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Gaussian-3 and related methods for accurate thermochemistry

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Abstract. In this paper, we present an overview of Gaussian-3 (G3) theory, a composite technique that employs a sequence of ab initio molecular orbital calculations to derive a total energy of a given molecular species. This method provides accurate energies of molecular systems for the calculation of enthalpies of formation, ionization potentials, electron affinities, proton affinities, etc. Also covered in this review are several variants of G3 theory including one based on scale factors (G3S) and an extended version (G3X) that uses improved geometries and larger Hartree-Fock basis sets. Finally, the G3/99 test set of accurate experimental data that is used for critical assessment is described. Overall, G3 theory has a mean absolute deviation from experiment of 1.07 kcal mol^{-1} for the G3/99 test set and G3S theory has a similar accuracy of 1.08 kcal mol^{-1}. G3X theory is significantly more accurate with the mean absolute deviation from experiment decreasing from 1.07 kcal mol^{-1} (G3) to 0.95 kcal mol^{-1} (G3X). The scaled version of G3X theory shows a similar improvement.

Key words: Computational thermochemistry – Ab initio molecular orbital theory – Molecular energies

Introduction

Knowledge of the thermochemistry of molecules is of major importance in the chemical sciences and is essential to many technologies. Computational methods can provide information on stabilities and reactivities of molecules that are used, for example, in modelling reactions occurring in combustion, the atmosphere, and chemical vapor deposition. In this paper, we present an overview of Gaussian-3 (G3) theory [1], a composite technique that employs a sequence of well-defined ab initio molecular orbital calculations to derive a total energy of a given molecular species. It is the latest method in the Gaussian-*n* series [2, 3] that is part of a long-term effort [4] to develop quantum chemical methods for the accurate computation of thermochemical data. G3 theory is significantly more accurate than its predecessors in the series and can be applied to larger systems. We also review several recent methods [5–7] based on variants of G3 theory and the G3/99 test set [8] of accurate experimental data that is used for critical assessment. There have also been other techniques that have been developed by other groups for calculating thermochemical data and the reader is referred to the literature [9–14] for information on such approaches.

This overview is organized as follows: we begin with a brief description of the G3/99 test set of experimental data. We then discuss the elements of G3 theory as well as the modified versions G3(MP3) and G3(MP2), and their performance for the G3/99 test set. Next we discuss the G3S method that includes multiplicative scale factors. The recently developed G3X method that corrects for many of the deficiencies of G3 theory for larger molecules is discussed in the last section. Finally, conclusions are drawn.

The G3/99 test set

We have assembled test sets of good, credible experimental data to perform assessments of quantum chemical models [Curtiss et al. (1991) 3, 8, 15]. The current test set, referred to as G3/99 [8], contains 376 energies (222 enthalpies of formation, 88 ionization energies, 58 electron affinities, and 8 proton affinities) that are known experimentally [16] to an accuracy of better than

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± 1 kcal mol^{-1}. It includes three subsets of energies, G2–1, G2–2, and G3–3. The G2–1 subset (original G2 test set from Curtiss et al. (1991) [3]) includes the energies for only very small molecules containing one to three heavy atoms (systems such as H_2O, C_2H_4, CO_2, and SO_2), whereas G2–2 [15] includes medium-sized molecules containing three to six heavy atoms (systems such as C_3H_6, C_4H_4O, and C_6H_6). The two subsets, G2–1 and G2–2, are together referred to as G2/97 and contain 301 test energies [Curtiss et al. (1998) 15]. The average number of bonds per molecule in this set is 4.8. The G3–3 test set [8] contains 75 new enthalpies of formation for molecules that are, on average, larger (containing three to ten heavy atoms). The average number of bonds per molecule in the G3–3 test set is 12.1 due to the presence of several larger hydrocarbons. The largest molecules in the G3–3 test set contain ten non-hydrogen atoms (naphthalene and azulene). It also contains several hypervalent molecules such as PF_5 or SF_6 that provide a challenge for many theoretical models.

The 222 enthalpies of formation included in the G3/99 test set contain a wide variety of molecules with many different kinds of bonds. They are conveniently classified into subgroups of molecules. They include 47 non-hydrogen-containing molecules, 38 hydrocarbons, 91 substituted hydrocarbons, 15 inorganic hydrides, and 31 open-shell radicals. Together, they provide a comprehensive assessment of new theoretical models in a wide variety of bonding environments. The average number of bonds per molecule in the entire G3/99 test set is 7.4.

The collection of such a large set of experimental data provides many challenges. All the experimental values that are included have a quoted uncertainty of less than 1 kcal mol^{-1} [16]. However, the evaluation of the experimental uncertainties is difficult or impossible in many cases. It is possible that some of the included values may turn out to be incorrect. For example, the G2/97 test set originally contained 302 energies, but the enthalpy of formation of COF_2 has been deleted because a new experimental upper limit [17] has been reported that casts doubt on the value used in the G2/97 test set. In our analysis, we have chosen not to discard experimental data unless there is new experimental evidence that warrants it. Another important factor is that the calculation of the enthalpies of formation for molecules requires the experimental atomic enthalpies of formation. Two of these (B and Si) have significant uncertainties and some authors have suggested the use of "theoretical" atomic enthalpies of formation for Si and B in the calculation of molecular enthalpies of formation [18–20]. We have consistently used experimental values for all elements, despite the uncertainty in the Si and Be values. The reason that we do not use these "theoretical" atomic enthalpies is that they are derived in part from an experimental molecular enthalpy that is part of the test set, which may bias the assessment process [21].

The geometries and energies of the molecules in these test sets are maintained at a web site, http://chemistry.anl.gov/compmat/comptherm.htm.

