Size-consistent quasiparticle representation of nonlinear optical susceptibilities in many-electron systems

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The optical response of a many-electron system is calculated by mapping it onto a coupled set of classical oscillators representing the electron–hole pair components of the reduced single-electron-density matrix. This classical representation is rigorously established using a Poisson bracket relation. Expressions for the nonlinear optical susceptibilities obtained using a Green's-function solution of the oscillator equations of motion are used to analyze the size scaling of the off-resonant response and the resonant structure of the response. © *1996 American Institute of Physics.* [S0021-9606(96)03401-6]

I. INTRODUCTION

The mechanism of optical nonlinearities constitutes an important fundamental problem with practical implications connected with the synthesis of new optical materials with large off-resonant nonlinear optical susceptibilities.[1–5] Optical susceptibilities of small molecules may be calculated by expanding them in the global (many-body) eigenstates of the system. The response is then related to the eigenvalues and the matrix elements of the polarization operator.[6] However, this approach becomes impractical for large systems since the number of eigenstates involved in the response grows rapidly with size. The response is in this case determined primarily by statistical properties such as level correlations which show up in multidimensional spectral densities rather than by properties of the individual eigenstates.[7] In addition, the global eigenstates representation faces some serious difficulties in predicting the size scaling of the polarizabilities since the $\sim N$ scaling for large sizes (where N is the number of atoms) results from cancellations of terms which scale as $\sim N^2$.[8] To obtain these cancellations by performing approximate calculations of the eigenstates one should ensure the compatability of approximations for the ground and excited states.[9] These difficulties, known as the size-consistency problem, can be overcome using many-body methods based on a reduced description.[10,11] This is obtained using equations of motion, which can be closed by invoking certain approximations. In these approaches the correct scaling for large sizes is built in from the start and it does not require a delicate cancellation of terms. An application of a many-body Green's-function technique to Frenkel exciton systems in molecular aggregates had clearly demonstrated these points.[7] The time-dependent Hartree–Fock (TDHF)[12] is a many-body technique which has been shown to be useful for predicting optical properties of many-electron systems with extended single-electron states and strong Coulomb interactions. The method has been applied to study the resonant as well as off-resonant optical properties of conjugated polymers.[13–15]

In this paper we recast the TDHF equation for a many-electron system driven by an external field in a form of Hamilton's classical equations of motion involving a classical Hamiltonian and a Poisson bracket[16] defined on the classical phase space: the manifold of all single Slater determinants representing the state of a many-electron problem. By expanding the solution of the TDHF equation in powers of the applied field we derive closed expressions for the lowest three optical response functions. We then establish a coupled oscillator (quasiparticle) picture for the response, and express the response functions in terms of eigenmodes (oscillators) of the linearized TDHF equation representing electron–hole excitation. For a system of M electrons with N available orbitals the number of oscillators is $M(N-M)$. The nonlinear response can be attributed to mode scattering. The expressions for the response contain commutators and traces in the phase space of reduced single-electron-density matrices. Size consistency, namely, the $\sim N$ scaling of hyperpolarizabilities for large sizes, is naturally built in and requires no delicate cancellations.

II. THE TIME-DEPENDENT HARTREE–FOCK EQUATIONS

We consider a many-fermion system with M electrons which can occupy N orthonormal states ($M \leqslant N$) denoted by Latin indices with overbars ($\bar{n},\bar{m},...$) and the indices include the spin.[17] Assuming two-body interactions, the general system Hamiltonian has the form

$$\hat{H}=\sum_{\bar{m}\bar{n}} \bar{t}_{\bar{m}\bar{n}}\hat{c}^{+}_{\bar{m}}\hat{c}_{\bar{n}}+\sum_{\bar{m}\bar{n}\bar{k}\bar{l}} \bar{V}_{\bar{m}\bar{n}\bar{k}\bar{l}}\hat{c}^{+}_{\bar{m}}\hat{c}^{+}_{\bar{n}}\hat{c}_{\bar{k}}\hat{c}_{\bar{l}}, \tag{2.1a}$$

where $\hat{c}(\hat{c}^{+})$ are the electron annihilation (creation) operators which satisfy the Fermi commutation relations

$$\hat{c}_{\bar{m}}\hat{c}^{+}_{\bar{n}}+\hat{c}^{+}_{\bar{n}}\hat{c}_{\bar{m}}=\delta_{\bar{m}\bar{n}}, \tag{2.1b}$$

and all other anticommutators of $\hat{c}$ and $\hat{c}^{+}$ vanish. Without loss of generality, the matrix $\bar{V}_{\bar{m}\bar{n}\bar{k}\bar{l}}$ is assumed to be antisymmetric with respect to permutations $\bar{m}$ with $\bar{n}$ and k with l.

We adopt the multipolar form of interaction with the transverse electric field,[18] and the total Hamiltonian $\hat{H}_T$ of the driven system is

$$\hat{H}_T(t)=\hat{H}-\sum_{\bar{m}\bar{n}} \mathscr{E}_{\bar{m}\bar{n}}(t)\hat{c}^{+}_{\bar{m}}\hat{c}_{\bar{n}}, \tag{2.2}$$

where $\mathscr{E}_{mn}(t)$ can be expressed in terms of the external field $\mathscr{E}(\mathbf{r},t)$

$$\mathscr{E}_{\bar{m}\bar{n}}(t)\equiv\int d\mathbf{r}\ \mathscr{E}(\mathbf{r},t)\mu_{\bar{m}\bar{n}}(\mathbf{r}). \tag{2.3}$$

Expressions for the matrix elements $\mu_{\bar{m}\bar{n}}(\mathbf{r})$ of the polarization operator were given in Refs. 14 and 17.

The TDHF procedure results in closed equations of motion for the reduced single-electron-density matrix $\rho_{\bar{m}\bar{n}}\equiv\langle c_{\bar{m}}^{+}c_{\bar{n}}\rangle$.[12–15] In this section we recast the time-dependent Hartree–Fock equations in a form of Hamilton's dynamical equations of classical mechanics. We will adopt the following convention. Let $\mathscr{A}$ be the space of linear operators acting on the N-dimensional space $\mathscr{V}$ of single-electron states; therefore, $\mathscr{A}$ is the single-electron Liouville space; we will use a caret to denote the elements of $\mathscr{A}$. Any $\hat{Q}\in\mathscr{A}$ can be viewed as a function on $\mathscr{A}$:

$$\hat{Q}(\hat{\rho})\equiv\mathrm{Tr}(\hat{\rho}\hat{Q})\quad\text{for}\quad\hat{\rho}\in\mathscr{A}, \tag{2.4}$$

and we will also use a caret to denote functions on $\mathscr{A}$. Let $\hat{\sigma}_{\bar{m}\bar{n}}$ be a basis set in $\mathscr{A}$. The components $\rho_{\bar{m}\bar{n}}$ of the reduced density matrix $\hat{\rho}$ are given by

$$\rho_{\bar{m}\bar{n}}=\hat{\sigma}_{\bar{m}\bar{n}}(\hat{\rho})=\mathrm{Tr}(\hat{\rho}\hat{\sigma}_{\bar{m}\bar{n}}). \tag{2.5a}$$

Any element $\hat{Q}\in\mathscr{A}$ can be represented in terms of its matrix elements $Q_{\bar{m}\bar{n}}$:

$$\hat{Q}=\sum_{\bar{m}\bar{n}}Q_{\bar{m}\bar{n}}\hat{\sigma}_{\bar{m}\bar{n}}. \tag{2.5b}$$

The associate algebra of functions on $\mathscr{A}$ is generated by $\hat{\sigma}_{\bar{m}\bar{n}}$ and we have

$$\begin{aligned}\hat{\sigma}_{\bar{m}_l\bar{n}_l}\cdots\hat{\sigma}_{\bar{m}_k\bar{n}_k}(\hat{\rho})&=\mathrm{Tr}(\hat{\sigma}_{\bar{m}_1\bar{n}_1}\hat{\rho})\cdots\mathrm{Tr}(\hat{\sigma}_{\bar{m}_k\bar{n}_k}\hat{\rho})\\&=\rho_{\bar{m}_1\bar{n}_1}\cdots\rho_{\bar{m}_k\bar{n}_k}.\end{aligned} \tag{2.5c}$$

Using this notation, the TDHF equation which describes the evolution of the reduced density matrix can be presented in a form

$$i\frac{\partial\hat{\rho}}{\partial\tau}=[\hat{t}+2V(\hat{\rho})-\hat{\mathscr{E}}(\tau),\hat{\rho}], \tag{2.6}$$

where

$$\hat{t}\equiv\sum_{\bar{m}\bar{n}}t_{\bar{m}\bar{n}}\hat{\sigma}_{\bar{m}\bar{n}}, \tag{2.7a}$$

$$\begin{aligned}\bar{V}(\hat{\rho})\equiv\frac{1}{2}\sum_{\bar{m}\bar{n}\bar{k}\bar{l}}&[\mathrm{Tr}(\hat{\rho}\hat{\sigma}_{\bar{m}\bar{l}})\hat{\sigma}_{\bar{n}\bar{k}}+\mathrm{Tr}(\hat{\rho}\hat{\sigma}_{\bar{n}\bar{k}})\hat{\sigma}_{\bar{m}\bar{l}}\\&-\mathrm{Tr}(\hat{\rho}\hat{\sigma}_{\bar{m}\bar{k}})\hat{\sigma}_{\bar{n}\bar{l}}-\mathrm{Tr}(\hat{\rho}\hat{\sigma}_{\bar{n}\bar{l}})\hat{\sigma}_{\bar{m}\bar{k}}]\bar{V}_{\bar{m}\bar{n}\bar{k}\bar{l}}.\end{aligned} \tag{2.7b}$$

To recast the TDHF equation in Hamilton's form we first obtain a classical Hamiltonian $\hat{H}$. We make use of the fact that the reduced density matrix $\hat{\rho}$ is a projection operator [see Eqs. (A1)] and associates with a given $\hat{\rho}$ an M-particle quantum state $\Omega(\hat{\rho})$ which is a single Slater determinant formed by M single-electron states belonging to $\mathscr{V}(\hat{\rho})\equiv\mathrm{im}(\hat{\rho})$ (see Appendix A). This allows us to define a classical Hamiltonian on the Grassman manifold $\mathscr{M}\subset\mathscr{A}$ (Ref. 19; see Appendix A):

$$\hat{H}(\hat{\rho})\equiv\langle\Omega(\hat{\rho})|\hat{H}|\Omega(\hat{\rho})\rangle. \tag{2.8}$$

To express this Hamiltonian in terms of matrix elements of $\hat{\rho}$ we make use of the fact that

$$\langle\Omega(\hat{\rho})|\hat{c}_{\bar{m}}^{+}\hat{c}_{\bar{n}}|\Omega(\hat{\rho})\rangle=\rho_{\bar{m}\bar{n}} \tag{2.9a}$$

and the Wick theorem[10] which gives

$$\begin{aligned}\langle\Omega|\hat{c}_{\bar{m}}^{+}\hat{c}_{\bar{n}}^{+}\hat{c}_{\bar{k}}\hat{c}_{\bar{l}}|\Omega\rangle&=\langle\Omega|\hat{c}_{\bar{m}}^{+}\hat{c}_{\bar{l}}|\Omega\rangle\langle\Omega|\hat{c}_{\bar{n}}^{+}\hat{c}_{\bar{k}}|\Omega\rangle\\&\quad-\langle\Omega|\hat{c}_{\bar{m}}^{+}\hat{c}_{\bar{k}}|\Omega\rangle\langle\Omega|\hat{c}_{\bar{n}}^{+}\hat{c}_{\bar{l}}|\Omega\rangle.\end{aligned} \tag{2.9b}$$

Substituting Eq. (2.1a) or Eq. (2.2) into Eq. (2.8) and making use of Eqs. (2.9) and (2.5) we obtain

$$\hat{H}=\sum_{\bar{m}\bar{n}}t_{\bar{m}\bar{n}}\hat{\sigma}_{\bar{m}\bar{n}}+\sum_{\bar{m}\bar{n}\bar{k}\bar{l}}\bar{V}_{\bar{m}\bar{n}\bar{k}\bar{l}}(\hat{\sigma}_{\bar{m}\bar{l}}\hat{\sigma}_{\bar{n}\bar{k}}-\hat{\sigma}_{\bar{m}\bar{k}}\hat{\sigma}_{\bar{n}\bar{l}}), \tag{2.10a}$$

$$\hat{H}_T(\tau)=\hat{H}-\hat{\mathscr{E}}(\tau), \tag{2.10b}$$

where the dipole interaction with the radiation field is

$$\hat{\mathscr{E}}(\tau)\equiv\int d\mathbf{r}\ \mathscr{E}(\mathbf{r},\tau)\hat{\mu}(\mathbf{r})=\sum_{\bar{m}\bar{n}}\mathscr{E}_{\bar{m}\bar{n}}(\tau)\hat{\sigma}_{\bar{m}\bar{n}}, \tag{2.10c}$$

with the dipole operator

$$\hat{\mu}(\mathbf{r})\equiv\sum_{\bar{m}\bar{n}}\mu_{\bar{m}\bar{n}}(\mathbf{r})\hat{\sigma}_{\bar{m}\bar{n}}. \tag{2.10d}$$

The Liouville equations of classical dynamics written for distributions (functions on $\mathscr{M}$) have the form[16]

$$\frac{d\hat{f}}{d\tau}=\{\hat{H},\hat{f}\} \tag{2.11a}$$

or, using our basis set,

$$\frac{d}{d\tau}\hat{\sigma}_{\bar{m}\bar{n}}=\{\hat{H},\hat{\sigma}_{\bar{m}\bar{n}}\}. \tag{2.11b}$$

$\{\hat{f},\hat{g}\}$ denotes the Poisson bracket of $\hat{f}$ and $\hat{g}$, defined as follows: We first introduce the elementary Poisson bracket

$$\{\hat{\sigma}_{\bar{m}\bar{n}},\hat{\sigma}_{\bar{k}\bar{l}}\}\equiv i[\hat{\sigma}_{\bar{m}\bar{n}},\hat{\sigma}_{\bar{k}\bar{l}}], \tag{2.12a}$$

where the matrix commutator is

$$[\hat{\sigma}_{\bar{m}\bar{n}},\hat{\sigma}_{\bar{k}\bar{l}}]\equiv\delta_{\bar{n}\bar{k}}\hat{\sigma}_{\bar{m}\bar{l}}-\delta_{\bar{m}\bar{l}}\hat{\sigma}_{\bar{k}\bar{n}}. \tag{2.12b}$$

Making use of the following properties of the Poisson bracket:

$$\{\hat{f},\hat{g}\}=-\{\hat{g},\hat{f}\}, \tag{2.13a}$$

$$\{\hat{f},\hat{g}\hat{h}\}=\{\hat{f},\hat{g}\}\hat{h}+\hat{g}\{\hat{f},\hat{h}\}, \tag{2.13b}$$

we can extend the Poisson bracket definition to arbitrary functions on our classical phase space $\mathscr{M}$.

