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Atomization energies were computed for 73 molecules, many of them chosen from the GAUSSIAN-2 and G2/97 test sets. A composite theoretical approach was adopted which incorporated estimated complete basis set binding energies based on frozen core coupled cluster theory with a quasiperturbative treatment of triple excitations and three corrections: (1) a coupled cluster core/valence correction; (2) a configuration interaction scalar relativistic correction; and (3) an atomic spin-orbital correction. A fourth correction, corresponding to more extensive correlation recovery via coupled cluster theory with an approximate treatment of quadruple excitations, was examined in a limited number of cases. For the molecules and basis sets considered in this study, failure to consider any of these contributions to the atomization energy can introduce errors on the order of 1–2 kcal/mol. Although some cancellation of error is common, it is by no means universal and cannot be relied upon for high accuracy. With the largest available basis sets (including, in some cases, up through aug-cc-pV6Z), the mean absolute deviation with respect to experiment was found to lie in the 0.7–0.8 kcal/mol range, neglecting the effects of higher order excitations. Worst case errors were 2–3 kcal/mol. Several complete basis set extrapolations were tested with regard to their effectiveness at improving agreement with experiment, but the statistical difference among the various approaches was small. © *1999 American Institute of Physics.* [S0021-9606(99)31517-8]

I. INTRODUCTION

We recently examined the accuracy of five popular electronic structure methods in reproducing experimental atomization energies (ΣD_e), electron affinities, proton affinities, ionization potentials, vibrational frequencies and geometries.[1] The methods consisted of Hartree-Fock (HF) theory, second- and fourth-order Møller-Plesset perturbation theory (MP2 and MP4), coupled cluster theory with single and double excitations (CCSD) and coupled cluster theory with a quasiperturbative treatment of triples [CCSD(T)]. In addition to the errors associated with each (method/basis set) pair, for the four energetic quantities we attempted to assess the method's intrinsic error, i.e., the deviation with respect to experiment in the limit of a complete one-particle basis set. Extrapolation to the complete basis set (CBS) limit was accomplished by fitting results obtained from the correlation consistent basis sets[2–5] with a simple exponential functional form. Although several alternative functions have been suggested,[6–10] we chose the empirically motivated exponential, given by

$$E(x)=E_{\mathrm{CBS}}+be^{-cx}, \tag{1}$$

where x is an index associated with each basis set, $x=2(DZ)$, $3(TZ)$, $4(QZ)$, etc., for describing the convergence of the total energy.[11–13] We also examined a related expression,

$$E(l_{\max})=E_{\mathrm{CBS}}+b/(l_{\max}+\tfrac{1}{2})^4, \tag{2}$$

where $l_{\max}$ is the maximum angular momentum present in the basis set.[9] For second and third row correlation consistent basis sets, $x[\mathrm{Eq.}\,(1)]=l_{\max}[\mathrm{Eq.}\,(2)]$.

Our original test suite consisted of the 220 chemical systems in the GAUSSIAN-2 (G2)[14] collection of molecules, plus N_2O. Because this collection contains anions, as well as several highly polar neutral species, our study used the diffuse function augmented family of correlation consistent basis sets. These sets are labeled aug-cc-pVxZ, where $x=D$, T, Q and 5.[15] Hardware and software limitations in effect in 1997 made it prohibitively expensive to perform geometry optimizations with the aug-cc-pVQZ basis set for the complete G2 collection. Of the 55 G2 molecules with the best experimental atomization energies, we were able to treat only 47 at the CCSD(T)/aug-cc-pVQZ level. Among the group of properties we examined, atomization energies are of particular interest, since errors in ΣD_e were noticeably larger than errors for the other five properties. Moreover, they often displayed very slow convergence with respect to improvements in the one-particle basis set.

In the present work we focus exclusively on atomization energies, using the highest level *ab initio* method that can routinely be applied to small molecules with extended basis sets. Our goal will be to refine the previous estimate of the intrinsic error in CCSD(T)-derived atomization energies by: (1) extending the quadruple zeta-based CBS extrapolations

to all 55 G2 molecules for which accurate experimental values exist, (2) including CBS results based on the even larger aug-cc-pV5Z or aug-cc-pV6Z basis sets, (3) improving our description of core/valence effects, (4) accounting for scalar relativistic corrections, and (5) correcting ΣD_e for spin-orbit effects in the atomic products. Although core/valence and relativistic corrections are small in an absolute sense, they constitute a significant fraction of the remaining error when the mean absolute deviation (ϵ_{MAD}) with respect to experiment falls into the 1–3 kcal/mol range, as it did in the previous study.[1] Statistics will also be presented for a larger group of molecules, including some with slightly bigger experimental uncertainties. While this manuscript was in preparation, the next development in the Gaussian-*x* series, GAUSSIAN-3 (G3), was reported.[16] Where appropriate, results of the present study will be contrasted to G3.

II. PROCEDURE

In the original study, energies were evaluated at the optimal geometries corresponding to each method and basis set. Most optimizations of polyatomic species were performed with a gradient convergence criterion of $1.5\times10^{-5}E_h/a_0$, corresponding to the ''tight'' criterion defined in GAUSSIAN-94.[17] However, due to the expense of frozen core CCSD(T) optimizations, for which analytical gradients were not available, a convergence criterion of $4.5\times10^{-4}E_h/a_0$ was adopted. Diatomic bond lengths were optimized using a seven-point Dunham fit. The convention of using CCSD(T) optimized geometries is continued in the present study. Optimizations with the aug-cc-pVQZ basis sets used a convergence threshold of $\sim1\times10^{-3}E_h/a_0$. Practical considerations required an even more approximate scheme with the aug-cc-pV5Z basis sets and polyatomic molecules. The procedure we followed consisted of fitting the optimal aug-cc-pVDZ, aug-cc-pVTZ and aug-cc-pVQZ internal coordinates with an exponential expression in order to obtain initial guesses for the aug-cc-pV5Z bond lengths and bond angles. With the exception of C_2H_6, this was followed by a single cycle of quadratic interpolation for each internal coordinate. Cross terms, corresponding to simultaneous displacements along two internal coordinates, were not computed. In no case did the cycle of quadratic interpolations lower the energy by more than $1\times10^{-5}E_h$. Finally, no attempt was made to optimize the geometries of polyatomic molecules with the aug-cc-pV6Z basis. Internal coordinates were simply extrapolated from the (aVTZ, aVQZ, aV5Z) sequence.

Unless otherwise noted, open shell energies were based on unrestricted Hartree-Fock (UHF) zeroth order wave functions and were performed with the GAUSSIAN-94 program.[17] Orbital symmetry and equivalence restrictions were not imposed in atomic calculations. Closed shell CCSD(T) calculations were performed with MOLPRO-97[18] and GAUSSIAN-94. CCSD(TQ) calculations were obtained from ACES II.[19] All calculations were performed on a 16 processor Silicon Graphics, Inc. PowerChallenge, a 32 processor SGI Origin 2000 or an SGI/Cray J90 at D.O.E.'s National Energy Research Supercomputing Center. The largest CCSD(T) calculation reported in this study included 734 functions. As in the previous study, results were stored and analyzed using the Environmental Molecular Sciences Laboratory (EMSL) Computational Results Database,[20] which currently contains over 30 000 entries.

At the time of the earlier study, augmented correlation consistent basis sets were not available for the alkali and alkaline earth metals. Consequently, molecules containing these elements were described with basis sets that combined augmented sets on other elements with nonaugmented sets on Li, Be, Na and Mg. For the sake of brevity, results obtained with these hybrid basis sets will be grouped under the aug-cc-pVxZ headings.

In order to accurately determine the impact of core/valence correlation on the binding energy, ΔE_{CV}, it would have been desirable to perform calculations with extra tight functions, in addition to the already present shell of diffuse functions in the aug-cc-pVxZ family of basis sets. Although core/valence correlation consistent basis sets have been described,[21,22] geometry optimizations with such basis sets would have been prohibitively expensive for polyatomic species. Even studies of diatomic molecules with such large sets are still rare.[23] A compromise approach, adopted here, was to apply a core/valence correction at geometries obtained from basis sets lacking the extra tight functions. In particular, we corrected our atomization energies by performing core/valence (CV) calculations at the optimal CCSD(T)/aug-cc-pVTZ geometries determined in the previous study. These calculations were performed with both the cc-pCVTZ and the cc-pCVQZ (or cc-pwCVQZ for third period elements) basis sets, in order to gauge the degree of convergence in ΔE_{CV}. Only the latter results will be reported. The 1*s* pairs of electrons for third period elements were treated as frozen cores.

