

Which Ab Initio Wave Function Methods Are Adequate for Quantitative Calculations of the Energies of Biradicals? The Performance of Coupled-Cluster and Multi-Reference Methods Along a Single-Bond Dissociation Coordinate

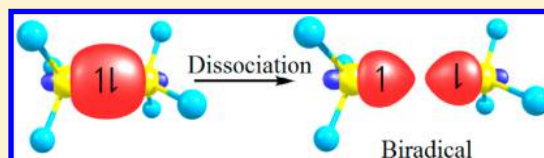
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S Supporting Information

ABSTRACT: We examine the accuracy of single-reference and multi-reference correlated wave function methods for predicting accurate energies and potential energy curves of biradicals. The biradicals considered are intermediate species along the bond dissociation coordinates for breaking the F–F bond in F₂, the O–O bond in H₂O₂, and the C–C bond in CH₃CH₃. We apply a host of single-reference and multireference approximations in a consistent way to the same cases to provide a better assessment of their relative accuracies than was previously possible. The most accurate method studied is coupled cluster theory with all connected excitations through quadruples, CCSDTQ. Without explicit quadruple excitations, the most accurate potential energy curves are obtained by the single-reference RCCSDt method, followed, in order of decreasing accuracy, by UCCSDT, RCCSDT, UCCSDt, seven multireference methods, including perturbation theory, configuration interaction, and coupled-cluster methods (with MRCI+Q being the best and Mk-MR-CCSD the least accurate), four CCSD(T) methods, and then CCSD.



1. INTRODUCTION

Dissociation of chemical bonds is a basic process in chemistry, yet it is far from trivial to describe the process of bond breaking with quantum chemical electronic structure methods. This epitomizes a larger problem because a molecule with a partially broken single covalent bond is an example of an incipient low-spin biradical, which is the most difficult kind of open-shell system to describe quantitatively in wave function theory (WFT). (Biradicals are also called diradicals, and we make no distinction between these two terms.) Despite the broad successes of WFT for thermochemical calculations,¹ we can hardly consider the situation satisfactory until we understand how to describe single-bond breaking in a practical, systematic, and quantitative way.

For a given one-electron basis set, all WFT electronic structure methods, as they are systematically improved, should tend to the same limit, which is called full configuration interaction (FCI). As the basis set is improved, the FCI results tend to the exact solution of the electronic Schrödinger equation, which is called complete configuration interaction (CCI). Unfortunately, there are only a few molecular systems for which the CCI limit has been obtained. Therefore, much of what we know about the quantitative validity of various biradical treatments is not based on comparisons to the CCI limit, and in fact it is not usually based on comparison to the FCI limit either, which is also expensive to obtain, and this adds uncertainty to the conclusions. In the present work we have selected three single-bond dissociation processes, namely, F₂ →

2 F, H₂O₂ → 2 OH, and CH₃CH₃ → 2 CH₃, as functions of the F–F, O–O, and C–C distances, respectively, since the FCI limit is known for a correlation-consistent polarized valence double- ζ (cc-pVDZ) basis set for F₂,² and we were able to generate near-FCI results for this basis for the other two systems. The O–O single bond is important in many interesting organic molecules such as 1,2-dioxetane and firefly dioxetanone,^{3–8} where O–O bond cleavage is an important step in the chemiluminescent decomposition of those molecules. C–C bonds are even more ubiquitous, and C–C bond breaking is very important in many organic reactions, such as some pericyclic reactions.^{9,10} By testing all the methods on the same three problems, we can make valid comparisons of their accuracy, and since we study the problem as a function of bond-breaking distances, we access a range of electronic coupling of the biradical centers, from strong at small distances to very weak at large distances. The methods tested in this work are introduced next.

It is a particularly opportune time for the tests mentioned above because recent improvements in algorithms and software have made it more practical to carry out a variety of calculations for including electron correlation to high order. We will divide the available methods into three categories based on the source of the orbitals used to construct configuration state functions (CSFs) for the final dynamically correlated wave function. In

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the methods tested here, such orbitals are obtained by self-consistent field (SCF) calculations; and the SCF wave function used for this purpose is called the reference wave function. The reference wave function may consist of either a single CSF or multiple configurations. In the former case the final dynamically correlated wave function is called a post-Hartree–Fock or single-reference (SR) treatment, and in the latter case it is called a multireference (MR) treatment. We may further divide SR treatment into those based on restricted Hartree–Fock (RHF) theory in which all spatial orbitals are doubly occupied and those based on unrestricted Hartree–Fock (UHF) theory that employs different orbitals for different spins; in both cases the reference wave function is a single Slater determinant for the problems treated here, where we only consider the ground electronic state. The MR treatments considered here are all based on complete-active-space SCF (CASSCF) wave functions. The final dynamically correlated SR wave functions considered here are all of the coupled-cluster (CC) type and have names beginning with RCC, RCR-CC, UCC, or UCR-CC, where the leading R or U denotes the restricted or unrestricted choice of reference (when we just refer to CC.... or CR-CC... methods, we do not specify whether the reference is restricted or unrestricted). Dynamically correlated wave functions of the MR type have names beginning with either MR or CASPT, as explained below. A further widely used notational issue is that molecules or systems for which SR wave functions provide a good zeroth-order description are often called SR molecules or systems, whereas those requiring multiple CSFs even for a reasonable zeroth-order treatment are often called MR molecules or systems. Biradicals are MR systems. Finally we note that SR methods are usually much more straightforward to apply than MR methods, so there is some interest in trying to treat MR systems by SR methods, and that is part of the present study.

The CC method is an effective tool for the accurate study of chemical systems.¹¹ Its origins are in many-body theory rather than in perturbation theory, and it does not yield variationally stationary wave functions, but it is the most promising method for treating MR systems by SR methods because it is well-known that CC methods are less sensitive to the choice of orbitals than are standard perturbation theory or variational methods. In the present article we consider both SR and MR versions of CC theory. The SR coupled-cluster treatment with single and double excitations (CCSD) can be used on its own but is usually not accurate enough for chemical applications. However, when combined with a particular quasi-perturbative treatment of connected triple excitations, labeled CCSD(T),¹² it becomes much more accurate and is even sometimes called “the gold standard of quantum chemistry”; this is a well-deserved name if one considers only molecules near equilibrium geometries. Unfortunately, for molecules with partially broken bonds significantly displaced from their equilibrium geometries, the restricted Hartree–Fock wave function is not a good reference wave function, and the perturbation approach of the CCSD(T) method with an RHF reference wave function fails.^{13,14} Therefore triple excitations must be treated nonperturbatively to describe bond-breaking.¹⁵ By including the triply and possibly the quadruply excited clusters in the iterative cluster expansion, the computational cost of the resulting coupled-cluster singles, doubles and triples (CCSDT)^{16,17} and coupled-cluster singles, doubles, triples, and quadruples (CCSDTQ)^{18–20} methods scale as $O(N^8)$ and $O(N^{10})$, where N is the number of atoms, as compared to

$O(N^6)$ and $O(N^7)$, respectively, for CCSD and CCSD(T). Hirata proposed a method called CCSDT(2)_Q, which treats the full singles, doubles, and triples iteratively and all of the second-order terms involving quadruples perturbatively.²¹ It has been shown to be quite accurate for the symmetric dissociation of H₂O and triple-bond dissociation in N₂. The CCSDT(2)_Q method is quite efficient compared to CCSDTQ, but it still scales as $O(N^9)$. Connected higher order excitation clusters such as triples and quadruples are necessary to describe bond dissociations. However, the complete inclusion of such excitations could be very expensive.

Piecuch and co-workers proposed the active-space coupled-cluster method called CCSDt,^{22,23} where the lower case t (“little t”) denotes that one includes the dominant connected triple excitations rather than all of them. In this method the connected triple excitations are limited to certain classes of excitations defined by active orbitals. (Note that the active orbitals here are selected HF orbitals, not orbitals from a multiconfigurational calculation, so the method retains the conceptual and algorithmic simplicity of a single-reference method, although its objective is to include multireference effects.) The CCSDt method is size extensive, and by increasing the number of active orbitals in a CCSDt calculation, one would reach the limit of CCSDT, without the perturbative approximation of CCSD(T), but the goal is to stop with a very small number of active orbitals, which provides a significant decrease in computation time, scaling behavior ($O(N^6)$ if the size of the active space is independent of the number of atoms), and storage requirements.

In other work designed to correct the unphysical results of CCSD(T) based on an RHF reference for bond dissociation without raising the scaling exponent, Piecuch and co-workers proposed renormalized (R-) and completely renormalized (CR-) coupled-cluster methods,^{24–28} such as CR-CCSD(T). These correct the breakdown of the perturbative treatment of triple excitations for breaking of a single bond.

An alternative practical way to describe bond breaking with SR coupled-cluster methods is to use a UHF wave function as the reference.^{11,13} We will compare the performance of all these various alternatives.

A quite different approach to describing bond dissociation is to construct the reference wave function with multiple Slater determinants to provide a better starting point. The CASSCF method,^{29–35} a specific case of multiconfiguration SCF,³⁶ is the most widely used way to construct multiconfiguration reference wave functions. Perturbation theory or configuration interaction can be built on CASSCF reference wave functions to recover dynamical electron correlation energy for better accuracy. Second-order perturbation theory with a CASSCF reference wave function (CASPT2) is one of the most widely used multireference methods.^{37–40} Multireference configuration interaction with single and double excitations^{41–43} (here called MRCI but sometimes called MR-CISD) is also widely used to add dynamical correlation to multiconfiguration SCF reference wave functions. However, MRCI suffers from not being size-extensive. This problem can be alleviated by adding Davidson’s correction⁴⁴ to approximately include the effects of high-order excitations, and the resulting method is called MRCI+Q. Multireference averaged coupled-pair functional (MR-ACPF)⁴⁵ and multireference averaged quadratic coupled-cluster (MR-AQCC)⁴⁶ methods represent other approaches to improving over MRCI; both of these may be considered as simplified versions of MR-CC theory.

