Multireference Møller–Plesset perturbation theory using spin-dependent orbital energies

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Abstract

The use of spin-dependent orbital energies is proposed in the multireference Møller–Plesset perturbation theory. In this method a single canonical Fock orbital set is used for both alpha and beta electrons, while the orbital energies depend on the spin of the electron that occupies the orbital. The method is tested on the energy splitting between states of different spins in the CH_2, CF_2, CO, O_2, N_2^+, and *o*-benzyne molecules. The results agree well with available experimental data; the deviations are within 4 kcal/mol in all cases considered. © 2001 Published by Elsevier Science B.V.

1. Introduction

Perturbation theory (PT) is a basic and essential tool for investigating the electronic structures of molecules in modern quantum chemistry. In particular, the single reference version of PT for closed-shell systems is now well established. On the other hand, it is only in relatively recent years that the multireference version of PT has made remarkable progress and comes in common use for studies of chemical reactions.

In the 1990s, many multireference perturbation theories were developed that are based on complete active space self-consistent field (CASSCF) reference wave functions. Multireference Møller–Plesset (MRMP) PT [1–4] and its generalization to multistate cases, quasi-degenerate PT with multiconfiguration self-consistent field reference functions

(MC-QDPT) [5,6], are examples of the CASSCF reference PT. We have applied them to various systems and demonstrated that they are powerful tools for investigating excitation spectra and potential energy surfaces of chemical reactions.

MRMP uses the zeroth-order energies defined through orbital energies,

$$E_I^{(0)} = \sum_{p\sigma} n_{p\sigma}(I)\varepsilon_{p\sigma}, \qquad (1)$$

where I denotes a basis (or zeroth-order) many-electron wave function, and $n_{p\sigma}$ and $\varepsilon_{p\sigma}$ are the occupation number and the energy of an orbital p with spin σ $(= \alpha, \beta)$, respectively. We have so far used a single orbital energy set for both alpha and beta orbitals: $\varepsilon_{p\alpha} = \varepsilon_p\beta$. However, it has been found that, for high-spin states of some molecules, this definition of the zeroth-order energies overestimates the second-order energy. The energy splitting between the $^1A_1$ and $^3B_1$ states in CH_2 is an example. A full configuration interaction (CI) results with the double zeta plus polarization basis

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set of Dunning is 12.0 kcal/mol [7]. In a previous calculation [2], MRMP with CAS[6e,6o] yielded 15.8 kcal/mol for the singlet–triplet (S–T) splitting. The deviation of 3.8 kcal/mol is not small for this small molecular size.

Several researchers have proposed definitions for H_0 to improve the convergence of the perturbation series [8–10], and some of them are particularly useful also for improving convergence for the high-spin state. Kozlowski and Davidson [8] proposed the MROPTn method and applied it to the CH_2 molecule. The values for the energy splitting are 12.3, 12.9, and 13.1 kcal/mol for MROPT2, 3, and 4, respectively. Dyall [9] also applied his CAS/A method to the same system and obtained 14.8 kcal/mol for the splitting. Andersson's CASPT2(g3) [10] yielded 13.0 kcal/mol.

In the single reference PT, an open-shell PT called the RMP method [11] or ROHF-MBPT [12], is available as a method for treating high-spin states. In this method, the ROHF orbitals are transformed to diagonalize the alpha and beta Fock matrices in occupied–occupied and virtual–virtual orbital blocks. Because the alpha and beta occupied/virtual orbital spaces are different, the resulting orbitals used in PT are necessarily of an unrestricted type.

In the present Letter, following the idea behind RMP, we propose the use of spin-dependent orbital energies in the definition of H_0 in the MRMP method. The orbitals used are the canonical orbitals, being the same as the conventional MRMP method, and hence the orbitals are of the restricted type. Only their energies are of the unrestricted type.

2. Method

In perturbation theory, a Hamiltonian H is split into an unperturbed part H_0 and the perturbation V,

$$H = H_0 + V. \tag{2}$$

The unperturbed Hamiltonian is expressed as

$$H_0 = \sum_I |\Phi_I\rangle E_I^{(0)} \langle\Phi_I|, \tag{3}$$

in a many-electron function basis $\{\Phi_I\}$, where $E_I^{(0)}$ is the zeroth-order energy and Φ_I corresponds to the zeroth-order wave functions. In MRMP, the zeroth-order energies are given by

$$E_I^{(0)} = \sum_{p\sigma} n_{p\sigma}(I)\varepsilon_{p\sigma}, \tag{4}$$

where $\varepsilon_{p\sigma}$ and $n_{p\sigma}(I)$ are the energy of orbital p with spin σ and the occupation number of orbital p with spin σ in wave function Φ_I, respectively.

