How Should We Calculate Transition State Geometries for Radical Reactions? The Effect of Spin Contamination on the Prediction of Geometries for Open-Shell Saddle Points

Yao-Yuan Chuang, Elena L. Coitiño, and Donald G. Truhlar*

Department of Chemistry and Supercomputer Institute, University of Minnesota, Minneapolis, Minnesota 55455-0431

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In this article we systematically examine the ability of current electronic structure methods to treat transition states whose unrestricted wave functions show significant spin contamination. Three H atom abstraction reactions have been selected as test cases for the study, namely the reactions of *trans*-N_2H_2 with H, CH_4 with OH, and C_2H_6 with OH. In each case we calculate the exoergicity, barrier heights, and transition state geometry at 3 to 26 levels of theory. The spin contamination in spin-unrestricted electronic structure calculations of the transition states is in the range of 0.755−0.9. Twelve different kinds of ab initio calculation with electron correlation (UMP2, ROMP2, UMP4, UCCD, UQCISD, UCCSD, UQCISD(T), UCCSD(T), RUCCSD, RCCSD, RUCCSD(T), and RCCSD(T)) are applied with two correlation-consistent basis sets (cc-pVDZ and cc-pVTZ). We conclude that quadratic configuration interaction and coupled cluster methods, even with unrestricted reference states, provide good approximations to transition state geometries and energies.

1. Introduction

A central problem in theoretical chemical dynamics is the calculation of barrier heights of chemical reactions. A special difficulty is encountered in the case of radical−molecule reactions because the transition state is an open-shell system with an odd number of electrons. Electronic structure calculations of such species present problems that do not occur for closed-shell singlets. The most widely used theoretical framework for electronic structure calculations on systems with an odd number of electrons is the unrestricted Hartree−Fock (UHF) method.[1] However, it has been recognized for many years that UHF methods systematically overestimate the barrier heights of reactions.[2] This overestimation results from a change in the dynamical electron correlation energy in proceeding from the reactants to the transition state. A further source of error may result from spin contamination of UHF wave functions. In general, UHF wave functions for open-shell systems are not eigenfunctions of the operator $\boldsymbol{S}^2$, where $\boldsymbol{S}$ is the electron spin operator. In particular, UHF wave functions for doublets are contaminated by quartets and higher multiplets.[3] UHF wave functions for transition states of radical-molecule reactions often suffer acutely from this so-called “spin contamination” effect,[4] and thus they do not provide suitable reference states for a perturbation theory treatment. Therefore, attempts to improve the accuracy of UHF wave functions by many-body perturbation theory, as in the popular unrestricted Møller−Plesset second-order (UMP2) theory[5,6] are not as reliable as using perturbation theory for closed-shell systems where spin contamination is not a problem.

The well-established method for circumventing the spin contamination problem at transition states is to use a multiconfiguration self-consistent-field (MCSCF) wave function[7] as the reference state for a treatment of dynamical correlation energy. Unfortunately, it is difficult to find a good multiconfiguration reference,[8] and multireference methods for treating electron correlation are generally very expensive or difficult to use, particularly when one needs gradients to search for the structure of a transition state and when one needs accurate second derivatives of the energy to perform a reaction-rate calculation.

Therefore, it is of great interest to understand better the performance of single-reference methods (i.e., methods based on a single-configuration reference state) that have the potential to make up for the spin contamination of the UHF reference, namely:

- restricted open-shell Möller−Plesset second-order (ROMP2) theory,[9] which is based on a restricted open-shell Hartree−Fock (ROHF) reference state;
- unrestricted coupled-cluster theory with single and double excitations (UCCSD);[10,11]
- unrestricted quadratic configuration interaction with single and double excitations (UQCISD);[12]
- restricted coupled cluster theory with single and double excitations[13] (either restricted to be a spin eigenfunction at the reference level but not at the coupled cluster level, which is called RUCCSD, or restricted to be a spin eigenfunction at both uncorrelated and correlated levels, which is called RCCSD);
- improved versions of UCCSD, UQCISD, RCCSD, and RUCCSD that include a quasiperturbative treatment of fourth-order and fifth-order connected triple-excitation terms, which yields the UCCSD(T),[14] UQCISD(T),[12] RCCSD(T), and RUCCSD(T)[13] methods.

