Full configuration interaction potential energy curves for breaking bonds to hydrogen: An assessment of single-reference correlation methods

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Several approximate correlation methods have been assessed for bond breaking reactions in BH, HF, and CH₄ by comparison to the full configuration interaction limit. Second-order Møller–Plesset perturbation theory, coupled-cluster singles and doubles (CCSD), coupled-cluster with perturbative triples [CCSD(T)], and the hybrid density-functional method Becke three parameter Lee–Yang–Parr have been considered. Both restricted and unrestricted references have been used along with the basis sets aug-cc-pVQZ, 6-31G**, and 6-31G* for BH, HF, and CH₄ respectively. Among the methods considered, unrestricted CCSD and CCSD(T) provide potential energy curves which are the most parallel to the benchmark full CI curves, but the nonparallelity errors are fairly large (up to 6 and 4 kcal mol⁻¹, respectively). Optimized-orbital coupled-cluster methods provide superior results but nevertheless exhibit approximately the same maximum errors. © 2003 American Institute of Physics. [DOI: 10.1063/1.1531658]

I. INTRODUCTION

It is well known that restricted Hartree–Fock (RHF) is qualitatively incorrect for bond breaking, because near the dissociation limit there are two or more degenerate electronic configurations which cannot be described simultaneously by a single restricted Slater determinant. One may also note that, by constraining both electrons in the breaking bond to occupy the same spatial orbital, the RHF wave function contains unphysical ionic terms at long distances. Although unrestricted Hartree–Fock (UHF) can provide a potential-energy curve that breaks a bond qualitatively correctly, the results may be quantitatively poor, and the wave function is no longer an eigenfunction of $\hat{S}^2$. One might expect the inclusion of electron correlation to improve results for bond breaking, since additional electron configurations are included in the wave function, but this is not always the case. Indeed, RHF-based second-order Møller–Plesset perturbation theory gives energies which diverge to negative infinity at the dissociation limit. While multireference methods like CASPT2¹ can handle any type of bond breaking problem in principle, in practice the computations can become intractable if large active spaces are required. Hence, an economical and reliable description of bond breaking remains a challenge for electronic structure theory.

Within the Born–Oppenheimer approximation, the full configuration interaction (FCI) model represents the exact solution of the electronic Schrödinger equation for the chosen one electron basis set. Because its computational cost increases factorially with the number of electrons or orbitals, full CI computations are only feasible for small chemical systems with moderately sized basis sets. Nevertheless, full CI benchmarks are invaluable for assessing the intrinsic errors in various approximate models of electron correlation. They are particularly valuable for generating potential energy curves, since they do not suffer from the multiconfigurational nature of the wave function near the dissociation limit. Several previous studies have provided full configuration interaction (CI) energies at a few (often three) geometries along a potential energy curve.²⁻⁶

Advances in algorithms and computer hardware have recently made it possible to obtain more complete full CI potential energy curves⁷⁻¹² for some simple systems. For example, Olsen and co-workers have presented very useful polarized double-zeta full CI potential energy curves for bond breaking in several electronic states of the N₂ molecule¹⁰,¹¹ and full CI energies for five geometries along the symmetric dissociation (breaking both bonds) of H₂O. The benchmark full CI 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.¹³⁻¹⁸

The present scarcity of such benchmark potential energy curves makes it unclear how well many of the standard correlation methods perform for different types of bond breaking. In the present study, we present full CI potential energy curves for three molecules (BH, HF, CH₄) in which a bond to hydrogen is broken. This should represent a common, chemically important process which one might expect to be the easiest bond breaking process for standard quantum-chemical methods to describe accurately. We compare various approximations to the full CI results, including second-order Møller–Plesset perturbation theory (MP2),¹⁹ coupled-cluster singles and doubles (CCSD),²⁰,²¹ coupled-cluster singles and doubles with perturbative triples [CCSD(T)],²² and the B3LYP gradient-corrected hybrid density-functional theory model.²³,²⁴ Both restricted and unrestricted orbitals are considered.

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Previous high-quality benchmarks for the molecules considered in this study include double zeta plus polarization (DZP) FCI results for three geometries of HF, a DZP FCI potential energy curve for BH, and 6-311+G(df,p) multireference CI results for the breaking of a single C–H bond in CH₄. The present work provides much more complete full CI potential energy curves, with a much larger basis set (aug-cc-pVQZ) in the case of BH. The role of spin contamination in some unrestricted perturbation theory and coupled-cluster descriptions of bond breaking in these molecules has previously been studied by Chen and Schlegel and by Krylov, who compared to earlier, more approximate benchmark potential energy curves. The present results should prove useful in the calibration of new theoretical methods for bond breaking.

