

Gaussian-3 (G3) theory for molecules containing first and second-row atoms

Larry A. Curtiss^{a)}

Chemistry and Materials Science Divisions, Argonne National Laboratory, Argonne, Illinois 60439

Krishnan Raghavachari

Bell Laboratories, Lucent Technologies, Murray Hill, New Jersey 07974

Paul C. Redfern

Chemistry and Materials Science Divisions, Argonne National Laboratory, Argonne, Illinois 60439

Vitaly Rassolov and John A. Pople

Department of Chemistry, Northwestern University, Evanston, Illinois 60208

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Gaussian-3 theory (G3 theory) for the calculation of molecular energies of compounds containing first (Li–F) and second row (Na–Cl) atoms is presented. This new theoretical procedure, which is based on *ab initio* molecular-orbital theory, modifies G2 theory [J. Chem. Phys. **94**, 7221 (1991)] in several ways including a new sequence of single point energy calculations using different basis sets, a new formulation of the higher level correction, a spin–orbit correction for atoms, and a correction for core correlation. G3 theory is assessed using 299 energies from the G2/97 test set including enthalpies of formation, ionization potentials, electron affinities, and proton affinities. This new procedure corrects many of the deficiencies of G2 theory. There is a large improvement for nonhydrogen systems such as SiF₄ and CF₄, substituted hydrocarbons, and unsaturated cyclic species. Core-related correlation is found to be a significant factor, especially for species with unsaturated rings. The average absolute deviation from experiment for the 148 calculated enthalpies of formation is reduced to under one kcal/mol, from 1.56 kcal/mol for G2 theory to 0.94 kcal/mol for G3 theory. Significant improvement is also found for ionization potentials and electron affinities. The overall average absolute deviation of G3 theory from experiment for the 299 energies is 1.02 kcal/mol compared to 1.48 kcal/mol for G2 theory. © 1998 American Institute of Physics. [S0021-9606(98)30640-6]

I. INTRODUCTION

Quantum chemical methods for the calculation of thermochemical data have developed beyond the level of just reproducing experimental data and can now make accurate predictions where the experimental data are unknown or uncertain. One of the more accurate of these methods is Gaussian-2 (G2) theory.^{1,2} It was the second in a series of methods,^{1,3,4} referred to as Gaussian-*n* theories, proposed for the calculation of energies of molecular systems containing the elements H–Cl. The goal of these methods was an accuracy of ± 2 kcal/mol for quantities such as atomization energies, ionization potentials, electron affinities, and proton affinities. In two recent papers^{5,6} we have developed a new test set of accurate experimental data for the assessment and development of new quantum chemical methods. This test set was given the name “G2/97” in Ref. 6 and contains 302 energies including 148 enthalpies of formation, 88 ionization potentials, 58 electron affinities, and 8 proton affinities. The G2/97 test set incorporates the 125 test energies from the original G2 test set¹ (referred to as the G2-1 subset) and 177 new energies (referred to as the G2-2 subset) which are mostly for larger and more diverse molecules. The 148 en-

thalpies are further broken down into five different subgroups: nonhydrogen, hydrocarbons, substituted hydrocarbons, inorganic hydrides, and radicals. This new test set provides a more rigorous database with which to evaluate quantum chemical methods than the original G2 test set.

In an assessment^{5,6} of G2 theory on the G2/97 test set, the energies of the new molecules have a larger average absolute deviation from experiment than the molecules in the original test set as shown in Fig. 1. The 55 enthalpies of formation of neutral molecules in the G2-1 subset of G2/97 have an average absolute deviation of 1.23 kcal/mol compared to 1.80 kcal/mol for the 93 enthalpies in the G2-2 subset. The 35 nonhydrogen molecules have the largest deficiency of any of the five subgroups of the 148 enthalpies with an average absolute deviation of 2.44 kcal/mol. For example, the calculated enthalpy of formation of CF₄ is too negative by 5.5 kcal/mol, whereas that of SiF₄ is too positive by 7.1 kcal/mol. The opposite signs of the deviations are especially puzzling. Another deficiency occurs for unsaturated cyclic systems. Although the average absolute deviation from experiment for hydrocarbons is 1.29 kcal/mol, the deviations are much larger for unsaturated ring systems than for saturated systems. For example, the enthalpy of formation of benzene differs from experiment by 3.9 kcal/mol. In addition, substituted hydrocarbons have a larger average ab-

^{a)}Electronic mail: curtiss@anlchm.chm.anl.gov

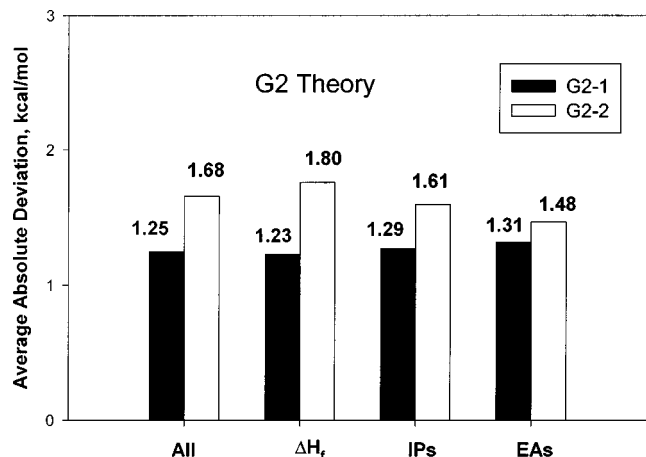


FIG. 1. Average absolute deviations with experiment for G2 theory on the G2/97 test set broken down into the G2-1 and G2-2 test sets.

solute deviation (1.48 kcal/mol) than hydrocarbons (1.29 kcal/mol). The average absolute deviations of the ionization potentials and electron affinities in the G2-2 subset also increase somewhat relative to the G2-1 subset: from 1.29 to 1.61 kcal/mol for ionization potentials and from 1.31 to 1.47 kcal/mol for electron affinities. About 84% of the deviations of G2 theory are in the range -2.0 to $+2.0$ kcal/mol for the G2-1 subset compared to 74% for the full G2/97 test set. It is clearly desirable to find ways to improve G2 theory.

In this paper we set forth Gaussian-3 theory (referred to as ‘‘G3 theory’’) which makes a significant improvement over G2 theory by eliminating many of the deficiencies described above. It has the following new features: 1) The fourth-order Moller–Plesset perturbation theory (MP4) and quadratic configuration interaction [QCISD(T)] single point calculations are based on the 6-31G(*d*) basis set instead of the 6-311G(*d,p*) basis set. 2) The second-order Moller–Plesset (MP2) single point calculation uses the G3large basis set, which is a modification of the 6-311+G(3*df*,2*p*) basis set used in G2 theory. 3) A spin–orbit correction is added to the energies of atomic species. 4) A correction for core correlation is added. 5) Finally, the higher level correction of G2 theory is separated into two parts, one for molecules and the other for atoms. It is derived to give the best fit to energies in the new test set. The first four features result in significant improvement in the enthalpies of formation of non-hydrogens and substituted hydrocarbons, while the last feature gives a significant improvement in ionization potentials and electron affinities. We find an average absolute deviation of 1.02 kcal/mol for G3 theory compared to 1.48 kcal/mol for G2.

In Sec. II, the specifics of G3 theory are given. In Sec. III, an assessment of G3 theory on the G2/97 test set is presented and a comparison is made with G2 theory. Finally, conclusions are presented in Sec. IV.

II. DESCRIPTION OF GAUSSIAN-3 THEORY

Gaussian-3 theory, like Gaussian-2 theory,¹ is a composite technique in which a sequence of well-defined *ab initio* molecular orbital calculations⁷ is performed to arrive at a

total energy of a given molecular species. The steps in G3 theory and the differences with G2 theory are as follows.

1. An initial equilibrium structure is obtained at the Hartree–Fock (HF) level with the 6-31G(*d*) basis.⁸ Spin-restricted (RHF) theory is used for singlet states and spin-unrestricted Hartree–Fock theory (UHF) for others. Step 1 is the same as in G2 theory.

2. 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.⁹ These frequencies give the zero-point energy, $E(\text{ZPE})$, used to obtain E_0 in step 7. Step 2 is the same as in G2 theory. This level of theory is adequate in most cases for the zero-point energies.¹⁰

3. 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 4. Except where otherwise noted by the symbol (full), these subsequent calculations include only valence electrons in the treatment of electron correlation. Step 3 is the same as in G2 theory.

4. A series of single-point energies calculations are carried out at higher levels of theory. The first higher level calculation is complete fourth-order Moller–Plesset perturbation theory¹¹ with the 6-31G(*d*) basis set, i.e., MP4/6-31G(*d*). This energy is then modified by a series of corrections from additional calculations.

(a) A correction for diffuse functions,¹² $\Delta E(+)$

$$\Delta E(+) = E[\text{MP4}/6-31+G(d)] - E[\text{MP4}/6-31G(d)]. \quad (1)$$

(b) A correction for higher polarization functions on nonhydrogen atoms and *p*-functions on hydrogens, $\Delta E(2df,p)$

$$\Delta E(2df,p) = E[\text{MP4}/6-31G(2df,p)] - E[\text{MP4}/6-31G(d)]. \quad (2)$$

The 2*d* symbol implies two sets of uncontracted *d*-primitives with exponents twice and half the standard values.⁸ The *p*-function exponent (1.1) for hydrogen is from Ref. 8(a) while the *f*-function exponents are from Ref. 12(a).

