Coupled cluster approach for static properties

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We review the coupled cluster (CC) methods for calculating static properties for closed and open-shell systems. In the response-type formulations, properties of various orders are derived as energy derivatives of corresponding orders. Among various CC response versions, the stationary formulation has the important advantage of an inbuilt $(2n+1)$ rule by which energy derivatives of higher order can be calculated using lower order derivative amplitudes. In this review we stress the importance and the difficulty of using a stationary formulation. We also discuss the first multideterminantal model space based CC response theory.

1. Introduction

COUPLED cluster (CC) methods have been established as accurate many-body methods to describe electron correlation[1-5]. Written in second quantized notation where the hamiltonian does not explicitly depend on the number of particles, the CC formulations are particularly suitable to describe neutral systems and their ions simultaneously. These methods have the attractive feature of satisfying the desired size-extensivity property (proper scaling with respect to the number of particles)[1]. In addition, this compactly sums up the correlation contribution of important terms to all orders in perturbation. This is achieved by the action of an exponential wave-operator on a suitable model space reference function; depending, however, on the choice of model space (single or multideterminantal), the nature of the ansatz and its consequences change. There have been a wide range of methods for calculating various atomic and molecular properties within the framework of CC theory. Traditionally, the nonvariational method of projection was used to derive pertinent equations for energy calculations for closed-shell systems[2,3]. Subsequently variational ways of determining energy and wave function were proposed. For closed-shell systems the CC wave operator acts on a single determinantal model space (Restricted Hartree–Fock). There have been developments (in nonvariational framework) starting from an unrestricted Hartree–Fock (UHF), or projected unrestricted Hartree–Fock (PUHF)[6] or quasi-restricted Hartree–Fock (QRHF)[7] model spaces to suit the open-shell cases. With the development of CC methods starting from multideterminantal model spaces[8-17], they have attained the status of far greater utility encompassing the more complex cases of open-shell correlation as well as pathological closed shell situations. Particularly of note are the developments with incomplete multideterminantal model spaces[12-14]. This has made the detailed open-shell electronic structure calculations more facile and rigorous[15-17]. Although the structure of the theory becomes much more complex when the wave operator acts on a multideterminantal model space, it is extremely important to start from such a model space in open-shell or near-quasidegenerate situations to avoid the potential divergence problems arising out of intruder states. This is attributed to the nondynamical-correlation involved in the open-shell states. CC methods have been extensively applied to the calculation of ground state electronic energy and its gradient[18-21], and in recent years, the multireference CC versions have been applied to the difference energy calculations[8,15-17,22-28] and potential energy surface (PES) studies[29]. There have been excellent reviews on the CC methods for energy calculations[1,30,31].

In comparison to the above developments, there has been much less work on the calculation of other electronic (static and dynamic) properties like the dipole moment, polarizability, dynamic dipole polarizability, etc. The formulation of these has been investigated and many general suggestions for handling property calculations are emerging, particularly in view of desirability features of stationarity, generalized Hellmann–Feynmann (GHF) principle, etc. In this context, different treatments for a stationary CC method and its response to the external field have surfaced. Understandably, they have been compared with the nonvariational method and the traditional expectation value approach. Recently these have been investigated into. It may be of great interest to bring all the current developments in this area on a common platform and analyse their structure and inter-relationships. The present work is an attempt in this direction and its purpose is to present a comprehensive review of the CC methods for property calculations. We will also mention in the passing a few actual calculations performed in this area. So far, to the best of our knowledge, no comprehensive review in this area exists. Traditionally, properties are calculated through the route of expectation value-like quantities with respect to the reference ground state wave function[3]. Martensson-Pendrill and Ynnerman[32] have recently suggested a general procedure for evaluation of matrix elements for an operator between CC wave functions. In expectation value approach for property, the ground state wave function is commonly found by

the nonvariational method of projection. However, the expectation value leads to a nonterminating series in cluster amplitudes. This line of calculation has been pursued by Noga and Urban[33] and the effect of truncation has been studied numerically. Alternatively, a response approach of calculating the properties of various orders can be formulated. Diercksen *et al.*[34] observed for some emperical CI calculations that the response approach is preferable to the expectation values when the GHF is not satisfied. In this class of response methods, finite field calculations have existed for a long time. This, however, entails the calculation of the derivatives numerically. Another related work was done by Koch and Jǿgensen[35] who determined linear and quadratic response functions for molecular systems described by a CC-response state. Quantities such as excitation energies, transition matrix elements, 2nd and 3rd order properties were then derived from response functions. Recent interest has been focused on analytic formulation of CC-response approach. In this approach, molecular properties of various orders are identified as energy derivatives of corresponding orders[36]. Determination of energy derivatives involves the calculation of analytic derivatives of the wave function. Here again both variational and nonvariational approaches can be pursued (as in the case of ground state energy calculation). The nonvariational response[37,38] does not generally satisfy the generalized Hellmann–Feynmann (GHF) theorem. However, some approximate schemes within this approach satisfy the GHF theorem as already observed[39]. We will review these interconnections in the course of our discussion.

A major theme of our review would be to discuss the response approach for the calculation of properties in the variational framework. This approach has many desirable features. For example, since it uses the stationary approach, there is a possibility of extracting bounds for various energy derivatives or properties. Another very attractive feature is the $(2n+1)$ rule built in the variational method so that calculation of higher $(2n+1)$ order properties needs the knowledge of stationary cluster amplitudes only up to nth order. This has been formally shown with derivation of the functional form in one of our recent works[40] and we will briefly discuss it in the later part of this review. The GHF theorem is a special case of the $(2n+1)$ rule which is more of a general utility from a computational point of view as has been demonstrated recently. In the context of a stationary CC response, various forms of functionals have been studied. We would discuss mainly two types of functionals: a) a normal Euler type, and b) an extended coupled cluster type. We advocate the use of the second type of functional. However, irrespective of the type of the functional chosen, a major difficulty arises in the scheme of variational response, namely, the redundancy in the number of equations in case the cluster amplitudes and all their relevant derivatives are not truncated to a uniform degree. Recently, we have been able to solve the redundancy problem[41,42] and we will focus our attention on this aspect later.

