Gaussian2 theory for molecular energies of first and secondrow compounds

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Gaussian-2 theory for molecular energies of first- and second-row compounds

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The Gaussian-2 theoretical procedure (G2 theory), based on *ab initio* molecular orbital theory, for calculation of molecular energies (atomization energies, ionization potentials, electron affinities, and proton affinities) of compounds containing first- (Li–F) and second-row atoms (Na–Cl) is presented. This new theoretical procedure adds three features to G1 theory [J. Chem. Phys. 90, 5622 (1989)] including a correction for nonadditivity of diffuse-*sp* and 2*df* basis set extensions, a basis set extension containing a third *d* function on nonhydrogen atoms and a second *p* function on hydrogen atoms, and a modification of the higher level correction. G2 theory is a significant improvement over G1 theory because it eliminates a number of deficiencies present in G1 theory. Of particular importance is the improvement in atomization energies of ionic molecules such as LiF and hydrides such as C_2H_6, NH_3, N_2H_4, H_2O_2, and CH_3SH. The average absolute deviation from experiment of atomization energies of 39 first-row compounds is reduced from 1.42 to 0.92 kcal/mol. In addition, G2 theory gives improved performance for hypervalent species and electron affinities of second-row species (the average deviation from experiment of electron affinities of second-row species is reduced from 1.94 to 1.08 kcal/mol). Finally, G2 atomization energies for another 43 molecules, not previously studied with G1 theory, many of which have uncertain experimental data, are presented and differences with experiment are assessed.

I. INTRODUCTION

In previous papers[1,2] we have presented a general theoretical procedure, based on *ab initio* molecular orbital theory, for the computation of total energies of molecules at their equilibrium geometries. The objective was to develop a general predictive procedure, applicable to any molecular system in an unambiguous manner, which can reproduce known experimental data to a prescribed accuracy of about ± 2 kcal/mol and can be applied with similar accuracy to species having larger experimental uncertainty. The theoretical procedure, referred to as "Gaussian-1 theory" ("G1 theory" for short), was a composite one, based on the 6–311G(*d,p*) basis set and two basis set extensions (diffuse-*sp* and 2*df*). Treatment of correlation is by Møller–Plesset (MP) perturbation theory and quadratic configuration interaction. The procedure was used to calculate atomization energies, ionization energies, proton affinities, and electron affinities of a large number of molecules for which these quantities have been well established experimentally. For compounds containing first-row elements agreement with experiment was found to be within ± 2 kcal/mol (± 0.1 eV) in most cases and for those containing second-row elements[2] agreement was found to be within ± 3 kcal/mol

(± 0.15 eV). G1 theory has also been applied to numerous molecules[3–9] where the experimental energies have not been as well established and in these cases it has provided valuable information.

G1 theory was conceived as the first in a series of well-defined methods that could be routinely applied to the calculation of molecular energies in a systematic manner. A number of deficiencies in G1 theory were noted and future developments to alleviate these deficiencies were indicated as being desirable. In particular G1 theory does poorly on dissociation energies of ionic molecules such as LiF (3.7 kcal/mol too high), on triplet state molecules such as O_2 (2.6 kcal/mol too low) and S_2 (2.3 kcal/mol too low), on singlet–triplet energy separations such as those of CH_2 (2.8 kcal/mol too small) and SiH_2 (2.7 kcal/mol too large), and on some hydrides such as NH_3 (2.5 kcal/mol too low) and N_2H_4 (4.1 kcal/mol too low). Also, G1 theory does poorly on the hypervalent species SO_2 and ClO_2 where the atomization energies are low by 6–8 kcal/mol. It was found that an additional *d* function may reduce this discrepancy.[2]

In this paper we set forth the Gaussian-2 theoretical procedure (referred to as "G2 theory"), which makes a significant improvement over G1 theory by eliminating some of the above deficiencies. It has the following new features: (1) It eliminates the assumption of additivity of the diffuse-*sp* (+) and 2*df* basis set extensions used in G1 theory. This

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change gives significant improvement for ionic species and some anions. (2) It adds a third d function on the nonhydrogen atoms and a second p function on the hydrogens. The third d function is especially important for some hypervalent molecules containing second-row atoms such as ClO_2 and SO_2, while the second p function significantly improves the atomization energies of some of the hydrogen containing molecules. (3) Finally, the higher level correction (HLC), which was determined in G1 theory by the error in the calculated energy of the H_2 molecule and the H atom, is determined from the best fit to the experimental atomization energies of 55 molecules for which the experimental value is well established. This also contributes to an improvement in calculated energies. In Sec. II the specifics of the G2 theory are given. In Sec. III the G2 and experimental values for 0 K atomization energies (ΣD_0), ionization potentials, proton affinities, and electron affinities are compared. These comparisons are restricted to examples where accurate experimental data are known and are the same ones that were used to test the performance of G1 theory.[1,2] Finally, in Sec. IV atomization energies from G2 theory are given for 79 molecules (including 43 which were not previously considered with G1 theory) for which the experimental data is less accurate. Species for which there are significant discrepancies between theory and experiment are discussed in this section.

II. DESCRIPTION OF THE THEORETICAL METHOD

G1 theory has been described in detail in Refs. 1 and 2. It is based on MP2 = FU/6–31G* (second-order MP perturbation) geometries using all electrons (MP2 = FU). Energies are calculated at the MP4SDTQ/6–311G(d,p) level (complete fourth-order MP perturbation) with corrections due to diffuse-sp functions on nonhydrogen atoms [$\Delta E(+)$], higher polarization functions on nonhydrogen atoms [($\Delta E(2df)$)], and for correlation beyond fourth-order perturbation theory using quadratic configuration interaction [$\Delta E(QCI)$]. A final higher level correction, $E(HLC)$, to make E_e exact for hydrogen atom and hydrogen molecule is added. This corresponds to 6.14 millihartrees for each valence electron pair and 0.19 millihartrees for each unpaired electron. (The justification and possible problems with the use of the higher level correction are discussed in detail in Ref. 1.) Finally, the energy E_0 is obtained by adding a zero-point energy [$\Delta E(ZPE)$, scaled HF/6–31G* frequencies] to E_e. In this paper we refer to this energy as E_0 (G1).

In G2 theory a correction Δ is added to the G1 energy. This is composed of two parts, both computed at the MP2 level. The first part Δ_1 corrects for nonadditivity caused by the assumption of separate basis set extensions for diffuse-sp functions (+) and higher polarization functions ($2df$) in G1 theory,

$$\Delta_1 = \Delta(+ 2df) - \Delta(+) - \Delta(2df), \qquad (1)$$

where $\Delta(+ 2df) = E\,[MP2/6–311 + G(2df,p)] - E[MP2/6–311G(d,p)]$, $\Delta(+) = E[MP2/6–311 + G(d,p)] - E[MP2/6–311G(d,p)]$,   and $\Delta(2df) = E[MP2/6–311G(2df,p)] - E[MP2/6–311G(d,p)]$.

The second part Δ_2 is a correction for addition of a third d function to the nonhydrogen atoms and a second p function to the hydrogens,

$$\Delta_2 = E\,[MP2/6–311 + G(3df,2p)]$$
$$- E\,[MP2/6–311 + G(2df,p)]. \qquad (2)$$

The total correction Δ is then

$$\Delta = \Delta_1 + \Delta_2 = E\,[MP2/6–311 + G(3df,2p)]$$
$$- E\,[MP2/6–311G(2df,p)] \qquad (3)$$
$$- E\,[MP2/6–311 + G(d,p)]$$
$$+ E\,[MP2/6–311G(d,p)].$$

Thus, G2 theory requires only one additional calculation, MP2/6–311 + G($3df,2p$), the other MP2 values in Eq. (3) already being done in G1 theory as part of the MP4 calculations.