(c) A correction for correlation effects beyond fourth-order perturbation theory using the method of quadratic configuration interaction,¹³ $\Delta E(\text{QCI})$

$$\Delta E(\text{QCI}) = E[\text{QCISD(T)}/6-31G(d)] - E[\text{MP4}/6-31G(d)]. \quad (3)$$

(d) A correction for larger basis set effects and for the nonadditivity caused by the assumption of separate basis set extensions for diffuse functions and higher polarization functions, $\Delta E(\text{G3large})$

$$\begin{aligned} \Delta E(\text{G3large}) = & E[\text{MP2}(\text{full})/\text{G3large}] \\ & - E[\text{MP2}/6-31G(2df,p)] \\ & - E[\text{MP2}/6-31+G(d)] \\ & + E[\text{MP2}/6-31G(d)]. \end{aligned} \quad (4)$$

G2	MP2	MP4	QCISD(T)	G3
6-311G(d,p)	X	X	X	6-31G(d)
6-311+G(d,p)	X	X		6-31+G(d)
6-311G(2df,p)	X	X		6-31G(2df,p)
6-311+G(3df,2p)	^{FC} X ^{FULL}			G3large

FIG. 2. Comparison of the basis sets used in the various steps in G2 and G3 theories. The MP2 calculation with the G3large basis includes all electrons in the correlation treatment [MP2(FULL)], whereas the MP2 calculation with the 6-311+G(3df,2p) basis treats only the valence electrons in the correlation treatment [MP2(FC)]. All other single-point energy calculations treat only the valence electrons.

Step 4 differs from G2 theory in several respects. First, the 6-31G(*d*) basis set is used as the starting point for the MP4 and QCISD(T) single-point calculations instead of 6-311G(*d*). This is because 6-311G(*d*) has been defined and used in a somewhat unsatisfactory manner. For the first row (Li–Ne), the basis has been criticized as being too “close-in” to be of triple-zeta quality by Grev and Shafer.¹⁴ For the second row (Na–Ar) 6-311G(*d*) has been implemented as a version of the segmented basis proposed by McLean and Chandler.¹⁵ This is defined in a nonuniform manner across the row and is in any case rather different from 6-31G(*d*) in its segmentation. To avoid these difficulties, we have chosen to use 6-31G(*d*) as a uniformly defined basis at this stage.

The second difference concerns the largest basis used at the MP2 level. In G2 theory, this was 6-311+G(3df,2p) with 3df polarization functions on first and second row atoms and 2p on hydrogen. Because of limitations of this ba-

sis, some of which have been noted above, we have modified it to include more polarization functions for the second row (3df), less on the first row (2df), and other changes to improve uniformity. In addition, some core polarization functions are added. This basis, which is termed G3large, is specified fully in the Appendix.^{16,17}

A third difference is that the largest basis set MP2 calculation in step 4(*d*) is carried out at the MP2(full) level. This is done to take some account of core-related correlation contributions to total energies. Such effects have been neglected in both G1 and G2 theories, but have been shown to be significant in several recent studies.^{18–21} The differences between G2 theory and G3 theory for Step 4 are summarized in Fig. 2. A full discussion of the effects of these changes is given in Sec. III.

5. The MP4/6-31G(*d*) energy and the four corrections from step 4 are combined in an additive manner along with a spin–orbit correction, $\Delta E(\text{SO})$, for atomic species only.

$$E(\text{combined}) = E[\text{MP4}/6\text{-}31\text{G}(d)] + \Delta E(+) + \Delta E(2df,p) + \Delta E(\text{QCI}) + \Delta E(\text{G3large}) + \Delta E(\text{SO}). \quad (5)$$

The spin–orbit correction is taken from experiment²² where available and accurate theoretical calculations²³ in other cases. The values are listed in Table I. The spin–orbit correction was not included in G2 theory, but was recently found to be important for halide-containing systems.⁵ About 30 diatomics in the G2/97 test set are ²Π states and have first-order spin–orbit corrections. Several of these diatomics, such as Cl₂⁺ and S₂⁺, have $\Delta E(\text{SO})$ values of about 1 kcal/mol; for most it is much less than 1 kcal/mol.²⁴ Inclusion of

TABLE I. Total G3 energies (in hartrees) of atomic species and spin–orbit corrections (in mhartrees).

Atomic species	$E_0(\text{G3})$	$\Delta E(\text{SO})^a$	Atomic species	$E_0(\text{G3})$	$\Delta E(\text{SO})^a$
H (² S)	−0.501 00	0.0	N ⁺ (³ P)	−54.031 23	−0.43
He (¹ S)	−2.902 35	0.0	O ⁺ (⁴ S)	−74.533 12	0.0
Li (² S)	−7.465 13	0.0	F ⁺ (³ P)	−99.045 19	−0.67
Be (¹ S)	−14.659 72	0.0	Ne ⁺ (² P)	−128.079 32	−1.19
B (² P)	−24.642 57	−0.05	Na ⁺ (¹ S)	−161.916 23	0.0
C (³ P)	−37.827 72	−0.14	Mg ⁺ (² S)	−199.621 31	0.0
N (⁴ S)	−54.564 34	0.0	Al ⁺ (¹ S)	−241.988 47	0.0
O (³ P)	−75.030 99	−0.36	Si ⁺ (² P)	−288.923 62	−0.93
F (² P)	−99.684 21	−0.61	P ⁺ (³ P)	−340.731 90	−1.43
Ne (¹ S)	−128.872 34	0.0	S ⁺ (⁴ S)	−397.583 73	0.0
Na (² S)	−162.104 15	0.0	Cl ⁺ (³ P)	−459.517 25	−1.68
Mg (¹ S)	−199.907 42	0.0	Ar ⁺ (² P)	−526.792 64	−2.18
Al (² P)	−242.207 47	−0.34	Li [−] (¹ S)	−7.492 39	0.0
Si (³ P)	−289.222 27	−0.68	B [−] (³ P)	−24.650 09	−0.03 ^b
P (⁴ S)	−341.116 43	0.0	C [−] (⁴ S)	−37.871 58	0.0
S (³ P)	−397.961 11	−0.89	O [−] (² P)	−75.080 14	−0.26 ^b
Cl (² P)	−459.990 96	−1.34	F [−] (¹ S)	−99.809 19	0.0
Ar (¹ S)	−527.369 22	0.0	Na [−] (¹ S)	−162.130 06	0.0
He ⁺ (² S)	−1.999 42	0.0	Al [−] (³ P)	−242.221 75	−0.28 ^b
Li ⁺ (¹ S)	−7.266 79	0.0	Si [−] (⁴ S)	−289.272 90	0.0
Be ⁺ (² S)	−14.312 14	0.0	P [−] (³ P)	−341.143 70	−0.45 ^b
B ⁺ (¹ S)	−24.340 00	0.0	S [−] (² P)	−398.037 01	−0.88 ^b
C ⁺ (² P)	−37.415 71	−0.2	Cl [−] (¹ S)	−460.123 60	0.0

^aSpin–orbit corrections are from Ref. 22 except where noted.

^bCalculated value, Ref. 23.

the spin-orbit corrections for the molecules does not improve the average absolute deviation of the G3 theory. We have not included the molecular spin-orbit correction in G3 theory since it gives no overall improvement in accuracy and also because calculations of this quantity are not routine when experimental values are not available.

6. A "higher level correction" (HLC) is added to take into account remaining deficiencies in the energy calculations:

$$E_e(\text{G3}) = E(\text{combined}) + E(\text{HLC}). \quad (6)$$

The 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 these extrapolations take some account of effects of basis functions with higher angular momentum, which are likely to be of more importance in molecules than in atoms. For G3 theory, $A=6.386$ mhartrees, $B=2.977$ mhartrees, $C=6.219$ mhartrees, $D=1.185$ mhartrees. The A , B , C , D values are chosen to give the smallest average absolute deviation from experiment for the G2/97 test set (less three ionization potentials as noted below). More discussion of the HLC is given in Sec. III.

7. Finally, the total energy at 0 K is obtained by adding the zero-point energy, obtained from the frequencies of step 2 to the total energy

$$E_0(\text{G3}) = E_e(\text{G3}) + E(\text{ZPE}). \quad (7)$$

The energy E_0 is referred to as the "G3 energy."

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.²⁵ All calculations in this paper were done with the GAUSSIAN94 computer program.²⁶ All of the basis sets in G3 theory, with the exception of G3large, are standard in GAUSSIAN94.

III. ASSESSMENT OF G3 THEORY ON THE G2/97 TEST SET

The G2/97 test set^{5,6} contains 148 enthalpies of formation of neutrals (at 298 K), 88 ionization potential 58 electron affinities, and eight proton affinities for a total of 302 reaction energies. In this assessment we have used the G2/97 test set less three ionization potentials ($\text{C}_6\text{H}_5\text{CH}_3 \rightarrow \text{C}_6\text{H}_5\text{CH}_3^+$, $\text{C}_6\text{H}_5\text{NH}_2 \rightarrow \text{C}_6\text{H}_5\text{NH}_2^+$, $\text{C}_6\text{H}_5\text{OH} \rightarrow \text{C}_6\text{H}_5\text{OH}^+$) resulting in a total of 299 energies. These three ionization potentials are not included in order to make comparison with G2 theory on an equal basis. These three ionization potentials were not calculated with G2 theory in Ref. 6 because of the size of the molecules. All of the average absolute deviations reported in this paper are for the 299 energies. The

enthalpies of formation at 298 K were calculated as in Ref. 5. The ionization potentials, electron affinities, and proton affinities were calculated at 0 K as in Ref. 6.

