Chinese Physics Letters

PAPER

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To cite this article: H. Aksu 2016 *Chinese Phys. Lett.* **33** 023102

CHIN. PHYS. LETT. Vol. 33, No. 2 (2016) 023102

Molecular Application of a State Specific Multi-Reference Brillouin–Wigner Perturbation Theory *

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(Received 9 September 2015)

The single reference second order Brillouin–Wigner perturbation theory recently developed, which eliminates its size-extensivity error, has been generalized to state-specific, multi-reference (SS-MR), BWPT2 providing a size-extensive correction to the electron correlation problem for systems that demand the use of a multi-reference function. Illustrative numerical tests of the size-extensivity corrections are made for widely used molecules in their ground states, which are pronounced multi-reference characteristics. We have implemented two-reference and three-reference cases for CH_2*, BH and bond breaking process in the ground states of HF molecules. The results are compared with the rigorously size-extensive methods such as the Møller–Plesset perturbation theory, i.e., MP2, full configuration interaction (Full-CI) and allied methods using the same basis sets.*

PACS: *31.15.xp*, *31.50.−x*, *31.50.Bc* DOI: 10.1088/0256-307X/33/2/023102

One of the main goals among the many electron theories is to obtain procedures which ensure the property of the size-extensivity. Size-extensivity requires that the method guarantees the additive result when applied to an assembly of an isolated system. The Brillouin–Wigner perturbation theory (BWPT), which was first published in the early 1930s,[1−3] has been noticed[4−7] to be unsuitable for many-body theories since it has the exact energy in the denominator which destroys its extensivity. Nevertheless, there have been some works[8,9] which prove that BW expansions can be subjected, a posteriori, to modification in the denominator so as to obtain a fully many-body theory.[9] Most of the studies have been made by the use of a single determinantal wave function, such as the Hartree–Fock determinant, which cannot be good approximation where near degeneration or bond breaking process occur in the molecular systems. As an example, single bond dissociation requires two determinants to obtain a compatible correct description. To show a better description for the degenerate or quasi degenerate systems, multi-reference (MR) character functions are required. It has been proven that the effective Hamiltonian concept has been applied to various chemical problems within the MR framework. Among the various perturbation methods, based on a multi-reference zero-order function, state-specific multi-reference perturbation theory (SS MRPT) developed by Mukherjee *et al.*[3,4,10,11] is the one which acquires the desirable features of size-extensivity and intruder-free character. In our previous studies[12,13] we have demonstrated an application of the single reference second order Brillouin–Wigner perturbation and only two references SS MRBWPT2 with its lack of size-extensivity correction to some closed shell atom and molecules. The purpose of this study is to critically study the use of size-extensivity correction to SS MRBWPT2 utilizing two and three references for multi-reference character molecules.

It is worthwhile to recall briefly some of the important results from previous works. First we write the BWPT2 expression[14,15] in the form as

$$E_{\rm BW}^{(2)}=\frac{1}{4}\sum_{ijab}\frac{\langle ab||ij\rangle\langle ij||ab\rangle}{(\varepsilon_0-E_0+\varepsilon_{ij}^{ab})},\tag{1}$$

where we use the convention in which i, j, $k,\ldots$ denote the occupied orbitals, and a, b, $c,\ldots$ denote unoccupied orbitals. The expressions ε_{ij}^{ab} and $\langle ij||ab\rangle$ indicate orbital energy differences between the occupied and unoccupied orbitals and doubly excited determinants, respectively. Equation (1) is similar to the Rayleigh Schrödinger perturbation theory (RSPT) except for ε_0 rather than E_0 in the denominator. It is well known that Eq. (1) is not size-extensive due to the fact that it has the exact energy in the denominator. The term ε_0-E_0 in the denominator is responsible for the correct size dependence of the system. Therefore we have to find a correct form for this term. We have shown this correction in previous works in the case of a single reference as

$$E_{\rm BW}^{(2)}=\frac{1}{4}\sum_{ijab}\frac{\langle ab||ij\rangle\langle ij||ab\rangle}{(E_{\rm BW}^{(2)}+\varepsilon_{ij}^{ab})}-[-E_{\rm MP}^{(2)}S]_{\rm EPV},\tag{2}$$

where the second term is the renormalization term which is explained in detail in Ref. [12].

