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The correlation consistent composite approach (ccCA): An alternative to the Gaussian-*n* methods

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An alternative to the Gaussian-*n* (G1, G2, and G3) composite methods of computing molecular energies is proposed and is named the “correlation consistent composite approach” (ccCA, ccCA-CBS-1, ccCA-CBS-2). This approach uses the correlation consistent polarized valence (cc-pVXZ) basis sets. The G2-1 test set of 48 enthalpies of formation (ΔH_f), 38 adiabatic ionization potentials (IPs), 25 adiabatic electron affinities (EAs), and 8 adiabatic proton affinities (PAs) are computed using this approach, as well as the ΔH_f values of 30 more systems. Equilibrium molecular geometries and vibrational frequencies are obtained using B3LYP density functional theory. When applying the ccCA-CBS method with the cc-pVXZ series of basis sets augmented with diffuse functions, mean absolute deviations within the G2-1 test set compared to experiment are 1.33 kcal mol⁻¹ for ΔH_f , 0.81 kcal mol⁻¹ for IPs, 1.02 kcal mol⁻¹ for EAs, and 1.51 kcal mol⁻¹ for PAs, *without* including the “high-level correction” (HLC) contained in the original *Gn* methods. Whereas the HLC originated in the Gaussian-1 method as an isogyric correction, it evolved into a fitted parameter that minimized the error of the composite methods, eliminating its physical meaning. Recomputing the G1 and G3 enthalpies of formation without the HLC reveals a systematic trend where most ΔH_f values are significantly higher than experimental values. By extrapolating electronic energies to the complete basis set (CBS) limit and adding G3-like corrections for the core-valence and infinite-order electron correlation effects, ccCA-CBS-2 often *underestimates* the experimental ΔH_f , especially for larger systems. This is desired as inclusion of relativistic and atomic spin-orbit effects subsequently improves theoretical ΔH_f values to give a 0.81 kcal mol⁻¹ mean absolute deviation with ccCA-CBS-2. The ccCA-CBS method is a viable “black box” method that can be used on systems with at least 10–15 heavy atoms. © 2006 American Institute of Physics. [DOI: 10.1063/1.2173988]

I. INTRODUCTION

The guiding principle of a “composite method” in *ab initio* quantum chemistry is straightforward, to mimic the accuracy of an expensive and often computationally intractable electronic structure computation using additive approximations obtained from multiple computations of higher efficiency and lower accuracy. The oldest, most widely used, and arguably most successful composite methods are the Gaussian-*n* or *Gn* methods of Pople, Curtiss, and co-workers.^{1–5} The specific goal of these methods was to create a “black box” procedure that could be applied to any (main group) molecular or atomic system and agree with known energetic experimental data [i.e., relative conformational energies, atomization energies, enthalpies of formation (ΔH_f), ionization potentials (IPs), electron affinities (EAs), and proton affinities (PAs)] to near-chemical accuracy, or within ± 2 kcal mol⁻¹. If the composite method achieved this goal over a training set of well-studied chemical species, the same level of accuracy was expected when utilized on species with larger experimental uncertainty or systems where experimental data were unavailable. The *Gn* methods have

proven to be quite robust in this respect, described in detail within numerous successful applications and reviews.^{6–10} Other composite methods have been created since the original formulation of the G1 method. Some of these, such as the complete basis set (CBS-*n*) model chemistries of Petersson and co-workers,^{11–14} the focal point method of Allen and co-workers^{15–20} and Császár *et al.*,^{21,22} the W1 and W2 methods of Parthiban and Martin²³ and Martin and de Oliveira,²⁴ and the High Accuracy Extrapolated *ab initio* Thermochemistry (HEAT) method of Stanton and co-workers,^{25,26} attempt to approach the complete basis set (CBS)/full-configuration interaction (FCI) limit of smaller systems, consistently obtaining accuracy better than within 0.5 kcal mol⁻¹ of experimental data. Dixon, Feller, and co-workers^{27–35} used large basis set coupled cluster equilibrium geometries and total energies while using smaller basis sets to perform further electron correlation and scalar relativistic corrections, in order to achieve at least chemical accuracy (± 1 kcal mol⁻¹) for enthalpies of formation. Feller and Peterson^{36,37} have also examined the performance of G2 methods compared to coupled cluster and perturbation theories. Other model chemistries, such as the multicoefficient correlation method (MCCM) of Truhlar and co-workers, optimize parameters to

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approach the CBS FCI correlation energy.^{38–40} Attempts to parametrize aspects of density functional theory⁴¹ (DFT) and perturbation theory⁴² (MP2) energy computations to attain accurate enthalpies of formation have also been attempted.

Preferably, a composite method should stay true to the tenets of “first principles” quantum chemistry, where accurate energies are obtained without semiempirical or optimized parameters. As is well known, the *Gn* methods include such an optimized parameter, the “high-level correction,” or HLC. Initially, the HLC of the Gaussian-1 (G1) method had a physical foundation, in that it equaled the difference between the G1 electronic energy of the primary systems (hydrogen atom and hydrogen molecule) and their near-exact analytical energies.³ It was then assumed that any unpaired valence electrons in a molecular system would also need a HLC equivalent to that of the H atom, and likewise that each pair of electrons would require the same HLC as the H₂ molecule. Thus within the G1 method, the HLC acted as an isogyric correction.

The simple physical implications of the G1 HLC were abandoned upon the advent of the Gaussian-2 (G2) method.⁴ The G2 HLC was optimized in order to minimize the mean absolute deviation from experiment for the 55 atomization energies investigated in the initial G2-1 training set. Henceforth, the HLC became a semiempirical parameter somewhat in opposition to the spirit of *ab initio* electronic structure methods. It is not well known if the HLC is needed because of the use of an incomplete basis set, incomplete treatment of electron correlation, the use of the harmonic approximation to compute vibrational zero-point energies, bond additivity effects, or even perhaps a combination of these effects. There are also smaller contributions to the electronic energy such as spin-orbit splitting, and relativistic effects that influence the HLC. To our knowledge, no work has been carried out to discern how these effects interplay with the magnitude of the HLC, nor has there been a focus on how *Gn* methods fare without inclusion of the HLC.

In 1989, the same year that the G1 method was published, Dunning⁴³ first introduced correlation consistent polarized valence (cc-pVXZ with $X=D, T, Q, 5, \dots$) basis sets for the first-row atoms. The correlation consistent basis sets were constructed by systematically expanding the higher angular momentum functions in shells. These basis sets were found to result in convergence toward the one-particle CBS limit for a number of properties for a given correlated method.^{43–45} The systematic nature of this convergence has enabled energies of increasing basis set size to be used to extrapolate to the CBS limit. By extrapolating to the CBS limit, the error coupling of the one-particle basis set expansion and the *n*-particle electron correlation is eliminated, leaving only the intrinsic error of the trial electronic wave function. Correlation consistent basis sets have since been reported for the second- and third-row elements,^{45–47} and have been modified to describe molecular systems where electron density is diffuse (aug-cc-pVXZ) (Refs. 48 and 49) or to account for core-valence electron correlation (cc-pCVXZ).^{50,51} Most recently, cc-pVXZ and their augmented and core-valence versions have been constructed for the 3*d* transition metals by Balabanov and Peterson.⁵²

With respect to basis set size, the poor scaling of *ab initio* theories that can account for high levels of electron correlation remains the limiting factor in the maximum molecular size that can be addressed by a composite method. Dixon and co-workers^{34,35} have demonstrated that employing quadruple- ζ (the minimum “zeta level” typically necessary for satisfactory CBS extrapolations) coupled cluster computations on molecules of modest size (e.g., *n*-octane) require extraordinary computational resources. Additionally, accounting for smaller, but significant energy corrections such as higher-order electron correlation, relativistic effects, spin-orbit coupling, and anharmonic zero-point energies can be time consuming and require more extensive expertise and software. These aspects prohibit the realization of a flexible “black box” composite method untethered by empirical or optimized parameters, that is also applicable to large molecules.

While composite methods utilizing cc-pVXZ basis sets and CBS extrapolation schemes exist, to our knowledge, no thorough attempt has been made to combine cc-pVXZ basis sets with the time-saving aspects of the *Gn* model chemistries. In this paper, the “Dunning-style” cc-pVXZ basis sets will replace the “Pople-style” basis sets traditionally used in the *Gn* methods. If the larger and more flexible cc-pVXZ families of basis set are used as the reference for the various *Gn* additive corrections, near-chemical accuracy of ± 2 kcal mol^{−1} can be achieved for properties on a variety of chemical systems. Our modifications to the *Gn* methods, called the “correlation consistent composite approach” or ccCA and ccCA-CBS were designed to include *no* semiempirical or optimized parameters. The ccCA-CBS methods could certainly be considered a more efficient approximation to the composite method of Dixon and co-workers, via substitution of coupled cluster geometry optimizations with perturbation theory single point energies applied to DFT equilibrium geometries. The ccCA and ccCA-CBS energies will be presented for 118 of the 125 atomic and molecular systems contained in the G2-1 subset,⁴ a selection of systems from the G2/97 (Ref. 6), and G3/99 (Ref. 8) test sets, and two large systems from the 600-molecule training set proposed by Cioslowski *et al.*⁴¹ The performance of the ccCA will be examined and compared to experiment, *Gn* methods (with and without their respective HLCs), and other theoretical studies.

II. DESCRIPTION OF THE ccCA THEORETICAL METHODS

Gn composite methods have been described in detail in Refs. 2–11, as well as references therein. They comprise of a set of *ab initio* molecular orbital (MO)-based computations performed to give an equilibrium geometry, a set of harmonic vibrational frequencies, and a total electronic energy at the equilibrium geometry. The determination of G3 geometries, frequencies, and total energies are described as follows.

To obtain the G3 equilibrium structure, a second-order Møller-Plesset perturbation theory^{53,54} (MP2) computation is run at the 6-31G(*d*) basis set level⁵⁵ with all electrons corre-

lated. Harmonic vibrational frequencies at 0 K are computed earlier, using the global minimum obtained at the HF/6-31G(*d*) level of theory and scaled by a factor of 0.8929 to give the zero-point energy [E (ZPE)].

In G3, a reference energy is computed with complete fourth-order Møller-Plesset perturbation theory⁵⁶ and the 6-31G(*d*) basis set at the MP2(full)/6-31G(*d*) equilibrium geometry. [In G1 and G2, the reference energy is computed at the MP4/6-311G(*d,p*) level.] Shown here for G3, additive single point energy corrections are obtained with the following additional computations.

- (a) $\Delta E(+)$, a MP4 computation where the 6-31G(*d*) basis set is augmented with diffuse functions, 6-31+G(*d*).^{57,58}
- (b) $\Delta E(2df,p)$, a MP4 computation where higher polarization functions are added to the 6-31G(*d*) basis set, 6-31G(2df,*p*).
- (c) $\Delta E(QCI)$, a correction to include correlation effects to infinite-order using quadratic configuration interaction with single, double, and perturbative triple excitations [QCISD(T)] (Ref. 59) with the 6-31G(*d*) basis set.
- (d) In the G3 method, an all-electron MP2 correction is included [ΔE (G3large)] with an even larger basis set to consider core-valence correlation effects.
- (e) In the G3 method, atomic spin-orbit corrections are taken from experimental results⁶⁰ or theoretical computations.⁵
- (f) Lastly, the HLC is added depending on the number of closed- and open-shell valence electrons. The actual value of the HLC for each open-shell electron or bound pair of closed shell electrons differs amongst the G_n methods.

