Scaled higher-order correlation energies: In pursuit of the complete basis set full configuration interaction limit

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A simple multiplicative approach is presented for approximating the full configuration interaction (FCI) limit at the complete basis set limit from the small basis set FCI and coupled cluster [most notably CCSD(T) and CCSDT] calculations. The proposed scaled higher-order correlation (SHOC) correction scheme is demonstrated to extrapolate CCSD(T) and CCSDT correlation energies for BH and AlH to the FCI limit with remarkable accuracy, and to correct the dissociation energies of $[CN,C_2,N_2]$ computed at the CCSD(T) and CCSDT levels by $[+1.4, +2.3, +1.5]$ kcal/mol, respectively, bringing them in much closer agreement with the best experimental values. The approach is also well suited for the generation of accurate potential energy hypersurfaces. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1351882]

I. INTRODUCTION

Recent developments in computer technology and electronic structure theory have facilitated the high accuracy computations necessary for the theoretical determination of many thermochemical properties. Theory is now capable of obtaining near chemical accuracy (± 1 kcal/mol) for the energies of small and medium sized molecular systems. The computational errors in today's approximate solutions to the time-independent nonrelativistic electronic Schrödinger equation result mainly from the truncation of the atomic orbital (AO) one-electron basis and the truncation of the *n*-electron basis of all Slater determinants that constitute the full configuration interaction (FCI) wave function. Techniques which aim to achieve chemical accuracy for energetic quantities include the Gaussian-X,[1–4] the complete basis set (CBS),[5,6] and the W-X (Ref. 7) model chemistries. These approaches may rely on empirical parameters which are optimized to minimize the thermochemical errors for a given training set of molecules. An alternative parameter-free method is the focal-point[8,9] approach, which seeks to achieve the complete one-electron basis set (CBS) and *n*-electron limit by performing a series of electronic structure computations employing convergent basis sets and correlation methods. The previously mentioned model chemistries are designed to represent approximations to the focal-point approach, and are therefore more computationally efficient but may be less accurate for certain troublesome cases. Furthermore, the focal-point approach allows efficient estimation of the remaining computational error[9–11] for the given problem, while in the case of model chemistries one needs to rely on average error estimates. Of particular interest here, the focal-point scheme assumes that the correlation energy increments have rather different convergence characteristics, with the higher-order correlation (HOC) increments showing diminishing basis set dependence. This assumption has allowed efficient estimation of molecular barriers at the CBS FCI limit.[9–11]

The determination of the complete one-electron basis set limit has received considerable attention in recent years.[7,9–17] Efficient formulas are now available which provide an estimate of the CBS energy limit from calculations employing the systematically constructed families of basis sets [e.g., the correlation-consistent (cc) basis sets of Dunning and co-workers[18]]. These studies clearly show that different levels of electronic structure theory follow distinct basis set extrapolation patterns; most notably, Hartree–Fock energies converge almost exponentially toward the CBS limit,[13,15] while correlation energies seem to follow an X^{-3} dependence,[9,12] where X is the cardinal number of the cc basis sets.[18] In certain cases, such as the relativistic two-electron Darwin correction,[16] the correlation contribution to the energy scales as slowly as X^{-1}.

Of equal importance is the determination of the FCI limit in a given one-particle basis from approximate *n*-electron methods. Numerous studies have shown the diminishing energy contribution of higher excitation levels. Coupled-cluster (CC) methods[19] including triple excitations[20–22] or configuration interaction with quadruple substitutions[23] typically provide accurate approximations to the FCI energy. Of these approaches CCSD(T) (Ref. 20) has proven to be the most reliable and affordable for predicting high-quality energies and properties.[24] To achieve chemical accuracy it is necessary to consider the typically neglected energy contributions from higher-order excitations, as well as special relativity (including spin–orbit effects), core-valence correlation, and nonadiabatic effects.[8,9,25] Feller and Sordo[26–28] have recently studied the HOC effects neglected in the CCSD(T) approach for a series of diatomic molecules.

