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Configuration-based multi-reference second order perturbation theory

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Abstract Various configuration-based multi-reference second order perturbation approaches were investigated and a new scheme averting intruder states was suggested. The codes based on these schemes were tested by example calculations.

Keywords: perturbation theory, multi-reference, configuration interaction.

The second order Moller-Plesset perturbation theory (MP2) is widely used as one of the most efficient methods for evaluating the electron correlation effect in molecules. Usually for systems where one configuration is strongly dominant in the wave-function, as this requirement is often fulfilled for molecules in their ground state around their equilibrium geometries, the single HF reference MP2 could provide a convenient and reliable description. However, for molecules in excited states and radicals and the large-scale PES calculations, where the degeneracy or quasi-degeneracy effects should be considered, multi-reference techniques would be the only choice to give a correct and balanced description of the electron structure. Among various multi- reference treatments, e.g. multi-reference configuration interaction (MRCI) and multi-reference perturbation theory (MRPT), only the second order perturbation theory (MRPT2) is efficient enough to be applied to the study for large-size systems. For this reason, much research interest has been focused on the development and application of MRPT2 methods since the past decades[1—12].

Various MRPT2 methods could be implemented by adopting different algorithms. Generally speaking, they can be viewed as either the method based on orbitals or that based on configurations. The differences between the both mainly come from the different definitions of the zeroth-order Hamiltonian operator H_0. Each method has its advantages as well as shortcomings. In the methods based on orbitals, graphical techniques and the linked graph theorem could be exploited to simplify the calculation[13]. However, the energy of the one-electron orbitals (especially of the active orbitals) should usually be redefined or modified, and the reordering of the orbital energy may lead to the convergence difficulty. In the methods based on configurations, the convergence could also fail when there is an intruder state encountered, but it is often comparably easier to find a suitable solution. The major computational task in the MRPT2 method based on configurations consists of CI matrix elements between configurations or the coupling coefficients. In the previous work we developed a series of advanced algorithms to obtain the coupling coefficients of CI matrix elements in a very efficient way[14] and therefore the efficiency of the method could be guaranteed in our codes. In addition, in this paper we propose an MPRT2 method, which may avoid intruder states. Practice calculations show that our proposed method has good convergence properties even for molecules far away from their equilibrium geometries.

1 Theory and algorithm

For a preselected reference space M_R with d_R configurations, the whole configuration space M is constructed through applying all possible single and double substitution operators to the reference configurations.

$$M_R = \{\ddot{O}_R \in M_R, R = 1,\ 2,\ \cdots,\ d_R\},$$

$$M = \left\{\ddot{O}_i, i = 1,2,\cdots,d_M \middle| \left\langle \ddot{O}_i \middle| \ddot{O}_j \right\rangle = d_{ij} \right\}$$

After diagonalization of Hamiltonian matrix in the reference space, the zeroth-order approximate wave function and zeroth-order energy could be obtained:

$$y_0 = \sum_{R \in M_R} C_R \ddot{O}_R, \quad E_0 = \langle \text{Ø}_0 | H | \text{Ø}_0 \rangle. \tag{1}$$

The complete configuration space could be partitioned into model space P and its complementary space Q. The project operators in spaces P and Q are then defined as

$$P = \sum_{a \in P} \left|\ddot{O}_a\right\rangle\left\langle\ddot{O}_a\right|, \quad Q = \sum_{b \in Q} \left|\ddot{O}_b\right\rangle\left\langle\ddot{O}_b\right|. \tag{2}$$