To present the equations in a compact form which suggests possible generalizations (see Appendix B) we note that $\mathscr{A}$ forms a Lie algebra with respect to the commutator given by Eq. (2.12b). Since in the following all indices come in

pairs, we shall adopt an abbreviated notation and hereafter use a single Latin index to represent a pair of indices with overbars. The basis set thus becomes

$$\hat{\sigma}_m \equiv \hat{\sigma}_{\bar{m}\bar{n}} \quad \text{for} \quad m=\bar{m}\bar{n}. \tag{2.14}$$

Writing the commutator in terms of structure constants f,

$$[\hat{\sigma}_m,\hat{\sigma}_n]=\sum_a f^a_{mn}\hat{\sigma}_a, \tag{2.15a}$$

we can extend the TDHF equation to an arbitrary Lie algebra $\mathscr{A}$ where $\hat{\sigma}_m$ are assumed to form an orthonormal basis set of $\mathscr{A}$:

$$\mathrm{Tr}(\hat{\sigma}_m\hat{\sigma}_n)=\delta_{mn}. \tag{2.15b}$$

For the initial case [algebra gl$(N;C)$], and using the new single-index notation, the Hamiltonians $\hat{H}$ and $\hat{H}_T$ can be written in a form

$$\hat{H}=\sum_m t_m\hat{\sigma}_m+\sum_{mn} V_{mn}\hat{\sigma}_m\hat{\sigma}_n, \tag{2.16a}$$

$$\hat{H}_T(\tau)=\hat{H}-\hat{\mathscr{E}}(\tau), \tag{2.16b}$$

where

$$\hat{\mathscr{E}}(\tau)\equiv\int d\mathbf{r}\ \mathscr{E}(\mathbf{r},\tau)\hat{\mu}(\mathbf{r})=\sum_m \mathscr{E}_m(\tau)\hat{\sigma}_m, \tag{2.16c}$$

with

$$\hat{\mu}(\mathbf{r})\equiv\sum_m \mu_m(\mathbf{r})\hat{\sigma}_m. \tag{2.16d}$$

Here

$$f^a_{mn}=\delta_{\bar{n}\bar{k}}\delta_{\bar{m}\bar{a}}\delta_{\bar{l}\bar{b}}-\delta_{\bar{m}\bar{l}}\delta_{\bar{k}\bar{a}}\delta_{\bar{n}\bar{b}}, \tag{2.17a}$$

$$t_m=\bar{t}_{\bar{m}\bar{n}}, \quad \mu_m(\mathbf{r})=\mu_{\bar{m}\bar{n}}(\mathbf{r}), \tag{2.17b}$$

$$V_{mn}=\tfrac{1}{2}(\bar{V}_{\bar{m}\bar{k}\bar{l}\bar{n}}-\bar{V}_{\bar{m}\bar{k}\bar{n}\bar{l}})+\tfrac{1}{2}(\bar{V}_{\bar{k}\bar{m}\bar{n}\bar{l}}-\bar{V}_{\bar{k}\bar{m}\bar{l}\bar{n}}), \tag{2.17c}$$

where $m=\bar{m}\bar{n}$, $n=\bar{k}\bar{l}$, $a=\bar{a}\bar{b}$.

The following equations hold for a general Hamiltonian given by Eq. (2.16) and the Poisson bracket [Eq. (2.15a)]. Equations (2.17) will be used only at the end (see Appendix F). To connect the Liouville equation of motion [Eqs. (2.11)] to the TDHF equations we recast the Liouville dynamical equation in a form of the Hamilton's equation for trajectories in phase space (see Appendix C for derivation) and obtain

$$i\frac{\partial\hat{\rho}}{\partial\tau}=[\hat{t}+2V(\hat{\rho})-\hat{\mathscr{E}}(\tau),\hat{\rho}] \tag{2.18a}$$

with

$$\hat{t}\equiv\sum_m t_m\hat{\sigma}_m, \quad V(\hat{\rho})\equiv\sum_{mn} V_{mn}\,\mathrm{Tr}(\hat{\rho}\hat{\sigma}_n)\hat{\sigma}_m, \tag{2.18b}$$

which coincides with the TDHF equation. Equation (2.18a) can also be written for the components $\rho_m\equiv\mathrm{Tr}(\hat{\rho}\hat{\sigma}_m)$,

$$i\frac{\partial\rho_a}{\partial\tau}=\sum_{mb} t_m f^b_{ma}\rho_b+2\sum_{mnb} V_{mn}f^b_{na}\rho_m\rho_b-\sum_{mb}\mathscr{E}_m(\tau)f^b_{ma}\rho_b. \tag{2.18c}$$

III. EXPANDING THE TDHF EQUATION IN THE VICINITY OF A STATIONARY SOLUTION

Before the external field is applied, the system is at equilibrium, and the reduced density matrix $\hat{\rho}$ does not depend on time [to avoid confusion between the time-dependent density matrix $\hat{\rho}(\tau)$ and the stationary density matrix we denote the latter using an overbar: $\bar{\rho}$, $\bar{\rho}$ is still an operator ($\bar{\rho}\in\mathscr{A}$); the overbar is also used to denote its components $\bar{\rho}_m\equiv\mathrm{Tr}(\bar{\rho}\hat{\sigma}_m)$]:

$$\hat{\rho}(\tau)\equiv\bar{\rho}. \tag{3.1}$$

From Eqs. (2.18) we see that the stationary density matrix $\bar{\rho}$ satisfies the nonlinear equation

$$\sum_{mb} t_m f^b_{ma}\bar{\rho}_b+2\sum_{mnb} V_{mn}f^b_{na}\bar{\rho}_m\bar{\rho}_b=0 \tag{3.2a}$$

which can also be written in a form

$$[\hat{t}+2V(\bar{\rho}),\bar{\rho}]=0. \tag{3.2b}$$

This constitutes the stationary Hartree–Fock equation (this is a system of equations for all components of the reduced density matrix $\bar{\rho}$) and its solution $\bar{\rho}$ represents the ground-state reduced density matrix in the Hartree–Fock approximation.

To calculate the optical susceptibilities, we expand the solution of the TDHF equations around their stationary point $\bar{\rho}$:

$$\hat{\rho}(\tau)=\bar{\rho}+\delta\hat{\rho}(\tau). \tag{3.3}$$

Substituting Eq. (3.3) into Eq. (2.18) and making use of Eq. (3.2b) we obtain

$$\begin{aligned}-i\frac{\partial\delta\rho_a}{\partial\tau}=&\sum_{mb} t_m f^b_{ma}\delta\rho_b+2\sum_{mnb} V_{mn}f^b_{na}\bar{\rho}_m\delta\rho_b\\&+2\sum_{mnb} V_{mn}f^b_{na}\bar{\rho}_m\delta\rho_b-\sum_{mb}\mathscr{E}_m(\tau)f^b_{ma}\bar{\rho}_b\\&+2\sum_{mnb} V_{mn}f^b_{na}\delta\rho_m\delta\rho_b-\sum_{mb} f^b_{mn}\mathscr{E}_m(\tau)\delta\rho_b\end{aligned} \tag{3.4a}$$

or, alternatively,

$$\begin{aligned}i\frac{\partial\delta\hat{\rho}}{\partial\tau}=&[\hat{t}+2V(\bar{\rho}),\delta\hat{\rho}]-2[\bar{\rho},V(\delta\hat{\rho})]-[\hat{\mathscr{E}},\bar{\rho}]\\&+2[V(\delta\hat{\rho}),\delta\hat{\rho}]-[\hat{\mathscr{E}},\delta\hat{\rho}],\end{aligned} \tag{3.4b}$$

and the polarization adopts the form (neglecting the equilibrium polarization $\mathrm{Tr}[\hat{\mu}(\mathbf{r})\bar{\rho}]$, which does not participate in the optical response)

$$P(\mathbf{r})=\mathrm{Tr}(\hat{\mu}(\mathbf{r})\,\delta\hat{\rho})=\sum_n \mu_n(\mathbf{r})\,\delta\rho_n. \tag{3.4c}$$

Equation (3.4b) is the TDHF equation for the deviation of the reduced density matrix from equilibrium. It can be solved pertubatively in $\mathscr{E}$, resulting in the optical susceptibilities. The first three terms in the rhs of Eq. (3.4b) describe a system of harmonic oscillators driven by an external field; the last two terms represent the anharmonicities which lead to the optical nonlinearities.

We shall now describe the "restricted scheme"[14,20] of the TDHF equation which allows us to work with fewer variables. This more compact scheme is based on the fact that the TDHF equation can be recast in a form [see Eq. (2.18a)]

$$\frac{\partial\hat{\rho}}{\partial\tau}=[\hat{h}(\hat{\rho},\tau),\hat{\rho}],\quad \hat{h}(\hat{\rho},\tau)\in\mathscr{A} \tag{3.5}$$

and, therefore, at any time, $\hat{\rho}(\tau)$ belongs to the orbit of the Lie group related to the Lie algebra $\mathscr{A}$ which starts at point $\bar{\rho}$. A convenient choice of local coordinates in the vicinity of $\bar{\rho}$ is obtained choosing the particle–hole components of the density matrix (we will denote the subspace of intraband and interband components by $\mathscr{A}_0$ and $\mathscr{A}_1$, respectively). We can use $\mathscr{A}_1$ as a system of local coordinates on the orbit in the vicinity of $\bar{\rho}$ by introducing a (nonlinear) mapping T: $\mathscr{A}_1\rightarrow\mathscr{A}_0$ so that any $\hat{\rho}$ which belongs to the orbit is represented as

$$\hat{\rho}=\bar{\rho}+\hat{\xi}+T(\hat{\xi}),\quad \hat{\xi}\in\mathscr{A}_1. \tag{3.6}$$

Hereafter, we use Latin indices with primes and double primes to denote the basis sets of $\mathscr{A}_1$ and $\mathscr{A}_0$, respectively. n' represents electron–hole pairs whereas n'' represents either electron–electron or hole–hole variables. In this notation we have

$$\delta\rho_{n'}\equiv\xi_{n'} \tag{3.7a}$$

and

$$\delta\rho_{n''}\equiv T_{n''}(\hat{\xi}), \tag{3.7b}$$

where T can be expanded in powers of ξ, starting with quadratic terms:

$$T_{n''}=\sum_{a'b'}T^{(2)}_{n'',a'b'}\xi_{a'}\xi_{b'}+\sum_{a'b'c'}T^{(3)}_{n'',a'b'c'}\xi_{a'}\xi_{b'}\xi_{c'}+\cdots. \tag{3.8}$$

{The operator T can be in principle obtained by solving the constraint $\hat{\rho}^2=\hat{\rho}$; however, the expansion coefficients Eq. (3.8) can be derived for a more general case because using the fact that $\mathscr{M}$ is an orbit, the coefficients can be expressed in terms of commutators (see Appendix B). In other words, the coefficients $T^{(j)}$ are universal functions of the structure constants f [Eq. (2.15a)] and do not depend on the model.}

Substituting Eq. (3.6) into Eq. (3.4b) and making use of Eqs. (B4) we obtain for $\hat{\xi}\in\mathscr{A}_1$

$$\begin{aligned}i\frac{\partial\hat{\xi}}{\partial t}=&L(\hat{\xi})-[\hat{\mathscr{E}},\bar{\rho}]+2[V^{(0)}(\hat{\xi}+T(\hat{\xi})),\hat{\xi}]\\&+2[V^{(1)}(T(\hat{\xi})),\bar{\rho}]+2[V^{(1)}(\hat{\xi}+T(\hat{\xi})),T(\hat{\xi})]\\&-[\hat{\mathscr{E}}^{(0)},\hat{\xi}]-[\hat{\mathscr{E}}^{(1)},T(\hat{\xi})],\end{aligned} \tag{3.9a}$$

where

$$L(\hat{\xi})\equiv[\hat{t}+2V(\bar{\rho}),\hat{\xi}]-2[\bar{\rho},V(\hat{\xi})], \tag{3.9b}$$

and $\hat{\mathscr{E}}^{(j)}$, $V^{(j)}$ for $j=0,1$ stand for partitions in $\mathscr{A}_0$ and $\mathscr{A}_1$, respectively:

$$\hat{\mathscr{E}}=\hat{\mathscr{E}}^{(0)}+\hat{\mathscr{E}}^{(1)},\quad V=V^{(0)}+V^{(1)}. \tag{3.9c}$$

Due to Eq. (2.10d) the polarization $\hat{\mu}(\mathbf{r})$ is a function on $\mathscr{M}$. It can be viewed as a function of $\hat{\xi}$ according to the representation of Eq. (3.6), and hence can be represented in a form

$$\hat{\mu}(\mathbf{r},\hat{\xi})=\mathrm{Tr}(\hat{\mu}(\mathbf{r})\hat{\xi})+\mathrm{Tr}(\hat{\mu}(\mathbf{r})T(\hat{\xi})),\quad \hat{\mu}(\mathbf{r})\in\mathscr{A}. \tag{3.10a}$$

The two terms in the rhs of Eq. (3.10a) represent linear and nonlinear terms in $\hat{\xi}$. The polarization $P(\mathbf{r},\tau)$ is given by

$$P(\mathbf{r},\tau)=\hat{\mu}(\mathbf{r},\hat{\xi}(\tau))=\sum_{n'}\mu_{n'}(\mathbf{r})\xi_{n'}+\sum_{n''}\mu_{n''}(\mathbf{r})T_{n''}. \tag{3.10b}$$

Equation (3.9a) together with Eq. (3.6) constitute the "restricted" system of TDHF equations which is based on electron–hole variables alone.

IV. LINEAR OPTICAL RESPONSE AND OSCILLATOR MODES

In this section we obtain a Green's-function expression for the linear response. This allows us to introduce the oscillator modes which map the system onto a set of classical oscillators, and provides a natural representation for the linear response. In the next section we calculate the nonlinear response using the oscillator modes and relate it to oscillator scattering.

We start by defining the response function corresponding to $\delta\hat{\rho}$, which represents the deviation of the reduced density matrix from its equilibrium value $\bar{\rho}$, expanded in powers of the external field $\mathscr{E}(\tau)$. Switching to the frequency domain:

$$\delta\rho_n(\tau)=\int\frac{d\omega}{2\pi}e^{-i\omega t}\delta\rho_n(\omega), \tag{4.1a}$$

$$\mathscr{E}_n(\tau)=\int\frac{d\omega}{2\pi}e^{-i\omega t}\mathscr{E}_n(\omega), \tag{4.1b}$$

we introduce the response functions

$$R^{(J)}_{nm_1\cdots m_J}(-\omega_s;\omega_1,\ldots,\omega_J),$$

defined by the expansion

$$\delta\rho_n(\omega_s)=\sum_{J=1}^{\infty}\sum_{m_1\cdots m_J}\int_{-\infty}^{\infty}\frac{d\omega_1\cdots d\omega_J}{(2\pi)^J}\times 2\pi\delta(\omega_1+\cdots+\omega_J-\omega_s)\times R^{(J)}_{nm_1\cdots m_J}(-\omega_s;\omega_1,\ldots,\omega_J)\times\mathscr{E}_{m_1}(\omega_1)\cdots\mathscr{E}_{m_J}(\omega_J). \tag{4.2a}$$

The response functions $R^{(J)}(-\omega_s\mathbf{r}_s;\omega_1\mathbf{r}_1,\ldots,\omega_J\mathbf{r}_J)$ which express the microscopic polarization in terms of the external field $\mathscr{E}(\mathbf{r})$ in the frequency domain are related to the response functions introduced by Eq. (4.2a) in the following way:

$$R^{(J)}(-\omega_s\mathbf{r}_s;\omega_1\mathbf{r}_1,\ldots,\omega_J\mathbf{r}_J)=\sum_{nm_1\cdots m_J}\mu_n(\mathbf{r}_s)\mu_{m_1}(\mathbf{r}_1)\cdots\mu_{m_J}(\mathbf{r}_J)\times R^{(J)}_{nm_1\cdots m_J}(-\omega_s;\omega_1,\ldots,\omega_J). \tag{4.2b}$$

Applying the restricted scheme, we can solve Eq. (3.9a) iteratively and find the expansion for $\delta\rho_{n'}(\omega_s)$. The expansion for $\delta\rho_{n''}(\omega_s)$ is obtained by applying Eq. (3.8), and the expansion coefficients give the response functions $R^{(J)}$.

