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Some aspects of the time-dependent coupled-cluster approach to dynamic response functions

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An approximation scheme for dynamic response functions within the coupled cluster or exp(T) method of Coester and Kümmel is described in this paper. Particular attention is given to the relationship between the "vacuum amplitude" $\langle 0 | U(t,-\infty) | 0 \rangle$ for the time development of an exact eigenstate of a many-electron Hamiltonian in the presence of an adiabatically switched-on perturbation, and the amplitude $\langle \Phi_0 | U(t,-\infty) | 0 \rangle$ for the time evolution into an independent-particle reference state $|\Phi_0\rangle$, which is not orthogonal to $|0\rangle$. The latter amplitude plays a prominent role in the time-dependent coupled-cluster calculation of response functions.

I. INTRODUCTION

The coupled-cluster or exp(T) approach to the many-fermion correlation problem[1] has by now become recognized as a viable alternative to current methods in electronic structure theory. A number of encouraging results have been obtained in molecular physics, the theory of Fermi liquids, and the electron gas. We refer the reader to a comprehensive review of Kümmel *et al.*[2] for an account on these developments.

Atomic and molecular applications were initiated by Cizek, Paldus, and Shavitt.[3] The algebraic structure of the highly nonlinear coupled-cluster equations, originated by Coester,[1] was examined in a series of papers by Harris[4] and Zivković and Monkhorst.[5,6] Recently accurate potential-energy—surface calculations for small molecules have been published.[7–9]

Most coupled-cluster calculations made so far have dealt with the ground-state correlation problem, but methods for excited states have been suggested. Harris[4] discussed the calculation of a manifold of states which are not orthogonal to a common independent-particle reference state. A formalism suggested by Emrich[10] can be applied to arbitrary excited states. However, both of these procedures suffer from the drawback that transition moments between excited states and the ground state are difficult to obtain.

One of the main advantages of a response function approach is that transition moments and energies are obtained simultaneously. The physical significance of the linear response functions, which we shall consider in this paper, is that the expectation value $\langle \psi | O | \psi \rangle$ in the presence of an adiabatically switched-on perturbation

$$W(t)=(Ve^{i\omega t}+V^{\dagger}e^{-i\omega t})e^{\alpha t} \quad (\alpha>0) \tag{1}$$

can be expressed in terms of them as[11,12]

$$\langle \psi | O | \psi \rangle = \langle 0 | O | 0 \rangle + \langle\langle O;V^{\dagger} \rangle\rangle_{\omega+i\alpha}\exp[-i(\omega+i\alpha)t] + \langle\langle O;V \rangle\rangle_{-\omega+i\alpha}\exp[-i(-\omega+i\alpha)t] + \cdots . \tag{2}$$

A derivation of the response function $\langle\langle O;V \rangle\rangle$ using Eq. (2) requires an evaluation of the time-dependent density matrices, a notoriously difficult task within the coupled-cluster method, unless one is satisfied with a perturbation expansion up to certain order in the electron-electron interaction. Mukherjee and his collaborators circumvented this problem by adding terms to the time-independent Hamiltonian H_0 which describe the coupling between photons and matter.[13] A calculation of the second-order energy corrections as a function of photon energy then provides information on the response functions.

A time-dependent coupled-cluster formalism aiming directly at the calculation of response functions has been suggested by one of us.[6] Similar methods have been introduced by other authors in nuclear and solid-state physics for various dynamical problems.[14,15] The purpose of this

paper is to examine the formal aspects of time-dependent coupled-cluster theory and its connection with adiabatic perturbation theory[16] and Green's-function methods.[17] The basic idea is to exploit a frequency-dependent level-shift function, which emerges naturally when the Coester-Kümmel projection technique is employed to solve the time-dependent coupled-cluster equations. This level-shift function contains information about dynamic response functions but the identification of these requires some results from adiabatic perturbation theory. These are briefly reviewed in Sec. II. The coupled-cluster response theory is then described in Sec. III and the response functions are analyzed with regard to poles and residues, i.e., transition energies and transition moments. Concluding remarks are stated in Sec. IV.