For the SS MRBWPT expressions we have obtained the following correction term and final equa-

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*Supported by the Scientific and Technological Research Council of Turkey (TUBİTAK) under Grant No 2219-1/2013.

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tion, respectively,

$$[-E_{\rm MP}^{(2)}S]_{\rm EPV}^{\mu,\nu} = \sum_{j\notin P} \frac{\langle \Phi_\mu|\hat{H}_1|\Phi_j\rangle\langle \Phi_j|\hat{H}_1|\Phi_\nu\rangle}{E_0 - E_j}\langle \Phi_\mu^1||\Phi_\nu^1\rangle, \tag{3}$$

and

$$\begin{aligned}\langle \Phi_\mu|\hat{V}_0|\Phi_\nu\rangle &= \langle \Phi_\mu|\hat{H}_1|\Phi_0\rangle \\ &\quad + \sum_{j\notin P} \frac{\langle \Phi_\mu|\hat{H}_1|\Phi_j\rangle\langle \Phi_j|\hat{H}_1|\Phi_\nu\rangle}{\varepsilon_0 - E_j} \\ &\quad - [-E_{\rm MP}^{(2)}S]_{\rm EPV}^{\mu,\nu}. \end{aligned} \tag{4}$$

For our calculations we propose to use the three-reference system

$$\Psi_0 = C_0\Phi_0 + C_1\Phi_1 + C_2\Phi_2, \tag{5}$$

and we have the following matrix form to find the energy

$$\begin{pmatrix} m_{11} & m_{12} & m_{13} \\ m_{21} & m_{22} & m_{23} \\ m_{31} & m_{32} & m_{33} \end{pmatrix} \begin{pmatrix} C_0 \\ C_1 \\ C_2 \end{pmatrix} = 0, \tag{6}$$

where

$$\begin{aligned} &m_{11} = \langle \Phi_0|\hat{H}_\alpha|\Phi_0\rangle - \varepsilon_0, \quad m_{12} = \langle \Phi_0|\hat{V}_0|\Phi_1\rangle, \\ &m_{13} = \langle \Phi_0|\hat{V}_0|\Phi_2\rangle, \quad m_{21} = \langle \Phi_1|\hat{V}_0|\Phi_0\rangle, \\ &m_{22} = \langle \Phi_1|\hat{H}_\alpha|\Phi_1\rangle - \varepsilon_0, \quad m_{23} = \langle \Phi_1|\hat{V}_0|\Phi_2\rangle, \\ &m_{31} = \langle \Phi_2|\hat{V}_0|\Phi_0\rangle, \quad m_{32} = \langle \Phi_2|\hat{V}_0|\Phi_1\rangle, \\ &m_{33} = \langle \Phi_2|\hat{H}_\alpha|\Phi_2\rangle - \varepsilon_0, \end{aligned}$$

from which we take the lower energy until we reach the self-consistency of exact energy ε_0. In this case all the general matrix elements in Eq. (6) were explained in Ref. [13].

The computational results addressed in this work have been obtained by using the Mathematica 9.0 programme language. We have written codes for those calculations demonstrated in the following. We have used all of the two electron molecular orbital values and orbital energies from GAMESS[16] calculations and we have used them in our code to perform the necessary computations. In this study we utilize DZ,[17] 6-31G**[18,19] and cc-pVDZ[20] (with five d functions) basis sets from GAMESS library. All the results are demonstrated in tables and figures in the following. Due to the small size of the matrix, the computing time is quite small and it is only a few seconds.

