J. Phys. Chem. A **2007,** *111,* 11189−11197

Reduced Multireference Coupled-Cluster Method: Barrier Heights for Heavy Atom Transfer, Nucleophilic Substitution, Association, and Unimolecular Reactions[†]

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Received: November 30, 2006; In Final Form: February 6, 2007

The recently developed reduced multireference coupled-cluster method with singles and doubles (RMR CCSD) that is perturbatively corrected for triples [RMR CCSD(T)] is employed to compute the forward and reverse barrier heights for 19 non-hydrogen-transfer reactions. The method represents an extension of the conventional single-reference (SR) CCSD(T) method to multireference situations. The results are compared with a benchmark database, which is essentially based on the SR CCSD(T) results. With the exception of seven cases, the RMR CCSD(T) results are almost identical with those based on SR CCSD(T), implying the abatement of MR effects at the SD(T) level relative to the SD level. Using the differences between the RMR CCSD(T) and CCSD(T) barrier heights as a measure of MR effects, modified values for barrier heights of studied reactions are given.

I. Introduction

In order to compute accurate barrier heights (BHs) for chemical reactions, one has to employ high level correlated methods, as well as large enough, suitably extended basis sets. There are, essentially, three types of ab initio methods that can reliably account for many-electron correlation effects, namely the configuration interaction (CI), many-body perturbation theory (MBPT), and coupled cluster (CC) methods. Although even the fourth order perturbation theory (MP4) cannot guarantee the results of a chemical accuracy (of 1 kcal/mol) for BHs, the large-scale multireference (MR) CI methods are capable of yielding very accurate results. The drawback of the latter methods is, however, their high cost. Moreover, since these methods rely on the linear Ansatz for the wave function, they cannot effectively describe dynamic correlations, unless they employ a very large number of references. This is the main reason why the CC methods[1−4] that are based on the exponential Ansatz for the wave function, which enables an efficient account of the dynamic correlation, are often employed for this purpose (for recent reviews, see refs 5−13, and see also refs 14 and 15 for a historical perspective). In particular, the standard single reference (SR) CCSD(T) method[16] provides a reasonable compromise between the accuracy and the cost and is easy to employ thanks to its SR nature and black-box character. These are the main reasons why CCSD(T) is very often used in actual applications. Of course, higher-level CC methods, such as the CCSDT, CCSDTQ, and similar higher-order approaches (CC with singles, doubles, triples, quadruples, etc.), yield more accurate results than does CCSD(T), but in view of their higher scaling with the number of orbitals, they soon become computationally too demanding, both in terms of the CPU and storage requirements.

Besides the just mentioned standard ab initio approaches, it is the density functional theory (DFT) that in many instances, particularly when dealing with the ground state geometry or energy properties, has become a very popular computational tool. It is characterized by a much lower-order scaling with the orbital number than are the standard ab initio methods, implying an attractive cost-to-performance ratio, and thus enables the handling of much larger molecular systems than do the high-level correlated methods. However, the favorite semiempirical hybrid DFT methods that are calibrated with the help of thermochemical data, such as the B3LYP version,[17,18] are generally not sufficiently accurate and reliable for the determination of the BHs. In order to develop a semiempirical DFT approach that is suitable for the computation of BHs, a different parametrization would be required. However, since the experimental BHs are not readily available, being inaccessible to a direct measurement, it is difficult to find such a suitable parametrization, not to mention the uncertainties in the experimentally determined BHs that are extracted from indirect experimental data. Thus, to obtain a reliable estimate of BHs, one generally relies on high-level ab initio methods that are capable of achieving the chemical accuracy, such as the CCSD(T) method. The results generated in this way are in turn employed as a benchmark for the assessment of the performance of various DFT approaches[19] or as a basis for the parametrization of semiemperical DFTs.

Although, generally, the CCSD(T) method works reasonably well even for systems with moderately stretched chemical bonds, such as encountered in transition complexes, it is well-known that its performance deteriorates with the increasing quasidegeneracy and utterly fails when generating full potential energy surfaces (PESs) or curves (PECs) once the dissociation limit, involving the breaking of true chemical bonds, is approached or, in fact, whenever the system acquires an open-shell or biradicaloid character. It is thus desirable to develop a MR version of CCSD(T) that would be applicable even in quasidegenerate situations, which in a moderate form could be encountered in some transition-state complexes. It would be, of course, highly desirable that such a method be characterized

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10.1021/jp068226x CCC: $37.00

by the same, or nearly the same, scaling with the orbital number as is CCSD(T) and thus require a similar computational effort.

Another important factor when considering MR approaches is the size of the required reference space. When we strive for the chemical accuracy, the MR CISD or similar methods are known to require a relatively large reference space, mainly due to the CI's inability to adequately describe dynamic correlation effects, which are much more efficiently handled by the CC approaches [primarily via the T_2^2 term at the CCSD level and via the (T) correction at the CCSD(T) level]. A search for methods that perform well with small reference spaces is very important, and MR CCSD(T), in particular the so-called reduced MR (RMR) CCSD(T), represents a viable option (see below). At a qualitative level, a small reference space is also implied by chemical intuition. As an example, let us mention the $^1A_1$ states of ozone, CH_2, and BN, in which case two references are essential even for a qualitative description and represent a straightforward choice for RMR CCSD(T). However, when such a two-reference space (or, in general, other minimal reference space) does not suffice, then there is no simple way how to choose additional references. In general, MR formalism assumes that certain subsets of higher excitations are of primary importance compared with the rest of the configuration state functions (CSFs). However, if for a chosen set of orbitals all higher excitations are more or less equally important then, at least theoretically, a MR approach will not lead to a faster convergence toward the full CI (FCI) result than does the corresponding SR approach.

