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An Assessment of the Accuracy of Multireference Configuration Interaction (MRCI) and Complete-Active-Space Second-Order Perturbation Theory (CASPT2) for Breaking Bonds to Hydrogen

Micah L. Abrams and C. David Sherrill*

Center for Computational Molecular Science and Technology, School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332-0400

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Complete-active-space self-consistent field (CASSCF), complete-active-space second-order perturbation theory (CASPT2), and two restricted active-space variants of multireference configuration interaction (singles, doubles, and limited triples and quadruples, CISD[TQ], and second-order configuration interaction, SOCI) have been assessed for bond-breaking reactions in BH, HF, and CH_4 by comparison to the full configuration interaction limit. These results allow one, for the first time, to ascertain typical errors for such reactions across the entire potential energy curve. They also provide an assessment of different prescriptions for choosing an active space. A valence active space and a one-to-one active space were considered along with the basis sets cc-pVQZ, 6-31G**, and 6-31G* for BH, HF, and CH_4, respectively. The valence active space performs better than the one-to-one active space for BH but is inferior for HF. Always choosing the larger of the two active spaces for a given molecule leads to the best results. When using the larger of the two active spaces, the nonparallelity errors for CASPT2, CISD[TQ], and SOCI were less than 3.3, 1.4, and 0.3 kcal mol^{-1}, respectively. These results are superior to those of unrestricted coupled-cluster with perturbative triples [UCCSD(T)] for these same systems.

1. Introduction

The last decade has seen a major advancement in electron correlation methods based on a multiconfiguration wave function, that is, multireference versions of configuration interaction (MRCI), perturbation theory (MRPT), and coupled-cluster theory (MRCC).[1] Although the idea of such methods is rather old,[2−4] significant new approximations and algorithms[1,5−14] have been developed. While these methods remain too computationally expensive to use on molecules with more than a few heavy atoms, they are nonetheless the only methods capable of accurately describing many chemical processes, particularly bond-breaking and bond-forming reactions.

Multireference configuration interaction has been the standard model for determining accurate potential energy surfaces of polyatomic molecules for the last 30 years. Problems with size consistency still remain, but thus far, alternative size-consistent methods are not yet in common use for generating potential energy surfaces of spectroscopic accuracy. Multireference perturbation theory has been applied to a number of chemical problems including molecular structure, electronic spectra, and transition metal chemistry. Perhaps the most popular variation of MRPT is the complete-active-space second-order perturbation theory (CASPT2) method of Andersson and Roos.[5] Errors in geometries, binding energies, and excitation energies have been systematically studied;[15] however, the error in CASPT2 along a full potential energy curve has not been thoroughly evaluated.

The most straightforward way to determine the error of a given correlation model is to compare it to the exact solution of the electronic Schrödinger equation for the given one-electron basis, which is the full configuration interaction (FCI) result. A series of studies by Bauschlicher in the late 1980s provided FCI energies at a few geometries along the potential energy curves of several small molecules.[16−20] Advances in CI algorithms and computer hardware have made it possible to obtain more complete FCI potential energy curves[21−26] for some simple systems. For example, Olsen and co-workers studied polarized double-ζ FCI potential energy curves for bond breaking in several electronic states of the N_2 molecule[24,27] and the symmetric dissociation (breaking both bonds) of H_2O. The benchmark FCI results were compared to perturbation theory and coupled-cluster models to indicate how these approximate methods perform for very challenging cases. Such benchmarks are essential for the calibration of new theoretical models meant to describe bond-breaking processes.[28−33]

In the present study, we compare to FCI potential energy curves for three molecules (BH, HF, CH_4) in which a bond to hydrogen is broken. This should represent a common, chemically important process that one might expect to be the easiest type of bond-breaking reaction for standard quantum chemical methods to describe accurately. However, we have recently shown[26] that single-reference methods, even when based on an unrestricted Hartree−Fock reference, are not very accurate for these simple systems; unrestricted coupled-cluster with perturbative triple excitations [UCCSD(T)] yields nonparallelity erorrs of about 4 kcal mol^{-1}. It is therefore of interest to compare the performance of multireference approaches for these molecules.

