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Hybrid correlation models based on active-space partitioning: Correcting second-order Møller–Plesset perturbation theory for bond-breaking reactions

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Møller–Plesset second-order (MP2) perturbation theory breaks down at molecular geometries which are far away from equilibrium. We decompose the MP2 energy into contributions from different orbital subspaces and show that the divergent behavior of the MP2 energy comes from the excitations located within a small (or sometimes even the minimal) active space. The divergent behavior of the MP2 energy at large interfragment distances may be corrected by replacing a small number of terms by their more robust counterparts from coupled-cluster (CCSD) theory. We investigated several schemes of such a substitution, and we find that a coupling between the active-space CCSD and the remaining MP2 amplitudes is necessary to obtain the best results. This naturally leads us to an approach which has previously been examined in the context of cost-saving approximations to CCSD for equilibrium properties by Nooijen [J. Chem. Phys. **111**, 10815 (1999)]. The hybrid MP2–CCSD approach, which has the same formal scaling as conventional MP2 theory, provides potential curves with a correct shape for bond-breaking reactions of BH, CH₄, and HF. The error of the MP2–CCSD method (measured against full configuration-interaction data) is smaller than that of MP2 at all interfragment separations and is qualitatively similar to that of full CCSD. © 2005 American Institute of Physics. [DOI: 10.1063/1.1935508]

I. INTRODUCTION

It is well known that restricted Hartree–Fock (RHF) theory provides a qualitatively incorrect description of homolytic bond-breaking reactions because it fails to include the additional electron configuration(s) which become degenerate when the fragments are far apart.^{1,2} Near degeneracies of electron configurations can also complicate theoretical predictions for diradicals, first-row transition metals, and other species. Unfortunately, popular post-Hartree–Fock theories which approximately account for electron correlation via singly and doubly-substituted Slater determinants are often incapable of fully overcoming the initial deficiencies of the Hartree–Fock wave function.^{3–5} Although unrestricted Hartree–Fock (UHF) gives much more accurate energies than RHF at large interfragment separations, this comes at the price of massive spin contamination and the wave function no longer having the proper spin character. Moreover, correlated computations using unrestricted orbitals can yield less accurate energies in the intermediate bond-breaking region.^{4,6,7}

Although multireference methods are designed to handle near degeneracies among electron configurations, they can be computationally costly and difficult to use for nonexperts. Thus it is useful to assess the accuracy of single-reference methods for bond-breaking reactions and other examples of electronic degeneracies to see if some of them may be sufficiently accurate for certain applications. This can be

done^{4,6,8,9} by comparing to full configuration-interaction (full CI) results, which are numerically exact solutions to the electronic Schrödinger equation within the space spanned by the given one-particle basis set. At the same time, it is important to investigate possible improvements to single-reference methods which might make them more reliable for bond-breaking problems while retaining their simplicity and “black-box” character. Some efforts along these lines include the spin-flip approach of Krylov and co-workers^{10–13} and the completely renormalized coupled-cluster methods of Piecuch *et al.*,^{14,15} among others.^{16–20}

The simplest single-reference treatment of electron correlation is second-order Møller–Plesset (MP2) perturbation theory. For many equilibrium properties, MP2 provides very reliable predictions which are suitable for all but the most demanding applications. Moreover, MP2 is the least expensive computationally of the conventional single-reference correlated methods. It is unfortunate, then, that RHF-based MP2 fails catastrophically for bond-breaking reactions or other cases where electron configurations become nearly degenerate. MP2 potential-energy curves “turn over” at large interfragment distances, and the energy appears to diverge toward negative infinity. This behavior can be understood by examination of the spin-orbital energy equation for MP2 (assuming Hartree–Fock orbitals),

$$E^{\text{MP2}} = E^{\text{HF}} + \frac{1}{4} \sum_{ijab} \frac{|\langle ij||ab \rangle|^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}, \quad (1)$$

where E^{HF} is the Hartree–Fock reference energy, ϵ_p is the energy of orbital p , and $\langle ij||ab \rangle$ are the usual antisymme-

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trized two-electron integrals. As the bonding and antibonding orbitals of the bond being broken approach degeneracy at large interfragment separations, then at least one term in the above sum becomes an unphysically large negative number; namely, the term where i and j are the indices corresponding to the α and β spin components of the bonding orbital, and a and b are those of the two spin components of the antibonding orbital which becomes nearly degenerate with it. One might optimistically hope that MP2 could be “fixed” for bond-breaking reactions by the replacement of this one offending term. As we will see, such a simple remedy does not appear to be satisfactory. Nevertheless, a more careful examination of the failure of MP2 at large distances (analyzed via a decomposition of the energetic contributions using active-space concepts) suggests that one should replace the offending terms from MP2 with analogous terms from more robust theories; a minimal number of terms will be replaced so as to retain the fifth-order scaling of the conventional MP2 method.

