Theor Chim Acta (1995) 90: 257–271

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Chimica Acta

Fock space multi-reference coupled cluster study of transition moment and oscillator strength

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Received January 10, 1994/Accepted August 17, 1994

Summary. A method of calculating transition moment and oscillator strength within the framework of the Fock space multi-reference coupled cluster method is described. Diagrammatic technique is used to obtain coupled cluster equations. The general form of equations for the transition moment between N-electron ground and excited states is obtained. MBPT analysis of the final equations is done. The excitation energies, dipole transition moments and oscillator strengths for the CH^+ molecule are calculated.

Key words: Coupled cluster method – Fock-space formalism – Excitation energies – Transition moment – Oscillator strength

1. Introduction

Coupled cluster methods (CCM [1] have been established as very convenient tools for introducing electron correlation. Extensive applications of CCM have been made in recent years to the calculation of electron correlation energies. Broadly, CCM can be classified into two distinct categories: one based on a single determinantal reference function, the other based on a multi-configurational model space. Single-reference CCM have been used very successfully for closed-shell situations. However, it has been realized that for certain cases, particularly when quasidegeneracy is involved, it is essential to start from a model space which consists of several configurations. The expanding literature [2–4] shows that both single- and multi-reference methods are taking leading positions among methods developed to describe the electron correlation effects.

While most of the attention has been focused on the electron correlation contributions to the state energies or on the energy differences, there has been recent interest in applying CCM to the studies on static and dynamic properties of molecules. A systematic treatment of these properties in a framework of CCM was proposed by Monkhorst [5]. In this approach [5, 6], suitable for calculating static first- and second-order properties as well as dynamic response functions, an explicit dependence of the CC operator on the perturbation parameter (and time – when dynamic properties are considered) is assumed. Similar formalisms were also studied in Refs. [7–10]. Arponen [11] initiated a different CC approach to the static first-order properties by employing the variational principle; this approach has been further developed by Pal [12]. We have to also mention a solution of the problem of analytical energy gradients [13] in the CC method and successful CC calculations of static properties of atomic and molecular systems performed by using a finite field perturbation approach [14]. Other attempts to apply the CC method to static electronic properties were due to Kummel [15], Mukherjee and co-workers [9, 16] and Geertsen and Oddershede [17]. Kummel [15] discussed a special form of the linked expression of expectation value. Mukherjee and co-workers extensively developed a linear-response approach. A CC-polarization propagator method was recently developed by Geertsen and Oddershede [17]. Noga and Urban [18] also studied one-electron properties in CC states. However most of the studies performed so far on the static properties have been based on a single reference function. From our experience on the CC studies of energies we expect that using a CC approach based on a multi-configurational model space for calculation of the open-shell system properties may also be essential. Such methods have been formulated by Pal [19] for response properties, and by Stolarczyk and Monkhorst [20] for expectation values and for transition properties. While the first one proposed by Pal is a kind of continuation of a response single-reference CC approach, Stolarczyk and Monkhorst developed a different idea. A characteristic feature of their method is that it enables to determine reduced density and transition matrices for the unperturbed system. Then the expectation values and the transition moments can easily be generated for any arbitrary perturbation operator. One should also mention a procedure used by Mårtenson–Pendrill [21] for calculation of the expectation value of a perturbation operator between unperturbed wave functions. Only the Mårtenson–Pendrill method has found some applications till now, but even in this case the final equations are far from being suitable for routine calculations.

Our attention has been focused on transition properties in the Fock space multi-reference coupled cluster (FSMRCC) approach. It is motivated by the fact that the FSMRCC method has been extensively applied in excitation energy calculations and the description of spectra would not be complete without transition moment or oscillator strength quantities. The paper is organized as follows. In the next section the FSMRCC theory [22, 26] is outlined. In Sect. 3 the method of Monkhorst and Stolarczyk [20] of evaluation of the first- and second-order static properties is applied to FSMRCC theory [22]. In order to give a more complete description of our approach the many-body perturbation theory (MBPT) analysis of FSMRCC equations and its diagrammatic representation is presented in Sect. 4. Finally, in Sect. 5 the theory is applied to evaluation of the excitation energies, transition moments and the oscillator strengths in CH^+. The results are compared with other methods, including full configuration interaction (FCI).

2. Theory

The nonrelativistic Hamiltonian within Born–Oppenheimer approximation is given as

$$H = \sum_i h(i) + \sum_{i>j} \frac{1}{r_{ij}}, \tag{1}$$

where the one-electron operator is defined as

$$h(i) = -\tfrac{1}{2} \nabla_i^2 - \sum_A \frac{Z_A}{r_{iA}}. \tag{2}$$

In the formalism of perturbation theory we assume the exact Hamiltonian H to be composed of two components: the zero-order H_0 and the perturbation V:

$$H = H_0 + V. \tag{3}$$

In the Møller–Pleset type of perturbation theory, we define H_0 as

$$H_0 = \sum_i f(i), \tag{4}$$

$$f(i) = h(i) + u(i), \tag{5}$$

$$f\phi_r = \varepsilon_r \phi_r \tag{6}$$

and $H\Phi_0 = E_0\Phi_0$ with Φ_0 – the Hartree–Fock antisymmetrized product of occupied spin orbitals (ϕ_r). Here $u(i)$ is an effective one-electron operator. The perturbation operator then becomes

