

## A Single Reference Perturbation Theory beyond the Møller–Plesset Partition

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**Abstract:** A new single reference perturbation partition is proposed for restricted open-shell Hartree–Fock (ROHF) and complete active space self-consistent field (CASSCF) orbitals. It is a sum of one-particle operator which is implicitly defined. When the operator acts on a ROHF or CASSCF orbital, the resultant eigenvalue is the orbital's corresponding orbital energy coming from the ROHF or CASSCF calculation. HF, F<sub>2</sub>, and N<sub>2</sub> with stretched bonds are used for the size extensivity test. Results indicate that the first three-order energies calculated with the new partition are size extensive. Single reference perturbation calculations for H<sub>2</sub>O, NH<sub>3</sub>, and CH<sub>4</sub> with CASSCF orbitals have been performed and compared with other methods like MRCI, MRCI+Q, MRPT2, and MRPT3. The single reference nature of the present perturbation theory is also shown with computations of the singlet–triplet separation of the CH<sub>2</sub> and SiH<sub>2</sub> radicals.

### 1. Introduction

The Rayleigh–Schrödinger perturbation theory with the Møller–Plesset partition (MP)<sup>1</sup> has been widely used in electronic structure calculations because of its inexpensive computational cost and size extensivity. MP partition is defined as a sum of the Fock operator which is only valid for restricted closed-shell problems. For open-shell problems, unrestricted Hartree–Fock (UHF), restricted open-shell Hartree–Fock (ROHF), and complete active space self-consistent field (CASSCF) computations are usually performed instead. Because of spin contamination, the UHF wave function and its corresponding MP perturbation series will not be discussed here further. Because no single particle operator is properly defined for ROHF and CASSCF orbitals, the application of MP perturbation series is largely limited. Although Epstein–Nesbet partition<sup>2</sup> can be used sometimes as an alternative, yet its corresponding perturbation series are not size extensive.<sup>3</sup> It is because the perturbation series are not invariant with respect to the orbital unitary transformation.<sup>4</sup>

Encouraged by the success of the MP partition for restricted closed-shell problems, many perturbation approaches<sup>3,5–19</sup> have been attempted for open-shell problems. The basic strategy is to define an analogous single particle

operator such as the Fock operator based on a physical intuition or a mathematical consideration. Among these methods, to list just a few, there are opt1 and opt2,<sup>6</sup> and MROPT,<sup>7</sup> of Davidson's group, and MRMP2<sup>8</sup> of Hirao, CASPT2 and CASPT3 of Roos.<sup>11</sup> The interested reader can find more details from ref 20.

Rintelman et al.<sup>21</sup> investigated extensively the size extensivity problem of MRMP2<sup>8</sup> and CASPT2<sup>11</sup> with a series of basis sets and three challenging molecules, HF, N<sub>2</sub>, and F<sub>2</sub>, which are stretched away from their equilibrium geometries to have some multireference character. Rolik et al. presented a multireference perturbation theory.<sup>17</sup> Szabados et al. reformulated it later and obtained a size extensive second-order theory.<sup>18</sup> However, higher orders of the series violate the size-extensivity requirement. On the basis of the multireference perturbation theory by Chen et al.,<sup>22</sup> we derived a size extensive second-order multireference perturbation theory through a theoretical analysis on a supermolecule consisting of *N* noninteracting H<sub>2</sub> molecules.<sup>19</sup>

In this paper, a new single reference perturbation partition is proposed for ROHF and CASSCF orbitals. The size extensivity as well as the accuracy of the first three-order perturbation energies based on this partition will be examined numerically. The single reference nature of the present partition will also be investigated with the CH<sub>2</sub> and SiH<sub>2</sub> radicals.

