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Simplified Reference Wave Functions for Multireference Perturbation Theory

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A number of simplifications in defining the reference wave functions used in multireference second-order Møller−Plesset perturbation theory (MRMP2) calculations are studied. The usual multiconfigurational orbital optimization is avoided by using Hartree−Fock or Kohn−Sham orbitals; the complete configuration expansion in the active-space orbitals is replaced by a severely truncated expansion, and the spin-component-scaling idea is applied to the multireference perturbation expansion. We assess these approximations to the full procedure by calculating the barrier heights for 15 processes taken from the Zhao−Gonzalez−Garcia−Truhlar database. Our results suggest that reliable and relatively cheap reference wave functions for MRMP2 calculations can be obtained from the simplifications introduced here. We hope that this will enable the application of the MRMP2 method to a larger range of chemical systems.

1. Introduction

In the area of wave-function-based quantum chemistry, there are essentially two broad approaches to the calculation of electronic structures; these are the single reference and the multireference philosophies. The former, which includes the Hartree−Fock (HF) method and the perturbational and coupled-cluster approaches, which use the HF determinant as the reference wave function, lends itself to the development of "black-box" computational strategies which require a minimal input from the user. The multireference approaches, by contrast, require a degree of subjective judgment from the user to render the calculations manageable and effective. An obvious example of this type of consideration is the choice of orbitals to be included in the active space of a multiconfigurational calculation. It is well-known that many chemical systems require multiconfigurational/multireference treatments for a reliable description of their electronic structures, and it is desirable to look for schemes which enable such calculations to be performed with computational efficiency and minimal user intervention.[1] In recent studies, we have investigated simplifications to the various steps required to perform multireference perturbation theory (MRPT) calculations.[2−4] The motivation for the work has been to enable a broader range of chemical problems to be treated by MRPT methods. This requires not only considerations of computational efficiency but also a simple conceptual approach to the use of multiconfigurational techniques so that such calculations may be performed by the "nonspecialist". Nevertheless, it must be stressed that while the simplifications we implement are applicable to many situations, they are not applicable to all situations. In ref 2, we studied ground- and excited-state potential energy curves of the C_2 molecule and found that our approximations were valid if not far from equilibrium, but for study of the entire potential energy curves, the full MRMP2 procedure was required. In ref 3, we studied a variety of reactions and found for the HCN → HNC reaction that the multiconfigurational orbital optimization produced much more compact orbitals and gave a correspondingly more accurate barrier height than other more approximate orbitals. In ref 4, we studied the use of a truncated configuration expansion and found again that in the region of equilibrium or even at bond lengths corresponding to transition state structures, the approximations held, but at longer bond distances, severe errors in the reference wave functions were obtained.

The first consideration in using multiconfigurational methods, as alluded to above, is the choice of active-space orbitals. For some systems, this is straightforward and guided by the chemistry of the situation. When the choice cannot be made simply on chemical grounds, various schemes based on indices computed for each orbital[5,6] can be used to assess whether an orbital should be included in the active space or not. Such schemes can be developed on sound theoretical arguments, but it is often found that the choice of orbitals arrived at is geometry-dependent. Hence, the choice of orbitals appropriate in one region of a potential energy surface may be inappropriate in another region. By contrast, the full valence shell of orbitals for each atom in the system is an automatic choice that can be made, provided a set of converged HF or Kohn−Sham (KS) orbitals is available. The drawback is that the number of valence shell orbitals grows quickly with the size of the molecule, and if a complete configuration expansion is used (as in the complete active-space self-consistent field CASSCF method[7]), the number of determinants increases exponentially with the number of valence shell orbitals. A further difficulty arises in that once an active space has been chosen, the orbitals must be optimized. The full-valence-shell-type active space can lead to the occurrence of redundant coordinates in the optimization process. For example, consider the F_2 molecule described by a full valence shell of 14 electrons in 8 orbitals. There is effectively only one correlating orbital ($3\sigma_u$) into which the $3\sigma_g$ donates, and the remaining orbitals are essentially doubly occupied. Active orbitals which have near-double occupancy or near-zero occupancy effectively correspond to inactive and virtual orbitals, respectively. This means that the inactive−active and active−virtual rotations involving these orbitals leave the energy invariant and can lead to problems in the orbital optimization. While there exist techniques for dealing with this problem, it nevertheless provides an additional complication. Hence, there

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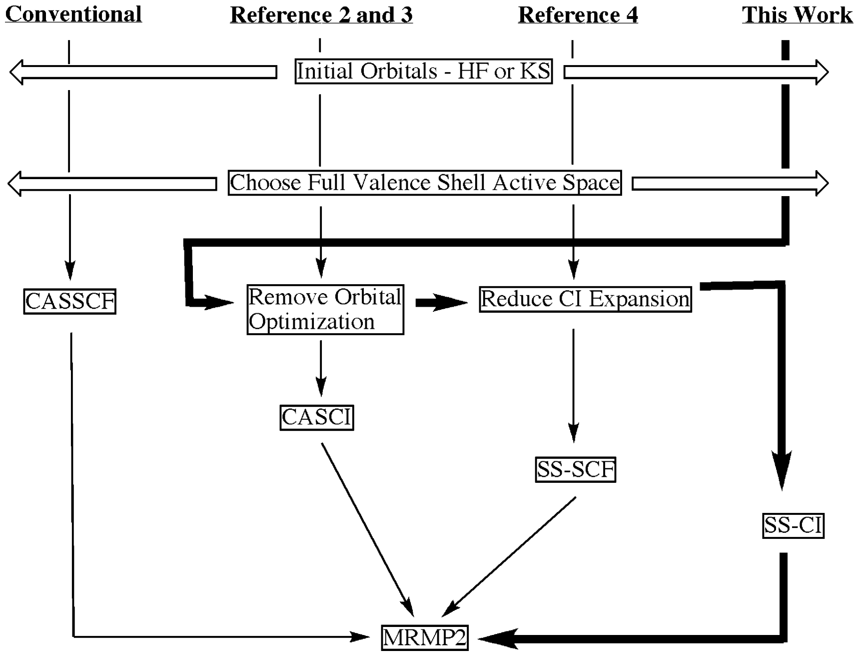
SCHEME 1



