Gaussian-2 theory using reduced Møller–Plesset orders

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Two variations of Gaussian-2 (G2) theory are presented. In the first, referred to as G2 (MP2) theory, the basis-set-extension energy corrections are obtained at the 2nd order Møller–Plesset (MP2) level and in the second, referred to as G2(MP3) theory, they are obtained at the MP3 level. The methods are tested out on the set of 125 systems used for validation of G2 theory [J. Chem Phys. **94**, 7221 (1991)]. The average absolute deviation of the G2(MP2) and G2(MP3) theories from experiment are 1.58 and 1.52 kcal/mol, respectively, compared to 1.21 kcal/mol for G2 theory. The new methods provide significant savings in computational time and disk storage.

I. INTRODUCTION

In a previous paper[1] we presented a general theoretical procedure referred to as Gaussian-2 (G2) theory, based on *ab initio* molecular orbital theory, for the computation of total energies of molecules at their equilibrium geometries. G2 theory uses the $6\text{-}311\text{G}(d,p)$ basis set and corrections for several basis set extensions. Treatment of correlation is by Møller–Plesset (MP) perturbation theory and quadratic configuration interaction (QCISD). The final total energies obtained in G2 theory are effectively at the $\text{QCISD(T)}/6\text{-}311\text{G}+\text{G}(3df,2p)$ level, making certain assumptions about additivity of the corrections. These additivity assumptions are supported by a recent full study.[2] G2 theory was tested on a total of 125 energies (dissociation energies, ionization energies, electron affinities, and proton affinities) having well-established experimental values and found to have an average absolute deviation from experiment of 1.21 kcal/mol. In subsequent work it has proved to be very useful in assessing thermochemical data of a large number of species for which less reliable experimental information is available.[3]

In this paper we present two variations of G2 theory which provide substantial savings in computational time and disk storage. In the first, referred to as G2(MP2) theory, the basis-set-extension corrections are obtained at the MP2 level and in the second, referred to as G2(MP3) theory they are obtained at the MP3 level. These new methods are tested out on the same set of 125 systems used for validation of G2 theory. In Sec. II the theoretical methods used are described. In Sec. III the G2(MP2) and G2(MP3) energies are presented and compared with experiment and the original G2 theory.

II. DESCRIPTION OF THE THEORETICAL METHOD

G2 theory has been described in detail in Ref. 1. It is based on $\text{MP2}=\text{FU}/6\text{-}31\text{G}(d)$ geometries using all electrons $(\text{MP2}=\text{FU})$. Energies are calculated at the $\text{MP4SDTQ}/6\text{-}311\text{G}(d,p)$ level (complete fourth-order MP perturbation) with corrections from higher level calculations. These include the following terms:

(1) A correction for diffuse functions is evaluated as

$$\Delta E(+)=E[\text{MP4}/6\text{-}311+\text{G}(d,p)]$$
$$-E[\text{MP4}/6\text{-}311\text{G}(d,p)].$$

(2) A correction for higher polarization on nonhydrogen atoms is evaluated as

$$\Delta E(2df)=E[\text{MP4}/6\text{-}311\text{G}(2df,p)]$$
$$-E[\text{MP4}/6\text{-}311\text{G}(d,p)].$$

(3) A correction for inclusion of a third d-function on nonhydrogen atoms and a second p-function on hydrogens is obtained from the relationship

$$\Delta=E[\text{MP2}/6\text{-}311+\text{G}(3df,2p)]$$
$$-E[\text{MP2}/6\text{-}311\text{G}(2df,p)]$$
$$-E[\text{MP2}/6\text{-}311+\text{G}(d,p)]$$
$$+E[\text{MP2}/6\text{-}311\text{G}(d,p)].$$

(4) A correction for correlation effects beyond fourth order perturbation theory is evaluated as

$$\Delta E(\text{QCI})=E[\text{QCISD(T)}/6\text{-}311\text{G}(d,p)]$$
$$-E[\text{MP4}/6\text{-}311\text{G}(d,p)].$$

using the method of quadratic configuration interaction.[4]

(5) A higher level correction (HLC) to account for remaining basis set deficiencies is added. This is $\text{HLC}=An_\beta-Bn_\alpha$, where $A=4.81$ mhartree, $B=0.19$ mhartree, and n_α and n_β are the number of α and β valence electrons, respectively, with $n_\alpha \geqslant n_\beta$. The value of A was derived to give the zero mean deviation from experiment of the calculated atomization energies of 55 molecules having well-established experimental values.[1] The value of B is the

TABLE I. Total G2(MP2) energies (in hartrees).

