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Z-vector formalism for the Fock space multireference coupled cluster method: Elimination of the response of the highest valence sector amplitudes

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In this paper we present Z-vector formalism for the Fock space multireference coupled cluster framework. We present detailed equations describing the derivative effective Hamiltonian, where the response amplitudes of the highest Fock sector are eliminated. We discuss the conditions and approximations under which the formalism is possible. We also discuss the implications and comparison with the similar formalism in the single reference framework. The computational advantages and feasibility are also commented upon in this paper. © 1999 American Institute of Physics. [S0021-9606(99)30433-5]

I. INTRODUCTION

In recent years, coupled cluster (CC) method has emerged as the method of choice in electronic structure calculation.^{1–5} The single reference variant of the CC method (SRCC) has been used successfully for the structure and properties of closed shell systems. Central to the success of the SRCC method is the development of analytic derivative technique, which has made SRCC a powerful tool for determination of geometry, vibrational frequencies as well as calculation of electric and magnetic properties of molecules.^{6–8} Although several stationary CC techniques have been investigated, the most standard CC technique is based on the nonvariational method of projection, which results in simplification of equations. However, because of the nonvariational character, the derivatives of energy do not satisfy Hellmann–Feynman theorem or general $(2n+1)$ rule. Hence, for example, the first derivative of the energy with respect to a perturbation parameter, e.g., external electric field vector or nuclear coordinates is dependent on the corresponding first derivative of the amplitudes. These derivatives are obtained from the solution of a linear equation, which is different for different perturbation parameters. From the structure of the linear equation in the SRCC case these derivative amplitudes can be written compactly as inverse of a matrix acting on a perturbation-dependent vector. Substituting this expression in the energy derivative and invoking the interchange theorem, one can cast the energy first derivative expression into a scalar product of perturbation-dependent vector and another vector consisting of perturbation-independent de-excitation amplitudes, which can be obtained by the solution of a linear equation. This makes the SRCC analytic derivative technique a computationally feasible one. This technique was first introduced by Handy and Schaefer⁹ in CI (configuration interaction) method and subsequently Bartlett and co-workers introduced

the technique SRCC method.¹⁰ The additional de-excitation amplitudes vector is called the Z-vector and the technique is commonly known as Z-vector technique.

The SRCC method has been used for some special open shell cases, where the model function can be represented as a single determinant. However, to treat the general quasi-degenerate cases dominated by the dynamical electron correlation, it is physically desirable to start from a multideterminantal model space. The CC methods based on this model space, known as multireference CC methods, have been studied extensively in recent years.^{11–17} There are three classes of MRCC (multireference coupled cluster) methods in the literature, (a) valence universal or Fock space method,^{11–14} (b) state universal or Hilbert space method,^{15,16} and (c) state specific method.¹⁷ The traditional approach is the effective Hamiltonian approach, where an effective Hamiltonian, defined over the principal or reference determinants, is diagonalized to yield the energies of exact states, the zeroth-order prescriptions of which lie in the model space. The effective Hamiltonian approach has been used in valence universal and state universal variants. Both these variants have been studied, although the efficacy of these variants is now established for specific studies. The state universal one is more suited for study of states with a fixed number of electrons. The valence universal variant, on the other hand, is efficient for the study of states with a specified number of valence electrons N_v and all the lower valence model spaces with fewer valence electrons m , ($0 \leq m \leq N_v$), which makes it suitable for studies of spectroscopic energies. The valence universal MRCC has been developed for accurate calculation of ionization and excitation energies. State specific MRCC addresses to the solution of a specific state of interest and is thus relatively free of intruder state problems.