$$V = \sum_{i>j} \frac{1}{r_{ij}} - \sum_i u(i). \tag{7}$$

In order to develop a diagrammatic approach, it is convenient to work within a second-quantized formalism. The expressions for H_0 and V then become

$$H_0 = \sum_r \varepsilon_r r^+ r, \tag{8}$$

$$V = V_2 + V_1, \tag{9}$$

$$V_2 = \frac{1}{4} \sum_{pqrs} \langle pq \| rs \rangle p^+ q^+ s r, \tag{10}$$

$$V_1 = -\sum_{pq} \langle p|u|q \rangle p^+ q, \tag{11}$$

or in the normal order

$$H_{\mathrm{N}} = H - \langle \Phi_0 | H | \Phi_0 \rangle, \tag{12}$$

$$H_{\mathrm{N}} = H_{\mathrm{N}}^0 + V_{\mathrm{N}}, \tag{13}$$

$$H_{\mathrm{N}}^0 = \sum \varepsilon_r \{r^+ r\}, \tag{14}$$

$$V_{\mathrm{N}} = V_1^{\mathrm{N}} + V_2^{\mathrm{N}}, \tag{15}$$

$$V_1^{\mathrm{N}} = \sum_{pq} \langle p | w - u | q \rangle \{p^+ q\}, \tag{16}$$

$$V_2^{\mathrm{N}} = \sum_{pq} \langle pq \| rs \rangle \{p^+ q^+ s r\}, \tag{17}$$

where the brackets { } indicate the normal order and $H_{\mathrm{N}}, H_{\mathrm{N}}^0, V_2^{\mathrm{N}}$ are normal ordered operators corresponding to the operators in Eqs. (8–11). In our case (Hartree–Fock reference function Φ_0), the one-electron potential $V_1^{\mathrm{N}} = 0$. In the Fock space multi-reference coupled cluster theory we solve the Schrödinger equation of the form

$$H_{\mathrm{N}} \Psi_{\mathrm{N}} = \Delta E_I \Psi_I, \tag{18}$$

$$\Delta E_I = E_I - E_0 \tag{19}$$

for several states I. The solution

$$\Psi_I = \Omega \Psi_I^0 = \Omega \sum_k \mathbf{C}_{I,k} \Phi_{I,k} = \Omega_I C_I \boldsymbol{\Phi}_I \tag{20}$$

is built from the multi-reference function Ψ_I^0 that is represented in a space of configurations $\{\Phi_I\}$. The space of functions is constructed from a set of active particle $(\alpha, \beta, \ldots)$/hole $(\mu, \nu, \ldots)$ creation/annihilation operators acting on the ground state (GS) wave function Φ_0. From this point of view every state Ψ_I is characterized by its multi-reference (model) wave function Ψ_I^0, expanded on the $\{\Phi_I\}$ space, and can be referred to by notation $\Psi_I^{(p,h)}$, where p refers to the number of electrons in the virtual space and h refers to the number of electrons removed from the occupied space of $\{\Phi_0\}$. The relevant reference spaces for the GS (0, 0), IP (0, 1), EA (1, 0) and EE (1, 1) cases are as follows:

$$\Phi_{\mathrm{GS}} = \Phi_0, \tag{21}$$

$$\Phi_{\mathrm{IP}} = \{\mu\}\Phi_0, \tag{22}$$

$$\Phi_{\mathrm{EA}} = \{\alpha^+\}\Phi_0, \tag{23}$$

$$\Phi_{\mathrm{EE}} = \{\alpha_+\mu\}\Phi_0, \tag{24}$$

where all active hole operators μ, and particle operators α are considered. Then, we can write the solution to the Schrödinger equation as

$$\Psi^{(0,0)} = \Omega\Psi^0_{\mathrm{GS}}, \tag{25}$$

$$\Psi^{(0,1)} = \Omega\Psi^0_{\mathrm{IP}}, \tag{26}$$

$$\Psi^{(1,0)} = \Omega\Psi^0_{\mathrm{EA}}, \tag{27}$$

$$\Psi^{(1,1)} = \Omega\Psi^0_{\mathrm{EE}}. \tag{28}$$

In this notation the GS is found in the solution of the (0, 0) problem; ionization potentials (IP) in the (0, 1) problem; electron affinities (EA) in the (1, 0) problem and excitation energies (EE) in the (1, 1) problem. In the FSMRCC, Ω is the wave universal operator. This means that the same Ω solves all eigenvalue problems.

$$\Omega = \{\exp(T^{(0,0)} + T^{(0,1)} + T^{(1,0)} + T^{(1,1)}) + \cdots\}, \tag{29}$$

where

$$T^{(0,0)} = \sum_{i,a} \langle a | T_1^{(0,0)} | i \rangle \{a^+ i\} + \frac{1}{4} \sum_{i,j,a,b} \langle ab | T_2^{(0,0)} | ij \rangle_A \{a^+ b^+ ji\} + \cdots. \tag{30}$$

a/i run over all unoccupied/occupied orbitals in Φ_0.