Gaussian-3 theory

Gaussian-3 theory, like its predecessor Gaussian-2 (G2) theory (Curtiss et al. (1991) [3]), is a composite technique in which a sequence of well-defined ab initio molecular orbital calculations [22] is performed to arrive at a total energy of a given molecular species. It is applicable to molecules containing atoms of the first (Li-F) and second (Na-Cl) rows of the periodic table. It was designed to correct some of the deficiencies of G2 theory for systems such as halogen-containing molecules, unsaturated hydrocarbons, etc. It also contains important physical effects such as core-valence correlation and spin-orbit contributions that were not included in G2 theory. G3 theory is computationally less demanding than G2 theory, though it is significantly more accurate. The detailed steps involved in G3 theory are as follows:

1. An initial equilibrium structure is obtained at the Hartree-Fock (HF) level with the 6–31G(d) basis [22]. Spin-restricted (RHF) theory is used for singlet states and spin-unrestricted Hartree-Fock theory (UHF) for others. The HF/6-31G(d) equilibrium structure is used to calculate harmonic frequencies, which are then scaled by a factor of 0.8929 to take account of known deficiencies at this level [23]. These frequencies are used to evaluate the zero-point energy (E(ZPE)) and thermal effects.
2. The equilibrium geometry is refined at the MP2(full)/6–31G(d) level, using all electrons for the calculation of correlation energies. This is the final equilibrium geometry in the theory and is used for all single-point calculations at higher levels of theory in step 3. Except where otherwise noted by the symbol (full), these subsequent calculations include only valence electrons in the treatment of electron correlation.
3. A series of single-point energies calculations are carried out at higher levels of theory. The first higher-level calculation is complete fourth-order Møller-Plesset perturbation theory [24] with the 6-31G(d) basis set, that is, MP4/6-31G(d). For convenience of notation, we represent this as MP4/d. This energy is then modified by a series of corrections from additional calculations.

(a) A correction for correlation effects beyond fourth-order perturbation theory using quadratic configuration interaction method [25], E(QCI):

$$E(\mathrm{QCI}) = \mathrm{QCISD(T)/d} - \mathrm{MP4/d} \tag{1}$$

(b) A correction for diffuse functions, E(plus):

$$E(\mathrm{plus}) = \mathrm{MP4/plus} - \mathrm{MP4/d} \tag{2}$$

where plus denotes the 6-31 + G(d) basis set [22].

(c) A correction for higher polarization functions on non-hydrogen atoms and p-functions on hydrogens, E(2df,p):

$$E(\mathrm{2df,p}) = \mathrm{MP4/2df,p} - \mathrm{MP4/d} \tag{3}$$

where 2df,p denoted the polarized 6-31G(2df,p) basis set [2].

(d) A correction for larger basis set effects and for the non-additivity caused by the assumption of separate basis set extensions for diffuse functions and higher polarization functions, E(G3Large):

$$E(\mathrm{G3Large}) = \mathrm{MP2(full)/G3L} - \mathrm{MP2/2df,p} - \mathrm{MP2/plus} + \mathrm{MP2/d} \quad (4)$$

The largest basis set, denoted as G3Large [1], (G3L) includes some core polarization functions as well as multiple sets of valence polarization functions. It should be noted that the largest basis set MP2 calculation in step 3d is carried out at the MP2(full) level. This is done to take account of core-related correlation contributions to total energies.

4. Spin-orbit correction, E(SO), is included for atomic species *only*. The spin-orbit correction is taken from experiment [26] where available and accurate theoretical calculations [27] in other cases. These are particularly important for halide-containing systems [1]. Molecular spin-orbit corrections are not included in G3 theory.
5. A "higher-level correction" (E(HLC)) is added to take into account remaining deficiencies in the energy calculations: 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. The use of different corrections for atoms and molecules can be justified, in part, by noting that effects of basis functions with higher angular momentum are likely to be of more importance in molecules than in atoms. The A, B, C, and D values are chosen to give the smallest average absolute deviation from experiment for the G2/97 test set. For G3 theory, A = 6.386 mhartrees, B = 2.977 mhartrees, C = 6.219 mhartrees, and D = 1.185 mhartrees.
6. Finally, the total energy at 0 °K ("G3 energy") is obtained by adding all the individual energy corrections in an additive manner.

$$E_0[\mathrm{G3}] = \mathrm{MP4/d} + E(\mathrm{QCI}) + E(\mathrm{plus}) + E(\mathrm{2df,p}) + E(\mathrm{G3L}) + E(\mathrm{SO}) + E(\mathrm{HLC}) + E(\mathrm{ZPE}). \quad (5)$$

The G3 energy can also be represented more fully as

$$\begin{aligned} E_0(\mathrm{G3}) = {} & \mathrm{MP4/d} + [\mathrm{QCISD(T)/d} - \mathrm{MP4/d}] \\ & + [\mathrm{MP4/plus} - \mathrm{MP4/d}] \\ & + [\mathrm{MP4/2df,p} - \mathrm{MP4/d}] + [\mathrm{MP2(full)} \\ & /\mathrm{G3L} - \mathrm{MP2/2df,p} - \mathrm{MP2/plus} + \mathrm{MP2/d}] \\ & + E(\mathrm{SO}) + E(\mathrm{HLC}) + E(\mathrm{ZPE}) \quad (6) \end{aligned}$$

The final total energy is effectively at the QCISD(T, full)/G3Large level if the different additivity approximations work well. The validity of such approximations has been previously investigated for G2 theory on the G2–1 subset of G2/97 and found to be satisfactory (Curtiss et al. (1992) [3]).

