

## CASCI Reference Wave Functions for Multireference Perturbation Theory Built from Hartree–Fock or Kohn–Sham Orbitals

David Robinson and Joseph J. W. McDouall\*

*School of Chemistry, The University of Manchester, Oxford Road,  
Manchester M13 9PL, U.K.*

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**Abstract:** The MRMP2 method and many similar variants of multireference perturbation theory have a potentially wide range of applicability. However they typically require a CASSCF calculation to define the reference wave function. It is worthwhile to investigate whether ‘simpler’ orbitals than those obtained from the full CASSCF procedure can provide useful accuracy. In this study we investigate six reactions taken from the Zhao–González-García–Truhlar database and investigate the MRMP2 procedure when used with a variety of different orbital sets in order to assess the reliability of such procedures. The results are encouraging and suggest that multireference perturbation theory may be used, for some systems, with the simplified procedures presented here.

### 1. Introduction

In studying the electronic structure of molecules there are many well-known situations that require a many determinant approach in order to obtain a description that is even qualitatively correct. Examples of such situations include the following: the computation of potential energy curves far from equilibrium; certain types of excited states; the location of transition structures containing diradical character; and the mapping of complete reaction paths. The most commonly used multideterminant method is the complete active space self-consistent field (CASSCF) method,<sup>1</sup> that deals with the nondynamic (structure-dependent) correlation, but does not account for the dynamic electron correlation to any significant degree. The dynamic electron correlation must be dealt with by the multireference analogues of perturbation,<sup>2</sup> configuration interaction,<sup>3</sup> and coupled-cluster<sup>4</sup> theories. In particular among these methods are a number of multireference perturbation theories<sup>5–11</sup> that have been developed and applied with considerable success. The popularity of these methods stems from their relative computational efficiency. This gives a manageable cost/accuracy ratio for dealing with multiconfigurational problems.

The use of CASSCF based methods presents additional levels of complexity for the user when compared with single reference methods. The most obvious conceptual challenge is to choose a meaningful active space for describing a given chemical problem.<sup>12</sup> Assuming this can be done reliably, the next challenge is to converge the CASSCF wave function. Each cycle of the CASSCF orbital optimization involves a partial integral transformation from the atomic orbital to the molecular orbital basis. When large active spaces are used, a substantial CI eigenvalue problem must also be solved in each cycle. These factors make the CASSCF procedure relatively demanding in terms of computational resources. A number of groups<sup>13–16</sup> 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. In a recent paper<sup>17</sup> we have also studied this matter for the case of the  $X^1\Sigma_g^+$ ,  $B^1\Delta_g$ , and  $B'^1\Sigma_g^+$  state potential energy curves of the  $C_2$  molecule. We used complete active space configuration interaction (CASI) reference wave functions in a multireference perturbation theory scheme. The CASI wave functions were built from Hartree–Fock or Kohn–Sham orbitals with no further refinement of the orbital sets. The  $C_2$  potential energy curves provide demanding multiconfigurational test cases for which full CI results have been published. In comparing our

\* Corresponding author phone: +44 (0)161-275-4720; fax: +44 (0)161-275-4598; e-mail: joe.mcdouall@manchester.ac.uk.

**Table 1.** Reference Values for the Forward ( $V_f^\infty$ ) and Reverse ( $V_r^\infty$ ) Reaction Barriers (kcal mol<sup>-1</sup>) for Reactions 1–6 Taken from the Minnesota Database Collection<sup>18,19</sup>

	reaction	barrier	database value
1	H + FH → HF + H	$V_{fr}^\infty$	42.18
2	H + ClH → HCl + H	$V_{fr}^\infty$	18.00
3	H + F <sub>2</sub> → HF + F	$V_f^\infty$	2.27
		$V_r^\infty$	106.18
4	H + N <sub>2</sub> → HN <sub>2</sub>	$V_f^\infty$	14.69
		$V_r^\infty$	10.72
5	H + CO → HCO	$V_f^\infty$	3.17
		$V_r^\infty$	22.68
6	HCN → HNC	$V_f^\infty$	48.16
		$V_r^\infty$	33.11

