Theor Chim Acta (1994) 88: 383–388

Theoretica Chimica Acta

On the calculation of expectation values and transition matrix elements by coupled cluster method

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Received January 4, 1993/Accepted December 2, 1993

Summary. Finite order expressions are derived for expectation values and transition matrix elements within the framework of the coupled cluster method.

Key words: Coupled cluster method – Expectation values and transition matrix elements

1 Introduction

The use of coupled cluster method (CCM) to obtain approximate solutions of the Schroedinger's equation has become widely popular in recent years [1–7]. For the ground state of a closed shell system, the CCM ansatz is given by [1–4]

$$|\psi_0\rangle = \exp(T)|\phi_0\rangle, \tag{1}$$

where $|\psi_0\rangle$ and $|\phi_0\rangle$ are the exact and the single determinantal reference wave functions respectively. The matrix elements of the cluster operator T and the ground state energy E_g are obtained from

$$\langle\phi_e|\bar{H}|\phi_0\rangle = 0, \tag{2a}$$

$$\langle\phi_0|\bar{H}|\phi_0\rangle = E_g. \tag{2b}$$

Here, $|\phi_e\rangle$ are the hole particle excited states orthogonal to $|\phi_0\rangle$, and

$$\bar{H} = \exp(-T)H\exp(T). \tag{2c}$$

The advantages of using this approach i.e. its size extensive nature and the general observation that even low order truncations to the cluster operator can yield energies comparable in accuracy to full CI stem from the exponential structure of the wave operator in Eq. (1).

Parallel to these developments, attempts have also been made to calculate other molecular properties [8–13]. Within the framework of the CCM formalism, the expectation value of an operator O is given by

$$\langle\psi_0|0|\psi_0\rangle = \frac{\langle\phi_0|\exp(T^+)\mathrm{O}\exp(T)|\phi_0\rangle}{\langle\phi_0|\exp(T^+)\exp(T)|\phi_0\rangle} = \langle\phi_0|\exp(T^+)\mathrm{O}\exp(T)|\phi_0\rangle_L, \tag{3}$$

the last expression following from the linked cluster theorem [1, 14]. Unlike the equations for the cluster matrix elements (2a), Eq. (3) is a non-terminating series. This has been the major bottleneck in extending CCM approaches to the calculation of non-energetic quantities. Consequently, very few attempts have been made to use Eq. (3) directly [9, 10]. Instead, several authors have attempted to formulate the expectation value problem in terms of response functions to avoid the infinite series [11–13]. Calculation of transition matrix elements using CCM wave functions also suffers from the same problem.

The purpose of the present paper is to outline an alternative method to calculate transition matrix elements between different eigenstates of the hamiltonian and also expectation values which to some extent eleminates the above mentioned problem. It is based on the observation that $\bar{H}$ defined in Eq. (2c) is related to the original hamiltonian via a similarity transformation. Given the eigenvectors of $\bar{H}$, it is now possible to construct the eigenvectors of H and thus determine the matrix elements of any arbitrary operator. This is presented in Section 2. The implication of this analysis to CCM are discussed in Section 3.

2 Similarity transformations and eigenvector relations

The problem at hand may be posed as follows. Given a hermitian operator H and its eigenvectors $|C_I\rangle$,

$$H|C_I\rangle = E_I|C_I\rangle, \tag{4}$$

we wish to calculate

$$O_{IJ} = \langle C_I|O|C_J\rangle / (\langle C_I|C_I\rangle\langle C_J|C_j\rangle)^{1/2}$$

for some hermitian operator O. Consider now the operator $\bar{H}$ related to H via a similarity transformation,

$$\bar{H} = U^{-1}HU. \tag{5}$$

$\bar{H}$ is not manifestly hermitian and its left and right eigenvectors are different in general,

$$\bar{H}|X_I\rangle = E_I|X_I\rangle, \tag{6a}$$

$$\langle Y_I|\bar{H} = \langle Y_I|E_I. \tag{6b}$$

From Eqs. (4)–(6), the following associations hold:

$$|C_I\rangle = U|X_I\rangle, \tag{7a}$$

$$\langle C_I| = \langle Y_I|U^{-1}N_I, \tag{7b}$$

with

$$N_I = \langle C_I|C_I\rangle, \tag{8}$$

if we set $\langle Y_I|X_I\rangle = 1$. Defining

$$\bar{O} = U^{-1}OU, \tag{9}$$

it can be readily verified that

$$\langle Y_I|\bar{O}|X_J\rangle = O_{IJ}(N_J/N_I)^{1/2}. \tag{10}$$

Since $O_{IJ}=O_{JI}^{*}=|O_{IJ}|\exp(i\theta)$ we get

$$|O_{IJ}|=(\langle Y_I|\bar{O}|X_J\rangle\langle Y_J|\bar{O}|X_I\rangle)^{1/2}, \tag{11a}$$

$$\theta=(1/2)\mathrm{Imag}\ln(\langle Y_I|\bar{O}|X_J\rangle/\langle Y_J|\bar{O}|X_I\rangle). \tag{11b}$$

The expectation value of O is given by

$$O_{II}=\langle Y_I|\bar{O}|X_I\rangle. \tag{12}$$

Thus the matrix elements of any operator between the eigenvectors of the original operator H can be calculated from a knowledge of the eigenvectors of $\bar{H}$.

