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A method of incorporating quadruple correction in the scheme of multi-reference singly and doubly excited configuration interaction—a CSF based coupled pair approximation

Kiyoshi Tanaka, Takeo Sakai, and Hidemi Terashima
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo, 060, Japan

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Summary. We develop an approximate size consistent method within a framework of the multi-reference configuration interaction scheme. The Rayleigh–Schrödinger perturbation theory is employed with a specific selection of the unperturbed part of the electronic Hamiltonian. The second order energy is obtained by a set of equations similar to the quasidegenerate variational perturbation theory of Cave and Davidson. The approximate fourth order energy is obtained by solving a set of equations similar to the coupled electron pair approximation (CEPA). The method has been tested for two simple systems, BeH_2 and N_2, and the results are quite encouraging.

Key words: MRSDCI — Non-linear expression — Size consistent — Coupled pair — Quadruple correction

1. Introduction

The configuration interaction (CI) method is a well-established method for obtaining wave functions of atoms and molecules including electron correlation [1]. The CI method employing only singly and doubly excited configuration state functions (CSFs) from several leading functions is widely used for drawing potential surfaces, describing wave functions of the excited states and so on. This procedure is called a multi-reference single and double excited configuration interaction (MRSDCI). A lot of trials have been made for improving the algorithm of the method [2]. By virtue of such efforts and the remarkable developments in high speed computers, quite large CI, say 10^6 dimensional CI, is now feasible; however, even with such large CI, chemical accuracy can be obtained only for small molecules. In considering larger molecules, inclusion of the configurations of the higher order excitation becomes important and the size consistency problem [3] arises in limited CI.

In order to overcome this difficulty at least partially, Peyerimhoff and Buenker incorporated Davidson's scheme of estimating quadruple correction [4] in the MRDCI method [5]. A few similar approaches have been put forward in MRSDCI [6]. Davidson further discussed a scheme based on second order Rayleigh–Schrödinger perturbation theory [7a], variational perturbation theory (VPT) [7b] and quasidegenerate version (QDVPT) [7c]. Ahlrichs proposed a coupled pair functional method (CPF) and multi-reference averaged coupled pair functional (ACPF) [8].

We are going to develop a new approach to achieve size consistency approximately on the MRSDCI level. The method is based on the Rayleigh–Schrödinger perturbation theory with a specific selection of the unperturbed part of the electronic Hamiltonian. We obtain a new set of equations similar to the coupled electron pair approximation (CEPA) [9] by making an approximation to the terms representing coupling between singly and doubly excited CSF's and triply and quadruply excited CSF's. Because of the resemblance of the equations to those of CEPA, we call this approach a multi-reference coupled pair approximation (MRCPA). The method is easily implemented in any of the MRSDCI program codes which have been extensively developed in recent years.

In addition to the various methods of improvement at the CI level, there have also been studies of size consistent methods, such as many body perturbation theory and cluster expansion theory [3, 10]. The extension of some of these methods to multi-reference theory has been devised by a few groups [11], and several simplified schemes have been proposed and examined [12].

The method developed in this work will be described in the next section. Test calculations on BeH_2 and N_2 were performed and are compared with the results of a few other methods in the Sect. 3.

2. Method

Suppose we have a complete orthonormal set of many electron functions. The set of functions is partitioned into three subsets ***P***, ***Q*** and ***R*** as follows:

P: reference functions	$\{\phi_a\}$,
Q: singly and doubly excited CSFs	$\{\psi_i\}$,
R: rest of CSFs	$\{\psi_s\}$.

Hereafter, we use suffices $a, b, c, \ldots$ to specify the ***P*** space elements, $i, j, k, \ldots$ for the ***Q*** space ones, and $s, t, u, \ldots$ the ***R*** space elements. As a matter of course, reference functions span a zero-th order space that gives a reasonable description of the exact total wave function.

