On the general properties of non-linear optical conductivities

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The optical conductivity is the basic defining property of materials characterizing the current response toward time-dependent electric fields. In this work, following the approach of Kubo’s linear response theory, we study the general properties of the nonlinear optical conductivities of quantum many-body systems both in equilibrium and non-equilibrium. We discuss a generalization of the $f$-sum rule to a non-equilibrium setting by focusing on the instantaneous response. Furthermore, we obtain an expression of the second- and the third-order optical conductivity in terms of correlation functions and present a perturbative proof of the generalized Kohn formula proposed recently.

I. INTRODUCTION

The electric conductivity describes the response of the current density $j_i(t)$ toward a time-dependent electric field $E_j(t)$. In the Fourier space, the linear optical conductivity $\sigma^j_i(\omega)$ ($i, j$ are the spatial indices) is the proportionality constant connecting $j_i(\omega)$ to $E_j(\omega)$:

$$j_i(\omega) = \sum_j \sigma^j_i(\omega) E_j(\omega) + O(E^2).$$

(1)

There has been a long history of studies on the general properties of $\sigma^j_i(\omega)$. For example, the optical conductivity obeys the frequency-sum rule ($f$-sum rule) [1]; that is, the integral

$$\int_{-\infty}^{\infty} d\omega \sigma^j_i(\omega)$$

(2)

is solely determined by an expectation value in the absence of the electric field. Furthermore, the optical conductivity is known to have the following generic structure:

$$\sigma^j_i(\omega) = \frac{i}{\omega + i\eta} D^j_i + \sigma^j_i(\text{regular})(\omega),$$

(3)

where $D^j_i$ is called the Drude weight that characterizes the singular part of $\sigma^j_i(\omega)$ around $\omega = 0$ and $\sigma^j_i(\text{regular})(\omega)$ is the regular part that includes all other terms. The Drude weight is a useful measure distinguishing ideal conductors from insulators and non-ideal conductors [2]. More than a half century ago, Kohn [3] showed that the Drude weight at zero temperature is given by the curvature of the ground state energy $E_0(\vec{A})$ as a function of the vector potential $\vec{A}$:

$$D^j_i = \left. \frac{1}{V} \frac{\partial^2 E_0(\vec{A})}{\partial A_i \partial A_j} \right|_{A=0}.$$  

(4)

This is nowadays known as the Kohn formula [1]. An extension to a finite temperature was achieved in Ref. [1].

Recently, two of us proposed [5] a generalization of the $f$-sum rule and the Kohn formula to the $N$-th order optical conductivity $\sigma^{1 \cdots N}_i(\omega_1, \ldots, \omega_N)$ [see Eqs. (25) and (28)] through a heuristic argument utilizing extreme quantum processes in the quench or the adiabatic limit. Historically, however, the $f$-sum rule and the Kohn formula for the linear optical conductivity were derived using the concrete expression of $\sigma^j_i(\omega)$ in terms of current-current correlation functions obtained from the linear response theory [6] as we review in Sec. IV [1, 3, 4]. The main result of this work is to put forward this analysis to higher-order conductivities and provide a proof of the generalized Kohn formula [in Eq. (28) below] via the perturbation theory for the second- and third-order response. On the way to achieve this goal, we also find it possible to further generalize the $f$-sum to non-equilibrium states by focusing on the instantaneous response [see Eq. (14)], which may be seen as another result of this work. This idea was briefly sketched in Ref. [5] without concrete formulation. For this purpose, we will keep the discussion applicable to general time-dependent, non-equilibrium states as much as possible.
II. SETUP AND DEFINITIONS

Here we explain the setting of our study and give the definition of the nonlinear optical conductivity and the nonlinear Drude weight.

A. Setup

We consider quantum many-body systems defined on the $d$-dimensional cubic lattice. The system size $V$ is kept finite with an arbitrary boundary condition. Let $H_0(t)$ be the Hamiltonian of the system, which is allowed to explicitly depend on $t$. The Hamiltonian may contain arbitrary forms of kinetic terms and interactions, but all terms are required to be short-ranged and U(1) symmetric. If the initial density matrix is $\hat{\rho}_0$, the density matrix at a later time $t$ is given by

$$\hat{\rho}_0(t) = \hat{S}_0(t)\hat{\rho}_0\hat{S}_0(t)\dagger,$$

where $\hat{S}_0(t)$ is the time-evolution operator

$$\hat{S}_0(t) = \mathcal{T}\exp \left(-i\int_0^t dt' \hat{H}_0(t')\right).$$

Since we have not put any restriction on the initial density matrix, $\hat{\rho}_0(t)$ can describe an arbitrary equilibrium and non-equilibrium state.

We perturb this system by applying a uniform electric field $\vec{E}(t) \equiv d\vec{A}(t)/dt$ via the vector potential $\vec{A}(t) = (A_x(t), A_y(t), \ldots)$. (Note that our sign convention of $\vec{A}(t)$ is opposite to the standard one.) The perturbed Hamiltonian is denoted by $\hat{H}(t, \vec{A}(t))$. $\vec{A}(t)$ is set to be $\vec{0}$ for $t \leq 0$ and is turned on continuously at $t = 0$. The word “perturbation” in this work is exclusively used regarding the external field; the effect of many-body interactions and disorders, if any, can be fully taken into account in $\hat{\rho}_0(t)$. We assume that $\hat{H}(t, \vec{A})$ is analytic with respect to $\vec{A}$ so that

$$\hat{H}_{i_1, \ldots, i_N}(t) = \left. \frac{\partial^N \hat{H}(t, \vec{A})}{\partial A_{i_1} \cdots \partial A_{i_N}} \right|_{\vec{A}=\vec{0}}$$

is well-defined for any integer $N \geq 1$.

We are interested in the response of the current density toward the applied electric field. The current density operator is defined by

$$\vec{j}(t, \vec{A}) = \frac{1}{V} \left[ \frac{\partial \hat{H}(t, \vec{A})}{\partial \vec{A}} \right].$$

If $\hat{\rho}(t)$ is the perturbed density matrix fully including the effect of $\vec{A}(t)$, the current expectation value at time $t$ reads

$$j_i(t) = \text{tr}(\vec{j}(t, \vec{A})\hat{\rho}(t)) \quad (i = x, y, \ldots).$$

The spontaneous current $j_i(t)|_{\vec{A}=0}$ vanishes in the Gibbs states and in the ground state [7–9], while it may be nonzero in other more general states. The $N$-th order response of $j_i(t)$ ($N \geq 1$) may be written as

$$j_i^{(N)}(t) = \frac{1}{N!} \sum_{i_1, \ldots, i_N} \int_0^{t+\epsilon} dt_1 \cdots \int_0^{t+\epsilon} dt_N \sigma_i^{i_1, \ldots, i_N}(t, t_1, \ldots, t_N) \prod_{\ell=1}^N E_{i_\ell}(t_\ell),$$

which gives the definition of the $N$-th order conductivity. Here, the summation of $i_\ell$’s ($\ell = 1, \ldots, N$) is taken over $x, y, \ldots$. An infinitesimal parameter $\epsilon > 0$ is included to properly treat possible $\delta$-functions. As $\sigma_i^{i_1, \ldots, i_N}(t, t_1, \ldots, t_N)$ vanishes whenever $t_\ell > t$ for any $\ell = 1, \ldots, N$ due to the causality, the value of $\epsilon$ does not affect the integral. The nonlinear conductivity $\sigma_i^{i_1, \ldots, i_N}(t, t_1, \ldots, t_N)$ is symmetric with respect to the exchange of any pair of $(i_\ell, t_\ell)$ and $(i_{\ell'}, t_{\ell'})$.

For our discussions below, we find it useful to introduce another set of response functions $\phi_i^{i_1, \ldots, i_N}(t, t_1, \ldots, t_N)$. They are defined similarly to $\sigma_i^{i_1, \ldots, i_N}(t, t_1, \ldots, t_N)$ in Eq. (10) but $\vec{E}(t)$ there is replaced with $\vec{A}(t)$:

$$j_i^{(N)}(t) = \frac{1}{N!} \sum_{i_1, \ldots, i_N} \int_0^{t+\epsilon} dt_1 \cdots \int_0^{t+\epsilon} dt_N \phi_i^{i_1, \ldots, i_N}(t, t_1, \ldots, t_N) \prod_{\ell=1}^N A_{i_\ell}(t_\ell).$$
In terms of the response function $\phi_i^{t_i-\cdots-t_N}(t, t_1, \ldots, t_N)$, the conductivity $\sigma_i^{t_i-\cdots-t_N}(t, t_1, \ldots, t_N)$ is given by

$$\sigma_i^{t_i-\cdots-t_N}(t, t_1, \ldots, t_N) = \int_{t_1}^{t+\epsilon} dt'_1 \cdots \int_{t_N}^{t+\epsilon} dt'_N \phi_i^{t_i-\cdots-t_N}(t, t'_1, \ldots, t'_N). \tag{12}$$

This can be seen by expressing $\tilde{A}(t)$ as $\tilde{A}(t) = \int_0^t dt' \tilde{E}(t')$ and by performing integration by parts one by one for $t_1, \ldots, t_N$ in Eq. (11).