3 Implications for CCM

We now address the problem of calculating expectation values and transition matrix elements in CCM. As noted in the introduction, $\bar{H}$ defined in Eq. (2) is related to the original hamiltonian via a similarity transformation, and as a consequence of Eq. (2a) $|\phi_0\rangle$ is the right eigenvector of it. The calculation of expectation values via Eq. (12) requires the knowledge of the corresponding left eigenvector $\langle Y_0|$ of $\bar{H}$. Expanding $\langle Y_0|$ as a *linear* superposition of the vacuum and hole particle states

$$\langle Y_0|=\langle\phi_0|+\sum_{\mathrm{e}} Y_{\mathrm{e}}\langle\phi_{\mathrm{e}}|, \tag{13}$$

we obtain, for Y_{e}

$$\sum_{\mathrm{e}'} Y_{\mathrm{e}'}\langle\phi_{\mathrm{e}'}|\bar{H}-E_{\mathrm{g}}|\phi_{\mathrm{e}}\rangle=-\langle\phi_0|\bar{H}|\phi_{\mathrm{e}}\rangle. \tag{14}$$

Thus the expectation values are given explicitly as

$$\langle\psi_0|O|\psi_0\rangle=\langle\phi_0|\bar{O}|\phi_0\rangle+\sum_{\mathrm{e}} Y_{\mathrm{e}}\langle\phi_{\mathrm{e}}|\bar{O}|\phi_0\rangle, \tag{15a}$$

where

$$\bar{O}=\exp(-T)O\exp(T). \tag{15b}$$

For an n-body operator O, the Housdorff expansion for $\bar{O}$ terminates after $2n$ commutators. Thus the expansion in Eq. (15) has finite number of terms in it. Secondly, the matrix elements Y_{e} obtained from Eq. (14) contain no unlinked terms. Consequently, the expectation values of any connected operator O as obtained from Eq. (15a) are also explicitly connected. This approach was discussed earlier by Salter et al. [12] and by Koch and Jorgensen [17] from a different point of view.

A second approach to obtain $\langle Y_0|$ is to expand it via an exponential ansatz:

$$\langle Y_0|=\langle\phi_0|\exp(\tilde{T}). \tag{16}$$

The $\tilde{T}$ amplitude satisfy the set of nonlinear simultaneous equations

$$\langle\phi_0|\exp(\tilde{T})\bar{H}\exp(-\tilde{T})|\phi_{\mathrm{e}}\rangle=0. \tag{17}$$

The expectation values are given, in this case, by

$$\langle\psi_0|O|\psi_0\rangle=\langle\phi_0|\bar{\bar{O}}|\phi_0\rangle, \tag{18a}$$

Again, by Hausdorf expansion $\bar{\bar{O}}$ also contains finite number of terms in it.

Note that the ansatz (16) for $\langle Y_0|$ is equivalent to the invocation of a double exponential wave operator to relate to the reference and exact wavefunctions:

$$|\psi_0\rangle = \exp(T)\exp(-\tilde{T})|\phi_0\rangle, \tag{19}$$

in the spirit of the extended coupled cluster method (ECCM) developed by Arponen and coworkers [18, 19]. The ECCM prescribes a variational procedure to obtain the cluster amplitudes. Consequently, the calculation of the T and $\tilde{T}$ matrix elements is coupled. The present approach differs from ECCM in that, the calculation of T matrix elements is done by solving Eq. (2b) and is thus decoupled from the calculation of the $\tilde{T}$ matrix elements which are then obtained from Eq. (17). Thus the original problem of solving for T and $\tilde{T}$ is broken down to two subproblems. Since the computational effort to solve simultaneous equations scales as N^3, we can expect the present approach to be more efficient than the ECCM. A particularly attractive feature of ECCM is that the cluster amplitudes by this theory contain infinite order sums of both upward and downward reducible diagrams to all orders [18]. The present approach, based on the normal CCM, sums up only downward reducible diagrams. To date, there have been no serious applications of ECCM to assess the importance of such generalized time ordered diagrams. On the other hand, numerical experience with the normal CCM gives the impression, that it suffices for most applications [3]. So, an approach based on Eqs. (16)–(18) might be expected to be fairly accurate.

We now compare the present method and formulations based on response functions which utilize the analytical derivatives of energy [11–13]. These approaches are based on the observation that the expectation values can be obtained as the derivatives of energy with respect to appropriate external fields. The advances made in the evaluation of analytical derivatives within the framework of CCM have made these approaches particularly popular [12, 13].

