

Assessment of Multireference Perturbation Methods for Chemical Reaction Barrier Heights.

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Abstract

A few flavours of multireference perturbation theory, two variants of the n -electron Valence State Perturbation Theory and two of the Complete Active Space Perturbation Theory, are here tested for the calculation of barrier heights for the set of chemical reactions included in the DBH24/08 database, for which very accurate values are available. The comparison of the results obtained with these approaches with those already published for other theoretical models indicates that multireference perturbation theory is a valuable tool for the description of a chemical reaction. Moreover, limiting the comparison to the perturbation theory approaches, one observes that the bad behavior found for single reference methods (such as Møller-Plesset to second and fourth order in the energy) is markedly improved moving to the multireference generalizations.

Introduction

The computational study of transition states is a key aspect to perform reliable simulations of the reactivity of chemical systems. Indeed, a good estimate of the chemical reaction barrier heights is essential to obtain accurate kinetic parameters, such as the rate constants. On the other hand, transition states represent a major challenge for quantum chemistry, since a single reference wave function often provides a poor description of the systems far from the minima of the potential energy surface (PES). Recently, Zheng *et al.*¹ carried out a comprehensive systematic study to evaluate the accuracy of different computational methods for the estimation of the barrier heights of a set of chemical reactions. They used as benchmark a set of twelve reactions, called the DBH24/08 database, for which very accurate estimates for the barrier heights are available. For this set they calculated the errors for 348 computational models, including wave functions based methods, density functional theory (DFT) methods, semi-empirical methods and multi-level methods. In that study they have not considered the multireference perturbation methods, while in a previous work² the same research group tested the performances of the multireference second order Møller-Plesset theory (MRMP2)³ on the twelve reactions of the DBH24/08 database. Since the formulation of

the MRMP2 method, further important advancements have been made in the multireference perturbation theory, which have proved valuable in challenging situations. For instance the n -electron valence state perturbation theory (NEVPT), developed by our group, has been very effective in the estimation of the electronic excitation energies⁴⁻⁷ and in the study of intermetallic bonds.⁸⁻¹⁰ In this work we intend to evaluate the accuracy of two different multireference perturbation approaches, namely NEVPT and the complete active space perturbation theory (CASPT) for the calculation of the barrier heights of the twelve reactions included in the DBH24/08 database.

Method

Theoretical Methods

NEVPT¹¹⁻¹⁴ is a form of multireference perturbation theory based on a CAS-SCF or CAS-CI zero order wave function which uses perturber functions of multireference type. The zero order Hamiltonian (H_0) is derived from Dyalls model Hamiltonian, it is bielectronic in the active orbital space and monolectronic in the core and virtual orbitals. The zero order energies and the perturber functions are obtained through the partition of the first order interacting space (FOIS) in subspaces, defined by the type of excited electrons (from core or active space) and by the type of orbitals occupied in the excitation (active or virtual), and then by diagonalizing Dyal's Hamiltonian on these subspaces. In the second order formulation of the NEVPT theory (NEVPT2), the only one considered in this paper, one only has to define the zero order Hamiltonian in the CAS and FOIS space, the latter being composed by eight subspaces. Two variants of the theory have been developed, they can be distinguished according to the degree of contraction of the FOIS. In the strongly contracted form (SC-NEVPT) the subspaces are contracted in order to obtain a single perturber function for each occurrence of a given excitation pattern in the doubly occupied and virtual orbitals spaces. The partially contracted version (PC-NEVPT) uses a larger number of perturber functions, thus it is more flexible and is in principle expected to provide better results. However, in general the two versions provide very similar results, provided that the reference function is chosen

appropriately. In the CASPT2¹⁵ method, the zero-order Hamiltonian is defined starting from a pure mono-electronic (Fock-like) model Hamiltonian and this is the fundamental difference with respect to NEVPT2. In 2004, Ghigo *et al.*¹⁶ introduced the so-called ionization potential-electron affinity (IPEA) shift of the zero-order CASPT2 Hamiltonian in order to correct the systematic overestimate of the correlation energy for the open shell systems. In our calculations we consider CASPT2 both in the original version (shift parameter equal to zero) and with the shift parameter fixed 0.25 a.u., that is the standard value suggested in Ref. 16. Both the CASPT2 and NEVPT2 methods coincide with the second-order Møller-Plesset perturbation theory (MP2) when just a single-determinant function is used as reference.