II. ADIABATIC PERTURBATION THEORY

A few results from adiabatic perturbation theory will be summarized here in a form which is suitable for the application to time-dependent coupled-cluster theory. For details the reader is referred to, e.g., the text by Fetter and Walecka.[6]

We start by considering the time evolution of the exact ground state, $|0\rangle$, which we assume to be nondegenerate:

$$H_0|0\rangle = |0\rangle E_0, \quad \langle 0|0\rangle = 1 . \tag{3}$$

A formal solution to the time-dependent Schrödinger equation

$$\left[H_0 + W - i\frac{d}{dt}\right]|\psi\rangle = 0 \tag{4}$$

corresponding to the initial condition

$$\lim_{t\to-\infty} |\psi(t)\rangle \exp(iE_0 t) = |0\rangle \tag{5}$$

can be expressed as

$$\begin{aligned}|\psi\rangle &= U(t,-\infty)|0\rangle \\ &= \sum |m\rangle \exp(-iE_m t)\langle m|U_I(t,-\infty)|0\rangle ,\end{aligned} \tag{6}$$

where we have introduced the spectral representation for the unperturbed evolution operator $\exp(-iH_0 t)$. U_I denotes the evolution operator in the interaction representation

$$U_I(t,-\infty) = 1 - i\int_{-\infty}^{t} W_I(s)U_I(s,-\infty)ds . \tag{7}$$

Following a suggestion by Langhoff *et al.*[18] we write Eq. (6) as

$$|\psi\rangle = \left[|0\rangle + \sum_{m\neq 0} |m\rangle a_m\right]\langle 0|U|0\rangle . \tag{8}$$

The matrix element $\langle 0|U|0\rangle$ is often called the vacuum amplitude. It is related to the complex level-shift function, ϕ, through the definition

$$\langle 0|U(t,-\infty)|0\rangle = \exp\left[-iE_0 t - i\int_{-\infty}^{t}\phi(s)ds\right] . \tag{9}$$

It is well known that so-called secular divergencies occur in connection with integrations over infinite time intervals in the limit $\alpha\to 0$. The advantage of introducing the forms (8) and (9) is that the coefficients a_m and the function ϕ are regular and the limit $\alpha\to 0$ can be determined provided that $\pm p\omega \neq \omega_{m0}$ for all m and all integers p.[18,19]

In perturbation theory one assumes that an expansion in powers of W can be made such that

$$\phi(s) = \phi_1(s) + \phi_2(s) + \phi_3(s) + \cdots . \tag{10}$$

By introducing Eqs. (7) and (10) on the left- and right-hand side of Eq. (9), respectively, explicit expressions are obtained for the low-order function ϕ:

$$\phi_1(s) = \sum_j \langle 0|V_j|0\rangle \exp[i(\omega_j - i\alpha)s] , \tag{11}$$

$$\phi_2(s) = -\sum_{\substack{j,j',\\ m}} \frac{\langle 0|\tilde{V}_j|m\rangle\langle m|\tilde{V}_{j'}|0\rangle}{\omega_{j'} - i\alpha + \omega_{m0}} \exp[i(\omega_j + \omega_{j'} - 2i\alpha)s] , \tag{12}$$

$$\phi_3(s) = \sum_{\substack{j,j',\\ m,m'}} \frac{\langle 0|\tilde{V}_j|m\rangle\langle m|\tilde{V}_{j'}|m'\rangle\langle m'|\tilde{V}_{j''}|0\rangle \exp[i(\omega_j + \omega_{j'} + \omega_{j''} - 3i\alpha)s]}{(\omega_{j'} + \omega_{j''} - 2i\alpha + \omega_{m0})(\omega_{j''} - i\alpha + \omega_{m'0})} . \tag{13}$$

An extra label $j = 1$ or 2, has been introduced to distinguish between V and $V^\dagger$, and ω and $-\omega$ as follows:

$$\begin{aligned} V_1 &= V, \quad \omega_1 = \omega , \\ V_2 &= V^\dagger, \quad \omega_2 = -\omega . \end{aligned} \tag{14}$$

Furthermore, we have defined $\tilde{V}_j$ as

$$\tilde{V}_j = V_j - \langle 0|V_j|0\rangle \tag{15}$$

so that the sums (11)–(13) do not contain any term with m or $m' = 0$.