G3 theory, as defined in Sec. II, was used to calculate the energies of atoms, molecules and ions in the G2/97 test set. Table I contains the G3 total energies of the atomic species and the spin-orbit corrections, $\Delta E(\text{SO})$, that are included in the total energies. The G3 total energies for the molecules and their geometries are available elsewhere.¹⁶ Tables II–V contain the deviations of the G3 enthalpies, ionization potentials, electron affinities, and proton affinities from experiment for the G2/97 test set. Also included in the tables are the results for G2 theory from Refs. 1, 5, and 6. Table VI contains a summary of the average absolute deviations and root-mean-square deviations of G3 theory from experiment. Results for G2 theory are also included in the table for comparison. The contributions of the new features to the improvement in G3 theory relative to G2 theory are listed in Table VII.

A. Comparison of G2 and G3 theories

The results in Table VI indicate that for the 299 energies the average absolute deviation from experiment at the G3 level is 1.02 kcal/mol compared to 1.48 kcal/mol for G2 theory. The root-mean-square deviation of G3 theory (1.45 kcal/mol) is also significantly improved compared to G2 theory (1.93 kcal/mol). G3 theory performs far better than G2 theory for enthalpies of formation, ionization potentials, and electron affinities. These three quantities have average absolute deviations of about 0.94, 1.13, and 1.00 kcal/mol, respectively, at the G3 level compared to 1.56, 1.45, and 1.41 kcal/mol at the G2 level. The only type of energy for which the accuracy decreases is proton affinities, which have an average absolute deviation of 1.34 kcal/mol at the G3 level compared to 1.08 kcal/mol at the G2 level. However, all of the deviations from experiment for the eight proton affinities in the test set are less than 2 kcal/mol at the G3 level (see Table V).

Table VI contains the average absolute deviations for the enthalpies of formation of neutrals broken down into five different types as in Ref. 5: Nonhydrogen, hydrocarbons, substituted hydrocarbons, inorganic hydrides, and radicals. G3 theory is more accurate than G2 theory for all five types of species. The largest improvement in accuracy occurs for the 47 substituted hydrocarbons for which the average absolute deviation is cut by more than a factor of 2, from 1.48 to 0.56 kcal/mol. The next largest improvement occurs for the 35 nonhydrogens for which the average absolute deviation decreases from 2.44 (G2) to 1.72 kcal/mol (G3). The average absolute deviation for the 22 hydrocarbons decreases from 1.29 to 0.68 kcal/mol while that for the 29 radicals decreases from 1.16 to 0.84 kcal/mol. Finally, the enthalpies for 15 inorganic hydrides improve slightly from 0.95 to 0.87 kcal/mol. With the exception of nonhydrogens, all of the subgroups have absolute average deviations of less than 1 kcal/mol using G3 theory.

The G3 average absolute deviations for the G2-1 and G2-2 subsets are shown in Fig. 3 for the different energies. In contrast to the G2 results in Fig. 1, G3 theory does not

TABLE II. Deviations of calculated enthalpies of formation from experiment.^a

Species	$\Delta H_f^0(298\text{ K})$		Deviation	
	Expt. ^b	G3	G3	G2
G2-1 test set				
LiH	33.3	33.0	0.3	0.6
BeH	81.7	82.2	-0.5	-1.5
CH	142.5	141.1	1.4	0.6
CH ₂ (³ B ₁)	93.7	92.4	1.3	-1.0
CH ₂ (¹ A ₁)	102.8	101.8	0.9	1.4
CH ₃	35.0	34.0	1.0	-0.1
CH ₄	-17.9	-18.2	0.3	0.7
NH	85.2	84.3	0.9	-1.1
NH ₂	45.1	44.5	0.6	0.1
NH ₃	-11.0	-10.2	-0.8	-0.2
OH	9.4	8.4	1.0	0.3
OH ₂	-57.8	-57.5	-0.3	0.3
FH	-65.1	-65.4	0.2	1.0
SiH ₂ (¹ A ₁)	65.2	63.1	2.1	2.9
SiH ₂ (³ B ₁)	86.2	84.9	1.3	0.5
SiH ₃	47.9	46.9	1.0	1.2
SiH ₄	8.2	7.3	0.9	2.2
PH ₂	33.1	32.6	0.5	0.2
PH ₃	1.3	3.1	-1.8	-0.7
SH ₂	-4.9	-4.5	-0.4	-0.1
CIH	-22.1	-21.9	-0.1	0.4
Li ₂	51.6	49.4	2.2	2.0
LiF	-80.1	-80.8	0.7	1.3
C ₂ H ₂	54.2	54.9	-0.7	-1.6
C ₂ H ₄	12.5	12.3	0.2	-0.2
C ₂ H ₆	-20.1	-20.4	0.3	0.5
CN	104.9	106.7	-1.8	-2.4
HCN	31.5	31.3	0.2	0.3
CO	-26.4	-26.7	0.3	1.8
HCO	10.0	9.7	0.3	0.7
H ₂ CO	-26.0	-26.6	0.6	2.0
H ₃ COH	-48.0	-48.1	0.1	1.4
N ₂	0.0	2.1	-2.1	-1.3
H ₂ NNH ₂	22.8	24.9	-2.1	-0.9
NO	21.6	21.8	-0.2	0.6
O ₂	0.0	1.1	-1.1	-2.4
HOOH	-32.5	-31.3	-1.2	-0.2
F ₂	0.0	0.7	-0.7	-0.3
CO ₂	-94.1	-95.3	1.2	2.7
Na ₂	34.0	30.0	4.0	2.4
Si ₂	139.9	138.0	1.9	-0.4
P ₂	34.3	35.5	-1.2	-1.3
S ₂	30.7	31.6	-0.9	-3.2
Cl ₂	0.0	1.1	-1.1	-1.4
NaCl	-43.6	-44.8	1.3	1.2
SiO	-24.6	-23.9	-0.7	-1.7
SC	66.9	65.8	1.1	1.0
SO	1.2	1.7	-0.5	-2.6
ClO	24.2	25.9	-1.7	-2.2
FCI	-13.2	-12.5	-0.7	0.7
Si ₂ H ₆	19.1	17.7	1.4	2.9
CH ₃ Cl	-19.6	-19.5	-0.1	0.9
H ₃ CSH	-5.5	-5.1	-0.4	-0.2
HOCl	-17.8	-17.4	-0.4	0.5
SO ₂	-71.0	-67.1	-3.8	-5.0
G2-2 test set				
BF ₃	-271.4	-270.9	-0.5	0.0
BCl ₃	-96.3	-96.3	0.0	2.0
AlF ₃	-289.0	-290.1	1.1	-1.4
AlCl ₃	-139.7	-143.0	3.3	2.8
CF ₄	-223.0	-223.9	0.9	5.5
CCl ₄	-22.9	-24.6	1.7	2.8
COS	-33.1	-35.9	2.8	2.7
CS ₂	28.0	24.7	3.3	2.1

TABLE II. (Continued.)