The G2 energy is then obtained as follows:

$$E_0\,(G2) = E_0\,(G1) + \Delta + 1.14n\text{pair}, \qquad (4)$$

where $n$pair is the number of valence pairs. The last term in Eq. (4) lowers the higher level correction (HLC) of 6.14 millihartrees per electron pair in G1 theory by 1.14 millihartrees. The value of 1.14 was determined to give the zero mean deviation from experiment of the calculated atomization energies of 55 molecules having well-established experimental values (Table III).

The use of MP2 instead of MP4 energies to obtain the correction Δ in Eq. (3) has been examined in several test calculations and found to be valid. The results are shown in Table I for the ΣD_0's of CH_4, HCCH, H_2S, CO, Cl_2, NaCl and the IP of HCCH. The differences between the MP4 calculation and the MP2 approximation used in Eq. (3) are small.

III. COMPARISON WITH ACCURATE EXPERIMENTAL DATA

G2 theory has been applied to the set of atoms, molecules and ions in Table II. This includes the species chosen in Refs. 1 and 2 to test the G1 theory. It also includes 79 species whose atomization energies are not as well known. Results for these species are discussed in Sec. IV. Table II contains

TABLE I. Comparison of use of MP2 and MP4 energies to calculate Δ [Eq. (3)].

	G2 reaction energies (in kcal/mol)	
	MP2 energies used to calculate Δ [a]	MP4 energies used to calculate Δ
$CH_4 \rightarrow C + 4H$	393.2	393.1
$CO \rightarrow C + O$	258.1	258.0
$HCCH \rightarrow 2H + 2C$	387.3	387.2
$H_2S \rightarrow 2H + S$	173.0	173.0
$Cl_2 \rightarrow 2Cl$	55.8	56.1
$NaCl \rightarrow Na + Cl$	98.8	98.9
$C_2H_2 \rightarrow C_2H_2^+ + e^-$	263.3	263.3

[a] Corresponds to method proposed in this paper.

TABLE II. G1 and G2 total energies.[a]

TABLE II (continued).

Molecule	E_0(G1)	Δ	E_0(G2)	Molecule	E_0(G1)	Δ	E_0(G2)
H	− 0.500 00	⋯	− 0.500 00	C_2H	− 76.473 45	− 4.15	− 76.473 04
H_2	− 1.165 01	− 2.49	− 1.166 36	C_2H_2	− 77.186 02	− 5.42	− 77.185 74
Li	− 7.432 22	⋯	− 7.432 22	C_2H_3	− 77.738 45	− 7.21	− 77.739 96
Be	− 14.623 37	− 0.11	− 14.622 34	C_2H_4	− 78.414 01	− 8.76	− 78.415 93
B	− 24.602 79	− 0.40	− 24.602 05	C_2H_5	− 78.966 61	− 10.57	− 78.970 34
C	− 37.784 64	− 0.82	− 37.784 32	C_2H_6	− 79.626 56	− 12.32	− 79.630 90
N	− 54.517 76	− 1.36	− 54.517 98	CN	− 92.583 36	− 3.96	− 92.582 76
O	− 74.982 04	− 2.27	− 74.982 03	HCN	− 93.285 47	− 5.12	− 93.284 89
F	− 99.632 75	− 3.49	− 99.632 82	H_2CNH	− 94.460 95	− 9.17	− 94.463 28
Na	− 161.846 18	⋯	− 161.846 18	H_3CNH_2	− 95.662 10	− 12.79	− 95.666 91
Mg	− 199.646 13	− 0.15	− 199.645 14	CO	− 113.177 22	− 5.97	− 113.177 49
Al	− 241.931 67	− 0.44	− 241.930 97	HCO	− 113.697 46	− 7.07	− 113.698 83
Si	− 288.933 78	− 0.61	− 288.933 25	H_2CO	− 114.337 24	− 8.48	− 114.338 88
P	− 340.818 00	− 1.36	− 340.818 22	H_3COH	− 115.530 59	− 12.28	− 115.534 89
S	− 397.654 93	− 2.30	− 397.654 95	CF	− 137.626 79	− 5.91	− 137.627 00
Cl	− 459.676 70	− 3.36	− 459.676 64	HCF	− 138.246 05	− 7.86	− 138.247 07
LiH	− 8.022 28	− 1.34	− 8.022 48	H_3CF	− 139.551 26	− 10.93	− 139.554 21
BeH	− 15.195 28	− 0.77	− 15.194 91	CSi	− 326.875 72	− 2.84	− 326.875 14
BeH_2	− 15.844 26	− 1.56	− 15.843 54	CP	− 378.798 14	− 4.82	− 378.798 40
BH	− 25.234 70	− 1.57	− 25.233 99	HCP	− 379.491 83	− 5.64	− 379.491 77
BH_2	− 25.856 51	− 3.03	− 25.857 26	H_2CPH	− 380.690 52	− 8.43	− 380.692 11
BH_3	− 26.524 07	− 4.21	− 26.524 86	H_3CPH	− 381.902 31	− 11.71	− 381.906 04
CH	− 38.412 20	− 2.66	− 38.412 58	CS	− 435.712 57	− 4.13	− 435.711 00
$CH_2(^3B_1)$	− 39.067 00	− 4.28	− 39.069 00	H_2CS	− 436.933 01	− 7.52	− 436.933 69
$CH_2(^1A_1)$	− 39.057 10	− 4.72	− 39.058 40	H_3CSH	− 438.145 32	− 11.13	− 438.148 47
CH_3	− 39.742 54	− 5.97	− 39.745 09	CCl	− 497.614 33	− 5.13	− 497.613 76
CH_4	− 40.407 72	− 7.72	− 40.410 88	H_3CCl	− 499.552 04	− 9.77	− 499.553 83
NH	− 55.140 77	− 3.68	− 55.142 17	N_2	− 109.393 72	− 4.59	− 109.392 61
NH_2	− 55.786 16	− 6.28	− 55.789 02	H_2NNH_2	− 111.675 21	− 13.22	− 111.680 45
NH_3	− 56.454 77	− 8.44	− 56.458 65	NO	− 129.739 12	− 6.53	− 129.739 95
OH	− 75.642 14	− 5.19	− 75.643 91	HNO	− 130.313 89	− 8.34	− 130.315 39
OH_2	− 76.328 34	− 8.27	− 76.332 05	NF	− 154.271 14	− 6.58	− 154.272 02
FH	− 100.347 13	− 7.44	− 100.350 01	NSi	− 343.626 48	− 3.74	− 343.624 52
NaH	− 162.416 99	− 2.11	− 162.417 96	NP	− 395.568 58	− 4.25	− 395.567 13
MgH	− 200.191 53	− 1.44	− 200.191 83	NS	− 452.344 17	− 6.93	− 452.345 40
MgH_2	− 200.804 04	− 2.49	− 200.804 25	O_2	− 150.147 90	− 6.02	− 150.148 22
AlH	− 242.546 70	− 1.77	− 242.546 19	HOO	− 150.725 66	− 8.91	− 150.727 73
AlH_2	− 243.118 73	− 2.51	− 243.118 96	HOOH	− 151.362 91	− 10.85	− 151.365 78
AlH_3	− 243.753 98	− 3.59	− 243.753 95	HOF	− 175.352 02	− 9.36	− 175.353 40
SiH	− 289.546 30	− 1.98	− 289.546 00	ONa	− 236.936 08	+ 1.71	− 236.930 95
$SiH_2(^1A_1)$	− 290.167 90	− 3.23	− 290.167 71	HONa	− 237.623 90	+ 0.87	− 237.618 47
$SiH_2(^3B_1)$	− 290.130 13	− 2.64	− 290.130 49	OMg	− 274.726 37	+ 0.30	− 274.721 52
SiH_3	− 290.773 21	− 3.73	− 290.773 51	HOMg	− 275.407 10	− 2.56	− 275.405 10
SiH_4	− 291.418 81	− 4.79	− 291.419 04	OSi	− 364.218 92	− 2.96	− 364.216 18
PH	− 341.427 35	− 3.36	− 341.428 43	OP	− 416.021 20	− 7.25	− 416.022 75
PH_2	− 342.047 25	− 5.30	− 342.049 13	OPH	− 416.627 99	− 7.62	− 416.628 77
PH_3	− 342.676 54	− 7.06	− 342.679 04	OS	− 472.828 54	− 6.65	− 472.829 49
SH	− 398.285 48	− 4.92	− 398.286 98	OCl	− 534.755 75	− 7.26	− 534.756 17
SH_2	− 398.927 82	− 7.47	− 398.930 73	HOCl	− 535.407 52	− 9.04	− 535.408 58
ClH	− 460.337 98	− 6.75	− 460.340 17	F_2	− 199.325 21	− 6.74	− 199.323 97
Li_2	− 14.907 04	+ 0.14	− 14.905 76	FNa	− 261.669 29	+ 3.11	− 261.661 62
LiN	− 62.012 72	+ 0.91	− 62.009 52	FMg	− 299.448 50	− 1.44	− 299.445 38
LiO	− 82.540 29	+ 1.31	− 82.535 56	FAl	− 341.825 83	− 1.14	− 341.821 27
LiOH	− 83.244 73	− 0.50	− 83.240 67	FSi	− 388.790 22	− 2.48	− 388.787 00
LiF	− 107.290 13	+ 1.36	− 107.284 21	$FSiH_3$	− 390.645 01	− 7.00	− 390.644 03
LiCl	− 467.290 09	− 2.08	− 467.287 61	FP	− 440.619 77	− 4.54	− 440.618 62
BeO	− 89.767 53	− 0.67	− 89.763 64	FS	− 497.418 68	− 6.34	− 497.418 18
BeOH	− 90.430 37	− 3.42	− 90.429 23	FCl	− 559.406 67	− 7.97	− 559.406 67
BeF	− 114.468 33	− 1.58	− 114.465 35	Na_2	− 323.724 10	− 0.04	− 323.723 00
BeS	− 412.397 58	− 3.14	− 412.396 16	NaCl	− 621.681 29	− 3.49	− 621.680 22
BeCl	− 474.440 70	− 4.07	− 474.440 21	MgS	− 597.383 42	− 3.05	− 597.381 91
BO	− 99.890 26	− 4.40	− 99.889 70	MgCl	− 659.442 75	− 3.08	− 659.441 27
HBO	− 100.566 37	− 5.71	− 100.566 38	AlCl	− 701.802 85	− 3.03	− 701.800 18
BS	− 422.467 82	− 3.61	− 422.466 87	Si_2	− 577.985 92	− 1.26	− 577.983 76
HBS	− 423.142 99	− 4.37	− 423.141 66	H_3SiSiH_3	− 581.668 99	− 7.07	− 581.668 08
BCl	− 484.475 76	− 4.57	− 484.474 63	SiS	− 686.821 69	− 3.22	− 686.819 21
C_2	− 75.804 02	− 4.33	− 75.803 79	SiCl	− 748.771 53	− 2.80	− 748.768 63

