Evaluation of Incremental Correlation Energies for Open-Shell Systems: Application to the Intermediates of the 4-Exo Cyclization, Arduengo Carbenes and an Anionic Water Cluster

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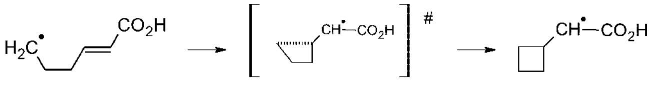
A fully automated procedure for incremental closed-shell CCSD calculations has been extended to open-shell cases tractable with the restricted open-shell CCSD method. It is demonstrated that for monoradical intermediates of the 4-exo cyclization, the triplet state of Arduengo carbenes as well as for water cluster anions chemical accuracy can be reached with respect to the error introduced by the local correlation treatment. Finally, it is shown that the computationally less demanding evaluation of higher-order increments in a smaller basis set does not lead to significant errors.

1. Introduction

An accurate description of the electronic structure of molecules requires us to go beyond Hartree−Fock theory and to include electron correlation. At the ab initio level this is usually achieved by means of many-body perturbation theory MBPT, configuration interaction theory (CI), or coupled cluster theory (CC). The steep scaling of these approaches with respect to the system size is the reason why the development of local correlation methods became a very active field in theoretical chemistry during the last two decades. Ground state methods like LMP2,[1–10] LCCD, NLSCC, LCCSD or LCCSD(T) [11–17] were developed by several groups and enable ab initio investigations of medium-sized molecules.

An alternative approach that in its simplest implementation can be performed with standard quantum chemical program packages without changing the correlation modules is the incremental scheme of Stoll,[18–20] which is related to an earlier proposal by Nesbet.[21–23] Within this approach the occupied HF orbitals are first localized and then grouped into local domains. The total correlation energy is evaluated as a sum over contributions of all individual domains as well as correction terms of increasing order and usually decreasing importance arising from interactions between the domains. In recent publications we presented a fully automated procedure to evaluate the closed-shell coupled cluster singles and doubles (CCSD) correlation energy for molecules by the method of increments.[24–26]

Despite various recent developments the extension of local correlation methods to the open-shell case is not yet solved completely. Local CI and multireference CI schemes (MRCI) suitable for open-shell applications were developed by Walter et al.[27–29] In the framework of the incremental scheme applications were published by Mödl et al.,[30] Paulus et al.[31] and Bezugly and Birkenheuer.[32] In this work we extend our recent fully automated implementation of the incremental scheme for CCSD energies to the restricted open-shell coupled cluster singles and doubles method (RCCSD) and present the results for the 4-exo cyclization,[33,34] the singlet−triplet excitation in an Arduengo carbene[35,36] and the correlation contribution to the electron affinity of the $(H_2O)_6^-$ cluster.[37]



1 **2** **3**

Figure 1. Intermediates of the 4-exo cyclization.

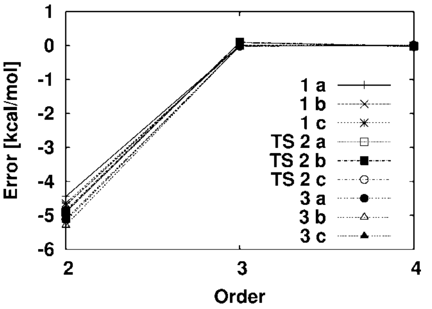


Figure 2. Convergence of the incremental RCCSD/cc-pVDZ correlation energies of the 4-exo cyclization for intermediates depicted in Figure 1. a, b, and c are different local minima of the corresponding molecule.

2. Theory

In an incremental calculation we divide the total system into small domains consisting of groups of localized orbitals according to the procedure outlined in refs 24−26 and calculate the correlation energies for these domains. To include the nonadditivity corrections, we also calculate correction energies of pairs, triples, etc. of domains, until we reach the desired accuracy. The correlation energy is then computed according to

$$E_{\mathrm{corr}} = \sum_{\substack{\mathrm{X} \\ X \in P(D) \wedge |X| \leq O}} \Delta\varepsilon_X \qquad (1)$$

D is the set of domains, $P(D)$ stands for the power set of the set of the domains and O denotes the order of the expansion. The summation index X in eq 1 runs over all increments up to the order O (see refs 24 and 26 for details). When ε_X represents the correlation energy of the unified subsystems of X, the general correlation energy increment $\Delta\varepsilon_X$ is given as

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$$\Delta\varepsilon_X = \varepsilon_X - \sum_{\substack{Y \\ Y \in P(X) \wedge |Y| < |X|}} \Delta\varepsilon_Y \qquad (2)$$

Here the summation index runs over the power set of X. On the basis of previous work, we expect the series to converge very rapidly if we use the approach of refs 24 and 26 to construct the domains.