Here, we assess the popular complete-active-space self-consistent field (CASSCF)[34,35] method and complete-active-space second-order perturbation theory (CASPT2) with the nondiagonal zero-order operator.[5] We also consider two multireference configuration interaction singles and doubles (MR-CISD) methods. One of these, the second-order CI (SOCI),[2] generates all possible singly and doubly substituted configurations from every active space configuration that can be formed

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by distributing the active electrons among the active orbitals. This is perhaps the most complete type of a MR-CISD wave function. The second MR-CISD approach considered here is the CISD[TQ] wave function of Schaefer and co-workers,[36,37] which generates all single and double substitutions from the reference set of all singly and doubly substituted configurations that can be formed in the active space. As such, CISD[TQ] may be thought of as an approximation to SOCI in which all configurations that are more than quadruply substituted (relative to the Hartree−Fock reference) are discarded.

Previous high-quality benchmarks for the molecules considered in this study include a cc-pVTZ FCI potential energy curve for BH,[38] a cc-pVDZ FCI potential energy curve for HF,[38] and 6-311++G(df,p) multireference CI results[39] for the breaking of a single C−H bond in CH_4. We have previously assessed[26] several single-reference correlated methods by comparison to FCI for BH, HF, and CH_4 in the aug-cc-pVQZ, 6-31G**, and 6-31G* basis sets, respectively, and we will refer to the FCI results of that study in the present work. Because of additional difficulties in converging CASSCF wave functions with basis sets containing many diffuse functions, for BH we will compare to cc-pVQZ FCI results, which were also generated in our previous study.

2. Theoretical Approach

Here, we use the cc-pVQZ, 6-31G**, and 6-31G* basis sets for BH, HF, and CH_4, respectively.[40] We have examined CASSCF,[35,34] CISD[TQ],[37] SOCI,[2] and CASPT2 with the nondiagonal zero-order operator.[5] The CISD[TQ] and SOCI computations were performed using CASSCF orbitals.

Two orbital active spaces were used in this study. The first active space is a valence active space, by which we mean that there is one active space orbital of a given irreducible representation for each molecular orbital of the same irreducible representation that can be formed from the valence orbitals on the atoms in the molecule. The valence orbitals of the atoms are of course the usual 1s for hydrogen and 2s, $2p_x$, $2p_y$, and $2p_z$ for B−F. The valence active space is commonly used in CASSCF computations, where it is sometimes referred to as full-valence CASSCF. This approach was also introduced by Ruedenberg under the name full optimized reaction space (FORS).[35]

The second active space, which we will refer to as one-to-one or 1:1, includes the occupied valence orbitals plus an active virtual orbital (of the same symmetry) for every occupied valence orbital. This is the active space used in generalized valence bond perfect pairing computations, and it is being considered in recent work by Head-Gordon and co-workers.[41,42] Its use in CASSCF computations dates back at least to a 1980 paper by Roos, which shows much better agreement with experiment than full-valence CASSCF for equilibrium properties of the water molecule.[43] The benefit of these two choices of active spaces, full-valence and one-to-one, is that they are a priori definitions that can be used to define the active space of a molecule in the absence of any preliminary computations or arbitrary choices of thresholds. These two active spaces were previously compared for the more challenging case of double dissociation in H_2O by Olsen and co-workers.[22]

More specifically, the active spaces for the molecules in the study are as follows: BH val = ($4e^-$/3011) and 1:1 = ($4e^-$/4000); HF val = ($8e^-$/3011) and 1:1=($8e^-$/4022); and CH_4 val = 1:1 = ($8e^-$/62), where the notation indicates (number of active electrons/number of active orbitals per irrep of the largest Abelian subgroup). For CH_4, definitions of the valence and 1:1 active spaces are equivalent. Note that the valence active space is larger than the 1:1 active space for the BH molecule, but it is smaller for HF. The core 1s orbitals were constrained to remain doubly occupied in all cases.