Obviously there is a relationship between the two operators:

$$P + Q = 1.$$

According to Lowdin[15], it is always possible to write Schrödinger equation in an equivalent form:

$$H_{\text{eff}}\,(PY) = E(P\ Y\ ), \tag{3}$$

where E is the exact energy and H_{eff} an effective Hamiltonian operator:

$$H_{\text{eff}} = PHP + PHQ\,(E - QHQ)^{-1}\,QHP. \tag{4}$$

In the perturbation theory, Hamiltonian operator is divided into the zeroth-order Hamiltonian and the perturbation operator:

$$H = H_0 + V.$$

Using the above relationship, the perturbation series could be obtained by expanding the factor $(E - QHQ)^{-1}$ by hierarchy. The equation

$$(X - Y)^{-1} = X^{-1} \sum_{i=0}^{\infty} (YX^{-1})^i \tag{5}$$

could be used to get the expansion result. There are different means to expand the term

$(E- QHQ)^{-1}$. In Brillouin-Wigner perturbation expansion we set

$$X = E - H_0\,,\ Y = V,$$

and the effective Hamiltonian is derived as

$$H_{\text{eff}} = P(H + VR_{\text{BW}}V + VR_{\text{BW}}VR_{\text{BW}}V + \cdots)P, \tag{6}$$

with

$$R_{\text{BW}} = \frac{Q}{E - H_0} = \sum_{b \in Q} \frac{\left|\ddot{O}_b\right\rangle\left\langle\ddot{O}_b\right|}{E - E_b}.$$

When truncating the series to the second-order, we have the second-order BW perturbation operator

$$(H_{\text{eff}})^{(0-2)} = P(H + VR_{\text{BW}}V)P. \tag{7}$$

In Rayleigh-Schrödinger perturbation expansion, we define

$$X = E' - H_0, \qquad Y = V - E + E' = V - \Delta E,$$

where E' could be the zeroth-order energy or any modified energy. The effective Hamiltonian for RS perturbation theory is expanded as

$$H_{\text{eff}} = P(H + VR_{\text{RS}}V + VR_{\text{RS}}(V - \Delta E)R_{\text{RS}}V + \cdots)P, \tag{8}$$

where

$$R_{\text{RS}} = \frac{Q}{E' - H_0} = \sum_{b \in Q} \frac{\left|\ddot{O}_b\right\rangle\left\langle\ddot{O}_b\right|}{E' - E_b}. \tag{9}$$

Thus the second-order RS effective Hamiltonian operator is obtained by truncating the expansion to the second-order:

$$(H_{\text{eff}})^{(0-2)} = P(H + VR_{\text{RS}}V)P. \tag{10}$$

In principle, the definition of the zeroth-order Hamiltonian and the choice of the model space in MRPT2 are arbitrary by its definition. In practice, however, the choice strongly determines the convergence properties of the perturbation expansion and is critical to the success of the perturbation theory. It is desirable to have the zeroth-order energy as close as possible to the total energy. At the same time, there are also other requirements, which may need to be considered, e.g. the size-consistency of the method, the treatment of intruder states, and the implementation of the algorithms. Several approaches are proposed in this paper in order to meet these requirements.

1.1 The model space P is equal to M_R

In the first approach, the reference space is chosen as the model space. Diagonalization of the Hamiltonian in the reference space will give the zeroth-order energy E_0^0 and wave function Y_0. Perturbation corrections are then to be found for this single reference wave function. The zeroth-order Hamiltonian H_0 could be defined as

$$H_0 = \sum_{R\in M_R} E_R \left|Ö_R\right\rangle\left\langle Ö_R\right| + \sum_{b\in Q} E_b \left|Ö_b\right\rangle\left\langle Ö_b\right|, \tag{11}$$

where

$$E_x = \left\langle Ö_x\right|H\left|Ö_x\right\rangle, x\in P,Q .$$

The above definition actually corresponds to Epstein-Nesbet (EN) partitioning scheme[13]. Because H_0 is defined as the diagonal operator in space M, the zeroth-order wave function is generally not the eigenfunction of H_0, unless all the configuration functions in the model space are degenerated. The zeroth-order energy can be written as

