Quasidegenerate perturbation theory with multiconfigurational self-consistent-field reference functions

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A quasidegenerate perturbation theory based on multiconfigurational self-consistent-field (MCSCF) reference functions is derived. The perturbation theory derived here is for multistate, where several MCSCF functions obtained by the state-averaged MCSCF method are used as the reference and an effective Hamiltonian is constructed by perturbation calculation. The energies of states interested in are obtained simultaneously by diagonalization of the effective Hamiltonian. An explicit formula of the effective Hamiltonian through second order is derived as well as general formalism, and is applied to calculate potential curves of the system H_2, Be–H_2, CO, NO, BN, and LiF. The results agree well with those of full configuration interaction or multireference single and double excitation configuration interaction methods for both the ground and the excited states.

I. INTRODUCTION

Many-body perturbation theory (MBPT) has been utilized as a convenient way of taking account of electron correlation beyond Hatree–Fock approximation. In particular, its single-reference version[1] seems to be fully established. Møller–Plesset perturbation method,[2] up to the fourth order, is equipped as a standard tool in program systems such as GAUSSIAN (Ref. 3) or HONDO (Ref. 4). However, the application of the single-reference many-body perturbation theories (SR-MBPT) is limited only to the system where the Hartree–Fock approximation is a good starting point. It cannot describe open-shell molecules, dissociation to open-shell fragment, and transition state of chemical reaction.

Quasidegenerate perturbation theory[5–9] (QDPT) has been developed to be applied to open-shell systems and excited states. Although much effort has been made to develop the quasidegenerate perturbation theory, it is not widely used among chemists. The major reason is that the QDPT often provides incorrect potential curves, since the perturbation series frequently diverges owing to the existence of intruder states.[10]

From the mid 1980's, multiconfigurational self-consistent-field (MC-SCF) reference perturbation theories[11–16] have been proposed to overcome the defects of the single-reference PT and the quasidegenerate PT, and some of them seem very promising. In fact, they have many advantages; (1) it is size consistent, (2) it yields fairly accurate results compared with traditional highly correlated methods, (3) it can be applied to the open shell and excited states, (4) it is stable on the wide region of potential surfaces, and (5) it is more efficient than other multireference based methods.

In the present paper, we propose a *multistate* perturbation theory based on several MCSCF wave functions, where several functions obtained by the state-averaged MCSCF method are used as the reference and an effective Hamiltonian is constructed by perturbation calculation. The states of interest are obtained by diagonalizing the effective Hamiltonian.

The MCSCF reference quasidegenerate perturbation theory retains all the advantages (1)–(5) of the previous MCSCF perturbation theories. Furthermore, it has the following advantages over the MCSCF perturbation theories: (1) the solutions interested can be obtained simultaneously, (2) it can be applied to degenerate or quasidegenerate systems, and states where the root flipping occurs, and (3) the interstate matrix elements, such as transition dipole moment, can be calculated in the same manner to obtain the effective Hamiltonian matrix in the energy calculation.

The organization of the present paper is as follows. In Sec. II, general formalism of MCSCF reference quasidegenerate perturbation theory and an explicit formula of the effective Hamiltonian through the second order of the perturbation are derived. In Sec. III, the present theory is applied to several systems H_2, Be–H_2, CO, NO, BN, and LiF, and the results are compared with those of full CI or multireference CI methods. Conclusions are made in Sec. IV.

II. THEORY

A. Formalism of MCSCF reference quasidegenerate perturbation theory

The total Hamiltonian is first split into

$$H = H^0 + V, \tag{1}$$

where H^0 is an unperturbed Hamiltonian and V is a perturbation. We assume that the Schrödinger equation for the unperturbed system,

$$H^0 | r \rangle = E_r^{(0)} | r \rangle \tag{2}$$

provides a complete set of eigenfunctions $\{ | r \rangle \}$ with corresponding eigenvalues $\{ E_r^{(0)} \}$. The exact eigenfunctions $\{ | \Psi_i \rangle \}$ can be expanded by the basis set $\{ | r \rangle \}$ as

$$| \Psi_i \rangle = \sum_r C_r | r \rangle . \tag{3}$$

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The zeroth-order wave functions (reference functions) in the present theory, which define P space, are state-averaged complete active space self-consistent-field (CASSCF) wave functions for target states (i). The complementary eigenfunctions of the CAS CI Hamiltonian (ii) and the CSF's generated by exciting electrons out of the CSF's in the active space (iii) are orthogonal to the reference functions and define Q space. These functions are used as the basis set to expand the exact wave functions for 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. Hereafter, Greek letters, capital letters, and lower case letters, are used to denote multiconfigurational states, single CSF's, and general states, respectively.

Since the Hamiltonian with the aforementioned basis is diagonal in the active space (R space), the following relations are satisfied:

$$(V_{RR})_{\alpha\beta}=(V)_{\alpha\beta}\delta_{\alpha\beta}=E_\alpha^{(1)}\delta_{\alpha\beta},$$

$$(V_{PP})_{\alpha\beta}=(V)_{\alpha\beta}\delta_{\alpha\beta}=E_\alpha^{(1)}\delta_{\alpha\beta},\tag{4}$$

$$V_{QP}=V_{SP},\qquad V_{PQ}=V_{PS}.\tag{5}$$

In a quasidegenerate perturbation theory, the Hamiltonian is block diagonalized by a similar transformation,[9]

$$\mathscr{H}=U^{-1}HU\tag{6}$$

or

$$HU=U\mathscr{H},\tag{7}$$

with

$$\mathscr{H}=\mathscr{H}_D,\tag{8}$$

$$\mathscr{H}_X=0,\tag{9}$$

where the suffix D and X denote a block-diagonal part and a block-off-diagonal part of an operator A,

$$A_D=A_{PP}+A_{QQ},\quad A_X=A_{PQ}+A_{QP}.\tag{10}$$

Rewriting Eq. (7) as

$$\begin{pmatrix} H_{PP} & H_{PQ}\\ H_{QP} & H_{QQ}\end{pmatrix}\begin{pmatrix} U_{PP} & U_{PQ}\\ U_{QP} & U_{QQ}\end{pmatrix}=\begin{pmatrix} U_{PP} & U_{PQ}\\ U_{QP} & U_{QQ}\end{pmatrix}\begin{pmatrix} \mathscr{H}_{\text{eff}} & 0\\ 0 & \mathscr{H}_{QQ}\end{pmatrix},\tag{11}$$

and splitting H into H^0 and V, we get the formulas,

$$[U_{QP},H^0]=V_{QQ}U_{QP}+V_{SP}U_{PP}-U_{QP}(\mathscr{H}_{\text{eff}}-H_{PP}^0),\tag{12}$$

$$\mathscr{H}_{\text{eff}}=H_{PP}^0U_{PP}+V_{PS}U_{SP}+V_{PP}U_{PP}-(U_{PP}-1)\mathscr{H}_{\text{eff}},\tag{13}$$

