MCSCF reference quasidegenerate perturbation theory with Epstein–Nesbet partitioning

Haruyuki Nakano

Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606, Japan

A quasidegenerate perturbation theory (QDPT) with Epstein–Nesbet partitioning based on MCSCF reference functions is presented. The formulas for CSF-based matrix operations are derived. They are applied to the systems Be–H_2 and CO, and compared with other methods. The potential energy curves agree well with those of the full-CI or MR-CI methods.

1. Introduction

In understanding chemical reaction mechanisms it is crucial to obtain the associated potential energy surfaces. Much effort, therefore, has been spent in developing reliable and practical methods for calculating the surfaces. At present, the most reliable and familiar method is the multireference configuration interaction (MR-CI) method, which is stable on the whole region of the potential surface and is fairly accurate. However, MR-CI is difficult to apply, except for systems containing a small number of atoms, because the order of the Hamiltonian matrix increases rapidly for larger systems. The multiconfigurational self-consistent field (MCSCF) method is also popular, since it provides a qualitatively accurate description of the potential surface. However, it is not sufficient to obtain quantitative results within chemical accuracy. A method which is as efficient as the MCSCF method, yet is as accurate as MR-CI, is needed.

Perturbation theories (PTs) based on the MCSCF reference function [1–5] have been proposed and are proving to be useful. Indeed, they have many attractive features. First, they are more efficient than the other multireference based methods such as MR-CI and MR-CC (multireference coupled cluster) methods, because they do not require iterations for diagonalization or for solving linear equations. Secondly, they can yield results within chemical accu-

racy. Thirdly, they can describe open shell or excited states as well as closed shell ground states in a single framework.

In a previous paper [6], we proposed MCSCF reference quasidegenerate perturbation theory (QDPT) based on Møller–Plesset partitioning [7], which can give the energies of several states simultaneously. This method has the following advantages compared to the single state MCSCF PTs: (1) it can be applied to degenerate or quasidegenerate systems, and (2) interstate matrix elements such as transition dipole moments and nonadiabatic coupling elements can be calculated. In the present Letter, we have developed a new MCSCF reference QDPT based on the Epstein–Nesbet partitioning [8]. We derive here formulae using the sum-over-states method instead of the sum-over-orbitals method applied in the previous work [6]. Although the calculation of the third- or higher-order effective Hamiltonian is difficult with the sum-over-orbitals method, it is feasible with the present procedure. Only single and double excited configuration state functions (CSFs) from the reference space are necessary to obtain the third-order effective Hamiltonian.

The organization of this Letter is as follows: In section 2 the MCSCF reference QDPT is derived and the computational formulae are shown. In section 3, the method is applied to two systems: Be–H_2 and CO, and the results are compared with the other meth-

ods. Conclusions are made in section 4.

2. Theory

The zeroth-order wavefunctions (reference functions) in the MCSCF reference QDPT, which define P space, are the state-averaged MCSCF wavefunctions for target states (i). The complementary eigenfunctions of the MCSCF CI Hamiltonian (ii) and the CSFs generated by exciting electrons out of the CSFs in MCSCF space (iii) are orthogonal to the reference functions and define Q space. These functions are used as the basis set to expand the exact wavefunctions for the target states. For convenience, we further denote the MCSCF space spanned by functions (i) and (ii), and its orthogonal complementary space spanned by functions (iii), R space and S space, respectively.

With this basis set and the Epstein–Nesbet partitioning, the following relations are satisfied since the Hamiltonian is diagonal in R space,

$$V_{RR} = 0 , \quad V_{PP} = 0 , \tag{1}$$

$$V_{QP} = V_{SP} , \quad V_{PQ} = V_{PS} . \tag{2}$$

In the QDPT the Hamiltonian is block-diagonalized by the similar transformation [9],

$$K = W^{-1} H W , \tag{3}$$

or in the matrix notation,

$$\begin{pmatrix} H_{PP} & H_{PQ} \\ H_{QP} & H_{QQ} \end{pmatrix} \begin{pmatrix} W_{PP} & W_{PQ} \\ W_{QP} & W_{QQ} \end{pmatrix}$$

$$= \begin{pmatrix} W_{PP} & W_{PQ} \\ W_{QP} & W_{QQ} \end{pmatrix} \begin{pmatrix} K_{eff} & 0 \\ 0 & K_{QQ} \end{pmatrix} , \tag{4}$$

where K_{eff} is termed an effective Hamiltonian. The energies of the target states are obtained by diagonalizing the effective Hamiltonian.