$$E_0^0 = \langle Ø_0 \mid H \mid Ø_0\rangle = \sum_R C_R^2 E_R . \tag{12}$$

By using formulae (7) and (10) we obtain the perturbation energy for the second-order BW and RS perturbation methods:

$$E_{\mathrm{BW}}^{(0-2)} = \left\langle Ø_0\right|H_{\mathrm{eff}}\left|Ø_0\right\rangle = E_0 + \sum_{b\in Q} \frac{\left|\left\langle Ø_0\right|V\left|Ö_b\right\rangle\right|^2}{E - E_b}, \tag{13a}$$

$$E_{\mathrm{RS}}^{(0-2)} = \left\langle Ø_0\right|H_{\mathrm{eff}}\left|Ø_0\right\rangle = E_0 + \sum_{b\in Q} \frac{\left|\left\langle Ø_0\right|V\left|Ö_b\right\rangle\right|^2}{E' - E_b} . \tag{13b}$$

Since H_0 is a diagonal operator, the perturbation matrix elements in eqs.(13a) and (13b) are essentially the off-diagonal elements of H. The only difference between the second-order BW and RS perturbation energy appears in the denominator of eqs. (13a) and (13b). In the RS formula E' is equal to E_0 or E_0^0**,**while in BW formula E is an unknown energy and should be determined iteratively.

1.2 The model space P is not equal to M_R

In order to accelerate the convergence of PT series and avoid the intruder states, the larger model space P could be selected, implying that all the configurations having a strong interaction with reference configurations or the energy which nears the zeroth-order energy should be included into P space. For this purpose, two thresholds T_1 and T_2 are defined as criteria parameters for selecting configurations:

$$\left\langle Ø_0\right|V\left|Ö_b\right\rangle \geqslant T_1, \quad \left|E(E') - E_b\right| \leqslant T_2.$$

The configurations which meet either of the above requirements are chosen to construct the P space, together with all the configurations in the reference space. The unselected configurations consist of the Q space. Thus the zeroth-order Hamiltonian is expressed as

$$H_0 = \sum_{a\in P} E_a \left|Ö_a\right\rangle\left\langle Ö_a\right| + \sum_{b\in Q} E_b \left|Ö_b\right\rangle\left\langle Ö_b\right| .$$

With the methods similar to the first scheme, the zeroth-order perturbation energy and corresponding wavefunction could be obtained by solving equations

$$H\O_0' = E^0\O_0' \ , \quad \O_0' = \sum_{a\in P} C_a \ddot{O}_a \, , \tag{14}$$

and the perturbation energy is

$$E_{\mathrm{CI-PT2}} = E^0 + \sum_{b\in Q} \frac{\left|\left\langle \O_0' \middle| V \middle| \ddot{O}_b \right\rangle\right|^2}{E^0 - E_b} . \tag{15}$$

The perturbation approach discussed above is analogous to A_k approximation method[16] and CIPSI (configuration interaction with perturbation selection iteratively)[17]. However, the zeroth model space is selected from different considerations. In our method the importance of avoiding intruder states is more emphasized.

1.3 Perturb-then-diagonalized method

Both the two approaches described above belong to the mode called "first-diagonalize-then-perturb", in which the reference space is represented as a single zeroth-order wave function, thus only one state and its energy could be generated once a time. Besides these, MRPT2 calculation could also be realized by the mode called "first-perturb-then-diagonalize". In this mode, the diagonalization of an effective Hamiltonian H_{eff} is performed after perturbation correlation is done. In this approach the same zeroth Hamiltonian H_0 of eq. (11) is employed, but the effective Hamiltonian matrix in the model space could be given by different ways, e. g.

$$(H_{\mathrm{eff}})_{aa'}^{(0-2)} = H_{aa'} + \sum_{b\in Q} \frac{H_{ab} H_{fa'}}{E_0 - E_b} , \tag{16}$$

$$(H_{\mathrm{eff}})_{aa'}^{(0-2)} = H_{aa'} + \sum_{b\in Q} \frac{H_{ab} H_{ba'} (E_a + E_{a'} - E_b - E_0)}{(E_a - E_b)(E_{a'} - E_b)} . \tag{17}$$