The correlation methods in G3 theory are still computationally demanding and it is of interest to find modifications to reduce the computational requirements. Two approximate versions of G3 theory have been proposed to make the methods more applicable. The first is G3(MP3) (first Ref. in [5]) that eliminates the expensive MP4/2df,p calculation by evaluating the larger basis set effects at the MP3 level. It also eliminates the MP4/plus calculation.

$$\begin{aligned} E_0(\mathrm{G3(MP3)}) = {} & \mathrm{MP4/d} + [\mathrm{QCISD(T)/d} - \mathrm{MP4/d}] \\ & + [\mathrm{MP3/2df,p} - \mathrm{MP3/d}] \\ & + [\mathrm{MP2(full)/G3L} - \mathrm{MP2/2df,p}] + E(\mathrm{SO}) \\ & + E(\mathrm{HLC}) + E(\mathrm{ZPE}) \quad (7) \end{aligned}$$

The second is G3(MP2) theory (second Ref. in [5]) that evaluates the larger basis set effects at the MP2 level, similar to the successful G2(MP2) theory.

$$\begin{aligned} E_0(\mathrm{G3(MP2)}) = {} & \mathrm{MP4/d} + [\mathrm{QCISD(T)/d} - \mathrm{MP4/d}] \\ & + [\mathrm{MP2/G3MP2L} - \mathrm{MP2/d}] \\ & + E(\mathrm{SO}) + E(\mathrm{HLC}) + E(\mathrm{ZPE}) \quad (8) \end{aligned}$$

In G3(MP2) theory, the MP2(full)/G2Large calculation in G3 is replaced with a frozen core calculation with the G3MP2Large basis set (second Ref. in [5]) (G3MP2L) that does not contain the core polarization functions in the G2Large basis set.

The enthalpies of formation for most molecules in the G2/97 and G3/99 test sets have been measured at 298 °K. In order to compare with experiment, the enthalpies of formation for molecules are calculated using a procedure described in detail previously [8]. Briefly, thermal corrections (298 °K) are first evaluated using the calculated vibrational frequencies and standard statistical mechanical methods [28]. The calculated total energies of the given molecule and its constituent atoms are used to evaluate its atomization energy. This value is then used along with the thermal corrections and the known experimental enthalpies of formation for the atomic species [1, Chase et al. 16] to calculate the enthalpy of formation for the molecule (298 °K). The electron affinities are calculated as the difference in total energies at 0 °K of the anion and the corresponding neutral species, at their respective MP2(full)/6-31G(d)-optimized geometries. Likewise, the ionization potentials are calculated as the difference in total energies at 0 °K of the cation and the corresponding neutral species, at their respective MP2(full)/6-31G(d)-optimized geometries. Many of the G3 techniques have been implemented in the Gaussian98 computer program [29].

The performance of G3, G3(MP3), and G3(MP2) theories for the energies in the G2/97 and G3/99 test sets are summarized in Table 1. Overall, the mean absolute deviations increase slightly for the G3/99 test set compared to that of the G2/97 test set. The mean absolute deviation of G3 theory increases from 1.01 to 1.07 kcal mol^{-1}, G3(MP3) theory increases from 1.21 to 1.27 kcal mol^{-1}, and G3(MP2) theory remains at

Table 1. Summary of mean absolute deviations (kcal mol^{-1}) for G3 theories[a]

	G3	G3(MP3)	G3(MP2)
G2/97 test set			
Enthalpies of formation (147)[a]	0.92(0.19)	1.19(0.25)	1.17(0.24)
Non-hydrogens (34)	1.68	2.09	2.06
Hydrocarbons (22)	0.68	0.86	0.70
Subst. hydrocarbons (47)	0.56	0.78	0.74
Inorganic hydrides (15)	0.87	1.18	1.03
Radicals (29)	0.84	1.05	1.23
All (301)[a]	1.01	1.21	1.31
Complete G3/99			
Enthalpies of formation (222)[a]	1.05(0.14)	1.29(0.18)	1.22(0.17)
Non-hydrogens (47)	2.11	2.74	2.45
Hydrocarbons (38)	0.69	0.77	0.71
Subst. hydrocarbons (91)	0.75	0.86	0.83
Inorganic hydrides (15)	0.87	1.18	1.03
Radicals (31)	0.87	1.06	1.21
Ionization energies (88)	1.14	1.24	1.46
Electron affinities (58)	0.98	1.24	1.46
Proton affinities (8)	1.34	1.25	1.02
All (376)[b]	1.07	1.27	1.31

[a] Values in parentheses are the average absolute error per bond. The average number of bonds is 4.8 for the G2/97 test set and 7.3 for the G3/99 test set

[b] The ionization energies, electron affinities, and proton affinities in the G2/97 test set are the same as in G3/99

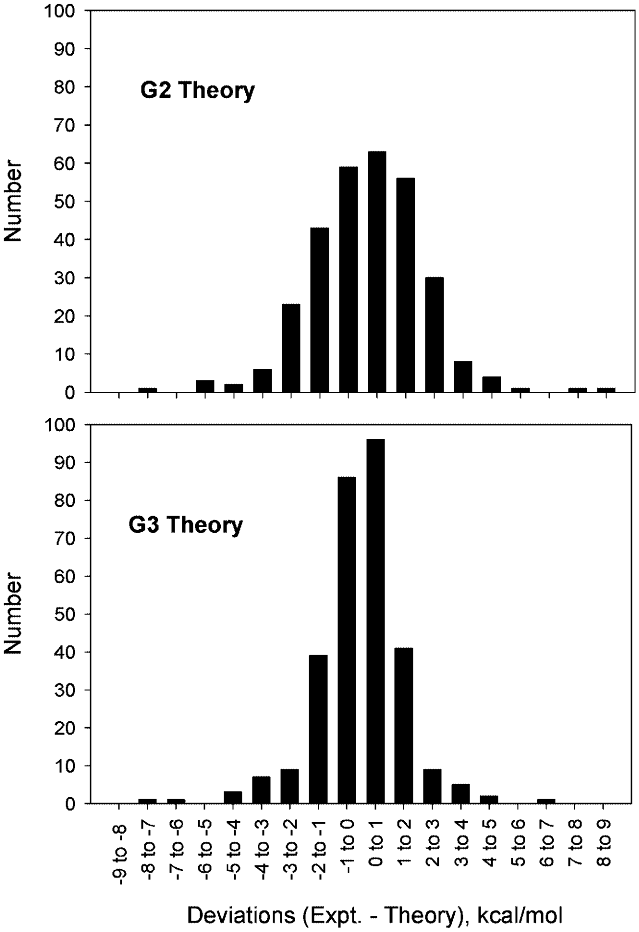

Fig. 1. Histograms of G2 and G3 deviations for the G2/97 test set. Each *vertical bar* represents deviations in a one kcal mol^{-1} range