The state-specific multireference coupled cluster approach proposed by Mukherjee and co-workers is rigorously size-extensive⁴⁷ and converges to the FCI limit rapidly.⁴⁸ The Mukherjee multireference coupled-cluster singles and doubles (Mk-MR-CCSD) has been implemented⁴⁹ and used to study biradicals.^{50,51} Although, Mk-MR-CCSD improves the performance of CCSD significantly, recent studies suggest the triples are necessary for quantitative results.^{52–54} This is a more general problem in that, because of the greater complexity of MR methods as compared to SR methods, dynamical electron correlation is usually treated to a much lower order than in single-reference coupled-cluster methods. For CASPT2, MRCI, MRCI+Q, MR-ACPF, MR-AQCC, and Mk-MR-CCSD, connected excitations are fully included only up to double excitations. Among methods in common use, only CASPT3,⁵⁵ which is a third-order multireference perturbation method, considers connected triple excitations. On the other hand, coupled-cluster methods based on single-reference HF wave functions can include much higher connected excitations. So it is very interesting to test the performance of various coupled-cluster and multireference methods for bond dissociation. That is the main motivation of the present study.

2. METHODS

The equilibrium geometry of H₂O₂ was optimized by the M06-2X⁵⁶ density functional with the MG3S basis set⁵⁷ (for systems containing only H, C, O, or F, such as those considered here, MG3S is equivalent to 6-311+G(2df,2p)^{58,59}). The equilibrium geometries of F₂ and CH₃CH₃ were taken from experiment.^{2,60} In the calculation of potential energy curves, only the X–X (X = F, O, or C) bond lengths were changed, while the other degrees of freedom were frozen. A correlation consistent polarized valence double- ζ (cc-pVDZ) basis set⁶¹ was used in all WFT calculations. Note that the cc-pVDZ basis set is inadequate to yield reliable results to compare with experiments; however, it is adequate for the present study since our aim is to test the performance of various wave function methods against the FCI (or near-FCI) results with this particular basis set. Since the available FCI results of F₂ only consider electron correlation in the valence shell,² excitations of the 1s electrons of F, O, and C atoms were excluded in all our correlation calculations, which is often called the frozen-core approximation.

Various coupled-cluster methods, CCSD(T),¹² CR-CCSD(T),²⁴ CCSDt,²² CCSDT,^{16,17} CCSDT(2)_Q,²¹ and CCSDTQ_{18–20} were used to calculate the potential energy curve as a function of the X–X bond distances.

The calculations by the CCSDt method involve the selection of active orbitals such that connected triple excitations are limited to those in which at least one hole is made in an occupied active orbital, and at least one particle is created in an unoccupied active orbital. This includes all internal excitations in which all orbitals involved in the excitation are active orbitals and semi-internal triple excitations that involve up to two core orbitals and up to two virtual orbitals. We chose active orbitals that correspond to the 2p orbitals of nonhydrogenic atoms and the 1s orbitals of hydrogen atoms—that is, the 5 highest occupied orbitals and 1 lowest unoccupied orbital for F–F, the 5 highest occupied orbitals and 3 lowest unoccupied orbitals for HO–OH, and the 5 highest occupied orbitals and 7 lowest unoccupied orbitals for H₃C–CH₃. Since these active spaces are much smaller than the whole space consisting of doubly occupied orbitals, active orbitals, and virtual orbitals, the savings

in computational time is enormous, even for the small molecules and basis sets considered here.

The coupled-cluster methods were tested with both RHF and UHF reference wave functions, and—as already mentioned—we put R or U in front of the method acronyms to indicate RHF or UHF reference wave functions. All Hartree–Fock and coupled-cluster calculations (except Mk-MR-CCSD) were carried with the tensor contraction engine (TCE)⁶² in *NWChem* version 6.0.⁶³

We did the Mk-MR-CCSD calculations with both the RHF orbitals and two-configuration self-consistent-field (TCSCF) orbitals.⁶⁴ In both cases, the zeroth-order wave function for Mk-MR-CCSD is a multiconfigurational reference function given by

$$|\Phi_0\rangle = c_1|(\text{core})^2\phi_1\alpha\phi_1\beta\rangle + c_2|(\text{core})^2\phi_2\alpha\phi_2\beta\rangle \quad (1)$$

where ϕ_1 and ϕ_2 are the two active orbitals, and c_1 and c_2 are the coefficients of two configurations. The two coefficients are obtained self-consistently for TCSCF orbitals or by a CAS-CI calculation for RHF orbitals. All Mk-MR-CCSD calculations were performed with the *PSI3* computer package.⁶⁵

In CASSCF calculations, the number N_e of active electrons and the number N_o of active orbitals need to be specified, which is typically denoted as CASSCF(N_e, N_o). To recover dynamical correlation, CASPT2, MRCI, MRCI+Q, MR-ACPF, and MR-AQCC calculations were carried out based on CASSCF reference wave functions. For all three systems, we performed multireference calculations based on CASSCF(2,2) wave functions, which include X–X bonding and antibonding orbitals in the active space. For H₂O₂ and F₂, we also performed CASSCF calculations with full valence active spaces; this yields CASSCF(14,10) for H₂O₂ and CASSCF(14,8) for F₂. All the CASSCF and multireference calculations based on CASSCF orbitals were performed with the *Molpro* program.⁶⁶ The MRCI, MRCI+Q, MR-ACPF, and MR-AQCC calculations were performed with the internally contracted MRCI algorithm^{42,43} of *Molpro*.

3. RESULTS

We first tested the performance of various coupled-cluster methods and multireference methods for the bond dissociation of F₂ since there are FCI results available.² As discussed in section 3.1.1, we found that the CCSDT(2)_Q results with RHF reference wave functions agree very well with the FCI results for F₂, and therefore RCCSDT(2)_Q was used to serve as benchmark to test the performance of other methods for the O–O bond dissociation in H₂O₂ and the C–C bond dissociation in CH₃CH₃.

For all three molecules, we consider the potential energy curve

$$\Delta E = E(R_{X-X}) - E(R_{X-X,\text{eq}}) \quad (2)$$

where E is the electronic energy including nuclear repulsion, R_{X-X} is the X–X distance, and $R_{X-X,\text{eq}}$ is its equilibrium value. The values used for the three equilibrium bond lengths are: O–O, 1.420 Å; F–F, 1.412 Å; and C–C, 1.523 Å.

The T_1 diagnostic of MR behavior will be useful in the discussion; the T_1 diagnostic has been defined as the norm of the vector of single-excitation amplitudes in the cluster expansion of the CCSD wave function, and it has been suggested that a value greater than 0.02 indicates the need for an MR treatment.⁶⁷

3.1. F_2 . The quantitative description of bond dissociation represents a very challenging problem for single-reference methods since the Hartree–Fock wave function is not a good zeroth-order reference wave function away from the equilibrium geometry. The potential energy curve of F_2 represents an even more challenging problem for single-reference methods than most bond dissociations since a restricted HF wave function is not a good zeroth-order reference wave function even at the experimental equilibrium geometry (which is close to its RHF equilibrium geometry⁶⁸). It is therefore very interesting to test the performance of single-reference coupled-cluster methods for the F–F bond dissociation in F_2 .

3.1.1. Potential Energy Curve of F_2 Calculated by Coupled-Cluster Methods with RHF Reference Wave Functions. The potential energy curves of F_2 calculated by various coupled-cluster methods with RHF reference wave functions, as well as the FCI results, are shown in Figure 1, and the corresponding

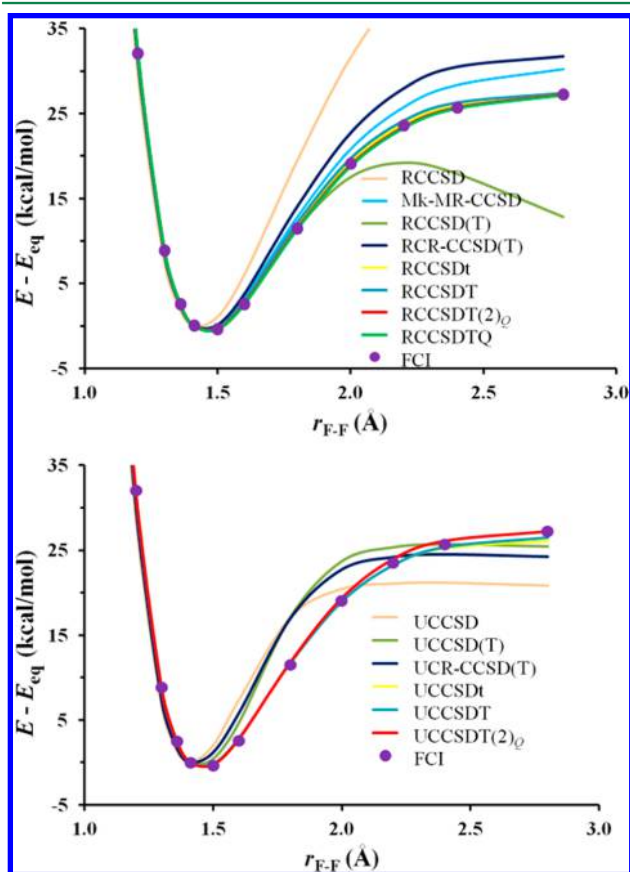


Figure 1. Dissociation curves of F_2 calculated by various coupled-cluster methods with RHF (top) and UHF (bottom) reference wave functions (the energy of experimental geometry is taken as the zero-reference for each method).