Our interest in the level-shift function ϕ arises from its connection with response functions. For frequencies ω away from resonance the most important identity is

$$\lim_{\alpha\to 0}(\omega/2\pi)\int_0^{2\pi/\omega}\phi_2(s)ds=\langle\langle V;V^\dagger\rangle\rangle_\omega$$
$$=\sum_{m\neq 0}\left[\frac{\langle 0\mid V\mid m\rangle\langle m\mid V^\dagger\mid 0\rangle}{\omega-\omega_{m0}}-\frac{\langle 0\mid V^\dagger\mid m\rangle\langle m\mid V\mid 0\rangle}{\omega+\omega_{m0}}\right], \tag{16}$$

where $\omega_{m0}=E_m-E_0$. Equation (12) shows that for Hermitian operators $V=V^\dagger$, we also have the identity

$$\frac{\phi_2(0)}{2}=\sum_m|\langle 0\mid\tilde{V}\mid m\rangle|^2\left[\frac{1}{\omega-\omega_{m0}+i\alpha}-\frac{1}{\omega+\omega_{m0}-i\alpha}\right], \tag{17}$$

where the singularities are shifted below and above the real axis, as in the Fourier transform of the causal two-time Green's function.[20]

More generally, nonlinear response functions of even order in V and $V^\dagger$ can be derived from integrals of the type

$$\int_0^{2\pi/\omega}\phi_{2k}(s)ds,\quad k=2,3,\ldots. \tag{18}$$

The odd order terms of the perturbation expansion for the level-shift function vanish in the average over one period. Odd order response functions can be deduced from $\phi_{2k+1}(0)$ and from integrals of the type

$$\int_0^{2\pi/\omega}\exp(ip\omega s)\phi_{2k+1}(s)ds \tag{19}$$

but these response functions will not be discussed here. Instead, we proceed to analyze the amplitudes

$$a_m(t)=\frac{\langle m\mid U(t,-\infty)\mid 0\rangle}{\langle 0\mid U(t,-\infty)\mid 0\rangle}$$
$$=\exp(i\omega_{0m}t)\frac{\langle m\mid U_I\mid 0\rangle}{\langle 0\mid U_I\mid 0\rangle}$$
$$\equiv b_m(t)\exp(i\omega_{0m}t)\,. \tag{20}$$

The amplitudes $b_m(t)$ satisfy the differential equations

$$i\frac{db_m(t)}{dt}=\langle m\mid W_I(t)\mid 0\rangle+\sum_{m'\neq 0}[\langle m\mid W_I(t)\mid m'\rangle-\delta_{mm'}\phi(t)]b_{m'}(t) \tag{21}$$

with the initial condition

$$\lim_{t\to-\infty}b_m(t)=0\,. \tag{22}$$

Equations (21) and (22) are direct consequences of Eq. (7). In order to solve Eq. (21) we again introduce a perturbation expansion for b_m or equivalently for a_m as

$$a_m=a_m^1+a_m^2+\cdots,\qquad \lim_{t\to-\infty}a_m^k(t)=0\,. \tag{23}$$

Explicit expressions for the first- and second-order amplitudes are (for $m\neq 0$)

$$a_m^1(t)=-\sum_{j,m}\frac{\langle m\mid V_j\mid 0\rangle\exp[i(\omega_j-i\alpha)t]}{\omega_j-i\alpha+\omega_{m0}}\,, \tag{24}$$

$$a_m^2(t)=\sum_{\substack{j,j',\\ m'}}\frac{\langle m\mid\tilde{V}_j\mid m'\rangle\langle m'\mid\tilde{V}_{j'}\mid 0\rangle\exp[i(\omega_j+\omega_{j'}-2i\alpha)t]}{(\omega_j+\omega_{j'}-2i\alpha+\omega_{m0})(\omega_{j'}-i\alpha+\omega_{m'0})}\,. \tag{25}$$

There are two basic properties of the coefficents a_m^k which we shall need in the following. First, the function a_m^k is regular in the limit $\alpha\to 0$ provided that

$$\pm p\omega\neq\omega_{m'0} \tag{26}$$

for all m' and $p\in\{1,2,\ldots,k\}$. Second, the limit

$$\lim_{\alpha\to 0}a_m^k(t) \tag{27}$$

is periodic as a function of t with the period $2\pi/\omega$.

