Multireference coupled-cluster response approach for the calculation of static properties

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We present in this paper a coupled-cluster method for the calculation of the response of properties of a system of various orders. This uses a multiconfigurational model space thus making it suitable for open-shell or quasidegenerate situations. We present the basic equations and the hierarchy for generating higher-order response.

I. INTRODUCTION

Coupled-cluster methods[1] (CCM's) have been established as very convenient tools for introducing electron correlation. Extensive applications of CCM's have been made in recent years to the calculation of electron correlation energies. Broadly, CCM's can be classified into two distinct categories—one based on a single-determinantal reference function,[1] usually a Hartree-Fock function, the other based on a multiconfigurational model space.[2] Single-reference CCM's have been used very successfully for closed-shell situations,[3,4] particularly some accurate calculations giving results within chemical accuracy.[5] However, it has been realized that for certain cases such as quasidegenerate situations it is essential to start from a model space which already consists of several configurations. There have been recent applications of multiconfigurational CCM's to the calculation of difference energies and the energies of open-shell systems.[6–8]

While most of the attention has been focused on the electronic correlation energies or difference energies, there has been recent interest in applying CCM's to the case of static electronic properties. For a first-order property one may evaluate the expectation value with respect to a stationary coupled-cluster (CC) wave function. However, in a formulation that we call the response approach, the response of the CC wave function and consequently the properties of various orders are described by the derivatives of the cluster parameters with respect to external perturbation. One can have analytical expressions for properties which are related to various-order derivatives of energy with respect to external perturbation in the limit where the perturbation parameter is set to zero. Monkhorst discussed such an approach and presented the equations for derivatives.[9] Sekino and Bartlett[10] additionally incorporated the change of orbitals to external fields and made some calculations for first-order and higher-order derivatives. Their calculations reflect the necessity of incorporating a high degree of electron correlation. With a similar wave function a stationary formulation was attempted by us.[11] A bivariational CC method which uses two different sets of cluster parameters depending on the perturbation parameter was also formulated by Pal[12] and Basu Ghose and Pal[13] in recent years. The idea of using a bivariational method stemmed from an earlier work of Arponen[14] using a functional involving different parametrization for the bra and ket states. However, since the approach by Arponen did not use the idea of a response of the wave function, it was limited to first-order properties. The other attempts to apply CCM's to static electronic properties were due to Kümmel,[15] Mukherjee and co-workers,[16] and Geertsen and Oddershede.[17] Kümmel discussed a special form of the linked expectation value. Mukherjee and co-workers extensively developed a linear-response approach. A CC polarization propagator method was recently developed by Geertsen and Oddershede. Noga and Urban[18] also studied the expectation value of a one-electron property in a CC state and the degree of non-Hellman-Feynman character.

However, most of the studies so far on static properties have been based on a single-reference function. From our experience on the CC studies of energies we expect that it may be essential to formulate a suitable CC approach based on a multiconfigurational model space for the calculation of properties for open-shell systems also. We shall, in this paper, attempt a response approach in the framework of a multideterminantal model space containing nondynamical electron correlation. We shall use much of the knowledge for description of the wave function that we have from multireference CC (MRCC) methods already used for energy calculations. The paper is organized as follows. In Sec. II A we describe the response approach for the single-reference model function. In Sec. II B we present the MRCC approach developed for energy calculation and in Sec. III we present our formulation of properties for a multiconfigurational model space. Section IV contains some relevant discussion.