where Eq. (5) was used. These are basic equations in the present quasidegenerate perturbation theory and are equivalent to Schrödinger equation. However, the transformation operator cannot be fully determined only from these equations, since there is no equation for U_{PP}. This freedom allow us to define some different versions of quasidegenerate perturbation theory. The most familiar condition for U_{PP} is the intermediate normalization,[5] namely, $U_{PP}=1$ through any order. However, the disadvantage of using intermediate normalization is yielding nonsymmetric transition dipole moment matrices since the wave functions are not orthonormal. Therefore, in the present study, we choose U_{PP} so that U is unitary through any order,[7,8]

$$U^\dagger U=1.\tag{14}$$

Expanding Eqs. (12), (13), and (14) as a perturbation series, we obtain

$$[U_{QP}^{(n)},H^0]=V_{QQ}U_{QP}^{(n-1)}+V_{SP}U_{PP}^{(n-1)}-\sum_{i=1}^{n-1}U_{QP}^{(i)}\mathscr{H}_{\text{eff}}^{(n-i)},\tag{15}$$

$$\mathscr{H}_{\text{eff}}^{(n)}=H_{PP}^0U_{PP}^{(n)}+V_{PS}U_{SP}^{(n-1)}+V_{PP}U_{PP}^{(n-1)}-\sum_{i=1}^{n}U_{PP}^{(i)}\mathscr{H}_{\text{eff}}^{(n-i)},\tag{16}$$

and

$$U_{PP}^{(n)}=\begin{cases}1 & (n=0),\\ -\displaystyle\sum_{i=1}^{\lfloor n/2\rfloor}(1-\tfrac{1}{2}\delta_{2i,n})(U_{PP}^{(i)\dagger}U_{PP}^{(n-i)}+U_{PQ}^{(i)\dagger}U_{QP}^{(n-i)}) & (n>0)\end{cases}\tag{17}$$

Equation (16) can be rewritten in explicit Hermite forms[9] as

$$\begin{aligned}\mathscr{H}_{\text{eff}}^{(2n)}=&\tfrac{1}{2}(U_{PP}^{(n-1)\dagger}V_{PP}U_{PP}^{(n)}+U_{PP}^{(n-1)\dagger}V_{PS}U_{SP}^{(n)}+U_{PS}^{(n-1)\dagger}V_{SP}U_{PP}^{(n)}+U_{PQ}^{(n-1)\dagger}V_{QQ}U_{QP}^{(n)})\\&-\sum_{i=1}^{n}\sum_{j=0}^{\lfloor i/2\rfloor}(1-\tfrac{1}{2}\delta_{0,j}-\tfrac{1}{2}\delta_{2j,i})(U_{PP}^{(n-j)\dagger}U_{PP}^{(n-i+j)}+U_{PQ}^{(n-j)\dagger}U_{QP}^{(n-i+j)})\mathscr{H}_{\text{eff}}^{(i)}+(\text{H.c.}),\end{aligned}\tag{18}$$

$$\begin{aligned}\mathscr{H}_{\text{eff}}^{(2n+1)}=\tfrac{1}{2}\Bigg(&U_{PP}^{(n)\dagger}V_{PP}U_{PP}^{(n)}+U_{PP}^{(n)\dagger}V_{PS}U_{SP}^{(n)}+U_{PS}^{(n)\dagger}V_{SP}U_{PP}^{(n)}+U_{PQ}^{(n)\dagger}V_{QQ}U_{QP}^{(n)}-\sum_{i=1}^{n}\sum_{j=0}^{\lfloor (i-1)/2\rfloor}(1-\tfrac{1}{2}\delta_{2j,i-1})\\&\times(U_{PP}^{(n-j)\dagger}U_{PP}^{(n-i+j+1)}+U_{PQ}^{(n-j)\dagger}U_{QP}^{(n-i+j+1)})\mathscr{H}_{\text{eff}}^{(i)}+\text{H.c.}\Bigg),\end{aligned}\tag{19}$$

where (H.c.) stands for Hermite conjugate terms. Explicit formulas at the lowest few orders are

$$\langle\alpha|\mathscr{H}_{\rm eff}^{(0-1)}|\beta\rangle = E_\beta^{\rm MCSCF}\delta_{\alpha\beta}, \tag{20}$$

$$\langle\alpha|\mathscr{H}_{\rm eff}^{(2)}|\beta\rangle = \tfrac{1}{2}\langle\alpha|V(R_SV)|\beta\rangle + ({\rm H.c.}), \tag{21}$$

$$\langle\alpha|\mathscr{H}_{\rm eff}^{(3)}|\beta\rangle = \tfrac{1}{2}\langle\alpha|(VR_S^\dagger)(V-E_\beta^{(1)})(R_SV)|\beta\rangle + ({\rm H.c.}), \tag{22}$$

$$\begin{aligned}\langle\alpha|\mathscr{H}_{\rm eff}^{(4)}|\beta\rangle = {}& \tfrac{1}{2}\langle\alpha|(VR_S^\dagger)(V-E_\alpha^{(1)})(R_Q(V-E_\beta^{(1)}) \\ &\times(R_SV))|\beta\rangle - \tfrac{1}{8}\langle\alpha|(VR_S^\dagger)(R_SV) \\ &\times[3V(R_SV)+(VR_S^\dagger)V]|\beta\rangle \\ &+({\rm H.c.}),\end{aligned} \tag{23}$$

etc., where R_S and R_Q denote resolvent operators for the S space and the Q space, respectively, and are defined for an arbitrary operator A as

$$\begin{aligned}&\langle i|(R_SA)|j\rangle \\ &= \langle i|S(R_SA)P|j\rangle \\ &= \begin{cases}\dfrac{1}{E_j^{(0)}-E_i^{(0)}}\langle i|A|j\rangle & (\text{if}\quad i\in S, j\in P), \\ 0 & (\text{else}),\end{cases}\end{aligned} \tag{24}$$

$$\begin{aligned}&\langle i|(AR_S^\dagger)|j\rangle \\ &= \langle i|P(AR_S^\dagger)S|j\rangle \\ &= \begin{cases}\dfrac{1}{E_i^{(0)}-E_j^{(0)}}\langle i|A|j\rangle & (\text{if}\quad i\in P, j\in S), \\ 0 & (\text{else}).\end{cases}\end{aligned} \tag{25}$$

Equation (4) was used to obtain the third- and the fourth-order effective Hamiltonian.

It is noteworthy that, up to the third order, the effective Hamiltonian is expressed by only the states in P and S space. Thus full diagonalization of the MCSCF Hamiltonian is not necessary to obtain the second- and third-order energy.

To formulate the perturbation theory uniquely, we must define the zeroth-order Hamiltonian. It is useful if the zeroth-order Hamiltonian is a sum of one-particle operators, since the zeroth-order energies are immediately obtained as sums of the eigenvalues. However, the MCSCF orbital is not an eigenvector of a one-particle operator, so that diagonal part of an operator, which is analogous to the Fock operator, is used:

$$H^0 = \sum_{pq\sigma} f_{pq}a_{p\sigma}^\dagger a_{q\sigma}\delta_{pq} = \sum_{p\sigma}\epsilon_p a_{p\sigma}^\dagger a_{p\sigma}, \tag{26}$$

where ϵ_p is defined as the orbital energy. The label σ denotes the spin label. As the matrix f_{pq}, we adopt

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

where $D_{rs}^{\rm av}$ denotes state-averaged one-particle density matrix.