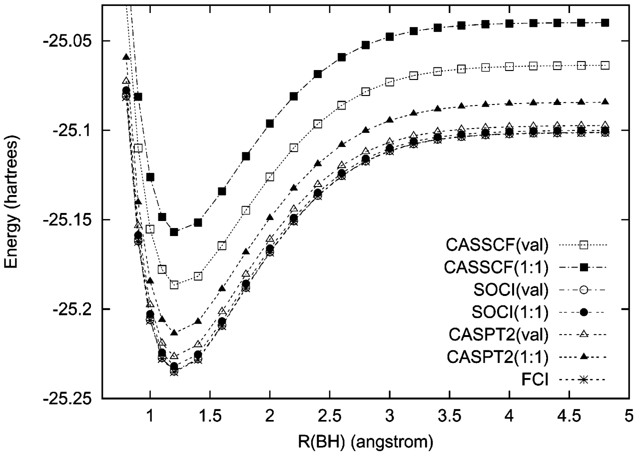

Figure 1. Potential energy curves (hartree) for BH using the cc-pVQZ basis set.

The CASPT2 calculations were performed with MOLCAS 5.2.[44] All other calculations were performed with the DETCAS and DETCI[11] modules of PSI 3.2.[45] The potential energy curve for methane was obtained by constraining three C−H bonds to their equilibrium bond length (1.086 Å)[46] and the HCH angles at the tetrahedral value while stretching a single C−H bond. Full CI results are taken from our previous work.[26]

3. Results and Discussion

The potential energy curves for BH are shown in Figure 1. From the figure, it is clear that all of the methods considered here provide qualitatively correct potential energy curves. This contrasts to the behavior of many single-reference correlation methods, evaluated previously.[26] Although the CASSCF potential energy curves are significantly higher in energy than the exact FCI curve (because of the limited treatment of electron correlation), they have approximately the correct shape. The CASPT2 curve with the smaller active space is also significantly higher than the FCI curve, but again it has the correct shape. The other methods considered are accurate enough that they are hard to distinguish from the FCI curve at this scale. Because the qualitative behavior of the potential energy curves is similar for the other two molecules, we omit figures of the curves for HF and CH_4. More instructive are plots of the errors versus FCI as a function of bond length, which are presented in Figures 2, 3, and 4 for BH, HF, and CH_4, respectively. These are discussed below.

Tables 1, 2, and 3 contain the error versus FCI, and Tables 4, 5, and 6 contain the maximum, minimum, and nonparallelity errors (NPE) for BH, HF, and CH_4, respectively. The NPEs are computed as the difference between the maximum and minimum errors along the potential energy curve, and they provide a measure of how well each method mimics the overall shape of the exact FCI potential energy curve. A NPE of zero would imply a complete match to the shape of the FCI curve.

It is well-known that the CASSCF wave function provides qualitatively correct potential energy surfaces if a proper active space is chosen, because it describes the interaction between important near-degenerate configurations, called nondynamical correlation. However, the method does not contain enough configurations to accurately describe the usual short-range electron−electron repulsions, called dynamical correlation.

TABLE 1: FCI Energy and Error Versus FCI (hartree) for BH Using the cc-pVQZ Basis Set