Effectively for G1 and G2 methods the result of these additive corrections to the MP4/6-311G(*d,p*) // MP2(full)/6-31G(*d*) total energy should be equal to the zero-point corrected (E_0) QCISD(T)/6-311+G(2df,*p*) and QCISD(T)/6-311+G(3df,2*p*) energies, respectively, while for G3, the composite method should give the E_0 at the QCISD(T,full)/G3large level of theory. The validity of using the G_n composite methods to reach the target total energy of the higher level of theory has been found to be satisfactory.⁶¹

Many modifications to the G_n methods have appeared such as reducing the basis set size,⁶² employing coupled cluster with single, double, and perturbative triple excitations [CCSD(T)] (Refs. 59 and 63) instead of QCISD(T), using second- or third-order MP n theory instead of MP4 to determine the reference electronic energy,^{64,65} and using scale factors to replace the HLC.^{66,67} The ccCA will adopt the use of B3LYP DFT equilibrium geometries and vibrational frequencies similar to the modifications of the G3 methods called G3/B3LYP (or G3B3) (Ref. 68) and G3X.⁶⁷ This variation generally retains sufficient accuracy while severely reducing the computational expense of geometry optimizations.^{68,69}

The first implementation of ccCA attempts to remain similar to the G3B3 algorithm due to the demonstrated success of the G3 approaches. Our main modification is based on the relationship between basis set size and correlation

energy in attaining accurate theoretical thermochemical values and relative energies. As basis sets and electron correlation effects are the two largest components which determine the accuracy of computing atomic and molecule electronic wave functions, these effects must be the focus of a composite *ab initio* technique. While the Gaussian-*n* methods account for a significant portion of the dynamical electron correlation with the MP4 level of theory, the additive corrections may not be balanced if employed in conjunction with rather small basis sets. This investigation will show that without an empirical or parametrized energy correction, small basis sets such as 6-31G(*d*) or cc-pVDZ are of insufficient quality to act as the reference electronic energy for additive corrections since the correlated methods used [MP2, MP4, QCISD(T)] are heavily basis set dependent. It will be demonstrated that if larger or CBS-extrapolated correlation consistent basis sets are employed as the foundation for additive corrections, the accuracy of ccCA improves dramatically. The algorithms of ccCA are outlined as follows.

The equilibrium geometries are obtained at the B3LYP/6-31G(*d*) level of theory (akin to G3B3 theory)⁶ and harmonic frequencies are also computed at the B3LYP/6-31G(*d*) level of theory and scaled by a factor of 0.9854 (equivalent to the scale factor used in G3X)^{67,70,71} in order to compute the zero-point vibrational energy correction at 0 K and the molecular enthalpy of formation correction at 298.15 K. The G3X scale factor (with G3B3 geometries) is used, which generally improves ccCA-derived enthalpies of formation by 0.10 kcal mol⁻¹ as compared to the G3B3 scale factor of 0.96. Again, the main impetus behind using the DFT geometries and harmonic ZPE corrections is that there is relatively little compromise in accuracy compared to the time savings achieved from avoiding expensive MP2 or CCSD(T) geometry optimizations. Geometry optimizations at the CCSD(T) level of theory are still prohibitively expensive for most large molecules, and efficient parallelized frozen-core coupled cluster energy gradients are nonexistent in most widely available *ab initio* software packages. Variation of ccCA accuracy based on different types of optimized geometries will be further investigated in future work, though we believe that the 6-31G(*d*) DFT geometries with the G3X zero-point energy scheme will be important for a successful “black box” implementation on large molecular systems.

We have initially implemented five variants of the ccCA methods. Three versions of ccCA begin with a single point frozen-core MP4 computation along with a correlation consistent basis set used as the reference energy at the B3LYP/6-31G(*d*) equilibrium geometry for subsequent additive corrections. If the reference energy is computed with the cc-pVDZ basis sets, the method is named ccCA-DZ. Likewise, with a cc-pVTZ reference energy the method is called ccCA-TZ, and an aug-cc-pVTZ reference energy is called ccCA-aTZ. Additive corrections are modeled from the original G_n methods. For example, if MP4/cc-pVTZ is the reference energy (as with ccCA-TZ), $\Delta E(+)$ is computed to correct for the addition of diffuse functions,

$$\Delta E(+) = E[\text{MP4/aug-cc-pVTZ}] - E[\text{MP4/cc-pVTZ}]. \quad (1)$$

The correction for higher polarization functions can be simply formulated with the cc-pVXZ basis sets by raising the “zeta level,” i.e., increasing from double-zeta to triple-zeta, or triple-zeta to quadruple-zeta level basis sets. This was designated as $\Delta E(2df, p)$ in *Gn* methods, and is now named $\Delta E(\zeta)$.

For the latter two variations of the ccCA methods (named ccCA-CBS), frozen-core MP2 energies are computed with the aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ basis sets, and extrapolated to the CBS limit. We determine the MP2 CBS energy in two ways, the first is the simple exponential form proposed by Xantheas and Dunning⁴⁴ and Feller,^{72,73} where x =the *zeta* level of the correlation consistent basis set [$2=\text{DZ}$, $3=\text{TZ}$, etc.]:

$$E(X) = A_{\text{CBS}} + B \exp(-Cx). \quad (2)$$

Alternatively, a mixed exponential/Gaussian functional devised by Peterson *et al.*⁷⁴ is expressed as

$$E(x) = A_{\text{CBS}} + B \exp[-(x-1)] + C \exp[-(x-1)^2]. \quad (3)$$

The ccCA energies determined with these two functional forms are referred to as ccCA-CBS-1 and ccCA-CBS-2, respectively. This MP2 CBS energy serves as the reference energy for additive corrections.

In order to properly account for high-order electron correlation effects, a small basis set single point energy is computed with the QCISD(T) wave function. If MP2 or MP4 levels of theory overestimate the amount of dynamical correlation in the system, the $\Delta E(\text{QCI})$ correction can actually raise the total energy of the system. The $\Delta E(\text{QCI})$ correction for the ccCA-aTZ method is expressed as

$$\begin{aligned} \Delta E(\text{QCI}) = & E[\text{QCISD(T)/cc-pVTZ}] \\ & - E[\text{MP4/cc-pVTZ}]. \end{aligned} \quad (4)$$

Within the ccCA-CBS methods $\Delta E(\text{QCI})$ is

$$\begin{aligned} \Delta E(\text{QCI}) = & E[\text{QCISD(T)/cc-pVTZ}] \\ & - E[\text{MP2/cc-pVTZ}]. \end{aligned} \quad (5)$$

The G3large correction is implemented as a simple correction for core-valence correlation effects and renamed $\Delta E(\text{CV})$. For the ccCA methods with triple-zeta reference energies, $\Delta E(\text{CV})$ is computed as

$$\begin{aligned} \Delta E(\text{CV}) = & E[\text{MP2(full)/aug-cc-pCVTZ}] \\ & - E[\text{MP2/aug-cc-pVTZ}]. \end{aligned} \quad (6)$$

All of the appropriate additive corrections, such as the zero-point energy correction [$\Delta E(\text{ZPE})$], $\Delta E(+)$, $\Delta E(\zeta)$, $\Delta E(\text{QCI})$, and $\Delta E(\text{CV})$, are added to the reference energy. Finally, depending on the basis set used to compute the reference energy, the ccCA energy is defined as

$$\begin{aligned} E_0(\text{ccCA-DZ}) = & E[\text{MP4/cc-pVDZ}] + \Delta E(+) + \Delta E(\zeta) \\ & + \Delta E(\text{QCI}) + \Delta E(\text{CV}) + \Delta E(\text{ZPE}), \end{aligned} \quad (7)$$

$$\begin{aligned} E_0(\text{ccCA-TZ}) = & E[\text{MP4/cc-pVTZ}] + \Delta E(+) + \Delta E(\zeta) \\ & + \Delta E(\text{QCI}) + \Delta E(\text{CV}) + \Delta E(\text{ZPE}), \end{aligned} \quad (8)$$

or

$$\begin{aligned} E_0(\text{ccCA-aTZ}) = & E[\text{MP4/aug-cc-pVTZ}] + \Delta E(\zeta) \\ & + \Delta E(\text{QCI}) + \Delta E(\text{CV}) + \Delta E(\text{ZPE}). \end{aligned} \quad (9)$$

Both of the ccCA-CBS energies are defined as

$$\begin{aligned} E_0(\text{ccCA-CBS-}n) = & E[\text{MP2/aug-cc-pV}\infty\text{Z}] + \Delta E(\text{QCI}) \\ & + \Delta E(\text{CV}) + \Delta E(\text{ZPE}). \end{aligned} \quad (10)$$

Table I pictorially represents the additive corrections used with the ccCA method and a direct comparison to the *Gn* algorithms. All computations were run with the GAUSSIAN03 software package⁷⁵ except for the *n*-octane, $\text{C}(\text{NO}_2)_4$, and adamantane QCISD(T) computations, for which MOLPRO 2002.6 was used.⁷⁶ Closed shell restricted Hartree-Fock (RHF) wave functions and open-shell unrestricted Hartree-Fock (UHF) reference wave functions were implemented. Newly optimized (aug)-cc-p(C)VXZ basis sets for Li, Be, Mg, and Na atoms were obtained from Peterson *et al.*⁷⁷

III. BASIS SET DEPENDENCE OF REFERENCE ENERGIES

In this study, a major goal is to examine the role of the initial electronic energy to be used as the foundation for additive corrections. The most crucial difference between the *Gn* composite methods and the ccCAs is that the ccCA basis set sizes are generally larger. To make a brief comparison of increasing the basis set size for the reference energy, atomic energies are listed in Table II obtained with the *Gn* methods, those utilizing cc-pVDZ (ccCA-DZ), cc-pVTZ (ccCA-TZ), and aug-cc-pVTZ (ccCA-aTZ) basis sets as the reference MP4 energy, and the ccCA-CBS-1 and ccCA-CBS-2 energies. The first point of comparison is between the G3 atomic energies and those obtained with the ccCA-DZ method. Of the non-noble gas first-row atomic electronic energies, the ccCA-DZ energies are higher (and none more than 10 mE_h) than the G3 energies, while the second-row ccCA-DZ energies are usually higher by $80\text{--}90 \text{ mE}_h$. However, the G3 energies include the HLC, which can contribute up to 24.56 mE_h to the electronic energy for the first- and second-row atoms. All computed ccCA-TZ, ccCA-aTZ, and ccCA-CBS atomic energies are significantly lower than the G3 energies, except for the hydrogen radical, which G3 predicts to violate the variational principle due to overcorrection of the parametrized HLC with an electronic energy of $-0.501 E_h$. Likewise, the hydrogen atom energy predicted with the ccCA-CBS-2 composite method is below the variational limit, in this case by $20 \mu\text{E}_h$. While none of these model chemistries strictly adhere to the variational principle, the recovery of more atomic correlation energy due to larger basis set size in the ccCA methods is an early indicator that molecular properties will achieve comparable or improved accuracy when compared to the *Gn* methods.

To examine the basis set dependence, Table III shows atomic IPs and EAs obtained with the *Gn* and ccCA meth-

TABLE I. Depiction of the G_n and ccCA algorithms.