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## 2. Theory

ROHF and CASSCF are two common approaches for open-shell problems. CASSCF are also widely used to account for the nondynamic correlation energy in multireference problems. ROHF orbitals and orbital energies are obtained for a given system by minimizing its electronic energy  $E^{37}$

$$E = 2 \sum_k \langle k | \hat{h} | k \rangle + \sum_{k,l} [2 \langle kl | \hat{g} | kl \rangle - \langle kl | \hat{g} | lk \rangle] + \\ f(2 \sum_m \langle m | \hat{h} | m \rangle + f \sum_{m,n} [2a \langle mn | \hat{g} | mn \rangle - b \langle mn | \hat{g} | nm \rangle] + \\ 2 \sum_k \sum_m [2 \langle km | \hat{g} | km \rangle - \langle km | \hat{g} | mk \rangle])$$

where  $a$ ,  $b$ , and  $f$  are constants, indices  $k$  and  $l$  are used for closed-shell orbitals,  $m$  and  $n$  for open-shell orbitals,  $\hat{h}$  and  $\hat{g}$  are one- and two-particle operators respectively. A CASSCF wave function for a given system has the following form

$$\Psi = \sum_k c_k \Phi_k$$

where  $\Phi_k$  is a configuration function. These configurations are constructed by a complete distribution of a number of active electrons among a set of active orbitals.<sup>38</sup> The CASSCF wave function can be regarded as a small full configuration interaction function. But it is optimized variationally not only with respect to the expansion coefficients  $c_k$  but also with respect to the orbitals within the configuration  $\Phi_k$ .

In order to apply Rayleigh–Schrödinger perturbation theory to the problems discussed above a zero-th Hamiltonian should be defined at first. Similar to the Fock operator, a single particle operator  $\hat{F}$  for a ROHF or CASSCF orbital  $\phi_i$  is defined implicitly below

$$\hat{F}\phi_i = \varepsilon_i \phi_i \quad (1)$$

provided that all orbitals are orthonormalized with each other. The eigenvalue  $\varepsilon_i$  is the orbital energy of the corresponding orbital  $\phi_i$ , which is originally from a ROHF or CASSCF calculation. For a restricted closed-shell problem the operator  $\hat{F}$  is reduced to the Fock operator. For other cases, an explicit form of the operator  $\hat{F}$  is in general unknown or maybe does not exist in reality. However, the information given in eq 1 is enough to define the zero-th Hamiltonian  $\hat{H}_0$  in Rayleigh–Schrödinger perturbation theory. Of course, some kind of generalized Fock operator may be defined explicitly for these cases. However, the reason that we do not follow this approach is that the orbitals optimized with ROHF and CASSCF have been well tested and widely used for years.

Corresponding to the single particle operator  $\hat{F}$  in eq 1, the zero-th Hamiltonian  $\hat{H}_0$  has the following form

$$\hat{H}_0 = \sum_i \hat{F}(i) \quad (2)$$

The summation in the above equation is carried out over all electrons in a system of interest. It is assumed that the eigenvalues and eigenfunctions of  $\hat{H}_0$  are known as

$$\hat{H}_0 \Phi_i^{(0)} = E_i^{(0)} \Phi_i^{(0)}, \quad i = 1, 2, 3, \dots$$

In the current implementation of this perturbation theory, spin-adapted configuration interaction functions are used as  $\Phi_i^{(0)}$ . Thus,  $E_i^{(0)}$  is just a sum of the orbital energies of those molecular orbitals in the corresponding configuration function  $\Phi_i^{(0)}$ . The system Hamiltonian operator  $\hat{H}$  can then be decomposed into two parts,  $\hat{H}_0$  and  $\hat{V}$ , i.e.

$$\hat{H} = \hat{H}_0 + \lambda \hat{V} \quad (3)$$

where  $\hat{V}$  is supposed to be a small perturbation operator to the unperturbed  $\hat{H}_0$ ,  $\lambda$  is a perturbation parameter. With these preparations, application of the Rayleigh–Schrödinger perturbation theory to the atomic and molecular systems is straightforward. The corresponding perturbation formula<sup>4,30</sup> is

$$E_i = E_i^{(0)} + V_{ii} \lambda + \sum_{j \neq i} \frac{V_{ij} V_{ji}}{E_i^{(0)} - E_j^{(0)}} \lambda^2 + \\ \left[ \sum_{j,k \neq i} \frac{V_{ij} V_{jk} V_{ki}}{(E_i^{(0)} - E_j^{(0)})(E_i^{(0)} - E_k^{(0)})} - V_{ii} \sum_{j \neq i} \frac{V_{ij} V_{ji}}{(E_i^{(0)} - E_j^{(0)})^2} \right] \lambda^3 + \dots \quad (4)$$

where  $V_{ij} = \langle \Phi_i^{(0)} | \hat{V} | \Phi_j^{(0)} \rangle$ ,  $\lambda$  is set equal to unity for the final energy  $E_i$ .

