J. Chem. Theory Comput. **2009,** *5,* 2687–2693

2687

JCTC Journal of Chemical Theory and Computation

Unrestricted Coupled Cluster and Brueckner Doubles Variations of W1 Theory

Ericka C. Barnes,[†] George A. Petersson,*,[†] John A. Montgomery, Jr.,[‡,¶]
Michael J. Frisch,[‡] and Jan M. L. Martin[¶,§]

*Hall-Atwater Laboratories of Chemistry, Wesleyan University, Middletown,
Connecticut 06459-0180, Gaussian, Incorporated, 340 Quinnipiac Street, Building 40,
Wallingford, Connecticut 06492-4050, and Department of Organic Chemistry,
Weizmann Institute of Science, IL-76100 Reovot, Israel*

Abstract: Unrestricted coupled cluster spin contamination corrected [UCCSD(T)] and unrestricted Brueckner doubles [UBD(T)] variations of the Weizmann-1 theory (W1), denoted as W1U, W1Usc, and W1BD, respectively, are compared with the restricted open-shell W1 theory [W1(RO)]. The performances of the four W1 variants are assessed with 220 total atomization energies, electron affinities, ionization potentials, and proton affinities in the G2/97 test set, for consistency with the error analysis of the original W1(RO) study. The root-mean-square deviations from the experiment of W1U (0.65 ± 0.48 kcal/mol), W1Usc (0.57 ± 0.48 kcal/mol), W1BD (0.62 ± 0.48 kcal/mol), and W1(RO) (0.57 ± 0.48 kcal/mol) show that the four methods are virtually indistinguishable. This error analysis excludes the "singlet biradicals," C_2 and O_3, since single determinantal methods are not really adequate for these strongly multireference systems. The unrestricted W1 variants perform poorly for such highly spin-contaminated and multireference species (the largest deviation from experiment for W1Usc is -4.2 ± 0.1 kcal/mol for the O_3 EA). W1(RO) performs much better than its unrestricted counterparts for these pathological cases (the deviation from experiment is reduced to -1.5 ± 0.1 kcal/mol for the O_3 EA), though the errors are significantly larger than those for the overall test set. The examples of C_2, O_3, and the F_2 potential energy curve indicate that an advantage to using W1BD is that the error in $\langle S^2 \rangle$ correlates with the magnitude of the error in energy, whereas W1(RO) loses accuracy without such a warning.

I. Introduction

Advances in computational methods and computer hardware have made possible the accurate ab initio calculation of energies for small- and medium-size molecules. Combined with Pople's model chemistry concept, these calculations provide reliable thermochemical predictions, which are a significant achievement of modern computational chemistry.[1]

* Corresponding author. E-mail: gpetersson@wesleyan.edu.

† Wesleyan University.

‡ Gaussian, Incorporated.

¶ Weizmann Institute of Science

§ Current address: Department of Physics, University of Connecticut, 2152 Hillside Road, U-3046, Storrs, CT 06269-3046

A "theoretical model chemistry" is a complete algorithm for the calculation of the energy of any molecular system.[2,3] It cannot involve subjective decisions in its application. It must be size extensive, giving energies that are additive for separated systems, so that the energy of every molecular species is uniquely defined. A model chemistry is useful if for some class of molecules it is the most accurate calculation we can afford to do. A number of "black-box" computational methods have emerged in the past two decades, through the development of composite theoretical model chemistry methods such as the complete basis set (CBS) model chemistries of Petersson et al.,[4−8] the Gaussian-*n* methods of Pople and co-workers,[9−12] the Weizmann-*n* (W*n*) theories of Martin and co-workers,[13−17] the high-accuracy extrapo-

lated ab initio thermochemistry (HEAT) protocol of the Gauss and Stanton groups,[18-20] and the correlation-consistent composite approach (ccCA) of Wilson and co-workers,[21,22] to name a few.

The Wn computational protocols of Martin and co-workers offer a sequence of models of increasing cost and accuracy,[23-26] the converging hierarchy of which currently ranges from W1 to W4.4. W1 theory, the most computationally accessible member of the evolving Wn family, is often employed as a benchmark for more approximate methods in the absence of accurate experimental data. Some of the key accomplishments of W1 theory are:

i. It achieves 0.44 kcal/mol mean absolute deviation (0.56 kcal/mol rms deviation) for 220 total atomization energies (TAEs), electron affinities (EAs), ionization potentials (IPs), and proton affinities (PAs) of the G2/97 set;

ii. As a properly defined theoretical model chemistry, it is applicable in a "black-box" manner by a nonspecialist; and

iii. It is completely devoid of parameters adjusted to fit experimental data.

The present study compares the performance of several unrestricted variants of W1 theory: unrestricted W1 (W1U), W1U with a spin contamination correction (W1Usc), and unrestricted Brueckner doubles W1 (W1BD). Standard W1 will be explicitly referred to as W1(RO) in this study, in order to avoid confusion in the comparison.