The exact total wave function, Ψ^a, is expanded in the CI method as

$$\Psi^a = \sum_b \phi_b \alpha_b^a + \sum_i \psi_i \beta_i^a + \sum_s \psi_s \gamma_s^a. \tag{1}$$

If H is defined as total electronic Hamiltonian, the secular equation of the CI is obtained by projecting

$$(H - E_a)\Psi^a = 0 \quad \text{onto subspaces } \boldsymbol{P}, \boldsymbol{Q}, \text{ and } \boldsymbol{R}.$$

Here we propose a non-linear expansion of the total wave function, Ψ^a:

$$\Psi^a = \sum_b \left\{ \phi_b + \sum_i \psi_i C_i^b + \sum_s \psi_s D_s^b \right\} \alpha_b^a, \tag{2}$$

where

$$\beta_i^a = \sum_b C_i^b \alpha_b^a \quad (\text{for all } i \text{ in } \boldsymbol{Q}) \tag{2a}$$

and

$$\gamma_s^a = \sum_b D_s^b \alpha_b^a \quad (\text{for all } s \text{ in } \boldsymbol{R}). \tag{2b}$$

As the matrix α is not singular, the coefficients $\{C_i^b\}$ and $\{D_s^b\}$ are uniquely defined. If we project $(H - E_a)\Psi^a = 0$ onto the space, $\boldsymbol{P}$, $\boldsymbol{Q}$, and $\boldsymbol{R}$, we obtain the following Eqs. (3), (4), and (5), respectively:

$$\sum_b \left\{ H_{cb} + \sum_i H_{ci} C_i^b - E_a \delta_{cb} \right\} \alpha_b^a = 0, \tag{3}$$

$$\sum_b \left\{ H_{jb} + \sum_i H_{ji} C_i^b + \sum_s H_{js} D_s^b - E_a C_j^b \right\} \alpha_b^a = 0, \tag{4}$$

$$\sum_b \left\{ \sum_i H_{ti} C_i^b + \sum_s H_{ts} D_s^b - E_a D_t^b \right\} \alpha_b^a = 0. \tag{5}$$

In this work, we consider a perturbation expansion of the wave function Ψ^a to determine $\{C_i^a\}$ and $\{D_t^a\}$. If the coefficients $\{C_i^a\}$ are obtained, the total wave functions and eigenvalues are then given by solving (3), i.e., the eigenvalue problem of the effective Hamiltonian acting only on the reference space. Of course it is impossible to obtain the solution for the coefficients $\{D_t^a\}$. We will make an approximation for $\{D_t^a\}$ and obtain a set of equations to determine $\{C_i^a\}$ where the effect of the correlation due to the space $\boldsymbol{R}$ is taken into account.

Let $\mathscr{P}$, $\mathscr{Q}$, and $\mathscr{R}$ be the projection operators on the spaces $\boldsymbol{P}$, $\boldsymbol{Q}$, and $\boldsymbol{R}$, respectively. The electronic Hamiltonian H is separated into the unperturbed part, H_0, and the perturbing term, V, as

$$H = H_0 + \lambda V, \tag{6}$$

where λ is introduced as an ordering parameter of the perturbation. The parameter λ is set to unity after the formulae are obtained. The unperturbed part of the Hamiltonian is defined as follows:

$$H_0 = \mathscr{P}H\mathscr{P} + \mathscr{Q}H\mathscr{Q} + \mathscr{R}H\mathscr{R}. \tag{7}$$

The perturbing term is then

$$V = \mathscr{P}H\mathscr{Q} + \mathscr{Q}H\mathscr{P} + \mathscr{Q}H\mathscr{R} + \mathscr{R}H\mathscr{Q}. \tag{8}$$

Kutzelnigg [13] obtained formulae for perturbation expansions using essentially the same partitioning of the Hamiltonian for the case of single function in the ***P*** space.