TABLE II (*continued*).

Molecule	E_0 (G1)	Δ	E_0 (G2)
ClSiH$_3$	-750.62354	-6.25	-750.62181
P$_2$	-681.82090	-4.10	-681.81930
H$_2$PPH$_2$	-684.18529	-9.57	-684.18688
PS	-738.63102	-5.49	-738.63081
PCl	-800.61462	-3.24	-800.61216
S$_2$	-795.46663	-4.19	-795.46512
HSSH	-796.67162	-8.24	-796.67187
ClS	-857.43660	-3.91	-857.43367
Cl$_2$	-919.44585	-4.33	-919.44220
CO$_2$	-188.36107	-9.36	-188.36131
COS	-510.94917	-7.95	-510.94800
CS$_2$	-833.53497	-7.70	-833.53355
O$_3$	-225.17516	-9.61	-225.17451
O$_2$Si	-439.36405	-6.07	-439.36100
O$_2$S	-548.01192	-14.06	-548.01572
O$_2$Cl	-609.82359	-18.96	-609.83229
Li$^+$	-7.23584	$\cdots$	-7.23584
Be$^+$	-14.27639	$\cdots$	-14.27639
B$^+$	-24.30175	-0.06	-24.30067
C$^+$	-37.37405	-0.54	-37.37345
N$^+$	-53.98600	-1.13	-53.98599
O$^{+\cdot}$	-74.48439	-1.73	-74.48498
F$^+$	-98.99362	-2.53	-98.99387
Na$^+$	-161.66423	-0.06	-161.66429
Mg$^+$	-199.36402	-0.06	-199.36408
Al$^+$	-241.71379	-0.39	-241.71304
Si$^+$	-288.63626	-0.53	-288.63565
P$^+$	-340.43437	-1.14	-340.43437
S$^+$	-397.27956	-1.74	-397.28016
Cl$^+$	-459.20384	-2.98	-459.20454
CH$_4^+$	-39.94173	-6.57	-39.94488
NH$_3^+$	-56.08110	-6.42	-56.08410
NH$_4^+$	-56.77782	-8.14	-56.78140
OH$^+$	-75.16545	-3.85	-75.16702
OH$_2^+$	-75.86523	-6.17	-75.86798
OH$_3^+$	-76.58866	-7.83	-76.59193
FH$^+$	-99.75667	-5.63	-99.75888
SiH$_4^+$	-291.01376	-3.95	-291.01429
SiH$_5^+$	-291.66246	-4.96	-291.66286
PH$^+$	-341.05702	-2.91	-341.05765
PH$_2^+$	-341.69049	-4.77	-341.69184
PH$_3^+$	-342.31424	-5.58	-342.31640
PH$_4^+$	-342.97317	-7.10	-342.97571
SH$^+$	-397.90666	-3.54	-397.90792
SH$_2^+$ ($^2B_1$)	-398.54531	-5.53	-398.54742
SH$_2^+$ ($^2A_1$)	-398.46036	-5.22	-398.46216
SH$_3^+$	-399.19521	-7.31	-399.19796
ClH$^+$	-459.87096	-5.36	-459.87290
ClH$_2^+$	-460.54882	-7.87	-460.55213
C$_2$H$_2^+$	-76.76565	-4.89	-76.76598
C$_2$H$_3^+$	-77.42907	-7.23	-77.43060
C$_2$H$_4^+$	-78.02469	-8.26	-78.02725
CO$^+$	-112.66023	-6.87	-112.66254
CS$^+$	-435.29103	-4.94	-435.29141
N$_2^+$ ($^2\Sigma_g^+$)	-108.82029	-4.90	-108.82063
N$_2^+$ ($^2\Pi_u$)	-108.78024	-4.47	-108.78015
O$_2^+$	-149.70094	-5.73	-149.70097
FCl$^+$	-558.93977	-8.96	-558.94189
P$_2^+$	-681.43345	-2.90	-681.43179
S$_2^+$	-795.12570	-4.11	-795.12411
Cl$_2^+$	-919.02169	-4.32	-919.01917
C$^-$	-37.82825	-0.95	-37.82806
O$^-$	-75.03385	-2.98	-75.03341
F$^-$	-99.75993	-5.32	-99.76069
Si$^-$	-288.98227	-1.91	-288.98304
P$^-$	-340.84018	-3.77	-340.84167

TABLE II (*continued*).