Atomic spin-orbit and molecular/atomic scalar relativistic corrections were also appended to our nonrelativistic atomization energies and are denoted ΔE_{SO} and ΔE_{SR}, respectively. The former account for the improper description of the atomic asymptotes, since atomic energies determined by our calculations correspond to an average over the possible spin multiplets. In some cases, such as the $^2\Pi$ states of molecules like CH and OH, there is an additional molecular spin-orbit correction due to the splitting of the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ states. Spin-orbit corrections were taken from the atomic and molecular values reported by Dunning and co-workers,[6,13] which are based on the experimental values of Herzberg[24] and Moore.[25] Scalar relativistic corrections were obtained from configuration interaction wave functions including single and double excitations (CISD) using the cc-pVTZ basis set. The CISD(FC) wave function was used to evaluate the dominant one-electron Darwin and mass-velocity terms in the Breit-Paul Hamiltonian.

Our results will be compared to experimental atomization energies extrapolated to 0 K, both with and without zero point energies (ZPEs), i.e., $\Sigma D_0(0\ \mathrm{K})$ and $\Sigma D_e(0\ \mathrm{K})$, respectively. In the original G1 paper,[26] most of the atomization energies were taken from the third edition of the JANAF tables.[27] The value for CN, 176.6 kcal/mol, was taken from work by Engleman and Rouse.[28] The same experimental value was used in the G2 paper, and in several subsequent papers.[29,30] A majority of the experimental data used in this

report was taken from the NIST-JANAF tables (4th, ed.)[31] and Huber and Herberg.[32] For the remainder of the experimental atomization energies, we adopted the values[33–42] reported in the G1 and G2 papers. Zero point energies for most molecules were taken from Huber and Herzberg,[32] Grev *et al.*[43] or, for O_3, from Barbe *et al.*[44] Several of the theoretical results for silicon compounds were taken from the work of Feller and Dixon.[45]

III. COMPLETE BASIS SET ESTIMATES

Due to the importance of the one-particle basis set truncation error in electronic structure calculations, theoreticians have long sought to develop methods for minimizing its adverse impact on their predictions. An approach which began with the pioneering work of Petersson and co-workers[46–49] is to extrapolate finite basis set results to the CBS limit by exploiting the convergence in atomic pair natural orbitals. Following the introduction of the correlation consistent basis sets and the observation that the total energies obtained from these sets converged roughly as an exponential function of the basis set index, a simple three-parameter function was used to estimate the CBS limit.[11–13] Peterson *et al.*[6,50] used an alternative form, based on a combined Gaussian/exponential function,

$$E(x)=E_{\mathrm{CBS}}+be^{-(x-1)}+ce^{-(x-1)**2}, \tag{3}$$

to extrapolate the dissociation energy of second row diatomics.

Martin[7,8] reported CBS results with an empirical correction based on the number of σ, π and lone pair electrons, and also explored expansions in inverse powers of $l_{\max}$, the maximum angular momentum present in the basis set.[9] The latter was suggested by the work of Schwartz,[51] Carroll *et al.*[52] and Hill[53] who demonstrated that the second-order correlation energy of a two-electron system approached the asymptotic limit as powers of $1/l_{\max}$. Improved agreement with experiment, compared to the exponential CBS estimates, was reported for 13 total atomization energies. Martin and co-workers[9,54] have used expressions of the form

$$E(l_{\max})=E_{\mathrm{CBS}}+\frac{B}{(l_{\max}+0.5)^4}+\frac{C}{(l_{\max}+0.5)^6}, \tag{4}$$

or a simpler two-parameter expression with $C=0$. Wilson and Dunning[10] also examined expressions of the general form

$$E^{(2)}(l_{\max})=E^{(2)}_{\mathrm{CBS}}+\frac{B}{(l_{\max}+d)^m}+\frac{C}{(l_{\max}+d)^{m+1}}+\frac{D}{(l_{\max}+d)^{m+2}}, \tag{5}$$

and found them to provide improved estimates of the CBS limit for the MP2 correlation energy. The best agreement between the correlation corrections predicted by Eq. (5) and the ''exact'' MP2-R12 values of Klopper[55] were obtained with values of $m=4$, $d=1$ and $D=0$. Strictly speaking, $1/l_{\max}$ describes just the convergence in the correlation energy. When using a $1/l_{\max}$ expansion, the convergence in the Hartree-Fock energy is often treated separately. However, since the increase in correlation energy dominates the increase in the Hartree-Fock energy, describing the total energy with Eq. (4) is a reasonable approximation for large basis sets.

More recently, Halkier *et al.*[56] and Klopper and Helgaker[57] investigated a number of different extrapolation schemes by comparing them to correlation energies obtained with r_{ij}-dependent methods. Their work illustrates one of the difficulties of measuring the effectiveness of complete basis set extrapolations. Because of their inherent expense, the number of calculations performed with very large basis sets, such as sets of sextuple zeta quality, is very limited. Thus, the amount of data available for judging the accuracy of CBS extrapolations is quite limited. While r_{ij}-dependent methods can, in principle, provide more rapid convergence to the CBS limit, in practice they suffer from the need for large, nonstandard basis sets and sometimes display larger uncertainties than is desirable. For example, the r_{ij} CBS estimates for the MP2(FC) energy of N_2 differed by as much as $3mE_h$, depending on which of two approaches was used to evaluate certain two-electron integrals.[56] Even for the Ne atom, the differences were $0.0005E_h$. Halkier *et al.*[56] conclude that a two-parameter linear Schwartz extrapolation of the core/valence quintuple and sextuple results yielded excellent agreement with their r_{ij}-based CBS estimates. However, the need for such enormous basis sets would preclude application to any but the smallest molecules.

Truhlar has recently discussed basis set extrapolations.[58] Building upon a suggestion by Halkier *et al.*[56] that the extrapolation should include parameters adjusted to improve the agreement with the best estimate for the CBS limit, Truhlar proposed an extrapolation based on only the double and triple zeta correlation consistent basis sets. In his approach, Hartree-Fock and correlation energies were fit separately.

The performance of a CBS extrapolation can be judged on the basis of several criteria. Absolute accuracy is one, but chemists are typically interested in energy differences. Thus, a method possessing systematic errors might conceivably be of as much practical value as another method which exhibited slightly better absolute accuracy, but whose errors were less systematic. In order to investigate these factors, we have performed CBS extrapolations using Eqs. (1), (2) and (3), denoted CBS($aDTQ/e^{-x}$) and CBS($aDTQ/l_{\max}$) and CBS($aDTQ$/mix), respectively, when based on results from the aug-cc-pVDZ through aug-cc-pVQZ basis sets. Similarly, CBS($aTQ5/e^{-x}$) would denote an extrapolation based on the augmented triple through quintuple zeta basis sets. Whenever the number of available energies exceeds the number of parameters in the CBS functional form (three for the exponential and mixed, two for the $1/l_{\max}$ function), it is possible to determine the adjustable parameters via a least squares fit. However, in the present work we have chosen instead to always discard the smallest basis set result.

As an illustration of the type of agreement these fits provide in absolute energies, we carried out R/UCCSD(T)(FC)[59–61] calculations on the oxygen atom. The resulting total energies were extrapolated with all three methods. No correlation consistent septuple zeta has been

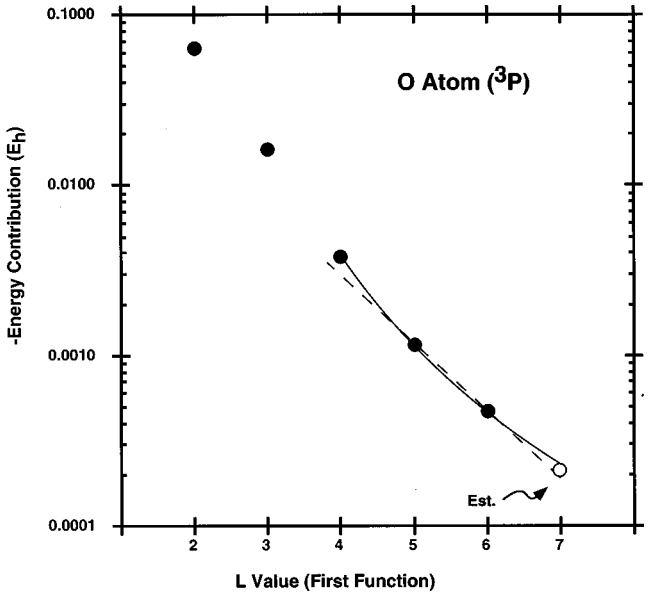

FIG. 1. The energy contribution to the frozen core R/UCCSD(T) energy of the oxygen atom obtained from the first function of each angular momentum.

published, so a new $(18s,12p,6d,5f,4g,3h,2i)\rightarrow[8s,7p,6d,5f,4g,3h,2i]$ contraction was developed. The (s,p) exponents were taken from Partridge.[62] All other exponents were constrained to follow an even-tempered progression, i.e., $\zeta(i)=\alpha\beta^i$, and were optimized in CISD(FC) calculations. Following the normal prescription for the correlation consistent basis sets, the cc-pV7Z set should contain a single set of k functions ($l=7$), but such functions were not supported by any of the integral programs at our disposal. We estimated the energy contribution of the missing k functions by averaging the results obtained from linear and exponential extrapolations of the energy contribution of the first function of each l value. As seen in Fig. 1, the convergence in the energy contributions is highly linear through $l=4$ or 5, but displays some curvature beyond that. Based on Fig. 1, we adopted a k-function correction of $-0.0002E_h$, which was added to the $-75.0028E_h$ directly computed value, to give $E^{\mathrm{pV7Z}}_{\mathrm{CCSD(T)}}=-75.0030E_h$ and a CBS limit of $-75.0039E_h$. A completely independent CBS estimate can be obtained from the aug-cc-pVxZ, $x=Q$, 5 and 6 sequence of energies. This avoids the need for estimating the energy of the missing k functions and yields a very similar energy of $-75.0038E_h$.