Let us assume that the reference functions, $\{\phi_a\}$, are eigenfunctions of $\mathscr{P}H\mathscr{P}$.

$$H_{ab} = H_{aa}\delta_{ab}. \tag{9}$$

By using (6) and (9), Eqs. (3), (4), and (5) may be rewritten as

$$\sum_b \left\{ (H_{bb} - E_a)\delta_{cb} + \lambda \sum_i H_{ci} C_i^b \right\} \alpha_b^a = 0, \tag{10}$$

$$\sum_b \left\{ \sum_i H_{ji} C_i^b - E_a C_j^b + \lambda H_{jb} + \lambda \sum_s H_{js} D_s^b \right\} \alpha_b^a = 0, \tag{11}$$

$$\sum_b \left\{ \sum_s H_{ts} D_s^b - E_a D_t^b + \lambda \sum_i H_{ti} C_i^b \right\} \alpha_b^a = 0. \tag{12}$$

Since CSFs $\{\psi_i\}$ in ***Q*** interact with the zero-th order wave functions (reference functions) and $\{\psi_s\}$ in ***R*** do not interact with the zero-th order wave function, the coefficients $\{C_i^a\}$ start from the first order and $\{D_s^a\}$ start from the second order.

$$C_i^a = \sum_{n=1} \lambda^n C_i^{a(n)}, \tag{13}$$

$$D_s^a = \sum_{n=2} \lambda^n D_s^{a(n)}, \tag{14}$$

$$\alpha_b^a = \delta_{ab} + \sum_{n=2} \lambda^n \alpha_b^{a(n)}, \tag{15}$$

$$E_a = H_{aa} + \sum_{n=2} \lambda^n \Delta E_a^{(n)}, \tag{16}$$

where δ_{ab} is Kronecker's delta. Collecting the second order terms in Eq. (10), we obtain the following equation:

$$-\Delta E_a^{(2)} \delta_{ca} + \sum_i H_{ci} C_i^{a(1)} + (H_{cc} - H_{aa})\alpha_c^{a(2)} = 0. \tag{17}$$

This leads to the following two equations:

$$\Delta E_a^{(2)} = \sum_i H_{ai} C_i^{a(1)}, \tag{17a}$$

$$\alpha_c^{a(2)} = (H_{cc} - H_{aa})^{-1} \sum_i H_{ci} C_i^{a(1)}. \tag{17b}$$

From the first, second and third order terms of Eq. (11), the equations,

$$\sum_i H_{ji} C_i^{a(1)} - H_{aa} C_j^{a(1)} + H_{ja} = 0, \tag{18}$$

$$\sum_i H_{ji} C_i^{a(2)} - H_{aa} C_j^{a(2)} = 0 \tag{19}$$

and

$$\sum_i H_{ji} C_i^{a(3)} - H_{aa} C_j^{a(3)} + \sum_b \left\{ \sum_i H_{ji} C_i^{b(1)} - H_{aa} C_j^{b(1)} + H_{jb} \right\} \alpha_b^{a(2)}$$

$$- \Delta E_a^{(2)} C_j^{a(1)} + \sum_s H_{js} D_s^{a(2)} = 0, \tag{20}$$

may be derived, while the second and third order terms of Eq. (12) give rise to the following equations:

$$\sum_s H_{ts} D_s^{a(2)} - H_{aa} D_t^{a(2)} + \sum_i H_{ti} C_i^{a(1)} = 0, \tag{21}$$

$$\sum_s H_{ts} D_s^{b(3)} - H_{aa} D_t^{a(3)} = 0. \tag{22}$$

The coefficients $C_i^{a(1)}$ may be obtained by solving Eq. (18). The coefficients $C_i^{a(2)}$ are all zero

$$C_i^{a(2)} = 0, \tag{23}$$

because of Eq. (19); H_{aa} is not the eigenvalue of $\mathcal{Q}H\mathcal{Q}$ but $\mathcal{P}H\mathcal{P}$. The coefficients $D_s^{a(2)}$ can be obtained by solving Eq. (21); they are coefficients for the higher order excited CSF's $\{\psi_s\}$ which belong to the space $\boldsymbol{R}$. The coefficients $D_s^{a(3)}$ are all zero as in the case of $C_i^{a(2)}$.

