# W3X: A Cost-Effective Post-CCSD(T) Composite Procedure

Bun Chan* and Leo Radom*

School of Chemistry and ARC Centre of Excellence for Free Radical Chemistry and Biotechnology, University of Sydney, Sydney, NSW 2006, Australia

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ABSTRACT: We have formulated the W3X procedure by incorporating cost-effective post-CCSD(T) components (up to the CCSDT(Q) level) into the W1X-1 protocol, the latter representing a recently reported economical yet accurate approximation to CCSD(T)/CBS. For medium-sized systems, W3X is moderately more computationally demanding than W1X-1, but it is significantly less costly than the W3.2lite and (especially) W3.2 procedures. Because of the use of the cost-effective W1X-1 method as the underlying CCSD(T) component, W3X is also less expensive than the W2.2 protocol, which does not incorporate post-CCSD(T) excitations. We find that, for single-reference systems (the G2/97 set and most of the W4-11 set), W3X is comparable in accuracy to the underlying W1X-1 protocol, as might have been expected. For the more challenging cases of the multireference systems within the W4-11 set, the dissociation of F_2 and the automerization of cyclobutadiene, W3X provides improved performance compared with the CCSD(T)-based procedures (W1X-1 and W2.2). Highly multireference chromium oxides CrO, CrO_2, and CrO_3 are still somewhat challenging for W3X (and even for the higher-level W3.2lite and W3.2 procedures), but the inclusion of the economical post-CCSD(T) terms in W3X already leads to a significant improvement over W1X-1. Thus, W3X provides a cost-effective means for treating systems with significant (but perhaps not excessive) multireference character that are otherwise not well-described by CCSD(T)-based methods.
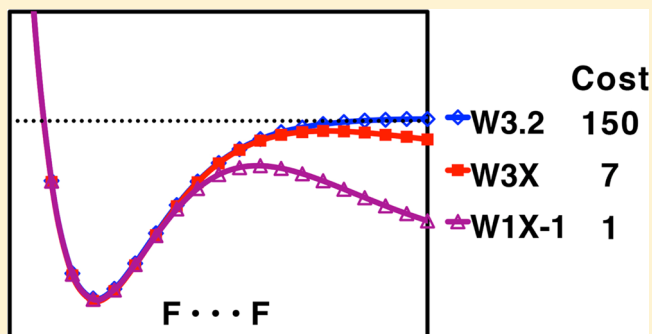
INTRODUCTION

In recent years, continuing advances in computational chemistry procedures have enabled the prediction of thermochemical properties to very high accuracy. The introduction of the W1 composite protocol[1] represented a major breakthrough in this area as one of the first generally formulated procedures capable of yielding, on average, relative energies of "chemical accuracy" ($\sim$5 kJ mol^{-1}) for a wide variety of thermochemical properties,[2] while, at the same time, being applicable to systems of moderate size.[3] The W1 procedure employs a series of CCSD and CCSD(T) calculations to provide a very good approximation to the all-electron scalar-relativistic CCSD(T) energy at the complete-basis-set (CBS) limit.

Further developments along the lines of the W1 protocol have led to the W3[4] and W4[5] methods. These more-sophisticated procedures additionally incorporate post-CCSD-(T) contributions (referred to as Δ(T)+ in the present study, up to CCSDTQ5 for W4), and they further improve the general accuracy to $\sim$1 kJ mol^{-1}.[6] Perhaps a more important attribute of these methods is the improved robustness due to the inclusion of the higher-order excitations, which to a large extent rectifies the problem for CCSD(T) in properly describing highly correlated systems such as ozone and the halogen oxides.[5,7] However, in contrast to W1, which nowadays is applicable to medium-sized systems, W3 and W4 are

currently only applicable to molecules consisting of just a few atoms.[8] In this regard, the W3.2lite procedure[9] has been proposed as an accurate alternative to W3 and W4 but with a reduced demand on computational resources. The W3.2lite protocol incorporates Δ(T)+ contributions up to CCSDT(Q) in combination with smaller basis sets than those used in W3 and W4. In some of our own investigations,[3b,10,11] however, we find that such an approach, while extending the range of W3 and W4, is still limited to relatively small molecules.

We have been interested in broadening the scope of computational thermochemistry, by formulating new theoretical chemistry procedures that are both accurate and have a moderate demand on computational resources.[12,13] In a recent study,[13] we formulated composite methods (W1X-1 and W1X-2) related to the W1w[4] and W1-F12[14] protocols, but with a cost that is $\sim$1/10 and $\sim$1/5 of those for W1w and W1-F12, respectively. In the present study, we build on the foundations of W1X, and develop cost-effective composite methods that include Δ(T)+ excitations in the spirit of W3.2lite but with an even lower demand on computational resources, and, hence, a broader applicability. We note that the outstanding accuracy of W3.2lite is in part associated with the use of the highly rigorous but computationally demanding W2.2 protocol[5] for the

CCSD(T)/CBS component. In this regard, we deem W1X already sufficiently accurate as an approximation to CCSD(T)/CBS for typical molecules, and aim to formulate a method that is generally of similar accuracy to that of W1X, but that is more robust for strongly correlated systems.

COMPUTATIONAL DETAILS

Standard ab initio molecular orbital theory and density functional theory (DFT) calculations[15] were carried out with the Gaussian 09[16] and Molpro 2010[17] programs. Unless otherwise noted, geometries were optimized with the B3-LYP/cc-pVTZ+d procedure. Following each geometry optimization, harmonic frequency analysis was carried out to confirm the nature of the stationary point as an equilibrium structure. For all W1-type methods, improved single-point energies for open-shell species were obtained using restricted-open-shell reference wave functions. The energy differences between CCSDT and CCSD(T) were also obtained with restricted-open-shell references, while the CCSDT(Q) − CCSDT differences were evaluated with unrestricted Hartree−Fock wave functions.

Two-point extrapolation schemes with the formula $E_L = E_{CBS} + AL^{-\alpha}$ were used in the evaluation of the CBS limit,[18] where L is the cardinal number of the basis set (i.e., 2 for double-ζ and 3 for triple-ζ basis sets, etc.) and α is an adjustable parameter. In the W1X-1 scheme, α is taken to be 5 for Hartree−Fock energies, while for correlation energies, α values of 3.67 and 2.04 are employed for the CCSD-F12b and conventional (T) correlation energy components, respectively. Scale coefficients for post-CCSD(T) contributions were optimized using the G2-1 training set by fitting the W3X reaction energies to the experimental values.[19] Following previous practice,[12b,c,13] our optimization procedures involved minimizing the average of the mean absolute deviation (MAD) from benchmark values and the standard deviation (SD) of these deviations.

Literature values for corrections for spin−orbit coupling, where available, were included for atomic species and several molecules.[19] To obtain the zero-point vibrational energies (ZPVEs) and thermal corrections for enthalpies at 298 K (ΔH_{298}), we used B3-LYP/cc-pVTZ+d harmonic vibrational frequencies, scaled by 0.985 as prescribed for W1w. All relative energies are given in units of kJ mol^{-1}.

THEORETICAL APPROACH

We will employ the performance of W3.2 and W3.2lite as yardsticks to assess the protocols devised in the present study. There are several existing variants of W3.2lite, namely versions a−d.[9] All of them, as well as W3.2, are based on a CCSD(T)/CBS component obtained at the W2.2 level, but they differ in the manner in which the post-CCSD(T) [Δ(T)+] components are obtained. Among the different versions of W3.2lite, we employ W3.2lite(c) in the present study, as we deem it to be the best compromise between accuracy and computational efficiency.[9] For the sake of simplicity, we will refer to this variant simply as W3.2lite.