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TABLE I. SHOC correction factors and correlation energy increments (mE_h) from valence-only CC and CI series for $X\ ^1\Sigma^+$ BH.[a,b]

Basis set, RHF/E_h	CI2	CI3	CCSD	CCSD(T)	CCSD(TQ)	CCSDT	FCI
cc-pVDZ(19)	1.051 869	1.031 209	1.020 865	1.005 380	1.000 684	1.000 758	1.000 000
−25.125 334	−85.379	−87.089	−87.972	−89.327	−89.746	−89.739	−89.807
cc-pVTZ(44)	1.057 290	1.031 884	1.025 895	1.005 172	1.000 863	1.000 848	1.000 000
−25.129 926	−95.724	−98.081	−98.654	−100.688	−101.121	−101.123	−101.208
cc-pVQZ(85)	1.057 936	1.031 735	1.026 778	1.004 856	1.000 975	1.000 864	1.000 000
−25.131 287	−98.570	−101.073	−101.561	−103.777	−104.179	−104.191	−104.281
cc-pV5Z(146)	1.057 992	1.031 622	1.026 975	1.004 620	–	1.000 857	1.000 000
−25.131 548	−99.384	−101.925	−102.386	−104.664	–	−105.058	−105.148
aug-cc-pVDZ(32)	1.054 303	1.031 764	1.022 687	1.005 740	1.000 812	1.000 849	1.000 000
−25.126 427	−87.1315	−89.035	−89.825	−91.339	−91.789	−91.785	−91.863
aug-cc-pVTZ(69)	1.057 915	1.031 887	1.026 500	1.005 254	1.000 943	1.000 876	1.000 000
−25.130 193	−96.243	−98.670	−99.188	−101.285	−101.721	−101.728	−101.817
aug-cc-pVQZ(126)	1.058 050	1.031 692	1.026 933	1.004 814	1.000 996	1.000 863	1.000 000
−25.131 262	−98.749	−101.272	−101.741	−103.980	−104.377	−104.391	−104.481

[a]The HF energies are reported below each basis set. For each basis set the total number of contracted Gaussian functions is given in parentheses. The correlation energy increments are always taken as the difference between the given level of correlation treatment [e.g., CI2 (CISD) or CI3 (CISDT)] and the HF level.

[b]All energies were computed at the aug-cc-pVQZ CCSD(T) (FC) optimized geometry of $r_{BH}=1.233\ 33$ Å taken from Ref. 42.

Their comparisons to experimental, and estimated FCI data with basis sets of quadruple-ζ quality, indicate that the CCSDT method is more reliable than CCSD(TQ) in approximating HOC effects. However, for certain troublesome cases an assessment of the HOC effects beyond those included in CCSDT is essential for obtaining ± 1 kcal/mol accuracy.

In this paper we investigate a simple linear, one-parameter scaling approach to arrive at the CBS FCI limit from truncated *n*-electron space computations. Since FCI computations are rather expensive, even with small basis sets, there is little hope that larger basis set FCI calculations will become routine in the near future. Even with the exponential growth in computing power, FCI benchmarks are currently limited to small basis sets and molecules with up to two heavy atoms.[29–42] However, large basis set coupled-cluster computations, which include through triple excitations [CCSD(T) (Ref. 20) and CCSDT (Refs. 21 and 22)], are viable for a large number of molecular systems where small basis set FCI computations are feasible. Therefore, we attempt to scale higher-order correlation energies (SHOC) obtained at lower levels of theory, to correct for neglected excitations, in order to arrive at the FCI limit within a particular one-particle basis set. The basis set dependence of the SHOC procedure is then examined to provide a scaling factor for the CBS FCI limit. Recommendations are then drawn from the existing data which provide a reliable scheme for obtaining the CBS FCI limit. At this point we note that linear scalings, though with different goals in mind, have been employed before, see, e.g., the SEC (Ref. 43) and SAC (Ref. 44) methods of Truhlar and co-workers, the PCI-X method of Siegbahn and co-workers,[45] and the G3S method of Pople and co-workers.[4]