One possibility is to replace the problematic MP2 terms with their counterparts from the more complete coupled-cluster theory. This is reminiscent of the strategy of using coupled-cluster theory for the more important “strong pairs” and MP2 for the less important “weak pairs” in local coupled-cluster theory.^{21–23} Although coupled-cluster theory including single and double substitutions²⁴ (CCSD, the cost of which scales as the sixth power of the system size) is not itself foolproof for bond-breaking reactions, it is at least qualitatively correct in most cases where a single bond is broken—a vast improvement over MP2. Moreover, the errors in CCSD remain modest for some simple reactions.⁴ Additionally, it seems likely that in some systems where the degeneracies are not too strong (e.g., certain transition metals), CCSD may yield reasonable results where MP2 would fail. Finally, the MP2 method can be regarded as a special case of CCSD under certain simplifying assumptions, making it theoretically appealing to consider replacing certain terms from MP2 with their CCSD counterparts. However, it is also clear that this would be one of the simplest approaches in a whole family of hybrid methods which could be made more robust via the inclusion of higher-order terms (via coupled-cluster or configuration-interaction approaches).

II. THEORY AND DISCUSSION

The CCSD energy expression, again assuming Hartree–Fock orbitals, may be written as

$$E^{\text{CCSD}} = E^{\text{HF}} + \frac{1}{4} \sum_{ijab} \langle ij || ab \rangle (t_{ij}^{ab} + 2t_i^a t_j^b). \quad (2)$$

It is clear that the MP2 energy expression can be obtained from the CCSD energy expression when single excitations are neglected and when the T_2 amplitudes are fixed at their first-order form $t_{ij}^{ab(1)} = \langle ij || ab \rangle / (\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)$. This connection between MP2 and CCSD theory will be exploited in the present work.

Although it is well appreciated that the MP2 and CCSD methods can give rather different numerical results, especially for nonequilibrium geometries, it is conceivable that

some terms constituting E^{MP2} and E^{CCSD} might be very similar. For instance, one might expect that the MP2 and CCSD theories describe the excitations from low-energy occupied to high-energy virtual orbitals equally well, whereas the excitations from highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) may be handled with a significant difference in quality. Indeed, bond dissociation is accompanied by the HOMO and LUMO energies’ gradually becoming degenerate, so that the denominator of the corresponding E^{MP2} term tends to zero, and at some point on the potential-energy surface the perturbation expansion is no longer valid. However, the analogous term of E^{CCSD} does not exhibit divergent behavior even at larger bond distances. As the number of terms in the sums (1) and (2) is on the order of $o^2 v^2$, where o is the number of doubly occupied orbitals and v is the number of virtual orbitals, it is impossible to compare the behavior of all the individual corresponding terms as a function of the bond length for a non-trivial molecule with a reasonable basis set. Instead, by using an appropriate active space, one can separate the occupied and virtual orbitals into restricted (R) and active (A) subsets, so that the correlation energy contributions to both (1) and (2) can be rewritten as

$$E_{\text{corr}}^Q = E_{AAAA}^Q + E_{AAAR}^Q + E_{AARR}^Q + E_{ARAA}^Q + E_{ARAR}^Q + E_{ARRR}^Q + E_{RRAA}^Q + E_{RRAR}^Q + E_{RRRR}^Q, \quad Q = \text{MP2, CCSD}, \quad (3)$$

so that only nine terms need to be compared. In the expression E_{WXYZ}^Q the first two lower indices (W and X) stand for the orbital subsets *from* which the electrons are excited, and the last two lower indices (Y and Z) stand for the orbital subsets *to* which the electrons are excited. At this stage, the distinction between the restricted and active orbitals is purely notational: no actual restrictions were imposed on the excitations either from or to the R orbitals.

In this initial study, we look at some simple bond-breaking reactions in BH, CH₄, and HF, where our previous full configuration-interaction benchmarking studies show that CCSD works reasonably well.⁴ For CH₄, the reaction considered is CH₄ → CH₃ + H, where we have fixed the C–H distances and HCH angles at 1.086 Å and the tetrahedral value, respectively, for convenience.⁴ In this study, we use the 6-31G* basis and correlate all electrons. For each molecule, we consider a minimal active space consisting only of the highest occupied and lowest unoccupied orbitals of the totally symmetric irreducible representation, which at large distances will correspond to the bonding and antibonding orbitals for the bond being broken. For HF and CH₄, we also consider larger active spaces, chosen somewhat arbitrarily as (6a₁2b₁2b₂) and (7a'3a'') respectively, where we give the number of active orbitals in each of the irreducible representations of the computational subgroup. All occupied orbitals except the core orbitals are made part of the active space. The results reported in this study were obtained using a simple spin-orbital coupled-cluster code which was easy to modify for our present purposes.²⁵ Transformed integrals were obtained using the PSI3 package.²⁶