errors are shown in Figure 2. RCCSD overestimates the dissociation energy of F_2 by giving too high energies at large bond distances. RCCSD(T) performs much better near the equilibrium bond length, with less than 2 kcal/mol discrepancies with FCI results. However, the performance of CCSD(T) deteriorates as the bond length increases. The RCCSD(T) potential energy curve has an unphysical hump around 2.2 Å, as observed earlier by other groups.^{11,15,24,25}

The error of RCCSD(T) with respect to FCI is shown in Figure 2, along with the T_1 diagnostics. As the T_1 diagnostic

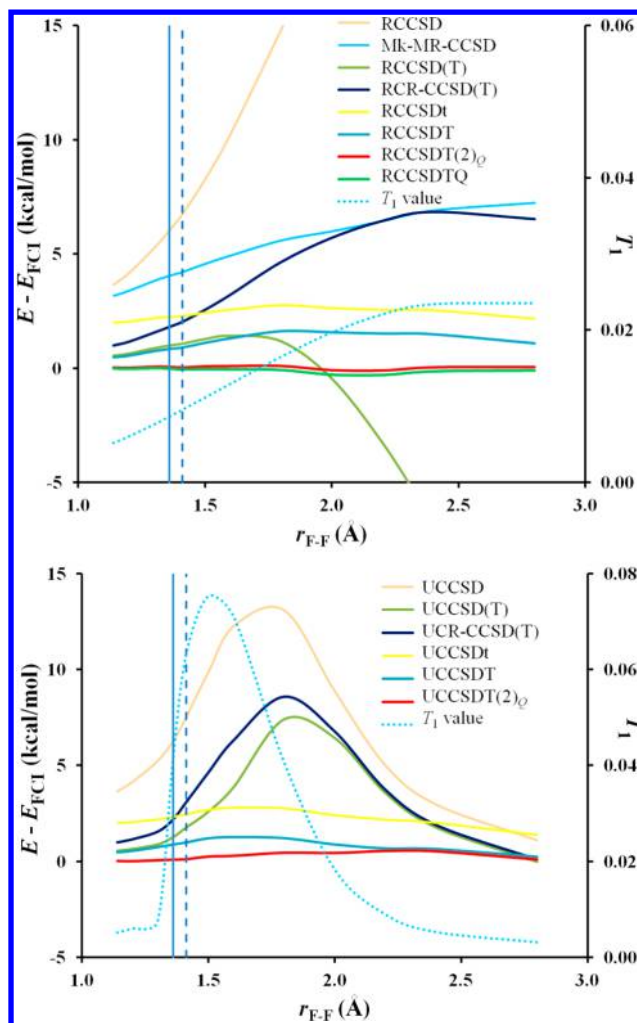


Figure 2. Errors of various coupled-cluster methods with RHF (top) and UHF (bottom) reference wave functions relative to the FCI energies of F_2 at different bond lengths (the vertical dash line denotes the experimental bond length; the vertical solid line denotes the bond length at which the RHF–UHF instability sets in).

approaches 0.02, the error of RCCSD(T) becomes negative. The unphysical lowering of the potential energy curve indicates the breakdown of RCCSD(T), suggesting that nonperturbative triple excitations need to be considered in the cluster expansion. The RCR-CCSD(T) method eliminates the hump in the potential energy curve. However, it always overestimates the relative energy along the potential energy curve, giving too large a bond dissociation energy. Figure 2 shows that even at the relatively short distance of 1.9 Å (a moderately coupled biradical) RCR-CCSD(T) overestimates the biradical energy with respect to the covalent bond energy by 5 kcal/mol.

Figure 2 also shows that coupled-cluster methods with triple or higher excitations in the cluster expansion are able to correctly describe the bond dissociation of F_2 . RCCSDT yields a reasonably accurate potential energy curve, with an absolute error of only about 1.5 kcal/mol at large bond lengths. By selecting important triples excited from the active orbitals (5 highest occupied and 1 lowest unoccupied orbitals), which are orbitals corresponding to the 2p orbitals of F atoms, the dissociation curve calculated by RCCSDt is almost identical to the RCCSDT one; this is quite encouraging since RCCSDt requires only a fraction of the computational requirements of

RCCSDT. The RCCSDT(2)_Q and RCCSDTQ potential energy curves agree very well with each other, and they both agree with FCI results extremely well, with the largest discrepancies being 0.1 kcal/mol for RCCSDT(2)_Q and 0.3 kcal/mol for RCCSDTQ. It is interesting to see that RCCSDT(2)_Q, which treats the quadruple excitations perturbatively, yields better agreement with FCI than RCCSDTQ which treats the quadruple excitations iteratively; this is reminiscent of the well-known fact that CCSD(T) is often more accurate than CCSDT (although not here).^{69–72} Because of the excellent performance of RCCSDT(2)_Q, we will use it as a benchmark for the other two molecules where FCI results are not currently available.

Although Mk-MR-CCSD is a multireference coupled-cluster method, we included it here for a direct comparison between Mk-MR-CCSD and RCCSD. We performed Mk-MR-CCSD calculations with both RHF and TCSCF orbitals. The results obtained with RHF and TCSCF orbitals are quite similar, so we only discuss the results with RHF orbitals. By using a multideterminant function as the zeroth-order reference wave function, Mk-MR-CCSD describes the dissociation curve much better than CCSD away from the equilibrium bond length, in both relative (Figure 1) and absolute senses (Figure 2). However, at large bond lengths, Mk-MR-CCSD still overestimates the relative energies of stretched F₂ by more than 3 kcal/mol, which indicates the necessity of higher order excitations for quantitative results.

3.1.2. Potential Energy Curve of F₂ Calculated by Coupled-Cluster Methods with UHF Reference Wave Functions. For F₂, the RHF wave function is unstable^{44,68} even at the experimental equilibrium geometry ($r_{\text{FF}} = 1.412$ Å); it leads to a broken-symmetry UHF wave function that is lower in energy. The UHF wave function, unlike the RHF one, dissociates to ground-state atoms. The potential energy curves calculated by various coupled-cluster methods with UHF reference wave functions are shown in Figure 1. With UHF reference wave functions, even CCSD(T) is able to yield the correct dissociation behavior at large bond lengths. However, at intermediate bond lengths (1.5 to 2.2 Å), UCCSD, UCCSD(T), and UCR-CCSD(T) all give energies much higher than those of FCI, both in a relative sense (Figure 1) and an absolute sense (Figure 2). Figure 2 shows clearly that the errors of the UCCSD(T) and UCR-CCSD(T) energies relative to FCI are quite small (less than 2 kcal/mol) at small and large bond lengths, but can be quite large (greater than 8 kcal/mol) at intermediate bond lengths (1.5 to 2.2 Å). The T_1 diagnostics for UCCSD(T) are also quite large at intermediate bond lengths, which suggests that the spin-contaminated UHF wave functions are not good reference wave functions at those bond lengths.

When triple or higher order excitations are considered, as in UCCSDT and UCCSDT(2)_Q, one is able to get results that agree well with FCI. However, the energies calculated by UCCSDT(2)_Q can differ from the FCI results by as much as 0.5 kcal/mol, which is much larger than the maximum error of RCCSDT(2)_Q, whose largest discrepancy is only 0.1 kcal/mol. In summary, the biradicals corresponding to partly dissociated F₂ are treated much better by RCCSDT(2)_Q than by UCCSDT(2)_Q. Again, with the inclusion of important triples, UCCSDt yields a dissociation curve in good agreement with the FCI one.

3.1.3. Potential Energy Curve of F₂ Calculated by Multireference Methods. To describe the dissociation process

of F₂, at least the σ_{FF} and σ_{FF}^* orbitals need to be included in the active space. This yields 2 active electrons in 2 active orbitals in the CASSCF calculations, which is denoted as CASSCF(2,2). We also test the performance of multireference methods based on CASSCF wave functions with a full valence active space, which is CASSCF(14,8) for F₂. The calculated potential energy curves of F₂ by multireference methods with CASSCF(2,2) reference wave functions are shown in Figure 3.

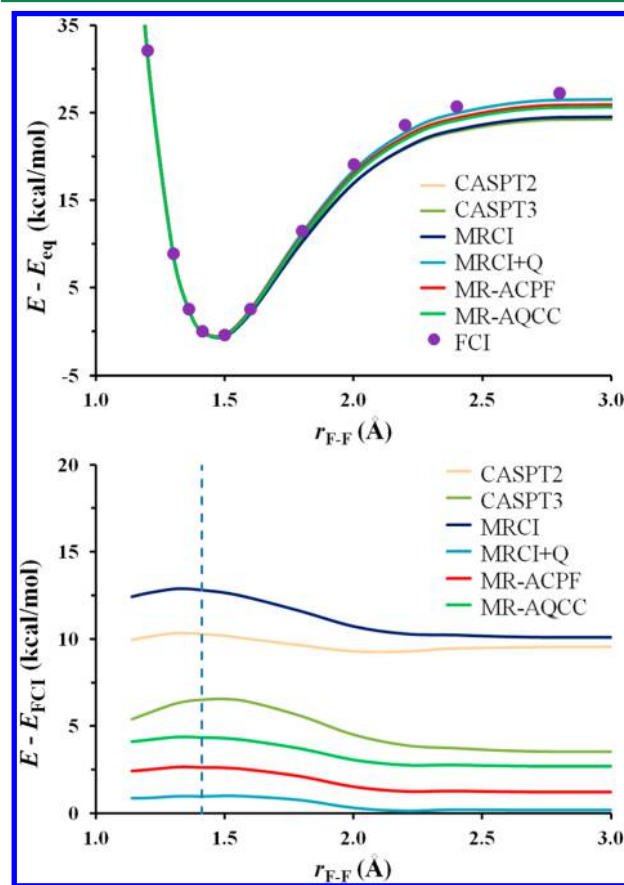


Figure 3. Dissociation curves of F₂ (top) and errors relative to FCI energies (bottom) calculated by various multireference methods with CASSCF(2,2) reference wave functions (the vertical dash line denotes the experimental bond length).

