Gaussian-3 theory using reduced Møller-Plesset order

Larry A. Curtiss[a] and Paul C. Redfern
Chemistry and Materials Science Divisions, Argonne National Laboratory, Argonne, Illinois 60439

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

Vitaly Rassolov and John A. Pople
Department of Chemistry, Northwestern University, Evanston, Illinois 60208

(Received 24 September 1998; accepted 23 November 1998)

A variation of Gaussian-3 (G3) theory is presented in which the basis set extensions are obtained at the second-order Møller–Plesset level. This method, referred to as G3(MP2) theory, is assessed on 299 energies from the G2/97 test set [J. Chem. Phys. **109**, 42 (1998)]. The average absolute deviation from experiment of G3(MP2) theory for the 299 energies is 1.30 kcal/mol and for the subset of 148 neutral enthalpies it is 1.18 kcal/mol. This is a significant improvement over the related G2(MP2) theory [J. Chem. Phys. **98**, 1293 (1993)], which has an average absolute deviation of 1.89 kcal/mol for all 299 energies and 2.03 kcal/mol for the 148 neutral enthalpies. The corresponding average absolute deviations for full G3 theory are 1.01 and 0.94 kcal/mol, respectively. The new method provides significant savings in computational time compared to G3 theory and, also, G2(MP2) theory. © *1999 American Institute of Physics.*
[S0021-9606(99)30309-3]

I. INTRODUCTION

The Gaussian-*n* series[1] of model chemistries have the goal of calculating molecular energies to high accuracy. We recently presented Gaussian-3 (G3) theory,[2] which achieves significantly improved accuracy compared to Gaussian-2 (G2) theory.[3] G3 theory is a new procedure for calculating energies of molecules containing atoms of the first and second row of the periodic chart based on *ab initio* molecular orbital theory. G3 theory uses geometries from second-order perturbation theory [MP2/6-31G(*d*)] and zero-point energies from Hartree–Fock theory [HF/6-31G(*d*)] followed by a series of single-point energy calculations at the second-order Møller–Plesset (MP2), fourth-order Møller–Plesset (MP4), and quadratic configuration interaction [QCISD(T)] levels of theory. The MP4 calculations are done with the 6-31G(*d*) basis set and several basis set extensions. The QCISD(T) calculation is done with the 6-31G(*d*) basis set. The MP2 calculation is done with a new basis set, referred to as G3large, and includes core correlation at this level. The other single point energy calculations are done with a frozen core approximation. G3 theory is effectively at the QCISD(T) (full)/G3large level, making certain assumptions about additivity of the calculations. It also includes a spin–orbit correction, and a higher-level empirical correction. G3 theory was assessed on a total of 299 energies (enthalpies of formation, ionization energies, electron affinities, and proton affinities) from the G2/97 test set.[4,5] The average absolute deviation from experiment of G3 theory for these energies is 1.01 kcal/mol. For the subset of 148 neutral enthalpies of formation the average absolute deviation is 0.94 kcal/mol. The corresponding deviations for G2 theory are 1.48 and 1.56 kcal/mol, respectively. In addition, G3 theory requires less computational resources than G2 theory because of the replacement of the 6-311G basis set by the 6-31G basis in G3 theory. For example, for benzene it requires about one-half the cpu time, while giving a deviation from experiment of 0.6 kcal/mol compared to 3.9 kcal/mol for G2 theory.

The correlation methods in G3 theory are still computationally intensive and it is of interest to find modifications to reduce the computational requirements. In G2 theory it was found that the most demanding steps, calculation of the MP4 energies, could be replaced by a MP2 calculation. This method, referred to as G2(MP2) theory,[6] requires significantly less computational time than G2 theory, but is less accurate. The average absolute deviation of G2(MP2) theory is 1.89 kcal/mol for the G2/97 test set. A further modification, G2(MP2,SVP) theory,[7] replaces the QCISD(T)/6-311G(*d,p*) calculation in G2(MP2) theory by a QCISD(T)/6-31G(*d*) calculation to save additional time with essentially no change in accuracy (1.89 kcal/mol) compared to G2(MP2).

In this paper we present a variation of G3 theory that uses a reduced Møller–Plesset order similar to what was done for G2(MP2) theory. In this method, referred to as G3(MP2) theory, the basis set extensions are obtained at the MP2 level, thus eliminating the MP4 calculations. The QCISD(T) calculation is the computationally most demanding step in G3(MP2) theory. G3(MP2) theory is assessed with the G2/97 test set and compared to the performance of G2(MP2) and G3 theory. In Sec. II the theoretical methods used are described. In Sec. III the G3(MP2) energies are presented and compared with experiment.

[a]Electronic mail: CURTISS@ANLCHM.CHM.ANL.GOV

 © 1999 American Institute of Physics

Downloaded 01 Sep 2002 to 163.28.96.12. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/jcpo/jcpcr.jsp

TABLE I. Total G3(MP2) energies (in hartrees) of atomic species and spin-orbit corrections (in mhartrees).