The desirability of methods that employ small reference spaces has also been discussed in some detail by Szalay.[20] For this purpose, he considered various versions of CEPA-type (coupled electron pair approximation) approaches in their MR version. The most promissing among these ad hoc approximations turned out to be the ACPF (approximate coupled pair functional) method,[21] which assumes a zero interaction between electron pairs, and a more realistic AQCC (averaged quadratic CC) approximation.[20,22,23]

Let us also briefly comment on the so-called T_1 diagnostics, proposed by Lee and Taylor,[24] that has been employed to discern the MR character. The usefulness of this diagnostics has been questioned by several researchers (see, e.g., ref 8), since the magnitude of T_1 is very much dependent on the orbital choice. Indeed, for Brueckner orbitals, $T_1 = 0$, yet this does not eliminate an eventual MR character. In fact, the latter often arises due to double excitations. In the RMR approach, we essentially adopt what can be referred to as a "large amplitude indicator": We simply identify large (e.g., >0.1) amplitudes and choose the corresponding excited configurations as additional references. The absence of such large amplitudes implies the adequacy of the SR approach.

At the SR level, the main shortcommings of the CCSD(T) approach, namely its failure when dissociating true chemical bonds, can also be largely overcome by the so-called completely renormalized (CR) and renormalized (R) CCSD(T) methods.[25−28] Although these methods slightly underperform SR CCSD(T) in the region of equilibrium geometries and suffer slightly from the lack of size-extensivity, this is not the case for the most recently designed CR−CC(2,3) method,[28−31] which seems to provide an excellent approximation in the entire range of geometries. However, without accounting for connected quadruples, these methods will not fully account for MR effects, as illustrated by a comparison of their performance with that of the RMR-type approaches for several demanding systems.[32] Clearly, a similar comparison for the BHs, including the AQCC approach, would be desirable.

We have recently developed two MR CCSD(T)-type approaches. The first one is a general-model-space (GMS) state-universal (SU) CCSD(T) method.[33,34] This method represents a version of the standard complete-model-space (CMS) SU CC theory[35] that employs, in principle, an incomplete model space spanned by an arbitrary set of references. Although the GMS SU CCSD method,[33] and its (T)-corrected variant,[34] are generally applicable, they are probably best suited for states in which several configurations play an equally important role, such as spin multiplets, requiring a multideterminantal CSF for their proper description.

The second type of MR states is those that are governed by a single leading configuration, so that other CSFs are of a secondary importance. For such states, it is easier to employ SR or state-specific (SS) MR approaches. For this purpose, we have recently developed the RMR CCSD(T) method,[36] which performs as well as CCSD(T) does in nondegenerate situations, and can also be relied upon in the presence of quasidegeneracy. This approach simply adds perturbative triple corrections to the RMR CCSD energies.[37] We recall that the RMR CCSD method represents an externally corrected (ec) variant[38] of the standard SR CCSD method, in which the most important triples and quadruples are accounted for by relying on a modest size MR CISD wave function. By taking care of the remaining triples via the standard perturbative (T)-type corrections, we arrive at the RMR CCSD(T) method.

The RMR CCSD approach, as well as its (T)-corrected version, represents a method that strives to benefit from the complementarity of CC and CI approaches in their ability to handle, respectively, the dynamic and nondynamic correlation effects. Thus, although the higher-than-pair cluster components are of a secondary importance in the case of a nondegenerate reference, and may thus be safely handled perturbatively, this is not the case when quasidegeneracy sets in and these cluster components gain on importance. The RMR approaches then rely on MR CISD wave function to provide information concerning the most important three- and four-body cluster amplitudes, while retaining a proper exponential Ansatz for the wave operator, guaranteeing size-extensivity. We should also mention at this opportunity that the just-mentioned reciprocity of CI and CC approaches has also been exploited in reverse direction when designing more realistic a posteriori Davidson-type corrections[39−43] and, similarly, in a priori-type corrections that are based on ad hoc linear-CC functionals mentioned above, namely in the MR-ACPF and MR-AQCC methods. The latter method has also been extended to handle the excited states.[44,45]

In this paper, we examine the performance of the RMR CCSD(T) method in computations of the BHs for 19 reactions, some involving a heavy atom transfer and others being nucleophilic substitution, unimolecular, and association reactions. This has been made possible thanks to recently developed benchmark databases for these reactions by Truhlar and coworkers.[46] The present study thus serves two purposes: First, it assesses the performance of the RMR CCSD(T) method in the computations of reaction BHs, and second, it points to a possible improvement of the currently best estimate of these BHs, that is essentially based on SR CCSD(T), by comparing the differences between the CCSD(T) and RMR CCSD(T) estimates, since the latter method also accounts for a quasidegeneracy, if present, as well as for the most important connected quadruples. We thus first recall the essential features of the RMR

CCSD and RMR CCSD(T) methods and, subsequently, present the results and their discussion for the 19 reactions just mentioned.

II. Method

In the CCSD(T) method,[16] the CCSD energy is corrected for the effect of connected triples by relying on a SR perturbation theory (PT) or MBPT. This is the reason why CCSD(T) fails, or even completely breaks down, in degenerate or quasidegenerate situations (such as the bond breaking, biradical systems, etc.), since singles and doubles (SDs) from other degenerate configurations become as important as SDs from the leading Hartree−Fock configuration and cannot be reliably accounted for via a SR PT, requiring a proper, preferably a MR, treatment. Moreover, in MR situations, some quadruply or higher-excited connected clusters can play a non-negligible role; yet, these clusters are missing in CCSD(T).

The RMR CCSD(T) method[36] alleviates the above-mentioned shortcomings of CCSD(T), while retaining the same computational scaling. It differs from CCSD(T) in two important aspects: First, the problematic triples that cannot be properly handled perturbatively are treated in a different way, namely via the externally corrected (ec) CCSD,[38] specifically via RMR CCSD.[37] Second, RMR CCSD(T) also accounts for the most important quadruply and even higher-excited connected cluster amplitudes.

In the RMR CCSD(T) method, perturbative (T)-type corrections for connected triples are employed only for the less important, or secondary triples (the set of which we designate by $\mathscr{M}_3^{\mathrm{s}}$), whose amplitudes are sufficiently small to be treated via SR PT, whereas the more important, or primary, triples (designated by $\mathscr{M}_3^{\mathrm{p}}$) are accounted for through the external corrections to CCSD, i.e., via the RMR CCSD method. The dividing line between the primary and the secondary triples is determined by the strength of the interaction with the zero-order wave function. In the case of a strong interaction, we can even employ a truncated version of RMR CCSD(T),[32] which is computationally less demanding than the standard, non-truncated version.