Unfortunately, these methods are not well tested for chemical dynamics calculations, especially for barrier heights. First, all these methods are newer than UMP2. Second, it is hard to test these methods for complex reactions because the true barrier height of a reaction is usually unknown (many workers equate the barrier height to the phenomenological experimental activation energy, but this can be unreliable by 2 kcal or more[15]). Third, one must be careful not to confuse errors due to the incompleteness of the one-electron basis set with errors due to the many-electron formulation of the correlation problem.

In the present paper we test the performance of the ROMP2, UQCISD, UCCSD, RUCCSD, RCCSD, UQCISD(T), UCCSD-

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(T), RUCCSD(T), and RCCSD(T) many-electron formulations with two one-electron basis sets on three hydrogen abstraction reactions:

$$\mathrm{H} + trans\text{-}\mathrm{N_2H_2} \rightarrow \mathrm{H_2} + \mathrm{N_2H} \qquad \text{(R1)}$$

$$\mathrm{OH} + \mathrm{CH_4} \rightarrow \mathrm{H_2O} + \mathrm{CH_3} \qquad \text{(R2)}$$

$$\mathrm{OH} + \mathrm{C_2H_6} \rightarrow \mathrm{H_2O} + \mathrm{C_2H_5} \qquad \text{(R3)}$$

To make our study more complete, we have also included second- and fourth-order perturbation theory based on the unrestricted Hartree−Fock reference state (UMP2 and UMP4[16]), and unrestricted coupled-cluster theory with double excitations[17] (UCCD). All of the calculations are performed with the ACES2,[18] GAUSSIAN94,[19] and MOLPRO[20] electronic structure programs.

A special feature of the present tests is that in all cases the geometries are optimized for reactants, products, and saddle points using the many-electron level and one-electron basis set being tested, even though the saddle point optimization is often difficult or expensive. We have found that rate calculations involving single-point energy calculations at geometries optimized with a lower level or smaller basis set are often quite inaccurate.[21] Previous tests of these levels of theory using saddle point optimization are sparse, but in one notable exception, Watt, Franz, and Bartlett reported a very encouraging test of ROMP2 theory for predicting the transition state geometry and barrier height of the radical hydrogen transfer reaction between ethylene and ethyl radical.[22] We also single out the work of Peterson and Dunning.[13d]

A comment on notation is in order here. The ROMP2 theory used here is the one called RMP2 in ref 9c (where a different theory[23] is called ROMP2). However, after the appearance of ref 9c, the theory called RMP2 has usually been called ROMP2. In particular we note that this is the theory called ROMP2 in refs 9a and 9b and in both the GAUSSIAN[19] AND ACES2[18] codes. ROMP2 is based on an ROHF reference, but the correlated wave function is *not* restricted to be a spin eigenfunction. Thus the theory might also be called RUMP2, by analogy to RUCCSD. However, the ROMP2 name is both descriptive and widely used, and so we adopt this notation here, preferring to use the most popular name for each method rather than the most systematic names. We also note that QCID is identical to CCD, and we use the more common name (CCD).

2. Most Accurate Available Data for Comparison

We use both classical barrier heights $V^‡$ and classical exoergicities ΔE to test the reliability of the predictions given by each of the theoretical methods examined in this work. Here, V or E denotes the electronic energy plus nuclear repulsion, excluding zero-point effects, and Δ denotes the value at products minus that at reactants. In this section we collect the data currently available for the three processes considered and discuss the reliability of the numbers given, to establish a clear base for the comparisons in this paper.

2.1. Classical Exoergicities ΔE. The classical exoergicity can be calculated directly,[24,25] or it can be estimated from the experimental enthalpy change ΔH at $T = 0$ K by subtracting the change in zero-point energy.[26,27] For reaction R1 we take our best estimate of ΔE as −37.3 kcal/mol, which is the MRCI55//MCSCF value calculated by Linder et al.[25] For reactions R2 and R3 we accept the estimates of Melissas and one of the authors,[26,27] which are −13.3 kcal/mol and −17.3 kcal/mol, respectively. In all cases we allow for an uncertainty of ∼0.7 kcal/mol.