While for closed shells, single determinant-based response CC theories have come to a reasonable standard of development, there has been only a recent interest in multireference CC-response theories[43,44]. In fact for open shells, variational formulations are considerably more difficult even for the energy calculations, although the problem has been tractable in Fock-space[45]. Naturally, such formulations have not yet been translated for response-based methods for properties.

2. Methods for energy calculation

Coupled cluster methods for energy calculations

The idea underlying the coupled cluster theory originates from the Linked diagram theorem which states that the exact electronic wave function and energy can be written as a sum of only linked diagrams or, equivalently, the wave operator as an exponential of cluster operators. This ensures correct scaling with the number of electrons or size extensivity. Cizec[2] first presented a diagrammatic approach to derive explicit working equations for the CC method. In this method, the exact wave function Ψ is generated by the action of an exponential operator on a reference function which is usually chosen as the HF closed shell function (Φ_0). The linked excitation operator T creates excitations from the independent particle reference. For a n-particle system, T is a sum of operators

$$T = T_1 + T_2 + \cdots + T_n, \tag{1a}$$

where T_n is n-particle excitation operator. The expression for two body T_2 is:

$$T_2 = \frac{1}{2!} \sum_{ijab} \langle ab | t_{ij}^{ab} | ij \rangle_a \{a^+ b^+ ji\}. \tag{1b}$$

The operator amplitudes $\{t_{ij}^{ab}\}$ are different from the DCI coefficients C_{ij}^{ab}. The relation between the CI excitation operators and cluster operators are as follows:

$$C_1 = T_1,$$

$$C_2 = T_2 + \frac{1}{2!} T_1 T_1,$$

$$C_3 = T_3 + T_1 T_2 + \frac{1}{3!} T_1 T_1 T_1. \tag{1c}$$

C_1, C_2 and C_3 are single, double and triple CI excitation operators respectively.

The Schrodinger equation for correlation energy can be written as

$$H_N e^T \Phi_0 = \Delta E\, e^T \Phi_0,$$
$$\Psi = e^T \Phi_0, \tag{2}$$

where the exact wave function is assumed to obey intermediate normalization, i.e. $\langle \Psi | \Phi_0 \rangle = \langle \Phi_0 | \Phi_0 \rangle = 1$. H_N is the normal order hamiltonian defined as $H_N = H - \langle \Phi_0 | H | \Phi_0 \rangle$. Various different versions of the CC method provide different expressions for correlation energy and different ways of solution of the amplitudes. They are discussed here in short.

Nonvariational method

In the traditional nonvariational approach, the starting equation is:

$$H_{\text{eff}}\, \Phi_0 = \Delta E\, \Phi_0,$$

$$\text{where } H_{\text{eff}} = \bar{e}^T H e^T, \tag{3a}$$

projecting on the left by Φ_0^* we get

$$\Delta E = \langle \Phi_0 | H_{\text{eff}} | \Phi_0 \rangle. \tag{3b}$$

The amplitudes are obtained by solving equations provided by projection of equation (3a) with different virtual states. These form a closed set of coupled non-linear equations in t coefficients and are to be solved iteratively.

Stationary methods

A stationary recipe to find out energy and amplitudes was given by Pal *et al.*[46] In this method, a suitable energy functional $E(t)$ is constructed and is made stationary with respect to the cluster amplitudes contained in the functional. Application of stationarity conditions $\partial E/\partial t = 0$ provides all the necessary equations to calculate the optimum amplitudes. Energy is then calculated with these amplitudes.

Stationary or variational methods have a great attraction. They have furnished bounds to useful chemical quantities. In the case of property calculations using variational response, the important theorem of GIIF is satisfied. Connected with this is the $(2n+1)$ type rule which essentially states that the energy derivative can be calculated to a much higher order than the knowledge of the derivatives of the cluster amplitudes in the wave function. A stationary recipe may furnish useful bounds to higher order properties. In the MBPT context, the formulation of such bounds has been attempted recently[47]. There are however many drawbacks related to the variational formulation of the CC method unlike linear variation methods like the Configuration Interaction (CI). CC-based variation, being nonlinear, does not have an eigenvalue-equation structure. Inconsistent truncation leads to loss in the variational bound property. The Euler type functional is nonterminating and the application of stationary condition yields disconnected terms. Arponen and coworkers[48-50] proposed an Extended Coupled Cluster (ECC) type functional which bypasses both the problems of nonterminating series and that of disconnected terms although by doing this the burden of computation is increased because of the presence of two different sets of amplitudes in the functional. Despite several problems, however, it may be sufficient here to stress the importance of using a variational approach. In the following, we dwell on various functionals and their interconnections.

Functionals for stationary coupled cluster approach

The Euler type functional is written as: $\langle \Psi | \hat{H} | \Psi \rangle / \langle \Psi | \Psi \rangle$. For groundstate energy, one needs to make this functional stationary with respect to the parameters in the wave function. Using a exp (T) CC wave function, the functional, on expanding by Generalized Wick's theorem (GWT), can be shown to yield

$$E = \langle \Phi_0 | e^{T+} \hat{H} e^T | \Phi_0 \rangle_L. \tag{4}$$

The functional is a nonterminating series in cluster amplitudes and can be made stationary with respect to these amplitudes. If we truncate the functional to degree n, using the stationarity we can write the stationary energy as a functional of the cluster amplitudes of degree $(n-1)$. Stationary conditions to this functional yield disconnected terms when the different n-body Ts are used. In this functional, a particular T/T^+ may be connected exclusively to a T^+/T vertex and when the stationary equations are obtained by deleting a T^+/T vertex from the linked diagrams of energy, the T^+/T vertex exclusively connected to the deleted (or differentiated) vertex becomes disconnected. A response approach built with this functional would inherit the above problems. For calculating the higher order properties, one needs an additional set of stationary equations to calculate the derivative of the T-amplitudes. This set of equations is the feature of the response type method. We will see in section 4 that in a stationary approach, this leads to a redundancy in the equations in a general truncation model. The bookkeeping of the equations may be bypassed, however, by a careful strategy.