To obtain the linear response we introduce the Green's function $G_{n'm'}(\omega)$ of the linearized TDHF equation [Eq. (4.5)],

$$G_{n'm'}(\omega)\equiv[(\omega-\bar{L})^{-1}]_{n'm'}, \tag{4.3}$$

where $\bar{L}$ is the linear operator L defined by Eq. (3.9b), confined to $\mathscr{A}_1$ [note that $L(\mathscr{A}_1)\subset\mathscr{A}_1$], and obtain the linear response function $R^{(1)}$ in a form

$$R^{(1)}_{n'm'}(\omega)\equiv R^{(1)}_{n'm'}(-\omega_s;\omega)=\sum_{a'b''}f^{a'}_{b''m'}\bar{\rho}_{b''}G_{n'a'}(\omega). \tag{4.4}$$

All other components (i.e., $R_{n''m'}$, $R_{n'm''}$, and $R_{n''m''}$) vanish.

Equations (4.3) and (4.4) show that the linear response function can be expressed in terms of the eigenmodes of the operator $\bar{L}$, denoted the oscillator modes (the reason will be clarified later). These modes can be obtained from the linearized TDHF equation which follows from Eq. (3.9a) if we set $\mathscr{E}(\tau)\equiv 0$ and only retain the linear terms,

$$i\frac{\partial\hat{\xi}}{\partial\tau}=L(\hat{\xi}). \tag{4.5}$$

The eigenmodes $\hat{\xi}_\alpha$ of Eq. (4.5) are defined by the equations

$$L(\hat{\xi}_\alpha)=\Omega_\alpha\hat{\xi}_\alpha,\quad \hat{\xi}_\alpha\in\mathscr{A}_1, \tag{4.6}$$

which implies that $\hat{\xi}_\alpha$ are the eigenmodes of the operator L confined on $\mathscr{A}_1$.

In order to show that Eq. (4.5) describes a set of harmonic oscillators we recast it in a form of a Hamilton's equation of classical dynamics. To that end, we expand the Hamiltonian $\hat{H}$ [Eq. (2.16a)] and the Poisson bracket [Eqs. (2.12a), (2.15a), and (2.13)] in the vicinity of $\bar{\rho}$ in powers of $\xi_{n'}$, making use of Eq. (3.8). To obtain the linearized TDHF equation we retain up to quadratic terms in the Hamiltonian. The linear terms of the expansion vanish due to the stationary Hartree–Fock equation [Eqs. (3.2)]. Neglecting the constant term $\hat{H}(\bar{\rho})$ which does not contribute to the equations of motion, the Hamiltonian becomes

$$\hat{H}=\frac{1}{2}\sum_{m'n'}H_{m'n'}\hat{\sigma}_{m'}\hat{\sigma}_{n'}. \tag{4.7}$$

We will keep only the zero-order terms in the expansion of the Poisson bracket $\{\hat{\xi},\hat{\xi}'\}$. $\{\hat{\xi},\hat{\xi}'\}$ under this approximation is a constant function equal to the value of $\{\hat{\xi},\hat{\xi}'\}$ at the point $\bar{\rho}$, which using Eq. (2.12a) yields

$$\{\hat{\xi},\hat{\xi}'\}=i\ \mathrm{Tr}(\bar{\rho}[\hat{\xi},\hat{\xi}']); \tag{4.8}$$

Eq. (4.5) can then be written in Liouville form [Eq. (2.11)] using Eqs. (4.7) and (4.8).

Equations (4.7) together with (4.8) define a harmonic system. To map it into a set of uncoupled harmonic oscillators we use the equations of motion [Eq. (4.5)]. It follows from the fact that Eq. (4.5) can be written in the form of Eq. (2.11) that the linear operator L satisfies the following properties [for example, Eq. (4.9a) follows from the representation $\{L(\hat{u}),\hat{v}\}=-\Sigma_{m'n'}\mathrm{Tr}(\hat{u}\hat{\sigma}_{m'})\mathrm{Tr}(\hat{v}\hat{\sigma}_{n'})H_{m'n'}$]:

$$\{L\hat{u},\hat{v}\}=-\{\hat{u},L\hat{v}\}, \tag{4.9a}$$

$$(L\hat{u})^+=-L\hat{u}^+, \tag{4.9b}$$

for any $\hat{u}$, $\hat{v}\in\mathscr{A}_1$ [Eq. (4.9a) means that L is "Hermitian" with respect to antisymmetric scalar product defined by Eq. (4.8)].

Equations (4.9) imply the following important properties of the eigenmodes:

$$\{\hat{\xi}_\alpha,\hat{\xi}_\beta\}=0,\quad \text{if } \Omega_\alpha\neq-\Omega_\beta \tag{4.10a}$$

and for each eigenmode ξ_α with $\Omega_\alpha>0$ we have an eigenmode $\hat{\xi}_{-\alpha}\equiv\hat{\xi}^+_\alpha$ with

$$\Omega_{-\alpha}=-\Omega_\alpha. \tag{4.10b}$$

Using Eq. (4.10b), we can consider the modes $\hat{\xi}_\alpha$ with $\alpha>0$ (which implies a positive frequency $\Omega_\alpha>0$) only. Normalizing the modes $\hat{\xi}_\alpha(\alpha>0)$ with the condition

$$\mathrm{Tr}(\bar{\rho}[\hat{\xi}^+_\alpha,\hat{\xi}_\alpha])=1, \tag{4.11}$$

we obtain the Poisson brackets for the modes:

$$\{\hat{\xi}_\alpha,\hat{\xi}_\beta\}=\{\hat{\xi}^+_\alpha,\hat{\xi}^+_\beta\}=0, \tag{4.12a}$$

$$\{\hat{\xi}^+_\beta,\hat{\xi}_\alpha\}=i\delta_{\alpha\beta}, \tag{4.12b}$$

for any α, $\beta>0$. The Hamiltonian $\hat{H}$ [Eq. (4.7)] now becomes

$$\hat{H}=\sum_{\alpha>0}\Omega_\alpha\hat{\xi}^+_\alpha\hat{\xi}_\alpha, \tag{4.13a}$$

where $\hat{\xi}_\alpha$ are functions related to an expansion of $\hat{\xi}$ in the modes

$$\hat{\xi}=\sum_\alpha(\zeta_\alpha\hat{\xi}_\alpha+\zeta^*_\alpha\hat{\xi}^+_\alpha) \tag{4.13b}$$

as follows

$$\hat{\zeta}_\alpha(\hat{\xi}) = \zeta_\alpha \tag{4.13c}$$

and, therefore,

$$\hat{\zeta}_\alpha = [\bar{\rho}, \hat{\xi}_\alpha^+] \tag{4.13d}$$

and

$$\{\hat{\zeta}_\alpha, \hat{\zeta}_\beta^+\} = i\delta_{\alpha\beta}. \tag{4.13e}$$

Equations (4.12) and (4.13) map the system onto a set of noninteracting harmonic oscillators labelled $\alpha>0$; Ω_α is an oscillator frequency and $\hat{\zeta}_\alpha$ and $\hat{\zeta}_\alpha^+$ are its variables. Alternatively, we can use the momentum-coordinate variables $\hat{P}_\alpha$, $\hat{Q}_\alpha$,

$$\hat{Q}_\alpha \equiv -\frac{i}{\sqrt{2}}(\hat{\xi}_\alpha - \hat{\xi}_\alpha^+), \tag{4.14a}$$

$$\hat{P}_\alpha \equiv \frac{1}{\sqrt{2}}(\hat{\xi}_\alpha + \hat{\xi}_\alpha^+), \tag{4.14b}$$

with the Poisson brackets

$$\{\hat{P}_\alpha, \hat{P}_\beta\} = \{\hat{Q}_\alpha, \hat{Q}_\beta\} = 0, \tag{4.15a}$$

$$\{\hat{P}_\alpha, \hat{Q}_\beta\} = \delta_{\alpha\beta}. \tag{4.15b}$$

We will use the abbreviated vector notation

$$\hat{X}_{1\alpha} \equiv \hat{P}_\alpha, \quad \hat{X}_{2\alpha} \equiv \hat{Q}_\alpha \tag{4.15c}$$

or equivalently

$$\{\hat{X}_{i\alpha}, \hat{X}_{j\beta}\} = \epsilon_{ij}\delta_{\alpha\beta}. \tag{4.15d}$$

It is important to note that the Poisson bracket is defined on functions on $\mathscr{M}$, whereas the eigenmodes $\hat{\xi}_\alpha$, $\hat{\xi}_\alpha^+$ as well as $\hat{X}_{j\alpha}$ are tangent vectors to $\mathscr{M}$ at the point $\bar{\rho} \in \mathscr{M}$, since that the Poisson bracket in Eqs. (4.9a), (4.10a), (4.12), (4.14), and (4.15), being an antisymmetric two-form defined on the tangent space, is the symplectic structure[21] rather than the Poisson bracket. However, since the scalar product on $\mathscr{A}$ denoted by Tr connects vectors to forms and the symplectic structure (when applying this connection) has the same form as the Poisson bracket, we will make no distinction between the two objects. However, this leads to a definition of $\hat{P}_\alpha$ and $\hat{Q}_\alpha$ in terms of left and right variables $\hat{\xi}_\alpha$ and $\hat{\xi}_\alpha^+$ which differs from the conventional. This can be rationalized as follows: The variables are actually the coefficient in the expansion of ξ in the modes rather than the modes themselves. The Poisson bracket and the transformation for these variables coincide with the conventional. In Eq. (4.15d) $i,j=1,2$ and ϵ_{ij} is the two-dimensional Levi–Cevita tensor with components $\epsilon_{12}=-\epsilon_{21}=1$, $\epsilon_{11}=\epsilon_{22}=0$.

The operator L is non-Hermitian. Nevertheless, one can use Eqs. (4.12) or Eqs. (4.15) to expand vectors $\hat{u} \in \mathscr{A}_1$ in the oscillator variables and avoid inverting of the operator $(\omega - L)^{-1}$ which was required in Ref. 15. To show this we expand the projector operator $\mathscr{P}: \mathscr{A} \to \mathscr{A}_1$ which adopts a form

$$\mathscr{P}(\hat{u}) = \sum_{\alpha>0} \mathrm{Tr}(\bar{\rho}[\hat{\xi}_\alpha^+, \hat{u}])\hat{\xi}_\alpha - \sum_{\alpha>0} \mathrm{Tr}(\bar{\rho}[\hat{\xi}_\alpha, \hat{u}])\hat{\xi}_\alpha^+, \tag{4.16a}$$

or alternatively

$$\mathscr{P}(\hat{u}) = \sum_{\alpha>0} \{\hat{u}, \hat{Q}_\alpha\}\hat{P}_\alpha - \sum_{\alpha>0} \{\hat{u}, \hat{P}_\alpha\}\hat{Q}_\alpha, \tag{4.16b}$$

for any $\hat{u} \in \mathscr{A}$.

Using the notation of Eqs. (4.14), Eq. (4.16) can also be presented in a form

$$\mathscr{P}(\hat{u}) = \sum_{\alpha>0} \epsilon_{ij}\{\hat{u}, \hat{X}_{j\alpha}\}\hat{X}_{i\alpha}. \tag{4.16c}$$

Hereafter we adopt the convention that repeated indices with values 1 and 2 should be summed over.

In summary, two eigenmodes $\hat{\xi}_\alpha$ and $\hat{\xi}_\alpha^+$ of the operator L are associated with an αth oscillator. Since $\hat{P}_\alpha$ and $\hat{Q}_\alpha$ which are not the eigenmodes of L are closely related to them [Eqs. (4.14)] and have a clear physical meaning we will refer to them as oscillator modes as well. Altogether there are $2M(N-M)$ modes. We can now represent the linear optical response in terms of the oscillator variables. To that end we note that the Green's function $G(\omega)$ in Eq. (4.3) is diagonal in the eigenmode basis set and make use of Eqs. (4.16). Introducing frequency-domain oscillator Green's functions $G_{ij}^\alpha(\omega)$ $(i,j=1,2)$, which are 2×2 matrices for each oscillator (since each oscillator represents a pair of phase space variables, a coordinate and a momentum),

$$G_{ij}^\alpha(\omega) \equiv \frac{\Omega_\alpha \delta_{ij} - i\omega\epsilon_{ij}}{\Omega_\alpha^2 - (\omega + i\gamma)^2}, \tag{4.17a}$$

where γ is phenomenological damping. These describe the solution of the linearized TDHF equation [Eq. (4.5)] in terms of the oscillator coordinate-momentum variables $\zeta_{i\alpha}$ introduced by Eq. (5.1),

$$\zeta_{m\alpha}(\tau) = G_{mn}^\alpha(\tau)\zeta_{n\alpha}(0), \tag{4.17b}$$

$$G_{mn}^\alpha(\tau) \equiv \int \frac{d\omega}{2\pi} \epsilon_{mj} G_{jn}^\alpha(\omega) \exp(-i\omega\tau), \tag{4.17c}$$

we obtain for the linear response, combining Eqs. (4.16) and (4.4),

$$R^{(1)}(-\omega_s \mathbf{r}_s; \omega\mathbf{r}) = \sum_\alpha \mu_{i\alpha}(\mathbf{r}_s) G_{ij}^\alpha(\omega) \mu_{j\alpha}(\mathbf{r}), \tag{4.18a}$$

where

$$\mu_{i\alpha}(\mathbf{r}) \equiv \mathrm{Tr}([\bar{\rho}, \hat{\mu}(\mathbf{r})][\hat{X}_{i\alpha}, \bar{\rho}]). \tag{4.18b}$$

Equations (4.17) and (4.18) constitute the linear response, expanded in the oscillator modes.