Species	Energy	Species	Energy	Species	Energy
H	$-0.500\ 00$	H_2CO	$-114.336\ 08$	SH^+	$-397.902\ 80$
Li	$-7.432\ 22$	CH_3OH	$-115.531\ 81$	$SH_2^+(^2B_1)$	$-398.541\ 95$
Be	$-14.623\ 51$	N_2	$-109.389\ 48$	$SH_2^+(^2A_1)$	$-398.455\ 72$
B	$-24.602\ 72$	N_2H_4	$-111.677\ 67$	ClH^+	$-459.864\ 87$
C	$-37.783\ 90$	NO	$-129.736\ 22$	$C_2H_2^+$	$-76.764\ 47$
N	$-54.516\ 31$	O_2	$-150.142\ 08$	$C_2H_4^+$	$-78.025\ 53$
O	$-74.978\ 68$	H_2O_2	$-151.361\ 32$	CO^+	$-112.660\ 32$
F	$-99.628\ 94$	F_2	$-199.317\ 80$	$N_2^+\ ^2\Sigma_g^+$	$-108.818\ 33$
Na	$-161.846\ 17$	CO_2	$-188.356\ 62$	$N_2^+\ ^2\Pi_u$	$-108.777\ 87$
Mg	$-199.646\ 20$	Na_2	$-323.723\ 58$	O_2^+	$-149.695\ 63$
Al	$-241.929\ 95$	Si_2	$-577.978\ 05$	P_2^+	$-681.425\ 12$
Si	$-288.930\ 02$	P_2	$-681.810\ 96$	S_2^+	$-795.112\ 81$
P	$-340.813\ 87$	S_2	$-795.452\ 17$	Cl_2^+	$-919.003\ 64$
S	$-397.646\ 99$	Cl_2	$-919.425\ 73$	ClF^+	$-558.931\ 16$
Cl	$-459.666\ 72$	NaCl	$-621.671\ 01$	SC^+	$-435.285\ 96$
LiH	$-8.021\ 79$	SiO	$-364.214\ 01$	C^-	$-37.824\ 66$
BeH	$-15.194\ 67$	CS	$-435.705\ 58$	O^-	$-75.028\ 18$
CH	$-38.411\ 70$	SO	$-472.819\ 30$	F^-	$-99.755\ 69$
$CH_2(^3B_1)$	$-39.067\ 81$	ClO	$-534.744\ 16$	Si^-	$-288.977\ 76$
$CH_2(^1A_1)$	$-39.057\ 44$	ClF	$-559.394\ 17$	P^-	$-340.834\ 13$
CH_3	$-39.743\ 91$	Si_2H_6	$-581.660\ 94$	S^-	$-397.719\ 64$
CH_4	$-40.409\ 66$	CH_3Cl	$-499.544\ 46$	Cl^-	$-459.799\ 72$
NH	$-55.140\ 03$	CH_3SH	$-438.141\ 23$	CH^-	$-38.451\ 38$
NH_2	$-55.787\ 11$	HOCl	$-535.397\ 72$	CH_2^-	$-39.091\ 57$
NH_3	$-56.457\ 18$	SO_2	$-548.007\ 09$	CH_3^-	$-39.745\ 45$
OH	$-75.640\ 92$	Li^+	$-7.235\ 84$	NH^-	$-55.149\ 42$
OH_2	$-76.330\ 01$	Be^+	$-14.276\ 39$	NH_2^-	$-55.816\ 38$
FH	$-100.347\ 04$	B^+	$-24.302\ 04$	OH^-	$-75.709\ 97$
SiH	$-289.542\ 51$	C^+	$-37.374\ 43$	SiH^-	$-289.583\ 95$
$SiH_2(^1A_1)$	$-290.164\ 26$	N^+	$-53.985\ 97$	SiH_2^-	$-290.199\ 00$
$SiH_2(^3B_1)$	$-290.127\ 03$	O^+	$-74.483\ 83$	SiH_3^-	$-290.820\ 96$
SiH_3	$-290.770\ 07$	F^+	$-98.991\ 00$	PH^-	$-341.456\ 82$
SiH_4	$-291.415\ 53$	Na^+	$-161.664\ 29$	PH_2^-	$-342.089\ 10$
PH	$-341.423\ 31$	Mg^+	$-199.364\ 08$	HS^-	$-398.364\ 36$
PH_2	$-342.044\ 07$	Al^+	$-241.713\ 81$	O_2^-	$-150.157\ 53$
PH_3	$-342.674\ 23$	Si^+	$-288.634\ 89$	NO^-	$-129.731\ 45$
SH	$-398.279\ 46$	P^+	$-340.432\ 22$	CN^-	$-92.725\ 92$
SH_2	$-398.924\ 08$	S^+	$-397.276\ 39$	PO^-	$-416.050\ 95$
ClH	$-460.331\ 62$	Cl^+	$-459.196\ 74$	PO	$-416.015\ 14$
Li_2	$-14.906\ 40$	CH_4^+	$-39.943\ 98$	S_2^-	$-795.512\ 51$
LiF	$-107.280\ 92$	NH_3^+	$-56.082\ 58$	Cl_2^-	$-919.511\ 32$
C_2H_2	$-77.184\ 08$	OH^+	$-75.164\ 95$	NH_4^+	$-56.779\ 88$
C_2H_4	$-78.414\ 31$	OH_2^+	$-75.865\ 72$	OH_3^+	$-76.589\ 90$
C_2H_6	$-79.628\ 93$	FH^+	$-99.755\ 87$	$C_2H_5^+$	$-77.428\ 97$
CN	$-92.580\ 35$	SiH_4^+	$-291.011\ 91$	SiH_5^+	$-291.660\ 13$
HCN	$-93.282\ 49$	PH^+	$-341.054\ 62$	PH_4^+	$-342.971\ 97$
CO	$-113.175\ 40$	PH_2^+	$-341.688\ 50$	SH_3^+	$-399.192\ 57$
HCO	$-113.695\ 97$	PH_3^+	$-342.312\ 68$	ClH_2^+	$-460.544\ 57$

