

Extension of Gaussian-3 theory to molecules containing third-row atoms K, Ca, Ga–Kr

Larry A. Curtiss^{a)} and Paul C. Redfern

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

Vitaly Rassolov, Gary Kedziora, and John A. Pople

Department of Chemistry, Northwestern University, Evanston, Illinois 60208

(Received 2 January 2001; accepted 28 February 2001)

Gaussian-3 (G3) theory is extended to molecules containing the third-row nontransition elements K, Ca, Ga–Kr. Basis sets compatible with those used in G3 theory for molecules containing first- and second-row atoms have been derived. The G3 average absolute deviation from experiment for a set of 47 test reactions containing these elements is 0.94 kcal/mol. This is a substantial improvement over Gaussian-2 theory, which has an average absolute deviation of 1.43 kcal/mol for the same set. Variations of G3 theory are also presented that are based on reduced orders of perturbation theory. These variations also show similar improvement over the corresponding G2 methods. The use of scaling parameters in G3 theory for the third row was investigated and found to perform nearly as well as use of the higher level correction. In addition, these methods are evaluated on a set of molecules containing K and Ca for which the experimental data are not accurate enough for them to be included in the test set. Results for this set indicate that G3 theory performs significantly better than G2 for molecules containing Ca. When the 47 third-row systems are added to the G3/99 database the complete G3 average absolute deviation becomes 1.06 kcal/mol for 423 energies.

© 2001 American Institute of Physics. [DOI: 10.1063/1.1366337]

I. INTRODUCTION

The Gaussian-2 (G2) theory¹ of molecular energies was introduced to provide a method for calculating accurate thermochemical data for molecules containing first- and second-row atoms. G2 theory is a composite procedure based on *ab initio* molecular orbital theory. G2 theory was extended to molecules containing the third-row nontransition elements K, Ca Ga–Kr.^{2,3} This extension of G2 theory required: (1) development of new basis sets for K, Ca Ga–Kr that were compatible with those of the first- and second-row atoms, (2) inclusion of spin–orbit corrections, which become significant for third-row atoms and for some molecules containing third-row atoms, and (3) assessment of the method on a suitable set of species for which accurate experimental data exist. Recently, we presented the third in the Gaussian-*n* series, Gaussian-3 (G3) theory,⁴ which achieved significantly improved accuracy compared to Gaussian-2 (G2) theory. G3 theory is a composite *ab initio* technique similar in spirit to G2 theory, but with some new features and several modifications including (1) single-point correlation energies calculated with different basis sets, the largest being the G3Large basis,⁴ (2) a spin–orbit correction for first- and second-row elements added to the total energy, (3) a modified higher level correction with four parameters instead of two, and (4) a core-correlation term added at the second-order Møller–Plesset level. The average absolute deviation of G3 theory from experiment for the 299 energies in the G2/97 test set^{5,6} is 1.01 kcal/mol compared to 1.48 kcal/mol for G2 theory.

For the recently introduced G3/99 test set⁷ that contains 376 energies, G3 theory has an average absolute deviation of 1.07 kcal/mol.

In this paper we describe the extension of G3 theory to the third-row nontransition elements K, Ca, Ga–Kr. In Sec. II, the theoretical procedures used in this extension are described. In Sec. III, the construction of the basis sets compatible with the ones for first and second row in G3 theory is described. In Sec. IV, G3 theory is evaluated for a set of test species. Finally, in Sec. V modifications of G3 theory based on reduced orders of perturbation theory and scaling parameters are presented.

II. THEORETICAL PROCEDURE

Gaussian-3 theory⁴ is based on standard *ab initio* molecular orbital methods. G3 theory involves approximating the quadratic configuration interaction QCISD(T) energy⁸ of a molecule at a large basis set assuming additivity of a series of calculations at lower levels of theories.⁹ The G3 energy is given by

$$\begin{aligned}
 E_0(\text{G3}) = & \text{MP4}/d + [\text{QCISD(T)}/d - \text{MP4}/d] \\
 & + [\text{MP4}/\text{plus} - \text{MP4}/d] + [\text{MP4}/2df,p - \text{MP4}/d] \\
 & + [\text{MP2(FU)}/\text{G3L} - \text{MP2}/2df,p \\
 & - \text{MP2}/\text{plus} + \text{MP2}/d] \\
 & + E(\text{SO}) + E(\text{HLC}) + E(\text{ZPE}), \quad (1)
 \end{aligned}$$

where $d = 6-31\text{G}(d)$, $\text{plus} = 6-31 + \text{G}(d)$, $2df,p = 6-31\text{G}(2df,p)$, $\text{G3L} = \text{G3Large}$ basis set,⁴ $E(\text{SO}) = \text{spin-orbit}$

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

TABLE I. Spin-orbit corrections^a (in mhartrees) of first- and second-row diatomics^b and third-row species.^c

Species	$E(\text{SO})$	Species	$E(\text{SO})$	Species	$E(\text{SO})$	Species	$E(\text{SO})$
CH $^2\Pi$	-0.07	P $_2^+ ^2\Pi_u$	-0.57	Ga 2P	-2.51	KBr $^+ ^2\Pi$	-2.99
OH $^2\Pi$	-0.30	S $_2^+ ^2\Pi_g$	-1.25	Ge 3P	-4.41	AsH $^+ ^2\Pi$	-3.54
NO $^2\Pi$	-0.27	Cl $_2^+ ^2\Pi_g^+$	-1.77	Ge $^+ ^2P$	-5.37	SeH $^+ ^2\Pi$	-4.21
ClO $^2\Pi$	-0.61	ClF $^+ ^2\Pi$	-1.60	As $^+ ^3P$	-8.04	HBr $^+ ^2\Pi$	-6.26
HS $^2\Pi$	-1.01	NH $^- ^2\Pi$	-0.12	Se 3P	-4.30	BrF $^+ ^2\Pi$	-6.10
FH $^+ ^2\Pi$	-0.62	PH $^- ^2\Pi$	-0.45	Br 2P	-5.60	BrO $^2\Pi$	-2.20
PH $^+ ^2\Pi$	-0.67	O $_2^- ^2\Pi_g$	-0.34	Br $^+ ^3P$	-6.71	NaBr $^+ ^2\Pi$	-3.93
ClH $^+ ^2\Pi$	-1.60	S $_2^- ^2\Pi_g$	-1.12	Kr $^+ ^2P$	-8.16	Br $_2^+ ^2\Pi_g$	-6.55
C $_2$ H $_2^+ ^2\Pi_u$	-0.07	PO $^2\Pi$	-0.53				
N $_2^+ ^2\Pi_u$	-0.17	SiH $^2\Pi$	-0.34				
O $_2^+ ^2\Pi_g$	-0.43						

^aValues for diatomics were calculated from experiment. Calculated using the COLUMBUS program (Refs. 11 and 12).

