Theor Chim Acta (1993) 85: 451–461

Theoretica
Chimica Acta

A CSF-based multireference coupled pair approximation.

II. As a size consistent method in the scheme of multireference singly and doubly excited configuration interaction

Takeo Sakai[1] **and Kiyoshi Tanaka**[2]

[1] Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan

[2] Division of Natural Science, The University of Electro-Communications, 1-5-1, Chofugaoka, Chofu, Tokyo 182, Japan

Received October 5, 1992/Accepted November 2, 1992

Summary: MRCPA (multireference coupled pair approximation) is formulated by the use of the wave operator formalism and Rayleigh–Schrödiner perturbation theory with special selection of the unperturbed part of the electronic Hamiltonian. By considering super molecule, it is shown that the theory is size consistent with the help of the new formalism. The method has been tested for three simple systems, H_2O, FH, and O_2.

Key words: MRCPA – MRSDCI – Wave operator – Bloch equation – Size consistency – Supermolecule

1. Introduction

Recent developments in computational quantum chemistry have increasingly shown the essential importance of adequate treatment of electron correlation in theory of the electronic structure of atoms and molecules [1, 2]. As a standard computation procedure for post Hartree–Fock calculations, the configuration interaction (CI) method has been well established in the field [3]. Its inherent simplicity and flexibility have led to various innovations of algorithm, such as direct CI [4], unitary group approach (UGA) [5], and so on. With remarkable development of computing facilities, such innovations now enable one to perform CI calculations including the order of 10^6 configurations routinely. Highly sophisticated CI program systems are now popularly used in the world [6]. In particular, multireference single and double excitation CI (MRSDCI) is one of the most versitile theoretical schemes, and has undoubtedly expanded the bounds of theoretical themistry in various aspects.

It is, however, well known that any truncated CI, including MRSDCI, suffers from severe principle difficulty, i.e., size inconsistency [7, 8]. Size inconsistency of truncated CI is caused by lack of configurations of the higher excitations responsible for canceling unlinked terms whose particle number dependence is incorrect. As a result, quality of truncated CI calculations is decreased as the number of correlating electrons increases. The inconsistency may lead to, for example, inappropriate or inaccurate potential energy surfaces. Size consistency in a correlated many-electron wavefunction is achieved by the full CI with a given basis, but this type of calculation is impractical for most systems of chemical interest even with a small basis set. In order to relax this difficulty without extra cost, several schemes have been proposed [9] for correcting and/or extrapolating a truncated CI energy.

The many-body perturbation theory (MBPT) and closely related coupled cluster method (CCM) constitute another predominant class of correlation methods [7, 8]. Unlike truncated CI, both methods have the advantage of size consistency at each level of approximation. The CCM presents a very efficient algorithm to account important parts of higher excitation effects, at the expense of rather complicated nonlinear structure of the resulting equations. Since the coupled pair many electron theory (CPMET) [10] and the coupled electron pair approximation (CEPA) [11], various coupled cluster approximations (CCA) [12] have been proposed. Applicability of these methods to real systems, however, has been relatively limited. The reason is that they are almost unexceptionally applicable to cases where the electronic state is lead by a configuration state function (CSF), i.e., the case of a single reference function. There are a lot of cases where usage of multireference functions is required: for example, proper description of potential surfaces both in the ground state and excited states. It is noted that some developments to incorporate multireference functions in MBPT/CCM have been made in the last decade [13, 14]. The formal structure of the theories are quite complicated and some simplified schemes have been proposed and examined [15].

Other than these efforts, some trials to develop approximate size consistent theories where one can take advantage of simple computational procedure of MRSDCI; ACPF (averaged coupled pair functional) [16a], QDVPT (quasi degenerate variation perturbation theory) [16b], and MRCPA (multireference coupled pair approximation) [16c]. Hereafter we designate our previous paper [16c] as **I**. In that paper, we proposed a nonlinear expression of a total wave function, Ψ_a,

$$\Psi_a = \sum_b \left(\phi_b + \sum_i \psi_i C_{ib} \right) \alpha_{ba}, \tag{1}$$

where ϕ_b and ψ_i represent a reference function and an excited function orthogonal to the reference functions, respectively. In obtaining a solution, we developed a Rayleigh–Schrödinger perturbation expansion with the special selection of the unperturbed part of the Hamiltonian. In this paper, we show that the MRCPA theory can be expressed more straightforwardly by the use of a perturbation theory within a wave operator formalism and consider the size consistency of this formalism. Further computational results on H_2O, FH, and O_2 are represented.