Molecule	E_0 (G1)	Δ	E_0 (G2)
S$^-$	-397.72683	-5.15	-397.72856
Cl$^-$	-459.80793	-5.62	-459.80899
CH$^-$	-38.45282	-3.49	-38.45403
CH$_2^-$	-39.09072	-5.99	-39.09329
CH$_3^-$	-39.74299	-8.05	-39.74648
NH$^-$	-55.15177	-4.84	-55.15319
NH$_2^-$	-55.81343	-8.56	-55.81743
OH$^-$	-75.70999	-7.33	-75.71276
SiH$^-$	-289.58845	-3.28	-289.58945
SiH$_2^-$	-290.20307	-4.39	-290.20404
SiH$_3^-$	-290.82434	-5.86	-290.82564
PH$^-$	-341.46082	-6.23	-341.46363
PH$_2^-$	-342.09131	-8.20	-342.09495
SH$^-$	-398.36764	-8.51	-398.37159
CN$^-$	-92.73158	-2.91	-92.72879
NO$^-$	-129.73689	-6.33	-129.73752
O$_2^-$	-150.16525	-6.95	-150.16536
OP$^-$	-416.06163	-4.98	-416.06091
S$_2^-$	-795.52697	-5.84	-795.52597
Cl$_2^-$	-919.52909	-8.41	-919.52952

*Total energies in hartrees; Δ is in mhartrees. Calculations done using the GAUSSIAN 88 series of computer programs: M. J. Frisch, M. Head-Gordon, H. B. Schlegel, K. Raghavachari, J. S. Binkley, C. Gonzalez, D. J. Defrees, D. J. Fox, R. A. Whitesides, R. Seeger, C. F. Melius, J. Baker, R. L. Martin, L. R. Kahn, J. J. P. Stewart, E. M. Fluder, S. Topiol, and J. A. Pople (Gaussian, Inc., Pittsburgh, PA, 1988).

G1 energies, the corrections Δ, and G2 energies for all species considered in this paper. The G2 energies were computed using Eq. (4). Tables III–VI contain G2 atomization energies, ionization energies, electron affinities, and proton affinities for the species that have well established experimental values and were studied with G1 theory in Refs. 1 and 2. Also included in these tables are the G1 and experimental values for comparison. Table VII contains a summary of the average absolute deviations of the theoretical values from experiment. For 125 energies the average absolute deviation at the G2 level is 1.21 kcal/mol compared to 1.53 kcal/mol at the G1 level. We now discuss the specific results.

Agreement between G2 theory and experiment is improved for atomization energies over the agreement with G1 theory. The G2 atomization energies have an average absolute deviation of 1.16 kcal/mol, a significant improvement over the deviation of 1.56 kcal/mol at the G1 level. The improvement is especially significant for the first row compounds (1.49 to 0.92 kcal/mol). At the G2 level, with the exception of O$_2$ (2.4 kcal/mol too high), H$_2$CO (2.1 kcal/mol too high), and CO$_2$ (2.7 kcal/mol too high), all of the first-row atomization energies differ from experiment by less than 2 kcal/mol and, with the exception of S$_2$ (3.3 kcal/mol too low) and SO$_2$ (5.1 kcal/mol too low), all of the second-row compounds differ by less than 3 kcal/mol.

The most dramatic improvement in atomization energy is that of LiF where the dissociation energy decreases from 141.3 kcal/mol (G1) to 137.5 kcal/mol (G2). The improvement is due to the large nonadditivity Δ_1 of the (+) and (2*df*) basis set expansions (6.83 millihartrees). Apparently,

TABLE III. Total atomization energies ΣD_0 (in kcal/mol).

Molecule	G1 theory	G2 theory	Expt.[a]
LiH	56.5	56.6	56.0
BeH	45.1	45.5	46.9
CH	80.0	80.5	79.9
CH_2 ($^3B_1$)	177.2	178.6	179.6
CH_2 ($^1A_1$)	171.0	172.0	170.6
CH_3	287.4	289.1	289.2
CH_4	391.0	393.2	392.5
NH	77.2	77.9	79.0
NH_2	168.4	170.1	170.0
NH_3	274.2	276.5	276.7
OH	100.5	101.6	101.3
OH_2	217.3	219.6	219.3
FH	134.5	136.3	135.2
SiH_2 ($^1A_1$)	146.9	147.1	144.4
SiH_2 ($^3B_1$)	123.2	123.8	123.4
SiH_3	213.1	213.5	214.0
SiH_4	304.4	304.8	302.8
PH_2	143.9	144.9	144.7
PH_3	225.0	226.4	227.4
SH_2	171.1	173.0	173.2
ClH	101.2	102.6	102.2
Li_2	26.7	25.9	24.0
LiF	141.3	137.5	137.6
HCCH	387.0	387.2	388.9
H_2CCH_2	530.1	531.7	531.9
H_3CCH_3	663.5	666.6	666.3
CN	176.3	176.0	176.6
HCN	303.1	302.8	301.8
CO	257.6	258.0	256.2
HCO	270.3	271.4	270.3
H_2CO	358.1	359.3	357.2
H_3COH	479.4	482.3	480.8
N_2	224.8	223.8	225.1
H_2NNH_2	401.4	404.4	405.4
NO	150.2	150.6	150.1
O_2	115.4	115.6	118.0
HOOH	250.3	252.1	252.3
F_2	37.5	36.6	36.9
CO_2	384.3	384.6	381.9
Na_2	19.8	19.2	16.6
Si_2	74.3	73.6	74.0
P_2	116.0	114.7	116.1
S_2	98.4	97.4	100.7
Cl_2	58.1	55.8	57.2
NaCl	99.4	98.8	97.5
SiO	190.2	188.8	190.5
SC	171.3	170.5	169.5
SO	120.1	120.8	123.5
ClO	60.9	61.2	63.3
ClF	60.9	61.0	60.3
Si_2H_6	502.9	503.0	500.1
CH_3Cl	370.6	372.1	371.0
CH_3SH	442.8	445.0	445.1
HOCl	156.1	156.8	156.3
SO_2	246.6	248.9	254.0

[a] Experimental references are given in Refs. 1 and 2.

TABLE IV. Ionization potentials (eV).