Species	$\Delta H_f^0(298\text{ K})$		Deviation	
	Expt. ^b	G3	G3	G2
COF ₂	-149.1 ^c	-145.7	-3.4	-0.5
SiF ₄	-386.0	-384.9	-1.1	-7.1
SiCl ₄	-158.4	-158.4	0.0	3.8
N ₂ O	19.6	21.4	-1.7	-0.6
ClNO	12.4	13.4	-1.0	0.8
NF ₃	-31.6	-31.6	0.1	3.7
PF ₃	-229.1	-224.2	-4.8	-5.4
O ₃	34.1	34.9	-0.8	1.1
F ₂ O	5.9	6.5	-0.6	0.5
ClF ₃	-38.0	-36.0	-1.9	0.4
C ₂ F ₄	-157.4	-162.3	4.9	8.2
C ₂ Cl ₄	-3.0	-6.4	3.4	4.6
CF ₃ CN	-118.4	-120.2	1.8	4.8
CH ₃ CCH (propyne)	44.2	44.4	-0.2	-1.5
CH ₂ =C=CH ₂ (allene)	45.5	45.0	0.5	-0.9
C ₃ H ₄ (cyclopropene)	66.2	68.4	-2.2	-2.9
CH ₃ CH=CH ₂ (propylene)	4.8	4.7	0.0	-0.5
C ₃ H ₆ (cyclopropane)	12.7	13.4	-0.7	-0.9
C ₃ H ₈ (propane)	-25.0	-25.3	0.3	0.4
CH ₂ CHCHCH ₂ (butadiene)	26.3	26.7	-0.4	-1.7
C ₄ H ₆ (2-butyne)	34.8	35.2	-0.4 ^d	-2.1
C ₄ H ₆ (methylene cyclopropane)	47.9	46.4	1.5	0.3
C ₄ H ₆ (bicyclobutane)	51.9	54.5	-2.6	-3.0
C ₄ H ₆ (cyclobutene)	37.4	39.5	-2.1	-2.9
C ₄ H ₈ (cyclobutane)	6.8	6.8	0.0	-0.2
C ₄ H ₈ (isobutene)	-4.0	-4.0	0.0	-0.6
C ₄ H ₁₀ (trans butane)	-30.0	-30.4	0.4	0.4
C ₄ H ₁₀ (isobutane)	-32.1	-32.3	0.2	0.3
C ₅ H ₈ (spiropentane)	44.3	44.7	-0.4	-1.4
C ₆ H ₆ (benzene)	19.7	20.4	-0.6	-3.9
CH ₂ F ₂	-107.7	-108.4	0.7	3.1
CHF ₃	-166.6	-167.1	0.5	4.3
CH ₂ Cl ₂	-22.8	-22.3	-0.5	0.6
CHCl ₃	-24.7	-24.6	0.0	1.0
CH ₃ NH ₂ (methylamine)	-5.5	-4.5	-1.0	0.0
CH ₃ CN (methyl cyanide)	18.0	17.8	0.2	-0.1
CH ₃ NO ₂ (nitromethane)	-17.8	-17.8	0.0	2.7
CH ₃ ONO (methyl nitrite)	-15.9	-15.7	-0.2	2.7
CH ₃ SiH ₃ (methyl silane)	-7.0	-6.8	-0.2	0.4
HCOOH (formic acid)	-90.5	-90.6	0.1	2.0
HCOOCH ₃ (methyl formate)	-85.0	-86.6	1.6	3.8
CH ₃ CONH ₂ (acetamide)	-57.0	-55.9	-1.1	0.2
C ₂ H ₄ NH (aziridine)	30.2	31.4	-1.2	-0.3
NCCN (cyanogen)	73.3	73.6	-0.3	-1.5
(CH ₃) ₂ NH (dimethylamine)	-4.4	-3.5	-0.9	0.3
CH ₃ CH ₂ NH ₂ (trans ethylamine)	-11.3	-11.3	0.0	0.8
CH ₂ CO (ketene)	-11.4	-12.1	0.8	0.8
C ₂ H ₄ O (oxirane)	-12.6	-12.6	0.0	1.3
CH ₃ CHO (acetaldehyde)	-39.7	-39.8	0.1	1.3
HCOCOH (glyoxal)	-50.7	-51.6	0.9	2.9
CH ₃ CH ₂ OH (ethanol)	-56.2	-56.3	0.1	1.0
CH ₃ OCH ₃ (dimethylether)	-44.0	-44.4	0.4	2.0
C ₂ H ₄ S (thiirane)	19.6	18.8	0.8	0.7
(CH ₃) ₂ SO (dimethyl sulfoxide)	-36.2	-34.7	-1.5	-1.4
C ₂ H ₅ SH (ethanethiol)	-11.1	-10.7	-0.4	-0.4
CH ₃ SCH ₃ (dimethyl sulfide)	-8.9	-8.9	0.0	0.2
CH ₂ =CHF (vinyl fluoride)	-33.2	-34.4	1.2	1.7
C ₂ H ₅ Cl (ethyl chloride)	-26.8	-26.7	-0.1	0.8
CH ₂ =CHCl (vinyl chloride)	8.9	5.3	3.6	3.7
CH ₂ =CHCN (acrylonitrile)	43.2	44.8	-1.6	-2.7
CH ₃ COCH ₃ (acetone)	-51.9	-52.0	0.0	1.1
CH ₃ COOH (acetic acid)	-103.4	-103.3	-0.1	1.5
CH ₃ COF (acetyl fluoride)	-105.7	-105.8	0.1	2.0

TABLE II. (Continued.)

Species	$\Delta H_f^0(298\text{ K})$		Deviation	
	Expt. ^b	G3	G3	G2
CH ₃ COCl (acetyl chloride)	-58.0	-58.2	0.2	1.8
CH ₃ CH ₂ CH ₂ Cl (propyl chloride)	-31.5	-31.9	0.4	1.1
(CH ₃) ₂ CHOH (isopropanol)	-65.2	-65.7	0.5	1.2
C ₂ H ₅ OCH ₃ (methyl ethyl ether)	-51.7	-52.8	1.1	2.3
(CH ₃) ₃ N (trimethylamine)	-5.7	-5.9	0.2	1.4
C ₄ H ₄ O (furan)	-8.3	-7.8	-0.5	-1.0
C ₄ H ₄ S (thiophene)	27.5	27.7	-0.2	-2.4
C ₄ H ₅ N (pyrrole)	25.9	27.1	-1.2	-2.2
C ₅ H ₅ N (pyridine)	33.6	33.7	-0.1	-2.2
H ₂	0.0	-0.5	0.5	1.1
HS	34.2	33.7	0.5	-0.3
CCH	135.1	136.3	-1.2	-3.6
C ₂ H ₃ (² A')	71.6	70.5	1.1	-1.1
CH ₃ CO (² A')	-2.4	-2.5	0.1	0.4
H ₂ COH (² A)	-4.1	-3.9	-0.1	-0.3
CH ₃ OCS (² A')	4.1	4.9	-0.8	-0.7
CH ₃ CH ₂ O (² A'')	-3.7	-2.5	-1.2	-1.4
CH ₃ S (² A')	29.8	29.0	0.8	-0.1
C ₂ H ₅ (² A')	28.9	28.7	0.2	-1.0
(CH ₃) ₂ CH (² A')	21.5	21.5	0.0	-1.3
(CH ₃) ₃ C (t-butyl radical)	12.3	13.0	-0.7	-2.0
NO ₂	7.9	8.1	-0.2	0.7

^aEnthalpies and deviations in kcal/mol. Deviation=Experiment-Theory.

^bSee Refs. 1, 3-5 for experimental references.

^cNew value from Ref. 32.

^dCalculated with the GAUSSIAN98 computer program.

decrease in accuracy for larger molecules in the G2-2 subset, with the exception of ionization energies. Thus, G3 theory has eliminated some significant deficiencies in G2 theory.

B. Assessment of the new features of G3 theory

In Table VII we separate the effects of the new features of G3 theory on the average absolute deviations for the 299 test energies. The results in the table indicate that all of the new features make a contribution to the improvement of G3 theory over G2 theory. We now discuss the role of the new features in more detail.

1. Basis sets

A significant decrease in the average absolute deviation (0.14 kcal/mol) results from use of the new basis set, G3large, in the MP2 calculation (step 4d). This basis set has a better balance of polarization functions, i.e., *3d2f* on the second-row and *2df* on the first-row, than the 6-311+G(*3df,2p*) basis set used in G2 theory. The polarization functions are similar to those used by Petersson *et al.*²⁷ in the CBS-Q method (see below). The G3large basis also uses a neutral atom basis set for P, S, and Cl, whereas 6-311+G(*3df,2p*) is based on an atomic anion basis set for these elements (see Appendix). These features, along with the spin-orbit correction (step 5), help eliminate deficiencies found in the G2 energies of nonhydrogen species. For example, the errors in the enthalpies of CF₄, CCl₄, SiF₄, and SiCl₄ are reduced from 5.5, 2.8, -7.1, and 3.8 kcal/mol, respectively, in G2 theory to 0.9, 1.7, -1.1, and 0.0 kcal/mol, respectively, in G3 theory. There remain several nonhydrogen systems with large errors and these are discussed

TABLE III. Deviations of calculated ionization potentials from experiment.^a

Species	Ionization potential		Deviation	
	Expt. ^b	G3	G3	G2
G2-1 test set				
Li	124.3	124.5	-0.2	1.1
Be	214.9	218.1	-3.2	-2.2
B	191.4	189.9	1.5	2.3
C	259.7	258.5	1.1	1.8
N	335.3	334.5	0.8	1.5
O	313.9	312.4	1.4	1.9
F	401.7	401.0	0.7	0.8
Na	118.5	117.9	0.6	4.4
Mg	176.3	179.5	-3.2	0.0
Al	138.0	137.4	0.6	1.2
Si	187.9	187.4	0.5	1.2
P	241.9	241.3	0.6	1.0
S	238.9	236.8	2.1	3.7
Cl	299.1	297.3	1.8	2.8
CH ₄	291.0	291.8	-0.8	-1.4
NH ₃	234.8	233.8	0.9	-0.3
OH	300.0	298.3	1.7	0.8
OH ₂	291.0	290.4	0.6	-0.2
FH	369.9	370.0	-0.1	-1.1
SiH ₄	253.7	254.2	-0.5	-0.3
PH	234.1	234.9	-0.8	1.4
PH ₂	226.5	226.4	0.0	2.2
PH ₃	227.6	227.9	-0.3	0.0
SH	239.1	238.1	1.0	1.3
SH ₂ (² B ₁)	241.4	240.8	0.6	0.9
SH ₂ (² A ₁)	294.7	294.3	0.4	0.7
ClH	294.0	293.3	0.7	0.8
C ₂ H ₂	262.9	263.1	-0.2	-0.5
C ₂ H ₄	242.4	243.5	-1.2	-1.6
CO	323.1	323.2	-0.1	-0.1
N ₂ (² Σ cation)	359.3	358.9	0.4	0.4
N ₂ (² Π cation)	385.1	384.4	0.7	0.8
O ₂	278.3	282.4	-4.0	-2.3
P ₂	242.8	243.3	-0.5	-0.3
S ₂	215.8	216.3	-0.5	1.9
Cl ₂	265.2	265.8	-0.6	-0.3
ClF	291.9	292.0	-0.1	0.3
SC	261.3	262.7	-1.4	-2.0
G2-2 test set				
H	313.6	314.4	-0.6	-0.1
He	567.0	566.6	0.5	1.1
Ne	497.2	497.6	-0.4	-1.2
Ar	363.4	361.8	1.6	1.5
BF ₃	358.8	359.9	-1.1	-1.2
BCl ₃	267.5	268.6	-1.1	-1.5
B ₂ F ₄	278.3	271.3	7.0	7.3
CO ₂	317.6	315.9	1.7	1.5
CF ₂	263.3	263.8	-0.5	-0.6
COS	257.7	257.8	-0.2	0.3
CS ₂	232.2	232.8	-0.6	-0.7
CH ₂	239.7	239.7	0.0	1.9
CH ₃	227.0	227.6	-0.6	1.4
C ₂ H ₅ (² A')	187.2	188.3	-1.1	1.1
C ₃ H ₄ (cyclopropene)	223.0	224.5	-1.5	-2.1
CH ₂ =C=CH ₂	223.5	223.6	-0.2	-1.0
sec-C ₃ H ₇	170.0	172.1	-2.2	-0.6
C ₆ H ₆	213.2	214.7	-1.5	-1.9
CN	313.6	319.6	-6.1	-3.1
CHO	187.7	188.2	-0.5	0.9
H ₂ COH (² A)	174.2	173.7	0.5	2.4
CH ₃ O (² A')	247.3	247.7	-0.3	-1.3
CH ₃ OH	250.2	251.8	-1.6	-2.5
CH ₃ F	287.6	292.5	-5.0	-5.3
CH ₂ S	216.2	215.8	0.4	0.0