Atomic species	E_0 [G3(MP2)]	ΔE(SO)[a]	Atomic species	E_0 [G3(MP2)]	ΔE (SO)[a]
H(^2S)	−0.501 84	0.0	N^+ (^3P)	−53.993 47	−0.43
He (^1S)	−2.902 54	0.0	O^+ (^4S)	−74.492 72	0.0
Li (^2S)	−7.434 05	0.0	F^+ (^3P)	−99.001 28	−0.67
Be (^1S)	−14.629 26	0.0	Ne^+ (^2P)	−128.033 71	−1.19
B (^2P)	−24.607 08	−0.05	Na^+ (^1S)	−161.664 29	0.0
C (^3P)	−37.789 34	−0.14	Mg^+ (^2S)	−199.365 91	0.0
N (^4S)	−54.525 19	0.0	Al^+ (^1S)	−241.718 72	0.0
O (^3P)	−74.989 77	−0.36	Si^+ (^2P)	−288.642 76	−0.93
F (^2P)	−99.640 94	−0.61	P^+ (^3P)	−340.444 18	−1.43
Ne (^1S)	−128.828 67	0.0	S^+ (^4S)	−397.288 70	0.0
Na (^2S)	−161.848 00	0.0	Cl^+ (^3P)	−459.214 12	−1.68
Mg (^1S)	−199.650 84	0.0	Ar^+ (^2P)	−526.483 31	−2.18
Al (^2P)	−241.936 95	−0.34	Li^- (^1S)	−7.468 65	0.0
Si (^3P)	−288.939 43	−0.68	B^- (^3P)	−24.610 10	−0.03[b]
P (^4S)	−340.826 65	0.0	C^- (^4S)	−37.829 90	0.0
S (^3P)	−397.663 76	−0.89	O^- (^2P)	−75.038 25	−0.26[b]
Cl (^2P)	−459.687 24	−1.34	F^- (^1S)	−99.766 29	0.0
Ar (^1S)	−527.060 96	0.0	Na^- (^1S)	−161.878 57	0.0
He^+ (^2S)	−2.000 25	0.0	Al^- (^3P)	−241.949 70	−0.28[b]
Li^+ (^1S)	−7.235 84	0.0	Si^- (^4S)	−288.988 45	0.0
Be^+ (^2S)	−14.278 22	0.0	P^- (^3P)	−340.850 81	−0.45[b]
B^+ (^1S)	−24.306 03	0.0	S^- (^2P)	−397.740 05	−0.88[b]
C^+ (^2P)	−37.379 24	−0.2	Cl^- (^1S)	−459.822 36	0.0

[a]Spin–orbit corrections are the same as used in G3 theory (Ref. 2) and are from Ref. 11, except where noted.
[b]Calculated value, Ref. 12. We have recently become aware of experimental values for the atomic anions from H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data **14**, 731 (1985). The experimental values for B^-, O^-, Al^-, P^-, and S^- are −0.03, −0.27, 0.23, −0.41, and −0.74 mhartrees, respectively. The differences with the calculated values are small (<0.1 kcal/mol).

II. DESCRIPTION OF G3(MP2) THEORY

G3(MP2) theory is based on MP2(full)/6-31G(*d*) geometries using all electrons. A series of single point energy calculations are carried out at higher levels of theory. The subsequent calculations include only valence electrons in the treatment of electron correlation, i.e., frozen core (fc). The first higher level calculation is at the quadratic configuration interaction level of theory[8] with the 6-31G(*d*) basis set, i.e., QCISD(T)/6-31G(*d*). This energy is then modified by a series of corrections to obtain a total energy, E_0

$$E_0[\mathrm{G3(MP2)}]=\mathrm{QCISD(T)/6\text{-}31G}(d)+\Delta E_{\mathrm{MP2}}+\Delta E(\mathrm{SO})+E(\mathrm{HLC})+E(\mathrm{ZPE}). \quad (1)$$

The correction at the second-order Møller–Plesset level[9] (MP2) is given by

$$\Delta E_{\mathrm{MP2}}=[E(\mathrm{MP2/G3MP2large})]-[E(\mathrm{MP2/6\text{-}31G}(d)]. \quad (2)$$

The G3MP2large basis set[10] is the same as the G3large basis set (see Ref. 2 for details) used in G3 theory, except that the core polarization functions (Table X in Ref. 2) are not included. The G3MP2large basis set differs from the 6-311+G(3*df*,2*p*) basis set used in G2(MP2) theory in three ways: (1) 2*df* polarization functions on the first-row atoms (Li–Ne) and 3*d*2*f* polarization functions on second-row atoms (Na–Ar), (2) a new 6-311G basis for S, Cl, and Ar which is optimized for the neutral atoms, and (3) diffuse functions on hydrogens. In addition, the MP2/G3MP2large calculation in G3(MP2) theory is done with a frozen core (fc) approximation, whereas the MP2/G3large calculation in G3 theory includes all electrons in the correlation treatment.