From the O (^3P) total energies and fitting errors shown in Table I it is clear that the exponential fits systematically underestimate the true correlation energy lowering as $l_{\max}$ increases. Contributions to the correlation energy from higher l functions fall off less rapidly than e^{-x}. At the opposite extreme, the $1/l_{\max}$ fits overestimate the CBS limit and do a particularly poor job of fitting the double zeta energy. However, the importance of the latter effect is marginal because the double zeta energies are typically not included when performing a $1/l_{\max}$ fit.

The observed errors for the $1/l_{\max}$ fits are not systematic. They both underestimate and overestimate the CCSD(T) energies, creating an uncertainty about the sign of the error in the CBS limit. In general, as the size of the basis set increases, the exponential CBS energy decreases, i.e., becomes more negative, while the $1/l_{\max}$ estimate increases. For oxygen, these two estimates initially differ by $0.0026E_h$ (based on the use of quadruple zeta energies in the fit). If energies through septuple zeta are used, the difference falls to less than $0.0006E_h$.

The mixed $e^{-x}+e^{-x**2}$ expression based on double through quadruple zeta results tends to predict energies for the largest basis set that are too low, but the errors with the triple through quintuple zeta basis sets are among the smallest in Table I (ignoring the $+0.0201E_h$ error for the cc-pVDZ entry). Furthermore, the mixed expression does not show the oscillating error sign of the $1/l_{\max}$ fits.

IV. ACCURACY CONSIDERATIONS

CCSD(T) results for the 55 molecules that served as the training set for G1[63] and G2,[14] as well as H_2 and N_2O, are

TABLE I. Comparison of predicted and calculated frozen core CCSD(T) energies for O (^3P).[a]

		e^{-x}		$e^{-x}+e^{-x**2}$		$1/l_{\max}$	
Basis set	$E_{\mathrm{CCSD(T)}}$	$DZ\rightarrow QZ$ error	$TZ\rightarrow 5Z$ error	$DZ\rightarrow QZ$ error	$TZ\rightarrow 5Z$ error	$TZ\rightarrow QZ$ error	$QZ\rightarrow 5Z$ error
cc-pVDZ	−74.9099	0.0000	−0.0011	0.0000	+0.0201	+0.0289	+0.0289
cc-pVTZ	−74.9738	0.0000	0.0000	0.0000	0.0000	0.0000	+0.0009
cc-pVQZ	−74.9934	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
cc-pV5Z	−75.0000	+0.0005	0.0000	−0.0004	0.0000	+0.0004	0.0000
cc-pV6Z	−75.0021	+0.0008	−0.0003	−0.0009	−0.0003	0.0000	−0.0005
Est. V7Z[b]	−75.0030	+0.0011	0.0000	−0.0009	−0.0003	−0.0002	−0.0008
Est. CBS[c]	−75.0039	+0.0018	+0.0007	−0.0006	+0.0001	−0.0008	−0.0014

[a]Energies and energy errors are in hartrees. The expressions used for fitting the energies are: $E(x)=E_{\mathrm{CBS}}+be^{-cx}$, $E(x)=E_{\mathrm{CBS}}+be^{-[x-1]}+ce^{-[x-1]**2}$ and $E(l_{\max})=E_{\mathrm{CBS}}+b/(l_{\max}+1/2)^4$, from left to right.

[b]Estimate based on $E_{\mathrm{CCSD(T)}}$ using an $[8s,7p,6d,5f,4g,3h,2i]$ basis set, plus a -0.0002 E_h correction for the missing k functions, as explained in the text. The optimal even-tempered parameters for the oxygen higher l functions, assuming $\zeta(i)=\alpha\beta^i$, are: $\alpha_d=0.125$, $\beta_d=2.078$; $\alpha_f=0.205$, $\beta_f=2.021$; $\alpha_g=0.359$, $\beta_g=2.119$; $\alpha_h=0.579$, $\beta_h=2.010$; $\alpha_i=0.897$, $\beta_i=2.316$.

[c]Estimate based on the average of CBS($567/e^{-x}$) and CBS($67/l_{\max}$) energies. $E[\mathrm{CBS}(567/e^{-x})]=-75.0036$ and $E[\mathrm{CBS}(67/l_{\max})]=-75.0042$ E_h. The average of the CBS($a567/e^{-x}$) and CBS($a67/l_{\max}$) energies $=-75.0038$ E_h.

presented in Table II. Before comparing our results with the experimental data, we discuss what the available theoretical evidence can tell us about the degree of convergence in our calculations. Of the four theoretically determined contributions to the atomization energy listed in Table II, the electronic components, ΣD_e, are the largest in magnitude. An indication of the sensitivity of this component to the size of the one-particle basis set can be found both in Fig. 2 and by examining the differences among the three columns of Table II that appear under the label ΣD_e. From Fig. 2, the mean absolute deviation, ϵ_{MAD}, can be seen to drop by over 1 kcal/mol when the basis set is expanded from quadruple to quintuple zeta. However, the change in CBS estimates based on the $aDZ \rightarrow aQZ$ and $aTZ \rightarrow a5Z$ sequences is noticeably smaller, as would be expected if the extrapolations were working effectively. Typical differences between the CBS($aDTQ/e^{-x}$) and CBS($aTQ5/e^{-x}$) values of ΣD_e are $\sim$0.5 kcal/mol, or less. However, in the worst case, SO_2, the difference is 7.2 kcal/mol.

The next larger basis set in the augmented correlation consistent sequence is a sextuple zeta set, denoted aug-cc-pV6Z. For second period elements, such as carbon, this basis set is a $(17s,11p,6d,5f,4g,3h,2i) \rightarrow [8s,7p,6d,5f,4g,3h,2i]$ contraction. Because of the expense of CCSD(T)/aug-cc-pV6Z calculations, there are currently very few in the literature. The EMSL Computational Results Database contains only 11 examples (H_2, N_2, F_2, HF, CO, H_2O, N_2O, HCl, Cl_2, SO_2 and CH_4). For the most problematic case, SO_2, the quintuple zeta-based CBS extrapolations differed from the sextuple zeta-based extrapolations by -4.51 (exp.) -1.88 ($1/l_{\max}$) and -1.35 (mixed) kcal/mol. Differences for the second worst case, Cl_2, were -1.26 (exp.), -0.54 ($1/l_{\max}$) and -0.31 (mixed) kcal/mol. The remaining eight cases had differences that were roughly half as large as those of Cl_2 or smaller. In several other cases the exponential CBS extrapolation produced variations between $aTQ5$ and $aQ56$ values that were twice as large as those for the other two extrapolations.

From this admittedly limited body of data, we conclude that CBS/mix and CBS/$l_{\max}$ extrapolations based on aug-cc-pV5Z total energies should generally yield atomization energies within 1 kcal/mol of the true complete basis set limit for 1st through 3rd period elements, with worse case errors running twice as large. When only quadruple zeta energies are available, an additional ± 0.5 kcal/mol uncertainty in the CBS estimate is introduced. Uncertainties in ΣD_e can be expected to grow with the size of the molecule because of the nature of total atomization energies. Even with aug-cc-pVQZ energies, any of the three CBS extrapolations we have examined are capable of improving agreement with experiment beyond what could be obtained from the raw aug-cc-pV5Z basis set values.

In order to gauge the accuracy of the cc-pCVQZ core/valence corrections to the atomization energies, we performed a parallel set of CCSD(T)/cc-pCVTZ calculations for each molecule. The average difference in the triple and quadruple zeta estimates of the core/valence correction, ΔE_{CV}, was 0.12 kcal/mol, with the largest difference being 0.59 kcal/mol. We therefore believe that the present core/valence corrections are accurate to several tenths of a kcal/mol. In some cases the present corrections differ by more than several tenths of a kcal/mol from previously published, large basis set core/valence corrections. For example, Martin[64] has reported a ΔE_{CV} for SO_2 of 0.77 kcal/mol, similar to the 0.73 kcal/mol (or 0.52 with counterpoise correction) given by Bauschlicher and Ricca.[30] Our value of $\Delta E_{\mathrm{CV}} = 1.01$ kcal/mol would seem to be too large by $\sim$0.2 kcal/mol. However, aside from small differences arising from the use of slightly different basis sets and geometries, the main reason for this discrepancy is the present use of UCCSD(T) for treating the atomic asymptotes, versus R/UCCSD(T)[59,60] in the work of Martin and Bauschlicher and Ricca. Frequently, however, the differences between UCCSD(T) and R/UCCSD(T) are much less. For example, the best R/UCCSD(T) estimate of the core/valence correction to $D_e(N_2)$, which was based on cc-pCV6Z calculations,[65] differs from the present estimate by only 0.1 kcal/mol.