There still remains an arbitrariness in choosing the MCSCF orbitals because the CASSCF energies are invariant under the rotation in doubly occupied, active, and external orbital spaces. The canonical Fock orbital set[11–13] which leads the partially diagonal form in each space of f_{pq} and natural orbital set[14–16] which leads the diagonal form of the one-particle density matrix have been used so far. In the present paper we used both the orbital sets.

Finally, we mention the size consistency of the present theory. From diagrammatic treatment, it was proved that the perturbation theory with the unitary normalization is size consistent through fourth order of the effective Hamiltonian, and is not from the fifth order.[8] However, this fact is not so disappointing, since rapid convergence is expected in the MCSCF perturbation theory, and thus such higher-order terms are not required in many practical calculations.

B. Explicit expression for the effective Hamiltonian through second order

It is easy to show that the effective Hamiltonian up to first order $\mathscr{H}_{\rm eff}^{(0-1)}$ is equivalent to the CAS CI in the reference space $\{|\alpha\rangle\}$ and is given by

$$|\alpha\rangle = \sum_A C_{\alpha A}|A\rangle, \tag{28}$$

$$\langle\alpha|\mathscr{H}_{\rm eff}^{(0-1)}|\beta\rangle = \delta_{\alpha\beta}E_\alpha^{\rm MCSCF}, \tag{29}$$

where $|A\rangle$ and $E_\alpha^{\rm MCSCF}$ denote the CSF belonging to the active space and the MCSCF energy, respectively.

From Eq. (21) the second-order effective Hamiltonian is written as the sum-over-states form,

$$\langle\alpha|\mathscr{H}_{\rm eff}^{(2)}|\beta\rangle = \tfrac{1}{2}\sum_I \langle\alpha|V|I\rangle\frac{1}{E_\beta^{(0)}-E_I^{(0)}}\langle I|V|\beta\rangle + ({\rm H.c.}), \tag{30}$$

where $|I\rangle$ denotes the CSF belonging to S space. Equation (30) is further reducible to the sum-over-orbitals form, if we use Eq. (28) and substitute the second quantized form of perturbation V in Eq. (30),

$$\begin{aligned}V &= \sum_{pq}(h_{pq}-\epsilon_p\delta_{pq})E_{pq} + \frac{1}{2}\sum_{pqrs}(pq|rs)E_{pq,rs} \\ &= \sum_{pq}v_{pq}E_{pq} + \tfrac{1}{2}\sum_{pqrs}(pq|rs)E_{pq,rs},\end{aligned} \tag{31}$$

where E_{pq} and $E_{pq,rs}$ are one- and two-particle generators of the unitary group, respectively, and are defined by

$$E_{pq} = \sum_\sigma a_{p\sigma}^\dagger a_{q\sigma}, \tag{32}$$

$$E_{pq,rs} = E_{pq}E_{rs} - \delta_{qr}E_{ps} = \sum_{\sigma\sigma'} a_{p\sigma}^\dagger a_{r\sigma'}^\dagger a_{s\sigma'}a_{q\sigma}. \tag{33}$$

Substituting Eqs. (28) and (31) into Eq. (30), we obtain

$$\begin{aligned}\langle\alpha|\mathscr{H}_{\text{eff}}^{(2)}|\beta\rangle=&-\frac{1}{2}\sum_{AB}C_{\alpha A}C_{\beta B}\left\langle A\left|\left(\sum_{pq}v_{pq}E_{pq}+\frac{1}{2}\sum_{pqrs}(pq|rs)E_{pq,rs}\right)\left(\sum_{p'q'}\frac{v_{p'q'}}{\epsilon_{p'}-\epsilon_{q'}+E_B^{(0)}-E_\beta^{(0)}}E_{p'q'}\right.\right.\right.\\&\left.\left.\left.+\frac{1}{2}\sum_{p'q'r's'}\frac{(p'q'|r's')}{\epsilon_{p'}-\epsilon_{q'}+\epsilon_{r'}-\epsilon_{s'}+E_B^{(0)}-E_\beta^{(0)}}E_{p'q',r's'}\right)\right|B\right\rangle+(\text{H.c.}),\end{aligned}\tag{34}$$

where $E_B^{(0)}$ and $E_\beta^{(0)}$ are the zeroth-order energies of the CSF $|B\rangle$ and the state $|\beta\rangle$, respectively; that is,

$$E_B^{(0)}=\sum_p\mu_p\epsilon_p\quad(\mu_p=0,1,\text{ or }2),\tag{35}$$

$$E_\beta^{(0)}=\sum_p\langle\beta|E_{pp}|\beta\rangle\epsilon_p,\tag{36}$$

where μ_p is the occupation number and $\langle\beta|E_{pp}|\beta\rangle$ the averaged occupation number. The set of suffix in the summation $\{p',q'\}$ and $\{p',q',r',s'\}$ are restricted so that the intermediate states belong to the S space. Hence, the following types of generators $E_{p'q'}$ and $E_{p'q',r's'}$ appear as

$$E_{p'q'}:E_{ea},\ E_{ei},\ E_{ai},$$

$$E_{p'q',r's'}:\begin{cases}E_{ea,ii}, & E_{ei,jj}, & E_{ai,jj}, & E_{ii,ea}, & E_{ii,ej}, & E_{ii,aj}\\ E_{ei,ia}, & E_{ei,ij}, & E_{ai,ij}, & E_{ia,ei}, & E_{ij,ei}, & E_{ij,ai}\\ E_{ea,fb}, & E_{ea,fi}, & E_{ei,fa}, & E_{ei,fj}, & & \\ E_{ea,bc}, & E_{ea,bi}, & E_{ei,ab}, & E_{ei,aj}, & E_{ab,ec}, & E_{ab,ei}, & E_{ai,eb}, & E_{ai,ej}\\ E_{ab,ci}, & E_{ai,bc}, & E_{ai,bj} & & & \end{cases},$$

where $\{i,j\}$, $\{a,b\}$, and $\{e,f\}$ denote doubly occupied, active, and external orbital labels, respectively.