Until now we have mainly used canonical Fock orbitals, which are defined so that the generalized Fock matrix,

$$F_{pq} = h_{pq} + \sum_{rs} \left(D_{rs}^\alpha + D_{rs}^\beta\right)\left[(pq|rs) - \tfrac{1}{2}(ps|rq)\right], \tag{5}$$

is partially diagonal in the core, active, and virtual orbital sub-blocks (D_{rs}^α and D_{rs}^β represent alpha and beta one-particle density matrices, respectively) and have adopted the diagonal elements of the generalized Fock matrix, F_{pp}, as orbital energies,

$$\varepsilon_{p\alpha} = \varepsilon_{p\beta} = h_{pp} + \sum_{rs} \left(D_{rs}^\alpha + D_{rs}^\beta\right)\left[(pp|rs) - \tfrac{1}{2}(ps|rp)\right]. \tag{6}$$

The use of a single orbital energy set for alpha and beta orbitals should be effective if the alpha and beta electrons are in the identical environment. However, in an open-shell system involving unpaired alpha electrons, the electron environment depends on whether the electron is in an alpha or a beta orbital. Thus, here we propose that we retain canonical Fock orbitals but adopt spin-dependent orbital energies defined by

$$\varepsilon_{p\alpha} = h_{pp} + \sum_{rs} \left\{D_{rs}^\alpha[(pp|rs) - (ps|rp)] + D_{rs}^\beta(pp|rs)\right\} \tag{7}$$

and

$$\varepsilon_{p\beta} = h_{pp} + \sum_{rs} \left\{D_{rs}^\beta[(pp|rs) - (ps|rp)] + D_{rs}^\alpha(pp|rs)\right\}, \tag{8}$$

for alpha- and beta-spin orbitals, respectively. This treatment of the orbital energies necessarily changes the zeroth-order energies $E_I^{(0)}$ but keep the zeroth-order wave functions.

A feature we should note concerning the present treatment is that it lifts the degeneracy of determinants that have a common spatial orbital occupation. This gives rise to a spin contamination

problem: the perturbed wave function (i.e., that higher than zeroth-order) is not S^2 adapted. From the practical point of view, however, this does not constitute a very serious drawback with MRMP calculations as they do not go beyond the second-order in energy. One more problem derived from the fact is that the present treatment does not give an identical energy for degenerate states of a spin magnetic quantum number M. The use of reference functions of $M = S$ is desirable because, in the function of $M < S$, the effect of spin-dependent orbital energy is reduced to some extent by spin coupling, such as $(\alpha\beta - \beta\alpha)/\sqrt{2}$.

The energy, Eq. (6), in the original MRMP is the average of the alpha and beta energies, Eqs. (7) and (8), respectively, in the new MRMP. Hereafter, we refer the original MRMP to MRMP(SA) (MRMP with spin-averaged orbital energies), and a new MRMP to MRMP(SD) (MRMP with spin-dependent orbital energies) for a shorthand notation.

3. Applications

The MRMP(SD) described in the preceding section was applied to six molecules, CH_2, CF_2, CO, O_2, N_2^+, and o-benzyne, to clarify its performance. In the following subsections the active space is indicated by the representation CAS[Ne,-Mo], which means that N electrons are distributed among the M orbitals.

3.1. CH_2 and CF_2

Various methods have been applied to the adiabatic (S–T) splitting of methylene with the same geometry, active space, and basis set given in Ref. [7]. We first calculated it with the same condition for comparison. The active space is a full-valence type CAS[6e,6o], and the basis set used is the double zeta plus polarization (DZP) basis [7]. The results are listed in Table 1. The S–T splitting by the original MRMP(SA) is 15.9 kcal/mol; the de-