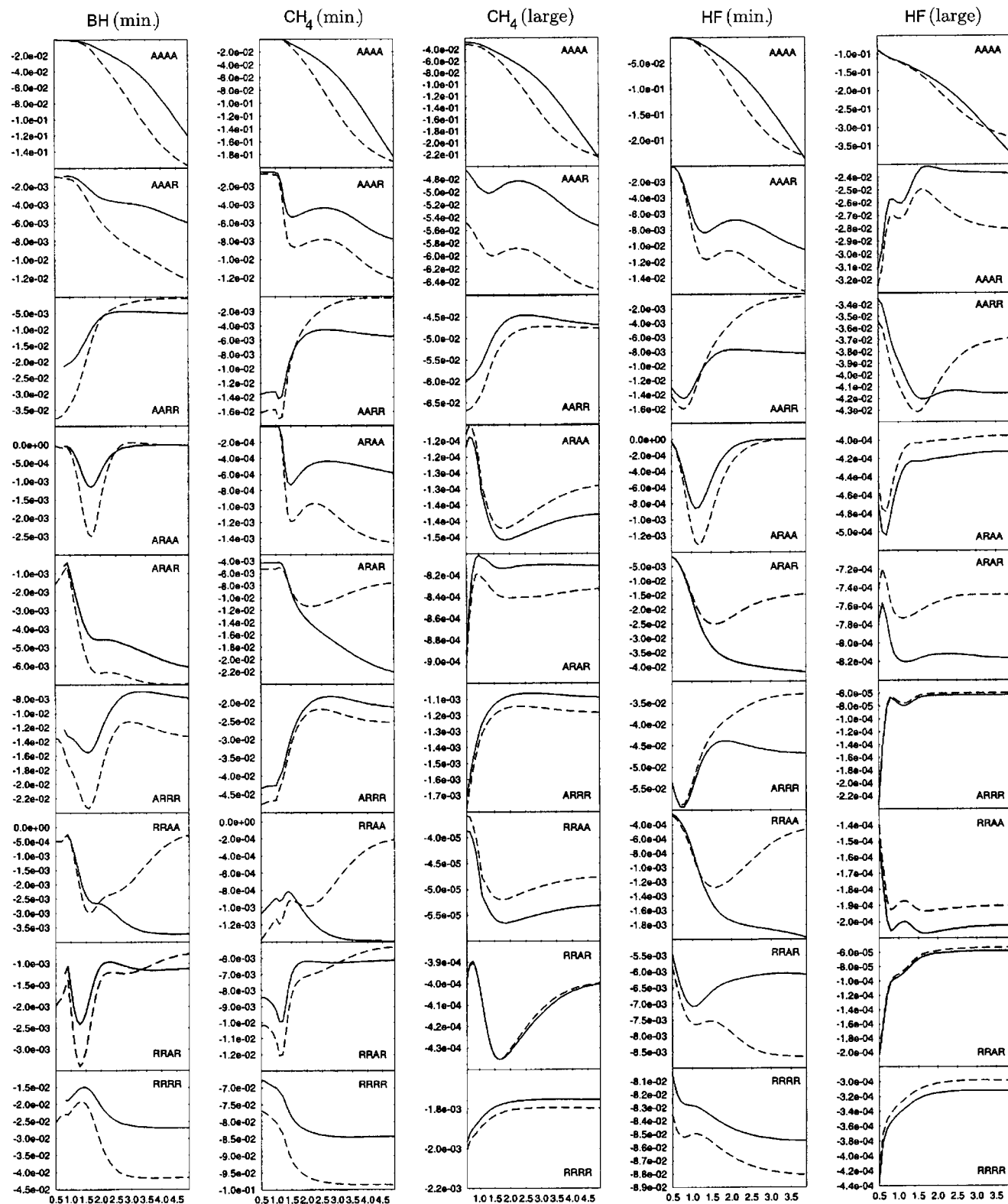


FIG. 1. The orbital excitation components of MP2 and CCSD energies. The minimal and large active spaces are described in the text. Distances (x axis) are in angstrom and energies (y axis) are in a.u.