III. TIME-DEPENDENT COUPLED-CLUSTER METHOD

In this section we shall describe the connection between the adiabatic perturbation theory and the time-dependent coupled-cluster approach to dynamic response functions suggested previously by one of us.[6] We start by a brief review of the static Coester-Kümmel equation in order to introduce the necessary notations.

Let $|\phi_0\rangle$ denote an independent particle reference state, which is not orthogonal to the exact ground state, for an N-electron system. The set of all particle-hole and multiple-hole excitations will be denoted by

$$\{q_\nu^\dagger\mid\nu=1,2,\ldots,D\} \tag{28}$$

where $D=\binom{M}{N}-1$ for a finite-basis-set approximation with M spin orbitals. Some of the basic properties of these operators are

$$q_\nu|\phi_0\rangle=0,\quad\langle\phi_0|q_\nu q_{\nu'}^\dagger|\phi_0\rangle=\delta_{\nu\nu'}\,,\qquad [q_\nu^\dagger,q_{\nu'}^\dagger]=0\,, \tag{29}$$

and the fact that the manifold of states

$$\{\,|\phi_0\rangle,\ q_\nu^\dagger|\phi_0\rangle\} \tag{30}$$

form an orthogonal basis for the linear space in which an approximate solution to the Schrödinger equation is sought.

The coupled-cluster ansatz for the ground state is

$$|0\rangle=\exp(T_0)|\phi_0\rangle N_0,\quad T_0=\sum_{\nu=1}^{d} q_\nu^\dagger T_\nu^0\quad (d\le D)\ , \tag{31}$$

where N_0 is a normalization constant and T_0 is the cluster generator, which is a linear combination of a subset of excitation operators. Introducing (31) into the Schrödinger equation, multiplying by $\exp(-T_0)$ and projecting onto the subspace spanned by

$$\{\,|\phi_0\rangle,\ q_\nu^\dagger|\phi_0\rangle\,|\,\nu=1,\ldots,d\} \tag{32}$$

we obtain a set of nonlinear equations for the amplitudes T_ν^0 and an expression for the total energy:

$$\langle\phi_0|\,q_\nu\exp(-T_0)H_0\exp(T_0)|\phi_0\rangle=0\ , \tag{33}$$

$$E_0=\langle\phi_0|\exp(-T_0)H_0\exp(T_0)|\phi_0\rangle\ . \tag{34}$$

Currently, we assume that Eqs. (33) and (34) have been solved.

For a system in the presence of an external perturbation given by Eq. (1) Monkhorst[6] suggested the form

$$\begin{aligned}|\psi\rangle&=\exp(T)|0\rangle\exp(-iE_0t-i\epsilon)\\&=\exp(T+T_0)|\phi_0\rangle N_0\exp(-iE_0t-i\epsilon)\ ,\end{aligned} \tag{35}$$

where

$$T=\sum_{\nu=1}^{d} T_\nu q_\nu^\dagger\ . \tag{36}$$

The amplitudes T_ν and the parameter ϵ are now time dependent. They are to be determined from the time-dependent Schrödinger equation, which after multiplication by $\exp(-T-T_0)$ and a projection onto the subspace spanned by the set (32) takes the form

$$\frac{d\epsilon}{dt}=\langle\phi_0|\exp(-T_0-T)(H_0+W-E_0)\exp(T_0+T)|\phi_0\rangle\ , \tag{37}$$

$$i\frac{dT_\nu}{dt}=\langle\phi_0|\,q_\nu\exp(-T_0-T)(H_0+W)\exp(T_0+T)|\phi_0\rangle\ . \tag{38}$$