	$G1^a$	$G2^b$	$G3B3^c$	ccCA-DZ	ccCA-TZ	ccCA-aTZ	ccCA CBS-1 / ccCA CBS-2
Geometry optimization	MP2(full)/6-311G**	MP2(full)/6-31G(d)	B3LYP/6-31G(d)	B3LYP/6-31G(d)	B3LYP/6-31G(d)	B3LYP/6-31G(d)	B3LYP/6-31G(d)
Harmonic vibrational frequencies	HF/6-31G(d)	HF/6-31G(d)	B3LYP/6-31G(d)	B3LYP/6-31G(d)	B3LYP/6-31G(d)	B3LYP/6-31G(d)	B3LYP/6-31G(d)
Scale factor	0.8929	0.8929	0.9854	0.9854	0.9854	0.9854	0.9854
Reference energy $E(\text{ref})$	MP4/6-311G**	MP4/6-311G(d,p)	MP4/6-31G(d)	MP4/cc-pVDZ	MP4/cc-pVTZ	MP4/aug-cc-pVTZ	MP2/CBS aug-cc-pVXZ
$\Delta E(+)$	MP4/6-311+G** − $E(\text{ref})$	MP4/6-311+G(d,p) − $E(\text{ref})$	MP4/6-31+G(d) − $E(\text{ref})$	MP4/aug-cc-pVDZ − $E(\text{ref})$	MP4/aug-cc-pVTZ − $E(\text{ref})$
$\Delta E(2df,p)/\Delta E(\zeta)$	MP4/6-311G**(2df) − $E(\text{ref})$	MP4/6-311G(2df,p) − $E(\text{ref})$	MP4/6-31G(2df,p) − $E(\text{ref})$	MP4/cc-pVTZ − $E(\text{ref})$	MP4/cc-pVQZ −MP4/ cc-pVTZ	MP2/aug-cc-pVQZ −MP2/aug-cc-pVTZ	...
$\Delta E(\text{QCI})$	QCISD(T)/6-311G** − $E(\text{ref})$	QCISD(T)/6-311AG(d,p) − $E(\text{ref})$	QCISD(T)/6-31G(d) − $E(\text{ref})$	QCISD(T)/cc-pVDZ − $E(\text{ref})$	QCISD(T)/cc-pVTZ − $E(\text{ref})$	QCISD(T)/cc-pVTZ −MP4/cc-pVTZ	QCISD(T)/cc-pVTZ −MP2/cc-pVTZ
$\Delta E(\text{G3large}) / \Delta E(\text{CV})$...	MP2/6-311+G(3df,2p) −MP2/6-311G(2df,p) −MP2/6-311+G(d,p) +MP2/6-311G(d,p)	MP2(full)/G3large −MP2/6-31G(2df,p) −MP2/6-31G(2df,p) −MP2/6-31+G(d) +MP2/6-31+G(d)	MP2(full)/ aug-cc-pCVDZ −MP2/aug-cc-pVTZ	MP2(full)/ aug-cc-pCVTZ −MP2/aug-cc-pVTZ	MP2(full)/ aug-cc-pCVTZ −MP2/aug-cc-pVTZ	MP2(full)/aug-cc-pCVTZ −MP2/aug-cc-pVTZ
$\Delta E(\text{HLC})$	$-0.19n_\alpha - 5.95n_\beta^d$	$-0.19n_\alpha - 4.81n_\beta^d$	$-An_\alpha - Bn_\beta^c$
Effective level of theory	QCISD(T)/ 6-311+G**(2df)	QCISD(T)/ 6-311+G(3df,2p)	QCISD(T,full)/ G3large	QCISD(T,full)/ aug-cc-pCVTZ	QCISD(T,full)/ aug-cc-pCVQZ	QCISD(T,full)/ aug-cc-pCVQZ	QCISD(T,full)/aug-cc- pCV ∞ Z

^aReference 3.^bReference 4. The G3 variants also include a spin-orbit correction to atomic energies.^cRef. 68.^d n_α and n_β represent the number of alpha- and beta-spin valence electrons, respectively.^eThe high-level correction parameter A equals 6.760 mE_h for molecules and 6.786 mE_h for atoms. The HLC parameter B equals 3.233 E_h for molecules and 1.269 mE_h for atoms.

TABLE II. Atomic energies (in E_h) using *Gn* methods.

	G1	G3	ccCA-DZ	ccCA-TZ	ccCA-aTZ	ccCA-CBS-1	ccCA-CBS-2
H(2S)	-0.500 00	-0.501 00	-0.499 87	-0.499 96	-0.499 95	-0.499 99	-0.500 02
Li(2S)	-7.432 22	-7.465 13	-7.461 81	-7.470 23	-7.470 23	-7.470 23	-7.470 23
Be(1S)	-14.623 37	-14.659 72	-14.650 37	-14.660 08	-14.660 90	-14.662 02	-14.661 84
B(2P)	-24.602 79	-24.642 57	-24.633 38	-24.645 31	-24.646 27	-24.648 93	-24.648 57
C(3P)	-37.784 64	-37.827 72	-37.820 36	-37.834 93	-37.835 53	-37.839 02	-37.839 28
N(4S)	-54.517 76	-54.564 34	-54.559 73	-54.577 99	-54.577 80	-54.582 41	-54.583 34
O(3P)	-74.982 04	-75.030 99	-75.028 08	-75.053 85	-75.051 75	-75.060 02	-75.061 30
F(2P)	-99.632 75	-99.684 21	-99.683 89	-99.718 00	-99.713 79	-99.726 44	-99.728 04
Na(2S)	-161.846 18	-162.104 15	-162.047 56	-162.147 60	-162.147 60	-162.147 71	-162.147 88
Mg(1S)	-199.646 13	-199.907 42	-199.820 32	-166.948 85	-199.949 45	-199.950 12	-199.950 49
Al(2P)	-241.931 67	-242.207 47	-242.133 19	-242.247 41	-242.248 30	-242.249 94	-242.250 25
Si(3P)	-288.933 78	-289.222 27	-289.141 36	-289.257 94	-289.258 82	-289.261 48	-289.261 88
P(4S)	-340.818 00	-341.116 43	-341.035 85	-341.154 22	-341.154 84	-341.158 14	-341.159 01
S(3P)	-397.654 93	-397.961 11	-397.876 59	-398.001 63	-398.000 61	-398.006 29	-398.007 58
Cl(2P)	-459.676 70	-459.990 96	-459.902 73	-460.038 21	-460.035 08	-460.041 68	-460.044 79
Li $^+$ (1S)	-7.235 84	7.266 79	-7.264 96	-7.272 73	-7.272 73	-7.272 73	-7.272 72
Be $^+$ (2S)	-14.276 39	-14.312 14	-14.309 41	-14.317 15	-14.317 14	-14.317 16	-14.317 19
B $^+$ (1S)	-24.301 75	-24.340 00	-24.331 53	-24.342 49	-24.343 24	-24.346 42	-24.344 98
C $^+$ (2P)	-37.374 05	-37.415 71	-37.407 50	-37.422 31	-37.423 05	-37.426 33	-37.426 23
N $^+$ (3P)	-53.986 00	-54.031 23	-54.023 75	-54.043 64	-54.044 25	-54.048 69	-54.049 35
O $^+$ (4S)	-74.484 39	-74.533 12	-74.527 68	-74.554.06	-74.554 33	-74.560 88	-74.562 27
F $^+$ (3P)	-98.993 62	-99.045 19	-99.038 48	-99.076 41	-99.075 53	-99.086 23	-99.088 39
Na $^+$ (1S)	-161.664 23	-161.916 23	-161.863 64	-161.961 35	-161.960 65	-161.961 46	-161.961 65
Mg $^+$ (2S)	-199.364 02	-199.621 31	-199.541 82	-199.667 94	-199.667 93	-199.668 12	-199.688 37
Al $^+$ (1S)	-241.713 79	-241.988 47	-241.914 43	-242.028 72	-242.029 38	-242.030 34	-242.030 66
Si $^+$ (2P)	-288.636 26	-288.923 62	-288.841 40	-288.958 83	-288.959 66	-288.962 02	-288.962 24
P $^+$ (3P)	-340.434 37	-340.731 90	-340.647 92	-340.767 60	-340.768 51	-340.771 57	-340.772 23
S $^+$ (4S)	-397.279 56	-397.583 73	-397.498 97	-397.623 10	-397.623 76	-397.627 64	-397.628 97
Cl $^+$ (3P)	-459.203 84	-459.517 25	-459.427 44	-459.561 97	-459.561 11	-459.567 33	-459.569 33
C $^-$ (4S)	-37.828 25	-37.871 58	-37.883 70	-37.888 80	-37.880 76	-37.883 46	-37.883 91
O $^-$ (2P)	-75.033 85	-75.080 14	-75.118 11	-75.125 84	-75.105 47	-75.113 84	-75.114 63
F $^-$ (1S)	-99.759 93	-99.809 19	-99.857 80	-99.869 41	-99.844 14	-99.855 85	-99.856 54
Si $^-$ (4S)	-288.982 27	-289.272 90	-289.200 80	-289.317 23	-289.310 23	-289.312 60	-289.313 19
P $^-$ (3P)	-340.840 18	-341.143 70	-341.077 90	-341.190 26	-341.179 73	-341.183 92	-341.184 84
S $^-$ (2P)	-397.726 83	-398.037 01	-397.970 26	-398.085 54	-398.075 37	-398.082 95	-398.083 58
Cl $^-$ (1S)	-459.807 93	-460.123 60	-460.052 32	-460.180 31	-460.167 83	-460.179 67	-460.179 47

ods. For the 14 atomic IPs, the accuracy improves when comparing ccCA-DZ and ccCA-TZ, as the average absolute deviation is reduced from 1.34 to 0.64 kcal mol $^{-1}$, compared to the G3 average absolute deviation of 1.24 kcal mol $^{-1}$. The ccCA-aTZ method performs slightly worse than other methods for atomic ionization potentials (1.01 kcal mol $^{-1}$ average absolute deviation), which can be explained by the contrasting way that $\Delta E(\zeta)$ is computed, i.e., using the difference between MP4 computations (ccCA-TZ) versus the difference between MP2 computations (ccCA-aTZ). This slim degradation in accuracy from using MP2 for the $\Delta E(\zeta)$ correction is tolerable since computations of MP4 cc-pVQZ or MP4 aug-cc-pVQZ energies would become the computational bottleneck of the ccCA methods and would limit the size of molecules that can be treated.

The mean absolute deviation of the ccCA-CBS-1 and ccCA-CBS-2 atomic IPs (0.80 and 0.71 kcal mol $^{-1}$, respectively) are comparable to the ccCA-TZ method and nearly half that of the G3 method (1.24 kcal mol $^{-1}$). The largest ccCA-CBS-2 absolute deviation (1.6 kcal mol $^{-1}$ for Na $^+$), is less than half that of G3 (3.5 kcal mol $^{-1}$ for both Mg $^+$ and

Be $^+$). It should be noted that the ccCA-CBS methods are faster and of equal or surpassed accuracy to the ccCA-TZ and ccCA-aTZ methods. Therefore, by removing basis set incompleteness effects and eliminating costly MP4 computations, the ccCA-CBS methods hold two distinct advantages over the ccCA-aTZ method.

Basis set deficiencies within the ccCA-DZ, ccCA-TZ, and ccCA-aTZ clearly arise when computing electron affinities; a traditionally more difficult atomic and molecular property to accurately describe. The ccCA-DZ method grossly overestimates electron affinities, with a maximum deviation of -30.7 kcal mol $^{-1}$ for F $^-$ and an average deviation of -14.3 kcal mol $^{-1}$. The average deviation is lessened but still unacceptable at the ccCA-TZ level, -7.6 kcal mol $^{-1}$. Our assessment is that the ccCA-DZ and ccCA-TZ $\Delta E(\zeta)$ additive correction for anions is overemphasized with the MP4 level of theory. Using the MP2 augmented CBS values as the reference energy seems to compensate for this problem. While it appears that the ccCA-aTZ method performs slightly worse than ccCA-TZ for atomic IPs, the ccCA-aTZ and ccCA-CBS methods perform splendidly for atomic EAs with

TABLE III. Atomic ionization potentials and electron affinities (both in kcal mol⁻¹) with *Gn* and ccCA methods.