$$D_s^{a(3)} = 0. \tag{24}$$

With the help of Eqs. (17a), (17b), and (18) Eq. (20) may be rewritten as

$$H_{aa} C_j^{a(3)} - \sum_i H_{ji} C_i^{a(3)} = \sum_s H_{js} D_s^{a(2)} - \left(\sum_i H_{ai} C_i^{a(1)} \right) C_j^{a(1)}$$

$$- \sum_{b \neq a} \sum_i H_{bi} C_i^{a(1)} C_j^{b(1)}. \tag{25}$$

The first term of the right hand side represents the correlation term due to the higher excitations from the space $\boldsymbol{P}$. This term is composed of, so to say, "connected" and "disconnected" contributions. The second term is the "disconnected" one including an "exclusion principle violating (EPV)" type contribution. The third term represents the indirect coupling between a reference function ϕ_a and other reference functions through the correlation in the first order of the perturbation expansion.

It is of course impossible to obtain the coefficients $\{D_s^{a(2)}\}$ which are the solution of Eq. (21)

$$D_s^{a(2)} = \sum_{it} (H_{aa}\mathbf{1} - \boldsymbol{H})^{-1}{}_{st} H_{ti} C_i^{a(1)}, \tag{26a}$$

where $\mathbf{1}$ is unit matrix for the $\boldsymbol{R}$ space. Various types of approximations to these coefficients have been made for the case of a single reference function. The CP-MET (coupled pair many electron theory) [10a] neglects the connected contributions, and pairs of disconnected double excitations are considered for the case of a single reference function. To be brief, $D_s^{a(2)}$ is written as

$$D_s^{a(2)} \cong \sum_{ki} C_k^{a(1)} C_i^{a(1)} \quad (i \neq k), \tag{26b}$$

where only four electron excitations are taken into account for $D_s^{a(2)}$ and combinations of pair excitations k and i fall into the four electron excited configuration s. Further approximations have been made in the treatment of the $D_s^{a(2)}$ in CEPA's. In CEPA2, the following approximation has been made:

$$\sum_s H_{js} D_s^{a(2)} \cong \sum_k H_{ak} C_k^{a(1)} C_j^{a(1)} \quad (j \neq k). \tag{26c}$$

Thus the approximate formula

$$\sum_s H_{js} D_s^{a(2)} - \left(\sum_i H_{ai} C_i^{a(1)} \right) C_j^{a(1)} \cong H_{aj} C_j^{a(1)} C_j^{a(1)} \tag{26d}$$

has been obtained.

Unfortunately it is difficult to introduce the idea of electron pairs in the multi-reference case. Further the EPV terms and non EPV terms are not identified in this case. Here we assume that the "connected" contribution in the first term, $\sum_s H_{js} D_s^{a(2)}$ can be neglected.

First we define e_j^a by

$$e_j^a C_j^{a(1)} = -\left\{ \sum_s H_{js} D_s^{a(2)} - \left(\sum_i H_{ai} C_i^{a(1)} \right) C_j^{a(1)} \right\}, \tag{27}$$

and further approximate e_j^a as follows. Assume that ψ_j is a doubly excited CSF relative to the reference space, which means, in this case, that ψ_j is not singly excited relative to any reference CSF. A similar approximation to the CEPA2 is then carried out on Eq. (27):

$$e_j^a = H_{aj} C_j^{a(1)} \quad (j\text{: double excitation}). \tag{28}$$

If, on the other hand ψ_j is a singly excited CSF relative to a reference function, ψ_j can interact only with triply excited CSFs in the space $\boldsymbol{R}$, and those interacting CSFs are not single excitations relative to ψ_j but double excitations. We assume that $\sum_s H_{js} D_s^{a(2)}$ cancels with the contribution from the double excitation in the summation over i: $(\sum_i H_{ai} C_i^{a(1)}) C_j^{a(1)}$. Thus e_j^a is given by