$$T^{(0,1)} = \sum_{i,\mu} \langle \mu | T_1^{(0,1)} | i > \{\mu^+ i\} + \frac{1}{2} \sum_{i,j,\mu,b} \langle \mu b | T_2^{(0,1)} | ij \rangle_A \{\mu^+ b^+ ji\} + \cdots, \tag{31}$$

$$T^{(1,0)} = \sum_{c,\alpha} \langle c | T_1^{(1,0)} | \alpha \rangle \{c^+ \alpha\} + \frac{1}{2} \sum_{c,d,\alpha,i} \langle cd | T_2^{(1,0)} | \alpha i \rangle_A \{c^+ d^+ i\alpha\} + \cdots, \tag{32}$$

$$T^{(1,1)} = \sum_{a,\mu} \langle \mu | T_1^{(1,1)} | \alpha \rangle \{\mu^+ \alpha\} + \frac{1}{2} \sum_{i,d,\mu,\alpha} \langle \mu d | T_2^{(1,1)} | \alpha i \rangle_A \{\mu^+ d^+ i\alpha\} + \cdots, \tag{33}$$

the indices μ, α are defined by the active holes and particles. From Eq. (18) and from the definition of the model space, inserting into the Schrödinger equation, we have

$$\Omega^{-1}H_N\Omega C_I\Phi_I = \Delta E_I C_I \Phi_I, \tag{34}$$

$$\langle \Phi_\nu | \Omega^{-1} H_N \Omega | C_I \Phi_I \rangle = C_I \Delta E_I \tag{35}$$

if we then define

$$H^{(k,l)}_{N,\text{eff}} = P^{(k,l)}(\Omega^{-1}H_N\Omega)P^{(k,l)}, \tag{36}$$

$$(H_{N,\text{eff}})^{(k,l)}_{\nu\mu} = \langle \Phi_\nu | P^{(k,l)}(\Omega^{-1}H_N\Omega)P^{(k,l)} | \Phi_\mu \rangle, \tag{37}$$

where

$$P^{(k,l)} = \sum_\mu | \Phi^{(k,l)}_\mu \rangle \langle \Phi^{(k,l)}_\mu | \tag{38}$$

is the projector onto the model space of k particles and l holes. Then,

$$C_I^{-1} H^{(k,l)}_{N,\text{eff}} C_I = \Delta E_I, \tag{39}$$

where ΔE_I is a diagonal matrix and C_I is an eigenvector which along with Ω define the wave function Ψ_I or $\Psi^{(k,l)}$. If we now define

$$Q^{(k,l)} = 1 - P^{(k,l)} = \sum_j | \Phi_j > \ < \Phi_j | \tag{40}$$

where

$$\Phi_j \neq \{\Phi^{(k,l)}_\mu\} \tag{41}$$

that is the projection operator over all function space not spanned by the model determinants, then projection by the Q-space the Bloch equation of the form

$$H_N \Omega P^{(k,l)} = \Omega H^{(k,l)}_{N,\text{eff}} P^{(k,l)} \tag{42}$$

will give us the multi-reference coupled cluster equations

$$Q^{(k,l)} \Omega H^{(k,l)}_{N,\text{eff}} P^{(k,l)} = Q^{(k,l)} H_N \Omega P^{(k,l)} \tag{43}$$

or

$$\langle \Phi^{(k,l)}_j | H_N \Omega - \Omega H^{(k,l)}_{N,\text{eff}} | \Phi^{(k,l)}_\mu \rangle = 0 \tag{44}$$

where $\Phi_j \neq \{\Phi^{(k,l)}\}$. The form of the Q-space set $\{\Phi_j\}$ will vary depending on the sector of interest. By analyzing the ansatz (29) it follows that we can write the wave operator in the following form:

$$\Omega = \{e^T\} = e^{T(0,0)}\{e^{T-T(0,0)}\} = e^{T(0,0)}\hat{\Omega}. \tag{45}$$

Making use of Eq. (45) we find that the Bloch equation (42) goes over into

$$\bar{H}\hat{\Omega}P^{(k,l)} = \hat{\Omega} H^{(k,l)}_{N,\text{eff}} P^{(k,l)}, \tag{46}$$

$$\bar{H} = [H_N e^{T(0,0)}]_C, \tag{47}$$

where

$$\bar{H}^{(k,l)}_{N,\text{eff}} = P^{(k,l)} \hat{\Omega}^{-1} \bar{H} \hat{\Omega} P^{(k,l)} \tag{48}$$

is a new effective Hamiltonian which upon diagonalization will give the energy difference, i.e. ionization energies, excitation energies, etc., and

$$Q^{(k,l)}(\bar{H}\hat{\Omega} - \hat{\Omega} H_{N,\text{eff}})^{(k,l)} P^{(k,l)} = 0 \tag{49}$$

give us the new multi-reference coupled cluster equations. Equation (48) has been derived and used by other authors (see e.g. refs. [22], [32]). Also the advantage of storing $\bar{H}$ has been noted earlier [9, 22].

The Bloch equation (46) is solved hierarchically, step by step, starting from the (0, 0) sector, using the fact that the higher valence quantities do not contribute in equations for lower valence cluster amplitudes. An advantage of the above formulation is that $\bar{H}$ has to be calculated only once. In practice, however, we only store the one and two body parts of $\bar{H}$ and calculate other parts directly.

3. First- and second-order static properties in the FSMRCC method

Let us assume that the set of eigenfunctions of H can be expressed as

$$\Psi_I = A\Phi_I, \tag{50}$$

where operator

$$A = \Omega B \tag{51}$$

is assumed to be unitary,

$$A^+A = B^+\Omega^+\Omega B = 1. \tag{52}$$

The Ω operator is the CC wave operator of the exponential form, B is the operator which results from the multi-reference character of the model space and expresses the coefficients of the linear combination of function from this space. Let us assume that operator O is a Hermitian operator representing a certain external perturbation to our many-fermion system described by Hamiltonian H. Quantity

$$O_I^J = \langle \Psi^I | O \Psi^J \rangle \tag{53}$$

is for $I = J$ called the expectation value of operator O, in a state Ψ^I, and for $I \neq J$, called the transition moment of O for states Ψ^I and Ψ^J. Below, a few examples of system properties which can be expressed in terms of integrals O_I^J are given.