DBH24/08 Database

In order to test the multireference perturbation methods in the calculation of chemical reaction barrier heights, we used as trial the DBH24/08 database,¹ for which several data are available for comparison. This database consists of twelve reactions selected to be statistically representative of the larger NHTBH38/04 database¹⁷ and Database/3.¹⁸ The reactions defining this database, together with the relative best references are shown in Table 1. The best estimates for the barrier heights are based on calculations at high level of theory (W4, W3.2 or MRCI) or are derived from experimental data (VSEC). For more details on the database we refer to the original publication.¹

Computational Details

As zero order description for the perturbation methods, we used the CASSCF wave functions with full valence active spaces. Namely, all the electrons and all the valence orbitals of the considered molecules are included in the active spaces. This choice was motivated by the purpose to obtain a balanced description of reactants, products and transition states. A procedure of this type is not scalable to larger systems, but it is useful to assess the accuracy of the considered methods. The only exception is the $\text{OH}^- + \text{CH}_3\text{F} \rightarrow \text{HOCH}_3 + \text{F}^-$ reaction for which we used smaller active spaces to circumvent computational problems arising from the use of too large active spaces. In

Table 1: Reactions and best estimates for the barrier heights (in kcal/mol) in the DBH24/08 database.

Reaction	forward/reverse BH	method
Heavy-Atom Transfer		
1) $\text{H} + \text{N}_2\text{O} \rightarrow \text{OH} + \text{N}_2$	17.13/82.47	W4
2) $\text{H} + \text{ClH} \rightarrow \text{HCl} + \text{H}$	18.00/18.00	MRCI
3) $\text{CH}_3 + \text{FCl} \rightarrow \text{CH}_3\text{F} + \text{Cl}$	6.75/60.00	W3.2
Nucleophilic Substitution		
4) $\text{Cl}^- \cdots \text{CH}_3\text{Cl} \rightarrow \text{ClCH}_3 \cdots \text{Cl}^-$	13.41/13.41	W3.2
5) $\text{F}^- \cdots \text{CH}_3\text{Cl} \rightarrow \text{FCH}_3 \cdots \text{Cl}^-$	3.44/29.42	W3.2
6) $\text{OH}^- + \text{CH}_3\text{F} \rightarrow \text{HOCH}_3 + \text{F}^-$	-2.44/17.66	W3.2
Unimolecular and Association		
7) $\text{H} + \text{N}_2 \rightarrow \text{HN}_2$	14.36/10.61	W4
8) $\text{H} + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_5$	1.72/41.75	VSEC
9) $\text{HCN} \rightarrow \text{HNC}$	48.07/32.82	W4
Hydrogen Transfer		
10) $\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2\text{O}$	6.7/19.6	experiment
11) $\text{H} + \text{OH} \rightarrow \text{O} + \text{H}_2$	10.7/13.1	MRCI
12) $\text{H} + \text{H}_2\text{S} \rightarrow \text{H}_2 + \text{HS}$	3.6/17.3	experiment

Table 2, we show the size of the active spaces for the molecules involved in our analysis. For the nucleophilic substitutions, 4) and 5) in Tab. 2, we kept frozen at the Hartree-Fock level the core orbitals in the CASSCF calculations to prevent the 1s orbital of carbon to enter in the active space. For all the calculations we employed the aug-cc-pVTZ basis set.^{19,20} The molecular geometries were taken from the DBH24/08 database where they have been optimized by the QCISD/MG3 method, where MG3 is the basis set reported in Ref. 21. For the transition state of the reaction 4), we modified slightly the geometry in order to increase the symmetry from the C_1 to the C_{2v} symmetry point group. This precaution promoted the convergence of the CASSCF calculations, without any appreciable change in the electronic energies (the energy difference between the two geometries, at QCISD/MG3 level, is less than 10^{-7} hartree). All the molecular geometries, CASSCF, NEVPT and CASPT energies are reported in the supporting information. The SC-NEVPT2 and PC-NEVPT2 calculations were performed using the version 2010.1 of the Molpro program.²² The CASPT2 calculations were performed using the version 7.6 of the Molcas program. The perturbation corrections have been calculated with frozen core electrons. All the heights of the barriers are

estimated as differences between the electronic energies, therefore they do not include the effects of the zero point energies. We have considered the effect of spin-orbit coupling for the molecules Cl, O, OH, HS lowering their energies, respectively, by 0.84, 0.22, 0.20 and 0.54 kcal/mol as reported in the work of Zheng *et al.*¹

Table 2: Active spaces used in the reference CASSCF wave functions for all the molecules considered.