For the purpose of comparison, the multireference perturbation series<sup>22</sup> are also included here

$$E_p = \varepsilon_p^{(0)} + \sum_{i,j \leq n} \sum_{a > n} \frac{u_p^{(0)}(i) H_{ia} H_{aj} u_p^{(0)}(j)}{\varepsilon_p^{(0)} - H_{aa}} \lambda^2 + \\ \sum_{i,j \leq n} \sum_{a,b > n} \frac{u_p^{(0)}(i) H_{ia} H_{ab} H_{bj} u_p^{(0)}(j)}{(\varepsilon_p^{(0)} - H_{aa})(\varepsilon_p^{(0)} - H_{bb})} \lambda^3 + \dots \quad (5)$$

where  $u_p^{(0)}(i)$  is the  $i$ -th component of the  $p$ -th eigenvector and  $\varepsilon_p^{(0)}$  is the  $p$ -th eigenvalue in the reference space. The dimension of the reference space is  $n$ .  $H_{ij}$  is the Hamiltonian matrix element with respect to the  $i$ -th and  $j$ -th configuration functions.  $\lambda$  is a perturbation parameter as described in eq 4 and is set equal to unity for the final energy  $E_p$ .

## 3. Results and Discussion

For a supermolecular system composed of  $m$  monomers, which are separated by so large a distance that the interaction among them can be negligible, the size extensivity error (SEE) can then be defined as

$$\text{SEE} = E(A_1 + A_2 + \dots + A_m) - [E(A_1) + E(A_2) + \dots + E(A_m)] \quad (6)$$

If the monomers are the same, the SEE can be computed as follows

$$\text{SEE} = E(m \times A)/m - E(A) \quad (7)$$

Equation 7 is used for all SEE calculations in this study.

All ROHF and CASSCF orbitals and orbital energies in this study were calculated with GAMESS<sup>23</sup> and Gaussian.<sup>36</sup>

**Table 1.** Size Extensivity Error (hartree) Check for N<sub>2</sub>, HF, and F<sub>2</sub> Supermolecules

method	SRPT1	SRPT2	SRPT3
no. of HF's		CASSCF(2,2)	
1	0	0	0
2	0.00000000	-0.00000000	0.00000000
3	0.00000000	-0.00000000	0.00000000
4	0.00000000	-0.00000000	0.00000000
no. of F <sub>2</sub> s		CASSCF(2,2)	
1	0	0	0
2	0.00000000	-0.00000008	0.00000005
3	0.00000000	-0.00000008	—
4	0.00000000	-0.00000008	—
		N <sub>2</sub> dimer	
CASSCF(2,2)	0.00000000	0.00000000	-0.00000000
CASSCF(4,4)	0.00000000	0.00000000	0.00000000
CASSCF(6,6)	0.00000000	0.00000000	-0.00000001

MELDF<sup>24</sup> and our group programs were used to calculate matrix elements and perturbation energies.

**A. Size Extensivity Test.** As discussed in the first part of this paper, Rintelman et al.<sup>21</sup> investigated the size extensivity error with three molecular series, HF, N<sub>2</sub>, and F<sub>2</sub>, and several different levels of basis sets, Pople's 6-31G(d,p),<sup>25,26</sup> 6-311G(d,p),<sup>27</sup> and Dunning's cc-pVDZ, cc-pVTZ, and cc-pVQZ.<sup>28</sup> It was shown that the SEEs increased as the basis set was enlarged. However, the changes are not so much, and the errors are almost at the same order of magnitude. On the basis of this observation, only 6-31G(d,p) for the above three molecular series is used in this study. The stretched bond lengths of HF, N<sub>2</sub>, and F<sub>2</sub> are the same as in ref 21 and are 1.60 Å, 1.50 Å, and 1.50 Å, respectively. The distance between monomers of N<sub>2</sub> and F<sub>2</sub> is 200 Å to make sure that interactions between monomers can be neglected. However, the distance between HF monomers is 2000 Å in order to quench the possible dipole-dipole interactions. The CASSCF convergence threshold is 10<sup>-8</sup> for supermolecular series of HF, F<sub>2</sub>, and N<sub>2</sub>.