^bReference 13.

^cReferences 2 and 3.

correction (for atoms only), $E(\text{HLC})$ =higher level correction, and $E(\text{ZPE})$ =zero-point energy correction.

In the extension of G3 theory to the third-row nontransition elements K, Ca, Ga–Kr the theoretical procedures are essentially the same as for first- and second-row elements.⁴ Equilibrium geometries are optimized with second-order Møller–Plesset perturbation theory (MP2), and single-point energies are calculated using second- and fourth-order Møller–Plesset perturbation theory (MP4) and quadratic configuration interaction [QCISD(T)] with basis sets described in Sec. III. All correlation calculations are done with a frozen core as described in the following, except for the MP2 calculation with the G3Large basis set that treats all electrons (FU), i.e., it includes core-related correlation. The basis sets used for first- and second-row atoms in G3 theory have been described in detail elsewhere.⁴ Those used for the third row are described in Sec. III. Harmonic vibrational frequencies are calculated at the Hartree–Fock (HF) level with the 6-31G* basis set described in the following to obtain zero-point vibrational energies and are scaled by 0.893.

A spin-orbit energy term [$E(\text{SO})$] is included for atomic species. The atomic spin-orbit energies used in the extension of G3 theory to K, Ca, Ga–Kr are given in Table I. Experimental¹⁰ spin-orbit corrections are used for the third-row atomic species, consistent with G3 theory for the first and second row. The spin-orbit term is also included for molecules having first-order corrections (diatomics having $^2\Pi$ states). Since experimental values are not available for some of these molecular species, we have used theoretical values computed using the COLUMBUS program.^{11,12} These values are given in Table I and are from Refs. 2 and 3. G3 theory for the first and second rows as defined in Ref. 4 does not include any spin-orbit energies for diatomic $^2\Pi$ species, of which there are 21 in the G3/99 test set. In order to have a consistent theory for all three rows we propose to include this energy term for first- and second-row elements in G3 theory. The spin-orbit energies for the first- and second-row diatomics calculated using the COLUMBUS code are included in Table I.¹³ Inclusion of the spin-orbit energies in the assessment of G3 theory on the G3/99 test set does not significantly change the overall accuracy of the method.

In G3 theory the frozen-core approximation is used in the single-point MP4 and QCISD(T) correlation calculations while no orbitals are frozen in the single point MP2 calculations with the G3Large basis set. For molecules containing first-row atoms, the doubly occupied orbital, which effectively corresponds to the 1s atomic orbital, is excluded from the correlation treatment at the MP4 level. For molecules containing second-row atoms, the doubly occupied molecular orbitals, which correspond approximately to the 1s, 2s, 2p_x, 2p_y, and 2p_z atomic orbitals, are defined as core orbitals and are therefore excluded. For molecules containing third-row Ga–Kr atoms, the inactive doubly occupied molecular orbitals are those which correspond approximately to the 1s, 2s, 2p_x, 2p_y, 2p_z, 3s, 3p_x, 3p_y, and 3p_z orbitals in the individual atoms. The treatment of the third-row Ga–Kr atoms thus follows the same pattern as for the first- and second-row atoms. However, this treatment is different than G2 theory for Ga–Kr since in that case the 3d orbitals were excluded from the correlation treatment. This is changed in G3 theory for two reasons. First, several previous studies^{14–16} have shown that for some molecules (e.g., GaF₃, GaOH) there is an inversion of the expected ordering of third-row core orbitals (e.g., Ga3d) with second-row valence orbitals (e.g., O2s or F2s). This may result in poor atomization energies. The addition of the 3d orbital to the valence space corrects the problem.^{14–16} Second, when G3 theory is extended to the transition metal elements of the third row, the 3d orbitals will have to be included in the correlation treatment, and thus they should be included for all elements in the third row for consistency.

For molecules containing K and Ca, we include in the core only the doubly occupied molecular orbitals corresponding to the 1s, 2s, 2p_x, 2p_y, and 2p_z orbitals in the individual atoms. The 3s, 3p_x, 3p_y, and 3p_z orbitals of K and Ca need to be included in the valence space because, for some molecules (such as KF), they are intermixed with the molecular orbitals containing valence orbitals. This also occurs in some cases for Na and Mg. Therefore, we modify G3 theory for Na and Mg to include in the core only the doubly occupied molecular orbitals that correspond to the 1s orbital in the individual atoms. The 2s, 2p_x, 2p_y, and 2p_z orbitals

TABLE II. Total Hartree–Fock level energies (in hartrees) for K, Ca, Ga–Kr.

	K	Ca	Ga	Ge	As	Se	Br	Kr
Numerical ^a			-1923.261 01	-2075.359 73	-2234.238 65	-2399.867 61	-2572.441 33	-2752.054 98
Uncontracted ^b			-1923.178 71	-2075.279 99	-2234.159 36	-2399.787 52	-2572.358 44	-2751.967 07
“6-311G” ^c	-599.149 001	-676.740 428	-1923.168 380	-2075.267 129	-2234.143 802	-2399.772 252	-2572.318 180	-2751.952 559
G3Large ^d	-599.158 264	-676.750 354	-1923.186 781	-2075.286 713	-2234.165 145	-2399.794 840	-2572.366 723	-2751.977 203

^aReference 38.^bReference 39. This is the uncontracted “6-311G” basis set.^cReferences 2 and 3.^dEnergies for the basis set without any supplementary functions included.

of Na and Mg are included in the valence space.

The G3 higher level correction (HLC) is based on four empirical parameters that correct remaining deficiencies in the total energies for pairs of valence electrons in molecules, unpaired electrons in molecules, pairs of valence electrons in atoms, and unpaired electrons in atoms. The HLC parameters used for third-row molecules are held fixed at the values used for the first- and second-row molecules.⁴

III. BASIS SETS

In the extension of G3 theory to the third row, we use the 6-31G* basis set recently derived for K, Ca, Ga–Kr by Rassolov *et al.*¹⁷ This is used for the 6-31G(*d*) basis set in Eq. (1). This basis set was constructed in a manner analogous to 6-31G* for the first and second rows and the 3*d* electrons are treated as part of the valence set. The polarization function is a *d* function with six second-order Cartesian Gaussians used for all atoms. We note that in previous work^{2,3} the nomenclature “6-31G*” was used for a different basis set, the 641(*d*) basis set of Binning and Curtiss.¹⁸ In subsequent work we refer to the latter basis set as 6-31G*(*C*) and the “true” 6-31G* basis set is now that of Rassolov *et al.*¹⁷ We also note that the 6-31G* basis set in Ref. 17 for K and Ca is an improved version of a 6-31G* basis set previously reported.¹⁹ The *f* polarization and diffuse functions for the 6-31G basis used in the calculation of the energies in Eq. (1) are described in the Appendix. We use a spherical harmonic representation (seven functions) for the *f*-polarization function.