same as was used in G1 theory,[5,6] where it was the error in the hydrogen atom energy.

(6) Finally, the energy E_0 is obtained by adding the zero-point correction, obtained from scaled (0.893) HF/6-31G* frequencies.

The resulting G2 energy is given by

$$E_0 = E[\text{MP4}/6\text{-}311G(d,p)] + \Delta E(+) + \Delta E(2df)$$
$$+ \Delta + \Delta E(\text{QCI}) + \text{HLC} + E(\text{ZPE}). \tag{1}$$

In G2(MP2) theory the basis set extension corrections in steps (1)–(3) are replaced by a single correction obtained at the MP2 level

$$\Delta_{\text{MP2}} = E[\text{MP2}/6\text{-}311+G(3df,2p)]$$
$$- E[\text{MP2}/6\text{-}311G(d,p)]. \tag{2}$$

The total G2(MP2) energy is thus given by

$$E_0 = E[\text{QCISD(T)}/6\text{-}311G(d,p)] + \Delta_{\text{MP2}} + \text{HLC}$$
$$+ E(\text{ZPE}). \tag{3}$$

The value of A used in the HLC for G2(MP2) theory was chosen to give the smallest average absolute deviation from experiment for the entire set of 125 energies. This turns out to be the same as that used for the HLC in G2 theory, i.e.,

TABLE II. Total G2(MP3) energies (in hartrees).