These equations should be solved with the initial conditions

$$\lim_{t\to-\infty}\epsilon(t)=\lim_{t\to-\infty}T_\nu(t)=0\ . \tag{39}$$

Before describing the perturbative solution to Eqs. (37) and (38), let us examine the relationship between the vacuum amplitude and ϵ. It follows from Eqs. (8), (9), and (35) that

$$\begin{aligned}\langle\phi_0|\psi\rangle&=\langle\phi_0|U(t,-\infty)|0\rangle\\&=\left[\langle\phi_0|0\rangle+\sum_{m\neq0}a_m\langle\phi_0|m\rangle\right]\\&\quad\times\exp\left[-iE_0t-i\int_{-\infty}^{t}\phi(s)ds\right]\\&\equiv\exp(-iE_0t-i\epsilon+\ln N_0)\end{aligned} \tag{40}$$

Thus we find that

$$\epsilon=\int_{-\infty}^{t}\phi(s)ds+i\ln\left[1+\sum_{m\neq0}\langle\phi_0|m\rangle(a_m/N_0)\right] \tag{41}$$

since $N_0=\langle\phi_0|0\rangle$, as can be seen from Eq. (31). The logarithm on the right-hand side of this equation is spurious and not simply related to response functions. To remove this part we consider the average level shift

$$\left[\epsilon\left[\frac{2\pi}{\omega}\right]-\epsilon(0)\right]\frac{\omega}{2\pi}=\frac{\omega}{2\pi}\int_0^{2\pi/\omega}\phi(s)ds+\frac{i\omega}{2\pi}\ln x\ , \tag{42}$$

where

$$x=1+\frac{\sum_{m\neq0}\langle\phi_0|m\rangle[a_m(2\pi/\omega)-a_m(0)]}{N_0+\sum_{m\neq0}\langle\phi_0|m\rangle a_m(0)}\ . \tag{43}$$

It follows from the results of the preceding section that

$$\lim_{\alpha\to0}x=1 \tag{44}$$

because the coefficients a_m become regular, periodic functions with period $2\pi/\omega$ in the limit $\alpha\to0$, when $\pm p\omega\neq\omega_{m0}$ for all integers p and m. For each term in the perturbation expansion

$$\epsilon=\epsilon_1+\epsilon_2+\cdots \tag{45}$$

we then have the identity

$$\begin{aligned}\lim_{\alpha\to0}\left[\epsilon_k\left[\frac{2\pi}{\omega}\right]-\epsilon_k(0)\right]&=\lim_{\alpha\to0}\int_0^{2\pi/\omega}\frac{d\epsilon_k(s)}{ds}ds\\&=\lim_{\alpha\to0}\int_0^{2\pi/\omega}\phi_k(s)ds\ .\end{aligned} \tag{46}$$

Linear response functions, in particular, can be calculated as

$$\langle\langle V;V^\dagger\rangle\rangle_\omega=\lim_{\alpha\to0}\frac{\omega}{2\pi}\int_0^{2\pi/\omega}\frac{d\epsilon_2(s)}{ds}ds\ . \tag{47}$$

In the remaining part of this section we shall discuss the calculation $d\epsilon_2/ds$ by matrix methods. First, we introduce a perturbation expansion for the operator T in (36) as

$$T=T_1+T_2+\cdots\ , \tag{48}$$

$$\begin{aligned}T_1&=\sum_\nu X_\nu q_\nu^\dagger\ ,\\T_2&=\sum_\nu Y_\nu q_\nu^\dagger\ .\end{aligned} \tag{49}$$

Differential equations for the first- and second-order coef-

ficients X_ν and Y_ν, and for the level shifts $d\epsilon_1/dt$ and $d\epsilon_2/dt$ are obtained from Eqs. (37) and (38) as

$$i\frac{dX_\nu}{dt}=\sum_{\nu'}A_{\nu\nu'}X_{\nu'}+B_\nu\ , \tag{50}$$

$$\frac{d\epsilon_1}{dt}=\langle\hat{W}\rangle+\langle[\hat{H}_0,T_1]\rangle\ , \tag{51}$$

$$i\frac{dY_\nu}{dt}=\sum_{\nu'}A_{\nu\nu'}Y_{\nu'}+C_\nu\ , \tag{52}$$

$$\frac{d\epsilon_2}{dt}=\langle[\hat{H}_0,T_2]\rangle+\langle[\hat{W},T_1]\rangle+\tfrac{1}{2}\langle[[\hat{H}_0,T_1],T_1]\rangle\ . \tag{53}$$

