# Generalized sum rules for optical nonlinearities of many-electron systems

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Sum rules which connect spectral moments of linear and nonlinear optical susceptibilities of nonrelativistic many-electron systems to their ground state properties are derived. These sum rules provide a direct connection between chemical bonding and optical properties and may assist in constructing tight-binding Hamiltonians for the effective modeling of electronic spectroscopy. In the time-dependent Hartree–Fock approximation, the only relevant ground state information is the Hartree–Fock ground stated reduced single-electron density matrix. © *1995 American Institute of Physics.*

## I. INTRODUCTION

Linear and nonlinear optical spectra are most commonly interpreted using the electronic energy levels and the dipole matrix elements of the system.[1,2] Consequently, their theoretical modeling requires an accurate calculation of the ground state as well as the relevant excited states.[3] Sum rules, which allow the calculation of some averaged global properties of optical spectra using a considerably reduced effort,[4–6] provide a powerful tool for the analysis of complex spectra. The simplest and the most widely used sum rule is known as the Thomas–Reiche–Kuhn (or the oscillator strength) sum rule, and relates the sum of the oscillator strengths of electronic transitions to the number of electrons in the system[7,8]

$$\sum_\alpha f_\alpha = N, \tag{1.1a}$$

where the oscillator strength is $f_\alpha \equiv (2m/e^2\hbar)\Omega_\alpha|\mu_\alpha|^2$; $\mu_\alpha$ and $\Omega_\alpha$ being the transition dipole and transition frequency and $m$ and $e$ are the electron mass and charge, respectively. This remarkably simple sum rule can also be written in terms of the imaginary part of the linear susceptibility $\chi^{(1)}(\omega)$ (i.e., the absorption line shape)

$$\int_0^\infty \frac{d\omega}{2\pi}\, 2\omega\, \mathrm{Im}[\chi^{(1)}(\omega)] = \frac{e^2}{2m} N. \tag{1.1b}$$

Sum rules which connect the higher-order moments of the absorption

$$\int_0^\infty \frac{d\omega}{2\pi}\, 2\omega^n [\mathrm{Im}\, \chi^{(1)}(\omega)]$$

to a hierarchy of ground state reduced (single-electron, two-electron, etc.) density matrices can be derived as well.[4,5]

Equations (1.1) hold for a system of electrons interacting with the potential of nuclei and with each other through the Coulomb interaction, and involves all transitions $\alpha$ [Eq. (1.1a)] or all frequencies $\omega$ [Eq. (1.1b)], including nonoptical (e.g., x-ray) frequencies. In this paper, we derive sum rules for general tight-binding many-electron models which are restricted to optical electronic transitions and, consequently, could be much more useful in analyzing optical properties. We further propose a new family of sum rules which connect nonlinear optical susceptibilities to ground state properties; these are of special interest for clarifying the mechanism of the nonlinear response and predicting its dependence on chemical bonding.

Sum rules based on higher-order moments generally connect optical properties to higher-order ground state reduced density matrices. The time-dependent Hartree–Fock (TDHF) approximation[9] has been successfully applied in studies of the nonlinear optical properties of many-electron systems.[10] Making use of the Hamilton's form of the TDHF equation,[11] we show that, within this approximation, all linear and nonlinear sum rules can be expressed in terms of the ground state single-electron reduced density matrix $\hat{\rho}_0$ representing the Hartree–Fock (HF) ground state.[12,13] Since the off-diagonal elements of $\hat{\rho}_0$ reflect the bond order, the TDHF sum rules provide direct relations between optical and chemical bonding properties.[14,15]

Our derivation starts with the following Hamiltonian representing a system driven by a uniform external field $\mathscr{E}(\tau)$

$$\hat{H}_T = \hat{H} - \hat{\mu}\mathscr{E}(\tau), \tag{1.2}$$

where $\hat{H}$ is the Hamiltonian of the unperturbed system and $\hat{\mu}$ is the system's dipole operator. We next introduce the time-domain optical response functions $R^{(n)}(t_n,\ldots,t_1)$ obtained by expanding the expectation value of the polarization $\langle P(\tau)\rangle \equiv \mathrm{Tr}[\hat{\mu}(\tau)\hat{\rho}]$ in powers of the external field:[1,2]

$$\langle P(\tau)\rangle = \sum_n \frac{1}{n!}\int_0^\infty dt_1 \cdots \int_0^\infty dt_n R^{(n)}(t_n, t_{n-1},\ldots,t_1) \times \mathscr{E}(\tau - t_1 - \cdots - t_n)\cdots\mathscr{E}(\tau - t_n). \tag{1.3}$$