The other corrections in Eq. (1) are similar to those in G3 theory and are discussed in more detail in Ref. 2. The spin–orbit correction, ΔE(SO), is included for atomic species *only*. The spin–orbit correction is taken from experiment[11] where available and accurate theoretical calculations[12] in other cases. The spin–orbit corrections are listed in Table I. The zero-point correction, E(ZPE), is obtained from scaled (0.8929) HF/6-31G(*d*) frequencies. A ''higher level correction'' (HLC) is added to take into account remaining deficiencies in the energy calculations. 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 $n_\alpha \geqslant n_\beta$. The *A*, *B*, *C*, *D* values are chosen to give the smallest average absolute deviation for the G2/97 test set of experimental energies. For G3(MP2) theory, A=9.279 mhar-

TABLE II. Relative cpu times used in single point energy calculations on benzene and silicon tetrachloride.

Method	Benzene (D_{6h})	$SiCl_4$ (T_d)
G3(MP2)	1	1
G2(MP2)	2.9	2.7
G3	7.8	6.6
G2	14.7	15.9

Downloaded 01 Sep 2002 to 163.28.96.12. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/jcpo/jcpcr.jsp

TABLE III. G3(MP2) enthalpies of formation and their deviations from experiment.[a]

Molecule	$\Delta H_f^0(298)$	Deviation	Molecule	$\Delta H_f^0(298)$	Deviation
LiH	33.3	0.0	C_2Cl_4	−7.9	5.0
BeH	84.5	−2.8	CF_3CN	−119.4	1.0
CH	140.7	1.8	CH_3CCH (propyne)	43.9	0.3
$CH_2(^3B_1)$	92.3	1.4	$CH_2{=}C{=}CH_2$ (allene)	44.1	1.4
$CH_2(^1A_1)$	101.7	1.1	C_3H_4 (cyclopropene)	67.8	−1.6
CH_3	34.2	0.8	$CH_3CH{=}CH2$(propylene)	4.3	0.5
CH_4	−17.8	−0.1	C_3H_6 (cyclopropane)	13.5	−0.8
NH	84.0	1.2	C_3H_8 (propane)	−25.1	0.1
NH_2	44.5	0.6	$CH_2CHCHCH_2$ (butadiene)	25.5	0.8
NH_3	−10.0	−1.0	C_4H_6 (2-butyne)	34.9	−0.1
OH	8.3	1.1	C_4H_6 (methylene cyclopropane)	45.9	2.0
OH_2	−57.4	−0.4	C_4H_6 (bicyclobutane)	54.2	−2.3
FH	−65.4	0.3	C_4H_6 (cyclobutene)	38.8	−1.4
$SiH_2(^1A_1)$	62.9	2.3	C_4H_8 (cyclobutane)	6.8	0.0
$SiH_2(^3B_1)$	83.4	2.8	C_4H_8 (isobutene)	−4.4	0.4
SiH_3	46.0	1.9	C_4H_{10} (trans butane)	−30.2	0.2
SiH_4	7.2	1.0	C_4H_{10} (isobutane)	−32.1	0.0
PH_2	31.8	1.3	C_5H_8 (spiropentane)	44.8	−0.5
PH_3	2.5	−1.2	C_6H_6 (benzene)	18.6	1.1
SH_2	−5.5	0.6	CH_2F_2	−107.9	0.2
ClH	−22.4	0.3	CHF_3	−166.5	−0.1
Li_2	48.7	2.9	CH_2Cl_2	−22.8	0.0
LiF	−80.2	0.1	$CHCl_3$	−25.3	0.7
C_2H_2	54.3	−0.1	CH_3NH_2 (methylamine)	−4.1	−1.4
C_2H_4	11.9	0.7	CH_3CN (methyl cyanide)	17.9	0.1
C_2H_6	−20.1	0.0	CH_3NO_2 (nitromethane)	−16.2	−1.6
CN	106.4	−1.5	CH_3ONO (methyl nitrite)	−14.7	−1.2
HCN	31.2	0.3	CH_3SiH_3 (methyl silane)	−6.7	−0.3
CO	−27.4	0.9	HCOOH (formic acid)	−90.0	−0.5
HCO	9.5	0.5	$HCOOCH_3$ (methyl formate)	−85.7	0.7
H_2CO	−26.5	0.6	CH_3CONH_2 (acetamide)	−54.9	−2.1
H_3COH	−47.7	−0.3	C_2H_4NH (aziridine)	31.6	−1.4
N_2	2.0	−2.0	NCCN (cyanogen)	73.9	−0.6
H_2NNH_2	25.3	−2.5	$(CH_3)_2NH$ (dimethylamine)	−2.9	−1.5
NO	21.9	−0.3	$CH_3CH_2NH_2$ (transethylamine)	−10.9	−0.4
O_2	2.0	−2.0	CH_2CO (ketene)	−12.2	0.8
HOOH	−30.8	−1.7	C_2H_4O (oxirane)	−12.1	−0.5
F_2	1.3	−1.3	CH_3CHO (acetaldehyde)	−39.5	−0.2
CO_2	−94.9	0.8	HCOCOH (glyoxal)	−51.2	0.5
Na_2	30.6	3.3	CH_3CH_2OH (ethanol)	−55.8	−0.5
Si_2	137.1	2.8	CH_3OCH_3 (dimethylether)	−43.7	−0.3
P_2	34.5	−0.2	C_2H_4S (thiirane)	18.1	1.5
S_2	30.2	0.5	$(CH_3)_2SO$ (dimethylsulfoxide)	−34.8	−1.4
Cl_2	0.4	−0.4	C_2H_5SH (ethanethiol)	−11.4	0.3
NaCl	−45.1	1.5	CH_3SCH_3 (dimethyl sulfide)	−9.5	0.6
SiO	−25.3	0.6	$CH_2{=}CHF$ (vinyl fluoride)	−34.6	1.4
SC	63.7	3.2	C_2H_5Cl (ethyl chloride)	−26.8	0.0
SO	2.3	−1.1	$CH_2{=}CHCl$ (vinyl chloride)	4.5	4.4
ClO	26.4	−2.2	$CH_2{=}CHCN$ (acrylonitrile)	44.4	−1.2
FCl	−11.8	−1.4	CH_3COCH_3 (acetone)	−51.5	−0.5
Si_2H_6	17.9	1.2	CH_3COOH (acetic acid)	−102.5	−0.9
CH_3Cl	−19.6	0.1	CH_3COF (acetyl fluoride)	−105.2	−0.5
H_3CSH	−5.9	0.4	CH_3COCl (acetyl chloride)	−58.0	0.0
HOCl	−17.1	−0.7	$CH_3CH_2CH_2Cl$ (propyl chloride)	−32.0	0.5
SO_2	−67.0	−3.9	$(CH_3)_2CHOH$ (isopropanol)	−65.1	−0.1
BF_3	−269.6	−1.8	$C_2H_5OCH_3$ (methyl ethylether)	−52.0	0.3
BCl_3	−95.7	−0.6	$(CH_3)_3N$ (trimethylamine)	−5.2	−0.5
AlF_3	−289.4	0.4	C_4H_4O (furan)	−8.3	0.0
$AlCl_3$	−142.7	3.0	C_4H_4S (thiophene)	25.5	2.0
CF_4	−223.0	0.0	C_4H_5N (pyrrole)	26.4	−0.5
CCl_4	−25.3	2.3	C_5H_5N (pyridine)	32.8	0.8
COS	−36.5	3.4	H_2	−1.1	1.1
CS_2	22.6	5.3	HS	33.0	1.2
COF_2	−145.1	−4.0	CCH	135.8	−0.7
SiF_4	−383.8	−2.1	C_2H_3 $(^2A')$	70.3	1.3
$SiCl_4$	−159.4	1.0	CH_3CO $(^2A')$	−2.4	0.0
N_2O	22.1	−2.4	H_2COH (^2A)	−3.6	−0.5