II. THEORETICAL APPROACH

The molecules considered in this study are BH, HF, and CH₄. For BH, we have used both standard and augmented correlation consistent polarized valence quadruple zeta basis sets, denoted by cc-pVQZ and aug-cc-pVQZ. The augmented basis set adds an extra set of diffuse functions for each angular momentum in the basis. We have used the standard split-valence polarized double-zeta basis sets 6-31G* for methane and 6-31G** for HF. The 6-31G** basis was recently shown to be among the best polarized double-zeta basis sets for full CI benchmarking. We have performed MP2, CCSD, CCSD(T), FCI, and B3LYP calculations for all three molecules over a wide range of geometries. FCI and all computations using restricted orbitals except for B3LYP are obtained using the PSI 3.0 package, and all other computations employed Q-CHEM 2.0. Full CI procedures employed the DETCI module of PSI. For convenience, methods using unrestricted orbitals are denoted with a prefix “U,” as in UMP2, UCCSD, etc. The frozen core approximation has been used for all three molecules. For BH, B3LYP results are not reported because of a limitation in the Q-CHEM program for density-functional theory computations with quadruple zeta basis sets. Results

![Potential energy curve for BH in an aug-cc-pVQZ basis using full configuration interaction and various approximate correlation methods with an RHF reference.](image1.png)

![Potential energy curve for BH in an aug-cc-pVQZ basis using various approximate correlation methods with a UHF reference.](image2.png)
TABLE I. Full CI total energies and errors for approximate correlation methods (hartrees) for BH using the aug-cc-pVQZ basis.

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<th>R(HF)/Å</th>
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<td>0.081 052</td>
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<td>0.073 793</td>
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<td>−0.036 800</td>
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</table>

have been obtained using the largest abelian subgroup, which is $C_{2v}$ for BH and HF and $C_{s}$ for CH$_4$. For methane, the potential energy curve was obtained by altering the length of a single C–H bond while keeping the remaining three C–H bonds at their equilibrium bond length (1.086 Å) and the HCH angles at the tetrahedral value. The number of determinants in the full CI wave functions are 15,132,412 (aug-cc-pVQZ BH); 3,756,816 (6-31G** HF); and 26,755,625 (6-31G* CH$_4$).

III. RESULTS AND DISCUSSION

The potential energy curves for the ground state of BH using the aug-cc-pVQZ basis set are displayed in Figs. 1 and 2 for RHF and UHF references, respectively. Tables I and II provide full CI benchmark energies and the relative errors for the different correlation methods considered. These errors are presented graphically in Fig. 3. Results using the nonaugmented basis cc-pVQZ were very similar and are available.
FIG. 4. Potential energy curves for HF in a 6-31G** basis using full configuration interaction and various approximate correlation methods with restricted orbitals.

FIG. 5. Potential energy curves for HF in a 6-31G** basis using various approximate correlation methods with unrestricted orbitals.

FIG. 6. Errors in potential energies for HF using various approximate correlation methods with a 6-31G** basis. B3LYP and UB3LYP error curves have been shifted up by 70 kcal mol$^{-1}$. 
from the authors. One striking feature of the results is the very poor behavior of MP2 and CCSD(T) at large distances when using an RHF reference. The MP2 energies diverge toward negative infinity, and the CCSD(T) energies drop below FCI around 3 Å and appear to level off around 6 Å at a value more than 20 kcal mol\(^{-1}\) below the FCI dissociation limit. These methods are able to produce energies below the FCI energy because they do not employ a symmetric expectation value formula for the energy, and hence they are not subject to the variational theorem. The poor performance of MP2 and CCSD(T) arises from the inapplicability of nondegenerate perturbation theory in cases of strong neardegeneracies as occur at large bond distances. RHF CCSD appears to be immune to these difficulties in this case, providing energies which never drop below FCI. However, the good performance of CCSD near equilibrium (absolute en-

<table>
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<th>TABLE IV. Error vs FCI for HF (hartrees) using the 6-31G** basis.</th>
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<td>R(HF)/Å</td>
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</tr>
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<tr>
<td>0.85</td>
</tr>
<tr>
<td>0.9</td>
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ergy errors of less than 2 kcal mol$^{-1}$ degrades significantly for larger bond distances and errors become more than 9 kcal mol$^{-1}$ near dissociation.