V. SECOND- AND THIRD-ORDER NONLINEAR OPTICAL RESPONSE AND MODE SCATTERING

In this section we calculate the second- and third-order nonlinear response functions and relate them to mode scat-

tering. To that end, we recast the equations of motion [Eq. (3.9)] in the oscillator form by introducing a coordinate system based on the modes (oscillators):

$$\hat{\xi}=\sum_{\alpha}\ \zeta_{m\alpha}\hat{X}_{m\alpha}. \tag{5.1}$$

Substituting Eq. (5.1) into Eqs. (3.9), making use of Eq. (4.16c), and neglecting all terms which lead to higher than the third-order response in the external field we obtain the TDHF equation

$$\begin{aligned}\frac{\partial\zeta_{m\alpha}}{\partial\tau}+\Omega_{\alpha}\epsilon_{mn}\zeta_{n\alpha}-\epsilon_{mn}\int d\mathbf{r}\ \mathscr{E}(\mathbf{r})\mu_{n\alpha}(\mathbf{r})\\ =\epsilon_{mn}\sum_{\alpha_1\alpha_2}A_{n\alpha,m_1\alpha_1,m_2\alpha_2}\zeta_{m_1\alpha_1}\zeta_{m_2\alpha_2}\\ +\epsilon_{mn}\sum_{\alpha'\alpha_1\alpha_2}A^{(1)}_{n\alpha,m'\alpha',m_1\alpha_1,m_2\alpha_2}\zeta_{m'\alpha'}\zeta_{m_1\alpha_1}\zeta_{m_2\alpha_2}\\ +\epsilon_{mn}\sum_{\alpha'}\int d\mathbf{r}\ \mathscr{E}(\mathbf{r})B_{n\alpha,m'\alpha'}(\mathbf{r})\zeta_{m'\alpha'}\\ +\epsilon_{mn}\sum_{\alpha_1\alpha_2}\int d\mathbf{r}\ \mathscr{E}(\mathbf{r})B^{(1)}_{n\alpha,m_1\alpha_1,m_2\alpha_2}(\mathbf{r})\zeta_{m_1\alpha_1}\zeta_{m_2\alpha_2}.\end{aligned} \tag{5.2}$$

In Eq. (5.2) we have used the following notation:

$$\begin{aligned}A_{n\alpha,m_1\alpha_1,m_2\alpha_2}\equiv&\ \mathrm{Tr}([\hat{X}_{n\alpha},\bar{\rho}][V(\hat{X}_{m_1\alpha_1}),\hat{X}_{m_2\alpha_2}])\\ &+\mathrm{Tr}([\hat{X}_{n\alpha},\bar{\rho}][V(\hat{X}_{m_2\alpha_2}),\hat{X}_{m_1\alpha_1}])\\ &+2\ \mathrm{Tr}([\hat{X}_{n\alpha},\bar{\rho}][V(\hat{W}_{m_1\alpha_1,m_2\alpha_2}),\bar{\rho}]),\end{aligned} \tag{5.3a}$$

$$B_{n\alpha,m'\alpha'}(\mathbf{r})\equiv\mathrm{Tr}([\bar{\rho},\hat{X}_{n\alpha}][\hat{\mu}(\mathbf{r}),\hat{X}_{m'\alpha'}]), \tag{5.3b}$$

$$\begin{aligned}A^{(1)}_{n\alpha,m'\alpha',m_1\alpha_1,m_2\alpha_2}\\ \equiv&\ 2\ \mathrm{Tr}([\hat{X}_{n\alpha},\bar{\rho}][V(\hat{X}_{m'\alpha'}),\hat{W}_{m_1\alpha_1,m_2\alpha_2}])\\ &+2\ \mathrm{Tr}([\hat{X}_{n\alpha},\bar{\rho}][V(\hat{W}_{m_1\alpha_1,m_2\alpha_2}),\hat{X}_{m'\alpha'}]),\end{aligned} \tag{5.3c}$$

$$B^{(1)}_{n\alpha,m_1\alpha_1,m_2\alpha_2}(\mathbf{r})\equiv\mathrm{Tr}([\hat{\mu}(\mathbf{r}),\hat{W}_{m_1\alpha_1,m_2\alpha_2}][\bar{\rho},\hat{X}_{n\alpha}]), \tag{5.3d}$$

$$\hat{W}_{i\alpha,j\beta}\equiv\tfrac{1}{4}[[\hat{X}_{i\alpha},\bar{\rho}],\hat{X}_{j\beta}]+\tfrac{1}{4}[[\hat{X}_{j\beta},\bar{\rho}],\hat{X}_{i\alpha}]\in\mathscr{A}. \tag{5.3e}$$

The polarization truncated to quadratic order in ζ (which is the order required for the third-order response) is

$$P(\mathbf{r})=\sum_{\alpha}\ \mu_{n\alpha}(\mathbf{r})\zeta_{n\alpha}+\sum_{\alpha\beta}\ S_{m\alpha,n\beta}(\mathbf{r})\zeta_{m\alpha}\zeta_{n\beta}. \tag{5.4a}$$

$\mu_{n\alpha}(\mathbf{r})$ was defined in Eq. (4.18b) and

$$\begin{aligned}S_{i\alpha,j\beta}(\mathbf{r})\equiv&\ \tfrac{1}{4}\ \mathrm{Tr}([\hat{X}_{i\alpha},\bar{\rho}][\hat{X}_{j\beta},\hat{\mu}(\mathbf{r})])+\tfrac{1}{4}\ \mathrm{Tr}([\hat{X}_{j\beta},\bar{\rho}]\\ &\times[\hat{X}_{i\alpha},\hat{\mu}(\mathbf{r})])=\tfrac{1}{4}B_{i\alpha,j\beta}(\mathbf{r})+\tfrac{1}{4}B_{j\beta,i\alpha}(\mathbf{r}).\end{aligned} \tag{5.4b}$$

Equations (5.2) and (5.4) can be alternatively derived by expressing the Poisson bracket and the Hamiltonian in terms of the variables given by Eq. (5.1) and applying Hamilton's equation of motion using these variables. The Poisson bracket and the Hamiltonian are expressed in terms of $\zeta_{m\alpha}$ in Appendix D.

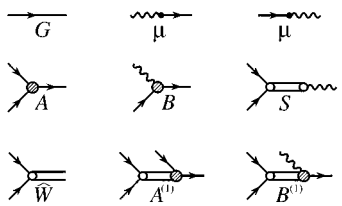

FIG. 1. Elements of the diagram technique related to scattering processes discussed in Sec. V, which contribute to the nonlinear response.

Setting the rhs of Eq. (5.2) to zero and neglecting the second term in the rhs of Eq. (5.4a) we obtain a system of uncoupled harmonic oscillators with zero nonlinear response. Equations (5.2) and (5.4a) express the nonlinear response in terms of mode scattering. The quantities entering Eqs. (5.2) and (5.4a) defined by Eqs. (5.3) and (5.4b) (see Fig. 1 for diagrammatic representation) have the following significance: $\mu_{i\alpha}(\mathbf{r})$ describes the creation of the mode $i\alpha$ by the external field acting at the point $\mathbf{r}$ or formation of polarization at $\mathbf{r}$ coming from the mode $i\alpha$, $S_{i\alpha,j\beta}(\mathbf{r})$ gives the polarization at $\mathbf{r}$ generated by a combination of the modes $i\alpha$ and $j\beta$, and A and B describe scattering of modes. $A_{i\alpha,m\mu,n\nu}$ represents a process whereby the mode $i\alpha$ is obtained out of a pair of modes $m\mu$ and $n\nu$; $B_{i\alpha,j\mu}(\mathbf{r})$ describes a scattering of the mode $j\mu$ on the external field at point $\mathbf{r}$, which creates the mode $i\alpha$. $A^{(1)}_{n\alpha,m'\alpha',m_1\alpha_1,m_2\alpha_2}$ describes a process of forming a particle–particle component of the density matrix $\hat{W}$ out of two modes $m_1\alpha_1$ and $m_2\alpha_2$ which forms the mode $n\alpha$ being scattered on the mode $m'\alpha'$. $B^{(1)}_{n\alpha,m_1\alpha_1,m_2\alpha_2}(\mathbf{r})$ is related to a similar process with the only difference that the mode $n\alpha$ is formed as a result of scattering of $\hat{W}$ on the external field at point $\mathbf{r}$. Optical response functions can be obtained by solving Eq. (5.2) iteratively and applying Eq. (5.4a). The second-order response has a form of three contributions (see Fig. 2 for diagrammatic representation),

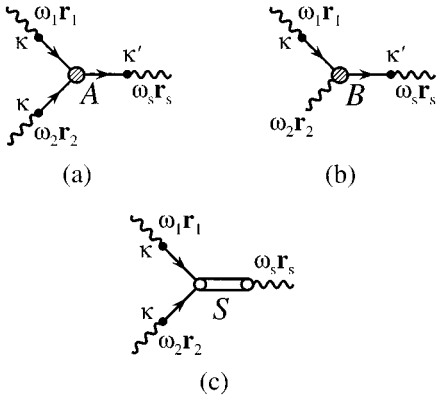

FIG. 2. Diagrammatic representation of three contributions to $R^{(2)}$ corresponding to Eqs. (5.6a)–(5.6c).

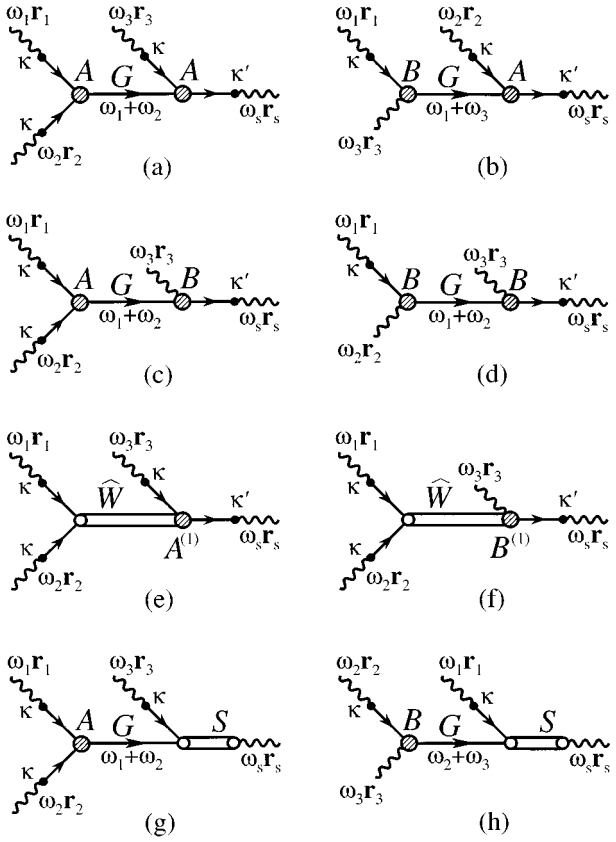

FIG. 3. Diagrammatic representation of eight contributions to $R^{(3)}$ corresponding to Eqs. (E1a)–(E1h).

$$R^{(2)}(-\omega_s\mathbf{r}_s;\omega_1\mathbf{r}_1,\omega_2\mathbf{r}_2)=\sum_{n=1}^{3}R_n^{(2)}(-\omega_s\mathbf{r}_s;\omega_1\mathbf{r}_1;\omega_2\mathbf{r}_2) \tag{5.5}$$

with

$$R_1^{(2)}(-\omega_s\mathbf{r}_s;\omega_1\mathbf{r}_1,\omega_2\mathbf{r}_2)=\sum_{\alpha\mu\nu}\kappa'_{i\alpha}(\omega_s\mathbf{r}_s)A_{i\alpha,j_1\mu,j_2\nu}\kappa_{j_1\mu}(\omega_1\mathbf{r}_1)\kappa_{j_2\nu}(\omega_2\mathbf{r}_2), \tag{5.6a}$$

$$R_2^{(2)}(-\omega_s\mathbf{r}_s;\omega_1\mathbf{r}_1,\omega_2\mathbf{r}_2)=\sum_{\alpha\mu}\kappa'_{i\alpha}(\omega_s\mathbf{r}_s)B_{i\alpha,j\mu}(\mathbf{r}_2)\kappa_{j\mu}(\omega_1\mathbf{r}_1), \tag{5.6b}$$

$$R_3^{(2)}(-\omega_s\mathbf{r}_s;\omega_1\mathbf{r}_1,\omega_2\mathbf{r}_2)=\sum_{\alpha\beta}S_{i\alpha,j\beta}(\mathbf{r}_s)\kappa_{i\alpha}(\omega_1\mathbf{r}_1)\kappa_{j\beta}(\omega_2\mathbf{r}_2), \tag{5.6c}$$

where

$$\kappa_{j\alpha}(\omega\mathbf{r})\equiv G^{\alpha}_{jm}(\omega)\mu_{m\alpha}(\mathbf{r}), \tag{5.7a}$$

$$\kappa'_{j\alpha}(\omega_s\mathbf{r}_s)\equiv\mu_{m\alpha}(\mathbf{r}_s)G^{\alpha}_{mj}(\omega_s). \tag{5.7b}$$

Similarly, the third-order nonlinear response $R^{(3)}$ can be represented as a sum of eight contributions (see Fig. 3):

$$R^{(3)}(-\omega_s\mathbf{r}_s;\omega_1\mathbf{r}_1,\omega_2\mathbf{r}_2,\omega_3\mathbf{r}_3)=\sum_{n=1}^{8}R_n^{(3)}(-\omega_s\mathbf{r}_s;\omega_1\mathbf{r}_1,\omega_2\mathbf{r}_2,\omega_3\mathbf{r}_3). \tag{5.8}$$

These contributions in the mode representation are given in Appendix E.

Expressions for the static response functions [$R^{(1)}(\mathbf{r}_s,\mathbf{r})$, $R^{(2)}(\mathbf{r}_s;\mathbf{r}_1,\mathbf{r}_2)$ and $R^{(3)}(\mathbf{r}_s;\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)$] can be obtained by setting all frequencies in Eqs. (4.18a), (5.6), and (E1) to zero. Equation (4.17a) for the Green's function $G^{\alpha}_{ij}(\omega)$ then yields $G^{\alpha}_{ij}(\omega)=\delta_{ij}/\Omega_\alpha$. For the linear response we have

$$R^{(1)}(\mathbf{r}_s,\mathbf{r})=\sum_{\alpha}\frac{\mu_{j\alpha}(\mathbf{r}_s)\mu_{j\alpha}(\mathbf{r})}{\Omega_\alpha}. \tag{5.9}$$

The second-order response function $R^{(2)}$ is a sum of three contributions,

$$R_1^{(2)}(\mathbf{r}_s;\mathbf{r}_1,\mathbf{r}_2)=\sum_{\alpha\mu\nu}\frac{\mu_{i\alpha}(\mathbf{r}_s)\mu_{j\mu}(\mathbf{r}_1)\mu_{s\nu}(\mathbf{r}_2)}{\Omega_\alpha\Omega_\mu\Omega_\nu}A_{i\alpha,j\mu,s\nu}, \tag{5.10a}$$

$$R_2^{(2)}(\mathbf{r}_s;\mathbf{r}_1,\mathbf{r}_2)=\sum_{\alpha\nu}\frac{\mu_{i\alpha}(\mathbf{r}_s)\mu_{j\nu}(\mathbf{r}_1)}{\Omega_\alpha\Omega_\nu}B_{i\alpha,j\nu}(\mathbf{r}_2), \tag{5.10b}$$

$$R_3^{(2)}(\mathbf{r}_s;\mathbf{r}_1,\mathbf{r}_2)=\sum_{\alpha\beta}\frac{\mu_{i\alpha}(\mathbf{r}_1)\mu_{j\beta}(\mathbf{r}_2)}{\Omega_\alpha\Omega_\beta}S_{i\alpha,j\beta}(\mathbf{r}_s). \tag{5.10c}$$

The corresponding expressions for the third-order response are given in Appendix E as well.