Thus, when a single Hartree−Fock determinant provides a good zero-order approximation, all triples may be considered to be of the secondary kind. In such a case RMR CCSD(T) reduces to the standard CCSD(T). A more general situation arises when the Hartree−Fock configuration $|\Phi_0\rangle$ is nearly degenerate with configurations $|\Phi_1\rangle, |\Phi_2\rangle, ..., |\Phi_{M-1}\rangle$. We then consider an M-dimensional reference space P that is spanned by these quasidegenerate configurations $|\Phi_i\rangle$, $i = 0, 1, 2, ..., (M - 1)$, and assume that it provides an adequate zero-order description for the lowest state of a given symmetry species we are interested in. All singly and doubly excited configurations with respect to those in P span the first-order interacting space Q. The triples and quadruples (relative to $|\Phi_0\rangle$) from $P \oplus Q$ are then regarded as the primary ones, and those in the orthogonal complement of $P \oplus Q$ in the entire N-electron space (as defined by the ab initio model employed) are classified as the secondary ones.

The approximate values of the primary triple and quadruple cluster amplitudes are obtained by the cluster analysis of the corresponding MR CISD wave function,[47] which in turn is obtained by diagonalizing the Hamiltonian in the $P \oplus Q$ space: The MR CISD wave function can be easily cast into the intermediately normalized form relative to the Hartree−Fock reference $|\Phi_0\rangle$ and then cluster analyzed in a standard way. The resulting three- and four-body cluster amplitudes $t_3^{(0)}$ and $t_4^{(0)}$ represent only a small subset of all triples and quadruples, respectively, and define the approximate $T_3^{(0)}$ and $T_4^{(0)}$ cluster operators.

Thus, an appropriate cluster Ansatz for the RMR CCSD wave operator W, $|\Psi\rangle = W|\Phi_0\rangle$, takes the form

$$W = \exp(T_1 + T_2 + T_3^{(0)} + T_4^{(0)} + ...) \tag{1}$$

where $T_3^{(0)}$ and $T_4^{(0)}$ designate the above-described approximate fixed three- and four-body cluster operators extracted from MR CISD wave function. These $T_3^{(0)}$ and $T_4^{(0)}$ cluster operators are then used to evaluate the relevant three- and four-body terms in singles and doubles ecCCSD equations[38]

$$\langle\Phi_i^{(1)}|\bar{H} + [H, T_3^{(0)}]|\Phi_0\rangle = 0 \tag{2}$$

$$\langle\Phi_i^{(2)}|\bar{H} + [H, T_3^{(0)} + T_4^{(0)}] + [[H, T_1], T_3^{(0)}]|\Phi_0\rangle = 0 \tag{3}$$

defining the RMR CCSD method. Here, $\bar{H}$ designates the $(e^{T_1+T_2})$-similarity-transformed Hamiltonian

$$\bar{H} = e^{-T_1-T_2} H_N e^{T_1+T_2} \tag{4}$$

and $|\Phi_i^{(k)}\rangle$ represents the ith (k)-times excited configuration relative to $|\Phi_0\rangle$. Note that no higher than quadruply excited clusters appear in ecCCSD eqs 2 and 3, and should such cluster contribute in any significant manner, they will be taken care of via the $T_3^{(0)}$ and $T_4^{(0)}$ clusters (assuming, of course, they are present in the MR CISD wave function employed). Once the ecCCSD or RMR CCSD t_1 and t_2 amplitudes have been obtained by solving eqs 2 and 3, the correlation energy is given by the standard CC energy expression

$$E_{\mathrm{RMR-CCSD}} = \left\langle \Phi_0 \middle| H\left(T_1 + T_2 + \frac{1}{2}T_1^{\,2}\right) \middle| \Phi_0 \right\rangle \tag{5}$$

This energy accounts for the MR effects and yields a superior result to the standard CCSD method.

We use the superscript (0) to emphasizes an approximate nature of the three- and four-body clusters resulting from the cluster analysis of the MR CISD wave function. These $T_3^{(0)}$ and $T_4^{(0)}$ cluster operators entering the above ecCCSD equations thus represent fixed, a priori known quantities, so that the correcting $T_3^{(0)}$ and $T_4^{(0)}$ dependent terms are evaluated only once (for a noniterative handling of the $[[H, T_1], T_3^{(0)}]$ term, see refs 37, 38, 48, and 49). Clearly, by setting the three- and four-body cluster operators to zero, $T_3^{(0)} = T_4^{(0)} = 0$, the above ecCCSD equations become the standard CCSD equations. On the other hand, by employing the exact three- and four-body cluster amplitudes (as given, e.g., by the cluster analysis of the FCI wave function), i.e., by setting $T_3^{(0)} = T_3^{(\mathrm{exact})}$ and $T_4^{(0)} = T_4^{(\mathrm{exact})}$, respectively, the ecCCSD eqs 2 and 3 will recover the exact FCI energy. Since the wave operator W, eq 1, has the exponential form, the method remains size-extensive, as are its two limiting cases just mentioned. Nonetheless, we should emphasize here that the size-extensivity per se is of a limited use when the basic assumption of the SR CCSD approach, namely the nondegeneracy of the reference $|\Phi_0\rangle$, is violated (see, e.g., the CCSD PEC for N_2, Figure 1, ref 50). Clearly, in the dissociation limit, the size-consistency will play a much more important role and can be largely accounted for via the essential three- and four-body clusters. For a genuine MR-type method to be size-consistent at any order requires the zero-order (i.e., the reference space) to be size-consistent as well. In other words,