Splitting H into H^0 and V in eq. (4), we obtain from the block-off-diagonal part of eq. (4)

$$[W_{QP}, H^0] = V_{QQ} W_{QP} + V_{SP} W_{PP}$$

$$- W_{QP}(K_{eff} - H^0_{PP}) , \tag{5}$$

and from the block-diagonal part

$$K_{eff} = H^0_{PP} W_{PP} + V_{PS} W_{SP} + (1 - W_{PP}) K_{eff} , \tag{6}$$

where we used eqs. (1) and (2). The W_{PP} part can be chosen arbitrarily, and this freedom allows us to define the various versions of the QDPT ("normalization condition"). To assure the hermiticity of the effective Hamiltonian, we utilize the unitary normalization [10],

$$W^\dagger W = 1 , \tag{7}$$

through any order. Eqs. (5), (6) and (7) are the basic equations of the present perturbation theory and are equivalent to the Schrödinger equation.

Expanding the operators in a perturbation series, recursive equations are obtained:

$$[W_{QP}^{(n)}, H^0] = V_{QQ} W_{QP}^{(n-1)} + V_{SP} W_{PP}^{(n-1)}$$

$$- \sum_{k=0}^{n-1} W_{QP}^{(k)} K_{eff}^{(n-k)} , \tag{8}$$

$$W_{PP}^{(n)} = - \sum_{k=1}^{[n/2]} (1 - \tfrac{1}{2}\delta_{n,2k}) (W_{PP}^{(k)\dagger} W_{PP}^{(n-k)}$$

$$+ W_{PQ}^{(k)\dagger} W_{QP}^{(n-k)} , \tag{9}$$

and

$$K_{eff}^{(n)} = V_{PS} W_{SP}^{(n-1)} - [W_{PP}^{(n)}, H^0_{PP}]$$

$$- \sum_{k=1}^{n-1} W_{PP}^{(k)} K_{eff}^{(n-k)} . \tag{10}$$

From these equations the effective Hamiltonians at the lowest few orders are obtained:

$$K_{eff}^{(1)} = 0 , \tag{11}$$

$$K_{eff}^{(2)} = \tfrac{1}{2} V_{PS} W_{SP}^{(1)} + \text{h.c.} , \tag{12}$$

$$K_{eff}^{(3)} = W_{PS}^{(1)\dagger} V_{SS} W_{SP}^{(1)} , \tag{13}$$

$$K_{eff}^{(4)} = \tfrac{1}{2} \{ W_{PQ}^{(2)\dagger} V_{QS} W_{SP}^{(1)}$$

$$- \tfrac{1}{2} W_{PS}^{(1)\dagger} W_{SP}^{(1)} (K_{eff}^{(2)} + V_{PS} W_{SP}^{(1)}) \} + \text{h.c.} , \tag{14}$$

etc., where h.c. stands for the hermite conjugate terms.

The matrix elements of the first- and the second-order transformation operators W in eqs. (12)–(14) are given by

$$\langle \alpha | W_{SP}^{(1)} | \beta \rangle = (E_\beta^{(0)} - E_\alpha^{(0)})^{-1} \langle \alpha | V | \beta \rangle$$

$$(\alpha \in S, \beta \in P) , \tag{15}$$

$$\langle \alpha | W^{(2)}_{QP} | \beta \rangle = (E^{(0)}_{\beta} - E^{(0)}_{\alpha})^{-1}$$

$$\times \sum_{\gamma \in S} \langle \alpha | V | \gamma \rangle \langle \gamma | W^{(1)}_{SP} | \beta \rangle \quad (\alpha \in Q, \beta \in P) .$$

$$(16)$$

Using the sum-over-states method, the second-, third-, and fourth-order effective Hamiltonians are calculated with matrix operations by the following:

(1) The second order:

$$K^{(2)}_{eff} = \tfrac{1}{2} w^{(1)T}_{SP} v^{(1)}_{SP} + h.c. , \tag{17}$$

with

$$v^{(1)}_{SP} = V_{SR} w^{(0)}_{RP} , \tag{18}$$

$$(w^{(1)}_{SP})_{ij} = (E^{(0)}_{j} - E^{(0)}_{i})^{-1} (v^{(1)}_{SP})_{ij} . \tag{19}$$

The $w^{(0)}_{RP}$ stores the eigenvectors of the MCSCF CI Hamiltonian for the target states, and V is the *CSF-based* perturbation matrix,

$$V = \begin{pmatrix} 0 & H_{RS} \\ H_{SR} & (H - H_{diag})_{SS} \end{pmatrix}, \tag{20}$$

where H denotes the CSF-based Hamiltonian matrix and H_{diag} is its diagonal part.

(2) The third order:

$$K^{(3)}_{eff} = w^{(1)T}_{SP} v^{(2)}_{SP} , \tag{21}$$

with

$$v^{(2)}_{SP} = V_{SS} w^{(1)}_{SP} . \tag{22}$$

(3) The fourth order:

$$K^{(4)}_{eff} = \tfrac{1}{2} [w^{(1)T}_{SP} v^{(3)}_{SP}$$

$$- \tfrac{1}{2} w^{(1)T}_{SP} w^{(1)}_{SP} (K^{(2)}_{eff} + v^{(1)T}_{SP} w^{(1)}_{SP})] + h.c. , \tag{23}$$

with

$$v^{(2)}_{CP} = w^{(0)T}_{RC} V_{RS} w^{(1)}_{SP} , \tag{24}$$

$$(w^{(2)}_{QP})_{ij} = (E^{(0)}_{j} - E^{(0)}_{i})^{-1} (v^{(2)}_{QP})_{ij} , \tag{25}$$

$$v^{(3)}_{SP} = V_{SS} w^{(2)}_{SP} + V_{SR} w^{(0)}_{RR} w^{(2)}_{RP} , \tag{26}$$

where the suffix C indicates the complementary space of the P space in the active (R) space, and $w^{(0)}_{RC}$ stores the eigenvectors of the MCSCF CI Hamiltonian other than the reference functions, i.e. the functions (ii).

The perturbation matrix V is the full-CI matrix at a general order; however in order to calculate the second- and the third-order effective Hamiltonian,

only single and double excited CSFs from the reference CSFs are necessary. In particular, for the second-order effective Hamiltonian only the SR part of the perturbation matrix is used. Moreover, full diagonalization of the MCSCF CI Hamiltonian is not necessary to obtain up to third-order energy. In section 3, the second- and the third-order results are presented.

3. Calculated results

The method developed in section 2 was applied to the systems Be–H$_2$ and CO, in order to illustrate its performance.

The state-averaged CASSCF calculation was carried out to obtain the orbital sets corresponding to the doubly occupied, the active, and the external subspaces. The orbitals in each space were defined so as to diagonalize the matrix [1–4],

$$f_{pq} = h_{pq} + \sum_{rs} D^{ave}_{rs} [(pq|rs) - \tfrac{1}{2}(pr|qs)] , \tag{27}$$

where D^{ave}_{rs} is the state-averaged one-particle density matrix.

The method was first applied to the lowest two $^1A_1$ states on the C$_{2v}$ insertion pathway for Be–H$_2$. The geometries and basis set were identical to those in refs. [11,12]. The orbitals $2a_1$, $3a_1$, $1b_1$, $1b_2$, $2b_2$, and $4a_1$ were regarded as active, and $1a_1$ was frozen in the perturbation calculation. The results are shown in table 1.

At most geometries, the energies up to the second order of the MCSCF reference QDPT with Epstein–Nesbet partitioning (EN2) are closer to full-CI energies than those with Møller–Plesset partitioning (MP2). The averages of the difference from the full-CI energies for MP2 are 1.35 and 1.67 mhartree for the $1\,^1A_1$ and $2\,^1A_1$ states, respectively; on the other hand those by EN2 are 0.60 and 1.32 mhartree. The energies were further improved by including the third-order contribution (EN3): the averages of the difference from full-CI were reduced to be 0.45 and 0.96 mhartree for the $1\,^1A_1$ and $2\,^1A_1$ states, respectively.