In summary, to calculate the optical response functions within the TDHF approximation one should proceed in the following steps. (i) Starting with the quantum Hamiltonian [Eqs. (2.1a) and (2.2)] determined by parameters $\bar{t}_{\bar{m}\bar{n}}$, $V_{\bar{m}\bar{n}\bar{k}\bar{l}}$, and $\mu_{\bar{m}\bar{n}}$ we obtain the classical Hamiltonian and expression for polarization [Eq. (2.10)] which are determined by the matrices $\hat{t}$ and $\hat{\mu}$ and a superoperator V acting in the space of reduced density matrices and defined by Eq. (2.18b). These are expressed in terms of the initial parameters of the model by means of Eqs. (2.17) and (2.18b). (ii) Solve the stationary Hartree–Fock equation [Eqs. (3.2)] which is written in terms of $\hat{t}$ and V, and obtain the ground-state density matrix $\bar{\rho}$. (iii) Find the eigenmodes $\hat{\xi}_\alpha$ of the linearized TDHF equation solving the linear problem [Eq. (4.6)]; the linear operator L is expressed in terms of $\hat{t}$, V, and $\bar{\rho}$ [Eq. (3.9b)]. (iv) Calculate the oscillator variables $\hat{X}_{i\alpha}$ [Eqs. (4.14) and (4.15c)]. (v) Calculate the dipole moments of the modes [Eq. (4.18b)] and the anharmonicity constants [Eqs. (5.3) and (5.4b)]. Upon substituting them into Eqs. (4.18a), (5.6), and (E1) we finally obtain the optical response functions.

VI. SIZE CONSISTENCY OF THE OSCILLATOR REPRESENTATION

In this section we consider the optical response of long one-dimensional chains (e.g., conjugated polymers or semiconductor quantum wires) with translational symmetry (i.e.,

a one-dimensional lattice).[2,3,14] We will show that the third-order polarizability scales linearly with the number of sites. More importantly, each of the eight terms in Eqs. (E1) has the correct scaling, and the problem of interference among large terms, which usually complicates the size consistency, does not exist in this picture. We consider a semiempirical model, with the Hamiltonian given by Eqs. (2.1) and (2.2), and with the parameters defined in Appendix F [Eqs. (F1) and (F2)]. We choose the z axis of our coordinate system in the chain direction, so that

$$\mathbf{R}_n=(0,0,z_n), \quad z_n\equiv na, \tag{6.1}$$

where a is the lattice constant (in this section we use Latin indices to denote the sites). We will treat $\mathscr{E}$ as the z component of the external electric field, and invoke the dipole approximation (assuming that the optical wavelength is larger than the chain size). This allows us to neglect the $\mathbf{r}$ dependence of $\mathscr{E}$, i.e., $\mathscr{E}(\mathbf{r},\tau)=\mathscr{E}(\tau)$, and leads to

$$\mu_n(\mathbf{r})=ez_n\delta(\mathbf{r}-\mathbf{R}_n), \tag{6.2a}$$

$$\mathscr{E}_n(\tau)=ez_n\mathscr{E}(\tau). \tag{6.2b}$$

We assume that the ground state is a singlet with respect to the spin variables, and as shown in Appendix F the spin variables can be omitted and we only need to follow the evolution of ρ_{mn} where m and n denote the sites.

If the chain is longer than all relevant coherence sizes but still shorter than the optical wavelength, we can invoke the dipole approximation, yet neglect boundary (edge) effects. The Hamiltonian $\hat{H}$ without the external field possesses the translational symmetry $n\rightarrow n+1$. In the conjugated phase the symmetry is spontaneously broken up to the symmetry $n\rightarrow n+2$, i.e., translations with respect to the unit cell which has the size of two lattice constants (2a). In the Hartree–Fock approximation this implies that the ground-state density matrix $\bar{\rho}_{mn}$ which is the solution of the stationary Hartree–Fock equation has the following properties:

$$\bar{\rho}_{m+1,n+1}\neq\bar{\rho}_{mn}, \tag{6.3a}$$

$$\bar{\rho}_{m+2,n+2}=\bar{\rho}_{mn}. \tag{6.3b}$$

The Hamiltonian is obtained from Eq. (F4a) by omitting the spin variables and assuming

$$\bar{t}_{mn}=\bar{t}_{m-n}, \quad U_{mn}=U_{m-n}, \tag{6.4}$$

resulting in

$$\hat{H}=\sum_{mn}\bar{t}_{m-n}\hat{\sigma}_{mn}+\sum_{mn}U_{m-n}\hat{\sigma}_{mm}\hat{\sigma}_{nn}-\sum_{mn}U_{m-n}\hat{\sigma}_{mn}\hat{\sigma}_{nm}. \tag{6.5a}$$

The Hamiltonian H_T of the driven system can be obtained from Eqs. (F4) by making use of Eqs. (6.2):

$$\hat{H}_T=\hat{H}-e\sum_n z_n\hat{\sigma}_{nn}\mathscr{E}(\tau). \tag{6.5b}$$

$\hat{H}$ possesses translational symmetry with respect to a unit cell; however, the Hamiltonian of the driven system $\hat{H}_T$ does not have such symmetry due to the factors z_n in the last term of Eq. (6.5b). Nevertheless, translational symmetry is recovered in the equations of motion, as can be seen from the TDHF equation, which follows from Eqs. (2.11), (6.5b), and (2.12):

$$i\frac{\partial\hat{\sigma}_{mn}}{\partial\tau}=i\{\hat{H},\hat{\sigma}_{mn}\}-e(z_m-z_n)\hat{\sigma}_{mn}\mathscr{E}(\tau). \tag{6.6}$$

This implies that Eq. (6.3b) holds at all times; i.e., the reduced density matrix possesses translational symmetry with respect to a unit cell at all times. Consequently, the relative motion of electron–hole pairs is factorized from their center of mass, and only electron–hole pairs with zero total momentum contribute to the response.

The TDHF equations [Eqs. (2.18)] and the expressions for the response functions [Eqs. (4.18), (E1), and (5.3)–(5.10)] have been obtained for an arbitrary algebra. In particular, they apply to the matrices obeying Eq. (6.3b) which form a closed algebra. As a result the modes will be represented by density matrices satisfying Eq. (6.3b) which describe the relative electron–hole motion.

We adopt the following representation for reduced density matrices ρ_{mn} satisfying Eq. (6.3b):

$$\begin{aligned}&\rho_{2n,2m}=\tilde{\rho}_{00}(n-m), \quad \rho_{2n+1,2m+1}=\tilde{\rho}_{11}(n-m),\\ &\rho_{2n+1,2m}=\tilde{\rho}_{10}(n-m), \quad \rho_{2n,2m+1}=\tilde{\rho}_{01}(n-m).\end{aligned} \tag{6.7}$$

Equations (6.7) represent ρ_{mn} in a form of n 2×2 matrices $\tilde{\rho}_{ij}(n)$, where $i,j=0,1$. The matrix product in the space of matrices $\hat{\rho}$ induces a product in the space of matrix functions $\tilde{\rho}(n)$:

$$(\tilde{\rho}\,\tilde{\eta})_{ij}(n)=\sum_{k=0,1}\sum_{m=-\infty}^{\infty}\tilde{\rho}_{ik}(n-m)\tilde{\rho}_{kj}(m). \tag{6.8}$$

Equation (6.8) implies that a product of matrix functions is a matrix product with respect to matrix indices and a convolution with respect to the argument. The definition of product given by Eq. (6.8) leads to the usual definition of the commutator (i.e., $[\tilde{\rho},\tilde{\eta}]\equiv\tilde{\rho}\tilde{\eta}-\tilde{\eta}\tilde{\rho}$).

We define $\mathrm{Tr}(\tilde{\rho})$ as

$$\mathrm{Tr}(\tilde{\rho})\equiv\tilde{\rho}_{00}(0)+\tilde{\rho}_{11}(0), \tag{6.9a}$$

which is related to $\mathrm{Tr}(\tilde{\rho})$ by

$$\mathrm{Tr}(\hat{\rho})\equiv(N/2)\mathrm{Tr}(\tilde{\rho}), \tag{6.9b}$$

where $N/2$ is the number of unit cells in the chain. The scalar product is defined by

$$\mathrm{Tr}(\tilde{\rho}\,\tilde{\eta})=\sum_{i,j=0,1}\sum_{m=-\infty}^{\infty}\tilde{\rho}_{ij}(m)\,\tilde{\eta}_{ji}(-m), \tag{6.10a}$$

and satisfies

$$\mathrm{Tr}(\hat{\rho}\,\hat{\eta})=(N/2)\mathrm{Tr}(\tilde{\rho}\,\tilde{\eta}). \tag{6.10b}$$

We can now apply the expressions of Sec. V to calculate the hyperpolarizabilities. The second-order polarizability $\beta(-\omega_s;\omega_1,\omega_2)$ vanishes in cenrosymmetric systems. We define the third-order polarizability γ

$$\gamma(-\omega_s;\omega_1,\omega_2,\omega_3)\equiv\int d\mathbf{r}_s\, d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{r}_3 \times R^{(3)}(-\omega_s\mathbf{r}_s;\omega_1\mathbf{r}_1,\omega_2\mathbf{r}_2,\omega_3\mathbf{r}_3). \tag{6.11a}$$

Normalizing the eigenmodes according to Eq. (4.11) or, equivalently, Eqs. (4.12) or Eqs. (4.15) using the definition of the trace given by Eqs. (6.9a) and (6.9b), we obtain

$$\gamma(-\omega_s;\omega_1,\omega_2,\omega_3)=(N/2)R^{(3)}(-\omega_s;\omega_1,\omega_2,\omega_3), \tag{6.11b}$$

where $R^{(3)}(-\omega_s;\omega_1,\omega_2,\omega_3)$ is a sum of eight contributions $R_1^{(3)},\ldots,R_8^{(3)}$ corresponding to Eqs. (E1a)–(E1h). These contributions have the form of Eqs. (E1) provided we omit the $\mathbf{r}$ arguments of B, S, $B^{(1)}$, κ, and κ' and define the coefficients in Eqs. (E1) in the following way: A, $A^{(1)}$, and $\hat{W}$ are given by Eqs. (5.3a), (5.3c), and (5.3e);

$$\kappa_{i\alpha}(\omega)\equiv G_{ij}^{\alpha}(\omega)\mathrm{Tr}(\mu(\bar{\rho})[\hat{X}_{j\alpha},\bar{\rho}]), \tag{6.12a}$$

$$\kappa'_{i\alpha}(\omega_s)\equiv\mathrm{Tr}(\mu(\bar{\rho})[\hat{X}_{j\alpha},\bar{\rho}])G_{ji}^{\alpha}(\omega_s), \tag{6.12b}$$

$$B_{i\alpha,j\mu}\equiv\mathrm{Tr}([\hat{X}_{i\alpha},\bar{\rho}]\mu(\hat{X}_{j\mu})), \tag{6.12c}$$

$$B^{(1)}_{i\alpha,i_1\alpha_1,i_2\alpha_2}\equiv\mathrm{Tr}([\hat{X}_{i\alpha},\bar{\rho}]\mu(\hat{W}_{i_1\alpha_1,i_2\alpha_2})), \tag{6.12d}$$

$$S_{i\alpha,j\beta}\equiv\tfrac{1}{4}\,\mathrm{Tr}([\hat{X}_{i\alpha},\bar{\rho}]\mu(\hat{X}_{j\beta}))+\tfrac{1}{4}\,\mathrm{Tr}([\hat{X}_{j\beta},\bar{\rho}]\mu(\hat{X}_{i\alpha})). \tag{6.12e}$$

The algebra $\mathscr{A}$ in this case is represented by 2×2 matrix functions $\tilde{\rho}_{ij}(n)$; $i,j=0,1$. In Eqs. (6.12) μ: $\mathscr{A}\to\mathscr{A}$, which acts as follows:

$$(\mu(\tilde{\rho}))_{ij}(n)\equiv -ea(2n+i-j)\tilde{\rho}_{ij}(n). \tag{6.13}$$

The operator V and the vector $\hat{t}\in\mathscr{A}$ enter in the definition of L [Eq. (3.9b)] which determines the modes [Eq. (4.6)]. They appear in the definition of A and $A^{(1)}$ [Eqs. (5.3a) and (5.3c)] and assume the form

$$\tilde{t}_{ij}(n)\equiv\bar{t}_{2n+i-j}, \tag{6.14a}$$

$$[V(\tilde{\rho})]_{ij}(n)\equiv\delta_{ij}\delta(n)\sum_{k=0,1}\sum_{m=-\infty}^{\infty}U_{2m+i-k}\tilde{\rho}_{kk}(0) - U_{2n+i-j}\tilde{\rho}_{ij}(n), \tag{6.14b}$$

where $i,j=0,1$.

Equations (E1) applied to the algebra defined by Eqs. (6.7)–(6.10) are expressed in terms of the modes of the relative motion of electrons and holes which do not depend on N. Therefore, $R_1^{(3)},\ldots,R_8^{(3)}$ do not depend on N as well, and Eq. (6.11b) yields the $\sim N$ scaling of all eight contributions to γ [Eqs. (E1a)–(E1h)]. The origin of the N factor in Eq. (6.11b) can be rationalized as follows: In order to obtain the perturbative expansion of the deviation of the reduced density matrix from its stationary value in the external field we can apply the results of Sec. V to the algebra defined by Eqs. (6.7)–(6.10) which does not contain N as a parameter. This yields Eqs. (E1) which do not contain N. However, in calculating the total polarization one needs to use the conventional definition of the trace which gives the $N/2$ factor in Eq. (6.11b) due to Eq. (6.10b).

Although we have already demonstrated the $\gamma\sim N$ scaling of the nonlinear response for each contribution [see Eqs. (6.11) and (E1)] it will be instructive to show how this scaling follows naturally from the normalization of the modes [Eq. (6.7)] with the usual definition of the trace. To that end we consider Eqs. (6.12) and (5.3), and make use of the translational symmetry which holds at large sizes, and implies that each oscillator mode has a factor of $N^{-1/2}$, the trace gives a factor of N, and the commutators do not yield any size-dependent factors. We then obtain the following large-size scaling properties of the parameters entering Eqs. (E1):

$$\kappa_{i\alpha}\sim N^{1/2},\quad A_{i\alpha,m\mu,n\nu}\sim N^{-1/2},\quad B_{i\alpha,j\mu}\sim N^{0}, \tag{6.15a}$$

$$A^{(1)}_{i\alpha,j\beta,i_1\alpha_1,i_2\alpha_2}\sim N^{-1},\quad B^{(1)}_{i\alpha,i_1\alpha_1,i_2\alpha_2}\sim N^{-1/2}, \tag{6.15b}$$

$$S_{i\alpha,j\beta}\sim N^{0},\quad G_{ij}^{\alpha}\sim N^{0}. \tag{6.15c}$$

Substituting Eqs. (6.15) into Eqs. (E1) we obtain the $\sim N$ scaling of each of the eight contributions given by Eqs. (E1a)–(E1h).