2. Method

2.1. Formal theory

Since quasi-degenerate perturbation theory (QDPT) based on the generalized Bloch equations [13b] is utilized to reformulate the MRCPA, we give a brief description of the formalism pertinent to the present method. First, we define an operator I projecting whole space spanned by a complete orthonormal N electron basis, $\{\Phi_I\}$:

$$I = \sum_k |\Phi_k\rangle\langle\Phi_k|. \tag{2}$$

As was done in **I**, the operator I is partitioned into three parts [17]:

$$I = P + Q + R, \tag{3}$$

where P projects a subspace spanned by preselected reference functions:

$$P = \sum_{\mu=1}^{d} |\Phi_\mu\rangle\langle\Phi_\mu| = \sum_{\mu=1}^{d} P_\mu, \tag{4}$$

and is assumed to diagonalize the total electronic Hamiltonian H within the subspace:

$$(PHP)P_\mu = E_\mu^{(0)} P_\mu, \quad \mu = 1, 2, \ldots, d \tag{5}$$

where d represents the number of reference functions. The operator Q projects a subspace spanned by single and double excitation functions from the reference space, and R projects the rest space spanned by many-electron excitations:

$$PHR = RHP = 0. \tag{6}$$

We use symbols P, Q, and R as operators and as the corresponding subspaces, interchangeably.

In the next step, we define a wave operator W as follows:

$$W = WP, \qquad PW = P, \tag{7}$$

$$WP\Psi_\mu = \Psi_\mu, \quad \mu = 1, 2, \ldots, d \tag{8}$$

where Ψ_μ represents an exact eigenfunction of the electronic Hamiltonian. It is noted that W is intermediately normalized. Once W is determined, exact energies associated with $\{\Psi_\mu\}$ $\mu = 1, 2, \ldots d$, are obtained by diagonalizing the effective Hamiltonian:

$$H_{\mathrm{eff}} = PHW, \tag{9}$$

which acts only on a reference space. It is noted that the present effective Hamiltonian is generally non-Hermitian.

In determining W, we utilize the perturbation theory of Lindgren [13b] with a specific choice of a perturbing term. According to the partitioning of the whole space as Eq. (3), the total Hamiltonian H is now partitioned into block-diagonal and off-block-diagonal parts, where the block-diagonal part is unperturbed part of the Hamiltonian (H_0) and the off-block-diagonal part is perturbing term (V).

$$H = H_0 + V, \tag{10}$$

where

$$H_0 = PHP + QHQ + RHR, \tag{11}$$

$$V = PHQ + QHP + QHR + RHQ. \tag{12}$$

The wave operator W obeys the generalized Bloch equation:

$$\begin{aligned} [W, H_0] &= VW - WVW, \\ &= VW - WT, \end{aligned} \tag{13}$$

where $T = VW$. Let us expand W in order of the perturbation:

$$W = \sum_{n=0} W^{(n)}. \tag{14}$$

Substituting it into Eq. (13) and rearranging the terms in order of the perturbation, one obtains the order-dependent Bloch equations starting from $W^{(0)} = P$:

$$[W^{(n)}, H_0] = VW^{(n-1)} - \sum_{k=1}^{n-1} W^{(n-k)}VW^{(k-1)}. \quad n \geqslant 1 \tag{15}$$

In the following, we show equations up to the 4th order using Eq. (12):

$$[W^{(1)}, H_0] = QHP, \tag{16}$$

$$[W^{(2)}, H_0] = RHQW^{(1)}, \tag{17}$$

$$[W^{(3)}, H_0] = QHRW^{(2)} - W^{(1)}PHQW^{(1)}, \tag{18}$$

$$[W^{(4)}, H_0] = RHQW^{(3)} - W^{(2)}PHQW^{(1)}. \tag{19}$$

As is seen in the above lower-order equations, one finds the present choice of the perturbing term in Eq. (12) leads to the following equation:

$$W = W^{(0)} + \sum_{k=1} [QW^{(2k-1)}P + RW^{(2k)}P], \tag{20}$$

i.e. W has $R - P$ components exclusively in even orders, and odd-order terms have $Q - P$ components. So the effective Hamiltonian given in Eq. (9) is expanded by:

$$H_{\text{eff}} = PHP + \sum_{k=1} H_{\text{eff}}^{(2k)}, \tag{21}$$

where $H_{\text{eff}}^{(2k)}$ is defined as follows:

$$H_{\text{eff}}^{(2k)} = PHW^{(2k-1)}. \tag{22}$$

In the next subsection, we will show that the MRCPA given in **I** is rewritten by the present perturbation theory.