To make the MRCC class of methods more useful, there have been recent efforts in developing strategy of linear response. In particular, Pal has developed the linear response of valence-universal MRCC method in the time-independent framework.¹⁸ Szalay¹⁹ has developed constrained varia-

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tional approach for the Fock space MRCC method, where the first derivative amplitudes are naturally not required in the expression of first derivative energy. Following the work of Pal,¹⁸ response to time-dependent field and its static limit yielding the time-independent equations has been derived by Ajitha and Pal.²⁰ The time-independent linear response formalism has been applied only recently to evaluate dipole moments for open shell radicals.²¹ However, the initial formulation did not include any prescription of Z-vector type technique and thus the energy derivatives depend explicitly on the corresponding wave function derivatives, i.e., the derivatives of the cluster amplitudes.

The objective of this paper is to introduce simplifications in the MRCC response equations, by introducing a Z-vector type formalism. We will show in the present paper that it is possible to eliminate the explicit dependence of the derivative effective Hamiltonian on the derivative of the highest Fock space sector amplitudes. We will discuss situations where such elimination will prove fruitful. The organization of the present paper is as follows. In Sec. II, we briefly present valence universal MRCC linear response approach with specific reference to the time-independent perturbation. In Sec. III, we will show that in the Fock space (valence universal) framework, the derivatives of the highest Fock space sector amplitudes with respect to different perturbations, e.g., external electric fields in three directions or the nuclear co-ordinates can be eliminated in favor of a single set of amplitudes under certain approximations. We will derive the pertinent equations and show how this simplifies the calculation of analytic derivatives in the MRCC valence universal framework. We will also discuss the situations where the approximations are valid.

II. FOCK SPACE MRCC AND LINEAR RESPONSE

In the Fock space MRCC method the model space of interest is generated from a single determinant which is a hole-particle vacuum. The model space $P_{(m,n)}$ containing m valence particles and n valence holes is defined as the linear space obtained by the action of a string of valence hole-particle creation operators (X^+). For the specific one hole sector, the model space is defined as the linear combination of the states $|\Phi_\mu\rangle$, where $|\Phi_\mu\rangle$ is the set of states obtained by creating a valence hole. The projection operator for the one hole model space is defined as

$$P_{(0,1)} = \sum_\mu |\Phi_\mu\rangle \langle \Phi_\mu| \quad \text{where} \quad |\Phi_\mu\rangle = Xi^+ |\Phi_0\rangle, \quad (1)$$

where $i \in \text{valence holes}$,

where Xi^+ is valence hole creation operator. Subscript (0,1) denotes that there is 0 particle and 1 hole in model space.

The effect of correlation is brought in by means of a valence universal wave operator. The wave operator for the general (m,n) sector model space is defined as

$$\Omega_{(m,n)} = \{\exp(\tilde{T}_{(m,n)})\}, \quad (2)$$

$$\tilde{T}_{(m,n)} = \sum_{k=0}^m \sum_{l=0}^n T_{(k,l)}. \quad (3)$$

Where, $\{\}$ denotes normal ordering. $T_{(k,l)}$ is an operator which, acting on the model space, destroys exactly k valence particles and l valence holes. Thus the $\tilde{T}_{(m,n)}$ operator can destroy any subset of m valence particles and n valence holes. The wave operator for the (m,n) sector simultaneously correlates all the lower sectors and thus is valence universal in nature. For the specific one hole sector, the wave operator can be written as follows:

$$\Omega_{(0,1)} = \{\exp(T_{(0,0)} + T_{(0,1)})\} = \exp T_{(0,0)} \{\exp T_{(0,1)}\}. \quad (4)$$

The operators $T_{(0,1)}$ and $T_{(0,0)}$ are generally truncated to one and two body parts. The one and two body parts of the (0,0) sector amplitudes are simply the SRCC hole-particle excitation amplitudes. The one and two body parts of $T_{(0,1)}$ operators, which destroy one active hole, are given by

$$T_{1(0,1)} = \sum_{i \in ah, j \notin ah} \langle i | t_{(0,1)} | j \rangle i^+ j, \quad (5)$$

$$T_{2(0,1)} = \sum_{i \in ah, j, k, a} \langle ia | t_{(0,1)} | jk \rangle i^+ a^+ k j, \quad (6)$$