The Δ(T)+ contributions to the energy for W3.2 consist of the following:[9]

- A "ΔT" component obtained using CCSDT and CCSD(T) calculations with the cc-pVDZ and cc-pVTZ basis sets. The CCSDT − CCSD(T) differences are then extrapolated to the CBS limit using the formula $E_L = E_{CBS} + AL^{-3}$.

- A "Δ(Q)" component calculated as CCSDT(Q)/cc-pVDZ − CCSDT/cc-pVDZ.

Further approximations to the above Δ(T)+ energies are made in W3.2lite. Thus, the following modified contributions are instead employed:[9]

- A "ΔT" term obtained using the formula −1.6 × [CCSDT/cc-pVDZ − CCSD(T)/cc-pVDZ] + 2.6 × [CCSDT/cc-pVTZ(2d no f)(no p on H) − CCSD(T)/cc-pVTZ(2d no f)(no p on H)], where (2d no f) indicates that, for heavy atoms, only the 2d polarization functions in cc-pVTZ are retained but the f functions are excluded, and (no p on H) signifies that only the s functions are retained for hydrogen.

- A "Δ(Q)" term calculated as 1.1 × [CCSDT(Q)/cc-pVDZ(no p on H) − CCSDT/cc-pVDZ(no p on H)].

For the new procedures devised in the present study, the W1X-1 protocol[13] is used to obtain the CCSD(T)/CBS component. We will not go into the details of this method, but simply note that the total W1X-1 electronic energy can be straightforwardly obtained in a single Molpro calculation. Detailed instructions and an input file template are given in the supporting information of ref 13.

For the Δ(T)+ contributions, we note that W3.2lite represents an excellent approximation to W3.2, which, in turn, represents a good approximation to W3 and W4.[9] The success of the more approximate protocols can be largely attributed to the relatively rapid basis-set convergence for Δ(T)+ energies, thus enabling the use of relatively small basis sets for their calculation. In the case of W3.2lite (versus W3.2), simplifications are made with truncations of polarization functions in the standard basis sets, and the use of a direct additivity scheme instead of extrapolation to estimate the basis-set limit. In addition, the use of empirical scaling exploits the systematic nature of the deviations introduced by the basis-set truncations and leads to a performance for W3.2lite that is comparable to that for W3.2.

In the present study, in addition to examining the use of the Δ(T)+ component in W3.2lite to complement W1X-1, we have investigated other simplifications to the calculation of Δ(T)+ energies. Thus, we have exploited further truncations of basis sets, and these are complemented by reoptimization of the scale factors in the Δ(T)+ terms. Specifically, the following components are included in our new Δ(T)+ schemes:

- A "ΔT" component calculated as a single-scaled CCSDT − CCSD(T) term, using a valence-triple-ζ basis set with no polarization functions (NP), i.e., $E(\Delta T) = c[\Delta T] \times [E(CCSDT/TZ\text{-}NP) − E(CCSD(T)/TZ\text{-}NP)]$, where $c[\Delta T]$ is a fitted parameter for this term. The TZ-NP basis sets examined are cc-VTZ, def2-TZV, and 6-311G, where cc-VTZ and def2-TZV correspond to cc-pVTZ and def2-TZVP but with the polarization functions removed.

- A "Δ(Q)" term obtained with the formula $c[\Delta Q] \times [E(CCSDT(Q)/DZ\text{-}NP) − E(CCSDT/DZ\text{-}NP)]$, where $c[\Delta Q]$ is a fitted parameter for this term and DZ-NP represents a double-ζ basis set with no polarization functions, analogous to the corresponding TZ-NP triple-ζ basis sets.

Table 1. Mean Absolute Deviations (kJ mol^{-1}) from Benchmark Values for the Wn-Type Procedures for the G2-1 Set, and Timing Comparisons

method[a]	W3.2	W3.2lite	W2.2	W3X(A)	W3X(B)	W3X(C)	W3X(D)	W1X-1
CCSD(T)	W2.2	W2.2	W2.2	W1X-1	W1X-1	W1X-1	W1X-1	W1X-1
ΔT	cc-pV[D,T]Z	$-1.6 \times$ cc-pVDZ + 2.6 $\times$ cc-pVTZ (2d no f) (no d on H)		$-0.6 \times$ cc-pVDZ + 1.6 $\times$ cc-pVTZ (2d no f) (no d on H)	1.14 $\times$ cc-VTZ	1.31 $\times$ def2-TZV	1.26 $\times$ 6-311G	
Δ(Q)	1.1 $\times$ cc-pVDZ	1.1 $\times$ cc-pVDZ (no p on H)		1.1 $\times$ cc-pVDZ (no p on H)	0.69 $\times$ cc-VDZ	0.64 $\times$ def2-SV	0.69 $\times$ 6-31G	
Mean Absolute Deviations								
G2-1[b]	1.4	1.4	1.6	1.5	1.6	1.6	1.6	1.7
ΔH_f	1.8	1.9	2.0	1.5	1.5	1.5	1.5	1.6
IE	0.8	0.9	1.0	1.3	1.3	1.4	1.3	1.5
EA	1.2	1.2	1.5	1.7	1.9	1.9	2.0	1.9
PA	1.9	1.8	1.8	2.3	2.3	2.4	2.4	2.3
Timing Comparisons[c]								
CCSD(T)	124.1	124.1	124.1	1.0	1.0	1.0	1.0	1.0
Δ(T)+	153.9	9.6		9.6	0.5	0.6	0.8	
total	278.0	133.6	124.1	10.6	1.5	1.6	1.8	1.0

[a]CCSD(T) represents the all-electron scalar relativistic CCSD(T)/CBS component. ΔT = CCSDT − CCSD(T), Δ(Q) = CCSDT(Q) − CCSDT, and Δ(T)+ = ΔT + Δ(Q). The cc-VnZ (n = D, T) and def2-nV (n = S, TZ) basis sets are derived from cc-pVnZ and def2-nZVP, respectively, with all polarization functions removed. [b]ΔH_f = heat of formation, IE = ionization energy, EA = electron affinity, and PA = proton affinity. [c]Relative to the total computational time consumed for all calculations in the G2-1 set for W1X-1.

■ RESULTS AND DISCUSSION

Performance of the W3-Type Protocols. The performance of the various W3-type procedures for the G2-1 set is shown in Table 1, along with timing comparisons. Four new W3-type procedures are examined in the present study. They are termed W3X(A−D) as they are all based on an all-electron scalar-relativistic CCSD(T)/CBS component as estimated with W1X-1. The W3X(A) protocol employs the Δ(T)+ term from W3.2lite but with redetermined scaling coefficients for these components. The variants B−D utilize the double-ζ basis sets cc-VDZ, def2-SV, and 6-31G, respectively, for the Δ(Q) component, together with matching triple-ζ basis sets for ΔT. The scaling coefficients for the ΔT and Δ(Q) terms that are fitted to the G2-1 set are also given.

It is noteworthy that the experimental data in the G2-1 set are associated with an uncertainty as large as 1 kcal mol^{-1} (4.2 kJ mol^{-1}). Thus, the high-level Wn-type procedures, especially the W3-type procedures, are arguably more accurate than some of the "benchmark" experimental data. In addition, we reiterate that the present study seeks to formulate a post-CCSD(T) procedure that is generally as accurate as W1-type procedures, but more robust in the cases where CCSD(T) performs poorly.