2.2 MRCPA

The simplest approximation which we call MRCPA(0) is the second-order perturbation theory:

$$H_{\text{eff}}^{(\text{MRCPA}(0))} = PHP + H_{\text{eff}}^{(2)}, \tag{23}$$

which is obtained by solving Eq. (16). More concrete form of the equation is given by:

$$\sum_{j}^{\text{SD}} \{E_v^{(0)}\delta_{ij} - H_{ij}\} W_{jv}^{(1)} = H_{iv}, \tag{24}$$

and this is equivalent to Eq. (18) of **I**. QDVPT of Cave and Davidson [16b] is obtained by setting *PHP* of Eq. (16) as:

$$PHP \cong E_\mu^{(0)}P, \tag{25}$$

where $E_\mu^{(0)}$ is the zeroth-order energy of the target state μ. It is also noted that the MRCPA(0) reduces to MRLCCM of Laidig and Bartlett [15b] if we calculate an energy without diagonalizing Eq. (23):

$$E_\mu^{\text{MRLCCM}} = \langle \Phi_\mu | H | \Phi_\mu \rangle + \langle \Phi_\mu | H_{\text{eff}}^{(2)} | \Phi_\mu \rangle. \tag{26}$$

Hoffmann and Simons [15e] solve an equation essentially similar as Eq. (24) where they take a single function expanded by multireference functions in P. It's orthogonal complements and SD space are included in the space Q. The method is similar to VPT (variation perturvation theory) of Cave and Davidson [15b].

As was shown in **I**, MRCPA(0) may overshoot the correlation energy in some cases and inclusion of the higher-order correction is desirable. In order to take the fourth-order correction into account in the effective Hamiltonian, we need to solve Eqs. (17) and (18) successively. It is, however, impossible to solve Eq. (17). By similar consideration given in the CEPA theory, as was discussed in **I**, we approximate the right-hand side of Eq. (18) as follows:

$$[\overline{W^{(3)}}, H_0] = -\sum_i \sum_{\mu=1}^{d} Q_i W^{(1)} P_\mu H Q_i W^{(1)} P_\mu, \tag{27}$$

where $\overline{W^{(3)}}$ means an approximation to $W^{(3)}$. This approximation corresponds to neglecting the "connected" contribution of the higher excitation in the first term of the right-hand side of Eq. (18) and keeping the "exclusion principle violating (EPV)" type contribution in the right-hand side of Eq. (18). Then we obtain:

$$[W^{(1)} + \overline{W^{(3)}}, H_0] = QHP - \sum_i \sum_{\mu=1}^{d} Q_i W^{(1)} P_\mu H Q_i W^{(1)} P_\mu. \tag{28}$$

Equation (28) is rewritten as:

$$[W^{(1)} + \overline{W^{(3)}}, H_0 + \Delta] = QHP - \sum_i \sum_{\mu=1}^{d} Q_i \overline{W^{(3)}} P_\mu H Q_i W^{(1)} P_\mu, \tag{29}$$

where Δ is defined as follows:

$$\Delta^{(j)} = \sum_{\mu=1}^{d} P_\mu H Q_j W^{(1)} P_\mu, \tag{30a}$$

$$Q_j (W^{(1)} + \overline{W^{(3)}}) P_\mu \Delta = Q_j (W^{(1)} + \overline{W^{(3)}}) \Delta^{(j)} P_\mu, \tag{30b}$$

$$\Delta Q_j = 0. \tag{30c}$$

The first term of the right-hand side of Eq. (29) is in the first order of the perturbation expansion, whereas the second term is of the fifth order. Neglecting the last term, we obtain the following equation:

$$[W^{(1)} + \overline{W^{(3)}}, H_0 + \Delta] = QHP. \tag{31}$$

If we rewrite this equation in a manner of Eq. (32) of **I**, we obtain the following equation:

$$\sum_i \{(H_{\mu\mu} + \Delta^{(j)}_{\mu\mu})\delta_{ji} - H_{ji}\}(W^{(1)}_{i\mu} + \overline{W^{(3)}_{i\mu}}) = H_{j\mu}, \tag{32a}$$

$$\Delta^{(j)}_{\mu\mu} = H_{\mu j} W^{(1)}_{j\mu}, \tag{32b}$$

where indices i and j represent the element of the space Q and μ the space P. This is a little bit different from the fourth-order (2) approximation of the paper **I**. This change is proposed to ensure the size consistency of the method through considering additive separability of the total energy under the model of supermolecule as shown in the following subsection. The equation determining coefficients of CSF's, Eq. (32a), is equivalent to ACPF (averaged coupled pair functional) by Gdanitz and Ahlrichs [16a], if we set $\Delta^{(j)}_{\mu\mu}$ independent of j and μ. The idea of higher-order correction by Rattink and co-workers [15f] is similar to the present approximation.