$$\begin{align*}
\int_0^{t+\epsilon} dt_1 \cdots \int_0^{t+\epsilon} dt_N \phi_i^{t_i-\cdots-t_N}(t, t_1, \ldots, t_N) \prod_{\ell=1}^N A_i(t_\ell) \\
= \int_0^{t+\epsilon} dt_1 \cdots \int_0^{t+\epsilon} dt_N \left( \frac{d}{dt_1} \int_0^{t_1} dt'_1 \phi_i^{t_i-\cdots-t_N}(t, t'_1, t_2, \ldots, t_N) \right) \left( \int_0^{t_1} dt''_1 E_i(t''_1) \right) \prod_{\ell=2}^N A_i(t_\ell) \\
= \int_0^{t+\epsilon} dt_2 \cdots \int_0^{t+\epsilon} dt_N \int_0^{t_2} dt'_2 \phi_i^{t_i-\cdots-t_N}(t, t'_2, t_3, \ldots, t_N) \int_0^{t_2} dt''_2 E_i(t''_2) \prod_{\ell=2}^N A_i(t_\ell) \\
- \int_0^{t+\epsilon} dt_1 \cdots \int_0^{t+\epsilon} dt_N \int_0^{t_1} dt'_1 \phi_i^{t_i-\cdots-t_N}(t, t'_1, t_2, \ldots, t_N) E_i(t_1) \prod_{\ell=2}^N A_i(t_\ell) \\
= \int_0^{t+\epsilon} dt_1 \cdots \int_0^{t+\epsilon} dt_N \int_0^{t_1} dt'_1 \phi_i^{t_i-\cdots-t_N}(t, t'_1, t_2, \ldots, t_N) E_i(t_1) \prod_{\ell=2}^N A_i(t_\ell) \\
= \cdots \\
= \int_0^{t+\epsilon} dt_1 \cdots \int_0^{t+\epsilon} dt_N \left( \int_0^{t_1} dt'_1 \cdots \int_{t_N}^{t+\epsilon} dt'_N \phi_i^{t_i-\cdots-t_N}(t, t'_1, \ldots, t'_N) \right) \prod_{\ell=1}^N E_i(t_\ell). \tag{13}
\end{align*}$$

Comparing the last line with Eq. (10), we obtain Eq. (12).

### B. Instantaneous response

Let us define the instantaneous conductivity by

$$\mathcal{I}_i^{t_i-\cdots-t_N}(t) \equiv \lim_{t' \to t-0} \sigma_i^{t_i-\cdots-t_N}(t, t', \ldots, t'). \tag{14}$$

In terms of $\phi_i^{t_i-\cdots-t_N}(t, t_1, \ldots, t_N)$, we have

$$\mathcal{I}_i^{t_i-\cdots-t_N}(t) = \lim_{t' \to t-0} \int_{t'}^{t+\epsilon} dt' \cdots \int_{t_N}^{t+\epsilon} dt'_N \phi_i^{t_i-\cdots-t_N}(t, t'_1, \ldots, t'_N), \tag{15}$$

which implies that $\phi_i^{t_i-\cdots-t_N}(t, t_1, \ldots, t_N)$ contains a term of the form

$$\phi_i^{t_i-\cdots-t_N}(t, t_1, \ldots, t_N) = \mathcal{I}_i^{t_i-\cdots-t_N}(t) \prod_{\ell=1}^N \delta(t - t_\ell). \tag{16}$$

One of the main results of this work is the following formula that gives $\mathcal{I}_i^{t_i-\cdots-t_N}(t)$ as the expectation value of $\hat{H}_{i_1\cdots i_N}(t)$ in Eq. (7):

$$\mathcal{I}_i^{t_i-\cdots-t_N}(t) = \lim_{t' \to t-0} \sigma_i^{t_i-\cdots-t_N}(t, t', \ldots, t') = \frac{1}{V} \text{tr}\left(\hat{H}_{i_1\cdots i_N}(t) \hat{\rho}_0(t)\right). \tag{17}$$

This relation can be interpreted as the generalized $f$-sum rule for non-equilibrium states as we discuss below.
C. Fourier transformation for stationary states

If the unperturbed Hamiltonian $\hat{H}_0$ lacks any time-dependence and if the initial density matrix $\hat{\rho}_0$ commutes with $\hat{H}_0$, the system becomes time-translation invariant. In such a case, $\hat{\rho}_0$ can be written as

$$\hat{\rho}_0 = \sum_n \rho_n |n\rangle \langle n|, \quad (18)$$

where $|n\rangle$ is the $N$-th eigenstate of $\hat{H}_0$ with the energy eigenvalue $E_n$. In the stationary state, both $\sigma^{i_1 \cdots i_N}_{t_1 \cdots t_N}$ and $\phi^{i_1 \cdots i_N}_{t_1 \cdots t_N}$ depend only on the difference $t - t'$.

We write

$$\sigma^{i_1 \cdots i_N}_{t_1 \cdots t_N} = \sigma^{i_1 \cdots i_N}_{t - t'}, \quad \phi^{i_1 \cdots i_N}_{t_1 \cdots t_N} = \phi^{i_1 \cdots i_N}_{t - t'}, \quad (19)$$

for which Eq. (12) becomes

$$\sigma^{i_1 \cdots i_N}_{t_1 \cdots t_N} = \int_{-\epsilon}^{t_1} dt_1' \cdots \int_{-\epsilon}^{t_N} dt_N \sigma^{i_1 \cdots i_N}_{t_1', \cdots, t_N}. \quad (21)$$

In the presence of the time-translation symmetry, it is customary to work in the Fourier space. The Fourier transformation is defined by

$$\sigma^{i_1 \cdots i_N}_{i_1 \cdots i_N} (\omega_1, \ldots, \omega_N) = \int_{-\epsilon}^{\infty} dt_1 \cdots \int_{-\epsilon}^{\infty} dt_N \sigma^{i_1 \cdots i_N}_{t_1, \ldots, t_N} \prod_{\ell=1}^{N} e^{i(\omega_\ell - \eta)t_\ell}, \quad (22)$$

$$\phi^{i_1 \cdots i_N}_{i_1 \cdots i_N} (\omega_1, \ldots, \omega_N) = \int_{-\epsilon}^{\infty} dt_1 \cdots \int_{-\epsilon}^{\infty} dt_N \phi^{i_1 \cdots i_N}_{t_1, \ldots, t_N} \prod_{\ell=1}^{N} e^{i(\omega_\ell - \eta)t_\ell}, \quad (23)$$

where $\eta > 0$ is an infinitesimal parameter ensuring the convergence of the integrand in the $t_\ell \to \infty$ limit. The Fourier component $\sigma^{i_1 \cdots i_N}_{i_1 \cdots i_N} (\omega_1, \ldots, \omega_N)$ is called the $N$-th order optical conductivity. In the Fourier space, Eq. (21) reduces to

$$\sigma^{i_1 \cdots i_N}_{i_1 \cdots i_N} (\omega_1, \ldots, \omega_N) = \phi^{i_1 \cdots i_N}_{i_1 \cdots i_N} (\omega_1, \ldots, \omega_N) \prod_{\ell=1}^{N} \frac{i}{\omega_\ell + i\eta}. \quad (24)$$

By the inverse Fourier transformation, the frequency integral of $\sigma^{i_1 \cdots i_N}_{i_1 \cdots i_N} (\omega_1, \ldots, \omega_N)$ can be related to the instantaneous conductivity in Eq. (17) that is time-independent in stationary states:

$$\int_{-\infty}^{\infty} \frac{d\omega_1}{2\pi} \cdots \int_{-\infty}^{\infty} \frac{d\omega_N}{2\pi} \sigma^{i_1 \cdots i_N}_{i_1 \cdots i_N} (\omega_1, \ldots, \omega_N)$$

$$= \frac{1}{2^N N} \int_{t'}^{t} \lim_{t' \to +0} \sigma^{i_1 \cdots i_N}_{i_1 \cdots i_N} (t', \ldots, t') = \frac{1}{2^N N} \sum_n \rho_n \langle n | \hat{H}_{i_1 \cdots i_N} | n \rangle. \quad (25)$$

The factor $2^{-N}$ originates from the discontinuity of $\sigma^{i_1 \cdots i_N}_{i_1 \cdots i_N} (t_1, \ldots, t_N)$ around $t_\ell = 0$. This is the generalized $f$-sum rule for non-linear conductivity proposed recently [5].