are several potentially difficult steps that must be carried out to obtain the reference wave function before the MRPT expansion can be built. In the next section, we discuss two approximations that we have investigated which simplify the procedure. We then proceed to combine these approximations and assess the performance of the resultant method in calculating the reaction barriers for a number of chemical reactions.

2. Approximations

Our multireference perturbation theory program follows the multireference second-order Møller−Plesset perturbation theory (MRMP2) formalism of Hirao.[8−10] This approach was introduced (initially) for use with CASSCF-type reference wave functions. The first-order density matrix, γ, obtained from the full CI expansion in the chosen active space is used to construct the matrix representation of the generalized Fock operator, ***F***

$$F_{\mathrm{pq}} = h_{\mathrm{pq}} + \sum_{ij}^{\text{occupied}} \gamma_{ij}\left[(pq|ij) - \frac{1}{2}(pj|iq)\right] \tag{1}$$

For a CASSCF expansion, the energy is invariant to rotations within the inactive, active, and virtual orbital subspaces. ***F*** is canonicalized within each subspace, and the resulting diagonal elements are used to define the eigenvalues, $E^{(0)}$, of the model Hamiltonian, H_0. The second-order correction to the energy is given by

$$E_P^{(2)} = -\sum_Q \frac{|\langle Q|H|P\rangle|^2}{E_Q^{(0)} - E_P^{(0)}} \tag{2}$$

In eq 2, the CASSCF state is labeled by P, and Q refers to one of the set of all allowed double excitations between the orbital subspaces. The occurrence of intruder states can seriously degrade the performance of multireference perturbation theory, and a simple scheme has been developed for intruder state avoidance (ISA) within the formalism of Hirao's MRMP2.[11,12] In this approach, eq 2 is modified by introducing a shift in the denominator

$$E_P^{(2)-\mathrm{ISA}} = -\sum_Q \frac{|\langle Q|H|P\rangle|^2}{E_Q^{(0)} - \mathrm{E}_P^{(0)} + \Delta_Q} \tag{3}$$

where

$$\Delta_Q = \frac{b}{E_Q^{(0)} - E_P^{(0)}}$$

A number of groups[1,13−15] have investigated the possibility of avoiding the CASSCF step by using orbitals obtained from simpler methods to define the active spaces for use in multireference treatments. We have also studied this matter using complete active-space configuration interaction (CASCI) reference wave functions in a MRPT scheme. In refs 2 and 3, the CASCI wave functions were built from Hartree−Fock or Kohn−Sham orbitals with no further refinement of the orbital sets. We have also studied the use of a very truncated configuration expansion in defining the reference wave function.[4] The truncation scheme we used was described by Rogers and McDouall[16] and is based on a CI expansion in Slater determinants. A brief outline of the scheme is as follows. In the CI methodology, the advantage of using Slater determinants is being able to split the determinants into an α-string, $\alpha(^{\alpha}I)$, and a β-string, $\beta(^{\beta}I)$[17,18]

$$\psi_{\det} = |\phi_i\bar{\phi}_j\phi_k\bar{\phi}_l...\rangle = |\phi_i\phi_k...\bar{\phi}_j\bar{\phi}_l...\rangle = |\alpha(^{\alpha}I)\beta(^{\beta}I)\rangle \tag{4}$$

The α-string is an ordered product of n_α creation operators with α spin, where the system contains $n_\alpha + n_\beta$ electrons. The β-string is similarly defined. The full space of Slater determinants can then be formed by building the sets of all α-strings $\{\alpha(^{\alpha}I)\}$ and β-strings $\{\beta(^{\beta}I)\}$ and taking all possible pairings between them. The number of determinants that are produced for M orbitals is given by

$$\mathrm{Dim}_{\mathrm{FullCI}} = \binom{M}{n_\alpha}\binom{M}{n_\beta} \tag{5}$$

Each member of $\{\alpha(^{\alpha}I)\}$ is an ordered set of creation operators and so can be related to every other member by a product of replacement operators $\hat{E}^{\alpha}_{pq}\hat{E}^{\alpha}_{rs}\hat{E}^{\alpha}_{tu}$..., where

$$\hat{E}^{\alpha}_{pq} = a^{\dagger}_{p\alpha}a_{q\alpha} \tag{6}$$

($a^{\dagger}$ and a are the usual fermion creation and annihilation operators, respectively). In order to span the full set, we must include up to n_α-fold products of the operators in eq 6. In the S-strings scheme, the excitations are restricted to just a single operator applied to the string from the reference determinant, $\alpha(^{\alpha}I)$

$$\alpha(^{\alpha}I^{p}_{q}) = \hat{E}^{\alpha}_{pq}\alpha(^{\alpha}I) \tag{7}$$

This produces a reduced set of strings which differ by a single spin orbital from the reference string. The same procedure is carried out for the β-strings. Using these restricted sets of strings, the number of Slater determinants that can be formed is

$$\mathrm{Dim}_{\mathrm{S-strings}} = [1 + n_\alpha(M - n_\alpha)][1 + n_\beta(M - n_\beta)] \tag{8}$$

