Theor Chim Acta (1985) 68, 379-388

THEORETICA CHIMICA ACTA

Study of approximate coupled cluster methods for first-order static properties*

Sourav Pal

Theoretical Chemistry Group, Physical Chemistry Division, National Chemical Laboratory, Pune 411 008, India

(Received January 31, revised May 29/Accepted June 18, 1985)

In this paper, we analyse the algebraic structure of the equations for calculating the first order static properties using several approximate versions of Coupled Cluster (CC) methods. In particular, the non-variational and the variational method using a CC wavefunction corresponding to an appropriately defined perturbed Hamiltonian as well as the simple expectation value expression using a CC stationary state are studied under different approximations. Two different models are proposed: (a) use of maximum overlap orbitals where the pertinent approximations are $T \sim T_2$, $T^{(1)} \sim T_2{}^{(1)}$, (b) use of Hartree-Fock orbitals and $T \sim (T_1 + T_2)$, $T^{(1)} \sim (T_1^{(1)} + T_2^{(1)})$ approximations. It is analytically shown that in both these models certain approximate versions of the methods under purview yield identical results for first order static properties.

Key words: Static properties — Coupled Cluster methods — Atoms and molecules

1. Introduction

The use of highly correlated methods like the Coupled Cluster Method (CCM) and Many Body Perturbation Theory (MBPT) has recently been made in the context of various static properties [1-6, 8, 9]. These methods have already been highly successful in the calculation of electron correlation energies. Hence recently it has been felt natural to study the use of these methods to the static properties. MBPT framework was used suitably by Sadlej for the calculation of static properties [8]. Čížek and Fink considered the expectation value of a property operator using a reference CC state. A CCM was advocated by Monkhorst [4]

* NCL Communication No. 3725

using a suitable form of the Coupled Cluster (CC) wave function. The method was nonvariational in nature. Taking cue from the ansatz proposed by Monkhorst, a variational CCM and a method using a unitary CC wave function were recently suggested by us [5, 6]. A CCM using bivariational expression has recently been advocated by Arponen [1]. Kümmel also proposed a CCM to calculate the first order of static properties [3]. However, so far no study has been undertaken to make a comparative analysis of the algebraic structure of the equations and show correspondences between these methods.

In this paper we want to keep on record a comparative study of some of these methods based on CC wave function aimed at calculating first order property in physically meaningful schemes. Certain correspondences will be shown on completely analytical grounds which will be very useful for later computations. We will study the nonvariational [4] and the variational method recently suggested for first order properties as well as the simple expectation value of the first order property operator using a stationary CC state.

2. Background of the pertinent theories

Let us first review these methods for first order properties in brief. Čížek and Fink [2] considered the simple expectation value of a one body operator $\hat{O}$ as,

$$\langle \hat{O} \rangle = \langle \psi | \hat{O} | \psi \rangle / \langle \psi | \psi \rangle \tag{1}$$

where ψ is a suitable stationary state. Using a CC form of the wave function ψ, $\hat{O}$ was shown to be a sum of linked diagrams.

$$\langle \hat{O} \rangle = \langle \phi_0 | e^{T^+} \hat{O} e^T \phi_0 \rangle_{\text{Linked}} \tag{2}$$

with

$$\psi = e^T \phi_0 \tag{3}$$

T is the logarithm of wave operator, ϕ_0 is the reference. function Equation (2) is a power series in T, and has to be truncated to a suitable degree for actual computation.