2.2. Classical Barrier Heights $V^‡$. As far as we know, there is no experimental information for the rate of the reaction of atomic hydrogen with *trans*-diazene. The accurate classical barrier height for reaction R1 was estimated theoretically to be 4.3 kcal/mol by Linder et al.[25] Their calculations involved transition state geometry optimization by MCSCF/cc-pVDZ calculations with a full-valence complete active space of eleven orbitals, followed by a multireference configuration interaction (MRCI) with the cc-pVTZ basis and including all single and double excitations out of a five-orbital complete active space. It is hard to estimate the reliability of this calculation, but we accept their estimate as the best available, with an uncertainty of ∼1 kcal/mol.

The barrier height for reaction R2 between methane and OH has been predicted by several authors, based both on experimental kinetic evidence[28,29] and theoretical calculations.[26,30−33] Experimental studies have estimated the activation energy for this reaction to be in the range from 4 to 7 kcal/mol.[28] However, it is hard to accurately predict the barrier height from the experimental data because the Ahrrenius plots obtained from kinetic measurements performed at several temperatures are curved.[29] Thus, the best estimate of the classical barrier of the reaction is obtained from dynamical calculations which were able to reproduce the observed kinetics for the reaction over a wide range of temperatures. Melissas and one of the authors[26] calculated the barrier height for this reaction by optimizing the structures at the UMP2/*adj*-cc-pVTZ level, where *adj* denotes that the basis set has been adjusted to match the calculated exoergicity at the UMP2−SAC level to the experimental one, and SAC denotes scaling all correlation energy.[34] Forcing the calculation to yield the correct exoergicity was expected to improve the reliability of the transition state geometry. The barrier height was estimated to be 7.4 kcal/mol with UMP2-SAC/*adj*-cc-pVTZ single point calculations. Then the potential surface was tested by comparing the reaction rates calculated by variational transition state theory with multidimensional semiclassical tunneling (VTST/MT) to the experimental reaction rates. The dynamical calculation at the UMP2-SAC/*adj*-cc-pVTZ//UMP2/cc-pVTZ electronic structure level yielded agreement with experimental rate constants within a factor of 2.0 over the entire 223−1512 K range. Furthermore, for 295−1000 K the calculations were systematically lower than experiment, indicating that the barrier may be slightly overestimated. From these calculations we estimate that the true barrier is about 7 kcal/mol. We note, however, that Malick et al.[35] have estimated a barrier of 5.1 kcal for this reaction by the CBS-QCI-APNO[36] method. Thus we will take the best estimate as 5−7 kcal/mol.

The Ahrrenius plots for reaction R3 show significant curvature at temperatures lower than 700 K.[37] Dynamics calculations were performed by Melissas and one of the authors;[27] for this reaction the best agreement with experimental rate constants is obtained with PMP2//UMP2/*adj*-cc-pVTZ calculations (where PMP2 is spin-projected[4] UMP2) instead of the UMP2-SAC//UMP2 ones. For ethane, the calculated classical barrier is 4.0 kcal/mol, and the reaction rates are in good agreement with experiment (within a factor of 2.0) between 200 and 800 K. More recently, Martell et al.[38] have report a Gaussian-2 (G2)[39] estimate of 3.0 kcal/mol for the activation energy at 0 K, which leads to a classical barrier height of 4.8 kcal/mol once the zero-point contribution is removed. It has been shown that the G2 method can have errors as large as 2.6 kcal in predicting classical barrier heights for reactions involving open-shell transition