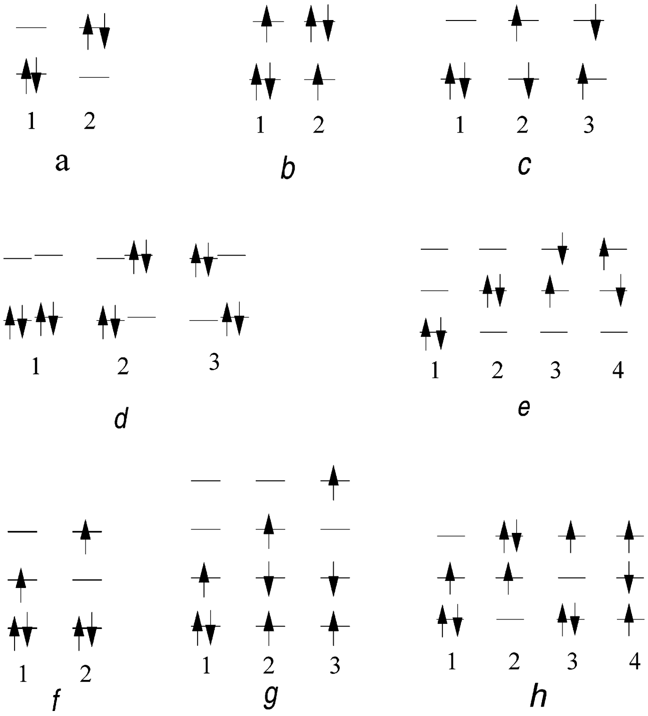

Figure 1. Schematic representation of reference configurations spanning the two-dimensional (a, b, and f), three-dimensional (c, d, and g), and four-dimensional (e and h) reference spaces used in the RMR-type CCSD methods.

this requires that in MR CC methods the reference space for a (super)system be a direct product of reference spaces for subsystems.[51]

The RMR CCSD method thus accounts for the nondynamic correlation by accounting for the primary triples and quadruples, while ignoring the secondary sets of the three- and four-body cluster amplitudes. These secondary triples and quadruples are responsible, by definition, for the dynamic correlation and can be reasonably well accounted for via PT. This is done in the RMR CCSD(T) method, in which the secondary set of triples, $\mathcal{M}_3^{\rm s}$, is taken care of through an additive (T)-type correction to the RMR CCSD energy. By using the converged RMR CCSD t_1 and t_2 amplitudes, we evaluate the contribution arising from each triply excited configuration $|\Phi_i^{(3)}\rangle$ via the CCSD(T)-type expression, namely

$$e(i) = \Big(\sum_{k=1}^{2} \sum_{l}\Big) \sum_{d} D(i)^{-1}\, t_l^{(k)}\, t_d^{(2)} \langle \Phi_l^{(k)}|H|\Phi_i^{(3)}\rangle \langle \Phi_i^{(3)}|H|\Phi_d^{(2)}\rangle \tag{6}$$

where the denominator $D(i)$ is given by the difference of the diagonal matrix elements of the Fock operator that are associated with the triply excited configuration $|\Phi_i^{(3)}\rangle$. The overall energy correction due to all secondary triples is then added to the RMR CCSD energy, obtaining the RMR CCSD(T) correlation energy

$$E_{\rm RMR-CCSD(T)} = E_{\rm RMR-CCSD} + \sum_{i \in \mathcal{M}_3^{\rm s}} e(i) \tag{7}$$

In summary, the RMR CCSD(T) method partitions the full set of triples and quadruples into the two subsets of unequal importance: the primary $\mathcal{M}_3^{\rm p}$ and $\mathcal{M}_4^{\rm p}$ subsets, and the secondary $\mathcal{M}_3^{\rm s}$ and $\mathcal{M}_4^{\rm s}$ ones. The primary subsets are handled nonperturbatively via RMR CCSD, whereas the secondary subset of triples $\mathcal{M}_3^{\rm s}$ is accounted for via perturbative (T)-type corrections. The secondary quadruples $\mathcal{M}_4^{\rm s}$ are at this stage ignored but, if desired, could be accounted for in a similar way to secondary triples via a CCSD(TQ)-type approach.

III. Computational Details

A. Basis Set and Geometry. We employ a modified G3Large (MG3) basis set,[52−54] also referred to as the G3LargeMP2 basis set, which is the same as the 6-311++G(3d2f,2df,2p) basis for H−Si but an improved one for P−Ar. These basis sets are of a triple-ζ quality, with additional diffuse functions on all atoms. They have two sets of p functions for hydrogen, two sets of d functions and one set of f functions for the first-row atoms, and three sets of d functions and two sets of f functions for the second row atoms. To facilitate a comparison with the results of Truhlar's group database,[46] we employ the same geometries for both the individual molecules and the transition complexes. We recall that these geometries were optimized at the QCISD/MG3 level of theory.

B. Computer Program. The results presented in this paper have been carried out with our codes for general MR CC methods that enable us to generate the standard SR CCSD and CCSD(T), as well as the RMR CCSD and RMR CCSD(T) energies, and, moreover, the general-model-space (GMS) state-universal (SU) CCSD results. These codes are based on the spin-orbital formalism, employ the restricted-open-shell HF (ROHF) reference for high-spin cases, and are interfaced with the GAMESS codes[55] generating the required molecular orbital (MO) integrals.

C. Choice of References. The main difference between the SR and RMR CC calculations is in the choice of references. In general, the selection of reference configurations can be based on various criteria. One obvious choice is based on the concept of an active space and another one on the importance of individual CSFs in a suitable test wave function. The concept that is based on the active orbitals seems to be simple and straightforward, yet in reality this is not the case, since the relevant active orbitals are not necessarily the frontier orbitals (see, e.g., ref 36), and the dimension of the so-called complete model space rapidly increases with the number of active orbitals. For these reasons, the latter approach offers a more practical and judicious way of choosing a model or reference space and can in fact be accomplished in a "quasi-black-box" fashion. Moreover, the references that are eventually selected in this way can often be described in terms of some simple active space formalism.

In the case of RMR CCSD(T), the choice of the model space is achieved via an automated, self-contained procedure, which selects the references according to the size of their CCSD amplitudes. For this purpose, we first perform a SR CCSD calculation. If all of the resulting CCSD amplitudes are smaller than a chosen threshold, we are likely dealing with a SR case when CCSD(T) yields satisfactory results, thus obviating the need for RMR CCSD(T). However, when some of the amplitudes are larger than a prescribed threshold, we select the corresponding configurations as references for RMR CCSD(T).