D. Drude weight and Kohn formula

The Drude weight, usually discussed for the linear optical conductivity as in Eq. (2), can be naturally extended to nonlinear responses. The $N$-th order Drude weight ($N \geq 1$) is the coefficient of the term proportional to $\prod_{\ell=1}^{N} i/(\omega_\ell + i\eta)$ in the $N$-th order optical conductivity [5]:

$$\sigma^{i_1 \cdots i_N}_{(Drude)} (\omega_1, \ldots, \omega_N) = D^{i_1 \cdots i_N}_{i_1 \cdots i_N} \prod_{\ell=1}^{N} \frac{i}{\omega_\ell + i\eta}. \quad (26)$$
Comparing with Eq. (24), we find

$$D_i^{i_1\cdots i_N} = \phi_i^{i_1\cdots i_N}(\omega_1 = 0, \ldots, \omega_N = 0) = \int_{-\epsilon}^{\infty} dt_1 \cdots \int_{-\epsilon}^{\infty} dt_N \phi_i^{i_1\cdots i_N}(t_1, \ldots, t_N) e^{-\sum_{i=1}^{N} t_i}. \quad (27)$$

The generalized Kohn formula proposed in Ref. [5] reads

$$D_i^{i_1\cdots i_N} = \frac{1}{V} \sum_n \rho_n \frac{\partial^{N+1} E_n(\mathbf{A})}{\partial A_i \partial A_{i_1} \cdots \partial A_{i_N}} \bigg| \mathbf{A} = \mathbf{0}. \quad (28)$$

Here, $E_n(\mathbf{A})$ is the energy eigenvalue of the (instantaneous) eigenstate $|n(\mathbf{A})\rangle$ of $\hat{H}(\mathbf{A})$. The weight $\rho_n$ appearing in $\hat{\rho}_0$ in Eq. (18) is kept independent of $\mathbf{A}$. The energy eigenvalue $E_n(\mathbf{A})$ and the eigenstate $|n(\mathbf{A})\rangle$ are assumed to be analytic around $\mathbf{A} = \mathbf{0}$, satisfying $E_n(\mathbf{0}) = E_n$ and $|n(\mathbf{0})\rangle = |n\rangle$. The case of $N = 1$ for Gibbs states (i.e., $\rho_n \propto e^{-\beta E_n}$) reduces to the finite-temperature extension of the original Kohn formula discussed in Ref. [4], and Eq. (28) is its generalization to the $N$-th order optical conductivity ($N \geq 1$) of general stationary states. In the following, we give a proof of Eq. (28) via the non-degenerate perturbation theory for $N = 2$ and 3.

As a by-product of this derivation, we obtain the following alternative formulas of the Drude weight up to the third-order response:

$$D_i^{i} = \frac{1}{V} \sum_n \rho_n \left( n|\hat{H}_{i i}|n \right) - \left( n|\hat{H}_i \frac{\hat{Q}_n}{H_0 - E_n} \hat{H}_i |n \rangle + \text{c.c.} \right), \quad (29)$$

$$D_i^{i_1 i_2} = S_{i i_1 i_2} \frac{1}{V} \sum_n \rho_n \left( n|\hat{H}_{i i_1 i_2}|n \right) - 3 \left( n|\hat{H}_i \frac{\hat{Q}_n}{H_0 - E_n} \hat{H}_{i i_1} |n \rangle + \text{c.c.} + 6 \left( n|\hat{H}_i \frac{\hat{Q}_n}{H_0 - E_n} \delta_n \hat{H}_i \frac{\hat{Q}_n}{H_0 - E_n} \hat{H}_{i_2} |n \rangle \right) \right), \quad (30)$$

$$D_i^{i_1 i_2 i_3} = S_{i i_1 i_2 i_3} \frac{1}{V} \sum_n \rho_n \left( n|\hat{H}_{i i_1 i_2 i_3}|n \right) - 6 \left( n|\hat{H}_{i i_1} \frac{\hat{Q}_n}{H_0 - E_n} \delta_n \hat{H}_{i_2 i_3} |n \rangle \right) - 4 \left( n|\hat{H}_i \frac{\hat{Q}_n}{H_0 - E_n} \delta_n \hat{H}_i \frac{\hat{Q}_n}{H_0 - E_n} \hat{H}_{i_3} |n \rangle \right) + \text{c.c.}$$

$$+ 12 S_{i i_1 i_2 i_3} \frac{1}{V} \sum_n \rho_n \left( n|\hat{H}_{i i_1} \frac{\hat{Q}_n}{H_0 - E_n} \delta_n \hat{H}_{i_2} |n \rangle + \langle n|\hat{H}_i \frac{\hat{Q}_n}{H_0 - E_n} \delta_n \hat{H}_i |n \rangle + \langle n|\hat{H}_i \frac{\hat{Q}_n}{H_0 - E_n} \delta_n \hat{H}_{i_3} |n \rangle + \text{c.c.} \right), \quad (31)$$

Here, $\hat{Q}_n = 1 - |n\rangle \langle n|$ is the projector onto the compliment of the space spanned by $|n\rangle$, c.c. represents the complex conjugation of the term right in front, $S_{i i_1 \cdots i_N}$ is the symmetrizing operation among $i$, $i_1$, $\ldots$, and $i_N$, and $\delta_n \hat{H}_i$ is a short-hand notation for $\hat{H}_i - \langle n|\hat{H}_i |n \rangle$. The expression (29) for the linear Drude weight has been used in the literature [1] [3] [4], and Eqs. (30) and (31) are its generalizations to the second- and the third order Drude weight. The advantage of these expressions is that the gauge field $\mathbf{A}$ is set to be $\mathbf{0}$ when diagonalizing the Hamiltonian $\hat{H}_0$ to find $|n\rangle$ and $E_n$. As a price to pay, one needs to know all excited states to compute the correlation functions. This is in contrast to the Kohn formula (28) at zero temperature, which uses only the ground state energy as a function of $\mathbf{A}$.

### III. KUBO THEORY

In this section, we derive the concrete expressions of $\phi_i^{i_1\cdots i_N}(t, t_1, \ldots, t_N)$ for $N = 1, 2$ and 3 by following Kubo’s work on the linear response theory [6]. This formulation naturally leads us to a proof of Eq. (17) on the instantaneous conductivity for a general $N \geq 1$.

Let us begin by expanding the perturbed Hamiltonian $\hat{H}(t, \mathbf{A}(t))$ as

$$\hat{H}(t, \mathbf{A}(t)) = \sum_{N=0}^{\infty} \hat{H}_N(t),$$

(32)
where \( \hat{H}_N(t) \) is the correction of all \( N \)-th order terms,

\[
\hat{H}_N(t) = \frac{1}{N!} \sum_{i_1, \ldots, i_N} \hat{H}_{i_1 \ldots i_N}(t) \prod_{\ell=1}^{N} A_{i_\ell}(t).
\]

The perturbed density matrix \( \hat{\rho}(t) \) can be accordingly written as

\[
\hat{\rho}(t) = \sum_{N=0}^{\infty} \hat{\rho}_N(t).
\]

Plugging Eqs. (32) and (34) into the von Neumann equation \( i \partial_t \hat{\rho}(t) = [\hat{H}(t, \vec{A}(t)), \hat{\rho}(t)] \), we find, order by order, that

\[
\partial_t \hat{\rho}_N(t) = \sum_{M=0}^{N} (-i) [\hat{H}_{N-M}(t), \hat{\rho}_M(t)].
\]

We can solve this equation for \( \hat{\rho}_N(t) \) by switching to the “interacting picture”

\[
\hat{O}(t) \equiv \hat{S}_0^\dagger(t) \hat{O}(t) \hat{S}_0(t),
\]

where \( \hat{S}_0(t) \) was defined in Eq. (36). Assuming \( \hat{\rho}_N(0) = 0 \) for \( N \geq 1 \), we find

\[
\hat{\rho}_N(t) = \sum_{M=0}^{N-1} \int_0^t dt' (-i) [\hat{H}_{N-M}(t'), \hat{\rho}_M(t')]
\]

\( (\geq 1) \).

Since the right-hand side contains only \( \hat{\rho}_M(t') \) with \( 0 \leq M \leq N-1 \), one can find \( \hat{\rho}_N(t) \) inductively. For example, we have \( \hat{\rho}_0(t) = \hat{\rho}_0 \),

\[
\hat{\rho}_1(t) = \int_0^t dt' (-i) [\hat{H}_1(t'), \hat{\rho}_0],
\]

and

\[
\hat{\rho}_2(t) = \int_0^t dt' (-i) [\hat{H}_2(t'), \hat{\rho}_0] + \int_0^t dt' \int_0^{t'} dt'' (-i) 2^2 [\hat{H}_1(t'), [\hat{H}_1(t''), \hat{\rho}_0]],
\]

and

\[
\hat{\rho}_3(t) = \int_0^t dt' (-i) [\hat{H}_3(t'), \hat{\rho}_0] + \int_0^t dt' \int_0^{t'} dt'' (-i)^2 [\hat{H}_2(t'), [\hat{H}_1(t''), \hat{\rho}_0]] + \hat{H}_1(t'), [\hat{H}_2(t''), \hat{\rho}_0])
\]

\( + \int_0^t dt' \int_0^{t'} dt'' \int_0^{t''} (-i)^3 [\hat{H}_1(t'), [\hat{H}_1(t''), [\hat{H}_1(t'''), \hat{\rho}_0]]].
\]

Expressions for higher-order terms can be derived, at least formally, in the same way. However, when expressed in terms of \( \hat{H}_M \) (\( 0 \leq M \leq N \)) and \( \hat{\rho}_0 \), the number of terms in \( \hat{\rho}_N(t) \) (\( N \geq 1 \)) is \( 2^{N-1} \), and it is practically not easy to keep track of them altogether. In what follows, we will mainly discuss corrections only up to the third order (\( N = 3 \)).