It can be seen from Table 1 that, for the G2-1 set of species that are, by and large, adequately treated by CCSD(T)-based procedures (W1X-1 and W2.2), the W3-type methods perform comparably to the already quite accurate W1- or W2-type protocols. Nonetheless, the W3-type procedures do give somewhat improved overall agreement with the experimental data.

In terms of timing comparisons, we can see that, even for the G2-1 set of relatively small molecules, the W2.2 protocol is already substantially more demanding than W1X-1, and it contributes significantly (through the CCSD(T) component) to the cost of W3.2 and W3.2lite. For W3.2, the calculation of the Δ(T)+ term is more expensive than the cost of obtaining the underlying W2.2 CCSD(T) energy. The simplification in W3.2lite dramatically reduces the cost for the evaluation of Δ(T)+ by more than an order of magnitude. However, the cost of calculating Δ(T)+ in this manner is still ∼10 times greater

than that for the underlying W1X-1 CCSD(T) component in W3X(A). Further simplifications in the W3X(B−D) protocols lead to costs for Δ(T)+ that are somewhat smaller than the cost for the underlying CCSD(T) component, i.e., W1X-1, for the G2-1 set. Among the B−D variants of W3X, the use of the Dunning basis sets in W3X(B) appears to be somewhat more efficient with the hardware and software employed. Therefore, we will focus on the W3X(B) procedure in the remainder of the present investigation, and we hereafter will refer to this protocol simply as W3X.

Evaluation of W3X with the G2/97 Test Set. We now further evaluate the performance of W3X for the larger G2/97 set (Table 2).[20,21] It can be seen that W3X generally leads to a performance comparable to that of W1X-1, with an overall MAD of 2.2 kJ mol^{-1}, vs 2.3 kJ mol^{-1} for W1X-1. The performances of the two methods for the subsets are also comparable. Among the four subsets, the largest deviations for

Table 2. Statistical Performance (kJ mol^{-1}) for W1X-1 and W3X Procedures for the G2/97 Set and Timing Comparisons

	Mean Absolute Deviation		Largest Deviation	
	W1X-1	W3X	W1X-1	W3X
G2/97	2.3	2.2	−17.4	−17.8
ΔH_f	2.4	2.4	−16.1 (C_2F_4)	−17.8 (C_2F_4)
IE	2.4	2.0	−17.4 (CN$^{\bullet}$)	+13.8 (BCl_3)
EA	1.9	1.8	+8.1 ($CH_2NC^{\bullet}$)	+8.4 ($CH_2NC^{\bullet}$)
PA	2.2	2.2	−5.4 (PH_3)	−5.3 (PH_3)
Timing Comparisons[a]				
			W1X-1	W3X
CCSD(T)			1.0	1.0
Δ(T)+				5.8
all			1.0	6.8

[a]Relative to the total computational time consumed for all calculations in the G2/97 set for W1X-1.

heats of formation (ΔH_f) and ionization energies (IEs) are larger than 10 kJ mol^{-1} for both W1X-1 and W3X.

For ΔH_f, the largest deviation occurs for C_2F_4 for both W1X-1 (−16.1 kJ mol^{-1}) and W3X (−17.8 kJ mol^{-1}). Large deviations from the experiment for ΔH_f (C_2F_4) have also been found previously for G4-type composite procedures.[12b] The *NIST Chemistry WebBook*[22] lists a range of experimental values (−658.6 to −686.0 kJ mol^{-1}) for ΔH_f (C_2F_4), and we find that the one obtained by Kirkbride and Davidson (−678.0 ± 4.0 kJ mol^{-1})[23] is in best agreement with our high-level theoretical values (W1X-1 = −674.7 and W3X = −676.4 kJ mol^{-1}). It should perhaps replace the benchmark experimental value (−658.6 ± 2.9 kJ mol^{-1}) currently used for $\Delta H_f(C_2F_4)$ in the G2/97 set.[20]

The largest deviation for IEs for W1X-1 is found for the CN$^{\bullet}$ radical (−17.4 kJ mol^{-1}). The cation that results from the ionization of CN$^{\bullet}$, i.e., CN$^+$, is essentially a singlet biradical. In the absence of higher-order correlation effects, the use of a single-determinant reference wavefunction is likely to be inadequate, and indeed it appears to be the case in this instance. The deviation for W3X for IE (CN$^{\bullet}$) is +9.1 kJ mol^{-1}. In comparison, we have also obtained W2.2 and W3.2lite values, and the corresponding deviations are −15.4 and −3.1 kJ mol^{-1}, respectively. Clearly there are large post-CCSD(T) contributions to the calculated IE of CN$^{\bullet}$. The largest deviation for IEs for W3X is for BCl$_3$ (+13.8 kJ mol^{-1}). For this quantity, we also observe large deviations for W1X-1 (+15.9 kJ mol^{-1}), W2.2 (+20.3), and W3.2lite (+17.4). Currently, the source of the discrepancy with experiment is unclear, but we note that the reported IE(BCl$_3$) values span a very wide range,[24] and the data given in a more recent photoelectron spectroscopy study[25] appear to imply a value (∼11.8 eV, 1133 kJ mol^{-1}) that is more consistent with our theoretical IEs (1135.1 (W1X-1) and 1133.0 (W3X) kJ mol^{-1}).

We now turn our attention to the timing comparisons for the G2/97 set, which contains larger molecules than G2-1. While the computational time for the Δ(T)+ component in W3X for the G2-1 set is less than that for the underlying W1X-1 calculations (Table 1), for G2/97 the Δ(T)+ component is more time-consuming than the W1X-1 component. Nonetheless, we emphasize that the W3X protocol is already applicable, reasonably straightforwardly, to systems as large as the toluene radical cation $C_6H_5Me^{\bullet+}$. For this molecule, the computational time required for the complete W3X calculation is ∼9.3 times that for W1X-1 (Table 3). In comparison, the computation of $C_6H_5Me^{\bullet+}$ with W1w requires a CPU time that is 6.4 times that for W1X-1. The W3X calculation for $C_6H_5Me^{\bullet+}$ consumed a maximum of 9.3 GB of memory, which is the same as that required for W1X-1, but it is less than that for W1w (15.2 GB). In terms of scratch disk space, the W3X calculation used a

maximum of 219 GB (for the CCSDT/cc-VTZ component), which is substantially more than the 71 GB consumed by W1X-1. However, this is still noticeably less than the corresponding requirement for W1w, which is 337 GB. Overall, for systems of sizes that are comparable to that for $C_6H_5Me^{\bullet+}$, the computational requirements for W3X are likely to be comparable to those for W1w.

Benchmarking with the W4-11 Set. Following the examination of the performance of W3X for the G2/97 set, we proceed to investigate its performance for systems that may have a higher demand on the level of theory. We will start with the W4-11 test set.[7] This compendium of data contains 140 atomization energies (AEs) obtained with W4-type protocols, which include high-order correlation effects up to CCSDTQ5. These extremely high-level theoretical AEs can be considered to be associated with an uncertainty of just 1 kJ mol^{-1}. Among the 140 systems, 124 are regarded as dominated by a single-reference (SR) wave function, while 16 species are deemed to have substantial multireference (MR) character.[7] It is of interest to examine how W1X-1 and W3X perform for this set of higher-level theoretical AEs, and how the incorporation of the Δ(T)+ term in W3X modifies the performance, in particular for the MR systems.