Before deriving the final form of the second-order effective Hamiltonian, we redefine the one-particle perturbation operator by

$$u_{pq}=v_{pq}+\sum_i[2(pq|ii)-(pi|iq)],\tag{37}$$

where the suffix i runs over doubly occupied orbitals, and define the difference between $E_B^{(0)}$ and $E_\beta^{(0)}$ by

$$\Delta E_{B\beta}=E_B^{(0)}-E_\beta^{(0)}.\tag{38}$$

Ordering the generators in Eq. (34) to normal products with only active orbital labels, we obtain

$$\begin{aligned}\langle\alpha|\mathscr{H}_{\text{eff}}^{(2)}|\beta\rangle=\frac{1}{2}\sum_{AB}C_{A\alpha}C_{B\beta}\Bigg[&-\delta_{AB}\left(\sum_{ia'}\frac{2u_{ia'}u_{a'i}}{\epsilon_{a'}-\epsilon_i+\Delta E_{B\beta}}+\sum_{ija'b'}\frac{(ia'|jb')[2(a'i|b'j)-(a'j|b'i)]}{\epsilon_{a'}-\epsilon_i+\epsilon_{b'}-\epsilon_j+\Delta E_{B\beta}}\right)\\&+\sum_{pq}\langle A|E_{pq}|B\rangle\Bigg[\sum_i\frac{u_{iq}u_{pi}}{\epsilon_p-\epsilon_i+\Delta E_{B\beta}}-\sum_e\frac{u_{pe}u_{eq}}{\epsilon_e-\epsilon_q+\Delta E_{B\beta}}-\sum_{ia'}\frac{u_{ia'}[2(a'i|pq)-(a'q|pi)]}{\epsilon_{a'}-\epsilon_i+\epsilon_p-\epsilon_q+\Delta E_{B\beta}}\\&-\sum_{ia'}\frac{[2(ia'|pq)-(iq|pa')]u_{a'i}}{\epsilon_{a'}-\epsilon_i+\Delta E_{B\beta}}+\sum_{ija'}\frac{(ja'|iq)[2(a'j|pi)-(a'i|pj)]}{\epsilon_{a'}-\epsilon_j+\epsilon_p-\epsilon_i+\Delta E_{B\beta}}\\&-\sum_{ia'b'}\frac{(ia'|pb')[2(a'i|b'q)-(a'q|b'i)]}{\epsilon_{a'}-\epsilon_i+\epsilon_{b'}-\epsilon_q+\Delta E_{B\beta}}\Bigg)+\sum_{pqrs}\langle A|E_{pq,rs}|B\rangle\left(\sum_i\frac{u_{iq}(pi|rs)}{\epsilon_p-\epsilon_i+\epsilon_r-\epsilon_s+\Delta E_{B\beta}}\right.\\&-\sum_e\frac{u_{pe}(eq|rs)}{\epsilon_e-\epsilon_q+\epsilon_r-\epsilon_s+\Delta E_{B\beta}}+\sum_i\frac{(iq|rs)u_{pi}}{\epsilon_p-\epsilon_i+\Delta E_{B\beta}}-\sum_e\frac{(pe|rs)u_{eq}}{\epsilon_e-\epsilon_q+\Delta E_{B\beta}}\\&-\frac{1}{2}\sum_{ij}\frac{(iq|js)(pi|rj)}{\epsilon_p-\epsilon_i+\epsilon_r-\epsilon_j+\Delta E_{B\beta}}-\frac{1}{2}\sum_{a'e}\frac{(pa'|re)(a'q|es)}{\epsilon_{a'}-\epsilon_q+\epsilon_e-\epsilon_s+\Delta E_{B\beta}}-\frac{1}{2}\sum_{ae}\frac{(pe|ra)(eq|as)}{\epsilon_e-\epsilon_q+\epsilon_a-\epsilon_s+\Delta E_{B\beta}}\\&+\sum_{ia'}\frac{(pa'|iq)(a'i|rs)}{\epsilon_{a'}-\epsilon_i+\epsilon_r-\epsilon_s+\Delta E_{B\beta}}+\sum_{ia'}\frac{(pa'|is)(a'q|ri)}{\epsilon_{a'}-\epsilon_q+\epsilon_r-\epsilon_i+\Delta E_{B\beta}}\end{aligned}$$

TABLE I. (a) Difference of total energy from full CI for $H_2(^1\Sigma_g^+)$ in a.u. (b) Difference of total energy from full CI for $H_2(^3\Sigma_u^+)$ in a.u. The symbol r_e denotes the bond length of the ground state, 1.4 a.u.

	Geometry	r_e	$1.5r_e$	$2.0r_e$	100 a.u.
(a)	First state				
	CASSCF	0.014 659	0.007 784	0.001 619	0.000 058
	Present (canonical)	0.001 620	0.000 670	0.000 276	0.000 007
	Present (natural)	0.001 447	0.000 613	0.000 283	0.000 007
	Full CI	−1.167 438	−1.121 311	−1.063 509	−0.999 619
	Second state				
	CASSCF	0.006 455	0.002 438	0.004 408	0.005 144
	Present (canonical)	0.000 773	0.000 278	0.000 448	0.000 191
	Present (natural)	0.000 851	0.000 296	0.000 444	0.000 185
	Full CI	−0.533 483	−0.533 899	−0.589 810	−0.496 940
(b)	First state				
	CASSCF	0.001 400	0.002 478	0.001 311	0.000 000
	Present (canonical)	0.000 179	0.000 294	0.000 122	0.000 000
	Present (natural)	0.000 079	−0.000 007	0.000 003	0.000 000
	Full CI	−0.777 953	−0.906 507	−0.961 301	−0.999 619
	Second state				
	CASSCF	0.001 975	0.001 960	0.000 878	0.000 000
	Present (canonical)	0.000 245	0.000 423	0.000 086	0.000 000
	Present (natural)	0.000 247	0.000 506	0.000 145	0.000 000
	Full CI	−0.381 853	−0.471 847	−0.477 448	−0.478 555

$$-\sum_{ia'}\frac{(ia'|pq)[2(a'i|rs)-(a's|ri)]}{\epsilon_{a'}-\epsilon_i+\epsilon_r-\epsilon_s+\Delta E_{B\beta}}\Bigg)+\sum_{pqrstu}\langle A|E_{pq,rs,tu}|B\rangle\Bigg(\sum_i\frac{(iq|rs)(pi|tu)}{\epsilon_p-\epsilon_i+\epsilon_t-\epsilon_u+\Delta E_{B\beta}}$$

$$-\sum_e\frac{(pe|rs)(eq|tu)}{\epsilon_e-\epsilon_q+\epsilon_t-\epsilon_u+\Delta E_{B\beta}}\Bigg)\Bigg]+(\text{H.c.}). \qquad (39)$$

The $E_{pq,rs,tu}$ is the three-particle generator defined by

$$E_{pq,rs,tu}=\sum_{\sigma\sigma'\sigma''}a^\dagger_{p\sigma}a^\dagger_{r\sigma'}a^\dagger_{t\sigma''}a_{u\sigma''}a_{s\sigma'}a_{q\sigma}. \qquad (40)$$

The orbital labels $\{i,j\}$, $\{a\}$, and $\{e\}$ are for doubly occupied, active, and external orbitals, respectively, and $\{a',b'\}$ run over both active and external orbitals, and the suffix of the generator $\{p,q,r,s,t,u\}$ run over only active orbitals.