All tested multireference methods are able to qualitatively describe the F–F bond dissociation of F₂. CASPT2, MRCI+Q, MR-ACPF, and MR-AQCC all yield potential energy curves in good agreement with the FCI curve, with the best agreement obtained by MRCI+Q. The CASPT2 dissociation curve almost overlaps with the MRCI+Q curve. The CASPT3 and MRCI calculations are less accurate; both of them underestimate relative energies by about 4 kcal/mol at large bond lengths. It is interesting to see that CASPT3, which recovers correlation energy better than CASPT2, actually performs worse for the potential energy curves. To understand the performance of multireference methods better, we also plotted the error of each multireference method with respect to FCI results versus the F–F bond length in Figure 3. CASPT3 does recover more correlation energy than CASPT2, as shown by the smaller errors relative to FCI, with the largest error of 7 kcal/mol. On the other hand, more than 10 kcal/mol of electron correlation energy is missing in CASPT2. However, the errors of CASPT2 do not vary much with F–F bond length; thus, by cancellation

of errors, CASPT2 yields a much better potential energy curve than CASPT3. The errors of MRCI are about the same as those of CASPT2, which is perhaps not surprising since both of them consider only up to double excitations. (For example, multireference coupled-cluster calculations provide a better treatment of diradicals if one explicitly includes the effects of connected triple excitations.)⁵⁴ The errors of MRCI also depend strongly on bond length, like CASPT3, with better recovery of electron correlation energies at large bond lengths. This explains why MRCI and CASPT3 underestimate the relative energies at large bond lengths. By adding Davidson's correction to approximate higher-order excitations, the MRCI+Q approximation reduces the errors of MRCI significantly, to less than 1 kcal/mol at all considered bond lengths. Since it is well-known that MRCI+Q overestimates the effect of quadruple excitations,^{73–75} it must get good results by canceling such errors against the neglect of quintuple and other higher-order excitations. The errors of MR-ACPF and MR-AQCC are less than 3 and 5 kcal/mol respectively near equilibrium bond lengths, and reduce further at large bond lengths, so both of them describe the potential energy curves very well, with slight underestimation of the relative energies at large bond lengths.

Intruder states plague some applications of CASPT2,^{76–78} but their spurious contributions can be ameliorated by introducing a level shift in the denominators of the CASPT2 energy expression.⁷⁹ When not mentioned, as in all calculations presented so far, we use a zero level shift. To check the effect on the results, we calculated the potential energy curves by CASPT2 with various values of the level shift, from 0.1 to 0.5 hartree; and we compared these to those obtained without a level shift. Figure 4 shows that the calculated potential energy curves with and without the level shift are almost identical. Figure 4 shows that though the absolute errors increase with the level shift, the calculated relative energies are almost the same since the curves are quite parallel to each other.

Perturbation methods require partitioning the Hamiltonian into a zeroth-order Hamiltonian and a perturbative term. The original CASPT2 algorithm uses the standard Fock matrix formulation for the zeroth-order Hamiltonian,^{37,38} and we denote such calculations as CASPT2[g0] when we want to explicitly indicate this. When it is not mentioned, as in all calculations presented so far, we use the g0 formulation. CASPT2[g0] has been shown to often underestimate the bond energies by an amount between 2 and 5 kcal/mol per bond,⁸⁰ as also found above for the bond dissociation of F₂. To improve the performance of CASPT2 for excitation energies and dissociation energies, three different modifications, namely, g1, g2, and g3, of the zeroth-order Hamiltonian were proposed by Andersson.⁸¹ In addition, a g4 modification was implemented in *Molpro* to make CASPT2 calculations size extensive for cases in which a molecule dissociates to high-spin open-shell atoms.⁸² As an alternative to these Andersson-type modifications, Ghigo, Roos, and Malmqvist argued that CASPT2 with the original zeroth-order Hamiltonian, denoted by CASPT2[g0] in this paper, tends to overestimate the correlation energy for open-shell systems, thus underestimating the bond dissociation and excitation energies. They proposed a modification of the zeroth-order Hamiltonian by shifting the diagonal elements of the Fock operator by a weighted average quantity motivated by considering the ionization potential and electron affinity. This modification is called the IPEA shift,⁸³ and is widely used because it is applied by default in the

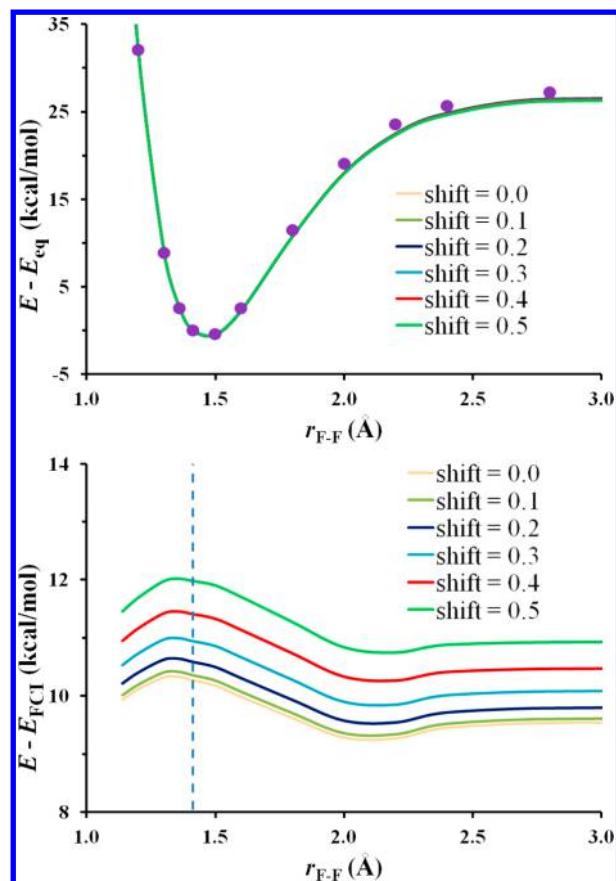


Figure 4. Dissociation curves of F₂ (top) and errors relative to FCI energies (bottom) calculated by CASPT2[g0] with different level shift values and with CASSCF(2, 2) reference wave functions (the vertical dash line denotes the experimental bond length).

MolCAS program⁸⁴ since version 6.4. Ghigo, Roos, and Malmqvist compared the calculated bond dissociation energies of 49 diatomic molecules with various IPEA shift values and recommended a value of 0.25 hartree. We calculated the potential energy curves of F₂ with different IPEA shift values, and the results are in Figure 5. The relative energies at large bond lengths increase with the IPEA shift, thus correcting the underestimation of CASPT2[g0] for bond dissociation energies. With an IPEA shift value of 0.25 hartree, the calculated CASPT2 potential energy curves almost pass through the FCI data points. The errors of CASPT2 energies with different IPEA shift values relative to FCI energies are also shown as functions of F–F bond length in Figure 5. The errors relative to FCI increase with the IPEA shift values, especially at large bond lengths (large biradical separations). Thus, CASPT2 with an IPEA shift value of 0.25 hartree has smaller errors in the bond dissociation energies; clearly this is a dangerous way to correct the theory since the correction results from a cancellation of errors.

The potential energy curves of F₂ were also calculated with Andersson-type zeroth-order Hamiltonians, namely, g1, g2, g3, and g4. Those results, as well as the original CASPT2[g0] results and the CASPT2[IPEA = 0.25 hartree] results are shown in Figure 6. All five modifications increase the relative energies at large bond length relative to CASPT2[g0]. However, CASPT2[g4] yields energies that are far from being parallel to the FCI results. The dependence of CASPT2 results on these choices makes them uncertain by at

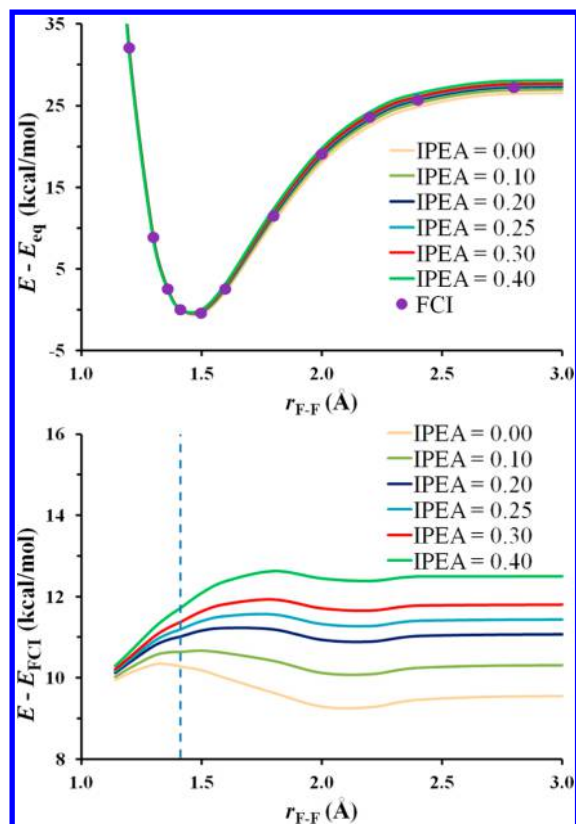


Figure 5. Dissociation curves of F_2 (top) and errors relative to FCI energies (bottom) calculated by CASPT2 with different IPEA shift values and with CASSCF(2, 2) reference wave functions (the vertical dash line denotes the experimental bond length).

least 1–3 kcal/mol. Consequently, one would be well advised to benchmark CASPT2 methods when they are applied to new systems. MR-AQCC, MR-ACPF, and especially MRCI+ Q_c recover much more correlation energy, and unlike CASPT2, their performance does not rely so strongly on the cancellation of errors.