Figure 1 compares each E_{WXYZ}^{MP2} component to the corresponding E_{WXYZ}^{CCSD} component as a function of bond lengths for each of our test cases. The minimal active-space results are of the greatest interest, since one may wonder whether only the AAAA contributions to the total energy differ markedly. If the rest of the terms are described quantitatively (or at least

qualitatively) in the same manner by both MP2 and CCSD theories, one could substitute the faulty E_{AAAA}^{MP2} term by the acceptable E_{AAAA}^{CCSD} term and in this way correct the total MP2 energy curve.

Let us discuss the minimal active-space curves first. From Fig. 1 we infer that, indeed, the greatest quantitative

difference between the E_{WXYZ}^{MP2} and E_{WXYZ}^{CCSD} contributions is in the case of the $AAAA$ term. Both E_{AAAA}^{MP2} and E_{AAAA}^{CCSD} terms decrease with bond distance, but while the CCSD term levels out, the MP2 term goes down sharply, making the total MP2 energy apparently divergent. Unfortunately, the E_{AAAA} contribution is not the only one where discrepancies are observed between the MP2 and CCSD methods. Each pair ($E_{WXYZ}^{\text{MP2}}, E_{WXYZ}^{\text{CCSD}}$) has a significant quantitative difference (although much smaller than that for the $AAAA$ term), and some pairs exhibit even qualitative differences. For example, the behavior of E_{RRAA}^{MP2} and E_{RRAA}^{CCSD} curves in the case of BH molecule is strikingly dissimilar after about 2 Å. The same observation concerns the $ARAR$ and $RRAA$ pairs of CH_4 as well as the $AARR$, $ARAR$, $ARRR$, $RRAA$, and $RRAR$ pairs of HF. It is pleasant to note though that for all the molecules studied the $RRRR$ pairs behave qualitatively in a similar way.

This analysis suggests that if we were to substitute only the E_{AAAA}^{MP2} term by the corresponding CCSD term in the MP2 energy expression,

$$E_{AAAA}^{\text{MP2}} \leftarrow E_{AAAA}^{\text{CCSD}}, \quad (4)$$

the resulting *modified* MP2 energy curve should avoid the disastrous turnover occasioned by the divergent E_{AAAA}^{MP2} term, but it might still exhibit some quantitative or even qualitative errors. This conclusion is tested in Fig. 2, which compares the total modified MP2 energy as obtained by Eq. (4) and the conventional MP2 and CCSD energies for our three test cases, BH, CH_4 , and HF. Here, the term E_{AAAA}^{CCSD} has been computed simply by a conventional CCSD computation. We will call this energy the MP2+CCSD(CCSD) energy, where “MP2+CCSD” indicates that we have simply added the E_{AAAA}^{CCSD} energy component to the complementary MP2 energy components, and “(CCSD)” denotes how the term E_{AAAA}^{CCSD} was obtained (through a conventional CCSD computation). We see that the MP2+CCSD(CCSD) potential curves are vastly improved over the MP2 curves, and the results for BH and CH_4 seem to provide an excellent match to the full CCSD results [the curves appear to be parallel, with the MP2+CCSD(CCSD) curves shifted slightly higher in energy]. A closer scrutiny of the energies reveals a very slow decrease in the MP2+CCSD(CCSD) energies at large distances, and this downward drift is much larger and clearly visible on the graph for HF. The MP2+CCSD(CCSD) scheme, then, provides a great improvement over MP2 for these cases, but it is not completely robust.

Now let us briefly discuss the results in the case of the extended active space. In the extreme case when *all* orbitals are considered active, the modified MP2 energy becomes equal to the CCSD energy. Therefore it is reasonable to suppose that the gradual increase of the active space will provide a gradual transition from the MP2 energy to the CCSD energy. It is easy to see from the large active-space curves presented in Fig. 1 that now the components E_{WXYZ}^{MP2} only slightly differ from the components E_{WXYZ}^{CCSD} for almost all the components $WXYZ$ except the $AAAA$ term. The MP2+CCSD(CCSD) potential curves calculated corresponding to large active spaces and presented in Fig. 3 also show a dramatic improvement in quality, and now they appear to be an excellent match for the CCSD curves for all three test cases.