Heavy-Atom Transfer				
H	N ₂ O	N ₂	OH	TS[N ₂ OH]
(1,1)	(16,12)	(10,8)	(7,5)	(17,13)
H	HCl			TS[H ₂ Cl]
(1,1)	(8,5)			(9,6)
CH ₃	FCl	CH ₃ F	Cl	TS[CH ₃ FCl]
(7,7)	(14,8)	(14,11)	(8,4)	(21,15)
Nucleophilic Substitution				
ClCH ₃ ...Cl ⁻				TS[ClCH ₃ Cl ⁻]
(22,15)				(22,15)
F ⁻ ...CH ₃ Cl	FCH ₃ ...Cl ⁻			TS[FCH ₃ Cl ⁻]
(22,15)	(22,15)			(22,15)
OH ⁻	CH ₃ F	HOCH ₃	F ⁻	TS[OHCH ₃ F ⁻]
(8,4)	(8,8)	(8,8)	(8,4)	(10,9)
Unimolecular and Association				
H	N ₂	N ₂ H		TS[N ₂ H]
(1,1)	(10,8)	(11,9)		(11,9)
H	C ₂ H ₄	C ₂ H ₅		TS[C ₂ H ₅]
(1,1)	(12,12)	(13,13)		(13,13)
HCN	CNH			TS[HCN]
(10,9)	(10,9)			(10,9)
Hydrogen Transfer				
OH	CH ₄	CH ₃	H ₂ O	TS[OHCH ₄]
(7,5)	(8,8)	(7,7)	(8,6)	(15,13)
H	OH	O	H ₂	TS[OH ₂]
(1,1)	(7,5)	(6,4)	(2,2)	(8,6)
H	H ₂ S	HS	H ₂	TS[H ₃ S]
(1,1)	(8,6)	(7,5)	(2,2)	(9,7)

Results

In Table 3 the results for the calculations with the CASSCF method are reported. The mean error for the estimation of the twenty-four barrier heights (one forward and one reverse barrier for each reaction) is of 9.28 kcal/mol, a result very far from the chemical accuracy, conventionally placed around 1 kcal/mol. The use of full valence active spaces guarantees a good description of the non-dynamic electron correlation and the poor performance of CASSCF implies that what is missing at this level, the dynamic correlation of the electrons, is crucial for the accurate estimation of the barrier heights of chemical reactions. Considering the average error for different classes of reactions, we notice that the worst performance are obtained for the heavy-atom transfer and the nucleophilic substitution reactions, for which the mean errors are respectively 10.87 and 10.25 kcal/mol. For the association/unimolecular and the hydrogen transfer reactions, the mean errors are lower and correspond to 7.46 and 8.52 kcal/mol. The high positive value of the mean signed error indicates a systematic overestimation of the barrier heights.

Table 3: Relative errors, mean absolute error and mean signed error (in kcal/mol) for the barrier heights computed with the CASSCF method respect to the best references reported in Tab. 1.

Reaction	forward BH	reverse BH
$\text{H} + \text{N}_2\text{O} \rightarrow \text{OH} + \text{N}_2$	12.14	12.88
$\text{H} + \text{ClH} \rightarrow \text{HCl} + \text{H}$	11.02	11.02
$\text{CH}_3 + \text{FCl} \rightarrow \text{CH}_3\text{F} + \text{Cl}$	5.65	12.53
$\text{Cl}^- \cdots \text{CH}_3\text{Cl} \rightarrow \text{ClCH}_3 \cdots \text{Cl}^-$	6.73	6.73
$\text{F}^- \cdots \text{CH}_3\text{Cl} \rightarrow \text{FCH}_3 \cdots \text{Cl}^-$	2.82	18.63
$\text{OH}^- + \text{CH}_3\text{F} \rightarrow \text{HOCH}_3 + \text{F}^-$	13.5	13.09
$\text{H} + \text{N}_2 \rightarrow \text{HN}_2$	11.71	-11.23
$\text{H} + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_5$	5.26	-7.11
$\text{HCN} \rightarrow \text{HNC}$	5.37	4.11
$\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2\text{O}$	11.21	4.76
$\text{H} + \text{OH} \rightarrow \text{O} + \text{H}_2$	6.59	14.11
$\text{H} + \text{H}_2\text{S} \rightarrow \text{H}_2 + \text{HS}$	7.39	7.05
Mean absolute error	9.28	
Mean signed error	7.75	