$$e_j^a = {\sum_i}' H_{ai} C_i^{a(1)} \quad (j\text{: single excitation}), \tag{29}$$

where summation $\sum_i'$ runs over only singly excited CSFs. Then we obtain the following equation:

$$H_{aa} C_j^{a(3)} - \sum_i H_{ji} C_i^{a(3)} = -e_j^a C_j^{a(1)} - \sum_{b \neq a} \sum_i H_{bi} C_i^{a(1)} C_j^{b(1)}. \tag{30}$$

By combining Eqs. (18) and (30), we obtain

$$\sum_i \left\{ (H_{aa} + e_j^a)\delta_{ji} - H_{ji} + \sum_{b \neq a} C_j^{b(1)} H_{bi} \right\} (C_i^{a(1)} + C_i^{a(3)})$$

$$= H_{ja} + e_j^a C_j^{a(3)} + \sum_{bi} C_j^{b(1)} H_{bi} C_i^{a(3)}. \tag{31}$$

The first term of the right hand side is first order in the magnitude of the perturbation whereas the second and third terms are the fifth order. If we neglect the fifth order term on the right hand side, the following equation results:

$$\sum_i \left\{ (H_{aa} + e_j^a)\delta_{ji} - H_{ji} + \sum_{b \neq a} C_j^{b(1)} H_{bi} \right\} (C_j^{a(1)} + C_j^{a(3)}) = H_{ja}. \tag{32}$$

We obtain a set of equations similar to that of the CEPA2 [8] except for the last term in the left hand side which originated from the indirect coupling between ϕ_a and other reference functions. Let us approximate C_i^a by

$$\underline{C}_i^a = C_i^{a(1)} + C_i^{a(2)} + C_i^{a(3)}. \tag{33}$$

By the use of Eq. (23) and the solutions of Eq. (32), we obtain approximate coefficients $\{\underline{C}_i^a\}$. The approximate solution for $\underline{E}_a$ and $\underline{\alpha}_c^a$ is then obtained from an equation corresponding to Eq. (10), but in which λ is set to be unity,

$$\sum_b \left\{ (H_{bb} - \underline{E}_a)\delta_{cb} + \sum_i H_{ci} \underline{C}_i^b \right\} \underline{\alpha}_b^a = 0. \tag{34}$$

The energy, $\underline{E}_a$, is the fourth order in the perturbation expansion. It is noted that the matrix of the effective Hamiltonian over the reference space is non-hermitian. The size consistency is obtained approximately due to the approximation on the right hand side of Eq. (25).

If we truncate the perturbation expansion at the first order, i.e. replace $\underline{C}_i^b$ by $C_i^{b(1)}$, and obtain the wave function using Eq. (34), the approximate total wave function corresponds to that of a linear cluster expansion including rotation among reference functions due to the inclusion of electron correlation. The resultant energy is correct up to the second order of the perturbation. Very recently Cave and Davidson [7c] proposed a QDVPT which provides a similar wave function to the second order approximation of the present method. If we neglect rotation among reference functions in this order, the resulting wave function corresponds to the one given by the linearized coupled-cluster method (LCCM) by Laidig and Bartlett [12d].

The fourth order energy is obtained by a scheme similar to the CEPA which includes the effect of the quadruple correction approximately with a MRSDCI framework. The rotation within the reference space is taken into account through Eq. (34). The averaged coupled-pair functional method (ACPF) [8b] is somewhat similar to the present method.

The process of the computation of the present method is as follows:

1) solve Eq. (18) to calculate $\{e_i^a\}$;
2) solve Eq. (32) to evaluate $\{\underline{C}_i^a\}$;
3) solve Eq. (34) to obtain $\{\underline{E}_a\}$ and $\{\underline{\alpha}_b^a\}$.