We will now write the expressions for first order static property using the two other methods to be studied here-nonvariational CCM of Monkhorst [4] and our variational CCM [5]. These approaches start from a perturbed Hamiltonian H (λ) including the perturbation due to the external fields.

$$H(\lambda) = H + \lambda \hat{O} \tag{4}$$

Where H is the Hamiltonian of the system and $\hat{O}$ is the corresponding property operator defining the interaction of the system with the external fields, λ is a coupling parameter. The wave function ψ (λ) is given by

$$\psi(\lambda) = e^{T(\lambda)} \phi_0 \tag{5a}$$

where

$$T(\lambda) = T + \lambda T^{(1)} + \lambda^2 T_+^{(2)} \tag{5b}$$

$$E(\lambda) = E + \lambda E^{(1)} + \lambda^2 E_+^{(2)}. \tag{6}$$

Operator T is the usual logarithm of the waveoperator for the wavefunction corresponding to the field-independent Hamiltonian H. $T^{(1)}$, $T^{(2)}$ etc appear as the response to the presence of the field. $E^{(1)}$ is associated with the first order property $E^{(2)}$ may be associated with second order property and so on. Let us use subscripts NV to $E(\lambda)$, $E^{(1)}$ etc. in (6) obtained by the nonvariational method and V to the same quantities obtained by the variational method.

$$E_{NV}(\lambda) = \langle \phi_0 | e^{-T(\lambda)} \mathrm{H}(\lambda) e^{T(\lambda)} | \phi_0 \rangle. \tag{7}$$

when

$$E_{NV}^{(1)} = \langle \phi_0 | e^{-T} \{ \hat{\mathrm{O}} + [\mathrm{H}, T^{(1)}] \} e^{T} | \phi_0 \rangle \tag{8}$$

with the equation determining parameters of $T^{(1)}$ in the nonvariational method given by

$$\langle \phi^* | e^{-T} \{ \hat{\mathrm{O}} + [\mathrm{H}, T^{(1)}] \} e^{T} | \phi_0 \rangle = 0 \tag{9}$$

ϕ^*'s being the relevant excited states, $E_{NV}^{(1)}$ is the first order property calculated by a nonvariational method. T-parameters are the parameters obtained through Čížek's CC equations for correlation energy. Equations (8) and (9) generate linked diagrams. T and $T^{(1)}$ can be written as the sum of various n-body operators.

$$T = \sum_m T_m \tag{10a}$$

$$T^{(1)} = \sum_m T_m^{(1)} \tag{10b}$$

where

$$T_1 = \sum_{\alpha,p} \langle p | t_1 | \alpha \rangle a_p^+ a_\alpha, \tag{11a}$$

$$T_2 = \frac{1}{2!} \sum_{\substack{\alpha,\beta \\ p,q}} \langle pq | t_2 | \alpha\beta \rangle a_p^+ a_q^+ a_\beta a_\alpha \tag{11b}$$

etc., where α, β denote occupied spin-orbitals, p, q, are unoccupied spin-orbitals

$T_1^{(1)}$, $T_2^{(1)}$ etc. can be written in a similar manner.

In the variational method, a linked perturbed expectation value functional

$$E_V(\lambda) = \langle \Phi_0 e^{T(\lambda)^+} H(\lambda)\, e^{T(\lambda)} | \phi_0 \rangle_{\text{Linked}} \tag{12}$$

$$E_V^{(1)} = \langle \Phi_o | N[e^{T^+} \{ \hat{\mathrm{O}} + T^{(1)+} \mathrm{H} + \mathrm{H} T^{(1)} \} e^{T}] | \Phi_0 \rangle_{\text{Linked}}. \tag{13}$$

The relevant equations for T, $T^{(1)}$ may be obtained by equating for λ^0, λ^1 terms in the following system of equations to zero.

$$\frac{\partial E(\lambda)}{\partial T^+} = 0. \tag{14}$$

As in the nonvariational method T, $T^{(1)}$ etc. are obtained hierarchically. In the variational method T's are obtained by putting the derivative of λ-independent term of (12) with respect to T^+ matrix elements to zero and then equating the derivative of $E_V^{(1)}$ with respect to T^+ matrix elements to zero gives us the $T^{(1)}$ matrix elements.