In Table 1, SEEs are calculated with the first-, second-, and third-order perturbation theory in eq 4 (denoted as SRPT1, SRPT2, and SRPT3) with partition eq 2. Results of HF supermolecules are listed in the upper part of the table. The complete active space is CASSCF(2,2). SEE is very small and is less than the CASSCF convergence threshold. As the basis set changes to 6-31G, the unpublished SEEs are still at about the same level. The effects of HF geometries on the SEE have also been investigated though the results have not been presented in the Table 1. The bond length of HF is chosen as 1.4 Å, which is between the equilibrium bond length<sup>30</sup> 0.92 Å and the elongated bond length 1.6 Å studied above. These unpublished SEEs calculated with basis set 6-31G and 6-31G(d,p) are all also less than the CASSCF convergence threshold.

In the middle part of the Table 1 are the results of F<sub>2</sub> supermolecules. They are more challenging examples for the SEE test. The active space is CASSCF(2,2) which is the same as used in the HF case. The core orbital 1s of the fluorine atom is frozen in the calculations. The SEEs are all at the order of 10<sup>-8</sup> hartree. Though they are slightly larger than the results of HF supermolecules, SEEs are still at the same level as the convergence threshold set for CASSCF calculations.

**Table 2.** Total Energies (hartree) for the Ground State of H<sub>2</sub>O Calculated with Different Methods

method	CASSCF(2,2)	CASSCF(4,4)	CASSCF(6,6)
CASSCF	-76.028093	-76.073481	-76.108960
MRCI	-76.214391	-76.227688	-76.229860
MRCI+Q	-76.232834	-76.241006	-76.243466
MRPT2	-76.261841	-76.249367	-76.234849
MRPT3	-76.214391	-76.221040	-76.227849
SRPT1	-76.023135	-76.022580	-76.022519
SRPT2	-76.215623	-76.223225	-76.223123
SRPT3	-76.223403	-76.220441	-76.220101

**Table 3.** Total Energies (hartree) for the Ground State of NH<sub>3</sub> Calculated with Different Methods

method	CASSCF(2,2)	CASSCF(4,4)	CASSCF(6,6)
CASSCF	-56.206428	-56.236639	-56.266567
MRCI	-56.392364	-56.396398	-56.399209
MRCI+Q	-56.405136	-56.410243	-56.413800
MRPT2	-56.423838	-56.413585	-56.403748
MRPT3	-56.389412	-56.392987	-56.397138
SRPT1	-56.195183	-56.194773	-56.194503
SRPT2	-56.381911	-56.383932	-56.385328
SRPT3	-56.393340	-56.391289	-56.389208

tions. Thus, the SEEs are not from the perturbation theory itself but due to the accuracy of CASSCF.

The SEE results of N<sub>2</sub> dimer are listed in the bottom of the Table 1. Three different complete active spaces, CASSCF(2,2), CASSCF(4,4), and CASSCF(6,6) are exploited to investigate the impact of active spaces on SEE. The absolute values of SEEs are below or close to the accuracy threshold 10<sup>-8</sup> set for CASSCF calculations. These results indicate that SEEs are not dependent on the active space.

The SEEs of the above three molecular series are the smallest numerical data available in the literature so far. They are only dependent on the accuracy of CASSCF calculations. On the basis of this numerical observation, it is concluded that the first three-order perturbation energies with the partition eq 2 are size extensive.

**B. Total Energies of H<sub>2</sub>O, NH<sub>3</sub>, and CH<sub>4</sub>.** Experimental geometries<sup>30</sup> of H<sub>2</sub>O, NH<sub>3</sub>, and CH<sub>4</sub> are used. The basis set is the Pople's 6-31G(d, p).<sup>25,26</sup> Total energies of H<sub>2</sub>O, NH<sub>3</sub>, and CH<sub>4</sub> at the ground states are calculated with the first three-order perturbation theory with partition eq 2 and are compared with other methods: CASSCF, multireference configuration interaction (MRCI), MRCI with Davidson correction<sup>29</sup> (MRCI + Q), and multireference second- and third-order perturbation theory (MRPT2 and MRPT3) in eq 5.