The order of Eq. (34) is usually very small but that of Eqs. (18) and (32) is the same and is equal to the number of CSFs of single and double excitations. As a secular equation of almost the same order of Eq. (32) is solved only once in the usual MRSDCI, the present method requires roughly twice as much processing time as in usual MRSDCI of the eigenvalue problem. Other computational processes such as integral transformation and Hamiltonian matrix elements are the same as in the usual MRSDCI scheme.

3. Results of test calculations and discussion

In order to test the reliability of the present method, we carried out test calculations on two small molecules, BeH_2 and N_2.

3.1. BeH_2

We carried out calculations at three geometrical points around the avoided crossing in the C_{2v} insertion pathway of Be into H_2 to yield BeH_2 in the lowest $^1A_1$ state [14]. We used the same basis set used by Purvis et al. [14], i.e., $[3s1p/2s]$ contracted from $(10s3p/4s)$. Firstly, a self consistent field (SCF) calculation was carried out using the electronic configuration $1a_1{}^2 2a_1{}^2 1b_2{}^2$ at the two geometry points other than the geometry point where the distance from Be to H_2 midpoint ($r(BeH_2)$) was $3.00a_0$; at that geometry $1a_1{}^2 2a_1{}^2 3a_1{}^2$ is used. Then we carried out a natural orbital (NO) iteration using CI with the singly excited configurations from the following two reference functions: $1a_1{}^2 2a_1{}^2 1b_2{}^2$ and $1a_1{}^2 2a_1{}^2 3a_1{}^2$. We expect this procedure to be a good approximation to an SCF procedure with the two configurations (TCSCF). Converged energies coincide with those given by Cave and Davidson [7b]. Using the molecular orbitals (MO's) thus obtained, we applied this method to the ground state surface using the two configurations as reference configurations. The number of CSFs was 182.

Results of the second order approximation and the fourth order energy are shown in Table 1 and compared with energies of some other calculations. Two types of approximation are carried out on the fourth order energy : (i) the fourth order(1), in which we neglect the last term of the left hand side of Eq. (31), i.e., indirect coupling between the reference functions, and (ii) the fourth order(2), in which Eq. (31) is solved exactly. The fourth order energies are improved much in comparison with the 2nd order energies throughout the three geometries. The ratio of the coefficient of the $1a_1{}^2 2a_1{}^2 3a_1{}^2$ configuration to that of the $1a_1{}^2 2a_1{}^2 1b_2{}^2$ at the geometry, $r(BeH_2) = 2.75a_0$, $r(H_2) = 2.55a_0$, is -1.02 in the 2nd order approximation, -0.97 in the fourth order(1) approximation, and -0.90 in the fourth order(2) approximation. The last one is in good agreement with the full CI result of -0.85 and comparable to -0.89 of QDVPT [7c].

Results by ACPF agree best with the full CI results. Next best agreement is obtained by the present fourth order(2) and the MRCEPM of Meissner et al. [11e] where the fourth order correction is taken into account. Comparable results

Table 1. The present results for the BeH_2 two-reference case and comparison with other results

$r(BeH_2)$[a]	2.50	2.75	3.00
$r(H_2)$[a]	2.78	2.55	2.32
Full CI[b]	−15.6229	−15.6029	−15.6250
ΔMRSDCI[c]	0.9	2.0	3.1
ΔMRLCCM[d]	−2.6	−2.4	−5.5
ΔMRCEPM[e]	−0.1	0.6	2.9
ΔACPF[f]	−0.9	−0.9	−0.5
ΔVPT[g]	−3.2	4.2	−5.5
ΔQDVPT[h]	−2.9	−4.7	−5.5
Present			
second order[i]	−13.6	−6.1	−5.6
fourth order(1)[j]	−2.6	−4.6	−4.1
fourth order(2)[k]	−1.2	−3.5	−4.5