II. Restricted vs Unrestricted Reference

One of the major issues in computational studies of open-shell species is the selection of a restricted or an unrestricted reference wave function. Each has its well-known advantages and disadvantages. For example, restricted open-shell coupled cluster singles and doubles[27-31] with perturbative triples,[32-35] [ROCCSD(T)], dissociate to the wrong energy limit, while the unrestricted coupled cluster [UCCSD(T)] wave function dissociates to the correct energy limit, but the wave function becomes significantly spin contaminated as a bond dissociates. Several approaches have been used through the years to alleviate the spin contamination problem. For example, the spin correction term in W1Usc was introduced for this purpose.[36]

Whether one chooses a restricted or an unrestricted reference determinant, it is best to be consistent. Although it is common practice in the application of unrestricted methods to treat many unrestricted Hartree−Fock (UHF)-unstable species (e.g., F_2, alkenes, or polyenes) with a restricted reference, problems arise in *reactions* involving these "closed-shell" molecules. For example, the methyl C−H bond dissociation energy (BDE) of UHF-unstable 1-butene gives a radical product, $H_2C=CHCH_2\dot{C}H_2$, that would be described by an unrestricted determinant. Employing a restricted reference for 1-butene and an unrestricted reference for the 1-buten-4-yl radical would create consistency problems between reactant and product energies and, thus, generate spurious BDE contributions. No matter how distant a radical center is, an unrestricted treatment of the radical will induce spin polarization of the UHF-unstable π-bond. These problems are eliminated if one employs a restricted open-shell Hartree−Fock (ROHF) reference for the radical or a UHF reference for the parent alkene.

Another alternative to unrestricted Hartree–Fock (HF) and coupled cluster is the use of charge coupled device (CCD) calculations with Brueckner orbitals,[37-42] coined as "Brueckner doubles" (BD) by Handy et al.[41] This method employs a reference configuration, BDRef (from which the singles coefficients are zero for the coupled cluster wave function truncated at the doubles level), in place of the HF reference typically employed in the coupled cluster ansatz. The Brueckner condition implies that the corresponding reference determinants give the best overlap of a one-configuration approximation of the wave function with the exact wave function.[39] Such a reference was introduced by its namesake Brueckner in 1954, as part of a self-consistent method in nuclear physics,[37] and was first employed by Nesbet[38] for use in the configuration interaction (CI) expansion of a wave function. In the field of computational chemistry, the resurgence of interest in Brueckner orbitals in the past two decades was prompted by Chiles and Dykstra[40] and later by Handy and co-workers.[41] Similar studies that demonstrate the robustness of BD as an alternative to its coupled cluster counterpart[42-45] have been carried out over the years. Since the species considered in the previous paragraph (i.e., F_2 and alkenes) are not UBD-unstable, the problems of consistency between the reactant and the radical product are also eliminated by using a BD-based method.

III. Computational Details

A. Components of W1. The justification for the selection of each component calculation in W1(RO) has been presented in detail[14,15] and will not be repeated here. The W1U and W1BD methods retain the essential features of standard W1(RO) but replace the sequence of ROHF, ROCCSD, and ROCCSD(T) calculations with their spin-unrestricted counterparts for W1U for calculations involving open-shell species and with the BDRef, BD, and BD(T)[46] sequence for W1BD theory. All calculations were carried out with Gaussian 09,[47] which uses the ROCCSD(T) definition of UCCSD(T) in a basis of semicanonicalized ROHF orbitals,[35,48] with the semicanonicalization carried out before the integral transformation. The triples contribution to BD(T) is evaluated with semicanonical Brueckner orbitals.

The UB3LYP/cc-pVTZ+1d geometry optimization and frequency calculations are retained from the original W1(RO) implementation. Optimized geometries and energy components for all species are available in the accompanying "geometries.txt" and "components.pdf" files as Supporting Information. In the original implementation of W1(RO), scalar relativistic corrections were obtained with the Martin−Taylor small (MTsmall) basis sets[49,50] as one-electron Darwin and mass−velocity terms[51,52] from averaged coupled pair wave functions,[53] while corresponding components in this study were obtained with Douglas−Kroll−Hess (DKH) second-order scalar relativistic calculations[54-58] using a Gaussian nuclear model[59] (also employing the MTsmall basis sets). Spin−orbit calculations were taken directly from ref 14. The spin correction term in W1Usc,

Variations of W1 Theory

J. Chem. Theory Comput., Vol. 5, No. 10, 2009 **2689**

$$\Delta E(\text{spin}) = -6.28 m E_h \times \Delta\langle S^2\rangle_{\text{UHF}} \qquad (1)$$

minimizes the difference between ROCCSD(T) and UCCSD(T) energies for some highly spin-contaminated species.[36]

B. Implementation of Brueckner Doubles. The BD algorithm employed throughout this study involves macro-iterations to update the orbitals, wherein each macroiteration involves an integral transformation and a CCD calculation. Thus, BD calculations appear, at first glance, to be significantly more expensive than the corresponding CCSD calculations. In practice, however, W1BD calculations are only slightly more expensive than the corresponding ones in W1U or W1(RO). The two main reasons for this are as follows: i. Since W1 involves a sequence of calculations, the converged orbitals and amplitudes from each step can be used to start the next. As a result, most of the extra CC iterations required are performed in the first BD(T) calculation, which uses the smallest basis set in the sequence of calculations. For the largest basis set (i.e., the BD/aug-cc-pVQZ+2df step), typically only two or three BD macroiterations are required, and the second and later macroiterations require only a few CC iterations. ii. Calculations involving even three heavy atoms spend a significant amount of time in the (T) steps, (the only $O(N^7)$ parts of W1), and calculations on systems having four or more heavy atoms are dominated by these steps. The triples calculations have the same cost for CCSD(T) and BD(T).