The results are listed in Table 2, Table 3, and Table 4. It can be seen from the tables that total energies are improved substantially with MRCI+Q over the results of MRCI. MRPT2 overestimates the energies especially with a small complete active space like CASSCF(2,2) in comparison with MRCI results. MRPT3 counteracts these discrepancies significantly. As the complete active space increases from CASSCF(2,2) to CASSCF(6,6) the MRPT2 and MRPT3 results converges very closely to MRCI energies. As expected, the CASSCF energies, which is actually the multireference zeroth-order energies, becomes lower as the CASSCF active space enlarged.

**Table 4.** Total Energies (hartree) for the Ground State of CH<sub>4</sub> Calculated with Different Methods

method	CASSCF(2,2)	CASSCF(4,4)	CASSCF(6,6)
CASSCF	-40.217021	-40.235347	-40.257266
MRCI	-40.385722	-40.383480	-40.385818
MRCI+Q	-40.397641	-40.395588	-40.398550
MRPT2	-40.405016	-40.392464	-40.387637
MRPT3	-40.386805	-40.382938	-40.384963
SRPT1	-40.201530	-40.201327	-40.201130
SRPT2	-40.369367	-40.364530	-40.365727
SRPT3	-40.386128	-40.379376	-40.378295

The single reference calculations are listed at the bottom of the Table 2, 3, and 4. Unlike the CASSCF energies, the ground-state energies of SRPT1 are almost unchanged with respect to the three types of CASSCF wave functions. This is also true for the energies calculated with SRPT2 and SRPT3. The reason for this is that the perturbation series in eq 4 considers only the ground-state configuration and its corresponding excitation configurations such as the single and double excitation configurations. Therefore, the nondynamical correlation from the CASSCF wave functions has not been taken into account. In this sense, it may be said that the present perturbation theory is not sensitive to the CASSCF orbitals. Nevertheless, like the Møller–Plesset second-order perturbation theory, SRPT2 recovers most of the correlation energy. The biggest energy difference between MRCI and SRPT3 is  $10^{-2}$  hartree for NH<sub>3</sub>. The energy differences for H<sub>2</sub>O and CH<sub>4</sub> are at the order of  $10^{-3}$  hartree. Considering the cheap computational cost of the single reference perturbation theory, the performances of SRPT2 and SRPT3 are satisfactory.

### C. The Singlet–Triplet Separation in CH<sub>2</sub> and SiH<sub>2</sub>

Computations of the singlet–triplet separation in CH<sub>2</sub> are a challenging problem for any perturbation theory. Detailed discussions on this can be found in ref 20. The purpose here is to investigate whether the present partition can be applied to a multireference problem. As can be seen from the above discussions in part B, the first three-order energies of the present partition are not changed so much though the complete active space is enlarged. Since they are essentially single reference problems in nature, the above three test cases may be not good enough to show the single reference character inherent in the present partition. Because of its well-known multireference character, CH<sub>2</sub> can be regarded as a proper example to fulfill the present purpose.

The calculations are performed with the DZP basis and the theoretically optimized geometry as used by Bauschlicher and Taylor.<sup>31</sup> The 1s orbital of CH<sub>2</sub> is frozen during the calculations. In Table 5 only single reference perturbation calculations are presented. The singlet–triplet separations are listed in the last column. It can be seen from the upper part of the table that the singlet–triplet gaps are still far away from the FCI result if only RHF orbitals for the singlet state and ROHF orbitals for the triplet state are used for the calculations. But the gaps listed in the lower part of the table are still not improved even with CASSCF(2,2) and CASSCF(6,6) orbitals for the singlet state. As pointed out by Bauschlicher and Taylor,<sup>31</sup> there are two important configurations in the singlet state. Thus, the possible reason for the