The G3Large basis set for the third-row atoms K, Ca, Ga–Kr is a contracted 8*s*7*p*3*d* Gaussian set with supplementary functions. The contracted set was derived by modification of the basis set referred to as “6-311G”² that is used

in G2 theory for the third row. This modification involves a different contraction of the *p* and *d* core functions and a full reoptimization of the basis set at the Hartree–Fock level. The optimizations were done on the ground state atoms for Ga–Kr. For K, Ca the ground state optimization leads to *d* and *p* functions that are too diffuse. Therefore, K and Ca basis sets were obtained first by optimizing the 7*s*7*p* contracted set on the ground states. Next, an additional uncontracted *s* function was added to the set with the exponent equal to the geometric mean of the two outermost valence *s* functions. Then, the 7*p* functions were reoptimized on the excited ²*P* state of K and the ³*D* state of Ca. Finally, a set of *d* functions was obtained by rescaling those from Sc by the ratio of squares of nuclear charges. The resulting basis set is a contraction of a 15*s*13*p*5*d* primitive set to 8*s*7*p*3*d*. The *p* contraction is 6211111 compared to 333111 in the “6-311G” basis set and the *d* contraction is 311 compared to 41 in “6-311G.” The new contraction and full optimization result in a lower energy compared to the “6-311G” basis set. The atomic energies are given in Table II and compared with “6-311G,” uncontracted, and numerical energies. The results show that the G3Large basis set gives a significantly lower energy (20–25 mH) than the “6-311G” basis set. The G3Large basis set also gives a lower energy (5–10 mH) than the uncontracted basis set because of added *sp* functions, but is still significantly higher (70–80 mH) than the numerical result.

The supplementary functions (diffuse and 3*d*2*f*) functions were derived in a manner similar to “6-311G” for G2 theory and are given in the Appendix along with information on where to obtain the G3Large basis set. In addition, tight polarization functions were derived for the G3Large basis set and the exponents are given in the Appendix. In the G3Large basis we use a spherical harmonic representation for the *d*-

TABLE III. Summary of the basis sets^a used in G3 theory for the first, second, and third rows.

		H	Li–Ne	Na–Ar	K, Ca, Ga–Kr
6-31G	Contracted set	4 <i>s</i> →2 <i>s</i> ^b	10 <i>s</i> 4 <i>p</i> →3 <i>s</i> 2 <i>p</i> ^b	16 <i>s</i> 10 <i>p</i> →4 <i>s</i> 3 <i>p</i> ^c	22 <i>s</i> 16 <i>p</i> 4 <i>d</i> →5 <i>s</i> 4 <i>p</i> 2 <i>d</i> ^d
G3Large ^e	Contracted set	5 <i>s</i> →3 <i>s</i>	11 <i>s</i> 5 <i>p</i> →4 <i>s</i> 3 <i>p</i>	13 <i>s</i> 9 <i>p</i> →6 <i>s</i> 5 <i>p</i>	15 <i>s</i> 13 <i>p</i> 5 <i>d</i> →8 <i>s</i> 7 <i>p</i> 3 <i>d</i>
	Supplemental functions	+ ,2 <i>p</i>	+ ,2 <i>df</i> , tight <i>p</i> , <i>d</i>	+ ,3 <i>d</i> 2 <i>f</i> , tight <i>d</i> , <i>f</i>	+ ,3 <i>d</i> 2 <i>f</i> , tight <i>d</i> , <i>f</i>

^aNumber of primitives is given to the left of the arrow and the number of contracted functions is given to the right. (+)=diffuse *sp* valence functions.^bFrom Ref. 40.^cFrom Ref. 41.^dFrom Ref. 17.^eFrom Ref. 4, except for K, Ca, Ga–Kr, which are from this work. The G3MP2Large basis set used in some modified versions of G3 theory does not include the tight polarization functions.

TABLE IV. Total atomic energies (in hartrees).^a

Species	G3	G3(MP3)	G3(MP2)	G3S	G3S(MP3)
K	-599.730 46	-599.735 83	-599.433 51	-599.776 07	-599.776 11
Ca	-677.384 50	-677.390 29	-677.084 27	-677.428 88	-677.429 39
Ga	-1924.286 20	-1924.287 58	-1923.537 28	-1924.440 47	-1924.438 51
Ge	-2076.378 34	-2076.379 77	-2075.638 44	-2076.530 32	-2076.527 86
As	-2235.249 71	-2235.252 11	-2234.516 55	-2235.400 91	-2235.398 42
Se	-2400.913 27	-2400.915 10	-2400.179 97	-2401.063 10	-2401.059 03
Br	-2573.517 47	-2573.518 77	-2572.783 86	-2573.665 98	-2573.660 79
Kr	-2753.154 51	-2753.155 50	-2752.417 87	-2753.302 12	-2753.296 17

^aSpin-orbit corrections are included in the total energies (see Table I).

and *f*-polarization functions (five and seven functions, respectively). The different basis sets used in G3 theory for the first, second, and third-rows are summarized in Table III.

Basis function optimizations were done with a modified version of the ATOM-SCF program.²⁰ The GAUSSIAN 98 computer program²¹ was used in all of the calculations reported in this paper.

IV. EVALUATION OF G3 THEORY AND RELATED METHODS FOR K, Ca, Ga–Kr

In this study we derive a test set from those used previously for molecules containing third-row atoms.^{2,3} For Ga–Kr a set of 40 reaction energies having experimental uncertainties of less than ± 1 kcal/mol was used in assessing G2 theory. For K, Ca a set of 18 energies was used. However, only 7 of these are known to an accuracy of ± 1 kcal/mol. Thus, these 7 were combined with the 40 for Ga–Kr for a test set of 47 reaction energies (23 atomization energies, 17 ionization potentials, 4 electron affinities, and 2 proton affinities). The other K, Ca energies with larger uncertainties are considered separately. The geometries for the test molecules are obtained at the MP2(FU) level using the new 6-31G* basis set.¹⁷ The geometries differ only slightly from the MP2 geometries from the old “6-31G*” basis [6-31G*(C)] basis set that was used previously.^{2,3} The new geometries are available on the internet.²²

G3 theory. The G3 atomic energies for the atomic species K, Ca, Ga–Kr are listed in Table IV. These energies include the spin–orbit corrections from Table I. The G3 molecular energies are not included here but are available on the internet.²² They also include spin–orbit energies listed in Table I.

