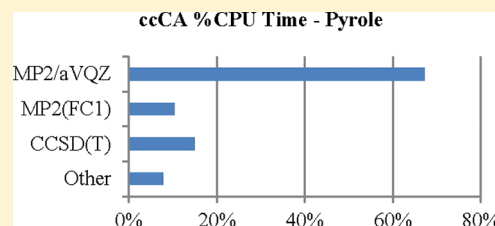


Explicitly Correlated Methods within the ccCA Methodology

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ABSTRACT: The prediction of energetic properties within “chemical accuracy” (1 kcal mol^{-1} from well-established experiment) can be a major challenge in computational quantum chemistry due to the computational requirements (computer time, memory, and disk space) needed to achieve this level of accuracy. Methodologies such as coupled cluster with single, double, and perturbative triple excitations (CCSD(T)) combined with very large basis sets are often required to reach this level of accuracy. Unfortunately, such calculations quickly become cost prohibitive as system size increases. Our group has developed an ab initio composite method, the correlation consistent Composite Approach (ccCA), which enables such accuracy to be possible, on average, but at reduced computational cost as compared with CCSD(T) in combination with a large basis set. While ccCA has proven quite useful, computational bottlenecks still occur. In this study, the means to reduce the computational cost of ccCA without compromising accuracy by utilizing explicitly correlated methods within ccCA have been considered, and an alternative formulation is described.



1. INTRODUCTION

The rapid proliferation and maturation of ab initio techniques available for the study of molecular and atomic systems is one of the great successes of computational quantum chemistry, enabling the study of species that were unfathomable only a decade or two ago. However, significant hurdles remain that drive development of computational methodologies. One limitation to the extension of commonly used single-reference computational methods to large chemical systems is the slow convergence of wave function-based methods utilizing atom-centered one-electron basis set functions to the complete basis set limit. This poor scaling is characteristic of wave function-based theories utilizing a configuration interaction expansion in one electron basis sets due to the poor description of the electron–electron cusp condition endemic to these one-particle basis set expansions.¹ The first derivative of the wave function with respect to r_{12} , the interelectron distance, is nonzero at $r_{12} = 0$, and this cusp cannot be easily reproduced with one-electron atom-centered basis sets, as very high angular momentum basis functions are required to properly characterize this behavior.² This difficulty in describing the electron–electron cusp behavior results in the slow convergence of calculated chemical properties when using one-particle basis functions at a rate of $(L + 1)^{-3}$, where L is the maximum angular quantum number in the basis set.³ With the steep computational scaling in conventional ab initio quantum chemistry methods, this convergence behavior imposes restrictions on the choices of basis set quality and appropriately robust electronic correlation methods that are feasible within the limitations imposed by available computational resources.

The problem of basis set convergence can be mitigated by inclusion of a term explicitly dependent on the interelectron distance r_{12} within the basis set expansion, which demonstrates a much more rapid convergence behavior of $(L + 1)^{-7}$ to the

complete basis set limit.^{4,5} Early implementation of this explicitly correlated term into wave function-based ab initio theory was performed by Slater,⁶ Hylleraas,⁷ and James and Coolidge⁸ in early quantum mechanical studies of two-electron systems such as the helium atom and the hydrogen molecule (H_2), but extending the use of explicitly correlated terms to larger molecular systems proved problematic due to computational limitations. While the basis set convergence was accelerated by using explicitly correlated terms, such terms require management of three- and four-electron integrals, which are significantly more computationally demanding compared to the two-electron integrals present in conventional one-particle basis set expansion methods. It was the introduction of the resolution-of-the-identity (RI) approximation to these three- and four-electron integrals that allowed for second-order perturbation and coupled cluster methods that include terms explicitly dependent on r_{12} to be extended to chemical systems of a similar size as their conventional counterparts without significantly increased computational requirements. The earliest of these approximations made use of the same basis set as the orbital expansion,⁴ but later approaches implemented auxiliary basis sets that removed the need for large atomic orbital basis set, which were required to avoid errors with the RI approximation.^{1,9} The rapid convergence behavior of explicitly correlated coupled cluster and second-order perturbation theory with correlation consistent basis sets typically yields energies of a quality that would require a basis set one L_{max} larger in a conventional method and, as such, has seen adoption in molecular thermochemical research.^{10–13} Explicitly correlated coupled cluster methods used in calculating both anharmonic and