3. Analysis of the approximate methods

We note that if we use full expansion with all possible cluster parameters in the wavefunction, the quantities obtained by both these methods are identical. Furthermore, the first order static property obtained by these methods $E_{NV}^{(1)}/E_V^{(1)}$ with the full expansion in $\psi(\lambda)$ in Eq. (5a) is identical to the expectation value of first order property with respect to an exact stationary CC state. However, it will be interesting to study them in various approximation schemes. In this context we will study two different kinds of truncation models (a) $T \sim T_2$, $T^{(1)} \sim T_2$ (b) $T \sim (T_1 + T_2)$, $T^{(1)} \sim (T_1^{(1)} + T_2)$. In both these schemes we ignore T's and $T^{(1)}$'s which are a higher body than T_2 and $T_2^{(1)}$. If we use maximum overlap orbitals as suggested by Kümmel [3] ($T_1 = 0$) we have the model (a). Model (b) includes both T_1 and T_2 generally. We will first show certain pertinent correspondences between the nonvariational method and the variational method under model (a) i.e. the truncation $T \sim T_2$, $T^{(1)} \sim T_2^{(1)}$ as well as the expectation value (2) in $T \sim T_2$ approximation. This amounts to a proper choice of orbitals where single excitations are negligible.

Let us study the nonvariational expression. We use Linearised-CPMET (L-CPMET) values for T_2-parameters (i.e. linearise the equations for T_2-matrix elements). Substituting these values for T_2-matrix elements in Eq. (9), we obtain $T_2^{(1)}$ matrix elements. Diagrammatically the equation means that the 2 particle-2hole ($2p$-$2h$) block consisting of the linked contractions of

$$(\overbrace{\hat{O}\ T_2} + \overbrace{v\ T_2^{(1)}} + \overbrace{f\ T_2^{(1)}} + \overbrace{v\ \overbrace{T_2\ {}^{(1)}T_2}}) = 0. \tag{15}$$

This is a linear equation in $T_2^{(1)}$ matrix elements. If we now make a further approximation in neglecting the terms due to $\overbrace{v\ \overbrace{T_2\ {}^{(1)}T_2}}$ contractions, then Eq. (15) may be written as,

$$\boldsymbol{A}T_2^{(1)} + \boldsymbol{B}'(T_2) = 0. \tag{16}$$

Where $\boldsymbol{A}$ is the usual (L-CPMET) matrix of coefficients, $\boldsymbol{T}_2^{(1)}$ is a column consisting of $T_2^{(1)}$ matrix elements. $\boldsymbol{B}'$ (T_2) is a column matrix consisting of various two particle-two hole ($2p$-$2h$) elements generated by contractions of $\overbrace{\hat{O}T_2}$ (with L-CPMET T_2-matrix elements). It can be shown that under these conditions, $E^{(1)}$ obtained via Eq. (8) is equal to the expectation value (as in Eq. 2) truncated to quadratic terms in T_2. From Eq. (16) one can write

$$\boldsymbol{T}_2^{(1)} = -\boldsymbol{A}^{-1}\boldsymbol{B}'(\boldsymbol{T}_2). \tag{17}$$

The nonvariational expression for first-order property $E^{(1)}$ is given by the sum of the contribution of the closed linked diagrams generated by contraction of v

and $T_2^{(1)}$ operators and the value corresponding to the stationary function ϕ_0 (reference value). An element of $\boldsymbol{T}_2^{(1)}$ i.e. $[\boldsymbol{T}_2^{(1)}]_i$ is given by

$$[T_2^{(1)}]_i = \sum_j (\boldsymbol{A}^{-1})_{ij} (\boldsymbol{B}')_j \tag{18}$$

where the index "j" runs over all the $2p$-$2h$ distinct elements. L-CPMET T_2' s satisfy the equation

$$\boldsymbol{A}\boldsymbol{T}_2 + \boldsymbol{B} = 0 \tag{19}$$

where $\boldsymbol{B}$ is a column matrix consisting of v-matrix elements.

$$\boldsymbol{T}_2 = -\boldsymbol{A}^{-1}\boldsymbol{B}. \tag{20}$$

Closed diagrams consisting of v and $T_2^{(1)}$ operators may be written as $\boldsymbol{B}^T\boldsymbol{T}_2^{(1)}$ where $\boldsymbol{B}^T$ is a row. Hence $E^{(1)}$, apart from its reference value, is given by

$$-\sum [B^T]_i \, (A^{-1})_{ij} [B'(T)]_j$$

The indices i and j run over all the $2p$-$2h$ matrix elements.