II. COMPUTATIONAL DETAILS

The molecular systems selected for this study are BH, C_2, CH_2, CN, N_2, H_2O, HF, AlH, and H_2S. The configuration interaction calculations utilized the DETCI code[23] interfaced with the PSI3 program system,[46] while the ACESII code[47] has been employed for the coupled-cluster calculations. Several high-level correlation methods have been proposed to improve upon the CCSD(T) description of electron correlation, most notably CCSDT,[21,22] CCSD(TQ),[48,49] CCSDT(Q_f),[50,51] and CCSDTQ.[52] The first two methods are considered in the present work and their reliability quantified. The correlation-consistent family of basis sets (aug)-cc-p(C)VXZ, with X=D(2), T(3), Q(4), and 5, have been employed in all calculations. All results obtained as part of this study are reported in Tables I–IV, separately for $X\ ^1\Sigma^+$ BH (Table I), $\tilde{X}\ ^3B_1$ and $\tilde{a}\ ^1A_1$ CH_2 (Table II), and $X\ ^1\Sigma^+$ AlH (Table IV), while Table III contains results for $X\ ^1\Sigma_g^+$ C_2, $X\ ^2\Sigma^+$ CN, $X\ ^1\Sigma_g^+$ N_2, $X\ ^1\Sigma^+$ HF, $\tilde{X}\ ^1A_1$ H_2O, and $\tilde{X}\ ^1A_1$ H_2S. The higher-order correlation factors are defined as the ratio of the FCI correlation energy to the approximate correlation energy.

III. RESULTS AND DISCUSSION

Examination of Tables I–IV reveals the following observations about SHOC correction factors and their utilization for computing energies at the CBS FCI limit.

First, approaching the *n*-particle limit requires the use of convergent quantum chemical methods. The SHOC factors systematically approach one (FCI) as the CI or CC excitation level increases. The SHOC scale factors show very limited

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TABLE II. SHOC factors and corresponding correlation energy increments (mE_h) from valence only CC and CI series for $\tilde{X}\,^3B_1$ and $\tilde{a}\,^1A_1$ CH_2.[a]

State	Basis set, R(O)HF/E_h	CI2	CI3	CI4	CI5	CCSD	CCSD(T)	CCSDT	FCI
$\tilde{a}\,^1A_1$	cc-pVDZ(24)	1.068 691	1.044 157	1.001 339	1.000 362	1.027 523	1.006 441	1.001 333	1.000 000
	−38.881 090	−132.730	−135.849	−141.658	−141.796	−138.048	−140.940	−141.659	−141.847
	cc-pV(T/D)Z(40)	1.076 658	1.044 864	1.001 606	1.000 368	1.035 262	1.006 303	1.001 298	1.000 000
	−38.888 569	−152.417	−157.054	−163.837	−164.040	−158.511	−163.073	−163.888	−164.100
	cc-pVTZ(58)	1.077 295	1.045 197	1.001 646	1.000 375	1.035 621	1.006 143	1.001 327	1.000 000
	−38.892 369	−157.836	−162.684	−169.757	−169.973	−164.188	−168.998	−169.811	−170.036
	aug-cc-pVDZ(41)	1.074 032	1.045 469	1.001 523	1.000 372	1.031 555	1.006 857	1.001 493	1.000 000
	−38.884 383	−137.566	−141.325	−147.526	−147.696	−143.231	−146.745	−147.531	−147.751
	aug-cc-pV(T/D)Z(64)	1.078 983	1.045 391	1.001 697	1.000 371	1.037 138	1.006 484	1.001 408	1.000 000
	−38.890 490	−154.932	−159.910	−166.886	−167.107	−161.183	−166.092	−166.934	−167.169
$\tilde{X}\,^3B_1$	cc-pVDZ(24)	1.039 479	1.016 306	1.000 376	1.000 045	1.018 711	1.003 734	1.000 626	1.000 000
	−38.921 413	−115.714	−118.353	−120.237	−120.277	−118.073	−119.835	−120.207	−120.283
	cc-pV(T/D)Z(40)	1.048 006	1.017 194	1.000 540	1.000 046	1.027 616	1.003 787	1.000 405	1.000 000
	−38.928 478	−134.191	−138.256	−140.557	−140.627	−136.854	−140.103	−140.577	−140.633
	cc-pVTZ(58)	1.048 807	1.017 512	1.000 559	1.000 048	1.028 187	1.003 738	1.000 459	1.000 000
	−38.932 172	−139.372	−143.658	−146.092	−146.167	−142.167	−145.630	−146.107	−146.174
	aug-cc-pVDZ(41)	1.044 431	1.017 221	1.000 474	1.000 049	1.023 170	1.004 357	1.000 648	1.000 000
	−38.922 891	−120.185	−123.400	−125.466	−125.519	−122.683	−124.981	−125.444	−125.525