Let us write the perturbed Hamiltonian for the system as

$$H(\lambda) = H + \lambda O, \tag{54}$$

where λ is a perturbation parameter. The Rayleigh–Schrödinger perturbation theory applied to the ground state of H leads to the following expansion for an eigenvalue of $H(\lambda)$:

$$E(\lambda) = E^0 + \lambda E^1 + \lambda^2 E^2 + \cdots, \tag{55}$$

where

$$E^0 = E_0, \tag{56}$$

$$E^1 = O_{\mathrm{GS}}^{\mathrm{GS}}, \tag{57}$$

$$E^2 = -\sum_{J(\neq 0)} \frac{|O^J|^2}{\Delta E^J}. \tag{58}$$

In Eqs. (56)–(58) E_0 is the ground state energy, $O_{\mathrm{GS}}^{\mathrm{GS}}$ is the expectation value of O in the eigenstate Ψ_{GS}, O^J is the transition moment of O for states Ψ_{GS} and Ψ^J, and ΔE^J is an excitation energy

$$\Delta E^J = E^J - E_0. \tag{59}$$

$E^{(1)}$ and $E^{(2)}$ correspond to first- and second-order properties of the system. In the approximation (52), the formula (53) becomes

$$\begin{aligned} O_J^I &= \langle \Phi_I | A^+ O A \Phi_J \rangle \\ &= \langle \Phi_I | A^{-1} O A \Phi_J \rangle \\ &= \langle (B^{-1})^+ \Phi_I | \Omega^{-1} O \Omega B \Phi_J \rangle. \end{aligned} \tag{60}$$

In a FSMRCC procedure however the operator A is not a unitary one and is of the form (20)

$$A' = \Omega C \tag{61}$$

and the application of formula (60) cannot be so straightforward. It can be shown [20] however that even if the operator $\Omega C_I \Phi_I$ from Eqs. (20) is not a unitary one, after some manipulations the following expressions for the expectation value and the square of the transition moment absolute value are valid:

$$O_I^I = \langle \Phi_I | (\Omega C_I)^{-1} O (\Omega C_I) \Phi_I \rangle, \tag{62}$$

$$|O_J^I|^2 = |\langle \Phi_I | (\Omega C_I)^{-1} O (\Omega C_J) \Phi_J \rangle|^2. \tag{63}$$

It is worthwhile to note a close correspondence between Eq. (63) and the CC-response expression of Koch and Jørgensen [32].

If one defines the operator

$$W = (\Omega^{-1} O \Omega)_C \tag{64}$$

and the matrix element

$$W_J^I = \langle \Phi_I | \Omega^{-1} O \Omega \Phi_J \rangle \tag{65}$$

and chooses

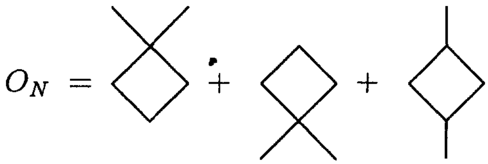
$$\Psi_I = \Psi^{(0,0)}, \tag{66}$$

$$\Psi_J = \Psi^{(1,1)}, \tag{67}$$

with the normal ordered perturbation

$$O_{\mathrm{N}} = \sum_{i,j} \langle i | r | j \rangle \{ i^+ j \} \tag{68}$$

as a one-electron dipole moment operator, which diagrammatically can be expressed as



then the transition moment between the ground state and excited states can be calculated from the expression

$$|O^J|^2 = |\langle \Phi_0 | \Omega^{-1} \mathrm{O}_{\mathrm{N}} (\Omega C_J) \Phi_J \rangle|^2 \tag{69}$$

in a matrix representation, where C^J indicates the Jth row of the matrix,

$$|\underline{O}^J|^2 = \underline{W}^J \underline{C}_J (\underline{C}^J)^{-1} \underline{W}_J, \tag{70}$$

The matrix elements $\underline{W}^J$ and $\underline{W}_J$ are

$$\underline{W}^J = \langle \Phi_{\mathrm{GS}} | W^J | \Phi_{\mathrm{EE},0} \rangle, \tag{71}$$

$$\underline{W}_J = \langle \Phi_{\mathrm{EE},0} | W_J | \Phi_{\mathrm{GS}} \rangle, \tag{72}$$

where $W^J(W_J)$ represents the connected part of $(\Omega^{-1} O \Omega)_C$ and can be divided into zero-, one-, two-particle operators

$$W = W_0 + W_1 + W_2 + \cdots . \tag{73}$$

In this application the highest particle operator considered is W_2. To be able to get transition moment amplitudes W_n one has to know the inverse of the wave operator Ω. Since Ω is the normal ordered operator the inverse of it is difficult to find. To solve this problem one can multiply Eq. (64) by Ω and gets

$$\Omega W = O\Omega. \tag{74}$$

From the power series of the exponential form of the wave operator we have

$$\left(1 + T + \frac{1}{2!}T*T + \frac{1}{3!}T*T*T + \cdots\right) W = O\left(1 + T + \frac{1}{2!}T*T + \frac{1}{3!}T*T*T + \cdots\right) \tag{75}$$

and

$$W = O + O\left(T + \frac{1}{2!}T*T + \frac{1}{3!}T*T*T + \cdots\right) - \left(T + \frac{1}{2!}T*T + \frac{1}{3!}T*T*T + \cdots\right)W. \tag{76}$$