If we start from the expectation value type expression as in Eq. (2) which is truncated to quadratic terms, $\langle \hat{O} \rangle$, apart from its reference value, is given by all the closed diagrams consisting of T_2^+, $\hat{O}$ and T_2 operators. Since $\hat{O}$ is a one-body operator, no closed diagram consisting of contractions $T_2^+ \hat{O}$, $\hat{O} T_2$ are possible. The diagrams consist of closed contractions of $T_2^+ \hat{O}$ and T_2 operators. This $2p$-$2h$ block is identical to the $\boldsymbol{B}'$ (T_2) block. Hence the closed diagrams involving T_2^+, $\hat{O}$ and T_2 operators may be written as,

$$\sum_i (\boldsymbol{T}_2^+)_i [\boldsymbol{B}'(T)]_i$$

where i again runs over all the partinent $2p$-$2h$ indices.

$\boldsymbol{T}_2^+$ is a row consisting of T_2^+ matrix elements. Using Eq. (20) and the hermiticity of $\boldsymbol{A}$ one can write,

$$\boldsymbol{T}_2^+ = -\boldsymbol{B}^T(\boldsymbol{A}^{-1}) \tag{21}$$

such that

$$(\boldsymbol{T}_2^+)_i = -\sum_j [\boldsymbol{B}^T]_j [(\boldsymbol{A}^{-1})]_{ji}. \tag{22}$$

Hence, the closed diagrams involving T_2^+, $\hat{O}$ and T_2 operators may be written as,

$$-\sum_i \sum_j [\boldsymbol{B}^T]_j (\boldsymbol{A}^{-1})_{ji} [\boldsymbol{B}'(\boldsymbol{T}_2)]_i$$

with i and j running over $2p$-$2h$ distinct elements.

Hence the nonvariational expression for calculating static property under the model (a) coupled with a further neglect of the terms due to contraction of $\overbrace{v \; T_2^{(1)}} \; T_2$ in Eq. (15) leads to a value identical to that generated by the expectation value expression (Eq. 2) truncated to a total of quadratic powers of T in $T \sim T_2$ approximations.

Now we show that the same value of $E^{(1)}$ as in the nonvariational method under the conditions discussed above is obtained if we follow a variational prescription for calculating $T_2^{(1)}$, T_2 matrix elements by taking a total of quadratic power in T_2, $T_2^{(1)}$ in E (λ). Indeed, this is very similar to our earlier observation in the context of correlation energy that the variational method with the inclusion of a total of quadratic power in the energy functional furnishes the L-CPMET energy [7]. With the quadratic terms included, the calculation of T_2 gives the L-CPMET T_2's as has been discussed in our work in [7]. Let us now analyse the expression for $E_v^{(1)}$ and the structure of the equations for calculating T_2, $T_2^{(1)}$ matrix elements. $E_v^{(1)}$ contains upto quadratic in T_2, $T_2^{(1)}$ the following terms

$$\begin{aligned} E_v^{(1)} = &\langle\phi_0|\hat{O}|\phi_0\rangle + \langle\phi_0|T_2^+\hat{O}T_2|\phi_0\rangle_L \\ &+\langle\phi_0|T_2^{(1)^+}fT_2|\phi_0\rangle_L + \langle\phi_0|T_2^{(1)^+}vT_2|\phi_0\rangle_L \\ &+\langle\phi_0|T_2^{(1)^+}v|\phi_0\rangle_L + \langle\phi_0|T_2^+vT_2^{(1)}|\phi_0\rangle_L \\ &+\langle\phi_0|T_2^+fT_2^{(1)}|\phi_0\rangle_L + \langle\phi_0|vT_2^{(1)}|\phi_0\rangle_L. \end{aligned} \tag{23}$$