Generalizing the previous ideas of Mödl et al.,[30] the extension of the incremental series in eq 1 to the multireference case reads

$$E_{\mathrm{corr}} = E_{\mathrm{corr}}^{\mathrm{active}} + \sum_{\substack{X \\ X \in P(D) \wedge |X| \leq O}} \Delta\varepsilon_X \qquad (3)$$

where $E_{\mathrm{corr}}^{\mathrm{active}}$ is the correlation energy of the active space using the whole virtual space V. The set of domains D is constructed from the occupied orbitals excluding the active space. The correlation energy increments are redefined as

$$\Delta\varepsilon_X = \varepsilon_X - E_{\mathrm{corr}}^{\mathrm{active}} - \sum_{\substack{Y \\ Y \in P(X) \wedge |Y| < |X|}} \Delta\varepsilon_Y \qquad (4)$$

Note that the active space is included in every correlated calculation, and the additional terms in the expansion ensure that its contribution to the correlation energy is counted only once.

If only one active electron is present, the correlation energy of the active space is zero. Thus the expansion eq 3 reduces to the standard incremental expansion and eq 1 can be used to expand the RCCSD correlation energy for calculations on monoradicals. The merely technical difference to the conventional incremental expansion is that we have to include the unpaired electron in every calculation. For more than one unpaired electron $E_{\mathrm{corr}}^{\mathrm{active}}$ does not vanish; however, the RCCSD approach can still be applied to all high-spin (single-reference) cases by merely including the unpaired electrons in every correlated calculation.

3. Obtaining the Correlation Energies

In the present work we apply the RCCSD approach as implemented in MOLPRO[38–40] to evaluate the correlation energies. For a domain K we correlate all electrons in the orbitals of K and the active space in the RCCSD calculation of ε_K whereas the rest of the occupied orbitals remain frozen. The approximate RCCSD correlation energy of the total system is then obtained according to eqs 1 and 2 truncated at the order O.

4. Computational Details

The current implementation contains an interface to the MOLPRO quantum chemistry package[38] to obtain the molecular orbital coefficient matrix, the overlap matrix in AO-basis and the dipole integrals in AO-basis from the previous HF self-consistent field (SCF) calculation. After extraction of the required data a Foster-Boys localization[41] with unitary 2 × 2 rotations in the doubly occupied space is performed. The localization is carried out by the procedure originally proposed by Edmiston and Ruedenberg[42] with a threshold of 10^{-12} (for details we refer to eq 26 in ref 42 and eq 15 in ref 43).

The active orbital and the orbitals that are treated as frozen cores in the subsequent correlation calculation are excluded from the unitary transformations. We use the procedure of ref 25 for the construction of the *l*-site domains.

Because the number of calculations increases quite fast, we had to tighten the threshold for the RHF energies (10^{-10} Hartree) and the RCCSD[44] energies (10^{-8} Hartree) as well as for the RCCSD amplitudes (10^{-5} au). If less strict convergence criteria are applied, numerical errors increase as demonstrated in.[25]

The number of frozen core orbitals in the coupled cluster calculations is given as core and the domain-size-parameter dsp corresponds roughly to the desired number of occupied orbitals in the one-site domains.[24]

5. Applications

5.1. Reaction Pathway of the 4-exo Cyclization. The RI-BP86/TZVP geometries of the molecules in Figure 1 were previously obtained by Friedrich et al.[34] For a detailed analysis of the competing 4-exo and 5-endo reactions we refer to refs 34, 45, and 46.

Figure 2 shows the convergence of the incremental RCCSD correlation energies of eq 3 for a set of intermediates in the 4-exo cyclization. The complete list of incremental correlation energies per order is given in the Supporting Information, whereas the exact RCCSD/cc-pVXZ (X = D, T) values are taken from ref 34. Considering the incremental RCCSD/cc-pVDZ correlation energies we find errors of 4.4−5.2 kcal/mol at the second-order level of the incremental expansion. At the third-order level we recover more than 99.9% of the correlation energy, which corresponds to a largest error of 0.1 kcal/mol. Due to the fast convergence in this case, the fourth-order corrections do not significantly improve the third-order energies. The good convergence and the rapid decrease of errors with increasing incremental order is demonstrated in Figure 2.