[a] $r(BeH_2)$ is the distance from Be to H_2 midpoint. $r(H_2)$ is the H_2 bond length in bohr

[b] The full CI energies given in hartree [14b]

[c] [7b]; relative to the full CI energies in millihartree

[d] [12d]; relative to the full CI energies in millihartree

[e] [11e]; relative to the full CI energies in millihartree

[f] [8b]; relative to the full CI energies in millihartree

[g] [7b]; relative to the full CI energies in millihartree

[h] [7c]; relative to the full CI energies in millihartree

[i] $\underset{\sim}{C}_i^a$ are replaced by the solution of Eq. (18). Energies are second order and relative to the full CI energies in millihartree

[j] $\underset{\sim}{C}_i^a$ are given by the solution of Eq. (31), neglecting the last term of the left hand side. Energies are relative to the full CI energies in millihartree

[k] $\underset{\sim}{C}_i^a$ are given by the solution of Eq. (31). Energies are relative to the full CI energies in millihartree

are given by QDVPT. As is expected for a molecule as small as BeH_2, the MRSDCI gives a very accurate energy in comparison with the full CI.

As was pointed out previously, the present second order approximation without rotation in the reference space is equivalent to MRLCCM by Laidig et al. [12d]. The energies of the second order without rotation in the reference space agree with those of MRLCCM. The energies of MRLCCM seem to be better than the present second order energies. This may be attributed to cancelation caused by neglecting rotation among reference functions.

3.2. N_2

The basis set used in this work was the [4*s*2*p*] Dunning contraction [15] of the Huzinagal [16] (9*s*5*p*) primitive set. A set of *d* polarization functions was added (3*s* component excluded) with exponents of 0.8. The internuclear distances employed were $2.05a_0$, $2.10a_0$, $2.15a_0$, and $50.0a_0$. The electronic wave function and energies of the ground state ($X^1\Sigma_g^+$) were calculated. First we carried out NO iteration with the 14 CSFs (20 by D_{2h} point group) of the following type of configurations:

$$1\sigma_g{}^2 1\sigma_u{}^2 2\sigma_g{}^2 2\sigma_u{}^2 (3\sigma_g, 3\sigma_u)^2 (1\pi_u, 1\pi_g)^4,$$

plus singly excited CSFs from these functions. We expect that the resulting NO set should be good approximation to the MCSCF orbital set for the 14 CSFs which are necessary to describe dissociation to the two nitrogen atoms in the $^4S°$ state properly. Using this NO set, we applied the present method to the ground state of N_2. At internuclear distances of $2.05a_0$, $2.10a_0$ and $2.15a_0$, we took the following four CSFs.

$$1\sigma_g{}^2 1\sigma_u{}^2 2\sigma_g{}^2 2\sigma_u{}^2 3\sigma_g{}^2 1\pi_u{}^4,$$

$$1\sigma_g{}^2 1\sigma_u{}^2 2\sigma_g{}^2 2\sigma_u{}^2 3\sigma_g{}^2 [(1\pi_u{}^2)^{{}^3\Sigma_g^-} (1\pi_g{}^2)^{{}^3\Sigma_g^-}],$$

$$1\sigma_g{}^2 1\sigma_u{}^2 2\sigma_g{}^2 2\sigma_u{}^2 3\sigma_g{}^2 [(1\pi_u{}^2)^{{}^1\Delta_g} (1\pi_g{}^2)^{{}^1\Delta_g}],$$

$$1\sigma_g{}^2 1\sigma_u{}^2 2\sigma_g{}^2 2\sigma_u{}^2 3\sigma_g{}^2 [(1\pi_u{}^2)^{{}^1\Sigma_g^+} (1\pi_g{}^2)^{{}^1\Sigma_g^+}],$$

as reference functions to generate singly and doubly excited CSF's, the weight of the other CSFs being negligibly small. At the internuclear distance of $50.0a_0$, the 14 CSFs are taken as reference functions. The singly and doubly excited CSFs so generated are restricted to the first order interacting functions [17]. In order to compare the present results with the bench mark full CI by Bauschlicher and Langhoff [18], we utilized the same level of active orbital space and kept $1\sigma_g$, $1\sigma_u$, $2\sigma_g$, and $2\sigma_u$ frozen. The number of CSF's was 1670 for the case of four