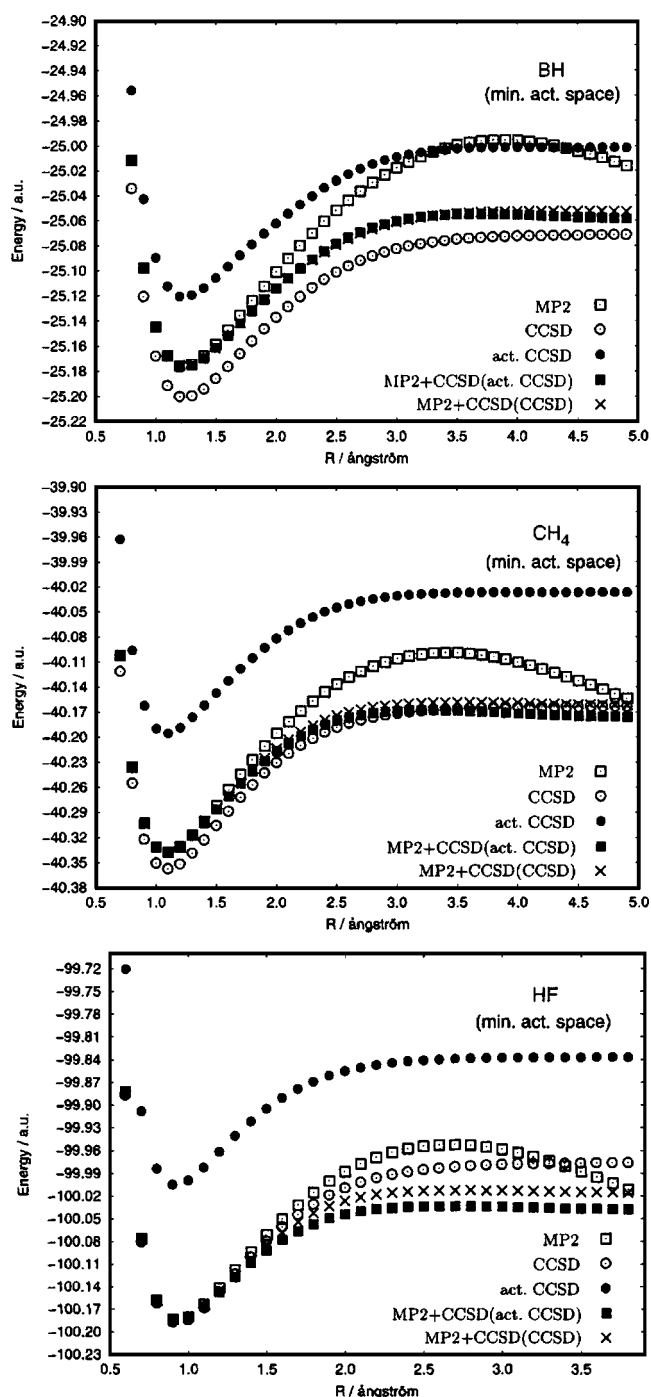


FIG. 2. The performance of different hybrid MP2+CCSD methods for minimal active spaces.

The computational scheme discussed so far, MP2+CCSD(CCSD), is no less expensive than the CCSD method itself, because for the E_{AAAA}^{CCSD} value is obtained only after the CCSD iterations have converged. Therefore, in order to make this combined scheme practical we would need to approximate the E_{AAAA}^{CCSD} value by the energy obtained from a CCSD computation of a moderate cost, for example, from a CCSD performed using active orbitals only. For a minimal active space, the cost of this CCSD computation would be negligible, and it would remain small so long as the number of active orbitals is small compared to the total number of orbitals. However, in using such an approximation