In our previous work,[32] a threshold of 0.1 proved to be sufficiently small to account for MR effects. However, the molecules in equilibrium and transition complexes in saddle-point geometries that are considered in this paper generally entail rather moderate MR effects, so that only in very few cases we encounter amplitudes that are larger than 0.1 (the largest one being 0.15). For this reason, we decided to use a smaller threshold of 0.05. Even so, the improvement due to RMR CCSD(T) over CCSD(T) is often insignificant. Nonetheless, we think it to be useful to confirm this fact relating to the role of MR or nondynamic correlation effects. Actually, in many instances, even with the 0.05 threshold, we end up with a single reference, so that RMR CCSD(T) reduces to CCSD(T). In the remaining cases, we used at most four references. When the formal selection process required 5 or 6 references, only the most important four references were chosen.

The configurations spanning the eight types of two- to four-dimensional reference spaces that are employed in this work are schematically represented in Figure 1. Such configurations and corresponding reference spaces often arise in MR situations. For example, type (a) involves one doubly excited configuration out of the RHF or ROHF reference and represents a two-electron/two-orbital (2,2) complete active space (CAS) when the bottom and top orbitals have a different symmetry. Type (c) is a (2,2) CAS excluding the doubly excited CSF. Type (e) then extends case (a) by one more virtual orbital, whereas type (b) represents a three-electron/two-orbital (3,2) CAS. Type (d) is typically associated with the active π orbitals: The two references complementing the ground state RHF or ROHF CSF correspond to double excitations $\pi_x^2 \rightarrow \pi_x^{*2}$ and $\pi_y^2 \rightarrow \pi_y^{*2}$. Finally, type (g) is a subspace of (3,4) CAS, and type (h) is a subspace of (3,3) CAS.

We must also emphasize that the doubly occupied orbitals in Figure 1 are not necessarily the highest occupied MOs (HOMOs) nor are the virtual ones necessarily the lowest unoccupied MOs (LUMOs) (cf. ref 36). For example, when considering the HN_2 species [case (2)], the relevant double excitation is from the sixth to the tenth MO. Likewise, for C_2H_4, our procedure selects a double involving the excitation from the eighth MO to the twentieth MO. This fact clearly demonstrates that, at a given geometry, it may not be immediately apparent which orbitals should be chosen as the active ones. In any case, our results seem to justify the selection procedure that is based on the weights of the CCSD cluster amplitudes, which enables us to carry out the computations in a "black-box" or, at least, a "quasi-black-box" manner. Thus, in comparison with the standard SR CC input, the only additional information that is required for RMR CC is the size of the chosen threshold.

IV. Results and Discussion

Before turning our attention to BHs, we first investigate the role of MR effects for the individual species appearing in the studied reactions, including the transition complexes. This is accomplished by comparing the relevant SR CC and RMR CC energies and will help us to better understand the results for the actual BHs. We shall see that in most cases the MR effects play a rather negligible role, so that only in a few cases it is worthwhile to account for the nondynamic correlation effects. We note that the same conclusion concerning the performance of SR-based approaches, be they of the Hartree−Fock or CISD variety, were pointed out already in an early study of the PES for the reaction of fluorin with the hydrogen molecule.[56] In most cases, although the absolute energies obtained at the SR and MR level may be significantly different, the relevant energy differences are very similar. We also recall that SR CCSD(T) works extremely well in the region of equilibrium geometries, and reasonably well even for slightly stretched bonds, usually up to the geometries characterizing the transition complex, where the new bond starts to form. For this reason, the *reaction* PESs obtained with SR CCSD(T) generally provide an adequate description. However, when describing the dissociation channels, or biradicaloid transition states, CCSD(T) breaks down.

TABLE 1: Energy Differences (in kcal/mol): $\Delta E_1 = E_{\mathrm{CCSD(T)}} - E_{\mathrm{RMRCCSD(T)}}$ and $\Delta E_2 = E_{\mathrm{CCSD}} - E_{\mathrm{RMRCCSD}}$

system[a]	M[b]	type[c]	ΔE_1	ΔE_2
HN_2	2	a	0.34	1.82
HN_2 (TS)	2	a	0.40	1.52
C_2H_4	2	a	0.11	1.10
$ClCH_3Cl^-$ (TS)	2	a	-0.06	0.79
$ClCH_3Cl^-$	2	a	0.03	0.59
CH_3FCl (TS)	2	a	0.16	2.19
ClF	2	a	0.08	1.01
HCO	2	b	0.36	1.75
HCO (TS)	2	b	-0.01	0.40
$CH_3CH_2CH_2$ (TS)	2	b	-0.14	0.58
FCH_3F^- (TS)	3	c	-0.08	1.50
FCH_3Cl^- (TS)	3	c	-0.16	1.13
N_2	3	d	0.49	2.26
HCN	3	d	0.28	1.66
F_2	4	e	0.80	4.66
HFH (TS)	2	f	0.07	0.60
HN_2O (TS)	2	f	0.50	1.15
HClH (TS)	3	g	0.24	1.09
$HFCH_3$ (TS)	3	g	-0.01	0.55
HF_2 (TS)	4	h	0.85	5.44

[a] TS designates a transition state. [b] M is the number of references. [c] Reference type in Figure 1.

In order to independently justify small corrections to the existing data that are based on CCSD(T) results, we carry out in section IV.C a case study, using a small basis set ab initio model that enables the FCI treatment, considering the reaction for which the MR effects are found to be most pronounced.

A. Energy Differences between the SR and RMR CC Methods. Molecules and transition state (TS) complexes that are considered in our RMR CCSD and RMR CCSD(T) study are listed in Table 1, where we also give the number of references employed in each case and the type of the reference configurations constituting the model space as defined in Figure 1 and indicate the importance of MR effects as measured by the difference between the CCSD and RMR CCSD energies, as well as between the CCSD(T) and RMR CCSD(T) energies. The RMR CCSD method always yields a lower energy than does CCSD, the largest improvement amounting to about 5 kcal/mol in the case of F_2 and HF_2(TS). In the remaining cases RMR CCSD improves CCSD by about 0.5−2 kcal/mol. The differences between the CCSD(T) and RMR CCSD(T) energies are smaller, the largest one being about 0.8 kcal/mol, implying the absence of major MR effects in the studied cases, as well as the fact that CCSD(T) is capable of handling, at least to some extent (i.e., for only moderately stretched bonds), the quasidegeneracy effects.

