Quadratic response functions within the time-dependent Hartree-Fock approximation

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The response of an atomic or molecular system to an external perturbation is studied within the framework of time-dependent Hartree-Fock theory. Quadratic response functions are defined and analyzed with regard to their poles and residues, from which an expression for matrix elements of an arbitrary operator between excited states is deduced. For one-particle operators the matrix elements $\langle m \mid A \mid n \rangle$ are correct through first order in correlation and the hypervirial relation $(E_1 - E_m) \langle m \mid A \mid n \rangle = \langle m \mid [A,H] \mid n \rangle$ is satisfied. Spurious poles, which have no counterpart in an exact theory, are encountered in the quadratic response functions. Their appearance is attributed to well-known deficiencies in the time-dependent Hartree-Fock approximation.

I. INTRODUCTION

The rapid development of laser spectroscopy in the nonlinear domain during the last decade calls for a theoretical description of second-order processes.[1] It is, of course, well known that a knowledge of the excitation energies of the system and the matrix elements of the various perturbation operators between the ground state and excited states and between excited states provide all necessary ingredients to obtain cross sections or transition probabilities for all types of linear and nonlinear optical processes. But the formal "sum-over-states" expressions are difficult to use in practice and a direct determination of response functions is often more feasible.[2]

Efficient calculations of linear response functions are now being carried out by several groups[3] and particularly encouraging results have been obtained recently within the framework of multiconfigurational Hartree-Fock theory.[4,5] Linear response functions provide by means of a pole and residue search the excitation energies and transition moments between ground and excited states but not between excited states. It is possible to establish plausible expressions for such matrix elements by using the excitation operators which are obtained from a spectral representation of the linear response functions.[6] These formulas are not unique, however, because they are based on consistency requirements on the approximate ground state, which are normally only approximately fulfilled.[7] An identification of the desired matrix elements from quadratic response functions appears

therefore to be a worthwhile approach to this problem.

It is the purpose of this paper to describe how quadratic response functions may be calculated in the time-dependent Hartree-Fock approximation (TDHF) as well as related schemes. Some formal aspects of response theory are reviewed in Sec. II, which include definitions of the quadratic response functions to be studied in the remaining part of the paper. In Sec. III an outline is given of the TDHF calculation of the linear and quadratic response to an adiabatically switched-on perturbation. We choose here the Hartree-Fock state as a ground- or reference-state representative, but the formalism can, with relatively little effort, be generalized to more involved schemes, in particular, the multiconfigurational TDHF approach.[8] Matrix elements of the type $\langle m \mid A \mid n \rangle$, where $\mid m \rangle$ and $\mid n \rangle$ denote excited states of the system, are derived from the spectral representation of the quadratic response functions in Sec. IV. It is proven that these matrix elements are correct through first order in correlation and that the hypervirial relation

$$(E_n - E_m)\langle m \mid A \mid n \rangle = \langle m \mid [A,H] \mid n \rangle$$

is satisfied for arbitrary one-particle operators. Conclusions concerning applications and possible generalizations of the TDHF quadratic response functions are stated in Sec. V.

II. ELEMENTS OF RESPONSE THEORY

Our aim is to analyze the response of an atom or molecule to an adiabatically switched-on perturba-

tion of the general form

$$W(t) = \int_{-\infty}^{\infty} d\omega \, V_\omega \exp[-i(\omega + i\alpha)t] \,, \qquad (1)$$

where α denotes a positive infinitesimal such that

$$\lim_{t \to -\infty} W(t) = 0 \,. \qquad (2)$$

For the perturbation operator to be Hermitian we also require that

$$V_\omega^+ = V_{-\omega} \,. \qquad (3)$$

Since response theory is a standard topic in quantum mechanics only the results will be stated here. An account on the subject, which is particularly

useful for our purpose, has been written by Zubarev.[9] Assume for the moment that $|0\rangle$ is the exact unperturbed reference state and that $|\psi\rangle$ is the corresponding solution to the time-dependent Schrödinger equation in the presence of the perturbation given by Eq. (1), i.e., with the initial condition

$$\lim_{t \to -\infty} |\psi\rangle\langle\psi| = |0\rangle\langle0| \,. \qquad (4)$$

The result, which we shall employ, is then that the expectation value at time t of an arbitrary operator A takes the form

$$\langle\psi|A|\psi\rangle = \langle0|A|0\rangle + \int d\omega \, ds \, \langle\langle A(t); V_\omega(s) \rangle\rangle \exp[-i(\omega + i\alpha)s]$$

$$+ \int d\omega \, d\omega' ds \, ds' \langle\langle A(t); V_\omega(s); V_{\omega'}(s') \rangle\rangle \exp[-i(\omega + i\alpha)s - i(\omega' + i\alpha)s'] + \cdots \,, \qquad (5)$$

where all integrations over frequency and time variables s, s' are from $-\infty$ to ∞. Several definitions have been introduced here. First, $A(t)$ and $V_\omega(s)$ are operators in the interaction representation, i.e., $A(t) = \exp(iHt)A\exp(-iHt)$. The quantities in the double angle brackets are the linear and quadratic response functions.[2,9] Zubarev defines the retarded two-time propagators or Green's functions as

$$\langle\langle A(t); B(s) \rangle\rangle = -i\langle0|[A(t), B(s)]|0\rangle\Theta(t-s) \,. \qquad (6)$$

Various definitions of Green's function of higher order have been discussed by Rickayzen.[10] For the present response calculation it is most convenient to adopt the following definition:

$$\langle\langle A(t); B(s); C(s') \rangle\rangle = -\tfrac{1}{2}\langle0|[[A(t), B(s)], C(s')]|0\rangle\Theta(t-s)\Theta(s-s')$$

$$-\tfrac{1}{2}\langle0|[[A(t), C(s')], B(s)]|0\rangle\Theta(t-s')\Theta(s'-s) \,, \qquad (7)$$

which arises naturally when using time-ordered products in perturbation theory. In a preliminary study[8] of quadratic response only the first part of the right-hand side of Eq. (7) was retained in the definition of second-order response functions. There are two reasons for the change made here. Firstly, the present definition is more directly related to observable molecular properties. Secondly, the Fourier transforms of each of the two terms in Eq. (7) contain singularities, which are absent in the sum.[8] It should be noted that

$$\langle\langle A(t); B(s); C(s') \rangle\rangle = \langle\langle A(t); C(s'); B(s) \rangle\rangle \,. \qquad (8)$$