We have performed one specific molecule which has a pronounced multi-reference character. Table 1 lists the results obtained for the CH_2 molecule for the two-reference (2R) and 3R-SS MRBWPT2$_{\rm corr}$ cases. Here we have chosen our complete active space (CAS) for the two-reference cases Φ_0: $1a_1^2 2a_1^2 1b_2^2 3a_1^2$, Φ_1: $1a_1^2 2a_1^2 1b_2^2 1b_1^2$, and we add only the triplet state open shell configuration of CH_2 molecules as Φ_2: $1a_1^2 2a_1^2 1b_2^2 3a_1^1 1b_1^1$.

Table 1. CH_2 molecule ground state calculations by using the cc-pVDZ basis set with five d functions, compared with various computing methods. Only valence electrons have been correlated. The geometry is taken from Refs. [21–23]. All entries are in atomic units.

Method	Singlet energy (a.u.)	ΔE
RHF	38.863609	−0.142692
CASSCF	38.883205	−0.123096
MBPT	38.977 001	−0.029300
MR AQCC[a]	39.002767	−0.003534
MR ACPF[a]	39.004310	−0.001991
MR CISD[a]	39.000608	−0.005693
MR CISD+Davidson[a]	39.006868	0.000567
MR CISD+Pople[a]	39.004854	−0.001447
MR RSPT2[a]	38.983980	−0.022321
MR RSPT3[a]	39.000320	−0.005981
SRCCSD	39.004326	−0.001975
SRCCSD(T)	39.007822	0.001521
SRCCSD[T]	39.007796	0.001495
SRBWPT2$_{\rm corr}$	38.977355	−0.028946
2RSSMRBWPT2$_{\rm corr}$	38.984514	−0.021787
3RSSMRBWPT2$_{\rm corr}$	38.989271	−0.017030
MR BWCCSD[a]	39.003592	−0.002709
FCI[a]	39.006301	

[a] Refs. [21–23].

In these calculations we have carried out Roothaan–Hartree–Fock (RHF), MP2, CAS self-consistent-field SCF(2, 2), single reference coupled cluster single and double (SRCCSD), SRCCSD triplets (T), SRCCSD[T] and finally our methods SRBWPT, 2R-SS MRBWPT2 and 3R-SS MRBWPT2 with their size-extensivity corrections. We compare our results with the well-known FCI and also apply the methods by using the cc-pVDZ basis sets with five d functions. Our results with the 2R and 3R-SS MRBWPT2$_{\rm corr}$ have a good agreement with the MR BW CCSD as well as with the FCI result. In the last column of Table 1 we have shown differences (ΔE) between FCI and every method presented in this study.

The absolute errors from RHF and CASSCF are quite large and to decrease errors one has to employ the multi-reference scheme. In this family we can mention the MR averaged coupled-pair function (ACPF)[21] and the MR averaged quadratic coupled cluster (AQCC)[22] methods which are based on the idea that there are independent coupled pairs and interaction between the independent coupled pairs, respectively. Since these methods have taken into account the electron correlation averaged way they may overestimate the electron correlation. However, the results from these two successful methods are satisfactory and are a good approximation to the multi-reference configuration interaction (MRCI). Similar to these methods there have been studied a posteriori corrections to the MRCI method from several researchers. Some of them are also listed in Table 1. It is easy to see that the MR CISD result with the Davidson correction overestimates the FCI one due to some unnecessary cancelation of unlinked terms in the MRCI. Since the CC method is not a variational method, the results from the CCSD(T) and CCSD[T] methods are below the FCI results. On the other hand, in this CC scheme the MR BWCCSD method is a more reliable approximation.

Because the second application is the potential energy curve (PECs) of the ground state ($X^1\Sigma^+$) of HF molecules in this work, we use only two configuration state functions (CSFs), i.e., Φ_0: $1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4$ and Φ_1: $1\sigma^2 2\sigma^2 4\sigma^2 1\pi^4$.