II. RESPONSE APPROACH AND MULTIREFERENCE MODEL SPACE

A. Response approach

The response approach is based on the CC wave function depending on a perturbation parameter introduced in the Hamiltonian. The Hamiltonian of a system interacting with external fields is expressed in terms of a perturbation parameter λ, as

$$H(\lambda)=H+\lambda\hat{O}\ , \tag{1}$$

where H is the Hamiltonian of the system, and $\hat{O}$ describes the interaction. The CC wave function $\Psi(\lambda)$ corresponding to the perturbed Hamiltonian $H(\lambda)$ is written as

$$\Psi(\lambda)=e^{T(\lambda)}\Phi_0 , \tag{2}$$

where Φ_0 is a reference state. In all earlier developments for calculating properties, Φ_0 is taken to be the single-reference model space. Following Refs. 9 and 10, $T(\lambda)$ and $E(\lambda)$, the eigenvalues of $H(\lambda)$, may be expanded as

$$T(\lambda)=T+\lambda T^{(1)}+\lambda^2 T^{(2)}+\cdots , \tag{3}$$

$$E(\lambda)=E+\lambda E^{(1)}+\lambda^2 E^{(2)}+\cdots . \tag{4}$$

T is the cluster operator corresponding to the system Hamiltonian. $T^{(1)}$ is the first derivative of $T(\lambda)$ with respect to λ at $\lambda=0$, and so on. E is the energy of the system without any perturbation, and $E^{(1)}$ is the first derivative of $E(\lambda)$ at $\lambda=0$. The Schrödinger equation for the perturbed Hamiltonian is given by

$$H(\lambda)\Psi(\lambda)=E(\lambda)\Psi(\lambda) . \tag{5}$$

Not allowing any change in orbital parameters due to the perturbation, which is a very reasonable approximation for static properties, one can write down the equations resulting from projection onto Φ_0 and the various excited states.[9] While terms independent of λ result in ordinary single-reference CC equations, terms linear in λ give the equation needed for first-order properties and the $T^{(1)}$ parameters. Similarly, terms quadratic in λ yield second-order properties. For example,

$$E^{(1)}=\langle\Phi_0|e^{-T}(\hat{O}+[H,T^{(1)}])e^{T}|\Phi_0\rangle , \tag{6a}$$

with

$$\langle\Phi^*|e^{-T}(\hat{O}+[H,T^{(1)}])e^{T}|\Phi_0\rangle=0 . \tag{6b}$$

For the approximate wave function, $E^{(1)}$ and $\langle\hat{O}\rangle$ are, in general, different, thus deviating from the Hellman-Feynman theorem. $E^{(1)}$ obtained by Eqs. (6a) and (6b) in the doubles-only approximation, however, gives the expectation value truncated to a total of quadratic power in amplitudes. Thus we established some conditions for the Hellman-Feynman theorem in approximate cases. In a recent study Noga and Urban[18] also studied the non-Hellman-Feynman contribution for a first-order property. There have been various other formulations of static properties in a single-reference space, notably a variational treatment by the present author[11,19] and a bivariational treatment by Arponen[14] and by Pal[12] and Basu Ghose and Pal.[13] While the normal variational method yields properties which are a terminating series in cluster amplitudes, the bivariational treatment furnishes terminating series. However, we will pursue the nonvariational approach for the multiconfigurational generalization for simplicity. A small review of the MRCC approach to energy calculations would be helpful for later discussions.

B. Multireference model space

In this section we first discuss the MRCC theories as they are used for the calculation of correlation energies of open-shell systems and difference energies such as the excitation energies. The model space for the μth state may be written as

$$\Psi_\mu^0=\sum_i C_{i\mu}\Phi_i . \tag{7}$$

The exact state Ψ_μ may then be written as

$$\Psi_\mu=\Omega P\Psi_\mu^0=\{e^T\}\left[\sum_i C_{i\mu}\Phi_i\right] , \tag{8}$$

where $\{\ \}$ denotes the normal ordering of the operators contained in the curly bracket. While the original developments of MRCC theories were based on the choice of a complete model space for the facility of satisfying the linked-diagram theorem, the recent work of Mukherjee[20] has made it possible to use a more general model space and still have a linked-cluster theorem. However, one needs to abandon the intermediate normalization. A detailed discussion pertaining to the theoretical developments and the applications for excitation energies using a particle-hole incomplete model space is contained in the work of Pal *et al.*[8] Here we fix the notation for T-matrix elements and mention the hierarchical strategy for the solution. Starting from Eq. (8) we define $(H_{\text{eff}})_{ij}$ as

$$(H_{\text{eff}})_{ij}=\langle\Phi_i\,|\,\Omega^{-1}H\Omega\,|\,\Phi_j\rangle . \tag{9}$$