where a_h is the subspace of active holes and the wave operator acting on the model space of interest can transform them in one shot to the corresponding exact states. The operator $T_{(0,1)}$ contains hole-particle annihilation operators in contrast to $T_{(0,0)}$ operator with only hole-particle creation operators. These operators in the Fock space multireference framework do contract among themselves. This situation is avoided by postulating the normal ordering of the wave operator and this ensures that there is no contraction between two valence operators of the highest (m,n) sector. However, it should be noted that in case of the truncation of the cluster amplitudes, we assume that they transform to the states close to the exact states. The exact states are obtained via the effective Hamiltonian approach. The effective Hamiltonian is defined over the model space. The equations describing the effective Hamiltonian and wave operator for the specific (0,1) sector are given as

$$P_{(0,1)} H_{\text{eff}(0,1)} P_{(0,1)} = P_{(0,1)} H \Omega_{(0,1)} P_{(0,1)}, \quad (7)$$

$$Q_{(0,1)} (H \Omega_{(0,1)} - \Omega_{(0,1)} H_{\text{eff}(0,1)}) P_{(0,1)} = 0,$$

where, $Q_{(0,1)}$ is the orthogonal complement of $P_{(0,1)}$ that is reached by the action of the excitation operators on the model space $P_{(0,1)}$. We see that effective Hamiltonian requires the knowledge of the wave operator and this set of equation has to be solved simultaneously as in the case of the single reference method. $H_{\text{eff}(0,1)}$ refers to the specific effective Hamiltonian for the one hole model space. Diagonalizing $H_{\text{eff}(0,1)}$ directly gives the energy difference of the hole state, i.e., ionization potential of the system.

Normal ordering of the wave operator ensures that there is no contribution of the higher valence sector amplitudes in the lower sector equations and thus enables a partial decoupling of the wave operator equations. Thus the Fock space equations can now be solved in a hierarchical manner starting from the lowest sector amplitudes and reaching to the higher sector equations. This is also referred to as the

sub-system embedding condition in the Fock space terminology. Thus in the case of one hole model spaces, we first solve the zero hole model space amplitudes and then solve the one hole sector equations. This brings in the Fock space hierarchy of sector solutions in this approach. Owing to the nature of the sector equations, it is easily adopted to calculate the direct energy differences like ionization potential and electron affinity. Normal ordering also ensures that the Fock space equation is at most quadratic in the unknown (m,n) sector amplitudes.

A. Response of multireference Fock space coupled cluster method

The Fock space MRCC effective Hamiltonian equation in the presence of external perturbation can be written as

$$\sum_i [H_{\text{eff}(0,1)}(g)]_{ji} C_{i\mu}(g) = \Delta E_\mu(g) C_{j\mu}(g), \quad (8)$$

where, $C_{j\mu}(g)$ are the field-dependent model space coefficients. The response of a specific Fock space sector is again described by a set of hierarchical equations describing the response of the lower sector amplitudes. For example, in order to evaluate the response of the $(0,1)$ sector, it is essential to solve the response equation of the lower valence $(0,0)$ amplitudes. To develop the analytic response of the system, we expand relevant field-dependent quantities as a Taylor series in g .

This has to be now written for the $(0,1)$ sector.

$$\begin{aligned} \Omega_{(0,1)}(g) &= \Omega_{(0,1)}^{(0)} + \Omega_{(0,1)}^{(1)} g + 1/2! \Omega_{(0,1)}^{(2)} g^2 + \dots, \\ H_{\text{eff}(0,1)}(g) &= H_{\text{eff}(0,1)}^{(0)} + H_{\text{eff}(0,1)}^{(1)} g + 1/2! H_{\text{eff}(0,1)}^{(2)} g^2 + \dots, \\ \Delta E_\mu(g) &= \Delta E_\mu^{(0)} + \Delta E_\mu^{(1)} g + 1/2! \Delta E_\mu^{(2)} g^2 + \dots, \\ C_{j\mu}(g) &= C_{j\mu}^{(0)} + C_{j\mu}^{(1)} g + 1/2! C_{j\mu}^{(2)} g^2 + \dots. \end{aligned} \quad (9)$$