calculations with the benchmark results we found that reliable results were obtained with a variety of orbitals provided that the region of interest was not too far from equilibrium. For accurate reproduction of full potential energy curves only the curves built from fully optimized CASSCF orbitals were adequate. However, since many studies are primarily concerned with regions of the potential energy surface not too far from equilibrium, one would like to encourage the use of orbitals generated by simpler techniques, provided that the results remain consistent in a wide range of applications. This will be important in enabling multireference perturbation theory methods to be applied to a wider variety of systems, given that the CASSCF step in the calculations is avoided.

In this work we wish to investigate whether the encouraging results we obtained in the study of diatomic potential energy curves carry over to the study of chemical reactions. In particular, transition states often possess electronic structures that are multideterminantal in nature, as they are typically intermediate between two different bonding situations. Zhao, González-García, and Truhlar<sup>18,19</sup> have produced a database of barrier heights for heavy atom transfer, nucleophilic substitution, and unimolecular and association reactions. We have chosen 6 examples, (1)–(6) below, from this database with which to test our procedure.



Calculating forward and backward reactions gives 10 barrier heights for comparison with our calculations. Reactions 1–5 possess an overall spin,  $s = 1/2$ , and so refer to doublet surfaces. Reaction 6, with  $s = 0$ , refers to a singlet surface. Table 1 collects the database reference values for the barrier heights.

These reference values have been obtained by the WI theory as described in ref 18 and include corrections for a variety of factors including relativistics, core correlation, and

spin–orbit effects. For the reactions we have studied, the net effect of these additional corrections is on average <0.07 kcal mol<sup>-1</sup> with a maximum correction of 0.43 kcal mol<sup>-1</sup> for reaction 3. Hence it is acceptable to compare our computed results directly with these reference values.

## 2. Computational Details

Our multireference perturbation theory program follows the multireference second-order Møller–Plesset perturbation theory (MRMP2) formalism of Hirao.<sup>7–9</sup> In this approach, the first-order density matrix,  $\gamma$ , obtained from the full CI expansion in the chosen active space is used to construct the matrix representation of the generalized Fock operator,  $F$ :

$$F_{pq} = h_{pq} + \sum_{ij}^{\text{occupied}} \gamma_{ij} \left[ (pq | ij) - \frac{1}{2} (pj | iq) \right] \quad (7)$$

For a CASCI 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

$$E_p^{(2)} = - \sum_Q \frac{|\langle Q | H | P \rangle|^2}{E_Q^{(0)} - E_p^{(0)}} \quad (8)$$

The CASSCF or CASCI state is labeled by  $P$ , and  $Q$  refers to one of the set of all allowed double excitations between the orbital subspaces. Calculations based on (7) and (8) with different types of orbital are denoted as the MRMP2(*method*), where *method* refers to the level of theory used to define the orbitals. We have investigated orbitals obtained from Hartree–Fock (HF) and Kohn–Sham (KS) calculations, the latter using the B3LYP and BLYP exchange–correlation functionals. Hence we report results at the MRMP2-(CASSCF), MRMP2(HF), MRMP2(BLYP), and MRMP2-(B3LYP) levels.

The issue of intruder states is important in multireference perturbation theory. A simple scheme has been developed for intruder state avoidance (ISA) within the formalism of Hirao's MRMP2.<sup>20,21</sup> In this approach, eq 8 is modified by introducing a shift in the denominator

$$E_p^{(2)-\text{ISA}} = - \sum_Q \frac{|\langle Q | H | P \rangle|^2}{E_Q^{(0)} - E_p^{(0)} + \Delta_Q}, \quad \text{where } \Delta_Q = \frac{b}{E_Q^{(0)} - E_p^{(0)}} \quad (9)$$

We have also recalculated all results using this technique. The value of the parameter,  $b$ , which is used to define the energy denominator shifts, is that recommended in ref 21 ( $b = 0.02$ ). These results are denoted as the MRMP2-ISA-(*method*).