Table 1
Energy splitting between the $^1A_1$ and $^3B_1$ states in CH_2 and CF_2

	Method	Energy (hartree)		ΔE (kcal/mol)
		$^1A_1$	$^3B_1$	
	CH_2			
	[6e,6o]CASSCF/DZP	−38.94532	−38.96578	12.8
	[6e,6o]MRMP(SA)/DZP	−39.01106	−39.03636	15.9
	[6e,6o]MRMP(SD)/DZP	−39.01106	−39.03115	12.6
	Full CI/DZP	−39.02718	−39.04626	12.0
	[6e,6o]CASSCF/cc-pVTZ	−38.95422	−38.97099	10.5
	[6e,6o]MRMP(SA)/cc-pVTZ	−39.04461	−39.06778	14.5
	[6e,6o]MROPT2/cc-pVTZ	−39.04461	−39.06138	10.5
	[6e,6o]MRMP(SD)/cc-pVTZ	−39.04461	−39.06064	10.1
	[6e,12o]CASSCF/cc-pVTZ	−39.02090	−39.02778	4.3
	[6e,12o]MRMP(SA)/cc-pVTZ	−39.06931	−39.08723	11.2
	[6e,12o]MROPT2/cc-pVTZ	−39.06931	−39.08513	9.9
	[6e,12o]MRMP(SD)/cc-pVTZ	−39.06931	−39.08504	9.9
	Exptl.[a]			9.4
CF_2				
	[12e,9o]CASSCF/cc-pVTZ	−236.85497	−236.76085	59.1
	[12e,9o]MRMP(SA)/cc-pVTZ	−237.38184	−237.30738	46.7
	[12e,9o]MROPT2/cc-pVTZ	−237.38184	−237.30391	48.9
	[12e,9o]MRMP(SD)/cc-pVTZ	−237.38184	−237.29807	52.6
	Exptl.[b]			56.6

[a] Ref. [14].
[b] Ref. [16].

viation from the full CI value of 12.0 kcal/mol is 3.9 kcal/mol. This is improved by MRMP(SD); the splitting is 12.6 kcal/mol, the discrepancy being only 0.6 kcal/mol.

We next carried out calculations with a larger basis set and active space to compare the calculated and experimental results. The splitting with Dunning's correlation consistent polarized valence triple zeta (cc-pVTZ) basis set [13] is 10.1 kcal/mol, which is in good agreement with the experimental value of 9.4 kcal/mol [14]. In the calculations with CAS[6e,6o], even the reference CASSCF gives good results: 12.8 (DZP) and 10.5 (cc-pVTZ) kcal/mol. The deviation from the full CI and experimental values are only 0.8 and 1.1 kcal/mol, respectively. However, it is known that the energy splitting at the CASSCF level gets worse if the active space is enlarged to CAS[6e,12o] [15]. We next calculated the splitting using CAS[6e,12o] as a further check. The result of CASSCF is 4.3 kcal/mol, which is rather poor compared with the CAS[6e,6o] value. To the contrary, the value 9.9 kcal/mol of MRMP(SD) is in much better agreement with experiment.

The geometry of CF_2 used in the calculations was determined with CASSCF[6e,6o]/cc-pVTZ. The active space and basis set for MRMP are CAS[12e,9o] and cc-pVTZ, respectively. The S–T splitting energy calculated with MRMP(SD) is 52.6 kcal/mol. This is a fairly good estimate of the experimental value, 56.6 kcal/mol [16]. On the other hand, the value from MRMP(SA), 46.7 kcal/mol, is too small compared with experiment.

MROPT2 by Kozlowski and Davidson [8] also reproduces the splitting, 10.5 (CAS[6e,6o]) and 9.9 kcal/mol (CAS[6e,12o]) for CH_2. These numbers are very close to those of MRMP(SD). For CF_2, however, it gives a slightly smaller splitting of 48.9 kcal/mol.