Obviously, this is a dramatic reduction in the number of determinants. The specific form of the determinants obtained is shown below

$$\begin{aligned}\Psi^{\alpha 0}_{\mathrm{det}} &= \hat{E}^{\alpha}_{pq}\alpha(^{\alpha}I)\beta(^{\beta}I) = \alpha(^{\alpha}I^{p}_{q})\beta(^{\beta}I)\\ \Psi^{\beta 0}_{\mathrm{det}} &= \alpha(^{\alpha}I)\hat{E}^{\beta}_{pq}\beta(^{\beta}I) = \alpha(^{\alpha}I)\beta(^{\beta}I^{p}_{q})\\ \Psi^{\alpha\beta}_{\mathrm{det}} &= \hat{E}^{\alpha}_{pq}\alpha(^{\alpha}I)\hat{E}^{\beta}_{rs}\beta(^{\beta}I) = \alpha(^{\alpha}I^{p}_{q})\beta(^{\beta}I^{r}_{s})\end{aligned} \tag{9}$$

In the space of determinants, we have the $\alpha\beta$-component of the double excitations, along with all of the α and β single excitations, relative to the reference determinant

$$\Psi^{00}_{\mathrm{det}} = \alpha(^{\alpha}I)\beta(^{\beta}I) \tag{10}$$

This S-strings (SS) truncation of the N-electron space is extreme, and we cannot expect it to reproduce the energy of the CASSCF or CASCI state in general. However, we have shown[4] that it leads to a manageable reference space that retains good accuracy in the MRMP2 scheme. A full discussion of the properties of the SS approximation may be found in ref 16. When using a CASSCF or CASCI reference, the active space is fully correlated. However, with a truncated reference space, the remaining correlation for the active space must be evaluated perturbatively.[19] All single and double excitations from the reference configurations in eq 9 will be treated in this manner. Since these terms involve excitations within the active space only, we shall denote these terms as $A \rightarrow A$. We shall also look at the effect of omitting any further treatment of the active-space correlation. This can be justified since the correlation in the space of active orbitals has been treated, to some degree, by the terms present in eq 9. Furthermore, the perturbative treatment of the remaining active-space correlation may be expected to be problematic since the opportunity for intruder state effects must increase, and we expect that the coupling between key configurations will be strongest for determinants which differ by excitation within the active space alone; these are situations which we can expect to be poorly described by a low-order perturbation treatment.

Our purpose here is to combine the approximations introduced in refs 2, 3, and 4. Scheme 1 shows our strategy and highlights the simplifications implemented.

Finally, we shall also look at the effect of using Grimme's spin-component scaling (SCS)[20−24] for the MRMP2 method. There are subtleties in the application of SCS to a multireference expansion, and we shall deal with these in section 4.2.

3. Computational Details

In this work, we assess the accuracy of our procedures in calculating the barrier heights of nine reactions. Transition states often possess electronic structures that are multiconfigurational in nature, as they are typically intermediate between two different bonding situations. We have selected reactions from the NHTBH38/04 database of Truhlar and co-workers.[25,26] Specifically the reactions we study are

$$\mathrm{H + FH \rightarrow HF + H} \tag{11}$$

$$\mathrm{H + ClH \rightarrow HCl + H} \tag{12}$$

$$\mathrm{H + F_2 \rightarrow HF + F} \tag{13}$$

$$\mathrm{H + N_2 \rightarrow HN_2} \tag{14}$$

$$\mathrm{H + CO \rightarrow HCO} \tag{15}$$

$$\mathrm{HCN \rightarrow HNC} \tag{16}$$

$$\mathrm{H + N_2O \rightarrow OH + N_2} \tag{17}$$

$$\mathrm{H + FCH_3 \rightarrow HF + CH_3} \tag{18}$$

$$\mathrm{F^- + CH_3F \rightarrow FCH_3 + F^-} \tag{19}$$

We refer to the reactions of eqs 11−16 as Set 1 and those of eqs 17−19 as Set 2. Calculating forward ($V^{\ddagger}_{\mathrm{f}}$) and reverse ($V^{\ddagger}_{\mathrm{r}}$) reactions gives 15 barrier heights for comparison with our calculations. For Set 1, the CASSCF references can be calculated easily, but for Set 2, the use of CASSCF references becomes computationally demanding. The Set 2 reactions contain significantly more multireference character; the reaction in eq 17 is particularly demanding and generally produces the largest errors in what follows.

All geometries for reactants and transition states were taken from ref 26 and refer to the QCISD/MG level. The MG basis consists of the 6-311++G(3d2f,2df,2p)[27] basis set for the atoms H−Si, with an extended basis for atoms P−Ar.[28,29] The notation (3d2f,2df,2p) indicates three sets of d functions and two sets of f functions for atoms Na−Ar, two sets of d functions and one set of f functions for atoms Li−Ne, and two sets of p functions for hydrogen. The calculations we report use the MGS basis, which is equivalent to the MG basis except for the case of the H atom, for which the diffuse functions are excluded. In calculating the energies of reactants and products, the systems were treated as supermolecules with a separation between moieties of 100 Å. This avoids any issues related to size consistency of the MRMP2 approach; a detailed discussion can be found in refs 30 and 31. All active spaces used were of the full-valence-shell-type.