It also follow from the definition (6) and (7) that the propagators are invariant under time translations, i.e.,

$$\langle\langle A(t); B(s) \rangle\rangle = \langle\langle A(0); B(s-t) \rangle\rangle \,, \qquad (9)$$

$$\langle\langle A(t); B(s); C(s') \rangle\rangle = \langle\langle A(0); B(s-t); C(s'-t) \rangle\rangle \,. \qquad (10)$$

Fourier transforms of the linear response function may therefore be calculated as[2,9]

$$\langle\langle A; B \rangle\rangle_E = \int_{-\infty}^{\infty} d\tau \exp(iE\tau)\langle\langle A(0); B(-\tau) \rangle\rangle \,, \qquad (11)$$

where E is a complex variable. The function $\langle\langle \,; \rangle\rangle_E$ is analytic in the upper half of the complex plane, and Eq. (11) has the inverse relation

$$\langle\langle A(t); B(s) \rangle\rangle = \lim_{\alpha \to 0^+} \left[\frac{1}{2\pi}\right] \int_{-\infty}^{\infty} d\epsilon \exp[-i\epsilon(t-s)]\langle\langle A; B \rangle\rangle_{\epsilon + i\alpha} \,. \qquad (12)$$

Similarly, we introduce a double Fourier transform for the quadratic response functions as

$$\langle\langle A; B; C \rangle\rangle_{EE'} = \langle\langle A; C; B \rangle\rangle_{E'E} = \int d\tau \, d\tau' \exp(iE\tau + iE'\tau')\langle\langle A(0); B(-\tau); C(-\tau') \rangle\rangle \,. \qquad (13)$$

Introducing formally a complete set of states $\{ \, | \, m \, \rangle \}$ which are eigenstates of H, we find by using Eqs. (6), (7), (12), and (13) that the spectral representations may be written

$$\langle\langle A;B \rangle\rangle_E = \sum \left[\frac{\langle 0 | A | m \rangle\langle m | B | 0 \rangle}{E - E_m + E_0} - \frac{\langle 0 | B | m \rangle\langle m | A | 0 \rangle}{E + E_m - E_0} \right] \tag{14}$$

and

$$\langle\langle A;B;C \rangle\rangle_{EE'} = \tfrac{1}{2} \sum \left\{ \frac{\langle 0 | A | m \rangle\langle m | B | m' \rangle\langle m' | C | 0 \rangle}{(E+E'-E_m+E_0)(E'-E_{m'}+E_0)} + \frac{\langle 0 | A | m \rangle\langle m | C | m' \rangle\langle m' | B | 0 \rangle}{(E+E'-E_m+E_0)(E-E_{m'}+E_0)} \right.$$

$$+ \frac{\langle 0 | C | m \rangle\langle m | B | m' \rangle\langle m' | A | 0 \rangle}{(E+E'+E_{m'}-E_0)(E'+E_m-E_0)} + \frac{\langle 0 | B | m \rangle\langle m | C | m' \rangle\langle m' | A | 0 \rangle}{(E+E'+E_{m'}-E_0)(E+E_m-E_0)}$$

$$\left. - \frac{\langle 0 | B | m \rangle\langle m | A | m' \rangle\langle m' | C | 0 \rangle}{(E+E_m-E_0)(E'-E_{m'}+E_0)} - \frac{\langle 0 | C | m \rangle\langle m | A | m' \rangle\langle m' | B | 0 \rangle}{(E'+E_m-E_0)(E-E_{m'}+E_0)} \right\} .$$

$$\tag{15}$$

It is apparent from Eq. (14) that the linear response function via its poles and residues provide transition energies and transition moments for transitions involving the ground state, or reference state, directly. In addition, the quadratic response functions furnish us with transition amplitudes between two excited states as can be seen in the following manner. Suppose that the linear and quadratic response functions have been calculated as functions of the complex variables E and E', and assume that the linear response function has a pole at $E = \omega_J \equiv (E_J - E_0)$ and at $\omega_{J'} = (E_{J'} - E_0)$. Then it follows from Eq. (15) that

$$\lim_{E' \to -\omega_{J'}} \left[\lim_{E \to \omega_J} (E - \omega_J)(E' + \omega_{J'})\langle\langle A;B;C \rangle\rangle_{EE'} \right] = -\tfrac{1}{2}\langle 0 | C | J' \rangle(\langle J' | A | J \rangle - \delta_{JJ'}\langle 0 | A | 0 \rangle)\langle J | B | 0 \rangle$$

$$\tag{16}$$

provided that the states involved are nondegenerate. Since the matrix elements $\langle 0 | C | J' \rangle$ and $\langle J | B | 0 \rangle$ are known from the linear response function we can determine $\langle J' | A | J \rangle$ as well.

The Fourier transforms of the response function or propagators provide an alternative expression for the influence of the external perturbation given by Eq. (1) on the expectation value of an arbitrary operator

$$\langle \psi | A | \psi \rangle - \langle 0 | A | 0 \rangle = \int d\omega \langle\langle A;V_\omega \rangle\rangle_E \exp(-iEt) + \int d\omega \, d\omega' \langle\langle A;V_\omega;V_{\omega'} \rangle\rangle_{EE'} \exp[-i(E+E')t] + \cdots$$

$$(E = \omega + i\alpha, \quad E' = \omega' + i\alpha) \tag{17}$$

where we have used Eqs. (5), (9), (10), (11), and (13). Equation (17) shows that, depending on the particular choice of operators, the quadratic response functions are proportional to the second-order nonlinear optical susceptibility,[11] and a description of the second harmonic generation in light scattering may be given in terms of the quadratic response function evaluated at the relevant frequencies. This fact together with the information on transition amplitudes between excited states gives the main motivation for extending current efforts in the theory of propagators to include the quadratic ones.