We call this scheme as MRCPA(2). The total energy is given by diagonalizing the following effective Hamiltonian:

$$H_{\text{eff}}^{(\text{MRCPA}(2))} = PHP + PH(W^{(1)} + \overline{W^{(3)}})P. \tag{33}$$

2.3 *Size consistency*

By considering an assembly of non interaction two molecules, i.e., supermolecule, it is tested if the total energy of the system results in addition of the two molecules which are obtained by the same computational scheme.

A Hamiltonian of the supermolecule composed of A and B is expressed as follows:

$$H = H_{\text{A}} + H_{\text{B}}. \tag{34}$$

We assume that reference functions are properly separated into leading CSF's (reference functions) of well-defined states of the two molecules and provide properly separated zeroth-order energies. It is well known that the total energy by MRSDCI does not correlate into addition of the energies of the two molecules obtained by SDCI with the separated reference function(s). Hereafter we will show that the size consistency is contained not only in the exact theory but also in the approximation presented in the preceding subsection.

Suppose that I_{A} and I_{B} are spanned by complete orthonormal functions which involve number of electrons requested in each molecule and possess proper boundary conditions. The projection operators P, Q, and R for the supermolecule may be given by:

$$P = P_{\text{A}}P_{\text{B}}, \tag{35a}$$

$$Q = P_{\text{A}}Q_{\text{B}} + Q_{\text{A}}P_{\text{B}}, \tag{35b}$$

$$R = Q_{\text{A}}Q_{\text{B}} + P_{\text{A}}R_{\text{B}} + R_{\text{A}}P_{\text{B}} + Q_{\text{A}}R_{\text{B}} + R_{\text{A}}Q_{\text{B}} + R_{\text{A}}R_{\text{B}}. \tag{35c}$$

The space Q is composed of those functions directly interacting with the space P. The Hamiltonian of each molecule is also partitioned as follows:

$$H_x = H_{0x} + V_x, \quad x = \text{A, B} \tag{36a}$$

$$H_{0x} = P_xHP_x + Q_xHQ_x + R_xHR_x. \quad x = \text{A, B} \tag{36b}$$

We assume that the relations shown in Eqs. (6) ~ (20) hold for either A or B. The wave operators W_{A} and W_{B} are specified in the respective molecules, A and B. Thus the Bloch equations are expressed as follows:

$$[W_{\text{A}}, H_{0\text{A}}] = V_{\text{A}}W_{\text{A}} - W_{\text{A}}T_{\text{A}}, \tag{37a}$$

$$[W_{\text{B}}, H_{0\text{B}}] = V_{\text{B}}W_{\text{B}} - W_{\text{B}}T_{\text{B}}. \tag{37b}$$

Noting that two operators associated with different molecules commute with each other, we obtain

$$\begin{aligned}[W_{\text{A}}W_{\text{B}}, H_0] &= VW_{\text{A}}W_{\text{B}} - W_{\text{A}}W_{\text{B}}(T_{\text{A}} + T_{\text{B}}),\\ &= VW_{\text{A}}W_{\text{B}} - W_{\text{A}}W_{\text{B}}VW_{\text{A}}W_{\text{B}}.\end{aligned} \tag{38}$$

Comparison of Eq. (38) with Eq. (13) reveals that the composite system satisfies the multiplicative separability [18, 19]:

$$W = W_{\text{A}}W_{\text{B}}, \tag{39}$$

and the effective Hamiltonian is rewritten as an additively separable form:

$$\begin{aligned} H_{\text{eff}} &= P_{\text{A}} P_{\text{B}} (H_{\text{A}} + H_{\text{B}}) W_{\text{A}} W_{\text{B}}, \\ &= (H_{\text{A,eff}} + H_{\text{B,eff}}) P_{\text{A}} P_{\text{B}}. \end{aligned} \tag{40}$$

The eigenvalue of H_{eff} is obtained by summation of eigenvalues of effective Hamiltonian of the subsystems and the multiplicative separability of W is a necessary condition for the size consistency in the present context.