R(B−H), Å	FCI	CASSCF (val)	CASSCF (1:1)	SOCI (val)	SOCI (1:1)	CASPT2 (val)	CASPT2 (1:1)
0.80	−25.081 355	0.052 543	0.081 702	0.000 543	0.003 673	0.008 719	0.022 021
0.90	−25.162 408	0.052 480	0.081 161	0.000 536	0.003 764	0.008 986	0.022 119
1.00	−25.206 390	0.051 187	0.080 188	0.000 496	0.003 628	0.008 822	0.021 979
1.10	−25.227 709	0.049 855	0.079 181	0.000 490	0.003 451	0.008 685	0.021 784
1.20	−25.235 155	0.048 658	0.078 273	0.000 479	0.003 286	0.008 565	0.021 599
1.40	−25.228 283	0.046 621	0.076 734	0.000 447	0.002 988	0.008 338	0.021 225
1.60	−25.209 491	0.044 943	0.075 332	0.000 408	0.002 717	0.008 073	0.020 788
1.80	−25.188 268	0.043 511	0.073 798	0.000 365	0.002 477	0.007 742	0.020 088
2.00	−25.168 318	0.042 268	0.071 984	0.000 325	0.002 256	0.007 346	0.019 317
2.20	−25.151 002	0.041 200	0.070 005	0.000 289	0.002 032	0.006 895	0.018 594
2.40	−25.136 762	0.040 307	0.068 116	0.000 256	0.001 833	0.006 396	0.017 990
2.60	−25.125 628	0.039 581	0.066 450	0.000 224	0.001 676	0.005 871	0.017 526
2.80	−25.117 376	0.039 010	0.065 052	0.000 193	0.001 557	0.005 366	0.017 217
3.00	−25.111 577	0.038 575	0.063 942	0.000 164	0.001 471	0.004 929	0.017 045
3.20	−25.107 695	0.038 256	0.063 116	0.000 138	0.001 410	0.004 589	0.016 965
3.40	−25.105 194	0.038 032	0.062 538	0.000 119	0.001 369	0.004 343	0.016 933
3.60	−25.103 629	0.037 878	0.062 151	0.000 106	0.001 342	0.004 174	0.016 923
3.80	−25.102 666	0.037 775	0.061 901	0.000 097	0.001 325	0.004 065	0.016 921
4.00	−25.102 081	0.037 706	0.061 740	0.000 091	0.001 315	0.004 002	0.016 921
4.20	−25.101 726	0.037 660	0.061 638	0.000 088	0.001 308	0.003 975	0.016 922
4.40	−25.101 512	0.037 629	0.061 573	0.000 087	0.001 304	0.003 962	0.016 922
4.60	−25.101 383	0.037 609	0.061 531	0.000 086	0.001 302	0.003 956	0.016 922
4.80	−25.101 305	0.037 594	0.061 503	0.000 086	0.001 300	0.003 957	0.016 922

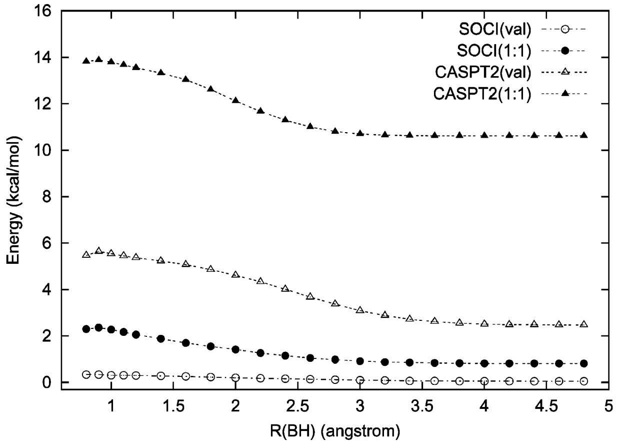

Figure 2. Error versus FCI (kcal mol^{-1}) for BH using the cc-pVQZ basis set. The cc-pVQZ FCI equilibrium bond distance is 1.2260 Å.

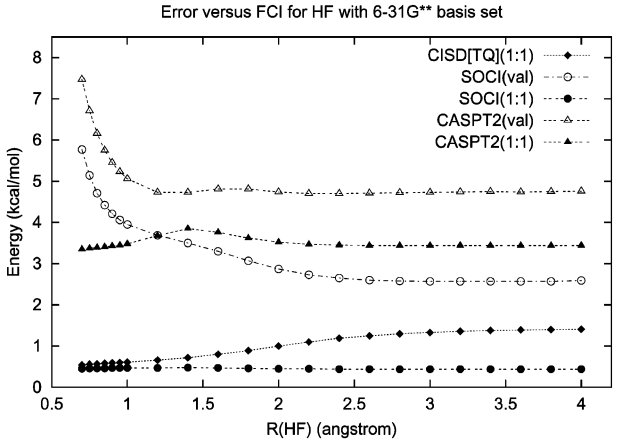

Figure 3. Error versus FCI (kcal mol^{-1}) for HF using the 6-31G** basis set. The 6-31G** FCI equilibrium bond distance is 0.9214 Å.