The present method has some computational merits as compared with the MR-CI method. First, neither diagonalization of large matrix nor solving large scale linear

TABLE II. Spectroscopic constants for H_2.

		r_e (Å)	D_e (eV)	ω_e (cm^{-1})
$X\,^1\Sigma_g^+$	CASSCF	0.7571	4.174	4329
	Present (canonical)	0.7426	4.523	4522
	Present (natural)	0.7423	4.527	4525
	Full CI	0.7401	4.567	4551
$E\,^1\Sigma_g^+$	CASSCF	0.9023	1.282	3116
	Present (canonical)	0.8893	1.268	3272
	Present (natural)	0.8895	1.267	3270
	Full CI	0.8875	1.278	3290
$F\,^1\Sigma_g^+$	CASSCF	2.3413	4.864	1371
	Present (canonical)	2.3367	4.870	1381
	Present (natural)	2.3367	4.870	1381
	Full CI	2.3363	4.870	1381
$e\,^3\Sigma_a^+$	CASSCF	1.3486		1688
	Present (canonical)	1.3396		1727
	Present (natural)	1.3398		1717
	Full CI	1.3356		1723

TABLE III. The difference of total energy from full CI on the C_{2v} insertion pathway for Be–$H_2(^1A_1)$ in a.u.

Geometry	*a*	*b*	*c*	*d*	*e*	*f*	*g*	*h*	*i*
First state									
CASSCF	0.006 11	0.006 88	0.006 36	0.004 79	0.005 25	0.008 13	0.009 60	0.008 11	0.007 44
CCMC[a]	0.000 30	0.000 54	0.001 50	0.002 63	0.002 33	0.001 83	0.001 18	0.000 16	0.000 29
QD-MBPT[b]	−0.007 96	−0.010 01	−0.008 51	−0.003 05	−0.001 90	−0.001 14	−0.003 15	−0.002 59	
Present (canonical)	0.001 35	0.001 51	0.001 42	0.001 09	0.001 06	0.001 33	0.001 13	0.001 73	0.001 50
Present (natural)	0.001 34	0.001 44	0.001 42	0.001 11	0.001 14	0.001 43	0.001 12	0.001 70	0.001 49
Full CI[c]	−15.778 84	−15.736 92	−15.674 51	−15.622 58	−15.602 63	−15.624 79	−15.692 97	−15.736 47	−15.762 63
Second state									
CASSCF	0.004 69	0.006 31	0.009 49	0.010 19	0.009 75	0.007 58	0.010 81	0.009 84	0.005 83
CCMC[c]	0.001 50	0.001 80	0.001 00	0.002 00	0.002 50	0.002 50	0.001 50	0.001 20	0.001 30
QD-MBPT[b]	−0.010 27	−0.004 80	0.001 10	0.000 09	−0.001 79	−0.003 01	−0.001 32	−0.020 89	
Present (canonical)	0.001 30	0.001 68	0.001 74	0.002 06	0.001 93	0.001 28	0.001 64	0.002 82	0.000 59
Present (natural)	0.001 31	0.001 74	0.002 07	0.002 24	0.002 00	0.001 33	0.001 77	0.002 92	0.000 59
Full CI[c]	−15.407 44	−15.414 03	−15.442 74	−15.524 50	−15.553 95	−15.535 21	−15.461 74	−15.453 22	−15.475 36

[a] Reference 19.
[b] Reference 21.
[c] Reference 20.

equation is necessary. Second, the larger block-diagonal part of the Hamiltonian, H_{QQ}, is not necessary. Thirdly, the integral transformation for the two-electron integrals with three and four external orbital labels is not necessary.

Since the codes of the present method and of the MR-CI method were not fully optimized, the comparison of the computational time is not so meaningful. However, the CPU time to compute Eq. (39) is less than or almost equal to the time of one iteration in the MR-CI method, which suggests the efficiency of the present method.

III. APPLICATIONS

The present method was applied to several molecular systems for illustrating its performance. The results will be compared with those of full CI or multireference CI method using the same basis set and the same reference space. The target states were the lowest two states in the same spin and symmetry.

A. Hydrogen molecule ($^1\Sigma_g^+$ states and $^3\Sigma_u^+$ states)

Calculations of potential curves for $^1\Sigma_g^+$ states and $^3\Sigma_u^+$ states of the hydrogen molecule have been performed using triple-zeta plus polarization (orbital exponent 1.0) basis set.[17] The orbitals, $1\sigma_g$, $1\sigma_u$, $2\sigma_g$, and $2\sigma_u$ were chosen to be active, which are necessary for proper dissociation of the lowest two states of $^1\Sigma_g^+$ and $^3\Sigma_u^+$.

The total energies at some selected internuclear distances are shown in Tables I(a) and I(b). These tables show that the present method provide very close energies to those of full CI method for both the ground and excited states. For $1\,^1\Sigma_g^+$ state, the CASSCF description was poor near the equilibrium structure; the deviation at $r=1.4$ bohr was 14.7 mhartree. The present method reduced it to 1.6 mhartree (for the canonical Fock orbital). For $^3\Sigma_u^+$ states, compared to the largest deviation of the CASSCF, 2.5 mhartree, that of the present method was only 0.5 mhartree. About 85%–90% of the dynamic correlation has been recovered by the present method.

Table II shows the spectroscopic constants for the bound states, i.e., $X\,^1\Sigma_g^+$, $E\,^1\Sigma_g^+$, $F\,^1\Sigma_g^+$, and $e^3\Sigma_u^+$. The present method provided very close values to the full CI results. The deviations for $X\,^1\Sigma_g^+$ state, for example, were only 0.0025 Å, 0.044 eV, and 29 cm^{-1}, in the bond length, the dissociation energy, and the vibrational frequency, respectively.

B. C_{2v} insertion pathway for BeH_2

The potential curves of the perpendicular (C_{2v}) insertion of Be into H_2 were calculated. Many works[18–20] have been done for this system for some reasons. First, several

TABLE IV. Vertical excitation energies for Be–$H_2(^1A_1)$ in a.u.

Geometry	*a*	*b*	*c*	*d*	*e*	*f*	*g*	*h*	*i*
CASSCF	0.369 98	0.322 32	0.234 90	0.103 48	0.053 18	0.089 03	0.232 44	0.284 98	0.285 66
CCMC[a]	0.372 60	0.324 15	0.231 27	0.097 45	0.048 85	0.090 25	0.231 55	0.284 61	0.288 28
QD-MBPT[b]	0.369 09	0.328 10	0.241 38	0.101 22	0.048 79	0.087 71	0.233 06	0.264 95	
Present (canonical)	0.371 35	0.323 06	0.232 09	0.099 05	0.049 55	0.089 53	0.231 74	0.284 34	0.286 36
Present (natural)	0.371 37	0.323 19	0.232 42	0.099 21	0.049 54	0.089 48	0.231 88	0.284 47	0.286 37
Full CI[a]	0.371 40	0.322 89	0.231 77	0.098 08	0.048 68	0.089 58	0.231 23	0.283 25	0.287 27

[a] Estimated from Refs. 19 and 20.
[b] Reference 21.