We conclude this section by noting that the propagators satisfy equations of motion[2]

$$E\langle\langle A;B \rangle\rangle_E = \langle 0 | [A,B] | 0 \rangle + \langle\langle [A,H];B \rangle\rangle_E \tag{18}$$

and

$$(E+E')\langle\langle A;B;C \rangle\rangle_{EE'} = \langle\langle [A,H];B;C \rangle\rangle_{EE'} + \tfrac{1}{2}\langle\langle [A,B];C \rangle\rangle_{E'} + \tfrac{1}{2}\langle\langle [A,C];B \rangle\rangle_E . \tag{19}$$

Most approximate calculations of propagators have been based on equations of motion or the moment expansions derived from it,[2,3] and also the quadratic response function can be calculated approxi- mately by forming Padé approximants to their moment expansions. This approach will not be pursued in this paper, however. Equations (18) and (19) can be proven by introducing the spectral rep-

resentations (14) and (15) into (18) and (19). A more illuminating approach is to require that Eq. (17) should be consistent with Ehrenfest's theorem[12]

$$i\frac{d}{dt}\langle\psi\mid A\mid\psi\rangle = i\Big\langle\psi\Big|\frac{\partial A}{\partial t}\Big|\psi\Big\rangle$$

$$+\langle\psi\mid[A,H+W]\mid\psi\rangle\ .\quad(20)$$

The steps which lead to Eqs. (18) and (19) are a differentiation of the right-hand side of (17), which gives an expansion in terms of $E\langle\langle A;V_\omega\rangle\rangle_E$ and $(E+E')\langle\langle A;V_\omega;V_{\omega'}\rangle\rangle_{EE'}$, where $E=\omega+i\alpha$ and $E'=\omega'+i\alpha$. This expansion is equated to a similar expansion involving the propagators appearing on the right-hand side of Eqs. (18) and (19), which is obtained by applying Eq. (17) with A replaced by $[A,H+W]$. Then Eqs. (18) and (19) follow from the properties of Fourier integrals.

III. TDHF RESPONSE FUNCTIONS

We proceed now to outline the calculation of linear and quadratic response functions in the TDHF approximation as well as related but more general schemes. An algebraic formulation is adopted here; the reader is referred to a recent paper by Smet et al.[13] for a second-order TDHF method, which employs effective one-particle operators and differential equations.

As an ansatz for a time-dependent reference state in the presence of the external perturbation given by Eq. (1) we introduce the expression[4,14]

$$\mid\psi\rangle=\exp(i\Lambda)\mid0\rangle\exp(-i\epsilon)\ ,\quad(21)$$

where Λ is a Hermitian one-particle operator, which generates unitary transformations of the orbitals, and ϵ is a real parameter. We choose ϵ such that[15]

$$\Big\langle\psi\Big|i\frac{d}{dt}-H-W\Big|\psi\Big\rangle=0\quad(22)$$

or

$$\frac{d\epsilon}{dt}=\Big\langle0\Big|\exp(-i\Lambda)\Big|H+W-i\frac{d}{dt}\Big|\exp(i\Lambda)\Big|0\Big\rangle\ ,$$
$$(23)$$

but in what follows we shall not concern ourselves with ϵ, since it does not enter the calculation of response functions.

The initial or unperturbed state $\mid0\rangle$ *is taken to be the Hartree-Fock state,* which we assume is stable[2] and nondegenerate. Throughout this paper we shall employ a finite basis set of spin orbitals $\{\ u_s(\zeta)\mid\ s=1,\ldots,M\ \}$, and the corresponding electron creation and annihilation operators will be denoted by $\{\ a_s^\dagger,a_s\mid s=1,\ldots,M\ \}$. Then the operator Λ may be expressed as

$$\Lambda=\sum(\Lambda_{kl}a_k^\dagger a_l+\Lambda_{lk}a_l^\dagger a_k)$$

$$\equiv\sum(\Lambda_v q_v^\dagger+\Lambda_v^* q_v);\quad v\equiv(kl)\ .\quad(24)$$

Labels l and k are used here to indicate orbitals, which are occupied and unoccupied in the Hartree-Fock state, respectively. The reader is referred to Refs. 7 and 16 for the details concerning orbital transformations; Ref. 7 provides proof that the variables $\Lambda_{kk'}$ and $\Lambda_{u'}$ are redundant and may be omitted in Eq. (24).

Most derivations of the time-dependent Hartree-Fock equations have taken the Frenkel variation principle[15] as the point of departure

$$\text{Re}\Big\langle\delta\psi\Big|i\frac{d}{dt}-H-W\Big|\psi\Big\rangle=0\ .\quad(25)$$

Equation (25) determines the variables $\Lambda_v=\Lambda_v(t)$ when the initial conditions

$$\lim_{t\to-\infty}\Lambda_v(t)=0\quad(\text{all }v)\quad(26)$$

are invoked. It was demonstrated recently,[8] however, that Eqs. (21) and (25) are equivalent to Ehrenfest's theorem for all one-particle operators, i.e.,

$$\Gamma(O)\equiv\langle\psi\mid O\mid\dot\psi\rangle+\langle\dot\psi\mid O\mid\psi\rangle$$

$$+i\langle\psi\mid[O,H+W]\mid\psi\rangle=0\ ,\quad(27)$$

where $O=\sum O_{rs}a_r^\dagger a_s$. There are M^2 independent one-particle operators but only $N(M-N)$ complex variables in Eq. (24) for an N-electron system so that Eq. (27) leads to more equations than variables. Any one-particle operator can be written as a linear combination of operators from the set

$$\{\ a_r^\dagger a_s\mid r,s=1,\ldots,M\ \}$$

or, alternatively, from the set

$$\{\ \tilde a_r^\dagger\tilde a_s\mid r,s=1,\ldots,M\ \}\ ,$$

where

$$\tilde a_r^\dagger=\exp(i\Lambda)a_r^\dagger\exp(-i\Lambda)\ .\quad(28)$$

It is easier to identify the nonredundant equations from (27), when the transformed field operators are

used. These operators have particle-hole characteristics with regard to the state $|\psi\rangle$ so that

$$\tilde{a}_k^\dagger \tilde{a}_{k'} |\psi\rangle = 0$$

and   (29)

$$\tilde{a}_l^\dagger \tilde{a}_{l'} |\psi\rangle = |\psi\rangle \delta_{ll'}$$

from which it follows that $\Gamma(\tilde{a}_k^\dagger \tilde{a}_{k'})$ and $\Gamma(\tilde{a}_l^\dagger \tilde{a}_{l'})$ vanish identically. Therefore Eq. (27) reduces to $N(M-N)$ essential, complex *first-order* differential equations

$$\Gamma(\tilde{a}_k^\dagger \tilde{a}_l) = 0 .$$ (30)

Equation (30) can also be obtained through a minimization of a positive semidefinite error functional for time-dependent density operators.[17] These features of the formalism guarantee the existence and uniqueness of the solution for specified initial conditions. We shall see shortly that the set of equations

$$\Gamma(a_k^\dagger a_l) = 0$$ (31)

in each order of perturbation theory also determines the solution for Λ_{kl} uniquely, and it follows from the discussion above that any set of equations of this type which determines the solution can be used. Equation (31) is simplest to apply in practice.