The current density operator in Eq. (3) depends on \( \vec{A}(t) \) explicitly, which can also be written as

\[
\hat{j}_i(t, \vec{A}(t)) = \sum_{N=0}^{\infty} \hat{j}_{iN}(t),
\]

\[
\hat{j}_{iN}(t) = \frac{1}{V} \sum_{N=0}^{\infty} \frac{1}{N!} \sum_{i_1, \ldots, i_N} \hat{H}_{i_1 \ldots i_N}(t) \prod_{\ell=1}^{N} A_{i_\ell}(t).
\]

The \( N \)-th order correction to the current expectation value is the sum of \( N + 1 \) contributions:

\[
\langle j_i^{(N)}(t) \rangle = \sum_{M=0}^{N} \text{tr}(\hat{\rho}_M(t) \hat{\rho}_M(t)),
\]

\( (43) \).
which contains $2^N$ terms in total. Using Eq. \[38\]–\[40\], we get

$$j_1^{(1)}(t) = \langle \hat{j}_{i1}(t) \rangle_0 + \int_0^t dt'(-i)\langle \hat{j}_{i0}(t), \hat{H}_1(t') \rangle_0,$$

$$j_1^{(2)}(t) = \langle \hat{j}_{i2}(t) \rangle_0 + \int_0^t dt'(-i)\langle \hat{j}_{i1}(t), \hat{H}_1(t') \rangle_0 + \int_0^t dt' \int_0^{t'} dt''(-i)^2 \langle \hat{j}_{i0}(t), \hat{H}_1(t'), \hat{H}_1(t'') \rangle_0,$$  \hspace{2cm} (44)

and

$$j_1^{(3)}(t) = \langle \hat{j}_{i3}(t) \rangle_0 + \int_0^t dt'(-i)\langle \hat{j}_{i2}(t), \hat{H}_1(t') \rangle_0 + \int_0^t dt' \int_0^{t'} dt''(-i)^2 \langle \hat{j}_{i1}(t), \hat{H}_1(t'), \hat{H}_1(t'') \rangle_0 + \int_0^t dt' \int_0^{t'} dt'' \int_0^{t''} dt'''(-i)^3 \langle \hat{j}_{i0}(t), \hat{H}_1(t'), \hat{H}_1(t''), \hat{H}_1(t''') \rangle_0.$$ \hspace{2cm} (45)

Here and hereafter, we write

$$\langle \hat{O} \rangle_0 \equiv \text{tr}(\hat{O}\hat{\rho}_0)$$ \hspace{2cm} (47)

for any operator $\hat{O}$. Plugging Eqs. \[33\] and \[42\] into these results, we can read off $\phi_{i_1\cdots i_N}^{(t_1, t_2, \ldots, t_N)}(t, t_1, \ldots, t_N)$:

$$V \phi_{i_1}^{(t_1, t_1)}(t, t_1) = \delta(t - t_1)\langle \hat{H}_{i_{11}}(t) \rangle_0 + \theta(t - t_1)(-i)\langle [\hat{H}_i(t), \hat{H}_{i_{11}}(t_{11})] \rangle_0,$$ \hspace{2cm} (48)

$$V \phi_{i_1 i_2}^{(t_1, t_1, t_2)}(t, t_1, t_2) = \delta(t - t_1)\delta(t - t_2)\langle \hat{H}_{i_{11} i_{12}}(t) \rangle_0 + 2S_{i_1 i_2}\delta(t - t_1)\theta(t - t_2)(-i)\langle [\hat{H}_{i_{11}}(t), \hat{H}_{i_{12}}(t_{12})] \rangle_0 + \delta(t_1 - t_2)\theta(t - t_1)(-i)\langle [\hat{H}_i(t), \hat{H}_{i_{11}}(t_{12})] \rangle_0 + 2S_{i_1 i_2}\theta(t - t_1)\theta(t_1 - t_2)(-i)^2\langle [\hat{H}_{i_{11}}(t), \hat{H}_{i_{11} i_{12}}(t_{12})] \rangle_0,$$ \hspace{2cm} (49)

and

$$V \phi_{i_1 i_2 i_3}^{(t_1, t_1, t_2, t_3)}(t, t_1, t_2, t_3) = \delta(t - t_1)\delta(t - t_2)\delta(t - t_3)\langle \hat{H}_{i_{11} i_{12} i_{13}}(t) \rangle_0 + 3S_{i_1 i_2 i_3}\delta(t - t_1)\delta(t - t_2)\theta(t - t_3)(-i)\langle [\hat{H}_{i_{11} i_{12}}(t), \hat{H}_{i_{13}}(t_{13})] \rangle_0 + 3S_{i_1 i_2 i_3}\delta(t - t_1)\delta(t - t_2)\theta(t - t_3)(-i)\langle [\hat{H}_{i_{11}}(t), \hat{H}_{i_{13}}(t_{13})] \rangle_0 + 6S_{i_1 i_2 i_3}\delta(t - t_1)\theta(t - t_2)\theta(t - t_3)(-i)^2\langle [\hat{H}_{i_{11}}(t), \hat{H}_{i_{12}}(t_{12})] \rangle_0 + \delta(t_1 - t_2)\delta(t_2 - t_3)\theta(t - t_1)(-i)\langle [\hat{H}_i(t), \hat{H}_{i_{11} i_{12}}(t_{13})] \rangle_0 + 3S_{i_1 i_2 i_3}\delta(t - t_1)\theta(t - t_2)\theta(t_1 - t_3)(-i)^2\langle [\hat{H}_{i_{11}}(t), \hat{H}_{i_{11} i_{12}}(t_{13})] \rangle_0 + 3S_{i_1 i_2 i_3}\theta(t - t_2)\theta(t - t_1)\theta(t_1 - t_3)(-i)^2\langle [\hat{H}_i(t), \hat{H}_{i_{11}}(t_{13})] \rangle_0 + 6S_{i_1 i_2 i_3}\theta(t - t_1)\theta(t - t_2)\theta(t - t_3)(-i)^3\langle [\hat{H}_i(t), \hat{H}_{i_{11}}(t_{13})] \rangle_0.$$ \hspace{2cm} (50)
Here, \( \theta(t) \) is the Heaviside step function and \( S_{i_1\ldots i_N} \) refers to the symmetrizing operation averaging over all \( N! \) permutations of \((i_1, t_1)\)’s. For example,

\[
S_{i_1i_2}f_{i_1i_2}(t_1, t_2) = \frac{1}{2} \left[ f_{i_1i_2}(t_1, t_2) + f_{i_2i_1}(t_2, t_1) \right],
\]

\[
S_{i_1i_2i_3}f_{i_1i_2i_3}(t_1, t_2, t_3) = \frac{1}{6} \left[ f_{i_1i_2i_3}(t_1, t_2, t_3) + f_{i_2i_3i_1}(t_2, t_3, t_1) + f_{i_3i_1i_2}(t_3, t_1, t_2) + f_{i_3i_1i_2}(t_3, t_1, t_2) + f_{i_1i_2i_3}(t_1, t_2, t_3) + f_{i_2i_3i_1}(t_2, t_3, t_1) \right].
\]

One can obtain the expression of the corresponding \( \sigma_{i_1\ldots i_N}^{\text{inst}}(t, t_1, \ldots, t_N) \) by using Eq. (12).

Let us switch back to the consideration for a general \( N \geq 1 \). In general, \( j_i^{(N)}(t) \) \((N \geq 0)\) contains \( \langle \hat{H}_{i_1\ldots i_N}(t) \rangle_0 = \frac{1}{V} \langle \hat{H}_{i_1\ldots i_N}(t) \rangle_0 \) that originates from the \( M = 0 \) contribution in Eq. (13). This term results in the instantaneous response

\[
\phi_{i_1}^{i_1\ldots i_N}(t, t_1, \ldots, t_N) = \frac{1}{V} \langle \hat{H}_{i_1i\ldots i_N}(t) \rangle_0 \prod_{\ell=1}^{N} \delta(t - t_\ell) = \frac{1}{V} \text{tr}(\hat{H}_{i_1i\ldots i_N}(t)\hat{\rho}_0(t)) \prod_{\ell=1}^{N} \delta(t - t_\ell).
\]

All other contributions to \( j_i^{(N)}(t) \) from \( M \geq 1 \) in Eq. (43) are retarded effect involving at least one temporal integration that can be traced back to Eq. (57). Comparing Eq. (53) with Eq. (16), we obtain our result in Eq. (17).

**IV. CONCRETE FORM OF THE OPTICAL CONDUCTIVITY**

In this section we perform the Fourier transformation to obtain the explicit form of \( \phi_{i_1}^{i_1\ldots i_N}(\omega_1, \ldots, \omega_N) \) for \( N = 1, 2 \) and 3. Then we use them to give a perturbative proof of the Kohn formula for the second- and third-order optical conductivity.