Ionization potential	Expt. ^a	G1	G2	G3	ccCA-DZ	ccCA-TZ	ccCA-aTZ	ccCA-CBS-1	ccCA-CBS-2
Li	124.3	123.2	124.5	124.5	123.5	123.9	123.9	123.9	123.9
Be	214.9	217.7	218.1	218.4	214.0	215.2	215.7	216.4	216.3
B	191.4	188.9	189.9	189.9	189.4	190.1	190.2	189.8	190.5
C	259.7	257.6	258.5	258.6	259.1	258.9	258.8	259.0	259.2
N	335.3	333.7	334.5	334.6	336.3	335.0	334.8	334.9	335.1
O	313.9	312.3	312.4	312.7	314.0	313.8	312.1	313.2	313.1
F	401.7	401.1	401.0	401.3	405.0	402.6	400.6	401.7	401.4
Na	118.5	114.2	117.9	118.0	115.4	116.9	116.9	116.9	116.9
Mg	176.3	177.0	179.5	179.8	174.8	176.3	176.7	177.0	177.0
Al	138.0	136.7	137.4	137.5	137.3	137.2	137.4	137.8	137.8
Si	187.9	186.7	187.4	187.5	188.2	187.7	187.7	187.9	188.0
P	241.9	240.7	241.3	241.3	243.4	242.6	242.4	242.6	242.7
S	238.9	235.5	236.8	237.1	237.0	237.5	236.5	237.6	237.6
Cl	299.1	296.7	297.3	297.6	298.3	298.8	297.4	297.7	298.4
Mean Dev. IP		1.41	1.54	0.21	0.45	0.38	0.76	0.39	0.28
Mean Abs. Dev.		1.91	1.85	1.24	1.34	0.64	1.98	0.80	0.71
Standard Dev.		1.71	1.59	1.66	1.63	0.75	0.94	0.93	0.82
Electron affinity									
C	29.1	27.4	27.5	27.6	39.7	33.7	28.4	27.9	28.0
O	33.7	32.5	30.8	31.1	56.5	45.1	33.7	33.8	33.5
F	78.4	79.8	78.4	78.7	109.1	94.6	81.7	81.2	80.6
Si	31.9	30.4	31.8	31.8	37.3	37.2	32.3	32.1	32.2
P	17.2	13.9	17.1	16.7	26.4	22.6	15.6	16.2	16.2
S	47.9	45.1	47.6	47.9	58.8	52.7	46.9	48.1	47.7
Cl	83.4	82.3	83.2	83.5	93.9	89.2	83.3	86.6	84.5
Mean Dev. EA		1.46	0.91	0.61	-14.31	-7.64	-0.04	-0.61	-0.16
Mean Abs. Dev.		1.86	1.43	0.73	14.31	7.64	1.01	1.24	0.87
Standard Dev.		1.51	1.39	1.06	9.02	4.46	1.59	1.73	1.17

^aSee Refs. 2 and 4 for experimental references.

average absolute deviations of 1.01, 1.24, and 0.87 kcal mol⁻¹ for ccCA-aTZ, ccCA-CBS-1, and ccCA-CBS-2, respectively. Though the basis set dependence of the ccCA methods has been shown here on only a small number of atomic properties, we find that molecular properties behave similarly. For example, the ccCA-TZ electron affinity of CH₂⁻ is predicted to be 19.5 kcal mol⁻¹, compared to the experimental value of 15.0 kcal mol⁻¹, while the ccCA-aTZ method predicts an EA of 14.4 kcal mol⁻¹, and the ccCA-CBS-1 and ccCA-CBS-2 methods both predict an EA of 15.1 kcal mol⁻¹.

IV. ASSESSMENT OF ccCA ON THE G2-1 TEST SET

The G2-1 test set contains 125 atomic and molecular electronic energies,⁴ and from those energies, 55 enthalpies of formation at 298.15 K (ΔH_f), 38 adiabatic ionization potentials (IPs), 25 adiabatic electron affinities (EAs), and 8 adiabatic proton affinities (PAs) can be determined and compared to reliable experimental data.

A. Performance of ccCA

Due to the persistent discrepancies over the ΔH_f value of silicon gas,^{34,78–82} seven molecules from the G2-1 test set containing silicon atoms have been removed from our initial test set. Work is currently being carried out upon small

silicon-containing compounds in order to assess and improve the errors of the ccCA-CBS methods, and more quantitatively address controversy in the gas phase enthalpy of formation of silicon.⁸³

In Table IV, the G2-1 test set standard enthalpies of formation at 298.15 K predicted with G1, G2, G3B3, ccCA-aTZ, ccCA-CBS-1, and ccCA-CBS-2 are compared. The mean deviations of the 48 ΔH_f values computed with ccCA-aTZ, ccCA-CBS-1, and ccCA-CBS-2 are -0.93, 1.02, and 1.23 kcal mol⁻¹, respectively. The mean absolute deviations for the three variants are 1.31, 1.45, and 1.33 kcal mol⁻¹, all within the desired ± 2 kcal mol⁻¹ range of near-chemical accuracy. Due to the nature of the HLC being optimized for a large test set that includes the G2-1 set, the G3B3 enthalpies of formation have a mean deviation of 0.03 kcal mol⁻¹, with no discernable pattern to allow inferences as to why some enthalpies of formation are higher or lower than the experimental values. In contrast, the most problematic cases within the G2-1 test set for the ccCA-aTZ method are structurally similar; hydrocarbons and small systems with multiple bonds where the ΔH_f values are always overestimated compared to the experimental quantity. However, the ccCA-CBS methods perform much better for hydrocarbons and multiply bonded systems while most of the larger errors from the ccCA-CBS methods come from molecules containing second-row main

TABLE IV. Computed enthalpies of formation (in kcal mol⁻¹) of G2-1 test set.

Species	Expt. ^a	$\Delta H_f(298.15\text{ K})$								
		G1	G1 w/o HLC	G2	G3B3	G3B3 w/o HLC	ccCA- aTZ	ccCA- CBS-1	ccCA- CBS-2	+SO+ SR ^b
G2-1 test set										
LiH	33.3	32.8	36.4	32.7	32.9	35.5	33.1	32.6	32.4	32.4
BeH	81.7	83.6	83.6	83.2	82.3	83.1	82.0	81.8	81.7	81.7
CH	142.4	142.4	146.0	141.9	141.0	144.4	142.8	142.6	142.2	142.3
CH ₂ (³ B ₁)	93.5	95.9	99.5	94.7	92.3	96.6	94.5	94.4	93.7	94.0
CH ₂ (¹ A ₁)	102.5	102.1	109.4	101.4	101.8	106.2	103.1	102.5	101.9	102.1
CH ₃	35.1	36.8	44.0	35.1	34.3	40.2	36.3	35.7	34.8	35.1
CH ₄	-17.9	-16.4	-5.5	-18.6	-17.9	-9.9	-16.1	-16.9	-18.0	-17.7
NH	85.2	87.0	90.6	86.3	84.1	88.8	86.6	86.0	85.8	85.9
NH ₂	44.5	46.7	53.9	45.0	44.3	50.2	45.7	44.5	44	44.2
NH ₃	-11.0	-8.5	2.4	-10.8	-10.3	-3.0	-9.3	-11.2	-11.8	-11.5
OH	8.9	10.2	13.8	9.1	8.4	11.3	9.2	8.3	8.2	8.6
OH ₂	-57.8	-55.7	-48.5	-58.1	-57.6	-53.3	-57.6	-59.4	-59.5	-59.0
FH	-65.1	-64.4	-60.8	-66.2	-65.2	-63.8	-65.8	-66.6	-66.7	-66.1
PH ₂	33.1	34.0	41.2	32.9	32.4	38.4	33.0	31.6	31.3	31.7
PH ₃	1.3	3.4	14.3	2.0	2.8	10.1	2.4	0.3	-0.1	0.5
SH ₂	-4.9	-3.0	4.2	-4.8	-4.5	-0.2	-5.8	-7.2	-7.5	-6.4
ClH	-22.1	-21.0	-17.4	-22.4	-21.6	-20.2	-23.1	-25.2	-24.3	-23.1
Li ₂	51.6	48.8	52.4	49.6	49.2	51.7	51.0	50.6	50.5	50.5
LiF	-80.1	-85.2	-81.6	-81.4	-80.4	-79.0	-81.4	-83.4	-82.8	-81.7
C ₂ H ₂	54.2	56.1	67.0	55.8	54.3	61.2	57.4	56.8	54.6	55.1
C ₂ H ₄	12.5	14.4	28.8	12.8	12.3	21.7	15.4	13.4	12.0	12.6
C ₂ H ₆	-20.1	-17.5	0.6	-20.6	-20.1	-8.1	-17.1	-18.7	-20.6	-20.0
CN	104.9	107.0	114.2	107.3	104.9	110.4	108.2	106.1	106.0	106.3
HCN	31.5	30.9	41.7	31.2	30.6	37.5	33.9	31.4	30.8	31.2
CO	-26.4	-27.9	-20.6	-28.2	-27.0	-23.1	-25.0	-27.8	-27.7	-27.2
HCO	10.0	9.4	16.6	9.3	9.4	13.6	10.6	8.3	8.0	8.7
H ₂ CO	-26.0	-26.8	-15.9	-27.9	-26.9	-20.4	-24.4	-26.8	-27.4	-26.7
H ₃ COH	-48.0	-46.5	-32.1	-49.4	-48.2	-35.0	-46.3	-48.5	-49.6	-48.7
N ₂	0.0	0.3	11.1	1.3	0.6	7.5	3.0	-0.5	-0.5	-0.3
H ₂ NNH ₂	22.8	26.9	44.9	23.7	24.2	36.2	26.1	22.4	21.6	22.2
NO	21.6	21.3	28.6	21.0	21.7	26.8	24.0	21.2	21.5	22.0
O ₂	0.0	2.6	6.2	2.4	-0.1	3.3	1.8	0.1	0.2	0.9
HOOH	-32.5	-30.7	-19.9	-32.3	-31.9	-25.8	-31.0	-33.2	-33.7	-32.8
F ₂	0.0	-0.5	3.1	0.3	1.2	1.5	0.2	0.6	-0.2	0.7
CO ₂	-94.1	-96.4	-85.5	-96.7	-95.7	-89.9	-91.7	-95.8	-95.9	-94.7
Na ₂	34.0	30.9	34.5	31.6	29.7	32.2	32.6	32.3	32.2	32.2
P ₂	34.3	34.4	45.2	35.7	34.9	41.8	37.4	33.1	33.7	34.2
S ₂	30.7	34.0	37.7	33.9	31.8	36.3	31.9	29.3	29.5	31.1
Cl ₂	0.0	-0.8	2.8	1.4	1.9	2.2	-0.5	-4.3	-2.6	-0.6
NaCl	-43.6	-45.5	-41.9	-44.8	-44.6	-43.2	-43.7	-47.0	-45.4	-44.1
SC	66.9	65.1	72.3	65.9	65.9	69.9	67.4	64.4	64.8	65.8
SO	1.2	4.4	8.1	3.8	1.5	4.9	1.9	0.0	-0.3	1.0
ClO	24.2	26.7	30.3	26.4	26.6	28.5	25.4	22.9	23.8	25.2
FCI	-13.2	-14.1	-10.5	-14.0	-12.0	-11.7	-14.4	-16.8	-15.7	-14.2
CH ₃ Cl	-19.6	-19.1	-8.3	-20.5	-19.1	-13.0	-19.2	-21.8	-21.9	-20.5
H ₃ CSH	-5.5	-3.2	11.3	-5.3	-4.9	4.2	-4.8	-6.8	-8.0	-6.6
HOCl	-17.8	-17.6	-10.4	-18.3	-17.2	-14.0	-18.6	-21.8	-20.9	-19.4
SO ₂	-71.0	-63.5	-52.7	-65.9	-68.4	-63.0	-71.3	-77.2	-77.9	-75.8
Mean Dev.		-0.80	-8.33	-0.13	0.03	-4.88	-0.93	1.02	1.23	0.51
Mean Abs.										
Dev.		1.80	8.39	1.16	0.85	4.96	1.31	1.45	1.33	0.81
Std. Dev.		2.13	5.26	1.53	1.18	3.30	1.34	1.66	1.28	0.99
Max.					Na ₂			SO ₂	SO ₂	SO ₂
Deviation		SO ₂ (-7.5)	H ₂ NNH ₂ (-22.1)	SO ₂ (-5.0)	(4.3)	H ₂ NNH ₂ (-13.4)	CN/H ₂ NNH ₂ (-3.3)	(6.2)	(6.9)	(4.8)

^aSee Refs. 2, 3, 6, 71, and 89 for experimental references.^bAtomic spin-orbit (SO) corrections and scalar relativistic (SR) SDPT corrections from Refs. 84 and 86 are added to the ccCA-CBS-2 atomization energies.

group atoms. For example, maximum deviation in ccCA-CBS theoretical ΔH_f values occurs with SO_2 , with the ccCA-CBS-1 method in error by $+6.2 \text{ kcal mol}^{-1}$ and the ccCA-CBS-2 method in error by $+6.9 \text{ kcal mol}^{-1}$. Modifications of ccCA to improve the treatment of molecules with second-row elements will be discussed in later sections.