In order to solve these equations we first introduce a perturbation expansion (with regard to W)

$$\Lambda = \Lambda(1) + \Lambda(2) + \cdots ;$$
$$\Lambda_v = \Lambda_v(1) + \Lambda_v(2) + \cdots ,$$ (32)

into Eq. (31). Collecting terms of the same order, as usual in perturbation theory, we find in zero order the condition

$$\langle [q_v, H] \rangle = 0$$ (33)

for the perturbation expansion to exist. This is the well-known Brillouin theorem.[18] We are using the notation $\langle \cdots \rangle \equiv \langle 0 | \cdots | 0 \rangle$ for the Hartree-Fock expectation values. The first- and second-order equations become

$$i\langle [q_v, \dot{\Lambda}(1)] \rangle - \langle [[q_v, H], \Lambda(1)] \rangle = -i\langle [q_v, W] \rangle ,$$ (34)

$$i\langle [q_v, \dot{\Lambda}(2)] \rangle - \langle [[q_v, H], \Lambda(2)] \rangle = \langle [[q_v, W], \Lambda(1)] \rangle + \frac{i}{2}\langle [[[q_v, H], \Lambda(1)], \Lambda(1)] \rangle$$

$$+ \frac{1}{2}\langle [[q_v, \dot{\Lambda}(1)], \Lambda(1)] \rangle + \frac{1}{2}\langle [[q_v, \Lambda(1)], \dot{\Lambda}(1)] \rangle .$$ (35)

The last two terms in Eq. (35) may be omitted in the TDHF approximation since the expectation value of any product of three particle-hole excitation or deexcitation operators vanish identically. In a more general scheme, e.g., multiconfigurational time-dependent Hartree-Fock, such terms must be included.

The solution of the first-order equation (34) is equivalent to an ordinary linearized TDHF calculation. The results of such calculations are conveniently presented as a set of excitation and deexcitation operators $\{ Q_j^\dagger, Q_j \}$, which are related to the set of particle-hole operators $\{ q_v^\dagger, q_v \}$ through a nonsingular transformation

$$Q_j^\dagger = \sum (q_v^\dagger Z_{vj} + q_v Y_{vj}) ,$$

$$j = 1, 2, \ldots, N(M-N) .$$ (36)

We refer the reader to previous work[2,7,14] for details of TDHF calculations. The basic properties of the excitation operators are given by the equations

$$\langle [[Q_j, H], Q_{j'}^\dagger] \rangle = \omega_j \delta_{jj'} ,$$ (37)

$$\langle [[Q_j, H], Q_{j'}] \rangle = 0 ,$$ (38)

$$\langle [Q_j, Q_{j'}^\dagger] \rangle = \delta_{jj'} ,$$ (39)

$$\langle [Q_j, Q_{j'}] \rangle = 0 ,$$ (40)

where the real and positive numbers ω_j are interpreted as excitation energies, $E_j - E_0$, of the system. Transition moments are calculated as

$$\langle 0 | A | j \rangle = \langle [A, Q_j^\dagger] \rangle .$$ (41)

In order to derive the linear and quadratic response functions in a reasonable compact form it is convenient to employ an alternative set of variables in the definition of Λ. There is no loss of generality by writing

$$\Lambda = \sum_1^d (a_j Q_j^\dagger + a_j^* Q_j) \equiv \sum_{-d}^d \alpha_j \kappa_j ,$$

$$d = N(M-N) ,$$ (42)

and taking the coefficients $\{ a_j \}$ to be the basic

variables to be determined from Eqs. (34) and (35). We also introduce the definitions

$$\alpha_j = a_j \quad \text{and} \quad \kappa_j = Q_j^\dagger \quad \text{for } j > 0 \tag{43}$$

$$\alpha_j = a^*_{|j|} \quad \text{and} \quad \kappa_j = Q_{|j|} \quad \text{for } j < 0 \; .$$

with this notation Eqs. (37), (38), (39), and (40) become

$$\delta_{jj'} = \langle [\kappa_{-j}, \kappa_{j'}] \rangle \mathrm{sgn}(j) \; , \tag{44}$$

$$\omega_j \delta_{jj'} = \langle [[\kappa_{-j}, H], \kappa_{j'}] \rangle \mathrm{sgn}(j) \; , \tag{45}$$

provided that we let

$$\omega_{-j} \equiv -\omega_j \; . \tag{46}$$

Corresponding to the perturbation expansion for Λ in Eq. (32) there will be first- and second-order contributions to the variables a_j or equivalently α_j, i.e.,

$$\alpha_j = \alpha_j(1) + \alpha_j(2) + \cdots \; , \tag{47}$$

and with this observation we are prepared to solve Eqs. (34) and (35) which now may be written

$$\left[i\frac{d}{dt} - \omega_j \right] \alpha_j(1) = -i \, \mathrm{sgn}(j) \langle [\kappa_{-j}, W] \rangle \tag{48}$$

and

$$\left[i\frac{d}{dt} - \omega_j \right] \alpha_j(2) = \mathrm{sgn}(j) \langle [[\kappa_{-j}, W], \Lambda(1)] \rangle + \frac{i}{2} \mathrm{sgn}(j) \langle [[[\kappa_{-j}, H], \Lambda(1)], \Lambda(1)] \rangle \; . \tag{49}$$