Where $\Omega_{(0,1)}^{(0)}$, $H_{\text{eff}(0,1)}^{(0)}$, $E_\mu^{(0)}$, and $C_{j\mu}^{(0)}$ are the wave operator, effective Hamiltonian, exact energies and the model space coefficients of the unperturbed problem, respectively. The auxiliary condition on the vector $C^{(1)}$ that has to be satisfied is

$$\begin{aligned} \sum_i C_{i\mu}^{(0)*} C_{iv}^{(0)} &= \delta_{\mu\nu}, \\ \sum_i C_{i\mu}^{(0)*} C_{iv}^{(1)} + \sum_i C_{i\mu}^{(1)*} C_{iv}^{(0)} &= 0. \end{aligned} \quad (10)$$

The field-dependent wave operator can be written as

$$\Omega_{(0,1)}(g) = [\exp T_{(0,0)}(g) \{ \exp T_{(0,1)}(g) \}]. \quad (11)$$

The symbol $\{ \}$ represents the normal ordering of the operator products inside the braces. $T_{(0,0)}$ and $T_{(0,1)}$ may be written as a Taylor's series in the field strength g .

$$\begin{aligned} T_{(0,1)}(g) &= T_{(0,1)}^{(0)} + g T_{(0,1)}^{(1)} + \frac{1}{2!} g^2 T_{(0,1)}^{(2)} + \dots, \\ T_{(0,0)}(g) &= T_{(0,0)}^{(0)} + g T_{(0,0)}^{(1)} + \frac{1}{2!} g^2 T_{(0,0)}^{(2)} + \dots. \end{aligned} \quad (12)$$

The use of one body and two body parts of these operators is known as MRCCSD scheme. The response of a specific Fock space sector is also described by a set of hierarchical equations. For the one hole problem of interest the solved amplitudes of the response of the $(0,0)$ sector, which is the response of the SRCC amplitudes, is a prerequisite. The derivative Bloch equation in terms of the perturbed quantities is given below.

III. ELIMINATION OF THE EVALUATION OF THE DERIVATIVE OF THE HIGHEST VALENCE SECTOR AMPLITUDES UNDER SOME APPROXIMATIONS

To obtain the energy first derivatives one needs to solve the derivative of the effective Hamiltonian eigenvalue equation. The dependence of the first derivative Hamiltonian on the first derivative of the cluster amplitudes demands that for each perturbation, one needs to solve the derivative Bloch equation. This is a time consuming step and makes this method particularly unsuitable for gradients. In this section we will attempt a partial elimination of the evaluation of derivatives of cluster amplitudes with respect to each perturbation. We will also show the conditions under which this partial elimination is possible.

To get a clearer picture we define the $H_{\text{eff}(0,1)}$ and the equations for the model space for the one hole sector. The equation for the one particle problem is similar with slight difference and so is for any general (m,n) sector amplitudes.

$$P_{(0,1)} H \Omega_{(0,1)} P_{(0,1)} = P_{(0,1)} H_{\text{eff}(0,1)} P_{(0,1)}. \quad (13)$$

The effective Hamiltonian is linear in the highest valence sector amplitudes due to normal ordering of the cluster amplitudes. Thus for the $(0,1)$ sector problem the effective Hamiltonian equation is linear in $T_{(0,1)}$ amplitudes. It is well established that the effective Hamiltonian is connected. Writing the connected part as commutators, we get

$$P_{(0,1)} (\bar{H} + [\bar{H}, T_{(0,1)}]) P_{(0,1)} = P_{(0,1)} H_{\text{eff}(0,1)} P_{(0,1)}. \quad (14)$$