As a general consideration, one has to stress that the nature of the chemical bonds in the tran-

sition states often shows a considerable complexity, given that in such a situation one can observe the simultaneous formation and breaking of the bonds, the hypervalency, the unusual bond lengths, many of these problems requiring in general the use of a multicentric description of the bond. The types of bonding models that can be used to describe the active site in the transition states of the reactions of the database DBH24/08 are collected in Table 4. For the heavy-atom transfer and hydrogen transfer reactions, we can represent the bonding in the active site with a three-center three-electron (3c3e) model, in which three orbitals are involved: a bonding, a non-bonding and an antibonding orbital. As an illustrative example the three orbitals for the transition state H_2Cl of the $\text{H} + \text{ClH} \rightarrow \text{HCl} + \text{H}$ reaction are shown in Figure 1.

Except for the case of the reaction $\text{H} + \text{N}_2\text{O} \rightarrow \text{OH} + \text{N}_2$, where the transition state has a N-O bond much stronger than the forming O-H bond, for all the atom transfer reactions here considered, the antibonding orbital of the multicentric system is the lowest unoccupied molecular orbital (LUMO) and it has the highest occupation number among the virtual orbitals of the full valence CASSCF wave functions. Moreover, if we compare the occupation numbers of the antibonding orbitals of the multicenter systems in the transition states with the analogous antibonding ones for the molecules of the reagents and products, the occupation numbers for the former are significantly larger than those for the latter. For example, the occupation number of the antibonding orbital in the HCl molecule is 0.024345, while for the antibonding orbital of the H_2Cl transition state is 0.050183. This is a consequence of the stretching of the H-Cl bond distance, which in the HCl molecule is 1.274 Å, whereas in the transition state it becomes 1.486 Å. Therefore, as the stretching of the bonds becomes important the multireference description of the molecule becomes more and more necessary. The nucleophilic substitutions have characteristics very similar to the atom transfer reactions, with the difference that the transition state is not a radical, and the active site can be described by a three-center four-electron (3c4e) bond. In the $\text{H} + \text{N}_2 \rightarrow \text{HN}_2$ and $\text{H} + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_5$ reactions, as happens in the $\text{H} + \text{N}_2\text{O} \rightarrow \text{OH} + \text{N}_2$ reaction, the N_2 and C_2H_4 molecules even if perturbed by the presence of the hydrogen atom, maintain their original nature also in the transition state. Therefore, the bonding and antibonding orbitals in the 3c3e system

are similar to those of the isolated molecules, while the non-bonding orbital is substantially the $1s$ orbital of the hydrogen atom. For the unimolecular reaction of the HCN system, the transition state has a compact triangular geometry and a simple model based on the three orbitals shared among the three atoms is no longer satisfactory. However, we can assume that according to a localized vision of the molecule, there are four electrons involved in the tricentric bond in such a case.

Table 4: The type of bonding models for the active site of the transition states of the reaction of the DBH24/08 database. 3c3e denotes a 3-center-3electron bonding model, 3c4e denotes a 3-center-4-electron model

Reaction	active site	bonding model
$\text{H} + \text{N}_2\text{O} \rightarrow \text{OH} + \text{N}_2$	N-O...H	3c3e
$\text{H} + \text{ClH} \rightarrow \text{HCl} + \text{H}$	H-Cl-H	3c3e
$\text{CH}_3 + \text{FCl} \rightarrow \text{CH}_3\text{F} + \text{Cl}$	C-F-Cl	3c3e
$\text{Cl}^- \cdots \text{CH}_3\text{Cl} \rightarrow \text{ClCH}_3 \cdots \text{Cl}^-$	Cl-C-Cl	3c4e
$\text{F}^- \cdots \text{CH}_3\text{Cl} \rightarrow \text{FCH}_3 \cdots \text{Cl}^-$	F-C-Cl	3c4e
$\text{OH}^- + \text{CH}_3\text{F} \rightarrow \text{HOCH}_3 + \text{F}^-$	O-C-F	3c4e
$\text{H} + \text{N}_2 \rightarrow \text{HN}_2$	N...H	3c3e
$\text{H} + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_5$	H...C-C	3c3e
$\text{HCN} \rightarrow \text{HNC}$	N-H-C	3c4e
$\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2\text{O}$	O-H-C	3c3e
$\text{H} + \text{OH} \rightarrow \text{O} + \text{H}_2$	H-H-O	3c3e
$\text{H} + \text{H}_2\text{S} \rightarrow \text{H}_2 + \text{HS}$	H-H-S	3c3e