[a]See footnote a to Table I for an explanation of the layout of the table. The reference geometries for the calculations are the aug-cc-pCVQZ CCSD(T) optimized geometries [$\tilde{X}\,^3B_1$: r_{CH}=1.075 98 Å and θ_{HCH}=133.85°, $\tilde{a}\,^1A_1$: r_{CH}=1.106 91 Å and θ_{HCH}=102.14°].

basis set dependence (e.g., Tables I and IV), with the variation in the SHOC factors due to changes in the one-electron basis being considerably smaller, even for low excitation levels (e.g., CISD), than that due to the excitation level. Therefore, the SHOC factors are much more readily applicable for extrapolation to the FCI limit; the SHOC correction factors from a small basis set computation can be utilized with larger basis sets and approximate correlation methods to extrapolate to the CBS FCI limit.

Second, from the results presented in Table III for a larger set of molecules it is clear that the SHOC correction factors vary greatly from one molecule to another, even at the same level of theory. For example, the CISD (CI2) SHOC factor is as small as 1.05 for H_2O and as large as 1.23 for C_2, with some degree of correlation with the multireference character of the wave function. Furthermore, for [BH, CH_2($\tilde{X}\,^3B_1$ and $\tilde{a}\,^1A_1$), H_2O, HF] the cc-pVDZ CI2 and CI3 SHOC factors are [1.052, 1.039, 1.069, 1.058, 1.044] and [1.031, 1.016, 1.044, 1.043, 1.035], respectively. Transfer of SHOC factors among molecules seems to be inaccurate, casting some doubts about the accuracy of an intrinsic approximation of the PCI-X (Ref. 45) methods assuming the transferability of the X factors from one molecule to another.

Third, for our test cases, CI2, CCSD, CCSD(TQ), and CCSDT SHOC factors usually converge from below, while CCSD(T) SHOC factors converge from above. It is also notable how different the CCSD(T) and CCSDT SHOC factors

TABLE III. SHOC factors and corresponding correlation energy increments (mE_h) from valence only CC and CI series.[a]