The result is that the extra cost of doing W1BD over W1U or W1(RO) is in the range of 20−40% for two heavy-atom systems, about 20% for three heavy-atom systems, and going down further to less than 20% for systems with more than three heavy atoms and/or those involving second-row atoms and beyond. (W1 calculations involving two or more second-row or heavier atoms are dominated by the last calculation, which includes triples and correlates core electrons. As noted previously, the triples part of this step has the same cost for CCSD(T) and BD(T), and the BD iterations converge quickly since they use the orbitals, amplitudes, and basis set from the preceding frozen-core calculation as an initial guess.)

All but one of the correlation energy calculations in W1 use the frozen-core (FC) approximation, which substantially speeds up the calculations as compared to correlating all electrons (Full). Previous papers on the BD method have not discussed the issue of frozen-core with this model, and some programs, such as Gaussian 03, freeze the core orbitals at their initial values during BD iterations. This means that the converged BD(FC) energy varies with different initial guess orbitals. For example, in CN, the UHF solution is highly spin contaminated, while the BD(Full) reference determinant has very minimal spin contamination. Hence, a BD(FC) calculation starting from the UHF orbitals will freeze a core that is more spin polarized than that of a BD(Full) calculation and produce a different energy than, say, a BD(FC) calculation that starts with (also much less spin contaminated) B3LYP orbitals. The consistent approach to frozen-core BD calculations is to update all orbitals, including the core, during the BD iterations but to restrict the amplitudes in the CCD calculations to those involving only

valence orbitals. The results are then independent of the initial orbitals, and the core is spin polarized only to the extent that the BD valence is. This approach is used in all BD results reported here.[47]

IV. Results and Discussion

Since the four flavors of W1 theory are virtually the same for closed-shell species, we shall focus on their performance for open-shell systems. The extent to which the ROHF and UHF reference determinants differ can be measured by the error in $\langle S^2\rangle$ for the reference configuration.

A. Spin-Contaminated Species. The restricted and unrestricted variations of W1 theory have been evaluated with bond dissociation enthalpies (BDEs), EAs, and IPs of some radicals and biradicals (Table 1). The sample of 11 reactions was selected on the basis of sizable errors in $\langle S^2\rangle_{\text{UHF}}$ and the availability of reliable experimental data.[60−67]

The rms deviation from experiment (Table 1) is not surprisingly the largest for W1U (1.3 ± 0.3 kcal/mol), in the absence of any rectification of the spin contamination problem. The spin correction in W1Usc indeed reduces the rms error to 0.6 ± 0.3 kcal/mol but is not always reliable. For example, $\Delta E(\text{spin})$ in eq 1 overestimates the correction for the first C−H bond dissociation in acetylene by 0.8 ± 0.02 kcal/mol and worsens the deviation with experiment of the first C−H bond dissociation of propene by 0.8 ± 0.4 kcal/mol (Table 1). The rms deviations for W1U, W1Usc, W1BD, and W1(RO) are 1.3 ± 0.3, 0.6 ± 0.3, 0.8 ± 0.3, and 0.6 ± 0.3 kcal/mol, respectively, demonstrating the comparable accuracy of W1Usc, W1BD, and W1(RO) in handling these UHF spin-contaminated species. Note that both W1BD and W1(RO) attain these results in the *absence* of the empirical spin correction in W1Usc.

The following interesting observations are made for the three most spin-contaminated species of the G2/97 test sets, C_2, O_3, and CS^+, selected on the basis of $\Delta\langle S^2\rangle_{\text{UHF}}$ values greater than 0.6:[68]

i. First is the existence of multiple solutions, which complicates the use of "black-box" methods. To compound the problem of multiple solutions for both restricted and unrestricted versions of both HF and Brueckner determinants for C_2, the relative energies of the solutions are switched between the HF vs the CCSD(T) levels of theory for both restricted and unrestricted reference configurations. That a single reference method produces several solutions comes as no surprise in these cases, since C_2 and O_3 are known to possess a significant multiconfigurational character in their wave functions. If there are indications of near degeneracies of configurations (such as a large error in $\langle S^2\rangle$ for UHF or UBDRef or a negative eigenvalue for a virtual orbital as in neutral C_2), then it is necessary to explore multiple solutions in addition to checking for the correct number of imaginary frequencies. A more thorough discussion is presented as Supporting Information (see "Problem_species.pdf" file), which includes an example of solutions crossing between the BD vs BD(T) levels of theory.

ii. Second, the reactions involving these severely spin-contaminated systems indicate that $\Delta\langle S^2\rangle_{\text{UHF}}$ values do not correlate as well with the energy error in a W1U calculation