In Table 5 the data for the SC-NEVPT2 method are collected. The mean absolute error for the twenty-four barrier heights is 1.42 kcal/mol, thus showing a marked improvement with respect to the CASSCF results, bringing the accuracy close to the chemical reference ($\simeq 1$ kcal/mol). The performance is quite uniform for the different types of reactions, with the mean errors amounting to 1.97, 1.58, 1.12 and 1.03 kcal/mol for the heavy-atom transfer, the nucleophilic substitution, the association/unimolecular and the hydrogen transfer reactions, respectively. The highest absolute deviation, 3.41 kcal/mol, is obtained for the forward barrier of the $\text{H} + \text{N}_2\text{O} \rightarrow \text{OH} + \text{N}_2$ reaction, a difficult case to study as noted in Ref. 23, where even high-level methods such as diffusion Monte Carlo and CCSD(T) have given unsatisfactory results. SC-NEVPT2 provides a low positive mean signed error, namely 0.61 kcal/mol, therefore it slightly overestimates the barrier heights.

The PC-NEVPT2 results are reported in Table 6. One finds that the mean absolute error is 1.64

Table 5: Relative errors, mean absolute error and mean signed error (in kcal/mol) for the barrier heights computed with the SC-NEVPT2 method respect to the best references reported in Tab. 1.

Reaction	forward BH	reverse BH
$\text{H} + \text{N}_2\text{O} \rightarrow \text{OH} + \text{N}_2$	3.41	1.24
$\text{H} + \text{ClH} \rightarrow \text{HCl} + \text{H}$	2.51	2.51
$\text{CH}_3 + \text{FCl} \rightarrow \text{CH}_3\text{F} + \text{Cl}$	0.44	1.69
$\text{Cl}^- \cdots \text{CH}_3\text{Cl} \rightarrow \text{ClCH}_3 \cdots \text{Cl}^-$	-1.79	-1.79
$\text{F}^- \cdots \text{CH}_3\text{Cl} \rightarrow \text{FCH}_3 \cdots \text{Cl}^-$	-1.16	3.09
$\text{OH}^- + \text{CH}_3\text{F} \rightarrow \text{HOCH}_3 + \text{F}^-$	0.28	-1.34
$\text{H} + \text{N}_2 \rightarrow \text{HN}_2$	2.47	-0.41
$\text{H} + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_5$	1.74	-1.45
$\text{HCN} \rightarrow \text{HNC}$	-0.63	-0.01
$\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2\text{O}$	-0.76	-0.04
$\text{H} + \text{OH} \rightarrow \text{O} + \text{H}_2$	2.82	-0.40
$\text{H} + \text{H}_2\text{S} \rightarrow \text{H}_2 + \text{HS}$	1.53	0.63
Mean absolute error	1.42	
Mean signed error	0.61	

kcal/mol, slightly greater than the SC-NEVPT2 value. The mean absolute error for the heavy-atom transfer reactions is 1.58 kcal/mol, in this case slightly better than the SC-NEVPT2 result. Instead, for the nucleophilic substitutions the average error of PC-NEVPT2 is greater by 0.55 kcal/mol than the corresponding SC-NEVPT2 value. For unimolecular/association reactions the two versions of the NEVPT method give average errors that differ only by 0.03 kcal/mol. The largest difference between the two contraction schemes occurs for the hydrogen transfer reactions, for which the SC-NEVPT2 provides a better average result by 0.68 kcal/mol. Overall, however, one can say that the SC-NEVPT2 and PC-NEVPT2 methods offer comparable and satisfactory performance, reducing by nearly 8 kcal/mol the average error obtained with the zero-order CASSCF approach. Although one would expect more accurate results for PC-NEVPT2, given the higher number of perturber functions used, the difference between the two versions is so small that it can be considered a fortuitous consequence of the balance of the errors due to the approximations employed. The value of the mean signed error for PC-NEVPT2 is negative and very low and, given that the ratio with the mean absolute error equals 0.28, it has the smallest bias among the methods considered.