To derive the above two formulae, the fact that the perturbation correction comes only from off-diagonal Hamiltonian elements was considered. Formula (17) is adopted from ref. [9], where the definition of configuration energy is different from that in ref. [9]. The eigenvalues and the wavefunctions could be obtained by solving the following equation,

$$H_{\mathrm{eff}}^{(0-2)} \O_i = E_i \O_i , \quad i = 1, \ 2, \ \cdots, \ d_R . \tag{18}$$

In principle, the diagonalization of the effective Hamiltonian could give us several lowest eigenvalues and the corresponding eigenfunctions.

In summary, the most costly computational task in the implementation of the three approaches discussed above is to calculate the matrix elements of the perturbation operator. In this paper they actually correspond to the off-diagonal elements of Hamiltonian matrix, i.e. $\left\langle \O_0 \middle| H \middle| \ddot{O}_b \right\rangle$ and $\left\langle \O_a \middle| H \middle| \ddot{O}_b \right\rangle$. The former term involves only the matrix elements between the reference space and the complementary space Q, and the calculation is very simple and efficient. This is because only the loops which appear in *V-D*, *V-T* and *V-S* pairs should be generated and considered, while the large amount loops relative to *S* (*T*)-*S* (*T*), *S* (*T*)-*D* and *D*-*D* interaction type are neglected. For the latter terms, some loops with interaction type like *S* (*T*)-*S* (*T*) should be calculated, but the number of such loops is cut down greatly compared with that in MRCISD calculations. Thus all MRPT2 approaches could improve the program efficiency to some extent, as shown by the example calculations.

2 Applications

2.1 Ground state energy of C_4H_6

The ground state energy obtained by the perturbation and MRCISD calculations having the same reference functions is given in table 1. The last column in the table lists the timing comparison.

The molecule has the symmetry C_{2h} and the basis set DZP is chosen. Thus there are 94 orbitals: 36 a_g , 36 b_u , 11 b_g and 11 a_u . The reference space is CAS(6/5), i.e. 6 electronics are distributed in 5 active orbitals: 1-2 b_g , 1-3 a_u. 4 lowest orbitals are frozen. The number of configurations involved in MRCISD space is 9 539 571. The MRPT2-1a energy is obtained from eq. (13a) by iteration, while the MRPT2-1 energy from eq. (13b), where $E' = E_0$ (eq. (1)). The energy for MRPT2-2 and MRPT2-3 is obtained by using eqs. (15) and (16), respectively.

Table 1 MRPT2 and MRCISD calculations for C_4H_6

Methods	No. of ref. func.	Dim. of *P* space	Dim. of CI space	Energy(a.u.)[a)]	Timing / s[b)]
MRCISD	56		9 539 571	−155.461 66	55 408 (22 293)
MRPT2-1a	56	56		−155.466 85	240
MRPT2-1b	56	56		−155.577 63	240
MRPT2-2[c)]	56	134		−155.466 49	4 095
MRPT2-3	56	56		−155.566 45	1 041

a) 1 a.u. = 2 624.87 kJ/mol; b) computer: K7-500. The time in the parenthesis is for the new MRCISD program; c) thresholds: $T_1 = 1.0\times10^{-2}$ and $T_2 = 1.0$.

It can be seen from table 1 that among all results presented, MRPT2-2 energy remains in better agreement with MRCISD' s, but takes more time than other perturbative schemes. The non-iterative RS scheme, MRPT2-1b, is the fastest and has larger deviation in energy with respect to MRCISD. The deviation can be reduced if the preliminary MCSCF calculation is performed. It seems that the iterative BW scheme, MRPT2-1a, works well in energy and efficiency, however is not generally size-consistent. The result based on formula (17) is not reported for its poor convergence.