Ideally, scalar relativistic corrections should be obtained from four-component calculations at some correlated level of theory. However, at present such calculations are prohibitively expensive to apply to polyatomic molecules of the size studied here. Due to the scarcity of four-component results, it is difficult to judge the accuracy of our CISD/first order perturbation theory approach. Visscher and Dyall[66] reported a Dirac-Coulomb CISD (DC-CISD) correction to the dissociation energy of F_2 of -0.9 kcal/mol, in (fortuitously) exact agreement with our -0.9 kcal/mol ($\Delta E_{\mathrm{SO}} + \Delta E_{\mathrm{SR}}$) result. Their CISD correction for Cl_2 (-0.8 kcal/mol) was also in good agreement with our -0.9 kcal/mol ($\Delta E_{\mathrm{SO}} + \Delta E_{\mathrm{SR}}$). Additional comparisons are possible for HF, -0.6 (DC-CISD)[67] vs -0.6 (present), and HCl, -1.1 (DC-CISD) vs -1.0 (present). The results were not sensitive to the level of theory, since CCSD(T) produced the same corrections as CISD to within 0.1 kcal/mol. Douglas-Kroll CCSD(T) scalar relativistic calculations predict $\Delta E_{\mathrm{SR}}(SiH_4) = -0.7$ kcal/mol,[68] whereas this work predicts -0.6 kcal/mol. Finally, four-component multireference configuration interaction (CI) predicts $\Delta E_{\mathrm{SR}}(SiH) = -0.09$ kcal/mol,[69] compared to the present -0.07 kcal/mol. Therefore, we conclude that for molecules composed of elements through the first three periods, CISD(FC)/cc-pVTZ is capable of predicting scalar relativistic corrections within several tenths of a kcal/mol of accurate, four-component or Douglas-Kroll results.

The only other widely applicable theoretical method with an accuracy comparable to CCSD(T) is complete active space (CAS), multireference configuration interaction. A substantial body of internally contracted Cl (iCAS-Cl) results are available in the literature using the same basis sets as were used in the present study. When iCAS-Cl statistics dealing with atomization energies are compiled for an identical set of molecules and basis sets, the mean absolute deviations are very similar to those found with CCSD(T). Since iCAS-Cl contains a step which grows extremely rapidly with the size of the molecule, the technique is usually limited to di- and triatomics. All of this makes it difficult to calibrate CCSD(T) without resorting to experimental data and the ambiguities associated with experimental uncertainties. Caution should be exercised so as not to reach conclusions that are

TABLE II. CCSD(T) atomization energies for a selected subset of the G2 molecules.[a]

Molecule	ΣD_e Exponential CBS est. (*aDTQ*)	(*aTQ5*)	(*aQ56*)	$1/2\Sigma\omega_i$	ZPE basis[b]	Expt. ZPE[c]	ΔE_{CV}[d]	ΔE_{SP}[e]	Expt. atomic ΔE_{SO}[f]	Expt. ΣD_0 (0 K)	Error w.r.t. Expt. exp.	Mixed	l_{max}
LiH($^1\Sigma^+$)	57.5	57.7		2.0	aVQZ	2.0	0.3	0.0	0.0	**56.00±0.01** WS 55.67±0.01 JANAF	0.0	0.0	0.0
BeH($^2\Sigma^+$)	50.1	50.1		2.9	aVQZ	2.9	0.4	0.0	0.0	**46.90±0.01** HH	0.7	0.7	0.7
CH($^2\Pi$)	83.3	83.8		4.1	aVQZ	4.0	0.2	0.0	0.0	**79.90±0.02** HH 80±4 JANAF	0.0	0.0	0.1
$CH_2(^3B_1)$	189.4	189.7		10.9	aVQZ	10.6	0.8	−0.2	−0.1	**179.6** LZ 181±1 JANAF	−0.3	−0.2	−0.1
$CH_2(^1A_1)$	180.0	180.4		10.5	aVQZ	10.3	0.4	−0.1	−0.1	**170.6** MBSESS	−0.5	−0.4	−0.2
$CH_3(^2A_2'')$	305.9	306.0		18.6	aVTZ		1.0	0.0	−0.1	**289.3±0.2** JANAF	−1.0	−0.5	−0.3
$CH_4(^1A_1)$	418.0	418.7	418.9	27.8	aVDZ	27.6	1.3	−0.2	−0.1	**392.5±0.1** JANAF	−0.4	−0.4	−0.3
NH($^3\Sigma^-$)	82.5	82.6		4.7	aVQZ	4.6	0.2	−0.1	0.0	**79.0±0.4** GGB 74.2±4 JANAF	−1.0	−0.9	−0.8
$NH_2(^2B_1)$	181.4	181.6		12.0	aVQZ		0.4	−0.2	0.0	**170.0±0.3** GGB	−1.0	−0.8	−0.6
$NH_3(^1A_1)$	296.5	296.6		21.4	aVDZ	21.3	0.7	−0.3	0.0	**276.7±0.1** JANAF	−1.1	−0.8	−0.5
OH($^2\Pi$)	106.9	106.7		5.3	aVQZ	5.3	0.2	−0.1	0.0	**101.4±0.3** JANAF	0.1	0.3	0.3
$H_2O(^1A_1)$	232.6	232.1	232.5	13.5	aVQZ	13.3	0.5	−0.3	−0.2	**219.35±0.01** JANAF	−0.4	−0.6	−0.4
HF($^1\Sigma^+$)	141.7	141.1	141.4	5.9	aVQZ	5.9	0.2	−0.2	−0.4	**135.2±0.2** JANAF	−0.1	−0.1	−0.1
$SiH_2(^1A_1)$	153.4	153.9[g]	153.6[g]	7.3	aVTZ		0.0	−0.2	−0.4	**144.4±0.7** BGCR	1.3	1.3	1.5
$SiH_2(^3B_1)$	133.2	133.5[g]		7.5	aVDZ		−0.5	−0.4	−0.4	**123.4±0.7** BGCR	1.3	1.1	1.2
$SiH_3(^2A_2'')$	227.5	228.7[g]		13.2	aVDZ		−0.2	−0.4	−0.4	**213.8±1.2** DW	0.5	0.2	0.5
$SiH_4(^1A_1)$	324.4	324.3[g]		19.4	aVDZ		−0.2	−0.6	−0.4	**302.6±0.5** JANAF 301.6±0.5 GG 302 LBLHLM	1.1	1.6	2.0
$PH_2(^2B_1)$	153.5	154.0		8.4	aVDZ		0.3	−0.2	0.0	**144.7±0.6** BCGGHP 152±23 JANAF	1.0	0.9	1.2
$PH_3(^1A_1)$	241.0	241.6		15.0	aVDZ		0.4	−0.4	0.0	**228.6±0.4** JANAF 227.4 JANAF (old)	−2.0	−2.0	−1.6
$H_2S(^1A_1)$	182.9	183.7		9.5	aVQZ	9.4	0.4	−0.3	−0.6	**173.1±0.2** JANAF	0.6	0.5	0.7
HCl($^1\Sigma^+$)	107.1	107.4	107.0	4.3	aVQZ	4.2	0.3	−0.2	−0.8	**102.24±0.5** JANAF	−0.2	0.0	0.1
$Li_2(^1\Sigma_g^+)$	24.1	24.1		0.5	aVQZ	0.5	0.2	0.0	0.0	**23.9±0.7** JANAF	−0.1	0.0	0.0
LiF($^1\Sigma^+$)	139.1	137.7		1.3	aVQZ	1.3	0.9	−0.2	−0.4	**137.6±2.0** JANAF	−0.9	−0.6	−0.5
$C_2H_2(^1\Sigma_g^+)$	401.5	402.1		15.7	aVDZ	16.5	2.4	−0.3	−0.2	**386.9±0.2** JANAF 388.9 WEPSHBCN	1.4	1.6	2.0
$C_2H_4(^1A_g')$	560.3	560.7		31.7	aVDZ	31.5	2.3	−0.3	−0.2	**531.9±0.1** JANAF	−1.1	−0.8	−0.3
$C_2H_6(^1A_{1g})$	708.8	709.8		46.5	aVDZ	46.4	2.4	−0.4	−0.2	**666.3** WEPSHBCN	−1.2	1.9	−0.4
CN($^2\Sigma^+$)	177.7	177.3		3.0	aVQZ	2.9	1.2	0.0	−0.1	**178.1±2.4** JANAF 178.5±0.5 HBH 176.6±1.1 ER 178.9±0.2 HH	−2.7	−2.5	−2.2
HCN($^1\Sigma^+$)	310.4	310.4		9.8	aVDZ	10.0	1.7	−0.2	−0.1	**301.7±2** JANAF	0.5	0.8	1.3
CO($^1\Sigma^+$)	258.6	257.8	258.2	3.1	aVQZ	3.1	0.9	−0.2	−0.3	**256.2±0.2** JANAF 255.8 HH	−0.7	−0.7	−0.5
HCO($^2A'$)	277.6	277.1		8.1	aVTZ	8.2	1.2	−0.3	−0.3	**270.3±2** JANAF	−0.7	−0.4	−0.2
$H_2CO(^1A_1)$	373.2	372.2		16.6	aVDZ	16.5	1.3	−0.4	−0.3	**357.2±0.1** BCCHKTW 359.0±1.5 JANAF	−1.0	−0.6	−0.3
$H_3COH(^1A')$	510.9			32.0	aVDZ		1.5	−0.5	−0.3	**480.8** WEPSHBCN 481.1 LBLHLM	−1.2	0.0	0.3
$N_2(^1\Sigma_g^+)$	226.5	226.1	226.1	3.4	aVQZ	3.4	1.0	−0.1	0.0	**225.1±0.4** JANAF	−1.5	−1.1	−0.8
$N_2H_4(^1A)$	435.8	435.7		33.2	aVDZ		1.3	−0.2	0.0	**405.4** JANAF	−1.8	−1.4	−0.8
NO($^2\Pi$)	151.5	150.7		2.8	aVQZ	2.7	0.6	−0.1	−0.2	**150.06±0.04** JANAF 149.8 HH	−1.9	−1.5	−1.3
$O_2(^3\Sigma g^-)$	119.8	119.9		2.3	aVQZ	2.3	0.3	−0.2	−0.4	**117.96±0.02** JANAF	−0.7	−1.5	−1.6
$H_2O_2(^1A)$	267.9	267.5		16.4	aVDZ		0.5	−0.5	−0.4	**252.3** JANAF	−1.6	−1.1	−1.0
$F_2(^1\Sigma_g^+)$	37.5	38.2	38.3	1.3	aVQZ	1.3	−0.1	−0.1	−0.8	**36.9±0.1** JANAF	−0.9	−0.9	−0.8
$CO_2(^1\Sigma_g^+)$	387.9	386.7		7.2	aVTZ	7.2	1.8	−0.6	−0.5	**381.93±0.01** JANAF	−1.7	−1.2	−0.7
$Na_2(^1\Sigma_g^+)$	16.6	16.7		0.2	aVQZ	0.2	0.3	0.0	0.0	**16.8±0.3** JANAF *16.6* HH	0.0	0.1	−0.4
$Si_2(^3\Sigma_g^-)$	75.1	76.2		0.7	aVQZ	0.7	0.5	−0.1	−0.9	**74.0** HH 73±3 JANAF	1.9	1.3	1.6
$P_2(^1\Sigma_g^+)$	114.8	115.7		1.1	aVQZ	1.1	0.8	0.2	0.0	**116.1±0.5** JANAF	−0.5	−0.9	−0.2
$S_2(^3\Sigma_g^-)$	102.1	103.8		1.0	aVQZ	1.0	0.6	−0.3	−1.1	**100.66±0.07** JANAF	1.3	0.8	0.9
$Cl_2(^1\Sigma_g^+)$	58.2	60.1	58.8	0.8	aVQZ	0.8	0.2	+0.7	−1.7	**57.18±0.01** JANAF	0.0	0.4	0.7
NaCl($^1\Sigma^+$)	100.0	99.3		0.5	aVQZ	0.5	−1.2	−0.3	−0.8	**97.3±0.5** JANAF 97.5 HH	−0.8	−0.6	−0.7