The eigenvectors of $(H_{\text{eff}})_{ij}$ are the coefficients $\{C_{i\mu}\}$, and the eigenvalues E_μ are the energies of μ states, where μ is the number of functions included in the model space. The various T amplitudes are obtained by the virtual-space projection of the Bloch equation

$$H\Omega P=\Omega H_{\text{eff}}P . \tag{10}$$

A consistent and systematic way of solving the equations is to use a Fock-space approach where one defines holes and particles with respect to a closed-shell reference determinant which, by definition, has no holes and particles. The determinants spanning the model space having, e.g., k holes and/or l particles which may be called "active," are denoted by the set $\{\Phi_i^{(k,l)}\}$ and the wave operator has operators capable of destroying any of the subset of k active holes and/or l active particles. The number of destruction operators of active holes and particles will be used as subscripts of the T operator:

$$T=\sum_{m=0}^{l}\sum_{n=0}^{k}T_{(m,n)} . \tag{11}$$

For any (k,l) model space the solution starts from the lowest-valence sector, progressively reaching the (k,l) sector. At any stage the lower-valence T amplitudes as obtained from the solution of the earlier sectors are kept frozen. With this background we now generalize the response approach to a multiconfigurational model space in Sec. III.

III. RESPONSE APPROACH IN A MULTIREFERENCE MODEL SPACE

For calculating static properties of a system the model space of which, in the absence of a perturbation, is best described by a linear combination of several deter-

minants, we suggest a response-type approach with a multiconfigurational model space. Let the Hamiltonian be described as before in Eq. (1). We attempt to solve the Schrödinger equation for $H(\lambda)$. The model space $\Psi_\mu^0(\lambda)$ having m active holes and n active particles may be written as

$$\Psi_\mu^{0^{(m,n)}}(\lambda)=\sum_i C_{i\mu}(\lambda)\Phi_i^{(m,n)} . \tag{12}$$

Although we use the same set of configurations $\{\Phi_i^{(m,n)}\}$ for different perturbation strengths, we allow the coefficients $\{C_{i\mu}\}$ to depend on λ. We do not, as in the case of a single-determinant-based approach, use molecular orbitals which depend on λ, for the orbital changes may not be as important for the static properties. We may write $C_{i\mu}(\lambda)$ as

$$C_{i\mu}(\lambda)=C_{i\mu}^{(0)}+\lambda C_{i\mu}^{(1)}+\lambda^2 C_{i\mu}^{(2)}+\cdots . \tag{13}$$

The exact μth state is given by

$$\Psi_\mu^{(m,n)}(\lambda)=e^{T(\lambda)}\Psi_\mu^{0^{(m,n)}}(\lambda)=\Omega(\lambda)\Psi_\mu^{0^{(m,n)}}(\lambda) . \tag{14}$$

We assume from now on the normal ordering of the wave operator. The Schrödinger equation for $H(\lambda)$ is set up as

$$H(\lambda)\Psi_\mu^{(m,n)}(\lambda)=E_\mu^{(m,n)}(\lambda)\Psi_\mu^{(m,n)}(\lambda) . \tag{15}$$

As is true for the normal MRCC methods for energy calculations, we can get the properties of various states at a time, the number depending on the number of model space functions. $T(\lambda)$ and $E_\mu(\lambda)$ may be expanded in a power series as

$$T(\lambda)=T+\lambda T^{(1)}+\lambda^2 T^{(2)}+\cdots , \tag{16a}$$

$$E_\mu(\lambda)=E_\mu+\lambda E_\mu^{(1)}+\lambda^2 E_\mu^{(2)}+\cdots . \tag{16b}$$