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harmonic vibrational frequencies in chemical systems with basis sets as low as aug-cc-pVTZ have been reported previously, with accuracy exceeding those of conventional coupled cluster calculations using aug-cc-pVQZ basis sets.¹⁴ Similar results were found by Feller et al. in the examination of atomization energies of fluorine-containing hydrocarbons, where explicitly correlated coupled cluster demonstrated results with a quadruple- ζ basis set comparable to a conventional coupled cluster method with a sextuple- ζ basis set.¹⁵ Basis sets for explicitly correlated methods have also been introduced that have been reoptimized for use within explicitly correlated methodologies^{16–18} and show improved performance over nonoptimized basis sets.¹¹

Increasing the basis set convergence rate is only one of many methods to have been introduced to reduce the computational resource costs of ab initio correlated methods. Other examples include local methods,¹⁹ hybrid quantum mechanics/molecular mechanics (QM/MM) approaches,^{20–22} and composite methods. In particular, composite methods, or “model chemistries”, are methods that describe chemical properties through multiple theoretical calculations rather than a single, highly robust theoretical method. Computational costs are saved by implementing multiple, less computationally expensive theoretical calculations to replicate results that would, in principle, be achieved with a much more sophisticated, albeit, more computationally expensive method. Composite approaches typically incorporate effects such as core–valence interactions, relativistic effects, and spin–orbit coupling, which can have significant impact on the energetic properties of molecules and atoms.

Examples of composite methods include the Feller–Peterson–Dixon (FPD),^{23–25} Weizman- n (Wn),^{26–28} complete basis set (CBS),^{29–31} Gaussian- n (Gn),^{32–35} multicoefficient composite (MCCM),^{36–40} and HEAT^{41,42} methods. The performance of these model chemistries is often analyzed against molecular sets with extensively studied gas-phase thermochemical data from experiment such as enthalpies of formation, ionization potentials, proton affinities, and electron affinities. The Gn and CBS model chemistries have demonstrated chemical accuracy (MAD from experiment of approximately 1.0 kcal mol^{−1} for main group species) across a wide range of main group organic and inorganic species, and the Wn and HEAT methods have demonstrated accuracies below a MAD of 1.0 kJ mol^{−1}. The mitigation of electron correlation and basis set incompleteness effects differ widely among the model chemistry approaches, such as Gn relying on empirical corrections and the Wn and HEAT methods relying on computationally demanding coupled cluster methods that prevent their use in large chemical systems.

Our laboratory’s own model chemistry, the correlation consistent Composite Approach (ccCA),^{43,44} uses the systematic convergence behavior of the correlation consistent basis sets first developed by Dunning,⁴⁵ to strive toward possible chemical accuracy via an all-electron coupled cluster calculation at a significantly reduced cost while simultaneously eschewing the need for parametrization required in the Gn methods. The ccCA methodology has been used effectively for main group species,⁴⁴ s -block compounds,⁴⁶ first-row transition metals,^{47–59} and second-row transition metals.⁵⁰ Recently, the resolution-of-the-identity (RI) approximation was applied to the ccCA methodology, demonstrating significant reduction in the computational resources required with no significant loss of accuracy.⁵¹