Molecule	Basis set, R(O)HF/E_h	CI2	CI3	CI4	CI5	CI6	CCSD	CCSD(T)	CCSD(TQ)	CCSDT	FCI
$X\,^1\Sigma_g^+C_2$	cc-pVDZ(24)	1.234 305	1.154 362	1.020 134	1.006 638	1.000 386	1.094 367	1.005 520	1.002 802	1.009 535	1.000 000
	−75.386 979	−276.939	−296.117	−335.080	−339.572	−341.694	−312.351	−339.950	−340.871	−338.598	−341.827
$X\,^1\Sigma_g^+N_2$	cc-pVDZ(24)	1.120 218	1.082 499	1.006 549	1.002 256	1.000 125	1.044 107	1.005 407	1.002 985	1.005 180	1.000 000
	−108.953 856	−288.650	−298.707	−321.247	−322.623	−323.310	−309.691	−321.611	−322.388	−321.684	−323.351
$X\,^1\Sigma^+HF$	cc-pVDZ(19)	1.044 123	1.034 685	1.000 929	1.000 414	1.000 008	1.011 681	1.002 367	1.000 637	1.001 937	1.000 000
	−100.019 385	−200.418	−202.246	−209.066	−209.174	−209.259	−206.844	−208.766	−209.128	−208.856	−209.261
	aug-cc-pVDZ(32)	1.056 925	1.038 994	1.001 634	1.000 484	1.000 016	1.020 669	1.002 299	1.002 819	1.001 434	1.000 000
	−100.033 437	−218.264	−222.031	−230.313	−230.577	−230.685	−226.017	−230.159	−230.041	−230.358	−230.689
$X\,^2\Sigma^+CN$	cc-pVDZ(19)	1.134 628	1.059 795	1.006 104	1.001 305	1.000 073	1.059 047	1.009 052	-	1.005 593	1.000 000
	−92.195 790	−262.325	−280.848	−295.835	−297.253	−297.619	−281.046	−294.971	-	−295.986	−297.641
$\tilde{X}\,^1A_1$ H_2O	cc-pVDZ(24)	1.057 714	1.042 599	1.001 464	1.000 614	1.000 012	1.017 414	1.002 972	1.000 551	1.002 210	1.000 000
	−76.026 719	−203.270	−206.217	−214.687	−214.870	−214.999	−211.322	−214.365	−214.884	−214.528	−215.002
$\tilde{X}\,^1A_1$ H_2S	cc-pVDZ(28)	1.072 519	1.050 120	1.001 945	1.000 685	1.000 012	1.023 957	1.003 975	1.000 648	1.001 564	1.000 000
	−398.694 572	−159.448	−162.849	−170.679	−170.894	−171.009	−167.010	−170.334	−170.900	−170.744	−171.011

[a]See footnote a to Table I for an explanation of the layout of the table. The reference geometries for the calculations are 1.2455 Å (C_2), 1.0996 Å (N_2), 0.9177 Å (HF), 1.1736 Å (CN), r_{OH}=0.958 85 Å, and θ_{HOH}=104.34°(H_2O), r_{SH}=1.337 30 Å, and θ_{HSH}=92.295° (H_2S).

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TABLE IV. SHOC factors and corresponding correlation energy increments (mE_h) from valence only CC and CI series for $X\,^1\Sigma^+$ AlH.[a]

Basis set, RHF/E_h	CI2	CI3	CCSD	CCSD(T)	CCSD(TQ)	CCSDT	FCI
cc-pVDZ(23)	1.049 726	1.031 052	1.018 731	1.005 218	1.001 095	1.000 520	1.000 000
−242.453 946	−71.469	−72.764	−73.644	−74.636	−74.942	−74.985	−75.024
cc-pVTZ(48)	1.055 443	1.032 946	1.022 594	1.005 214	1.001 278	1.000 713	1.000 000
−242.461 822	−79.853	−81.592	−82.418	−83.843	−84.172	−84.220	−84.280
cc-pVQZ(89)	1.056 667	1.033 065	1.023 684	1.004 980	1.001 637	1.000 767	1.000 000
−242.463 755	−82.061	−83.936	−84.705	−86.282	−86.569	−86.645	−86.711
cc-pV5Z(150)	1.056 626	1.032 882	1.023 828	1.004 714	–	1.000 775	1.000 000
−242.464 438	−82.759	−84.661	−85.410	−87.035	–	−87.377	−87.445
aug-cc-pVDZ(36)	1.053 034	1.032 568	1.020 412	1.005 574	1.001 170	1.000 610	1.000 000
−242.454 370	−74.049	−75.516	−76.416	−77.543	−77.885	−77.928	−77.976
aug-cc-pVTZ(73)	1.056 502	1.033 136	1.023 533	1.005 449	1.001 487	1.000 758	1.000 000
−242.461 908	−80.602	−82.425	−83.198	−84.694	−85.030	−85.081	−85.156
aug-cc-pVQZ(130)	1.056 814	1.033 005	1.023 885	1.004 922	1.001 628	1.000 781	1.000 000
−242.463 800	−82.303	−84.200	−84.950	−86.553	−86.838	−86.911	−86.979