Although in most cases RMR CCSD(T) gives a lower energy than does CCSD(T), in a few cases, it yields a slightly higher energy. This is understandable if we recall that in degenerate situations CCSD(T) has a tendency to overshoot the exact FCI energy, especially in the bond breaking situations.[36] However, this can arise even in the vicinity of the equilibrium geometry: For example, in the case of the BN molecule, CCSD(T) overestimates the energy of the lowest singlet state and predicts the singlet rather than the triplet ground state, contrary to the experiment, whereas RMR CCSD(T) corrects this failure.[57]

The size of the CCSD cluster amplitudes, which is used as a basis for the selection of references, is also indicative of a possible improvement due to the RMR CCSD(T) approach. For example, the cluster amplitude that is associated with the second reference configuration for F_2 and HF_2(TS) is about 0.13−0.15, which in turn can be related to the largest observed difference between the RMR CCSD(T) and CCSD(T) energies and,

TABLE 2: CCSD, RMR CCSD, CCSD(T), and RMR CCSD(T) Forward and Reverse Barrier Heights (in kcal/mol) for the 19 Reactions Considered

reaction		CCSD	RMR CCSD	CCSD(T)	RMR CCSD(T)	best estimate[a]
heavy-atom transfer reactions						
(1) $H + N_2O \rightarrow OH + N_2$	$V_f^\ddagger$	20.25	19.10	18.58	18.08	18.14
	$V_r^\ddagger$	92.21	93.33	83.55	83.54	83.22
(2) $H + FH \rightarrow HF + H$	$V_f^\ddagger$	45.01	44.41	43.42	43.35	42.18
	$V_r^\ddagger$	45.01	44.41	43.42	43.35	42.18
(3) $H + ClH \rightarrow HCl + H$	$V_f^\ddagger$	20.97	19.89	19.19	18.95	18.00
	$V_r^\ddagger$	20.97	19.89	19.19	18.95	18.00
(4) $H + FCH_3 \rightarrow HF + CH_3$	$V_f^\ddagger$	34.06	33.51	31.68	31.68	30.38
	$V_r^\ddagger$	61.10	60.55	57.55	57.56	57.02
(5) $H + F_2 \rightarrow HF + F$	$V_f^\ddagger$	4.07	3.30	2.30	2.25	2.27
	$V_r^\ddagger$	112.34	106.90	105.98	105.51	105.13
(6) $CH_3 + FCl \rightarrow CH_3F + Cl$	$V_f^\ddagger$	9.44	8.27	6.11	6.02	7.43
	$V_r^\ddagger$	66.36	64.17	61.54	61.38	60.17
nucleophilic substitution reactions						
(7) $F^- + CH_3F \rightarrow FCH_3 + F^-$	$V_f^\ddagger$	1.29	−0.21	−1.30	−1.22	−0.34
	$V_r^\ddagger$	1.29	−0.21	−1.30	−1.22	−0.34
(8) $F^-\cdots CH_3F \rightarrow FCH_3\cdots F^-$	$V_f^\ddagger$	15.48	13.98	13.34	13.42	13.38
	$V_r^\ddagger$	15.48	13.98	13.34	13.42	13.38
(9) $Cl^- + CH_3Cl \rightarrow ClCH_3 + Cl^-$	$V_f^\ddagger$	4.75	3.96	2.37	2.43	3.10
	$V_r^\ddagger$	4.75	3.96	2.37	2.43	3.10
(10) $Cl^-\cdots CH_3Cl \rightarrow ClCH_3\cdots Cl^-$	$V_f^\ddagger$	14.94	14.74	13.02	13.11	13.61
	$V_r^\ddagger$	14.94	14.74	13.02	13.11	13.61
(11) $F^- + CH_3Cl \rightarrow FCH_3 + Cl^-$	$V_f^\ddagger$	−12.40	−13.53	−14.51	−14.34	−12.54
	$V_r^\ddagger$	24.97	23.84	22.28	22.45	20.11
(12) $F^-\cdots CH_3Cl \rightarrow FCH_3\cdots Cl^-$	$V_f^\ddagger$	3.66	2.53	2.30	2.46	2.89
	$V_r^\ddagger$	34.07	32.95	31.70	31.86	29.62
(13) $OH^- + CH_3F \rightarrow HOCH_3 + F^-$	$V_f^\ddagger$	−1.02	−1.02	−3.89	−3.89	−2.78
	$V_r^\ddagger$	19.50	19.50	16.23	16.23	17.33
(14) $OH^-\cdots CH_3F \rightarrow HOCH_3\cdots F^-$	$V_f^\ddagger$	13.09	13.09	10.67	10.67	10.96
	$V_r^\ddagger$	50.01	50.01	47.87	47.87	47.20
unimolecular and association reactions						
(15) $H + N_2 \rightarrow HN_2$	$V_f^\ddagger$	16.84	17.57	15.42	15.50	14.69
	$V_r^\ddagger$	11.90	12.20	10.84	10.78	10.72
(16) $H + CO \rightarrow HCO$	$V_f^\ddagger$	4.61	4.21	4.02	4.03	3.17
	$V_r^\ddagger$	22.38	23.73	22.29	22.65	22.68
(17) $H + C_2H_4 \rightarrow CH_3CH_2$	$V_f^\ddagger$	3.18	4.28	2.64	2.74	1.72
	$V_r^\ddagger$	44.07	44.07	41.95	41.95	41.75
(18) $CH_3+C_2H_4 \rightarrow CH_3CH_2CH_2$	$V_f^\ddagger$	8.82	9.34	6.43	6.67	6.85
	$V_r^\ddagger$	34.49	33.91	32.26	32.39	32.97
(19) $HCN \rightarrow HNC$	$V_f^\ddagger$	48.89	50.55	48.49	48.77	48.16
	$V_r^\ddagger$	34.36	34.85	33.58	33.39	33.11

[a] From ref 46.

likewise, between the RMR CCSD and CCSD energies (cf. Table 1). Similarly, the CCSD amplitude that is associated with the second reference for HN_2O(TS) [type (f) in Figure 1] is 0.15. In this case, the energy improvement due to the RMR treatment amounts to 0.5 kcal/mol. Here it is interesting to point out that the second reference is singly excited relative to the Hartree−Fock reference, so that RMR CCSD(T) does not bring in quadruples. The difference between RMR CCSD(T) and CCSD(T) is in this case solely due to the difference in the treatment of triples.