The maximum deviation of the G3B3 method is $+4.3 \text{ kcal mol}^{-1}$ with Na_2 , while the ccCA-aTZ maximum deviation is $-3.3 \text{ kcal mol}^{-1}$ with CN. The ccCA-aTZ, ccCA-CBS-1, and ccCA-CBS-2 methods, respectively, have 10, 11, and 10 species over the $\pm 2 \text{ kcal mol}^{-1}$ range whereas only four systems are outside this error range using G3B3. Compared to using ccCA-aTZ, extrapolations to the one-particle CBS limit lower the total energy of molecules relative to the component atoms. This in turn raises computed atomization energies and proportionally lowers the computed value of ΔH_f .

For the 38 adiabatic ionization potentials contained in the G2-1 test set (shown in Table V), ccCA-aTZ, ccCA-CBS-1, and ccCA-CBS-2 have mean absolute deviations of 0.63, 0.91, and $0.81 \text{ kcal mol}^{-1}$, respectively. This compares well to G3B3, which has a mean absolute deviation of $0.89 \text{ kcal mol}^{-1}$. The ccCA-CBS-2 has two IPs with deviations over $\pm 2 \text{ kcal mol}^{-1}$, CH_4^+ and SC^+ . Two atomic ionization potentials over the $\pm 2 \text{ kcal mol}^{-1}$ error limit (Be and Mg) occur using G3B3, while CH_4^+ is the only molecular ionization potential in the G2-1 test set poorly described by G3B3.

The 25 computed adiabatic electron affinities (shown in Table VI) have ccCA-aTZ, ccCA-CBS-1, and ccCA-CBS-2 mean absolute deviations of 0.93, 1.10, and $1.02 \text{ kcal mol}^{-1}$, respectively. Three of the ccCA-CBS-2 electron affinities exceed the $\pm 2 \text{ kcal mol}^{-1}$ error range, compared to ten systems using G1, six using G2, three using G3, and four using G3B3. The eight proton affinities (shown in Table VII) have ccCA-aTZ, ccCA-CBS-1, and ccCA-CBS-2 mean absolute deviations of 1.48, 1.49, and $1.51 \text{ kcal mol}^{-1}$, respectively. Because the protonated species have the same number of valence electrons as their neutral counterparts, their G_n HLCs will be equivalent. Since there is no difference in the HLCs of the neutral and protonated species, removal of the HLC will not change the G_n PA values. Thus the G_n methods slightly outperform ccCA for overall computation of proton affinities.

B. Removal of the HLC

In order to more directly compare the basis set difference between G_n methods and ccCA, the high-level correction has been subtracted from the G1 and G3B3 atomic and molecular energies in order to assess the quality of the purely *ab initio* portions of the G_n methods. In Table IV, the deficiency of the G1 and G3 MP4/6-31G(d) reference energy is obvious. Whereas G3B3 with the HLC only predicts four of the 48 G2-1 ΔH_f values to have a deviation from experiment larger than $\pm 2 \text{ kcal mol}^{-1}$, uncorrected G3B3 has 37 systems outside the range of near-chemical accuracy. The G1 method, with its supposedly more physically sound “isogyric” HLC, only has five G2-1 systems with absolute deviations *within*

2 kcal mol^{-1} of the experimental values! Without the HLC, the mean absolute deviation for the 48 G2-1 enthalpies of formation (silicon-containing molecules excluded) with G3B3 is $4.96 \text{ kcal mol}^{-1}$. The implementation of standard DFT with a large basis set [B3LYP/6-311+G(3df,2p)] to compute G2-1 enthalpies of formation has a mean absolute deviation of only $2.36 \text{ kcal mol}^{-1}$.⁶ Almost all uncorrected G1 and G3B3 enthalpies of formation are severely overestimated, especially hydrocarbons and multiply bonded systems. The most problematic systems for uncorrected G_n methods correlate well with the problematic systems using ccCA with an incomplete basis set treatment.

As a testament to the relative ease in computing ionization potentials rather than enthalpies of formation, the G3B3 method still performs reliably without the HLC. The mean absolute deviation of IPs for G3B3 without the HLC is $1.79 \text{ kcal mol}^{-1}$, with 12 species outside the 2 kcal mol^{-1} range. Uncorrected electron affinities, however, are quite poor, with an average deviation of $3.15 \text{ kcal mol}^{-1}$ and all but five systems outside the 2 kcal mol^{-1} accuracy range. The noncorrected G3B3 always overestimates both IPs and EAs, except for two cases, CH_4^+ and SC^+ .

C. Atomic spin-orbit corrections

Enthalpies of formation predicted by the ccCA-CBS- n methods are predominantly overestimated, whereas the G3 and G3B3 enthalpies of formation are more evenly distributed around the experimental result. For G3 methods, this is because effects such as atomic spin-orbit splitting are folded into the total energies, and hence the HLC parametrization. Removal of atomic spin-orbit effects from the G3 methods will lower atomization energies. This trend, pictorially represented in Fig. 1, is the basis for our predilection towards the ccCA-CBS-2 method. Of the 48 nonsilicon-containing enthalpies of formation within the G2-1 test set, all have a negative deviation except Na_2 when employing the G3B3 method without a high-level correction. Removal of atomic spin-orbit corrections will shift calculated ΔH_f deviations even *further* in the negative direction. The ccCA-aTZ method predicts 35 values of ΔH_f with a negative deviation, while conversely the ccCA-CBS-1 method predicts 13 systems with negative deviation in ΔH_f , and the ccCA-CBS-2 method predicts only 4 systems with a negative deviation. When atomic spin-orbit splitting and relativistic effects are computed in conjunction with the ccCA-CBS- n methods, these combined corrections will generally lower atomization energies and proportionally raise the computed ΔH_f , therefore increasing the overall accuracy in computing ΔH_f . Using the same spin-orbit corrections as those in the original G3 method,⁵ the average ΔH_f deviation of the ccCA-aTZ method is more negative (-0.95 to $-1.30 \text{ kcal mol}^{-1}$) while the ccCA-CBS-1 average deviation improves, changing from $+1.03$ to $+0.65 \text{ kcal mol}^{-1}$. Mean absolute deviations of the various composite methods are shown in Fig. 2. The ccCA-CBS-2 average deviation in ΔH_f improves from $+1.24$ to $+0.55 \text{ kcal mol}^{-1}$. Due to the shift in atomization energies, the mean absolute deviation of the ccCA-aTZ method for the entire data set worsens from 1.29 to $1.46 \text{ kcal mol}^{-1}$, while

TABLE V. Computed ionization potentials (in kcal mol⁻¹) of G2-1 test set.

Species	Expt. ^a	G1	Ionization potential				ccCA-aTZ	ccCA-CBS-1	ccCA-CBS-2	+SO+SR ^b
			w/o HLC	G2	G3B3	w/o HLC				
G2-1 test set										
Li	124.3	123.2	123.1	124.5	124.5	123.7	123.9	123.9	123.9	123.9
Be	214.9	217.7	214.0	218.1	218.4	214.6	215.7	216.4	216.3	216.3
B	191.4	188.9	188.8	189.9	189.9	188.7	190.2	189.8	190.5	190.4
C	259.7	257.6	257.5	258.5	258.6	257.3	258.8	259.0	259.2	258.7
N	335.3	333.7	333.6	334.5	334.6	333.3	334.8	334.9	335.1	334.6
O	313.9	312.3	308.5	312.4	312.7	308.4	312.1	313.2	313.1	313.1
F	401.7	401.1	397.3	401.0	401.3	396.7	400.6	401.7	401.4	401.1
Na	118.5	114.2	114.1	117.9	118.0	117.1	116.9	116.9	116.9	117.0
Mg	176.3	177.0	173.3	179.5	179.8	176.1	176.7	177.0	177.0	177.2
Al	138.0	136.7	136.6	137.4	137.5	136.6	137.4	137.8	137.8	137.8
Si	187.9	186.7	186.6	187.4	187.5	186.6	187.7	187.9	188.0	187.5
P	241.9	240.7	240.6	241.3	241.3	240.5	242.4	242.6	242.7	241.5
S	238.9	235.5	231.8	236.8	237.1	233.3	236.5	237.6	237.6	237.8
Cl	299.1	296.7	293.0	297.3	297.6	293.8	297.4	297.7	298.4	297.8
CH ₄	291.0	292.4	288.7	291.8	293.7	291.5	293.1	293.3	293.5	293.5
NH ₃	234.8	234.5	230.7	233.8	234.0	231.8	235.0	235.6	235.8	235.8
OH	300.0	299.1	295.4	298.3	298.4	296.2	299.5	299.5	299.9	299.7
OH ₂	291.0	290.6	286.9	290.4	290.5	288.3	290.8	291.9	291.7	291.5
FH	369.9	370.5	366.8	370.0	370.2	368.0	370.3	371.6	371.1	370.8
SiH ₄	253.7	254.1	250.4	254.2	254.6	252.8	254.3	255.5	255.4	255.1
PH	234.1	232.4	232.3	234.9	235.0	233.7	234.3	234.3	234.4	234.1
PH ₂	226.5	223.9	223.8	226.4	226.4	225.2	226.0	226.0	226.1	225.8
PH ₃	227.6	227.3	223.6	227.9	227.9	226.7	227.8	228.2	228.4	228.6
SH	239.1	237.7	234.0	238.1	238.1	236.8	238.9	239.8	239.8	239.5
SH ₂ (² B ₁)	241.4	240.0	236.3	240.8	240.7	239.5	241.1	241.8	241.8	241.5
SH ₂ (² A ₁)	294.7	293.3	289.6	294.3	294.2	293.0	294.1	294.9	294.9	295.1
ClH	294.0	293.1	289.3	293.3	293.3	292.0	293.9	295.3	294.9	294.5
C ₂ H ₂	262.9	263.8	260.1	263.1	263.5	261.3	262.9	262.6	263.6	263.5
C ₂ H ₄	242.4	244.3	240.6	243.5	243.0	240.8	242.5	243.1	243.3	243.3
CO	323.1	324.4	320.7	323.2	323.4	321.2	323.4	324.6	324.5	324.5
N ₂ (² Σcation)	359.3	359.8	356.1	358.9	359.4	359.2	358.9	359.7	359.7	359.6
N ₂ (² Πcation)	385.1	385.0	381.2	384.4	385.2	383.0	384.7	385.6	385.8	385.6
O ₂	278.3	280.5	280.4	282.4	278.8	276.8	278.2	277.7	277.8	277.6
P ₂	242.8	243.1	239.4	243.3	243.6	242.8	242.6	243.9	243.7	243.3
S ₂	215.8	213.9	213.8	216.3	215.7	215.7	215.4	215.3	215.3	214.9
Cl ₂	265.2	266.2	262.4	265.8	265.8	265.1	265.2	266.4	265.8	265.4
ClF	291.9	293.0	289.3	292.0	292.4	291.5	291.9	293.2	292.4	292.1
SC	261.3	264.5	260.8	262.7	262.4	261.7	263.1	264.6	264.2	264.1
Mean Dev.		0.48	3.06	0.59	−0.03	1.75	0.23	−0.34	−0.37	−0.17
Mean Abs. Dev.		1.44	3.17	1.26	0.89	1.79	0.63	0.91	0.81	0.80
Std. Dev.		1.68	1.76	1.50	1.22	1.59	0.87	1.09	0.95	0.99
Max. Dev.		Na	S	Na	Mg	S	S	SC	SC	SC
		(4.3)	(7.1)	(4.4)	(−3.5)	(5.6)	(2.4)	(−3.3)	(−2.9)	(−2.8)

^aSee Refs. 2 and 4 for experimental references.^bAtomic spin-orbit (SO) corrections and scalar relativistic (SR) SDPT corrections from Refs. 84 and 86 are added to the ccCA-CBS-2 total energies.

ccCA-CBS-1 improves from 1.47 to 1.17 kcal mol⁻¹, and ccCA-CBS-2 improves from 1.34 to 0.84 kcal mol⁻¹. The inclusion of spin-orbit effects will also affect the computed atomic IPs and EAs, but has little effect on the overall deviation of these two quantities.