In case of the response equations \bar{H} and $H_{\text{eff}(0,1)}$ are expanded as Taylor series in the field strength. Let us denote from now onwards $\bar{H}^{(1)}$, $T_{(0,1)}^{(1)}$, $H_{\text{eff}(0,1)}^{(1)}$ as the linear response of \bar{H} , $T_{(0,1)}$, and $H_{\text{eff}(0,1)}$ in the presence of weak external perturbation. The linear response equation in terms of the response terms are given below

$$\begin{aligned} P_{(0,1)} (\bar{H}^{(1)} + [\bar{H}^{(1)}, T_{(0,1)}] + [\bar{H}, T_{(0,1)}^{(1)}]) P_{(0,1)} \\ = P_{(0,1)} H_{\text{eff}(0,1)}^{(1)} P_{(0,1)}. \end{aligned} \quad (15)$$

From the above equation we see that the derivative effective Hamiltonian is linearly dependent on the derivative of the sector amplitudes. Our interest is to eliminate this field-dependent perturbed amplitudes in favor of a set of amplitudes, the solution of which is independent of perturbation. To achieve this elimination, we project the Lindgren–Bloch equation to the $Q_{(0,1)}$ space. Thus the wave operator response equation in terms of $\bar{H}^{(1)}$, $H_{\text{eff}(0,1)}^{(1)}$, and $T_{(0,1)}^{(1)}$ amplitudes is as given below.

$$Q_{(0,1)}(\bar{H}^{(1)} + [\bar{H}^{(1)}, T_{(0,1)}] + [\bar{H}, T_{(0,1)}^{(1)}] - [T_{(0,1)}^{(1)}, H_{\text{eff}(0,1)}] - [T_{(0,1)}, H_{\text{eff}(0,1)}^{(1)}])P_{(0,1)} = 0. \quad (16)$$

Collecting the terms containing the $T_{(0,1)}^{(1)}$ on one side we can write as

$$Q_{(0,1)}(\bar{H}T_{(0,1)}^{(1)} - T_{(0,1)}^{(1)}\bar{H} - T_{(0,1)}^{(1)}H_{\text{eff}(0,1)} - T_{(0,1)}H_{\text{eff}(0,1)}^{(1)})P_{(0,1)} = Q_{(0,1)}(\bar{H}^{(1)} + [\bar{H}^{(1)}, T_{(0,1)}])P_{(0,1)}. \quad (17)$$

It should be noted that $H_{\text{eff}}^{(1)}$ contains $T_{(0,1)}^{(1)}$. Expanding commutator and applying resolution of identity to separate out the perturbed amplitudes we get

$$\begin{aligned} &\langle Q_{(0,1)}|\bar{H}|Q_{(0,1)}\rangle\langle Q_{(0,1)}|T_{(0,1)}^{(1)}|P_{(0,1)}\rangle \\ &- \langle Q_{(0,1)}|T_{(0,1)}^{(1)}|P_{(0,1)}\rangle\langle P_{(0,1)}|\bar{H}|P_{(0,1)}\rangle \\ &- \langle Q_{(0,1)}|T_{(0,1)}^{(1)}|P_{(0,1)}\rangle\langle P_{(0,1)}|H_{\text{eff}(0,1)}|P_{(0,1)}\rangle \\ &- \langle Q_{(0,1)}|T_{(0,1)}|P_{(0,1)}\rangle\langle P_{(0,1)}|H_{\text{eff}(0,1)}^{(1)}|P_{(0,1)}\rangle \\ &= \langle Q_{(0,1)}|(\bar{H}^{(1)} + [\bar{H}^{(1)}, T_{(0,1)}])|P_{(0,1)}\rangle. \end{aligned} \quad (18)$$