Here $\hat{\mu}(\tau)$ is the dipole operator in the Heisenberg picture and $\hat{\rho}$ is the system's equilibrium density matrix. The arguments of the response functions $R^{(n)}$ are the time intervals $t_1,\ldots,t_n$ between successive interactions with the radiation field. Switching to the frequency domain and using the convention

$$f(\tau) = \int \frac{d\omega}{2\pi}\, e^{-i\omega\tau} f(\omega), \tag{1.4a}$$

we can relate the polarization and the external field in the frequency domain using the optical susceptibilities $\chi^{(n)}(-\omega_s;\omega_1,\ldots,\omega_n)$ defined as

$$\langle P(\omega_s)\rangle=\sum_n \frac{1}{n!}\int_{-\infty}^{\infty}\frac{d\omega_1}{2\pi}\cdots\int_{-\infty}^{\infty}\frac{d\omega_n}{2\pi} \times 2\pi\delta(\omega_1+\cdots+\omega_n-\omega_s) \times\chi^{(n)}(-\omega_s;\omega_1,\ldots,\omega_n)\mathscr{E}(\omega_1)\ldots\mathscr{E}(\omega_n). \tag{1.4b}$$

Comparing Eqs. (1.3) and (1.4) we obtain the general multidimensional Fourier transform relationship between optical susceptibilities and response functions

$$R^{(n)}(t_n,t_{n-1},\ldots t_1)=\int_{-\infty}^{\infty}\frac{d\omega_1}{2\pi}\cdots\int_{-\infty}^{\infty}\frac{d\omega_n}{2\pi} \times\chi^{(n)} \times(-\omega_s;\omega_1,\ldots,\omega_n) \times e^{-i\omega_1 t_1-i(\omega_1+\omega_2)t_2-\cdots-i(\omega_1+\cdots+\omega_n)t_n}. \tag{1.5}$$

We next adopt the following notation. For an arbitrary operator $\hat{A}$ we introduce a superoperator (also denoted as Liouville space operator) $\tilde{A}$, defined by its action on another operator $\hat{B}$

$$\tilde{A}\hat{B}\equiv[\hat{A},\hat{B}]. \tag{1.6a}$$

The superoperator $\tilde{H}$ corresponding to the Hamiltonian $\hat{H}$ is known as the Liouville operator. The Greens function of the Liouville operator is given by

$$\mathscr{G}(t)=\exp(i\tilde{H}t). \tag{1.6b}$$

We also define the expectation value of an operator $\hat{A}$ with respect to the equilibrium density matrix $\hat{\rho}$ as

$$\langle\hat{A}|\hat{\rho}\rangle\equiv\mathrm{Tr}(\hat{\rho}\hat{A}). \tag{1.6c}$$

Using this notation, the nonlinear response function is given by[2]

$$R^{(n)}(t_n,t_{n-1},\ldots,t_1) =(-1)^n\langle\tilde{\mu}\mathscr{G}(t_1)\tilde{\mu}\mathscr{G}(t_2)\tilde{\mu}\ldots\tilde{\mu}\mathscr{G}(t_n)\hat{\mu}|\hat{\rho}\rangle. \tag{1.7}$$

Equation (1.7) can be obtained using the Heisenberg picture of quantum evolution

$$\frac{\partial\hat{Q}(\tau)}{\partial\tau}=i\tilde{H}_T(\tau)\hat{Q}(\tau), \tag{1.8a}$$

$$\langle\hat{Q}(\tau)\rangle=\langle\hat{Q}(\tau)|\hat{\rho}\rangle. \tag{1.8b}$$

To derive the sum rules we first introduce the spectral moments of the optical susceptibilities.

$$K^{(n)}_{m_1\ldots m_n}\equiv(-1)^n(-i)^{m_1+\cdots+m_n}\int\frac{d\omega_1\ldots d\omega_n}{(2\pi)^n} \times\chi^{(n)}(-\omega_s;\omega_1,\ldots,\omega_n)\omega_1^{m_1}(\omega_1+\omega_2)^{m_2}\cdots \times(\omega_1+\cdots+\omega_n)^{m_n}. \tag{1.9a}$$