The procedure we used involved running an initial HF or KS calculation followed by a stability analysis. Where instabilities existed, the wave function was reoptimized until a stable wave function was found (UHF or UKS). The natural orbitals formed from these were used in the following CI calculation. Where no instabilities existed, a spin-restricted wave function

TABLE 1: Database and Calculated Barrier Heights for the Reactions in Eqs 11−19; Absolute Barriers and Errors (ϵ) Are in kcal mol^{-1}

reaction	barrier	database value[a]	SS-CI (HF)	ϵ	SS-CI (B3LYP)	ϵ	SS-CI (BLYP)	ϵ
$H + FH \rightarrow HF + H$	$V^{\ddagger}_{f,r}$	42.18	42.33	0.15	44.33	2.15	45.89	3.71
$H + ClH \rightarrow HCl + H$	$V^{\ddagger}_{f,r}$	18.00	40.56	22.56	36.59	18.59	21.38	3.38
$H + F_2 \rightarrow HF + F$	$V^{\ddagger}_{f}$	2.27	20.15	17.88	10.39	8.12	11.80	9.53
	$V^{\ddagger}_{r}$	106.18	128.09	21.91	100.47	−5.71	107.35	1.17
$H + N_2 \rightarrow HN_2$	$V^{\ddagger}_{f}$	14.69	35.64	20.95	31.52	16.83	30.33	15.64
	$V^{\ddagger}_{r}$	10.72	19.06	8.34	1.26	−9.46	−1.38	−12.10
$H + CO \rightarrow HCO$	$V^{\ddagger}_{f}$	3.17	10.90	7.73	15.44	12.27	13.98	10.81
	$V^{\ddagger}_{r}$	22.68	54.22	31.54	9.87	−12.81	6.34	−16.34
$HCN \rightarrow HNC$	$V^{\ddagger}_{f}$	48.16	43.60	−4.56	42.27	−5.89	44.80	−3.36
	$V^{\ddagger}_{r}$	33.11	33.80	0.69	30.97	−2.14	31.38	−1.73
$H + N_2O \rightarrow OH + N_2$	$V^{\ddagger}_{f}$	18.14	20.25	2.11	−36.08	−54.22	−23.70	−41.84
	$V^{\ddagger}_{r}$	83.22	114.77	31.55	87.52	4.30	102.44	19.22
$H + FCH_3 \rightarrow HF + CH_3$	$V^{\ddagger}_{f}$	30.38	9.51	−20.87	12.37	−18.01	16.13	−14.25
	$V^{\ddagger}_{r}$	57.02	32.96	−24.06	58.55	1.53	61.30	4.28
$F^- + CH_3F \rightarrow FCH_3 + F^-$	$V^{\ddagger}_{f,r}$	−0.34	7.74	8.08	11.99	12.33	14.64	14.98
Set 1 $\lvert\bar{\epsilon}\rvert$				13.63		9.40		7.78
max $\lvert\epsilon\rvert$				31.54		18.59		16.34
Set 2 $\lvert\bar{\epsilon}\rvert$				17.33		18.08		18.91
max $\lvert\epsilon\rvert$				31.55		54.22		41.84
combined $\lvert\bar{\epsilon}\rvert$				14.87		12.29		11.49
max $\lvert\epsilon\rvert$				31.55		54.22		41.84

[a] Ref 26.

TABLE 2: Barrier Heights at the MRMP2 + $A \rightarrow A$ Level; Absolute Barriers and Errors (ϵ) Are in kcal mol^{-1}

Reaction	Barrier	MRMP2 (HF) + $A \rightarrow A$	ϵ	MRMP2 (B3LYP) + $A \rightarrow A$	ϵ	MRMP2 (BLYP) + $A \rightarrow A$	ϵ
$H + FH \rightarrow HF + H$	$V^{\ddagger}_{f,r}$	42.36	0.18	44.20	2.02	45.34	3.16
$H + ClH \rightarrow HCl + H$	$V^{\ddagger}_{f,r}$	16.20	−1.80	15.88	−2.12	17.92	−0.08
$H + F_2 \rightarrow HF + F$	$V^{\ddagger}_{f}$	1.40	−0.87	−1.04	−3.31	0.48	−1.79
	$V^{\ddagger}_{r}$	104.64	−1.54	101.19	−4.99	95.20	−10.98
$H + N_2 \rightarrow HN_2$	$V^{\ddagger}_{f}$	15.80	1.11	5.05	−9.64	1.93	−12.76
	$V^{\ddagger}_{r}$	8.86	−1.86	1.48	−9.24	−0.53	−11.25
$H + CO \rightarrow HCO$	$V^{\ddagger}_{f}$	4.16	0.99	4.27	1.10	1.77	−1.40
	$V^{\ddagger}_{r}$	27.56	4.88	24.44	1.76	23.42	0.74
$HCN \rightarrow HNC$	$V^{\ddagger}_{f}$	52.29	4.13	52.36	4.20	56.28	8.12
	$V^{\ddagger}_{r}$	34.57	1.46	31.00	−2.11	30.72	−2.39
$H + N_2O \rightarrow OH + N_2$	$V^{\ddagger}_{f}$	−19.27	−37.41	−25.89	−44.03	−8.43	−26.57
	$V^{\ddagger}_{r}$	27.73	−55.49	34.30	−48.92	46.09	−37.13
$H + FCH_3 \rightarrow HF + CH_3$	$V^{\ddagger}_{f}$	22.75	−7.63	31.50	1.12	35.75	5.37
	$V^{\ddagger}_{r}$	47.58	−9.44	52.03	−4.99	53.31	−3.71
$F^- + CH_3F \rightarrow FCH_3 + F^-$	$V^{\ddagger}_{f,r}$	0.00	0.34	−6.28	−5.94	−8.36	−8.02
Set 1 $\lvert\bar{\epsilon}\rvert$			1.88		4.05		5.27
max $\lvert\epsilon\rvert$			4.88		9.64		12.76
Set 2 $\lvert\bar{\epsilon}\rvert$			22.06		21.00		16.16
max $\lvert\epsilon\rvert$			55.49		48.92		37.13
combined $\lvert\bar{\epsilon}\rvert$			8.61		9.70		8.90
max $\lvert\epsilon\rvert$			55.49		48.92		37.13