Table 1. Deviations (Experiment−theory) of Calculated BDEs and adiabatic IPs and EAs from Experiment of Selected Spin-Contaminated Species, in kcal/mol

species[a]	reaction	W1U Δ⟨S²⟩		W1BD Δ⟨S²⟩		deviation (experiment−theory)				experiment
		reactant	product	reactant	product	W1U	W1Usc	W1BD	W1RO[b]	
				σ-Radicals						
BDE ΔH_{298}	H−CN → H + ·C≡N	0.00	0.37	0.00	0.01	−1.9	−0.4	−1.0	−0.8	126.29 ± 0.2[c]
	H−C≡CH → H + ·C≡CH	0.00	0.35	0.00	0.03	−0.6	0.8	0.0	0.1	133.46 ± 0.02[d]
	H−CH=CH₂ → H + ·CH=CH₂	0.00	0.18	0.00	0.01	−0.4	0.3	−0.1	−0.1	110.71 ± 0.6[c]
IP ΔE_0	C=O → e⁻ + C=O⁺	0.00	0.21	0.00	0.02	−0.9	−0.1	−0.6	−0.2	323.17 ± 0.01[e]
	N≡C−C≡N → e⁻ + N≡C−C≡N⁺	0.00	0.35	0.00	0.03	−1.8	−0.4	−1.3	−1.0	308.42 ± 0.2[f]
EA ΔE_0	CH₂=C=CH⁻ → e⁻ + CH₂=C=CH	0.00	0.21	0.00	0.03	−0.7	0.1	−0.4	−0.3	20.59 ± 0.1[f]
	C=N → e⁻ + C=N	0.00	0.37	0.00	0.01	−1.8	−0.3	−1.0	−0.7	89.06 ± 0.1[e]
				π-Radicals						
BDE ΔH_{298}	HCH₂−CH=CH₂ → H + ·CH₂−CH=CH₂	0.00	0.20	0.00	0.04	0.5	1.3	0.8	0.9	88.79 ± 0.4[g]
EA ΔE_0	CH₂CHCH₂⁻ → e⁻ + CH₂CHCH₂	0.00	0.20	0.00	0.04	−0.5	0.3	−0.3	−0.1	11.09 ± 0.2[f]
				Singlet Biradicals						
BDE ΔH_{298}	F−F → F + F	0.30	0.01	0.00	0.01	1.8	0.6	1.1	1.0	38.00 ± 0.2[f]
				Triplet Biradicals						
EA ΔE_0	H−C−C≡N⁻ → e⁻ + H−C−C≡N	0.12	0.36	0.02	0.07	−0.5	0.5	−0.3	−0.2	46.20 ± 0.3[h]
MAD						1.1	0.5	0.6	0.5	± 0.2
rms						1.3	0.6	0.8	0.6	± 0.3
LD						−2.1	1.3	−1.3	−1.0	

[a] Geometries are optimized at the UB3LYP/cc-pVTZ+1d level and available as Supporting Information. [b] W1(RO) energies were calculated with Gaussian 09 (ref 47). [c] ref 60. [d] ref 61. [e] ref 62. [f] ref 63. [g] ref 64. [h] ref 65.

as $\Delta\langle S^2\rangle_{\text{UBDRef}}$ values do for W1BD errors (vide infra). A sizable $\Delta\langle S^2\rangle_{\text{UBDRef}}$ value appears to be a useful warning of when to be skeptical of W1BD results (refer to Supporting Information Table S−III and discussion on pages 11−12 of "Problem_species.pdf" file for details).

B. G2/97 Test Set. The G2−1[9−11] and the G2−2[69,70] test sets, collectively referred to as the G2/97 data set of Curtiss et al. were employed to calibrate the accuracy of W1(RO) for EAs, IPs, and PAs, while the G2−1 test set and a subset of the G2−2 data set (26 out of 93) of heats of formation were used in the calibration of total atomization energies (TAEs).[14] The selection of TAEs, EAs, IPs, and PAs is retained in assessing the performance of W1U, W1Usc, and W1BD, in order to facilitate comparisons with W1(RO) values in the literature.[14,15] A thorough discussion on the notable discrepancies with experiment for some problematic cases has already been presented by one of the authors.[14] A comprehensive breakdown of the G2−1 and the G2−2 TAE, EA, IP, and PA energetic components and error statistics for W1U, W1Usc, W1BD, and W1(RO) are available as Supporting Information. The error analyses for 220 reactions from the G2/97 data set are summarized in Table 2. The reported uncertainties in the deviations from experiment represent the uncertainties in the experimental data.[36]

The overall G2/97 rms errors for W1U, W1Usc, W1BD, and W1(RO) (excluding C₂ and O₃) are 0.65, 0.57, 0.62, and 0.57 ± 0.48 kcal/mol, respectively. Comparison of the calculated energies with experiment is rather problematic due to the large experimental uncertainties (± 0.65 for TAEs, ± 0.32 for EAs, and ± 0.35 kcal/mol for IPs, Table 2). The experimental uncertainties are of greater magnitude than the differences in rms errors between the methods themselves, making W1 variants virtually indistinguishable from one another for the G2/97 test set (Table 2).

C. F₂ Potential Energy Curve. Although the W*n* methods are intended for the thermochemistry of molecular systems at equilibrium geometries, the potential energy curve for the F₂ $^1\Sigma_g^+$ ground-state dissociation provides insight into the differences between the UCCSD(T), the spin-corrected UCCSD(T), the UBD(T), and the ROCCSD(T) levels of theory. Deviations of the potential energy curves from the exact solution in the cc-pVDZ basis are shown in Figure 1. A constant geometry-independent shift of the energy from the full configuration interaction (FCI) reference would display as zero error throughout the potential energy curve.