The solution for $\alpha_j(1)$ and hence $\Lambda(1)$ which satisfies the initial condition given by Eq. (26) may be written

$$\alpha_j(1) = -\exp(-i\omega_j t) \int_{-\infty}^{t} ds \, \exp(i\omega_j s) \langle [\kappa_{-j}, W(s)] \rangle \mathrm{sgn}(j) \; , \tag{50}$$

and introducing Eq. (1) for the time-dependent perturbation in this expression we find

$$\alpha_j(1) = -i \, \mathrm{sgn}(j) \int_{-\infty}^{\infty} d\omega \langle [\kappa_{-j}, V_\omega] \rangle \frac{\exp[-i(\omega + i\alpha)t]}{(\omega - \omega_j + i\alpha)} \; . \tag{51}$$

Inserting

$$\Lambda(1) = \sum \alpha_j(1) \kappa_j \tag{52}$$

into the right-hand side of Eq. (49) and carrying out a time integration similar to the one in Eq. (50), an expression for $\alpha_j(2)$ is obtained,

$$\alpha_j(2) = -i \, \mathrm{sgn}(j) \int d\omega \, d\omega' \frac{X_j(\omega, \omega') \exp[-i(\omega + \omega' + 2i\alpha)t]}{(\omega + \omega' + 2i\alpha - \omega_j)} \; . \tag{53}$$

Here we have introduced the definition

$$X_j(\omega, \omega') = \sum \frac{\langle [[\kappa_{-j}, V_\omega], \kappa_n] \rangle \langle [\kappa_{-n}, V_{\omega'}] \rangle \mathrm{sgn}(n)}{(\omega' - \omega_n + i\alpha)}$$

$$+ \sum \frac{\langle [[[\kappa_{-j}, H], \kappa_n], \kappa_m] \rangle \langle [\kappa_{-n}, V_\omega] \rangle \langle [\kappa_{-m}, V_{\omega'}] \rangle}{2(\omega - \omega_n + i\alpha)(\omega' - \omega_m + i\alpha)} \mathrm{sgn}(nm) \; , \tag{54}$$

where the summations are over n and n,m, respectively. Having these results we are able to deduce formulas for the linear and quadratic response functions from the expansion

$$\langle \psi | A | \psi \rangle - \langle A \rangle = i \langle [A, \Lambda] \rangle - \tfrac{1}{2} \langle [[A, \Lambda], \Lambda] \rangle + \cdots$$

$$= i \sum \langle [A, \kappa_j] \rangle [\alpha_j(1) + \alpha_j(2)] - \tfrac{1}{2} \sum \langle [[A, \kappa_j], \kappa_{j'}] \rangle \alpha_j(1) \alpha_{j'}(1) + \cdots \; . \tag{55}$$

This expansion should exhibit the same frequency dependence as Eq. (17). Therefore we can make the identifications

$$\langle\langle A; V_\omega \rangle\rangle_E = \sum \mathrm{sgn}(j) \langle [A, \kappa_j] \rangle \langle [\kappa_{-j}, V_\omega] \rangle (E - \omega_j)^{-1} \tag{56}$$

and

$$\langle\!\langle A;V_\omega;V_{\omega'}\rangle\!\rangle_{EE'}=\sum\frac{\text{sgn}(jn)\langle[A,\kappa_j]\rangle\langle[[\kappa_{-j},V_\omega],\kappa_n]\rangle\langle[\kappa_{-n},V_{\omega'}]\rangle}{2(E+E'-\omega_j)(E'-\omega_n)}$$

$$+\sum\frac{\text{sgn}(jn)\langle[A,\kappa_j]\rangle\langle[[\kappa_{-j},V_{\omega'}],\kappa_n]\rangle\langle[\kappa_{-n},V_\omega]\rangle}{2(E+E'-\omega_j)(E-\omega_n)}$$

$$-\sum\frac{\text{sgn}(jj')\langle(\kappa_j,A,\kappa_{j'})\rangle\langle[\kappa_{-j},V_\omega]\rangle\langle[\kappa_{-j'},V_{\omega'}]\rangle}{2(E-\omega_j)(E'-\omega_{j'})}$$

$$-\sum\frac{\text{sgn}(jnm)\langle[A,\kappa_j]\rangle\langle(\kappa_n,[\kappa_{-j},H],\kappa_m)\rangle\langle[\kappa_{-n},V_\omega]\rangle\langle[\kappa_{-m},V_{\omega'}]\rangle}{2(E+E'-\omega_j)(E-\omega_n)(E'-\omega_m)}\;,\qquad(57)$$

where $E=\omega+i\alpha$ and $E'=\omega'+i\alpha$. The notation $(\ldots,\ldots,\ldots)$ is used for the symmetric double commutator, i.e.,

$$(A,B,C)=\tfrac{1}{2}[[A,B],C]+\tfrac{1}{2}[A,[B,C]]\qquad(58)$$

for arbitrary operators A, B, and C. In all summations above the indices j, n and m run from $-d$ to $d=N(M-N)$.

Thus we have achieved our goal of obtaining explicit expressions for linear and quadratic response functions in the TDHF approximation. Some fundamental properties of these response functions will be discussed in Sec. IV.

IV. TRANSITION AMPLITUDES

The properties of the residues and poles of the TDHF linear response functions have been discussed in the literature several times, and only some of the most important aspects are mentioned here. First we employ Eqs. (43) and (56) to express the spectral representation of the propagator $\langle\!\langle A;A\rangle\!\rangle_E$ in the TDHF approximation as

$$\langle\!\langle A;A\rangle\!\rangle_E=\sum_{j=1}^{d}|\langle[A,Q_j^\dagger]\rangle|^2\left[\frac{1}{E-\omega_j}-\frac{1}{E+\omega_j}\right].$$
$$(59)$$

A comparison with the formally exact spectral representation in Eq. (14) lead us to interpret the positive, real numbers $\{\omega_j\}$ as excitation energies, while the quantities $\langle[A,Q_j^\dagger]\rangle$ are identified as the corresponding transition amplitudes between an excited state labeled j and the ground state. Thus we write

$$\langle0|A|j\rangle=\langle[A,Q_j^\dagger]\rangle\qquad(60)$$

and

$$(E_j-E_0)=\omega_j$$

but the reader should be aware that even if we use this notation we do not claim that explicit expressions for the excited states $|j\rangle$ can be provided.