Several definitions have been introduced here in order to simplify the notation. Average values are with regard to the independent particle state $|\phi_0\rangle$, i.e., $\langle O\rangle \equiv\langle\phi_0|O|\phi_0\rangle$. Transformed operators $\hat{O}$ are defined as

$$\hat{O}=\exp(-T_0)O\exp(T_0) \tag{54}$$

and the matrices A, B, and C are given by

$$A_{\nu\nu'}=\langle q_\nu[\hat{H}_0,q_{\nu'}^\dagger]\rangle=\langle q_\nu\hat{H}_0q_{\nu'}^\dagger\rangle-\delta_{\nu\nu'}E_0\ , \tag{55}$$

$$B_\nu=\langle q_\nu\hat{W}\rangle\ , \tag{56}$$

$$C_\nu=\langle q_\nu[\hat{W},T_1]\rangle+\tfrac{1}{2}\langle q_\nu[[\hat{H}_0,T_1],T_1]\rangle\ . \tag{57}$$

It follows from Eq. (1) that

$$B_\nu=B_\nu^+\exp[i(\omega-i\alpha)t]+B_\nu^-\exp[i(-\omega-i\alpha)t]\ , \tag{58}$$

where

$$B_\nu^+=\langle q_\nu\hat{V}\rangle,\quad B_\nu^-=\langle q_\nu\hat{V}^+\rangle\ . \tag{59}$$

It should be noted that $\hat{V}^+=\exp(-T_0)V^\dagger\exp(T_0)$ is not the adjoint of $\hat{V}$. Then we see from Eq. (50) that X_ν can be expressed as

$$X_\nu=X_\nu^+\exp[i(\omega-i\alpha)t]+X_\nu^-\exp[i(-\omega-i\alpha)t]\ , \tag{60}$$

where

$$X_\nu^\pm=\sum_{\nu'}[(\mp\omega+i\alpha)1-A]^{-1}_{\nu\nu'}B_{\nu'}^\pm\ . \tag{61}$$

In order to calculate the second-order coefficients Y_ν from Eq. (52) we first write the matrix elements C_ν as

$$C_\nu=C_\nu^+\exp[2i(\omega-i\alpha)t]+C_\nu^0\exp(2\alpha t)+C_\nu^-\exp[2i(-\omega-i\alpha)t]\ , \tag{62}$$

where

$$C_\nu^0=\sum_{\nu'}(\langle q_\nu[\hat{V},q_{\nu'}^\dagger]\rangle X_{\nu'}^-+\langle q_\nu[\hat{V}^+,q_{\nu'}^\dagger]\rangle X_{\nu'}^+)+\sum_{\nu',\nu''}\langle q_\nu[[\hat{H}_0,q_{\nu'}^\dagger],q_{\nu''}^\dagger]\rangle X_{\nu'}^+X_{\nu''}^-\ . \tag{63}$$

Similar expressions hold for $C_\nu^\pm$. Equations (52) and (62) now show that Y_ν can be written

$$Y_\nu=Y_\nu^+\exp[2i(\omega-i\alpha)t]+Y_\nu^0\exp(2\alpha t)+Y_\nu^-\exp[2i(-\omega-i\alpha)t]\ , \tag{64}$$

$$Y_\nu^\pm=\sum_{\nu'}\{[2(\mp\omega+i\alpha)\underline{1}-\underline{A}]^{-1}\}_{\nu\nu'}C_{\nu'}^\pm\ ,$$

$$Y_\nu^0=\sum_{\nu'}\{[2i\alpha\underline{1}-\underline{A}]^{-1}\}_{\nu\nu'}C_{\nu'}^0\ . \tag{65}$$