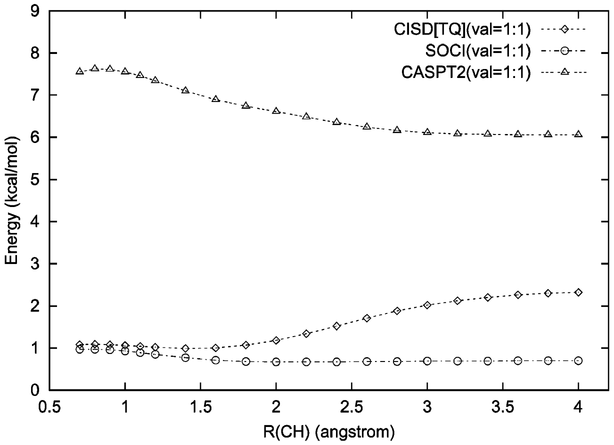

Figure 4. Error versus FCI (kcal mol^{-1}) for CH_4 using the 6-31G* basis set. The equilibrium bond distance is 1.086 Å from ref 46.

Because more electrons are closer together near equilibrium than at the dissociation limit, the degree of dynamical correlation is larger there and so are the CASSCF errors. This is seen quantitatively in Tables 1−3. The only exception is for HF with the 1:1 active space, for which the CASSCF error is fairly constant and rises slightly with distance. Here, the 1:1 active space is sufficient to capture a significant portion of the dynamical correlation near equilibrium.

Given that the degree of dynamical correlation is larger near equilibrium, one would expect that increasing the size of the active space would cause a greater improvement in the error at equilibrium than at dissociation. The nonparallelity errors in Tables 4 and 5 verify this expectation, keeping in mind that the valence active space is larger for BH but smaller for HF. Enlarging the active space from 1:1 to valence for BH decreases the error at 1.2 Å by 18.6 kcal mol^{-1} and at 4.8 Å by 15.0 kcal mol^{-1}. Likewise, for HF enlarging the active space from valence to 1:1 reduces the error at 0.9 Å by 63.5 kcal mol^{-1} and at 4.0 Å by 41.2 kcal mol^{-1}.

Across all three molecules, the CASSCF nonparallelity error is as small as 4.8 kcal mol^{-1} and as large as 18.0 kcal mol^{-1}. This is roughly comparable to the NPEs for CCSD based on RHF orbitals (8−13 kcal mol^{-1}) and represents a definite improvement over UHF or UMP2 but not UCCSD, UCCSD(T), or UB3LYP.[26] However, for more challenging bond-breaking cases, CASSCF should continue to work as well, while the quality of the single-reference approaches will degrade, as demonstrated by Olsen et al. for the simultaneous breaking of both bonds in H_2O.[22] We plan to examine bond breaking in additional molecules in future work.