TABLE 1: Energies (kcal/mol) and Bond Lengths (Å) of R1[a,b]

theory	ΔE	$V^{\ddagger}$	$R^{\ddagger}$(H−H)	$R^{\ddagger}$(N−H)	$\langle S^2\rangle^{\ddagger}$
UHF/cc-pVDZ	37.4	10.8	1.11	1.15	0.970
ROHF/cc-pVDZ	−32.2	19.6	1.02	1.17	0.750
UMP2/cc-pVDZ	−28.0	13.5	1.12	1.15	0.819[c]
ROMP2/cc-pVDZ	−33.7	6.9	1.14	1.13	
UMP4/cc-pVDZ	−32.9	10.1	1.19	1.12	
UCCD/cc-pVDZ	−32.8	10.3	1.16	1.13	
UQCISD/cc-pVDZ	−38.7	3.7	1.23	1.11	
UCCSD/cc-pVDZ	−38.0	4.0	1.23	1.11	
RUCCSD/cc-pVDZ	−37.9	4.0	1.21	1.12	0.754
RCCSD/cc-pVDZ	−37.5	4.5	1.18	1.13	0.750
UQCISD(T)/cc-pVDZ	−37.9	3.4	1.25	1.11	
UCCSD(T)/cc-pVDZ	−37.4	3.7	1.25	1.11	
RUCCSD(T)/cc-pVDZ	−37.7	3.3	1.25	1.11	0.754
RCCSD(T)/cc-pVDZ	−37.4	3.7	1.22	1.11	0.750
UMP2/cc-pVTZ	−29.1	12.8	1.09	1.14	0.810[d]
ROMP2/cc-pVTZ	−34.1	7.0	1.13	1.12	0.750
UMP4/cc-pVTZ	−33.8	9.1	1.16	1.12	
UCCD/cc-pVTZ	−34.4	9.1	1.13	1.13	
UQCISD/cc-pVTZ	−39.1	3.7	1.20	1.11	
UCCSD/cc-pVTZ	−38.6	4.0	1.19	1.11	
RUCCSD/cc-pVTZ	−38.4	3.9	1.18	1.12	0.755
RCCSD/cc-pVTZ	−38.0	4.5	1.15	1.12	0.750
UQCISD(T)/cc-pVTZ	−38.2	3.0	1.22	1.11	
UCCSD(T)/CC−PVTZ	−37.8	3.4	1.22	1.11	
RUCCSD(T)/cc-PVTZ	−38.1	3.0	1.22	1.11	0.755
RCCSD(T)/ cc-PVTZ	−37.6	3.5	1.18	1.12	0.750
best estimate	−37−38	3−5			0.750

[a] All basis sets use spherical harmonic d and f shells. [b] All calculations are done with uncorrelated core. [c] UHF/cc-pVDZ value of $\langle S^2\rangle^{\ddagger}$ at UMP2 geometry is 0.860. [d] UHF/cc-pVTZ value of $\langle S^2\rangle^{\ddagger}$ at UMP2 geometry is 0.849.

states.[40] Considering all these pieces of information, we estimate that the true barrier is in the range 3−4 kcal/mol.

3. Results and Discussion

We carried out calculations with a polarized double-ζ (cc-pVDZ)[41] and a polarized triple-ζ (cc-pVTZ)[41] basis set.

Table 1 shows the results for reaction R1 at various levels of theory. The unrestricted MP2 treatment suffers from severe spin contamination and overestimates the classical barrier height $V^{\ddagger}$; in particular, UMP2 with the cc-pVDZ and cc-pVTZ basis sets gives $V^{\ddagger}$ equal to 13.5 and 12.8 kcal/mol, respectively. When we increase the order of perturbation theory to fourth order, the UMP4 calculation only lowers $V^{\ddagger}$ by 3.4−3.7 kcal/mol. The restricted-open-shell MP2 calculation (ROMP2) lower the UMP2 barrier heights by ∼50%, but still appear to give too high a value of $V^{\ddagger}$, as does coupled cluster theory with only double excitations. If we include single and double excitations in the QCI or CC treatments, the $V^{\ddagger}$ values are close to the estimation from Linder et al., which is 4.3 kcal/mol. Thus either UQCISD or UCCSD gives a reasonable barrier height for reaction R1. The unrestricted methods with quasiperturbtive triple excitations (UQCISD(T) and UCCSD(T)) result in a $V^{\ddagger}$ value that is 0.3−0.6 kcal/mol lower than without triples. Some confirmation that coupled-cluster theory at the SD or SD(T) levels is valid is provided by the ΔE values. Furthermore, and most important of all, we note that RUCC and RCC calculations are in encouragingly good agreement with the UQCI and UCC calculations.