2.2 Splitting energy between the singlet and triplet states of CH_2

The computation results of different methods and the experiment values are compared in table 2. It could be seen from the table that both the HF method and the single reference MP2 have very poor results compared with the experimental values, while all the multi-reference methods predict much better values. The results obtained by MRPT2-1a are in the best agreement with the experimental values, however, this does not indicate MRPT2-1a method is more theoretically advantageous because of possible error cancellation. The results of MRCISD are not as good as expected because the configuration spaces for singlet and triplet states have many different sizes. For calculation of triplet, the dimension of the configuration space is 257 791, while for singlet the dimension is 163 115. The weight ratio for the reference configurations in the final wavefunction is 0.947 1 and 0.944 5, respectively. The computed results could be improved if a larger configuration space is used for singlet. In fact, if 16 reference configurations are selected for singlet calculation and 6 reference configurations for triplet calculation, the dimension of the configuration is 219 492 and 226 556, and the weight actor for reference space is 0.950 7 and 0.951 1 respectively. The splitting energy using the balanced configuration spaces is 9.95 kcal/mol for MRCISD and 9.86 kcal/mol after the Davidson correction (MRCISD+Q), which are in excellent agreement with the experimental value[19]. However, such a reference space is not suitable for perturbation calculations.

Table 2 Energy splitting of $^3B_1$ and $^1A_1$ for CH_2 (kcal / mol)

Methods	$E\ (^3B_1)$	$E(^1A_1)$	Splitting
HF	−38.932 36	−38.892 33	25.12
MP2	−39.070 99	−39.046 06	15.64
MRPT2-1a[a)]	−39.100 85	−39.085 06	9.91
MRPT2-1b[a)]	−39.091 19	−39.072 35	11.82
MRPT2-2[b)]	−39.087 59	−39.069 19	11.55
MRPT2-3	−39.101 16	−39.082 99	11.40
MRCISD	−39.087 51	−39.069 33	11.41
MRCISD+Q[c)]	−39.096 64	−39.079 45	10.78
Experiment (T_e)[d)]			9.65

a) Active orbitals : $1a_1$, $2a_1$, $3a_1$, $1b_2$, $1b_1$, $2b_1$. The dimension of the complete is 257 791(triplets) and 163 115 (singlets); b) thresholds: $T_1=1.0\times10^{-3}$ and $T_2 = 2.0$. The dimension of the P space is 2 806 (triplets) and 2 241 (singlets); c) the Davidson correction: $\Delta E = (E_{\mathrm{MRCISD}} - E_{\mathrm{REF}})(1-C_0)/(2C_0-1)$, where C_0 is the square sum of coefficients in MRCISD function; d) the relativism and zeroth-energy revision are not included in T_e[18].

2.3 Potential energy curves of BH

The determination of the ground-state potential energy curve of BH molecule is a “touchstone” for many *ab initio* methods and gives ones useful direction for selecting proper theoretical methods to calculate potential energy curves. Many methods, including HF and various post-HF, are tested in this paper. The basis set cc-pVTZ is selected. In order to determine the potential energy curves of BH under multi-reference condition, a preliminary CASSCF calculation is first performed for reference space CAS(4/5), i.e. 4 electrons are distributed in 5 active orbitals: 2σ, 3σ, 1π, 2π, and 4π. The results for single and multiple references are shown in fig. 1(a) and (b), respectively. Fig. 1 (a) was obtained by Gaussian-98w[20]. We notice that MP2, MP3 and MP4 of single reference perturbation methods cannot lead to correct decomposing limit and therefore are not reliable for the calculation of potential energy surfaces. As is well known that MP*n* are a kind of perturbation schemes based on orbital energy, whose difference between occupied and non-occupied orbitals is involved in the denominator and molecular integrals in the numerator of the energy formula. Let us investigate the energy at the two different nuclear separations, 0.32 nm (near the top of the MP4 potential energy curve) and 0.6 nm(the point having lower energy), and we found out that the energy deference between HOMO and LUMO at 0.6 nm decreases more than that of molecular integrals, which leads to the decreasing of the total energy. This is why MP*n* are not successful for the geometry far away from equilibrium. The curves for QCISD and QCISD (T) are basically correct though the QCISD(T) curve slightly descents owing to the perturbation treatment in the third order.