Equations (6.15) are useful for studying the size dependence of hyperpolarizabilities. Adopting the dominant mode picture[14,15] which means that only a few modes (in the simplest case, one B_u and one A_g mode) contribute to Eqs. (E1), we can express the response in terms of specific properties of the modes [i.e., the parameters in Eqs. (6.15)]. This means that the dominant modes constitute the collective variables (quasiparticles) of the system. Deviations from the $\sim N$ scaling of nonlinear hyperpolarizabilities for smaller sizes is then due to deviations of the scaling properties of these parameters, Eqs. (6.15).

Finally, we note that the expressions for the optical response derived in this section hold for a more general model with an arbitrary number L of orbitals per unit cell, irrespective of the mechanism of formation of a unit cell (here we have considered the translational symmetry-breaking mechanism). In this case matrices $\tilde{\rho}_{ij}(n)$ become $L\times L$ (instead of 2×2) n-dependent matrices.

VII. DISCUSSION

In this paper we represented the TDHF equation for a nonrelativistic many-electron system (whose Hamiltonian conserves the number of particles) in a form of the Hamilton's classical equation of motion. Since the optical response functions are determined by dynamics in the vicinity of the stationary point $\bar{\rho}$, the global geometric properties of the phase space (which is the manifold of all single Slater determinants) do not affect the response to weak fields. We can therefore introduce a system of local coordinates in the vicinity of $\bar{\rho}$ and expand the Poisson bracket and the Hamiltonian in these coordinates. This was done in Appendix D for a particular choice of coordinates representing the particle–hole eigenmodes of the linearized TDHF equation. These results establish an oscillator picture of the response in the following sense: Using this coordinate system in phase

space, we obtain the Poisson bracket which is canonical to first nonvanishing order (in powers of coordinates) and the Hamiltonian which starts with quadratic terms. This implies that in zeroth order we have a system of uncoupled harmonic oscillators. Optical nonlinearities are induced by higher-order terms in the expansion of the Hamiltonian as well as the Poisson bracket in powers of the phase-space coordinates; the former terms can be considered as nonlinearities induced by anharmonicities, and the latter represent nonlinearities due to nonboson statistics of quasiparticles. The Poisson bracket up to the terms in the expansion which contribute to the second- and third-order response is given in Appendix D [Eqs. (D7)]. The corresponding expansions for the dipole operator and the Hamiltonian are

$$\hat{\mu}(\mathbf{r})=\sum_{\alpha}\ \mu_{i\alpha}(\mathbf{r})\hat{\zeta}_{i\alpha}+\sum_{\mu\nu}\ S_{i\mu,j\nu}(\mathbf{r})\hat{\zeta}_{i\mu}\hat{\zeta}_{j\nu}, \tag{7.1}$$

$$\begin{aligned}\hat{H}=&\sum_{\alpha}\ \Omega_{\alpha}\hat{\zeta}_{m\alpha}\hat{\zeta}_{m\alpha}-\frac{1}{3}\sum_{\alpha\mu\nu}A_{i\alpha,m\mu,n\nu}\hat{\zeta}_{i\alpha}\hat{\zeta}_{m\mu}\hat{\zeta}_{n\nu}\\&-\frac{1}{4}\sum_{\alpha_1\alpha_2\beta_1\beta_2}A^{(1)}_{m_1\alpha_1,m_2\alpha_2,n_1\beta_1,n_2\beta_2}\hat{\zeta}_{m_1\alpha_1}\hat{\zeta}_{m_2\alpha_2}\hat{\zeta}_{n_1\beta_1}\hat{\zeta}_{n_2\beta_2}\\&+\frac{1}{4}\sum_{\alpha_1\alpha_2\beta_1\beta_2}\Omega_{\alpha_2}\epsilon_{m_1n}F_{n\alpha_1,m_2\alpha_2,n_1\beta_1,n_2\beta_2}\\&\times\hat{\zeta}_{m_1\alpha_1}\hat{\zeta}_{m_2\alpha_2}\hat{\zeta}_{n_1\beta_1}\hat{\zeta}_{n_2\beta_2},\end{aligned} \tag{7.2}$$

where the functions $\hat{\zeta}_{m\alpha}$ are defined in Appendix D [Eqs. (D3)] and A, $A^{(1)}$, S, and F are given by Eqs. (5.3a), (5.3c), (5.4b), and (D7b). The equation of motion for the $\zeta_{m\alpha}$ variables [Eq. (5.2)] can be obtained by substituting the Hamiltonian [Eqs. (7.1) and (7.2)] and the Poisson bracket [Eqs. (D7)] into the Liouville equation [Eq. (D2)]. This derivation which leads to the same equation of motion [Eq. (5.2)] is different from those used in Sec. V, where we adopted the following scheme: Starting with the Liouville equation in an invariant form we derived the Hamilton's equation in an invariant form [Eq. (3.4b) or Eq. (3.9a)] and then switched to the $\zeta_{m\alpha}$ variables. The alternative derivation presented here starts by recasting the Poisson bracket and the Hamiltonian in terms of the $\zeta_{m\alpha}$ variables which leads to the Liouville and then to the Hamilton's equation of motion, both written using these variables. The latter derivation, though more complicated in practice, highlights the Hamilton's structure of Eq. (5.2) and describes the anharmonicity constants as coefficients in the expansion of the Poisson bracket and the Hamiltonian in powers of the oscillator variables.

Classification of different contributions (i.e., originating either from statistics or anharmonicity) to the response can be made in the following way. Since a Poisson bracket can be always presented locally in the canonical form after a proper coordinate transformation, and since our Poisson bracket is canonical to first nonvanishing order, we can make it exactly canonical by applying a transformation which does not contain linear terms. In practice it can be obtained in a form of an expansion in coordinates which starts with quadratic terms. Since the Poisson bracket becomes canonical, the system can be treated as a set of coupled oscillators with anharmonicities given by the higher than quadratic terms in the Hamiltonian. Optical nonlinearities are induced by the higher-order terms in the Hamiltonian (anharmonicities) as well as the nonlinear terms in the expansion of the dipole moment (effects of statistics).

Hamilton's form of the TDHF equations is crucial for obtaining simple expressions for ''scattering'' constants (anharmonicities) entering the nonlinear response functions in the oscillator representation. The matrix L in Eq. (4.3) for the Green's function of the linearized TDHF equation [Eq. (4.5)] is non-Hermitian, and one cannot use projections onto modes for inverting the matrix $(\omega-L)^{-1}$. A direct numerical inversion procedure has been used in Ref. 15. This poses, however, the following problem: To obtain an anharmonicity constant related to a scattering process of, say, a pair of modes, we need to have information about all modes of the linearized TDHF equation. This seriously complicates the dominant mode representation;[14,15] although the response involves only a few modes, the anharmonicity constants and hence the response cannot be expressed in terms of these modes alone [one needs information about all modes to invert $(\omega-L)$], and the dominant modes cannot be regarded as genuine collective variables. This problem can be overcome using the Hamilton's origin of the TDHF equation: The matrix L is symplectic, i.e., ''Hermitian,'' with respect to the antisymmetric ''scalar product'' defined by the Poisson bracket [see Eqs. (4.8) and (4.9)], and a projection technique using an antisymmetric ''scalar'' product can be used [see Eqs. (4.16)].

Another important consequence of Hamilton's form of the TDHF equation is that the response functions can be written in terms of commutators and traces for a general algebra which makes it possible to prove easily the $\sim N$ scaling of the response functions for large sizes; it is important to note that even though the response functions contain a large number of contributions, they all scale as $\sim N$ and we need not worry about cancellations of $\sim N^2$ terms.[8]

Alternatively, it is possible to consider the entire reduced density matrix elements as oscillators.[15] In that case, we obtain N^2 [rather than $M(N-M)$] oscillators. Although the two approaches are mathematically equivalent, the present restricted scheme has several advantages. First, it requires considerably fewer oscillators, which simplifies the calculation as well as the analysis. Second, Hamilton's form of the TDHF equation makes it possible to express the anharmonicity constants representing mode scattering in terms of the modes involved in a particular elementary scattering process. This is particularly useful for analyzing the dynamical behavior of the system. In the other approach, the expression for each scattering process involves all the modes of the linearized TDHF equation. This becomes particularly advantageous in the ''dominant mode picture,''[14] i.e., when only a

few modes (oscillators) contribute to the response. The dominant modes then become well-defined collective variables, and the response is expressed in terms of their individual properties.

Finally, we note that Hamilton's form of the TDHF equations allows us to derive a family of sum rules[22] connecting the optical response to the ground-state reduced single-electron-density matrix.[23] In addition, since we consider a general Lie algebra, the analog of the TDHF equations (generalized TDHF equations) can be derived for a more general class of systems.

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APPENDIX A: THE GRASSMAN MANIFOLD AND POISSON BRACKET RELATIONS

In this appendix we discuss the Grassman manifold in the TDHF equation. Within the TDHF approximation the reduced density matrix $\hat{\rho}(\tau)$ remains a projector operator at all times, i.e.,

$$\hat{\rho}^2=\hat{\rho} \tag{A1a}$$

and

$$\mathrm{rank}(\hat{\rho})=M, \tag{A1b}$$

where M is the number of electrons. Let $\mathscr{M}$ be the space of Hermitian matrices $\hat{\rho}$ satisfying Eqs. (A1). Any matrix of this type can be uniquely associated with an M-dimensional subspace $\mathscr{V}(\hat{\rho})$ of the N-dimensional complex vector space of single-electron states $\mathscr{V}=C^N$,

$$\mathscr{V}(\hat{\rho})\equiv \mathrm{im}(\hat{\rho}), \tag{A2}$$

where $\mathrm{im}(\hat{\rho})$ is the image of $\hat{\rho}$, i.e., a vector subspace consisting of vectors v which can be represented as $v_{\bar{m}}=\Sigma_{\bar{n}}\rho_{\bar{m}\bar{n}}u_{\bar{n}}$, $u_{\bar{n}}$ being basis set vectors. This implies that the reduced density matrices which satisfy the conditions of Eqs. (A1b) form a Grassman manifold $G(M,N;C)$ defined as the set of all M-dimensional complex vector subspaces of a complex N-dimensional vector space.[19] We can therefore treat the TDHF equation as a dynamical equation on the Grassman manifold $G(M,N;C)$. In order to express the TDHF equation in a form of Hamilton's classical dynamics we need to introduce a Poisson bracket on $\mathscr{M}=G(M,N;C)$ and a classical Hamiltonian $\hat{H}$ (which is a function on $\mathscr{M}$) so that the equation can be represented as in the Liouville form [Eq. (2.11)]. A Poisson bracket on $\mathscr{M}$ can, in principle, be induced by the canonical symplectic structure on a Grassman manifold.[19] However, in Sec. II we introduced it algebraically. It is easy to show that the Poisson bracket defined by Eqs. (2.12) and (2.13) coincides with the canonical Poisson bracket on $G(M,N;C)$.[19]

APPENDIX B: ALGEBRAIC ASPECTS OF THE TDHF EQUATIONS

In this appendix we present the TDHF equations on an orbit $\mathscr{M}$ of a Lie algebra $\mathscr{A}$ [the conventional TDHF equations are related to the case when $\mathscr{A}=\mathrm{gl}(N,C)$ is a full linear matrix algebra].

Let $\mathscr{A}$ be a complex Lie algebra with a nondegenerate invariant scalar product denoted $\mathrm{Tr}(\hat{u}\hat{v})$ for any $\hat{u},\hat{v}\in\mathscr{A}$ and a real structure $r:\mathscr{A}\to\mathscr{A}$, which is an antilinear mapping [i.e., $r(\lambda\hat{u})=\lambda^* r(\hat{u})$ for any $\lambda\in C$, $\hat{u}\in\mathscr{A}$]. The invariance of the scalar product means

$$\mathrm{Tr}(\hat{u}[\hat{v},\hat{w}])=\mathrm{Tr}(\hat{v}[\hat{w},\hat{u}]) \tag{B1}$$

for any $\hat{u},\hat{v},\hat{w}\in\mathscr{A}$. We will also use a notation $\hat{u}^+\equiv r(\hat{u})$.

Each orbit $\mathscr{M}$ of the coadjoint representation of the Lie group G associated with the real form of $\mathscr{A}$ (which consists of all $\hat{u}\in\mathscr{A}$ with $\hat{u}^+=\hat{u}$) has a symplectic structure, i.e., a nondegenerate closed two-form ω on $\mathscr{M}$ which defines a Hamilton structure.[21]

Since the scalar product forms an isomorphism between $\mathscr{A}$ and $\mathscr{A}^*$ (the space of linear functionals on $\mathscr{A}$) there is no difference between coadjoint and adjoint representations and we will work with the latter. Therefore, points $\hat{\rho}\in\mathscr{M}$ can be considered as elements of $\mathscr{A}$ (since $\mathscr{M}\subset\mathscr{A}^*\cong\mathscr{A}$). Elements $\hat{u}\in\mathscr{A}$ can be viewed as functions on $\mathscr{M}$ defined as

$$\hat{u}(\hat{\rho})\equiv\mathrm{Tr}(\hat{u}\hat{\rho}) \quad \text{for} \quad \hat{\rho}\in\mathscr{M}. \tag{B2}$$

The algebra of functions on $\mathscr{M}$ is generated (as an associative algebra) by elements of $\mathscr{A}$. The Poisson bracket on $\mathscr{M}$ associated with the canonical sympectic structure on $\mathscr{M}$ can be defined algebraically,

$$\{\hat{f},\hat{g}\}\equiv i[\hat{f},\hat{g}], \tag{B3}$$

for any $\hat{f},\hat{g}\in\mathscr{A}$ and then extended to any functions $\hat{f}$ and $\hat{g}$ using Eqs. (2.13).

The TDHF equations have been derived in Sec. II for this general case when $\hat{\sigma}_m$ in the expression for the Hamiltonian [Eqs. (2.16)] form a basis set of $\mathscr{A}$. The conventional TDHF equations correspond to the particular case when $\mathscr{A}=\mathrm{gl}(N,C)$, and $\mathscr{M}$ is the Grassman manifold.

A local coordinate system on $\mathscr{M}$ in the vicinity of the stationary point $\bar{\rho}\in\mathscr{M}$ can be introduced as follows. Let $\mathscr{A}$ be represented in a form

$$\mathscr{A}=\mathscr{A}_0\oplus\mathscr{A}_1, \tag{B4a}$$

where $\mathscr{A}_0$ is the stabilizer of the orbit; i.e., it consists of all $\hat{u}\in\mathscr{A}$ commuting with $\bar{\rho}$. $\mathscr{A}_1$ satisfies the following conditions:

$$[\hat{u},\hat{v}]\in\mathscr{A}_0, \quad \text{if } \hat{u},\hat{v}\in\mathscr{A}_1, \tag{B4b}$$

$$[\hat{u},\hat{v}]\in\mathscr{A}_1, \quad \text{if } \hat{u}\in\mathscr{A}_0,\hat{v}\in\mathscr{A}_1, \tag{B4c}$$

and $\mathscr{A}_1$ can be considered as a local coordinate system in view of Eq. (3.6).