The deviations of the atomization energies (0 K), ionization energies, electron affinities calculated from G3 theory are given in Tables V and VI. The average absolute deviations of G3 theory for the complete test set are given in Table VII. Also given in these tables are the G2 results. The overall average absolute deviation of G3 theory from experiment is 0.94 for the complete set of 47 test cases (Table VII), a significant improvement compared to 1.43 kcal/mol for G2 theory. When these results are added to those for the G3/99 test set,⁷ the overall average absolute deviation for 423 experimental comparisons is 1.06 kcal/mol.

The 23 third-row G3 atomization energies have an average absolute deviation from experiment of 1.01 kcal/mol compared to the G2 result of 1.29 kcal/mol. The largest G3

deviations are -3.1 kcal/mol for K_2 , -2.5 kcal/mol for GeH_4 , and -2.1 kcal/mol for NaBr; all of the other atomization energies differ from experiment by less than 2 kcal/mol. The 17 ionization energies have an average absolute deviation of 0.89 kcal/mol, a significant improvement over the G2 result of 1.80 kcal/mol. The largest deviation is -4.9 kcal/mol for the ionization energy of NaBr, all of the other energies differ with experiment by less than 2 kcal/mol. The error in the ionization potential of NaBr increases from -2.4 kcal/mol (G2) to -4.9 kcal/mol (G3). The reason for the problem with NaBr for G3 theory is unclear. The 5 electron affinities have an average absolute deviation of 1.06 kcal/mol compared to the G2 result of 1.25 kcal/mol. The largest deviation is -2.6 kcal/mol for the electron affinity of the K atom.

It has been shown that scalar relativistic effects systematically reduce binding energies in molecules containing first- and second-row atoms.²³ The scalar relativistic correc-

TABLE V. Deviation of calculated atomization energies (ΣD_0) from experiment (in kcal/mol).^a

Species	Expt ^b	G2 ^c	G3	G3(MP3)	G3(MP2)	G3S	G3S(MP3)
K_2	12.6	-2.0	-3.1	-4.9	-2.9	-0.7	-0.9
KBr	90.5	2.7	-1.0	-1.9	0.0	0.5	1.0
KCl	101.0	1.3	-0.6	-2.2	-0.6	0.5	0.1
KF	117.6	-0.1	1.7	0.9	2.1	2.5	2.6
GeH_4	270.5	-5.3	-2.5	-2.3	-3.1	-1.8	-1.0
AsH	64.6	1.4	-0.1	-0.1	-0.7	2.5	2.8
AsH_2	131.1	-0.7	-0.8	-0.7	-1.2	0.9	1.4
AsH_3	206.0	0.4	1.4	1.5	1.1	2.5	3.0
SeH	74.3	0.1	-1.1	-1.4	-1.6	0.4	0.4
SeH_2	153.2	1.1	0.9	0.5	0.1	1.5	1.5
HBr	86.5	0.6	-0.2	-0.6	-0.4	0.2	0.2
GaCl	109.9	-0.2	-1.5	-2.3	-1.9	-0.7	-1.1
GeO	155.2	-0.5	-1.6	-3.9	-4.0	-1.4	-3.0
As_2	91.3	0.1	-0.4	0.0	-0.4	1.9	2.6
BrCl	51.5	1.5	0.3	-0.4	0.1	0.9	0.8
BrF	58.9	-0.2	0.3	1.0	1.5	1.1	1.8
BrO	55.3	1.7	0.1	0.6	0.9	0.5	1.2
Br_2	45.4	2.4	-0.1	-0.7	0.4	0.7	0.9
BBr	103.5	2.3	0.7	0.1	0.3	1.5	1.3
NaBr	86.2	-0.2	-2.1	-2.2	-1.6	-1.2	-0.8
CH_3Br	358.2	0.7	-0.3	-0.6	-0.1	0.1	0.3
GeS_2	191.7	-2.2	-1.9	-3.6	-4.0	-0.5	-1.8
KrF_2	21.9	-1.9	-0.6	2.4	3.2	-0.8	1.0

^aExpt—theory.

^bSame experimental references as in Refs. 2 and 3.

^cFrom Refs. 2 and 3.

TABLE VI. Deviation of ionization potentials (IP), electron affinities (EA), and proton affinities (PA) from experiment (in kcal/mol).^a

	Species	Expt ^b	G2 ^c	G3	G3(MP3)	G3(MP2)	G3S	G3S(MP3)	
IP	K	100.1	1.6	0.8	0.3	0.4	1.0	0.9	
	Ca	140.9	-1.5	-1.7	-2.0	-3.6	0.1	-0.2	
	Ga	138.3	1.6	-0.2	-0.6	-0.9	-0.1	0.0	
	Ge	182.2	2.2	-0.1	-0.4	-0.4	-0.4	0.0	
	As	225.7	2.1	-0.4	-0.4	-0.2	-0.8	-0.2	
	Se	224.9	2.5	1.0	1.6	1.9	1.6	2.9	
	Br	272.4	2.2	0.5	0.8	0.5	1.4	2.2	
	Kr	322.8	3.4	1.3	1.7	0.7	2.6	3.3	
	AsH	222.3	2.3	-1.0	-1.0	-1.3	-0.3	0.3	
	AsH ₂	217.8	2.5	-0.8	-0.9	-1.1	-0.2	0.4	
	SeH	227.0	1.0	0.1	0.2	0.9	-0.3	0.6	
	SeH ₂	228.0	0.8	-0.3	-0.3	0.0	-0.6	0.1	
	HBr	268.9	1.9	0.8	0.9	0.9	0.8	1.4	
	Br ₂	242.6	0.8	-0.2	-0.1	-0.3	0.8	1.4	
	HOBr	245.3	-0.2	-0.4	-0.1	-0.3	0.5	1.0	
	BrF	271.6	1.6	0.7	1.1	1.3	1.3	2.0	
	NaBr	191.6	-2.4	-4.9	-4.8	-4.8	-5.0	-4.5	
	EA	K	11.5	-2.9	-2.6	-3.2	-4.9	-0.2	-0.8
		Ge	28.4	0.3	-0.5	-0.4	-0.2	-1.2	-0.5
Br		77.6	1.0	-0.5	-0.1	-1.3	0.2	0.8	
BrO		54.4	-2.0	-1.3	-0.5	-1.8	-1.1	-1.4	
SeH		51.0	0.0	-0.4	-0.3	-0.4	-1.0	-0.4	
PA	Br ⁻	322.6	-0.4	-0.3	-1.7	-0.4	0.0	-0.6	
	CH ₃ Br	157.3	-0.2	0.4	-0.1	-0.3	0.0	-0.5	