We are now prepared to set up a closed expression for the coupled-cluster response function as

$$\lim_{\alpha\to0}\frac{\omega}{2\pi}\int_0^{2\pi/\omega}ds\frac{d\epsilon_2}{ds}=\sum_\nu(\langle\hat{V}q_\nu^\dagger\rangle X_\nu^-+\langle\hat{V}^+q_\nu^\dagger\rangle X_\nu^+)+\sum_\nu\langle\hat{H}_0q_\nu^\dagger\rangle Y_\nu^0+\sum_{\nu,\nu'}\langle\hat{H}_0q_\nu^\dagger q_{\nu'}^\dagger\rangle X_\nu^+X_{\nu'}^-\ . \tag{66}$$

The limit $\alpha\to0$ can here be taken without difficulty provided that the ground state is nondegenerate and provided that neither $\pm\omega$ nor $\pm2\omega$ equal any of the resonance frequencies. Using Eq. (63) to eliminate Y_ν^0, we finally get the result that

$$\langle\langle V;V^\dagger\rangle\rangle_\omega=\sum_\nu(D_\nu^-X_\nu^++D_\nu^+X_\nu^-)+\sum_{\nu,\nu'}F_{\nu\nu'}X_\nu^+X_{\nu'}^-\ , \tag{67}$$

where

$$F_{\nu\nu'}=\langle\hat{H}_0q_\nu^\dagger q_{\nu'}^\dagger\rangle-\sum_{\mu,\mu'}\langle\hat{H}_0q_\mu^\dagger\rangle(\underline{A}^{-1})_{\mu\mu'}\langle q_{\mu'}[[\hat{H}_0,q_\nu^\dagger]q_{\nu'}^\dagger]\rangle\ , \tag{68}$$

$$D_\nu^+=\langle\hat{V}q_\nu^\dagger\rangle-\sum_{\mu,\mu'}\langle\hat{H}_0q_\mu^\dagger\rangle(\underline{A}^{-1})_{\mu\mu'}\langle q_{\mu'}[\hat{V},q_\nu^\dagger]\rangle\ . \tag{69}$$

A similar expression for D_ν^- is obtained by replacing V by $V^\dagger$.

The transition frequencies are given by the roots of the determinant

$$|E\underline{1}-\underline{A}|=0\ . \tag{70}$$

The matrix $\underline{A}$ is not Hermitian and we cannot, in general, be sure that $\underline{A}$ can be diagonalized. All matrices can, however, be brought to Jordan's normal form by a similarity transformation

$$\underline{A}=\underline{S}\,\underline{\Omega}\,\underline{S}^{-1}\ . \tag{71}$$

We assume here that all Segrè characteristics of $\underline{A}$ are equal to one, since it would otherwise be impossible to express the spectral representation for $\langle\langle V;V^\dagger\rangle\rangle_\omega$ in the correct form, where all poles are of first order. An occurrence of Segrè characteristics of higher order is a pathological case, which should be cured by changing (extending) the subset of operators, which are employed in the coupled-cluster calculation. Thus we assume that Ω is a diagonal matrix with elements $\{\omega_m\}$.

We close this section by giving the formal spectral representation for $\langle\langle V;V^\dagger\rangle\rangle_\omega$, which is obtained from Eqs. (61) and (67)—(71) as

$$\langle\langle V;V^\dagger\rangle\rangle_\omega=\sum_m\left[\frac{a_m^+}{\omega-\omega_m}-\frac{a_m^-}{\omega+\omega_m}\right], \tag{72}$$

where $a_m^\pm$ can be calculated from the definitions

$$a_m^\pm=d_m^\pm b_m^\mp-h_m^\pm , \tag{73}$$

$$d_m^\pm=\sum_\nu D_\nu^\pm S_{\nu m} , \tag{74}$$

$$b_m^\pm=\sum_\nu(\underline{S}^{-1})_{m\nu}B_\nu^\pm , \tag{75}$$

$$h_m^\pm=\sum_{\substack{\nu,\nu',\\ m'}}(b_m^\mp S_{\nu m}F_{\nu\nu'}S_{\nu' m'}b_{m'}^\pm)/(\omega_m+\omega_{m'}) . \tag{76}$$

The summation in Eq. (76) is over m', ν', and ν. It follows now from the general spectral representation (16) that ω_m should be interpreted as a transition energy and a_m^+ as $\langle 0\,|\,V\,|\,m\rangle\langle m\,|\,V^\dagger\,|\,0\rangle$.