1.31 kcal mol^{-1}. This increase in the mean absolute deviation is primarily due to large deviations in the calculated enthalpies of formation of some of the non-hydrogen species in the expanded test set. In particular, the mean absolute deviation of 3.24 kcal mol^{-1} for the 13 non-hydrogen species in the G3–3 subset is nearly twice that of the 35 non-hydrogens in the G2/97 set (1.68 kcal mol^{-1}). Especially large deviations (G3 theory) occur for SF_6 (−6.22 kcal mol^{-1}), PF_5 (−7.05 kcal mol^{-1}), SO_3 (−5.14 kcal mol^{-1}), P_4 (−4.15 kcal mol^{-1}), and Cl_2O_2S (−4.37 kcal mol^{-1}). Among these, P_4 is an unusually strained molecule with a bond angle of 60°. The remaining systems are hypervalent. Overall, the G3 deviations for nearly all of the new non-hydrogen species are negative indicating underbinding. Part of the error for these species is due to the use of MP2/6-31G(d) geometries. The remainder of the deficiency for non-hydrogen systems is largely due to basis set deficiencies (see below). The mean absolute deviations for the other types of molecules in the G3/99 test set are similar to that in the G2/97 test set. The average error per bond is 0.19 kcal mol^{-1} in the G2/97 test set and 0.14 kcal mol^{-1} for the G3/99 test set. The smaller error per bond in the later test set is due to the larger proportion of hydrocarbons in the G3–3 test set, the type of molecule for which G3 theory is most accurate.

As mentioned earlier, G3 theory was designed to correct some of the deficiencies in G2 theory. The histograms in Fig. 1 show the range of deviations of G2 and G3 theories from experiment for the G2/97 test set. Nearly 88% of the G3 deviations fall within the range of −2.0 to +2.0 kcal mol^{-1}. This is substantially better than G2 theory for which about 74% of the deviations fall in this range. In addition to improving the accuracy, the use of the 6-31G(d) basis set-based calculations in G3 theory substantially decreases the computer time and disk space requirements relative to G2 theory (which uses the larger 6-311G(d, p) basis set-based calculations). For example, the computer time for a G3 calculation on benzene is nearly a factor two faster than a G2 calculation.

Other variations of G3 theory have been proposed that use alternate geometries, zero-point energies, or higher-order correlation methods. G3 theory uses MP2(full)/6-31G(d) geometries and scaled HF/6-31G(d) frequencies and zero-point energies. A method using B3LYP/6-31G(d) geometries and scaled B3LYP/6-31G(d) zero-point energies (0.96) was considered to make it more uniform. Denoted as G3//B3LYP [30], its performance is very similar to that of G3 theory though it may be useful in cases where the MP2 theory is deficient for geometries. Another variation [31] involves the use of coupled clustered energies [32] [CCSD(T)/6-31G(d)] instead of quadratic configuration interaction [25] [QCISD(T)/6-31G(d)] to evaluate the contribution of higher-order correlation effects. The resulting G3(CCSD) method has an accuracy very similar to that of G3 theory and may be useful in cases where the QCISD(T) method is not available or deficient. Apart from these minor variations, two major variations (G3S and G3X) have been proposed to address some of the main deficiencies of G3 theory. These are discussed in detail below.

Finally, G3 theory and some modifications of it have recently been extended to third-row atoms K, Ca, Ga-Kr [33]. This has involved development of new basis sets [34] analogous to the ones used in G3 theory for the first- and second-row and the use of the same higher-level corrections. The G3 mean absolute deviation from experiment for a set of 47 test reactions containing these elements is 0.94 kcal mol^{-1}, which is a substantial improvement over G2 theory for the same set (1.43 kcal mol^{-1}) [35].

G3S theory

G3 theory and the other variants discussed thus far include a higher-level correction term (HLC) to correct for the remaining deficiencies that result from basis set incompleteness, etc. The HLC term in G3 theory consists of four molecule-independent additive parameters that depend only on the number of paired and unpaired electrons in the system. Such an approach will work if the deficiencies are systematic and scale as the number of electrons. The parameters in G3 theory were obtained by minimizing the mean absolute deviation from experiment of the energies in the G2/97 test set. This approach is indeed successful as indicated by the overall accuracy of 1 kcal mol^{-1} for this test set. However, one of the limitations of G3 theory is that the HLC parameters do not depend on the geometry and thus do not vary on the potential energy surface. This may cause deficiencies for regions near transition states that contain partially broken bonds. Even more importantly, G3 theory cannot be used to study potential energy surfaces for reactions in which the reactants and products have a different number of electron pairs.

An alternative approach for calculating accurate thermochemical data is to scale the calculated correlation energy using multiplicative parameters determined by fitting to the experimental data. Pioneering methods using such an approach include the scaling all correlation (SAC) method of Gordon and Truhlar [36], the parameterized correlation (PCI-X) method of Seigbahn et al. [37], and the multi-coefficient correlation methods (MCCM) of Truhlar et al. [14]. Such methods can be used to yield continuous potential energy surfaces even for reactions in which the reactants and products contain different numbers of electron pairs.