We also tested the multireference methods with a full valence active space in the CASSCF, which includes 14 active electrons in 8 active orbitals. The main conclusions are similar to those obtained with CASSCF(2, 2), so we have relegated these calculations to the Supporting Information, and do not discuss them here. However, we want to point out that with the full valence active space, CASPT2[g0] slightly overestimates the bond dissociation energy by about 0.5 kcal/mol, and as a result, CASPT2 methods with all modified Hamiltonians overestimate the relative energies at large distances by at least 2 kcal/mol.

3.2. H_2O_2 and CH_3CH_3 . H_2O_2 and CH_3CH_3 are isoelectronic with F_2 , and the O–O and C–C dissociation processes are isoelectronic to the F–F dissociation process that we have considered so far. Similar to the situation in F_2 , the RHF wave function of H_2O_2 becomes unstable just a short distance away from the equilibrium O–O bond distance. On the basis of the excellent agreement of RCCSDT(2) $_Q$ with FCI for F_2 , we used the RCCSDT(2) $_Q$ results as the benchmark to test the performance of electronic structure methods for these interesting bond breaking processes.

3.2.1. Potential Energy Curves of H_2O_2 and CH_3CH_3 Calculated by Coupled-Cluster Methods with RHF Reference Wave Functions. The potential energy curves of H_2O_2 and CH_3CH_3 as calculated by various coupled-cluster methods are

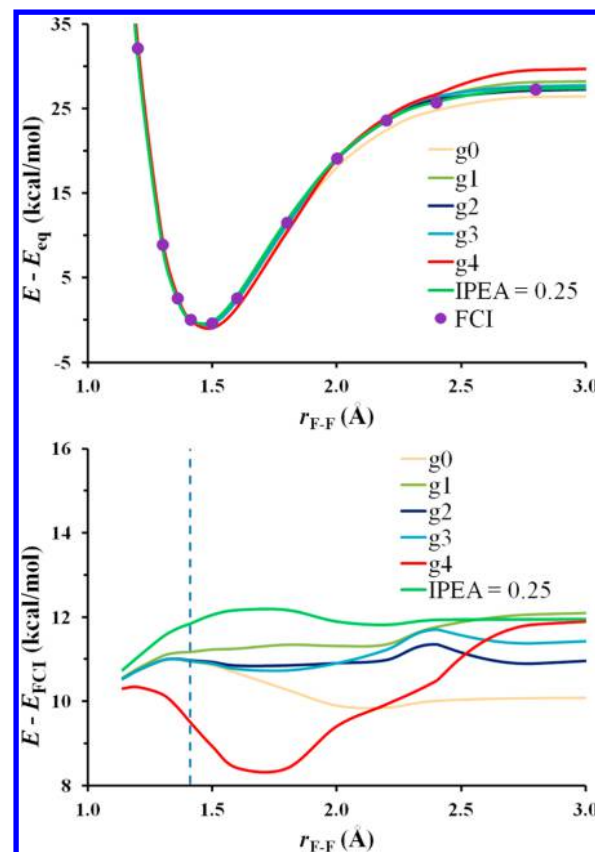


Figure 6. Dissociation curves of F_2 (top) and errors relative to FCI energies (bottom) calculated by CASPT2 with different zeroth-order of Hamiltonians (g_0 , g_1 , g_2 , g_3 , g_4) and IPEA shift = 0.25 a. u. (the vertical dash line denotes the experimental bond length).

shown in Figure 7. The RCCSD method overestimates the bond dissociation energy of H_2O_2 and CH_3CH_3 , and therefore it yields relatively too high energies at large bond distances. As for F_2 , this results from the failure of using perturbative triple excitations at large bond lengths, as may be inferred from Figure 8. The RCCSD(T) potential energy curves of H_2O_2 and CH_3CH_3 have unphysical humps, the one for H_2O_2 appearing at a relatively small bond distance of about 2.2 Å, while the RCCSD(T) potential energy curve of CH_3CH_3 is still in good agreement with RCCSDT(2) $_Q$, with discrepancies of less than 1 kcal/mol, until 3 Å. As shown in Figure 8, when the T_1 values are less than 0.02, the errors of RCCSD(T) are typically less than 1 kcal/mol. However, when T_1 values are larger than 0.02, the perturbation treatment fails and RCCSD(T) gives unphysically low energies as shown by the negative errors in Figure 8. The RCR-CCSD(T) approximation proposed by Piecuch and co-workers is able to dissociate the O–O bond in H_2O_2 and C–C bond in CH_3CH_3 correctly. But it is not as effective as RCCSD(T) to recover correlation energy near the equilibrium bond distance, as shown by the larger errors near equilibrium geometries. Moreover, the errors of RCR-CCSD(T) increase with the bond length. So, RCR-CCSD(T) tends to overestimate the relative energies at large bond lengths yielding too large dissociation energies.

Energies of selected points along the dissociation curve of H_2O_2 were calculated by RCCSDTQ. The energies calculated by RCCSDT(2) $_Q$ and RCCSDTQ agree very well, with the largest discrepancy being 0.2 kcal/mol. The RCCSDT potential energy curves also agree well with those from RCCSDT(2) $_Q$.

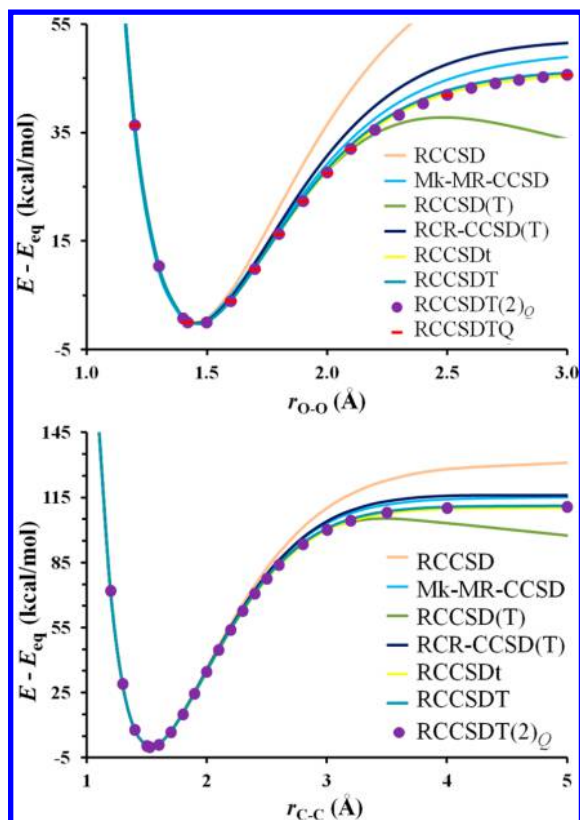


Figure 7. Dissociation curves of H_2O_2 (top) and CH_3CH_3 (bottom) calculated by various coupled-cluster methods with RHF reference wave functions (the energy of equilibrium geometries were taken as the zero-reference for each method).

with a slight overestimation of the relative energies by about 0.5 kcal/mol for H_2O_2 and 0.2 kcal/mol for CH_3CH_3 at large bond lengths. RCCSDt yields very accurate dissociation curves and has almost constant absolute errors close to 3 kcal/mol at different bond lengths for H_2O_2 and CH_3CH_3 , suggesting its applicability for diradicals.

Mk-MR-CCSD improves the performance of RCCSD for bond dissociations in H_2O_2 and CH_3CH_3 . However, as in F_2 , it tends to overestimate the relative energies at large bond lengths.