Despite this success, computational bottlenecks in ccCA still occur, as in all ab initio methodologies, and further reduction of the computational cost of the steps comprising ccCA is of great interest. The primary computational bottleneck encountered in the ccCA methodology is the computationally intensive CCSD(T) theory⁵² used to calculate high-order correlation effects due to the formal scaling of CCSD(T) as $O(n_{\text{occ}}^3 n_{\text{vir}}^4)$, where n_{occ} is the number of occupied orbitals and n_{vir} is the number of virtual orbitals. A second computational bottleneck is found in the MP2 calculation utilizing the aug-cc-pVQZ basis set. The formal computational scaling of the MP2 method is $O(n_{\text{occ}} N^4)$, where n_{occ} is the number of occupied orbitals and N is the total number of basis functions,⁵³ but the number of functions in an augmented correlation consistent basis set grows according to the maximum angular quantum number,⁵⁴

$$N_{\text{aug-cc-pVXZ}} = 0.33(L_{\text{max}} + 1)(L_{\text{max}} + 1.5)(L_{\text{max}} + 2) + (L_{\text{max}} + 1)^2 \quad (1)$$

where N is the number of basis functions and L_{max} is the maximum angular quantum number in the basis set. The rapid increase in the number of basis functions as the quality of the basis set increases leads to undesirable scaling of computational resources in the ccCA methodology, making explicitly correlated methods utilizing smaller basis sets a highly appealing potential alternative to the computational bottlenecks present in the ccCA methodology by removing dependence of the ccCA methodology on CCSD(T) and second-order perturbation methods relying on cc-pVTZ and aug-cc-pVQZ basis sets, respectively.

In this paper, both second-order perturbation theory and coupled cluster methods with explicitly correlated wave function descriptions and small basis sets have been considered for use within ccCA for main group species, the computational bottlenecks associated with this methodology and potential modifications to the ccCA methodology using explicitly correlated methods are presented, as well as the analysis of the computational bottlenecks, the accuracies of ccCA with explicitly correlated modifications, and CPU time savings due to these modifications.

2. METHODOLOGY

The ccCA method combines several computational techniques to approach the energy that would be achieved in principle by an all-electron CCSD(T) calculation with a relativistic two-component Douglas–Kroll–Hess Hamiltonian at the complete basis set limit (ae-CCSD(T)-DK/aug-cc-pCV ∞ Z-DK). The recommended ccCA formulation for main group species, available in previous work,⁴⁴ is based upon an optimized geometry performed at the B3LYP/cc-pVTZ level of theory and a theoretically determined frequency scaling factor of 0.989 applied to the calculated harmonic zero-point energy (ΔE_{ZPE}) and thermal enthalpy corrections. From the calculated geometry, an extrapolated CBS energy is determined at the MP2 level of theory (E_{ref}), followed by a series of additive single-point calculations to account for high-order correlation (ΔE_{CC}), scalar-relativistic effects (ΔE_{SR}), core–valence interactions (ΔE_{CV}), and spin–orbit coupling (where applicable) (ΔE_{SO}) that yield the total ccCA energy (E_{ccCA}):

$$E_{\text{ccCA}} = E_{\text{Ref}} + \Delta E_{\text{CC}} + \Delta E_{\text{CV}} + \Delta E_{\text{SR}} + \Delta E_{\text{ZPE}} + \Delta E_{\text{SO}} \quad (2)$$

For use with explicitly correlated methods in the ccCA methodology, two extrapolation schemes have been chosen.^{55,56} The first scheme is the L_{\max}^{-7} extrapolation first proposed by Yamaki et al., based on the theoretical $(L_{\max}+1)^{-7}$ convergence behavior of explicitly correlated wave functions in a configuration interaction type expansion:⁵⁷

$$E(n) = E_{\text{CBS}} + B(L_{\max})^{-7} \quad (3)$$

where E_{CBS} is the complete basis set energy, $E(n)$ is the energy associated with the n - ζ basis set, and L_{\max} is the maximum angular momentum quantum number associated with the n - ζ basis set. The authors reported two point CBS limit extrapolations with explicitly correlated second-order perturbation theory that approximated a conventional second order perturbation theory extrapolation with basis sets of an L_{\max} number one larger than those used in the explicitly correlated methods. More recent work by Hill et al.,⁵⁸ however, demonstrated that for small molecules, the double-, triple-, and quadruple- ζ basis sets may not have enough basis functions of sufficient angular momentum to exhibit the theoretical $(L_{\max} + 1)^{-7}$ convergence behavior of explicitly correlated wave functions. Thus, a second extrapolation scheme based on this apparent convergence behavior for low L_{\max} cardinal number basis sets was also used,