Downloaded 01 Sep 2002 to 163.28.96.12. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/jcpo/jcpcr.jsp

TABLE III. (*Continued.*)

Molecule	$\Delta H_f^0(298)$	Deviation	Molecule	$\Delta H_f^0(298)$	Deviation
ClNO	12.9	−0.5	CH_3O CS ($^2A'$)	5.3	−1.2
NF_3	−30.7	−0.8	CH_3CH_2O ($^2A''$)	−2.0	−1.7
PF_3	−223.9	−5.2	CH_3S ($^2A'$)	28.6	1.2
O_3	36.4	−2.3	C_2H_5 ($^2A'$)	28.9	0.0
F_2O	7.6	−1.7	$(CH_3)_2CH$ ($^2A'$)	21.7	−0.2
ClF_3	−33.6	−4.3	$(CH_3)_3C$ (*t*-butyl radical)	13.3	−1.0
C_2F_4	−161.7	4.3	NO_2	9.1	−1.2

[a]In kcal/mol. Deviation=experiment−theory.

trees, B=4.471 mhartrees, C=9.345 mhartrees, and D=2.021 mhartrees. This is a modification of the HLC used in G2(MP2) theory which has two parameters, one for pairs of electrons in molecules and atoms and one for unpaired electrons in molecules and atoms.

Modification of G3 theory to obtain G3(MP2) theory is analogous to the modification of G2 theory to obtain G2(MP2) theory. As in the case of G2(MP2) theory, the G3(MP2) energy requires only two single-point energy calculations. For G3(MP2) theory the two calculations are QCISD(T)/6-31G(*d*) and MP2(fc)/G3MP2large. The former calculation also provides the MP2(fc)/6-31G(*d*) energy required for Eq. (2). The absence of the MP4/6-31G(2*df,p*) calculation in G3(MP2) theory compared to G3 theory provides significant savings in computational time and disk storage such that larger systems can be calculated. The relative cpu times are given for two examples, benzene and silicon tetrachloride, in Table II. The limiting calculation in G3(MP2) theory is the QCISD(T)/6-31G(*d*) calculation. For benzene, G3(MP2) theory is about eight times faster than G3 theory. Compared to G2(MP2) theory it is about three times faster for benzene. G3(MP2) theory is similar in speed to G2(MP2,SVP) theory.[7]

All calculations in this paper were done with the GAUSSIAN94 computer program.[13]

III. ASSESSMENT OF G3(MP2) THEORY ON THE G2/97 TEST SET

The G2/97 test set[4,5] contains 148 enthalpies of formation of neutrals (at 298 K), 88 ionization potentials, 58 electron affinities, and 8 proton affinities for a total of 302 reaction energies. In this assessment we have used the G2/97 test set less three ionization potentials ($C_6H_5CH_3 \rightarrow C_6H_5CH_3^+$, $C_6H_5NH_2 \rightarrow C_6H_5NH_2^+$, $C_6H_5OH \rightarrow C_6H_5OH^+$) resulting in a total of 299 energies. These three ionization potentials are not included in order to make comparison with G2 and G2(MP2) theories on an equal basis. These three ionization potentials were not calculated with G2 theory in Ref. 5 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. 4. The ionization potentials, electron affinities, and proton affinities were calculated at 0 K as in Ref. 5.