It can be seen from Table 4 that W1X-1 performs quite well for the full W4-11 set of AEs, with an MAD of 2.1 kJ mol^{-1}. We

Table 4. Statistical Performance (kJ mol^{-1}) for the W*n*-Type Procedures for the W4-11 Set of Atomization Energies (AEs) and an Evaluation of the Post-CCSD(T) Contributions to AEs for These Procedures against W4 Values

| | W4-11 AEs | | Δ(T)+ Contributions to AEs | | |
	W1X-1	W3X	W3.2^{a,b}	W3X^a	HK^c
MAD^d	2.1	1.9	0.6	1.0	2.5
SR^e	1.8	1.7	0.5	0.8	2.4
MR^f	3.9	3.2	1.8	2.5	3.8
MD^g	−1.8	−0.2	−0.2	+0.3	+2.5
LD^h	−10.5	−9.3	−9.7	−10.7	+7.8
SD^i	2.4	2.5	1.3	1.6	1.6

^{a}See Table 1 for the definition of the Δ(T)+ components. ^{b}Statistics obtained using the data in the supporting information of ref 7. ^{c}CCSDT(Q)/cc-pV(D+d)Z − CCSD(T)/cc-pV(D+d)Z; data taken from ref 27. ^{d}Mean absolute deviation. ^{e}Mean absolute deviation for single-reference systems. ^{f}Mean absolute deviation for multireference systems. ^{g}Mean deviation. ^{h}Largest deviation. ^{i}Standard deviation.

note that this is similar to the MADs for W1w (2.0 kJ mol^{-1}) and W1-F12 (2.1 kJ mol^{-1}).[14] The AEs calculated with W1X-1 are typically underestimated, as indicated by the MD value of −1.8 kJ mol^{-1}. This is in accord with the previous observation that the W2.2 protocol also underestimates the AEs in the W4-11 set.[7] For W3X, the overall MAD improves slightly to 1.9 kJ mol^{-1} when compared with that for W1X-1. Such a modest improvement may in the first instance appear to be somewhat surprising, as one may consider a major difference between W1-type and W4-type procedures to be the inclusion of higher-order excitations, which is what W3X attempts to address. However, we note that, in ref 14, when the W1w, W2w,[4] and W3w[14] methods were benchmarked against the W4-11 set, the major improvement occurs in going from W1w (MAD = 2.0 kJ mol^{-1}) to W2w (MAD = 1.0 kJ mol^{-1}), i.e., an improvement in the underlying CCSD(T)/CBS approximation, with a further

Table 3. Computational Resources Utilized for the Calculation of the Energies for $C_6H_5Me^{\bullet+}$ with W*n*-Type Procedures

	CPU time (h)	memory (GB)	disk (GB)
W3X	319.1	9.3	219.1
W1X-1	34.4	9.3	71.1
CCSD(T)/cc-VTZ	0.1	0.1	0.6
CCSDT/cc-VTZ	187.7	7.8	219.1
CCSDT(Q)/cc-VDZ	96.8	3.3	98.9
W1w	220.9	15.2	336.8

Table 5. Comparison of the Mean Absolute Deviations from W4 Atomization Energies (MADs, kJ mol^{-1}) for the W4-11 Set for Various W*n*-Type Procedures, Divided into Four Groups of Species According to the #CCSD(T) (kJ mol^{-1}) and %(T) (%) Diagnostics

	number of species	#CCSD(T)	%(T)	W1X-1	W3X	W2.2	W3.2	suggested method
A	82	≤3	≤5	1.2	1.1	0.7	0.3	W1X-1
B	29	≤3	>5	2.6	2.0	2.9	1.1	W3X
C	15	>3	≤5	4.3	3.9	0.7	0.4	W2.2
D	14	>3	>5	2.9	3.7	6.5	1.4	W3.2[a]

[a]For a method that combines W2.2 and W3X Δ(T)+, i.e., W3X$_{(W2.2)}$, the MAD for group D is 2.4 kJ mol^{-1}.

smaller improvement accompanying the inclusion of higher-order excitations in W3w (MAD = 0.6 kJ mol^{-1}). Nevertheless, we note that the use of the more rigorous post-CCSD(T) components in W3w (identical to those for W3.2, see Table 1) does lead to a larger improvement for W2w than that resulting from the addition of the W3X Δ(T)+ term to W1X-1.

We can see that, for the SR systems, the MADs of W1X-1 (1.8 kJ mol^{-1}) and W3X (1.7 kJ mol^{-1}) are quite similar to each other. However, there is a more significant improvement for the MR species when the Δ(T)+ component is included (MAD = 3.9 kJ mol^{-1} for W1X-1 and 3.2 kJ mol^{-1} for W3X). It is noteworthy that the MD for W3X is −0.2 kJ mol^{-1}. Thus, a major consequence of the inclusion of higher-order correlation effects in W3X is the offsetting of the systematic under-estimation of the AEs by W1X-1. This observation is again consistent with the previous comparison between the W2.2, W3.2, and W4 methods for this dataset.[7]

Among the 16 MR systems, the largest improvement is found for S$_4$, for which the deviations from the W4 benchmark for W1X-1 and W3X are −10.5 and −3.8 kJ mol^{-1}, respectively. However, we note that the deviation for BN for W3X (−8.8 kJ mol^{-1}) is considerably larger in magnitude than that for W1X-1 (+3.2 kJ mol^{-1}). The larger deviation for W3X can be attributed to the Δ(T)+ term being not sufficiently converged.[26] When the Δ(T)+ term from the more rigorous W3.2 procedure is used to complement W1X-1, the deviation from W4 is just +2.1 kJ mol^{-1}. Similarly, the W3X deviation for F$_2$O$_2$ (+8.4 kJ mol^{-1}) is significantly larger than that for W1X-1 (+0.3 kJ mol^{-1}). Closer examination shows that W1X-1 deviates from the CCSD(T)/CBS component of W4 by +8.1 kJ mol^{-1}. This is very close to either the W4 (+7.6 kJ mol^{-1}) or W3X (+8.1 kJ mol^{-1}) estimates of Δ(T)+, which leads to a fortuitously good result for W1X-1 and a poorer result for W3X. Alternatively, when we combine the AE(F$_2$O$_2$) value from W2.2 with the corresponding Δ(T)+ term from W3X, the resulting AE deviates from W4 by just −1.3 kJ mol^{-1}. When these two systems are excluded from our analysis, the MADs for the remaining 14 MR systems are 4.2 and 2.4 kJ mol^{-1}, respectively, for W1X-1 and W3X, versus 3.9 and 3.2 kJ mol^{-1}, respectively, when BN and F$_2$O$_2$ are included.

We now turn our attention to the Δ(T)+ component used in the various post-CCSD(T)-type composite schemes. For W3.2, for which the Δ(T)+ term is formulated in the most rigorous manner among the three methods listed in Table 4, the overall MAD from W4 values is just 0.6 kJ mol^{-1}. Perhaps not unexpectedly, the agreement is slightly better for the SR systems (MAD = 0.5 kJ mol^{-1}) than for the MR species (1.8 kJ mol^{-1}). We can also see that W3.2 has an MD of −0.2 kJ mol^{-1}, which indicates that there is no notable systematic deviation from the W4 Δ(T)+ values for the species in the W4-11 set. The Δ(T)+ term used in W3X performs quite comparably to that for W3.2 for SR systems (0.8 kJ mol^{-1}), but the MAD for

MR species is larger (2.5 kJ mol^{-1}). There are only very mild systematic deviations, with an MD value of +0.3 kJ mol^{-1}.