Since our recent work[21] has shown that the use of accurate transition state geometries is a critical factor in the prediction of accurate reaction rates, it is very important to look at the predicted transition state geometries, and in fact these geometries are the main focus of the present study. Table 1 shows the breaking N−H and the forming H−H bond distances at the transition state geometries at different levels of theory. The calculations in Table 1 that yield accurate values for ΔE and $V^{\ddagger}$ indicate that the internuclear distance of the making H−H bond is about 0.1 Å longer than the internuclear distance of the breaking N−H bond. The transition state geometries predicted by the UMP2, ROMP2, and UCCD methods all appear qualitatively incorrect. The UMP4 results are slightly better but still differ significantly from the results of the UQCISD, UCCSD, RUCCSD, UQCISD(T), UCCSD(T), RUCCSD(T), and RCCSD(T) methods, which form a reasonably consistent set.

Probably the most disappointing aspect of these results is the poor performance of the ROMP2 method for the geometry of the transition state. In fact this result causes one to revise the usual interpretation of the poor performance of UMP2 for cases such as this. The usual interpretation is spin contamination, and one would hope that ROMP2 would overcome this. But the ROMP2 transition state geometry is very similar to the UMP2 one. In contrast, UMP4 is closer to the consistent UQCISD, UCCSD, RUCCSD, UQCISD(T), UCCSD(T), and RUCCSD(T) values than is ROMP2. Thus higher-order correlation effects (singles, triples, and quadruples) may be more important than ensuring a spin eigenfunction. At the very least, attributing the poor performance solely to spin contamination appears to be an oversimplification. An important consideration to keep in mind is that spin contamination is a symptom of a deeper malady, namely the inadequacy of a single-configuration description, and ROHF and ROMP2 do not correct this. In particular the ROHF wave function may provide a qualitatively incorrect description in some cases under the same circumstances where UHF shows large spin contamination. However QCISD and CCSD methods show much more invariance than perturbation theory to the quality of the reference state and therefore do have the potentiality to obtain a qualitatively correct result even when the reference state does not provide a good starting point.

The MCSCF/cc-pVDZ saddle point geometry of Linder et al. has $R^{\ddagger}$(H−H) = 1.20 Å and $R^{\ddagger}$(N−H) = 1.17 Å. This is in poor agreement with the consistent higher-level results. This finding is perhaps not surprising since the MCSCF calculation does not include external (dynamical) correlation. However, MCSCF calculations are a popular approach to calculating saddle point geometries and reaction paths; confidence in this approach has been buoyed by the belief that a multi-configuration calculation might provide a balanced treatment of bond breaking and bond making, but such optimism is apparently unjustified.

The uneven performance of RCCSD(T) for geometries is consistent with the finding of Perterson and Dunning[13d] that RUCCSD(T) yields more systematic potential energy surface predictions than RCCSD(T).

Tables 2 and 3 provide a considerably different story from Table 1. Here ROMP2, UQCISD, and UCCSD no longer appear to provide more accurate barrier heights than UMP2 for the basis sets tested. This seems to be correlated to the fact that spin contamination is much less severe in these cases. Again, however, the transition state geometries indicate that it is more important for geometry that the correlated treatment goes beyond second order than that it eliminates spin contamination. (We note from the tables that reaction R1 is much less sensitive to the one-electron basis set (polarized triple-ζ vs polarized double-ζ) than are the OH reactions, but that issue is peripheral to our focus here.)