The sum rules are obtained by expressing the short-time optical response in terms of the frequency-domain optical susceptibilities as well as in terms of ground-state properties. The short-time optical response thus provides a bridge between optical and ground state (chemical) properties of the system. Expanding Eq. (1.7) in a Taylor series with respect to the (positive) time arguments $t_1,\ldots,t_n$, we obtain

$$K^{(n)}_{m_1\ldots m_n}=i^{m_1+\cdots+m_n+n}\langle\tilde{\mu}(\tilde{H})^{m_1}\tilde{\mu}(\tilde{H})^{m_2}\tilde{\mu}\ldots(\tilde{H})^{m_n}\hat{\mu}|\hat{\rho}\rangle. \tag{1.9b}$$

Equation (1.9a), together with Eq. (1.9b), constitute a family of generalized sum rules, each labeled by integers $n>0$ and $m_1,\ldots,m_n$. They relate the spectral moments to a combination of commutators and the density matrix of the system. In the remainder of this paper we apply the formal expression (1.9) to various cases. In Sec. II we consider a many-electron system and show how the sum rules are connected with a hierarchy of reduced electronic density matrices. In Sec. III we specialize to the time dependent Hartree–Fock (TDHF) approximation where the reduced single-electron density matrix $\hat{\rho}_0$ is the only relevant ground state property. Our results are summarized and discussed in Sec. IV.

## II. SUM RULES FOR MANY-ELECTRON SYSTEMS

We consider a many-electron system described by the Hamiltonian

$$\hat{H}_T(\tau)=\hat{t}+\hat{U}-\hat{\mu}\mathscr{E}(\tau), \tag{2.1a}$$

with the hopping (transfer) coupling

$$\hat{t}=\sum_{\bar{m}\bar{n}} t_{\bar{m}\bar{n}}\hat{c}^+_{\bar{m}}\hat{c}^-_{\bar{n}}, \tag{2.1b}$$

the Coulomb interaction

$$\hat{U}\equiv\sum_{\bar{m}\bar{n}\bar{k}\bar{l}} U_{\bar{m}\bar{n}\bar{k}\bar{l}}\hat{c}^+_{\bar{m}}\hat{c}^+_{\bar{n}}\hat{c}^-_{\bar{k}}\hat{c}^-_{\bar{l}}, \tag{2.1c}$$

and the dipole operator

$$\hat{\mu}\equiv\sum_{\bar{m}\bar{n}}\mu_{\bar{m}\bar{n}}\hat{c}^+_{\bar{m}}\hat{c}^-_{\bar{n}}. \tag{2.1d}$$

The Hamiltonian is written using a general basis set of single-electron states (labeled by latin indices with overbars) represented by the electron creation (annihilation) operators $\hat{c}^+_{\bar{m}}(\hat{c}^-_{\bar{m}})$.[16]

In this section we use Eq. (1.9b) to evaluate the moments $K^{(n)}_{m_1,\ldots,m_n}$ for some particular cases. This requires calculating commutators of operators [Eq. (1.6a)]. $K^{(n)}_{m_1,\ldots,m_n}$ then adopt a form of a sum of terms proportional to $\langle\hat{c}^+_{\bar{m}_1},\ldots,\hat{c}^+_{\bar{m}_k}\hat{c}^-_{\bar{n}_1},\ldots,\hat{c}^-_{\bar{n}_k}|\hat{\rho}\rangle$ and can thus be written in terms of the ground state reduced $k$-electron density matrices

$$\bar{\rho}^{(k)}_{\bar{m}_1,\ldots,\bar{m}_k,\bar{n}_1,\ldots,\bar{n}_k}\equiv\mathrm{Tr}(\hat{\rho}\hat{c}^+_{\bar{m}_1},\ldots,\hat{c}^+_{\bar{m}_k}\hat{c}^-_{\bar{n}_1},\ldots,\hat{c}^-_{\bar{n}_k}). \tag{2.2}$$

We consider a class of models which satisfy

$$\hat{\mu}=\sum_{\bar{n}}\mu_{\bar{n}}\hat{c}^+_{\bar{n}}\hat{c}^-_{\bar{n}}, \tag{2.3a}$$

$$[\hat{\mu},\hat{U}]=0. \tag{2.3b}$$

Equation (2.3b) holds, for example, for the following form for the Coulomb interaction commonly used in semiempirical models[16]

$$\hat{U}=\sum_{\bar{m}\bar{n}} U_{\bar{m}\bar{n}}\hat{c}^{+}_{\bar{m}}\hat{c}^{+}_{\bar{n}}\hat{c}_{\bar{n}}\hat{c}_{\bar{m}}. \tag{2.4}$$