(RHF, RKS, ROHF, or ROKS) was used (provided convergence was possible) in order to avoid spin contamination of the wave function. These orbitals were then used in an SS-CI calculation to define the target state for the MRMP2 calculation. We carried out analogous calculations using KS orbitals obtained with the popular BLYP[32−34] and B3LYP[35] exchange-correlation functionals. Calculations at the SS-CI level with different types of orbital will be denoted SS−CI(*method*), where *method* refers to the level of theory used to obtain the orbitals. Similarly, perturbation theory calculations will be denoted MRMP2(*method*). When using multireference perturbation theories, it is important to consider the effect of intruder states; in the approach used here, eq 2 is replaced by eq 3. The value of the parameter used to define the energy denominator shifts, b, is that recommended in ref 12 ($b = 0.02$ au). The MRMP2-ISA scheme only makes significant shifts when the denominator is very small, while under normal circumstances, the denominators are changed only slightly. This method is applicable when the intruder state makes a negligible contribution to the target state. When the intruder state makes a significant contribution to the target state, the ISA scheme effectively removes the intruder state from the perturbation expansion. This can cause significant errors in the second-order energy, and other approaches should be sought (e.g., enlarging the active space or using a multistate method); see ref 12 for a full discussion.

All SS-CI/MRMP2 calculations were performed using our in-house codes, which we have interfaced with the Gaussian 03 suite of programs.[36] All atomic orbital integrals were obtained using standard procedures in Gaussian 03.

TABLE 3: Barrier Heights at the MRMP2 Level; Absolute Barriers and Errors (ϵ) Are in kcal mol^{-1}

reaction	barrier	MRMP2 (HF)	ϵ	MRMP2 (B3LYP)	ϵ	MRMP2 (BLYP)	ϵ
$H + FH \rightarrow HF + H$	$V^{\ddagger}_{f,r}$	42.62	0.44	44.45	2.27	45.59	3.41
$H + ClH \rightarrow HCl + H$	$V^{\ddagger}_{f,r}$	16.27	−1.73	16.04	−1.96	18.17	0.17
$H + F_2 \rightarrow HF + F$	$V^{\ddagger}_{f}$	2.12	−0.15	0.55	−1.72	0.91	−1.36
	$V^{\ddagger}_{r}$	105.36	−0.82	102.78	−3.40	95.63	−10.55
$H + N_2 \rightarrow HN_2$	$V^{\ddagger}_{f}$	13.76	−0.93	12.92	−1.77	12.97	−1.72
	$V^{\ddagger}_{r}$	8.97	−1.75	13.26	2.54	14.73	4.01
$H + CO \rightarrow HCO$	$V^{\ddagger}_{f}$	5.47	2.30	1.96	−1.21	2.46	−0.71
	$V^{\ddagger}_{r}$	19.67	−3.01	24.41	1.73	25.84	3.16
$HCN \rightarrow HNC$	$V^{\ddagger}_{f}$	53.31	5.15	52.76	4.60	52.05	3.89
	$V^{\ddagger}_{r}$	35.67	2.56	36.12	3.01	36.23	3.12
$H + N_2O \rightarrow OH + N_2$	$V^{\ddagger}_{f}$	22.80	4.66	42.20	24.06	42.35	24.21
	$V^{\ddagger}_{r}$	80.15	−3.07	99.07	15.85	93.70	10.48
$H + FCH_3 \rightarrow HF + CH_3$	$V^{\ddagger}_{f}$	33.21	2.83	39.65	9.27	42.48	12.10
	$V^{\ddagger}_{r}$	59.29	2.27	59.07	2.05	59.28	2.26
$F^- + CH_3F \rightarrow FCH_3 + F^-$	$V^{\ddagger}_{f,r}$	0.01	0.35	−6.15	−5.81	−7.86	−7.52
Set 1 $\lvert\bar{\epsilon}\rvert$			1.88		2.42		3.21
max $\lvert\epsilon\rvert$			5.15		4.60		10.55
Set 2 $\lvert\bar{\epsilon}\rvert$			2.64		11.41		11.31
max $\lvert\epsilon\rvert$			4.66		24.06		24.21
combined $\lvert\bar{\epsilon}\rvert$			2.13		5.42		5.91
max $\lvert\epsilon\rvert$			5.15		24.06		24.21