Fig. 1 shows the orbital energies of the core and active orbitals of the $^3B_1$ state of CF_2 used in MRMP(SA) and MRMP(SD). The active orbitals can be classified as doubly-occupied, singly-occupied, and unoccupied, according to their occupation numbers in this case. In MRMP(SD) the alpha- and beta-orbital energies are close to each other in the doubly-occupied and unoccupied orbitals, while those for singly-occupied orbitals
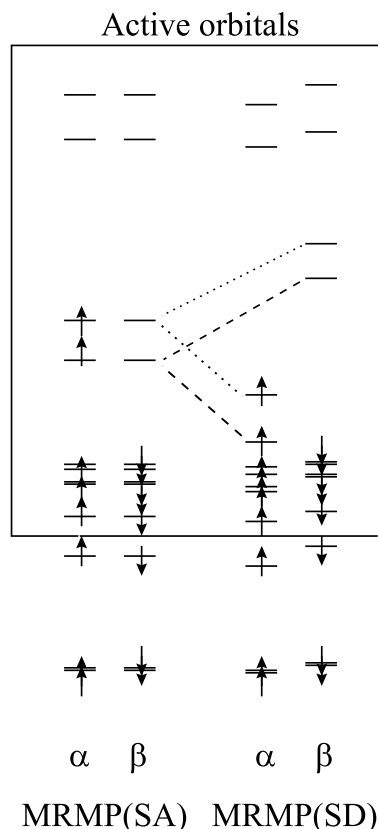

Fig. 1. Orbital energy pattern of the $^3B_1$ state of CF_2 in the spin-averaged and spin-dependent cases.

are quite different. The alpha- and beta-orbital energies in MRMP(SA) are equal and lie at the average of the alpha- and beta-orbital energies of MRMP(SD), by definition. Obviously, the large splitting of the alpha- and beta-orbital energies of singly-occupied orbitals is mainly responsible for the difference in energy between MRMP(SD) and MRMP(SA).

We can also see from Fig. 1 the reason why the MRMP(SD) energies are higher than the corresponding MRMP(SA) energies. The excitation energy from a singly-occupied orbital into a virtual orbital and that from a core orbital to a singly-occupied orbital in MRMP(SD) are larger than those in MRMP(SA), providing larger energy denominators in the second-order perturbation term, which gives a smaller correlation energy.

3.2. Diatomic molecules: CO, O_2, and N_2^+

The energy splitting between the ground state and the lowest state in the next higher spin multiplicity was calculated for these diatomic molecules: $X^1\Sigma^+$ and $a^3\Pi$ in CO, $X^3\Sigma_g^-$ and $a^1\Delta_g$ in O_2, and $X^2\Sigma_g^+$ and $a^4\Sigma_u^+$ in N_2^+. The bond lengths for each state in CO and O_2 were taken from experimental values [17]. For the states of N_2^+, theoretical values of the bond length [17] were used since no experimental values for $a^4\Sigma_u^+$ were available. The cc-pVTZ basis set was used for all these molecules. The active spaces are CAS[10e,8o], [8e,8o], and [9e,8o] for CO, O_2, and N_2^+, respectively. The results are summarized in Table 2.

The S–T splitting energy for the CO molecule at the CASSCF level is 154.8 kcal/mol, being overestimated by 15.6 kcal/mol from the experimental value. In contrast, the splitting is underestimated with the original MRMP(SA); the value is 127.5 kcal/mol, which is 11.7 kcal/mol smaller than the experimental value, and MRMP(SD) also underestimates the splitting. However, the deviation is reduced to only 3.5 kcal/mol, and thus the estimate of the splitting is improved from both the CASSCF and MRMP(SA) values.

In the O_2 molecule, the S–T splitting computed with MRMP(SD) is 18.2 kcal/mol, which is 4.4 kcal/mol smaller than the experimental value of 22.6 kcal/mol [17]. The accuracy is almost comparable to the case of CO. The original MRMP(SA), as well as CASSCF, also gives an accurate estimation in this case; the splittings by MRMP(SA) and CASSCF are 22.7 and 19.5 kcal/mol, respectively, both agreeing well with the experimental value.

No experimental spectroscopic information for $a^4\Sigma_u^+$ in N_2^+ is available. Hence, we used a theoretical value from a multireference (MR) CI method [18] as reference. The MRCI value for the splitting between $X^2\Sigma_g^+$ and $a^4\Sigma_u^+$ is 109.7 kcal/mol. CASSCF gives a splitting of 108.0 kcal/mol, which is very close to the MRCI value, whereas the value from MRMP(SA), 100.7 kcal/mol, is 9.0 kcal/mol smaller than that from MRCI. MRMP(SD) also gives a result whose deviation is larger than that from the CASSCF value though the deviation, only 3.1 kcal/mol, is comparable to the cases of CO and O_2.