$$E(n) = E_{\text{CBS}} + B(L_{\max})^{-4} \quad (4)$$

in light of the number of small molecules present in our chosen molecule set. The ccCA energies calculated from these correlation energy extrapolation schemes are referred to as ccCA-F12-S7 and ccCA-F12-S4 for eqs 3 and 4, respectively, from this point forward.

Modification of the ccCA framework to include explicitly correlated coupled cluster methods for electron correlation beyond second-order perturbation theory is performed by replacement of the methods in conventional ccCA methodology with their explicitly correlated analogs:

$$\begin{aligned} \Delta E_{\text{CC}} = & E[\text{CCSD(T)-F12/VDZ-F12}] \\ & - E[\text{MP2-F12/VDZ-F12}] \end{aligned} \quad (5)$$

Equation 5 will be referred to as the double- ζ correction from this point forward to distinguish the calculation from the conventional ΔE_{CC} expression.

The MP2-F12/3C and RMP2-F12/3C methods developed by Knizia and Werner⁵⁹ were used as replacements for the conventional MP2 and RMP2 theories used to calculate ccCA correlation reference energies. The coupled cluster methods used in the double- ζ correction were the CCSD(T)-F12x and UCCSD(T)-F12x ($x = \text{a,b}$) where the conventional perturbative triples correction is added to the CCSD-F12x and UCCSD-F12x ($x = \text{a,b}$) methods developed by Adler, Knizia, and Werner.^{60,61} Both CCSD(T)-F12 approaches are nearly identical in their approximations except for an addition energy correction included in the F12b approach. The inclusion of the additional correction has been shown to provide monotonic convergence of the F12b approach to the complete basis set limit with increasing basis set size, but the F12a approach generally provides better total energies, dissociation energies, and bond lengths than F12b with correlation consistent basis sets of double- or triple- ζ quality.⁶² Both coupled cluster and perturbation theory calculations were performed under fixed diagonal conditions. The VDZ-F12 and VTZ-F12 optimized basis sets^{15,16} and the matching optimized auxiliary basis

sets^{17,63} developed by Peterson et al. were used in the explicitly correlated calculations and density fitting approximations were made using the cc-pVTZ/JKFIT sets of Weigend.⁶⁴ For all explicitly correlated methods used, a Slater-type frozen geminal was used with the recommended geminal exponents of 0.9, 1.0, and 1.1 for VDZ-F12, VTZ-F12, and VQZ-F12 basis sets, respectively.¹⁵ In this work, analysis of the CPU resource usage and modifications to the ccCA methodology using explicitly correlated methods was performed by application of the methodology to the 148 enthalpies of formation (ΔH_f°) values in the G2/97 molecule set.³² All DFT geometry optimizations were performed using the Gaussian03 quantum chemistry package,⁶⁵ while all other calculations, including calculations using explicitly correlated methods, were performed using version 2009.1 of the MOLPRO quantum chemistry package.⁶⁶ The ΔH_f° values of Li_2 , LiH , LiF , BeH , Na_2 , and NaCl were not included in the following calculations due to a lack of chosen density-fitting sets available by default in the MOLPRO package. In total, 142 of the 148 ΔH_f° contained in the G2/97 test set were analyzed.