All geometries were taken from ref 19 and refer to the QCISD/MG3 level. The MG3 basis consists of the 6-311++G(3d2f,2df,2p)<sup>22</sup> basis set for the atoms H–Si, with an extended basis for atoms P–Ar.<sup>23,24</sup> The calculations we report use the MG3S basis, which is equivalent to the MG3

**Table 2.** Barrier Heights for Reactions 1–6 at the CASSCF, MRMP2(CASSCF), and MRMP2-ISA(CASSCF) Levels<sup>a</sup>

reaction	barrier	CASSCF	€	MRMP2	€	MRMP2-ISA	€
1	$V_{fr}^{\ddagger}$	55.08	12.90	41.62	−0.56	41.77	−0.41
2	$V_{fr}^{\ddagger}$	29.08	11.08	17.23	−0.77	17.35	−0.65
3	$V_f^{\ddagger}$	7.66	5.39	2.04	−0.23	2.09	−0.18
	$V_r^{\ddagger}$	105.48	−0.70	104.19	−1.99	104.27	−1.91
4	$V_f^{\ddagger}$	26.34	11.65	14.56	−0.13	14.69	0.00
	$V_r^{\ddagger}$	−0.56	11.28	11.74	1.02	11.74	1.02
5	$V_f^{\ddagger}$	10.02	6.85	3.36	0.19	3.42	0.25
	$V_r^{\ddagger}$	11.16	−11.52	22.86	0.18	22.85	0.17
6	$V_f^{\ddagger}$	53.89	5.73	48.38	0.22	48.42	0.26
	$V_r^{\ddagger}$	37.49	4.38	33.55	0.44	33.57	0.46
€			8.15		0.57		0.53
max  €			12.90		1.99		1.91

<sup>a</sup> Absolute values and errors (€) are given in kcal mol<sup>−1</sup>.

basis except for the case of H atom, for which the diffuse functions are excluded. We also include a wider study of basis set influence, which is given in the Supporting Information and discussed at the end of the next section. 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, and a detailed discussion can be found in refs 25 and 26.

In all cases, a HF or KS calculation was run, followed by a wave function stability analysis and, if necessary, reoptimization of the wave function. For stable wave functions, spin-restricted calculations (for closed- and open-shell systems, respectively) were used to generate the initial orbitals for the CASSCF calculation. In the cases where wave function instabilities were found, the spin-unrestricted natural orbitals were used as the initial orbitals for the CASSCF calculation. The same initial orbitals were also used, without further optimization, to perform a CASCI calculation to define the target state used in MRMP2 calculations. The active space in all calculations consists of the full valence shell orbitals of all atoms. The CASSCF/CASCI and MRMP2/MRMP2-ISA calculations were performed using our in-house codes which we have interfaced with the Gaussian 03 suite of programs.<sup>27</sup> All atomic orbital integrals were obtained using standard procedures in Gaussian 03, as were the HF, BLYP, B3LYP, and stability calculations.

### 3. Results

We begin with the CASSCF and MRMP2(CASSCF) and MRMP2-ISA(CASSCF) results, given in Table 2. The MRMP2 and MRMP2-ISA calculations based on CASSCF orbitals are our best estimates of the barriers for reactions 1–6.