Species	Energy	Species	Energy	Species	Energy
H	−0.500 00	H_2CO	−114.338 11	SH^+	−397.906 88
Li	−7.432 22	CH_3OH	−115.533 43	$SH_2^+(^2B_1)$	−398.546 67
Be	−14.622 89	N_2	−109.392 04	$SH_2^+(^2A_1)$	−398.461 12
B	−24.602 45	N_2H_4	−111.679 14	ClH^+	−459.871 29
C	−37.784 32	NO	−129.738 58	$C_2H_2^+$	−76.766 32
N	−54.517 47	O_2	−150.146 21	$C_2H_4^+$	−78.027 65
O	−74.981 32	H_2O_2	−151.363 03	CO^+	−112.662 42
F	−99.631 94	F_2	−199.321 29	$N_2^+\ ^2\Sigma_g^+$	−108.821 44
Na	−161.846 17	CO_2	−188.361 05	$N_2^+\ ^2\Pi u$	−108.780 32
Mg	−199.645 65	Na_2	−323.723 40	O_2^+	−149.701 13
Al	−241.930 94	Si_2	−577.983 05	P_2^+	−681.431 60
Si	−288.932 72	P_2	−681.818 66	S_2^+	−795.122 17
P	−340.817 34	S_2	−795.461 60	Cl_2^+	−919.014 52
S	−397.653 26	Cl_2	−919.437 63	ClF^+	−558.937 44
Cl	−459.674 63	NaCl	−621.678 57	SC^+	−435.290 54
LiH	−8.022 63	SiO	−364.218 37	C^-	−37.826 56
BeH	−15.195 15	CS	−435.710 79	O^-	−75.027 08
CH	−38.412 79	SO	−472.825 05	F^-	−99.749 39
$CH_2(^3B_1)$	−39.069 02	ClO	−534.751 71	Si^-	−288.982 06
$CH_2(^1A_1)$	−39.058 80	ClF	−559.401 06	P^-	−340.840 22
CH_3	−39.745 27	Si_2H_6	−581.668 27	S^-	−397.727 13
CH_4	−40.411 13	CH_3Cl	−499.551 78	Cl^-	−459.807 13
NH	−55.141 78	CH_3SH	−438.147 30	CH^-	−38.452 70
NH_2	−55.788 73	HOCl	−535.404 32	CH_2^-	−39.091 91
NH_3	−56.458 24	SO_2	−548.015 79	CH_3^-	−39.744 74
OH	−75.643 07	Li^+	−7.235 84	NH^-	−55.148 54
OH_2	−76.330 63	Be^+	−14.276 39	NH_2^-	−55.811 66
FH	−100.348 02	B^+	−24.301 30	OH^-	−75.702 15
SiH	−289.545 63	C^+	−37.374 01	SiH^-	−289.588 49
$SiH_2(^1A_1)$	−290.167 78	N^+	−53.986 19	SiH_2^-	−290.203 52
$SiH_2(^3B_1)$	−290.130 14	O^+	−74.484 77	SiH_3^-	−290.825 56
SiH_3	−290.773 51	F^+	−98.993 66	PH^-	−341.462 58
SiH_4	−291.419 39	Na^+	−161.664 29	PH_2^-	−342.094 27
PH	−341.427 50	Mg^+	−199.364 08	HS^-	−398.370 57
PH_2	−342.048 56	Al^+	−241.713 50	O_2^-	−150.157 84
PH_3	−342.678 83	Si^+	−288.635 66	NO^-	−129.732 01
SH	−398.285 77	P^+	−340.433 98	CN^-	−92.725 85
SH_2	−398.929 91	S^+	−397.279 18	PO^-	−416.053 70
ClH	−460.338 66	Cl^+	−459.202 58	PO	−416.020 41
Li_2	−14.906 19	CH_4^+	−39.945 17	S_2^-	−795.522 00
LiF	−107.281 31	NH_3^+	−56.084 33	Cl_2^-	−919.525 38
C_2H_2	−77.185 91	OH^+	−75.166 95	NH_4^+	−56.781 72
C_2H_4	−78.416 09	OH_2^+	−75.868 10	OH_3^+	−76.592 09
C_2H_6	−79.631 11	FH^+	−99.758 90	$C_2H_3^+$	−77.430 80
CN	−92.581 97	SiH_4^+	−291.014 54	SiH_5^+	−291.663 39
HCN	−93.284 55	PH^+	−341.057 33	PH_4^+	−342.975 90
CO	−113.177 73	PH_2^+	−341.691 86	SH_3^+	−399.197 49
HCO	−113.698 12	PH_3^+	−342.316 25	ClH_2^+	−460.550 83