If the Hamiltonian

$$H=\sum h_{rs}a_r^\dagger a_s+\tfrac{1}{2}\sum(rs|r's')a_r^\dagger a_r^\dagger a_s a_s\qquad(61)$$

is expressed in terms of canonical Hartree-Fock orbitals as a zero-order part

$$H_0=\sum\epsilon_s a_s^\dagger a_s\;,\qquad(62)$$

and a perturbation

$$V=(H-H_0)=\tfrac{1}{2}\sum(rs|r's')a_r^\dagger a_{r'}^\dagger a_{s'}a_s$$
$$-\sum v_{rs}a_r^\dagger a_s\;,\qquad(63)$$

where as usual $h_{rs}+v_{rs}=\epsilon_s\delta_{rs}$, then it is well known that the TDHF transition moments and energies for transitions from the ground state to an excited state are correct through first order.[3] Therefore the TDHF method is said to be correct through first order in "electronic correlation."

Another observation to be made here is that

$$\langle\!\langle Q_j;Q_j^\dagger\rangle\!\rangle_E=\delta_{jj'}(E-\omega_j)^{-1}\qquad(64)$$

as may be seen from Eqs. (43), (44), and (56). However, Eq. (64) is only consistent with the general spectral representation (14) if[6,19]

$$(Q_j^\dagger-\langle Q_j^\dagger\rangle)|0\rangle=|j\rangle\qquad(65)$$

and

$$(Q_j-\langle Q_j\rangle)|0\rangle=0\;.\qquad(66)$$

These equations were used by Yeager et al.[6] to suggest the following expression for matrix elements of an arbitrary operator A between two excited states:

$$\langle m|A|n\rangle\equiv\langle(Q_m-\langle Q_m\rangle)A(Q_n^\dagger-\langle Q_n^\dagger\rangle)\rangle\qquad(67)$$

$$=\langle(Q_m,A,Q_n^\dagger)\rangle+\tfrac{1}{2}\langle[Q_m,Q_n^\dagger]A+A[Q_m,Q_n^\dagger]\rangle\;,\qquad(68)$$

where the last identity is a consequence of Eq. (66). Formally, Eqs. (67) and (68) are equivalent, but the latter has a computational advantage, since density matrices of lower particle-hole rank are involved. Equation (68) has been applied by Jamieson and Watts, who calculated transition moments and oscillator strengths for a pair of excited states in helium and its isoelectronic sequence.[20] The results were quite satisfactory, but it must be pointed out that the interpretation of the TDHF excitation operators, which lead to Eq. (68) rests completely on (66), which within the TDHF approximation is violated in first order. This can be seen from

$$Q_j \mid 0 \rangle = \sum (q_v Z_{vj}^* + q_v^\dagger Y_{vj}^*) \mid 0 \rangle$$

$$= \sum q_v^\dagger \mid 0 \rangle Y_{vj}^* \qquad (69)$$

since the coefficients Y_{vj} are of first order in the electron-electron interaction.

The TDHF excitation operators are themselves in error in first order of perturbation theory because there are first-order contributions from double excitations, $q_v^\dagger q_{v'}^\dagger$, to an electronic excitation from the ground state. For a one-particle operator A, terms like $\langle [A, q_v^\dagger q_{v'}^\dagger] \rangle$ vanish identically so that

the one-particle transition moments are correct through first order. But the missing double excitations give rise to an error of first order, when Eq. (68) is used, since terms like $\langle (q_v, A, q_v^\dagger q_{v'}^\dagger) \rangle$ do not vanish even for a one-particle operator, A. Therefore the assertion by Jamieson and Watts that (68) is correct through first order is seen to be incorrect.[20]

Currently we shall adopt the view that while Eqs. (65) and (66) must be fulfilled in an exact theory, there is no need to insist on these consistency requirements in approximate response function calculations. The TDHF approximation and related schemes are basically sound in the sense that the ground-state representative is calculated from the energy variation principle and the response functions are determined by minimizing a positive semidefinite functional which can vanish only for an exact time evolution of the initial state.[17]

We proceed then to analyze the residues of the quadratic response functions derived in Sec. III. Equation (16) provides together with Eqs. (57) and (60) the following result for a matrix element between two excited states:

$$\langle m \mid A \mid n \rangle - \delta_{mn}\langle 0 \mid A \mid 0 \rangle = \langle (Q_m, A, Q_n^\dagger) \rangle + \sum_{j=1}^d \frac{\langle [A, Q_j^\dagger] \rangle \langle (Q_m, [Q_j, H], Q_n^\dagger) \rangle}{(\omega_n - \omega_m - \omega_j)}$$

$$- \sum_{j=1}^d \frac{\langle [A, Q_j] \rangle \langle (Q_m, [Q_j^\dagger, H], Q_n^\dagger) \rangle}{(\omega_n - \omega_m + \omega_j)} , \qquad (70)$$

where as before the expectation values $\langle \cdots \rangle$ should be evaluated in the Hartree-Fock state. Equation (70) is more complicated than (68), but still manageable in practical calculations and it has two distinctive advantages: The hypervirial relation $(E_n - E_m)\langle m \mid A \mid n \rangle = \langle m \mid [A, H] \mid n \rangle$ is satisfied for arbitrary one-particle operators and the matrix elements $\langle m \mid A \mid n \rangle$ given by (70) are correct through first order of perturbation theory in the electron-electron interaction. These claims will now be proven.

It is well known that $(E_n - E_0)\langle 0 \mid A \mid n \rangle = \langle 0 \mid [A, H] \mid n \rangle$ within the TDHF approximation,[21] i.e., $\omega_n \langle [A, Q_n^\dagger] \rangle = \langle [[A, H], Q_n^\dagger] \rangle$. Using this relation and some properties of one-particle operators, the hypervirial relation may be proven by direct substitution in (70). Alternatively, we may employ the fact that Ehrenfest's theorem is fulfilled for one-particle operators in the present scheme. Then we know from the discussion in Sec. II that the equations of motion (18) and (19) are valid as well and therefore

$$(E_n - E_m)\langle m \mid A \mid n \rangle = -2 \lim_{E' \to -\omega_m} [\lim_{E \to \omega_n} (E - \omega_n)(E' + \omega_m)(E_n - E_m)\langle\!\langle A; Q_n^\dagger; Q_m \rangle\!\rangle_{EE'}]$$

$$= -2 \lim_{E' \to -\omega_m} [\lim_{E \to \omega_n} (E - \omega_n)(E' + \omega_m)(E + E')\langle\!\langle A; Q_n^\dagger; Q_m \rangle\!\rangle_{EE'}]$$

$$= -2 \lim_{E' \to -\omega_m} [\lim_{E \to \omega_n} (E - \omega_n)(E' + \omega_m)\langle\!\langle [A, H]; Q_n^\dagger; Q_m \rangle\!\rangle_{EE'}]$$

$$= \langle m \mid [A, H] \mid n \rangle \quad (n \neq m) \qquad (71)$$

where we used Eqs. (16), (19), (39), and (41).