TABLE 2: Energies (kcal/mol) and Bond Lengths (Å) of R2[a,b]

theory	ΔE	$V^\ddagger$	$R^\ddagger$(O−H)	$R^\ddagger$(H−C)	$\langle S^2 \rangle^\ddagger$
UHF/cc-pVDZ	1.1	27.3	1.20	1.30	0.794
ROHF/cc-pVDZ	1.4	34.1	1.19	1.28	0.750
UMP2/cc-pVDZ	−10.2(−14.9)[c]	10.5	1.29	1.21	0.760[d]
ROMP2/cc-pVDZ	−10.2(−14.9)	10.3	1.31	1.20	
UMP4/cc-pVDZ	−6.7(−8.6)	10.8	1.26	1.24	
UCCD/cc-pVDZ	−6.4(−10.2)	13.9	1.25	1.25	
UQCISD/cc-pVDZ	−6.5(−10.3)	11.2	1.25	1.26	
UCCSD/cc-pVDZ	−6.5(−10.3)	11.5	1.25	1.25	
RUCCSD/cc-pVDZ	−6.5	11.8	1.24	1.26	0.754
RCCSD/cc-pVDZ	−6.5	12.4	1.24	1.25	0.750
UQCISD(T)/cc-pVDZ	−6.7(−10.9)	9.7	1.26	1.25	
RUCCSD(T)/cc-pVDZ	−6.7	9.8	1.26	1.25	0.754
RCCSD(T)/cc-pVDZ	−6.7	10.4	1.26	1.25	0.750
UMP2/cc-pVTZ	−14.9	8.8	1.32	1.19	0.759[e]
UCCD/cc-pVTZ	−10.2	12.5	1.27	1.22	
best estimate	−13−14	5−7			0.750

[a] All basis sets use spherical harmonic d and f shells. [b] All calculations are done with uncorrelated core. [c] Values in parentheses are ΔE with cc-pVTZ basis set. [d] UHF/cc-pVDZ value of $\langle S^2 \rangle^\ddagger$ at UMP2 geometry is 0.781. [e] UHF/cc-pVTZ value of $\langle S^2 \rangle^\ddagger$ at UMP2 geometry is 0.779.

TABLE 3: Energies and Bond Lengths of R3[a,b]

theory	ΔE	$V^\ddagger$	$R^\ddagger$ (O−H)	$R^\ddagger$ (H−C)	$\langle S^2 \rangle^\ddagger$
UMP2/cc-pVDZ	−12.9(−17.9)[c,d]	8.0	1.33	1.20	0.759[e]
UCCD/cc-pVDZ	−9.2(−13.1)	11.4	1.28	1.23	
UQCISD/cc-pVDZ	−9.5(13.5)	8.5	1.29	1.23	
best estimate	−17−18	3−4			0.750

[a] All basis sets use spherical harmonic d and f shells. [b] All calculations are done with uncorrelated core. [c] Values in parentheses are ΔE with cc-pVTZ basis set. [d] ROMP2 values of ΔE are −13.0 kcal/mol with cc-pVDZ and −18.0 kcal/mol with cc-pVTZ. [e] UHF/cc-pVDZ value of $\langle S^2 \rangle^\ddagger$ at UMP2 geometry is 0.779.

Melissas and Truhlar[42] used the calculations of ref 26 to predict the $^{12}CH_4/^{12}CD_4$ and $^{12}CH_4/^{13}CH_4$ kinetic isotope effects on reaction R2. The latter was in good agreement with existing experiments and the former was not; however, new experiments[43] confirmed the prediction. Since kinetic isotope effects are usually sensitive to the transition state geometry (typically because of the indirect effect that vibrational frequencies are sensitive to the extent of progress along the reaction path), this gave some credence to the UMP2/*adj*-cc-pVTZ transition state geometry that was obtained in these calculations, which was $R^\ddagger$(O−H) = 1.30 Å and $R^\ddagger$ (H−C) = 1.19 Å. Table 2 shows though that this is in better agreement with the UMP2/cc-pVTZ result than with the UCCD/cc-pVTZ result, which (on the basis of the trends at the cc-pVDZ level) is probably more accurate. Thus we conclude that the true saddle point geometry may be later (smaller O−H distance, larger C−H distance) than that on the potential energy surface of refs 26 and 42, because the surface of those references was based on UMP2 calculations.

Another (perhaps unexpected) feature of the results in Tables 2 and 3 is the good geometries obtained by UCCD and UQCISD calculations. The improvement of UQCISD and UCCSD methods over UMP2 method for cases with significant multi-configuration character is often attributed to the single-excitation operator, and this assumption is seldom checked by carrying out UCCD calculations. However, for reactions R2 and R3, UCCD geometries are very similar to UQCISD ones. Energies, however, are significantly worse, and the trend in geometries does *not* hold for reaction R1, so we conclude that UCCD is less reliable than UCCSD. The poor performance of the UCCD method for energies could perhaps be anticipated from its poor performance[4c] for $\langle S^2 \rangle$ in other applications. However, UQCISD does consistently perform as well as UCCSD.