**Table 5.** The Singlet–Triplet Separation in CH<sub>2</sub> Calculated with Single Reference Perturbation Theory

method	<sup>1</sup> A <sub>1</sub> (hartree)	3B <sub>1</sub> (hartree)	Δ (kcal/mol)
FCI <sup>a</sup>	-39.027183	-39.046260	11.97
method	RHF	ROHF	Δ (kcal/mol)
SRPT1	-38.886297	-38.927947	26.14
SRPT2	-38.996127	-39.042348	29.00
SRPT3	-39.016593	-39.043335	16.78
method	CASSCF(2,2)	ROHF	Δ (kcal/mol)
SRPT1	-38.885662	-38.927947	26.53
SRPT2	-38.998686	-39.042348	27.40
SRPT3	-39.017087	-39.043335	16.47
method	CASSCF(6,6)	ROHF	Δ (kcal/mol)
SRPT1	-38.885298	-38.927947	26.76
SRPT2	-39.000520	-39.042348	26.25
SRPT3	-39.015873	-39.043335	17.23

<sup>a</sup> See ref 31.

**Table 6.** The Singlet–Triplet Separation in CH<sub>2</sub> Calculated with the Single- And Multireference Perturbation Theory

method	<sup>1</sup> A <sub>1</sub> (hartree)	3B <sub>1</sub> (hartree)	Δ (kcal/mol)
FCI <sup>a</sup>	-39.027183	-39.046260	11.97
method	MRPT + CASSCF(2,2)	SRPT + ROHF	Δ (kcal/mol)
2nd order	-39.027875	-39.042348	9.08
3rd order	-39.023129	-39.043335	12.68
method	MRPT + CASSCF(6,6)	SRPT + ROHF	Δ (kcal/mol)
2nd order	-39.025273	-39.042348	10.71
3rd order	-39.023912	-39.043335	12.19

<sup>a</sup> See ref 31.

above failure may be due to the fact that the perturbation series with partition eq 2 is a single reference perturbation theory and cannot solve the multireference problem of the singlet state. In order to check this, the multireference second- and third-order calculations, MRPT2 and MRPT3 in eq 4, have been performed for the singlet state with CASSCF(2,2) and CASSCF(6,6) active spaces. The results are presented in Table 6. It can be seen clearly from the table that the singlet–triplet gaps are improved considerably in comparison with the results listed in Table 5 and are close to the FCI result.<sup>31</sup> As the active spaces are increased from CASSCF(2,2) to CASSCF(6,6), the gaps are getting much closer to the FCI result. The best result was obtained with CASSCF(6,6) at the third-order level. The gap is only 0.22 kcal/mol bigger than the FCI result.

Another example for this preliminary test is SiH<sub>2</sub>. The geometries for the singlet and triplet state are the same as that used by Bauschlicher and Taylor.<sup>32</sup> The basis sets for H is the Dunning's double- $\zeta$  basis set<sup>33</sup> with a 2p polarization function ( $\alpha = 1.0$ ) added. The basis set for Si is [5s3p] contractions of the Huzinaga<sup>34</sup> (12s8p) Si basis given by McLean and Chandler<sup>35</sup> with a 3d polarization function ( $\alpha = 0.3$ ) added. The 3s component of the 3d set is deleted. These basis sets for SiH<sub>2</sub> are the same as that in the original work of Bauschlicher and Taylor.<sup>32</sup>



**Table 7.** The Singlet–Triplet Separation in SiH<sub>2</sub> Calculated with the Single- and Multireference Perturbation Theory

method	<sup>1</sup> A <sub>1</sub> (hartree)	3B <sub>1</sub> (hartree)	Δ (kcal/mol)
FCI <sup>a</sup>	−290.110207	−290.082313	17.5
<hr/>			
	MRPT + CASSCF(2,2)	SRPT + ROHF	
2nd order	−290.106628	−290.072361	21.5
3rd order	−290.106525	−290.078602	17.5
<hr/>			
	MRPT + CASSCF(6,6)	SRPT + ROHF	
2nd order	−290.104278	−290.072361	20.0
3rd order	−290.106201	−290.078602	17.3

<sup>a</sup> See ref 32.