Finally, we show how to obtain the expansion of $T(\hat{\xi})$ in powers of $\hat{\xi}$. Since $\hat{\rho}$ belongs to an orbit of the adjoint representation we obtain, making use of Eq. (3.6),

$$\bar{\rho}+\hat{\xi}+T(\hat{\xi})=\bar{\rho}+[\hat{\eta},\bar{\rho}]+\tfrac{1}{2}[\hat{\eta},[\hat{\eta},\bar{\rho}]]+\cdots \tag{B5}$$

for some $\hat{\eta}\in\mathscr{A}_1$ and in the first nonvanishing order we obtain

$$\hat{\xi}=[\hat{\eta},\bar{\rho}], \tag{B6a}$$

$$T(\hat{\xi})=\tfrac{1}{2}[\hat{\eta},[\hat{\eta},\bar{\rho}]]. \tag{B6b}$$

Since $[\hat{\eta},\bar{\rho}]\neq 0$ for any $\hat{\eta}\in\mathscr{A}_1$, Eq. (B6a) can be solved with respect to $\hat{\eta}$, the solution, when substituted into Eq. (B6b), expresses T in terms of $\hat{\xi}$. In the case of the matrix algebra Eq. (B6a) can be easily solved using the relation $[\bar{\rho},[\bar{\rho},\hat{\xi}]]=\hat{\xi}$ for any $\hat{\xi}\in\mathscr{A}_1$, which yields

$$T(\hat{\xi})=\tfrac{1}{2}[[\hat{\xi},\bar{\rho}],\hat{\xi}]. \tag{B7}$$

APPENDIX C: DERIVATION OF THE TIME-DEPENDENT HARTREE–FOCK EQUATION [EQ. (2.18a)]

Equation (2.18a) can be derived in an invariant way without introducing an orthonormal basis set. To that end we recast Eq. (2.11a) making use of Eqs. (2.12), (2.13), and (2.16) in a form

$$i\frac{\partial\hat{\rho}'}{\partial\tau}=\sum_m t_m[\hat{\rho}',\hat{\sigma}_m]+2\sum_{mn}V_{mn}[\hat{\rho}',\hat{\sigma}_m]\hat{\sigma}_n - \sum_m \mathscr{E}_m(\tau)[\hat{\rho}',\hat{\sigma}_m]. \tag{C1}$$

Equation (C1) describes the evolution of functions on phase space. To write it in a form of an equation for phase-space trajectories we note that the value of a function $\hat{\rho}'$ at point $\hat{\rho}$ is $\mathrm{Tr}(\hat{\rho}'\hat{\rho})$, and recast Eqs. (C1) in a form

$$i\,\mathrm{Tr}\left(\frac{\partial\hat{\rho}}{\partial\tau}\hat{\rho}'\right)=\sum_m t_m\,\mathrm{Tr}([\hat{\rho}',\hat{\sigma}_m]\hat{\rho}) +2\sum_{mn}V_{mn}\,\mathrm{Tr}([\hat{\rho}',\hat{\sigma}_m]\hat{\rho})\mathrm{Tr}(\hat{\sigma}_n\hat{\rho}) -\sum_m \mathscr{E}_m(\tau)\mathrm{Tr}([\hat{\rho}',\hat{\sigma}_m]\hat{\rho}),\quad \forall\hat{\rho}'\in\mathscr{A}. \tag{C2}$$

Since the scalar product is invariant we obtain immediately from Eq. (C2)

$$i\frac{\partial\hat{\rho}}{\partial\tau}=\sum_m t_m[\hat{\sigma}_m,\hat{\rho}]+2\sum_{mn}V_{mn}\,\mathrm{Tr}(\hat{\sigma}_n\hat{\rho})[\hat{\sigma}_m,\hat{\rho}] -\sum_m \mathscr{E}_m(\tau)[\hat{\sigma}_m,\hat{\rho}]. \tag{C3}$$

Defining

$$V(\hat{\rho})\equiv\sum_{mn}V_{mn}\,\mathrm{Tr}(\hat{\sigma}_n\hat{\rho})\hat{\sigma}_m, \tag{C4a}$$

$$\hat{t}\equiv\sum_m t_m\hat{\sigma}_m, \tag{C4b}$$

we obtain Eq. (C3) in the form of Eq. (2.18a).

APPENDIX D: TIME-DEPENDENT HARTREE–FOCK EQUATION IN THE OSCILLATOR REPRESENTATION

In this Appendix we obtain the Poisson bracket, the Hamiltonian, and the TDHF equation in terms of the oscillator variables. The Liouville form of the TDHF equation [Eq. (2.11)] makes it possible to recast it for any coordinate system on the phase space $\mathscr{M}$. To that end we represent an arbitrary $\hat{\rho}\in M$ in the vicinity of the stationary solution $\bar{\rho}$ in a form of Eq. (3.6),

$$\hat{\rho}=\bar{\rho}+\hat{\xi}+T(\hat{\xi}),\quad \hat{\xi}\in\mathscr{A}_1, \tag{D1a}$$

and expand $\hat{\xi}$ in terms of the oscillator modes $\hat{X}_{i\alpha}$:

$$\hat{\xi}=\sum_\alpha \zeta_{i\alpha}\hat{X}_{i\alpha}. \tag{D1b}$$

It follows from Eq. (4.16c) that

$$\zeta_{i\alpha}=\epsilon_{ij}i\,\mathrm{Tr}(\bar{\rho}[\hat{\xi},\hat{X}_{j\alpha}]). \tag{D1c}$$

Equations (D1) introduce $\zeta_{i\alpha}$ as a set of coordinates on $\mathscr{M}$ in the vicinity of $\bar{\rho}$; we will call them oscillator variables.

The TDHF equation for oscillator variables follows from Eq. (2.11) and has the form

$$\frac{\partial\hat{\zeta}_{j\alpha}}{\partial\tau}=\{\hat{H},\hat{\zeta}_{j\alpha}\}, \tag{D2}$$

where $\hat{\zeta}_{m\mu}$ are functions satisfying the condition

$$\hat{\zeta}_{m\mu}(\hat{\rho})=\mathrm{Tr}(\hat{\zeta}_{m\mu}\hat{\xi})=\zeta_{m\mu}, \tag{D3a}$$

so that

$$\hat{\zeta}_{m\mu}\equiv i\epsilon_{mn}[\hat{X}_{n\mu},\bar{\rho}]\in\mathscr{A}_1. \tag{D3b}$$

To obtain the TDHF equations we need to express the Poisson bracket and the Hamiltonian $\hat{H}$ in terms of the oscillator variables $\zeta_{j\alpha}$.

It follows from Eqs. (D3) and the definition of the Poisson bracket [Eq. (2.12a)] that the value of $\{\hat{\xi}_{m\mu},\hat{\xi}_{n\nu}\}$ on $\hat{\rho}\in\mathscr{M}$ is

$$\{\hat{\xi}_{m\mu},\hat{\xi}_{n\nu}\}(\hat{\rho})=\mathrm{Tr}(i[\hat{\zeta}_{m\mu},\hat{\zeta}_{n\nu}]\hat{\rho}). \tag{D4a}$$

Taking $\hat{\rho}$ in a form of Eq. (D1a) with $\hat{\xi}$ given by Eq. (D1b) and making use of Eq. (D3) we obtain, since $\mathrm{Tr}([\hat{\zeta}_{m\mu},\hat{\zeta}_{n\nu}]\hat{\xi})=0$,

$$\{\hat{\zeta}_{m\mu},\hat{\zeta}_{n\nu}\}(\hat{\rho})=-i\epsilon_{ma}\epsilon_{nb}\,\mathrm{Tr}\{[[\hat{X}_{a\mu},\bar{\rho}],[\hat{X}_{b\nu},\bar{\rho}]]\bar{\rho}\} -i\epsilon_{ma}\epsilon_{nb}\,\mathrm{Tr}\left\{[[\hat{X}_{a\mu},\bar{\rho}],[\hat{X}_{b\nu},\bar{\rho}]]\times T\left(\sum_\alpha \zeta_{j\alpha}(\hat{\rho})\hat{X}_{j\alpha}\right)\right\}. \tag{D4b}$$

Taking into account Eq. (4.15d) we obtain from Eq. (D4) the Poisson bracket in terms of the oscillator variables [the caret

in $\hat{\zeta}_{j\alpha}$ in the rhs of Eq. (D5) denotes that $\hat{\zeta}_{j\alpha}$ is a function on $\mathscr{M}$. The rhs of Eq. (D5) should be calculated by treating $\hat{\zeta}_{j\alpha}$ as numbers rather than operators; the resulting expansion yields the Poisson bracket of $\hat{\zeta}_{m\mu}$ and $\hat{\zeta}_{n\nu}$ in powers of $\hat{\zeta}_{j\alpha}$ and the same applies to Eq. (D6)]:

$$\{\hat{\zeta}_{m\mu},\hat{\zeta}_{n\nu}\}=\epsilon_{mn}\delta_{\mu\nu}-i\epsilon_{ma}\epsilon_{nb}\ \mathrm{Tr}\Big\{[[\hat{X}_{a\mu},\bar{\rho}],[\hat{X}_{b\nu},\bar{\rho}]]\times T\Big(\sum_{\alpha}\hat{\zeta}_{j\alpha}\hat{X}_{j\alpha}\Big)\Big\}. \tag{D5}$$

The first term in the rhs of Eq. (D5) describes the canonical Poisson bracket of a system of uncoupled oscillators; the second terms describes coupling of oscillators due to effects of statistics.

To obtain the Hamiltonian we can use Eqs. (2.16) and express the functions $\hat{\sigma}_m$ in terms of $\hat{\zeta}_{j\alpha}$:

$$\hat{\sigma}_m=\mathrm{Tr}(\hat{\sigma}_m\bar{\rho})+\sum_{\mu}\ \mathrm{Tr}(\hat{\sigma}_m\hat{X}_{j\mu})\hat{\zeta}_{j\mu}+\mathrm{Tr}\Big\{\hat{\sigma}_m T\Big(\sum_{\mu}\hat{\zeta}_{j\mu}\hat{X}_{j\mu}\Big)\Big\}. \tag{D6}$$

Equations (D2), (D5), (2.16), and (D6) constitute the TDHF equation written in terms of the oscillator variables. Applying the expansion of Eq. (3.8) we can obtain the Poisson bracket and the Hamiltonian as an expansion in powers of oscillator variables. The Poisson bracket up to quadratic in $\xi_{j\alpha}$ terms adopts a form

$$\{\hat{\zeta}_{m\mu},\hat{\zeta}_{n\nu}\}=\epsilon_{mn}\delta_{\mu\nu}+\sum_{\alpha\beta}F_{m\mu,n\nu,k\alpha,j\beta}\hat{\zeta}_{k\alpha}\hat{\zeta}_{j\beta}, \tag{D7a}$$

with

$$F_{m\mu,n\nu,k\alpha,j\beta}\equiv-\frac{i}{2}\epsilon_{ma}\epsilon_{nb}\ \mathrm{Tr}\{[[\hat{X}_{a\mu},\bar{\rho}],[\hat{X}_{b\nu},\bar{\rho}]]\times[[\hat{X}_{k\alpha},\bar{\rho}],\hat{X}_{j\beta}]\}. \tag{D7b}$$

The Hamiltonian is given by Eqs. (7.1) and (7.2).

APPENDIX E: THE THIRD-ORDER RESPONSE FUNCTION

In this appendix we present the expression for the third-order nonlinear response which is given by Eq. (5.8) with

$$R_1^{(3)}(-\omega_s\mathbf{r}_s;\omega_1\mathbf{r}_1,\omega_2\mathbf{r}_2,\omega_3\mathbf{r}_3)=2\sum_{\substack{\alpha_1\alpha_2\alpha_3\\ \alpha\beta}}\kappa'_{i\alpha}(\omega_s\mathbf{r}_s)A_{i\alpha,j\beta,i_1\alpha_3}G^{\beta}_{jk}(\omega_1+\omega_2)\times A_{k\beta,i_1\alpha_1,i_2\alpha_2}\kappa_{i_1\alpha_1}(\omega_1\mathbf{r}_1)\kappa_{i_2\alpha_2}(\omega_2\mathbf{r}_2)\kappa_{i_3\alpha_3}(\omega_3\mathbf{r}_3), \tag{E1a}$$

$$R_2^{(3)}(-\omega_s\mathbf{r}_s;\omega_1\mathbf{r}_1,\omega_2\mathbf{r}_2,\omega_3\mathbf{r}_3)=2\sum_{\alpha\beta\alpha_1\alpha_2}\kappa'_{i\alpha}(\omega_s\mathbf{r}_s)A_{i\alpha,j\beta,i_2\alpha_2}G^{\beta}_{jk}(\omega_1+\omega_3)\times B_{k\beta,i_1\alpha_1}(\mathbf{r}_3)\kappa_{i_1\alpha_1}(\omega_1\mathbf{r}_1)\kappa_{i_2\alpha_2}(\omega_2\mathbf{r}_2), \tag{E1b}$$

$$R_3^{(3)}(-\omega_s\mathbf{r}_s;\omega_1\mathbf{r}_1,\omega_2\mathbf{r}_2,\omega_3\mathbf{r}_3)=\sum_{\alpha\beta\alpha_1\alpha_2}\kappa'_{i\alpha}(\omega_s\mathbf{r}_s)B_{i\alpha,j\beta}(\mathbf{r}_3)G^{\beta}_{jk}(\omega_1+\omega_2)\times A_{k\beta,i_1\alpha_1,i_2\alpha_2}\kappa_{i_1\alpha_1}(\omega_1\mathbf{r}_1)\kappa_{i_2\alpha_2}(\omega_2\mathbf{r}_2), \tag{E1c}$$

$$R_4^{(3)}(-\omega_s\mathbf{r}_s;\omega_1\mathbf{r}_1,\omega_2\mathbf{r}_2,\omega_3\mathbf{r}_3)=\sum_{\alpha\beta\alpha_1}\kappa'_{i\alpha}(\omega_s\mathbf{r}_s)B_{i\alpha,j\beta}(\mathbf{r}_3)G^{\beta}_{jk}(\omega_1+\omega_2)B_{k\beta,i_1\alpha_1}(\mathbf{r}_2)\times\kappa_{i_1\alpha_1}(\omega_1\mathbf{r}_1), \tag{E1d}$$

$$R_5^{(3)}(-\omega_s\mathbf{r}_s;\omega_1\mathbf{r}_1,\omega_2\mathbf{r}_2,\omega_3\mathbf{r}_3)=\sum_{\alpha_1\alpha_2\alpha_3\alpha}\kappa'_{i\alpha}(\omega_s\mathbf{r}_s)A^{(1)}_{i\alpha,i_3\alpha_3,i_1\alpha_1,i_2\alpha_2}\kappa_{i_3\alpha_3}(\omega_3\mathbf{r}_3)\times\kappa_{i_1\alpha_1}(\omega_1\mathbf{r}_1)\kappa_{i_2\alpha_2}(\omega_2\mathbf{r}_2), \tag{E1e}$$

$$R_6^{(3)}(-\omega_s\mathbf{r}_s;\omega_1\mathbf{r}_1,\omega_2\mathbf{r}_2,\omega_3\mathbf{r}_3)=\sum_{\alpha_1\alpha_2\alpha}\kappa'_{i\alpha}(\omega_s\mathbf{r}_s)B^{(1)}_{i\alpha,i_1\alpha_1,i_2\alpha_2}(\mathbf{r}_3)\times\kappa_{i_1\alpha_1}(\omega_1\mathbf{r}_1)\kappa_{i_2\alpha_2}(\omega_2\mathbf{r}_2), \tag{E1f}$$

$$R_7^{(3)}(-\omega_s\mathbf{r}_s;\omega_1\mathbf{r}_1,\omega_2\mathbf{r}_2,\omega_3\mathbf{r}_3)=2\sum_{\alpha_1\alpha_2\alpha_3\beta}S_{i_3\alpha_3,j\beta}(\mathbf{r}_s)\kappa_{i_3\alpha_3}(\omega_3\mathbf{r}_3)G^{\beta}_{jk}(\omega_1+\omega_2)\times A_{k\beta,i_1\alpha_1,i_2\alpha_2}\kappa_{i_1\alpha_1}(\omega_1\mathbf{r}_1)\kappa_{i_2\alpha_2}(\omega_2\mathbf{r}_2), \tag{E1g}$$

$$R_8^{(3)}(-\omega_s\mathbf{r}_s;\omega_1\mathbf{r}_1,\omega_2\mathbf{r}_2,\omega_3\mathbf{r}_3)=2\sum_{\alpha_1\alpha_2\beta}S_{i_1\alpha_1,j\beta}(\mathbf{r}_s)\kappa_{i_1\alpha_1}(\omega_1\mathbf{r}_1)G^{\beta}_{jk}(\omega_2+\omega_3)\times B_{k\beta,i_2\alpha_2}(\mathbf{r}_3)\kappa_{i_2\alpha_2}(\omega_2\mathbf{r}_2). \tag{E1h}$$