G3(MP2) 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(MP2) total energies of the atomic species and the spin–orbit corrections, $\Delta E(\mathrm{SO})$, that are included in the total energies. The G3(MP2) total energies for the molecules and the MP2(full)/6-31G(*d*) geometries are available elsewhere.[10] Table III contains the deviations of the G3(MP2) enthalpies of formation from

TABLE IV. G3(MP2) ionization potentials (IP) and their deviations from experiment.[a]

Molecule	IP	Deviation	Molecule	IP	Deviation
Li	124.4	−0.1	BCl_3	268.4	−0.9
Be	220.3	−5.4	B_2F_4	271.2	7.1
B	188.9	2.5	CO_2	316.0	1.6
C	257.3	2.3	CF_2	263.8	−0.4
N	333.7	1.6	COS	257.6	0.0
O	311.9	1.9	CS_2	233.1	−0.9
F	401.4	0.3	CH_2	239.8	0.0
Na	115.3	3.2	CH_3	227.9	−0.9
Mg	178.8	−2.5	C_2H_5 ($^2A'$)	188.4	−1.3
Al	136.9	1.1	C_3H_4 (cyclopropene)	225.2	−2.3
Si	186.2	1.8	$CH_2{=}C{=}CH_2$	224.9	−1.4
P	240.0	1.9	sec-C_3H_7	172.4	−2.5
S	235.4	3.6	C_6H_6	215.8	−2.6
Cl	296.9	2.2	CN	318.3	−4.7
CH_4	291.8	−0.8	CHO	188.5	−0.8
NH_3	234.2	0.5	H_2COH (^2A)	173.8	0.4
OH	297.7	2.3	CH_3O CS ($^2A'$)	247.5	−0.1
OH_2	290.3	0.7	CH_3OH	251.9	−1.7
FH	370.2	−0.4	CH_3F	293.0	−5.4
SiH_4	252.8	0.9	CH_2S	215.9	0.3
PH	234.3	−0.2	CH_2SH	172.7	1.1
PH_2	226.2	0.2	CH_3SH	217.9	−0.2
PH_3	227.2	0.4	CH_3Cl	260.6	−1.8
SH	237.0	2.2	C_2H_5OH	240.1	1.4
SH_2 $^2B_1$	240.4	1.0	CH_3CHO	236.9	−1.0
SH_2 $^2A_1$	294.5	0.2	CH_3OF	262.7	−1.2
ClH	293.4	0.6	C_2H_4S (thiirane)	209.0	−0.3
C_2H_2	263.6	−0.7	NCCN	310.9	−2.6
C_2H_4	244.5	−2.2	C_4H_4O (furan)	205.6	−2.0
CO	323.5	−0.4	C_4H_5N (pyrrole)	189.6	−0.3
N_2($^2\Sigma$ cation)	358.7	0.5	B_2H_4	221.6	2.0
N_2($^2\Pi$ cation)	383.9	1.2	NH	310.9	0.2
O_2	282.3	−4.0	NH_2	256.3	0.6
P_2	242.6	0.2	N_2H_2	223.9	−2.8
S_2	216.1	−0.2	N_2H_3	175.6	−0.2
Cl_2	265.9	−0.7	HOF	293.1	0.0
ClF	291.4	0.5	SiH_2 $^1A_1$	210.6	0.4
SC	263.4	−2.1	SiH_3	188.1	−0.5
H	314.9	−1.1	Si_2H_2	190.0	−0.9
He	566.2	0.9	Si_2H_4	187.9	−1.3
Ne	498.8	−1.7	Si_2H_5	177.6	−2.4
Ar	362.5	0.9	Si_2H_6	222.8	1.8
BF_3	359.7	−0.9			

[a]In kcal/mol. Deviation=experiment−theory.

Downloaded 01 Sep 2002 to 163.28.96.12. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/jcpo/jcpcr.jsp

TABLE V. G3(MP2) electron affinities (EA) and their deviations from experiment.[a]