A new family of methods [6], referred to as G3S (G3 Scaled), has been developed recently where the additive higher-level correction is replaced by a multiplicative scaling of the correlation and Hartree-Fock components of the G3 energy. The scale factors have been obtained by fitting to the G2/97 test set of energies. This test set is substantially larger than that used in previous scaled methods and can provide a reliable assessment of the use of this approach to computational thermochemistry.

Traditionally, the G3 energy is written in terms of corrections (basis set extensions and correlation energy contributions) to the MP4/d energy. Alternatively, the G3 energy can be specified in terms of HF and perturbation energy components. Denoting E2, E3, and E4 as the second-, third-, and fourth-order contributions from perturbation theory, and ΔQCI as the contributions beyond fourth order in a QCISD(T) calculation, the G3 energy expression can be expressed as

$$\begin{aligned}E_0[\mathrm{G3}] = {} & \mathrm{HF/d} + [\mathrm{HF/G3L} - \mathrm{HF/d}] + \mathrm{E2/d} + \mathrm{E3/d} \\ & + \mathrm{E4/d} + \Delta\mathrm{QCI/d} \\ & + [\mathrm{E2(full)/G3L} - \mathrm{E2/d}] + [\mathrm{E3/plus} - \mathrm{E3/d}] \\ & + [\mathrm{E3/2df,p} - \mathrm{E3/d}] + [\mathrm{E4/plus} - \mathrm{E4/d}] \\ & + [\mathrm{E4/2df,p} - \mathrm{E4/d}] + \mathrm{E(SO)} + \mathrm{E(HLC)} + \mathrm{E(ZPE)}.\end{aligned} \tag{9}$$

In deriving the scaled methods, the HLC term is set to zero and parameters are introduced that scale the different terms in the energy expression. A systematic study has been performed to investigate the performance of different scaled methods as the number of parameters is increased. In each case, the parameters have been optimized to give the smallest root mean square deviation from experiment for the energies in the G2/97 test set. The addition of scale factors to all 11 terms in Eq. (9) yields a method with a mean absolute deviation of only 0.97 kcal mol^{-1}. However, most of this improvement is obtained on using only six parameters (mean absolute deviation of 0.99 kcal mol^{-1}). Such a method is referred to as G3S theory.

The G3S energy expression is given in Eq. (10).

$$\begin{aligned}E_0[\mathrm{G3S}] = {} & \mathrm{HF/d} + S_{\mathrm{E234}} * [\mathrm{E2/d} + \mathrm{E3/d} + \mathrm{E4/d}] \\ & + S_{\mathrm{QCI}} * [\Delta\mathrm{QCI/d}] \\ & + S_{\mathrm{HF'}} * [\mathrm{HF/G3L} - \mathrm{HF/d}] + S_{\mathrm{E2'}} \\ & * [\mathrm{E2(full)/G3L} - \mathrm{E2/d}] \\ & + S_{\mathrm{E3'}} * \{[\mathrm{E3/plus} - \mathrm{E3/d}] + [\mathrm{E3/2df,p} - \mathrm{E3/d}]\} \\ & + S_{\mathrm{E4'}} * \{[\mathrm{E4/plus} - \mathrm{E4/d}] + [\mathrm{E4/2df,p} - \mathrm{E4/d}]\} \\ & + \mathrm{E(SO)} + \mathrm{E(ZPE)}.\end{aligned} \tag{10}$$

The scale factors for the basis set extension terms ($S_{\mathrm{HF'}}$, $S_{\mathrm{E2'}}$, $S_{\mathrm{E3'}}$, $S_{\mathrm{E4'}}$) are denoted by primes, the scale factor for the second-, third-, and fourth-order perturbation terms at the 6-31G(d) level is denoted by S_{E234}, and the scale factor for the QCI correction beyond MP4 at the 6-31G(d) level is denoted by S_{QCI}. Optimization of all six parameters in Eq. (10) gives a mean absolute deviation of 0.99 kcal mol^{-1}, which is slightly better than standard G3 theory with the HLC correction (mean absolute deviation of 1.01 kcal mol^{-1}). The optimized values (see Ref. [6]) for the parameters in the six-parameter fit are all of reasonable magnitude and range from 0.95 to 1.38. The largest scale factor occurs for the basis set extensions at the third-order of perturbation theory. Only one scale factor is less than unity – the scale factor for the basis set extensions at fourth-order perturbation theory (0.95). Thus, it is possible to obtain a very accurate version of G3 theory with scaling of energies when the basis set extensions are included in the fitting procedure.

In a similar manner, the approximate G3(MP3) method can be modified to use multiplicative scale factors. The resulting G3S(MP3) energy expression contains five parameters (see Ref. [6]) and yields a mean absolute deviation of 1.16 kcal mol^{-1} for the energies in the G2/97 test set (compared to the corresponding G3(MP3) deviation of 1.22 kcal mol^{-1}). An MP2 version of G3S theory, G3S(MP2) has been published [6]. While its performance is reasonable, the G3S(MP2) total energies are very different from those of G3S and G3S(MP3). Thus, we have not included it in the discussion here.