Neither restricted nor unrestricted CCSD(T) give a reliable description of bond-breaking reactions. These qualitative features of restricted and unrestricted methods along a potential energy curve for bond dissociation are well-known.[71] The spin correction successfully reduces the UCCSD(T) error in energy but shows fluctuation and dissociates improperly, reminiscent of problems encountered with a restricted reference (Figure 1). Furthermore, Ochterski et al. pointed out that the spin contamination error increases linearly with $\Delta\langle S^2\rangle_{\text{UHF}}$ for $\Delta\langle S^2\rangle_{\text{UHF}}$ less than 0.6.[68] This is consistent with our observations for C₂, O₃, and CS⁺ (see "Problem_species.pdf" file given as Supporting Information) and strongly suggests that eq 1 is also not applicable for $\Delta\langle S^2\rangle_{\text{UHF}} > 0.6$ on the F₂ potential energy curve ($\Delta\langle S^2\rangle_{\text{UHF}} = 0.6$ is marked by the vertical dashed line at 1.5 Å in Figure 1).

The Brueckner doubles approach possesses compensating advantages over both the RHF- and the UHF-based methods. First, there is very good agreement between the UBD(T) and the ROCCSD(T) potential energy curves in the vicinity of the equilibrium geometry, where UCCSD(T) is already contaminated with unwanted contributions from higher spin multiplicities. This efficacy of Brueckner orbitals in reducing spin contamination over a wider range of geometries compared to UHF-based methods is also well documented.[72] Furthermore, the Brueckner doubles curve is practically indistinguishable from that of ROCCSD(T), up to the point where the UBD(T) energy errors exhibit extreme sensitivity

Variations of W1 Theory

J. Chem. Theory Comput., Vol. 5, No. 10, 2009 **2691**

Table 2. Error Analysis (kcal/mol) for TAEs (298 K), EAs, IPs, and PAs of Select Molecules in the G2/97 Test Set for the Different Variations of W1 Theory[a]

G2/97 subset[b]	method	MAD	rms	LD	species/LD
TAE$_{298K}$ (81)[c]					
	W1U	0.60 ± 0.41	0.75 ± 0.65	1.72 ± 0.10	ClNO
	W1Usc	0.56 ± 0.41	0.70 ± 0.65	1.79 ± 0.10	ClNO
	W1BD	0.61 ± 0.41	0.77 ± 0.65	1.97 ± 0.10	ClNO
	W1(RO)	0.55 ± 0.41	0.67 ± 0.65	1.75 ± 0.10	ClNO
EA (55)[d]					
	W1U	0.46 ± 0.22	0.60 ± 0.32	−1.96 ± 0.60	CH$_2$NC
	W1Usc	0.41 ± 0.22	0.53 ± 0.32	−1.64 ± 0.60	CH$_2$NC
	W1BD	0.43 ± 0.22	0.55 ± 0.32	−1.81 ± 0.60	CH$_2$NC
	W1(RO)	0.43 ± 0.22	0.53 ± 0.32	−1.74 ± 0.60	CH$_2$NC
IP (76)[e,f]					
	W1U	0.41 ± 0.16	0.57 ± 0.35	−2.10 ± 0.23	CS
	W1Usc	0.33 ± 0.16	0.42 ± 0.35	1.39 ± 0.05	P$_2$
	W1BD	0.37 ± 0.16	0.49 ± 0.35	−1.48 ± 0.18	N$_2$ ($^2\Sigma$ cation)
	W1(RO)	0.35 ± 0.16	0.46 ± 0.35	1.42 ± 0.05	P$_2$
PA (8)[g]					
	W1U	0.42	0.48	−0.83	C$_2$H$_2$
	W1BD	0.42	0.49	−0.88	C$_2$H$_2$
	W1(RO)	0.43	0.49	−0.83	C$_2$H$_2$
Total (220)					
	W1U	0.49 ± 0.27	0.65 ± 0.48		
	W1Usc	0.44 ± 0.27	0.57 ± 0.48		
	W1BD	0.48 ± 0.27	0.62 ± 0.48		
	W1(RO)	0.44 ± 0.27	0.57 ± 0.48		