There have been developments based on a related functional using the Unitary Coupled Cluster (UCC) ansatz[51-54]. Various versions of the UCC have been attempted and in the following we summarise some of the conclusions. UCC wave function used in the non-variational context ensures a hermitian effective hamiltonian. Nonvariational energy expression with this ansatz may be written as:

$$E^{\nu} = \langle \Phi_0 | e^{\tau^+} H e^{\tau} | \Phi_0 \rangle = \langle \Phi_0 | e^{-\tau} H e^{\tau} | \Phi_0 \rangle. \quad (5)$$

The UCC (n) method, proposed by Bartlett *et al.*[54], however, eliminates the problems of disconnected terms by expanding the energy functional in orders of perturbation theory and selectively including terms whose initial contribution appears at a given perturbation order (n). This way one can make sure that disconnected terms in stationary set of equations are cancelled and the energy functional at the stationary point becomes size extensive.

Another functional, known as the ECC functional, was recently suggested by Arponen and coworkers[48-50]. This functional deals with the dual space of bra and ket vectors. The form of the functional for any operator $\hat{A}$ may be written as:

$$\langle \hat{A} \rangle = \langle \Psi' | \hat{A} | \Psi \rangle / \langle \Psi' | \Psi \rangle = \frac{\langle \Phi_0 | e^{T'} \hat{A} e^{T} | \Phi_0 \rangle}{\langle \Phi_0 | e^{T'} e^{T} | \Phi_0 \rangle}. \quad (6a)$$

It was shown[48] that this expectation value may be factored into a completely linked and connected expression. The linked cluster theorem essentially states that $\langle \Phi_0 | e^{T'} e^{T} / \langle \Phi_0 | e^{T'} e^{T} | \Phi_0 \rangle$ can be written as $\langle \Phi_0 | e^{T''}$, where T'' is a linked hole-particle destruction operator. In terms of diagrams, it has structural similarity with a T^+ vertex with a different set of amplitudes. The entire functional becomes a sum of connected terms yielding

$$\langle \hat{A} \rangle = \langle \Phi_0 | e^{T^*} e^{-T} \hat{A} e^{T} | \Phi_0 \rangle. \quad (6b)$$

With the structure of $e^{-T} A e^{T}$ the functional $\langle \hat{A} \rangle$ leads to a terminating series. For finite particle operator, $(e^{-T} \hat{A} e^{T})$ terminates to a finite order and this contributes to the terminating structure to $\langle \hat{A} \rangle$. However, there is still the possibility of a T'' exclusively linked to a T-vertex (while all the T-vertices must be connected to the operator $\hat{A}$) and hence the appearance of disconnected terms in the stationary equations. Later, Arponen defined two sets of transformed amplitudes σ'', σ in terms of which the functional may be written as

$$\langle A \rangle = \langle \Phi_0 | e^{\sigma^*} e^{-\sigma} \hat{A} e^{\sigma} | \Phi_0 \rangle_{DL}, \quad (6c)$$

where DL means double linking structure. σ vertices, by definition, are all connected to the operator $\hat{A}$. σ'' vertices, by construction of double linking, must be either connected to the operator $\hat{A}$ or to two different σ vertices. The latter eliminates the possibility of appearance of disconnected terms in the stationary equations. This form of the functional is inherently superior in terms of both the terminating structure and size-extensivity points of view. One important difference is that the functional has a nonhermitian structure. While the σ vertices are always linked to the operator, σ'' vertices have only the above mentioned double linking structure. It seems that it is impossible to retain the above desirable feature within a hermitian structure. A response approach has been built with this structure which we have termed bivariational response[55,56].

3. Nonvariational response

In the CC context, nonvariational methods have always been more traditional. Monkhorst[37] suggested that as a response of the external perturbation, the static properties may be calculated in a nonvariational way. The field dependent hamiltonian and the corresponding CC ansatz may be written as:

$$\hat{\mathscr{H}}(\lambda) = \hat{H} + \lambda \hat{O}, \quad (7a)$$

$$\Psi(\lambda) = e^{T(\lambda)} \Phi_0, \quad (7b)$$

so that the nonvariational expression for energy becomes:

$$\tilde{E}(\lambda) = \langle \Phi_0 | e^{-T(\lambda)} \hat{\mathscr{H}}(\lambda) e^{T(\lambda)} | \Phi_0 \rangle. \quad (7c)$$

Power series expansions of $\tilde{E}(\lambda)$ and $T(\lambda)$ are introduced as:

$$\tilde{E}(\lambda) = \tilde{E}^{(0)} + \lambda \tilde{E}^{(1)} + \lambda^2 \tilde{E}^{(2)} + \cdots, \quad (8a)$$

$$T(\lambda) = T^{(0)} + \lambda T^{(1)} + \lambda^2 T^{(2)} + \cdots, \quad (8b)$$

where $1/i![\tilde{E}^{(i)}]$ is identified as the ith order property. The nonvariational expressions for $\tilde{E}^{(i)}$

$$\tilde{E}^{(i)} = \frac{\partial^i}{\partial \lambda^i} \tilde{E}(\lambda) \Big|_{\lambda = 0} \quad (9a)$$

contains cluster amplitudes $T^{(0)} \cdots T^{(i)}$. The equations to determine these cluster amplitudes are given as:

$$\left\langle \Phi^* \left| \frac{\partial^i}{\partial \lambda^i} \left[e^{-T(\lambda)} \hat{\mathscr{H}}(\lambda) e^{T(\lambda)} \right] \right|_{\lambda = 0} \right| \Phi_0 \Big\rangle = 0 \quad (9b)$$

Φ_0 and Φ^* are the reference model space determinant and virtual space determinant respectively. In a CCSD model, including the orbital relaxation, Bartlett and coworkers[38] have used this method to calculate dipole moment, polarizability and hyperpolarizability for small systems like HF, CO, etc.

For an exact state, where all possible clusters $(T_1 \cdots T_n)$ for an n-body system are taken in determining $T(\lambda)$, the first order property satisfies the GHF $\tilde{E}^{(1)}=\langle\hat{O}\rangle$. For approximate wave function, though, this is true only under certain specific truncation scheme[39a]. In a later work[39b] we have shown that if one takes a linearized nonvariational energy functional with $T=T_2$, the expression for energy derivative and the equations for cluster amplitudes at each order become identical with those of a bivariational response under quadratic truncation scheme. The latter satisfies the $(2n+1)$ rule. Thus within such a scheme, the nonvariational expression for energy derivative also satisfies the more general $(2n+1)$ rule. While a nonvariational way of calculating energy derivatives satisfies $(2n+1)$ rule under specific conditions, a variational response automatically satisfies this[57].