TABLE II. (*Continued.*)

Molecule	ΣD_e Exponential CBS est. (*aDTQ*)	(*aTQ5*)	(*aQ56*)	$1/2\Sigma\omega_i$	ZPE basis[b]	Expt. ZPE[c]	ΔE_{CV}[d]	ΔE_{SP}[e]	Expt. atomic ΔE_{SO}[f]	Expt. ΣD_0 (0 K)	Error w.r.t. Expt. exp.	Mixed	l_{max}
$SiO(^1\Sigma^+)$	190.5	192.0		1.8	aVQZ	1.8	0.9	−0.2	−0.6	**189.9±2** JANAF 190.5 HH	0.4	−0.1	0.4
$CS(^1\Sigma^+)$	170.2	170.9		1.8	aVQZ	1.8	0.9	−0.1	−0.6	**169.4±6** JANAF 169.6 HH	−0.1	−0.4	0.0
$SO(^3\Sigma^-)$	124.2	125.7		1.6	aVQZ	1.6	0.6	−0.3	−0.8	**123.4±0.3** JANAF	0.2	0.0	0.4
$ClO(^2\Pi)$	63.3	64.8		1.2	aVQZ	1.2	0.3	−0.2	−1.1	**63.42±0.02** JANAF	−0.8	−1.2	−0.9
$ClF(^1\Sigma^+)$	62.1	62.6		1.1	aVTZ	1.1	0.2	−0.2	−1.2	**60.4** HH 59.1±0.1 JANAF	−0.1	−0.3	0.0
$Si_2H_6(^1A_{1g})$	535.0[g]			30.5	aVDZ		0.0	−1.1	−0.9	**500.1** LBLHLM	2.4	3.5	3.6
$CH_3Cl(^1A_1)$	393.6	394.6		23.5	aVDZ	23.5	1.2	−0.5	−0.9	**371.0** GGBVMKY	−0.1	−0.1	0.3
$H_3CSH(^1A')$	472.3			28.6	aVDZ		1.5	−0.6	−0.6	**445.1** LBLHLM	−1.1	0.1	0.2
$HOCl(^1A')$	165.2	165.6		8.3	aVTZ		0.4	−0.4	−1.1	**156.3±0.5** JANAF	−0.1	−0.1	0.2
$SO_2(^1A_1)$	254.9	262.1	257.6	3.9	aVDZ	4.4[h]	1.0	−0.9	−1.0	**254.0±0.2** JANAF	−1.2	−0.3	0.4
$N_2O(^1\Sigma)$	268.1	267.0	267.9	6.7	aVDZ	6.8	1.4	−0.5	−0.2	**263.6±0.1** JANAF	−1.7	−1.7	−1.3
$H_2(^1\Sigma_g^+)$	109.3	109.4	109.5	6.3	aVQZ	6.2	0.0	0.0	0.0	**103.2767** HH	−0.1	−0.1	−0.1

[a]Results are given in kcal/mol. The atomic asymptotes were described with the UCCSD(T) method. Errors for the exponential, mixed and $1/l_{max}$ CBS atomization energies (ΣD_0), which appear in the three right-most columns, were computed as the difference between the theoretical value, defined as: E[CCSD(T)(FC)/CBS]−1/2$\Sigma\nu_i$+CV+scalar relativistic+atomic/molecular S.O. and the bolded experimental value. The highest level basis set extrapolations were used. Experimental values in bold were used to compute the statistics quoted in the text. Values in italics were used in the original G1 and G2 papers, Refs. 26 and 14. If the currently listed values differed from the values listed in the G1 and G2 papers by ≤0.2 kcal/mol, the differences were attributed to roundoff errors and were not considered significant. The exponential CBS estimates in columns 2–4 were based on aug-cc-pVDZ→aug-cc-pVQZ basis sets (denoted *aDTQ*), etc. Experimental values are denoted as follows: WS=Way and Stwalley, Ref. 33; HH=Huber and Herzberg, Ref. 32; JANAF=Chase, Ref. 31; HBH=Huang *et al.*, Ref. 34; LZ=Lengel and Zare, Ref. 35; MBSESS=McKellar *et al.*, Ref. 36; BCCHKTW=Baulch *et al.*, Ref. 37; GGB=Gibson *et al.*, Ref. 38; LBLHLM=Lias *et al.*, Ref. 40; GG=Gunn and Green, Ref. 41; WEPSHBCN=Wagman *et al.*, Ref. 39; GGBVMKY=Glushko *et al.*, Ref. 42, BCGGHP=Berkowitz *et al.*, Ref. 72, BGCR=Berkowitz *et al.*, Ref. 80, DW=Doncaster and Walsch, Ref. 81.

[b]Basis set used for evaluating the harmonic zero point vibrational energy: aVDZ=aug-cc-pVDZ, aVTZ=aug-cc-pVTZ, etc.

[c]The experimental, anharmonic zero point energies are taken from the following sources: (1) diatomics were taken from Huber and Herberg, Ref. 32, and computed as $1/2\omega_e - 1/4\omega_e\chi_e$. (2) Polyatomics were taken from Grev *et al.*, Ref. 43.

[d]Core/valence corrections were obtained with the cc-pCVQZ or cc-pwCVQZ (for second row elements) basis sets at the optimized CCSD(T)/aug-cc-pVTZ geometries. A positive sign indicates that CV effects increase the stability of the molecule relative to the atomic asymptotes.