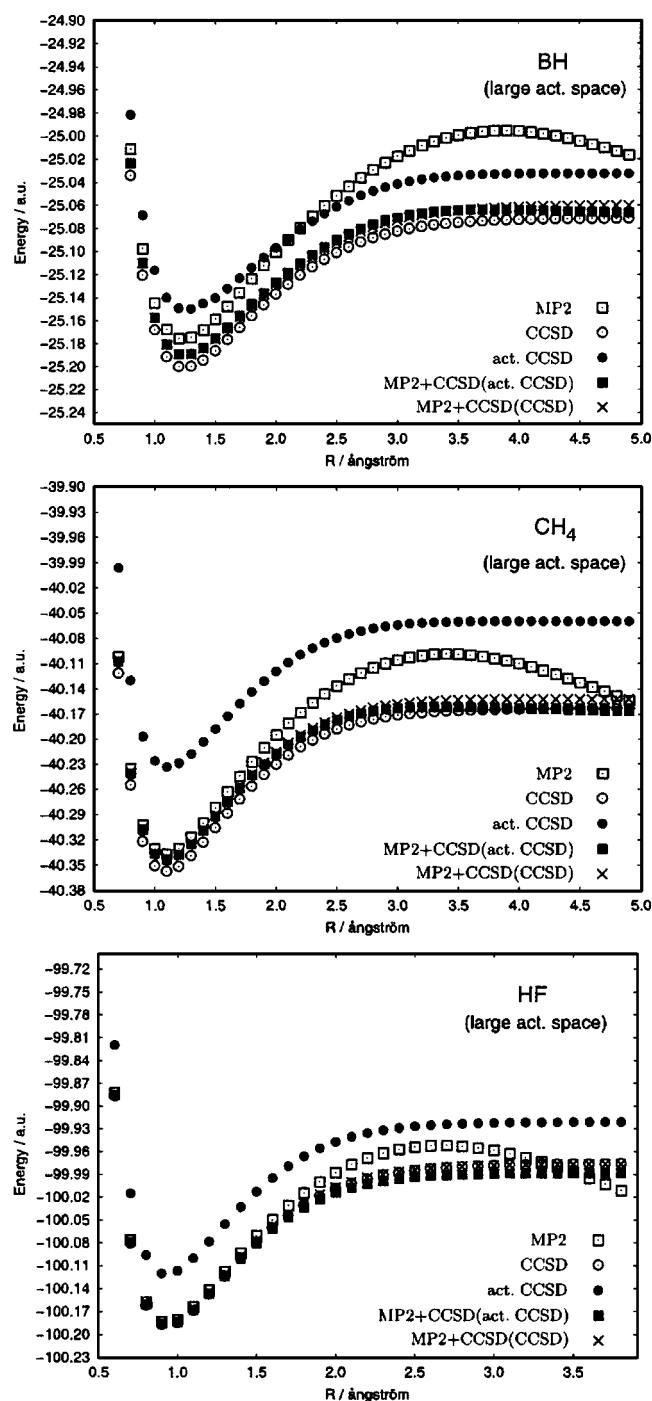


FIG. 3. The performance of different hybrid MP2+CCSD methods for large active spaces.

to the E_{AAAA}^{CCSD} term, we introduce an additional error into the MP2+CCSD energy. We will call the energy of this less expensive procedure the MP2+CCSD(active CCSD) procedure, indicating that the term E_{AAAA}^{CCSD} is obtained from an active-space CCSD computation. Figures 2 and 3 demonstrate that this approximation to E_{AAAA}^{CCSD} makes the MP2+CCSD(active CCSD) potential curve significantly worse than the MP2+CCSD(CCSD) curve. Of course, the larger the active space the smaller the error of the E_{AAAA}^{CCSD} approximation, but the computational cost of making this approximation becomes larger. An additional problem is that

the scheme ceases to be a black-box method if active spaces other than the minimal active space are used.

The results for MP2+CCSD(active CCSD) indicate that one cannot safely neglect the coupling between the active-only electron configurations and the other configurations. At the same time, however, to obtain a practical advantage over conventional CCSD, the computation of the full CCSD wave function to obtain E_{AAAA}^{CCSD} must be avoided. How can these two requirements be satisfied? The most obvious solution is to solve for the coupled-cluster amplitudes giving rise to E_{AAAA}^{CCSD} in the presence of the other amplitudes fixed in their MP2 form. Indeed, one might hope that the explicit coupling of the coupled-cluster amplitudes to the MP2 amplitudes might improve results over the MP2+CCSD(CCSD) approach discussed above. We will denote this new alternative as MP2–CCSD, where the dash will indicate a coupling between the methods rather than a simple addition of terms obtained from separate computations. This form of hybrid MP2 and CCSD was previously investigated by Nooijen²⁷ in a different context; namely, as a promising way to reduce the cost of CCSD for computations of equilibrium properties and excited-state energies. The general idea of reducing costs by restricting higher-order correlation terms to have at least a certain number of indices corresponding to active orbitals has ample precedent in coupled-cluster and configuration-interaction methods (see, for example, Refs. 17 and 28–34).

It is easy to implement the coupled, hybrid MP2–CCSD approach. CCSD programs generally use the MP2 amplitudes as an initial guess in the iterative solution of the cluster amplitudes, and the MP2 energy is obtained in the first iteration of a CCSD procedure.³⁵ To implement the hybrid MP2–CCSD approach, one needs only to fix all amplitudes in their initial MP2 form except for those “internal” amplitudes t_{ij}^{ab} and t_i^a , all of whose indices belong to the active-space orbitals. The final, converged energy may be written as

$$E_{\text{corr}}^{\text{MP2-CCSD}} = E_{AAAA}^{\text{MP2-CCSD}} + E_{AAAR}^{\text{MP2}} + E_{AARR}^{\text{MP2}} + E_{ARAA}^{\text{MP2}} + E_{ARAR}^{\text{MP2}} + E_{ARRR}^{\text{MP2}} + E_{RRAA}^{\text{MP2}} + E_{RRAR}^{\text{MP2}} + E_{RRRR}^{\text{MP2}}, \quad (5)$$

where

$$E_{AAAA}^{\text{MP2-CCSD}} = \frac{1}{4} \sum_{ijab}^{\text{act}} \langle ij || ab \rangle (t_{ij}^{ab} + 2t_i^a t_j^b), \quad (6)$$

assuming Hartree–Fock orbitals. The summation in the formula for $E_{AAAA}^{\text{MP2-CCSD}}$ is restricted to the active orbital space.