^aExpt-theory.^bSame experimental references as in Refs. 2 and 3.^cFrom Refs. 2 and 3.

tion is likely to be significant for molecules containing third-row atoms. We have investigated inclusion of scalar relativistic effects in G3 theory for first- and second-row molecules (including a reoptimization of the higher level correction) and found no overall improvement in G3 theory when it is included.²³ This result suggests that the scalar relativistic effects for light atomic systems are fairly systematic and are approximately accounted for by readjustment of the higher level correction in G3 theory. We have investigated scalar relativistic effects for the molecules containing Ga–Kr in the third-row test set. Similar to the first and second rows, there is a reduction in the atomization energies with the range being from 0.03 kcal/mol (KrF₂) to 4.24 kcal/mol (GeH₄).²⁴ We have not included scalar relativistic effects in the extension of G3 theory to the third row to be consistent with the first and second rows.

A comparison between experiment and G3 theory for some additional atomization and ionization energies of K and Ca is given in Table VIII. Also included are the G2

results for these energies. We did not include these molecules in the test set because of the large uncertainties in some of the experimental numbers. However, from examination of the G2 and G3 results in Table VIII it is clear that G3 is more accurate for this set of molecules. For the atomization energies, six G3 energies (CaO, CaS, CaOH, CaF, CaCl, CaCl₂) are significantly improved over the G2 energies. For the other 3 species (KH, KOH, CaF₂) the errors are similar. Hence, G3 performs better than G2 for molecules containing Ca. For the two ionization potentials in Table VIII G3 theory does slightly better for CaH and G2 does slightly better for KBr.

Several papers^{14,15} have reported that G2 theory does very poorly for some molecules (e.g., GaF₃, GaOH) that have an inversion of third-row core orbitals (e.g., Ga 3*d*) with second-row valence orbitals (e.g., O 2*s* or F 2*s*). Bauschlicher *et al.*¹⁵ and Duke and Radom¹⁴ proposed adding the 3*d* orbitals to the valence space to correct the problem. Duke and Radom refer to this modification of G2 theory as G2(*d*).

TABLE VII. Average absolute deviations (in kcal/mol) from experiment for K, Ca, Ga–Kr species.^a

Property ^b	G2	G3	G3(MP3)	G3(MP2)	G3S	G3S(MP3)
Σ <i>D</i> ₀ (23)	1.29(-5.29)	1.01(-3.14)	1.52 (-4.91)	1.41 (-4.02)	1.09(2.48)	1.37 (-3.04)
EA (5)	1.25(-2.85)	1.06(-2.60)	0.89 (-3.15)	1.72 (-4.91)	0.74(-1.21)	0.78 (-1.39)
IP (17)	1.80(3.35)	0.89(-4.94)	1.01 (-4.83)	1.15 (-4.80)	1.04(-5.03)	1.26 (-4.48)
PA (2)	0.32(-0.42)	0.33(0.37)	0.92 (-1.72)	0.31 (-0.36)	0.04(0.05)	0.54 (-0.60)
Total (47)	1.43(-5.29)	0.94(-4.94)	1.24 (-4.91)	1.30 (-4.91)	0.99(-5.03)	1.23 (-4.48)

^aMaximum deviations in parentheses.^bThe number of each type of energy is given in parentheses.

TABLE VIII. Atomization and ionization energies (kcal/mol) of K and Ca species.^a

	Species	Experiment	G2	G3	G3(MP3)	G3(MP2)	G3S	G3S(MP3)
ΣD_0	KH	43.1±3.5, ^b 42.9, ^c 42.5±4.3 ^d	40.1	40.9	42.0	41.1	40.1	40.3
	KOH	186.7±3.0, ^b 185.6±1.9 ^d	184.3	183.0	183.3	182.8	182.9	182.7
	CaO	90.6±5.0, ^b ≥109.8, ^{c,e} 90.8±3.6 ^d	83.6	89.0	94.3	91.1	90.9	93.6
	CaS	78.3±2.0, ^b 79.8, ^c 78.9±3.6 ^d	71.3	77.3	80.3	78.0	78.6	80.1
	CaOH	198.4±5.0, ^b 196.5±4.8 ^d	192.0	194.3	194.8	192.7	194.8	194.1
	CaF	125.6±1.9, ^b 126.4, ^c 126.7±1.2 ^d	122.7	124.6	125.7	123.2	124.2	123.8
	CaCl	95.8±3.1, ^b 94.3, ^c 95.6±1.5 ^d	92.0	96.1	97.7	94.9	95.7	95.6
	CaF ₂	266.4±1.9, ^b 267.9±1.6 ^d	263.6	262.6	263.5	260.7	262.6	262.0
	CaCl ₂	212.3±1.0, ^b 215.5±1.2 ^d	205.0	211.3	213.5	209.8	211.5	211.5
	IP	KBr	181.0±2.3 ^c	183.2	185.0	184.9	185.2	185.1
CaH		135.1±2.1 ^c	129.2	130.7	131.1	131.4	129.2	129.1

^aSame experimental references as in Refs. 2 and 3. Because of difficulties in the QCISD(T) procedure for CaO (see Ref. 2) a CCSD(T)/6-31G* was energy used for CaO. The G3(CCSD) method (Ref. 33) was used.

^bReference 42.

^cReference 43.

^dReference 25.

^eHuber and Herzberg also report 93.2 kcal/mol.

We have investigated not including the $3d$ orbitals in the correlation treatment for G3 theory as well as not including the $2s$ and $2p$ orbitals of Na. A summary of the results for the set of 47 energies is given in Table IX. The same higher level correction (HLC) parameters are used. The average absolute deviation increases slightly from 0.94 to 1.00 kcal/mol when this is done. These results are similar to those of Duke and Radom, who found that the average absolute deviation of G2 theory decreases from 1.38 to 1.31 kcal/mol when the $3d$ orbitals were included for the test set of 40 reactions containing Ga–Kr elements. Freezing the $3d$ orbitals in the correlation treatment significantly decreases the amount of computational time required and could be done without much loss of accuracy in most cases. However, for the reasons stated in Sec. II, we have included the $3d$ orbitals in the correlation treatment so these difficulties are largely avoided.