As is to be expected the CASSCF results show significant errors, since no appreciable account of the effects of dynamic electron correlation is included at this level. The MRMP2-(CASSCF) results show good agreement with the database values. With a full valence shell active space and a large basis set, the MRMP2(CASSCF) method should provide

**Table 3.** Barrier Heights for Reactions 1–6 Obtained from CASCI Wave Functions Built from HF, B3LYP, and BLYP Orbitals<sup>a</sup>

reaction	barrier	CASCI-(HF)	€	CASCI-(B3LYP)	€	CASCI-(BLYP)	€
1	$V_{fr}^{\ddagger}$	41.96	−0.22	57.42	15.24	56.14	13.96
2	$V_{fr}^{\ddagger}$	40.49	22.49	19.66	1.66	21.00	3.00
3	$V_f^{\ddagger}$	44.41	42.14	4.45	2.18	11.57	9.30
	$V_r^{\ddagger}$	127.93	21.75	94.53	−11.65	107.12	0.94
4	$V_f^{\ddagger}$	−33.17	−47.86	31.46	16.77	30.36	15.67
	$V_r^{\ddagger}$	−5.17	−15.89	−0.86	−11.58	−3.95	−14.67
5	$V_f^{\ddagger}$	10.61	7.44	15.66	12.49	13.81	10.64
	$V_r^{\ddagger}$	60.52	37.84	8.84	−13.84	4.52	−18.16
6	$V_f^{\ddagger}$	43.01	−5.15	40.95	−7.21	43.38	−4.78
	$V_r^{\ddagger}$	33.16	0.05	30.22	−2.89	30.54	−2.57
€			20.08		9.55		9.37
max  €			47.86		16.77		18.16

<sup>a</sup> Absolute values and errors (€) are given in kcal mol<sup>−1</sup>.

good accuracy and the mean absolute error of 0.57 kcal mol<sup>−1</sup> is very acceptable. The MRMP2-ISA(CASSCF) results show a slight improvement over the MRMP2(CASSCF) giving a mean absolute error of 0.53 kcal mol<sup>−1</sup>. Considering the shift,  $\Delta_Q$ , in eq 9, its effect is to essentially remove the contribution of a double excitation from the perturbation expansion if the energy of that determinant approaches the energy of the reference state. If the contribution of such an intruder state is significant, then eq 9 will not correct the situation, and a substantial error in the perturbation energy may be expected. In such circumstances one must either expand the reference space to include the intruder state or use a multistate method. Given the relatively small effect on the barriers dealt with here, we may conclude that there are no major intruder state problems associated with the systems studied.

We next consider the barrier heights calculated using a CASCI reference wave function, in which the CAS expansion is built from orbitals obtained by standard HF or KS methods. As with the CASSCF results, the CASCI errors are generally quite large and can be attributed to the lack of sufficient dynamical correlation within the CASCI wave function. It is noteworthy that the average error obtained with HF orbitals is significantly larger than when KS orbitals are employed. Typically the KS orbitals reduce the average error by a factor of 2, and the maximum error is reduced by a factor of approximately 3. Table 3 gives the relevant results.

Now adding the dynamic electron correlation we find that the MRMP2 correction to the CASCI reference shows quite good agreement with the database values. The mean absolute errors are 1.43, 1.40, and 1.87 kcal mol<sup>−1</sup> for MRMP2(HF), MRMP2(B3LYP), and MRMP2(BLYP), respectively. The results are shown in Table 4. The HF and B3LYP orbitals behave quite similarly, whereas the BLYP orbitals show significantly increased mean and maximum errors.

In the case of the HF and B3LYP orbitals, the maximum error occurs for reaction 6. Comparing the CI vectors for the CASCI wave functions with that of the CASSCF reveals a need for CASSCF orbitals in this case. In HCN, the contribution of the determinants describing the  $\pi \rightarrow \pi^*$  (doubly degenerate) excitation is underestimated via the CASCI methods. In the CASSCF calculation the HF