Noga *et al.*[33] numerically studied the Hellmann–Feynmann contribution of the first order energy derivative $\tilde{E}^{(1)}$. They showed that the first non-HFT terms arise from a wave function contribution which is one order higher than the last complete order of the wave function (e.g. for CCSD, they come from T_3). Their study on the effect of truncation on the expectation value showed that while contributions from $T_2^+\hat{O}T_2$, $\hat{O}T_1$ and mixed terms like $T_1^+\hat{O}T_2$, $T_2^+\hat{O}T_3$ are considerable, contributions from $T_1^+\hat{O}T_1$, $T_3^+\hat{O}T_3$ are negligible.

4. Stationary response

The basic approach of a stationary response method and its limitations are independent of the exact nature of the functional chosen although to avoid redundancy problem and to achieve highest efficiency (satisfying the $2n+1$ rule), the method has to be carefully executed. In the following, a critical analysis of the approach and the current state of art in this theme will be presented using a simple Euler type functional as an example. We start by giving the form of the energy functional $E(\lambda)$ in the presence of an external field.

$$E(\lambda)=\left\langle\Phi_0\left|N\left[e^{T^+(\lambda)}\hat{\mathcal{H}}(\lambda)e^{T(\lambda)}\right]\right|\Phi_0\right\rangle_L. \tag{10}$$

Subscript L denotes that only linked or connected diagrams need be considered. $N[\ ]$ denotes normal ordering of the operator products contained in the bracket. In stationary response, the functional $E(\lambda)$, the ansatz $e^{T(\lambda)}$ and the cluster amplitude operator $T(\lambda)$ are expanded in power series of λ as:

$$E(\lambda)=E^{(0)}+\lambda E^{(1)}+\lambda^2 E^{(2)}+\cdots+\lambda^n E^{(n)}+\cdots,$$

$$e^{T(\lambda)}=C^{(0)}+\lambda C^{(1)}+\lambda^2 C^{(2)}+\cdots+\lambda^n C^{(n)}+\cdots,$$

$$T(\lambda)=T^{(0)}+\lambda T^{(1)}+\lambda^2 T^{(2)}+\cdots+\lambda^n T^{(n)}+\cdots,$$

such that any nth order property is now identified as $n!E^{(n)}$, where $E^{(n)}$ is nth order derivative of the functional $E(\lambda)$ with respect to λ at $\lambda=0$. $\{C^{(n)}\}$ are related to the $\{T^{(n)}\}$ as:

$$C^{(0)}=e^{T(0)};\quad C^{(1)}=T^{(1)}e^{T(0)},$$

$$C^{(n)}=\left[T^{(n)}+\sum_{k=1}^{n-1}\sum_{m=1}^{k}T^{(k)}T^{(m)}a^{km}+\sum_{k=1}^{n-2}\sum_{m=1}^{k}\sum_{l=1}^{m}T^{(k)}T^{(m)}T^{(l)}a^{kml}+\cdots\right]e^{T^{(0)}},$$

coefficients $\{a^{km}\}$ are such that value of $a^{km}=1$ if $k\neq m$; $a^{km}=1/2!$ if $k=m$; $a^{kml}=1$ if $k\neq m\neq 1$; $a^{kml}=1/3!$ if $k=m=1$; $a^{klm}=1/2!$ if any two dummy indices are same.

Before application of stationary conditions, $E^{(n)}$ contains the amplitudes $(T^{(0)}\cdots T^{(n)})$. These may be obtained by solving either of the following sets of equations which are complex conjugates of each other.

$$\partial E(\lambda)/\partial T^{+(i)}=0\quad(i=0\cdots n), \tag{11a}$$

$$\partial E(\lambda)/\partial T^{(i)}=0\quad(i=0\cdots n). \tag{11b}$$

Since $E^{(n)}$ contains the amplitude $T^{(n)}$ as the highest order derivative amplitude along with all the lower order ones, the equation (11a) assumes a triangular form

$$\frac{\partial E(\lambda)}{\partial T^{+(i)}}=\sum_{j=1}^{n}\lambda^j\frac{\partial E^{(j)}}{\partial T^{+(i)}}=0. \tag{12}$$

Each of the above $n+1$ equations has a power series structure. The equations hold good for all λ, hence to solve for $n+1$ variables $T^{(0)}\cdots T^{(n)}$, we obtain a set of ${}^{n+1}C_2$ number of equations

$$\frac{\partial E^{(j)}}{\partial T^{+(i)}}=0. \tag{13}$$

This redundancy in the number of equations disappears in the case where each $T^{(i)}$ is truncated consistently up to a fixed k-body, thus consisting of all the amplitudes up to T_k at each order. It can be shown as a consequence of the exponential nature of the ansatz that these ${}^{(n+1)}C_2$ number of equations reduce to a unique and sufficient set of $(n+1)$ equations. There is a

great amount of equality in these set of equations[41]. In view of its importance in a variational response theory, we present a general proof. $E^{(n)}$ is a homogeneous polynomial and can be written as:

$$E^{(n)} = C^{(n)} H C^{(0)} + \sum_{k=0}^{n-1} C^{(k)} [\hat{H} C^{(n-k)} + \hat{O} C^{(n-1-k)}]. \tag{14}$$

Differentiation of $E^{(n)}$ with respect to $T_p^{+(q)}$ gives p-body open diagrams which translate to the algebraic equation:

$$\frac{\partial E^{(n)}}{\partial T_p^{+(q)}} = C^{(n-q)} H C^{(0)} + \sum_{k=0}^{n-q-1} C^{(k)} [\hat{H} C^{(n-q-k)} + \hat{O} C^{(n-q-1-k)}]. \tag{15}$$

It is obvious that as long as $(n-q)$ is constant, the p-body equations (15) will always have identical terms. Thus.

$$\frac{\partial E^{(n)}}{\partial T_p^{+(q)}} = \frac{\partial E^{(n-1)}}{\partial T_p^{+(q-1)}} = \cdots = \frac{\partial E^{(n-q)}}{\partial T^{+(0)}} = 0. \tag{16}$$