In all calculations only the outer-shell six electrons of the SiH<sub>2</sub> radical are considered for correlation. Like the CH<sub>2</sub> case, the single reference perturbation theory is also not enough to describe the singlet state. Therefore, multireference perturbation calculations with CASSCF(2,2) and CASSCF(6,6) orbitals have been carried out instead. As for the triplet state, it is found that the energies calculated with ROHF orbitals and single reference perturbation theory, especially the SRPT3, are comparable to the full CI result obtained by Bauschlicher and Taylor.<sup>32</sup> All results are summarized in Table 7. In comparison with the FCI result, the errors of the singlet–triplet gaps calculated with SRPT2 and MRPT2 are 4 and 3.5 kcal/mol for CASSCF(2,2) and CASSCF(6,6), respectively. However, as the perturbation level increases to the third-order, i.e., SRPT3 for the triplet and MRPT3 for the singlet, the errors of the singlet–triplet gaps becomes surprisingly small, i.e., zero for CASSCF(2,2) and 0.2 kcal/mol for CASSCF(6,6).

The above calculations in parts B and C demonstrate that the single reference perturbation theory with the partition eq 2 is valid and effective for single reference problems whenever ROHF and CASSCF orbitals are available. More studies with the present theory for open-shell problems such as the geometry optimization are under investigation.

#### 4. Conclusions

A single reference perturbation theory with a new partition is presented. The perturbation partition has been proposed for ROHF and CASSCF orbitals. Through numerical studies on the size extensivity test with HF, F<sub>2</sub>, and N<sub>2</sub> supermolecules, it has been shown that the first three-order perturbation series with the present partition are size extensive. The ground-state energies of H<sub>2</sub>O, NH<sub>3</sub>, and CH<sub>4</sub> calculated with the present perturbation partition are accurate. The biggest energy difference between MRCI and SRPT3 is 10<sup>−2</sup> hartree for NH<sub>3</sub>. The energy differences for H<sub>2</sub>O and CH<sub>4</sub> are at the order of 10<sup>−3</sup> hartree. The single reference nature of present partition has also been demonstrated with the computations on the singlet–triplet gap of the CH<sub>2</sub> and SiH<sub>2</sub> radicals.

The present perturbation partition can be considered as a natural extension of Møller–Plesset partition beyond Hartree–Fock orbitals and can be used for single reference problems where the perturbation theory with the Møller–Plesset partition is not applicable.