It is pertinent to note here that within the CCM framework the energy differentiation and the evaluation of expectation values do not in general lead to the same result for approximate wavefunctions, since the Hellman–Feynman theorem is valid only for exact wavefunctions or wavefunctions determined variationally in the complete functional space defined by the method. In addition to the expectation value of the operator concerned, the energy derivative contains the non-Hellman–Feynman term (non HFT)

$$\frac{2\left\langle \psi(0)|H(0)-E(0)|\left(\frac{\partial\psi(\lambda)}{\partial\lambda}\right)_{\lambda=0}\right\rangle}{\langle\psi(0)|\psi(0)\rangle}.$$

Here $\psi(\lambda)$ is the wavefunction at field strength λ. To calculate the expectation values, this term must be subtracted from the energy derivative. Noga and Urban [10] have presented a thorough analysis of this term when ψ is represented by CCM ansatz. They found that this term contains contributions from cluster operators which were not included in T. Since these terms are often quite small, the non HFT term is simply neglected. It is generally accepted that the energy derivatives provide a superior approach since it can absorb to a limited extent some deficiencies of the wavefunction. However, Noga and Urban found that the two methods give results of comparable accuracy at CCSDT level of approximation. Indeed the agreement of these two approaches can be used to assess the quality of the CCM wavefunction.

We next turn to the calculation of transition matrix elements. In one of the formulations of CCM for excited states called variously as the coupled cluster based linear response theory [15] or the Emrich formalism [16], the excited state energies are obtained by diagonalising $\bar{H}$ in the space of the hole particle excited states.

$$\bar{H}|X_I\rangle = E_I|X_I\rangle. \tag{20}$$

Transition matrix elements can thus be obtained using Eq. (11). For example, the magnitude of the transition matrix element between the ground state ψ_0 and one of the excited states ψ_I is given by

$$|\langle\psi_I|O|\psi_0\rangle| = (\langle Y_I|\bar{O}|\phi_0\rangle\langle Y_0|\bar{O}|X_I\rangle)^{1/2}. \tag{21}$$

where Y_I and X_I are the left and right eigenvectors of $\bar{H}$ corresponding to ψ_I and Y_0 is obtained from Eq. (13).

In summary, the linked cluster theorem from which the size consistency of CCM stems, leads to nonterminating serieses for expectation values and transition matrix elements. Consequently it is not practical to evaluate these quantities from a CCM ansatz directly. On the other hand, the CCM defines an intermediate effective hamiltonian $\bar{H}$ related to the original hamiltonian via a similarity transformation. The parameters of the similarity transformation (the cluster amplitudes) are chosen such that the reference determinant is the right eigenvector of $\bar{H}$. All information regarding the normalization constant of this state is then contained in the left eigenvector. Once it is obtained no infinite serieses are encountered in the calculation of expectation values. The left eigenvectors of $\bar{H}$ can be obtained either by expanding them as a linear superposition of the hole-particle states or by a second exponential operator. The former approach leads to a set of linear equations while the latter requires the solution of non-linear equations. In either case, the expressions for the expectation values would contain finite number of terms.

The methodology presented here can easily be generalised to CCM based on multi determinantal reference functions (MRCCM). Depending upon the form of the wave operator employed, MRCCM can be divided into two broad classes– Fock space [5–7] and Hilbert space [20, 21] MRCCM. Most of the applications to date are based on the Fock space approach. In this, a common wave operator is defined to relate a group of unperturbed states (spanning the model space) characterized by the projection operator P to an equal number of final states

$$\psi_I = \Omega\phi_I. \tag{22}$$

The wave operator is posited as a normally ordered exponential operator

$$\Omega = N[\exp(S)]. \tag{23}$$

The operator S induces excitations out of the model space. A model space effective hamiltonian H_{eff} is now constructed and ϕ_I are required to be its right eigenvectors

$$H_{\text{eff}}\phi_I = E_I\phi_I. \tag{24}$$

In one of the strategies adapted to obtain the cluster amplitudes S (called the similarity transformation based methods [7]), H_{eff} is defined as

$$H_{\text{eff}} = P\bar{H}P, \tag{25}$$

where,

$$\bar{H} = \Omega^{-1}H\Omega. \tag{26}$$

The cluster amplitudes are defined by requiring

$$Q\bar{H}P=0, \tag{27}$$

where Q is the projection operator on the virtual space.

Note that, Eq. (26) defines $\bar{H}$ as a similarity transformation from H. Thus the analysis of Section 2 is applicable here also. One only needs to evaluate the left eigenvectors of $\bar{H}$ to evaluate transition matrix elements between different ψ_I. Again either a linear expansion similar to Eq. (13) or a second exponential transformation similar to Eq. (16) can be used. These lead to multi-reference generalisation of Eq. (14) and Eq. (17) respectively. Once the left eigenvectors are obtained, Eq. (11), (12) can be used to obtain the transition matrix elements and expectation values.

Acknowledgements. I am grateful to Professor Dabashis Mukherjee for teaching me much of what I know of the coupled cluster method. Financial support from INSA is gratefully acknowledged.

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