TABLE 1: Performance of Different Quantum Chemical Methods for the Reaction Energies of the 4-*Exo* Cyclization Relative to 1 b in kcal/mol[a]

method:	RCCSD							RI-CC2	RI-MP2	RI-BP86	HF
basis set:	cc-pVDZ				cc-pVTZ			TZVPP	TZVPP	TZVP	cc-pVTZ
	incremental			exact	incremental		exact				
molecule/order	2	3	4		2	3					
1 a	3.3	3.1	3.1	3.1	3.3	3.1	3.1	3.3	3.4	2.8	4.0
1 b	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1 c	0.4	0.3	0.3	0.3	0.4	0.3	0.3	0.4	0.5	0.2	0.2
TS **2** a	19.1	19.4	19.3	19.3	18.4	18.8	18.7	17.8	23.4	11.6	27.9
TS **2** b	19.6	19.9	19.8	19.8	19.3	19.7	19.6	18.1	24.1	12.2	30.1
TS **2** c	17.4	17.6	17.5	17.5	16.9	17.1	17.0	15.7	21.4	9.9	26.5
3 a	−0.3	0.1	0.2	0.1	0.1	0.3	0.4	−0.4	0.9	−1.3	6.7
3 b	−1.5	−1.0	−0.9	−1.0	−0.9	−0.4	−0.4	−1.7	−0.4	−1.1	6.7
3 c	−1.8	−1.4	−1.3	−1.3	−1.4	−1.1	−1.1	−2.0	−0.6	−2.6	5.1

[a] The geometries were optimized at the RI-BP86/TZVP level. The zero-point energy correction was approximately included from the RI-BP86/TZVP values for all calculations. a,b,c denote different conformers of the molecules **1**−**3**.

TABLE 2: Convergence of the Incremental RCCSD/cc-pVDZ Correlation Energy of the Singlet and Triplet States of 1,3-Dimethylimidazol-2-ylidene at Their DFT Optimized Equilibrium Geometries (Figure 3)

order	*i*th order correction (au)	$E_{\mathrm{corr}}(i)$ (au)	error (kcal/mol)	% E_{corr}
		Singlet[a]		
1	−0.755405	−0.755405	188.26	71.57
2	−0.309756	−1.065162	−6.11	100.92
3	0.009729	−1.055433	−0.01	100.00
4	0.000008	−1.055425	0.00	100.00
exact CCSD		−1.055420		
		Triplet[b]		
E_{active}	−0.005780			
1	−0.802229	−0.808010	140.11	78.35
2	−0.230110	−1.038119	−4.29	100.66
3	0.006802	−1.031317	−0.02	100.00
4	0.000026	−1.031291	0.00	100.00
exact RCCSD		−1.031287		

[a] 6 domains, dsp = 3, core = 7. [b] 7 domains, dsp = 3, core = 7.

Comparing the relative incremental energies of the different intermediates (using the conformers a, b, c) in Table 1 with respect to the order, we find a better accuracy of the relative energies compared to the absolute energies, because of a beneficial error cancelation. The first-order incremental RCCSD energies lead to inaccurate results for all points in Table 1. The resulting error is already below 1 kcal/mol for the second-order level. This is because the spread of the errors at second-order level (Figure 2) is relatively small for the set of molecules in this study. At the third-order level we observe accurate relative CCSD energies, because even the absolute energies are already accurate at this level (Figure 2).

A comparison of the performance of the different quantum chemical methods in Table 1 for the educts and the products yields similar energies for all applied methods. On the basis of the fact that the HF results do not agree with the other methods, we conclude that electron correlation plays an important role in the quantitative description of the 4-exo cyclization. Comparing the incremental RCCSD results for the transition states, with those obtained by the MP2 method, we find in this case that the cheap second-order incremental expansion is much closer to the exact RCCSD results (cc-pVDZ, cc-pVTZ). Comparing the relative RCCSD energies of the transition states with the DFT results we find a quite large discrepancy. Guided by the results for the 3-exo cyclization, we would expect that the perturbative triples correction is quite important and shifts the coupled cluster results somewhat toward the DFT result.[47] Another aspect is the single-point approximation in the RCCSD calculations, which might also cause errors of a few kcal/mol. Because the RCCSD/cc-pVDZ geometry optimizations were already too time-consuming, we were not able to check how the relative RCCSD energies are affected by the usage of the DFT geometries for the RCCSD calculations. Finally, we conclude that the relative energies at second-order level are fairly accurate and agree better with the exact RCCSD results than the MP2 results do.