Subscript "L" denotes linked diagrams. All operator products in (23) are in normal order. The above terms are the only contributing terms. T_2-matrix elements are obtained by equating the λ-independent term in Eq. (14) to zero. The equation obtained will be identical to the ones obtained by making the energy functional $(\langle\phi_0|e^{T_2^+}\mathrm{H}e^{T_2}|\phi_0\rangle)$ (truncated to quadratic power) stationary with respect to T_2^+ matrix elements. As has been discussed in [7], we get L-CPMET T_2''s. The equations for $T_2^{(1)}$ matrix elements are obtained by equating the derivative of terms linear in λ in $E(\lambda)$ i.e. $E^{(1)}$ in Eq. (23) with respect to the matrix elements of T_2^+ to zero. Diagrammatically, $E^{(1)}$ consists of closed diagrams only. When the differentiation with respect to T_2^+ is done, $2p$-$2h$ block is generated consisting of the linked contractions. The variational equation may be diagramatically interpreted as $2p$-$2h$ block generated from the contractions

$$(\overbrace{\hat{O}\ T_2} + \overbrace{v\ T_2^{(1)}} + \overbrace{f\ T_2^{(1)}}) = 0 \tag{24}$$

Eq. (24) defining the $T_2^{(1)}$ matrix elements is identical to Eq. (16). Consequently, the closed contractions involving

$$\overbrace{T_2^+\ \hat{O}\ T_2} + \overbrace{T_2^+\ f\ T_2^{(1)}} + \overbrace{T_2^+\ v\ T_2^{(1)}} = 0. \tag{25}$$

Similarly, the L-CPMET $T_2's$ satisfy the condition that the closed contractions involving

$$\overbrace{T_2^{(1)+}\ v} + \overbrace{T_2^{(1)+}\ f\ T_2} + \overbrace{T_2^{(1)+}\ v\ T_2} = 0. \tag{26}$$

Because of Eqs. (23), (24), (25) and (26) $E_v^{(1)}$, apart from the reference value, is given by the closed diagrams involving the v, $T_2^{(1)}$ operators. Hence, this completes the derivation of our assertion.

Using one-hole one-particle orbitals (2-state model) for a 2-electron system let us write down the algebraic expressions for the first order property in the above methods using model (a). If we have α as the hole orbital (spatial), p as the

particle orbital, then from Eq. (16) we have

$$\langle pp|t_2^1|\alpha\alpha\rangle = \frac{(\hat{O}_{\alpha\alpha} - \hat{O}_{pp})\langle pp|t_2|\alpha\alpha\rangle}{[f_{pp} - f_{\alpha\alpha} + \langle p\alpha|v|\alpha p\rangle - 2\langle p\alpha|v|p\alpha\rangle + \tfrac{1}{2}\langle\alpha\alpha|v|\alpha\alpha\rangle + \tfrac{1}{2}\langle pp|v|pp\rangle]}. \tag{27}$$

where Goldstone matrix element convention has been used.

The same value of $\langle pp|t_2'|\alpha\alpha\rangle$ is obtained by use of the variational method under the model (a) with $E_v^{(1)}$ truncated to a total of quadratic power in T_2, $T_2^{(1)}$ (i.e. the Eq. (24)). If $\langle pp|t_2|\alpha\alpha\rangle$ is the linearised CPMET value, $E^{(1)}$ in both these variational and non-variational methods as well as the expectation value $\langle\hat{O}\rangle$ truncated to quadratic power in $T \sim T_2$ approximation are identical and equal to

$$\frac{\langle\alpha\alpha|v|pp\rangle(\hat{O}_{\alpha\alpha} - \hat{O}_{pp})\langle pp|t_2|\alpha\alpha\rangle}{[f_{pp} - f_{\alpha\alpha} + \langle p\alpha|v|\alpha p\rangle - 2\langle p\alpha|v|p\alpha\rangle + \tfrac{1}{2}\langle\alpha\alpha|v|\alpha\alpha\rangle + \tfrac{1}{2}\langle pp|v|pp\rangle]}.$$