[a]See footnote a to Table I for an explanation of the layout of the table. All computations used the cc-pVQZ CCSD(T) optimized bond length of 1.6519 Å.

can be, the CCSDT factors being smaller in all cases except C_2. While for BH the CCSDT and CCSD(TQ) factors are quantitatively very similar, for the larger set of molecules of Table III this dose not seem to hold as a general rule, the changes between CCSD(T), CCSD(TQ), and CCSDT being somewhat erratic.

Fourth, at least in the case of BH and AlH, SHOC factors obtained with cc-pVXZ and aug-cc-pVXZ basis sets can be considered to be the same; they converge to the same limiting values of [1.057–1.058, 1.032–1.033] at the [CI2, CI3] levels. This suggests the expected similarity in the valence-only description of the ground electronic states of BH and its congener, AlH.

Fifth, in the case of BH, employing a two-point X^{-3} extrapolation with X=4 and 5 results in valence-only CBS [CCSD, CCSD(T), CCSDT] correlation energy estimates of $[-103.252,-105.595,-105.968]\,mE_h$. Correcting these values with the relevant cc-pVDZ SHOC factors provides the much more uniform CBS FCI estimates of $[-105.406, -106.163,-106.048]\,mE_h$. The same X^{-3} estimate, with $X=4$ and 5 FCI energies, gives $-106.058\,mE_h$. As expected, this result is closest to the doubly extrapolated CBS FCI estimate from the highest-quality explicit CCSDT computations. Very similar results are obtained from the available AlH data: the valence-only CBS [CCSD, CCSD(T), CCSDT] correlation energy estimates are $[-86.150, -87.825,-88.145]\,mE_h$, the corresponding SHOC FCI estimates are $[-87.763,-88.283,-88.191]\,mE_h$, while the extrapolated CBS FCI correlation energy is $-88.215\,mE_h$. Note here that, as expected, scaling CISD results to the FCI limit is much less successful; using cc-pVDZ SHOC factors for cc-pV5Z CISD correlation energies for BH and AlH results in deviations of 0.61 and $0.57\,mE_h$ from the corresponding explicitly computed FCI limit.

Sixth, extrapolating the best three cc-pVXZ HF energies with the three-point exponential form and the best two cc-pVXZ FCI correlation energies with the two-point X^{-3} form, one arrives at the following valence-only CBS FCI energies (in E_h) for BH and AlH: −25.237 67 and −242.553 09, respectively. Assuming that only cc-pVDZ FCI and large basis set CCSD(T) calculations were feasible for these molecular systems, the following HOC-corrected CBS FCI energies are obtained: −25.237 77 and $-242.553\,09\,E_h$. If we consider the large basis set CCSDT calculations, the following HOC-scaled valence-only CBS FCI energies are obtained: −25.237 58 and $-242.553\,00\,E_h$. The agreement to within $100\,\mu E_h$ between all sets of energies is very encouraging.

Since the proposed SHOC scheme is multiplicative, it could be applied to the study of potential energy hypersurfaces (PESs) in a simple fashion if FCI computations can be afforded at each grid point. For cases where performing a large number of FCI calculations is not feasible or desirable, it is worth assuming that the SHOC scale factor does not change significantly with the geometry. The effectiveness of the use of a single SHOC factor has been tested on the ground-state PES of a molecule of recent interest to us, H_2S.[11,53] Six geometries[54] have been selected to test the geometry dependence of the SHOC correction factor, covering an energy range of 0–30 000 cm^{-1}. Valence-only cc-pVDZ FCI and CCSD(T) computations have been performed at these geometries, resulting in two sets of estimates of valence-only correlation energies. The FCI−CCSD(T) energy differences, in μE_h, before and after the SHOC scaling, performed with the arithmetic average of the six scale factors, 1.004 54, are as follows: [678, 797, 1096, 634, 887, 741] and [−95, −10, 255, −131, 56, −49], respectively. It is clear that the SHOC corrections result in an order of magnitude *uniform* reduction of the valence-only correlation energy error of the CCSD(T) calculation.