3.2.2. Potential Energy Curves of H_2O_2 and CH_3CH_3 Calculated by Coupled-Cluster Methods with UHF Reference Wave Functions. All the tested coupled-cluster methods yield monotonically increasing potential energy curves for O–O and C–C bond cleavage, as shown in Figure 9. The UCCSD method underestimates the bond dissociation energy since it picks up more correlation energy at large bond lengths than near the equilibrium bond length, which is confirmed by the smaller errors at large bond length (larger than 2.5 Å for H_2O_2 and larger than 3 Å for CH_3CH_3) than those at equilibrium bond lengths shown in Figure 10. UCCSD, UCCSD(T), and UCR-CCSD(T) all overestimate the relative energies at intermediate bond lengths. The errors of these methods relative to $\text{RCCSDT}(2)_Q$ have maxima at intermediate bond lengths, which indicates that UCCSD, UCCSD(T), and UCR-CCSD(T) are not accurate for moderately coupled biradicals; this is probably due to the spin-contaminated UHF wave functions being poor reference wave functions. Higher excitations are needed to recover correlation energies for those geometries as suggested by the large T_1 values in

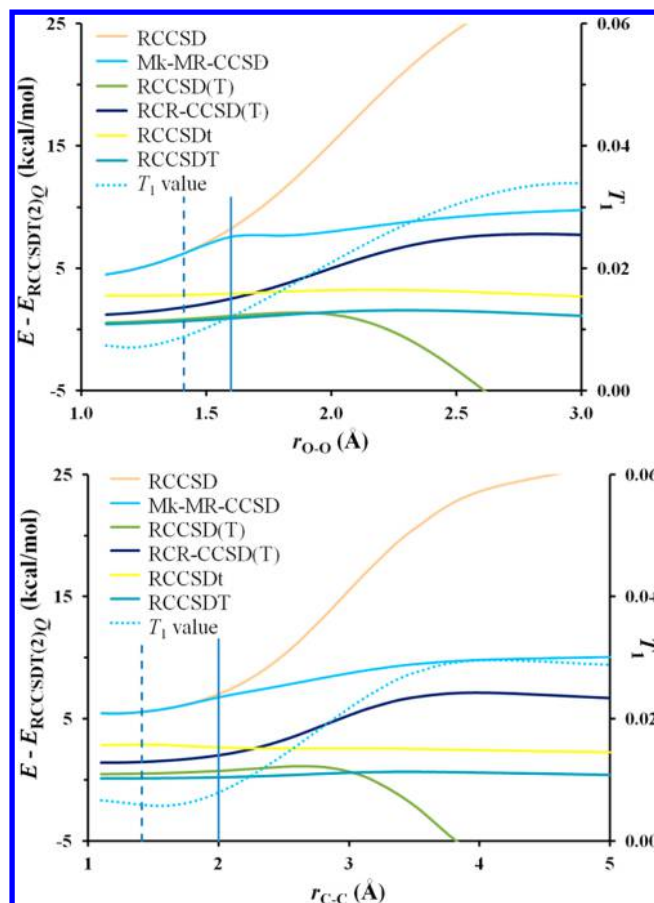


Figure 8. Errors of various coupled-cluster methods with RHF reference wave functions relative to the $\text{RCCSDT}(2)_Q$ energies of H_2O_2 (top) and CH_3CH_3 (bottom) at different bond lengths (the vertical dash line denotes the experimental bond length; the vertical solid line denotes the bond length at which the RHF-UHF instability sets in).

Figure 10. The UCCSDt method describes the O–O and C–C bond dissociations quite well; however, it underestimates the relative energies by about 0.9 kcal/mol at large bond lengths. Both UCCSDt and $\text{UCCSDT}(2)_Q$ describe the O–O dissociation very well. The difference of CCSDT energies from $\text{CCSDT}(2)_Q$ energies is typically less than 1 millihartree (0.6 kcal/mol) for both RHF and UHF reference wave functions.

3.2.3. Potential Energy Curves of H_2O_2 and CH_3CH_3 Calculated by Multireference Methods. With σ_{XX} and σ_{XX}^* ($X = \text{O}$ for H_2O_2 and C for CH_3CH_3) orbitals included in the active space, all tested multireference methods are able to describe the bond dissociation quite well. However, all the methods underestimate the bond dissociation energies as shown in Figure 11. Looking at the errors of each MR method relative to $\text{RCCSDT}(2)_Q$ in Figure 12, we can see that all tested MR methods recover more correlation energy at large bond lengths than near the equilibrium geometry. This explains why all tested multireference methods underestimate the bond dissociation energies.

Note that CASPT2 and MRCI have the largest errors relative to $\text{RCCSDT}(2)_Q$, probably since they only consider up to double excitations. However, the performance of CASPT2 for bond dissociation process is much better than that of MRCI since the errors of CASPT2 do not change much at different

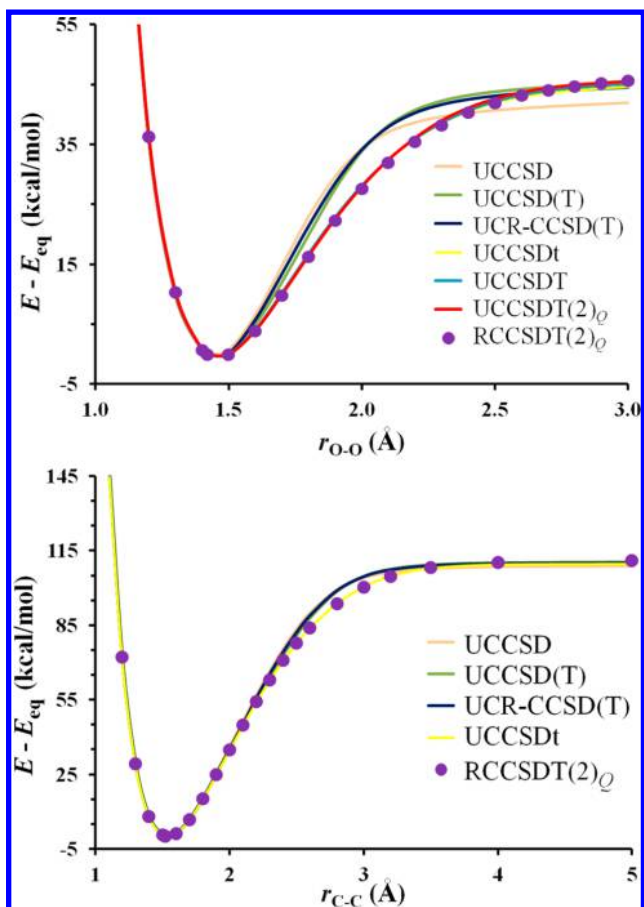


Figure 9. Dissociation curves of H_2O_2 (top) and CH_3CH_3 (bottom) calculated by various coupled-cluster methods with UHF reference wave functions (the energy of equilibrium geometries were taken as the zero-reference for each method).

bond lengths. CASPT3 recovers much more correlation energy than CASPT2, but its performance is not better than CASPT2 since its errors are more sensitive to changes in bond length, taking away the benefit arising from cancellation of errors. Again, by adding Davidson's correction for higher order excitations, MRCI+Q recovers correlation energy very effectively, with the largest discrepancy of 3 kcal/mol for CH_3CH_3 and H_2O_2 . MR-ACPF and MR-AQCC are also very good at recovering correlation energy, with the largest discrepancy of 4 and 6 kcal/mol respectively for CH_3CH_3 and H_2O_2 .

The effect of zeroth-order Hamiltonians was also considered for the bond dissociation in CH_3CH_3 and H_2O_2 . As for the F–F bond dissociation, the errors of CASPT2 with various zeroth-order Hamiltonians relative to $\text{RCCSDT}(2)_Q$ absolute energies are quite large (about 17 kcal/mol for H_2O_2 and 30 kcal/mol for CH_3CH_3), and the performance of those CASPT2 methods depends on the cancellation of errors.

3.3. Quantitative Discussion of the Accuracy and Performance of Coupled-Cluster and Multireference Methods for Bond Dissociation. We have presented the potential energy curves of F–F bond dissociation in F_2 , O–O bond dissociation in H_2O_2 , and C–C bond dissociation in CH_3CH_3 calculated by various coupled-cluster methods and multireference methods. Also, we have calculated the errors of each method relative to the most accurate results available (FCI results for F_2 and $\text{RCCSDT}(2)_Q$ results for H_2O_2 and

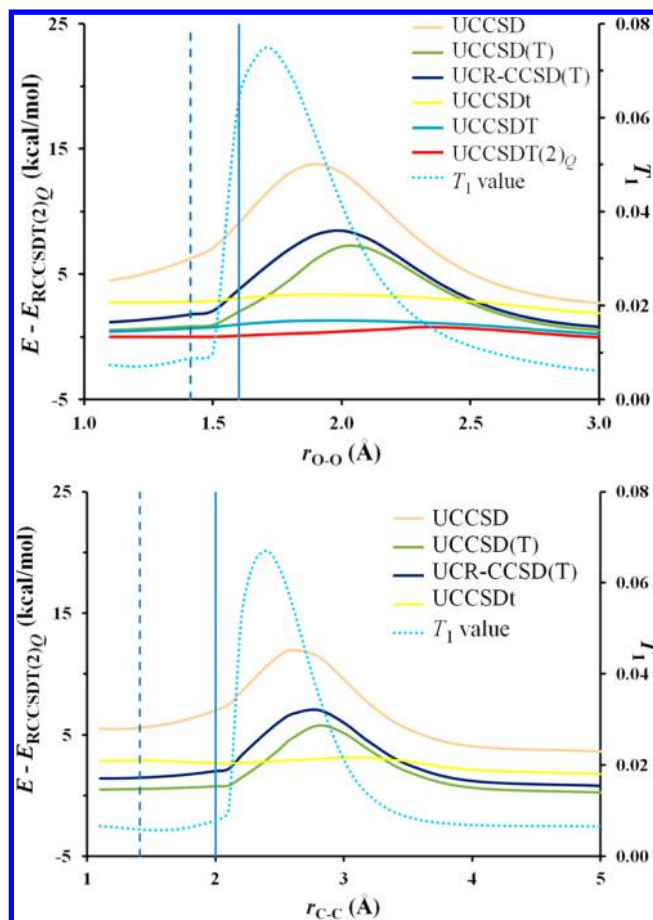


Figure 10. Errors of various coupled-cluster methods with UHF reference wave functions relative to the $\text{RCCSDT}(2)_Q$ energies of H_2O_2 (top) and CH_3CH_3 (bottom) at different bond lengths (the vertical dash lines denote the equilibrium bond lengths; the vertical solid line denotes the bond length at which the RHF–UHF instability sets in).