In many cases, the relative energies between different geometries or different electronic states other than the total energy itself are important to char-

Table 1
Total energies on the C_{2v} insertion pathway for Be-H_2 ($^1A_1$) in au [a]

Geometry	a	b	c	d	e	f	g	h
1 $^1A_1$								
CASSCF	−15.77273	−15.73004	−15.66815	−15.61779	−15.59738	−15.61666	−15.68337	−15.72836
	(0.00611)	(0.00688)	(0.00636)	(0.00479)	(0.00525)	(0.00813)	(0.00960)	(0.00811)
MP2 [b]	−15.77749	−15.73541	−15.67309	−15.62149	−15.60157	−15.62346	−15.69184	−15.73474
	(0.00135)	(0.00151)	(0.00142)	(0.00109)	(0.00106)	(0.00133)	(0.00113)	(0.00173)
EN2 [c]	−15.77811	−15.73622	−15.67372	−15.62186	−15.60188	−15.62383	−15.69284	−15.73602
	(0.00073)	(0.00070)	(0.00079)	(0.00072)	(0.00075)	(0.00096)	(0.00013)	(0.00045)
EN3 [c]	−15.77853	−15.73641	−15.67396	−15.62210	−15.60215	−15.62403	−15.69246	−15.73622
	(0.00031)	(0.00051)	(0.00055)	(0.00048)	(0.00048)	(0.00076)	(0.00051)	(0.00025)
full-CI [d]	−15.77884	−15.73692	−15.67451	−15.62258	−15.60263	−15.62479	−15.69297	−15.73647
2 $^1A_1$								
CASSCF	−15.40275	−15.40772	−15.43325	−15.51431	−15.54420	−15.52763	−15.45093	−15.44338
	(0.00469)	(0.00631)	(0.00949)	(0.01019)	(0.00975)	(0.00758)	(0.01081)	(0.00984)
MP2	−15.40614	−15.41235	−15.44100	−15.52244	−15.55202	−15.53393	−15.46010	−15.45040
	(0.00130)	(0.00168)	(0.00174)	(0.00206)	(0.00193)	(0.00128)	(0.00164)	(0.00282)
EN2	−15.40686	−15.41309	−15.44034	−15.52245	−15.55244	−15.53435	−15.46032	−15.45257
	(0.00058)	(0.00094)	(0.00240)	(0.00205)	(0.00151)	(0.00086)	(0.00142)	(0.00065)
EN3	−15.40714	−15.41340	−15.44150	−15.52335	−15.55295	−15.53449	−15.46005	−15.45274
	(0.00030)	(0.00063)	(0.00124)	(0.00115)	(0.00100)	(0.00072)	(0.00169)	(0.00048)
full-CI [e]	−15.40744	−15.41403	−15.44274	−15.52450	−15.55395	−15.53521	−15.46174	−15.45322

[a] Values in parentheses are differences from full-CI energies.
[b] Second-order results of MCSCF reference QDPT with Møller–Plesset partitioning [6].
[c] Second-(EN2) and third-(EN3) order results by the present method.
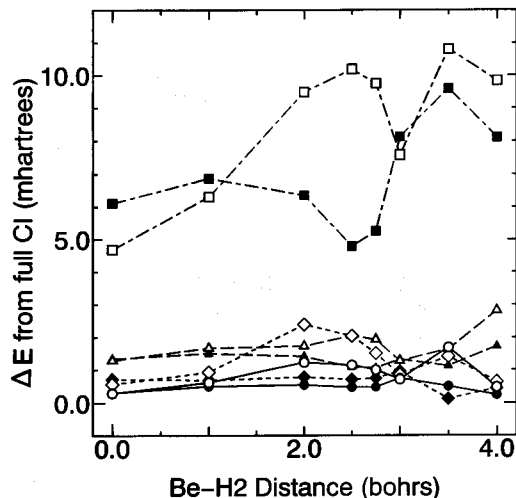[d] Ref. [11].   [e] Ref. [12].