This equality will provide the set of equations (13) a band diagonal structure so that there remains only a set of $(n+1)$ unique equations. The set of equations $\partial E^{(i)}/\partial T_p^{(0)} = 0$ $(i = 0 \cdots n)$ is hierarchical in nature: the $i=0$ part simply furnishes $T^{(0)}$ amplitudes and keeping them fixed, the $i=1$ part yields $T^{(1)}$ amplitudes etc. Identity of equations $\partial E^{(n)}/\partial T_p^{+(q)} = 0$ and $\partial E^{(n')}/\partial T^{+(q')} = 0$ for $(n-q) = (n'-q')$ however breaks down if all the cluster operators and their derivative operators are not truncated at the same level of approximation giving rise to a redundancy in the number of equations. In the following, we will discuss this problem and propose in improved variational strategy to be implemented for a flexible trancation scheme in CC response approach for first and higher order properties. Let us first take a simple example for calculating up to first order derivative amplitudes $\{T_1^{(1)}\}$ in a sub 2 truncation scheme. We show that there is a unique set of equations in this case.

$$T^{(0)} = T_1^{(0)} + T_2^{(0)},$$
$$T^{(1)} = T_1^{(1)} + T_2^{(1)}. \tag{17}$$

$\partial L^{(m)}/\partial T^{(n)} = 0$ with $m, n, p = 1, 2$ provide the following two sets of equations.

1. The one-body set:

$$\frac{\partial L^{(0)}}{\partial T_1^{+(0)}} = 0, \tag{18a}$$

$$\frac{\partial E^{(1)}}{\partial T_1^{+(0)}} = 0, \tag{18b}$$

$$\frac{\partial E^{(1)}}{\partial T_1^{+(1)}} = 0. \tag{18c}$$

2. The two-body set:

$$\frac{\partial E^{(0)}}{\partial T_2^{+(0)}} = 0, \tag{19a}$$

$$\partial E^{(1)}/\partial T_2^{+(0)} = 0, \tag{19b}$$

$$\partial E^{(1)}/\partial T_2^{+(1)} = 0. \tag{19c}$$

Since the truncation level is consistent for $T^{(0)}$ and $T^{(1)}$, the band diagonal identity holds for both the pairs of equations (18a, c) and (19a, c). As a result, one can obtain a unique set of 4 equations to solve for $T_1^{(0)}$, $T_2^{(0)}$, $T_1^{(1)}$, $T_2^{(1)}$.

In the case of an inconsistent truncation scheme, either $T^{(0)}$ or $T^{(1)}$ will have its p-body ($p=1$ or 2) amplitudes dropped. We continue with our earlier example and assume that $T^{(1)}$ has only two-body part, i.e.

$$T^{(0)} = T_1^{(0)} + T_2^{(0)}, \tag{20}$$
$$T^{(1)} = T_2^{(1)}.$$

As a result, out of the previous set of six equations (18a, b, c) and (19a, b, c):

1. equation (18c) will now be absent;
2. equations (18b) and (19b) now will no longer contain $T_1^{(1)}$ containing terms;
3. equations (18a), (19a), and (19c) will remain unaffected;
4. identity of the pair equations (19a) and (19c) will remain intact.

What we have in hand now is a redundant set of five equations for solving only three variables $T_1^{(0)}$, $T_2^{(0)}$ and $T_2^{(1)}$. Thus we have to keep either of equations (19a) or (19c), which are anyway identical and then choose any two from the remaining three equations (18a), (18b), (19b). To pick up the right option, we may now look at the functional forms of $E^{(0)}$ and $E^{(1)}$.

$$E^{(0)} = f^{(0)}(T_1^{(0)} T_2^{(0)}).$$
$$E^{(1)} = f^{(1)}(T_1^{(0)} T_2^{(0)} T_2^{(1)}). \tag{21}$$

If we retain the equation (18a) and choose one of the two equations (18b) and (19b), then together with equations (19a) or (19c) we obtain a necessary set of three equations which can be solved hierarchically but

this choice suffers from ambiguity. Since $E^{(1)}$ contains both $T_1^{(0)}$ and $T_2^{(0)}$, it is not clear which one of the equations (18b) and (19b) is to be selectively dropped and why. However, if we drop the equation (18a) and instead take both equations (18b) and (19b), then along with equation (19c) we end up with the correct set of equations. Similarly, for any general truncation, since $E^{(n)}$ contains all the T amplitudes and their derivatives, stationarities of $E^{(n)}$ with respect to all possible amplitudes form a sufficient set though the hierarchical structure is generally lost.

In retrospect, it may be said that this process is to choose the functional of variation for calculating the stationary amplitudes and their derivatives. From our above analysis we find it consistent to select $E^{(n)}$ as the given variational functional for calculating optimum cluster amplitudes of $T^{(0)}$, $T^{(1)}$, $T^{(n)}$.

With the knowledge of the stationary amplitudes up to a given order n, one can obtain property of much higher order $(2n+1)$. This is a specific advantage of stationary CC response method for the calculation of higher order properties. In fact, the GHF theorem is a special case of the more general $(2n+1)$ rule. In the following, we briefly prove this rule and write a general expression for $(2n)$th and $(2n+1)$th order property using nth order stationary amplitude derivatives.

It is apparent from the equation (14) that the expression for $E^{(2n)}$ would contain at the most up to the coefficients $T^{+(2n)}/T^{(2n)}$. If we collect terms in $E^{(2n)}$ which have on the right or left side of the operator $\hat{H}/\hat{O}$ derivative amplitudes $t^{(i)}$ of the order i greater than n and separate the rest in D, we may write

$$E^{(2n)} = \sum_{i=n+1}^{2n} (B^{(2n-i)} T^{(i)}) + \sum_{i=n+1}^{2n} (T^{+(i)} B^{+(2n-i)}) + D. \tag{22}$$

The remainder D contains terms involving $t_2^{(n)}/t_2^{+(n)}$ and lower order derivatives. In the expression for $E^{(2n)}$ in equation (22), the coefficients in the block $B^{(2n-i)}$ must contain only up to the $(n-1)$th order derivative t's. Thus for each amplitude $t^{(i)}$ with $i>n$, the corresponding block of coefficients $B^{(2n-i)}$ is unique which, as explained above, comprises only of several lower order derivative amplitudes $t^{(j)}$, $j\leqslant(n-1)$. Thus each term within the circular brackets of equation 22 is linear with respect to the amplitudes $t^{(i)}$, $i>n$. The remainder D, however, contains terms linear as well as nonlinear in nth and lower order t derivative amplitudes. Using the identity among the sets of equations for fixed $(n-p)$ we choose the following set of equations for the calculation of derivative amplitude $t^{(0)}$, $t^{(1)} \cdots t^{(n)}$ and their adjoints.