CH_3CH_3). However, a method with good accuracy does not necessarily have good performance for potential energy curves (that is, for the energies of biradicals relative to closed-shell covalently bonded species) and vice versa. For example, CASPT3 recovers more correlation energy and has smaller errors relative to benchmark results than CASPT2, but the performance of CASPT3 is not as good as CASPT2 and it underestimates the relative energies at large bond lengths.

To make a more comprehensive assessment of the performance of electronic structure methods for biradicals, we calculated the mean unsigned errors (MUEs) relative to best available results for points along the dissociation path. Tables 1 to 4 present the mean signed error (MSE) and the mean unsigned error (MUE) in E . Both quantities depend on the choice of bond lengths at which they are computed; and we used the following sets of distances: $R_{\text{F-F}}$: 1.14, 1.2, 1.3, 1.36, 1.41193, 1.5, 1.6, 1.8, 2, 2.2, 2.4, and 2.8 Å; $R_{\text{O-O}}$: 1.1–3.0 Å with a step size of 0.1 Å plus 1.42 Å; $R_{\text{C-C}}$: 1.1–2.6 Å with a step size of 0.1 Å, plus 1.5227, 2.8, 3.0, 3.5, 4.0, and 5.0 Å. We also tabulated the difference between the maximum and minimum signed error along the potential energy curve; this quantity is the maximum relative error and is abbreviated MaxRelE. It reflects the performance of a method for applications where we only care about relative energies.

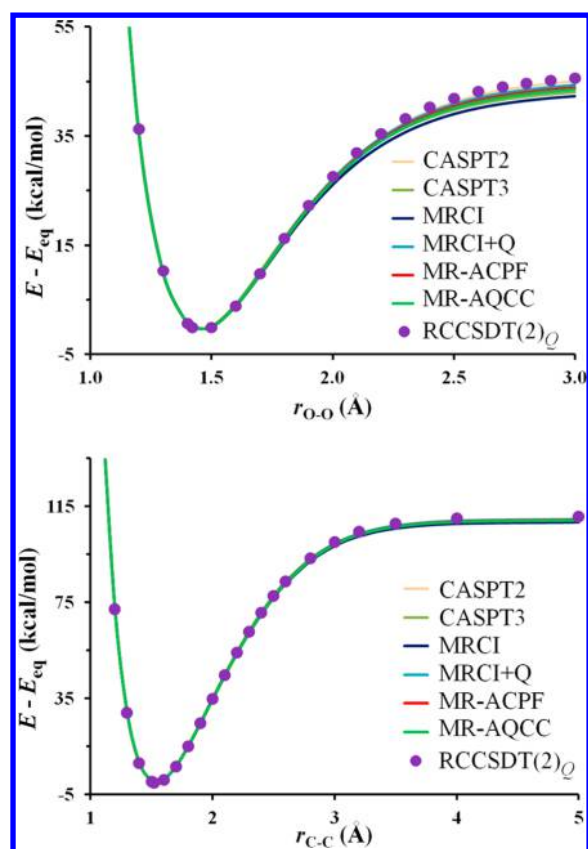


Figure 11. Dissociation curves of H_2O_2 (top) and CH_3CH_3 (bottom) calculated by various multireference methods with CASSCF(2e, 2o) reference wave functions (the energy of equilibrium geometries were taken as the zero-reference for each method).

The MSEs, MUEs, and MaxRelEs of the coupled-cluster methods with RHF reference wave functions are shown in Table 1. RCCSD has quite large MUEs (~ 10 kcal/mol), and its MaxRelEs lie in the range of 20–26 kcal/mol. The MUEs of Mk-MR-CCSD are in the range of 5–8 kcal/mol, and its MaxRelE is only ~ 5 kcal/mol. It improves over RCCSD significantly, in both the absolute and the relative sense; however, it is still not accurate enough for quantitative studies in which chemical accuracy (1 kcal/mol) is needed. The negative MSEs for RCCSD(T) are due to its unphysical behavior at large bond lengths. The errors of RCCSD(T) become quite large at large bond lengths, as shown by the large MaxRelE, which prevents the application of RCCSD(T) for bond dissociation. RCR-CCSD(T) does correct the unphysical low energies of RCCSD(T) at large bond lengths. However, as discussed in the previous sections, RCR-CCSD(T) tends to overestimate the relative energies at large bond lengths, and it suffers from a large MaxRelE (~ 6 kcal/mol). RCCSDT has lower values for both MUEs and MaxRelEs, indicating the applicability of RCCSDT for bond dissociation. By including important triple excitations, RCCSDt has relatively low MUEs (~ 3 kcal/mol) and a very small MaxRelE (less than 1 kcal/mol). The effectiveness and the efficiency of RCCSDt mean that it can be a useful alternative to RCCSDT when the biradicals are too large for RCCSDT. It is interesting to point out that RCCSDt has smaller MaxRelEs than RCCSDT, probably because of a favorable cancellation of errors. For F–F bond dissociation, RCCSDT(2)_Q and RCCSDTQ have MUEs of 0.1 kcal/mol, and MaxRelE of 0.2 and 0.3 kcal/mol,

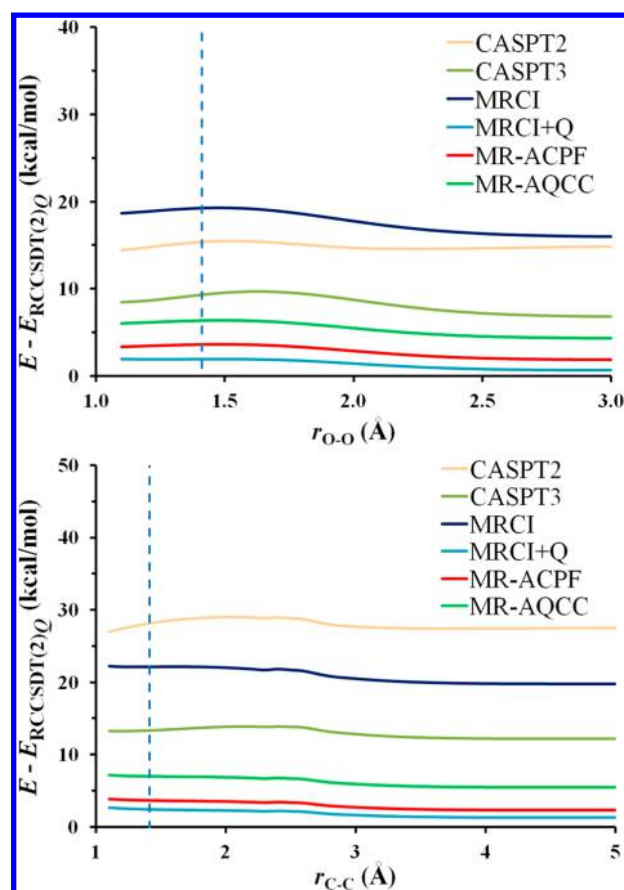


Figure 12. Errors of various multireference methods with CASSCF(2, 2) reference wave functions relative to the RCCSDT(2)_Q energies of H_2O_2 (top) and CH_3CH_3 (bottom) at different bond lengths (the vertical dash lines denote the equilibrium bond lengths).

respectively. Since CCSDT(2)_Q scales as $O(N^9)$ and CCSDTQ scales as $O(N^{10})$, and their performances are quite similar, we recommend using RCCSDT(2)_Q when highly accurate benchmark results are needed.

With UHF reference wave functions (Table 2), all tested coupled-cluster methods are able to yield qualitatively correct potential energy curves. The MUEs of UCCSD(T) and UCR-CCSD(T) are only 3 kcal/mol, as shown in Table 2. Since they have about the same cost, it is interesting to ask which of the four CCSD(T) methods in Tables 1 and 2 is the most successful. For F_2 and H_2O_2 , RCCSD(T) and UCCSD(T) have the same MUEs, and both are better than the corresponding renormalized methods; however, if one looks at MaxRelE, then RCR-CCSD(T) is the best of the four for both molecules. One draws different conclusions for CH_3CH_3 , here RCCSD(T) has the lowest MUE and UCCSD(T) is best for MaxRelE. So there is no definite winner. Furthermore, since the twelve MaxRelE values for the (T) methods in Tables 1 and 2 are all in the range 5.5–14.7 kcal/mol (i.e., all quite large), none of the (T) methods (golden or not) can be considered satisfactory for biradicals.