Methods using a UHF reference perform significantly better in general, which is not surprising given that UHF is able to dissociate BH at least qualitatively correctly, unlike RHF. BH is unusual in that it is a closed-shell molecule with a UHF solution below the RHF solution even at the equilibrium geometry. UHF and UMP2 both significantly underestimate the dissociation energy, by $\sim 18$ and 7 kcal mol$^{-1}$, respectively. The UMP2 potential energy curve has an unusual shape in the intermediate bond breaking region, with the energy rising too rapidly around 2 Å and eventually leveling off to a dissociation limit which is too low. It is interesting to note that the error for UMP2 is larger than for restricted MP2 around equilibrium, and this difference increases in the intermediate bond breaking region to around 9 kcal mol$^{-1}$. Near 2.4 Å the MP2 and UMP2 error curves intersect, and the UMP2 errors become smaller at larger internuclear distances.

The unrestricted CCSD and CCSD(T) results are much better and match full CI very closely around equilibrium and near dissociation. Like UMP2, they also rise too rapidly in the intermediate region, although not as severely. There is a small region of intermediate geometries (2.2–2.6 Å) in which errors for CCSD with unrestricted orbitals becomes noticeably larger than CCSD with restricted orbitals, although the difference is much less (around 1 kcal mol$^{-1}$) than for MP2 versus UMP2.

To help quantify how well the approximate methods parallel the full CI potential energy curves, we have computed “nonparallelity” errors (NPE) for each approximate method. This error is defined as the difference between the absolute maximum and minimum deviations from the FCI potential curve over the points considered. The NPE would, therefore, be zero if a curve differed from the FCI curve by a constant shift. The NPE’s are tabulated in Table VII, along with the minimum and maximum errors. Generally, the smallest errors occur near equilibrium for RHF references, but at the dissociation limit for UHF references. NPE’s are not given for RHF and restricted MP2 and B3LYP, since the maximum error is not well defined for these cases. For BH, we find that unrestricted orbitals give much smaller NPE’s than restricted orbitals, but the errors remain fairly large, around 5 and 3
same trends as in BH, except that the UHF solution now
in Tables III and IV. The potential energy curves follow the
given in Figs. 4 and 5 for restricted and unrestricted orbitals,
CCSD was superior to CCSD
more reliable than CCSD.

Potential energy curves for HF in a 6-31G ** basis are
obtained results using the popular B3L YP density-functional
and restricted orbitals, CCSD(T) is once again
more reliable than CCSD.

Potential energy curves for HF in a 6-31G ** basis are
given in Figs. 4 and 5 for restricted and unrestricted orbitals,
respectively. Errors against full CI are presented in Fig. 6 and
in Tables III and IV. The potential energy curves follow the
same trends as in BH, except that the UHF solution now
matches RHF up to a certain critical bond length (around 1.4
Å), which is the more typical situation. Again, restricted
MP2 diverges to negative infinity for large bond distances,
and restricted CCSD(T) gives energies which are far too low
at dissociation. Unrestricted orbitals generally improve the
MP2 and coupled-cluster results except for the intermediate
region around the RHF–UHF instability point, where they
introduce a slightly larger error for UCCSD and a signifi-
cantly larger error for UMP2. The nonparallelity errors in
Table VII show similar trends as for BH, but they are uni-
formly larger (NPE’s for restricted CCSD, UHF, and UMP2
are all larger by several kcal mol⁻¹). For HF, we have also
obtained results using the popular B3LYP density-functional

<table>
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<tr>
<th>R(HF)/Å</th>
<th>FCI</th>
<th>UHF</th>
<th>MP2</th>
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<td>4.6</td>
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<td>0.000 432</td>
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TABLE V. Full CI total energies and errors for approximate correlation methods (hartrees) for CH₄ using the
6-31G* basis. 
method. The B3LYP energies are much lower than full CI and the B3LYP curves have been shifted upward in Figs. 4 and 5 for easier comparison to the wave function based methods. Although B3LYP exhibits large errors for restricted orbitals, unrestricted B3LYP remains fairly parallel to the full CI curve. The NPE of UB3LYP and UCCSD are both about 6 kcal mol$^{-1}$; of the methods considered, only UCCSD(T) provides a better result (3.7 kcal mol$^{-1}$).