We first consider sum rules based on $K^{(n)}_{0\ldots01}$. Making use of Eqs. (2.3) we obtain

$$K^{(n)}_{0\ldots01}=i^{n+1}\langle[\hat{\mu},[\hat{\mu},\ldots[\hat{t},\hat{\mu}]\ldots]|\hat{\rho}\rangle$$

$$=i^{n-1}\sum_{\bar{p}\bar{q}}(\mu_{\bar{p}}-\mu_{\bar{q}})^{n+1}t_{\bar{p}\bar{q}}\bar{\rho}^{(1)}_{\bar{p}\bar{q}}. \tag{2.5}$$

For any order $n$ of the response, these sum rules involve only the single-electron reduced density matrix and do not depend on the Coulomb interaction.

Sum rules related to higher moments can be represented in a compact form by adopting the following notation. Let $W^{(k)}$ be the space of $k$-electron states, $\hat{\sigma}^{(k)}_{\bar{m}_1,\ldots,\bar{m}_k,\bar{n}_1,\ldots,\bar{n}_k} \equiv \hat{c}^{+}_{\bar{m}_1}\ldots\hat{c}^{+}_{\bar{m}_k}\hat{c}^{+}_{\bar{n}_1}\ldots\hat{c}_{\bar{n}_k}$ be a basis set in the corresponding Liouville space $L^{(k)}$ of operators acting in $W^{(k)}$, and $\mathrm{Tr}_k$ be the trace in $W^{(k)}$. We can associate with each operator $\hat{A}\in L^{(1)}$ a superoperator $\tilde{A}^{(k)}$ acting in $L^{(k)}$. To that end we define the superoperators corresponding to the basis set $\hat{\sigma}^{(k)}$

$$\tilde{\sigma}^{(k)}_{\bar{m}\bar{n}}(\hat{\sigma}^{(k)}_{\bar{m}_1,\ldots,\bar{m}_k,\bar{n}_1\ldots,\bar{n}_k})$$

$$=\sum_{p=1}^{k}\delta_{\bar{n}\bar{m}_p}\hat{\sigma}^{(k)}_{\bar{m}_1\ldots\bar{m}_{p-1}\bar{m}\bar{m}_{p+1}\ldots\bar{m}_k,\bar{n}_1\ldots\bar{n}_k}$$

$$-\sum_{p=1}^{k}\delta_{\bar{m}\bar{n}_p}\hat{\sigma}^{(k)}_{\bar{m}_1\ldots\bar{m}_k,\bar{n}_1,\ldots\bar{n}_{p-1}\bar{n}\bar{n}_{p+1}\ldots\bar{n}_k}. \tag{2.6a}$$

The reduced density operators $\hat{\rho}^{(k)}\in L^{(k)}$ are given by

$$\mathrm{Tr}(\hat{\rho}^{(k)}\hat{\sigma}^{(k)}_{\bar{m}_1\ldots\bar{m}_k,\bar{n}_1\ldots\bar{n}_k})=\bar{\rho}_{\bar{m}_1\ldots\bar{m}_k,\bar{n}_1\ldots\bar{n}_k}. \tag{2.6b}$$

We further introduce $\hat{U}\in L^{(2)}$ by

$$\hat{U}\equiv\sum_{\bar{m}\bar{n}\bar{k}\bar{l}}U_{\bar{m}\bar{n}\bar{k}\bar{l}}\hat{\sigma}^{(2)}_{\bar{m}\bar{n},\bar{k}\bar{l}}. \tag{2.6c}$$

We next consider the sum rules for the linear response. Noting that by symmetry $[\chi^{(1)}(-\omega)=-\chi^{(1)}(\omega)]$, all even moments vanish identically

$$K^{(1)}_{2n}=0,\quad n=0,1,2,\ldots\ . \tag{2.7a}$$

$K^{(1)}_{1}$ gives the oscillator strength sum rule [Eq. (2.5) for $n=1$]. The next nanovanishing sum rule is, therefore,

$$K^{(1)}_{3}=\mathrm{Tr}_1(\hat{\rho}^{(1)}\tilde{t}^{(1)}\tilde{t}^{(1)}\hat{t})+\mathrm{Tr}_2(\hat{\rho}^{(2)}\tilde{t}^{(1)}\tilde{t}^{(1)}\hat{U}). \tag{2.7b}$$