3.3. o-Benzyne

The geometries of the target states $^1A_1$ and $^3B_2$ were optimized at the CASSCF [8e,9o]/cc-pVDZ level. Single point calculations were performed with modified cc-pVTZ (a single exponent 0.55 for

Table 2
Energy splitting in CO, O_2, and N_2^+

	Method	Energy (hartree)		ΔE (kcal/mol)
CO		$X_1\Sigma^+$	$a^3\Pi$	
	[10e,8o]CASSCF/cc-pVTZ	−112.91228	−112.66558	154.8
	[10e,8o]MRMP(SA)/cc-pVTZ	−113.13270	−112.92948	127.5
	[10e,8o]MRMP(SD)/cc-pVTZ	−113.13270	−112.91634	135.8
	Exptl.[a]			139.2
O_2		$X^3\Sigma_g^-$	$a^1\Delta_g$	
	[8e,8o]CASSCF/cc-pVTZ	−149.77175	−149.74067	19.5
	[8e,8o]MRMP(SA)/cc-pVTZ	−149.95184	−149.91560	22.7
	[8e,8o]MRMP(SD)/cc-pVTZ	−149.94453	−149.91560	18.2
	Exptl.[a]			22.6
N_2^+		$X^2\Sigma_g^+$	$a^4\Sigma_u^+$	
	[9e,8o]CASSCF/cc-pVTZ	−108.55776	−108.38561	108.0
	[9e,8o]MRMP(SA)/cc-pVTZ	−108.74737	−108.58684	100.7
	[9e,8o]MRMP(SD)/cc-pVTZ	−108.74393	−108.57409	106.6
	MRCI[b]			109.7

[a] Ref. [17].
[b] Ref. [18].

Table 3
Energy splitting between the $^1A_1$ and $^3B_2$ states in o-benzyne

Method	Energy (hartree)		ΔE
	$^1A_1$	$^3B_2$	(kcal/mol)
[8e,8o]CASSCF/cc-pVTZ	−229.54776	−229.49187	35.1
[8e,8o]MRMP(SA)/cc-pVTZ	−230.26959	−230.21563	33.9
[8e,8o]MROPT2/cc-pVTZ	−230.26959	−230.21241	35.9
[8e,8o]CASPT2/aANO	–	–	32.6
CCSD(T)/pVTZ	–	–	35.3
[8e,8o]MRMP(SD)/cc-pVTZ	−230.26959	−230.20416	41.1
Exptl.[a]			37.5

[a] Ref. [19].

d orbitals). The active space used was CAS[8e,8o] in the perturbation method.

The results are listed in Table 3. The splitting by the original MRMP(SA) is 33.9 kcal/mol, which is 3.6 kcal/mol smaller than the experimental value, 37.5 kcal/mol [19]. On the other hand, the splitting computed with MRMP(SD), 41.1 kcal/mol, is larger than the experiment by 3.6 kcal/mol. The experimental splitting of 37.5 kcal/mol lies in the middle of these values. There have been several theoretical calculations for o-benzyne. MROPT2/cc-pVTZ gave 35.9 kcal/mol for the splitting, CASPT2/aANO evaluated it as 32.6 kcal/mol and CCSD(T)/pVTZ provided 35.3 kcal/mol [20]. The splitting is underestimated in these methods. Only MRMP(SD) gives a larger splitting than the experimental value.

4. Conclusions

We have proposed a multireference Møller–Plesset perturbation method using spin-dependent orbital energies (MRMP(SD)). In this method a single canonical Fock orbital set is used for both alpha and beta electrons, while the energies are dependent on the spin of the electron that occupies the orbital.

MRMP(SD) is tested on several molecules to evaluate its performance. In CH_2 and CF_2, MRMP(SD) improve the values of the S–T splitting over the original MRMP(SA) as well as those of the reference CASSCF method. The error from the full CI method or the experimental value is within 1 kcal/mol in CH_2 and is 4.0 kcal/mol in

CF_2. In diatomic molecules, the errors in the splitting energy from the experimental or MRCI values are a few kcal/mol: 3.4, 3.6, and 3.1 kcal/mol for CO, O_2, and N_2^+, respectively. Similarly, in o-benzyne, the error is in the order of a few kcal/mol, 3.6 kcal/mol. Although the original MRMP(SA) gives better results in some cases, its error is larger than 10 kcal/mol in other cases. These results indicate the reliability of the present method, MRMP(SD).

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