In order to prove the second claim above, we first observe that within perturbation theory the excited states can be labeled by particle-hole indices $kk' \cdots l'l$, and only the subset of excited states, which can be labeled by single-particle-hole excitation indices, can be described in a TDHF calculation. Let now $q_m^\dagger$ and $q_n^\dagger$ denote the particle-hole excitation operators which correspond to the excited states $|m\rangle$ and $|n\rangle$ in Eq. (70). Rayleigh-Schrödinger perturbation theory then gives the following expression for the matrix element of a one-particle operator between these states:

$$\langle m|A|n\rangle - \delta_{mn}\langle 0|A|0\rangle = \langle(q_m,A,q_n^\dagger)\rangle + \sum' \langle q_m A q_\nu^\dagger\rangle\langle q_\nu V q_n^\dagger\rangle(\omega_n^0 - \omega_\nu^0)^{-1} \qquad (\nu \neq n)$$

$$+ \sum' \langle q_m V q_\nu^\dagger\rangle\langle q_\nu A q_n^\dagger\rangle(\omega_m^0 - \omega_\nu^0)^{-1} \qquad (\nu \neq m)$$

$$+ \tfrac{1}{4} \sum \langle q_m A q_\nu^\dagger q_\nu^\dagger\rangle\langle q_\nu q_\nu V q_n^\dagger\rangle(\omega_n^0 - \omega_\nu^0 - \omega_\nu^0)^{-1}$$

$$+ \tfrac{1}{4} \sum \langle q_m V q_\nu^\dagger q_\nu^\dagger\rangle\langle q_\nu q_\nu A q_n^\dagger\rangle(\omega_m^0 - \omega_\nu^0 - \omega_\nu^0)^{-1} + \cdots , \qquad (72)$$

where the ellipsis represents terms of second order in V. We have here made use of the Brillouin theorem $\langle V q_n^\dagger\rangle = \langle[H,q_n^\dagger]\rangle = 0$, and the symmetric double commutator is introduced only in order to compare with the right-hand side of Eq. (70). All averages $\langle \cdots \rangle$ are as before evaluated in the Hartree-Fock state. ω_ν^0 denotes zero-order excitation energies, i.e., $(\epsilon_k - \epsilon_l)$.

Consider for a moment Eq. (36). Both the coefficients $Z_{\nu m}$ and $Y_{\nu m}$ have first-order contributions. The zero-order part of $Z_{\nu m}$ is simply $\delta_{\nu m}$. Owing to the properties of particle-hole excitation operators there is no first-order contribution from the Y coefficients to the term $\langle(Q_m,A,Q_n^\dagger)\rangle$, and the two summations denoted $\sum'$ above represent the first-order contributions from the Z coefficients. Symmetric double commutators may be introduced by noting that

$$\langle q_m A q_\nu^\dagger\rangle = \langle(q_m,A,q_\nu^\dagger)\rangle + \delta_{m\nu}\langle A\rangle . \qquad (73)$$

These remarks allow us to conclude that the first three terms of Eq. (72) can be written as $\langle(Q_m,A,Q_n^\dagger)\rangle$ + second-order terms. In the last two summations in Eq. (72) only the particle-hole part of A can contribute so that we can introduce the replacement

$$A \rightarrow \sum_j (\langle[A,q_j^\dagger]\rangle q_j - \langle[A,q_j]\rangle q_j^\dagger) \qquad (74)$$

and we need to consider matrix elements of the type

$$\langle q_m q_j q_\nu^\dagger q_\nu^\dagger\rangle , \qquad (75)$$

which can be nonvanishing if and only if $q_\nu^\dagger q_\nu^\dagger = \pm q_j^\dagger q_m^\dagger$. This can be achieved in four ways so that the factor $\tfrac{1}{4}$ is canceled. We are then able to rewrite Eq. (72) as

$$\langle m|A|n\rangle - \delta_{mn}\langle A\rangle = \langle(Q_m,A,Q_n^\dagger)\rangle + \sum \langle[A,Q_j^\dagger]\rangle\langle q_m q_j V q_n^\dagger\rangle(\omega_n - \omega_j - \omega_m)^{-1}$$

$$- \sum \langle[A,Q_j]\rangle\langle q_m V q_j^\dagger q_n^\dagger\rangle(\omega_m - \omega_j - \omega_n)^{-1} + \cdots , \qquad (76)$$

where the ellipsis represents second-order terms [also in Eqs. (77) and (78)]. Finally we use the Brillouin theorem to rewrite the matrix elements

$$\langle q_m q_j V q_n^\dagger\rangle = \langle q_m[q_j,H]q_n^\dagger\rangle + \langle q_m H q_j q_n^\dagger\rangle$$

$$= \langle q_m[q_j,H]q_n^\dagger\rangle + \delta_{jn}\langle[q_m,H]\rangle$$

$$= \langle(q_m,[q_j,H],q_n^\dagger)\rangle$$

$$= \langle(Q_m,[Q_j,H],Q_n^\dagger)\rangle + \cdots . \qquad (77)$$

Similarly, we find that

$$\langle q_m V q_j^\dagger q_n^\dagger\rangle = -\langle(Q_m,[Q_j^\dagger,H],Q_n^\dagger)\rangle + \cdots . \qquad (78)$$

This completes the proof that the matrix elements of one-particle operators between excited states derived from the residues of the quadratic response functions are correct through first order in electron-electron in-

teraction. At the same time we have obtained an interpretation of the last two summations in Eq. (70), namely, that they represent "two-particles—two-holes" corrections to the TDHF excitation operators.