Haunschild and Klopper (HK) have recently used a different composite protocol for the estimation of CCSDT(Q) energies.[27] It employs a single Δ(T)+ term obtained as CCSDT(Q)/cc-pV(D+d)Z − CCSD(T)/cc-pV(D+d)Z. It is of interest to make a comparison of the W3X Δ(T)+ values with the corresponding term in the HK procedure. For the HK Δ(T)+ term, the deviations from the W4 values for the W4-11 set are more substantial (MADs = 2.5 (overall), 2.4 (SR) and 3.8 (MR) kJ mol^{-1}) than those for W3X (1.0, 0.8, and 2.5 kJ mol^{-1}, respectively), which can largely be attributed to a systematic overstabilization of the molecules relative to the constituent atoms (MD = +2.5 kJ mol^{-1}).

A Diagnostic Protocol for the Anticipated Performance of W1X-1 and W3X. In previous sections, we have demonstrated that W3X provides an overall improvement over W1X-1 for diverse sets of small to medium-sized species, especially the MR systems, at a cost that is comparable to that for the original W1. However, for larger species, the cost associated with the calculation of the Δ(T)+ component can be expected to increase considerably. Therefore, it is of practical interest to ask: under what circumstances can we reasonably expect an improvement to W1X-1 by including the Δ(T)+ term? In this section, we present a set of diagnostics with the aim of addressing this matter, with the quantities used in this diagnosis protocol being obtained from the components of W1X-1. The details for the derivation of this protocol and the associated recommendations are given in the Supporting Information.

The performance of W3X depends partly on the quality of W1X-1 as an approximation to all-electron scalar-relativistic CCSD(T)/CBS, and partly on the adequacy of the Δ(T)+ term as an estimate of post-CCSD(T) effects. For the CCSD(T)/CBS component, our diagnostic is designed to take into account the smaller basis sets used for the valence CCSD(T) energies in W1X-1 when compared with the more rigorous treatment used in W4, as well as the use of MP2 (instead of CCSD(T) used in W4) for the calculation of core−valence and scalar-relativistic effects. We term this diagnostic tool #CCSD(T). Our analysis suggests that, when #CCSD(T) is less than ~3 kJ mol^{-1}, then W1X-1 is likely to be a good approximation to CCSD(T)/CBS, with an MAD from the W4 estimate of 1.3 kJ mol^{-1} for the systems for which #CCSD(T) ≤ 3 kJ mol^{-1} (for the W4-11 test set), versus 4.9 kJ mol^{-1} for #CCSD(T) > 3 kJ mol^{-1}. In fact, for the 111 (out of 140) systems of the W4-11 set for which #CCSD(T) ≤ 3 kJ mol^{-1}, the absolute deviations from W4 values of the W1X-1 total CCSD(T) correlation energy contribution to the AE are always < 5 kJ mol^{-1}. We note that a looser threshold of #CCSD(T) ≤ 4 kJ mol^{-1} covers 124 species with an MAD increased only slightly to 1.5 kJ mol^{-1}, but this choice does result in the

inclusion of SO_3 (#CCSD(T) = 3.7 kJ mol^{-1}), which shows a deviation of 8.2 kJ mol^{-1}.

With regard to post-CCSD(T) contributions, first of all, we note that there are several existing straightforward diagnostics for the importance of higher-order correlation effects.[5,28] Of these, the percentage contribution from the (T) correlation energy to the CCSD(T) atomization energy [%(T)] represents a reasonably reliable diagnostic for this purpose.[5,28d] Needless to say, whether W3X provides a sufficiently accurate estimate of energies depends also on the quality of the Δ(T)+ term. To this end, we again note that, when compared with the W4 Δ(T)+, the MAD for W3X Δ(T)+ is only 1.0 kJ mol^{-1}, with all but two systems showing a deviation that is smaller than 5 kJ mol^{-1}.

We now classify the molecules in the W4-11 set into four categories using the #CCSD(T) and %(T) diagnostics (Table 5). The criteria used are (1) #CCSD(T) $\leq$ 3 kJ mol^{-1}, which suggests that W1X-1 is likely to be a good approximation to the all-electron scalar-relativistic CCSD(T)/CBS limit, and (2) %(T) $\leq$ 5%, which is indicative of a system with small post-CCSD(T) effects, in accordance with the previously proposed guidelines.[5]

The diagnostics suggest that W1X-1 alone is likely to be sufficient for a set of 82 molecules (#CCSD(T) $\leq$ 3 kJ mol^{-1} and %(T) $\leq$ 5%, group A). For this group, the MAD for W1X-1 is indeed quite small (1.2 kJ mol^{-1}). For group B, the %(T) values (> 5%) indicate that post-CCSD(T) effects are likely to be important. We can see that W1X-1 and W2.2 have similar MADs ($\sim$2.5–3 kJ mol^{-1}), which are both notably larger than the corresponding group A values (1.2 kJ mol^{-1} for W1X-1 and 0.7 kJ mol^{-1} for W2.2). For this group, W3X represents a cost-effective means for obtaining reliable energies (MAD = 2.0 kJ mol^{-1}, vs 2.9 and 1.1 kJ mol^{-1} for W2.2 and W3.2, respectively).

The 29 molecules that belong to group B are shown in Table 6. We can see that W3X provides a generally improved performance when compared with W1X-1 and even W2.2. For example, there are six systems for which the absolute deviations for W1X-1 exceed 5 kJ mol^{-1}. In all these cases, the W3X results are significantly better, the improvements averaging 4.5 kJ mol^{-1}. We note that this group includes S_4, for which the improvement in going from W1X-1 ($-$10.5 kJ mol^{-1}) to W3X ($-$3.8 kJ mol^{-1}) is the most prominent among the species in the W4-11 set. There is just one case for which the deviation of W3X from W4 benchmarks is significant, namely singlet BN ($-$8.8 kJ mol^{-1}). The large deviation here is associated with an uncharacteristically large deviation for the W3X Δ(T)+ term [$-$10.7 kJ mol^{-1}, versus +0.6 kJ mol^{-1} for W3.2 Δ(T)+], attributable to basis-set effects, as discussed earlier.[26]

For groups C and D, the #CCSD(T) diagnostic indicates that these systems can potentially benefit from a more rigorous CCSD(T)/CBS approximation (Table 6). In these cases, the use of W2.2 or, perhaps more cost effectively, W1-F12[14] or W2-F12[14] may provide an improvement over W1X-1. It is noteworthy that one of the two problematic species discussed in the previous section, namely F_2O_2, for which we find that the difficulty for W3X lies in the underlying W1X-1 component, belongs to group D. The group D set of molecules have large post-CCSD(T) correlation effects, as evident from the large difference between the MADs for W2.2 (6.5 kJ mol^{-1}) and W3.2 (1.4 kJ mol^{-1}). To this end, we note that, when we incorporate W3X Δ(T)+ into W2.2 [W3X$_{(W2.2)}$], the resulting method has an MAD of 2.4 kJ mol^{-1} for group D.