**A. Optical conductivity and \( f \)-sum rules**

In the presence of the time-translation symmetry, Eqs. (48) and (49) reduce to

\[
V \phi_{i_1}^{i_1}(t_1) = \delta(t_1)(\hat{H}_{i_1i_1})_0
+ \theta(t_1)(-i)[\hat{H}_{i_1}e^{-i\hat{H}_0t_1}\hat{H}_{i_1}e^{i\hat{H}_0t_1}]_0
\]

and

\[
V \phi_{i_1i_2}^{i_1i_2}(t_1, t_2) = \delta(t_1)\delta(t_2)(\hat{H}_{i_1i_2})_0
+ 2S_{i_1i_2}\delta(t_1)\theta(t_2)(-i)[\hat{H}_{i_1i_2}e^{-i\hat{H}_0t_2}\hat{H}_{i_2}e^{i\hat{H}_0t_2}]_0
+ \delta(t_2 - t_1)\theta(t_1)(-i)[\hat{H}_{i_2}e^{-i\hat{H}_0t_1}\hat{H}_{i_1}e^{i\hat{H}_0t_1}]_0
+ 2S_{i_1i_2}\theta(t_1)\theta(t_2 - t_1)(-i)^2[\hat{H}_{i_2}e^{-i\hat{H}_0t_1}\hat{H}_{i_1}e^{i\hat{H}_0t_1}, e^{-i\hat{H}_0t_2}\hat{H}_{i_2}e^{i\hat{H}_0t_2}]_0.
\]

We perform the Fourier transformation (23) assuming the form of the density matrix in Eq. (18). We find

\[
V \phi_{i_1}^{i_1}(\omega_1) = (\hat{H}_{i_1i_1})_0
+ \sum_n \rho_n \langle n | \left( \delta_n \hat{H}_{i_1} \frac{\hat{Q}_n}{\omega_1 - \hat{H}_0 + \mathcal{E}_n + in\eta} - \delta_n \hat{H}_{i_1} \frac{\hat{Q}_n}{\omega_1 + \hat{H}_0 - \mathcal{E}_n + in\eta} \right) | n \rangle
\]

(56)
and
\[
V \phi_i^i \omega_1, \omega_2 = \langle \tilde{H}_{ii} \rangle_0^i + 2S_{ii} \sum_n \rho_n \langle n| \left( \delta_n \tilde{H}_{ii} \omega_2 - \tilde{Q}_n \delta_n \tilde{H}_{ii} \omega_2 + \tilde{H}_0 - \varepsilon_n + i\eta \right) \rangle|n\rangle
\]
\[
+ \sum_n \rho_n \langle n| \left( \delta_n \tilde{H}_i \omega_1 + \omega_2 - \tilde{Q}_n \delta_n \tilde{H}_{ii} \omega_1 + \omega_2 + \tilde{H}_0 - \varepsilon_n + 2i\eta \right) \rangle|n\rangle
\]
\[
+ 2S_{ii} \sum_n \rho_n \left[ \langle n| \delta_n \tilde{H}_i \omega_1 + \omega_2 - \tilde{Q}_n \delta_n \tilde{H}_{ii} \omega_2 + \tilde{H}_0 - \varepsilon_n + i\eta \rangle|n\rangle \right]
\]
\[
- \langle n| \delta_n \tilde{H}_i \omega_1 + \omega_2 - \tilde{Q}_n \delta_n \tilde{H}_{ii} \omega_2 + \tilde{H}_0 - \varepsilon_n + i\eta \delta_n \tilde{H}_{ii} |n\rangle \right]
\]
\[
+ \langle n| \delta_n \tilde{H}_i \omega_1 + \omega_2 + \tilde{H}_0 - \varepsilon_n + i\eta \delta_n \tilde{H}_{ii} |n\rangle \right].
\]
(57)

Here, \(\delta_n \tilde{H}_i \equiv \tilde{H}_i - \langle n| \tilde{H}_i |n\rangle \), \(\tilde{Q}_n \equiv 1 - |n\rangle \langle n|\) is the projector onto the compliment of the space spanned by \(|n\rangle\), and \(S_{ii} \) is the symmetrization among \((i, \omega)\)'s. The corresponding optical conductivity is then given by Eq. (24). The expression of \(\phi_i^i \omega_1, \omega_2 \) and \(\phi_i^i \omega_3 \) are too long to be presented here and are included in Appendix A.

More generally, the instantaneous contribution in Eq. (53) gives rise to
\[
\sigma_i^{i \ldots i N} (\omega_1, \ldots, \omega_N) = \frac{1}{V} \langle \tilde{H}_{ii} \rangle_0^i \prod_{\ell=1}^N \frac{i}{\omega_\ell + i\eta}
\]
(58)
in the \(N\)-th other optical conductivity. All other terms in \(\sigma_i^{i \ldots i N} (\omega_1, \ldots, \omega_N)\) are suppressed by \(|\omega_\ell|^{-2}\) for large \(|\omega_\ell|\) for at least one \(1 \leq \ell \leq N\) as a result of the temporal integration in Eq. (37). This observation immediately implies the \(f\)-sum rule (25). To see this, let us perform the frequency integration in Eq. (25) using techniques of complex analysis. Except for the instantaneous term in Eq. (58), all other terms in \(\sigma_i^{i \ldots i N} (\omega_1, \ldots, \omega_N)\) do not contribute to this integral. This is because, if a term is suppressed by \(|\omega_\ell|^{-2}\) for large \(|\omega_\ell|\), one can form a closed integration path by adding a large half circle in the upper half of the complex \(\omega_\ell\)-plane and apply the Cauchy’s integral theorem. All poles of \(\sigma_i^{i \ldots i N} (\omega_1, \ldots, \omega_N)\) are located in the lower-half of the complex plane and thus the integral vanishes. Therefore, taking into account only the contribution from the instantaneous term (58) using the formula
\[
\int_{-\infty}^{\infty} \frac{d\omega}{2\pi i} \frac{i}{\omega + i\eta} = \theta(0) = \frac{1}{2}
\]
(59)
we reproduce the \(f\)-sum rule (25).

**B. Drude weight**

Here we derive the Kohn formula based on the concrete expressions of \(\phi_i^{i \ldots i N} (\omega_1, \ldots, \omega_N)\) obtained above. For the brevity of the presentation, let us write
\[
|n_{i_1 \ldots i_N}\rangle = \frac{\partial^N |n(\tilde{A})\rangle}{\partial A_{i_1} \ldots \partial A_{i_N}} \bigg|_{\tilde{A} = 0}
\]
(60)

The linear Drude weight is given by \(D_i^{\omega_1} = \phi_i^i |\omega_1 = 0\rangle\). Let us make this into the form of the Kohn formula following the discussions in Refs. 13 and 14. Using the standard formulas
\[
\langle n|n_{i_1}\rangle + c.c. = 0,
\]
(61)
\[
\tilde{Q}_n|n_{i_1}\rangle = -\frac{\tilde{Q}_n}{\tilde{H}_0 - \varepsilon_n} \tilde{H}_{i_1} |n\rangle
\]
(62)
in the first-order nondegenerate perturbation theory, we find,

\[
V D_i^{(1)} = V \phi_i^{(1)}(\omega_1 = 0) \\
= \sum_n \rho_n \left( \langle n | \hat{H}_{ii_i} | n \rangle - \langle n | \hat{H}_i - \hat{Q}_n \hat{H}_{0} - \varepsilon_n \hat{H}_{1i} | n \rangle \right) + \text{c.c.} \\
= \sum_n \rho_n \left( \langle n | \hat{H}_{ii_i} | n \rangle + \langle n | \hat{H}_i \hat{Q}_n | n_{i_1} \rangle + \text{c.c.} \right) \\
= \sum_n \rho_n \left( \langle n | \hat{H}_{ii_i} | n \rangle + \langle n | \hat{H}_i | n_{i_2} \rangle + \text{c.c.} \right) \\
= \sum_n \rho_n \left( \frac{\partial}{\partial A_i} \left( \langle n(A) | \frac{\partial \hat{H}(A)}{\partial A_i} | n(A) \rangle \right) \right)_{A = 0} \\
= \sum_n \rho_n \left( \frac{\partial^2 \varepsilon_n(A)}{\partial A_i \partial A_{i_1} \partial A_{i_2}} \right)_{A = 0}. (63)
\]

Here, c.c. represents the complex conjugation of the term right in front. Thus Eq. (28) for \( N = 1 \) is verified. Strictly speaking, this proof applies only to the cases where all energy levels \( \varepsilon_n \) with \( \rho_n \neq 0 \) are non-degenerate. It was argued in Ref. 4 that the first-order degenerate perturbation theory lifts the degeneracy and the same procedure should work.