Figure 4 shows the performance of MP2–CCSD for various molecules and different active spaces. We may observe that even in the case of the minimal active spaces, the total energies derived from $E_{AAAA}^{\text{MP2-CCSD}}$ are qualitatively correct for every test case; in contrast with some of the MP2+CCSD approaches discussed above, the tendency of the potential curves to bend downward at large distances has been eliminated by the coupling of the coupled-cluster amplitudes to the MP2 amplitudes. At bond lengths close to equilibrium, the MP2–CCSD curves follow the MP2 curves very closely, but at larger separations, when the MP2 energies start to behave incorrectly, the MP2–CCSD curves remain almost

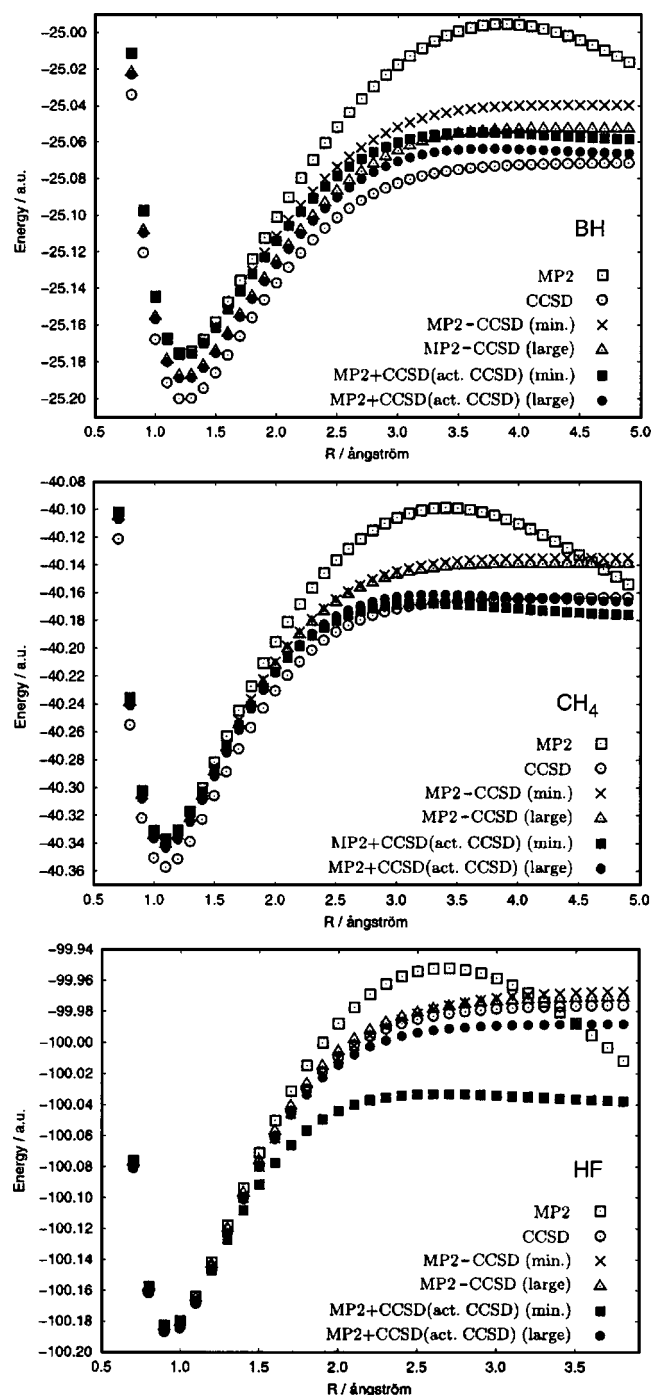


FIG. 4. The performance of the coupled, hybrid MP2-CCSD method.

parallel to the CCSD total-energy curves and at small and intermediate distances fall between the MP2 and CCSD curves. Increasing the size of the active space improves the picture even further.