Now, let us improve the model and include T_1 and $T_1^{(1)}$ as well. Inclusion of singly excited configurations is important for the calculation of first order property when we use the Hartree-Fock (HF) orbitals. We will study some interesting analytical correspondence between these methods in this improved i.e. the model (b). In such a model, $E_v^{(1)}$ is given by,

$$E_v^{(1)} = \langle\phi_0|e^{(T_1+T_2)^+}\{\hat{O} + (T_1^{(1)} + T_2^{(1)})^+ H + H(T_1^{(1)} + T_2^{(1)})\}e^{(T_1+T_2)}|\phi_0\rangle_{\text{Linked}}. \tag{28}$$

Let us retain terms up to a total of quadratic power of T_1, T_2, $T_1^{(1)}$, $T_2^{(1)}$ except for $\langle\phi_0|vT_1^{(1)}T_1|\phi_0\rangle$ and its conjugate (T_1, $T_1^{(1)}$ being small, this is not unreasonable). In this approximation we can show that the variational method yields the same first order property as the expectation value $\langle\phi_0|e^{T^+}\hat{O}e^{T}|\phi_0\rangle$ in $T \sim (T_1 + T_2)$ approximation if we use the values of T_1, T_2 matrix elements obtained by a linearised CCM with Singles and Doubles (LCCSD) calculation. Neglecting $\langle\phi_0|vT_1^{(1)}T_1|\phi_0\rangle$ and its conjugate terms, the variational equations for $T_1^{(1)}$, $T_2^{(1)}$ may be shown to be the following set: 1 particle-1 hole ($1p$-$1h$) block consisting of the following contractions

$$(\hat{O} + \overbrace{\hat{O}\ T_1} + \overbrace{\hat{O}\ T_2} + \overbrace{f\ T_1^{(1)}} + \overbrace{v\ T_2^{(1)}} + \overbrace{v\ T_1^{(1)}}) = 0 \tag{29}$$

$2p$-$2h$ block consisting of the contractions

$$(\hat{O}T_1 \text{ (Disconnected) } \overbrace{\hat{O}\ T_2} + \overbrace{f\ T_1^{(1)}} + \overbrace{v\ T_2^{(1)}} + \overbrace{v\ T_1^{(1)}}) = 0. \tag{30}$$

It may be noted that the variational equation contains a disconnected $2p$-$2h$ term, $\hat{O}T_1$ coming from the closed diagram in $E_v^{(1)}$ involving T_2^+, $\hat{O}$, T_1 operators. The rest of the diagrams are all connected.

The equations for T_1, T_2 (L-CCSD) are given in diagrammatic language by $1p$-$1h$ block generated from the contractions

$$(\overbrace{f\ T_1} + \overbrace{v\ T_1} + \overbrace{v\ T_2}) = 0 \tag{31}$$

$2p$-$2h$ block generated from the contractions

$$(v+\overbrace{v\ T_2}+\overbrace{f\ T_2}+\overbrace{v\ T_1})=0. \tag{32}$$

Because of Eqs. (29)-(30), the sum of the closed diagrams involving the following contractions is equal to zero i.e.

$$\begin{aligned}&\overbrace{T_1^+\ \hat{O}}+\overbrace{T_1^+\ \hat{O}\ T_1}+\overbrace{T_1^+\ \hat{O}\ T_2}+\overbrace{T_1^+\ f\ T_1^{(1)}}+\overbrace{T_1^+\ v T_2^{(1)}}\\&+\overbrace{T_1^+\ v T_1^{(1)}}+\overbrace{T_2^+\ \hat{O} T_1}+\overbrace{T_2^+\ \hat{O}\ T_2}+\overbrace{T_2^+\ v\ T_2^{(1)}}\\&+\overbrace{T_2^+\ f T_2^{(1)}}+\overbrace{T_2^+\ v\ T_1^{(1)}}+\overbrace{T^{(1)+}\ f T_1}+\overbrace{T_1^{(1)+}\ v\ T_1}\\&+\overbrace{T_1^{(1)+}\ v\ T_2}+\overbrace{T_2^{(1)+}\ v}+\overbrace{T_2^{(1)+}\ v\ T_2}+\overbrace{T_2^{(1)+}\ f\ T_2}\\&\overbrace{T_2^{(1)+}\ v\ T_1}=0.\end{aligned} \tag{33}$$