[a] C$_2$ and O$_3$ are excluded in all statistics. Optimized geometries, total energies, and energy changes of species and reactions in the G2/97 sets are given in the Supporting Information "geometries.txt", "components.pdf", and "Test_set.pdf" files, respectively. The uncertainties in the deviations from experiment represent the uncertainties in the experimental data (see "Test_set.pdf"). [b] The number of reactions considered in each subset is indicated as the number in the parentheses in the first column. [c] See Supporting Information Tables S−III and S−IV for individual TAEs. [d] See Supporting Information Tables S−V and S−VI for individual EAs. [e] See Supporting Information Tables S−VII and S−VIII for individual IPs. [f] Excludes CN ($^3\Pi$), CN ($^1\Sigma^+$), B$_2$H$_4$, sec−C$_3$H$_7$, and Si2H$_6$ (see ref 14). [g] See Supporting Information Table S−IX for individual PAs. Calculated proton affinities are considered converged at the W1 level (ref 14), agreeing well with experiment.
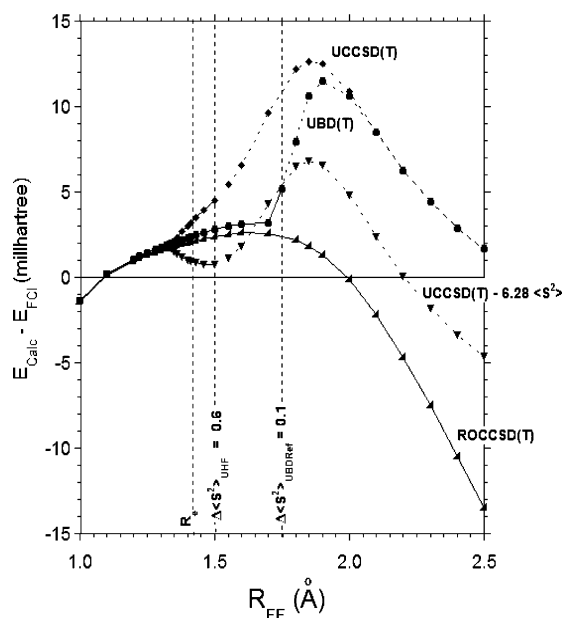
Figure 1. The error (mE_h) in the UCCSD(T), the spin-corrected UCCSD(T), the UBD(T), and the ROCCSD(T)/cc-pVDZ potential energy curves for the F$_2$ $^1\Sigma_g^+$ ground state. W1U/W1Usc and W1BD results beyond $\Delta\langle S^2\rangle_{UHF} = 0.6$ (1.5 Å) and $\Delta\langle S^2\rangle_{UBDRef} = 0.1$ (1.75 Å), respectively, (indicated by dashed rather than solid curves) are considered unreliable. Spin contamination errors cease to have a linear relationship with energetic errors beyond these cut-offs.

to geometry changes and the restricted coupled cluster begins to break down (1.2R$_e$ or 1.75 Å in Figure 1). This RBD(T)/ UBD(T) instability point is an unambiguous demarcation between the absence and the onset of significant BD energy errors, holding promise as a diagnostic tool for assessing the reliability of BD calculations. The good correlation between the W1BD $\Delta\langle S^2\rangle$ values and the energy errors is consistent with the results for CS$^+$ and O$_3$. The potential energy curve for the restricted wave function proceeds toward the wrong energy limit without such a warning.

V. Conclusions

The unrestricted flavors of W1 theory presented in this study are viable alternatives to W1(RO). W1U benefits significantly from a spin correction term for the 11 spin-contaminated reactions (Table 1), reducing the rms error from 1.3 to 0.6 ± 0.4 kcal/mol. The accuracy of the W1Usc, the W1BD, and the W1(RO) theories are indistinguishable from one another when evaluated with the moderately spin-contaminated data set (Table 1) and the 220 total atomization energies, electron affinities, ionization potentials, and proton affinities in the G2/97 test set (Table 2). Unlike W1U, the W1BD method demonstrates good correlation between the $\Delta\langle S^2\rangle_{UBDRef}$ and the energetic errors and, thus, gives a clear indication of the onset of energetic errors associated with spin contamination. W1(RO) gives no such straightforward warning when its single determinant reference wave function is inadequate. We, therefore, recommend the use

of W1BD, rather than W1Usc, as an unrestricted alternative to W1(RO) in studies of potentially pathological cases. Multiple solutions were obtained for both the restricted and the unrestricted methods for C_2 and O_3, demonstrating the need for exploring multiple solutions with single-reference wave functions even in the "black-box" context. Of course, testing for the correct number of imaginary vibrational frequencies is always necessary.

Supporting Information Available: Optimized geometries, energy components, and chemical energy differences for all species in this study, as well as additional discussion on the problematic species C_2, O_3, and CS^+, are available in the accompanying "geometries.txt", "components.pdf", "Test-_set.pdf", and "Problem_species.pdf" files, respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) For recent reviews on accurate computational thermochemistry, see for example:Helgaker, T.; Klopper, W.; Halkier, A.; Bak, K. L.; Jørgensen, P. Olsen, J. In *Quantum-Mechanical Prediction of Thermochemical Data*, Cioslowski, J., Ed.; Kluwer Academic: Dordrecht, The Netherlands, 2001; pp. 1−30; Martin, J. M. L.; Parthiban, S. In *Quantum-Mechanical Prediction of Thermochemical Data*, Cioslowski, J., Ed.; Kluwer Academic: Dordrecht, The Netherlands, 2001; pp. 31−65; Raghavachari, K.; Curtiss, L. A. In *Quantum-Mechanical Prediction of Thermochemical Data*, Cioslowski, J., Ed.; Kluwer Academic: Dordrecht, The Netherlands, 2001; pp. 67−98; Petersson, G. A. In *Quantum-Mechanical Prediction of Thermochemical Data*, Cioslowski, J., Ed.; Kluwer Academic: Dordrecht, The Netherlands, 2001; pp. 99−130; Henry, D. J.; Radom, L. In *Quantum-Mechanical Prediction of Thermochemical Data*, Cioslowski, J., Ed.; Kluwer Academic: Dordrecht, The Netherlands, 2001; pp. 161−197.

(2) Pople, J. A. Theoretical Models for Chemistry. *Proceedings of the Summer Research Conference on Theoretical Chemistry, Energy Structure and Reactivity*, 1973; p 51.