B. Barrier Heights. We computed forward and reverse BHs for 19 chemical reactions, six of which involve a heavy atom transfer, eight are nucleophilic substitution reactions, and five represent unimolecular and association reactions. The results for these BHs, as obtained with the CCSD, RMR CCSD, CCSD(T), and RMR CCSD(T) methods, are summarized in Table 2 and do not account for the core correlation and relativistic effects or for the spin−orbit coupling. For a comparison, we also included in Table 2 the benchmark best estimates[19] for these BHs, which represent the best theoretical

TABLE 3: Multireference Effect for Barrier Heights (BHs) (in kcal/mol)

reaction[c]	ΔBH(SD)[a] $V_f^‡$	ΔBH(SD)[a] $V_r^‡$	ΔBH[SD(T)][b] $V_f^‡$	ΔBH[SD(T)][b] $V_r^‡$
(1)	−1.15	1.12	−0.50	−0.01
(2)	−0.60	−0.60	−0.07	−0.07
(3)	−1.08	−1.08	−0.24	−0.24
(4)	−0.55	−0.55	0.00	0.01
(5)	−0.77	−5.44	−0.05	−0.85
(6)	−1.17	−2.19	−0.09	−0.16
(7)	−1.50	−1.50	0.08	0.08
(8)	−1.50	−1.50	0.08	0.08
(9)	−0.79	−0.79	0.06	0.06
(10)	−0.20	−0.20	0.09	0.09
(11)	−1.13	−1.13	0.17	0.17
(12)	−1.13	−1.12	0.16	0.16
(13)	0.00	0.00	0.00	0.00
(14)	0.00	0.00	0.00	0.00
(15)	0.73	0.30	0.08	−0.06
(16)	−0.40	1.35	0.01	0.36
(17)	1.10	0.00	0.10	0.00
(18)	0.52	−0.58	0.24	0.13
(19)	1.66	0.49	0.28	−0.19

[a] Denotes the difference between the RMR CCSD and CCSD BHs. [b] Denotes the difference between the RMR CCSD(T) and CCSD(T) BHs. [c] See Table 2 for the numbering of reactions.

estimates as obtained with the W1 (and in some cases with the W2) theory[58,59] that is based on the CCSD(T) results extrapolated to the complete basis set limit, supplemented by the corrections for the core correlation, relativistic effects, and spin−orbit coupling.

Unless the MR effects are roughly the same for both reactants, the transition state, and the product(s), their role will manifest itself in the computed BHs. For example, reaction 15 represents the case when the RMR CCSD(T) energy is lower than the CCSD(T) one by about 0.4 ± 0.1 kcal/mol for both reactants, the transition state, and the product. Hence, the RMR CCSD(T) and CCSD(T) results for both the forward and backward BHs differ by less than 0.1 kcal/mol.

The role of the MR effects in the computations of BHs, as determined by the differences between the RMR CCSD or RMR CCSD(T) and, respectively, CCSD or CCSD(T) results are listed in Table 3 for the 19 reactions considered (the reactions are numbered as in Table 2). The MR effects at the CCSD level, assessed by the difference between the RMR CCSD and CCSD BHs, can be as large as 5 kcal/mol for reaction 5, greatly reducing the CCSD error for that BH. Relative to the best benchmark estimates for 38 BHs, the mean absolute error for the CCSD and RMR CCSD values are 2.46 and 1.95 kcal/mol, respectively, whereas the corresponding mean signed errors are only slightly lower, namely 2.44 and 1.88 kcal/mol. Both of these averages indicate that the RMR CCSD approach improves the CCSD results by about 0.5 kcal/mol.

At a higher level of theory, the differences between the RMR CCSD(T) and CCSD(T) BHs are smaller (see Table 3), since the (T) corrections partially account for the MR effects. At this (T) level of approximation, we find the largest MR effect for the reverse barrier of reaction 5, amounting to 0.85 kcal/mol. Nonetheless, in seven cases of forward and reverse BHs, the differences between the RMR CCSD(T) and CCSD(T) estimates are greater than 0.24 kcal/mol (1 kJ/mol), an amount that is sometimes referred to as the "benchmark accuracy". Relative to the best benchmark estimates, the mean absolute errors for CCSD(T) and RMR CCSD(T) BHs are, respectively, 0.79 and 0.76 kcal/mol, whereas the corresponding signed mean errors are 0.12 and 0.12 kcal/mol. In view of this fact, we present in Table 4 slightly modified estimates for the BHs of the 19 reactions considered, which are based on our RMR CCSD(T) results. This modification is achieved by adding the difference between the RMR CCSD(T) and CCSD(T) BHs to Truhlar's best estimates.[19] Thus modified values are implicitly accounting for the core correlation, relativistic effects, and spin−orbit coupling. It should also be noted that the recommended BHs for reactions 3, 4, 13, 14, and 17, given in Table 4, are the same as those given by Zhao et al.[19] In fact the recommended BHs for reactions 3, 9, and 17 were taken over from ref 19, since they were obtained in a different way.

TABLE 4: Modified Final Estimate of BHs for the 19 Reactions Considered (in kcal/mol)

reaction[a]	$V_f^‡$	$V_r^‡$	reaction[a]	$V_f^‡$	$V_r^‡$
(1)	17.64	83.21	(11)	−12.37	20.28
(2)	42.11	42.11	(12)	3.05	29.78
(3)[b]	18.00	18.00	(13)[b]	−2.78	17.33
(4)[b]	30.38	57.03	(14)[b]	10.96	47.20
(5)	2.22	105.33	(15)	14.77	10.66
(6)	7.34	60.01	(16)	3.18	23.04
(7)	−0.26	−0.26	(17)[b]	1.72	41.75
(8)	13.46	13.46	(18)	7.09	33.10
(9)[b]	3.10	3.10	(19)	48.44	32.92
(10)	13.70	13.70			

[a] See Table 2 for the numbering of reactions. [b] These BHs are the same as those recommended by Zhao et al. in ref 19 (see the text for details).