(The sign $*$ in Eqs. (76) and (77) means that due to the normal order of the wave operator Ω, there are not contractions between coupled cluster amplitudes.) To be

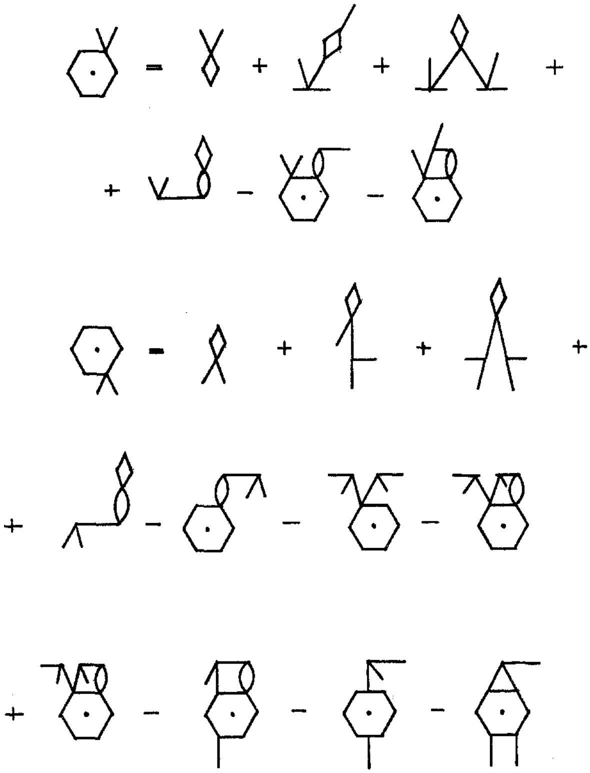


Fig. 1. W_1^{exc} and W_1^{dex} transition moment amplitudes. MRCC amplitudes are depicted by full lines

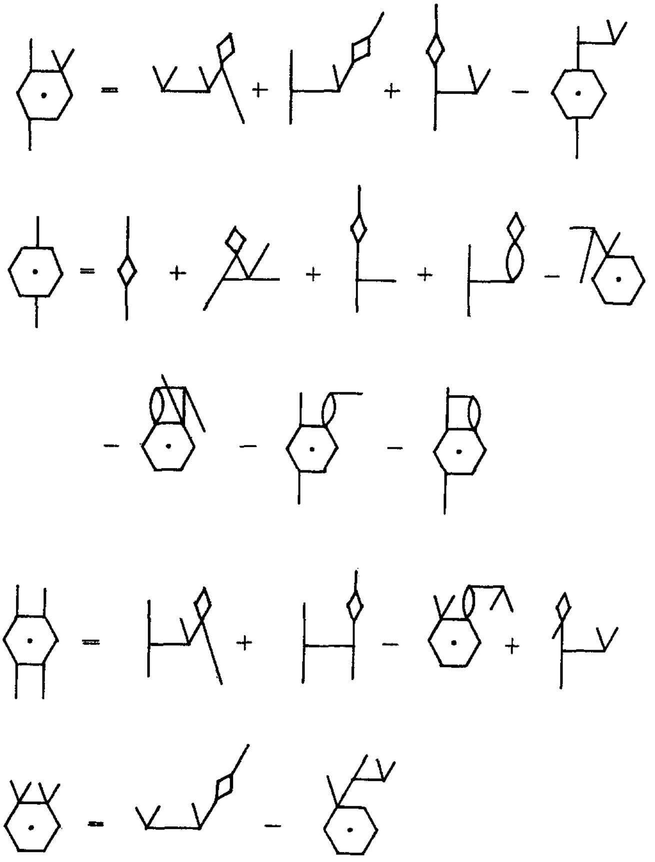


Fig. 2. The intermediate transition moment amplitudes W_1 and W_2 (see also Fig. 1)

able to get transition moment between two N-electron states (0,0) and (1,1) sectors we need W_1 excitation and deexcitation amplitudes. From diagrammatic equations presented in Figs. 1 and 2 one can see that these amplitudes depend on other W_1 and W_2 amplitudes. In consequence we get a set of linearly dependent equations which can be solved in an iterative way. Besides, in our approximations, i.e. $W = W_0 + W_1 + W_2$, $T = T_1 + T_2$, the infinite expansions in Eqs. (75) and (76) terminate.

One can see that to get transition moment amplitudes is not easy. The main reason is the presence of deexcitation amplitudes: $T_1^{(1,1)}$; $T_2^{(1,2)}$ and $T_2^{(2,1)}$; $T_2^{(2,2)}$ and the necessity to perform calculations in a higher than (1,1) sector.