$A=4.81$ mhartree. We note that the calculation of the G2(MP2) energy requires only two calculations, QCISD(T)/6-311G(d,p) and MP2/6-311+G$(3df,2p)$.

In G2(MP3) theory the basis set extension corrections in steps (1) and (2) are replaced by corrections obtained at the MP3 level,

$$\Delta_{MP3}(+)=E[\text{MP3/6-311}+\text{G}(d,p)]$$
$$-E[\text{MP3/6-311G}(d,p)], \qquad (4)$$

$$\Delta_{MP3}(2df)=E[\text{MP3/6-311G}(2df,p)]$$
$$-E[\text{MP3/6-311G}(d,p)]. \qquad (5)$$

The total G2(MP3) energy is thus given by

$$E_0=[\text{QCISD(T)/6-311G}(d,p)]+\Delta_{MP3}(+)$$
$$+\Delta_{MP3}(2df)+\Delta+\text{HLC}+E(\text{ZPE}). \qquad (6)$$

The value of A used in the HLC for G2(MP3) theory was chosen in a similar way as for G2(MP2) theory. For G2(MP3) theory $A=5.13$ mhartree. The G2(MP3) level requires four calculations, QCISD(T)/6-311G(d,p), MP3/6-311+G(d,p), MP3/6-311G$(2df,p)$, and MP2(6-311+G$(3df,2p)$.

TABLE III. G2(MP2) dissociation energies, ionization energies, and electron affinities (in kcal/mol). Values in parentheses are the difference between the G2(MP2) and experimental energies [expt −G2(MP2)].