In Table X, G3 results are presented for GaOH and GaF₃, two molecules that have been the subject of previous studies concerning inclusion of $3d$ orbitals in the core.^{14–16} The third-row molecule with the most dramatic failure at the

G2 level is the atomization energy of GaF₃, which has a deviation of 108 kcal/mol from experiment as noted by Bauschlicher *et al.*¹⁵ Inclusion of the $3d$ orbitals in the correlation treatment, G2(+ d), reduces the deviation to only 0.1 kcal/mol (see Table X). Similar results are obtained at the G2(MP2) level by Bauschlicher *et al.* When the $3d$ orbitals are frozen, the G3 deviation is 17.2 kcal/mol. This is much less than for G2 theory due to the inclusion of all electrons in the correlation treatment in the MP2/G3Large calculation. At the G3 level with $3d$ orbitals included, the deviation decreases to 8.2 kcal/mol. This is close to the uncertainty of the experimental value (6.5 kcal/mol).²⁵ A calculation on GaF₃ with a complete basis set extrapolation technique by Bauschlicher *et al.* gives an atomization energy that differs by only 2 kcal/mol from experiment. Also included in Table X are results for the atomization energy of NaBr and the ionization potential of NaBr. They indicate that inclusion of the $2s$ and $2p$ orbitals of Na in the correlation treatment has little effect on the deviations with experiment.

TABLE IX. Dependence of G3 and G2 average absolute deviations (in kcal/mol) on inclusion of $3d$ and $2s,2p$ (Na only) orbitals in the valence space for the correlation treatment.^a

Property ^b	G2	G2(+ d)	G3	G3(- d)	G3S	G3S(- d)
$\Sigma D_0(23)$	1.29	1.69	1.01	1.00	1.09	0.88
EA (5)	1.25	1.26	1.06	1.35	0.74	1.01
IP (17)	1.80	1.07	0.89	0.96	1.04	1.06
PA (2)	0.32	0.46	0.33	0.30	0.04	0.13
Total (47)	1.43	1.37	0.94	1.00	0.99	0.93

^aAverage absolute deviation from experiment for K, Ca, Ga–Kr species. G2(+ d) includes $3d$ and $2s,2p$ (Na only) orbitals in correlation treatment while G3(- d) does not include $3d$ and $2s,2p$ (Na only) orbitals in correlation treatment. The G2 results are from Refs. 2 and 3. The G2(+ d) results for Ga–Kr are taken from Ref. 14.

^bThe number of each type of energy is given in parentheses.

TABLE X. Dependence of G3 and G3S results for selected species on inclusion of Ga $3d$ and Na $2s,2p$ orbitals in the valence space for the correlation treatment.^a

	Expt (kcal/mol)	Deviation (expt-theory) (kcal/mol)			
		G3(- d)	G3	G3S(- d)	G3S
$\Sigma D_0(\text{GaF}_3)$	339.6±6.5 ^b	17.2	8.2	17.4	10.2
$\Sigma D_0(\text{GaOH})$	209.4±2.9 ^b	0.8	-3.4	-1.3	-4.5
$\Sigma D_0(\text{NaBr})$	86.2	-2.8	-2.1	-2.2	-1.2
IP ₀ (NaBr)	191.6	-5.4	-4.9	-5.6	-5.0

^aG3(- d) does not include $3d$ and $2s,2p$ (Na only) orbitals in correlation treatment.

^bReference 25.

V. MODIFIED G3 METHODS BASED ON REDUCED PERTURBATION ORDERS AND SCALED ENERGIES

A. G3(MP3) and G3(MP2)

G3(MP2)²⁶ and G3(MP3)²⁷ theories are modifications of G3 theory that use reduced orders of perturbation theory. The G3(MP3) method eliminates the expensive MP4/2df,p calculation in Eq. (1) by evaluating the larger basis set effects at the MP3 and MP2 levels of theory. It also eliminates the MP4/plus calculation. The G3(MP2) method evaluates the larger basis set effects at the MP2 level and the MP2(FU) calculation is replaced by a frozen core calculation (FC) with the G3MP2Large basis set.²⁷ Both methods save significant amounts of computer time compared to G3 theory. The formulation of G3(MP3) and G3(MP2) theories for the molecules containing K, Ca, Ga–Kr is analogous to that of the first and second rows. The basis sets are the same as used in G3 theory and are defined in Sec. III. The only difference is the use, in G3(MP2) theory, of the G3MP2Large basis set that does not have tight polarization functions (see Table III). In addition, the same higher level corrections^{26,27} used for the first and second rows are used for the third row.

The average absolute deviations for G3(MP2) and G3(MP3) theories for the 47 energy test set are given in Table VII and the individual deviations are given in Tables V and VI. The G3(MP2) average absolute deviation from experiment is 1.30 kcal/mol. This is a significant decrease from 1.92 kcal/mol for G2(MP2) theory for this same set.²⁸ The G3(MP3) average absolute deviation from experiment is 1.24 kcal/mol, about the same as G3(MP2). The results of these methods for K- and Ca-containing molecules with larger experimental uncertainty are given in Table VIII. Both the G3(MP3) and G3(MP2) methods give results for the Ca-containing molecules that are generally in agreement with experiment, similar to G3 theory.

B. Scaled methods

Scaled Gaussian-3 (G3S) theory²⁹ uses multiplicative scale factors, instead of the additive higher level correction. It is similar in spirit to several methods developed by Truhlar *et al.*^{30–32} and Siegbahn *et al.*^{33,34} In G3S theory the correlation energy is scaled by five parameters and the Hartree–Fock energy by one parameter,

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

The six parameters ($S_{E234}, S_{\text{QCI}}, S_{\text{HF}'}, S_{E2'}, S_{E3'}, S_{E4'}$) are fitted to the G2/97 test set of 299 energies and are given in Ref. 29. The $E2$, $E3$, and $E4$ refer to the energy contributions from second-, third-, and fourth-order perturbation

theory. For further details see Ref. 29. The G3S method has the advantage compared to G3 theory in that it can be used for studying potential energy surfaces where the products and reactants have a different number of paired electrons. G3S theory with reduced orders of perturbation similar to G3(MP3) has also been published and is called G3S(MP3).²⁹ The formulation of G3S and G3S(MP3) theories for the molecules containing K, Ca, Ga–Kr is analogous to that of the first and second rows. The same scale factors as reported in Ref. 29 are used and the basis sets are defined in Sec. III. The spin–orbit corrections are the same as is used for G3 theory. In Ref. 29 we defined G3S(MP2) theory, which is based on second-order perturbation theory. However, the total energies obtained from G3(MP2) theory are much different from the other methods in this series and we have not included it in this study.