**Table 4.** Barrier Heights for Reactions 1–6 Obtained from MRMP2 Calculations in Which the Reference CASCI Wave Function Is Built from HF, B3LYP, and BLYP Orbitals<sup>a</sup>

reaction	barrier	MRMP2- (HF)	€	MRMP2- (B3LYP)	€	MRMP2- (BLYP)	€
1	$V_{f,r}^{\text{cc}}$	42.42	0.24	40.98	-1.20	40.92	-1.26
2	$V_{f,r}^{\text{cc}}$	16.30	-1.70	17.26	-0.74	17.87	-0.13
3	$V_f^{\text{cc}}$	2.31	0.04	1.42	-0.85	0.57	-1.70
	$V_r^{\text{cc}}$	105.22	-0.96	103.65	-2.53	100.35	-5.83
4	$V_f^{\text{cc}}$	15.11	0.42	13.04	-1.65	13.17	-1.52
	$V_r^{\text{cc}}$	10.07	-0.65	10.92	0.20	12.04	1.32
5	$V_f^{\text{cc}}$	5.30	2.13	1.97	-1.20	2.27	-0.90
	$V_r^{\text{cc}}$	23.89	1.21	23.01	0.33	23.91	1.23
6	$V_f^{\text{cc}}$	52.95	4.79	51.55	3.39	51.06	2.90
	$V_r^{\text{cc}}$	35.31	2.20	34.97	1.86	35.00	1.89
$ \bar{\epsilon} $			1.43		1.40		1.87
max $ \epsilon $			4.79		3.39		5.83

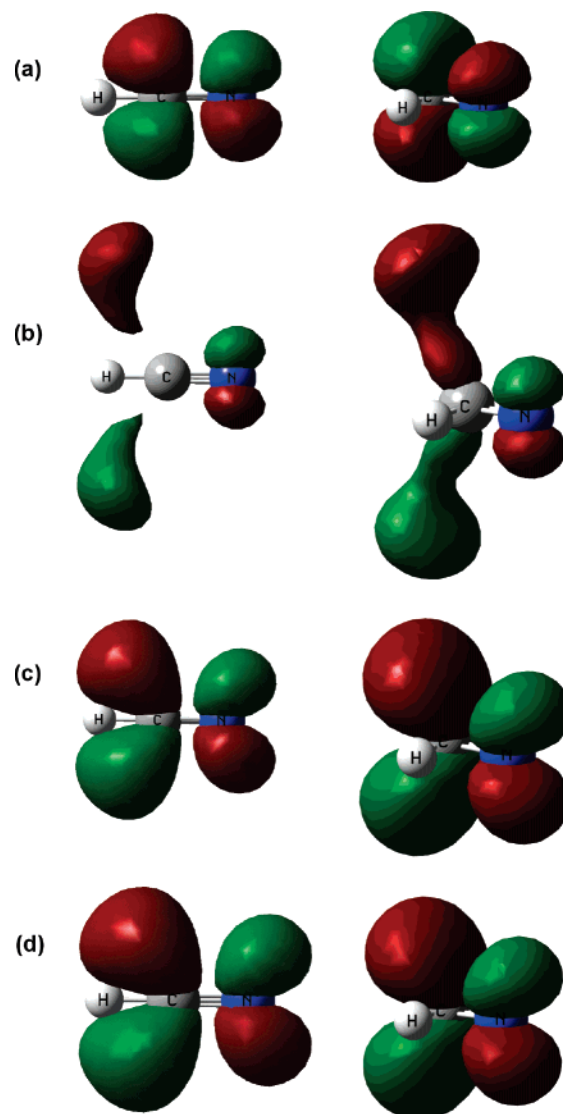
<sup>a</sup> Absolute values and errors ( $\epsilon$ ) are given in kcal mol<sup>-1</sup>.