TABLE 3: Correlation Contributions to the Singlet−Triplet Excitation and the Errors of the Correlation Contributions for the Carbenes in Figure 3

order	*i*th order contribution (kcal/mol)	error (kcal/mol)
1	−33.01	−48.15
2	16.97	1.83
3	15.13	−0.01
4	15.14	0.00
exact	15.14	

TABLE 4: Convergence of the Incremental RCCSD/6-31++G Correlation Energy for the $(H_2O)_6^-$ and the Cluster $(H_2O)_6$ Cluster of in Figure 4 (6 Domains, dsp = 4, core = 6)**

order	*i*th order correction (au)	$E_{\mathrm{corr}}(i)$ (au)	error (kcal/mol)	% E_{corr}
		$(H_2O)_6^-$		
1	−1.279021	−1.279021	8.72	98.92
2	−0.013790	−1.292811	0.07	99.99
3	−0.000115	−1.292926	0.00	100.00
4	0.000002	−1.292924	0.00	100.00
exact RCCSD		−1.292924		
		$(H_2O)_6$		
1	−1.249244	−1.249244	20.49	97.45
2	−0.032630	−1.281874	0.02	100.00
3	−0.000019	−1.281893	0.01	100.00
4	−0.000012	−1.281905	0.00	100.00
exact CCSD		−1.281905		

TABLE 5: Correlation Contributions to the Electron Affinity and Errors with Respect to the Exact Correlation Energy of $(H_2O)_6^-$ and $(H_2O)_6$ of Figure 4

order	*i*th order contribution (kcal/mol)	error (kcal/mol)
1	−18.69	−11.77
2	−6.86	0.05
3	−6.92	−0.01
4	−6.91	0.00
exact	−6.92	

5.2. An Arduengo Carbene. RI-BP86/TZVP optimized structures of the singlet and the triplet states of 1,3-dimethylimidazol-2-ylidene. After the first isolation of a stable carbene by Arduengo and co-workers,[48] a series of experimental[35,49–51,36,52] and theoretical[53–56] investigations were performed to explain the stability of such carbenes as well as their chemical bonding. To test our incremental RCCSD method for compounds with two unpaired electrons, we decided to study the singlet−triplet excitation of 1,3-dimethylimidazol-2-ylidene (**4**), which was first synthesized by Arduengo et al.[35] In Table 2 we see that the convergence of the incremental correlation energy is rapid for both the singlet and the triplet state. At the third-order level we already have errors below 0.02 kcal/mol. Because the convergence of the correlation energy for the triplet state is as fast as for the singlet state, we conclude that our incremental approach works in the more general case of eq 4, too. If we compare the singlet−triplet excitation energies of Table 3, we find a smaller error in the incremental excitation energies than in the absolute correlation energies, because of a beneficial error cancelation. At the cheap second-order level we obtain already a reasonable error of 1.83 kcal/mol. At the third-order level we have already chemical accuracy with respect to the exact RCCSD energy.

5.3. A Water Cluster Anion. Anionic compounds are usually challenging systems for local correlation methods, because the shape of the localized orbitals is usually more diffuse than the shape of the corresponding orbitals in cationic or neutral compounds. On the other hand, we have shown that water clusters can be calculated very efficiently with the incremental scheme, because the many-body perturbation series converges very fast for this class of compounds.[26] To see which effect dominates for water cluster anions, we decided to study the performance of our approach for a small water cluster anion that is similar to recently studied systems by other groups.[57,58,37,59–61]

If we consider the convergence of the incremental RCCSD correlation energies in Table 4, we find a fast decay of the errors

TABLE 6: High-Order CCSD Increments in cc-pVDZ and cc-pVTZ Basis Sets[a]

	error (kcal/mol)			third-order correction (kcal/mol)		
molecule	2nd order	3rd order	basis aprox[b]	cc-pVTZ	cc-pVDZ	difference
1 a	−5.08	−0.02	0.64	5.09	4.43	−0.66
1 b	−5.22	−0.04	0.51	5.25	4.71	−0.55
1 c	−5.15	−0.03	0.50	5.17	4.64	−0.53
TS **2** a	−5.54	−0.12	0.54	5.66	4.99	−0.66
TS **2** b	−5.54	−0.14	0.55	5.68	4.99	−0.69
TS **2** c	−5.37	−0.12	0.44	5.50	4.93	−0.56
3 a	−5.51	0.02	0.41	5.48	5.09	−0.39
3 b	−5.74	−0.02	0.45	5.75	5.29	−0.47
3 c	−5.55	0.02	0.41	5.52	5.13	−0.39

[a] Errors of the absolute energies with respect to the exact CCSD calculation in a cc-pVTZ basis. a, b, and c denote different conformers of the molecules **1**−**3**. [b] The low-order increments where calculated in the cc-pVTZ basis and the highest order increments in cc-pVDZ basis.