C. Full CI Case Study. In order to provide an additional justification for the superiority of the RMR CCSD(T) BHs relative to those based on the standard CCSD(T) method, however small the differences between them may turn out to be, we examine reaction 5 using a double-ζ (DZ) basis set model, which enables us to generate FCI results.[55] Of course, for such a model, we cannot expect the resulting BHs to be realistic and the only meaningful comparison is with the FCI BHs.

The F_2 molecule represents a weakly bound system, and the Hartree−Fock-level PECs, at either the RHF or UHF level, are purely repulsive.[60,61] In reaction 5, this reactant molecule, as well as the transition complex HF_2(TS), shows the largest MR effect among the systems considered in this work (cf. Table 1). In contrast, the product HF molecule is strongly bound, and both HF and F have a strong SR character. As a consequence, the MR effects should play a relatively important role for the reverse BH, since they are important for the transition complex and unimportant for the products but not for the forward BH, since the MR effects are of a roughly equal importance for the reactants and for the transition complex.

The computed CCSD(T), RMR CCSD(T), and FCI energies for reactants, transition state complex, and products, as well as the implied BHs, are summarized in Table 5 (all results are obtained with the same QCISD/MG3 geometries[46] that are used throughout this paper). Unfortunately, when all of the valence electrons are correlated, our computer facilities do not allow us to carry out the FCI calculation for the transition state complex. We have thus performed another set of calculations, in which both 1s and 2s core electrons of the fluorine atom are not correlated. In both sets of calculations (i.e., without and with freezing of the 2s electrons on F), the RMR CCSD(T) energies of F_2 and HF_2(TS) are lower than the CCSD(T) ones by 0.8−1 kcal/mol. This is consistent with the energy differences that were obtained with the large MG3 basis (cf. Table 1). The RMR CCSD(T) energies are closer to the FCI ones than are the CCSD(T) energies, implying that RMR CCSD(T) represents an improvement over CCSD(T).

TABLE 5: DZ Basis Set Model for Reaction 5[a]

	CCSD(T)	RMR CCSD(T)[b]	FCI
H	−0.497637	-0.497637	−0.497637
F_2	−198.963961	−198.965600	−198.965549
HF_2 (TS)	−199.464697	−199.466201	
HF	−100.146545	−100.146545	−100.146868
F	−99.472381	−99.472381	−99.472415
$V^{\ddagger}_{f}$	−1.94	−1.86	
$V^{\ddagger}_{r}$	96.78	95.84	
	Freeze 1s and 2s Electrons of F		
F_2	−198.893897	−198.895201	−198.895179
HF_2 (TS)	−199.396584	−199.397793	−199.398175
HF	−100.108481	−100.108481	−100.108665
F	−99.442741	−99.442741	−99.442787
$V^{\ddagger}_{f}$	−3.17	−3.11	−3.36
$V^{\ddagger}_{r}$	97.04	96.28	96.18

[a] Energies are in a.u. and barrier heights in kcal/mol. [b] Single reference for HF and F, four references for F_2 and HF_2 (TS).

Turning to the BHs and using the available FCI results as a benchmark, we see that for the forward barrier the RMR CCSD(T) result is similar to the CCSD(T) one, as can be expected in view of the cancellation of the MR effects for the reactant F_2 and the transition complex HF_2(TS). On the other hand, for the reverse barrier, the RMR CCSD(T) result is closer to the FCI one and represents an improvement over the CCSD(T) BH, since the MR effects contribute about 0.8 kcal/mol in this case. This result clearly indicates that RMR CCSD(T) can improve BHs in the presence of MR effects, even though the DZ model we employ is patently unrealistic, yielding even a negative forward BH.

V. Conclusions

We have employed the recently developed RMR CCSD(T) method[36] to investigate BHs for 19 chemical reactions, for which a highly accurate and reliable database[46] is available for comparison. In most cases, these results were based on the standard SR CCSD(T) results. In the absence of quasidegeneracy, the CCSD(T) method is known to yield very accurate results, representing an excellent, computationally affordable alternative to higher-order CC approaches that become unaffordable for larger ab initio models. Yet, in the presence of a near degeneracy, or when the system possesses a biradicaloid character, the role of nondynamic correlation effects begins to manifest itself through the enhanced importance of higher-than-pair cluster amplitudes. In such cases, in addition to an increased importance of triples, the account of which is always required if we strive for the chemical accuracy, even certain quadruples begin to play a non-negligible role. When this happens, the performance of SR CCSD(T) deteriorates due to the inadequacy of PT for the handling of triples and due to the complete neglect of quadruples.

The RMR CCSD(T) method[36] has been designed with an objective to avoid the shortcommings of the standard CCSD(T) method by accounting for, in an affordable and simple way, the nondynamic correlation due to the higher-than-pair cluster amplitudes. This is achieved in two steps: First, by externally correcting the standard CCSD approach using a small subset of the most important three- and four-body connected cluster amplitudes. These amplitudes are extracted by the cluster analysis of a modest-size MR CISD wave function. As is well-known, the variational methods are excellent in accounting for nondynamic correlation, while lacking in their description of dynamic correlation effects, thus complementing the CC methods. Second, since RMR CCSD corrects only for the most important triples, we employ the standard (T)-type correction for the remaining triples, which are huge in number, but individually making a small enough contribution to enable a perturbative treatment. The resulting method is referred to by the acronym RMR CCSD(T).

All tests of the RMR CCSD(T) approach that have been carried out so far[36,32,57,62,63] indicate an excellent performance of this approach (see also ref 34), as well as its computational affordability, particularly in its truncated form.[32] Even in cases when the standard CCSD(T) fails for systems in their equilibrium geometry, as is the case, for example, for the ground state of the BN molecule [where CCSD(T) predicts a singlet rather than a triplet ground state], the RMR CCSD(T) method yields the correct result.[57] Exploiting this approach for the determination of BHs, we find that in most cases RMR CCSD(T) either reduces to CCSD(T) or yields very similar results, indicating the negligibility of MR effects in these cases. Nonetheless, for seven cases, the MR effects are larger than 1 kJ/mol. Assuming the additive nature of such small corrections, we can thus provide a slightly modified estimate that should include the MR effects, however small, for the just mentioned seven cases.

Acknowledgment. The continued support (J.P.) by the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

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