The third-order nonlinear response function is

$$R^{(3)}=\sum_{n=1}^{8}R_n^{(3)} \tag{E2}$$

with

$$R_1^{(3)}(\mathbf{r}_s;\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)=2\sum_{\substack{\alpha_1\alpha_2\alpha_3\\ \alpha\beta}}\frac{\mu_{i\alpha}(\mathbf{r}_s)\mu_{i_1\alpha_1}(\mathbf{r}_1)\mu_{i_2\alpha_2}(\mathbf{r}_2)\mu_{i_3\alpha_3}(r_3)}{\Omega_{\alpha}\Omega_{\alpha_1}\Omega_{\alpha_2}\Omega_{\alpha_3}\Omega_{\beta}}\times A_{i\alpha,j\beta,i_3\alpha_3}A_{j\beta,i_1\alpha_1,i_2\alpha_2}, \tag{E3a}$$

$$R_2^3(\mathbf{r}_s;\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)=2\sum_{\alpha\beta\alpha_1\alpha_2}\frac{\mu_{i\alpha}(\mathbf{r}_s)\mu_{i_1\alpha_1}(\mathbf{r}_1)\mu_{i_2\alpha_2}(\mathbf{r}_2)}{\Omega_\alpha\Omega_{\alpha_1}\Omega_{\alpha_2}\Omega_\beta}\times A_{i\alpha,j\beta,i_2\alpha_2}B_{j\beta,i_1\alpha_1}(\mathbf{r}_3), \tag{E3b}$$

$$R_3^{(3)}(\mathbf{r}_s;\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)=\sum_{\alpha\beta\alpha_1\alpha_2}\frac{\mu_{i\alpha}(\mathbf{r}_s)\mu_{i_1\alpha_1}(\mathbf{r}_1)\mu_{i_2\alpha_2}(\mathbf{r}_2)}{\Omega_\alpha\Omega_{\alpha_1}\Omega_{\alpha_2}\Omega_\beta}\times B_{i\alpha,j\beta}(\mathbf{r}_3)A_{j\beta,i_1\alpha_1,i_2\alpha_2}, \tag{E3c}$$

$$R_4^{(3)}(\mathbf{r}_s;\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)=\sum_{\alpha\beta\alpha_1}\frac{\mu_{i\alpha}(\mathbf{r}_s)\mu_{i_1\alpha_1}(\mathbf{r}_1)}{\Omega_\alpha\Omega_{\alpha_1}\Omega_\beta}\times B_{i\alpha,j\beta}(\mathbf{r}_3)B_{j\beta,i_1\alpha_1}(\mathbf{r}_2), \tag{E3d}$$

$$R_5^{(3)}(\mathbf{r}_s;\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)=\sum_{\alpha_1\alpha_2\alpha_3\alpha}\frac{\mu_{i\alpha}(\mathbf{r}_s)\mu_{i_1\alpha_1}(\mathbf{r}_1)\mu_{i_2\alpha_2}(\mathbf{r}_2)\mu_{i_3\alpha_3}(\mathbf{r}_3)}{\Omega_{\alpha_1}\Omega_{\alpha_2}\Omega_{\alpha_3}\Omega_\alpha}\times A^{(1)}_{i\alpha,i_3\alpha_3,i_1\alpha_1,i_2\alpha_2}, \tag{E3e}$$

$$R_6^{(3)}(\mathbf{r}_s;\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)=\sum_{\alpha_1\alpha_2\alpha}\frac{\mu_{i\alpha}(\mathbf{r}_s)\mu_{i_1\alpha_1}(\mathbf{r}_1)\mu_{i_2\alpha_2}(\mathbf{r}_2)}{\Omega_{\alpha_1}\Omega_{\alpha_2}\Omega_\alpha}\times B^{(1)}_{i\alpha,i_1\alpha_1,i_2\alpha_2}(\mathbf{r}_3), \tag{E3f}$$

$$R_7^{(3)}(\mathbf{r}_s;\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)=2\sum_{\alpha_1\alpha_2\alpha_3\beta}\frac{\mu_{i_1\alpha_1}(\mathbf{r}_1)\mu_{i_2\alpha_2}(\mathbf{r}_2)\mu_{i_3\alpha_3}(\mathbf{r}_3)}{\Omega_{\alpha_1}\Omega_{\alpha_2}\Omega_{\alpha_3}\Omega_\beta}\times S_{i_3\alpha_3,j\beta}(\mathbf{r}_s)A_{j\beta,i_1\alpha_1,i_2\alpha_2}, \tag{E3g}$$

$$R_8^{(3)}(\mathbf{r}_s;\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)=2\sum_{\alpha_1\alpha_2\beta}\frac{\mu_{i_1\alpha_1}(\mathbf{r}_1)\mu_{i_2\alpha_2}(\mathbf{r}_2)}{\Omega_{\alpha_1}\Omega_{\alpha_2}\Omega_\beta}\times S_{i_1\alpha_1,j\beta}(\mathbf{r}_s)B_{j\beta,i_2\alpha_2}(\mathbf{r}_3). \tag{E3h}$$

APPENDIX F: ELIMINATION OF SPIN VARIABLES

In this appendix we apply the Green's-function expressions for optical response derived in Secs. IV and V to a tight-binding model of interacting electrons, and show that the TDHF equation can be written without spin variables, provided the ground state is a singlet. We consider a set of sites located at points $\mathbf{R}_{\bar{n}'}$ (we will use Latin indices with primes and overbars to denote the sites). Using Greek indices with overbars for the projection of electron spin we choose a basis set in the space of single-electron states to be electrons with a fixed projection of spin and located on a site; we then have

$$\bar{m}=(\bar{m}',\bar{\alpha}). \tag{F1}$$

Assuming that the hopping matrix $\bar{t}$ and the interaction matrix $\bar{V}$ do not depend on spin, we obtain

$$\bar{t}_{\bar{m}',\bar{\alpha},\bar{n}',\bar{\beta}}=\bar{t}_{\bar{m}',\bar{n}'}\delta_{\bar{\alpha}\bar{\beta}}, \tag{F2a}$$

$$\bar{V}_{\bar{m}',\bar{\alpha},\bar{n}',\bar{\beta},\bar{k}',\bar{\mu},\bar{e}',\bar{\nu}}=\tfrac{1}{2}U_{\bar{m}',\bar{n}'}(\delta_{\bar{n}',\bar{k}'}\delta_{\bar{m}',\bar{e}'}\delta_{\bar{\beta}\bar{\mu}}\delta_{\bar{\alpha}\bar{\nu}}-\delta_{\bar{n}',\bar{e}'}\delta_{\bar{m}',\bar{k}'}\delta_{\bar{\beta}\bar{\nu}}\delta_{\bar{\alpha}\bar{\mu}}), \tag{F2b}$$

with

$$U_{\bar{m}',\bar{n}'}=U_{\bar{n}',\bar{m}'}. \tag{F2c}$$

Assuming further that interaction with the external field is spin independent, we have

$$\mu_{\bar{m}',\bar{\alpha},\bar{n}',\bar{\beta}}(\mathbf{r})=\mu_{\bar{m}',\bar{n}'}(\mathbf{r})\,\delta_{\bar{\alpha}\bar{\beta}}\delta_{\bar{m}',\bar{n}'}. \tag{F2d}$$

The reduced single-electron-density matrix $\hat{\rho}$ (which has components $\rho_{\bar{m}\bar{n}}=\rho_{\bar{m}',\bar{\alpha},\bar{n}',\bar{\beta}}$ in the spin-coordinate space), using a notation $\rho_{\bar{m}',\bar{n}',\bar{\alpha}\bar{\beta}}\equiv\rho_{\bar{m}',\bar{\alpha},\bar{n}',\bar{\beta}}$, can be decomposed in the following way:

$$\hat{\rho}=\hat{\rho}^{(0)}\otimes\hat{I}+\hat{\rho}^{(z)}\otimes\hat{\sigma}_z+\hat{\rho}^{(+)}\otimes\hat{\sigma}_-+\hat{\rho}^{(-)}\otimes\hat{\sigma}_+, \tag{F3}$$

where $\hat{\rho}^{(0)}$, $\hat{\rho}^{(z)}$, $\hat{\rho}^{(+)}$, and $\hat{\rho}^{(-)}$ are the density matrices in the coordinate (site) space; $\hat{I}$, $\hat{\sigma}_z$, $\hat{\sigma}_+$, and $\hat{\sigma}_-$ are the 2×2 unit and the Pauli matrices acting in the spin space. Adopting this notation and making use of Eqs. (F2) we can recast the classical Hamiltonian given by Eqs. (2.10) in the form

$$\hat{H}=\sum_{\bar{m}'\bar{n}'}\bar{t}_{\bar{m}',\bar{n}'}\hat{\sigma}_{\bar{m}',\bar{n}'}\otimes\hat{I}+\sum_{\bar{m}'\bar{n}'}U_{\bar{m}',\bar{n}'}\hat{\sigma}_{\bar{m}',\bar{m}'}\hat{\sigma}_{\bar{n}',\bar{n}'}\otimes(\hat{I}\otimes\hat{I})-\sum_{\bar{m}'\bar{n}'}U_{\bar{m}',\bar{n}'}\hat{\sigma}_{\bar{m}',\bar{n}'}\hat{\sigma}_{\bar{n}',\bar{m}'}\otimes(\tfrac{1}{2}\hat{I}\otimes\hat{I}+\tfrac{1}{2}\hat{\sigma}_z\otimes\hat{\sigma}_z+\hat{\sigma}_+\otimes\hat{\sigma}_-+\hat{\sigma}_-\otimes\hat{\sigma}_+), \tag{F4a}$$

$$\hat{H}_T=\hat{H}-\sum_{\bar{m}'}\int d\mathbf{r}\;\mathscr{E}(\mathbf{r},\tau)\mu_{\bar{m}'}(\mathbf{r})\hat{\sigma}_{\bar{m}',\bar{m}'}\otimes\hat{I}. \tag{F4b}$$

Introducing operators V_0 and V_1 acting only on the space components of the reduced density matrix,

$$V_0(\hat{\rho})\equiv2\sum_{\bar{m}'\bar{n}'}U_{\bar{m}',\bar{n}'}\;\mathrm{Tr}(\hat{\sigma}_{\bar{m}',\bar{m}'}\hat{\rho})\hat{\sigma}_{\bar{n}',\bar{n}'}-\sum_{\bar{m}'\bar{n}'}U_{\bar{m}',\bar{n}'}\;\mathrm{Tr}(\hat{\sigma}_{\bar{m}',\bar{n}'}\hat{\rho})\hat{\sigma}_{\bar{n}',\bar{m}'}, \tag{F5a}$$

$$V_1(\hat{\rho})=-\sum_{\bar{m}'\bar{n}'}U_{\bar{m}',\bar{n}'}\;\mathrm{Tr}(\hat{\sigma}_{\bar{m}',\bar{n}'}\hat{\rho})\hat{\sigma}_{\bar{n}',\bar{m}'}, \tag{F5b}$$

and switching from the components $\hat{\rho}^{(z)}$, $\hat{\rho}^{(+)}$, and $\hat{\rho}^{(-)}$ to $\hat{\rho}^{(i)}$, $i=1,2,3$, by

$$\hat{\rho}^{(3)}=\hat{\rho}^{(z)},\quad \hat{\rho}^{(1)}=\tfrac{1}{2}(\hat{\rho}^{(+)}+\hat{\rho}^{(-)}),\quad \hat{\rho}^{(2)}=\frac{1}{2i}(\hat{\rho}^{(+)}-\hat{\rho}^{(-)}), \tag{F6}$$

we obtain the TDHF equations in the component form

$$i\frac{\partial\hat{\rho}^{(0)}}{\partial\tau}=[\hat{t}+2V_0(\hat{\rho}^{(0)})-\hat{\mathscr{E}}(\tau),\hat{\rho}^{(0)}]+\sum_j[V_1(\hat{\rho}^{(j)}),\hat{\rho}^{(j)}], \tag{F7a}$$

$$i\frac{\partial\hat{\rho}^{(k)}}{\partial\tau}=[\hat{t}+2V_0(\hat{\rho}^{(0)})-\hat{\mathscr{E}}(\tau),\hat{\rho}^{(k)}]+2[V_1(\hat{\rho}^{(k)}),\hat{\rho}^{(0)}]$$

$$-i\sum_{mn}\epsilon_{mnk}[V_1(\hat{\rho}^{(n)}),\hat{\rho}^{(m)}]_+\,, \tag{F7b}$$

where $[\ ,\ ]_+$ denotes the anticommutator, ϵ_{mnk} is the antisymmetric Levi–Cevita tensor, and

$$\hat{t}=\sum_{\bar{m}'\bar{n}'}\bar{t}_{\bar{m}'\bar{n}'}\hat{\sigma}_{\bar{m}'\bar{n}'}\,, \tag{F8a}$$

$$\hat{\mathscr{E}}(\tau)=\sum_{\bar{m}'}\int d\mathbf{r}\ \mathscr{E}(\mathbf{r},\tau)\mu_{\bar{m}'}(\mathbf{r})\hat{\sigma}_{\bar{m}'\bar{m}'}\,. \tag{F8b}$$

It follows from Eqs. (F7) that if the ground state is a singlet, i.e., $\bar{\rho}^{(k)}=0$, then $\hat{\rho}^{(k)}(\tau)\equiv 0$ and the response is given by $\hat{\rho}^{(0)}(\tau)$ which satisfies Eqs. (2.18) if we omit the spin variables.

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