Let us do the same for the second-order Drude weight, given by \( D_i^{(2)} = \phi_i^{(2)}(\omega_1 = 0, \omega_2 = 0) \). Knowing the answer, we find it easier to go backward:

\[
\sum_n \rho_n \frac{\partial^3 \varepsilon_n(A)}{\partial A_i \partial A_{i_1} \partial A_{i_2}} \bigg|_{A = 0} \\
= \sum_n \rho_n \frac{\partial^2}{\partial A_i \partial A_{i_2}} \left( n(A) \left| \frac{\partial \hat{H}(A)}{\partial A_i} \right| n(A) \right) \bigg|_{A = 0} \\
= S_{i_1 i_2} \sum_n \rho_n \left( \langle n | \hat{H}_{ii_i} | n \rangle + 2 \langle n_{i_1} | \hat{H}_i | n_{i_2} \rangle \right) + S_{i_1 i_2} \sum_n \rho_n \left( 2 \langle n | \hat{H}_{ii_i} | n_{i_1} \rangle + \langle n | \hat{H}_i | n_{i_1 i_2} \rangle \right) + \text{c.c.} \\
= S_{i_1 i_2} \sum_n \rho_n \left( \langle n | \hat{H}_{ii_i} | n \rangle + 2 \langle n_{i_1} | \hat{Q}_n \delta_n \hat{H}_i \hat{Q}_n | n_{i_2} \rangle \right) + S_{i_1 i_2} \sum_n \rho_n \left( 2 \langle n | \hat{H}_{ii_i} \hat{Q}_n | n_{i_2} \rangle + \langle n | \hat{H}_i \hat{Q}_n | n_{i_1 i_2} \rangle \right) + \text{c.c.} \\
+ 2S_{i_1 i_2} \sum_n \rho_n \langle n_{i_1} | \hat{Q}_n \hat{H}_i | n \rangle \langle n_{i_2} \rangle + \text{c.c.} \\
= S_{i_1 i_2} \sum_n \rho_n \left[ \langle n | \hat{H}_{ii_i} | n \rangle - 3 \langle n | \hat{H}_i \hat{Q}_n \hat{H}_0 - \varepsilon_n \hat{H}_{1i} | n \rangle + \text{c.c.} + 6 \langle n | \hat{H}_i \hat{Q}_n \delta_n \hat{H}_i \hat{Q}_n \hat{H}_0 - \varepsilon_n \hat{H}_{1i} | n \rangle \right] \\
= V \phi_i^{(2)}(\omega_1 = 0, \omega_2 = 0) = V D_i^{(2)}. (64)
\]

This reproduces Eq. (28) for \( N = 2 \). In the derivation, we used the standard formulas in Eqs. (61), (62), and

\[
(\langle n | n_{i_1 i_2} \rangle + \langle n_{i_2} | n_{i_1} \rangle) + \text{c.c.} = 0, (65)
\]

\[
\hat{Q}_n | n_{i_1 i_2} \rangle = -S_{i_1 i_2} \left[ \frac{\hat{Q}_n}{\hat{H}_0 - \varepsilon_n} \hat{H}_{1i} | n \rangle + 2 \frac{\hat{Q}_n}{\hat{H}_0 - \varepsilon_n} \delta_n \hat{H}_i | n_{i_2} \rangle \right]. (66)
\]
Finally, for the third-order response, we have

\[ \sum_n \rho_n \frac{\partial^3 \mathcal{E}_n(\vec{A})}{\partial A_i \partial A_j \partial A_k} \bigg|_{\vec{A}=\vec{0}} = \sum_n \rho_n \frac{\partial^3}{\partial A_i \partial A_j \partial A_k} \langle n(\vec{A}) \big| \frac{\partial \hat{H}(\vec{A})}{\partial A_i} \big| n(\vec{A}) \rangle \bigg|_{\vec{A}=\vec{0}} \]

\[ = S_{i_1i_2i_3} \sum_n \rho_n \left( 6\langle n|\hat{H}_{i_1i_2i_3}|n \rangle + 3\langle n|\hat{H}_{i_1}|n_{i_2i_3} \rangle + 3\langle n_1|\hat{H}_{i_1}|n_{i_2i_3} \rangle + 3\langle n_1|\hat{H}_{i_1}|n_{i_2i_3} \rangle + 6\langle n_2|\hat{Q}_n\delta_n\hat{H}_{i_2i_3}|n_{i_1i_2i_3} \rangle \right) + \text{c.c.} \]

\[ = S_{i_1i_2i_3} \sum_n \rho_n \left( 6\langle n|\hat{H}_{i_1i_2i_3}|n \rangle + 3\langle n|\hat{H}_{i_1}|n_{i_2i_3} \rangle + 3\langle n|\hat{H}_{i_1}|n_{i_2i_3} \rangle + 3\langle n|\hat{Q}_n\delta_n\hat{H}_{i_2i_3}|n_{i_1i_2i_3} \rangle \right) + \text{c.c.} \]

\[ + S_{i_1i_2i_3} \sum_n \rho_n \left( 6\langle n_2|n|\hat{Q}_n\delta_n\hat{H}_{i_2i_3}|n_{i_1i_2i_3} \rangle + 3\langle n_1|n|\hat{Q}_n\delta_n\hat{H}_{i_2i_3}|n_{i_1i_2i_3} \rangle + 3\langle n_1|n|\hat{Q}_n\delta_n\hat{H}_{i_2i_3}|n_{i_1i_2i_3} \rangle \right) + \text{c.c.} \]

\[ = S_{i_1i_2i_3} \sum_n \rho_n \left( 6\langle n|\hat{H}_{i_1i_2i_3}|n \rangle - 6\langle n|\hat{H}_{i_1} \hat{H}_{i_2i_3}|n \rangle - 4\langle n|\hat{H}_{i_1} \hat{Q}_n\delta_n\hat{H}_{i_2i_3}|n \rangle + c.c. \right) \]

\[ + 12S_{i_1i_2i_3} \sum_n \rho_n \left( 6\langle n|\hat{H}_{i_1i_2i_3}|n \rangle - 6\langle n|\hat{H}_{i_1} \hat{H}_{i_2i_3}|n \rangle - 4\langle n|\hat{H}_{i_1} \hat{Q}_n\delta_n\hat{H}_{i_2i_3}|n \rangle + c.c. \right) \]

\[ - 24S_{i_1i_2i_3} \sum_n \rho_n \langle n|\hat{H}_{i_1} \hat{H}_{i_2i_3}|n \rangle \hat{Q}_n \hat{H}_{i_2i_3}|n \rangle - 3\langle n|\hat{H}_{i_1i_2i_3}|n \rangle + c.c. \right) \]

\[ + 24S_{i_1i_2i_3} \sum_n \rho_n \langle n|\hat{H}_{i_1} \hat{H}_{i_2i_3}|n \rangle \hat{Q}_n \hat{H}_{i_2i_3}|n \rangle - 3\langle n|\hat{H}_{i_1i_2i_3}|n \rangle + c.c. \right) \]

\[ = V\phi_i^{i_1i_2i_3}(\omega_1 = 0, \omega_2 = 0, \omega_3 = 0) = V\phi_i^{i_1i_2i_3}. \]  \hspace{1cm} (67)

In passing to the last line we set \( \omega_1 = \omega_2 = \omega_3 = 0 \) in Eq. (A2). In the derivation, we used

\[ S_{i_1i_2i_3} \left( \langle n|n_{i_1i_2i_3} \rangle + 3\langle n_1|n_{i_2i_3} \rangle \right) + c.c. = 0 \]  \hspace{1cm} (68)

and

\[ \hat{Q}_n|n_{i_1i_2i_3} \rangle = S_{i_1i_2i_3} \left[ - \frac{\hat{Q}_n}{H_0 - \varepsilon_n} \hat{H}_{i_1i_2i_3}|n \rangle - 3\frac{\hat{Q}_n}{H_0 - \varepsilon_n} \hat{H}_{i_1i_2}|n_{i_3} \rangle - \frac{6\hat{Q}_n}{H_0 - \varepsilon_n} \hat{H}_{i_1i_2}|n_{i_3} \rangle - 3\frac{\hat{Q}_n}{H_0 - \varepsilon_n} \hat{H}_{i_1i_2}|n_{i_3} \rangle \right], \]  \hspace{1cm} (69)

in addition to the above first- and second-order relations.

V. TIGHT-BINDING MODEL

Let us demonstrate our results with a simple example of a tight-binding model. We diagonalize the unperturbed Hamiltonian as

\[ \hat{H}_0 = \sum_{k,n} \varepsilon_{kn} \hat{c}_{kn}^\dagger \hat{c}_{kn}. \]  \hspace{1cm} (70)

In this basis, \( \hat{H}_{i_1...i_N} \) in Eq. (7) can be written as

\[ \hat{H}_{i_1...i_N} = \sum_{k,m,n} \hat{c}_{km}^\dagger \hat{h}_{i_1...i_N}^{kmn} \hat{c}_{kn}. \]  \hspace{1cm} (71)
The response function \( \phi_i^{(1)}(\omega_1) \) and \( \phi_i^{(1,2)}(\omega_1, \omega_2) \) are then given by

\[
V \phi_i^{(1)}(\omega_1) = \sum_{k,n<0} h_{i_1}^{k,n} + \sum_{k,n<0,m>0} \left( \frac{h_{k}^{k,n} h_{i_1}^{k,m}}{\omega_1 - (\varepsilon_{km} - \varepsilon_{kn}) + i\eta} - \frac{h_{k}^{k,n} h_{i_1}^{k,m}}{\omega_1 + (\varepsilon_{km} - \varepsilon_{kn}) + i\eta} \right)
\]