	G1 theory	G2 theory	Expt.[a]
$Li \rightarrow Li^+$	5.34	5.34	5.39
$Be \rightarrow Be^+$	9.44	9.41	9.32
$B \rightarrow B^+$	8.19	8.20	8.30
$C \rightarrow C^+$	11.17	11.18	11.26
$N \rightarrow N^+$	14.47	14.48	14.54
$O \rightarrow O^+$	13.54	13.52	13.61
$F \rightarrow F^+$	17.39	17.39	17.42
$CH_4 \rightarrow CH_4^+$	12.68	12.68	12.62
$NH_3 \rightarrow NH_3^+$	10.17	10.19	10.18
$OH \rightarrow OH^+$	12.97	12.98	13.01
$OH_2 \rightarrow OH_2^+$	12.60	12.63	12.62
$FH \rightarrow FH^+$	16.07	16.08	16.04
$Na \rightarrow Na^+$	4.95	4.95	5.139
$Mg \rightarrow Mg^+$	7.68	7.65	7.646
$Al \rightarrow Al^+$	5.93	5.93	5.984
$Si \rightarrow Si^+$	8.09	8.10	8.15
$P \rightarrow P^+$	10.44	10.44	10.49
$S \rightarrow S^+$	10.21	10.20	10.36
$Cl \rightarrow Cl^+$	12.86	12.85	12.97
$SiH_4 \rightarrow SiH_4^+$	11.02	11.01	11.00
$PH \rightarrow PH^+$	10.08	10.09	10.15
$PH_2 \rightarrow PH_2^+$ ($^1A_1$)	9.71	9.72	9.82
$PH_3 \rightarrow PH_3^+$	9.86	9.87	9.87
$SH \rightarrow SH^+$	10.30	10.31	10.37
$SH_2 \rightarrow SH_2^+$ ($^2B_1$)	10.41	10.43	10.47
$SH_2 \rightarrow SH_2^+$ ($^2A_1$)	12.72	12.75	12.78
$ClH \rightarrow ClH^+$	12.71	12.71	12.75
$C_2H_2 \rightarrow C_2H_2^+$	11.44	11.42	11.40
$C_2H_4 \rightarrow C_2H_4^+$	10.59	10.58	10.51
$CO \rightarrow CO^+$	14.07	14.01	14.01
$N_2 \rightarrow N_2^+$ ($^2\Sigma_g$)	15.59	15.56	15.58
$N_2 \rightarrow N_2^+$ ($^2\Pi_u$)	16.69	16.67	16.70
$O_2 \rightarrow O_2^+$	12.16	12.17	12.07
$P_2 \rightarrow P_2^+$	10.54	10.54	10.53
$S_2 \rightarrow S_2^+$	9.28	9.28	9.36
$Cl_2 \rightarrow Cl_2^+$	11.53	11.51	11.50
$ClF \rightarrow ClF^+$	12.70	12.65	12.66
$SC \rightarrow SC^+$	11.47	11.42	11.33

[a] Experimental references given in Refs. 1 and 2.

only 1.9 kcal/mol at the G1 level, the change is not as dramatic. More ionic species are considered in Sec. IV and significant changes due to Δ_1 are also found for these species.

The addition of the third d function and the second p function to the basis set contributes to improvement in the atomization energies at the G2 level. The increase in basis set size, along with the modification in the higher level correction (HLC), has the largest effect on hydrides of the first-row compounds. In the majority of cases, the G2 value is in better agreement with experiment and contributes to the overall improvement in G2 theory compared to G1 theory. The atomization energies of C_2H_6 [2.8 kcal/mol too low (G1) compared to 0.3 kcal/mol too high (G2)], NH_3 [2.5 kcal/mol too low (G1) compared to 0.2 kcal/mol too low (G2)], N_2H_4 [4.0 kcal/mol too low (G1) compared to 1.0 kcal/mol too low (G2)], and H_2O_2 [2.0 kcal/mol too low (G1) compared to 0.2 kcal/mol too low (G2)] are notable for their improved agreement with experiment at the G2 level. Also, the addition of the third d function is largely responsible for the increase by 2 kcal/mol of the dissociation

in ionic systems the polarization extension ($2df$) on the positive center (Li) duplicates some of the contribution of the diffuse function (+) on the negative center (F). This is corrected in G2 theory. The only other ionic species considered in this set, NaCl, also improves, but since it was off by

TABLE V. Electron affinities (in eV).

	G1 theory	G2 theory	Expt.[a]
C	1.19	1.19	1.26
CH	1.11	1.13	1.24
CH$_2$	0.65	0.66	0.65
CH$_3$	0.01	0.04	0.08
NH	0.28	0.30	0.38
NH$_2$	0.74	0.77	0.74
O	1.41	1.40	1.46
OH	1.85	1.87	1.83
F	3.46	3.48	3.40
O$_2$	0.47	0.47	0.44
NO	− 0.06	− 0.07	0.02
CN	4.03	3.97	3.82
Si	1.32	1.35	1.385
P	0.60	0.64	0.746
S	1.96	2.00	2.077
Cl	3.57	3.60	3.615
SiH	1.15	1.18	1.277
SiH$_2$	0.96	0.99	1.124
SiH$_3$	1.39	1.42	1.44
PH	0.91	0.96	1.00,1.028
PH$_2$	1.20	1.25	1.26,1.271
HS	2.24	2.30	2.314
PO	1.10	1.04	1.09
S$_2$	1.64	1.66	1.663
Cl$_2$	2.26	2.38	2.39

[a] Experimental references given in Refs. 1 and 2.

energy of SO$_2$ [from 246.6 (G1) to 248.9 kcal/mol (G2)]. However, it still remains 5.1 kcal/mol below the experimental value. The reason for the remaining discrepancy is unclear and needs further study. The singlet–triplet energy differences for CH$_2$ and SiH$_2$ are improved somewhat at the G2 level with the triplet stabilized relative to the singlet. For CH$_2$ the difference increases from 6.2 (G1) to 6.6 kcal/mol (G2), while for SiH$_2$ where the singlet is more stable, it decreases from 23.7 (G1) to 23.3 kcal/mol (G2). The experimental values are 9.0 and 21.0 kcal/mol, respectively. Finally, the dissociation energies of the triplet molecules O$_2$, S$_2$, and SO remain in error by more than 2 kcal/mol at the G2 level with no significant improvement over the G1 level. The values for SO and S$_2$ are actually somewhat worse. Hence, this remains another area for further improvement.

TABLE VI. Proton affinities (kcal/mol).[a]

	G1 theory	G2 theory	Expt.[b]
NH$_3$	202.7	202.5	202.5
OH$_2$	163.3	163.1	165.1
C$_2$H$_2$	152.5	153.6	152.3
SiH$_4$	152.9	153.0	154
PH$_3$	186.1	186.2	187.1
SH$_2$	167.8	167.7	168.8
ClH	132.3	133.0	133.6

[a] At 0 K.
[b] From S. G. Lias, J. F. Liebman, and R. D. Levin, J. Phys. Chem. Ref. Data **13**, 695 (1984).
Corrections to 0 K from J. A. Pople and L. A. Curtiss, J. Phys. Chem. **91**, 155 (1987).

TABLE VII. Average absolute deviations of G1 and G2 results compared to experiment (from Tables III–VI).[a]

		Ave. Abs. Dev.			
		G1		G2	
	Species	kcal/mol	eV	kcal/mol	eV
ΣD_0	1st row	1.49	0.065	0.92	0.040
	2nd row	1.71	0.074	1.47	0.064
	1st + 2nd row	1.56	0.068	1.16	0.050
IP$_0$	1st row	1.27	0.055	1.13	0.049
	2nd row	1.59	0.069	1.34	0.058
	1st + 2nd row	1.43	0.062	1.24	0.054
EA$_0$	1st row	1.57	0.068	1.52	0.066
	2nd row	1.94	0.084	1.08	0.047
	1st + 2nd row	1.75	0.076	1.29	0.056
PA$_0$	1st + 2nd row	1.00	0.043	1.04	0.045

[a] ΣD_0 = atomization energy, IP$_0$ = ionization potential, EA$_0$ = electron affinity, PA$_0$ = proton affinity.

The absolute average deviations listed in Table VII indicate that, for the ionization potentials of the 37 atoms and molecules in Table IV, the deviation decreases from 0.063 (G1) to 0.055 eV (G2). For the 24 molecules in Table IV the deviation improves from 0.050 (G1) to 0.039 eV (G2). The largest change is for the ionization potential of CO which decreases from 14.07 (G1) to 14.01 eV (G2), in good agreement with the experimental value of 14.01 eV. The deviation for G2 theory is ⩽0.1 eV from experiment for all 24 molecules considered. Of the atoms considered in Table IV, only Na, S, and Cl differ by more than 0.1 eV from experiment. As discussed in Ref. 2, the error for Na is due to neglect of inner shell correlation energy.