Molecule	EA	Deviation	Molecule	EA	Deviation
C	25.5	3.6	C_2	72.4	3.1
O	30.4	3.3	C_2O	53.1	−0.3
F	78.7	−0.3	CF_2 $^1A_1$	3.2	0.9
Si	30.8	1.2	NCO	82.8	0.4
P	15.2	0.8	NO_2	52.5	−0.1
S	47.9	0.0	O_3	48.2	0.3
Cl	84.8	−1.4	OF	50.8	1.6
CH	26.5	2.1	SO_2	26.4	−0.9
CH_2	13.7	1.3	S_2O	45.4	−2.1
CH_3	0.1	1.7	C_2H	70.5	−2.0
NH	4.2	4.5	C_2H_3	16.6	−1.2
NH_2	17.2	0.5	$H_2C{=}C{=}C$ ($^1A_1$)	41.8	−0.4
OH	41.3	0.9	$H_2C{=}C{=}CH$	22.8	−2.2
SiH	28.9	0.6	CH_2CHCH_2	12.0	−1.1
SiH_2	24.9	1.1	HCO	7.5	−0.3
SiH_3	32.3	0.2	HCF $^1A'$	11.6	0.9
PH	21.8	2.0	CH_3O	36.3	−0.1
PH_2	29.3	0.0	CH_3S	43.5	−0.4
HS	54.1	0.3	CH_2S	10.7	0.0
O_2	8.5	1.6	CH_2CN	36.3	−0.7
NO	−0.6	1.0	CH_2NC	26.5	−2.1
CN	91.2	−2.2	CHCO	54.1	0.1
PO	25.0	0.1	CH_2CHO	43.1	−1.0
S_2	38.8	−0.5	CH_3CO	9.7	0.1
Cl_2	57.2	−2.1	CH_3CH_2O	40.7	−1.2
Li	21.7	−7.5	CH_3CH_2S	46.9	−1.9
B	1.9	4.5	LiH	10.0	−2.2
Na	19.2	−6.5	HNO	6.3	1.5
Al	8.0	2.2	HO_2 ($^2A''$)	24.2	0.6

[a]In kcal/mol. Deviation=experiment−theory.

TABLE VI. G3(MP2) proton affinities (PA) and their deviations from experiment.[a]

Molecule	PA	Deviation
NH_3	202.9	−0.4
OH_2	163.3	1.8
C_2H_2	152.9	−0.6
SiH_4	153.4	0.6
PH_3	185.9	1.2
SH_2	167.5	1.3
ClH	132.9	0.7
H_2	99.2	1.6

[a]In kcal/mol. Deviation=experiment−theory.

experiment for the G2/97 test set. The deviations of the ionization potentials, electron affinities, and proton affinities from experiment for the G2/97 test set are given in Tables IV, V, and VI, respectively. Table VII contains a summary of the average absolute deviations of G3(MP2) theory from experiment. Results for G2(MP2) theory and G2 theory are also included in the table for comparison.

A. Comparison of G3(MP2) theory with other Gn theories

G3(MP2) theory is significantly more accurate than G2(MP2) theory. The results in Table IV for the 299 energies in the G2/97 test set indicate that the average absolute deviation from experiment improves from 1.89 kcal/mol for G2(MP2) theory to 1.30 kcal/mol for G3(MP2) theory. Similarly, G3(MP2) theory is a significant improvement over G2(MP2,SVP) theory, which also has an average absolute deviation of 1.89 kcal/mol. Contributions to the improvement come from the three modifications included in G3(MP2) theory: The new higher level correction (HLC), the spin–orbit correction, and the G3MP2large basis set. Interestingly, G3(MP2) theory also performs better than G2 theory, which has an average absolute deviation of 1.48 kcal/mol. A detailed breakdown of the sources of improvement of G3 theory relative to G2 theory is given in Ref. 2. For example, use of a four parameter HLC in G2 theory improves the average absolute deviation of G2 theory for the same set of 299 energies used here to 1.28 kcal/mol.

The average absolute deviations of G3(MP2) theory are smaller than those of G2(MP2) theory for enthalpies of formation, ionization potentials, and electron affinities (see Table VII). These three quantities have average absolute deviations of 1.18, 1.41, and 1.46 kcal/mol, respectively, at the G3(MP2) level compared to 2.03, 1.72, and 1.94 kcal/mol at the G2(MP2) level. The only type of energy for which the accuracy decreases in G3(MP2) theory is proton affinities, which has an average absolute deviation of 1.02 kcal/mol at the G3(MP2) level compared to 0.77 kcal/mol at the G2(MP2) level. In comparison to G2 theory, G3(MP2) theory performs significantly better for enthalpies of formation of neutral species (1.56 vs. 1.18 kcal/mol). The average absolute deviations for ionization energies and electron affinities are only slightly larger for G3(MP2) theory than for G2 theory.

The average absolute deviation of G3(MP2) theory with G3 theory is also listed in Table VII. Overall the deviation is 0.61 kcal/mol. The largest absolute deviations between G3(MP2) and G3 occur for enthalpies of formation of nonhydrogens (0.87 kcal/mol) and electron affinities (0.86 kcal/mol).

Table VII presents the average absolute deviations for the enthalpies of formation of neutrals broken down into five different types: Nonhydrogen, hydrocarbons, substituted hydrocarbons, inorganic hydrides, and radicals. The results are improved compared to G2(MP2) theory for all five subsets. The largest improvement in accuracy from G2(MP2) to G3(MP2) occurs for the substituted hydrocarbons for which the average absolute deviation decreases from 1.89 to 0.74 kcal/mol. The improvement for hydrocarbons is also very large: From 1.83 to 0.70 kcal/mol. For inorganic hydrides the improvement is from 1.20 kcal/mol to 1.03 kcal/mol, while for radicals the improvement is from 1.36 to 1.23 kcal/mol. G3(MP2) theory improves for nonhydrogens compared to G2(MP2) theory, from 3.24 to 2.12 kcal/mol. Despite the improvement, the average absolute deviation for nonhydrogens is still quite large.