and

\[
V \phi_i^{(1,2)}(\omega_1, \omega_2) = \sum_{k,n<0} h_{i_1}^{k,n} + 2S_{i_1,2} \sum_{k,n<0,m>0} \left( \frac{h_{k}^{k,n} h_{i_1}^{k,m}}{\omega_1 - (\varepsilon_{km} - \varepsilon_{kn}) + i\eta} - \frac{h_{k}^{k,n} h_{i_1}^{k,m}}{\omega_1 + (\varepsilon_{km} - \varepsilon_{kn}) + i\eta} \right)
+ \sum_{k,n<0,m>0} \left( \frac{h_{i_1}^{k,n} h_{i_1}^{k,m}}{\omega_1 + \omega_2 - (\varepsilon_{km} - \varepsilon_{kn}) + 2i\eta} - \frac{h_{i_1}^{k,n} h_{i_1}^{k,m}}{\omega_1 + \omega_2 + (\varepsilon_{km} - \varepsilon_{kn}) + 2i\eta} \right)
+ 2S_{i_1,2} \sum_{k,n,n'<0,m,m'>0} \left[ \frac{h_{i_1}^{k,n} (h_{i_1}^{k,n'} \delta_{n,n'} - h_{i_1}^{k,n'} \delta_{m,m'}) h_{i_1}^{k,m'}}{\omega_1 + \omega_2 - (\varepsilon_{km} - \varepsilon_{kn}) + 2i\eta} \left[ \omega_2 - (\varepsilon_{km'} - \varepsilon_{kn'}) + i\eta \right] \right]
- 2S_{i_1,2} \sum_{k,n,n'<0,m,m'>0} \left[ \frac{h_{i_1}^{k,n} (h_{i_1}^{k,n'} \delta_{n,n'} - h_{i_1}^{k,n'} \delta_{m,m'}) h_{i_1}^{k,m'}}{\omega_1 + \omega_2 - (\varepsilon_{km} - \varepsilon_{kn}) + 2i\eta} \left[ \omega_2 - (\varepsilon_{km'} - \varepsilon_{kn'}) + i\eta \right] \right]
+ 2S_{i_1,2} \sum_{k,n,n'<0,m,m'>0} \left[ \frac{h_{i_1}^{k,n} (h_{i_1}^{k,n'} \delta_{n,n'} - h_{i_1}^{k,n'} \delta_{m,m'}) h_{i_1}^{k,m'}}{\omega_1 + \omega_2 + (\varepsilon_{km} - \varepsilon_{kn}) + 2i\eta} \right].
\]

We use the following two-band model, illustrated in Fig. 1(a), in \( d = 1 \) at zero temperature for the demonstration.

\[
H_{k_x} = \begin{pmatrix}
-\delta - 2t_2 \sin(k_x + A_x) & t_1 (e^{iA_x/2} e^{-i(k_x + A_x/2)}) \\
t_1 (e^{-iA_x/2} e^{i(k_x + A_x/2)}) & \delta + 2t_2 \sin(k_x + A_x)
\end{pmatrix}.
\]

This model breaks both the inversion symmetry and the time-reversal symmetry, resulting in a nonzero \( f \)-sum for the second-order conductivity. We set \( t_1 = 0.5, \delta = 0.5, \) and \( t_2 = 0.125 \). The crystal momentum \( k_x \) takes values \( 2\pi i_x/L_x \) with \( i_x = 1, 2, \cdots L_x \) and \( L_x = 501 \). When the chemical potential is set to be \(-1\), the system is metallic and partially fills the lower band as shown in Fig. 1(b). The optical conductivities \( \sigma_x^{(1)}(\omega_1) \) and \( \sigma_x^{(1,2)}(\omega_1, \omega_2) \) are computed based on...
TABLE I. Numerical results for the tight-binding model in Eq. (74). See the main text for the definitions of these quantities in the actual calculation.

| Linear response $\sigma^x(\omega_1)$ | Second-order response $\sigma^{xx}(\omega_1, \omega_2)$ |
|--------------------------------------|---------------------------------------------------------|
| Drude weight $D^x_z$ | $f$-sum $\frac{\partial^2 E_0 (A_z)}{\partial A_z^2}$ | Drude weight $D^{xx}_z$ | $f$-sum $\frac{\partial^3 E_0 (A_z)}{\partial A_z^3}$ |
| $0.495265$ | $0.495260$ | $0.306013$ | $0.306208$ | $0.076977$ | $0.077003$ | $0.0373262$ | $0.0374834$ |

Eqs. (24), (22), and (23) with $\eta = 0.01$ for the range of $\omega_1$ and $\omega_2$ in $|\omega_\ell| < 10$. The frequencies are discretized with $\Delta \omega = 1/200$. The obtained optical conductivities as a function of $\omega$ are shown in Fig. 1(c) and (e).

The Drude weights $D^x_z$ and $D^{xx}_z$ are then determined by fitting $\text{Re}[\sigma^x(\omega_1)]$ and $\text{Re}[\sigma^{xx}(\omega_1, \omega_2)]$ for small $\omega_\ell$’s [Fig. 1(d) and (f)] by

$$\text{Re}[\sigma^x(\omega_1)] = \frac{\eta}{\omega^2 + \eta^2} D^x_z, \quad \text{Re}[\sigma^{xx}(\omega_1, \omega_2)] = \frac{\eta^2 - \omega_1 \omega_2}{(\omega_1^2 + \eta^2)(\omega_2^2 + \eta^2)} D^{xx}_z \quad (|\omega_\ell| \ll 1).$$

For this fit, we use frequencies in the range $|\omega| < 0.2$. The Drude weights $D^x_z$ and $D^{xx}_z$ obtained this way are compared with $\partial^2 E_0 (A_z)/\partial A_z^2$ and $\partial^3 E_0 (A_z)/\partial A_z^3$ computed separately. As summarized in Table I, we observe good agreement, confirming the Kohn formula.

The frequency integration of $\sigma^x(\omega_1)$ and $\sigma^{xx}(\omega_1, \omega_2)$ in Eq. (25) are approximated by the Riemannian summation, i.e.,

$$\sum_{-10 < \omega_1 < 10} \frac{\Delta \omega}{2\pi} \sigma^x(\omega_1), \quad \sum_{-10 < \omega_1 < 10} \sum_{-10 < \omega_2 < 10} \frac{(\Delta \omega)^2}{2\pi^2} \sigma^{xx}(\omega_1, \omega_2).$$

The results are compared with $(1/2)\langle \partial^2 \hat{H}(A_z)/\partial A_z^2 \rangle_0$ and $(1/4)\langle \partial^3 \hat{H}(A_z)/\partial A_z^3 \rangle_0$ computed separately. Again, we find that they agree well, verifying the $f$-sum rule.

VI. CONCLUSION

In this work, we studied the non-linear conductivity $\sigma^{i_1 \ldots i_N}(t_1, \ldots, t_N)$ with respect to the spatially uniform electric field. We provided the detailed discussion on the relation between the instantaneous response and the $f$-sum rule, hinted in Ref. [5]. We also derived explicit expressions of the nonlinear optical conductivity $\sigma^{i_1 \ldots i_N}(\omega_1, \ldots, \omega_N)$ of the orders $N = 2$ and 3 for general quantum many-body systems, in terms of correlation functions. Based on the explicit formulas obtained, we proved the nonlinear generalizations of the Kohn formula to the second- and third-order optical conductivity, confirming the results in Ref. [3] derived in a general framework but without explicit expressions of the non-linear conductivities. As a demonstration, we applied our formulation to a simple tight-binding model in one dimension, and numerically verified the non-linear $f$-sum rule and Drude weight of the second order. While this demonstration was done for the non-interacting electrons, we emphasize that our formulation and results of the present paper is applicable to very general quantum many-body systems with interactions.

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Appendix A: Expression of $\phi_i^{(123)}$

Here we present the expression of $\phi_i^{(123)}(t_1, t_2, t_3)$ and $\phi_i^{(123)}(\omega_1, \omega_2, \omega_3)$. In the presence of the time-translation symmetry, Eq. (50) becomes

$$V\phi_i^{(123)}(t_1, t_2, t_3) = \langle \hat{H}_{ii_{1}i_{2}i_{3}} \rangle_0 + I_1 + I_2 + I_3,$$  \tag{A2}

where

$$I_1 = 3S_{i_1i_2i_3} \sum_n \rho_n \langle n | \left( \frac{\hat{Q}_n}{\omega_3 - \hat{H}_0 + \varepsilon_n + \imath \eta} - \frac{\hat{Q}_n}{\omega_3 + \hat{H}_0 - \varepsilon_n - \imath \eta} \right) | n \rangle,$$

$$I_2 = 3S_{i_1i_2i_3} \sum_n \rho_n \langle n | \left( \frac{\hat{Q}_n}{\omega_2 + \omega_3 - \hat{H}_0 + \varepsilon_n + 2\imath \eta} - \frac{\hat{Q}_n}{\omega_2 + \omega_3 + \hat{H}_0 - \varepsilon_n - 2\imath \eta} \right) | n \rangle,$$