One can then show that under the approximations $E_v^{(1)}$ is, apart from its HF value, given by the closed contractions of $\hat{O}$ and T_1 operators as well as v and $T_2^{(1)}$ operators.

$$E_v^{(1)}=\hat{O}_{HF}+\overbrace{\hat{O}T_1}+\overbrace{v\ T_2^{(1)}}. \tag{34}$$

Eq. (29-32) can be compactly written as,

$$\boldsymbol{X}\boldsymbol{T}^{(1)}+\boldsymbol{y}'(T)=0 \tag{35a}$$

$$\boldsymbol{X}\boldsymbol{T}+\boldsymbol{y}=0, \tag{35b}$$

where, as before, T and $T^{(1)}$ matrix elements are arranged in columns $\boldsymbol{T}$ and $\boldsymbol{T}^{(1)}$ respectively. $\boldsymbol{X}$ is the matrix of coefficients which is identical for T and $T^{(1)}$ determining equations under the approximations we have discussed.

$[\boldsymbol{y}'(\boldsymbol{T})]_i=$ ($1p$-$1h$) block consisting of contractions of $(\hat{O}+\overbrace{\hat{O}T_1}+\overbrace{\hat{O}T_2})$ (36a)

$$i=1, M$$

$[\boldsymbol{y}'(\boldsymbol{T})]_i=2p$-$2h$ block generated from the contractions of $(\overbrace{\hat{O}T_2})$ and disconnected $\hat{O}T_1$ term.

$$i=(M+1), N. \tag{36b}$$

The first M indices refer to distinct T_1 or $T_1^{(1)}$ matrix elements. The rest of the $(N-M)$ indices refer to distinct T_2 or $T_2^{(1)}$ matrix elements. Similarly,

$$y_i=0 \qquad i=1,\ldots,M \tag{37a}$$

$$y_i=v_i \qquad i=M+1,\ldots,N \tag{37b}$$

$v_i=$ Collection of distinct 2p-2h v-matrix elements. Closed contractions of v and $T_2^{(1)}$ operators again may be written as $\sum_{i=M+1}^{N}(\boldsymbol{y}^T)_i T_i^{(1)}$

$$\overbrace{v\ T_2^{(1)}}=-\sum_{i=1}^{N}\sum_{j=1}^{N}(\boldsymbol{y}^T)_i(\boldsymbol{X}^{-1})_{ij}[\boldsymbol{y}(\boldsymbol{T})]_j \tag{38a}$$

(Because $[\boldsymbol{y}^T]_i=0, i=1,\ldots,M$). (38b)

Let us start from the expectation value type expression in $T \sim (T_1 + T_2)$ approximation with L-CSSD T_1, T_2 values.

$$\langle \hat{O} \rangle = \hat{O}_{HF} + [\langle \phi_0 | T_2^+ \hat{O} T_2 | \phi_0 \rangle + \langle \phi_0 | T_2^+ \hat{O} T_1 | \phi_0 \rangle + \langle \phi_0 | T_1^+ \hat{O} | \phi_0 \rangle + \langle \phi_0 | T_1^+ \hat{O} T_1 | \phi_0 \rangle + \langle \phi_0 | T_1^+ \hat{O} T_2 | \phi_0 \rangle] + \langle \phi_0 | \hat{O} T_1 | \phi_0 \rangle. \quad (39)$$