4. FSMRCC theory for properties and MBPT analysis

Transition moment is the first-order property due to the external perturbation O. The diagrammatic equations (Figs. 1 and 2) show it is calculated as a sum of diagrams which are products of the matrix elements of the perturbation O and MRCC amplitudes. These amplitudes have been calculated in SD approximation and can be considered in a content of perturbation V [see Eq. (3)].

$$H(\lambda) = H_0 + \lambda V. \tag{77}$$

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

$$H(\lambda)\Omega(\lambda)P^{(k,l)} = \Omega(\lambda)H_{\text{eff}}^{(k,l)}(\lambda)P^{(k,l)}, \tag{78}$$

the universal wave operator $\Omega(\lambda)$ may be written as

$$\Omega(\lambda) = \{\exp(T(\lambda)\}. \tag{79}$$

For a model space containing k active particles and l active holes $T(\lambda)$ may be expanded as a Taylor's series consisting of the derivatives that can destroy at most k active particles and l active holes. These derivatives have to be calculated for each active hole–particle sector for open-shell systems. In this notation, we follow

$$T^{(\lambda)}_{(k,l)} = T^{(0)}_{(k,l)} + \lambda T^{(1)}_{(k,l)} + \lambda^2 T^{(2)}_{(k,l)} + \cdots. \tag{80}$$

Being universal in nature, each of the terms $T^{(\lambda)}_{(k,l)}$ may be written in terms of the cluster operators of a lower number of hole–particle sectors. The effective Hamiltonian H_{eff} corresponding to perturbed $H(\lambda)$ may also be written in terms of various order derivatives

$$H_{\text{eff}}(\lambda) = H_{\text{eff}}^{(0)} + \lambda H_{\text{eff}}^{(1)} + \lambda^2 H_{\text{eff}}^{(2)} + \cdots. \tag{81}$$

The projection of the Bloch equation to the model space and orthogonal space yields

$$P^{(k,l)}H(\lambda)\Omega(\lambda)P^{(k,l)} = P^{(k.l)}H_{\text{eff}}^{(k,l)}(\lambda)P^{(k,l)}, \tag{82}$$

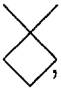
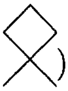
$$Q^{(k,l)}H(\lambda)\Omega(\lambda)P^{(k,l)} = Q^{(k.l)}\Omega(\lambda)H_{\text{eff}}^{(k,l)}(\lambda)P^{(k,l)}. \tag{83}$$

One can calculate the various derivatives of $H_{\text{eff}}(\lambda)$ in terms of the Fock space cluster operators and their derivatives. We will describe now how Eq. (43) may be solved in a manner that shows the connection between the MRCC and the different orders of the MBPT approaches.

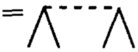
We start with the ground state, (0,0) sector, and solve Eq. (43) in an iterative manner, by performing an initial guess of $\{T^{(ab)}_{(ij)}\}$ and $\{T^a_j\}$ and then inserting these values on the right-hand side into Eq. (43) to obtain an improved set of values of $\{T^{(ab)}_{(ij)}\}$ and $\{T^a_j\}$. These are then inserted back to the right-hand side of Eq. (43) and again give us improved values of amplitudes, etc. As an initial guess of the cluster amplitudes we set those amplitudes that appear on the right-hand side of Eq. (43) equal to zero. The motivation for this choice is that the terms containing T on the right-hand side of Eq. (43) are assumed to be smaller than those on the left-hand side of this equation. Inserting these values of amplitudes into the CC expression for the total energy, we obtain the expression which is the result obtained in a second-order perturbation theory. A second iteration may be carried out by inserting into the right-hand side of Eq. (43) cluster amplitudes obtained in the first iteration. If we then neglect the terms that are quadratic in the T amplitudes, we obtain coupled cluster amplitudes that, when used to compute the energy, give the same algebraic expression as is obtained in the third-order MBPT. The iterative process carried out when determining the cluster amplitudes from Eq. (43) may be continued by inserting the cluster amplitudes from one iteration into the right-hand side of Eq. (43) to obtain the new amplitudes. The whole procedure is already very well known and a detailed description for single-reference CC had been given [31]. Similar analysis can be done for higher sectors. The pictures of this study will be simpler if we start with $\bar{H}$ expressions. By means of $T^{(\lambda)}_{(0,0)}$, the different orders of $\bar{H}^{(\lambda)}$ can be derived [31]. Following the presented idea above the PT analysis can be done for (0,1), (1,0) and (1,1) sectors.

It should be pointed out that the MRCC equations in SD approximation (similarly to the single-reference ones) are exact only till the second order of the perturbation V. The third- and the higher-order equations include T_3 and T_4 amplitudes.

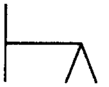
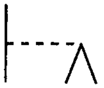
Our attention in this paper has been focused on the transition moment between the N-electron ground (0,0) and excited (1,1) states. Zero-, first-, and second-order equations on transition moment amplitudes W_1^{dex} and W_1^{exc}, necessary to calculate transition moments and oscillator strengths, have been shown in Fig. 3. Zero-order amplitudes are expressed by one-electron integrals

(, )

in Fig. 3a, b. First-order equations contain the first-order $T_2^{(2,2)}$ amplitudes (Fig. 3, d2). These contributions are rather easy to calculate:

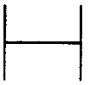
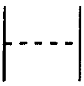
 = 

The dashed lines in the diagrams represent H_N integrals. Second-order equations (Fig. 3e, f) are slightly more difficult to get since besides the first-order $T_2^{(1,2)}$ and $T_2^{(2,1)}$ amplitudes (e3)

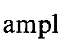
 = 

one need to calculate the second-order $T_2^{(2,2)}$ amplitudes.