Table 6. Deviations from W4 Benchmark Atomization Energies for Species in the W4-11 Set Characterized by the Diagnostics #CCSD(T) $\leq$ 3 kJ mol^{-1} and %(T) > 5% (Group B in Table 5)

species	#CCSD(T)	%(T)	W1X-1	W3X	W2.2	W3.2
HCNO	1.3	5	$-$1.3	0.3	$-$2.9	$-$0.8
HNO	2.8	5	0.8	2.2	$-$2.2	$-$0.4
HOO	2.7	5	0.3	3.0	$-$2.6	$-$0.2
CCl$_2$	0.4	6	$-$0.6	2.0	$-$2.9	$-$2.4
CN	1.1	6	$-$2.6	1.5	$-$4.0	$-$0.1
CS$_2$	1.5	6	$-$2.5	$-$0.5	$-$1.8	$-$2.3
CS	0.7	6	$-$2.1	$-$0.3	$-$1.6	$-$1.7
HOF	2.3	6	1.0	2.1	$-$1.9	$-$0.3
BN($^3\pi$)	1.1	7	$-$3.8	0.7	$-$3.3	0.4
NO	2.5	7	$-$0.3	1.5	$-$2.3	$-$0.8
SO$_2$	0.4	7	$-$6.8	$-$4.4	$-$3.1	$-$0.7
SO	1.5	7	$-$1.3	0.5	$-$0.9	$-$0.8
Cl$_2$	0.6	8	$-$1.1	$-$0.5	0.2	$-$0.3
P$_2$	0.1	8	$-$5.4	$-$1.8	$-$2.7	$-$2.5
S$_2$	0.2	8	$-$1.8	0.0	$-$0.8	$-$1.8
S$_2$O	2.6	8	$-$7.4	$-$3.1	$-$4.4	$-$2.0
ClF	0.9	9	$-$0.3	0.5	$-$1.0	$-$0.4
ClO	1.7	10	$-$3.5	$-$1.3	$-$2.9	$-$0.8
S$_3$	0.9	10	$-$7.7	$-$2.3	$-$5.6	$-$3.8
Cl$_2$O	2.5	12	0.2	1.8	$-$1.4	$-$1.0
S$_4$	0.3	13	$-$10.5	$-$3.8	$-$10.4	$-$6.0
C$_2$	1.2	14	$-$0.3	$-$2.8	$-$2.0	0.1
OClO	1.3	14	$-$2.7	1.8	$-$3.4	$-$0.8
FO	1.7	14	$-$1.7	1.9	$-$3.7	$-$0.3
B$_2$	0.3	15	$-$6.0	$-$1.4	$-$6.7	$-$2.2
F$_2$O	2.9	16	1.2	4.0	$-$4.8	$-$1.0
BN($^1\sigma$)	1.1	19	3.2	$-$8.8	1.3	0.6
F$_2$	1.9	21	0.8	2.1	$-$2.9	$-$0.5
Be$_2$	0.2	130	$-$2.4	$-$0.5	$-$3.1	$-$0.6

Further Tests: F_2 Dissociation, Cyclobutadiene Automerization and Higher-Order Excitations in Chromium Oxides.

We now further probe the applicability of several Wn-type procedures for cases that are more challenging than the systems in W4-11. The homolytic dissociation curve of F_2 represents a useful example for scrutinizing the performance of single-reference-based procedures, and has been previously used as a diagnostic tool in the development of the W1BD procedure.[29]

Figure 1 shows the potential energy curves for F_2 homolytic dissociation obtained with the W1X-1, W2.2, W3X, W3.2lite,
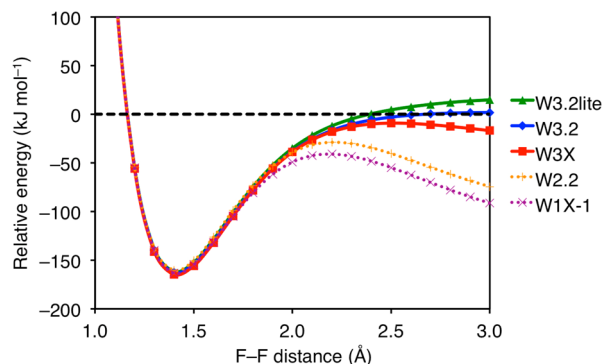

Figure 1. F_2 homolytic dissociation curves for Wn-type procedures with zero defined as the energy for $2 \times F^\bullet$ at the respective level.

and W3.2 procedures. It is apparent that only W3.2, being the theoretically most rigorous method among the five Wn-type protocols examined, gives an appropriate description of the dissociation process for the entire range of F−F distances.

Among the computationally less-demanding procedures, W1X-1, which is the least expensive method, begins to show a significant deviation (> 5 kJ mol^{-1}) from the W3.2 curve at an F−F distance of ∼1.9 Å, while the onset of significant deviation from the benchmark for W2.2 occurs at a slightly longer F−F distance of ∼2.1 Å. For both of these CCSD(T)-based methods, the deviations rapidly become larger with further lengthening of the F−F bond, with the largest deviations occurring at the longest distance examined (3.0 Å) and amounting to −93.2 kJ mol^{-1} for W1X-1 and −76.3 kJ mol^{-1} for W2.2. These findings are qualitatively consistent with those of Barnes et al.[29] For W3X and W3.2lite, the onsets for deviations with magnitudes of > 5 kJ mol^{-1} are 2.5 and 2.3 Å, respectively. Thus, both of these post-CCSD(T) Wn-type methods are applicable to a wider range of F−F distances than W1X-1 and W2.2. Perhaps a more important feature for W3X and W3.2lite, relative to the CCSD(T)-based protocols, is that even at ∼2.6−2.7 Å, the deviations for W3X and W3.2lite are still quite moderate at ∼10 kJ mol^{-1}, while the corresponding deviations for W1X-1 and W2.2 already exceed 50 kJ mol^{-1}. At the longest F−F distance of 3.0 Å, the deviations for W3X and W3.2lite are −18.6 and +13.0 kJ mol^{-1}, respectively, which are considerably smaller than those for W1X-1 and W2.2.

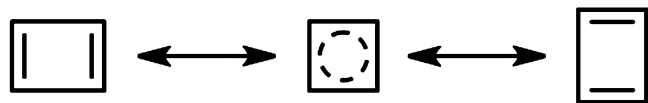The automerization of cyclobutadiene (Figure 2) via a doubly degenerate transition structure is another challenging

Figure 2. Automerization of cyclobutatiene via the multireference D$_{4h}$ transition structure.

problem for single-reference methods. The experimentally determined barrier for this reaction lies in a very wide range of 6.7−41.8 kJ mol^{-1}.[30] This reaction has been the subject of many theoretical studies by both single-reference as well as multireference methods. In a recent paper,[31] Shen and Piecuch (SP) have summarized some key theoretical results. In the present study, we have calculated the barrier for the automerization at the W3X and W3.2lite level. The results, together with selected barriers reported by SP, are shown in Table 7.

The best theoretical values are considered by SP to be those obtained with multireference-type procedures, namely, RMRCCSD(T), MkCCSD(T), CAS-BCCC4, MR-AQCC, and EOM-CCSD[+2]. These procedures point toward a barrier of ∼35−40 kJ mol^{-1} with the VTZ basis set. If one also takes into account the probable effect of basis-set incompleteness (as suggested by the significant differences between VDZ and VTZ), the barrier at the CBS limit is likely to be in the range 40−45 kJ mol^{-1}. Standard CCSD(T) and even some of its more sophisticated variants [CR-CC(2,3) and ΛCCSD(T)] significantly overestimate the barrier by ∼40 kJ mol^{-1}. As pointed out by SP, the good performance of CCSDT indicates that the large deviation of the CCSD(T) barrier from the multireference values can mostly be attributed to the decoupling of triple excitations from the singles and doubles.