(3) (a) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem. Symp.* **1976**, *10*, 1−19. (b) Krishnan, R.; Pople, J. A. *Int. J. Quantum Chem.* **1978**, *14*, 91−100.

(4) Petersson, G. A.; Bennett, A.; Tensfeldt, T. G.; Al-Laham, M. A.; Shirley, W. A.; Mantzaris, J. *J. Chem. Phys.* **1988**, *89*, 2193−2218.

(5) Montgomery, J. A., Jr.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys.* **1994**, *101*, 5900−5909.

(6) Ochterski, J. W.; Petersson, G. A.; Montgomery, J. A., Jr. *J. Chem. Phys.* **1996**, *104*, 2598−2619.

(7) Montgomery, J. A., Jr.; Frisch, M. J.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys.* **1999**, *110*, 2822−2827.

(8) Montgomery, J. A., Jr.; Frisch, M. J.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys.* **2000**, *112*, 6532−6542.

(9) Pople, J. A.; Head-Gordon, M.; Fox, D. J.; Raghavachari, K.; Curtiss, L. A. *J. Chem. Phys.* **1989**, *90*, 5622−5629.

(10) Curtiss, L. A.; Jones, C.; Trucks, G. W.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1990**, *93*, 2537−2545.

(11) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221−7230.

(12) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764−7776.

(13) Martin, J. M. L.; Oliveira, G. D. *J. Chem. Phys.* **1999**, *111*, 1843−1856.

(14) Parthiban, S.; Martin, J. M. L. *J. Chem. Phys.* **2001**, *114*, 6014−6029.

(15) Martin, J. M. L.; Parthiban, S. In *W1 and W2 theory and their variants: thermochemistry in the kJ/mol accuracy range*; Cioslowski, J., Ed.; Kluwer Academic: Dordrecht, The Netherlands, 2001; pp 1−30.

(16) Boese, A. D.; Oren, M.; Atasoylu, O.; Martin, J. M. L.; Kállay, M.; Gauss, J. *J. Chem. Phys.* **2004**, *120*, 4129−4141.

(17) Karton, A.; Rabinovich, E.; Martin, J. M. L.; Ruscic, B. *J. Chem. Phys.* **2006**, *125*, 144108−1144108−17.

(18) Tajti, A.; Szalay, P. G.; Császár, A. G.; Kállay, M.; Gauss, J.; Valeev, E. F.; Flowers, B. A.; Vázquez, J.; Stanton, J. F. *J. Chem. Phys.* **2004**, *121*, 11599−11613.

(19) Bomble, Y. J.; Vázquez, J.; Kállay, M.; Michauk, C.; Szalay, P. G.; Császár, A. G.; Gauss, J.; Stanton, J. F. *J. Chem. Phys.* **2006**, *125*, 064108−1−064108−8.

(20) Harding, M. E.; Vázquez, J.; Ruscic, B.; Wilson, A. K.; Gauss, J.; Stanton, J. F. *J. Chem. Phys.* **2008**, *128*, 114111−1114111−15.

(21) DeYonker, N. J.; Cundari, T. R.; Wilson, A. K. *J. Chem. Phys.* **2006**, *124*, 11410−1114104−17.

(22) DeYonker, N. J.; Grimes, T.; Yockel, S.; Dinescu, A.; Mintz, B.; Cundari, T. R.; Wilson, A. K. *J. Chem. Phys.* **2006**, *125*, 104111−1104111−15.

(23) Karton, A.; Ruscic, B.; Martin, J. M. L. *J. Mol. Struct. (THEOCHEM)* **2007**, *811*, 345−353.

(24) Karton, A.; Taylor, P. R.; Martin, J. M. L. *J. Chem. Phys.* **2007**, *127*, 064104−1−064104−11.

(25) Karton, A.; Martin, J. M. L. *J. Phys. Chem. A* **2007**, *111*, 5936−5944.

(26) Karton, A.; Martin, J. M. L. *Mol. Phys.* **2007**, *105*, 2499−2505.

(27) Roothaan, C. C. J. *Rev. Mod. Phys.* **1951**, *23*, 69−89.

(28) Bartlett, R. J.; Purvis, G. D. *Int. J. Quantum Chem.* **1978**, *14*, 561−581.

(29) Rittby, M.; Bartlett, R. *J. Phys. Chem.* **1988**, *92*, 3033−3036.

(30) Lauderdale, W. J.; Stanton, J. F.; Gauss, J.; Watts, J. D.; Bartlett, R. J. *Chem. Phys. Lett.* **1991**, *187*, 21−28.

(31) Bartlett, R. J. In *Coupled-Cluster Theory: An Overview of Recent Developments*; Yarkony, D. R., Ed.; World Scientific, Singapore, 1995; pp 1047−1131.

(32) Purvis, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910−1918.

(33) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968−5975.

(34) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479−483.

Variations of W1 Theory

J. Chem. Theory Comput., Vol. 5, No. 10, 2009 **2693**

(35) Watts, J. D.; Gauss, J.; Bartlett, R. J. *J. Chem. Phys.* **1993**, *98*, 8718–8733.