3. RESULTS AND DISCUSSION

3.1. MP2/aug-cc-pVQZ within ccCA. Within ccCA, the most computationally costly step is the MP2/aug-cc-pVQZ calculation. To illustrate, for pyridine, the MP2/aug-cc-pVQZ calculation requires well over one-half of the total CPU time required for the ccCA energy calculation (after the geometry optimization). This is illustrated in Figure 1. To further

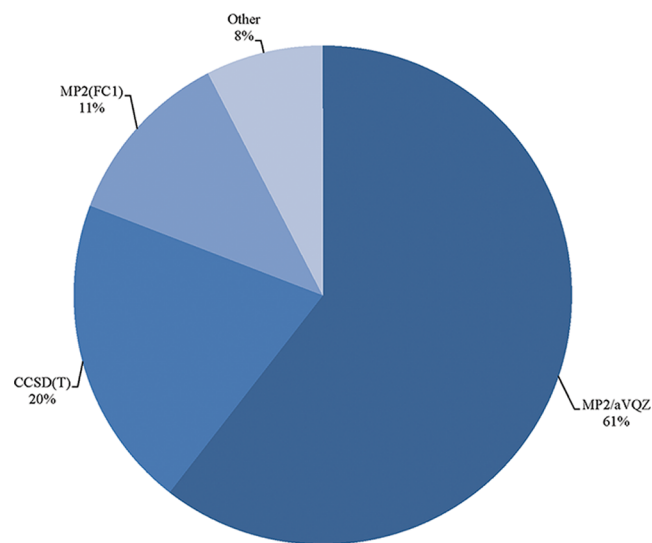


Figure 1. Percentage of total ccCA correlation energy CPU time by component. “Other” includes all correlation energy calculations of <10% total CPU time each.

illustrate the relative computation costs, eleven of the largest molecules within the G2/97 set have been considered. The relative computational requirements is similar to those demonstrated by pyridine, with the MP2/aug-cc-pVQZ computational step requiring greater than 50% of the total CPU time invested in the ccCA calculations, as shown in Figure 2. Furthermore, as the number of atoms increases in the molecules, the CPU time required by the MP2/aug-cc-pVQZ calculation does not show a corresponding decrease in favor of the CCSD(T)/cc-pVTZ calculations. The effects of the aug-cc-pVQZ basis set in ccCA calculations become more pronounced

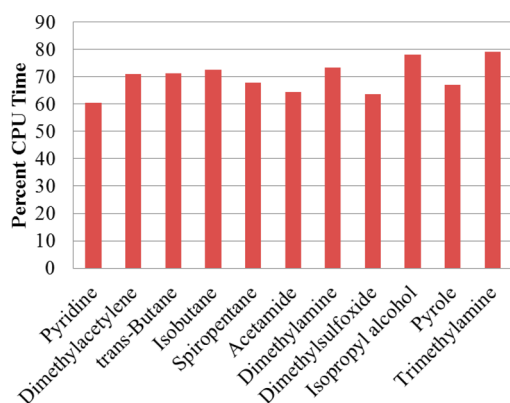


Figure 2. Percentage of total ccCA correlation energy CPU time required by MP2/aug-cc-pVQZ in select molecules.

for the largest of the molecules: trimethylamine (79%), trans-butane (71%), and isobutane (72%). When there are fewer basis functions in aug-cc-pVQZ, the resource usage is slightly less pronounced, as demonstrated by slightly smaller molecules such as pyroole (67%), pyridine (60%), acetamide (64%), and dimethylsulfoxide (63%).

3.2. Explicit Correlation in ccCA Reference Energies.

The results of the replacement of conventional MP2 with augmented double-, triple-, and quadruple- ζ basis sets within ccCA with explicitly correlated MP2-F12 utilizing double- and triple- ζ basis sets on the predicted enthalpies of formation are shown in Table 1. Both ccCA-F12-S7 and ccCA-F12-S4

Table 1. Comparison of Enthalpies of Formation in the G2/97 Set between Conventional ccCA Schemes and Explicitly Correlated Schemes^a

ccCA scheme	mean signed deviation	mean absolute deviation	max. deviation
ccCA-P	−0.83	1.07	4.29
ccCA-PS3	−0.36	0.84	4.56
ccCA-F12-S7	0.63	1.05	3.98
ccCA-F12-S4	0.15	1.02	4.89