In G3 theory it was found that the inclusion of core correlation improved the accuracy of the method as it decreased the average absolute deviation for the G2/97 test set from 1.09 to 1.01 kcal/mol.[2] The core correlation was found to be especially important for unsaturated ring systems such as benzene. Surprisingly, inclusion of core correlation using the G3large basis set that has core polarization functions

Downloaded 01 Sep 2002 to 163.28.96.12. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/jcpo/jcpcr.jsp

TABLE VII. Comparison of average absolute deviations (in kcal/mol) for G3(MP2), G2(MP2), G3, and G2 theories.[a,b]

Type	Average absolute deviation from experiment				G3(MP2)-G3[c]
	G3(MP2)	G2(MP2)	G3	G2	
Enthalpies of formation (148)	1.18	2.03	0.94	1.56	0.59
Nonhydrogen (35)	2.12	3.24	1.72	2.44	0.87
Hydrocarbons (22)	0.70	1.83	0.68	1.29	0.48
Subst. hydrocarbons (47)	0.74	1.89	0.56	1.48	0.55
Inorganic hydrides (15)	1.03	1.20	0.87	0.95	0.38
Radical (29)	1.23	1.36	0.84	1.16	0.54
Ionization energies (85)	1.41	1.72	1.13	1.41	0.53
Electron affinities (58)	1.46	1.94	0.98	1.41	0.86
Proton affinities (8)	1.02	0.77	1.34	1.08	0.39
All (299)[d]	1.30	1.89	1.01	1.48	0.62

[a]HLC parameters for G3(MP2) theory: A=9.279 mhartrees, B=4.471 mhartrees, C=9.345 mhartrees, D=2.021 mhartrees.
[b]G2(MP2) and G2 results from Refs. 2, 4, and 5, and G3 results are from Ref. 2. Some average absolute deviations vary slightly from those in previous publications because of corrections including the use of a new value for the enthalpy of formation of COF_2 (Ref. 2) and a revised geometry for the ethanol cation (Ref. 2).
[c]Average absolute deviation of G3(MP2) from G3 theory.
[d]Root-mean-square deviations for G3(MP2), G2(MP2), G3, and G2 are 1.81, 2.45, 1.45, and 1.93, repectively.

(and re-optimization of the HLC) in G3(MP2) theory in place of the G3MP2large basis increases the average absolute deviation from 1.30 to 1.43 kcal/mol (1.18 to 1.46 kcal/mol for enthalpies of formation). We have not included core correlation in G3(MP2) theory because it makes the method less accurate and, in addition, it requires more cpu time. The increase in the average deviation is unsatisfactory and we are investigating the underlying reasons.

B. Results for specific species

About 80% of the G3(MP2) deviations fall within the range −2.0 to +2.0 kcal/mol. This is substantially better than G2(MP2) theory for which only 60% of the deviations fall in this range. For G3 and G2 theories 88% and 74% of the deviations, respectively, fall in this range.

1. Enthalpies of formation

Twenty-five of the 148 enthalpies of formation in the G2/97 test deviate by more than ±2 kcal/mol from experiment at the G3(MP2) level of theory compared to 59 for G2(MP2) theory. Only eleven deviate by more than ±3 kcal/mol at the G3(MP2) level compared to 31 for G2(MP2) theory. The maximum deviation for G3(MP2) theory is +5.3 kcal/mol (CS_2) compared to 10.1 kcal/mol (C_2F_4) for G2(MP2) theory. Hence, G3(MP2) theory is a significant improvement over G2(MP2) theory both in terms of average absolute deviation and the number of species that have very large deviations (>3 kcal/mol). G3(MP2) theory also does better than G2: 41 of the 148 enthalpies of formation at the G2 level deviate by more than ±2 kcal/mol from experiment and the maximum deviation is 8.2 kcal/mol (C_2F_4).

Sixteen of the enthalpies that have deviations of more than 2 kcal/mol at the G3(MP2) level are in the nonhydrogen subset. Ten of these are in common with G3 theory (SO_2, PF_3, C_2F_4, C_2Cl_4, COF_2, Li_2, Na_2, $AlCl_3$, CS_2, COS). The C_2F_4 and C_2Cl_4 molecules have deviations of 4.3 and 5.0 kcal/mol from experiment. The reason for these large deviations is unclear, although we note that an isodesmic bond separation scheme[14] using some accurate experimental data also gives similarly large deviations with experiment. The seven other nonhydrogen species having deviations greater than 2 kcal/mol at the G3(MP2) level are SC, CCl_4, SiF_4, N_2O, O_3, and ClF_3.

Only one hydrocarbon has a deviation greater than 2.0 kcal/mol: Bicyclobutane (−2.3 kcal/mol). Of the 47 substituted hydrocarbons only two have deviations greater than ±2 kcal/mol: CH_3CONH_2 (−2.1 kcal/mol) and CH_2CHCl (4.4 kcal/mol). We note that an isodesmic scheme[14] 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 $^1A_1$ (2.3 kcal/mol) and H_4N_2 (−2.5 kcal/mol). Finally, four of the 29 neutral radicals have a deviation greater than ±2 kcal/mol: BeH (−2.8 kcal/mol), SiH_2 $^3B_1$ (2.8 kcal/mol), Si_2 (2.8 kcal/mol), ClO (−2.2 kcal/mol).