(36) Wood, G. P. F.; Radom, L.; Petersson, G. A.; Barnes, E. C.; Frisch, M. J.; Montgomery, J. A., Jr. *J. Chem. Phys.* **2006**, *125*, 094106−1−094106−16.

(37) Brueckner, K. A. *Phys. Rev.* **1954**, *96*, 508–516.

(38) Nesbet, R. K. *Phys. Rev.* **1958**, *109*, 1632–1638.

(39) Larsson, S.; Smith, V. *Phys. Rev.* **1969**, *178*, 137–152.

(40) Chiles, R. A.; Dykstra, C. E. *J. Chem. Phys.* **1981**, *74*, 4544–4556.

(41) Handy, N. C.; Pople, J. A.; Head-Gordon, M.; Raghavachari, K.; Trucks, G. W. *Chem. Phys. Lett.* **1989**, *164*, 185–192.

(42) Stanton, J. F.; Gauss, J.; Bartlett, R. J. *J. Chem. Phys.* **1992**, *97*, 5554–5559.

(43) Hampel, C.; Peterson, K. A.; Werner, H. J. *Chem. Phys. Lett.* **1992**, *190*, 1–12.

(44) Barnes, L. A.; Lindh, R. *Chem. Phys. Lett.* **1994**, *223*, 207–214.

(45) Watts, J. D.; Bartlett, R. J. *Int. J. Quantum Chem.* **1994**, *52*, 195–203.

(46) Scuseria, G. E. *Chem. Phys. Lett.* **1994**, *226*, 251–256.

(47) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M. Knox, J. E. Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09, Revision A.2,* Gaussian, Inc.: Wallingford, CT, 2009.

(48) Knowles, P. J.; Andrews, J. S.; Amos, R. D.; Handy, N. C.; Pople, J. A. *Chem. Phys. Lett.* **1991**, *186*, 130–136.

(49) Martin, J. M. L.; Taylor, P. R. *Chem. Phys. Lett.* **1994**, *225*, 473–479.

(50) Martin, J. M. L. *Chem. Phys. Lett.* **1995**, *242*, 343–350.

(51) Cowan, R. D.; Griffin, D. C. *J. Opt. Soc. Am.* **1976**, *66*, 1010–1014.

(52) Martin, R. L. *J. Phys. Chem.* **1983**, *87*, 750–754.

(53) Gdanitz, R. J.; Ahlrichs, R. *Chem. Phys. Lett.* **1988**, *143*, 413–420.

(54) Douglas, M.; Kroll, N. M. *Ann. Phys.* **1974**, *82*, 89–155.

(55) Hess, B. A. *Phys. Rev. A* **1985**, *32*, 756–763.

(56) Hess, B. A. *Phys. Rev. A* **1986**, *33*, 3742–3748.

(57) Barysz, M.; Sadlej, A. J. *J. Mol. Struct. (THEOCHEM)* **2001**, *573*, 181–200.

(58) de Jong, W. A.; Harrison, R. J.; Dixon, D. A. *J. Chem. Phys.* **2001**, *114*, 48–53.

(59) Visscher, L.; Dyall, K. G. *At. Data and Nucl. Data Tables* **1997**, *67*, 207–224.

(60) Ervin, K. M.; DeTuri, V. F. *J. Phys. Chem. A* **2002**, *106*, 9947–9956.

(61) Mordaunt, D. H.; Ashfold, M. N. R. *J. Chem. Phys.* **1994**, *101*, 2630–2631.

(62) Afeefy, H. Y.; Liebman, J. F.; Stein, S. E. NIST Chemistry Webbook. In *NIST Standard Reference Database*; Mallard, W. G., Linstrom, P. J., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, 1998; Vol. 69.

(63) *CODATA Key Values for Thermodynamics*; Cox, J. D., Wagman, D. D., Medvedev, V. A., Eds.; Hemisphere Pub. Corp: New York, 1989.

(64) Ellison, G. B.; Davico, G. E.; Bierbaum, V. M.; DePuy, C. H. *Int. J. Mass Spectrom. Ion Process.* **1996**, *156*, 109–131.

(65) Nimlos, M. R.; Davico, G.; Geise, C. M.; Wenthold, P. G.; Lineberger, W. C.; Blanksby, S. R.; Hadad, C. M.; Petersson, G. A.; Ellison, G. B. *J. Chem. Phys.* **2002**, *117*, 4323–4339.

(66) Blanksby, S. J.; Ellison, G. B. *Acc. Chem. Res.* **2003**, *36*, 255–263.

(67) Wenthold, P. G.; Squires, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 6401–6412.

(68) Ochterski, J. W.; Petersson, G. A.; Montgomery, J. A., Jr. *J. Chem. Phys.* **1995**, *104*, 2598–2619.

(69) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **1997**, *106*, 1063–1079.

(70) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 42–55.

(71) Schlegel, H. B. *J. Chem. Phys.* **1986**, *84*, 4530–4534.

(72) See, for example Watts, J. D.; Bartlett, R. J. *Int. J. Quantum Chem.* **1994**, *52*, 195–203.

(73) Catlett, C. In *TeraGrid: Analysis of Organization, System Architecture, and Middleware Enabling New Types of Applications*; Grandinetti, L., Ed.; Advances in Parallel Computing Series; IOS Press: Amsterdam, The Netherlands, 2007.