^aValues are in kcal mol^{−1}.

extrapolation schemes yielded MADs comparable to the ccCA-P and ccCA-PS3 schemes. The maximum deviations in the ΔH_f values from experiment, also shown in Table 1, are similar for both conventional and explicitly correlated ccCA, further indicating that the inclusion of F12 within the MP2 steps of ccCA provides a suitable approximation. Though these maximum deviations are 3–4 kcal mol^{−1}, it is anticipated from prior studies on the prediction of enthalpies of hydrocarbons using composite schemes including ccCA that a homodesmotic (or better) scheme will reduce this deviation, as compared with the atomization energy approach that was used not only for simplicity but also because it is the most widely used approach for the determination of ΔH_f values.^{67,68} It is of interest that the ccCA-F12-S7 and ccCA-F12-S4 ΔH_f values yield nearly identical MADs but show different bias. Both explicitly correlated schemes yield overestimations of the G2/97 enthalpies of formation while the conventional ccCA-P and ccCA-PS3 schemes underestimate these quantities.

3.3. CPU Time Analysis. The comparison of CPU time savings from the removal of the MP2 calculation with the quadruple- ζ level basis set is shown in Figure 3 for the same set

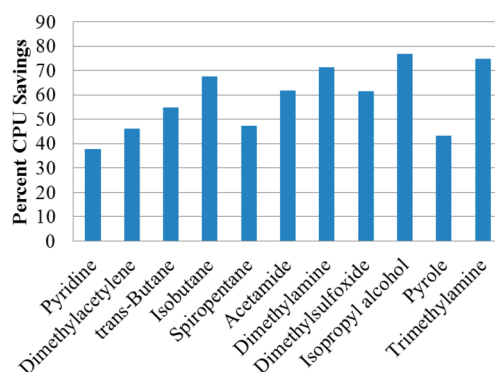


Figure 3. Percent CPU savings with alternative explicitly correlated extrapolation scheme.

of molecules, as shown in Figure 2. Overall, the omission of the MP2/aug-cc-pVQZ step in the determination of the MP2 reference energy in ccCA yielded a 58% reduction in CPU time required, with significant savings for trimethylamine (74% reduction), dimethylamine (71% reduction), and isopropyl alcohol (76% reduction). Both dimethylacetylene and pyroole, though, do not show such a dramatic decrease in CPU time despite the significant CPU time requirements exhibited by these molecules the MP2/aug-cc-pVQZ in the conventional ccCA correlation energy computation, 71% and 67%, respectively; the time savings using explicitly correlated methods was only 46% and 43% respectively despite a similar contribution to the overall ccCA CPU time requirements for these molecules compared to trimethylamine, dimethylamine, and isopropyl alcohol. In the pyroole calculations, the MP2-F12/VTZ-F12 step represents a 5-fold increase in computational effort compared to the MP2/aug-cc-pVTZ step in the conventional ccCA calculations, offsetting the gains in CPU time made through removal of the MP2/aug-cc-pVQZ calculation. In comparison, the CPU time increase from MP2/aug-cc-pVTZ to MP2-F12/VTZ-F12 is only a 2-fold increase in the calculations on trimethylamine, and as a result, the CPU time savings are far more significant. Similarly, trans-butane and isobutane have nearly the same percentage of CPU time consumed by the MP2/aug-cc-pVQZ calculation (71% and 72%, respectively), but the savings upon replacing the conventional MP2 methods with MP2-F12 are not similar (55% and 67%, respectively). Analysis of the CPU time contributions shows that the MP2-F12/VTZ-F12 computation in trans-butane results in a 3.5-time increase over the MP2/aug-cc-pVTZ computation it replaces in the reference energy calculation. In isobutane, the MP2-F12/VTZ-F12 computation represents only a 1.8-time increase in CPU time over the MP2/aug-cc-pVTZ computation.