Fig. 1. Energy differences from full-CI result of CASSCF (■), (□), MCSCF reference QDPT with Møller–Plesset partitioning (2nd) (▲), (△), and the present method ((♦), (◇) 2nd and (●), (○) 3rd) on the C_{2v} insertion pathway for Be-H_2($^1A_1$). The filled symbols denote the ground state.

acterize the potential surfaces. The differences from full-CI energies are drawn in fig. 1, where it can be seen that by EN2 and EN3 fairly balanced potential curves were obtained. In EN2 and EN3 method, the change of the error along the path is only 2 mhartree; on the other hand, in the CASSCF method the change is about 5–6 mhartree.

In table 2, vertical excitation energies are summarized with results by other methods. The results by EN3 are better than those by the CASSCF at all geometries a–h, and similarly the EN2 improved the CASSCF results except the value at geometry g. We can say that the MCSCF reference QDPT with Epstein–Nesbet partitioning provides a reliable estimate for the excitation energies as well as the potential energies of the reaction. The multiconfigurational coupled cluster method (CCMC) [11,12] also provided accurate results comparable to our method; however, its computational cost is much larger than that of the present method, since iterations are necessary to solve the CCMC equation. The traditional quasidegenerate many-body

Table 2
Vertical excitation energies for Be–H$_2$(^{1}A$_1$) in au

Geometry	a	b	c	d	e	f	g	h
CASSCF	0.36998	0.32232	0.23490	0.10348	0.05318	0.08903	0.23244	0.28498
CCMC [a]	0.37260	0.32415	0.23127	0.09745	0.04885	0.09025	0.23155	0.28461
QDMBPT [b] (2nd)	–	–	–	0.1030	0.0501	0.0764	–	–
QDMBPT [b] (3rd)	–	–	–	0.1180	0.0592	0.0818	–	–
QDMBPT [c] (2nd)	0.36909	0.32810	0.24138	0.10122	0.04879	0.08771	0.23306	0.26495
MP2 [d]	0.37135	0.32306	0.23209	0.09905	0.04955	0.08953	0.23174	0.28434
EN2	0.37125	0.32313	0.23338	0.09941	0.04944	0.08948	0.23252	0.28345
EN3	0.37139	0.32332	0.23246	0.09875	0.04920	0.08954	0.23241	0.28348
full-CI [a]	0.37140	0.32289	0.23177	0.09808	0.04868	0.08958	0.23123	0.28325

[a] Estimated from refs. [11,12].
[b] Estimated from ref. [13].
[c] Ref. [14].   [d] Ref. [6].

perturbation theory (QDMBPT) [13,14] based on the Hartree–Fock method did not give a better description than CASSCF for this system.

The second sample is carbon monoxide (CO). We calculated the lowest two states in $^1\Sigma^+$, namely the X $^1\Sigma^+$ and B $^1\Sigma^+$ states. The basis set used is a double zeta basis set: [4s2p] Dunning contraction of the Huzinaga (9s5p) primitive set [15]. This is too small to obtain quantitative results, but is sufficient for investigating the performance of the present perturbation method. The six orbitals, 3σ, 4σ, 1π, and 2π, were used as the active orbitals, and the 1s core or-

Table 3
Total energies for CO($^1\Sigma^+$) in au [a]