determinant has a coefficient of 0.961, and the  $\pi \rightarrow \pi^*$  excitations have a coefficient of -0.111. When HF orbitals are used the coefficient of the HF determinant in the CASCI wave function is 0.998, with negligible contribution from the  $\pi \rightarrow \pi^*$  excitations. The situation is somewhat improved when KS orbitals are used, and the coefficients then become for B3LYP orbitals 0.976 (HF determinant) and -0.103 ( $\pi \rightarrow \pi^*$  excitations). BLYP orbitals produce coefficients of 0.970 (HF determinant) and -0.114 ( $\pi \rightarrow \pi^*$  excitations). In the transition structure, a similar situation is found. In Figure 1, one of the symmetry unique  $\pi^*$  orbitals of HCN and the corresponding orbital in the transition structure are shown for the different levels of theory considered. These are the orbitals obtained following canonicalization and are shown on an equal scale and orientation and so may be directly compared. On the left-hand side is shown the reactant and on the right-hand side the transition structure. Looking down either column of Figure 1 we immediately note that the most compact  $\pi^*$  orbitals are obtained by the full CASSCF optimization, Figure 1(a). Conversely the most diffuse orbitals are obtained by the HF procedure, Figure 1(b). The KS orbitals (Figure 1(c),(d)) are intermediate between those of the CASSCF and HF orbitals. The B3LYP orbitals are slightly more compact for HCN than the BLYP orbitals; however, both sets of KS orbitals show an exaggerated polarization of the lobes away from each other. These are subtle effects but clearly have an effect on the CI coefficients and consequently the predicted barrier heights.

Clearly the poor description of these virtual orbitals by the non-CASSCF methods leads to the underestimation of the above determinants in the CASCI wave functions.

Finally the MRMP2-ISA results are shown in Table 5. Small improvements are observed for the KS orbitals, while the HF results change by only 0.01 kcal mol<sup>-1</sup> on average. There is no significant difference between the results with and without the ISA corrections, implying that the set of reactions chosen is not plagued by intruder state problems.

**3.1. Influence of Basis Sets.** To assess the influence of a basis set on the MRMP2 procedures we also carried out calculations on the reaction set using the cc-pVDZ and cc-

**Figure 1.** Canonical  $\pi^*$  orbitals of HCN (left-hand side) and the isomerization transition state (right-hand side) shown at an isosurface value of 0.05 au obtained by different methods: (a) CASSCF, (b) HF, (c) B3LYP, and (d) BLYP.

pVTZ basis sets of Dunning.<sup>28,29</sup> The detailed results can be found in the Supporting Information.

For the CASSCF results, the mean absolute errors are 8.47 kcal mol<sup>-1</sup>, 8.41 kcal mol<sup>-1</sup>, and 8.15 kcal mol<sup>-1</sup> for the cc-pVDZ, cc-pVTZ, and MG3S bases, respectively. At the CASCI(HF) level, the mean absolute errors are 10.39 kcal mol<sup>-1</sup> (cc-pVDZ), 10.37 kcal mol<sup>-1</sup> (cc-pVTZ), and 20.08 kcal mol<sup>-1</sup> (MG3S). The large discrepancy between the correlation consistent bases and the MG3S must be attributed to the presence of diffuse functions in the latter, since the MG3S and cc-pVTZ bases are quite similar in other respects. Additionally, the MG3S basis includes *3d2f* polarization functions for chlorine (reaction 2), whereas the cc-pVTZ includes only *2d1f* polarization functions. This interpretation is also borne out by the HF orbitals shown in Figure 1(b). The KS orbitals do not show the same dependence on the presence of diffuse functions, and we find that for the CASCI(B3LYP) level the mean absolute errors are 10.09 kcal mol<sup>-1</sup> (cc-pVDZ), 10.25 kcal mol<sup>-1</sup> (cc-pVTZ), and 9.55