Table 2. Total energies of the $X^1\Sigma_g^+$ state of N_2

$r(N_2)$[a]	2.05	2.10	2.15	50.0
Full CI[b]	−109.1469	−109.1506	−109.1505	−108.8295
MR-CI[c]	—	0.8	—	—
Present				
SDCI	2.2	2.3	2.6	0.5
second order[d]	−1.4	−2.6	−2.6	−0.1
fourth order(1)[e]	−1.4	−1.4	−1.5	−0.1
fourth order(2)[f]	−1.4	0.01	−0.3	−0.1

[a] $r(N_2)$: the N_2 bond distance in bohr (a_0)

[b] The full CI energies given in [18]

[c] The internally contracted MRCI energies given in [19]. Energies are relative to the full CI energies in millihartree

[d] $\underline{C}_i^a$ are replaced by the solution of Eq. (18). Energies are relative to the full CI energies in millihartree

[e] $\underline{C}_i^a$ are given by the solution of Eq. (31), neglecting the last term of the left hand side. Energies are relative to the full CI energies in millihartree

[f] $\underline{C}_i^a$ are given by the solution of Eq. (31). Energies are relative to the full CI energies in millihartree

Table 3. Some spectroscopic constants of the $X^1\Sigma_g^+$ state of N_2

	R_e (a_0)	D_e (eV)	ω_e (cm^{-1})
Full CI[a]	2.12	8.75	2333
Present			
SDCI	2.12	8.69	2359
second order[b]	2.12	8.82	2640
fourth order[c]	2.12	8.78	2327
fourth order[d]	2.13	8.74	1723

[a] The full CI energies given in [18]

[b] $\underline{C}_i^a$ are replaced by the solution of Eq. (18)

[c] $\underline{C}_i^a$ are given by the solution of Eq. (31), neglecting the last term of the left hand side

[d] $\underline{C}_i^a$ are given by the solution of Eq. (31)

reference functions and 4188 for 14 reference functions. Ordinary SDCI with these CSF's was also carried out.

Calculated energies and some spectroscopic constants are summarized in Table 2 and Table 3, respectively. The fourth order(2) approximation provides quite good agreement with the full CI energy except for $r(N_2) = 2.05a_0$, as is shown in Table 2. The fourth order(1) energies are also in good agreement with the full CI energies and errors are almost constant for the three near equilibrium internuclear distances. The equilibrium distance, R_e, by the four approaches is in good agreement with the full CI results. Excellent agreement for D_e with full CI was obtained by both the fourth order approaches. For ω_e, the fourth order(1) approximation gave very good agreement with the full CI value. SDCI also provided a good result. Unfortunately the fourth order(2) gave the worst result for ω_e. This was caused by the unstable error of energies against the three internuclear distances in the fourth order(2) approximation.

In this subsection, we have considered the accuracy of the computed total energy, R_e, D_e and ω_e of N_2: on the whole the fourth order(2) approximation is superior to the fourth order(1). The difference between the two approaches is only in the approximation of the right hand side of Eq. (25). In order to obtain more stable results, further consideration of this approximation may be interesting.

4. Summary

Using a non-linear expression for the wave function and Rayleigh–Schrödinger perturbation theory, we have developed a method of incorporating quadruple correction within the framework of the MRSDCI. Size consistency is approximately obtained by this method. The reference space is treated as quasidegenerate, and rotation in the reference space is taken into account.

This method has been used to calculate the total energies of BeH_2 and N_2, and good agreement with full CI results is obtained.

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