Substituting for $PH_{\text{eff}}^{(1)}P$ in terms of Eq. (15) we get the equation for the derivative amplitudes as

$$\begin{aligned} &\langle Q_{(0,1)}|\bar{H}|Q_{(0,1)}\rangle\langle Q_{(0,1)}|T_{(0,1)}^{(1)}|P_{(0,1)}\rangle - \langle Q_{(0,1)}|T_{(0,1)}^{(1)}|P_{(0,1)}\rangle \\ &\times \langle P_{(0,1)}|\bar{H}|P_{(0,1)}\rangle - \langle Q_{(0,1)}|T_{(0,1)}^{(1)}|P_{(0,1)}\rangle \\ &\times \langle P_{(0,1)}|H_{\text{eff}(0,1)}|P_{(0,1)}\rangle - \langle Q_{(0,1)}|T_{(0,1)}|P_{(0,1)}\rangle \\ &\times \langle P_{(0,1)}|\bar{H}T_{(0,1)}^{(1)}|P_{(0,1)}\rangle \end{aligned}$$

$$\begin{aligned} &= \langle Q_{(0,1)}|(\bar{H}^{(1)} + \bar{H}^{(1)}T_{(0,1)} - T_{(0,1)}\bar{H}^{(1)})|P_{(0,1)}\rangle \\ &+ \langle Q_{(0,1)}|T_{(0,1)}|P_{(0,1)}\rangle \\ &\times \langle P_{(0,1)}|(\bar{H}^{(1)} + \bar{H}^{(1)}T_{(0,1)})|P_{(0,1)}\rangle. \end{aligned} \quad (19)$$

From the above equation we can see that $T_{(0,1)}^{(1)}$ in the left hand side appears in the right of \bar{H} in Q space and to the left of $H_{\text{eff}(0,1)}$ in the P space. Since, in general, H_{eff} has a matrix structure, the factorization of the $T_{(0,1)}^{(1)}$ part can be effected only upon a diagonal assumption of H_{eff} . In the case of single reference model space, this is one particular number E_μ and thus no such approximation is necessary to have an analytic solved solution of the derivative amplitudes. In the present case, this approximation is appropriate in case of degenerate states, and in case of states with different symmetries as in both these case the H_{eff} is diagonal. Thus under the diagonal approximation the equation of the $T_{(0,1)}^{(1)}$ amplitudes can be written as follows:

$$\begin{aligned} &[\langle Q_{(0,1)}|\bar{H}|Q_{(0,1)}\rangle - \langle P_{(0,1)}|\bar{H}|P_{(0,1)}\rangle \\ &- \langle P_{(0,1)}|H_{\text{eff}(0,1)}|P_{(0,1)}\rangle - \langle Q_{(0,1)}|T_{(0,1)}\bar{H}|P_{(0,1)}\rangle \\ &- \langle Q_{(0,1)}|T_{(0,1)}\bar{H}|P_{(0,1)}\rangle]\langle Q_{(0,1)}|T_{(0,1)}^{(1)}|P_{(0,1)}\rangle \\ &= \langle Q_{(0,1)}|(\bar{H}^{(1)} + \bar{H}^{(1)}T_{(0,1)} - T_{(0,1)}\bar{H}^{(1)}) \\ &+ T_{(0,1)}(\bar{H}^{(1)} + \bar{H}^{(1)}T_{(0,1)})|P_{(0,1)}\rangle. \end{aligned} \quad (20)$$

Writing the explicit expression for derivative sector amplitudes we have:

$$\begin{aligned} \langle Q_{(0,1)}|T_{(0,1)}^{(1)}|P_{(0,1)}\rangle &= [\langle Q_{(0,1)}|(\bar{H}^{(1)} + \bar{H}^{(1)}T_{(0,1)} - T_{(0,1)}\bar{H}^{(1)}) + T_{(0,1)}(\bar{H}^{(1)} + \bar{H}^{(1)}T_{(0,1)})|P_{(0,1)}\rangle]^* \\ &\times \left[\begin{aligned} &\langle Q_{(0,1)}|\bar{H}|Q_{(0,1)}\rangle - \langle P_{(0,1)}|\bar{H}|P_{(0,1)}\rangle - \langle P_{(0,1)}|H_{\text{eff}(0,1)}|P_{(0,1)}\rangle \\ &- \langle Q_{(0,1)}|T_{(0,1)}\bar{H}|P_{(0,1)}\rangle - \langle Q_{(0,1)}|T_{(0,1)}\bar{H}|P_{(0,1)}\rangle \end{aligned} \right]^{-1}. \end{aligned} \quad (21)$$