The electron affinities (see Table V) calculated at the G2 level improve significantly with the average absolute deviation decreasing from 0.076 (G1) to 0.056 eV (G2). Most of the improvement occurs for the electron affinities of the species containing second row atoms [0.084 eV (G1) compared to 0.047 eV (G2)]. The largest improvements are for CN and Cl$_2$. For CN the error in the electron affinity is reduced from 0.21 (G1) to 0.15 eV (G2). The error is further reduced to 0.07 eV if QCISD(T)/6–31G* geometries are used instead of MP2 = FU/6–31G* geometries.[10] (The MP2 = FU/6–31G* geometry is poor for CN.) For Cl$_2$ the error decreases from 0.13 (G1) to 0.01 eV (G2). Much of the improvement in the G2 electron affinities can be traced to the correction for the nonadditivity of the diffuse-sp and 2df basis set extensions in the G1 procedure. At the G2 level all of the electron affinities are now within 0.15 eV of experiment. Only four are off by more than 0.1 eV. These are CH (0.11 eV too low), CN (0.15 eV too high), P (0.11 eV too low), and SiH$_2$ (0.13 too low).

The G2 level proton affinities (see Table VI) show little change from the G1 level values which were already in good agreement with experiment. All values are within 2 kcal/mol of the experimental value with an absolute average deviation of 1.04 kcal/mol for 7 species.

IV. PREDICTIONS OF ATOMIZATION ENERGIES OF OTHER COMPOUNDS

In this section we report the results of applying the G2 procedure to a large number of neutral molecules most of which have experimental atomization energies with an uncertainty of greater than 1 kcal/mol. The G2 atomization energies of the 36 molecules in this category, considered in the study on second-row compounds,[2] are listed in Table VIII. The G2 results for an additional 43 molecules, not included in the previous studies,[1,2] are listed in Table IX. Experimental and G1 values of ΣD_0 are also listed in Tables VIII and IX for comparison with the G2 values. Most of the experimental ΣD_0 values were derived from enthalpies of formation (0 K) in the JANAF tables.[11]

TABLE VIII. Total atomization energies (in kcal/mol), ΣD_0, for other species studied in Ref. 2.

	G1 theory	G2 theory	Expt.[a]
NaH	44.4	45.0	47.2 ± 5
MgH	28.5	29.3	46 ± 12,30.9 [b]
MgH$_2$	99.1	99.8	
AlH	72.2	72.3	67.0 ± 5, < 70.6 [b]
AlH$_2$	117.4	118.0	
AlH$_3$	202.2	202.7	
SiH	70.6	70.8	68.7, < 70.6 [b]
PH	68.6	69.2	70.5 ± 2 [c]
HS	81.9	82.8	87.7 ± 1.2,81.7 [b]
AlCl	122.0	120.8	119.2, 118.1 [b]
AlF	164.0	161.6	160.0 ± 1.6,158.9 [b]
SiS	146.2	145.0	147.4 ± 3.0
PN	146.1	144.9	165.8 ± 1.2,146.6 ± 5.0 [b,d]
PO	138.8	139.6	140.7 ± 0.9, 141.8 [b]
SF	82.2	81.8	81.2 ± 2.1
ClSi	101.1	99.6	88.3 ± 3
MgO	61.6	59.2	80 ± 6,81.4 [b]
LiCl	113.7	112.2	113.0 ± 3.0
NaF	119.5	114.6	113.2 ± 0.5, 122.9 [b]
SiF	140.4	138.6	130.3 ± 3, 128.4 [b]
SiC	98.7	98.9	106.5 ± 8, 107.0 [b]
SN	107.6	108.2	110.7 ± 6 [c]
BeCl	88.3	88.6	91.1 ± 3, 104.5 [b]
H$_3$CPH$_2$	501.8	504.2	507.9 [f]
H$_2$CPH	368.9	370.0	
H$_2$CS	309.6	310.3	317.4 ± 2 [g]
HCP	244.2	244.3	260.9 ± 15 [h]
CP	122.7	122.9	121.8 ± 2
HPO	205.8	206.2	198.7 ± 10
NaOH	185.5	182.1	182.7 ± 3
P$_2$H$_4$	344.7	345.4	338.1 [f]
S$_2$H$_2$	227.0	227.2	237.0 [i]
H$_3$SiCl	321.9	321.2	321.8 ± 2 [h]
H$_3$SiF	363.0	362.7	367.7 ± 5 [h]
SiO$_2$	292.5	291.0	297.2 ± 8
ClO$_2$	114.6	120.2	121.0 ± 1.5

[a] From JANAF tables (Ref. 11) unless otherwise specified.
[b] Reference 15.
[c] J. Berkowitz, L. A. Curtiss, S. T. Gibson, J. P. Greene, G. L. Hillhouse, and J. A. Pople, J. Chem. Phys. **84**, 375 (1986).
[d] K. A. Gingerich, J. Chem. Phys. **73**, 2735 (1969).
[e] P. O'Hare, J. Chem. Phys. **52**, 2992 (1970).
[f] Reference 25, estimated.
[g] M. Roy and T. B. McMahon, J. Organic Mass Spectrosc. **17**, 392 (1982).
[h] JANAF tables (Ref. 11), estimated.
[i] Reference 26.

TABLE IX. Total atomization energies (in kcal/mol), ΣD_0, for other species.[a]

	G1 theory	G2 theory	Expt.[b]
BeH$_2$	138.6	138.8	149.3 [c]
BH ($^1\Sigma^+$)	82.8	82.8	78.2 ± 2 [d]
BH$_2$	159.2	160.1	188.8 ± 15.2
BH$_3$	264.4	265.3	262.3 ± 2.4
LiN ($^3\Sigma^-$)	39.4	37.2	70.2 ± 40 [c]
LiO ($^2\Pi$)	79.1	76.1	76.6 ± 5
LiOH ($^1\Sigma^+$)	207.4	204.8	203.8 ± 1.5
BeO ($^1\Sigma^+$)	101.7	99.9	104.2 ± 3
BeOH ($^2A'$)	203.9	203.8	214.3 ± 10
BeF ($^2\Sigma^+$)	133.2	131.9	136.1 ± 2
BeS ($^1\Sigma^+$)	74.8	74.6	79.8 ± 15 [c]
BO ($^2\Sigma^+$)	191.7	191.8	192.4 ± 2
HBO ($^1\Sigma^+$)	302.2	302.6	291.7 ± 3
BS ($^2\Sigma^+$)	131.8	131.7	140.0 ± 4
HBS ($^1\Sigma$)	241.8	241.4	239.0 ± 10 [c]
BCl ($^1\Sigma^+$)	123.2	123.0	129.4 ± 4
C$_2$ ($^1\Sigma_g^+$)	147.3	147.6	140.95 ± 0.9
C$_2$H	253.6	253.8	[e]
C$_2$H$_3$	419.9	421.3	[e]
C$_2$H$_5$	563.1	565.8	[e]
H$_2$CNH	413.2	414.8	
H$_3$CNH$_2$	539.5	542.5	542.7 ± 0.1 [f]
CF ($^2\Pi$)	131.4	131.7	128.3 ± 2
HCF ($^1A'$)	206.2	207.0	210.2 ± 7
H$_3$CF	397.8	399.8	397.4 ± 8
CCl($^2\Pi$)	96.0	95.9	80 ± 5
HNO($^1A'$)	197.1	197.9	198.7
NF($^3\Sigma^-$)	75.7	76.1	71.4 ± 8 [c]
NSi ($^2\Sigma^+$)	105.9	105.6	130 ± 15
HOO($^2A''$)	164.1	165.5	161.1 ± 2
HOF	148.9	149.7	151.9 ± 1 [g]
ONa ($^2\Pi$)	67.7	64.5	64.3 ± 10
HONa	185.5	182.1	182.7 ± 3
HOMg ($^2\Sigma^+$)	175.0	174.4	184.9 ± 9 [c]
FMg ($^2\Sigma^+$)	106.4	105.1	109.8 ± 2
FP ($^3\Sigma^-$)	106.1	105.2	106.1 ± 4.6 [c]
MgS ($^1\Sigma^+$)	51.7	51.3	<66 ± 16
MgCl ($^2\Sigma^+$)	75.3	75.0	73.8 ± 10
PS ($^2\Pi$)	99.2	98.9	140 ± 25 [c]
PCl ($^3\Sigma^-$)	75.3	73.6	73.0 [c]
ClS ($^2\Pi$)	65.9	64.1	57.1 ± 4 [c]
COS	331.1	330.5	327.7 ± .2
CS2	276.4	275.7	273.5 ± .2
O$_3$ ($^1A_1$)	143.7	143.3	142.2 ± 0.5