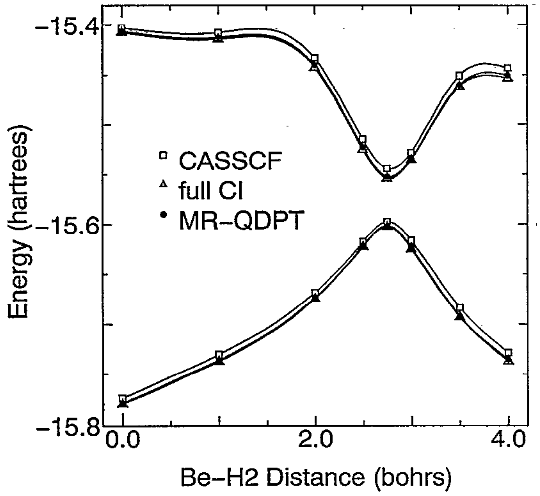

FIG. 1. CASSCF, full CI, and MCSCF reference QDPT potential curves on C_{2v} insertion path way for Be–$H_2(^1A_1)$.

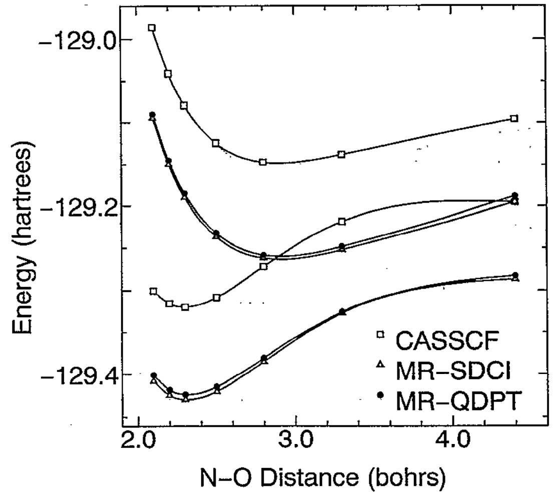

FIG. 3. CASSCF, MR-SCDI, and MCSCF reference QDPT potential curves of two lowest states of NO ($^2\Pi$).

configurations are necessary to describe the reaction, and thus it is suited to test the reliability of multireference based methods. Second, the system is small enough to allow us to carry out the full CI calculation.

The geometries and the basis set were identical to those in Refs. 20 and 21. The orbitals $2a_1$, $3a_1$, $1b_1$, $1b_2$, $2b_2$, and $4a_1$ were active, and $1a_1$, which corresponds to the $1s$ orbital of Be, was optimized in the CASSCF calculation, but frozen in the perturbation calculation. The results are shown in Table III(a) with those of multiconfigurational coupled cluster method[19,20] (CCMC), quasidegenerate many-body perturbation theory (QD-MBPT),[21] and full CI method.[19,20] The potential curves are illustrated in Fig. 1. From Table III it is estimated that the present method yielded 77%–88% and 72%–90% of dynamical correlation energy for the ground and the excited states, respectively; and the percentage averaged over the geometries and the states is 80%. In the CCMC method, 45%–98% and 67%–88% of dynamical correlation were reproduced for the ground and the excited states, respectively; and the average is 79%. We can say that the present method is comparable to the CCMC method as for energy. However, the present method is more efficient, since in the CCMC method, the reference MCSCF (18 CSF's) wave function was optimized for each state and coupled cluster equation was also solved separately; on the other hand, in the present method, state-averaged CASSCF (37 CSFs) was performed to construct the reference states once, and the two states were obtained simultaneously in perturbation calculation. We note that the state-specific 18-CSF MCSCF energies used in the CCMC calculations were lower than those of the present state-averaged 37-CSF CASSCF for the excited state. The 18-CSF MCSCF ground state energies were not given in Ref. 20.

The quasidegenerate perturbation method[21] overestimated the correlation energies. At geometries *d, e, f,* and *g*, this method gave good results; however at geometries *a, b,* and *c*, the errors were greater than those of CASSCF.

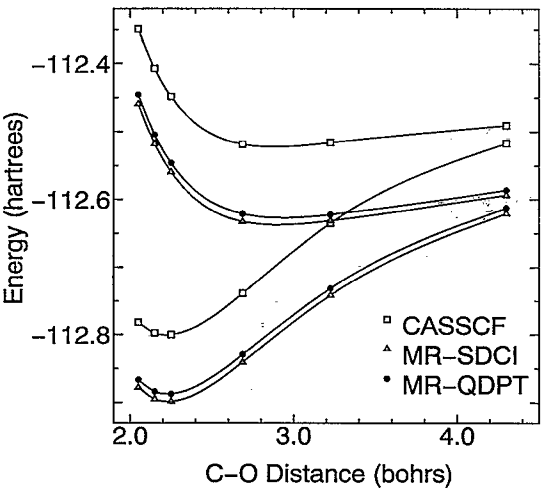

FIG. 2. CASSCF, MR-SDCI, and MCSCF reference QDPT potential curves of two lowest states of CO($^1\Sigma^+$).

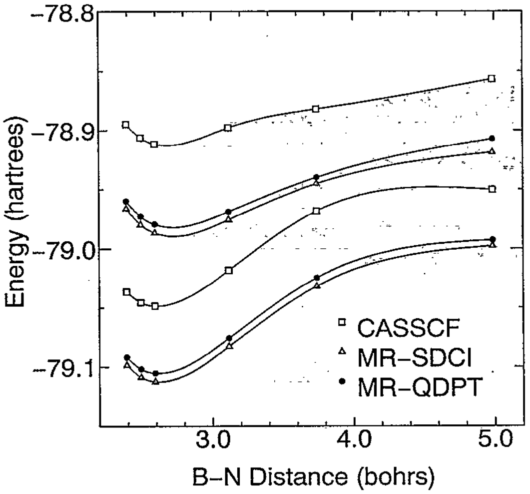

FIG. 4. CASSCF, MR-SDCI, and MCSCF reference QDPT potential curves of two lowest states of BN($^3\Pi$).

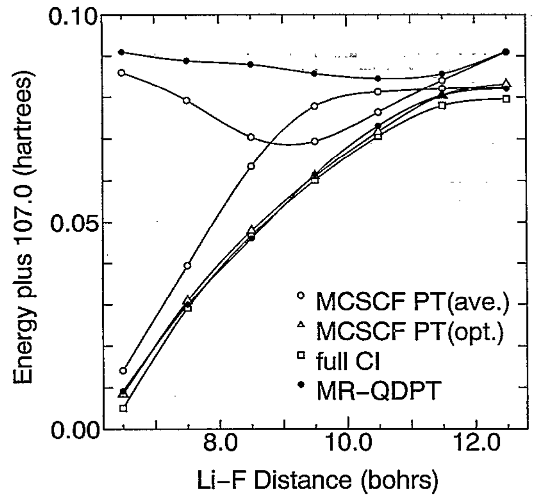

FIG. 5. Single-reference-state MCSCF PT, full CI, and MCSCF reference QDPT potential curves in avoided crossing region for LiF, where "CASSCF PT(ave.)" and "CASSCF PT(opt.)" denote single-reference-state MCSCF PT using state-averaged CASSCF orbital and that using state-specific CASSCF orbital optimized for the ground state, respectively.