TABLE 4: Barrier Heights at the MRMP2-ISA Level; Absolute Barriers and Errors (ϵ) Are in kcal mol^{-1}

reaction	barrier	MRMP2-ISA (HF)	ϵ	MRMP2-ISA (B3LYP)	ϵ	MRMP2-ISA (BLYP)	ϵ
$H + FH \rightarrow HF + H$	$V^{\ddagger}_{f,r}$	42.70	0.52	44.48	2.30	45.58	3.40
$H + ClH \rightarrow HCl + H$	$V^{\ddagger}_{f,r}$	16.61	−1.39	16.30	−1.70	18.27	0.27
$H + F_2 \rightarrow HF + F$	$V^{\ddagger}_{f}$	2.33	0.06	0.66	−1.61	0.91	−1.36
	$V^{\ddagger}_{r}$	105.64	−0.54	102.98	−3.20	95.82	−10.36
$H + N_2 \rightarrow HN_2$	$V^{\ddagger}_{f}$	13.94	−0.75	13.16	−1.53	13.10	−1.59
	$V^{\ddagger}_{r}$	9.09	−1.63	13.33	2.61	14.73	4.01
$H + CO \rightarrow HCO$	$V^{\ddagger}_{f}$	5.57	2.40	2.18	−0.99	2.67	−0.50
	$V^{\ddagger}_{r}$	19.74	−2.94	24.54	1.86	25.96	3.28
$HCN \rightarrow HNC$	$V^{\ddagger}_{f}$	53.35	5.19	52.71	4.55	52.02	3.86
	$V^{\ddagger}_{r}$	35.74	2.63	36.14	3.03	36.24	3.13
$H + N_2O \rightarrow OH + N_2$	$V^{\ddagger}_{f}$	22.58	4.44	41.64	23.50	41.76	23.62
	$V^{\ddagger}_{r}$	80.41	−2.81	99.37	16.15	93.56	10.34
$H + FCH_3 \rightarrow HF + CH_3$	$V^{\ddagger}_{f}$	33.21	2.83	39.67	9.29	42.48	12.10
	$V^{\ddagger}_{r}$	59.22	2.20	59.13	2.11	59.30	2.28
$F^- + CH_3F \rightarrow FCH_3 + F^-$	$V^{\ddagger}_{f,r}$	0.04	0.38	−6.47	−6.13	−7.58	−7.24
Set 1 $\lvert\bar{\epsilon}\rvert$			1.81		2.34		3.18
max $\lvert\epsilon\rvert$			5.19		4.55		10.36
Set 2 $\lvert\bar{\epsilon}\rvert$			2.53		11.44		11.12
max $\lvert\epsilon\rvert$			4.44		23.50		23.62
combined $\lvert\bar{\epsilon}\rvert$			2.05		5.37		5.82
max $\lvert\epsilon\rvert$			5.19		23.50		23.62

4. Results

4.1. MRMP2 Results with SS-CI Reference Wave Functions. In Table 1, we list the database values for the activation barriers we studied. Also shown are the results obtained with the SS-CI wave function built from different orbital sets. From these data, it can be seen that, with a few exceptions, the differences from the database values are quite large. The barrier heights also vary depending on which type of orbital the SS-CI is based on. These results are not so surprising since the dynamic electron correlation is not included to any significant degree. We note for comparison that the CASSCF results for Set 1 produce a mean absolute error of 8.19 kcal mol^{-1}, and the SS-SCF results produce an error of 8.39 kcal mol^{-1}. This gives an indication of the effects of eliminating the orbital relaxation and reducing the full CI expansion. For the SS-CI(HF) case, the mean absolute error is 13.63 kcal mol^{-1} but is significantly reduced when KS orbitals are used. In particular, the BLYP orbitals almost halve the error. When the set of reactions is expanded to include Set 2, the errors grow quite significantly.

In Table 2, MRMP2 results with the inclusion of the $A \rightarrow A$ term are shown. For the reactions of Set 1, MRMP2(HF) + $A \rightarrow A$ performs reasonably well, with a mean absolute error of 1.88 kcal mol^{-1}, whereas the MRMP2(B3LYP) + $A \rightarrow A$ and MRMP2(BLYP) + $A \rightarrow A$ results show considerably worse barriers. The reactions of Set 2 show a degradation of accuracy, with large errors for all methods. By contrast, when the $A \rightarrow A$ term is omitted, the results are much improved for all types of orbital used (Table 3). MRMP2(HF) performs significantly better, with a maximum error of 5.15 kcal mol^{-1} and a mean absolute error of 2.13 kcal mol^{-1}. MRMP2(B3LYP) and MRMP2(BLYP) perform somewhat better when the internal term is omitted; however, they both suffer from unacceptably large maximum errors of 24.06 and 24.21 kcal mol^{-1}, respectively, for the reactions of Set 2. For all methods, inclusion of