Table 7. Vibrationless Barriers (kJ mol^{-1}) for the Automerization of Cyclobutadiene at the W3X and W3.2lite Levels and Their Components, and Selected Theoretical Values from Previous Studies

	W3X	W3.2lite
CCSD(T)[a]	77.7	78.8
ΔT[b]	−28.0	−29.8
Δ(Q)[c]	0.6	−3.5
total	50.4	45.5
	Previous Work[d]	
	cc-pVDZ	cc-pVTZ
CCSD(T)	66.1	75.7
CR-CC(2,3)	68.2	77.8
ΛCCSD(T)	70.3	80.3
CC(t;3)	32.6	41.8
TCCSD(T)	19.2	29.3
CCSDT	31.8	44.4
RMRCCSD(T)	30.1	39.7
MkCCSD(T)	32.6	37.2
CAS-BCCC4	31.8	36.4
MR-AQCC	30.5	35.1
EOM-CCSD[+2]	34.7	39.7
Expt[e]	6.7−41.8	

[a]Correspond to W1X-1 for W3X and W2.2 for W3.2lite. [b]CCSDT − CCSD(T). [c]CCSDT(Q) − CCSDT. [d]Obtained from Table 3 of ref 31. [e]Data taken from ref 30.

How do the Wn methods perform in comparison with these previous findings? We can see that the CCSD(T) components for W3X and W3.2lite, namely, W1X-1 and W2.2, give barriers of ∼80 kJ mol^{-1}, which is consistent with the previous CCSD(T) value. The corrections for CCSDT (ΔT) in both W3X and W3.2lite lead to a lowering of the barrier by ∼30 kJ mol^{-1}, which is again in accord with the previous findings. The correction terms for CCSDT(Q) [Δ(Q)] are small (+0.6 kJ mol^{-1} for W3X and −3.5 kJ mol^{-1} for W3.2lite). This is supportive of the argument that post-CCSD(T) correlation effects in the transition structure can be largely described by the explicit inclusion of coupled triples. Overall, the barriers obtained with W3X and W3.2lite are 50.4 and 45.5 kJ mol^{-1}, respectively. These values are in reasonable agreement with the best multireference theoretical results, when account is taken of the smaller basis sets used in the latter treatments.

An arguably even more challenging problem for Wn-type procedures would be to adequately describe transition-metal species that are often highly multireference in character. Indeed, in a recent study (Chan et al., CKRR),[10] it was found that the theoretical determination of the ΔH_f values for the chromium oxides CrO, CrO$_2$, and (especially) CrO$_3$ represents an extremely difficult case for CCSD(T)-based composite methods, including several variants of W1. For CrO$_3$, there remains a considerable contribution to the ΔH_f of 10 kJ mol^{-1}, even at the CCSDTQ(5)$_\Lambda$ level! Admittedly, for these systems, it would be naive to expect some of the theoretically less rigorous W3-type methods to perform as well as the post-CCSDTQ composite protocols used by CKRR. Nevertheless, it would be of interest to put the W3-type procedures through a "stress test" with these systems.

Since the W3X procedure relies on the cc-pVnZ-F12 basis sets for its HF and CCSD components, and these basis sets currently are not available for transition metals, we will instead focus only on the Δ(T)+ component of W3-type procedures in

comparison with those used by CKRR. It is apparent that the $\Delta(T)+$ protocols used in W3X, W3.2lite, and W3.2 (Table 8)

Table 8. Post-CCSD(T) Contributions to Atomization Energies (kJ mol^{-1}) for Chromium Oxides Obtained According to the Various W3-Type Protocols Compared with Benchmark (CKRR) Values^a

	W3X	W3.2lite	W3.2	CKRR^a
CrO	8.9	6.4	9.7	2.4
CrO$_2$	13.3	21.5	24.8	8.9
CrO$_3$	14.9	−1.3	8.4	24.9

^{a}Post-CCSD(T) excitations up to CCSDTQ5 were included; data taken from ref 10.

do not have the same accuracy for these challenging species as they do for main-group molecules. While the $\Delta(T)+$ component of W3X appears to give the best agreement with the benchmark, it still deviates from the more-rigorous values, by up to 10 kJ mol^{-1} (for CrO$_3$). In addition, it predicts the post-CCSD(T) contributions for CrO$_2$ and CrO$_3$ to be comparable to each other, while the more-rigorous CKRR methods estimate $\Delta(T)+$ for CrO$_3$ to be considerably larger than that for CrO$_2$. Although the use of W3X $\Delta(T)+$ for systems of this type requires some caution, we note that, in conjunction with a rigorous estimation for CCSD(T)/CBS, it does lead to an accuracy comparable to that of the underlying CCSD(T) component for CrO, and an improvement for CrO$_2$ and (especially) CrO$_3$.

An Illustrative Application: W3X Energies for the Mindless Benchmark Set. In the previous sections, we have seen that the W3X protocol, as expected, performs quite well for the G2/97 and W4-11 sets, as does W1X-1 for most of the relatively straightforward systems in these sets. The incorporation of higher-order excitations in W3X substantially improves on W1X-1 for the dissociation of F$_2$ and the automerization of cyclobutadiene, but it is still insufficient to achieve the highest accuracies for the extremely challenging cases of highly multireference transition-metal species, such as the chromium oxides.

In this section, as an illustrative example for the application of W3X, we now apply it to Grimme's "mindless" benchmark set (MB08) of decomposition energies for artificial molecules.[32,33] These are eight-atom species that contain main-group elements (hydrogen and first- and second-row heavy atoms). They represent random minima on the potential energy surface and often contain, to a certain degree, stretched bonds. While all of the species in the MB08 set have been screened for potential multireference character with the %(T) diagnostic, such that the systems are likely to be largely of single-reference character,[32] currently, there is no diagnostic tool that is definitive in predicting the importance of post-CCSD(T) excitations. Therefore, it is of interest to explicitly examine higher-order excitations in these "exotic" chemical species.

The W1X-1 and W3X reaction energies for the MB08 set are given in the Supporting Information. Here, we simply note that the MAD of W1X-1 from the W3X values is 1.8 kJ mol^{-1}. Thus, overall, MB08 is indeed dominated by single-reference species. However, as with most medium-sized to large datasets, there exist certain outliers within the MB08 set. Figure 3 shows the distribution of the deviations. There are 53 occurrences among the 165 energies where the deviation is larger than 2 kJ mol^{-1} in
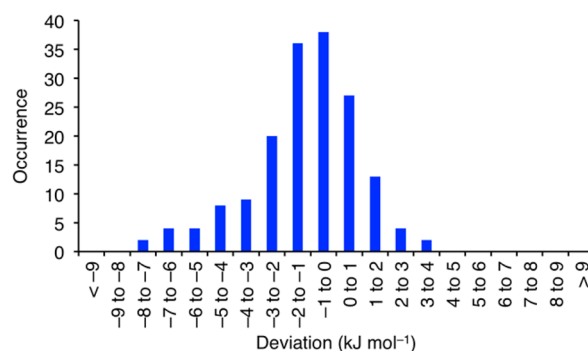

Figure 3. Distribution of deviations of W1X-1 reaction energies from W3X values for the MB08 set.

magnitude, with 18 of those having a deviation larger than 4 kJ mol^{-1}. The largest deviation is −7.8 kJ mol^{-1}. We note that, with the absence of transition metals, we can reasonably expect the $\Delta(T)+$ contributions in W3X to be quite accurate.