Tables 7 and 8 report the absolute deviations of the barrier heights computed with CASPT2

Table 6: Relative errors, mean absolute error and mean signed error (in kcal/mol) for the barrier heights computed with the PC-NEVPT2 method respect to the best references reported in Tab. 1.

Reaction	forward BH	reverse BH
$\text{H} + \text{N}_2\text{O} \rightarrow \text{OH} + \text{N}_2$	1.53	-2.59
$\text{H} + \text{ClH} \rightarrow \text{HCl} + \text{H}$	1.88	1.88
$\text{CH}_3 + \text{FCl} \rightarrow \text{CH}_3\text{F} + \text{Cl}$	-1.16	-0.46
$\text{Cl}^- \cdots \text{CH}_3\text{Cl} \rightarrow \text{ClCH}_3 \cdots \text{Cl}^-$	-2.39	-2.39
$\text{F}^- \cdots \text{CH}_3\text{Cl} \rightarrow \text{FCH}_3 \cdots \text{Cl}^-$	-1.85	3.88
$\text{OH}^- + \text{CH}_3\text{F} \rightarrow \text{HOCH}_3 + \text{F}^-$	-0.36	-1.92
$\text{H} + \text{N}_2 \rightarrow \text{HN}_2$	1.09	-0.29
$\text{H} + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_5$	1.14	-1.85
$\text{HCN} \rightarrow \text{HNC}$	-1.88	-0.69
$\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2\text{O}$	-3.08	-1.59
$\text{H} + \text{OH} \rightarrow \text{O} + \text{H}_2$	1.87	-2.48
$\text{H} + \text{H}_2\text{S} \rightarrow \text{H}_2 + \text{HS}$	1.02	-0.20
Mean absolute error	1.64	
Mean signed error	-0.45	

without the IPEA correction and with the IPEA shift set to 0.25, respectively. The two variants of the CASPT2 method provide the same mean absolute error, namely 1.10 kcal/mol, although the performance for the individual reactions differ perceptibly. In comparison to SC-NEVPT2 and PC-NEVPT2, CASPT2 reduces the average error by 0.32 and 0.54 kcal/mol, respectively. The improvement in performance is fairly uniform for all classes of reactions, we observe particularly good results for the unimolecular and association reactions for which the chemical accuracy is satisfied. The mean signed errors indicate that CASPT2 tends to underestimate the barrier heights, this is particularly true for the nucleophilic substitutions and it is more pronounced without the IPEA shift correction.

Table 9 shows the comparison of the data obtained in this work with the multireference methods with the results of the best wave function based methods, considered in the work of Zheng *et al.*,¹ namely Møller-Plesset perturbation theory and coupled cluster. NEVPT2 and CASPT2 give a significant increase in accuracy compared to MP2, the reduction in the mean absolute error is more than 3 kcal/mol for both methods. Even the fourth order of the Møller-Plesset perturbation theory is not able to approach the accuracy of the multireference methods, with the mean absolute error of

Table 7: Relative errors, mean absolute error and mean signed error (in kcal/mol) for the barrier heights computed with the CASPT2 (IPEA = 0.00) method respect to the best references reported in Tab. 1.

Reaction	forward BH	reverse BH
$\text{H} + \text{N}_2\text{O} \rightarrow \text{OH} + \text{N}_2$	0.09	-1.97
$\text{H} + \text{ClH} \rightarrow \text{HCl} + \text{H}$	-0.47	-0.47
$\text{CH}_3 + \text{FCl} \rightarrow \text{CH}_3\text{F} + \text{Cl}$	-3.49	-1.49
$\text{Cl}^- \cdots \text{CH}_3\text{Cl} \rightarrow \text{ClCH}_3 \cdots \text{Cl}^-$	-1.69	-1.69
$\text{F}^- \cdots \text{CH}_3\text{Cl} \rightarrow \text{FCH}_3 \cdots \text{Cl}^-$	-0.41	-4.06
$\text{OH}^- + \text{CH}_3\text{F} \rightarrow \text{HOCH}_3 + \text{F}^-$	-0.57	-0.69
$\text{H} + \text{N}_2 \rightarrow \text{HN}_2$	-0.44	0.92
$\text{H} + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_5$	0.08	-0.27
$\text{HCN} \rightarrow \text{HNC}$	-1.05	0.05
$\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2\text{O}$	-0.47	-3.11
$\text{H} + \text{OH} \rightarrow \text{O} + \text{H}_2$	-0.64	0.02
$\text{H} + \text{H}_2\text{S} \rightarrow \text{H}_2 + \text{HS}$	-0.26	1.99
Mean absolute error		1.10
Mean signed error		-0.84

Table 8: Relative errors, mean absolute error and mean signed error (in kcal/mol) for the barrier heights computed with the CASPT2 (IPEA = 0.25) method respect to the best references reported in Tab. 1.