The present SHOC scheme can also be employed to improve upon recent high-quality dissociation energies, D_e (all values reported henceforth are in kcal/mol), of diatomics re-

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ported by Feller and Sordo.[26–28] We take $C_2[C_2(^1\Sigma_g^+) \rightarrow C(^3P)+C(^3P)]$, $CN[CN(^2\Sigma^+) \rightarrow C(^3P)+N(^4S)]$, and N_2 $[N_2(^1\Sigma_g^+) \rightarrow N(^4S)+N(^4S)]$ as representative examples, the former two molecules having considerable multireference character in their ground electronic states and thus posing difficulties for single-reference CC techniques. The molecular CCSDT SHOC factors, 1.005 595, 1.009 536, 1.005 182 for CN, C_2, and N_2, respectively, are computed with a cc-pVDZ basis at the cc-pVQZ CCSDT optimized geometries.[27] The atomic limits are determined from explicit and approximate cc-pVXZ (X=2, 3, 4) FCI data[26] extrapolated here to the CBS FCI limit. For CN, the CBS ROCCSD(T) dissociation energy, corrected for core-valence, special relativity (including spin–orbit), and full triples, is 180.05.[26] Scaling the correlation energy using our present SHOC correction scheme gives 181.46, embarrassingly close to the best experimental result of 181.4 ± 0.5.[55] For C_2, the similarly corrected CBS ROCCSD(T) prediction is 143.61,[26] as compared to the best experimental result of 147.8 ± 0.5.[56] Using our SHOC scheme results in 146.02, suggesting a fairly large, +2.3 kcal/mol valence-only correction for quadruple and higher excitations and decreasing the original discrepancy of +4.2 to +1.8. For N_2, Feller and Sordo reported (Table II of Ref. 27) a corrected CBS ROCCSD(T) atomization energy of 227.1. This value changes, when corrected here for HOC effects, to 228.6. Therefore, following our simple SHOC scheme, the discrepancy between theory and experiment (228.42) for the dissociation energy of N_2 decreases from +1.3 to +0.2. Most importantly, the present results along with those of Feller and Sordo suggest that in the determination of diatomic dissociation energies HOC effects are rather substantial and should not be neglected during *ab initio* calculations aimed at surpassing chemical accuracy.

IV. CONCLUSIONS

Based on the molecular examples BH, C_2, CN, N_2, CH_2, H_2O, HF, AlH, and H_2S, it is shown in this work that a simple, linear scaling of the higher-order correlation energy (SHOC) determined at levels including only single, double, and triple excitations [such as CCSD(T) and CCSDT] allows efficient estimation of the FCI correlation energy. Application of the SHOC scheme to lower-level methods such as CISD is not recommended. Performing HOC scaling at the complete basis set (CBS) limit one can thus arrive at the penultimate, CBS FCI limit of electronic structure theory. The SHOC scheme is very effective in correcting the cc-pVDZ CCSD(T) potential energy hypersurface of H_2S, resulting in a factor of 4–5 *uniform* improvement in the correlation energy over the whole surface, as compared to cc-pVDZ FCI. The proposed scaling scheme can also be employed in the theoretical determination of atomization energies. For the ground electronic states of C_2, CN, and N_2, the SHOC scheme suggests that HOC effects are rather substantial [may exceed 2 kcal/mol at the CBS CCSD(T) level] and should not be neglected in *ab initio* calculations aimed at surpassing the chemical accuracy limit.

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