$$\frac{\partial E^{(2n)}}{\partial T^{(i)}} = 0 \quad i=(n+1)\cdots 2n, \tag{23a}$$

$$\frac{\partial E^{(2n)}}{\partial T^{(n)}} = 0, \tag{23b}$$

$$\frac{\partial E^{(2n)}}{\partial T^{+(i)}} = 0 \quad i=(n+1)\cdots 2n, \tag{24a}$$

$$\frac{\partial E^{(2n)}}{\partial T^{+(n)}} = 0, \tag{24b}$$

If the equations (23a) and (24a) are multiplied with the corresponding $t^{(i)}$ and $t^{+(i)}$'s (with i matching the equation indices $(n+1)$, $(n+2)\cdots(2n)$) and the resulting expression put back in the expression for $E^{(2n)}$, we obtain at the stationarity $E^{(2n)}=D$. As D or $E^{(2n)}$ would be nonlinear, in general, with respect to the amplitudes $t^{(n)}$, the application of equations (23b) and (24b) would not remove these variables in $E^{(2n)}$ at stationary points, but would serve to simplify the expressions further. Similar analysis can be made for the stationary expression for $E^{(2n+1)}$. Following the above lines, $E^{(2n+1)}$ may be written as

$$E^{(2n+1)} = \sum_{i=n+1}^{2n+1} (B'^{(2n+1-i)} T^{(i)}) + \sum_{i=n+1}^{2n+1} (B'^{+(2n+1-i)} T^{+(i)}) + D'. \tag{25}$$

The terms within the circular brackets are linear with respect to the amplitudes $t_2^{(i)}$, $i>n$ and D' contains terms linear as well as nonlinear in nth and lower order derivative t amplitudes. In the lines of the above arguments we may use the following $(n+1)$ set of equations and their adjoints.

$$\frac{\partial E^{(2n+1)}}{\partial t^{(i)}} = 0, \frac{\partial E^{(2n+1)}}{\partial t^{+(i)}} = 0 \quad i=(n+1)\cdots(2n+1), \tag{26}$$

so that the resulting stationary expressions for $E^{(2n+1)}$ contains only D'. D' contains the amplitude sets $t^{(i)}$, $i=0\cdots n$. In this case the set of equations $((\partial E^{(2n+1)}/\partial t^{(n)})=0$, $(\partial E^{(2n+1)}/\partial t^{+(n)})=0$ need not be considered. This is in contrast to the case of $E^{(2n)}$ where the stationary equations with respect to the amplitudes $t^{(n)}$ were necessary and served to simplify the remainder D. In any case the point is that for the calculation of $(2n)$th and $(2n+1)$th order derivative of energy, the amplitude derivatives up to the nth order are sufficient. This sums up the $(2n+1)$ rule for computing the properties.

For the practicability of numerical calculation, if we systematically truncate all the energy derivatives up to a total of quadratic power of amplitudes, the general expressions for $E^{(2n)}$ and $E^{(2n+1)}$ become:

$$E^{(2n)} = \langle \Phi_0 / T^{+(n)} \hat{O}\, T^{(n-1)}, \Phi_0 \rangle, \tag{27a}$$

$$L^{(2n+1)} = \langle \Phi_0 \, T^{+(n)} \hat{O} \, T^{(n)} / \Phi_0 \rangle. \quad (27b)$$

We have numerically tested the $(2n+1)$ rule for a few model systems (HF, N_2, CO) to calculate the dipole moment, a few polarizabilities and hyper-polarizabilities. The results agreed quite well with those of exact CCSD nonvariational non-relaxed calculation of Bartlett and coworkers[58]. Even with quadratic truncation the values agree quite well with the non-variational calculation as well as with the experimental number[40]. These results are presented in Tables 1 and 2.

The basic approach of a stationary response method and the consequent $2n+1$ rule is the same irrespective of whether variational or bivariational response has been used. However, a special feature of the variational response is that in case the cluster amplitude (or its derivative) comprises of more than a single k-body term, then the expression for energy derivative may contain terms like $T_1^{+(p)} \hat{O} \, T_2^{(q)}$ and $T_2^{+(p)} \hat{O} \, T_1^{(q)}$ which, on application of stationarity, give rise to disconnected terms like $\hat{O} \, T_1^{(q)}$. Numerical calculations however show that even if the disconnected term is dropped from the equation for solving the cluster amplitudes, the results are not much affected[40]. In bivariational response such terms are altogether absent. In the special case where the functionals are truncated at quadratic degree of amplitude and it is assumed that amplitudes in both cases comprise of a single k-body term, the expressions for energy derivative and the equations for cluster amplitudes are identical in a variational and a bivariational response. Additionally, if one imposes the restriction that only those terms which have a maximum of one T amplitude on either side of the vertex H are to be included in the expression for energy derivative $E^{(n)}$, that is,

$$E^{(n)} = [T^{+(n)} \hat{H}(1+T)] + [T^{+(n-1)} \{\hat{H} \, T^{(1)} + \hat{O}(1+T)\}]$$

$$+ \sum_{k=0}^{n-2} T^{+(k)} \{\hat{H} \, T^{(n-k)} + \hat{O} \, T^{(n-1-k)}\} + [H \, T^{(n)} + \hat{O} \, T^{(n-1)}]. \quad (28)$$

then the stationary equations for cluster amplitudes turn out to be identical to those of a nonvariational response approach. At the stationary point, therefore, the expression for $E^{(n)}$ will also be identical to the nonvariational expression for nth order property. Under this approximate scheme, even the nonvariationally derived expressions for first and higher order properties obey the $2n+1$ rule (of which GHF is a special case).