D. Scalar relativistic effects

Relativistic effects are obviously significant when comparing atoms or molecules containing elements including and

beyond the 3*d* transition metals. However, in investigations of relativistic effects on the molecular energies of the G3/99 test set, Kedziora and co-workers^{84–86} have found that scalar relativistic effects can have a contribution to atomization energies that is the same order of magnitude as atomic spin-orbit splitting effects. To generate an approximation of scalar relativistic corrections, we have shifted G2-1 atomization energies using the G3large stationary direct perturbation theory⁸⁷ (SDPT) results obtained by Kedziora and

TABLE VI. Computed electron affinities (in kcal mol⁻¹) of G2-1 test set.

Species	Expt. ^a	G1	w/o HLC	G2	G3B3	Electron affinity				
						w/o HLC	ccCA- aTZ	ccCA-CBS- 1	ccCA- CBS-2	+SO+ SR ^b
G2-1 test set										
C	29.1	27.4	27.2	27.5	27.6	27.2	28.4	27.9	28.0	27.9
O	33.7	32.5	28.8	30.8	31.1	28.5	33.7	33.8	33.5	33.3
F	78.4	79.8	76.1	78.4	78.7	76.4	81.7	81.2	80.6	80.3
Si	31.9	30.4	30.3	31.8	31.8	28.3	32.3	32.1	32.2	32.0
P	17.2	13.9	10.2	17.1	16.7	13.7	15.6	16.2	16.2	15.9
S	47.9	45.1	41.4	47.6	47.9	44.2	46.9	48.1	47.7	47.4
Cl	83.4	82.3	78.6	83.2	83.5	79.8	83.3	86.6	84.5	84.1
CH	28.6	25.5	25.4	27.2	27.1	25.0	27.2	27.2	27.2	27.1
CH ₂	15.0	14.9	11.2	13.4	13.0	10.8	14.4	15.1	15.1	15.1
CH ₃	1.8	0.3	−3.5	−0.9	−1.2	−3.4	0.0	1.0	1.0	1.0
NH	8.8	6.5	2.8	4.5	4.4	2.4	6.5	6.5	6.7	6.6
NH ₂	17.8	17.1	13.4	16.1	15.9	13.7	18.6	19.8	19.7	19.6
OH	42.2	42.6	38.8	41.0	41.0	38.8	45.1	45.2	45.0	44.8
SiH	29.4	26.4	26.3	29.3	29.4	27.4	28.7	28.6	28.7	28.5
SiH ₂	25.9	22.1	22.1	24.8	24.8	22.8	24.5	24.5	24.6	24.4
SiH ₃	32.5	32.1	28.4	32.9	32.8	30.6	32.5	32.9	33.0	33.1
PH	23.8	21.0	17.4	22.6	22.6	20.4	22.8	22.2	22.2	22.0
PH ₂	29.3	27.6	23.9	29.3	29.2	27.0	29.2	29.9	29.9	29.7
SH	54.4	51.6	47.8	53.5	53.5	51.3	53.6	54.8	54.5	54.2
O ₂	10.1	10.9	7.2	9.2	8.6	6.3	10.2	9.2	9.3	9.1
NO	0.5	−1.4	−1.5	−0.1	0.0	−2.0	0.5	−0.2	−0.2	−0.4
CN	89.0	93.0	89.3	90.6	89.4	87.2	89.5	90.6	90.6	90.6
PO	25.1	25.4	25.2	22.6	25.5	23.4	25.2	24.7	24.6	24.3
S ₂	38.3	37.9	34.1	38.5	38.5	36.3	37.8	38.2	38.1	37.8
Cl ₂	55.1	52.2	52.1	56.9	56.3	54.3	54.0	54.8	53.3	53.2
Mean Dev.		1.28	3.85	0.80	0.84	3.15	0.28	−0.07	0.13	0.30
Mean Abs. Dev.		1.84	3.88	1.32	1.08	3.15	0.93	1.10	1.02	1.09
Std. Dev.		1.78	1.97	1.40	1.28	1.29	1.27	1.46	1.28	1.27
Max. Dev.		CN	P	SiH ₂	NH	NH	F	Cl	OH	OH
	(−4.0)	(7.0)	(3.1)	(4.4)	(6.4)	(−3.3)	(−3.2)	(−2.8)	(−2.6)	

^aSee Refs. 2 and 4 for experimental references.^bAtomic spin-orbit (SO) corrections and scalar relativistic (SR) SDPT corrections from Refs. 84 and 86 are added to the ccCA-CBS-2 total energies.

co-workers.^{84,86} Of all 55 enthalpies of formation in the G2-1 test set, only the Na₂ system shows an increase in atomization energy when scalar relativistic effects are included. Thus, implemented scalar relativistic corrections will increase the average deviation in ΔH_f for G3 methods as well

as the ccCA-aTZ method. Curtiss and co-workers have noted⁸⁸ that scalar relativistic effects do not have a significant effect on the accuracy of G3 methods once the HLC has been reparametrized. Though the G3 relativistic HLC parameters are not revealed in Ref. 88, it is likely that if the bias of

TABLE VII. Computed proton affinities (in kcal mol⁻¹) of G2-1 test set.

		Proton affinity						
Species	Expt. ^a	G1	G2	G3B3	ccCA-aTZ	ccCA-CBS-1	ccCA-CBS-2	+SR ^b
G2-1 test set								
NH ₃	202.5	202.7	203.1	203.0	202.1	202.0	202.1	202.1
OH ₂	165.1	163.4	163.4	163.3	163.0	162.8	163.0	162.9
C ₂ H ₂	152.3	152.5	152.8	152.3	148.7	149.3	148.5	148.5
SiH ₄	154.0	152.9	152.3	151.8	152.1	151.6	151.8	151.9
PH ₃	187.1	186.1	185.3	185.4	185.7	186.2	186.1	185.8
SH ₂	168.8	167.8	167.0	167.3	167.7	167.6	167.8	167.8
ClH	133.6	132.3	132.6	132.7	133.3	132.7	133.2	133.2
H ₂	100.8		99.3	99.6	99.7	99.6	99.6	99.6

^aSee Refs. 2 and 4 for experimental references.^bScalar relativistic (SR) SDPT corrections from Refs. 84 and 86 are added to the ccCA-CBS-2 total energies.

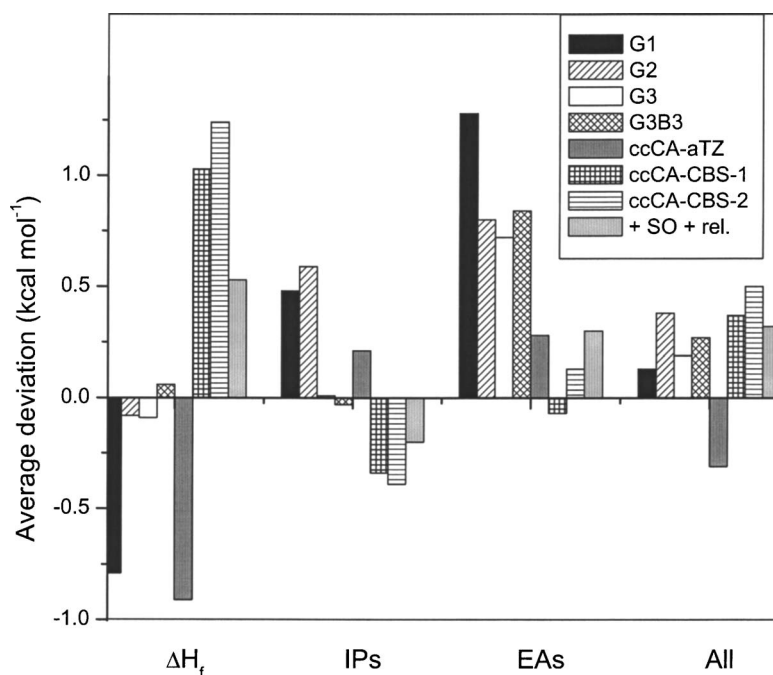


FIG. 1. Signed errors (in kcal mol⁻¹) for the various methods applied to experimentally known properties of the G2-1 test set.

the relativistic correction on enthalpies of formation uniformly increases the deviation from experiment in the same direction as basis set and spin-orbit effects, then the molecular HLC must increase in magnitude in order to account for more physical phenomena.

With the G3large SDPT relativistic correction, the mean absolute deviations in the 48 theoretical ΔH_f values with the ccCA-CBS-1 and ccCA-CBS-2 methods are 1.02 and 0.81 kcal mol⁻¹. This ccCA-CBS-2 mean absolute deviation for the G2-1 test set, obtained with no empirical or optimized parameters, is 0.04 kcal mol⁻¹ lower than that of G3B3. The scalar relativistic correction has a slight worsening effect on the accuracy of IPs, EAs, and PAs, but the change in the mean absolute deviations of all three of these quantities is less than 0.1 kcal mol⁻¹. The average absolute deviation of 38 IPs is 0.81 kcal mol⁻¹, 1.09 kcal mol⁻¹ for the 25 EAs,

and 1.55 kcal mol⁻¹ for the 8 PAs. Concerning these four major benchmarking experimental properties, ccCA-CBS-2 outperforms or matches the accuracy of the G3B3 method for all but the computation of proton affinities. Future studies will explore possible basis set, method, and geometry dependence of the relativistic corrections. Finally, after the scalar relativistic and spin-orbit effects are added to the 119 experimental values, the ccCA-CBS-2 method has an average deviation of 0.30 kcal mol⁻¹ and an average absolute deviation of 0.92 kcal mol⁻¹. For this data set, the average absolute deviation of the ccCA-CBS-2 method almost exactly matches that of G3B3 (0.93 kcal mol⁻¹). The ccCA-CBS-2 method achieves this accuracy without employing empirical corrections, nor involving expensive coupled cluster computations.