A summary of the mean absolute deviations of the G3S and G3S(MP3) theories is given in Table 2 for the entire G3/99 test set. The mean absolute deviations are 1.08 and 1.21 kcal mol^{-1}, respectively. Overall, the mean absolute deviations increase slightly for the G3/99 test set compared to the G2/97 test set on which they were parameterized. The mean absolute deviation of G3S theory increases from 0.99 to 1.08 kcal mol^{-1} and G3S(MP3) increases from 1.15 to 1.21 kcal mol^{-1} on going from the G2/97 to the G3/99 test set. The increase in the mean absolute deviation for both methods is primarily due to large deviations in the calculated enthalpies of formation of some of the non-hydrogen species in the expanded G3/99 test set. This is similar to the results for the G3 methods based on the higher-level correction per electron pair. The G3S mean absolute deviation of 3.37 kcal mol^{-1} for the 13 non-hydrogen species in the G3–3 subset is more than twice that of the 35 non-hydrogens in the G2/97 set (1.60 kcal mol^{-1}). Similar increases in the mean absolute deviations occur for G3S(MP3) theory.

G3X theory

A new family of G3 methods, referred to as G3X (G3 eXtended) has been developed recently [7] to improve the accuracy of the results for some of the larger molecules included in the G3/99 test set. In the assessment of G3 theory [8] on the G3/99 test set, the mean absolute deviation from experiment (1.07 kcal mol^{-1}) was slightly larger than the corresponding value found originally for the smaller G2/97 test set (1.01 kcal mol^{-1}). However, significantly larger deviations were found for the larger non-hydrogen systems containing second-row atoms (Fig. 2).

Table 2. Summary of mean absolute deviations (kcal mol^{-1}) for G3S theories

	G3S	G3S(MP3)
Complete G3/99		
Enthalpies of formation (222)[a]	1.12(0.15)	1.19(0.16)
Non-hydrogens (47)	2.09	2.49
Hydrocarbons (38)	0.79	0.98
Subst. hydrocarbons (91)	0.92	0.75
Inorganic hydrides (15)	0.63	0.79
Radicals (31)	0.86	0.96
Ionization energies (88)	1.09	1.27
Electron affinities (58)	0.90	1.24
Proton affinities (8)	1.17	1.10
All (376)	1.08	1.21

[a] Values in parentheses are the average absolute error per bond

The larger non-hydrogen systems have deviations (3.24 kcal mol^{-1}) almost twice as large as those in the smaller G2/97 test set (1.68 kcal mol^{-1}). In particular, hypervalent molecules such as SO_3, SF_6, and PF_5 have deviations in the range 5–7 kcal mol^{-1}. Part of the source of error for the non-hydrogen species in the G3 results was traced to the MP2/6-31G(d) geometries used for the single point energies. Use of experimental geometries instead of MP2/6-31G(d) in a small subset of non-hydrogens reduced the deviations in those molecules, but they still remained around 3–4 kcal mol^{-1}. The remainder of the error was assigned to basis set deficiencies.

Three modifications have been included in the G3X method to correct these deficiencies:

(1) B3LYP/6-31G(2df,p) geometries are used in place of the MP2(full)/6-31G(d) geometries. These new geometries were found to have significantly smaller deviations from experiment than the original geometries.

(2) B3LYP/6-31G(2df,p) zero-point energies (scaled by 0.9854) are used in place of the HF/6-31G(d) zero-point energies (scaled by 0.8929). The scale factor (0.9854) was derived from fitting the set of zero-point energies compiled by Scott and Radom [38]. This choice differs in two ways from that in the original G3 procedure. Firstly, in G3 theory the zero-point energies and geometries are calculated at two different levels of theory (HF/6-31G(d) and MP2(full)/6-31G(d), respectively). Secondly, the HF/6-31G(d) scale factor was based on fitting of experimental vibrational frequencies, not zero-point energies. Thus, the new procedure for calculating zero-point energies in G3X theory is more logical than that in the G3 procedure.

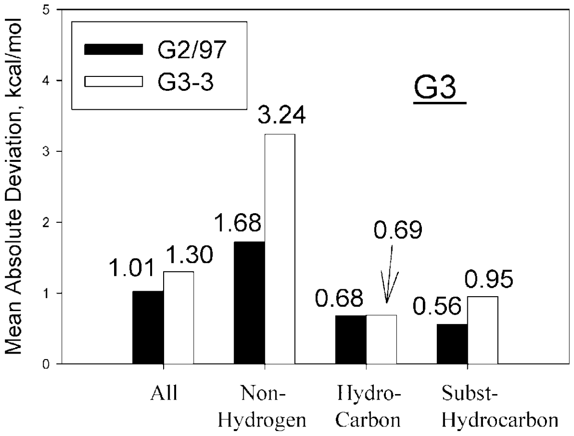

Fig. 2. Mean absolute deviation from experiment for G3 theory on the G3/99 test set broken down into the G2/97 (G2–1 + G2–2) and G3–3 subset

(3) A set of *g* valence polarization functions [7] are added to the G3Large basis set for second-row atoms at the Hartree-Fock level. Significant improvements in the calculated atomization energies were found for some representative molecules. For example, the addition of a single *g* function to the second-row atoms (Si-Cl) increases the binding in SiF_4, PF_5, and SF_6 by 3.6, 5.1, and 5.5 kcal mol^{-1}, respectively, at the Hartree-Fock level. 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. Addition of more polarization functions (2*g*, 2*gh*) on the second-row atoms results in substantially smaller changes in the atomization energies [7]. Thus, a single set of *g* polarization functions (7 pure functions) is added to the second-row G3Large basis set at the HF level in G3X theory. No *g* function was used on Na or Mg. This new basis set is referred to as G3Xlarge (G3XL). It should be noted that similar basis set deficiencies occur at correlated levels also. Correcting such deficiencies at the correlated level is more difficult due to their slow convergence, though the HLC parameters offer partial remedy.