For the case of the perturbation expansion, we expand Eq. (39) in order of the perturbation:

$$W^{(n)} = \sum_{k=0}^{n} W_{\text{A}}^{(k)} W_{\text{B}}^{(n-k)}. \tag{41}$$

Because of Eqs. (20) and (35b), any odd-order term of the wave operators are expressed as:

$$\begin{aligned} W^{(2k-1)} &= W_{\text{A}}^{(2k-1)} W_{\text{B}}^{(0)} + W_{\text{A}}^{(0)} W_{\text{B}}^{(2k-1)} \\ &= W_{\text{A}}^{(2k-1)} P_{\text{B}} + P_{\text{A}} W_{\text{B}}^{(2k-1)} \quad (k \geqslant 1). \end{aligned} \tag{42}$$

The effective Hamiltonian is given in the separated form by the use of Eq. (42):

$$H_{\text{eff}} = \sum_{k=0} (H_{\text{A,eff}}^{(2k)} + H_{\text{B,eff}}^{(2k)}) P_{\text{A}} P_{\text{B}}. \tag{43}$$

If $W^{(2k-1)}$ obeys properly separable equations, the theory is size consistent in the present context. In order to check if $W^{(1)}$ and $W^{(3)}$ obey properly separable equation, we apply Eqs. (34), (35), and (36) to Eqs. (16) and (18), we obtain the following equations:

$$\begin{aligned} [W^{(1)}, H_0] &= [W_{\text{A}}^{(1)}, H_{0,\text{A}}] P_{\text{B}} + P_{\text{A}} [W_{\text{B}}^{(1)}, H_{0,\text{B}}] \\ &= QHP = Q_{\text{A}} H_{\text{A}} P_{\text{A}} P_{\text{B}} + P_{\text{A}} Q_{\text{B}} H_{B} P_{\text{B}}, \end{aligned} \tag{44}$$

$$\begin{aligned} [W^{(3)}, H_0] &= [W_{\text{A}}^{(3)}, H_{0,\text{A}}] P_{\text{B}} + P_{\text{A}} [W_{\text{B}}^{(3)}, H_{0,\text{B}}] \\ &= QHRW^{(2)} - W^{(1)} PHQW^{(1)} \\ &= Q_{\text{A}} H_{\text{A}} R_{\text{A}} W_{\text{A}}^{(2)} P_{\text{B}} + Q_{\text{B}} H_{\text{B}} R_{\text{B}} W_{\text{B}}^{(2)} P_{\text{A}} \\ &\quad + P_{\text{A}} H_{\text{A}} Q_{\text{A}} W_{\text{A}}^{(1)} W_{\text{B}}^{(1)} + P_{\text{B}} H_{\text{B}} Q_{\text{B}} W_{\text{B}}^{(1)} W_{\text{A}}^{(1)} \\ &\quad - (W_{\text{A}}^{(1)} H_{\text{A}} Q_{\text{A}} W_{\text{A}}^{(1)} P_{\text{B}} + W_{\text{B}}^{(1)} H_{\text{B}} Q_{\text{B}} W_{\text{B}}^{(1)} P_{\text{A}} \\ &\quad + P_{\text{A}} H_{\text{A}} Q_{\text{A}} W_{\text{A}}^{(1)} W_{\text{B}}^{(1)} + P_{\text{B}} H_{\text{B}} Q_{\text{B}} W_{\text{B}}^{(1)} W_{\text{A}}^{(1)}) \\ &= (Q_{\text{A}} H_{\text{A}} R_{\text{A}} W_{\text{A}}^{(2)} - W_{\text{A}}^{(1)} H_{\text{A}} Q_{\text{A}} W_{\text{A}}^{(1)}) P_{\text{B}} \\ &\quad + (Q_{\text{B}} H_{\text{B}} R_{\text{B}} W_{\text{B}}^{(2)} - W_{\text{B}}^{(1)} H_{\text{B}} Q_{\text{B}} W_{\text{B}}^{(1)}) P_{\text{A}}. \end{aligned} \tag{45}$$

It is noted that two of the first four terms of the right-hand side of Eq. (45) are canceled by two of the last four terms of the right-hand side of Eq. (45). Equations (44) and (45) indicate that $W^{(1)}$ and $W^{(3)}$ obey properly separable equations.