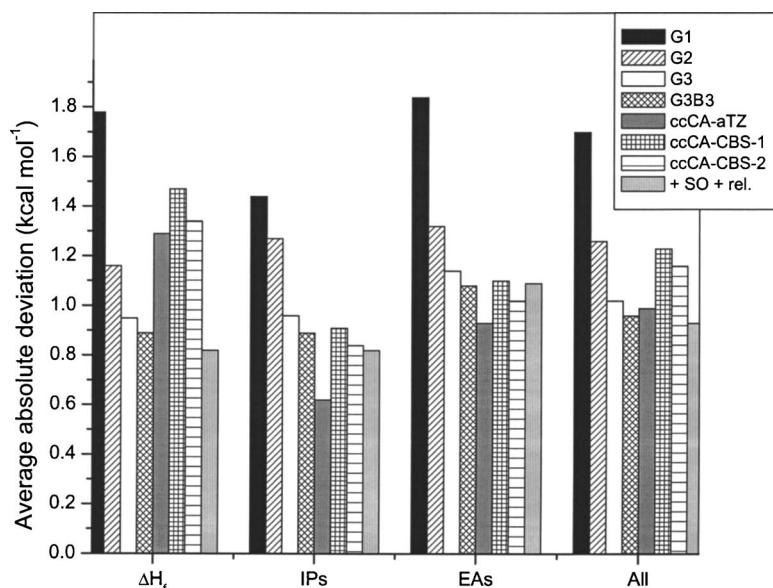


FIG. 2. Average absolute deviations (in kcal mol⁻¹) for the various methods applied to experimentally known properties of the G2-1 test set.

TABLE VIII. Computed enthalpies of formation (in kcal mol⁻¹) of larger training set.

Species	Expt. ^a	G2	G3B3	ccCA-aTZ	$\Delta H_f(298\text{ K})$		ccCA-aTZ +SO+SR ^b	ccCA-CBS-1 +SO+SR ^b	ccCA-CBS-2 +SO+SR ^b
					ccCA-CBS-1	ccCA-CBS-2			
BCl ₃	-96.3	-98.3	-95.1	-96.4	-104.3	-100.9	-92.9	-100.8	-97.4
F ₂ O	5.9	5.3	6.7	6.3	6.2	5.2	7.6	7.5	6.5
CF ₄	-223.0	-228.6	-223.1	-223.1	-224.9	-226.6	-220.3	-222.1	-223.8
C ₂ F ₄	-157.4	-165.6	-161.7	-159.0	-162.3	-164.0	-155.9	-159.2	-160.9
CCl ₄	-22.9	-25.7	-23.0	-24.5	-33.7	-29.5	-20.1	-29.4	-25.1
AlCl ₃	-139.7	-142.5	-141.6	-142.2	-151.5	-147.9	-137.8	-147.1	-143.5
PF ₃	-229.1	-223.7	-223.3	-227.6	-231.5	-232.7	-225.2	-229.1	-230.3
SF ₆	-291.7		-291.2	-294.0	-300.5	-302.4	-287.1	-293.6	-295.5
Linear alkanes									
C ₃ H ₈ (propane)	-25.0	-25.4	-25.0	-20.8	-23.2	-25.8	-19.9	-22.3	-24.9
C ₄ H ₁₀ (<i>n</i> -butane)	-30.0	-30.4	-30.0	-25.0	-28.3	-31.6	-23.8	-27.1	-30.4
C ₅ H ₁₂ (<i>n</i> -pentane)	-35.1		-34.9	-29.6	-32.7	-36.7	-28.0	-31.1	-35.1
C ₆ H ₁₄ (<i>n</i> -hexane)	-39.9		-40.0	-32.0	-36.9	-41.6	-30.1	-35.0	-39.7
C ₈ H ₁₈ (<i>n</i> -octane)	-49.9		-50.0		-45.9	-52.1		-43.4 ^c	-49.6 ^c
Other hydrocarbons									
C ₃ H ₄ (cyclopropene)	68.2	69.1	68.2	72.2	69.6	67.5	73.1	70.5	68.4
C ₄ H ₁₀ (isobutane)	-32.1	-32.4	-31.9	-26.8	-30.1	-33.4	-25.6	-28.9	-32.2
C ₆ H ₆ (benzene)	19.7	23.7	20.3	28.5	22.6	19.5	30.7	24.3	21.2
C ₁₀ H ₈ (naphthalene)	36.1		34.6	49.6	40.4	35.5	52.6	43.4	38.5
Substituted hydrocarbons									
CH ₃ NH ₂ (methylamine)	-5.5	-5.5	-4.6	-2.1	-4.8	-6.1	-1.5	-4.2	-5.5
HCOOCH ₃ (methyl formate)	-85.0	-88.8	-86.9	-82.1	-86.2	-87.8	-80.8	-84.9	-86.5
C ₂ H ₅ OCH ₃ (methyl ethyl ether)	-51.7	-54.0	-52.7	-47.5	-50.8	-53.7	-46.0	-49.3	-52.3
C ₆ H ₅ Cl (chlorobenzene)	12.4		12.1	19.7	11.8	10.0	21.5	13.6	12.8
C ₂ H ₆ O (ethanol)	-56.2	-57.2	-56.3	-53.0	-56.0	-57.8	-51.8	-54.8	-56.6
Organic radicals									
CH ₃ O	5.0	4.8	4.4	6.9	5.5	4.5	7.6	6.2	5.2
H ₂ COH	-4.1	-3.8	-4.1	-2.2	-4.2	-5.1	-1.4	-3.4	-4.3
CH ₃ CO	-2.5	-2.8	-2.7	1.0	-1.9	-3.1	2.0	-0.9	-2.1
CH ₃ CH ₂ O	-3.3	-2.3	-2.4	0.4	-1.8	-3.6	1.7	-0.5	-2.3
Inorganic hydrides									
H ₂	0.0	-1.1	-0.4	0.1	-0.1	-0.4	0.1	-0.1	-0.4
HS	33.7	34.4	33.7	33.8	33.1	33.0	34.6	33.9	33.8

^aSee Refs. 2, 3, 6, 71, and 89 for experimental references.^bAtomic spin-orbit (SO) corrections and scalar relativistic (SR) SDPT corrections from Refs. 84 and 86 are added to ccCA-CBS-2 total energies.^cScalar relativistic correction is taken from SDPT atomization energy correction in Ref. 84 using the 6-31G(*d*) basis set.

V. SPECIFIC TEST CASES

The ccCA methods were tested on a small subset of the G2-2 and G3/99 molecules as well as C(NO₂)₃ and adamantane from the set of 600 molecules compiled by Cioslowski *et al.*⁴¹ Benchmarking of the ccCA methods on larger training sets will be published in due course, but we believe that merits and deficiencies of the ccCA methods will be evident in the following discussion.

A. Some G2-2 / G3/99 test cases

Table VIII displays the ccCA ΔH_f results for a selection of 28 systems from the G2-2 and G3/99 test sets. We have attempted to include some common organic and nonhydrocarbon species that perform with varying degrees of success when using G3 and G3B3. Some of the radical organic mol-

ecules from the G2-2 test set whose enthalpies of formation have recently been revised by Ruscic *et al.*⁸⁹ are also included.

When employing the ccCA methods with larger test cases, similar patterns as those discussed for the G2-1 test set emerge. The mean deviation for all types of molecules with the G3B3 method is very close to zero, an indicator of the success of the HLC in accounting for the variety of basis set and correlation deficiencies in the Gaussian-*n* composite methods. The ccCA-aTZ method performs best with nonhydrocarbon species, resulting in a mean deviation of +0.78 kcal mol⁻¹ for the 8 systems studied, and performs poorly with both hydrocarbons and substituted hydrocarbons resulting in a mean deviation of -5.54 kcal mol⁻¹ for the 14 organic systems. As with the systems from the G2-1 training set, ccCA-CBS methods predict ΔH_f values significantly

higher than the experimental values for nonhydrocarbons. The ccCA-CBS-1 method generally overestimates ΔH_f values for organic species, while the ccCA-CBS-2 method underestimates ΔH_f . Once spin-orbit splitting and scalar relativistic effects are included, enthalpies of formation increase thereby improving the accuracy of the ccCA-CBS-2 method for all 28 species. The mean deviation of the ccCA-CBS-2 method is $0.51 \text{ kcal mol}^{-1}$ while the absolute mean deviation is $1.16 \text{ kcal mol}^{-1}$, comparable to the absolute mean deviation of the G3B3 method ($0.99 \text{ kcal mol}^{-1}$).

The quality of ccCA-CBS-2 results for this set of hydrocarbon, substituted hydrocarbon, and organic radical molecules is nearly equivalent to the G3B3 method. On the other hand, the accuracy of the ccCA methods is worse with nonhydrocarbon systems. Modifications to the ccCA may increase the accuracy of species containing second-row atoms without significantly adding to the computational cost of the ccCA methods. First, Curtiss *et al.* showed significant geometry differences (as large as 0.03 \AA) in molecules containing second-row atoms when the DFT basis set size used in geometry optimizations was increased from 6-31G(*d*) to 6-31G(2*df*,*p*) in their formulation of the G3X variant.⁶⁷ Second, Dunning, *et al.*⁴⁵ have found the addition of extra *d* functions to the second-row correlation consistent basis sets [cc-pV(*X*+*d*)Z] to drastically improve the quality of basis set convergence and dissociation energies owing to a better description of molecular core polarization effects.

B. Linear *n*-alkanes

The theoretical enthalpies of formation for the *n*-alkanes clearly show the basis set and size dependence of the HLC, and also accentuate the efficiency of the ccCA method compared to running large basis set coupled cluster calculations. The ΔH_f values obtained with various levels of theory have been recently explored by Pollack *et al.*³⁵ using a composite method of CCSD(T)/CBS energies combined with the ZPE, core-valence effects, spin-orbit splitting, and relativistic corrections. Pollack *et al.* exceed chemical accuracy in determining enthalpies of formation for the series of *n*-alkanes from methane (CH_4) to *n*-octane (C_8H_{18}), excluding heptane, via both the method of comparing atomization energies and the use of isodesmic equations. The mean absolute deviation of their seven ΔH_f values computed via atomization energies is only $0.23 \text{ kcal mol}^{-1}$. Redfern, *et al.*⁹⁰ have also studied the *n*-alkane series up to hexadecane ($\text{C}_{16}\text{H}_{34}$) using variants of the G3 method and density functional theories. Even with the HLC, G3 and reduced-order G3 (G3[MP2/CCSD]) results showed an increasing deviation proportional to the size of the alkane system. However, most G3 methods still had computed enthalpies of formation with deviations within the range of $\pm 2 \text{ kcal mol}^{-1}$. Their average absolute deviation from experiment for the seven straight alkanes is $0.43 \text{ kcal mol}^{-1}$. By comparison, the increasing deviation when utilizing B3LYP 6-311+G(3*df*,2*p*) is quite substantial, resulting in an average absolute deviation of $5.49 \text{ kcal mol}^{-1}$. For larger hydrocarbons, calculation of enthalpies of formation from atomization energies creates a significant differential in the number of unpaired carbon-atom electrons com-

pared to paired valence electrons. With the various *Gn* implementations, this differential proportionally increases the magnitude of the HLC. Removal of the HLC is disastrous, as the error in computed ΔH_f values increases in the negative direction linearly and rapidly. The uncorrected G3B3 ΔH_f of methane has an absolute deviation of $7.3 \text{ kcal mol}^{-1}$, increasing to an error of $20.9 \text{ kcal mol}^{-1}$ for butane. In fact, this slope of deviation from experiment is much larger than that of standard B3LYP as the alkane chain size increases!