Reaction	forward BH	reverse BH
$\text{H} + \text{N}_2\text{O} \rightarrow \text{OH} + \text{N}_2$	1.71	-1.68
$\text{H} + \text{ClH} \rightarrow \text{HCl} + \text{H}$	0.29	0.29
$\text{CH}_3 + \text{FCl} \rightarrow \text{CH}_3\text{F} + \text{Cl}$	-3.59	-1.63
$\text{Cl}^- \cdots \text{CH}_3\text{Cl} \rightarrow \text{ClCH}_3 \cdots \text{Cl}^-$	-1.60	-1.60
$\text{F}^- \cdots \text{CH}_3\text{Cl} \rightarrow \text{FCH}_3 \cdots \text{Cl}^-$	-0.32	-3.88
$\text{OH}^- + \text{CH}_3\text{F} \rightarrow \text{HOCH}_3 + \text{F}^-$	-0.14	-0.28
$\text{H} + \text{N}_2 \rightarrow \text{HN}_2$	0.89	0.49
$\text{H} + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_5$	0.99	-0.52
$\text{HCN} \rightarrow \text{HNC}$	-0.94	0.15
$\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2\text{O}$	-0.55	-2.78
$\text{H} + \text{OH} \rightarrow \text{O} + \text{H}_2$	0.48	-0.46
$\text{H} + \text{H}_2\text{S} \rightarrow \text{H}_2 + \text{HS}$	0.95	0.24
Mean absolute error		1.10
Mean signed error		-0.56

Table 9: Mean absolute errors for the estimate of the barrier heights of the DBH24/08 database for the methods considered in this work, compared with some wave function based methods discussed in Ref.¹ Where not indicated the employed basis set is aug-cc-pVTZ.

Method	Mean Absolute Error	Source
CCSD(T)	0.69	ref. ¹
CASPT2 (IPEA = 0.00)	1.10	this work
CASPT2 (IPEA = 0.25)	1.10	this work
SC-NEVPT2	1.42	this work
PC-NEVPT2	1.64	this work
CCSD	2.18	ref. ¹
MP4/MG3S	3.81	ref. ¹
MP2	5.02	ref. ¹
CASSCF	9.28	ref. ¹

MP4 higher than the NEVPT2 and CASPT2 values by more than 2 kcal/mol. The multireference methods behave well even when compared with coupled cluster. Only the formulation that includes single, double and an approximate treatment of the triple excitations (CCSD(T)) allows to obtain results of a better quality than NEVPT2 and CASPT2.

In Table 10 are collected the mean absolute errors for the methods considered in this work compared with the MRMP2 results obtained in the reference of Tishchenko *et al.*² In addition to the data for the DBH24/08 database, the table includes the results for the subsets DBH22/08, DBH20/08, DBH12/08 (DBH22/08 is missing 1) reaction; DBH20/08 is missing 4) and 5) reactions; and subset DBH12/08 is missing 1) - 6) reactions). The various types of the MRMP2 data are distinguished by the sizes of the active spaces in the zero order wave functions. For the details on the sizes of the active spaces we refer to the work of Tishchenko *et al.*,² the aspect to note here is that the nom-CPO, mod-CPO and ext-CPO schemes use active spaces of increasing size and that all are smaller than those exploited here. The errors for the MRMP2 data are updated to the references of the Zheng *et al.*¹ While the NEVPT2 and CASPT2 calculations were performed at the geometries optimized at QCISD/MG3 level, MRMP2 calculations have been run at the geometries optimized with the corresponding methods. This is a possible source of deviations in the comparison between the results. However, as shown in the work of Zheng *et al.*,¹ the deviations of the errors obtained with the QCISD/MG3 geometries and those at the geometries optimized with

Table 10: Mean absolute errors for the estimate of the barrier heights of the DBH24/08 database and the subsets DBH22/08, DBH20/08, DBH12/08 for the methods considered in this work, compared with the MRMP2 results obtained in Ref.² DBH22/08 is missing 1) reaction; DBH20/08 is missing 4) and 5) reactions; and subset DBH12/08 is missing 1) - 6) reactions.