Separability of the case of approximation given by Eqs. (27)–(31) is explained as follows. As is valid for the exact case:

$$W^{(1)} + W^{(3)} = (W_{\text{A}}^{(1)} + W_{\text{A}}^{(3)}) P_{\text{B}} + P_{\text{A}} (W_{\text{B}}^{(1)} + W_{\text{B}}^{(3)}), \tag{46}$$

the following equation holds:

$$W^{(1)} + \overline{W^{(3)}} = (W_{\rm A}^{(1)} + \overline{W_{\rm A}^{(3)}})P_{\rm B} + P_{\rm A}(W_{\rm B}^{(1)} + \overline{W_{\rm B}^{(3)}}). \tag{47}$$

Because of Eqs. (30) and (35), Δ is also separated:

$$\Delta = \Delta_{\rm A} + \Delta_{\rm B}. \tag{48}$$

It is easily shown that following separable equation obtained from Eq. (31):

$$\begin{aligned}&[W_{\rm A}^{(1)} + \overline{W_{\rm A}^{(3)}}, H_{0,{\rm A}} + \Delta_{\rm A}]P_{\rm B} + P_{\rm A}[W_{\rm B}^{(1)} + \overline{W_{\rm B}^{(3)}}, H_{0,{\rm B}} + \Delta_{\rm B}]\\ &\quad = Q_{\rm A}H_{\rm A}P_{\rm A}P_{\rm B} + P_{\rm A}Q_{\rm B}H_{\rm B}P_{\rm B}.\end{aligned} \tag{49}$$

The MRCPA(2), therefore, has additive separability and is size consistent in this context.

The MRCPA(0) and MRCPA(2) use CSF's of multireference single and double excitation CI. So it is notified that result is not invariant with respect to rotation in the occupied orbital space as is the case for MRSDCI except in special cases.

3. Test calculations

Test calculations on BeH_2 and N_2 were presented in the previous paper **I**. Further test calculations on H_2O, FH, and O_2 are reported and they are compared with the full valence electron CI energies in this paper.

3.1. H_2O

By the use of the contracted gaussian-type orbitals (CGTO's) of double zeta (DZ) quality, we calculate the electronic ground-state energies of H_2O at three geometrical points. First we carry out multiconfiguration self-consistent field (MCSCF) calculations with 12 CSF's which are obtained by assigning four valence electrons to the $3a_1$, $4a_1$, $1b_2$, and $2b_2$ MO's, where $1a_1$ and $2a_1$ are doubly occupied. By the use of the MO's thus obtained, single and double (SD) excited CSF's are generated from the 12 CSF's. The number of CSF's is 2148. The calculated energies are presented in Table 1 relative to the energies by the full CI whose number of CSF's is 256,473. They are taken from the work of Saxe and co-workers [20].

Table 1. Results of H_2O

R(OH)	FVCI[a]	SDCI[b]	CPA(0)[b]	CPA(2)[b]
1.0 Re[c]	−76.1579	2.0	0.7	0.1
1.5 Re	−76.0145	2.2	1.0	0.5
2.0 Re	−75.9053	2.0	1.1	0.8

[a] Total energies are given in hartree (a.u.). They are taken from [20]

[b] Energies are given relative to the FVCI energies and presented in mhartree

[c] Re = 1.843 a.u., <HOH = 110.6°

Table 2. Results of FH

R(FH)	FVCI[a]	SDCI[b]	CPA(0)[b]	CPA(2)[b]
1.0 Re[c]	−100.2510	6.5	0.8	0.4
1.5 Re	−100.1604	6.7	0.5	0.1
2.0 Re	−100.0811	6.0	2.6	0.5

[a] Total energies are given in hartree (a.u.). They are taken from [9c]
[b] Energies are given relative to the FVCI energies and presented in mhartree
[c] Re = 1.733 a.u.

3.2. FH

A set of CGTO's of DZ plus polarization function (P) is used for the FH molecule. First we carry out two configuration SCF (TCSCF) calculation with the configurations $1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4$ and $1\sigma^2 2\sigma^2 4\sigma^2 1\pi^4$ for the ground state, $^1\Sigma^+$. By the use of these two functions as reference functions, an SD excited space is generated with 1σ (F 1*s*) kept frozen. The number of CSF's is 1092. In Table 2, the calculated energies are compared with full valence electron CI (number of CSF's; 944,348) of Bauschlicher and co-workers [9c], where 1σ is kept frozen.

3.3. O_2

A DZP CGTO basis set is used for O_2 ground state, $^3\Sigma g^-$. First we carry out MCSCF calculation with the six CSF's generated from the following five configurations:

$$...3\sigma_g^2 1\pi_u^4 1\pi_g^2, \qquad ...3\sigma_g^2 1\pi_u^2 1\pi_g^4, \qquad ...3\sigma_u^2 1\pi_u^4 1\pi_g^2,$$

$$...3\sigma_g^2 1\pi_u^4 1\pi_g^2, \quad \text{and} \quad ...3\sigma_g^1 3\sigma_u^1 1\pi_u^3 1\pi_g^3 \text{ (two spin couplings).}$$

By the use of these six CSF's as reference functions, an SD excited space is generated with frozen cores of $1\sigma_g$, $1\sigma_u$, $2\sigma_g$, and $2\sigma_u$. The number of CSF's is 3715. The calculated energies are compared with the full valence electron CI energies in which $1\sigma_g$, $1\sigma_u$, $2\sigma_g$, and $2\sigma_u$ are kept frozen. The calculation was done by Bauschlicher and Langhoff [21]. The number of determinants included in the full valence electron CI is 21,382,384 in which cores orbitals of $1\sigma_g$, $1\sigma_u$, $2\sigma_g$, and $2\sigma_u$ are kept frozen.