Proceeding in the same way we obtain the complete the set of sum rules related to third moments of $\chi^{(3)}$

$$K^{(3)}_{111}=-\mathrm{Tr}_1(\hat{\rho}^{(1)}\tilde{t}^{(1)}\tilde{\mu}\tilde{t}^{(2)}\hat{t})-\mathrm{Tr}_2(\hat{\rho}^{(2)}\tilde{t}^{(1)}\tilde{\mu}\tilde{t}^{(2)}\hat{U}), \tag{2.8a}$$

$$K^{(3)}_{021}=\mathrm{Tr}_1(\hat{\rho}^{(1)}\tilde{t}^{(2)}\tilde{t}^{(2)}\hat{t})-2\ \mathrm{Tr}_1(\hat{\rho}^{(1)}\tilde{\mu}\tilde{t}^{(1)}\tilde{t}^{(2)}\hat{t})$$

$$+\mathrm{Tr}_2(\hat{\rho}^{(2)}\tilde{t}^{(2)}\tilde{t}^{(2)}\hat{U})-2\ \mathrm{Tr}_2(\hat{\rho}^{(2)}\tilde{\mu}\tilde{t}^{(1)}\tilde{t}^{(2)}\hat{U}), \tag{2.8b}$$

$$K^{(3)}_{102}=K^{(3)}_{111},\quad K^{(3)}_{012}=K^{(3)}_{021}, \tag{2.8c}$$

$$K^{(3)}_{201}=-\mathrm{Tr}_1(\hat{\rho}^{(1)}\tilde{t}^{(1)}\tilde{t}^{(3)}\hat{t})-\mathrm{Tr}_2(\hat{\rho}^{(2)}\tilde{t}^{(1)}\tilde{t}^{(3)}\hat{U}), \tag{2.8d}$$

$$K^{(3)}_{003}=3\ \mathrm{Tr}_1(\hat{\rho}^{(1)}\tilde{\mu}\tilde{t}^{(2)}\tilde{t}^{(1)}\hat{t})-3\ \mathrm{Tr}_1(\hat{\rho}^{(1)}\tilde{\mu}\tilde{\mu}\tilde{t}^{(1)}\tilde{t}^{(1)}\hat{t})$$

$$-\mathrm{Tr}_1(\hat{\rho}^{(1)}\tilde{t}^{(3)}\tilde{t}^{(1)}\hat{t})+3\ \mathrm{Tr}_2(\hat{\rho}^{(2)}\tilde{\mu}\tilde{t}^{(2)}\tilde{t}^{(1)}\hat{U})$$

$$-3\ \mathrm{Tr}_2(\hat{\rho}^{(2)}\tilde{\mu}\tilde{\mu}\tilde{t}^{(1)}\tilde{t}^{(1)}\hat{U})-\mathrm{Tr}_2(\hat{\rho}^{(2)}\tilde{t}^{(3)}\tilde{t}^{(1)}\hat{U}) \tag{2.8e}$$

with

$$\hat{t}^{(j)}\equiv[\hat{\mu},[\hat{\mu},[\ldots,[\hat{\mu},\hat{t}]\ldots]=\sum_{\bar{p}\bar{q}}t_{\bar{p}\bar{q}}(\mu_{\bar{p}}-\mu_{\bar{q}})^{j}\hat{\sigma}_{\bar{p}\bar{q}}. \tag{2.9}$$