The transition states studied here were selected because they provide a complementary pair of situations in that the first has very large spin contamination at the unrestricted level (UMP2 $\langle S^2 \rangle = 0.819$ for R1) and the other reactions have very small spin contamination (UMP2 $\langle S^2 \rangle = 0.759{-}0.760$). In many other cases the spin contamination is intermediate, e.g., the UMP2 $\langle S^2 \rangle$ for the transition state of the OH + HCl reaction is 0.78.[44]

4. Concluding Remarks

Ideally one would include open-shell effects in the reference configuration in a more satisfactory way than UHF. However, improving the reference function is very expensive and still presents numerous questions about how to choose a satisfactory multi-configuration reference state in a systematic yet affordable way. Thus one goal of the present work is to explore more fully the question of quantitatively how well the single excitations and triple excitations in currently available CC and QCI methods make up for deficiencies in the open-shell UHF reference.

QCISD and CCSD methods often give similar results. Although CCSD contains more terms, QCISD sometimes gives more accurate answers, due to cancellation of errors.[45] In other cases, though, the more complete CC formalism appears superior to QCI. A noteworthy aspect of both QCISD and CCSD is the inclusion of the T_1T_2 excitation operator, where T_1 and T_2 are operators generating single and double excitations, and T_1T_2 is an unconnected triple excitation. The CCSD formalism also includes $^1/_2T_1^2$, $^1/_6T_1^3$, $^1/_{24}T_1^4$, and $^1/_2T_1^2T_2$ and, in fact, it couples the single and double excitations to infinite order. All these operators containing T_1 give the methods a modicum of invariance to the reference state. Despite this, CCSD-like methods are still known to break down for structures far from equilibrium.[46] Transition states can present an intermediate case, and the calculations in the previous section were designed to test how well CCSD-like methods perform in practice for radical−molecule transition states, even when connected triple excitations are included only quasiperturbatively. Two questions arise: (i) Are UQCISD and UCCSD more successful than UMP2 when the unrestricted Hartree−Fock reference is bad? (ii) Is UCCSD systematically better than UQCISD in such cases because it includes more terms? Our results answer these questions yes and no, respectively. Usually the connected triples operator T_3 is also important if T_1T_2 is important, but inclusion of T_3, as in QCISD(T) and CCSD(T), greatly increases the computational cost. Our results show that the UQCISD and UCCSD methods predict surprisingly accurate saddle point geometries, but the connected triples are needed for reliable saddle point energies.

Probably the most popular method for optimizing geometries for open-shell transition states is UMP2, because it is affordable even for medium-sized molecules. However, it has not been clear what is the preferred way to go beyond UMP2 when UMP2 is not reliable. The present study was motivated by the observation that ROMP2 and UCCSD(T) geometries differ significantly for reactions R1 and R2. The question arose: which is more reliable—ROMP2 because it eliminates spin contamination in the reference or UCCSD(T) because it includes higher excitations? We have settled this question by carrying out RUCCSD(T) geometry optimizations for both molecules. The RUCCSD(T) method simultaneously removes spin contamination in the reference state and also includes higher excitations. The RUCCSD(T) geometries are in much better agreement with the UCCSD(T) results than with the ROMP2 results. Interestingly they are also in good agreement with UQCISD(T), UCCSD, and UQCISD geometries. We conclude that these three methods and UCCSD(T) should be preferred to UMP2 and ROMP2 for transition state geometry optimization. This conclusion is particularly encouraging for UQCISD geometries because the GAUSSIAN package, which is widely available and has very good transition state optimization algorithms, contains UQCISD gradients. Our conclusion is consistent with the finding by Durant and Rohlfing[40,47] that QCISD geometries lead to empirically improved agreement (compared to UMP2 geometries) of higher-level calculations with MRCI calculations.

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