The total G3X energy incorporating all three features is given by the equation

$$\begin{aligned}E_0(\mathrm{G3X}) = {} & \mathrm{MP4/d} + [\mathrm{QCISD(T)/d} - \mathrm{MP4/d}] \\ & + [\mathrm{MP4/plus} - \mathrm{MP4/d}] \\ & + [\mathrm{MP4/2df,p} - \mathrm{MP4/d}] + [\mathrm{MP2(full)} \\ & \quad \mathrm{/G3L} - \mathrm{MP2/2df,p} - \mathrm{MP2/plus} + \mathrm{MP2/d}] \\ & + [\mathrm{HF/G3XL} - \mathrm{HF/G3L}] + E(\mathrm{SO}) \\ & + E(\mathrm{HLC}) + E(\mathrm{ZPE}) \qquad (11)\end{aligned}$$

Equation (11) 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(full)/G3L energy, to the G3XL basis set. As in G3 theory, all correlation calculations are done with a frozen core, except the MP2 calculation with the G3large basis set.

As discussed earlier, the single-point energies in Eq. (11) are calculated at B3LYP/6-31G(2df,p) geometries and the zero-point energies E(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. 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 G3X method takes about 10–15% more time than G3 due to the B3LYP/6-31G(2df,p) frequency calculation.

G3X theory gives significantly better agreement with experiment for the G3/99 test set of 376 energies. A summary of the results is given in Table 3. Overall, the mean absolute deviation from experiment decreases from 1.07 kcal mol^{-1} (G3) to 0.95 kcal mol^{-1} (G3X). The mean absolute deviation for the 222 enthalpies of formation decreases from 1.05 kcal mol^{-1} (G3) to 0.88 kcal mol^{-1} (G3X). The improvement is largely due to the non-hydrogen systems for which the mean absolute deviation decreases from 2.11 to 1.49 kcal mol^{-1}. 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.

Table 3. Summary of mean absolute deviations (kcal mol^{-1}) for the G3X, G3X(MP3), and G3X(MP2) methods for the G3/99 test set

	G3	G3X	G3X(MP3)	G3X(MP2)
Enthalpies of formation (222)	1.05	0.88	1.07	1.05
Non-hydrogens (47)	2.11	1.49	2.05	1.75
Hydrocarbons (38)	0.69	0.56	0.68	0.76
Subst. hydrocarbons (91)	0.75	0.75	0.76	0.78
Inorganic hydrides (15)	0.87	0.81	1.12	1.01
Radicals (31)	0.87	0.76	0.96	1.17
Ionization energies (88)	1.14	1.07	1.16	1.36
Electron affinities (58)	0.98	0.98	1.29	1.51
Proton affinities (8)	1.34	1.21	1.09	0.79
All (376)[a]	1.07 (1.54)	0.95 (1.35)	1.13 (1.63)	1.19 (1.69)

[a] Root mean square deviation in parentheses

Unlike G3 theory, there is very little degradation of G3X theory for larger molecules. The overall mean absolute deviation from experiment is nearly the same for the larger G3/99 test set (0.95 kcal mol^{-1}) as for the smaller G2/97 test set (0.96 kcal mol^{-1}). Similarly, the mean absolute deviation from experiment for enthalpies is nearly the same for the larger G3/99 test set (0.88 kcal mol^{-1}) as for the smaller G2/97 test set (0.86 kcal mol^{-1}). It is also important to note that this result is not dependent on the data set that is used to obtain the higher-level correction parameters since both sets give essentially the same values.

Some examples of the changes on going from G3 to G3X theory for selected non-hydrogen systems can be seen in Table 4. Significant improvements are seen in most cases though errors in the range of 2–3 kcal mol^{-1} remain in some molecules. The reliability of the G3X method is illustrated by the fact that only one molecule (C_2F_4) has an error of more than 4 kcal mol^{-1} and even that experimental value has been recently called into question.

The three new features of G3X theory can also be easily included in the G3(MP3) and G3(MP2) methods [7]. The resulting methods are referred to as G3X(MP3) and G3X(MP2), respectively (see Ref. [7] for details). The equations for the G3X(MP3) and G3X(MP2) energies are the same as for G3(MP3) and G3(MP2) in Eqns. (7) and (8), respectively, 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. Again, the single-point energies are calculated at the B3LYP/6-31G(2df,p) geometry and the

Table 4. Deviations from experiment for the calculated enthalpies of formation of some non-hydrogen systems (experiment – theory, kcal mol^{-1})

Molecule	G3	G3X	G3S	G3SX
SO_2	−3.81	−0.73	−2.00	0.40
SO_3	−5.17	−1.54	−2.15	0.54
PF_3	−4.84	−1.85	−6.21	−2.96
PF_5	−7.05	−1.80	−7.32	−1.18
SF_6	−6.22	−0.47	−4.23	2.66
SiF_4	−1.12	2.27	−1.76	2.48
$SiCl_4$	0.02	−0.63	−1.97	0.13
P_4	−4.15	−2.18	−10.01	−8.79
PCl_3	−3.19	−3.30	−5.04	−3.15
PCl_5	2.40	1.74	1.09	3.44
$POCl_3$	−3.07	−2.32	−3.94	−1.88
Cl_2O_2S	−4.37	−2.55	−2.32	0.11

zero-point energies E(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.

Summaries of G3X(MP3) and G3X(MP2) mean absolute deviations from experiment for the G3/99 test set are given in Table 3. The overall mean absolute deviations for G3X(MP3) and G3X(MP2) for the 376 energies are 1.13 and 1.19 kcal mol^{-1}, respectively. These are improvements over G3(MP3) and G3(MP2), which have mean absolute deviations of 1.27 and 1.31 kcal mol^{-1}, respectively, for the same set of energies. For enthalpies of formation the mean absolute deviations decrease from 1.29 to 1.07 kcal mol^{-1} (G3X(MP3)) and from 1.22 to 1.05 kcal mol^{-1} (G3X(MP2)). Much of the improvement in enthalpies is due to non-hydrogens species, although the other types of species also improve slightly or stay the same. The G3X(MP3) and G3X(MP2) methods save considerable computational time and have a reasonable accuracy.