TABLE 5: Barrier Heights at the MRMP2-SCS Level; Absolute Barriers and Errors (ϵ) Are in kcal mol^{-1}

reaction	barrier	MRMP2-SCS (HF)	ϵ	MRMP2-SCS (B3LYP)	ϵ	MRMP2-SCS (BLYP)	ϵ
Optimized Parameters	SCS	$p_S = 1.20$ $p_T = 0.31$	$p_S = 1.07$ $p_T = 0.40$	$p_S = 1.07$ $p_T = 0.37$			
$H + FH \rightarrow HF + H$	$V^{\ddagger}_{f,r}$	40.99	−1.19	40.92	−1.26	42.15	−0.03
$H + ClH \rightarrow HCl + H$	$V^{\ddagger}_{f,r}$	17.39	−0.61	16.59	−1.41	17.07	−0.93
$H + F_2 \rightarrow HF + F$	$V^{\ddagger}_{f}$	3.04	0.77	1.12	−1.15	1.08	−1.19
	$V^{\ddagger}_{r}$	105.14	−1.04	97.75	−8.43	90.88	−15.30
$H + N_2 \rightarrow HN_2$	$V^{\ddagger}_{f}$	15.03	0.34	13.67	−1.02	13.63	−1.06
	$V^{\ddagger}_{r}$	10.23	−0.49	11.15	0.43	12.18	1.46
$H + CO \rightarrow HCO$	$V^{\ddagger}_{f}$	5.78	2.61	2.87	−0.30	3.17	0.00
	$V^{\ddagger}_{r}$	23.35	0.67	22.30	−0.38	23.06	0.38
$HCN \rightarrow HNC$	$V^{\ddagger}_{f}$	52.41	4.25	51.28	3.12	50.76	2.60
	$V^{\ddagger}_{r}$	35.23	2.12	34.89	1.78	34.98	1.87
$H + N_2O \rightarrow OH + N_2$	$V^{\ddagger}_{f}$	21.09	2.95	18.15	0.01	18.36	0.22
	$V^{\ddagger}_{r}$	82.95	−0.27	88.88	5.66	85.95	2.73
$H + FCH_3 \rightarrow HF + CH_3$	$V^{\ddagger}_{f}$	30.95	0.57	31.32	0.94	34.22	3.84
	$V^{\ddagger}_{r}$	56.99	−0.03	53.71	−3.31	53.82	−3.20
$F^- + CH_3F \rightarrow FCH_3 + F^-$	$V^{\ddagger}_{f,r}$	0.84	1.18	−4.29	−3.95	−6.00	−5.66
Set 1 $\lvert\bar{\epsilon}\rvert$			1.41		1.93		2.48
max $\lvert\epsilon\rvert$			4.25		8.43		15.30
Set 2 $\lvert\bar{\epsilon}\rvert$			1.00		2.77		3.13
max $\lvert\epsilon\rvert$			2.95		5.66		5.66
combined $\lvert\bar{\epsilon}\rvert$			1.27		2.21		2.70
max $\lvert\epsilon\rvert$			4.25		8.43		15.30

the $A \rightarrow A$ term gives poorer results, particularly for MRMP2-(HF) + $A \rightarrow A$, where the maximum error is more than an order of magnitude larger and the mean absolute error is approximately four times greater than that when the $A \rightarrow A$ term is omitted.

Intruder states are known to cause problems in MRPT. The treatment described above, in eq 3, has been applied here. Table 4 shows the results of the MRMP2-ISA calculations. The results show only a very small improvement over the MRMP2 results. From this, we may conclude that there are no major intruder state problems in any of the reactions considered.

4.2. Spin-Component Scaling in MRMP2 Theory. On the basis of a detailed comparison of low-order perturbation theory results with those of infinite-order analogues (quadratic CI, QCISD/QCISD(T)), Grimme[20] has suggested that single-reference MP2 suffers from a “systematic energy bias toward unpaired electrons”. The correlation energy given by the single-reference MP2 theory can be separated into antiparallel-($\alpha\beta$, “singlet”) and parallel-spin ($\alpha\alpha$ and $\beta\beta$, “triplet”) contributions

$$E_{\mathrm{corr}} = E_{\mathrm{S}} + E_{\mathrm{T}} \tag{20}$$

Grimme has proposed that separate scaling of the $\alpha\beta$ contribution and the $\alpha\alpha$ and $\beta\beta$ contributions to the correlation energy should correct this bias. To this end, parameters are introduced to scale the components of the correlation energy; this is termed spin-component scaling (SCS)

$$E^{\mathrm{SCS}}_{\mathrm{corr}} = p_{\mathrm{S}}E_{\mathrm{S}} + p_{\mathrm{T}}\,E_{\mathrm{T}} \tag{21}$$

Grimme has given the parameters as

$$p_{\mathrm{S}} = \frac{6}{5} \quad p_{\mathrm{T}} = \frac{1}{3} \tag{22}$$

and further details and examples of successful applications may be found in refs 20−24. The scheme is applicable to any correlation scheme, and here, we investigate how it might be used in the context of the MRMP2 method.