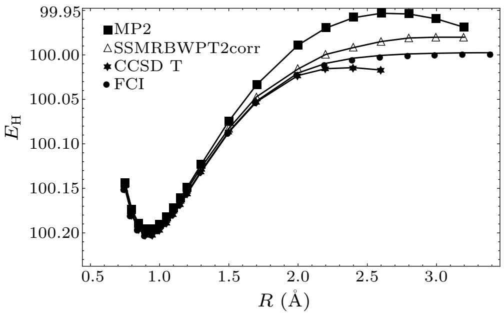

Fig. 1. PECs of ground state ($X^1\Sigma^+$) HF molecules computed by using the 6-31G** basis set. All electrons were correlated. All entries in a.u.

In the present study, we have performed the ground state calculations using again 6-31G** basis set for two energetically close 3σ and 4σ orbitals for which FCI calculations are available. We have chosen two closed shells for the two-reference configuration functions (2R-SS MRBWPT2). The results are shown in Fig. 1 for the 2R-SS MRBWPT2 including MP2 and CCSD(T) results. As seen from Fig. 1, the SS MRBWPT2 method works well during the PECs of HF molecules until $R = 2.20$ a.u. distance. When we look at Fig. 1 we can observe very poor behaviors of MP2 and CCSD(T) at large distances when using an RHF reference. The MP2 energies diverge faster toward negative infinity, and the CCSD(T) energies start to drop below FCI around 1.70–2.00 Å. These methods are able to produce energies below the FCI energy due to the fact that they do not employ a symmetric expectation value formula for the energy, and hence they are not subject to the variational theorem.[14] 2R-SS MRBWPT2$_{\rm corr}$ results have deviation from the FCI ones in the large bond distance where MR character methods should be used. As seen from Fig. 1 we could not put more information about CCSD(T) since it does not converge anymore. As it is seen from Fig. 1, the application of the a posteriori correction reduces the magnitude of the errors.

Lastly, we have implemented the boron hydride (BH) molecule since a number of theoretical studies are available for BH molecules in addition to their small size for implementing. To describe the dissociation of the BH molecule better we have used three references which are degenerate in the large bond distance. The Hartree–Fock description of the ground state ($X^1\Sigma^+$) of the BH molecule has the electronic form Φ_0: $1\sigma^2 2\sigma^2 3\sigma^2$. Since in the large bond distance, 3σ and 4σ orbitals become of near degeneration we have chosen our model spaces as follows: Φ_1: $1\sigma^2 2\sigma^2 3\sigma 4\sigma$ and Φ_2: $1\sigma^2 2\sigma^2 4\sigma^2$. It is obvious that our active space is constructed by 3σ and 4σ orbitals. For the three-reference calculations, 6-31G** basis sets were used and all electrons were correlated.

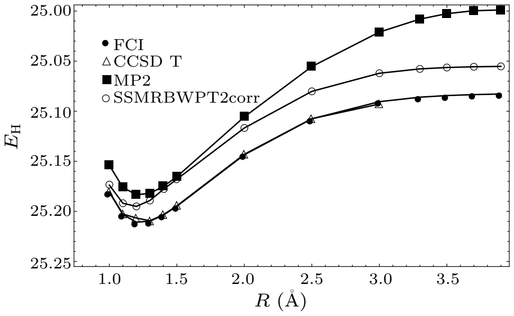

Fig. 2. PECs of ground state ($X^1\Sigma^+$) BH molecules computed by using the 6-31G** basis set. All electrons were correlated. All entries are in a.u.

The detailed behavior of these energies for the calculated methods as a function of r is plotted in Fig. 2. As seen from Fig. 2, SS MR BWPT2 with correction shows parallelity with the FCI while MP2 and CCSD(T) methods tend to converge or diverge above and below the FCI results, respectively.

As mentioned above, we have found the renormalization term,[14] which first appears exactly in quadruple excitation in the fourth-order many-body perturbation theory. The importance of this renormalization term is to cancel the non-physical terms. It is well known that fourth-order and higher-order perturbations have non-physical and renormalization terms together. Finally, they are canceled out naturally by themselves. In our case we construct an approximation to find out such a correction term which comes out as a renormalization term.