TABLE 2: Error Versus FCI (hartree) for HF Using the 6-31G Basis Set**

R(H−F), Å	CASSCF (val)	CASSCF (1:1)	CISD[TQ] (1:1)	SOCI (val)	SOCI (1:1)	CASPT2 (val)	CASPT2 (1:1)
0.70	0.162 876	0.063 955	0.000 867	0.009 195	0.000 716	0.011 912	0.005 343
0.75	0.163 972	0.064 196	0.000 886	0.008 197	0.000 726	0.010 698	0.005 374
0.80	0.164 811	0.064 369	0.000 904	0.007 510	0.000 733	0.009 819	0.005 404
0.85	0.165 401	0.064 491	0.000 920	0.007 037	0.000 738	0.009 168	0.005 434
0.90	0.165 754	0.064 589	0.000 936	0.006 706	0.000 742	0.008 688	0.005 466
0.95	0.165 890	0.064 691	0.000 951	0.006 469	0.000 744	0.008 328	0.005 504
1.00	0.165 824	0.064 822	0.000 967	0.006 293	0.000 746	0.008 056	0.005 552
1.20	0.163 754	0.065 908	0.001 045	0.005 878	0.000 756	0.007 540	0.005 872
1.40	0.159 260	0.067 861	0.001 147	0.005 585	0.000 761	0.007 543	0.006 140
1.60	0.153 437	0.069 764	0.001 267	0.005 257	0.000 747	0.007 666	0.005 996
1.80	0.147 734	0.070 855	0.001 421	0.004 894	0.000 731	0.007 659	0.005 766
2.00	0.143 307	0.071 317	0.001 593	0.004 572	0.000 719	0.007 561	0.005 612
2.20	0.140 478	0.071 503	0.001 756	0.004 347	0.000 712	0.007 494	0.005 529
2.40	0.138 900	0.071 590	0.001 891	0.004 216	0.000 709	0.007 484	0.005 494
2.60	0.138 081	0.071 633	0.001 993	0.004 146	0.000 707	0.007 501	0.005 483
2.80	0.137 669	0.071 651	0.002 069	0.004 112	0.000 706	0.007 521	0.005 481
3.00	0.137 462	0.071 655	0.002 125	0.004 095	0.000 706	0.007 537	0.005 484
3.20	0.137 360	0.071 654	0.002 167	0.004 089	0.000 706	0.007 551	0.005 485
3.40	0.137 309	0.071 651	0.002 197	0.004 088	0.000 705	0.007 565	0.005 486
3.60	0.137 285	0.071 648	0.002 218	0.004 090	0.000 705	0.007 556	0.005 486
3.80	0.137 273	0.071 646	0.002 232	0.004 094	0.000 705	0.007 576	0.005 486
4.00	0.137 268	0.071 645	0.002 242	0.004 133	0.000 705	0.007 579	0.005 486

TABLE 3: Error Versus FCI (hartree) for CH_4 Using the 6-31G* Basis Set

R(C−H), Å	CASSCF (val = 1:1)	CISD[TQ] (val = 1:1)	SOCI (val = 1:1)	CASPT2 (val = 1:1)
0.70	0.082 722	0.001 716	0.001 550	0.012 026
0.80	0.081 922	0.001 733	0.001 551	0.012 138
0.90	0.080 894	0.001 722	0.001 523	0.012 128
1.00	0.079 746	0.001 696	0.001 475	0.012 034
1.10	0.078 547	0.001 663	0.001 415	0.011 883
1.20	0.077 354	0.001 628	0.001 350	0.011 698
1.40	0.075 191	0.001 583	0.001 226	0.011 309
1.60	0.073 614	0.001 601	0.001 134	0.010 986
1.80	0.072 781	0.001 702	0.001 082	0.010 742
2.00	0.072 627	0.001 885	0.001 061	0.010 533
2.20	0.072 942	0.002 137	0.001 060	0.010 326
2.40	0.073 469	0.002 429	0.001 069	0.010 122
2.60	0.073 997	0.002 724	0.001 081	0.009 943
2.80	0.074 414	0.002 991	0.001 091	0.009 815
3.00	0.074 697	0.003 213	0.001 099	0.009 734
3.20	0.074 872	0.003 384	0.001 104	0.009 689
3.40	0.074 971	0.003 510	0.001 107	0.009 667
3.60	0.075 024	0.003 599	0.001 109	0.009 657
3.80	0.075 051	0.003 659	0.001 110	0.009 652
4.00	0.075 064	0.003 699	0.001 110	0.009 650

TABLE 4: Maximum, Minimum, and Nonparallelity Error (kcal mol^{-1}) for BH Using the cc-pVQZ Basis Set[a]

method	max error	min error	NPE
CASSCF (val)	32.97 (0.80)	23.59 (4.80)	9.38
CASSCF (1:1)	51.27 (0.80)	38.59 (4.80)	12.68
SOCI (val)	0.34 (0.80)	0.05 (4.40)	0.29
SOCI (1:1)	2.36 (0.90)	0.82 (4.00)	1.54
CASPT2 (val)	5.64 (0.90)	2.48 (4.60)	3.16
CASPT2 (1:1)	13.88 (0.90)	10.62 (3.60)	3.26

[a] Values in parentheses indicate the corresponding bond distance (Å).