A complication arises from the multiconfigurational nature of the reference wave function. The orbital space is partitioned into inactive (i), active (a) and virtual (v) subspaces. In the inactive space, all orbitals are doubly occupied in all reference configurations. The active space orbitals are allowed variable occupancy in the reference wave function, for example, as in a CAS expansion or a restricted expansion such as that of eq 9. The orbitals of the virtual space are unoccupied in the reference wave function. There are nine types of double excitation that must be considered in the MRMP2 expansion, and these may be classified by referring to the two types of orbitals (subspace) the electrons are removed from and the two types of orbital the electrons are excited into, that is

(i) ii → aa
(ii) ii → av
(iii) ii → vv
(iv) ia → aa
(v) ia → av
(vi) ia → vv
(vii) aa → aa
(viii) aa → av
(ix) aa → vv (23)

The excitations in eq 23vii are the $A \rightarrow A$-type terms referred to above and need not be considered for CASSCF/CASCI-type reference states as these are already included in the reference wave function. We have observed above that it is beneficial to omit these terms in the perturbation expansion. In applying the SCS to a multireference expansion, we encounter a complication. This is because the determinants arising from eq 23iv, v, vii, and viii cannot be unambiguously considered as $\alpha\beta$ or $\alpha\alpha/\beta\beta$ double excitations. To illustrate the point, consider an example in which the orbitals are partitioned is as follows: $\{\phi_1,\phi_2\}_{\mathrm{inactive}}$;

$\{\phi_3 - \phi_6\}_{\text{active}}$ and $\{\phi_7,\phi_8,...\}_{\text{virtual}}$. Now, consider an excitation of the type in eq 23iv, for example

$$\hat{E}^{\alpha}_{5,1}\hat{E}^{\beta}_{5,3}|\phi_1\phi_2\phi_3\phi_4\bar{\phi}_1\bar{\phi}_2\bar{\phi}_3\bar{\phi}_4\rangle = |\phi_5\phi_2\phi_3\phi_4\bar{\phi}_1\bar{\phi}_2\bar{\phi}_5\bar{\phi}_4\rangle$$
$$= -\hat{E}^{\alpha}_{5,1}|\phi_1\phi_2\phi_3\phi_4\bar{\phi}_1\bar{\phi}_2\bar{\phi}_4\bar{\phi}_5\rangle \qquad (24)$$

This $\alpha\beta$ double excitation is equivalent to a single excitation of α-type from a different reference configuration. Hence, we are left with the question as to whether we scale the contribution as part of E_S or E_T in eq 21. It is simple to show that a similar situation holds for the excitations given in eq 23v, vii, and viii, as well. In applying the SCS to the results presented here, we have excluded the SCS for the terms mentioned, and we apply the scaling only to determinants arising from eq 23i, ii, iii, vi, and ix.

Table 5 shows the results of MRMP2-SCS calculations on the two reaction sets. The parameters were optimized for each type of orbital set by minimizing the rms error obtained for all 15 barriers. It is encouraging to find that our optimized values of the parameters for HF orbitals are very close to Grimme's original values of $p_S = 1.20$ and $p_T = 0.33$. For the case of B3LYP and BLYP orbitals, the parameters are somewhat different; the results are also less satisfactory, with maximum errors for B3LYP orbitals twice as large as those obtained with the HF orbitals (with BLYP orbitals, the maximum error is almost four times larger). The MRMP2-SCS(HF) results are the best we obtain, and we recommend that this procedure be used in general with Grimme's original parameters.

Finally, we notice consistently from Tables 3−5 that the errors obtained when the reference wave function is built from HF orbitals is smaller than those obtained when KS orbitals are used. In contradiction to this observation, we would generally expect orbitals obtained in the presence of correlation (i.e., KS) to be superior to those obtained from the HF method. To understand the origin of this, we need to recall that the expansion used here consists of all double excitations from the reference wave function. If the reference wave function contains a complete expansion (CASSCF/CASCI), then the single excitations are linear combinations of the double replacements. When the CI expansion is not complete in the active space, as in this work, then there will be a contribution from the single excitations, which we have not included. However, the better the approximation to the complete expansion, the less significant will be this omission. In the HF method, at convergence, the occupied virtual block of the Fock matrix is zero by Brillouin's theorem. When (for multireference treatment) the active space is chosen, some of the occupied orbitals become active orbitals, and some of the virtual orbitals also become active orbitals. The generalized Fock operator in eq 1 is then canonicalized within each of the inactive, active, and virtual subspaces. This mixing of the (HF) occupied orbitals with the virtual orbitals in the active space eliminates the Brillouin condition between these orbitals. However, the Brillouin condition between the (HF) occupied and virtual orbitals that are not in the active space is maintained. This Brillouin condition applies only between the HF determinant and a single excitation from it, but provided that the multireference wave function is dominated by the HF determinant (even in the presence of many other significant contributions), this will reduce the significance of the singles contribution. By contrast, the Brillouin theorem does not apply to KS orbitals at all, and when KS orbitals are used, the singles contribution must be included. We have not included the singles contribution in our calculations and believe this is what accounts for the superiority of the results obtained using HF orbitals.

5. Conclusions

The reliability of the MRMP2 method has been assessed with non-MCSCF/non-CASSCF-optimized orbitals and a truncated CI space. This work suggests that HF orbitals (RHF, UHF, or ROHF) with an SS-CI expansion within a full valence shell active space provides a reliable and relatively cheap reference wave function for MRMP2 calculations. For example, the largest active space used here is for the reaction in eq 19, which involves 22 electrons in 15 orbitals. For a CASSCF (or CASCI) wave function, this would give 1 863 225 determinants, which, though quite achievable, would be very time-consuming in comparison to the SS-CI having just 2025 determinants. The results can be further improved by using the SCS scheme, and the choice of active space orbitals is essentially automatic given a converged set of HF or KS orbitals. This should enable the application of MRPT to larger systems since there are no MCSCF convergence problems to deal with and the number of determinants in the active space grows quite modestly with the number of active orbitals.

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