[a] This table contains additional species that were not considered in Refs. 1 and 2. Many have significant uncertainties in the experimental values.
[b] From JANAF tables (Ref. 11) unless otherwise specified.
[c] JANAF tables (Ref. 11), estimated values.
[d] See Ref. 4 for more discussion.
[e] See Table X.
[f] From ΔH_{f0}^{298} in Ref. 25, adjusted to 0 K using scaled HF/6–31G* frequencies.
[g] See Ref. 8 for more discussion.

The basic conclusions concerning the atomization energies of the molecules in Table VIII which have been made in Ref. 2 from the G1 results remained unchanged at the G2 level. Therefore, we will not repeat our discussion of the specific experimental values here except to point out significant differences between G1 and G2 theory. The G2 atomization energies of 11 of the 36 molecules in Table VIII differ by more than 1 kcal/mol from the G1 values. Five of these are "ionic" molecules including AlF (decreases by 2.4 kcal/

TABLE X. C–H bond dissociation energies at 0 K (in kcal/mol) in C_2H_n, $n = 2,4,6$.

	G1	G2	Other theory	Expt.
$C_2H_2 \rightarrow C_2H + H$	133.4 [a]	133.4	131.5,[b] 129.7,[c] 130.1 [d]	126–133 [e]
$C_2H_4 \rightarrow C_2H_3 + H$	110.1 [f]	110.4	109.5 [c]	98–117 [g]
$C_2H_6 \rightarrow C_2H_5 + H$	100.4 [h]	100.8		97–100 [i]

[a] Reference 9.
[b] Reference 22.
[c] Reference 23.
[d] Reference 24.
[e] Range of values quoted in Ref. 19.
[f] Reference 3.
[g] Range of values quoted in Ref. 27.
[h] Reference 7.
[i] Range of values quoted in Ref. 7.

mol), MgO (decreases by 2.4 kcal/mol), LiCl (decreases by 1.5 kcal/mol), NaF (decreases by 4.9 kcal/mol), and NaOH (decreases by 3.4 kcal/mol). The G2 values should be more reliable. The decreases are largely due to the correction in G2 theory for the nonadditivity of the diffuse-sp and $2df$ basis set extensions in G1 theory. The G2 results for these five species are generally in better agreement with experiment, and, for MgO and NaF, with previous high level calculations by Bauschlicher et al.[12] For NaF there are two experimental numbers: 113.2 kcal/mol (JANAF[11]) and 122.9 kcal/mol (Huber and Herzberg[15]). The G1 number of 119.5 kcal/mol is between the two values while the G2 value of 114.6 kcal/mol supports the JANAF value. This is also in agreement with the results of Bauschlicher et al.[12] who calculate a value of 115.1 kcal/mol for the dissociation energy of NaF. Two of the 11 molecules are triatomics which have significant contributions from the third d function. These are SiO_2 and ClO_2. The atomization energy of SiO_2 decreases by 1.5 kcal/mol and that of ClO_2 increases by 5.6 kcal/mol. The ClO_2 atomization energy of 120.2 kcal/mol is now in good agreement with the experimental value of 121.0 ± 1.5 kcal/mol. The SiO_2 atomization energy of 291.0 kcal/mol is about 6 kcal/mol lower than the experimental value of 297.2 kcal/mol, but this has a large uncertainty of ± 8 kcal/mol. The remaining five molecules that change by more than 1 kcal/mol all contain second-row atoms and are SiS (decreases by 1.2 kcal/mol), PN (decreases by 1.2 kcal/mol), ClSi (decreases by 1.5 kcal/mol), SiF (decreases by 1.5 kcal/mol), and H_3CPH_2 (increases by 2.4 kcal/mol). These changes are due to both corrections (Δ_1 and Δ_2) in G2 theory.

We now turn to the atomization energies of the molecules in Table IX. The changes in the G2 energies compared to the G1 energies in Table IX are similar to those discussed previously for molecules in Tables III and VIII. Significant changes occur for ionic molecules (LiN, LiO, LiOH, BeO, BeF, ONa, HONa, FMg) where the nonadditivity correction is important, hydrides (C_2H_3, C_2H_5, H_2CNH, H_3CNH_2, H_3CF, HOO) where the second p function is important, and some second-row molecules (PCl, ClS) where the third d function is important. The G2 values should be

more reliable for these cases. The G2 values for about three-quarters of the molecules in Table IX are in reasonable agreement with the experimental values. For the remaining one-quarter there is significant disagreement and we comment on these cases.

LiN: The JANAF[11] value of 70.2 ± 40 kcal/mol is estimated from dissociation energies of related molecules. The G2 value of 39.4 kcal/mol is much lower and more reliable. *BeOH:* The G2 atomization energy of BeOH is 203.8 kcal/mol. This is about 10 kcal/mol lower than the JANAF value of 214.3 kcal from mass spectral data which has a large uncertainty of ± 10 kcal/mol. Bauschlicher et al.[13] report a theoretical value of 108.4 kcal/mol for the dissociation energy of the Be–O bond in BeOH. Using the experimental value for the dissociation energy of OH radical in Table II, this corresponds to an atomization energy for BeOH of 209.7 kcal/mol also significantly lower than the experimental value. Hence, our results and those of Bauschlicher et al.[13] suggest that the experimental atomization energy of BeOH in the JANAF tables is too high by 5–10 kcal/mol. At the G1 and G2 levels of theory BeOH is predicted to be nonlinear, but the energy difference with linear BeOH is very small, 0.4 and 0.2 kcal/mol, respectively.

HBO: The G2 atomization energy of HBO is 302.6 kcal/mol. This is about 10 kcal/mol higher in energy than the JANAF value of 291.7 ± 1 kcal/mol which is derived from mass spectrometric data on DBO. The difference is much larger than is expected of G2 theory which does well on the dissociation energy of BO (see Table IX). The disagreement between the G2 result and the mass spectrometric value suggests that the latter may be unreliable.

BS: The G2 dissociation energy of BS is 131.7 kcal/mol. This is about 8 kcal/mol lower than the JANAF value of 140.0 ± 4 kcal/mol derived from mass spectral data. Gaydon[14] recommends a value of 118 from spectroscopic data, but this has a very large uncertainty of ± 18 kcal/mol. Since the G2 result for isovalent BO is in good agreement with experiment (see Table IX), the G2 value for the D_0 of BS should be more reliable than the experimental values.