Potential energy curves for CH$_4$ in a 6-31G* basis are presented in Figs. 7 and 8; errors are given in Tables V and VI and displayed in Fig. 9. Although the errors for restricted CCSD and CCSD(T) are a mere 3.3 and 0.4 millihartree around equilibrium, they increase to around 19 and ~22 millihartree, respectively, around the dissociation limit (4.6 Å). The trends in the curves are very similar as for HF, although the difference between MP2 and UMP2 near the RHF–UHF instability is smaller than in HF and is more similar to that in BH. The quality of UB3LYP is not as good for CH$_4$ as for HF, with the NPE growing to more than 11 kcal mol$^{-1}$. UCCSD and UCCSD(T) are the two best methods in this case, with NPE’s of about 5 and 3 kcal mol$^{-1}$, respectively.

The observation that unrestricted orbitals lead to larger errors for MP2 and CCSD in the intermediate bond breaking region deserves further discussion. It should be pointed out once again that in this study we are examining the breaking of bonds to hydrogen atoms, which ought to be the simplest case for single-reference methods. Indeed, Krylov$^{15}$ has shown that in the unusually challenging case of F$_2$, unrestricted orbitals can cause CCSD to exhibit unphysical behavior with very large errors in the bond breaking region. Ideally, one would like some way to obtain results like CCSD with restricted orbitals around equilibrium and in the intermediate region, with a smooth transition to UCCSD at the dissociation limit. Fortunately, there is a way to achieve this. Purvis$^{36}$ suggested that orbitals which minimized the CCD energy might prove useful in going between limits like this for bond breaking problems. This optimized-orbital coupled-cluster doubles (OO-CCD) approach was first tested by Purvis and Bartlett$^{20}$ and examined more fully by Scuseria and Schaefer,$^{37}$ with the first efficient implementation and examination of molecular properties by Sherrill$^{38}$ et al. Consistent with previous work,$^{15}$ we find that OO-CCD allowing
unrestricted orbitals (denoted here UOO-CCD) connects smoothly between the CCSD and UCCSD behaviors at short and long distances, respectively. Figure 10 demonstrates results for UOO-CCD and UOO-CCD(T) for the HF molecule. Although UOO-CCD does not include single excitations, the orbital optimization plays essentially the same role; UOO–CCD acts remarkably similar to CCSD to the left of the bond breaking region, and it switches smoothly to near UCCSD behavior at long distances. Although the error for UOO–CCD is usually smaller in the intermediate region, the maximum error is unfortunately about the same as in UCCSD. We also tested OO-CCD with restricted orbitals but found that it does not improve significantly upon CCSD with RHF orbitals. UOO-CCD(T) behaves in the same qualitative manner as UOO-CCD, acting as CCSD(T) before the bond breaking region, and as UCCSD(T) afterward. UOO-CCD(T) shifts from restricted to unrestricted behavior over the range $R_{HF} = 1.8–2.2$ Å, compared to 1.4–2.0 Å for OO-CCD. Although the errors for UOO-CCD(T) are generally less than for UCCSD(T), the maximum errors, near 2.0 Å, are nearly the same (3.5 and 3.8 kcal mol$^{-1}$, respectively).

**IV. CONCLUSIONS**

In this paper we have analyzed the performance of the MP2, CCSD, CCSD(T), and B3LYP methods for bond breaking reactions in the BH, HF, and CH$_4$ molecules by comparison to full CI results. In all three cases, in addition to the anticipated divergence of RHF and restricted MP2, we see very large errors in UHF and UMP2 at intermediate distances, and in restricted CCSD(T) at large distances. CCSD and especially MP2 exhibit larger errors with unrestricted than restricted Hartree–Fock orbitals in the intermediate bond breaking region. UB3LYP appears to improve upon UMP2 but is inferior to UCCSD and UCCSD(T) for breaking bonds to hydrogen. Among the investigated models, unrestricted CCSD and CCSD(T) are preferred because they remain the most parallel to the full CI curve for all three molecules. However, it must be noted that all of the methods considered give rather large nonparallelity errors, about 3 to 4 kcal mol$^{-1}$ for UCCSD(T), and larger for the other methods. Accounting for orbital relaxation by variational optimization of the orbitals at the CCD level, rather than by single excitations, gives a method which behaves as well as CCSD at short internuclear distances and as well as UCCSD at large distances. The resulting UOO-CCD and UOO-CCD(T) approaches clearly improve upon their counterparts based on Hartree–Fock orbitals, but have nearly the same maximum errors as UCCSD and UCCSD(T), respectively. Breaking bonds to atoms other than hydrogen is expected to be even more challenging for single-reference methods, and we will pursue such systems in future work.

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