5. Multi-reference nonvariational CC response approach

The calculation of properties via the CC approach either through the expectation values or response approach has been much more intensely pursued for closed shell systems than for the open shell ones. However, if the open-shell systems can be described as starting from an adequate single determinantal model space the closed shell CC theories can be applied to these systems with reasonable degree of confidence. There are still the cases where the model spaces cannot be described by a single determinant. These are more

Table 1[a]. Properties of hydrogen fluoride (DZ basis)

Property	SCF	Variational (N dis = 0)	Variational (N dis = 1)	Nonvariational Nonrelaxed[b]	Expt
Basis I[c]					
	0.936	0.897	0.894	0.896	0.707[d]
	4.002	4.277	4.525	4.179	6.40[e]
	−17.59	−23.05	−26.98	−17.52	—
	0.739	0.888	0.890	0.811	5.08[e,f]

[a]All results in atomic units; [b]From reference 58, [c]Double zeta (DZ) basis ref. 60; [d]Reference 61, [e]Reference 62; [f]Reference 63 Ndis = 0 means disconnected terms have been included in the cluster amplitude equations, Ndis = 1 means disconnected terms have been ignored in the cluster amplitude equations.

Table 2[a]. Properties of hydrogen fluoride (DZP basis)

Property	SCF	Variational (Ndis = 0)	Variational (Ndis = 1)	Nonvariational[b] Nonrelaxed	Expt.
Basis II[c]					
	0.807	0.754	0.750	0.756	0.707[d]
	4.294	4.626	4.967	4.570	6.40[e]
	−14.47	−20.840	−25.690	−15.36	—
	1.557	1.740	1.780	1.638	5.08[e,f]

[a]All results in atomic units, [b]From reference 58, [c]Double zeta plus polarization (DZP) basis; [d]Ref. 61, [e]Ref 62; [f]Ref. 63.

complex cases where electron correlation is predominantly nondynamical and has to be introduced through a multideterminantal model space. The open shell electron correlation, in general, encompasses these cases although this is only a loose definition. One may say that such a multideterminantal model space may be necessary for many pathological closed shell systems, in particular, those which are far away from equilibrium. Extensive review of the nature of electron correlation to open-shell systems has been made[31].

It is necessary to develop a response approach for such multideterminantal model space-based CC approaches (known as MRCC response theories). However, it is more complex to introduce response for MRCC wave function. In particular, a variational response approach will have far more complexities. Variational MRCC approach for energy calculation has been attempted in Fockspace[45]. Only recently a nonvariational response has been done with a MRCC wave function[43] and we will review this in the course of this section. The development of MRCC response theories is on a line similar to the MRCC theories for energy calculations (in zero field) where a manifold of energies are obtained in a single-shot calculation as eigenvalues of an effective hamiltonian defined over the model space. However, when we calculate properties as a response to the field, we will observe some very important differences in the structure of the theory.

As a response to external fields, the combination coefficients of the multideterminantal model space are allowed to vary. The orbitals may also be varied, but this variation can be taken care of by the standard coupled perturbed Hartree–Fock (CPHF) method. Instead of orbital variation, we will discuss here the Fock space approach where a suitable core is chosen with respect to which holes and particles are defined. The model space can be built so as to consist of a subset of holes and particles which may be called active orbitals. For example, a model space of m active holes and n active particles can be written as:

$$\psi_{\mu}^{(0)(m,n)} = \sum_i C_{i\mu}(\lambda)\,\Phi_i^{(m,n)} \tag{29}$$

The conventional Fock space Bloch equation for the perturbed hamiltonian can be written for all λ as,

$$\hat{H}(\lambda)\Omega(\lambda)P = \Omega(\lambda)H_{\text{eff}}(\lambda)P, \tag{30}$$

where P is a projector onto the model space. The universal wave operator $\Omega(\lambda)$, may be written as,

$$\Omega(\lambda) = \{\exp[\tilde{T}(\lambda)]\}P. \tag{31}$$

Corresponding to model space $\psi_{\mu}^{(0)(m,n)}$, the cluster operator has derivatives which can destroy a maximum of m active particles and n active holes.

$$\tilde{T}_{(m,n)}^{(\lambda)} = \tilde{T}_{(m,n)}^{(0)} + \lambda\tilde{T}_{(m,n)}^{(1)} + \lambda^2\,\tilde{T}_{(m,n)}^{(2)} + \cdots \tag{32a}$$

Being universal in nature, each of the terms $T_{(m,n)}^{(\lambda)}$ may be written as

$$\tilde{T}_{(m,n)}^{(0)} = \sum_{k=0}^{m}\ \sum_{l=0}^{m} T_{(k,l)}^{(0)}, \tag{32b}$$

$$\tilde{T}_{(m,n)}^{(1)} = \sum_{k=0}^{m}\ \sum_{l=0}^{m} T_{(k,l)}^{(1)}. \tag{32c}$$

The effective hamiltonian $H_{\text{eff}}(\lambda)$ will also depend on the external field strength parameter and can be written in terms of various order derivatives as:

$$H_{\text{eff}}(\lambda) = H_{\text{eff}}^{(0)} + \lambda H_{\text{eff}}^{(1)} + \lambda^2 H_{\text{eff}}^{(2)} + \cdots \tag{33}$$

The projection of the Bloch equation to the model space yields

$$\begin{aligned} PH(\lambda)\Omega(\lambda)P &= P_{\Omega}(\lambda)H_{\text{eff}}(\lambda)P \\ &= PH_{\text{eff}}(\lambda)P. \end{aligned} \tag{34}$$

(The latter identity follows only in case intermediate normalization is obeyed.) If the manifold of eigenvalues of $\{E_{\mu}(\lambda)\}$ satisfy the Schrodinger's equation for the perturbed hamiltonian $H(\lambda)$, they are, by extension of the familiar equations in zero field, eigenvalues of $H_{\text{eff}}(\lambda)$ too.

$$\sum_i [H_{\text{eff}}(\lambda)]_{ji}\,C_{i\mu}(\lambda) = E_{\mu}(\lambda)\,C_{j\mu}(\lambda), \tag{35}$$

where

$$E_{\mu}(\lambda) = E_{\mu}^{(0)} + \lambda E_{\mu}^{(1)} + \lambda^2 E_{\mu}^{(2)} + \cdots, \tag{36}$$

where the set $\{E_{\mu}^{(n)}\}$ may now defined as the manifold of nth order properties. To calculate $E_{\mu}^{(n)}$ (with $n=1$ say) one has to solve,

$$\sum \{H_{\text{eff}}^{(1)}\}_{ji} C_{i\mu}^{(0)} + (H_{\text{eff}}^{(0)})_{ji} C_{i\mu}^{(1)} = E_{\mu}^{(1)} C_{j\mu}^{(0)} + E_{\mu}^{(0)} C_{j\mu}^{(1)}. \tag{37}$$