The deviations of the atomization energies, ionization energies, and electron affinities calculated from G3S theory are given in Tables V and VI. The average absolute deviations of G3S theory for the Ga–Kr test set are given in Table VII. The overall average absolute deviation of G3S theory from experiment is 0.99 for the complete set of 47 test cases (Table VII), compared to 0.94 kcal/mol for G3 theory. The 23 atomization energies have an average absolute deviation from experiment of 1.09 kcal/mol, similar to the G3 result of 1.01 kcal/mol. The largest deviations are for the atomization energies of AsH and KF (2.5 kcal/mol). The 17 ionization energies have an average absolute deviation of 1.04 kcal/mol. Similar to G3 theory the largest deviation (−5.0 kcal/mol) is for the ionization energy of NaBr. The G3S deviations for the K, Ca molecules with larger experimental uncertainties are given in Tables VIII and IX. The G3S method gives results for these K- and Ca-containing molecules that are similar to G3 theory.

The average absolute deviation for G3S(MP3) theory for the 47 energy test set is given in Table VII and the individual deviations are given in Tables V and VI. The G3S(MP3) average absolute deviation from experiment is 1.23 kcal/mol with a maximum deviation of 4.5 kcal/mol, which is similar to G3(MP3) theory.

VI. CONCLUSIONS

Gaussian-3 (G3) theory is extended to molecules containing the third-row nontransition elements K, Ca, Ga–Kr. This new theoretical procedure modifies G2 theory for the third row in several ways including (1) the use of the 6-31G basis set as the underlying basis for the MP4 and QCISD(T) single point corrections, (2) a new formulation of the higher level correction, and (3) inclusion of core-related correlation. Basis sets compatible with those used in G3 theory for molecules containing first- and second-row atoms have been derived. The following conclusions are made from this study

(1) G3 theory is a significant improvement over G2 theory for third-row molecules similar to results previously reported for first- and second-row molecules. The average absolute deviation from experiment for the set of 47 test reactions improves from 1.43 kcal/mol for G2 theory to 0.94 kcal/mol for G3 theory. In addition, G3 theory performs sig-

TABLE XI. Polarization and diffuse functions for K, Ca, Ga–Kr.^a

		K	Ca	Ga	Ge	As	Se	Br	Kr
6-31G	d^b	0.0449	0.0502	0.2289	0.2772	0.3277	0.3810	0.4366	0.4948
	f	0.0448	0.0696	0.2636	0.4729	0.4090	0.3798	0.5777	0.5164
	+	0.0050	0.0071	0.0141	0.0223	0.0318	0.0339	0.0390	0.0352
G3large	d	0.05	0.05	0.3	0.3	0.3	0.3	0.3	0.3
	f	1.2	1.2	0.4	0.4	0.4	0.4	0.4	0.4
	+	0.007	0.015	0.0138	0.0317	0.0315	0.0345	0.0382	0.0525
	d (tight)	15	16	49	53	58	63	68	73
	f (tight)	17	19	5	6	6	7	7	8

^aThe $2d$ and $2f$ splits are obtained by $2a$ and $a/2$ split. The $3d$ split is obtained by a $4a, a, a/4$ split.

^bFrom Ref. 17.

nificantly better than G2 on atomization energies of molecules containing Ca, not included in the test set because of larger experimental uncertainties.

(2) G3(MP2) theory for third-row molecules has an average absolute deviation from experiment of 1.30 kcal/mol, which is significantly more accurate than G2(MP2). The G3 method based on third-order perturbation theory, G3(MP3), has an average absolute deviation of 1.24 kcal/mol.

(3) The G3 methods based on scaling parameters, G3S and G3S(MP3), have an accuracy similar to the corresponding methods based on the higher level correction.

There have also been a number of G3 methods that have been proposed, including ones based on B3LYP geometries³⁵ and CCSD(T) energies.³⁶ Although we have not included these methods in this paper, the methodologies can be easily extended to the third row with the basis sets given here.

ACKNOWLEDGMENTS

We thank Dr. J.-P. Blaudeau for permitting us to use his calculated spin-orbit corrections for first- and second-row diatomics. We acknowledge grants of computer time at the National Energy Research Supercomputer Center. The work at Argonne National Laboratory was supported by the U.S. Department of Energy, Division of Materials Sciences, under Contract No. W-31-109-ENG-38.

APPENDIX

The G3Large basis set for K, Ca, Ga–Kr, without the supplementary functions, is available on the internet.^{22,37} The derivation of this basis set is described in the text of this paper. The full G3Large basis set also includes a diffuse sp function, three d valence uncontracted primitive polarization functions, two f valence uncontracted primitive polarization functions, and tight d and f uncontracted primitive polarization functions. The three d polarization functions are obtained with exponents four times, equal to, and a quarter of the single function value in Table XI. The two f polarization functions are obtained with exponents twice and half the single function value in Table XI. The d and f exponents for the single uncontracted functions were obtained by optimizing the MP2 energies of KH, KOH, KF, KCl, CaO, CaF₂, GaCl, GeH₄, GeO, AsH₃, SeH₂, BrOH, KrF₂. The diffuse sp exponents in G3Large basis set are given in Table XI and were obtained by optimizing the MP2 energies of K⁻, Ca, Ga⁻, GeH₃⁻, AsH₂⁻, SeH⁻, Br⁻, Kr. The tight polarization

functions for the G3Large basis set were derived by adding single d and f functions with large exponents to the atoms. The exponents for these functions were obtained by optimizing the MP2(full) energy for the ground state neutral atoms. The exponents for the tight polarization functions used in the G3Large basis set are given in Table XI. The tight polarization functions are included in G3Large to recover core-related correlation energy.

The MP4 single point calculations include a sp diffuse function, two d valence uncontracted primitive polarization functions, and one f valence uncontracted primitive polarization functions as supplementary functions for the 6-31G* basis set. The two d polarization functions are obtained with exponents twice and half the standard 6-31G* value¹⁷ given in Table XI. Table XI also includes the f -polarization function exponents and the diffuse function exponents. The f exponents were obtained by optimizing HF energies of K⁻, Ga⁻, Ge⁻, AsH₂⁻, SeH⁻, Br⁻, Kr. The diffuse sp exponents were obtained by optimizing HF energies of K⁻, Ca⁻, Ga⁻, GeH₃⁻, AsH₂⁻, SeH⁻, Br⁻, Kr. The Ca exponent was taken from Ref. 3.

¹L. A. Curtiss, K. Raghavachari, G. W. Trucks, and J. A. Pople, *J. Chem. Phys.* **94**, 7221 (1991).