C_2: The G2 method gives 147.6 kcal/mol for the dissociation energy of the $^1\Sigma_g^+$ ground state of C_2. The JANAF tables give a value of 141.0 ± 1 kcal/mol from a spectroscopic study. However, Huber and Herzberg[15] give a value of 143.2 kcal/mol which is the average of two thermochemical values of 142.3 ± 2.5 and 144.1 kcal/mol. Bauschlicher et al.[16] report a theoretical value of 140.9 kcal/mol, but indicate that remaining basis set saturation would increase the value. The G2 value may be too large because the higher level correction may overestimate the basis set deficiency in singlet C_2 molecule relative to two triplet carbon atoms. Further study of the dissociation energy of C_2 is required, both by experiment and theory, to pin down a more accurate value for its D_0.

CCl: The G2 value for the dissociation energy of CCl is 95.9 kcal/mol. This is about 16 kcal/mol higher than the JANAF value of 80 ± 5 kcal/mol which is from chemiluminescence of flame reactions. However, Gaydon[14] recommends a value of 88 ± 11 kcal/mol based on spectroscopic evidence. The G2 results suggest that both of these values

may be low.

NF: The G2 value for the D_0 of the triplet ground state of NF is 76.1 kcal/mol. The JANAF value is 71.4 kcal/mol with a large uncertainty of ± 8 kcal/mol. Since the G2 method is low by about 2 kcal/mol for O_2 which is also a triplet and isoelectronic with NF, the G2 value for NF may be low by a similar amount. Montgomery et al.[17] have recently reported a theoretical study of the dissociation energy of NF using their complete basis set (CBS) method. They obtain a D_0 value of 76.1 $\pm$ 0.9 kcal/mol in agreement with the G2 results.

NSi: The G2 method gives a D_0 value of 105.6 kcal/mol for NSi. This is about 24 kcal/mol lower than the JANAF value of 130 $\pm$ 15 kcal/mol, based on spectroscopic data. Gaydon[14] recommends a value of 104 $\pm$ 9 kcal/mol from spectroscopic data. The G2 value supports the value of Gaydon over that of the JANAF tables.

HOMg: The results for magnesium hydroxide are similar to that for beryllium hydroxide. The G2 atomization energy of 174.4 kcal/mol is about 10 kcal/mol lower than the JANAF value of 184.9 $\pm$ 9 kcal/mol. Bauschlicher et al.[13] report a theoretical for D_0 (Mg–OH) of 76.3 kcal/mol. This corresponds to an atomization energy for MgOH of 177.6 kcal/mol. Hence, theory suggests that the experimental atomization energy of HOMg is too high.

MgS: The G2 method gives a dissociation energy of 51.3 kcal/mol for MgS. There is considerable uncertainty in the experimental value. The JANAF tables adopt D_0 (MgS) $\leqslant 66 \pm 16$ kcal/mol while Huber and Herzberg[15] and Gaydon[14] recommend < 55 kcal/mol. The G2 value should be more reliable than the experimental values.

PS: The G2 value for the D_0 of PS is 98.9 kcal/mol. The JANAF tables list an estimated value of 140 $\pm$ 25 kcal/mol. Gaydon[14] recommends 120 $\pm$ 23 kcal/mol based on spectroscopic data and Huber and Herzberg[15] list a value of 104 kcal/mol from mass spectrometric data. The G2 result supports the value chosen by Huber and Herzberg and suggests that it might even be lower.

ClS: The G2 value of D_0 for ClS is 64.1 kcal/mol. This should be considered more reliable than the estimated value listed in JANAF of 57.1 $\pm$ 4 kcal/mol.

There are four one-heavy atom hydrides (BeH_2, BH, BH_2, and BH_3) listed in Table VIII. These were studied previously in separate studies with the G1 method[4] and with a G1-like theory without the QCI correction.[18] The G2 atomization energies for these species do not change significantly from the previous studies and the assessment of the experimental data remains unchanged.

There are four molecules in Table IX with accurate experimental atomization energies. These are H_3CNH_2, COS, CS_2, and O_3. Ozone has been studied previously at the G1 level of theory.[6] The other three were not studied with the G1 method. The ΣD_0 values for all four molecules are in agreement with the experimental values. Little change occurs from G1 to G2 theory, except for H_3CNH_2 where the addition of the second p function makes a significant improvement.

Finally, Table IX lists atomization energies for the C_2H, C_2H_3, and C_2H_5 radicals. These species have previously

been studied at the G1 level of theory.[3,7,9] The experimental enthalpies of formation of these species, especially C_2H, have been the subject of some uncertainty in recent years. In Table X we list the energies for breaking the first CH bond in acetylene, ethylene, and ethane. The G1 and G2 energies for these bond breakings are nearly the same. For acetylene the experimental D_0 (HCC–H) values have fallen in two groups,[19] one at around 126 kcal/mol and the other at 131–132 kcal/mol. The most recent experimental measurements[20,21] support the latter value as do recent theoretical calculations.[9,22–24] The G1 and G2 values are 2–3 kcal/mol higher than the three theoretical values from other groups.[22–24] Use of QCISD(T)/6–31G* geometries, which is important for the C_2H radical, reduces the G2 value to 132.3 kcal/mol,[10] in good agreement with the most recent experimental values of 131.3 $\pm$ 0.7 (Ref. 20) to 131.1 $\pm$ 0.7 (Ref. 21) kcal/mol. The G2 values for D_0 (H_2CCH–H) and D_0 (H_3CCH$_2$–H) of 110.4 and 100.8 kcal/mol, respectively, are also in good agreement with the recent experimental values of Berkowitz et al.[7,27] of $\geqslant 106.6 \pm 1$ and 99.6 kcal/mol, respectively.

V. CONCLUSIONS

The Gaussian-2 theoretical procedure (G2 theory), based on *ab initio* molecular orbital theory, for calculation of molecular energies (atomization energies, ionization potentials, electron affinities, and proton affinities) of compounds containing first- (Li–F) and second-row atoms (Na–Cl) has been presented. This new theoretical procedure adds three features to G1 theory including a correction for nonadditivity of diffuse-sp and 2df basis set extensions, a basis set extension containing a third d function and a second p function, and a modification of the higher level correction. In tests carried out in this study, we have found G2 theory to be a significant improvement over G1 theory because it eliminates a number of deficiencies present in G1 theory. Of particular importance is the improvement in atomization energies of ionic molecules such as LiF and hydrides such as C_2H_6, NH_3, N_2H_4, H_2O_2, and CH_3SH. The average absolute deviation from experiment of atomization energies of 39 first-row compounds is reduced from 1.42 to 0.92 kcal/mol. In addition, G2 theory gives improved performance for hypervalent species and electron affinities of second-row species (the average deviation from experiment of electron affinities of second-row species is reduced from 1.94 to 1.08 kcal/mol). G2 theory is still inadequate (low by about 3 kcal/mol) for triplet states of molecules such as O_2 and S_2, as was G1 theory, and although the atomization energy of SO_2 is improved, it still remains about 5 kcal/mol below experiment. These remain problems for further study.

G2 atomization energies for 43 molecules not previously studied with G1 theory, many of which have uncertain experimental data, have also been presented and differences with experiment are assessed. For a number of species the results of G2 theory indicate that values in thermochemical tables are in error and should be re-examined. Among these are LiN, BeOH, HBO, BS, CCl, NSi, MgOH, MgS, PS, and ClS. In addition, G2 results for five ionic species (AlF, MgO, LiCl, NaF, NaOH) studied previously by G1 theory[2] show

significant decreases (greater than 1 kcal/mol) in atomization energies. The results are generally in better agreement with experiment and, for MgO and NaF, with previous high level calculations by Bauschlicher *et al.*[12]

Finally, while G1 theory has proved to be remarkably accurate in many applications, G2 theory strengthens G1 theory by eliminating several deficiencies. We are currently using G2 theory for a number of systems where the improvements over G1 theory should provide more reliable results including studies of N_2H_n and H_2O_n species.

ACKNOWLEDGMENTS

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