[e]The scalar relativistic correction is based on CISD(FC)/cc-pVTZ calculations of the one-electron Darwin and mass-velocity terms evaluated at the CCSD(T)(FC)/aug-cc-pVTZ geometry.

[f]Correction due to the incorrect treatment of the atomic asymptotes as an average of spin multiplets. For diatomics with a nonzero molecular spin-orbit contribution, e.g., $OH(^2\Pi)$, the sum of the atomic and molecular contributions is included here.

[g]Feller and Dixon, Ref. 45.

[h]Best anharmonic ZPE=4.378 kcal/mol quoted by J. Martin, Ref. 64.

broader than the data warrants. When ϵ_{MAD} reaches 1 kcal/mol or less, many effects which would otherwise have been inconsequential suddenly become significant. For example, even the method for treating the open shell atomic fragments can affect ΣD_e by up to 0.9 kcal/mol for some of the molecules included in this study.

In an attempt to check the convergence of our results with respect to the correlation treatment, we performed CCSD(TQ) calculations on HF N_2 and CO. At the estimated CBS limit, the effect of the quadruples was to reduce D_e(HF) by −0.32 kcal/mol. The memory requirements for CCSD(TQ) are such that we were prevented from using the aug-cc-pVQZ basis set with N_2 and CO, as such calculations would have required in excess of 3 GB of memory. By removing the shell of diffuse functions we were ultimately able to carry out VDZ, VTZ and VQZ CCSD(TQ) calculations. Comparison of the aug-cc-pVTZ and cc-pVTZ results showed that the effect of the diffuse functions was a modest 0.03 kcal/mol. At the CBS limit D_e decreased by −0.80 (N_2) and −1.43 (CO) kcal/mol. In each of these three cases the devia-

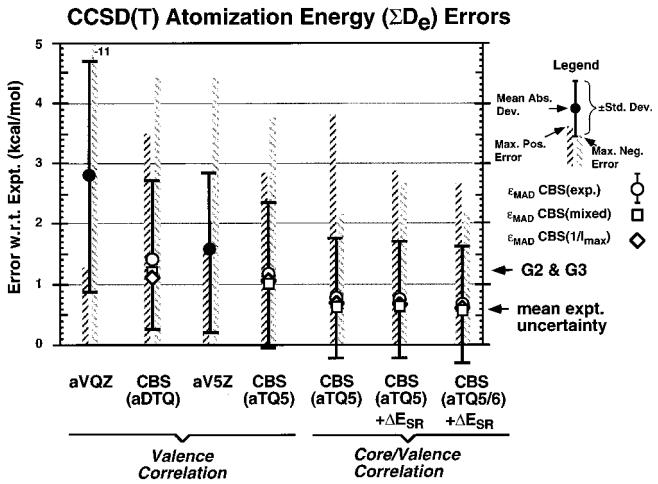

FIG. 2. ΣD_e errors with respect to experiment for the 55 G2 molecules, plus N_2O and H_2. The columns labeled as "$+\Delta E_{SR}$" have been corrected for scalar relativistic effects. "CBS(*aTQ*5/6)" refers to a combination of results obtained from extrapolations based on aug-cc-pV6Z energies (whenever available) and aug-cc-pV5Z energies in all other cases.

tion with respect to experiment was increased. It is difficult to know whether CCSD(TQ) accurately reflects the contribution of higher order excitation because of the lack of sufficiently accurate independent measurements. Results from iCAS-Cl calculations were less clear-cut. Expanded reference space calculations showed a reduction of D_e, as did the application of the multireference analog of the Davidson correction, denoted as iCAS-Cl+Q.[70] In fact, in all three cases the $+Q$ correction predicted a reduction in D_e, in qualitative agreement with CCSD(TQ), although the numerical values were sometimes off by 100%.

V. ATOMIZATION ENERGIES

In Table II we compared experimental values for ΣD_0 with the three CBS estimates. In order to differentiate the errors arising from ZPEs and purely electronic atomization energies, we first focus on ΣD_e. Our standard for comparison will be the ''experimental'' values, obtained from ΣD_0 simply by accounting for molecular zero point effects. The theoretical atomization energies will include the effects of an atomic spin-orbit correction. Where experimental ZPEs are not available, the best CCSD(T) values were used. Figure 2 shows the trends in ϵ_{MAD}, ϵ_{MAX} and ϵ_{MIN} for ΣD_e as the level of theory increases from left to right. For this set of 57 molecules, CCSD(T)(FC) appears capable of predicting atomization energies with an accuracy of roughly 1 kcal/mol at the complete basis set limit. In each case where sextuple zeta extrapolations were available, the error was decreased, so the true CBS limit for ϵ_{MAD} may fall slightly below 1 kcal/mol. Within the framework of frozen core calculations, the mixed CBS extrapolation showed the closest agreement with experiment, but the entire spread in ϵ_{MAD} among the three extrapolations was only 0.13 kcal/mol. Maximum errors exceeded 3 kcal/mol.

When core/valence corrections are included, ϵ_{MAD} for the 57 cases depicted in Fig. 2 drops into the 0.7–0.8 kcal/mol range. Relativistic corrections produce no overall change in ϵ_{MAD}, but did reduce the maximum errors. The reason for the lack of change in ϵ_{MAD} was that the experimental values were already underestimated for roughly half of the molecules and the relativistic correction almost always further reduced the theoretical value. For some molecules, especially those involving silicon, ΔE_{SR} can exceed 1 kcal/mol. For SiF_4, a molecule in the so-called ''G2/97'' test set,[71,72] $\Delta E_{\mathrm{SR}} = 2.4$ kcal/mol,[45] dramatically improving agreement with experiment.

Across all 57 molecules listed in Table II, the mean absolute deviations in ΣD_e for the three CBS extrapolations, including all energy corrections previously discussed, were 0.87 (exponential), 0.69 (mixed) and 0.72 kcal/mol ($1/l_{\mathrm{max}}$). These deviations were based on extrapolations utilizing aug-cc-pV5Z energies whenever available, and aug-cc-pVQZ results in all other cases. If the ten aug-cc-pV6Z results are used, ϵ_{MAD} decreases by 0.09 (exponential), 0.02 (mixed) and 0.05 kcal/mol ($1/l_{\mathrm{max}}$). Given the uncertainties in the experimental values and the remaining uncertainties in each of the components to the energy, this spread in ϵ_{MAD} is not felt to be statistically significant. Using R/UCCSD(T) for the atoms would result in a small increase in $\epsilon_{\mathrm{MAD}}(1/l_{\mathrm{max}})$ because more of the closed shell molecules' atomization energies already overshoot experiment, compared to the other two extrapolations. Conversely, ϵ_{MAD} for the exponential and mixed extrapolations will slightly decrease. The signed average deviations were -0.26 (exponential), -0.27 (mixed) and 0.04 kcal/mol ($1/l_{\mathrm{max}}$).

In view of the magnitude of the one-particle, *n*-particle, core/valence, scalar relativistic and atomic spin-orbital contributions to ΣD_e for the G2 molecules, it is not surprising that G2 theory sometimes yields significant deviations from experiment, e.g., $\Delta E_{\mathrm{error}} = -5.5$ kcal/mol for CF_4, $+7.1$ kcal/mol for SiF_4 and -3.9 for C_6H_6. Because G2 theory was formulated without explicit consideration of three of the five effects, the job of accounting for them falls to the so-called ''higher level correction.'' By explicitly including core/valence and atomic spin-orbital corrections, as well as doubling the number of fitting parameters to four, the prospects for achieving improved accuracy from G3 theory over a wider range of chemical systems appears better. However, as noted in our earlier paper[1] on the G2 molecules, the ZPEs which are common to G2 and G3 can be in error by more than 1 kcal/mol. Likewise, while scalar relativistic effects are sometimes unimportant for second period elements, they can easily contribute more than 1 kcal/mol to the atomization energy of molecules containing third period elements. Even molecules formed from second period elements can sometimes show a significant scalar relativistic effect, e.g., $\Delta E_{\mathrm{SR}}(CF_4) = 1.5$ kcal/mol. We note that while G3 reduces the mean absolute deviation for the heat of formation of the G2/97 test set of 148 molecules (from 1.56 to 0.94 kcal/mol), for the 57 molecules listed in Table II, $\epsilon_{\mathrm{MAD}}(\Sigma D_e)$ remains basically unchanged, 1.32 (G2) vs 1.30 (G3) kcal/mol. Similarly, the maximum negative deviation with respect to experiment remains close to -5 kcal/mol and the maximum positive deviation has grown under G3 from 2.4 to 4.0 kcal/mol.