TABLE III. (Continued.)

Species	Ionization potential		Deviation	
	Expt. ^b	G3	G3	G2
CH ₂ SH	173.8	173.0	0.8	2.7
CH ₃ SH	217.7	218.1	-0.4	-0.5
CH ₃ Cl	258.7	260.4	-1.7	-1.9
C ₂ H ₅ OH ^c	241.4	239.7	1.7	1.4
CH ₃ CHO	235.9	236.9	-1.0	-1.8
CH ₃ OF	261.5	262.9	-1.4	-1.5
C ₂ H ₄ S (thiirane)	208.7	209.1	-0.3	-0.4
NCCN	308.3	309.0	-0.6	-0.5
C ₄ H ₄ O (furan)	203.6	205.0	-1.3	-1.8
C ₄ H ₅ N (pyrrole)	189.3	188.7	0.6	2.9
B ₂ H ₄	223.7	221.6	2.1	1.6
NH	311.1	311.2	-0.1	1.8
NH ₂	256.9	256.4	0.5	-0.8
N ₂ H ₂	221.1	223.1	-2.0	-3.0
N ₂ H ₃	175.5	175.6	-0.1	1.6
HOF	293.1	293.3	-0.2	0.1
SiH ₂ (¹ A ₁)	211.0	212.0	-1.0	-0.5
SiH ₃	187.6	188.0	-0.4	1.9
Si ₂ H ₂	189.1	190.4	-1.4	-1.8
Si ₂ H ₄	186.6	187.8	-1.2	-0.7
Si ₂ H ₅	175.3	177.5	-2.3	-0.2
Si ₂ H ₆	224.6	223.6	1.0	0.8

^aIonization potentials and deviations in kcal/mol. Deviation=Experiment - Theory.

^bSee Refs. 1, 3, 4, 6 for experimental references.

^cIn the calculation of the G3 ionization potential of C₂H₅OH, a lower energy structure was found for C₂H₅OH⁺ than was used in Ref. 6. The G2 ionization potential has been revised accordingly. The new structure can be found at the web site in Ref. 16.

in the next section. The G3large basis is also responsible for a significant part of the large decrease in the average absolute deviation of the substituted hydrocarbons from 1.48 (G2) to 0.56 (G3) kcal/mol.

The use of the 6-31G basis in place of 6-311G in steps 4a-4c contributes to a lesser degree to the better agreement with experiment for G3 enthalpies of formation for neutrals (see Table VII). This change also results in significant savings of computer resources (see below).

The complete basis-set CBS-Q method of Petersson *et al.*²⁷ is a composite technique for calculation of thermochemical data similar in nature to G2 theory. The largest basis set used in this method is the 6-311+ +G(3d2f,2df,2p) basis set, which is similar to the G3large basis in that it also uses 3d2f polarization on the second-row and 2df polarization on the first-row. Overall, the CBS-Q method has an average absolute deviation about the same as G2 theory for the 148 enthalpies in the G2/97 test set.²⁸ G3 theory has a significantly lower average absolute deviation.

2. Higher level correction

A significant decrease in the average absolute deviation for the 299 test cases of the G2/97 test set (0.21 kcal/mol) occurs from use of the new higher level correction. There is a large improvement in the average absolute deviation for electron affinities and ionization potentials (see Table VII): The average absolute deviation of ionization potentials de-

TABLE IV. Deviations of calculated electron affinities from experiment.^a

Species	Electron affinity		Deviation	
	Expt. ^b	G3	G3	G2
G2-1 test set				
C	29.1	27.5	1.5	1.6
O	33.7	30.8	2.8	1.4
F	78.4	78.4	0.0	-1.8
Si	31.9	31.8	0.2	0.7
P	17.2	16.4	0.8	2.5
S	47.9	47.6	0.3	1.7
Cl	83.4	83.2	0.1	0.3
CH	28.6	27.2	1.4	2.6
CH ₂	15.0	13.4	1.5	-0.3
CH ₃	1.8	-0.9	2.8	1.0
NH	8.8	4.5	4.2	2.2
NH ₂	17.8	16.1	1.7	-0.1
OH	42.2	41.0	1.2	-1.0
SiH	29.4	29.3	0.2	2.2
SiH ₂	25.9	24.8	1.1	3.1
SiH ₃	32.5	32.9	-0.4	-0.2
PH	23.8	22.6	1.1	1.7
PH ₂	29.3	29.3	0.0	0.5
HS	54.4	53.5	0.9	1.3
O ₂	10.1	9.2	0.9	-0.6
NO	0.5	-0.1	0.5	2.0
CN	89.0	90.6	-1.6	-2.6
PO	25.1	26.5	-1.4	1.2
S ₂	38.3	38.5	-0.2	0.2
Cl ₂	55.1	56.9	-1.7	0.3
G2-2 test set				
Li	14.3	17.1	-2.9	-3.1
B	6.4	4.7	1.7	2.0
Na	12.6	16.3	-3.6	-2.9
Al	10.2	9.0	1.2	2.0
C ₂	75.5	72.8	2.7	3.9
C ₂ O	52.8	52.8	0.0	-0.9
CF ₂	4.1	4.1	0.1	2.0
NCO	83.2	82.5	0.7	-0.3
NO ₂	52.4	52.6	-0.1	-1.6
O ₃	48.5	48.5	0.0	0.9
OF	52.4	51.9	0.4	-0.8
SO ₂	25.5	27.3	-1.7	-1.1
S ₂ O	43.3	45.9	-2.6	-0.8
C ₂ H	68.5	69.1	-0.6	-2.7
C ₂ H ₃	15.4	15.1	0.3	-1.8
H ₂ C=C=C	41.4	42.0	-0.6	1.1
H ₂ C=C=CH	20.6	20.9	-0.3	-2.4
CH ₂ CHCH ₂	10.9	10.2	0.7	-1.2
HCO	7.2	7.1	0.1	-0.6
HCF	12.5	12.2	0.3	1.9
CH ₃ O	36.2	35.8	0.4	-1.2
CH ₃ S	43.1	42.9	0.2	0.1
CH ₂ S	10.7	10.7	0.0	1.8
CH ₂ CN	35.6	35.0	0.6	-0.9
CH ₂ NC	24.4	25.5	-1.1	-2.7
CHCO	54.2	53.3	0.9	-0.3
CH ₂ CHO	42.1	42.3	-0.2	-1.2
CH ₃ CO	9.8	9.3	0.5	-0.5
CH ₃ CH ₂ O	39.5	40.4	-0.9	-2.2
CH ₃ CH ₂ S	45.0	45.2	-0.2	-0.2
LiH	7.9	9.1	-1.2	0.5
HNO	7.8	6.8	1.0	2.2
HO ₂	24.9	24.2	0.6	-0.8

^aElectron affinities and deviations in kcal/mol. Deviation=Experiment - Theory.

^bSee Refs. 1, 3, 4, 6 for experimental references.

creases by 0.24 kcal/mol and that of electron affinities decreases by 0.32 kcal/mol. The new higher level correction also contributes to better agreement with experiment for enthalpies of the neutrals, especially radicals. For example, for

TABLE V. Deviations of calculated proton affinities from experiment.^a

Species	Proton affinity		Deviation	
	Expt. ^b	G3	G3	G2
NH ₃	202.5	203.1	-0.6	0.0
OH ₂	165.1	163.4	1.7	2.0
C ₂ H ₂	152.3	152.8	-0.5	-1.3
SiH ₄	154.0	152.3	1.7	1.0
PH ₃	187.1	185.3	1.8	0.9
SH ₂	168.8	167.0	1.8	1.1
ClH	133.6	132.6	1.0	0.6
H ₂	100.8	99.3	1.5	1.6

^aProton affinities and deviations in kcal/mol. Deviation=Experiment - Theory.