3.4. Explicit Correlation in ΔE_{CC} . The replacement of the CCSD(T)/cc-pVTZ step within ccCA with CCSD(T)-F12/VDZ-F12 (using a double- ζ ΔE_{CC} correction rather than a triple- ζ ΔE_{CC} correction) was also considered for both ccCA-F12-S7 and ccCA-F12-S4, and the results are shown in Table 2. The CCSD(T)-F12a approach provides better results in the ccCA framework in calculating ΔH_f with the VDZ-F12 basis set when compared to the CCSD(T)-F12b approach, but the application of the double- ζ ΔE_{CC} correction utilizing either CCSD(T)-F12 approach introduces significant errors, in excess of 3 kcal mol^{−1} MAD and 10 kcal mol^{−1} maximum deviation from experimental values for both ccCA-F12-S7 and ccCA-F12-S4 methodologies. These findings are consistent with the

Table 2. Comparison of Enthalpies of Formation in the G2/97 Set Using the High Order Correlation Correction (CCSD(T)-F12x) with the Newly Introduced Explicitly Correlated Schemes^a

ccCA scheme	mean signed deviation	mean absolute deviation	maximum deviation
$(x = a)$			
ccCA-F12-S7	−3.17	3.21	9.42
ccCA-F12-S4	−3.66	3.68	10.39
$(x = b)$			
ccCA-F12-S7	−4.97	4.97	12.45
ccCA-F12-S4	−5.45	5.45	13.41

^aValues are in kcal mol^{−1}.

results from a previous calibration study performed on C₂ and other selected small hydrocarbon molecules, which utilized the two CCSD(T)-F12 approaches in combination with the VnZ-F12 basis sets.⁶² This earlier study showed that while CCSD(T)-F12a/VDZ-F12 calculations provided total energies in much closer agreement with extrapolated CCSD(T)/CBS energies than those calculated with CCSD(T)-F12b/VDZ-F12, significant errors from the calculated CCSD(T)/CBS total energy still occurred, with a minimum error of 1.88 kcal mol^{−1} calculated for the CH molecule up to a maximum error of 18.2 kcal mol^{−1} for C₆H₁₄.⁶² Thus, though the ccCA-F12 framework enables a reduction in the levels of basis sets needed within ccCA-F12 as compared with conventional MP2, this is not at all the case for ΔE_{CC} , as the CCSD(T)-F12/cc-pVDZ-F12 can not be used as a rigorous replacement for CCSD(T)/cc-pVTZ, despite the faster convergence of the former.

4. CONCLUSIONS

Explicitly correlated methods were considered as a means to reduce the computational cost of ccCA. Conventional MP2 calculations with double-, triple-, and quadruple- ζ basis sets used in calculating the ccCA reference energy were replaced with explicitly correlated MP2 calculations with double- and triple- ζ basis sets only. When the reference energy arising from explicitly correlated MP2 replaces the reference energy obtained using conventional MP2 calculations a MAD of 1.0 kcal mol^{−1} for ΔH_f values was obtained for the G2/97 molecule set, a MSD of less than 1.0 kcal mol^{−1} was obtained, very similar to the results of conventional ccCA. The removal of the quadruple- ζ basis set from the ccCA reference energy calculation further results in a significant reduction of the CPU time required in the ccCA-F12 methodology. The use of explicitly correlated coupled cluster with a double- ζ basis set was also investigated to determine its potential utility as an alternative to the use of CCSD(T)/cc-pVTZ within ccCA. However, this replacement resulted in a significant loss of accuracy.

Our findings show that explicitly correlated methods show great promise in offering new alternatives to conventional ab initio composite methodologies by reducing the associated computational costs. Implementing these methods into the ccCA reference energy will enable the extension of ccCA to larger chemical species.

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Notes

The authors declare no competing financial interest.

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