The equation for the second-order $T_2^{(2,2)}$ amplitudes may be derived from Eq. (49). The formalism is more complicated now, since the equations include the unknown (0,2) and (2,0) amplitudes. Fortunately the first-order (0,2) and (2,0) amplitudes can be again expressed via simple integrals:

 = 

One can extend this analysis for higher orders. Since we work in the SD approximation, the third-order equations are not exact. Equations for the deexcitation W_1^{dex} amplitudes would contain the second-order ($T_1(1,1)$ and $T_2(2,2)$) and the third-order ($T_1^{(0,1)}$, $T_1^{(1,0)}$, $T_1^{(1,1)}$ and $T_2^{(1,1)}$ amplitudes. They are not exact as long as they do not contain T_3 amplitudes. If we would like to improve the results, then T_3 amplitudes could be, for example, included in an approximate, noniterative way using SD amplitudes.

In the present implementation we use the following approach: By the analogy to the single-reference CCSD method with $T_1^{(0,0)}$, and $T_2^{(0,0)}$, (, ) amplitudes we have taken into account $T_1^{(0,0)}, T_2^{(0,0)}, T_1^{(0,1)}, T_1^{(1,0)}, T_2^{(0,1)}, T_2^{(1,0)}$, $T_2^{(1,1)}$ excitations and $T_1^{(1,1)}, T_2^{(2,2)}$, (, ) deexcitation amplitudes. In this way we get zero- to fourth- and higher-order expressions, but PT analysis

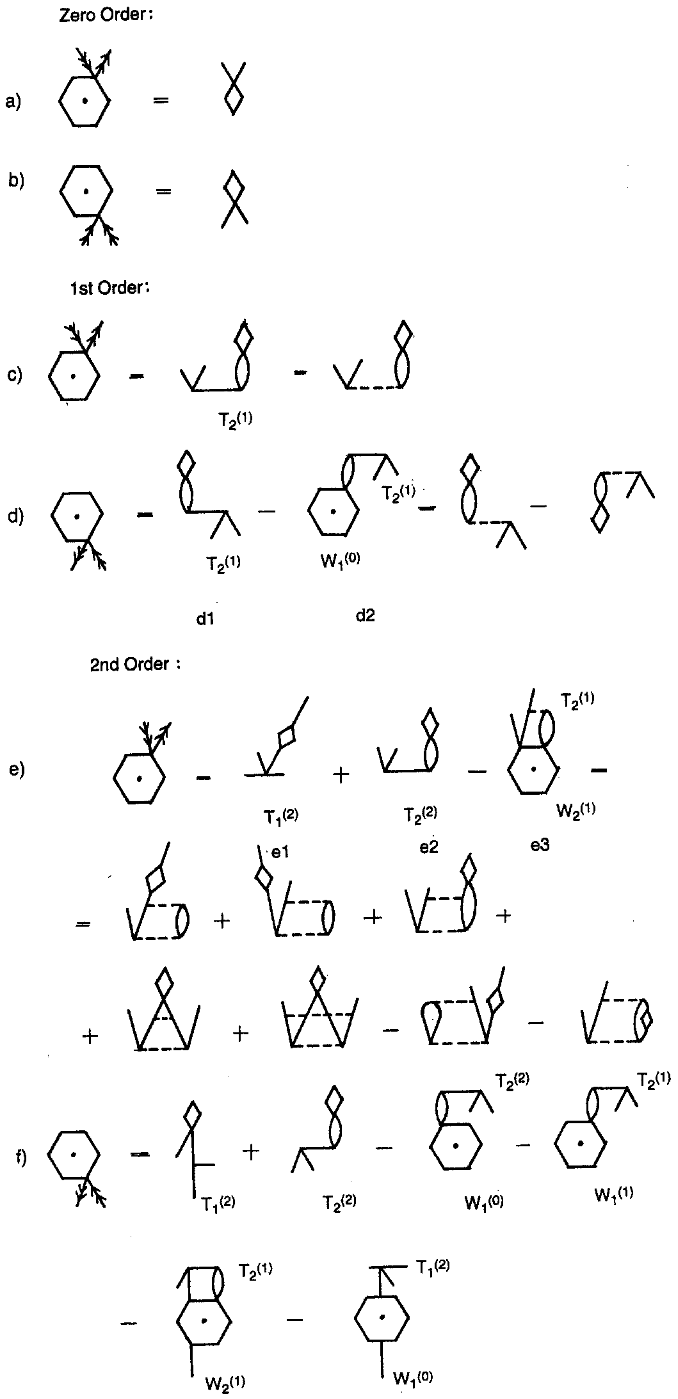

Zero Order:
a)
b)
1st Order:
c)
T2(1)
d)
T2(1)
T2(1)
W1(0)
d1
d2
2nd Order :
e)
T2(1)
T1(2)
T2(2)
W2(1)
e1
e2
e3
f)
T2(2)
T2(1)
T1(2)
T2(2)
W1(0)
W1(1)
T2(1)
T1(2)
W2(1)
W1(0)

Fig. 3.