## III. APPLICATION TO THE TDHF APPROXIMATION: THE SINGLE ELECTRON DENSITY MATRIX

It has been shown in Ref. 11 that the TDHF equation can be viewed as Hamilton's classical equation of motion on the phase space $\mathscr{M}$ of all single Slater determinants which can be described by single-electron reduced density matrices $\hat{\rho}_0$ satisfying the condition $\hat{\rho}_0^2=\hat{\rho}_0$. Each quantum operator $\hat{Q}$ then becomes a function on $\mathscr{M}$, defined as the expectation value of $\hat{Q}$ with respect to the Slater determinant represented by $\hat{\rho}_0$. [The algebra of functions of $\mathscr{M}$ is generated (as an associative algebra) by the functions $\hat{\sigma}_a\in\mathscr{A}$ which form a basis set of a matrix Lie algebra $\mathscr{A}$ generated by operators $\hat{c}^{+}_{\bar{m}}\hat{c}_{\bar{n}}$. For arbitrary function $\xi\in\mathscr{A}$ its value on $\hat{\rho}_0\in\mathscr{M}$ is $\hat{\xi}(\hat{\rho}_0)=\mathrm{Tr}(\hat{\xi}\hat{\rho}_0)$.] The classical Hamiltonian corresponding to the quantum Hamiltonian [Eqs. (1.2)] which yields the TDHF equation, has the form

$$\hat{H}_T(\tau)=\hat{H}-\hat{\mu}\mathscr{E}(\tau)=\hat{t}+\hat{V}-\hat{\mu}\mathscr{E}(\tau), \tag{3.1a}$$

with

$$\hat{t}=\sum_{m}t_m\hat{\sigma}_m,\quad \hat{V}=\sum_{mn}V_{mn}\hat{\sigma}_m\hat{\sigma}_n,\quad \hat{\mu}=\sum_{m}\mu_m\hat{\sigma}_m. \tag{3.1b}$$

Expressions for $t_m$, $V_{mn}$, and $\mu_m$ in terms of $t_{\bar{m}\bar{n}}$, $U_{\bar{m}\bar{n}\bar{k}\bar{l}}$, and $\mu_{\bar{m}\bar{n}}$ were given in Ref. 11. The Poisson bracket for any $\hat{\xi}$, $\hat{\eta}\in\mathscr{A}$ is determined by the commutator on $\mathscr{A}$ which is the algebra of single-electron reduced density matrices

$$\{\hat{\xi},\hat{\eta}\}=i[\hat{\xi},\hat{\eta}]. \tag{3.2a}$$

This definition can be extended to arbitrary functions on $\mathscr{M}$, making use of the property

$$\{\hat{\xi},\hat{\eta}_1\hat{\eta}_2\}=\{\hat{\xi},\hat{\eta}_1\}\hat{\eta}_2+\hat{\eta}_1\{\hat{\xi},\hat{\eta}_2\}. \tag{3.2b}$$

We shall use the Heisenberg picture (which appears very similar for the quantum and classical, i.e., TDHF cases) to derive the TDHF sum rules. {The classical analog of the Schrodinger–Liouville picture is based on following the evolution of $\hat{\rho}\in\mathscr{M}$:

$$\langle\hat{Q}(\tau)\rangle=\hat{Q}[\hat{\rho}(\tau)],\quad i\,\frac{\partial\hat{\rho}(\tau)}{\partial\tau}=[\hat{t}+2V(\hat{\rho})-\mathscr{E}(\tau)\hat{\mu},\hat{\rho}],$$

where $V(\hat{\rho})\equiv\Sigma_{mn}V_{mn}\mathrm{Tr}(\hat{\rho}\hat{\sigma}_n)\hat{\sigma}_m$. This constitutes the standard form of the TDHF equation}. In this case an operator $\hat{Q}$ becomes a distribution (a function in phase space $\mathscr{M}$). Equations (1.8) apply here as well with the following differences: the superoperator $\tilde{A}$ acting in the space of distributions is defined as

$$\tilde{A}\hat{B} \equiv -i\{\hat{A},\hat{B}\}, \tag{3.3}$$

and $\langle \hat{B}|\hat{\rho}_0\rangle$ for any distribution $\hat{B}$ denotes its value on a reduced density matrix $\hat{\rho}_0$:

$$\langle \hat{B}|\hat{\rho}_0\rangle \equiv \hat{B}(\hat{\rho}_0). \tag{3.4}$$

In addition, $\hat{\rho}$ should be replaced by $\hat{\rho}_0$ denoting the HF ground state reduced density matrix (the stationary point of the TDHF equation).

Since the classical and the quantum Liouville equations are formally identical, the TDHF sum rules have the form of Eqs. (1.9), except that the superoperators are defined by Eq. (3.3), the operator $\hat{\mu}$ on right-hand side of Eq. (1.9b) should be understood as a distribution (i.e., a function on $\mathscr{M}$), and $\langle \hat{B}|\hat{\rho}_0\rangle$ for a distribution $\hat{B}$ denotes its value at $\hat{\rho}_0 \in \mathscr{M}$, and $\hat{\rho}_0$ is the HF ground state density matrix [see Eq. (3.4)].