For the ccCA-aTZ and ccCA-CBS-1 methods, the signed deviation also becomes more negative as the molecular size increases. The ccCA-aTZ deviation of $\Delta H_f(\text{CH}_4)$ is $-1.8 \text{ kcal mol}^{-1}$, increasing in magnitude to a deviation of $-7.9 \text{ kcal mol}^{-1}$ for hexane. With the ccCA-CBS-1 method, this increase in deviation has a smaller slope, from $-1.0 \text{ kcal mol}^{-1}$ for methane to $-4.0 \text{ kcal mol}^{-1}$ for octane. Again, the ccCA-CBS-2 technique is a vast improvement. For these alkane chains, the predicted enthalpy of formation is too small (giving a positive signed deviation), and the slope is smaller than all other methods with the deviation increasing from $+0.1 \text{ kcal mol}^{-1}$ with methane to $+2.2 \text{ kcal mol}^{-1}$ with octane. Adding the relativistic and atomic spin-orbit corrections described in Sec. IV C and IV D will act to further improve the enthalpies of formation, and the ccCA-CBS-2 mean absolute deviation of the seven straight alkane chains is $0.21 \text{ kcal mol}^{-1}$, nearly equivalent to the composite method of Pollack *et al.*³⁵ and an improvement upon the G3 variants. Figure 3 shows the deviation of ΔH_f with various approaches.

While the composite method in use by Pollack *et al.* shows impressive accuracy, few computational research groups currently have the computational resources to perform CCSD(T)/aug-cc-pVQZ single-point energies for molecular systems as large or larger than *n*-octane. The tractability of running the CCSD(T)/aug-cc-pVQZ octane computations (run on 1400 Itanium-2 processors for 23 h to compute the triples contribution to the coupled cluster energy alone)³⁵ is questionable with mainstream technology. The most time- and disk-space consuming steps of the ccCA methods are the MP2/aug-cc-pVQZ and QCISD(T)/cc-pVTZ computations, which require significant but by no means extraordinary resources. On four SGI Origin MIPS R16000 processors, obtaining the ccCA energy of *n*-octane required nearly six days of CPU time, with the MP2/aug-cc-pVQZ step taking 45% of the CPU time, and the CCSD(T)/cc-pVTZ step taking 46% of the CPU time. On the same SGI Origin computer, the G3B3 energy of *n*-octane required 12 CPU hours. For large systems, G3B3 is likely to be an order of magnitude faster than the ccCA-CBS method. However, by including the most valuable shortcuts devised by the authors of the *Gn* methods, i.e., DFT geometries and frequencies, and perturbation theory as the reference energy, the ccCA-CBS methods should provide chemical accuracy for a wide variety of systems that possess significant molecular size.

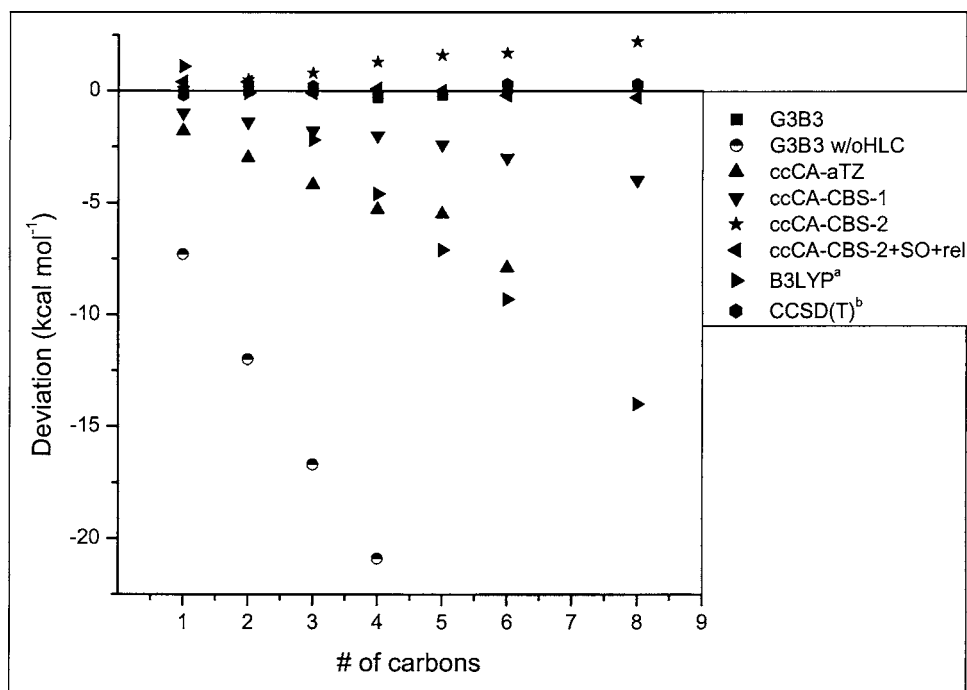


FIG. 3. A comparison of the deviation of enthalpies of formation (in kcal mol⁻¹) for *n*-alkanes using *Gn* methods, ccCA methods, DFT, and the composite coupled cluster method of Feller and Dixon [CCSD(T)].

C. Larger systems [C(NO₂)₄ and adamantane]

Lastly, we attempt to find the enthalpy of formation for two model systems where large basis set coupled cluster computations are prohibitive, tetranitromethane [C(NO₂)₄] and adamantane (C₁₀H₁₆). Tetranitromethane (TNM) can be used as a reagent for photonitration, for example, in syntheses of high-energy materials⁹¹ or the heterocyclization of alkenes.⁹² Early infrared⁹³ and electron gas diffraction studies^{94,95} showed the structure of TNM to possess *S*₄ point group symmetry. Theoretical studies on this molecule are scarce. The first appears to be a RHF/3-21G vibrational frequency computation supplementing a condensed phase study involving Raman spectra,⁹⁶ and most recently DFT and MP2 studies, by Vladimiroff using the 6-31G(*d*) basis set.⁹⁷ The ccCA geometries and harmonic frequencies obtained for this molecule should not improve on the results of the study by Vladimiroff. The enthalpy of formation for TNM at 298.15 K was reported in 1933 to be 19.7±0.5 kcal mol⁻¹.⁹⁸ As a molecule with more than ten nonhydrogen atoms and low Abelian point group symmetry (*C_s*), TNM is a good candidate to test the ccCA methods. The ccCA-CBS-1 and ccCA-CBS-2 methods predict a ΔH_f of 14.5 and 15.7 kcal mol⁻¹, respectively. When atomic spin-orbit splitting is added to atomization energies, ΔH_f becomes 16.4 and 17.6 kcal mol⁻¹. A scalar relativistic correction was obtained for C(NO₂)₄ from a frozen-core CCSD(T) wave functions using the cc-pVTZ-DK (Ref. 99) basis sets and the spin-free, one-electron Douglas-Kroll-Hess (DKH) Hamiltonian.¹⁰⁰⁻¹⁰² The Douglas-Kroll correction shifts the enthalpies of formation by +2.3 kcal mol⁻¹, giving final ccCA-CBS ΔH_f values of 18.7 and 19.9 kcal mol⁻¹, respectively. The ccCA-CBS-2 enthalpy of formation for TNM is within the experimental error bars.

In terms of the number of contracted basis functions, adamantane is the largest ccCA computation to date. The

largest MP2 computations were run on our SGI Origin 3900 with four MIPS R16000 processors using 16 Gbytes of RAM. The MP2/aug-cc-pVQZ computation had 1536 basis functions and took 51 CPU hours to complete. For the ccCA methods, the limit for molecular size involves the necessary disk space required for these large MP2 computations. For example, the MP2/aug-cc-pVQZ adamantane computation used 456 Gbytes of disk space. When employing the ccCA-CBS-2 method with spin-orbit splitting, the ΔH_f value of adamantane is determined to be -32.4 kcal mol⁻¹. The ccCA-CBS-2 result is quite close to the experimental enthalpy of formation for adamantane (-31.8 kcal mol⁻¹).¹⁰³ Relativistic effects should increase the enthalpy of formation, but even with further energy corrections, the theoretical value should be at least within 2 kcal mol⁻¹ of experiment. Compared to DFT methods, ccCA-CBS-2 should perform very well for large organic molecules. To contrast, the computed enthalpy of formation using B3LYP/6-311+G(3*d*2*f*,2*p*) energies at MP2/6-31G(*d*) geometries is off by almost 33 kcal mol⁻¹ from the experimental value.¹⁰⁴ In fact, all seven of the set of DFT functionals tested in Ref. 104, some of which are relatively new, have an error in excess of 4 kcal mol⁻¹ for the ΔH_f value of adamantane. Clearly for large molecules, DFT is not fundamentally sound for computation of theoretical ΔH_f values without some sort of parametrization. On the contrary, the ccCA-CBS-2 method can be expected to determine enthalpies of formation within 2 kcal mol⁻¹ of the experimental value, even for substantially large molecules.

VI. CONCLUSIONS

The Gaussian-*n* "high-level correction" is primarily a basis set effect, as there is a nearly uniform bias to the deviation for enthalpies of formation. Spin-orbit splitting and relativistic effects further offset these quantities in the

“wrong” direction, i.e., further from experiment. This results in a HLC that must not only be reparametrized for the various deficiencies in the one- and n -particle treatment of the electronic Schrödinger equation but also for smaller additive physical corrections. Upon increasing size of even well-behaved single-reference molecular systems, basis set deficiencies in the Gn model chemistries become exacerbated relative to the component atoms of the molecule; thus the quality of computing molecular properties that compare total energies of molecules to the energies of their component atoms will deteriorate rapidly without inclusion of a HLC.

If optimized parameters such as the HLC are avoided, the accuracy of theoretical electron affinities and enthalpies of formation will improve as the reference basis set used in the composite method is enlarged. When MP2 energies obtained with the correlation consistent one-particle basis sets are extrapolated to the CBS limit as in the ccCA-CBS-1 and ccCA-CBS-2 methods, then ionization potentials, electron affinities, and proton affinities compare satisfactorily to experiment. On the other hand, the initial accuracy of enthalpies of formation is modest, but with the ccCA-CBS-2 method, the error is biased in the favorable direction such that additive corrections improve the mean average deviation. When atomic spin-orbit and approximate scalar relativistic effects are included in the total energies, the ccCA-CBS-2 average absolute deviations are 0.81 kcal mol⁻¹ for 48 enthalpies of formation, 0.80 kcal mol⁻¹ for 38 ionization potentials, 1.09 kcal mol⁻¹ for 25 electron affinities, and 1.55 kcal mol⁻¹ for 8 proton affinities. In total for the G2-1 test set, excluding the seven enthalpies of formation for silicon-containing compounds, the ccCA-CBS-2 method with relativistic and spin-orbit splitting corrections has an average absolute deviation of 0.92 kcal mol⁻¹. For larger organic systems, the ccCA-CBS-2 method gives the results comparable and sometimes better than those obtained with G3B3.

Enthalpies of formation for two large molecules, C(NO₂)₄ with 13 heavy atoms and low point group symmetry and adamantane with 26 total atoms, are computed to be within 2 kcal mol⁻¹ of experimental estimates. While a composite approach free of empirical parameters (i.e., the HLC) is of great utility, the main drawback is the higher computational cost requirements. In terms of CPU time, the computational cost of the ccCA-CBS methods are at least an order of magnitude larger than that of the G3 methods. For the ccCA methods, the primary technological limitation of tractable molecular size is disk space. Our MP2/aug-cc-pVQZ adamantane computation required almost 500 Gbytes of disk, which is a large but not extraordinary amount. Therefore, employing the ccCA-CBS methods to compute energies of molecules substantially larger than adamantane is currently possible. Computing ccCA-CBS-2 energies for medium-sized systems is reasonable with typical computational resources.

The ccCA approach provides a “black box” means to obtain the atomic and molecular energies, resulting in near-chemical accuracy for energy-related properties of most systems studied to date. Further systematic improvement planned for the approach includes modifications of second-

row basis sets, imposing state averaging on open-shell atomic computations, improving geometry optimizations and electron correlation treatments, and employing a more systematic treatment of scalar relativistic effects. All of these modifications should systematically improve the accuracy of molecular energies, especially on molecules containing second-row atoms, with little sacrifice in computational cost. These modifications are currently being explored with the larger and more diverse G3/99 training set.

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