^bSee Refs. 1, 3, 4 for experimental references.

triplet molecules such as O₂ and S₂ the deviations with experiment decrease from -2.4 to -1.1 kcal/mol and -3.2 to -0.9 kcal/mol, respectively. Another example is singlet-triplet energy differences. The G2 and G3 singlet-triplet energy differences for CH₂ are 6.7 and 9.5 kcal/mol, respectively, compared to 9.1 from experiment and for SiH₂ they are 23.4 and 21.9 kcal/mol, respectively, compared to 21.0 from experiment.

The higher level correction (HLC) in G3 theory has been modified in several respects from that in G2 theory. First, a separate correction is used for atoms and molecules. This distinction is not very important for pairs of electrons as *A* (6.386 mhartrees) and *C* (6.219 mhartrees) have similar values. The distinction is significant for unpaired electrons as the correction for each unpaired electron is larger in molecules (*B*=2.977 mhartrees) than in atoms (*D*=1.185 mhartrees). This reflects a larger deficiency in the energy of an unpaired electron in a molecule than in an atom and is especially important for the evaluation of ionization potentials, electron affinities, and triplet state energies as noted above. Secondly, the HLC per unpaired electron is optimized in G3 theory, whereas in G2 theory it was arbi-

TABLE VI. Comparison of average absolute deviations and root-mean-square deviations for G2 and G3 theory.^a

Type	Average absolute deviation, kcal/mol		Root-mean-square deviation, kcal/mol	
	G2	G3	G2	G3
Enthalpies of formation (148)	1.56	0.94	2.10	1.35
Nonhydrogen (35)	2.44	1.72	3.14	2.19
Hydrocarbons (22)	1.29	0.68	1.66	1.00
Subst. hydrocarbons (47)	1.48	0.56	1.81	0.85
Inorganic hydrides (15)	0.95	0.87	1.32	1.09
Radical (29)	1.16	0.84	2.25	0.98
Ionization energies (85)	1.41	1.13	1.84	1.65
Electron affinities (58)	1.41	1.00	1.68	1.38
Proton affinities (8)	1.08	1.34	1.22	1.44
All (299)	1.48	1.02	1.93	1.45

^aHLC parameters for G3 theory: *A*=6.386 mhartrees, *B*=2.977 mhartrees, *C*=6.219 mhartrees, *D*=1.185 mhartrees. The average absolute deviations for G2 theory are slightly different from those reported in Refs. 5 and 6 due to the use of a new value for the enthalpy of formation of COF₂ (see Table II) and ionization potential of C₂H₅OH (see Table III).

TABLE VII. Effect of different modifications on G2 theory.^a

	Average Absolute deviation, kcal/mol				
	All (299)	Neutral enthalpies (148)	IPs	EAs	PAs
G2	1.48	1.56	1.41	1.41	1.08
G2+ <i>I</i>	1.46	1.50	1.41	1.44	1.10
G2+ <i>II</i>	1.34	1.28	1.43	1.35	1.21
G2+ <i>III</i>	1.44	1.44	1.45	1.45	1.08
G2+ <i>IV</i>	1.27	1.42	1.18	1.09	1.08
G2+ <i>I,II,III,IV</i>	1.09	1.09	1.15	1.00	1.21
[G3(noFULL)]					
G2+ <i>I,II,III,IV,V</i> [G3]	1.02	0.94	1.13	1.00	1.34

^a*I*=use of 6-31G(*d*) basis set for MP4 and QCISD(T) calculations [steps 4(a), 4(b), 4(c)]; *II*=use of G3large basis set in MP2 calculation [step 4(d), MP2(FC result)]; *III*=include spin-orbit correction [$\Delta E(\text{SO})$]; *IV*=use of new higher level correction [step 6, without inclusion of the spin-orbit correction]; *V*=includes correction for core correlation. In each case the HLC as defined for G2 theory was re-optimized, except for G3(noFULL) and G2+*IV* for which the G3 definition of the HLC was optimized.

trarily set to 0.19 mhartrees based on the difference between the exact and the calculated energy of hydrogen atom. Finally, the parameters for the HLC are obtained from a fit to the full set of experimental energies in G3 theory, whereas the HLC was obtained from a fit to only the atomization energies of the neutral molecules in G2 theory. The HLC in G3 theory is empirical in nature similar to G2 theory, although it now is based on four parameters compared to two in G2 theory. It remains molecule independent as in G2 theory.

The correction for breaking an electron pair is smaller in G3 theory compared to what it is for G2 theory due to reduced deficiencies in the energy calculation. The HLC in G3 theory corresponds to 3.20 and 3.11 mhartrees per paired electron in molecules and atoms, respectively, and 2.98 and 1.18 mhartrees per unpaired electron in molecules and atoms, respectively. Thus, the correction for breaking an electron pair in an atomization reaction is twice (3.20-1.18) or 4.04 mhartrees. This is smaller than the correction for breaking an electron pair in G2 theory (4.62 mhartrees). Surprisingly, the correction for breaking an electron pair in a bond separation reaction in which the products are both molecules, e.g., C₂H₆→2CH₃, is only 0.44 mhartrees [twice (3.20-

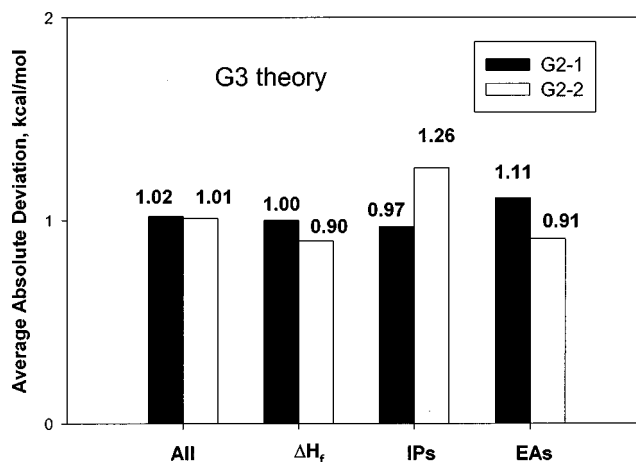


FIG. 3. Average absolute deviations with experiment for G3 theory on the G2/97 test set broken down into the G2-1 and G2-2 test sets.

2.98)]. In G2 theory the correction for this type of electron pair breaking is 4.62 mhartrees since the HLC parameters are the same for both atoms and molecules. Similarly, the correction for breaking an electron pair in ionization potentials and electron affinities is smaller in G3 than G2 theory.

We tested several constraints of the parameters in the higher level correction. A two parameter fit ($A, C=A, B=A/2, D$) with the same correction for pairs of electrons in molecules and atoms ($C=A$) and the correction for unpaired electrons in molecules equal to one-half that of paired electrons in molecules ($B=A/2$) gives an average absolute deviation of 1.04 kcal/mol. This result is slightly larger than the average absolute deviation of G3 theory (1.02 kcal/mol). An alternate two parameter fit ($A, C=A, B, D=B$), having the same correction for pairs of electrons in molecules and atoms ($C=A$) and the same correction for unpaired electrons in molecules and atoms ($D=B$), results in an average absolute deviation from experiment of 1.21 kcal/mol. The larger average absolute deviation for the latter case indicates the importance of having separate corrections for unpaired electrons in atoms and molecules.

3. Core-related correlation

The incorporation of the correction taking into account some core-related correlation in Eqn. (4), i.e., the MP2(full)/G3large calculation, improves the average absolute deviation from 1.09 to 1.02 kcal/mol (1.09→0.94 kcal/mol for the 148 enthalpies of formation). This correction eliminates some large errors for species with unsaturated rings such as benzene. Inclusion of this correction [G3(noFULL)→G3] reduces the deviation from experiment for benzene from -2.8 to -0.6 kcal/mol. At the G2 level the deviation was -3.9 kcal/mol. The other species with unsaturated rings such as cyclopropene, cyclobutene, thiophene, pyrrole, and pyridine also improve with inclusion of this term.

The significance of core-related correlation in the calculation of atomization energies of some small hydrocarbons has been noted by others.¹⁸⁻²⁰ Martin¹⁸ used a decontraction of Woon and Dunning's²⁹ correlation consistent triple-zeta basis set with core polarization functions added and found an increase in the atomization energies of CH₄ and C₂H₂ of 1.25 and 2.44 kcal/mol, respectively, when core correlation was included in the calculation. Partridge and Bauschlicher²⁰ reported similar results for these molecules. Increases of 1.16 and 2.08 kcal/mol are found for the atomization energies of CH₄ and C₂H₂, respectively, from a comparison of MP2(full)/G3large and MP2(frozen core)/G3large calculations. A more detailed analysis of the effect of core-related correlation will be presented in a separate study.³⁰

We note that the total energies from G3 theory remain significantly above the exact energies. For example, the G3 energy of fluorine atoms is 40.6 mhartrees above the estimated exact energy.³ However, this is an improvement compared to G2 theory which gives a fluorine energy that is 92.8 mhartrees above the exact value. The improvement compared to G2 theory is due to the inclusion of core correlation; the remaining deficiency is because the G3large basis set is not large enough in the core region.