We next evaluate Eq. (1.9b), for a few cases. In the TDHF case $K^{(n)}_{m_1,\ldots,m_n}$ has contributions of the form

$$\langle \hat{\sigma}_{a_1}\ldots\hat{\sigma}_{a_k}|\hat{\rho}_0\rangle = \bar{\rho}_{a_1},\ldots,\bar{\rho}_{a_k}, \tag{3.5a}$$

where

$$\bar{\rho}_a \equiv \langle \hat{\sigma}_a|\hat{\rho}_0\rangle \equiv \mathrm{Tr}(\hat{\sigma}_a\hat{\rho}_0). \tag{3.5b}$$

We shall consider systems satisfying Eqs. (2.3). In the TDHF approximation this implies

$$\{\hat{\mu},\hat{V}\} = 0, \quad \hat{\mu} = \sum_{\bar{n}} \mu_{\bar{n}}\hat{\sigma}_{\bar{n}\bar{n}}. \tag{3.6}$$

The TDHF sum rules related to $K^{(n)}_{0\ldots01}$ have the same form as the exact ones. The only difference is that the ground-state single-electron reduced density matrix on the right-hand side of Eqs. (2.5) is now the HF (rather than the exact) density matrix.

We next derive the lowest higher-order sum rules for $n=1$, 3 which are different for the quantum and classical cases. We find

$$K^{(1)}_2 = 0, \tag{3.7a}$$

and

$$K^{(1)}_3 = \langle \{\hat{\mu},\{\hat{H},\{\hat{H},\{\hat{H},\hat{\mu}\}\}\}\}|\hat{\rho}_0\rangle. \tag{3.7b}$$

Making use of the Jacobi identity for the Poisson bracket which reads as

$$\{\hat{f},\{\hat{g},\hat{h}\}\} + \{\hat{g},\{\hat{h},\hat{f}\}\} + \{\hat{h},\{\hat{f},\hat{g}\}\} = 0$$

for any functions $\hat{f}$, $\hat{g}$, and $\hat{h}$, and the fact that $\langle\{\hat{H},\hat{g}\}|\hat{\rho}_0\rangle = 0$, $\forall \hat{g}$ (which implies that $\hat{\rho}_0$ is a stationary point of the TDHF equation), we can recast Eq. (3.7b) in the form

$$K^{(1)}_3 = \langle \{\{\hat{\mu},\hat{H}\},\{\hat{H},\{\hat{H},\hat{\mu}\}\}\}|\hat{\rho}_0\rangle.$$

Noting that

$$\{\hat{\mu},\hat{H}\} = i[\hat{\mu},\hat{t}] \equiv i\hat{t}^{(1)} = i\sum_{\bar{m}\bar{n}} (\mu_{\bar{m}} - \mu_{\bar{n}})\bar{t}_{\bar{m}\bar{n}}\hat{\sigma}_{\bar{m}\bar{n}},$$

we get

$$K^{(1)}_3 = -\langle \{\hat{t}^{(1)},\{\hat{t}^{(1)},\hat{H}\}\}|\hat{\rho}_0\rangle.$$

Evaluating the right-hand side of this equation we finally obtain

$$K^{(1)}_3 = \mathrm{Tr}\{[\hat{t}+2V(\hat{\rho}_0),\hat{t}^{(1)}][\hat{t}^{(1)},\hat{\rho}_0]\} + 2\ \mathrm{Tr}\{[\hat{t}^{(1)},\hat{\rho}_0]V([\hat{t}^{(1)},\hat{\rho}_0])\}. \tag{3.7c}$$