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#### References

- (1) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.
- (2) (a) Epstein, P. S. *Phys. Rev.* **1926**, *28*, 695. (b) Nesbet, R. K. *Proc. R. Soc. London Ser. A* **1955**, *230*, 312.
- (3) Witek, H. A.; Nakano, H.; Hirao, K. *J. Chem. Phys.* **2003**, *118*, 8197.
- (4) Chen, F. *Computational methods in quantum chemistry*; Science Press: Beijing, P. R. China, 2008; pp 166–170.
- (5) Davidson, E. R.; MacMurchie, L. E.; Day, S. J. *J. Chem. Phys.* **1981**, *74*, 5491.
- (6) Murray, C. W.; Davidson, E. R. *Chem. Phys. Lett.* **1991**, *187*, 451.
- (7) (a) Kozłowski, P. W.; Davidson, E. R. *J. Chem. Phys.* **1994**, *100*, 3672. (b) Kozłowski, P. W.; Davidson, E. R. *Chem. Phys. Lett.* **1994**, *222*, 615. (c) Kozłowski, P. W.; Davidson, E. R. *Chem. Phys. Lett.* **1994**, *226*, 440. (d) Kozłowski, P. W.; Davidson, E. R. *Int. J. Quantum Chem.* **1995**, *53*, 149.
- (8) (a) Hirao, K. *Chem. Phys. Lett.* **1992**, *190*, 374–380. (b) Hirao, K. *Chem. Phys. Lett.* **1992**, *196*, 397–403. (c) Hirao, K. *Chem. Phys. Lett.* **1993**, *201*, 59.
- (9) Dyll, K. G. *J. Chem. Phys.* **1995**, *102*, 4909.
- (10) Werner, H. J. *Mol. Phys.* **1996**, *89*, 645.
- (11) Roos, B. O.; Andersson, K.; Fulscher, M. K.; Malmqvist, P.-A.; Serrano-Andres, L.; Pierloot, K.; Merchán, M. *Adv. Chem. Phys.* **1996**, *93*, 219.
- (12) Knowles, P. J.; Andrews, J. S.; Amos, R. D.; Handy, N. C.; Pople, J. A. *Chem. Phys. Lett.* **1991**, *186*, 130.
- (13) Lauderdale, W. J.; Stanton, J. F.; Gauss, J.; Watts, J. D.; Bartlett, R. J. *Chem. Phys. Lett.* **1991**, *87*, 21.
- (14) (a) Head-Gordon, M.; Oumi, M.; Maurice, D. *Mol. Phys.* **1999**, *96*, 593. (b) Head-Gordon, M.; Maslen, P. E.; White, C. A. *J. Chem. Phys.* **1998**, *108*, 616. (c) Maslen, P. E.; Head-Gordon, M. *Chem. Phys. Lett.* **1998**, *283*, 102.
- (15) Angeli, C.; Cimraglia, R.; Evangelisti, S.; Leininger, T.; Malrieu, J.-P. *J. Chem. Phys.* **2001**, *114*, 10252.
- (16) (a) Wolinski, K.; Seller, H. L.; Pulay, P. *Chem. Phys. Lett.* **1987**, *140*, 225–231. (b) Wolinski, K.; Pulay, P. *J. Chem. Phys.* **1989**, *90*, 3647. (c) Van Dam, B. J. J.; Van Lenthe, J. H.; Pulay, P. *Mol. Phys.* **1998**, *93*, 431.
- (17) Rolik, Z.; Szabados, Á.; Surján, P. R. *J. Chem. Phys.* **2003**, *119*, 1922.
- (18) Szabados, A.; Rolik, Z.; Tóth, G.; Surján, P. R. *J. Chem. Phys.* **2005**, *122*, 114104.
- (19) Chen, F. *Sci. China Ser. B* **2007**, *50*, 483.
- (20) Davidson, E. R.; Jarzecki, A. A. Multi-reference perturbation theory. In *Recent Advances in Computational Chemistry*; Hirao, K., Ed.; World Scientific Publishing: Singapore, 1999; Vol. 4, pp31–63.
- (21) Rintelman, J. M.; Adamovic, I.; Varganov, S.; Gordon, M. S. *J. Chem. Phys.* **2005**, *122*, 044105.
- (22) Chen, F.; Davidson, E. R.; Iwata, S. *Int. J. Quantum Chem.* **2002**, *86*, 256.

- (23) Gamess Schmidt, M. W.; Baldrige, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Natsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.
- (24) MELD is a set of electronic structure programs written by McMurchie L. E., Elbert, S. T.; Langhoff S. R.; Davidson, E. R. with extensive modifications by Feller, D.; Rawlings, D. C. Available from <http://php.indiana.edu/~davidson>.
- (25) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.
- (26) (a) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724. (b) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.
- (27) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.
- (28) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.
- (29) Langhoff, S. R.; Davidson, E. R. *Int. J. Quantum Chem.* **1974**, *8*, 61.
- (30) Szabo, A.; Ostlund, N. S. *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory*; Macmillan: New York, 1982.
- (31) Bauschlicher, C. W.; Taylor, R. P. *J. Chem. Phys.* **1986**, *85*, 6510.
- (32) Bauschlicher, C. W.; Taylor, R. P. *J. Chem. Phys.* **1987**, *86*, 1420.
- (33) Dunning, Jr., T. H. *J. Chem. Phys.* **1970**, *53*, 2823.
- (34) Huzinaga, S. Department of Chemistry Report, University of Alberta, Edmonton, Alberta, Canada, 1971.
- (35) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639.
- (36) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03W, revision D.01*; Gaussian, Inc.: Wallingford, CT, 2004.
- (37) Roothaan, C. C. *Rev. Mod. Phys.* **1960**, *32*, 179.
- (38) (a) Roos, B.; Taylor, P.; Siegbahn, P. *Chem. Phys.* **1980**, *48*, 157. (b) Siegbahn, P.; Heiberg, A.; Roos, B.; Levy, B. *Phys. Scr.* **1980**, *21*, 323. (c) Siegbahn, P.; Almlöf, J.; Heiberg, A.; Roos, B. *J. Chem. Phys.* **1981**, *74*, 2384.

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