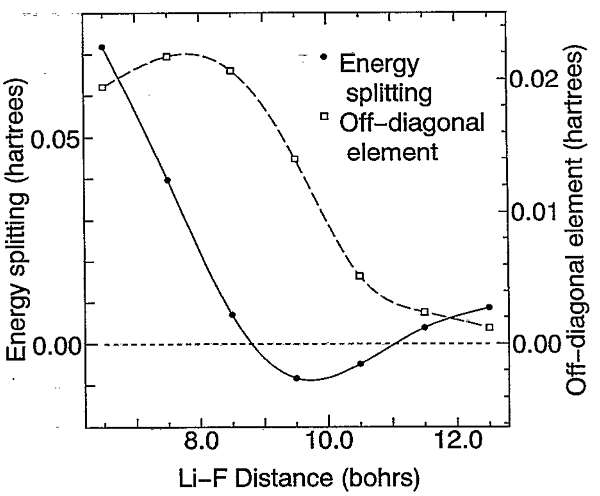

FIG. 6. Difference between the two diagonal elements of the effective Hamiltonian which are equivalent to the ground and excited states energy splitting by the single-reference-state MCSCF PT, and off-diagonal element.

In Table IV, the vertical excitation energies are shown. The present method improved the CASSCF excitation energies at all geometries, while the other methods did not at some geometries. This indicates that the present method provides reliable estimates for, not only the absolute value of energy, but also the relative value.

C. CO ($X\ ^1\Sigma^+$ and $B\ ^1\Sigma^+$), NO ($X\ ^2\Pi$ and $B\ ^2\Pi$), and BN ($X\ ^3\Pi$ and $A\ ^3\Pi$)

The potential curves of CO, NO, and BN were calculated using double-zeta basis set,[22] which is the $[4s2p]$ Dunning contraction of the Huzinaga $(9s5p)$ primitive set. Although the basis set is small, it is sufficient to check the performance of the present method. Since the full CI calculation is difficult to be performed, the multireference single and double excited CI (MR-SDCI) method using the same orbital and reference space was employed for comparison.

In the CASSCF calculations, six orbitals (3σ, 4σ, 1π, and 2π) were used to construct the active space for CO and NO, and seven orbitals (2σ, 3σ, 4σ, 1π, and 2π) for BN. The 1σ core orbitals and its corresponding virtual orbitals were not correlated in the present and the MR-SDCI method in order to reduce the number of CSF in the CI method.

The potential curves in the region $r_e-2.0r_e$ are illustrated in Figs. 2, 3, and 4. In this region, the deviations of the CASSCF energy from the MR-SDCI results were 0.10–0.11 hartree for CO and NO, and 0.05–0.08 hartree for BN. These were reduced by the present method to 14, 8, and 12 mhartree for CO, NO, and BN, respectively. The 81%–99 % of the error from the MR-SDCI results has been recovered by the present method.

In many cases, the relative energies between different geometries or different electronic states other than the total energy itself are important to characterize the potential curves. In Table V, vertical excitation energies are shown. The results of the present method agreed well with the MR-SDCI data. The difference was less than 3 mhartree. To estimate the shapes of the potential curves, which is crucial for dynamics, we further examined the change of the error along the bond distance, and found that the present method gave the improved potential curves where the changes were smaller than those of CASSCF. In the present method, the changes of the error were 7, 6, and 7 mhartree for CO, NO, and BN, respectively; on the other hand, they were 19, 23, and 30 mhartree in the CASSCF method.

D. Ionic-neutral curve crossing in $^1\Sigma^+$ states of LiF

Finally, we investigated ionic-neutral curve crossing between the two lowest $^1\Sigma^+$ states of LiF as an example of

TABLE V. Vertical excitation energies for CO, NO, and BN in a.u.

r	CO($X\,^1\Sigma^+ \rightarrow B\,^1\Sigma^+$) 2.1504 bohr	NO($X\,^2\Pi \rightarrow B\,^2\Pi$) 2.20 bohr	BN($X\,^3\Pi \rightarrow A\,^3\Pi$) 2.4931 bohr
CASSCF	0.39043	0.27480	0.13921
Present (canonical)	0.37887	0.27303	0.12922
Present (natural)	0.37870	0.27271	0.12956
MR-SDCI	0.37630	0.27442	0.12922

TABLE VI. Total energies for LiF in a.u.

r (a.u.)	6.5	7.5	8.5	9.5	10.5	11.5	12.5
First state							
CASSCF (av.)[a]	−106.885 92	−106.865 72	−106.853 10	−106.848 36	−106.847 23	−106.846 96	−106.846 90
CASSCF (opt.)[b]	−106.938 77	−106.899 36	−106.886 09	−106.875 48	−106.866 83	−106.862 30	−106.862 30
MCSCF PT (av.)	−106.985 83	−106.960 45	−106.936 50	−106.922 16	−106.918 67	−106.917 92	−106.917 73
MCSCF PT (opt.)	−106.991 48	−106.969 10	−106.952 10	−106.938 82	−106.928 20	−106.919 54	−106.916 84
Present[c]	−106.990 75	−106.970 03	−106.953 97	−106.938 46	−106.926 80	−106.919 53	−106.917 89
Full CI[d]	−106.994 85	−106.970 82	−106.953 23	−106.939 80	−106.929 28	−106.921 99	−106.920 46
Second state							
CASSCF (av.)	−106.832 10	−106.834 21	−106.832 30	−106.825 13	−106.816 41	−106.808 45	−106.801 60
MCSCF PT (av.)	−106.913 91	−106.920 73	−106.929 52	−106.930 49	−106.923 54	−106.915 88	−106.909 05
Present	−106.908 99	−106.911 15	−106.912 06	−106.914 19	−106.915 41	−106.914 27	−106.908 88

[a] State-averaged CASSCF.
[b] State-specific CASSCF optimized for the ground state.
[c] Only canonical Fock orbital was used.
[d] Reference 23.

a system which complicated by root flipping due to strong interaction. Bauschlicher *et al.*[23] studied this system with full CI and MR-CI methods. We also calculated potential curves of the two lowest states in the ionic-neutral curve crossing region using the present theory and the single-reference-state MCSCF perturbation theory for comparison. The basis set used was the same as that used by Bauschlicher *et al.*[23] Active orbitals were 4σ, 5σ, 1π, and 2π orbitals, which corresponds to F($2p\sigma$), Li($2s$), F($2p\pi$), and Li($2p\pi$), respectively, in the dissociation limit. The orbitals 1σ, 2σ, and 3σ were frozen in the perturbation calculation. Only the canonical Fock orbital was used.

Results are shown in Table VI and Fig. 5. The single-reference-state MCSCF perturbation theory using the state-averaged CASSCF orbital did not yield correct potential curves, since the two curves are crossing. The two energies at 9.5 bohr and 10.5 bohr are in the reverse order to those of CASSCF. On the contrary, the present method gave correct potential curves, and the maximum error from full CI energy was 4.1 mhartree for the ground state. (For the excited state, results by the full CI method have not been reported.)