In analogy with the above derivation we have calculated the complete set of sum rules representing the third moments of the third order response:

$$K^{(3)}_{111} = A_{13} + B, \tag{3.8a}$$

$$K^{(3)}_{201} = A_{13}, \quad K^{(3)}_{021} = 2A_{13} + 2B + A_{22}, \tag{3.8b}$$

$$K^{(3)}_{012} = K^{(3)}_{021}, \quad K^{(3)}_{102} = K^{(3)}_{111}, \tag{3.8c}$$

$$K^{(3)}_{003} = 3A_{13} + 3B + 3A_{22} + A_{31}. \tag{3.8d}$$

Here we have introduce the notation:

$$A_{kj} \equiv \mathrm{Tr}\{[\hat{\rho}_0,\hat{t}^{(k)}][\hat{t}+2V(\hat{\rho}_0),\hat{t}^{(j)}]\} + 2\ \mathrm{Tr}\{[\hat{\rho}_0,\hat{t}^{(k)}]V([\hat{t}^{(j)},\hat{\rho}_0])\}, \tag{3.9a}$$

$$B \equiv \mathrm{Tr}([\hat{\rho}_0,\hat{t}^{(1)}][\hat{t}^{(1)},\hat{t}^{(2)}]), \tag{3.9b}$$

and $\hat{t}^{(j)}$ were defined in Eq. (2.9).

## IV. DISCUSSION

In this paper we have introduced generalized sum rules for the optical response of many-electron systems. In each order of nonlinear response we obtain a family of sum rules, analogous to the moments of linear absorption, which connect the response functions to ground state properties. These relations generally involve detailed ground state information expressed in terms of a hierarchy of reduced density matrices (i.e., single electron, two electron, three electron, etc.). We have shown that at each order the response there is one sum rule [Eq. (2.5)] which only depends on the single-electron ground-state reduced density matrices.

Making use of Hamilton's form of the ''classical'' TDHF equation, we have applied methods of classical dynamics and derived a family of simplified sum rules, which connect optical response functions to the single-electron reduced density matrix of the HF ground state. It is interesting to note that the sum rule is an exact relation between these two approximate quantities, i.e., a response function in the TDHF approximation and the HF ground state single-electron reduced density matrix. This is a consequence of the fact that the TDHF approach is a classical analog of the original quantum model and reflects an inherent consistency of the TDHF approach to the optical response and the stationary HF approximation for the ground state. Since the ''classical'' sum rules only depend on the ground state single-electron reduced density matrix which controls the chemical bond order, these sum rules provide very powerful relations between optical and chemical properties of molecules. We have calculated the complete set of exact and TDHF sum rules related to the first and third moments of $\chi^{(1)}$ and $\chi^{(3)}$ [see Eqs. (2.5), (2.7), (2.8), (3.7c), and (3.8)].

The sum rules derived here can be applied to construct effective Hamiltonians for many-electron systems using as an input optical and ground state properties which may be either calculated or taken from experiment.[17–19] This is accomplished by treating the sum rules as a system of equations for the parameters of the Hamiltonian. For the wide class of Hamiltonians defined by Eqs. (2.1) or Eqs. (3.1) which satisfy Eqs. (2.3) the sum rules related to $K^{(n)}_{0\dots01}$ involve the hopping matrix $\hat{t}$ alone and do not contain the Coulomb interaction parameters. These can be used to determine the hopping matrix. Since hopping is usually short-range we need only a few sum rules. For example, if a molecule has a geometry of a long chain[3,10,14] we can make use of translational symmetry and require only one sum rule for the nearest-neighbor hopping and two sum rules (involving $\chi^{(1)}$ and $\chi^{(3)}$) in the case of next nearest-neighbor hopping. Sum rules related to higher-order moments can be used to determine the Coulomb interaction parameters. The sum rules derived in Secs. II and III. [Eqs. (2.7), (2.8), (3.7), and (3.8)] contain only the first power of the Coulomb interaction matrix [which is a consequence of the conditions given by Eqs. (2.3)], and provide linear equations for the Coulomb interaction. It directly follows from Eqs. (2.3) that all the sum rules related to the third moments of any $\chi^{(n)}$ (i.e., connected with $K^{(n)}_{m_1\dots m_n}$ for $m_1+\cdots+m_n=3$) involve only the first power of the Coulomb interaction and in the quantum case do not involve higher than the two-electron density matrix (i.e., $K^{(n)}_{m_1\dots m_n}$ for $m_1+\cdots+m_3=n$ can be expressed in terms of $\hat{\rho}^{(1)}$ and $\hat{\rho}^{(2)}$ for any $n$). The sum rules presented here are particularly attractive for calculating the optical response of conjugated polymers. It has been demonstrated that only a few dominant collective modes contribute to their optical susceptibilities. Therefore, they can be described in terms of a few parameters which can be determined using a finite number of sum rules. This should result in a direct connection between off-resonant nonlinear response and the ground-state single-electron reduced density matrix.

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