Fig. 1 (b) shows the multi-reference results obtained by the program of this paper except for CASSCF. The multi-reference methods, no matter whether they are MRPT2 or MRCISD, give the correct shape of a potential energy curve for a stable molecule.

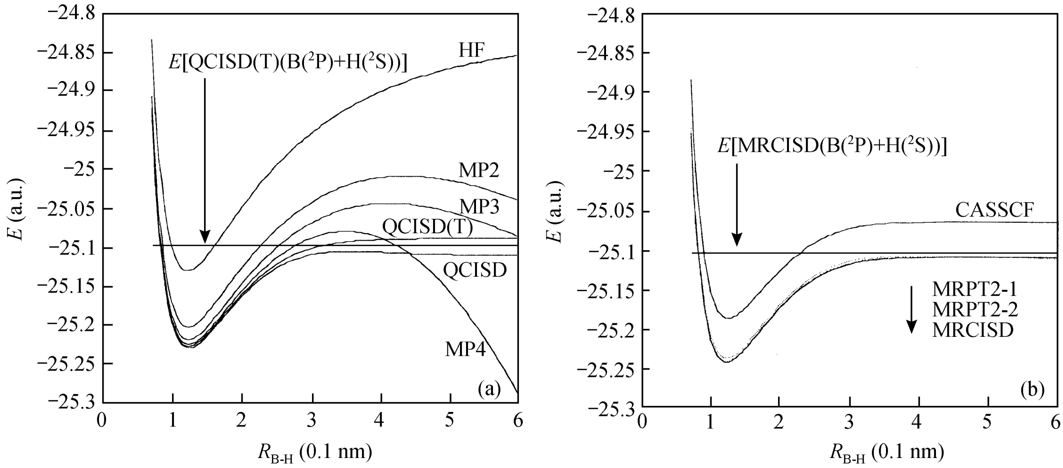

Fig. 1. The potential energy curves of BH.

3 Conclusions

Several multi-reference perturbation theories based on configurations are investigated in this paper. For the second-order perturbation calculations, the major computation task involves only the matrix elements in MRCISD. So our previous UGA methods to fast determine the coupling coefficients could be employed in the new MRPT2 codes. In MPRT2 methods based on configurations, the zeroth-order Hamiltonian operator is defined as the diagonal operator, whose expectation value is the diagonal element of Hamiltonian matrix. By this definition the matrix elements of a perturbation operator are actually the off-diagonal elements of Hamiltonian matrix. Four conclusions could be drawn from the studies in this paper. (i) All MP2 methods are much more efficient than the standard MRCISD calculations. The first method can reduce the computation time by more than two scales, and the accuracy of results is comparable to that of contracted CI methods. It is thus possible to extend this method into larger systems. (ii) Compared with the single reference MP2 methods, the multi-reference perturbation theory gives a more reliable and correct description for open-shelled systems and for molecules far away from its equilibrium geometry. (ⅲ) The second MRPT2 method could give results very close to that of MRCISD calculations and has the advantage avoiding intruder states. However, its efficiency is not very satisfactory and the size-consistency property always fails. For the other two methods the size-consistency is also not obvious because it is difficult to apply the linked graph theorem directly to the methods based on configurations. (ⅳ) Multi-reference techniques are extremely important in the investigation of the potential energy surface. Even for SCF calculation, MR techniques should be employed if the quasi degeneracy exists.

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