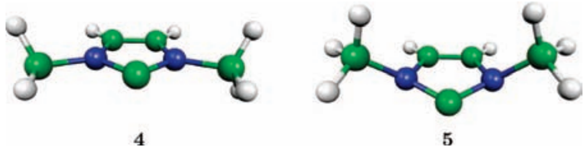

Figure 3. RI-BP86/TZVP optimized structures of the singlet and the triplet states of 1,3,-dimethylimidazol-2-ylidene.

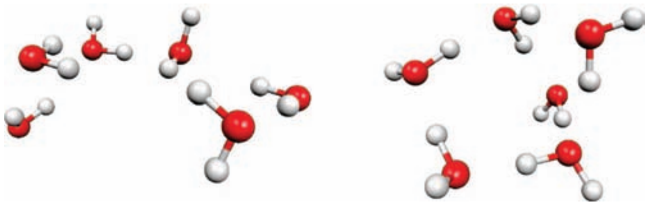

Figure 4. RI-BP86/TZVP optimized structures of $(H_2O)_6^-$ and $(H_2O)_6$.

with respect to the exact result for the anionic cluster and the neutral cluster. This can also be seen in the contributions of the correlation energy to the electron affnity given in Table 5.

In this case even the cheap second-order expansion is suffcient to obtain chemical accuracy. Therefore we conclude that the incremental scheme is a useful tool to obtain highly accurate energies not only for neutral water clusters[26] but also for water cluster anions.

5.4. Approximation of Higher-Order Increments. The evaluation of higher order increments becomes costly due to the increasing number of correlated electrons whereas their contributions usually become quite small and finally negligible. Therefore it is desirable to find an approximate scheme to evaluate the highest order increments in a given expansion at a moderate cost. Using the earlier ideas of Stoll and co-workers,[62,63] we approximate the higher-order increments by small basis set calculations. Here we check the accuracy of this approximation in a rigorous way for the intermediates of the 4-exo cyclization. The motivation of this approximation is as follows: because the third- or fourth-order contributions in the incremental series only contribute by a few kcal/mol, it might be sufficient to have only the first digit correct. This criterion is met if two basis sets are not too different because the correlation energies will be similar in this case. In Table 6 we show the accuracy of this approximation and compare the contribution of the higher orders with respect to the basis set. Considering the results in Table 6, we find that it is indeed possible to approximate the highest order in an incremental calculation by the incremental energy correction in a smaller basis set. In all considered cases we find that the error in the absolute energy decreases by about 5 kcal/mol compared to the uncorrected energy, and the error is below 1 kcal/mol; e.g., by replacing the cc-pVTZ by the cc-pVDZ basis set, we still get 87−93% of the exact third order corrections. We checked the performance of the basis set approximation with respect to the calculation time for a transition state and a product. For these two cases we found a reduction to 28−29% of the total computation time using the exact third order terms in the cc-pVTZ basis set.

To see if the approximation works for difficult cases too, we checked the basis set approximation for the closed-shell $MoCl_6$ complex.[24,64] In this case we approximated the fourth-order terms by a small basis set calculation, because the third order correction is very large (cc-pVTZ 19.02 kcal/mol; cc-pVDZ 14.99 kcal/mol) and the error at the third-order level is still 4.98 kcal/mol in the cc-pVTZ basis set. This error is reduced to 0.18 kcal/mol if the fourth-order terms are approximated by the corresponding calculations in the cc-pVDZ basis set (cc-pVDZ −4.80 kcal/mol).

6. Conclusion

We extended the closed-shell incremental CCSD method to the restricted open-shell case. The application to the reaction energies of the 4-exo cyclization, the Arduengo carbene and the water cluster anion showed that the errors in the correlation energies are below 1 kcal/mol for a third-order calculation. The fourth-order correction gave no significant improvement to the results for most of the systems in this study. Therefore we conclude that the incremental scheme is also able to provide accurate correlation energies for open-shell cases. Furthermore, we demonstrated that the convergence of the incremental series is fast and that it is an alternative method to obtain accurate reaction energies.

Considering the convergence of the incremental series, we did not observe a significant dependence on the one-particle basis set comparing the cc-pVDZ and the cc-pVTZ calculations. Finally, we found that the third-order or fourth-order summation can be approximated by an incremental expansion, using a smaller basis set, without significant loss of accuracy.

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Supporting Information Available: Tables of convergence behavior data. This material is available free of charge via the Internet at http://pubs.acs.org.

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