Including the important triple excitations leads to considerably lower MaxRelEs for UCCSDt. However, the MaxRelE of UCCSDt is larger than that for RCCSDt. The MUEs decrease when full triple excitations are included in the cluster expansion. Interestingly, UCCSDT is better than RCCSDT for both F_2 and H_2O_2 , with MUEs of only 0.8 kcal/mol and a smaller MaxRelE as well. For F_2 , including quadruples leads to

Table 1. Performance of Various Coupled-Cluster Methods with RHF Reference Orbitals for Bond Dissociations^a

	RCCSD	Mk-MR-CCSD	RCCSD(T)	RCR-CCSD(T)	RCCSDt ^b	RCCSDT	RCCSDT(2) _Q	RCCSDTQ
F_2								
MSE	13.1	5.0	−1.3	3.6	2.4	1.1	0.0	−0.1
MUE	13.1	5.0	2.6	3.6	2.4	1.1	0.1	0.1
MaxRelE	25.8	4.1	14.7	5.9	0.7	1.2	0.2	0.3
H_2O_2								
MSE	16.0	7.8	−1.6	4.8	3.0	1.1		
MUE	16.0	7.8	2.7	4.8	3.0	1.1		
MaxRelE	24.8	5.3	12.3	6.6	0.5	1.2		
CH_3CH_3								
MSE	10.3	7.2	−0.3	3.1	2.7	0.3		
MUE	10.3	7.2	1.5	3.1	2.7	0.3		
MaxRelE	20.4	4.6	13.9	5.8	0.6	0.5		

^aThe MSE is the mean signed error along the potential energy curve; the MUE is the mean unsigned error along the potential energy curve; and MaxRelE is the absolute value of the difference of the largest error and the smallest error to reflect the performance of the method for relative energies. For F_2 , errors are calculated relative to FCI energies; for H_2O_2 and CH_3CH_3 , errors are calculated relative to RCCSDT(2)_Q energies. ^bThe active space includes 5 highest occupied orbitals and 1 lowest unoccupied orbital for F_2 , 5 highest occupied orbitals and 3 lowest unoccupied orbitals for H_2O_2 , and 5 highest occupied orbitals and 7 lowest unoccupied orbitals for CH_3CH_3 ; in all cases these choices correspond to the 2p orbitals of nonhydrogenic atoms and the 1s orbital of H atoms.

Table 2. Performance of Various Coupled-Cluster Methods with UHF Reference Orbitals for Bond Dissociations^a

	UCCSD	UCCSD(T)	UCR-CCSD(T)	UCCSDt ^b	UCCSDT	UCCSDT(2) _Q
F_2						
MUE	6.7	2.6	3.4	2.3	0.8	0.2
MaxRelE	12.0	7.4	8.5	1.4	1.0	0.5
H_2O_2						
MUE	7.2	2.7	3.6	2.9	0.8	0.3
MaxRelE	11.1	6.7	7.7	1.5	1.1	0.8
CH_3CH_3						
MUE	7.3	1.7	2.9	3.0		
MaxRelE	8.4	5.5	6.2	1.3		

^aThe MSEs are the same as the MUEs for all tested methods, so they are not shown here. ^bThe active space includes 5 highest occupied orbitals and 1 lowest unoccupied orbital for F_2 , 5 highest occupied orbitals and 3 lowest unoccupied orbitals for H_2O_2 , and 5 highest occupied orbitals and 7 lowest unoccupied orbitals for CH_3CH_3 ; in all cases these choices correspond to the 2p orbitals of nonhydrogenic atoms and the 1s orbital of H atoms.

essentially converged results for RHF references, and slightly less accuracy for UHF references.

Both MUEs and MaxRelEs of all MR methods (Table 3, using the original zeroth-order Hamiltonian for CASPT2), are larger than the errors of either RCCSDT or UCCSDT with the exception of MRCI+Q for F_2 . As far as MUEs are concerned, RCCSD(T) and UCCSD(T) also compete well with MR

methods, except for MR-ACPF and MRCI+Q for F_2 and MRCI+Q for H_2O_2 . However, MR methods do much better for potential energy curves than all (T) methods, whether renormalized or not, with MaxRelE values in the range 0.8–3.3 kcal/mol in all cases and 11 out of 18 MaxRelE values below 2.0 kcal/mol.

Table 3 shows that the errors of CASPT2 actually are quite large, varying from 10 kcal/mol (F_2) to 30 kcal/mol (CH_3CH_3). However, as noted earlier, the bond-length dependence of the errors of CASPT2 is small, so CASPT2 has relatively small MaxRelEs. CASPT3, on the other hand, has MUEs about two times smaller than CASPT2; however, the bond-length dependence of the errors is much larger than for CASPT2, which leads to larger MaxRelEs.

The MUEs and MaxRelEs of CASPT2 with various zeroth-order Hamiltonians are tabulated in Table 4. The MUEs of CASPT2 are about the same for different zeroth-order Hamiltonians, about 11 kcal/mol for F_2 , 17 kcal/mol for H_2O_2 , and 30 kcal/mol for CH_3CH_3 . The MaxRelE is smallest for CASPT2[g2] for F–F dissociation in F_2 . But this is not true for O–O dissociation in H_2O_2 and C–C dissociation in CH_3CH_3 , where CASPT2[g0] is the best. CASPT2 with an IPEA shift of 0.25 hartree, although shown previously to give very good bond dissociation energies and excitation energies,⁵⁰ does not perform very well for our tested bond dissociation

Table 3. Performance of Various Multi-Reference Methods for Bond Dissociations^a

	CASPT2 ^b	MRCI	CASPT3	MR-AQCC	MR-ACPF	MRCI+Q
F_2						
MUE	9.9	11.8	5.4	3.7	2.1	0.7
MaxRelE	1.1	2.8	3.0	1.7	1.4	0.8
H_2O_2						
MUE	14.9	17.7	8.3	5.4	2.8	1.3
MaxRelE	1.0	3.3	2.9	2.0	1.7	1.2
CH_3CH_3						
MUE	28.3	21.5	13.4	6.6	3.3	2.1
MaxRelE	2.0	2.4	1.7	1.7	1.5	1.4

^aThe MSEs are the same as the MUEs for all tested methods, so they are not shown here. ^bCASPT2 denotes using of the standard Fock operator as the zeroth-order Hamiltonian without a level shift.

Table 4. Performance of CASPT2 with Various Zeroth-Order Hamiltonians and a Level Shift Value of 0.3 Hartree for Bond Dissociations^a

	g ⁰	g ¹	g ²	g ³	g ⁴	IPEA ^b
F_2						
MUE	10.5	11.3	10.9	11.0	9.8	11.7
MaxRelE	1.1	1.5	0.8	1.2	3.4	1.4
H_2O_2						
MUE	16.0	17.3	17.2	17.1	16.2	17.8
MaxRelE	1.2	3.2	3.4	3.4	4.5	2.9
CH_3CH_3						
MUE	30.0	30.6	30.5	30.5	30.1	31.0
MaxRelE	2.2	3.1	3.3	3.3	3.3	3.3

^aThe MSEs are the same as the MUEs for all tested methods, so they are not shown here. ^bAn IPEA shift value of 0.25 hartrees was used for CASPT2 calculations with the IPEA modified zeroth-order Hamiltonian.

processes. Since there are several methods named CASPT2 but with different zeroth-order Hamiltonians, and since the accuracy of CASPT2 can depend strongly (although not here) on the size and nature of the active space, we recommend benchmarking CASPT2 when applying it to new systems.

4. CONCLUSIONS

We have performed comprehensive studies of the performance of coupled-cluster and multireference methods for F–F, O–O, and C–C bond dissociation in F_2 , H_2O_2 , and CH_3CH_3 . The FCI potential energy curve of F_2 was used to verify the effectiveness of $RCCSDT(2)_Q$ and $RCCSTDQ$ in recovering electron correlation energies. The $RCCSDT(2)_Q$ method is recommended as a benchmark when highly accurate results are required. Mk-MR-CCSD improves the performance of CCSD for bond dissociation; however, it is not accurate enough for quantitative studies. The RCR-CCSD(T) corrects the unphysical hump in $RCCSD(T)$ potential energy curves; however, it overestimates the relative energies as the bond length increases, which means that it tends to overestimate the bond dissociation energies. When triple excitations are included, either limited to important triples as in CCSDt or full triples as in CCSDT, coupled-cluster methods can describe the single-bond dissociation properly even where the RHF wave function is a poor reference wave function. The effectiveness and efficiency of CCSDt should make it a preferred choice to study biradicals for many cases. With a UHF reference wave function, UCCSD, UCCSD(T), and UCR-CCSD(T) are able to give qualitatively correct potential energy curves; however, they overestimate the relative energies at intermediate bond lengths. As a result, they may overestimate barrier heights since in transition structures usually one or more bonds are stretched.

With CASSCF reference wave functions, all tested multireference methods can describe the dissociation of chemical bonds qualitatively correctly. The CASPT3 method has much smaller intrinsic errors relative to FCI or $RCCSDT(2)_Q$ than CASPT2; however, its performance for bond dissociation is not as good as CASPT2 since CASPT2 benefits from cancellation of errors. The level shift values can be used to remove intruder-state effects on the calculated energies, but this hardly affects the relative energies. Testing the performance of CASPT2 with different zeroth-order Hamiltonians shows that the good performance of different versions of CASPT2 relies on the cancellation of errors and also depends on the systems tested.

So we recommend benchmarking the performance of CASPT2 with different zeroth-order Hamiltonians when it is applied to new systems.

An analysis of the intrinsic errors and performance of all tested methods relative to FCI or $RCCSDT(2)_Q$ suggests that MR-AQCC and MR-ACPF are quite reliable for both absolute and relative energies, even though they are not as quantitatively accurate as CCSDT or the very efficient CCSDt. MRCI+Q is more quantitatively accurate than MR-AQCC and MR-ACPF, although apparently it achieves this by cancellation of errors.

■ ASSOCIATED CONTENT

Supporting Information

Relative energies calculated by various coupled-cluster methods and multireference methods of CH_3CH_3 (with (2,2) active space) and H_2O_2 and F_2 (with both (2,2) and full valence active space), calculated S^2 expectation values of UHF wave functions and T_1 values of coupled-cluster calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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