Some of the additional molecules in the G2/97 set are also included in the EMSL Computational Results Database. Table III lists these, as well as others that do not appear in the G2/97 set. All are believed to possess reliable experimental atomization energies.[73–83] Results for CF, CF_2 and CH_2F_2 were taken, in part, from the work of Dixon and Feller.[84,85] Results for SiF_4 are from Feller and Dixon.[85]

The older JANAF heat of formation of boron (132.6 ± 2.9 kcal/mol at 0 K) has been criticized as being too small. Therefore, the present atomization energies for boron-containing molecules in Table III were based on the newer ΔH_f^0 of 136.2 ± 0.2 kcal/mol.[86–88] This is the same value used in other high-level theoretical work on simple boron compounds,[89] but differs slightly from the value of 136.0 ± 0.4 kcal/mol recommended by Martin and Taylor.[90]

Agreement with experiment for the expanded list of molecules is generally good, with the exception of O_3. As seen in Table III, the CBS($aTQ5/e^{-x}$) atomization energy, 142.3 kcal/mol, including core/valence, scalar relativistic and atomic spin-orbital corrections, is 4 kcal/mol less than the experimental value listed in the most recent JANAF tables. The mixed and $1/l_{\mathrm{max}}$ extrapolations predict a value closer to 143.4 kcal/mol larger, only 0.5 kcal/mol larger. Overall, the

TABLE III. Results for additional molecules.

Molecule	G2/97[a]	ΣD_e[b]	Extrap. basis[c]	Expt. ΣD_e[d]	Expt. ref.[e]
$C_2(^1\Sigma_g^+)$		145.6	aV5Z	147.8±0.5	UBJ
				146±3	HH
				144.4±0.9	JANAF
$O_3(^1A_1)$	√	142.3	aV5Z	146.4±0.4	JANAF
$SiH(^2\Pi)$		73.7	aV5Z	71.6±0.7	BGCR
$SiF_4(^1A_1)$	√	573.5[f]	aV5Z	572.9±0.1	Johnson
				572.6±0.2	JANAF
$HS(^2\Pi)$	√	88.2	aV5Z	88.5±1.1	JANAF
				87.3±0.7	CBL
$CF(^2\Pi)$		131.3	aV5Z	132.7	HH
				130±2	JANAF
$CF_2(^1A_1)$		256.2	aV5Z	254.9±1.5	JANAF
$CF4(^1A_1)$	√	476.0[g]	aVQZ	475.9±0.3	JANAF
$AlH(^1\Sigma^+)$		74.1	aV5Z	73.1±0.2	BN
				70.2±5	JANAF
				<70.6	HH
$BH(^1\Sigma^+)$		84.8	aV5Z	85.0±0.6	JGP[h]
				82±2	JANAF[h]
$BF(^1\Sigma^+)$		181.2	aV5Z	182.1±0.2	HH
				183±3	JANAF[h]
$BF_3(^1A_1')$	√	467.1	aV5Z	470.6±0.5	CODATA[h]
				470.1±0.5	JANAF[h]
$CH_2Cl_2(^1A_1)$	√	368.4	aVQZ	369.9±0.3	JANAF
$PO(^2\Pi)$		143.2	aV5Z	143.6	BKH
				142±3	JANAF
$HNO(^1A')$		204.0	aV5Z	205.5	Dixon
				207.2	JANAF
$NO_2(^2A_1)$	√	226.3	aVQZ	227.3±0.2	JANAF

[a]Contained in the G2/97 test set.
[b]CCSD(T)-based, exponential CBS atomization energy (kcal/mol), including core/valence, scalar relativistic and corrected for atomic (and possible molecular) spin-orbit effects.
[c]Largest basis set used in the extrapolation.
[d]ZPE based on experimental value or CCSD(T) harmonic frequencies, with the exception of BF_3. The ZPE for BF_3 was taken from the work of Martin and Taylor, Ref. 86, who combined experimental fundamentals and theoretical anharmonicities to obtain ZPE=7.83 kcal/mol.
[e]Experimental values (without correcting for atomic S.O. effects) are denoted as follows: UBJ=Urdahl *et al.*, Ref. 77; JANAF=Chase, Ref. 31; HH=Huber and Herzberg, Ref. 32; BGCR=Berkowitz *et al.*, Ref. 73; CBL=Continetti *et al.*, Ref. 74; BN=Baltayan and Nedelec, Ref. 75; JGP=Johns *et al.*, Ref. 76; CODATA=Cox *et al.*, Ref. 79; BKH=R. N. Dixon, Ref. 78 and Butler *et al.*, Ref. 80; Johnson=G. K. Johnson, Ref. 83.
[f]Dixon and Feller, Ref. 45.
[g]Feller and Dixon, Ref. 85.
[h]Based on $\Delta H_f^0(B)=136.2\pm0.2$ kcal/mol, taken from work by Ochterski *et al.*, Ref. 85; Ruscic *et al.*, Ref. 86 and Storms and Mueller, Ref. 87.

mean absolute deviations with respect to experiment show about a 0.1 kcal/mol increase relative to the smaller 57 molecule set.

VI. SPECIAL CASES

CN, SO_2 and NaCl are worthy of special consideration. For CN the deviation with respect to experiment was unusually large, while SO_2 exhibited extremely slow convergence with respect to the normal correlation consistent basis set progression. NaCl displays an anomolously large core/valence correction that decreases the binding energy, in contrast to the majority of cases where D_e increases.

Table II lists four experimental values for $D_0(\mathrm{CN})$, only one of which lies within 2 kcal/mol of our best UCCSD(T) theoretical estimate at 175.4 kcal/mol. Pradhan *et al.*[91] recently reported an aug-cc-pV5Z iCAS-CI(FC) value of D_e =179.0 kcal/mol (178.3 kcal/mol with the Davidson correction).[70] Our CCSD(T)/aV5Z value is 1.6 kcal/mol smaller. Pradhan *et al.*'s preferred core/valence correction, +1.18 kcal/mol, is almost identical to our +1.17 kcal/mol, although the basis sets and methods differed. We believe that the primary difference in the predicted values of D_e is due to our use of UHF orbitals, since the UHF wave function displays a large amount of spin contamination ($S^2=1.17$ vs 0.75 for a pure doublet). By treating this open shell system with the R/UCCSD(T) method, we find that D_e increases by 1.4 kcal/mol, to 178.1 kcal/mol. A secondary contribution to the difference between the CI and UCCSD(T) binding energies is the amount of multiconfigurational nature in CN. Besides the Hartree-Fock configuration ($c_{\mathrm{HF}}=0.92$), the CI wave function, expressed in terms of natural orbitals, contains four expansion coefficients with magnitudes $\geqslant 0.1$.

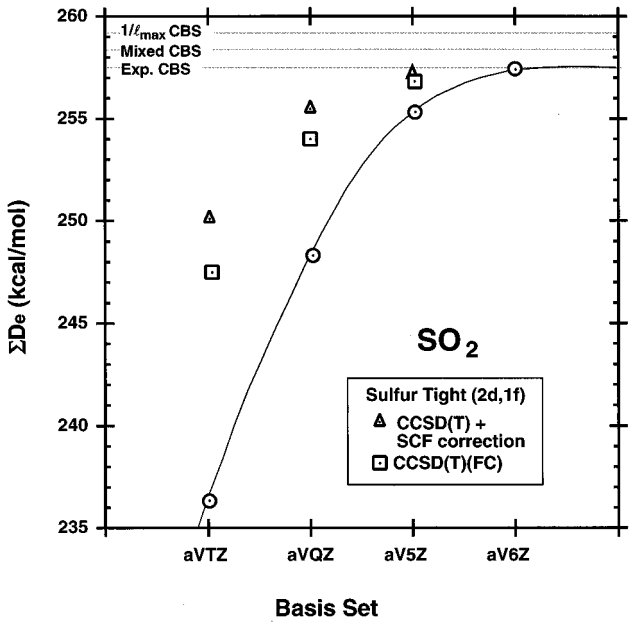

FIG. 3. Convergence of the CCSD(T)(FC) SO_2 atomization energy with respect to the size of the basis set. Triangles represent the binding energy obtained by adding a correction due to tight functions computed at the SCF level.

Very little change is observed in the CBS binding energies as the basis set is increased from quadruple to quintuple zeta, suggesting that very little of the error arises from errors in the one-particle basis set completeness.

SO_2 has been the subject of two recent high-level studies. Work by Martin[64] has emphasized the importance of tight (i.e., large exponent) d and f polarization functions on sulfur. By adding a $(2d,1f)$ set of tight functions to the aug-cc-pV5Z basis set, ΣD_e is increased by 1.4 kcal/mol. Exponents for the additional Gaussians are considerably larger than those found in either the cc-V5Z or cc-pV6Z basis sets, $\zeta_d = 20.0188$, 8.0075 (Martin) vs $\zeta_{d(\max)} = 5.0755$ (cc-pV6Z); $\zeta_f = 2.70$ (Martin) vs $\zeta_{f(\max)} = 1.3222$ (cc-pV6Z). Martin's best CBS estimate, including a 0.77 kcal/mol core/valence correction, was $\Sigma D_e = 259.4$ kcal/mol. Bauschlicher and Ricca[30] reported a similar CBS estimate ($\Sigma D_e = 260.5$ kcal/mol), but they also accounted for scalar relativistic (-0.8 kcal/mol) and basis set superposition effects, to arrive at a final ''best estimate'' for ΣD_e of 258.7 kcal/mol. Both Martin[64] and Bauschlicher and co-workers[30,92] obtained their best raw binding energies by adding tight functions to quintuple zeta level basis sets.