Curiously, we find our W1X-1 reaction energies to be considerably different from those obtained by Korth and Grimme (KG) using CCSD(T)/cc-pVTZ and CCSD(T)/cc-pVQZ as the major components in the CCSD(T)/CBS extrapolation.[32] We have carried out further calculations using the W2w protocol, which is theoretically more rigorous than both W1X-1 and the KG method. We find that the MADs from the W2w benchmark for W1X-1 and the KG procedure are 2.9 and 6.7 kJ mol^{-1}, respectively. We have thus included our W2w values plus the $\Delta(T)+$ contributions from W3X as our best estimate for the reaction energies for the MB08 dataset (see Table S3 in the Supporting Information), and believe that this provides an improved set of benchmark values that will be of use in future comparisons. We label this level of theory W3X$_{(W2w)}$. We note that, as with W4-11, for MB08, the use of a more-rigorous CCSD(T)/CBS (in going from W1X-1 to W2w) also leads to a larger improvement in performance (with a reduction in MAD by 1.4 kJ mol^{-1}) than the incorporation of $\Delta(T)+$ in W3X (ΔMAD = 0.3 kJ mol^{-1}). However, the move to W2w from W1X-1 places a greater requirement on the computational resources than the move to W3X. For the calculation of the complete MB08 set, W2w took ∼40 times more CPU time than W1X-1, while W3X consumed 5 times more CPU time than that for W1X-1.

Description of the W3X Protocol. At this point, we have demonstrated the utility of the W3X protocol as a cost-effective means for treating systems with significant (but not excessive) multireference character that are not well described by CCSD(T)-based methods. For convenience, we now briefly summarize the steps involved in carrying out a W3X calculation.

The all-electron relativistic CCSD(T)/CBS component of W3X involves the W1X-1 protocol:[13]

- The geometries and vibrational frequencies are obtained at the B3-LYP/cc-pVTZ+d level. A frequency scale factor of 0.985 is applied in the evaluation of ZPVEs and ΔH_{298}.
- The HF/CBS energy is obtained by extrapolating the HF(CABS)/cc-pVDZ-F12 and HF(CABS)/cc-pVTZ-F12 energies with the formula $E_L = E_{CBS} + AL^{-5}$.
- The valence ΔCCSD/CBS component is obtained by extrapolating the frozen-core CCSD-F12b/cc-pVDZ-F12 and CCSD-F12b/cc-pVTZ-F12 correlation energies using the formula $E_L = E_{CBS} + AL^{-3.67}$.

- The $\Delta(T)$ portion of the valence CCSD(T) correlation energy is obtained with the aug′-cc-pV(D+d)Z and aug′-cc-pV(T+d)Z basis sets, and extrapolated using the formula $E_L = E_{CBS} + AL^{-2.04}$.
- A combined core-correlation and scalar-relativistic component is obtained as the difference between the frozen-core and all-electron Douglas−Kroll−Hess MP2/cc-pCVTZ energies.

The W1X-1 energy is combined with the following valence post-CCSD(T) $[\Delta(T)+]$ components:

- A ΔT component is calculated as $1.14 \times [E(\text{CCSDT/cc-VTZ}) - E(\text{CCSD(T)/cc-VTZ})]$, where the cc-VTZ basis set is based on cc-pVTZ but with the polarization functions removed.
- A $\Delta(Q)$ term is obtained as $0.69 \times [E(\text{CCSDT(Q)/cc-VDZ}) - E(\text{CCSDT/cc-VDZ})]$, where cc-VDZ represents cc-pVDZ with polarization functions removed.

■ CONCLUDING REMARKS

We have examined several computationally cost-effective approaches for the incorporation of post-CCSD(T) correlation energies into the recently proposed W1X-1 protocol, the latter representing an economical yet accurate approximation to CCSD(T)/CBS. The resulting method includes excitations up to the CCSDT(Q) level. In spirit, it is comparable to the W3-type procedures of Martin, and we term the new protocol W3X. The key attributes of this new procedure are as follows:

(1) For medium-sized systems such as toluene radical cation, W3X is computationally more demanding than W1X-1 by up to an order of magnitude, but it is comparable in cost to the W1w procedure, which does not incorporate post-CCSD(T) effects. In order to account for post-CCSD(T) effects, we note that, even for smaller systems in the G2-1 test set, the W3.2 and W3.2lite procedures are already substantially more expensive than W3X.

(2) In terms of accuracy, for systems that can be suitably treated by CCSD(T)-based methods, such as those in the G2/97 test set and most of the W4-11 test set, W3X performs comparably to W1X-1. It generally improves on the accuracy of W1X-1 for the multireference systems in the W4-11 set.

(3) For the species with predominant single-reference character, the use of the W2.2 procedure, which is a theoretically more rigorous approximation to CCSD(T)/CBS than W1X-1, often leads to a somewhat larger improvement over W1X-1 than the incorporation of post-CCSD(T) terms in W3X. However, the use of W2.2 is often computationally more demanding than W3X, with the differences in the computational requirements being quite significant in some cases.

(4) To predict the likely accuracy of W1X-1 and W3X for specific systems, we have developed the #CCSD(T) diagnostic (see the Supporting Information for details) for estimating the quality of W1X-1 as an approximation to CCSD(T)/CBS. We note that the post-CCSD(T) term in W3X generally provides a good estimate of the effects of higher-order excitations when compared with W4. We put forward a set of recommended Wn-type procedures based on the values of #CCSD(T), and the %(T) diagnostic proposed by Martin and co-workers.

(5) We have examined more challenging instances where CCSD(T)-based methods such as W1-type and W2-type protocols are less adequate. We find that, in the case of the dissociation of F_2, W3X performs comparably to the theoretically more rigorous W3.2 procedure for F−F distances

up to 2.5 Å. It starts to deviate to a noticeable extent beyond this point. However, even at 3.0 Å, the deviation from the ideal behavior is still just −18 kJ mol^{-1}, which is comparable to that for the computationally more demanding W3.2lite protocol (+13 kJ mol^{-1}) and is significantly better than the deviations for W1X-1 (−93 kJ mol^{-1}) and the more expensive W2.2 (−76 kJ mol^{-1}).

(6) For the automerization of cyclobutadiene, W3X yields a barrier (50.4 kJ mol^{-1}) that is in reasonable agreement with those determined previously by the most rigorous multi-reference treatments ($\sim$40−45 kJ mol^{-1} when the effect of basis set incompleteness is taken into account). It represents a significant improvement over W1X-1 (77.7 kJ mol^{-1}) and W2.2 (78.8 kJ mol^{-1}), and is comparable in performance to W3.2lite (45.5 kJ mol^{-1}).

(7) For the even more difficult problem of the calculation of the heats of formation for the highly multireference chromium oxides, we find that the W3-type procedures examined, namely, W3X, W3.2lite, and W3.2, do not perform as well as they do for typical main-group species. Thus, multireference transition-metal species still represent a substantial challenge even to these high-level (single-reference) procedures.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information
Instructions for carrying out W3X calculations, sample Molpro input and output files, incorporated in a single zip archive (w3x.zip), zero-point vibrational energies (ZPVEs), enthalpy corrections at 298 K (ΔH_{298}), and total electronic energies for Wn-type procedures (Table S1), deviations from benchmark values (Table S2), components of Wn energies for the W4-11 set and related diagnostics (Table S3), Wn relative energies for the MB08 set (Table S4), and description of the diagnostics for W1X-1 (section S1). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors
*Tel.: +61-2-9351 5361. Fax: +61-2-9351 3329. E-mail: bun.chan@sydney.edu.au.
*Tel.: +61-2-9351 2733. Fax: +61-2-9351 3329. E-mail: radom@chem.usyd.edu.au, leo.radom@sydney.edu.au.

Notes
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