$$I_3 = 6S_{i_1i_2i_3} \sum_n \rho_n \left[ \langle n | \delta_n \hat{H}_{i1i} \hat{Q}_n \omega_2 + \omega_3 - \hat{H}_0 + \varepsilon_n + 2\imath \eta \frac{\delta_n \hat{H}_{i2i} \hat{Q}_n}{\omega_3 - \hat{H}_0 + \varepsilon_n + \imath \eta} \frac{\delta_n \hat{H}_{i3i} \hat{Q}_n}{\omega_2 + \omega_3 - \hat{H}_0 + \varepsilon_n + \imath \eta} | n \rangle - \langle n | \delta_n \hat{H}_{i1i} \hat{Q}_n \omega_2 + \omega_3 + \hat{H}_0 - \varepsilon_n + 2\imath \eta \frac{\delta_n \hat{H}_{i2i} \hat{Q}_n}{\omega_3 - \hat{H}_0 + \varepsilon_n + \imath \eta} \frac{\delta_n \hat{H}_{i3i} \hat{Q}_n}{\omega_2 + \omega_3 + \hat{H}_0 - \varepsilon_n - 2\imath \eta} | n \rangle + \langle n | \delta_n \hat{H}_{i3i} \hat{Q}_n \omega_2 + \omega_3 + \hat{H}_0 + \varepsilon_n + 2\imath \eta \frac{\delta_n \hat{H}_{i1i} \hat{Q}_n}{\omega_3 + \hat{H}_0 + \varepsilon_n + \imath \eta} \frac{\delta_n \hat{H}_{i2i} \hat{Q}_n}{\omega_2 + \omega_3 + \hat{H}_0 + \varepsilon_n + \imath \eta} | n \rangle \right].$$  \tag{A3}
\[ I_2 = 3S_{1i2i3} \sum_n \rho_n \left[ \langle n| \delta_n \hat{H}_1 \frac{\hat{Q}_n}{\omega_1 + \omega_2 + \omega_3 - H_0 + \epsilon_n + 3i\eta} \delta_n \hat{H}_{i12} \frac{\hat{Q}_n}{\omega_3 - H_0 + \epsilon_n + i\eta} \delta_n \hat{H}_{i3}|n\rangle 
\right. \\
- \langle n| \delta_n \hat{H}_{i12} \frac{\hat{Q}_n}{\omega_1 + \omega_2 + \omega_3 - H_0 + \epsilon_n + 2i\eta} \delta_n \hat{H}_i \frac{\hat{Q}_n}{\omega_3 - H_0 + \epsilon_n + i\eta} \delta_n \hat{H}_{i3}|n\rangle \\
+ \langle n| \delta_n \hat{H}_{i3} \frac{\hat{Q}_n}{\omega_3 - H_0 + \epsilon_n + i\eta} \delta_n \hat{H}_{i12} \frac{\hat{Q}_n}{\omega_1 + \omega_2 + \omega_3 + H_0 - \epsilon_n + 3i\eta} \delta_n \hat{H}_i|n\rangle \right] \\
+ 3S_{1i2i3} \sum_n \rho_n \left[ \langle n| \delta_n \hat{H}_1 \frac{\hat{Q}_n}{\omega_1 + \omega_2 + \omega_3 - H_0 + \epsilon_n + 3i\eta} \delta_n \hat{H}_{i12} \frac{\hat{Q}_n}{\omega_2 + \omega_3 - H_0 + \epsilon_n + 2i\eta} \delta_n \hat{H}_i \frac{\hat{Q}_n}{\omega_3 - H_0 + \epsilon_n + i\eta} \delta_n \hat{H}_{i3}|n\rangle 
\right. \\
- \langle n| \delta_n \hat{H}_{i12} \frac{\hat{Q}_n}{\omega_1 + H_0 - \epsilon_n + i\eta} \delta_n \hat{H}_i \frac{\hat{Q}_n}{\omega_2 + \omega_3 - H_0 + \epsilon_n + 2i\eta} \delta_n \hat{H}_{i3}|n\rangle \\
+ \langle n| \delta_n \hat{H}_{i3} \frac{\hat{Q}_n}{\omega_3 - H_0 + \epsilon_n + i\eta} \delta_n \hat{H}_{i12} \frac{\hat{Q}_n}{\omega_1 + \omega_2 + \omega_3 + H_0 - \epsilon_n + 2i\eta} \delta_n \hat{H}_i|n\rangle \right], 
\text{(A4)}
\]

and

\[ I_3 = 6S_{1i2i3} \sum_n \rho_n \langle n| \delta_n \hat{H}_1 \frac{\hat{Q}_n}{\omega_1 + \omega_2 + \omega_3 - H_0 + \epsilon_n + 3i\eta} \delta_n \hat{H}_{i1} \frac{\hat{Q}_n}{\omega_2 + \omega_3 - H_0 + \epsilon_n + 2i\eta} \delta_n \hat{H}_{i2} \frac{\hat{Q}_n}{\omega_3 - H_0 + \epsilon_n + i\eta} \delta_n \hat{H}_{i3}|n\rangle \\
- 6S_{1i2i3} \sum_n \rho_n \langle n| \delta_n \hat{H}_{i1} \frac{\hat{Q}_n}{\omega_1 + H_0 - \epsilon_n + i\eta} \delta_n \hat{H}_i \frac{\hat{Q}_n}{\omega_2 + \omega_3 - H_0 + \epsilon_n + 2i\eta} \delta_n \hat{H}_{i2} \frac{\hat{Q}_n}{\omega_3 - H_0 + \epsilon_n + i\eta} \delta_n \hat{H}_{i3}|n\rangle \\
+ 6S_{1i2i3} \sum_n \rho_n \langle n| \delta_n \hat{H}_{i3} \frac{\hat{Q}_n}{\omega_3 - H_0 + \epsilon_n + i\eta} \delta_n \hat{H}_{i1} \frac{\hat{Q}_n}{\omega_2 + \omega_3 - H_0 + \epsilon_n + 2i\eta} \delta_n \hat{H}_{i2} \frac{\hat{Q}_n}{\omega_1 + \omega_2 + \omega_3 + H_0 - \epsilon_n + 3i\eta} \delta_n \hat{H}_i|n\rangle \\
- 6S_{1i2i3} \sum_n \rho_n \langle n| \delta_n \hat{H}_i \frac{\hat{Q}_n}{\omega_1 - H_0 + \epsilon_n + i\eta} \delta_n \hat{H}_{i3} |n\rangle \langle n| \delta_n \hat{H}_{i12} \frac{\hat{Q}_n}{\omega_3 - H_0 + \epsilon_n + i\eta} \langle \omega_2 + H_0 - \epsilon_n + i\eta \rangle \delta_n \hat{H}_i|n\rangle \\
+ 3S_{1i2i3} \sum_n \rho_n \langle n| \delta_n \hat{H}_1 \frac{\hat{Q}_n}{\omega_1 + \omega_2 + \omega_3 - H_0 + \epsilon_n + 3i\eta} \delta_n \hat{H}_{i2} \frac{\hat{Q}_n}{\omega_2 + \omega_3 - H_0 + \epsilon_n + 2i\eta} \delta_n \hat{H}_{i1} \frac{\hat{Q}_n}{\omega_3 - H_0 + \epsilon_n + i\eta} \delta_n \hat{H}_{i3}|n\rangle \\
- 3S_{1i2i3} \sum_n \rho_n \langle n| \delta_n \hat{H}_{i1} \frac{\hat{Q}_n}{\omega_2 - H_0 + \epsilon_n + i\eta} \frac{\hat{Q}_n}{\omega_3 - H_0 + \epsilon_n + i\eta} \delta_n \hat{H}_{i3} |n\rangle \langle n| \delta_n \hat{H}_{i12} \frac{\hat{Q}_n}{\omega_1 + H_0 - \epsilon_n + i\eta} \delta_n \hat{H}_i|n\rangle \\
- 3S_{1i2i3} \sum_n \rho_n \langle n| \delta_n \hat{H}_{i1} \frac{\hat{Q}_n}{\omega_2 - H_0 + \epsilon_n + i\eta} \frac{\hat{Q}_n}{\omega_3 - H_0 + \epsilon_n + i\eta} \delta_n \hat{H}_{i3} |n\rangle \langle n| \delta_n \hat{H}_{i12} \frac{\hat{Q}_n}{\omega_1 + H_0 - \epsilon_n + i\eta} \delta_n \hat{H}_i|n\rangle \\
- 6S_{1i2i3} \sum_n \rho_n \langle n| \delta_n \hat{H}_1 \frac{\hat{Q}_n}{\omega_1 - H_0 + \epsilon_n + i\eta} \delta_n \hat{H}_{i12} \frac{\hat{Q}_n}{\omega_3 - H_0 + \epsilon_n + i\eta} \delta_n \hat{H}_i|n\rangle \\
\times \langle n| \delta_n \hat{H}_{i2} \frac{\hat{Q}_n}{\omega_3 - H_0 + \epsilon_n + i\eta} \delta_n \hat{H}_{i1}|n\rangle \\
- 6S_{1i2i3} \sum_n \rho_n \langle n| \delta_n \hat{H}_{i1} \frac{\hat{Q}_n}{\omega_1 - H_0 + \epsilon_n + i\eta} \delta_n \hat{H}_{i3} |n\rangle \langle n| \delta_n \hat{H}_{i2} \frac{\hat{Q}_n}{\omega_2 - H_0 + \epsilon_n + i\eta} \delta_n \hat{H}_i|n\rangle \\
\times \langle n| \delta_n \hat{H}_1 \frac{\hat{Q}_n}{\omega_1 + \omega_2 + \omega_3 + H_0 - \epsilon_n + 3i\eta} \delta_n \hat{H}_{i3}|n\rangle \rangle. 
\text{(A5)}
\]