It is easy to estimate the cost of such a coupled, hybrid method. In the notation of Stanton *et al.*,³⁶ the most time-consuming step of the CCSD procedure is the evaluation of the $\mathcal{W}_{abef} \rightarrow \Delta t_{ij}^{ab}$ contribution, which includes the four-virtual $\langle ab || ef \rangle$ components. This step normally scales as o^2v^4 , where o and v are the number of occupied and virtual orbitals, respectively. In the MP2-CCSD approach, the cost reduces to $v^2O^2V^2$, where O and V represent the number of

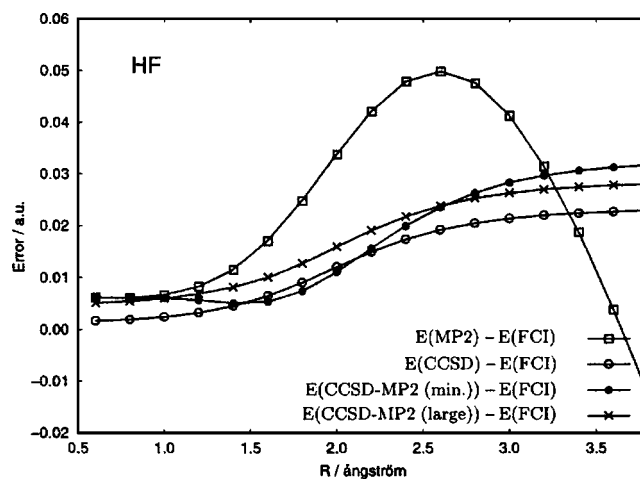


FIG. 5. Errors for the coupled, hybrid MP2-CCSD method and for conventional MP2 and CCSD compared to full configuration interaction for the HF molecule.

active occupied and active virtual orbitals, respectively. In the minimal active spaces considered here, $O=V=1$, and typically O and V will be of order 1. The cost of forming the \mathcal{W}_{mbej} intermediate is reduced from o^3v^3 to o^2v^2OV , and the cost of forming the \mathcal{W}_{mnij} intermediate is reduced from o^4v^2 to $o^2v^2O^2$. For a minimal active space, then, the computational scaling is no worse than that of MP2 theory, and for larger active spaces, the cost is still considerably less than that of conventional CCSD.

In order to investigate the errors of these hybrid methods more carefully, we present errors versus full CI energies for the HF molecule in Fig. 5.³⁷ The full CI results may be considered numerically exact solutions of the electronic Schrödinger equation within the given basis set. One wishes for flat error curves, which indicate that an approximation is yielding a potential curve parallel to the full CI curve (a mere shift in the potential, giving a constant error across the surface, is of no chemical significance). The figure reveals that the MP2-CCSD error curve tracks that of CCSD extremely well when the large active space is used. For the minimal active space, the MP2-CCSD error curve follows the general shape of the CCSD error curve at short and long distances, but the errors happen to dip slightly below the CCSD errors at intermediate distances. Both the small and large active-space MP2-CCSD error curves are tremendously improved over those of conventional MP2.

III. CONCLUSIONS

We have analyzed the failure of RHF-based MP2 for bond-breaking reactions in terms of energetic contributions from different orbital subspaces. The one double excitation from the sigma bonding orbital of the bond being broken to its antibonding counterpart accounts for the majority of the error in MP2 at large interfragment separations due to the energy denominator becoming nearly zero. Using more robust methods such as coupled-cluster theory to replace this one term vastly improves results, but there remains a slight, unphysical drift downward in the energy at large separations

due to some other energy components involving the active orbitals. This residual problematic behavior can be eliminated by coupling the solution of the active-space coupled-cluster problem to the MP2 amplitudes for the remaining excitations. This results in a method with a computational cost similar to that of MP2 (for minimal active spaces) but which behaves qualitatively correctly for reactions in which a single bond breaks, the error being roughly comparable to that observed for the much more complete CCSD method. Results of CCSD quality can be systematically approached using larger active spaces for the CCSD part of the CCSD–MP2 hybrid wave function.

Many other approaches to bond-breaking reactions and near degeneracies of electron configurations begin with a robust active-space computation [e.g., complete-active-space self-consistent-field (CASSCF)] and then proceed to add a description of electron correlation involving nonactive (restricted) orbitals. Here, we have followed something of a reversed procedure, fixing the description of electron correlation involving restricted orbitals at the MP2 level and then proceeding to solve for a more robust description of the active space. It is perhaps surprising that this approach works as well as it does for the cases considered. It is encouraging that the all-restricted (*RRRR*) energy component appears to be estimated well by MP2 even in the presence of nearly degenerate electron configurations, but we did notice some differences between MP2 and CCSD for some of the other components which we nevertheless fixed in their MP2 form. The coupling of the active-space coupled-cluster amplitudes to the fixed MP2 amplitudes allows them to respond in such a way as to produce qualitatively correct potentials.

The current results suggest that even in the presence of nearly degenerate electron configurations, MP2 theory may remain useful for estimating correlation coefficients except for those in which all indices correspond to active orbitals. In future work, we will investigate this possibility more fully by examining additional bond-breaking situations. Clearly, MP2–CCSD will not work for breaking double or triple bonds, because CCSD itself fails in these situations. However, one can easily imagine more sophisticated approaches which build upon the ones investigated here.

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