2. Ionization potentials, electron affinities, and proton affinities

Twenty-one of the 85 ionization potentials from G3(MP2) theory in Table IV deviate by more than ±2 kcal/mol from experiment compared to 33 of the G2(MP2) ionization potentials. The largest deviation occurs for B_2F_4 (7.1 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] In addition to B_2F_4, six of the G3(MP2) ionization potentials differ by more than 3 kcal/mol: Be (−5.4 kcal/mol), Na (3.2 kcal/mol), S (3.6 kcal/mol). O_2 (−4.0 kcal/mol), CN (−4.7 kcal/mol), CH_3F (−5.4 kcal/mol).

Fifteen of the 58 electron affinities from G3(MP2) theory in Table V deviate by more than 2 kcal/mol compared to 28 for G2(MP2) theory. Seven of the G3(MP2) electron affinities deviate by more than 3 kcal/mol: Li (−7.5 kcal/

Downloaded 01 Sep 2002 to 163.28.96.12. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/jcpo/jcpcr.jsp

mol), B (4.5 kcal/mol), C (3.6 kcal/mol), O (3.3 kcal/mol), Na (−6.5 kcal/mol), NH (4.5 kcal/mol), C_2 (3.1 kcal/mol).

Eight proton affinities are included in the G2/97 test set. The G3(MP2) method performs very well for them(see Table VI), 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(MP2) theory should meet the target accuracy of 2 kcal/mol.

IV. CONCLUSIONS

Gaussian-3 (G3) theory with a reduced order of perturbation theory, G3(MP2) theory, has been presented. It is analogous to the variation of G2 theory referred to as G2(MP2) theory. The average absolute deviation from experiment of G3(MP2) theory for the 299 energies is 1.30 kcal/mol and for the subset of 148 neutral enthalpies it is 1.18 kcal/mol. This is a significant improvement over G2(MP2) theory, which has an average absolute deviation 1.89 kcal/mol for all 299 energies and 2.03 kcal/mol for the 148 neutral enthalpies. G3(MP2) theory also does better than G2 theory which has an average absolute deviation of 1.48 kcal/mol. The G3(MP2) method provides significant savings in computational time and disk storage.

ACKNOWLEDGMENTS

We acknowledge grants of computer time at the National Energy Research Supercomputer Center and Argonne's Center for Computational Science and Technology. We thank Dr. Jean-Philippe Blaudeau for the calculation of spin–orbit corrections for several atomic ions. This work was supported by the U.S. Department of Energy, Division of Materials Sciences, under contract No. W-31-109-ENG-38 and the National Science Foundation.

[1] For reviews see, L. A. Curtiss and K. Raghavachari, in *Quantum Mechanical Electronic Structure Calculations with Chemical Accuracy,* edited by S. R. Langhoff (Kluwer Academic press, Netherlands, 1995), p. 139; K. Raghavachari and L. A. Curtiss, in *Modern Electronic Structure Theory,* edited by D. R. Yarkony (World Scientific, Singapore, 1995), p. 991.
[2] L. A. Curtiss, K. Raghavachari, P. C. Redfern, V. Rassolov, and J. A. Pople, J. Chem. Phys. **109**, 7764 (1998).
[3] L. A. Curtiss, K. Raghavachari, G. W. Trucks, and J. A. Pople, J. Chem. Phys. **94**, 7221 (1991).
[4] L. A. Curtiss, K. Raghavachari, P. C. Redfern, and J. A. Pople, J. Chem. Phys. **106**, 1063 (1997).
[5] L. A. Curtiss, P. C. Redfern, K. Raghavachari, and J. A. Pople, J. Chem. Phys. **109**, 42 (1998).
[6] L. A. Curtiss, K. Raghavachari, and J. A. Pople, J. Chem. Phys. **98**, 1293 (1993).
[7] B. J. Smith and L. Radom, J. Phys. Chem. **99**, 6468 (1995); L. A. Curtiss, P. Redfern, B. J. Smith, and L. Radom, J. Chem. Phys. **104**, 5148 (1996).
[8] J. A. Pople, N. Head-Gordon, and K. Raghavachari, J. Chem. Phys. **87**, 5968 (1987).
[9] W. J. Hehre, L. Radom, J. A. Pople, P. von R. Schleyer, *Ab Initio Molecular Orbital Theory* (Wiley, New York, 1987).
[10] The G3MP2Large basis set can be downloaded from the website http://chemistry.anl.gov/compmat/g3theory.htm. The G3(MP2) total energies of the molecules and a complete tabulation of deviations with experiment are also available from this website.
[11] C. Moore, Natl. Bur. Stand. (U.S.) Circ 467 (1952).
[12] J.-P. Blaudeau (private communication).
[13] GAUSSIAN94, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzales, and J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 1995.
[14] K. Raghavachari (unpublished results).

Downloaded 01 Sep 2002 to 163.28.96.12. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/jcpo/jcpcr.jsp