²L. A. Curtiss, M. P. McGrath, J.-P. Blaudeau, N. E. Davis, and R. Binding, *J. Chem. Phys.* **103**, 6104 (1995).

³J.-P. Blaudeau, M. P. McGrath, L. A. Curtiss, and L. Radom, *J. Chem. Phys.* **107**, 5016 (1997).

⁴L. A. Curtiss, K. Raghavachari, P. C. Redfern, V. Rassolov, and J. A. Pople, *J. Chem. Phys.* **109**, 7764 (1998).

⁵L. A. Curtiss, K. Raghavachari, P. C. Redfern, and J. A. Pople, *J. Chem. Phys.* **106**, 1063 (1997).

⁶L. A. Curtiss, P. C. Redfern, K. Raghavachari, and J. A. Pople, *J. Chem. Phys.* **109**, 42 (1998).

⁷L. A. Curtiss, P. C. Redfern, K. Raghavachari, and J. A. Pople, *J. Chem. Phys.* **112**, 7374 (2000).

⁸J. A. Pople, M. Head-Gordon, and K. Raghavachari, *J. Chem. Phys.* **87**, 5968 (1987).

⁹L. A. Curtiss, J. E. Carpenter, K. Raghavachari, and J. A. Pople, *J. Chem. Phys.* **96**, 9030 (1992).

¹⁰C. Moore, National Bureau of Standards (U.S.) Circular No. 467, 1952.

¹¹R. Shepard, I. Shavitt, R. M. Pitzer, D. C. Comeau, M. Pepper, H. Lishka, P. G. Szalay, R. Ahlrichs, F. B. Brown, and J. G. Zhao, *Int. J. Quantum Chem., Quantum Chem. Symp.* **22**, 149 (1988).

¹²J.-P. Blaudeau and L. A. Curtiss, *Int. J. Quantum Chem.* **60**, 943 (1997).

¹³J.-P. Blaudeau (private communication).

¹⁴B. J. Duke and L. Radom, *J. Chem. Phys.* **109**, 3352 (1998).

¹⁵C. W. Bauschlicher, Jr., C. F. Melius, and M. D. Allendorf, *J. Chem. Phys.* **110**, 1879 (1999).

¹⁶C. A. Richards, Y. Yamaguchi, S.-J. Kim, and H. F. Schaefer, *J. Chem. Phys.* **104**, 8516 (1996).

- ¹⁷V. A. Rassolov, M. A. Ratner, J. A. Pople, P. C. Redfern, and L. A. Curtiss, *J. Comput. Chem.* (in press).
- ¹⁸R. C. Binning, Jr. and L. A. Curtiss, *J. Comput. Chem.* **11**, 1206 (1990).
- ¹⁹V. A. Rassolov, J. A. Pople, M. A. Ratner, and T. L. Windus, *J. Chem. Phys.* **109**, 1223 (1998).
- ²⁰C. C. J. Roothaan and P. S. Bagus, IBM Research Report No. RJ518, 1968.
- ²¹M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 98, Revision A.7, Gaussian, Inc., Pittsburgh PA (1998).
- ²²<http://chemistry.anl.gov/compmat/compterm.htm>
- ²³G. S. Kedziora, J. A. Pople, V. Rassolov, M. A. Ratner, P. C. Redfern, and L. A. Curtiss, *J. Chem. Phys.* **110**, 7123 (1999).
- ²⁴R. Sharp, G. Kedziora, P. Redfern, L. A. Curtiss, and J. A. Pople (unpublished).
- ²⁵L. V. Gurvich, I. V. Veys, and C. B. Alcock, *Thermodynamic Properties of Individual Substances*, 4th ed. (Hemisphere, New York, 1989), Vols. I–III.
- ²⁶L. A. Curtiss, P. C. Redfern, K. Raghavachari, V. Rassolov, and J. A. Pople, *J. Chem. Phys.* **110**, 4703 (1999).
- ²⁷L. A. Curtiss, P. C. Redfern, K. Raghavachari, and J. A. Pople, *Chem. Phys. Lett.* **313**, 600 (1999).
- ²⁸P. C. Redfern, J.-P. Blaudeau, and L. A. Curtiss, *J. Phys. Chem.* **101**, 8701 (1997).
- ²⁹L. A. Curtiss, K. Raghavachari, P. C. Redfern, and J. A. Pople, *J. Chem. Phys.* **112**, 1125 (2000).
- ³⁰P. L. Fast, M. L. Sanchez, and D. G. Truhlar, *Chem. Phys. Lett.* **306**, 407 (1999).
- ³¹P. L. Fast, M. L. Sanchez, J. C. Corchado, and D. G. Truhlar, *J. Chem. Phys.* **110**, 11679 (1999).
- ³²P. L. Fast, J. C. Corchado, M. L. Sanchez, and D. G. Truhlar, *J. Phys. Chem. A* **103**, 5129 (1999).
- ³³P. E. M. Siegbahn, R. A. M. Blomberg, and M. Svensson, *J. Chem. Phys.* **102**, 5377 (1995).
- ³⁴P. E. M. Siegbahn, R. A. M. Blomberg, and M. Svensson, *Chem. Phys. Lett.* **223**, 35 (1994).
- ³⁵A. G. Baboul, L. A. Curtiss, P. C. Redfern, and K. Raghavachari, *J. Chem. Phys.* **110**, 7650 (1999).
- ³⁶L. A. Curtiss, K. Raghavachari, P. C. Redfern, A. G. Baboul, and J. A. Pople, *Chem. Phys. Lett.* **314**, 101 (1999).
- ³⁷See EPAPS Document No. E-JCPA6-114-313119 for the G3Large basis set without diffuse or polarization functions added. This document may be retrieved via the EPAPS homepage (<http://www.aip.org/pubservs/epaps.html>) or from <ftp.aip.org> in the directory/epaps/. See the EPAPS homepage for more information.
- ³⁸H. Partridge, *J. Chem. Phys.* **90**, 1043 (1989).
- ³⁹T. H. Dunning, Jr., *J. Chem. Phys.* **66**, 1382 (1979).
- ⁴⁰P. C. Hariharan and J. A. Pople, *Chem. Phys. Lett.* **66**, 217 (1972).
- ⁴¹M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. Defrees, and J. A. Pople, *J. Chem. Phys.* **77**, 3654 (1982).
- ⁴²M. W. Chaese, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud, *J. Phys. Chem. Ref. Data Suppl.* **14**, 1 (1985). JANAF Thermochemical Tasks Third Edition.
- ⁴³K. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure 4. Constants of Diatomic Molecules* (Van Nostrand, Princeton, 1979).