In the Fock-space approach, various T's, $T^{(1)}$'s, etc. can again be written in terms of various lower-valence ranks. $\Omega(\lambda)$ may be written as

$$\Omega(\lambda)=\Omega^{(0)}+\lambda\Omega^{(1)}+\lambda^2\Omega^{(2)}+\cdots . \tag{17}$$

Premultiplying Eq. (15) by $\Omega^{-1}(\lambda)$ and projecting onto $\{\Phi_l^*\}$ states orthogonal to the model space functions one obtains

$$\sum_i \langle \Phi_l^{*(m,n)}|\Omega^{-1}(\lambda)H(\lambda)\Omega(\lambda)|\Phi_i^{(m,n)}\rangle C_{i\mu}(\lambda)=0 \quad \forall l,m,n . \tag{18}$$

Since Eq. (18) is true for any λ, one may write equations for various powers of λ. Terms independent of λ may be regrouped as

$$\sum_i \langle \Phi_l^{*(m,n)}|\Omega^{(0)^{-1}}H\Omega^{(0)}|\Phi_i^{(m,n)}\rangle C_{i\mu}^{(0)}=0 \quad \forall l,m,n . \tag{19a}$$

Similarly, for terms depending only linearly on λ,

$$\sum_i \left\langle \Phi_l^{*(m,n)}\left|\frac{\partial}{\partial\lambda}[\Omega^{-1}(\lambda)H(\lambda)\Omega(\lambda)]_{\lambda=0}\right|\Phi_i^{(m,n)}\right\rangle C_{i\mu}^{(0)} + \sum_i \langle \Phi_l^{*(m,n)}|\Omega^{(0)^{-1}}H\Omega^{(0)}|\Phi_i^{(m,n)}\rangle C_{i\mu}^{(1)}=0 \quad \forall l,m,n , \tag{19b}$$

and so on.

One may show that for a first-order property these equations suffice. However, for a second-order property one needs the solution of Eq. (18) arising from terms quadratic in λ. From Eq. (19a), since the $\{C_{i\mu}^{(0)}\}$'s are linearly independent, one may write

$$\langle \Phi_l^{*(m,n)}\,|\,\Omega^{(0)^{-1}}H\Omega^{(0)}\,|\,\Phi_i^{(m,n)}\rangle=0 \quad \forall i,l,m,n , \tag{20a}$$

which is the normal MRCC equation for evaluating T parameters. Then substituting Eq. (20a) one obtains

$$\left\langle \Phi_l^{*(m,n)}\left|\frac{\partial}{\partial\lambda}[\Omega^{-1}(\lambda)H(\lambda)\Omega(\lambda)]_{\lambda=0}\right|\Phi_i^{m,n}\right\rangle=0 \quad \forall i,l,m,n , \tag{20b}$$

etc. Equation (20b) may be used for evaluating $T^{(1)}$ parameters. Alternatively, these sets of equations may be derived by observing that the $\{C_{i\mu}(\lambda)\}$'s are linearly independent and then writing down order by order the left-hand side of Eq. (18) for each i,l.

As stated earlier, the T's or $T^{(1)}$'s would have a similar structure as in the MRCC method. In a Fock space approach they can be classified by the number of active holes and/or active particles they can destroy.

One may have to adopt a similar strategy to solve each set of equations (20a), (20b), etc. as is done in the MRCC method for energy calculations, i.e., to start from the lowest sector, then progressively solve up to the highest sector needed. The solution of the T parameters from Eq. (20a) would be carried over to Eq. (20b), which would be solved for the $T^{(1)}$ parameters similarly, sector by sector. For example, for a first-order property which may be defined as $(\partial E_\mu/\partial\lambda)_{\lambda=0}$ or $E_\mu^{(1)}$ one needs only the knowledge of T and $T^{(1)}$ amplitudes up to the sector included in the model space. For calculating E_μ, $E_\mu^{(1)}$, etc. as well as the coefficients, one premultiplies Eq. (15) by $\Omega^{-1}(\lambda)$ and projects onto the model space functions thus giving

$$\sum_i \langle \Phi_j^{(m,n)}\,|\,\Omega^{-1}(\lambda)H(\lambda)\Omega(\lambda)\,|\,\Phi_i^{(m,n)}\rangle C_{i\mu}(\lambda)=E_\mu(\lambda)C_{\mu j}(\lambda) \quad \forall j,\mu$$