One can readily see that for MRCC first-order property, the structure of an eigenvalue equation no longer holds good. One can identify the form of $(H_{\text{eff}}^{(1)})_{ji}$ as

$$P\frac{\partial}{\partial\lambda}[\hat{H}(\lambda)\Omega(\lambda)]_{\lambda=0}P \tag{38}$$

and so on. The projection of the Fock space Bloch's equation to Q space i.e. the space consisting of virtual space determinants yields

$$\varphi[\hat{H}(\lambda)\Omega(\lambda) - \Omega(\lambda)H_{\text{eff}}(\lambda)]P = 0. \tag{39}$$

The zeroth order part of equation (39) provides the MRCC equation for the cluster operators necessary for the calculation of energies. Solutions of the derivative amplitudes in (0,1) sector needed for the 1st order property is given by the first derivative of equation (39) at $\lambda=0$. This is as follows:

$$\sum_i \langle \Phi_i^* \left| \frac{\partial}{\partial \lambda} \left[\hat{H}(\lambda)\Omega(\lambda) - \Omega(\lambda) H_{\text{eff}}^{(\lambda)} \right]_{\lambda=0} \right| \Phi_i \rangle C_{i\mu}^{(0)} + \sum \langle \Phi_i^* | [\hat{H}^{(0)}\Omega^{(0)} - \Omega^{(0)} H_{\text{eff}}^{(0)}] | \Phi_i \rangle C_{i\mu}^{(1)} = 0, \quad (40)$$

$\forall_{i,i}$

which can be written as

$$\langle \Phi_i^* \left| \frac{\partial}{\partial \lambda} \left[\hat{H}(\lambda)\Omega(\lambda) - \Omega(\lambda) H_{\text{eff}}^{(\lambda)} \right]_{\lambda=0} \right| \Phi_i \rangle = 0 \quad (41)$$

$\forall_{i,i}$

Equation (41) yields the parameters which define the derivative of $\Omega(\lambda)$ at $\lambda=0$. $H_{\text{eff}}^{(0)}$ and $H_{\text{eff}}^{(1)}$ may now be found as:

$$(H_{\text{eff}}^{(0)})_{ji} = \langle \Phi_j | \hat{H}^{(0)}\Omega^{(0)} | \Phi_i \rangle, \quad (42a)$$

$$(H_{\text{eff}}^{(1)})_{ji} = \left\langle \Phi_j \left| \frac{\partial}{\partial \lambda} \left[\hat{H}(\lambda)\Omega(\lambda) \right]_{\lambda=0} \right| \Phi_i \right\rangle \; i,j \in P \quad (42b)$$

Equation (37) along with the normalization conditions

$$\sum_i C_{i\mu}^{*(0)} C_{i\mu}^{(0)} = 1, \quad (43a)$$

$$\sum_i C_{i\mu}^{*(0)} C_{i\mu}^{(1)} + \sum_i C_{i\mu}^{*(1)} C_{i\mu}^{(0)} = 0, \quad (43b)$$

yields $E_\mu^{(1)}$, the first order property. Hence the properties of a number of states are obtained in a single calculation. The number of states, however, depends on the number of configuration included in the model space. Recently equations for one valence hole/particle system have been explicitly presented[43].

This is the first response approach in MRCC framework for quasidegenerate systems. It may be desirable, as seen from our discussions at the beginning of this review, to find a variational principle with MRCC model space. However, formulation of the open shell variational principle is far more complex and a suitable one in Fock space for energy calculations has recently been done. It is pertinent at this juncture to mention the MRCC developments for energy calculations using Hilbert space for general model spaces[59]. The Hilbert space formulations may seem to be the more natural ones, although the formal as well as the computational developments in the Hilbert space approach are lagging. Future trends in the formulation of open shell CC response theories for properties will be in the direction of variational formulations in Fock space and/or Hilbert space. This seems to be the natural culmination in the efforts of developing desirable CC methods for property calculations. Needless to say these have to be accompanied by the necessary code development, particularly for open shell cases and actual applications using these theories.

6. Conclusion

In this review we have discussed the coupled cluster response methods for calculation of properties. Special emphasis has been given on the stationary approach which has the inbuilt advantage of satisfying the $(2n+1)$ rule. This facilitates the computational task enormously. Numerical results from stationary response calculations are given in Tables 1 and 2.

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RESEARCH COMMUNICATIONS

An algorithm for conducting hypotheses testing based on Neyman–Pearson Lemma. I. The case of continuous univariates

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Neyman–Pearson Lemma provides a method for constructing the best critical region in hypotheses testing problems involving two simple hypotheses H_0 and H_1. In many applications H_0 and H_1 are expressed as probability density functions $f_0(x)$ and $f_1(x)$. In practical situations the functions $f_0(x)$ and $f_1(x)$ are either too complicated to be amenable for straightforward theoretical treatment by Neyman–Pearson Lemma or given only as a table of numerical values. An algorithm to conduct the Neyman–Pearson test for such a complicated situation is proposed. A Fortran program, called NPTEST, for implementing the algorithm has also been developed and tested.

In many hypotheses testing problems one has to decide between two probability density functions (PDF) $f_0(x)$ and $f_1(x)$ and the Neyman–Pearson Lemma[1] can be used to construct the best critical region for the test. In many practical situations the PDF $f_0(x)$ defining the null hypothesis H_0 and the PDF $f_1(x)$ defining the alternative hypothesis H_1 are either too complicated to be amenable for straightforward theoretical treatment by Neyman–Pearson Lemma or are given only as a table of numerical values. For example, in statistical tests for determining the space group symmetry of a crystal one meets with such a situation. It would therefore be quite useful to develop an algorithm for conducting the Neyman–Pearson test for such complicated situations and in this paper we shall describe one such algorithm. A Fortran program, called NPTEST, for implementing the algorithm has also been developed and tested using random samples generated from a few known probability distributions. NPTEST has also