	Species		Species		Species	
Dissociation energies	LiH	56.2(−0.2)	SH_2	173.9(−0.7)	CO_2	386.1(−4.2)
	BeH	44.7(2.2)	ClH	103.5(−1.3)	Na_2	19.6(−3.0)
	CH	80.2(−0.3)	Li_2	26.3(−2.3)	Si_2	74.1(−0.1)
	$CH_2(^3B_1)$	178.2(1.4)	LiF	137.9(−0.3)	P_2	115.0(1.1)
	$CH_2(^1A_1)$	171.6(−1.0)	HCCH	386.2(2.2)	S_2	99.3(1.4)
	CH_3	288.7(0.5)	C_2H_4	531.2(0.7)	Cl_2	57.9(−0.7)
	CH_4	392.7(−0.2)	C_2H_6	665.9(0.4)	NaCl	99.2(−1.7)
	NH	77.6(1.4)	CN	175.8(0.8)	SiO	191.6(−1.1)
	NH_2	169.9(0.1)	HCN	302.6(−0.8)	SC	172.4(−2.9)
	NH_3	276.6(0.1)	CO	259.0(−2.8)	SO	121.5(2.0)
	OH	101.8(−0.5)	HCO	272.0(−1.7)	ClO	62.0(1.3)
	OH_2	220.5(−1.2)	H_2CO	359.9(−2.7)	ClF	61.8(−1.5)
	FH	136.9(−1.7)	H_3COH	482.7(−1.9)	Si_2H_6	502.6(−2.5)
	$SiH_2(^1A_1)$	147.0(−2.6)	N_2	223.9(1.2)	CH_3Cl	372.6(−1.6)
	$SiH_2(^3B_1)$	123.6(−0.2)	H_4N_2	404.8(0.6)	CH_3SH	445.7(−0.6)
	SiH_3	213.4(0.6)	NO	151.4(−1.3)	HOCl	158.3(−2.0)
	SiH_4	304.7(−1.9)	O_2	115.9(2.1)	SO_2	252.7(1.3)
	PH_2	144.4(0.3)	HOOH	253.5(−1.2)		
	PH_3	226.1(1.3)	F_2	37.6(−0.7)		
Ionization energies	Li	123.2(1.1)	Cl	294.9(4.2)	ClH	292.9(1.1)
	Be	217.8(−2.9)	CH_4	292.2(−1.2)	C_2H_2	263.3(−0.4)
	B	188.7(2.7)	NH_3	235.1(−0.3)	C_2H_4	244.0(−1.6)
	C	256.9(2.7)	OH	298.7(1.3)	CO	323.2(−0.1)
	N	332.8(2.5)	OH_2	291.3(−0.3)	$N_2\ ^2\Sigma_g^+$	358.4(0.9)
	O	310.5(3.3)	FH	371.0(−1.1)	$N_2\ ^2\Pi_u$	383.8(1.3)
	F	400.3(1.4)	SiH_4	253.3(0.4)	O_2	280.1(−1.8)
	Na	114.1(4.4)	PH	231.4(2.7)	P_2	242.1(0.7)
	Mg	177.0(−0.7)	PH_2	223.1(3.3)	S_2	212.9(2.9)
	Al	135.6(2.4)	PH_3	226.9(0.7)	Cl_2	264.9(0.3)
	Si	185.2(2.7)	SH	236.4(2.8)	ClF	290.5(1.4)
	P	239.5(2.4)	$SH_2(^2B_1)$	239.8(1.7)	SC	263.3(−2.0)
	S	232.6(6.3)	$SH_2(^2A_1)$	293.9(0.8)		
Electron affinities	C	25.6(3.5)	CH_3	1.0(0.9)	HS	53.3(0.1)
	O	31.1(2.6)	NH	5.9(2.9)	O_2	9.7(0.5)
	F	79.5(−1.1)	NH_2	18.4(−1.3)	NO	−3.0(3.5)
	Si	30.0(2.0)	OH	43.3(−1.1)	CN	91.3(−3.3)
	P	12.7(4.5)	SiH	26.0(3.4)	PO	22.5(2.7)
	S	45.6(2.3)	SiH_2	21.8(4.1)	S_2	37.9(0.5)
	Cl	83.5(−0.1)	SiH_3	31.9(1.3)	Cl_2	53.7(1.4)
	CH	24.9(3.7)	PH	21.0(2.0)		
	CH_2	14.9(0.1)	PH_2	28.3(0.8)		
Proton affinities	NH_3	202.5(0.0)	SiH_4	153.5(0.5)	ClH	133.6(0.0)
	OH_2	163.1(2.0)	PH_3	186.8(0.3)		
	C_2H_2	153.7(−1.4)	SH_2	168.5(0.3)		

III. RESULTS AND DISCUSSION

The G2(MP2) and G2(MP3) total energies obtained from Eqs. (3) and (6), respectively, are given in Tables I and II. Tables III and IV contain atomization energies, ionization energies, electron affinities, and proton affinities derived from the energies in Tables I and II. The average absolute deviation of the G2(MP2) energies from experiment of the set of 125 species in Table III is 1.58 kcal/mol compared to the corresponding average absolute deviation of the G2 energies of 1.21 kcal/mol.[1] The average absolute deviation of the G2(MP2) energies from the G2 energies for the set of 125 species in Tables II is 0.74 kcal/mol.

Thus, the two theories agree more closely with each other than either does with experiment.

G2(MP2) theory does best for dissociation energies and proton affinities. Of the 55 dissociation energies in Table III the average absolute deviation from experiment is 1.31 kcal/mol compared to an average absolute deviation for G2 theory of 1.16 kcal/mol. For the most part the molecules which deviated by more than 2 kcal/mol from experiment are similar in G2 and G2(MP2) theory; these include SiH_2, O_2, H_2CO, Na_2, CO_2, Si_2H_6. G2 theory is also in error by more than 2 kcal/mol for S_2, SO, ClO, and SO_2 while G2(MP2) theory is in error by more than 2

TABLE IV. G2(MP3) dissociation energies, ionization energies, and electron affinities (in kcal/mol). Values in parentheses are the difference between the G2(MP3) and experimental energies [expt−G2 (MP3)].