The three new features of G3X theory can also be included in the G3S method [7]. The resulting method is referred to as G3SX and the energy is given by

$$\begin{aligned} E_0[\mathrm{G3SX}] = {} & \mathrm{HF/d} + S_{E234} * [\mathrm{E2/d} + \mathrm{E3/d} + \mathrm{E4/d}] \\ & + S_{QCI} * [\Delta\mathrm{QCI/d}] + S_{HF'} * [\mathrm{HF/G3XL} - \mathrm{HF/d}] \\ & + S_{E2'} * [\mathrm{E2(full)/G3L} - \mathrm{E2/d} \\ & + S_{E3'} * \{[\mathrm{E3/plus} - \mathrm{E3/d}] + [\mathrm{E3/2df,p} - \mathrm{E3/d}]\} \\ & + S_{E4'} * \{[\mathrm{E4/plus} - \mathrm{E4/d}] + [\mathrm{E4/2df,p} - \mathrm{E4/d}]\} \\ & + \mathrm{E(SO)} + \mathrm{E(ZPE)}. \end{aligned} \qquad (12)$$

Equation (12) is identical to that of the corresponding G3S method, except for the use of the G3XLarge basis set [7] in the Hartree-Fock term instead of the G3Large basis. Also, the single-point energies are calculated at the B3LYP/6-31G(2df,p) geometry and the zero-point energy E(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 (see Ref. [7]). G3SX has six parameters, one for the Hartree-Fock energy extension and five for the correlation terms. In a similar manner, a method based on reduced perturbation orders, G3SX(MP3), is derived by adding the three new features to the G3S(MP3) method (not shown).

A summary of G3SX mean absolute deviations from experiment for the G3/99 test set is given in Table 5. The mean absolute deviation for G3SX for the 376 energies is 0.95 kcal mol^{-1}. 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 to 0.88 kcal mol^{-1}. The improvement is due to the non-hydrogen species (2.09 vs. 1.60 kcal mol^{-1}) and the substituted hydrocarbons (0.92 vs. 0.72 kcal mol^{-1}), hydrocarbons (0.79 vs. 0.64 kcal mol^{-1}), and radicals (0.86 vs. 0.67 kcal mol^{-1}). However, consideration of the specific deviations for non-hydrogens indicates that G3SX does not do as well as G3X for these non-hydrogens. Eight of the 222 enthalpies of formation differ by more than 3 kcal mol^{-1} (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^{-1}. This is probably due to a small scaling factor for the MP4 term. Otherwise, the overall accuracy of G3SX theory, as assessed in terms of the mean absolute deviations on the G3/99 test set, is very similar to that attained by G3X theory, suggesting that both types of parameterizations work equally well. 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^{-1} for the 376 energies in the G3/99 test set and 0.90 kcal mol^{-1} for the 222 enthalpies of formation. In this respect it is as accurate as G3 theory and much less expensive.

Variations of G3X theory have also been developed in which the quadratic configuration interaction (QCISD(T)) energy calculation is replaced by either a Brueckner doubles (BD(T)) [39] or coupled cluster (CCSD(T)) energy [32]. This modification has been done for five G3X methods including G3X, G3X(MP3), G3X(MP2), G3SX, and G3SX(MP3) [40]. In most cases the replacement of the QCISD(T) energy by one of these alternative energies results in a slight improvement in the

Table 5. Mean absolute deviations (kcal mol^{-1}) from experiment for the G3/99 test set for the scaled G3S and G3SX methods

	G3S	G3SX	G3SX(MP3)
Enthalpies of formation (222)	1.12	0.88	0.90
Non-hydrogens (47)	2.09	1.60	1.70
Hydrocarbons (38)	0.79	0.64	0.66
Subst. Hydrocarbons (91)	0.92	0.72	0.65
Inorganic hydrides (15)	0.63	0.61	0.65
Radicals (31)	0.86	0.67	0.88
Ionization energies (88)	1.09	1.05	1.16
Electron affinities (58)	0.90	1.02	1.32
Proton affinities (8)	1.17	1.23	1.29
All (376)	1.08	0.95	1.04

accuracy of these methods as assessed on the G3/99 test set, which is limited to the first and second row. This is in contrast to G3 theory where use of these alternative energies leads to slightly poorer agreement with experiment [31]. The best agreement with experiment is obtained for G3SX(BD) and G3SX(CCSD), which have average absolute deviations with experiment of 0.92 kcal mol^{-1} for the G3/99 test set of 376 energies. These new G3X methods are useful alternatives to the G3X methods based on quadratic configuration interaction.

Conclusions

Gaussian-3 theory is a general predictive procedure for thermochemical calculations of molecules containing first- and second-row atoms. It is a significant improvement over the previous method in this series, G2 theory, while also being computationally more efficient. Overall, G3 theory has a mean absolute deviation of 1.07 kcal mol^{-1} for the G3/99 test set. G3 theory based on multiplicative scaling of the energy terms (G3S) instead of the additive higher-level correction has a mean absolute deviation of 1.08 for the G3/99 test set. G3X theory was introduced to correct some deficiencies of G3 theory for larger non-hydrogen containing molecules. It includes better geometries as well as *g* polarization functions on second-row atoms to correct for the deficiencies of G3 theory for hypervalent molecules. The overall mean absolute deviation from experiment decreases from 1.07 kcal mol^{-1} (G3) to 0.95 kcal mol^{-1} (G3X). The scaled version of G3X theory also shows a similar improvement. Despite the successes of methods such as G3 theory, much remains to be done in the future to further develop capabilities for accurate prediction of thermochemical data. Among the challenges will be extension of the methods to larger molecules, increased accuracy in predictions, and extension to heavier elements.

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