The terms in the square bracket may be analysed as follows. $\langle \phi_0 | T_2^+ \hat{O} T_2 | \phi_0 \rangle + \langle \phi_0 | T_2^+ \hat{O} T_1 | \phi_0 \rangle$ may be viewed as closed diagram resulting from the contraction of T_2^+ operator with $[y'(T)]_i$ with i being $2p$-$2h$ indices. The rest of the terms in the square bracket may be similarly seen as the closed contraction of T_1^+ operator with $[y'(T)]_i$ with i being $1p$-$1h$ indices. Hence, terms in the square bracket may be written as,

$$\sum_{i=1}^{N} T_i^+ [y'(T)]_i$$

We see that,

$$\sum_{i=1}^{N} T_i^+ [y'(T)]_i = - \sum_{i=1}^{N} \sum_{j=1}^{N} [y^T]_j (X^{-1})_{ji} [y'(T)]_i. \quad (40)$$

Comparing Eqs. (40), (39), (38), and (34) we find that if we invoke the model (b) and truncate $E_V^{(1)}$ to a total of quadratic terms in T, $T^{(1)}$ as well as neglect the contraction $\overbrace{v\, T_1^{(1)}}\, T_1$ and its conjugate term, the variational method yields an identical result to the expectation value quantity in $T \sim (T_1 + T_2)$ approximation. However, unlike in the case of model (a), no correspondence can be established with the nonvariational method. The equations for $T^{(1)}$ matrix elements in the nonvariational case are entirely different. If we write the nonvariational equations in the form of (35a), (35b), we will find that $[y'(T)]_i$ for $2p$-$2h$ indices of i will not contain the disconnected term. Hence no correspondences with the nonvariational method are established.

4. Summary

We have established some analytic connection between a variational and a nonvariational CC method as well as the expectation value in a CC stationary state for first order static property. In $T \sim T_2$, $T^{(1)} \sim T_2^{(1)}$ model, we have derived some approximate versions of the theory which will yield identical results. When additionally we include T_1, $T_1^{(1)}$ in the wavefunction, we see that an approximate variational and expectation vaue quantity truncated to a total of quadratic terms in T furnish the same results. However, correspondence with the nonvariational method is not transparent and we have also discussed the reason for this.

Acknowledgements. The author wishes to thank Dr. Debashis Mukherjee of the Indian Association for the Cultivation of Science, Calcutta for valuable discussions. The author also acknowledges the support of Dr. A. P. B. Sinha and Dr. G. P. Das of NCL, Pune in the progress of the work. Thanks are also due to the referee for his comments which have helped the author to improve the manuscript.

References

1. Arponen, J.: Ann. Phys. **151,** 311 (1983); Arponen, J.: Pajanne, E.; Lect. Notes Phys. **198,** 319 (1984)
2. Čížek, J.; Adv. Chem. Phys. **14,** 35 (1969); Fink, M.; Nucl. Phys. **A221,** 163 (1974)
3. Kümmel, H. G.; Int. J. Quantum Chem. **24,** 79 (1983)
4. Monkhorst, H. J.: Int. J. Quantum Chem. **S11,** 421 (1977) Dalgaard, E., Monkhorst, H. J.: Phys. Rev. **A28,** 1217 (1983)
5. Pal, S.: Theoret. Chim. Acta (Berl.), **66,** 151 (1984)
6. Pal, S.: Theoret. Chim. Acta (Berl.), **66,** 207 (1984)
7. Pal, S., Durga Prasad, M., Mukherjee, D.: Theoret. Chim. Acta (Berl.), **62** 523 (1983); Pramána, **18,** 261 (1982)
8. Sadlej, A. J.: Int. J. Quantum Chem. **23** 147 (1983); Buckingham, A. D.: Adv. Chem. Phys. **12** 107 (1967); Sadlej, A. J.: Acta Phys. Polon. **A59** 669 (1981)
9. Sekino, H., Bartlett, R. J.: Int. J. Quantum Chem. **S18** 255 (1984)