	Species		Species		Species	
Dissociation energies	LiH	56.7(−0.7)	SH_2	173.6(−0.4)	CO_2	385.3(−3.4)
	BeH	45.3(1.6)	ClH	102.9(−0.7)	Na_2	19.5(−2.9)
	CH	80.6(−0.7)	Li_2	26.2(−2.2)	Si_2	73.8(0.2)
	$CH_2(^3B_1)$	178.6(1.0)	LiF	136.3(1.3)	P_2	115.4(0.7)
	$CH_2(^1A_1)$	172.2(−1.6)	HCCH	387.3(1.6)	S_2	97.3(3.4)
	CH_3	289.2(0.0)	C_2H_4	531.8(0.1)	Cl_2	55.5(1.7)
	CH_4	393.3(−0.8)	C_2H_6	666.7(−0.4)	NaCl	99.0(−1.5)
	NH	78.0(1.0)	CN	175.8(0.8)	SiO	191.0(−0.5)
	NH_2	170.2(−0.2)	HCN	302.9(−1.1)	SC	171.4(−1.9)
	NH_3	276.6(0.1)	CO	258.6(−2.4)	SO	119.5(4.0)
	OH	101.5(−0.2)	HCO	271.4(−1.1)	ClO	60.1(3.2)
	OH_2	219.2(0.1)	H_2CO	359.2(−2.0)	ClF	59.3(1.0)
	FH	135.6(−0.4)	H_3COH	481.8(−1.0)	Si_2H_6	503.8(−3.7)
	$SiH_2(^1A_1)$	147.5(−3.1)	N_2	224.1(1.0)	CH_3Cl	372.0(−1.0)
	$SiH_2(^3B_1)$	123.9(−0.5)	H_4N_2	404.2(1.2)	CH_3SH	445.3(−0.2)
	SiH_3	213.8(0.2)	NO	150.5(−0.4)	HOCl	155.9(0.4)
	SiH_4	305.4(−2.6)	O_2	115.2(2.8)	SO_2	250.9(3.1)
	PH_2	145.1(−0.4)	HOOH	251.2(1.1)		
	PH_3	226.8(0.6)	F_2	36.0(0.9)		
Ionization energies	Li	123.2(1.1)	Cl	296.2(2.9)	ClH	293.3(0.7)
	Be	217.4(−2.5)	CH_4	292.4(−1.4)	C_2H_2	263.3(−0.4)
	B	189.0(2.4)	NH_3	234.6(0.1)	C_2H_4	243.7(−1.4)
	C	257.5(2.2)	OH	298.8(1.2)	CO	323.2(−0.3)
	N	333.4(1.9)	OH_2	290.2(0.8)	$N_2\,^2\Sigma_g^+$	358.1(1.2)
	O	311.6(2.3)	FH	369.7(0.2)	$N_2\,^2\Pi_u$	383.9(1.2)
	F	400.5(1.2)	SiH_4	254.0(−0.4)	O_2	279.3(−1.0)
	Na	114.1(4.4)	PH	232.3(1.8)	P_2	242.9(−0.1)
	Mg	176.7(−0.4)	PH_2	223.8(2.6)	S_2	213.0(2.8)
	Al	136.4(1.5)	PH_3	227.5(0.1)	Cl_2	265.5(−0.3)
	Si	186.4(1.5)	SH	237.8(1.4)	ClF	290.9(1.0)
	P	240.6(1.3)	$SH_2(^2B_1)$	240.5(1.0)	SC	263.7(−2.4)
	S	234.7(4.2)	$SH_2(^2A_1)$	294.2(0.5)		
Electron affinities	C	26.5(2.5)	CH_3	−0.3(2.2)	HS	53.2(0.1)
	O	28.7(5.0)	NH	4.2(4.5)	$O_2\cdot$	7.3(2.8)
	F	73.7(4.7)	NH_2	14.4(2.7)	NO	−4.1(4.6)
	Si	31.0(1.0)	OH	37.1(5.1)	CN	90.3(−2.2)
	P	14.4(2.8)	SiH	26.9(2.6)	PO	20.9(4.2)
	S	46.4(1.5)	SiH_2	22.4(3.5)	S_2	37.9(0.4)
	Cl	83.1(0.2)	SiH_3	32.7(0.5)	Cl_2	55.1(0.1)
	CH	25.0(3.6)	PH	22.0(1.0)		
	CH_2	14.4(0.6)	PH_2	28.7(0.4)		
Proton affinities	NH_3	203.0(−0.5)	SiH_4	153.1(0.9)	ClH	133.1(0.5)
	OH_2	164.1(1.0)	PH_3	186.4(0.7)		
	C_2H_2	153.7(−1.4)	SH_2	167.9(0.9)		