3.4. Results

The calculated total energies are given relative to the full valence electron CI energies in Table 1, Table 2, and Table 3 for H_2O, FH, and O_2, respectively. The total energies by the full valence electron CI are also included in the tables. The results show that the best agreement with full valence electron CI is obtained by MRCPA(2) for the given range of the molecular geometry for the three molecules. The errors by MRCPA(0) is larger than those by MRCPA(2) and the former is less stable than the latter. The largest errors are given by the MRSDCI among the approximations used in the present theory.

Table 3. Results of O_2

R(FH)	FVCI[a]	SDCI[b]	CPA(0)[b]	CPA(2)[b]
2.25 a.u.	−149.8751	5.7	3.2	1.8
2.30 a.u.	−149.8769	5.5	3.1	1.4
2.35 a.u.	−149.8767	6.0	3.6	1.6
100.0 a.u.	−149.7067	4.6	1.4	1.5

[a] Total energies are given in hartree (a.u.). They are taken from [21]

[b] Energies are given relative to the FVCI energies and presented in mhartree

4. Conclusion

The MRCPA theory is reformulated by the use of the Rayleigh–Schrödinger perturbation theory with the help of the wave operator and generalized Bloch equation. The set of CSF's employed in the theory is equal to that of SDCI with the same reference functions. It is shown that the theory is size consistent by the use of a model of a supermolecule.

Test calculations by MRCPA(2), MRCPA(0), and MRSDCI are carried out for H_2O, FH, and O_2. The best agreement with the energies of the full valence electron CI is obtained by MRCPA(2). The MRSDCI gives the largest errors among the three methods.

Acknowledgements. The authors are grateful to Professors K. Ohno and F. Sasaki for their helpful comments and encouragement, and express their thanks to Professor K. Yamaguchi for his interest and encouragement. The present work is supported partially by Grant-in-Aid for Scientific Research on Priority Area "Theory of Chemical Reactions" and "New Functionality Materials" from the Ministry of Education, Science, and Culture. Computations are carried out with the program systems of JAMOL3 [22], MICA3 [23], and its modified version for CPA on a HITAC M680 system at the Center for Information Processing Education of Hokkaido University.

References

1. Löwdin PO (1957) Adv Chem Phys 2:207–322
2. Wilson S (1984) Electron correlation in molecules. Clarendon, Oxford
3. Shavitt I (1977) The method of configuration interaction. In: Schaefer III HF (ed) Methods of electronic structure theory, vol 3. Plenum, NY, p 189–276
4. Roos BO, Siegbahn PEM (1977) The direct configuration interaction method from molecular integrals. In: Schaefer III HF (ed) Methods of electronic structure theory, vol 3. Plenum, NY, p 277–318
5. (a) Paldus J (1974) J Chem Phys 61:5321–5330
   (b) Shavitt I (1978) Int J Quantum Chem S11:131–148
6. (a) Davidson ER (1974) Int J Quantum Chem VII:83–89
   (b) Buenker RJ, Peyerimhoff SD (1975) Theoret Chim Acta 35:33–58, ibid 39:217–228
   (c) Liu B, Yoshimine M (1981) J Chem Phys 74:612–616
   (d) Knowles PJ, Handy NC (1984) Chem Phys Lett 111:315–321
   (e) Sasaki F, Tanaka K, Noro T, Togasi M, Nomura T, Sekiya M, Gonoi T, Ohno K (1987) Theoret Chim Acta 72:123–138
   (f) Werner HJ, Knowles PJ (1988) J Chem Phys 89:5803–5814
7. Bartlett RJ (1981) Ann Rev Phys Chem 32:359–401
8. Urban M, Cernusak I, Kellö V, Noga J (1987) Electron correlation in molecules. In: Wilson S (ed) Methods in Computational Chemistry, vol 1. Plenum, NY