In Fig. 3 the impact of additional tight functions on the atomization energy of SO_2 can be viewed from the perspective of the entire aVTZ→aV6Z portion of the convergence plot. As noted by Martin,[64] the majority of the effect is evident at the Hartree-Fock level, in accord with much earlier work by Magnusson and Schaefer,[93] who pointed out the importance of d functions to the description of SO_2. Depending upon which CBS estimate is adopted as the reference point, the tight $(2d,1f)$ set of functions picked up somewhere between 50% and 99% of the difference between the aug-cc-pV5Z value and the CBS limit. The present CBS/aQ56 ΣD_e extrapolations, adjusted for core/valence effects, fall into the 258.5–259.5 kcal/mol range, in good agreement with the previously published theoretical estimates and the experimentally derived value. Atomization energies for SO_2 that are based on R/UCCSDT(T) atomic energies, such as those of Martin and Bauschlicher and co-workers, will be ~0.3 kcal/mol larger than values based on UCCSD(T) atoms.

The large difference between the raw CCSD(T)/aug-cc-pVQZ value of ΣD_e and the CBS values should be interpreted as a warning that extrapolations based on double through quadruple zeta energies might be less reliable than normal. As with any *ad hoc* numerical procedure, complete basis set extrapolations should be applied with care.

Of the additional molecules given in Table III, the result for ozone exhibits the largest error with respect to the JANAF value (142.3 vs 146.4 ± 0.4 kcal/mol). Some of this error was found to arise from the exponential CBS estimate, since extrapolations based on either the mixed or $1/l_{\max}$ functions yielded a value for ΣD_e that was ~0.5 kcal/mol larger. Another contribution to the error arose from the use of UHF wave functions for the atoms. Comparison of the UCCSD(T) and RCCSD(T) total energies for the oxygen atom revealed that the spin unrestricted formalism resulted in an increase in ΣD_e of -0.81 kcal/mol. While the sum of these two effects totals 1.3 kcal/mol, the theoretical value is still smaller than the experimental value by 2.8 kcal/mol. If the atomization energy is broken down into two steps, $O_3 \rightarrow O_2 + O$ and $O_2 \rightarrow 2O$, we see that about 1.6 kcal/mol of this error is due to the underestimation of the first dissociation energy, while the remaining 1.2 kcal/mol arises from the O_2 dissociation energy.

Since the core/valence correction to the D_0(NaCl) was relatively large and negative (-1.2 kcal/mol), more extensive core/valence calculations were carried out. In these calculations, the results of which are summarized in Fig. 4, the RCCSD(T) method was chosen for the atomic asymptotes. Basis sets from both the cc-pwCVnZ and aug-cc-pCVnZ sequences were used, including up to aug-cc-pCV5Z. Core/valence functions were included on both atoms and the $(2s,2p)$ electrons were correlated. Optimal geometries were employed in all cases. Recently, Bauschlicher and Ricca[30] have recommended that calculations of the core/valence correction should include function counterpoise (CP) adjustments[94] to correct for basis set superposition error (BSSE). Hence, CP-corrected core/valence effects were also calculated.

As shown in Fig. 4, the effects of the CP correction are significant, especially at the double and triple zeta levels. When augmenting diffuse functions are present, the CP correction results in smoother convergence to the basis set limit. However, the magnitude of ΔE_{CV} predicted through the use of the CP correction is significantly overestimated for NaCl with the smaller basis sets. When diffuse functions are present on the chlorine atom, ΔE_{CV} is observed to decrease by 0.4, 0.1, and 0.05 kcal/mol for the DZ, TZ, and QZ basis sets, without adjusting for BSSE. However, much of this difference is directly related to BSSE since the counterpoise-corrected results show nearly no difference between the cc-

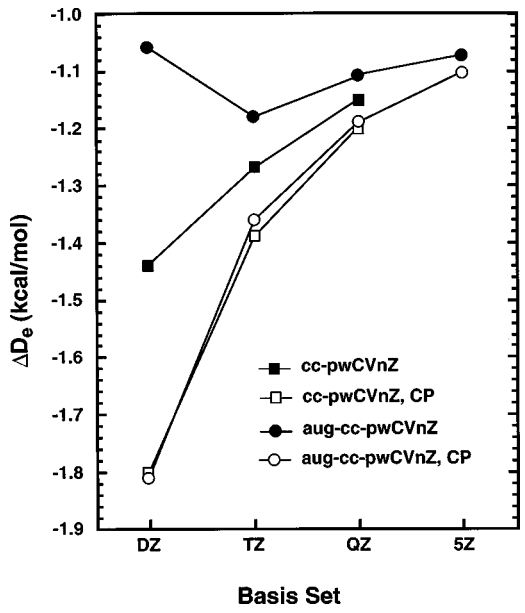

FIG. 4. Core/valence corrections to NaCl as a function of the basis set set size.

pwCVnZ and aug-cc-pCVnZ results. The basis set limit for the effect of core/valence correlation on the D_e of NaCl, as judged by the aug-cc-pwCV5Z results, is calculated to be -1.05 kcal/mol, i.e., the dissociation energy of NaCl is decreased when the core electrons are included in the correlation treatment. This is principally due to the lack of core/valence correlation contribution to Na^+ in the molecule, whereas the sodium atom has a non-negligible core/valence correction.

VII. CONCLUSIONS

CCSD(T) atomization energies were computed for a set of 73 molecules with reliable experimental values. The underlying one-particle basis sets were taken from the augmented correlation consistent family and represent some of the largest Gaussian basis sets currently available. By employing any of the three complete basis set extrapolations examined in this study, it is possible to enter a regime where core/valence, scalar relativistic, atomic spin-orbit and anharmonic ZPE effects can become as important as the remaining error in the one-particle basis set for the small molecules we studied. Failure to account for any one of these effects can lead to errors on the order of several kcal/mol or more in particularly troublesome cases. On the other hand, in fortunate cases, ΔE_{CV} and ΔE_{SR} effects may nearly cancel.

Due to the variation in size of the corrections to the baseline CCSD(T)(FC) atomization energies from molecule to molecule, a single, meaningful ranking of the relative importance of each correction was not possible. For most molecules, the deviation of raw CCSD(T)(FC)/aug-cc-pVQZ values with respect to experiment were still dominated by errors associated with the finite one-particle basis set expansion. At the highest level of theory used in the present study, ϵ_{MAD} fell into the 0.7–0.8 kcal/mol range. By separately fitting the self consistent field (SCF) and correlation energies, Martin has been able to achieve a ϵ_{MAD} of 0.12 kcal/mol for 15 first row molecules.[95] However, it was not clear if scalar relativistic corrections were considered. Given the size of the ΔE_{SR} correction, the potential residual error in the CCSD(T) treatment and the uncertainty in the experimental measurements, a mean absolute deviation of less than 0.5 kcal/mol for larger collections of molecules will be hard to maintain.

In light of the experimental uncertainties and the small spread in ϵ_{MAD} values among the exponential, mixed and $1/l_{\max}$ CBS extrapolations, it was difficult to characterize any one of the approaches as superior based solely on the level of agreement with experiment. The mixed extrapolation performed slightly better than the other two, and displayed somewhat better agreement with the apparent CBS energy of the oxygen atom, derived from a septuple zeta calculation. While the exponential functional form fit the entire double through septuple sequence better than any other two- or three-parameter fit, it systematically underestimates the contribution from functions with $l>4$, i.e., *h*-, *i*-, *k*-functions, etc. Because the error in the exponential fit is systematic, the resulting error in energy differences is very similar to what is observed for the other extrapolations. For problematic cases, such as SO_2, the exponential fit displayed twice as much variation in the CBS estimate for ΣD_e as the basis set was enlarged, as did the other two extrapolations.

Although CCSD(T) suffers from some of the same limitations as other single-reference methods, it is currently the most accurate *ab initio* electronic structure technique that can be applied with large basis sets to small molecules. Coupled cluster theory without the inclusion of triple excitations was found in our original study to be frequently less accurate for atomization energies than second order perturbation theory. The effects of higher order excitations, as estimated from CCSD(TQ) calculations, was substantial. However, the lack of corroborating evidence from comparable full CI calculations, makes this a tentative conclusion.

Finding a suitable reference set of highly accurate binding energies, whether obtained from experiment, theory or a combination of both, will be essential for measuring future improvements in methods focused on relative energetics, such as ΣD_e. Theoretical advances in predicting accurate bond energies may be hampered by the relatively small number of converged experimental measurements. The leading source of theoretical error in atomization energies for most small molecules has for many years been the error associated with the finite one-particle basis set. This problem is gradually yielding to improved, systematic sequences of basis sets, better software and faster computer hardware.

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