The difference between the two diagonal elements and the off-diagonal element of the effective Hamiltonian are shown in Fig. 6. From Fig. 6 it can be seen that the off-diagonal element is very large ($\sim 2\times 10^{-2}$ hartree). If we apply the single-reference-state MCSCF perturbation theory with state-averaged MCSCF orbitals, which is equivalent to the diagonal elements of the effective Hamiltonian, such strong interaction cannot be taken into account. On the contrary, in the present theory the interaction can be included as the off-diagonal element of the effective Hamiltonian naturally.

The single-reference-state MCSCF perturbation theory using the CASSCF orbital optimized for the ground state yielded good results. The maximum error was 3.6 mhartree, which is nearly equal to that of the present method. However, for the excited state at all geometries shown in Table V, CASSCF itself did not converge. Both the single-reference-state MCSCF perturbation theory based on state-averaged CASSCF and that based on state-specific CASSCF failed to describe the excited state. It is noted that the present method could obtain both of them.

IV. CONCLUDING REMARKS

A quasidegenerate perturbation theory based on MCSCF reference functions has been derived. The theory retains all of the attractive features of single-reference-state MCSCF perturbation theory and, moreover, has the advantages of traditional quasidegenerate perturbation theory as (1) several states interested in can be obtained simultaneously, (2) it can be applied to the degenerate or quasidegenerate systems, and (3) the interstate matrix elements, such as transition dipole moment, can be calculated in the same manner to obtain the effective Hamiltonian.

The formalism of MCSCF reference quasidegenerate perturbation theory has been presented and the working expression for the second order effective Hamiltonian, which has been reduced to molecular integrals and orbital energies, has been derived. It was applied to several systems as H_2, Be–H_2, CO, NO, BN, and LiF; and it was shown that the present method yields good results which agrees well with those of full CI or MR-CI. In particular, in the case of LiF, the single-reference-state MCSCF perturbation method could not provide both the ground and the excited states, while the present method could give both.

The present perturbation theory can provide several solutions even if they interact strongly, and the results are fairly good. Moreover, computational costs of the present method are much smaller than that of MR-CI. We expect the MCSCF reference quasidegenerate perturbation theory is useful in the wide region of the calculations for electronic state.

In forthcoming papers, the CSF based calculation of the MCSCF reference QDPT with Epstein–Nesbet partition[24] and dipole and transition dipole moments calculations will be presented.

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[1] K. A. Brueckner, Phys. Rev. **97**, 1353 (1955); **100**, 36 (1957); J. Goldstone, Proc. R. Soc. (London) Ser. A **239**, 267 (1957); H. P. Kelly, Adv. Chem. Phys. **14**, 129 (1969).

[2] C. Møller and M. S. Plesset, Phys. Rev. **46**, 618 (1934).

[3] M. J. Frisch, M. Head-Gordon, G. W. Trucks, J. B. Foreman, H. B. Schlegel, K. Raghavachari, M. Robb, J. S. Binkley, C. Gonzalez, D. J. Defrees, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. L. Martin, L. R. Kahn, J. J. P. Stewart, S. Topiol, and J. A. Pople, GAUSSIAN 90, Gaussian Inc., Pittsburgh, PA.

[4] M. Dupuis, J. D. Watts, H. O. Villar, and G. J. B. Hurst, HONDO version 7.0, QCPE Program No. 544, University of Indiana.

[5] B. H. Brandow, Rev. Mod. Phys. **39**, 771 (1967); I. Lindgren, Int. J. Quantum Chem. Symp. **12**, 33 (1978); B. H. Brandow, Int. J. Quantum Chem. **15**, 207 (1979); G. Hose and U. Kaldor, J. Phys. B **12**, 3827 (1981); K. F. Freed and M. G. Sheppard, J. Chem. Phys. **75**, 4507 (1981); **75**, 4525 (1981).

[6] H. Primas, Helv. Phys. Acta **34**, 331 (1961); H. Primas, Rev. Mod. Phys. **35**, 710 (1963).

[7] B. Kirtman, J. Chem. Phys. **49**, 3890 (1968); P. R. Certain and J. O. Hirschfelder, *ibid.* **52**, 5977 (1970); **53**, 2992 (1970); J. O. Hirschfelder, Chem. Phys. Lett. **54**, 1 (1978).

[8] B. Kirtman, J. Chem. Phys. **75**, 798 (1981).

[9] I. Shavitt and L. R. Redmon, J. Chem. Phys. **73**, 5711 (1980).

[10] T. H. Schucan and H. A. Weidenmuller, Ann. Phys. (N.Y.) **76**, 483 (1973).

[11] K. Wolinski, H. L. Sellers, and P. Pulay, Chem. Phys. Lett. **140**, 225 (1987).

[12] J. J. W. McDouall, K. Peasley, and M. A. Robb, Chem. Phys. Lett. **148**, 183 (1988).

[13] K. Andersson, P. Malmqvist, B. O. Roos, A. J. Sadlej and, K. Wolinski, J. Phys. Chem. **94**, 5483 (1990); K. Andersson, P. Malmqvist, and B. O. Roos, J. Chem. Phys. **96**, 1218 (1992).

[14] R. B. Murphy and R. P. Messmer, Chem. Phys. Lett. **183**, 443 (1991); J. Chem. Phys. **97**, 4170 (1992).

[15] K. Hirao, Chem. Phys. Lett. **190**, 374 (1992).

[16] K. Hirao, Chem. Phys. Lett. **196**, 397 (1992); Int. J. Quantum Chem. **S26**, 517 (1992).

[17] T. H. Dunning, J. Chem. Phys. **55**, 716 (1955).

[18] G. D. Purvis, R. Shepard, F. B. Brown, and R. J. Bartlett, Int. J. Quantum Chem. **23**, 835 (1983).

[19] A. Banerjee and J. Simons, Chem. Phys. **81**, 297 (1983).

[20] A. Banerjee and J. Simons, Chem. Phys. **87**, 215 (1984).

[21] M. R. Hoffmann, X. Wang, and K. F. Freed, Chem. Phys. Lett. **136**, 392 (1987).

[22] T. H. Dunning, J. Chem. Phys. **53**, 2823 (1953).

[23] C. W. Bauschlicher and S. R. Langhoff, J. Chem. Phys. **89**, 4246 (1988).

[24] P. S. Epstein, Phys. Rev. **28**, 695 (1926); R. D. Nesbet, Proc. R. Soc. (London) Ser. A **230**, 312 (1955).

[25] COLUMBUS, the graphical unitary group approach CI by I. Shavitt, IMS Computer Center Library Program No. 0444. The programs have been adapted for IBM by F. Brown and for the IMS HITAC by I. Shavitt. Other changes and additions have been made by P. Laidig, B. Saxe, F. Brown, and I. Shavitt, and the registration on IMS by S. Obara and S. Yamamoto. COLUMBUS contains Ohio state SCF/CI programs based on the R. M. Pitzer integrals/SCF programs and the Berkeley (B. R. Brooks and H. F. Schaefer) graphical unitary group approach CI programs.

[26] S. Obara, M. Honda, H. Nakano, F. Sakano, S. Takada, Y. Miyake, K. Sato, and T. Nakajima, KOTO92, Kyoto University.