We close this section by pointing out a defect in the TDHF quadratic response functions: The pole structure of the propagator, given by Eq. (57), is not compatible with Eq. (15). Consider as an example the following residue search:

$$-2 \lim_{E \to -\omega_n} [\lim_{E' \to -\omega_m} (E+\omega_n)(E'+\omega_m) \langle\!\langle A_j; Q_n; Q_m \rangle\!\rangle_{EE'}] \, . \tag{79}$$

The exact propagator gives zero identically, but from Eq. (57) we obtain a generally nonvanishing result,

$$\langle\!\langle Q_m, A, Q_n \rangle\!\rangle - \sum_j \langle [A, \kappa_j] \rangle \text{sgn}(j) \frac{\langle\!\langle Q_m, [\kappa_{-j}, H], Q_n \rangle\!\rangle}{(\omega_n + \omega_m + \omega_j)} \, , \tag{80}$$

where κ_j, as before, is defined in Eq. (43). A perturbation analysis shows that this expression is of first order in electron-electron interaction. All nonvanishing parts coming from $\langle\!\langle Q_m, A, Q_n \rangle\!\rangle$ contain the coefficients Y_{vm} or Y_{vn} and are therefore related to the violation of the reference-state annihilation condition as given by Eqs. (66) and (69), while the last term contains contributions from $Z_{vn} Z_{v'm}$ as well. Even in a fully self-consistent random-phase-approximation calculation,[7,2] such terms would appear in the quadratic response function. A detailed analysis of the conditions under which the quadratic response functions exhibit a pole structure that is compatible with the formally exact spectral representation given by Eq. (15) will not be given here, but it is clear that this defect in the TDHF procedure is difficult to overcome as long as the exact Hamiltonian is used in connection with decoupling schemes based on limited operator mainfolds.

In an analysis of this problem it must be borne in mind that the most general solution to Eqs. (37), (38), (39), (40), (65), and (66) is of the form[6]

$$Q_j^\dagger = |j\rangle\langle 0| + \sum |m\rangle \alpha_{mn}\langle n| + |0\rangle \alpha_0 \langle 0| \, , \tag{81}$$

where we sum over all $m, n \neq 0$ and all states are eigenstates of the Hamiltonian. In the exact limit all spurious terms cancel, when contributions from the last two terms in Eq. (35) are included, but this is, of course, only a check on the derivations.

V. DISCUSSION

A procedure for the calculation of quadratic response properties of atoms and molecules in the presence of external fields has been developed by using the time-dependent Hartree-Fock approximation. Particular attention has been given to the

determination of matrix elements between excited states by means of an analysis of the residues of the quadratic response functions. The main result is that these matrix elements for one-particle operators are correct through first order in correlation and that they satisfy the hypervirial relation. On the negative side the quadratic response functions turned out to have spurious poles, which had no counterpart in an exact theory. The occurrence of these poles was attributed to the use of inconsistent ground-state representatives in connection with the use of a limited operator manifold in the ansatz for a time-dependent reference state in Eqs. (21) and (24). Such defects in the nonlinear TDHF molecular properties do not appear explicitly in a numerical solution of the TDHF equations or a formulation which concentrates on the oscillating time-dependent orbitals.[13]

Although the advances in large scale *ab initio* quantum chemistry during the last few years may draw the attention away from a simple-minded formalism such as the TDHF approximation there are several incitements to seek a thorough understanding of this method and its consequences. The ground-state problem in TDHF theory has been effectively solved through the work of Linderberg and Öhrn[7,22] but there are still intricate questions in general, nonlinear time-dependent Hartree-Fock. If, e.g., we wish to follow the evolution of the electronic structure during an atomic collision within a classical trajectory description of the nuclear motion, we may let W in Eq. (25) include all terms, which describes the time-dependent interaction between the atoms. Equation (25) could then be solved numerically. But there are unsolved questions related to the interpretation of the time-dependent density operator after the collision and the calculation of cross sections for the various electronic processes.

TDHF theory rests upon a variational calculation of a ground-state representative followed by a

minimization of a positive semidefinite error functional for the evolution of the density operator.[17] At the same time Ehrenfest's theorem is valid for one-particle operators and this property of the equations make it possible to draw upon the quantum-mechanical correspondence principle in order to identify certain collective modes of motion. This aspect has been explored in nuclear physics.[23]

Having the virtues of TDHF theory in mind, it is interesting to ask the question: what type of extension of the method would preserve these features? It follows from the preceding sections and from previous work that such a theory should be based upon a variational ground-state approximation and an operator manifold $\{ b_j \}$, which form a Lie algebra. This operator manifold should be used as in Eqs. (21) and (24) to construct a time-dependent reference state or density operator $\rho = |\psi\rangle\langle\psi|$. Ehrenfest's theorem and the variational determination of response functions[17] is preserved if, furthermore, there is a nonsingular transformation of the operator manifold $\{ b_j \} \rightarrow \{ q_j^\dagger, q_j, A_\mu \}$ such that

$$q_j \rho = 0, \quad A_\mu \rho = \rho \langle A_\mu \rangle .\qquad(82)$$

Currently, the recently formulated multiconfigura-

tional time-dependent Hartree-Fock (MCTDHF) appears to be a useful and viable extension[4,5] but in this case the relevant operator manifold does not form a Lie algebra and the associated response functions do not seem to be derivable from a positive semidefinite error functional. An interesting possibility would be to introduce correlation effects into the ground-state representative by means of a unitary transformation

$$|\psi_0\rangle = \exp(iS)|0\rangle, \quad S = S^+ ,\qquad(83)$$

where the operator S contains cluster generators,[24] and then carry out the same transformation of the operator manifold which is used in Eqs. (21) and (24), i.e., we would employ the set

$$\{ \tilde{a}_k^\dagger \tilde{a}_l; \tilde{a}_l^\dagger \tilde{a}_k \mid l = 1, \ldots, N; k = N+1, \ldots, M \} ,$$

where

$$\tilde{a}_r^\dagger = \exp(iS) a_r^\dagger \exp(-iS) .\qquad(84)$$

This transformation would allow us to use the labels of TDHF theory throughout, but it remains to be seen if there is a cluster generator S, which will provide a balanced description of ground-state and excited-state correlation effects in such a framework.

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