TABLE 5: Maximum, Minimum, and Nonparallelity Error (kcal mol^{-1}) for HF Using the 6-31G Basis Set[a]**

method	max error	min error	NPE
CASSCF (val)	104.10 (0.95)	86.14 (3.80)	17.96
CASSCF (1:1)	44.96 (2.80)	40.13 (0.70)	4.83
SOCI (val)	5.77 (0.70)	2.57 (3.00)	3.20
SOCI (1:1)	0.48 (1.40)	0.44 (2.40)	0.04
CISD[TQ] (1:1)	1.41 (4.00)	0.54 (0.70)	0.87
CASPT2 (val)	7.47 (0.70)	4.70 (2.20)	2.77
CASPT2 (1:1)	3.85 (1.40)	3.35 (0.70)	0.50

[a] Values in parentheses indicate the corresponding bond distance (Å).

TABLE 6: Maximum, Minimum, and Nonparallelity Error (kcal mol^{-1}) for CH_4 Using the 6-31G* Basis Set[a]

method	max error	min error	NPE
CASSCF (val = 1:1)	51.91 (0.7)	45.57 (2.0)	6.34
CISD[TQ] (val = 1:1)	2.32 (4.0)	0.99 (1.4)	1.33
SOCI (val = 1:1)	0.97 (0.7)	0.67 (2.0)	0.30
CASPT2 (val = 1:1)	7.62 (0.8)	6.06 (3.6)	1.56

[a] Values in parentheses indicate the corresponding bond distance (Å).

CISD[TQ] is a restricted active space (RAS)[47] variant of MRCI in which RAS I is composed of active occupied orbitals and RAS II is composed of the active unoccupied orbitals. The inactive virtual orbitals comprise RAS III. The configurations are selected according to the following criteria: a maximum of two electrons are allowed in RAS III, and a maximum of four holes are allowed in RAS I. There are no restrictions on the occupancy of the orbitals in RAS II. These rules are equivalent to generating a MR-CISD in which the reference configurations are all singles and doubles within the active space. Results are not given for CISD[TQ] for BH because for four valence electrons, CISD[TQ] is equivalent to SOCI (discussed below). Likewise, for the small valence active space in HF (only one active virtual orbital), again CISD[TQ] and SOCI are equivalent.

It has been shown[37] that the error versus FCI for CISD[TQ] along a potential energy curve is the opposite of CASSCF: the maximum error occurs near dissociation, while the minimum error occurs near equilibrium. Figures 3 and 4 verify this trend. The error at 0.7 Å is quite small for HF and CH_4 (0.5 and 1.1 kcal mol^{-1}, respectively). The error begins to increase at 1.0 Å for HF but decreases slightly for CH_4 before beginning to climb at 1.8 Å. The nonparallelity error does achieve chemical accuracy (1.0 kcal mol^{-1}) for HF. In both cases, the NPE is 2−4 times less than that obtained with UCCSD(T).[26]

The second-order CI wave function can also be defined in the restricted active space framework by placing the active space orbitals in RAS II and inactive virtual orbitals in RAS III. It is not necessary to employ the RAS I orbital space in this case. Configurations are selected by allowing all possible distributions of electrons in RAS II but a maximum of two electrons in RAS III. Because this is equivalent to a MR-CISD in which every possible active space configuration is used as a reference, SOCI represents an idealized limit of MR-CISD, which would be very difficult to employ for all but the smallest chemical systems.

When the active space is small, SOCI describes the region near dissociation more accurately than that around equilibrium.

This trend is seen for BH with SOCI (1:1) and HF with SOCI (val); the associated nonparallelity errors (1.5 and 3.2 kcal mol^{-1}) are surprisingly large considering the very extensive description of electron correlation in SOCI. However, it must be kept in mind that the valence active space contains only one active unoccupied orbital for HF and the 1:1 active space contains no b_1 or b_2 orbitals for BH, which are important for dynamical correlation near equilibrium.