Now we propose a perturbation independent set of amplitudes called Λ set of amplitudes such that for every $Q_{(0,1)}T_{(0,1)}P_{(0,1)}$ sector amplitudes there is a corresponding $P_{(0,1)}\Lambda_{(0,1)}Q_{(0,1)}$ amplitude. If we require that these new set of amplitudes satisfy the equation

$$\begin{aligned} \langle P_{(0,1)}|\Lambda|Q_{(0,1)}\rangle &= [\langle P_{(0,1)}|(\bar{H}^{(1)} + \bar{H}^{(1)}T_{(0,1)} - T_{(0,1)}\bar{H}^{(1)}) + T_{(0,1)}(\bar{H}^{(1)} + \bar{H}^{(1)}T_{(0,1)})|Q_{(0,1)}\rangle]^* \\ &\times \left[\begin{aligned} &\langle Q_{(0,1)}|\bar{H}|Q_{(0,1)}\rangle - \langle P_{(0,1)}|\bar{H}|P_{(0,1)}\rangle - \langle P_{(0,1)}|H_{\text{eff}(0,1)}|P_{(0,1)}\rangle \\ &- \langle Q_{(0,1)}|T_{(0,1)}\bar{H}|P_{(0,1)}\rangle - \langle Q_{(0,1)}|T_{(0,1)}\bar{H}|P_{(0,1)}\rangle \end{aligned} \right]^{-1}, \end{aligned} \quad (22)$$

we can write the derivative effective Hamiltonian equation in terms of these Λ amplitudes as

$$\begin{aligned} &\langle P_{(0,1)}|(\bar{H}^{(1)} + \bar{H}^{(1)}T_{(0,1)})|P_{(0,1)}\rangle + \langle Q_{(0,1)}|\Lambda_{(0,1)}|Q_{(0,1)}\rangle \\ &\times \langle Q_{(0,1)}|\bar{H}|P_{(0,1)}\rangle = \langle P_{(0,1)}|H_{\text{eff}(0,1)}^{(1)}|P_{(0,1)}\rangle. \end{aligned} \quad (23)$$

This expansion (23) is a consequence of interchange theorem. We observe that the derivative effective Hamiltonian is written in terms of Λ amplitudes, which does not contain the

derivative of the $(0,1)$ sector amplitudes explicitly, and the derivative of the \bar{H} . The coupled linear equation of Λ amplitudes does not depend on perturbation and hence this equation needs to be solved only once. This will lead to considerable computational simplicity. However, although the derivatives of the one valence amplitudes need not be computed, the derivative amplitudes of the zero valence amplitudes are present in the \bar{H} derivative. They still appear explicitly. In general, through the interchange theorem, it is

possible to eliminate the highest valence amplitudes only. We believe that this is due to the nature of the Fock space, where amplitudes of different sectors are coupled hierarchically.

IV. CONCLUSIONS

In this paper we have attempted a Z-vector type of formalism for the Fock space multireference coupled-cluster analytical response approach. With the example of one valence problem we have shown that the dependence on the derivative amplitudes of the one valence sector can be eliminated in the derivative of the effective Hamiltonian in favor of a new set of perturbation-independent amplitudes which take functions in $Q^{(0,1)}$ space to the $P^{(0,1)}$ space. We show the approximations under which this elimination is possible and discuss the appropriate situations where these approximations are valid. Explicit equations for the derivative effective Hamiltonian in terms of these perturbation-independent amplitudes are given. The reasons as to why a total elimination is not achievable are also analyzed.

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