TABLE VIII. Comparison of cpu times and disk storage used in single point energy calculations on benzene and silicon tetrachloride.^a

Method	Benzene (D_{6h})		SiCl ₄ (T_d)	
	Cpu time	disk storage	cpu time	disk storage
G2	851	4.3	606	2.3
G3	455	3.4	249	1.2

^aCalculations done on a Cray YMP-C90. Total time in minutes and maximum storage in Gb (times for geometry optimization and zero-point energy calculation are not included).

4. Timings

In addition to improving the accuracy, the use of the 6-31G(*d*) basis set in step 4 substantially decreases the amount of computational time and disk space needed in calculations. Timings for two large molecules, benzene and silicon tetrachloride, are given in Table VIII. The main reduction in time comes from the use of MP4/6-31G(2*df*,*p*) in place of MP4/6-311G(2*df*,*p*) and QCISD(T)/6-31G(*d*) in place of QCISD(T)/6-311G(*d*,*p*) in G3 theory compared to G2 theory. The decrease in cpu time is nearly a factor of 2 for benzene and nearly a factor of 3 for SiCl₄.

C. Results for specific systems

The histograms in Fig. 4 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 -2.0 to +2.0 kcal/mol. This is substantially better than G2 theory for which about 74% of the deviations fall in this range. The

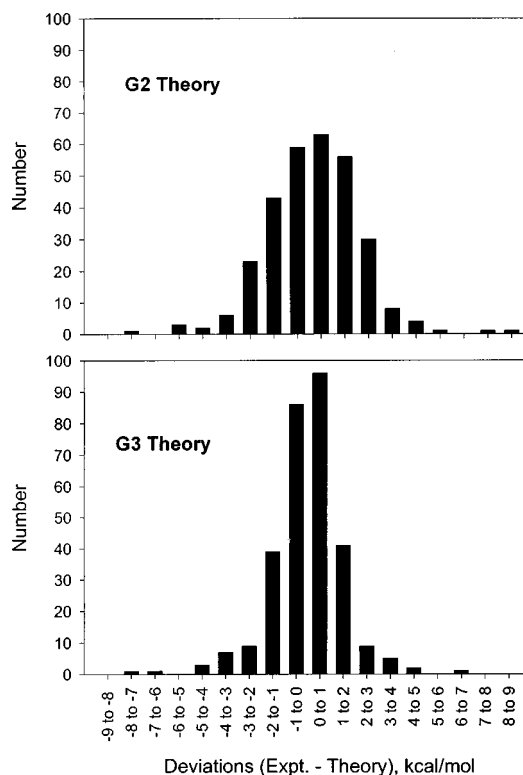


FIG. 4. Histogram of G2 and G3 deviations for the G2/97 test set. Each vertical bar represents deviations in a one kcal/mol range.

percentage for G3 theory is even better than that of G2 theory for the original G2 test set of small molecules. We now discuss some of the larger deviations and possible reasons for them.

1. Enthalpies of formation of neutrals

Seventeen of the 148 enthalpies of formation in the G2/97 test deviate by more than ± 2 kcal/mol from experiment at the G3 level of theory (compared to 41 for G2 theory) and of these nine deviate by more than ± 3 kcal/mol. Eleven of the problem systems are in the nonhydrogen subgroup. The C_2F_4 and C_2Cl_4 molecules have deviations of 4.9 and 3.4 kcal/mol from experiment. The reason for these large deviations is unclear, although we note that an isodesmic bond separation scheme³¹ using some accurate experimental data also gives similarly large deviations with experiment. The deviation for COF_2 is -3.4 kcal/mol based on a recent experimental study by Ruscic³² which gave a lower limit of -149.1 kcal/mol for the enthalpy of formation of COF_2 compared to the JANAF³³ value of -152.7 kcal/mol that we previously used. We have used the new and more accurate value in this analysis. The G3 enthalpy of formation of SO_2 has a deviation of -3.8 kcal/mol from experiment, which is slightly better than the deviation for G2 theory. Recent studies^{34,35} have shown the need for very large basis sets to describe the bonding in SO_2 . The PF_3 molecule also has a large negative deviation from experiment (-4.8 kcal/mol). A similar deviation is present at the G2 level. The negative deviation could be for the same reason as SO_2 . In both cases the first row analogs (O_3 and NF_3) are in good agreement with experiment. The sodium dimer has a deviation of 4.0 kcal/mol at the G3 level. The weak nature of this bond may require a higher level of theory. G3 theory has positive deviations of 2 to 3 kcal/mol with experiment for CS_2 (3.3 kcal/mol), COS (2.8 kcal/mol), and $AlCl_3$ (3.3 kcal/mol).

Three hydrocarbons with strained ring systems have deviations slightly greater than 2.0 kcal/mol Cyclopropene (-2.2 kcal/mol), cyclobutene (-2.1 kcal/mol), and bicyclobutane (-2.6 kcal/mol). Of the 47 substituted hydrocarbons only one has a deviation slightly greater than ± 2 kcal/mol: CH_2CHCl (3.6 kcal/mol). We note that an isodesmic scheme³¹ also gives an unusually large deviation for the latter species and may indicate a problem with the experimental value. Two of the 15 inorganic hydrides have deviations slightly greater than ± 2 kcal/mol: SiH_2 (2.1 kcal/mol) and H_4N_2 (-2.1 kcal/mol). Finally, the enthalpies of formation of all 29 neutral radicals in the G2/97 test set have deviations within the range ± 2 kcal/mol.

2. Ionization potentials, electron affinities, and proton affinities

Ten of the 85 ionization potentials from G3 theory in Table III deviate by more than ± 2 kcal/mol from experiment compared to sixteen of the G2 ionization potentials. The largest deviation occurs for B_2F_4 (7.0 kcal/mol) and we have previously suggested that even though the quoted experimental uncertainty is small, there may be a problem with the experimental value because of the large geometry change.⁶

Three of the atomic ionization energies deviate by more than ± 2.0 kcal/mol: Be (-3.2 kcal/mol), Mg (-3.2 kcal/mol), and S (2.1 kcal/mol). The other six ionization potentials (IPs) that deviate by more than 2 kcal/mol are O_2 (-4.0 kcal/mol), C_3H_7 (-2.2 kcal/mol), CN (-6.1 kcal/mol), CH_3F (-5.0 kcal/mol), B_2H_4 (2.1 kcal/mol), and Si_2H_5 (-2.3 kcal/mol).

Six of the 58 electron affinities from G3 theory in Table IV deviate by more than 2 kcal/mol compared to 14 for G2 theory. Three of the G3 values that deviate by more than 2.0 kcal/mol are atomic electron affinities (O, Li, Na). The other three electron affinity (EAs) that deviate by more than 2 kcal/mol are CH_3 (2.8 kcal/mol), NH (4.2 kcal/mol), and C_2 (2.7 kcal/mol).

Eight proton affinities are included in the G2/97 test set. The G3 method performs very well for them, with all of the deviations being less than 2 kcal/mol. The number of proton affinities in the G2/97 test set is limited, but the results suggest that G3 theory should do as well as G2 theory for these energies.

IV. CONCLUSIONS

Gaussian-3 theory (G3 theory) for the calculation of molecular energies (atomization energies, enthalpies of formation, ionization potentials, electron affinities, proton affinities) of molecules containing first- (Li-F) and second-row (Na-Cl) atoms has been presented. This new theoretical procedure modifies G2 theory in several ways including (1) the use of the 6-31G basis set as the underlying basis for the MP4 and QCISD(T) single point corrections, (2) the use of $3d2f$ polarization functions on second row atoms and $2df$ on first-row atoms in the MP2 single point calculation, (3) inclusion of a spin-orbit correction for atoms, (4) a new formulation of the higher level correction, and (5) inclusion of core-related correlation. The latter feature uses a basis set introduced in this paper, referred to as G3large, which includes core polarization functions and a new derivation of the underlying 6-311G basis for the elements P, S, Cl, and Ar.

These changes correct many of the deficiencies found for G2 theory for the G2/97 test set^{5,6} of experimental energies. Of particular importance is the improvement for 35 nonhydrogen systems, such as SiF_4 and CF_4 , for which the average absolute deviation decreases from 2.44 kcal/mol (G2 theory) to 1.72 kcal/mol (G3 theory). Another significant improvement is found for the 47 substituted hydrocarbons in the test set for which the average absolute deviation decreases from 1.48 to 0.56 kcal/mol and only one molecule out of this subgroup deviates by more than 2 kcal/mol. The average absolute deviation for hydrocarbons decreases from 1.29 to 0.68 kcal/mol. Core-related correlation is found to be a significant factor, especially for species with unsaturated rings. The average absolute deviation for the 148 enthalpies of formation is reduced from 1.56 kcal/mol for G2 theory to 0.94 kcal/mol for G3 theory. The agreement with experiment improves for ionization energies and electron affinities as well. The overall average absolute deviation of G3 theory with experiment for the 299 energies is 1.02 kcal/mol com-

pared to 1.48 kcal/mol for G2 theory. Finally, G3 theory uses significantly less computational time than G2 theory because of the changes in the basis sets.