kcal/mol for Li_2, CO, SC, and BeH. Of these problem molecules G2 theory deviates by more than 3 kcal/mol for two of them (SO_2 and S_2) while G2(MP2) theory deviates by more than 3 kcal/mol for only one (CO_2). G2(MP2) theory is comparable to G2 theory on the seven proton affinities examined with an average absolute deviation of 0.65 kcal/mol compared to 1.0 for G2 theory. G2(MP2) theory does more poorly on ionization energies and electron affinities than G2 theory. This is largely due to the results for the atoms where apparently the higher levels of correlation are more important in obtaining the energy differences. Aside from the atoms, G2(MP2) theory is off by by more than 3 kcal/mol in the electron affinities of SiH,

SiH_2, CN, and NO and the ionization energy of PH_2.

The average absolute deviation of the G2(MP3) energies from experiment of the set of 125 species in Table IV is 1.52 kcal/mol and the average absolute deviation of the G2(MP3) energies from the G2 energies in Tables IV is 0.62 kcal/mol. G2(MP3) theory also does best for dissociation energies and proton affinities. Of the 55 dissociation energies in Table IV the average absolute deviation is 1.29 kcal/mol. G2(MP3) theory is off by more than 2 kcal/mol for 12 molecules; these include SiH_2, SiH_4, Li_2, CO, O_2, Na_2, CO_2, S_2, SO, ClO, SO_2, and Si_2H_6. Of these problem molecules G2(MP3) theory deviates by more than 3 kcal/ mol for seven of them (SO_2, Si_2H_6, ClO, SO, S_2, CO_2,

SiH_2). G2(MP3) theory has an average absolute deviation of 0.84 kcal/mol for proton affinities. G2(MP3) theory also does more poorly on ionization energies and electron affinities than G2 theory, especially the atoms. Aside from the atoms G2(MP3) theory is off by more than 3 kcal/mol in the electron affinities of NH, OH, SiH_2, NO, and PO and none of the ionization energies.

Both G2(MP2) and G2(MP3) theories eliminate the MP4/6-311G($2df,p$) calculation which is the largest calculation in G2 theory. Use of direct calculations makes the MP2/6-311+G($3df,2p$) calculation in step (3) feasible. In G2(MP2) and G2(MP3) theories the limiting calculation is now the QCISD(T)/6-311G(d,p) calculation.

IV. CONCLUSIONS

The two variations of the (G2) theory presented here, G2(MP2) and G2(MP3), perform reasonably well when compared with G2 theory. The average absolute deviations with experiment of 1.58 and 1.52 kcal/mol, respectively (compared to 1.21 kcal/mol for G2 theory) suggest that they should be accurate to ±3 kcal. The absence of the MP4/6-311G($2df,p$) calculation in the two new methods provides significant savings in computational time and disk storage. Thus, the G2(MP2) and G2(MP3) methods can handle larger systems than are possible with G2 theory. G2(MP3) appears to have little advantage over G2(MP2), so the latter is preferable for studies of large molecules for which G2 theory is not feasible.

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