9. (a) Langhoff SR, Davidson ER (1974) Int J Quantum Chem VIII:61–72; Davidson ER, Silver DW (1977) Chem Phys Lett 52:403–406
   (b) Buenker RJ, Shih SK, Peyerimhoff SD (1979) Chem Phys 36:97–112
   (c) Bauschlicher CW Jr, Langhoff SR, Taylor PR, Handy NC, Knowles PJ (1986) J Chem Phys 85:1469–1474
   (d) Bauschlicher CW Jr, Taylor PR (1986) Chem Phys 85:6510–6512; (1987) ibid 86:1420–1424, (1987) Theoret Chim Acta 71:263–276
   (e) Knowles DB, Alvarez-Collado JR, Hirsch G, Buenker RJ (1990) J Chem Phys 92:585–596
10. Cizek J (1966) J Chem Phys 45:4256–4266; (1969) Adv Chem Phys 14:35–91
11. Meyer W (1971) Int J Quantum Chem S5:341–348; (1972) J Chem Phys 58:1017–1035; (1977) Configuration expansion by means of pseudonatural orbitals. In: Schaefer III HF (ed) Methods of electronic structure theory, vol 3. Plenum, NY, p 413–446
12. (a) Hurley AC (1976) Electron correlation in small molecules, Academic, NY
   (b) Kutzelnigg W (1977) Pair correlation theories. In: Schaefer III HF (ed) Methods of electronic structure theory, vol 3. Plenum, NY, p 129–188
   (c) Ahlrichs R (1979) Comput Phys Comm 17:31–45
13. (a) Brandow BH (1967) Rev Modern Phys 39:771–828
   (b) Lindgren I (1974) J Phys B (London) 7:2441–2470
   (c) Hose G, Kaldor U (1979) J Phys B (London) 12:3827–3855
   (d) Shavitt I, Redmon LT (1980) J Chem Phys 83:5711–5717
14. (a) Jeziorski B, Monkhorst HJ (1981) Phys Rev A24:1668–1681
   (b) Lindgren I (1978) Int J Quanum Chem S12:33–58
   (c) Mukherjee D (1986) Chem Phys Lett 125:207–212
   (d) Nakatsuji H (1985) J Chem Phys 83:713–722
   (e) Lindgren I, Mukherjee D (1987) Phys Rep 151:93–127
   (f) Meissner L, Jankowski K, and Wasilewski J (1988) Int J Quantum Chem XXXIV:535–557
   (g) Kutzelnigg W (1988) Quantum chemistry in Fock space. In: Mukherjee D (ed) Aspects of many-body effects in molecules and extended systems. Lecture Notes in Chemistry, vol 50. Springer-Verlag, Berlin, NY, p 35–67
   (h) Mukherjee D, Pal S (1989) Adv Quantum Chem 20:291–373
15. (a) Baker H and Robb MA (1983) Mol Phys 50:1077–1082
   (b) Banerjee A, Simons J (1981) Int J Quantum Chem 19:207–216; (1982) J Chem Phys 76:4548–4559
   (c) Laidig WD, Bartlett RJ (1984) Chem Phys Lett 104:424–430; Laidig WD, Saxe P, Bartlett RJ (1987) J Chem Phys 86:887–907
   (d) Tanaka K and Terashima H (1984) Chem Phys Lett 106:558–562
   (e) Hoffmann MR and Simons J (1989) J Chem Phys 90:3671–3679
   (f) Ruttink PJA, van Lenthe JH, Zwaans R, Groenenboom GC (1991) J Chem Phys 94:7212–7220
16. (a) Gdanitz RJ, Ahlrichs R (1988) Chem Phys Lett 143:413–420
   (b) Cave RJ, Davidson ER (1988) J Chem Phys 89:6798–6814; (1988) ibid 88:5770–5778
   (c) Tanaka K, Sakai T, Terashima H (1989) Theoret Chim Acta 76:213–225
17. Kutzelnigg W (1975) Chem Phys Lett 35:283–285
18. Primas H (1965) Separability in Many-electron systems. In: Sinanoglu O (ed) Modern Quantum Chemistry Part II, Academic, NY, p 33–74
19. Kvasnicka V (1977) Adv Chem Phys 36:345–412
20. Saxe P, Schaefer III HF, Handy NC (1981) Chem Phys Lett 79:202–204
21. Bauschlicher CW Jr, Langhoff SR (1987) J Chem Phys 86:5595–5599
22. Kashiwagi H, Takada T, Miyoshi E, Obara S, Sasaki F (1977) Library program of the computer center of Institute for Molecular Science. Okazaki, Japan
23. Murakami A, Iwaki H, Terashima H, Shoda T, Kawaguchi T, Noro T (1985) Library program of the computing center. Hokkaido Univ, Sapporo, Japan