Method	DBH24/08	DBH22/08	DBH20/08	DBH12/08
SC-NEVPT2	1.42	1.34	1.32	1.08
PC-NEVPT2	1.64	1.61	1.45	1.43
CASPT2 (IPEA = 0.00)	1.10	1.11	0.93	0.77
CASPT2 (IPEA = 0.25)	1.10	1.05	0.95	0.79
MRMP2/nom-CPO/MG3S	1.35	1.28	1.45	1.31
MRMP2/nom-CPO/aug-cc-pVTZ	-	1.33	-	1.12
MRMP2/mod-CPO/MG3S	-	-	1.67	1.45
MRMP2/ext-CPO/MG3S	-	-	-	1.14

the corresponding methods differ by around 0.4 kcal/mol or less if high level methods are used. Observing the results, we note that the multireference perturbation methods provide very close performances, only CASPT2 is distinguished by a slight higher accuracy.

Conclusions

In the present work, we have tested the NEVPT2 and CASPT2 methods for the estimation of the barrier heights of the chemical reactions included in the standard DBH24/08 database. The results confirm the theoretical consideration that a multireference approach is important for the accurate description of the transition states, systems often characterized by stretched bonds and hypervalency. The mean absolute error for the CASPT2 method, in both variants considered, is 1.10 kcal/mol, a value very close to what is usually called the chemical accuracy. For the SC-NEVPT2 method the error is slightly larger, namely 1.42 kcal/mol, while for PC-NEVPT2 is 1.64 kcal/mol. The increase in accuracy compared to the perturbation single reference methods is very significant, since the reduction in the mean absolute error is more than 3 kcal/mol compared to MP2 and more than 2 kcal/mol with respect to MP4. These data suggest that the use of perturbation multireference methods may find convenient application whenever reliable references for the barrier heights are required. In fact, among the methods considered in our comparison, only CCSD(T) provides

better performances than NEVPT2 and CASPT2. However, CCSD(T) has a field of applicability more limited than the multireference methods due to a worst scaling of the computational costs with respect to the size of the molecules studied (namely N^7 vs N^5).

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Supporting Information Available

The molecular geometries, CASSCF, NEVPT and CASPT energies are given. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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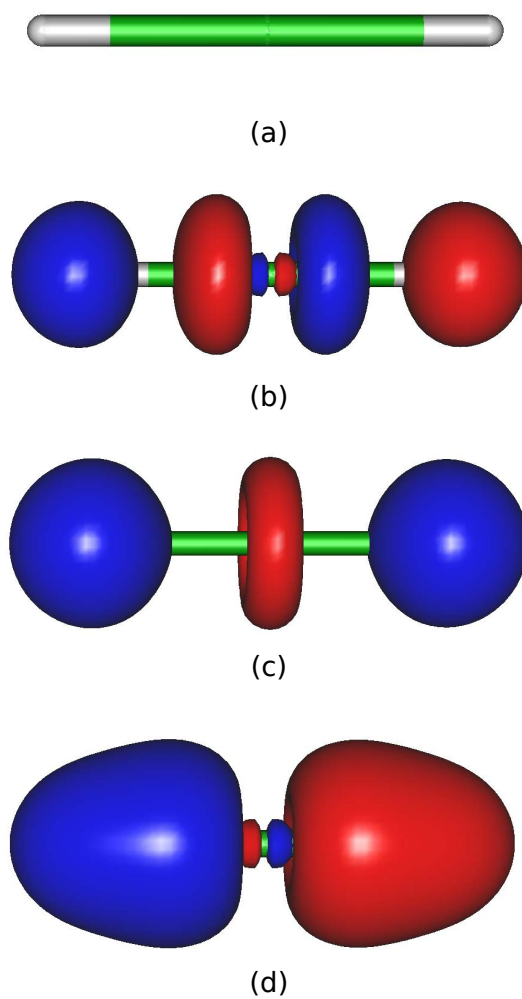


Figure 1: The three orbitals involved in the 3c3e bond of the transition state of the $\text{H} + \text{ClH} \rightarrow \text{HCl} + \text{H}$ reaction. (a) the structure of the H_2Cl system, the geometry is linear and his point group is $D_{\infty h}$ (b) the antibonding orbital (c) the non-bonding orbital (d) the bonding orbital.