**Table 5.** Barrier Heights for Reactions 1–6 Obtained from MRMP2-ISA Calculations in Which the Reference CASCI Wave Function Is Built from HF, B3LYP, and BLYP Orbitals<sup>a</sup>

reaction	barrier	MRMP2- (HF)	€	MRMP2- (B3LYP)	€	MRMP2- (BLYP)	€
1	$V_{f,r}^{\text{cc}}$	42.47	0.29	41.11	−1.07	41.12	−1.06
2	$V_{f,r}^{\text{cc}}$	16.64	−1.36	17.36	−0.64	17.98	−0.02
3	$V_f^{\text{cc}}$	2.47	0.20	1.45	−0.82	0.57	−1.70
	$V_r^{\text{cc}}$	105.36	−0.82	103.76	−2.42	100.51	−5.67
4	$V_f^{\text{cc}}$	14.92	0.23	13.43	−1.26	13.57	−1.12
	$V_r^{\text{cc}}$	10.10	−0.62	10.98	0.26	12.02	1.30
5	$V_f^{\text{cc}}$	5.37	2.20	2.22	−0.95	2.51	−0.66
	$V_r^{\text{cc}}$	24.24	1.56	23.13	0.45	24.04	1.36
6	$V_f^{\text{cc}}$	52.99	4.83	51.51	3.35	51.03	2.87
	$V_r^{\text{cc}}$	35.38	2.27	34.99	1.88	35.02	1.91
€			1.44		1.31		1.77
max  €			4.83		3.35		5.67

<sup>a</sup> Absolute values and errors (€) are given in kcal mol<sup>−1</sup>.**Table 6.** Mean and Maximum Absolute Errors (kcal Mol<sup>−1</sup>) in Barrier Heights for Reactions 1–6 Obtained with Different Types of Orbitals

method		orbitals used to build CASCI reference space			
		CASSCF	HF	B3LYP	BLYP
CASCI	€	8.15	20.08	9.55	9.37
	max  €	12.90	47.86	16.77	18.16
MRMP2	€	0.59	1.43	1.40	1.87
	max  €	1.99	4.79	3.39	5.83
MRMP2-ISA	€	0.53	1.44	1.31	1.77
	max  €	1.91	4.83	3.35	5.67

kcal mol<sup>−1</sup> (MG3S). The situation changes slightly at the CASCI(BLYP) level, see the Supporting Information.

For the MRMP2(CASSCF) level, the mean absolute errors are 2.56 kcal mol<sup>−1</sup> (cc-pVDZ), 1.05 kcal mol<sup>−1</sup> (cc-pVTZ), and 0.57 kcal mol<sup>−1</sup> (MG3S). The influence of the diffuse functions is much reduced at the MRMP2(HF) level, which gives mean absolute errors of 2.13 kcal mol<sup>−1</sup> (cc-pVDZ), 1.13 kcal mol<sup>−1</sup> (cc-pVTZ), and 1.43 kcal mol<sup>−1</sup> (MG3S). Finally, at the MRMP2(B3LYP) level we find errors of 2.00 kcal mol<sup>−1</sup> (cc-pVDZ), 1.24 kcal mol<sup>−1</sup> (cc-pVTZ), and 1.40 kcal mol<sup>−1</sup> (MG3S). We may conclude that for quantitative accuracy a large basis set (better than cc-pVDZ) is required.

#### 4. Conclusions

This study has looked at the feasibility of using orbitals obtained from simpler methods than CASSCF optimization for building reference wave functions for multireference perturbation theory. However one must be conscious of the errors that can be introduced by adopting such a strategy, for example, the generalized Brillouin conditions of CASSCF theory are not satisfied, and some multireference perturbation theories (including MRMP2) are built on the assumption that these conditions are met. Table 6 summarizes our findings. We believe these results suggest that our strategy of avoiding the CASSCF step and using HF or B3LYP orbitals can be justified for many situations, though not for all. We are investigating other simplifications that may be applied to

multireference perturbation theory calculations. Ultimately we hope to see the methodology adopted for a much larger class of problems than has traditionally been the case. The elimination of the CASSCF step in the process should go a ways in achieving this aim.

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**Supporting Information Available:** Detailed results with the cc-pVDZ and cc-pVTZ basis sets. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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