(because of the orthonormality of the set $\{\Phi_i\}$) , (21)

where $\Phi_j^{(m,n)}$ is a function belonging to the model space of the (m,n) sector. One can make an order-by-order expansion of Eq. (21) and obtain for the λ-independent case the MRCC eigenvalue equation for energy:

$$\sum_i \langle \Phi_j^{(m,n)}\,|\,\Omega^{(0)^{-1}}H\Omega^{(0)}\,|\,\Phi_i^{(m,n)}\rangle C_{i\mu}^{(0)}=E_\mu C_{\mu j}^{(0)} \quad \forall j,\mu . \tag{22}$$

However, collecting terms linear in λ, Eq. (21) yields

$$\sum_i \left\langle \Phi_j^{(m,n)} \left| \frac{\partial}{\partial\lambda}[\Omega^{-1}(\lambda)H(\lambda)\Omega(\lambda)]_{\lambda=0} \right| \Phi_i^{(m,n)} \right\rangle C_{i\mu}^{(0)} + \sum_i \langle \Phi_j^{(m,n)} | \Omega^{(0)^{-1}} H \Omega^{(0)} | \Phi_i^{(m,n)} \rangle C_{i\mu}^{(1)} = E_\mu C_{\mu j}^{(1)} + E_\mu^{(1)} C_{\mu j}^{(0)} \quad \forall j,\mu \ . \tag{23}$$

At this stage we have the knowledge of the necessary T amplitudes, E_μ, and $\{C_{\mu j}^{(0)}\}$. However, we need to know $E_\mu^{(1)}$ and $\{C_{\mu j}^{(1)}\}$ to have a solution of Eq. (23). We have still an insufficient number of equations. But the auxiliary normalization condition for the model space may be used, i.e.,

$$\langle \Psi_\mu^{0^{(m,n)}}(\lambda) \mid \Psi_\mu^{0^{(m,n)}}(\lambda) \rangle = 1 \ , \tag{24}$$

which yields

$$\sum_i C_{i\mu}^{(0)^*} C_{i\mu}^{(0)} = 1 \ . \tag{25}$$

More importantly, for terms linear in λ,

$$\sum_i C_{i\mu}^{(0)^*} C_{i\mu}^{(1)} + \sum_i C_{i\mu}^{(1)^*} C_{i\mu}^{(0)} = 0 \ . \tag{26}$$

We use the normalized values of $\{C_{i\mu}^{(0)}\}$. Equation (26) coupled with Eq. (23) would give us the sufficient number of equations to solve for $E_\mu^{(1)}$, $\{C_{\mu j}^{(1)}\}$, etc. At this stage we do not have a simple structure of an eigenvalue equation structure. In a similar manner one can set up equations for higher-order response properties, too.

IV. DISCUSSION

We have set up the hierarchy of equations for static properties at any order in a MRCC model. Essentially, there are two distinct types of hierarchies. One is related to the order of the response property and the other is related to the valence rank associated with the multireference CC equation for any order of property. Explicitly for a first-order property one first solves Eq. (20a), which is the MRCC equation for energy and which needs a solution starting from the lowest sector. For an $(N-1)$-electron state, if we identify the closed N-electron state as the reference, the problem may be identified as the (0,1) sector in our notation. One solves Eq. (20a) for the (0,0) sector and the (0,1) sector to obtain the $T_{(0,0)}, T_{(0,1)}$ amplitudes. Then one solves the eigenvalue equation (22). Subsequently, Eq. (20b) has to be solved sectorwise to obtain the $T_{(0,0)}^{(1)}, T_{(0,1)}^{(1)}$ amplitudes. At the end the coupled sets of equations (23) and (26) furnish the value of $E_\mu^{(1)}$.

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