In summary, we have demonstrated the use of SS MRBWPT2 approximation. Our aim is to test the size-extensivity on more realistic molecular systems by the use of three-reference configurations and comparing with the two-references and other allied methods. First, applications to the dissociation of two first-row diatomic hydride molecules, three-reference cases BH and two- and three-reference cases HF have been carried out, respectively. We have also implemented the ground state of CH_2 molecules and compared with the variety of known methods.

In particular, non-parallelity errors (NPEs) are generally satisfactory with respect to the full configuration interaction curves in the cases of HF and CH_2 molecules based on the SS MRBWPT2 results. However, SS MR BWPT2 results show erratic behaviors in terms of NPEs when applied to the large distance of HF molecules (as seen in Fig. 1 at $R = 2.2$ Å).

We have identified the size-inextensive terms in the working equations and we eliminate them in the last iterations to make SS MRBWPT2 theory size-extensive. Based on the information given above, we should consider the approximation we propose carefully to avoid the reasons why we have some erratic behavior SS MRBWPT2 curves in long distance.

References

[1] Papp P, Mach P, Hubač I and Wilson S 2007 *Int. J. Quantum Chem.* **107** 2622
[2] Brandow B H 1967 *Rev. Mod. Phys.* **39** 771
[3] Ghosh P, Chattopadhyay S, Jana D and Mukherjee D 2002 *Int. J. Mol. Sci.* **3** 733
[4] Mahapartra U S, Datta B and Mukherjee D 1999 *Chem. Phys. Lett.* **301** 206
[5] Mášik J and Hubač I 1997 *Quantum Systems in Chemistry and Physics: Trends in Methods and Applications* (Dordrecht: Kluwer Academic Publisher)
[6] Hubač I and Wilson S 2000 *J. Phys.* B **33** 365
Hubač I, Pittner J and čársky P 2000 *J. Chem. Phys.* **112** 8779
[7] Mao S, Cheng L, Liu W and Mukherjee D 2012 *J. Chem. Phys.* **136** 024105
[8] Mao S, Cheng L, Liu W and Mukherjee D 2012 *J. Chem. Phys.* **136** 024106
[9] Das S, Mukherjee D and Kallay M 2010 *J. Chem. Phys.* **132** 074103
[10] Mahapartra U S, Datta B and Mukherjee D 1999 *J. Phys. Chem.* A **103** 1822
[11] Mahapartra U S, Datta B and Mukherjee S 1999 *Chem. Phys. Lett.* **299** 42
[12] Aksu H 2012 *Theor. Chem. Acc.* **131** 1285
[13] Aksu H 2013 *Theor. Chem. Acc.* **132** 1325
[14] Shavitt I and Bartlett R J 2009 *Many-Body Methods in Chemistry and Physics* (Cambridge: Cambridge University Press)
[15] Hirata S 2011 *Theor. Chem. Acc.* **129** 727
[16] Schmidt M W, Baldridge K K, Boatz J A, Elbert S E et al 1993 *J. Comput. Chem.* **14** 1347
[17] Dunning T H 1970 *J. Chem. Phys.* **53** 2823
[18] Hehre W J, Ditchfield R and Pople J A 1972 *J. Chem. Phys.* **56** 2257
[19] Hariharan P C and Pople J A 1973 *Theor. Chim. Acta* **28** 213
[20] Dunning T H 1989 *J. Chem. Phys.* **90** 1007
[21] Gdanitz R J and Ahlrichs R 1988 *Chem. Phys. Lett.* **143** 413
[22] Szalay P and Bartlett R J 1993 *Chem. Phys. Lett.* **214** 481
[23] Pittner J, Nachtigall P, čársky P, Mášik J and Hubač I 1999 *J. Chem. Phys.* **110** 10275