	Distance (au)					
	2.0504	2.1504	2.2504	2.6880	3.2256	4.3008
X $^1\Sigma^+$						
CASSCF	–112.78144	–112.79744	–112.80004	–112.73833	–112.63484	–112.51691
	(0.09577)	(0.09657)	(0.09748)	(0.10195)	(0.10632)	(0.10353)
MP2	–112.86653	–112.88319	–112.88659	–112.82920	–112.73091	–112.61269
	(0.01068)	(0.01082)	(0.01093)	(0.01108)	(0.01025)	(0.00775)
EN2	–112.88106	–112.89747	–112.90057	–112.84110	–112.73913	–112.61807
	(–0.00385)	(–0.00346)	(–0.00305)	(–0.00082)	(0.00203)	(0.00237)
EN3	–112.87034	–112.88711	–112.89059	–112.83339	–112.73410	–112.61426
	(0.00687)	(0.00690)	(0.00693)	(0.00689)	(0.00706)	(0.00618)
MR-SDCI	–112.87721	–112.89401	–112.89752	–112.84028	–112.74116	–112.62044
B $^1\Sigma^+$						
CASSCF	–112.34886	–112.40701	–112.44814	–112.51839	–112.51600	–112.49039
	(0.11034)	(0.11070)	(0.11119)	(0.11391)	(0.11495)	(0.10288)
MP2	–112.44544	–112.50432	–112.54631	–112.62098	–112.62204	–112.58587
	(0.01376)	(0.01339)	(0.01302)	(0.01132)	(0.00891)	(0.00740)
EN2	–112.45442	–112.51336	–112.55538	–112.62972	–112.62949	–112.59230
	(0.00478)	(0.00435)	(0.00395)	(0.00258)	(0.00146)	(0.00097)
EN3	–112.45129	–112.51008	–112.55196	–112.62581	–112.62505	–112.58910
	(0.00791)	(0.00763)	(0.00737)	(0.00649)	(0.00590)	(0.00417)
MR-SDCI	–112.45920	–112.51771	–112.55933	–112.63230	–112.63095	–112.59327

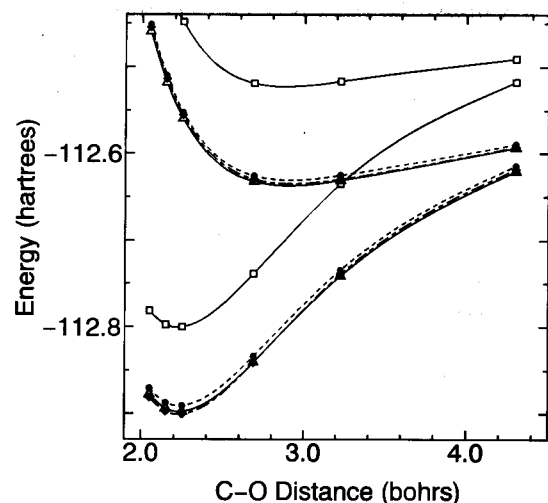[a] Values in parentheses are differences Irom MR-SDCI energies.

Fig. 2. (□) CASSCF, (△) MR-SDCI, and MCSCF reference QDPT with Epstein–Nesbet partitioning potential curves of two lowest states of CO($^1\Sigma^+$), (♦) EN2, (●) EN3.

bitals of the O and C (1σ and 2σ) and its corresponding virtual orbitals were frozen. The MR-SDCI calculation was also carried out with the same orbitals and reference space. The results are shown in table 3, and the potential curves in fig. 2. As seen in table 3, the EN2 gave a better description than the MP2 for both X $^1\Sigma^+$ and B $^1\Sigma^+$ states, as well as in the case of Be–H$_2$. The third-order correction, however, did not improve EN2 energies, which indicates that the convergence is not so rapid for this system. Nevertheless, the third-order contribution gave balanced potential curves compared with EN2 potential curves, since the change of the error of the EN3 is smaller than that of the EN2. The maximum deviation of the error by EN3 is only 3.74 mhartree; in other words, to an accuracy of 3.74 mhartree the shape of MR-CI potential curves could be obtained by EN3 method, where the computational cost is much less than the MR-CI method. This feature of the present method, EN2 and EN3, was found also for other molecular systems: H$_2$, NO and BN.

4. Summary

A new quasidegenerate perturbation theory based on the MCSCF reference functions with Epstein–Nesbet partitioning has been presented. Formulae for CSF-based matrix operation have been derived,

and the second- and third-order formulae were applied to the systems BeH$_2$ and CO. It was found that the second-order energies were more accurate than those by Møller–Plesset partitioning. The third-order contributions decrease the errors of the energies in the case of BeH$_2$. On the other hand, for the case of CO they did not improve the absolute energies, but by including the third-order contribution we obtained well-balanced potential curves being comparable to those of MR-SDCI. A similar feature has been confirmed in calculations for the molecules H$_2$, NO and BN.

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