ACKNOWLEDGMENTS

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APPENDIX

Here we define the G3large basis used in the full MP2 calculation (step 4). This consists of an underlying *sp* basis, together with added diffuse and polarization functions. The underlying basis is:

Atoms H to Ne: 6-311G as defined by Krishnan *et al.*³⁶

Atoms Na to Ar: A modification of the McLean–Chandler basis.¹⁵

The modified McLean–Chandler basis is a segmented set, based on the (12*s*,9*p*) uncontracted exponents originally obtained by Huzinaga.³⁷ The segmentation used is [6,5] or

$$(12,9) \rightarrow (631111/42111), \quad (A1)$$

where one *s*-exponent is repeated in the first two contracted

TABLE IX. Exponents and coefficients of the G3large basis set for P, S, Cl, and Ar.^a The supplementary basis functions for this basis set are given in the Appendix and the core polarization functions are given in Table X.

Atom	Shell	Exponent	Coefficient	Atom	Shell	Exponent	Coefficient		
Phosphorus	<i>s</i>	77 492.400 000	7.869 212E-04	Chlorine	<i>s</i>	10 5819.000 000	7.423 627E-04		
		11 605.800 000	6.108 245E-03			15 872.000 000	5.747 318E-03		
		2645.960 000	3.139 689E-02			3619.650 000	2.964 876E-02		
		754.976 000	1.242 379E-01			1030.800 000	1.178 998E-01		
		248.755 000	3.811 538E-01			339.908 000	3.648 532E-01		
	91.156 500	5.595 372E-01	124.538 000		5.816 968E-01				
	<i>s</i>	91.156 500	1.641 617E-01		<i>s</i>	124.538 000	1.370 443E-01		
		36.225 700	6.259 097E-01			49.513 500	6.231 380E-01		
		15.211 300	2.620 744E-01			20.805 600	2.903 279E-01		
		4.713 800	1.000 000E+00			6.464 800	0.1000 00D+01		
		1.782 700	1.000 000E+00			2.525 400	0.1000 00D+01		
	<i>s</i>	0.342 500	1.000 000E+00		<i>s</i>	0.537 800	0.1000 00D+01		
		0.124 600	1.000 000E+00			0.193 500	0.1000 00D+01		
		<i>p</i>	384.840 000			8.967 875E-03	<i>p</i>	589.780 000	7.873 332E-03
			90.552 000			6.904 902E-02		139.850 000	6.155 460E-02
			28.806 000			2.928 770E-01		44.795 000	2.742 514E-01
	10.688 00		7.292 494E-01		16.612 000	7.498 994E-01			
	4.252 100		6.325 822E-01		6.599 500	6.147 640E-01			
	<i>p</i>	1.740 500	4.232 996E-01		<i>p</i>	2.714 100	4.413 416E-01		
		0.597 900	1.000 000E+00			0.952 800	1.000 000E+00		
0.229 200		1.000 000E+00	0.358 000	1.000 000E+00					
0.083 800		1.000 000E+00	0.125 000	1.000 000E+00					
Sulfur		<i>s</i>	93413.400 000	7.420 791E-04		Argon	<i>s</i>	118022.000 000	7.416 902E-04
	13961.700 000		5.787 658E-03	17683.500 000	5.786 362E-03				
	3169.910 000		2.994 067E-02	4027.770 000	2.990 098E-02				
	902.456 000		1.189 282E-01	1145.400 000	1.191 287E-01				
	297.158 000		3.681 822E-01	377.164 000	3.687 839E-01				
	<i>s</i>	108.702 000	5.776 336E-01	<i>s</i>	138.160 000		5.767 726E-01		
		108.702 000	1.427 905E-01		138.160 000		1.435 931E-01		
		43.155 300	6.246 934E-01		54.989 100		6.231 142E-01		
		18.107 900	2.834 835E-01		23.170 700		2.840 810E-01		
		5.570 500	1.000 000E+00		7.377 860		1.000 000E+00		
	<i>s</i>	2.142 700	1.000 000E+00	<i>s</i>	2.923 690		1.000 000E+00		
		0.434 000	1.000 000E+00		0.650 405		1.000 000E+00		
		0.157 000	1.000 000E+00		0.232 825		1.000 000E+00		
		495.040 000	8.196 253E-03		663.062 000		7.820 021E-03		
		117.220 000	6.364 204E-02		157.093 000		6.148 333E-02		
<i>p</i>	37.507 000	2.788 060E-01	<i>p</i>	50.231 100	2.754 731E-01				
	13.910 000	7.447 404E-01		18.635 300	7.488 402E-01				
	5.504 500	6.168 248E-01		7.446 540	6.282 210E-01				
	2.243 300	4.402 946E-01		3.095 700	4.260 202E-01				
	0.776 200	1.000 000E+00		1.106 460	1.000 000E+00				
<i>p</i>	0.291 900	1.000 000E+00	<i>p</i>	0.415 601	1.000 000E+00				
	0.102 900	1.000 000E+00		0.145 449	1.000 000E+00				

^aThe exponents and coefficients for the other elements (H–Si) are the same as the 6-311G basis set (see Appendix). The complete basis set is available on the internet. (Ref. 16).

s-functions. For Na, Mg, Al, and Si, the contraction coefficients are those listed by McLean and Chandler;¹⁵ the basis is then exactly as returned by 6-311G in the GAUSSIAN 94 program.²⁷ For neutral P, S, Cl, and Ar, McLean and Chandler use a segmentation (631111/52111). In G3large, we use the segmentation (A1) over the whole row to give a uniform type of splitting in the atomic *2p*-region. This turns out to be important in getting satisfactory results for core-related correlation effects. The new contraction coefficients were obtained by minimization of the (spin-restricted) atomic energy of the neutral ground-state atoms, using a modified version of the ATOMSCF program.³⁸ The new bases for P, S, Cl, and Ar are listed in Table IX.¹⁶ (Note that the symbol 6311G returns McLean–Chandler sets appropriate to anions for P, S and Cl in the GAUSSIAN94 program.²⁷)

The supplementary diffuse functions consist of a single uncontracted *s*-function for H, He (exponents 0.036, 0.086) and a single uncontracted set of (*sp*) functions for atoms Li to Ar, using standard exponents:

Li(0.0074), Be(0.0207), B(0.0315), C(0.0438), N(0.0639),
O(0.0845), F(0.1076), Ne(0.1300),
Na(0.0076), Mg(0.0146), Al(0.0318), Si(0.0331),
P(0.0348), S(0.0405), Cl(0.0483), Ar(0.0600).

Polarization functions used are *2p* for H, He, *2df* for Li to Ne and *3d2f* for Na to Ar. Symbols *2p*, *2d*, and *2f* imply two sets of uncontracted primitives with exponents twice and half standard values. The *3d* means three sets using exponents four times, equal to, and a quarter of standard values. Standard *p*-exponents are 0.75 for H, He. Standard *d*-exponents for Li to Ar are:

Li(0.2), Be(0.255), B(0.401), C(0.626), N(0.913),
O(1.292), F(1.75), Ne(2.304),
Na(0.175), Mg(0.175), Al(0.325), Si(0.45), P(0.55),
S(0.65), Cl(0.75), Ar(0.85).

Standard *f*-exponents are:

Li(0.15), Be(0.26), B(0.50), C(0.80), N(1.00), O(1.40),
F(1.85), Ne(2.50),
Na(0.15), Mg(0.20), Al(0.25), Si(0.32), P(0.45), S(0.55),
Cl(0.70), Ar(0.85).

These supplementary functions¹² are the default in the GAUSSIAN94 program²⁷ for the 6-311G basis set. [Note that the *d*-exponents of Li–Ne (and *p*-exponent of H) for the 6-31G basis set used in the single point MP4 and QCISD(T) calculations in G3 theory are different from those used in the G3large basis set. The former are from Ref. 8(a).]

The core polarization functions for the G3large basis set were derived by adding single *p* and *d* functions with tight exponents to the first row atoms Li–Ne and single *d* and *f* functions with tight exponents to the second row atoms Na–Ar. The exponents for these functions were obtained by optimizing the MP2(full) energy for the ground-state neutral

TABLE X. Core polarization exponents used in the G3large basis set.

Atom	Exponent			Energy ^a
	<i>p</i>	<i>d</i>	<i>f</i>	
Li	4.0	7.0		−7.46394
Be	7.0	9.0		−14.63554
B	11.0	13.0		−24.61330
C	16.0	15.0		−37.79707
N	22.0	15.0		−54.53644
O	27.0	16.0		−74.99599
F	33.0	18.0		−99.64716
Ne	40.0	22.0		−128.83870
Na		4.0	4.0	−162.10297
Mg		4.0	5.0	−199.89069
Al		6.0	6.0	−242.18347
Si		8.0	7.0	−289.19227
P		10.0	9.0	−341.08484
S		11.0	10.0	−397.91806
Cl		13.0	12.0	−459.94148
Ar		15.0	14.0	−527.31993

^aMP2(full)/G3large energy in hartrees.

atoms. The exponents for the core polarization functions used in the G3large basis set are given in Table X.¹⁶ The core polarization functions included in G3large recover a large portion of the core-related correlation energy. We have not added *s* functions to the first row atoms or *sp* functions to the second row as there are multiple minima in the exponent space and they do not contribute as much to the energy lowering as the other core functions. A more detailed analysis of the core-related correlation will be presented in a separate study.³⁰

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