When one uses the larger active space in each case, the SOCI parallels the FCI limit very well, as seen for BH with SOCI (val), HF with SOCI (1:1), and CH_4 with SOCI (val = 1:1). The nonparallelity errors for SOCI with the larger active space (0.29−0.04 kcal mol^{-1}) are about an order of magnitude smaller than those for UCCSD(T) for these molecules.[26] The significantly larger nonparallelity errors for the smaller active space show that even for very extensive MR-CISD computations, the active space must be chosen carefully if subchemical accuracy is to be achieved.

Since its inception in 1990,[48] many papers have been published using the CASPT2 variant of MRPT. Because CASPT2 is approximately size-consistent[49] and will generally be more computationally efficient than MRCI, it may be attractive as an alternative approach for the determination of accurate potential energy surfaces. Previous studies[48,50] have shown that the CASPT2 error mimics the trend of SOCI—maximum error near equilibrium and minimum error near dissociation. This trend is seen here in Figures 2 and 3. As one would expect, the error for CASPT2 decreases with the larger active space. In the case of HF, the larger active space also leads to a smaller NPE, but in BH, the NPE is hardly improved. It is interesting to note that the NPEs for CASPT2 are less sensitive to the active space than are the NPEs for SOCI. Except for HF with the valence active space, the CASPT2 NPEs are always larger than the SOCI NPEs, by a factor of around 2−10. This indicates that SOCI or similar large MR-CISD wave functions are preferable to CASPT2 for obtaining very accurate potential energy surfaces, such as might be required for high-accuracy vibrational level prediction. Nevertheless, the CASPT2 errors are modest, and they tend to compare well with CISD-[TQ]. Compared to the single-reference results of our previous study, we find that CASPT2 does as well as UCCSD(T) for BH and much better for HF and CH_4. We expect the improvement over UCCSD(T) to be larger for more challenging cases such as the homolytic dissociation of bonds between two non-hydrogen atoms.

4. Conclusions

We have assessed various multireference methods for their performance in bond breaking reactions in BH, CH_4, and HF. This represents the first detailed evaluation of multireference methods across the entire potential energy curve for single bond-breaking reactions, and it is made possible by our determination of computationally demanding full configuration interaction potential curves, which represent the exact solution for the given basis set. Although breaking bonds to hydrogen should represent one of the easiest types of bond-breaking reactions for theoretical methods, nevertheless our recent evaluation of single-reference methods indicated surprisingly large errors.[26] For the present molecules, the multireference methods including dynamical correlation (CISD[TQ], SOCI, and CASPT2) all give more accurate results than the best standard single-reference method, UCCSD(T), even for these simple reactions.

With current technology, multireference configuration interaction is the only method in common use for determining spectroscopic-quality potential energy surfaces. As the size of the system increases, the quality of the MRCI wave function will degrade, leading to a need for size-consistent (or at least approximately size-consistent) methods, including multireference perturbation theory or multireference coupled-cluster. The CASPT2 approach is a widely used multireference perturbation theory method which, according to the present study, appears to be somewhat less sensitive to the choice of active space than MRCI. However, the perturbative treatment of dynamical electron correlation does not seem as effective as extensive MRCI for the small systems considered here. Unfortunately, the prospects of improving the CASPT2 model by employing higher orders of perturbation theory does not seem promising, because Olsen and co-workers[51] have shown that the multireference perturbation expansion does not converge. Nevertheless, if the proper active orbital space is chosen, CASPT2 is still preferred to spin-unrestricted single-reference methods for describing potential energy curves.

Comparison of active space definitions, valence or one-to-one, demonstrates that the best definition for a given molecule is that which produces the larger active space. The smaller active space led to relatively large errors in some cases. The ideal active space for multireference computations, which may be too large to employ in practice, would be one that is the union of the valence and one-to-one active spaces: that is, it should include all valence orbitals *and* ensure the presence of at least one active unoccupied orbital per active occupied orbital.

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