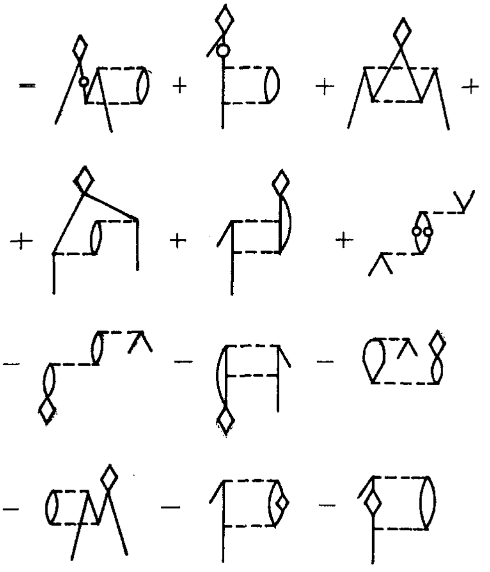


Fig. 3. Zero-, first-, and second-order equations for the amplitudes necessary to calculate the transition moments and oscillator strengths from the ground (0, 0) to the excited (1,1) states. One- and two-body parts of H_N are represented by dashed lines, the active lines by double arrows and the non active by circles (see also Fig. 1)

shows that several diagrams are omitted. We have also seen that the equation can be improved, without too large a computational effort, by including first-order amplitudes from higher sectors (0,2), (2,0), (1,2) and (2,1). Then one can get exact second-order transition moment, almost complete third-order (even without T_3) and a lot of higher-order terms not shown here. We will develop the method in this direction.

5. Applications

Here we present results for the CH$^+$ molecule. Our attention is focused mainly on two quantities: transition moment and oscillator strength in dipole representation. The oscillator strength in this representation is defined as

$$\tfrac{2}{3} * |\textit{transition moment}|^2 * \textit{excitation energy} \tag{84}$$

and depends on excitation energies and transition moment. The CH$^+$ calculations have been carried out at an internuclear distance of 2.13713 a.u. and using the basis given in [25]. For carbon atom a split valence basis set was used augmented with two diffuse *s* and *p* functions and one *d* polarization function. For hydrogen the 2*s* basis set was augmented with one diffuse *s* function and one *p* polarization function. The basis set contains a total of 26 Gaussian orbitals. CH$^+$ has a ground state electronic configuration $1\sigma^2 2\sigma^2 3\sigma^2$ and a large nondynamical correlation contribution originating from the $1\sigma^2 2\sigma^2 2\pi^2$ configuration. Table 1 reports FSMRCC and FCI calculations of excitation energies from the CH$^+$ $X^1\Sigma^+$ ground state to the lowest states of $^1\Pi$ symmetry and appropriate transition moments and oscillator strengths. We also make a comparison to TDA, RPA and MCLR calculations performed in the same basis set. The comparison with available experimental results has been done too. The lowest state of $^1\Pi$ symmetry has an electronic configuration $1\sigma^2 2\sigma^2 3\sigma^1 1\pi^1$ and excitation to this state has a dominant single replacement nature. Since the model space in the (1,1) sector of

Table 1. Excitation energies, transition moments and oscillator strengths with respect to ${}^1\Sigma^+$ and ${}^1\Pi_x$ states in the dipole length approximation for the TDA, RPA, MCLR, FSMRCC and FCI excitations

Method	Excitation energy (eV)	Transition moment (a.u.)	Oscillator strength (a.u.)
TDA[a]	2.926	0.441	0.014
RPA[b]	2.650	0.331	0.007
MCLR[b]	3.230	0.300	0.007
FSCC	3.241	0.243	0.005
FCI[b]	3.320	0.299	0.007
Exp.	3.07[c]	—	(0.00566 ∓ 0.0002)[d]
TDA[a]	15.231	− 1.081	0.436
RPA[b]	14.841	0.944	0.324
MCLR[b]	14.197	0.799	0.222
FSCC	15.005	0.700	0.180
FCI[b]	14.127	0.767	0.214

[a] Ref. [27]
[b] Ref. [25]
[c] Ref. [28]
[d] Ref. [29]

FSMRCC has been created by single excited configurations too, one should expect good excitation energies. The agreement with FCI is very good. The energies obtained in a small active space are of the same quality as of the MCLR method and much better than those obtained in RPA and TDA calculations. Transition moment and oscillator strength, which are rather small quantities, are well reproduced too.

The second state of ${}^1\Pi$ symmetry is dominated by higher excited configurations. Then, it is not surprising that the FSMRCC method gives bad excitation energies. Similar behavior can be observed in RPA and TDA. However, the FSMRCC method, which is optimized for several states at the same time, gives much better transition moment and oscillator strength in comparison to others. It means that the quality of the wave function is not bad. The MCLR method gives better numbers but, again, rather a big model space has been used.

Conclusions

We have presented the method of calculating expectation values and transition moments within the framework of the Fock space coupled cluster method. We have shown the excitation energies, transition moments and dipole oscillator strengths for the CH^+ molecule and have made a comparison with the TDA, RPA, MCLR and FCI methods. If one realizes that the method describes several states at the same time, the agreement with FCI is quite good. More advanced studies have been performed on the example of the O_3 molecule [26] which confirmed the conclusions. The final results are promising. Only the deexcitation amplitudes $T_1^{(1,1)}$ and $T_2^{(2,2)}$ have been calculated, but they both appear in considered N-electron states. We are aware of the fact that the results have to be improved and it will be a part of our next work.

We would like to emphasize that the transition moment amplitudes have been fast and well converged. Once the energy is given, the oscillator strength in fast calculations can be achieved.

Acknowledgements. The author would like to thank very much R. J. Bartlett for the inspiration to do the work and for valuable discussions. The author would also like to thank L. Stolarczyk for many comments and suggestions. This work has been supported by the US Office of Naval Research ONR-N00014-91-J-1282 and by the Polish KBN, contract no. 2 P303 10407.

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