IV. DISCUSSION

A time-dependent coupled-cluster approximation scheme has been outlined in this paper. We have emphasized the connection between ordinary adiabatic perturbation theory for the "vacuum amplitude" and the level-shift function $d\epsilon/dt$ of the coupled-cluster method. A result of this analysis is a procedure for the calculation of linear response functions $\langle\langle V;V^\dagger\rangle\rangle_\omega$ and thereby also transition moments and excitation energies. The excitation energies which are obtained by the present approach are identical to those obtained by the "equation-of-motion" formulation of Emrich and Zaboltizky.[10] Their numerical results have been very encouraging.

We have concentrated on the formal aspects of a coupled-cluster response theory, because the structure of the theory has to be described before the development of computer programs. But of course, as always in quantum chemistry, the fate of the proposed method will be decided by its numerical performance.

[1]F. Coester, Nucl. Phys. 7, 421 (1958); F. Coester and H. Kümmel, *ibid.* 17, 477 (1960).

[2]H. Kümmel, K. H. Lührmann, and J. G. Zabolitzky, Phys. Rep. 36C, 1 (1978).

[3]J. Cizek, J. Chem. Phys. 45, 4256 (1966); J. Cizek and J. Paldus, Int. J. Quantum Chem. 5, 359 (1971); J. Paldus, J. Cizek, and I. Shavitt, Phys. Rev. A 5, 50 (1972).

[4]F. E. Harris, Int. J. Quantum Chem. Symp. 11, 403 (1977).

[5]T. P. Zivković, Int. J. Quantum Chem. Symp. 11, 413 (1977); T. P. Zivković and H. J. Monkhorst, J. Math. Phys. 19, 1007 (1978).

[6]H. J. Monkhorst, Int. J. Quantum Chem. Symp. 11, 421 (1977).

[7]R. J. Bartlett and G. D. Purvis III, Proceedings of the Nobel Symposium 46, Sweden, 1979 [Phys. Scr. 21, 255 (1980)].

[8]G. D. Purvis III and R. J. Bartlett, J. Chem. Phys. 75, 1284 (1981).

[9]G. F. Adams, G. D. Bent, R. J. Bartlett, and G. D. Purvis, J. Chem. Phys. 75, 834 (1981).

[10]K. Emrich, Nucl. Phys. A 351, 379 (1981); 351, 397 (1981); K. Emrich and J. G. Zabolitizky, *ibid.* 351, 439 (1981).

[11]E. Dalgaard, Phys. Rev. A 26, 42 (1982), and references therein.

[12]E. Dalgaard, J. Chem. Phys. 72, 816 (1980).

[13]S. S. Z. Adnan, S. Bhattacharay, and D. Mukherjee, Mol. Phys. 39, 519 (1980).

[14]P. Hoodbhoy and J. W. Negele, Phys. Rev. C 18, 2380 (1978).

[15]K. Schönhammer and O. Gunnarsson, Phys. Rev. B 18, 6606 (1978).

[16]A. L. Fetter and J. D. Walecka, *Quantum Theory of Many-Particle Systems* (McGraw-Hill, New York, 1971).

[17]For a comprehensive survey, see J. Oddershede, Adv. Quantum Chem. 11, 275 (1978).

[18]P. W. Langhoff, S. T. Epstein, and M. Karplus, Rev. Mod. Phys. 44, 602 (1972).

[19]K. T. Chung, Phys. Rev. 163, 1343 (1967).

[20]See, e.g., J. Linderberg and Y. Öhrn, *Propagators in Quantum Chemistry* (Academic, New York, 1973), Chap. 5.