Quantum-statistical theory of nonlinear optical conductivity for an electron-phonon system

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A general theory is presented for the nonlinear optical conductivities of a system of electrons interacting with a phonon field. A formal solution of the Liouville equation for the system subjected to an arbitrary number of electromagnetic wave modes is obtained by applying the *K*-operator technique developed by Fujita and Lodder [Physica (Amsterdam) **50**, 541 (1970)]. By using this result, a rigorous expression $\langle \mathbf{J}(\mathbf{q},z)\rangle$ for the Fourier-Laplace transform of the electric current $\langle \mathbf{J}(\mathbf{r},t)\rangle$ is derived for an electron-phonon system in a compact general form. Conversely, the current density can be expressed in terms of the complex inversion integral of Laplace transform theory. In order to obtain a nonlinear conductivity of an arbitrary rank, one only needs to find the residue of $\langle \mathbf{J}(\mathbf{q},z)\rangle$ at an appropriate pole, from which one can extract a formula for the conductivity tensor. The method is simpler and more transparent than the usual perturbation formalism. Damping due to scattering can be also incorporated properly into the conductivities of any ranks and can be evaluated in terms of a resolvent expansion with respect to an electron-phonon interaction in a systematic manner. We illustrate a formalism and a method to obtain the general formula for a nonlinear conductivity of any rank and calculate the linear and the lowest-order nonlinear conductivities with the damping terms (matrices), which include the exchange effect among electrons as well as the contributing frequencies of applied radiation fields. [S1063-651X(98)07610-7]

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I. INTRODUCTION

The response theory is one of the standard methods with which to study many effects due to various interactions between matter and electromagnetic radiation. The density operator method has been shown to be a useful device for the calculation of macroscopic tensor conductivities required in nonlinear optical mixing problems in solids. The nth-order perturbational solution to the density operator has been obtained by several different authors and has been expressed in several different forms. In standard treatments [1], the density operator ρ is defined to be a quantity satisfying the quantum Liouville equation. Since the structure of the system Hamiltonian $H=H_0+H'(t)$ is, in general, very complicated, exact solutions are rarely obtainable and one must resort to approximation techniques. Writing the equivalent integral equation in the interaction representation

$$\rho_{\rm I}(t)=\rho_0+\frac{1}{i\hbar}\int_0^t [H'(t'),\rho_{\rm I}(t')]dt', \tag{1.1}$$

with ρ_0 a known initial value in the absence of the time-dependent perturbation H', one can apply successive approximations to obtain the series solution

$$\rho_{\rm I}(t)=\sum_{n=0}^{\infty}\rho_{\rm I}^{(n)}(t), \tag{1.2}$$

where $\rho_{\rm I}(0)=\rho_0$ and $\rho_{\rm I}^{(n)}(0)=0$ if $n\neq 0$ and, in general,

$$\rho_I^{(n)}(t)=\frac{1}{(i\hbar)^n}\int_0^t dt_1\int_0^{t_1}dt_2\cdots\int_0^{t_{n-1}}dt_n \times[H'(t_1),[H'(t_2),\cdots,[H'(t_n),\rho_0]\cdots]], \tag{1.3}$$

with the time ordering $t_n\leqslant t_{n-1}\leqslant\cdots\leqslant t_1\leqslant t$. With the correction of order n to the density operator known, we can calculate the correction to the mean value of an arbitrary physical quantity such as an electric current $\mathbf{J}(\mathbf{r},t)$. The calculation that involves finding the system density and the mean value of the physical quantity is straightforward, but becomes quite tedious. In addition, the time-ordered integrals of the nested commutator brackets arising in these equations tend to obscure the physical content of the problem.

A main purpose of this paper is to show a general theoretical method to obtain linear and nonlinear conductivity tensors for an electron-phonon system. We will give rigorous explicit expressions for the linear and the lowest-order nonlinear conductivity tensors, which include the exchange effect among electrons moving in a phonon field as well as a collisional decay processes of those electrons due to an electron-phonon interaction. In the present work, the formal solution of the Liouville equation is obtained by means of the *K*-operator technique developed by Fujita and Lodder [2], where the density operator $\rho(t)$ can then be expressible in a single line (2.26) and thereby time-ordered integrals do not appear in this expression. This form turns out to be very convenient, though not essential, in the subsequent development of the theory of nonlinear conductivities. In addition to yielding a significant computational simplification over the usual iterative perturbation approach, this technique provides a systematic method for representing and classifying arbitrary density perturbation terms in a natural and compact manner. Since a physical observable (i.e., the mean value of physical quantity) is a linear function of the density operator, contributions to the perturbation expansion of the density operator may be directly interpreted in terms of observable. The K-operator technique to obtain the density operator and the resolvent expansion method [3] of the observable in the Laplace-Fourier representation would be particularly useful for obtaining linear and nonlinear optical conductivities since the conductivity of an arbitrary rank can be extracted simply by finding the residue of a current density $\langle \mathbf{J}(\mathbf{q},z)\rangle/\Omega$ at an appropriate pole in Laplace(-Fourier) space. The inclusion of damping (i.e., decay processes) due to the electron scattering by phonons (and/or static impurities), which contributes to the frequency resonance linewidths and temporal response of the system, can be also easily incorporated into the linear and nonlinear conductivity formulas in a rigorous manner. In contrast to the density-operator phenomenological damping terms [1], we can evaluate those terms by utilizing the Argyres-Sigel projection operator technique [4–7], which takes into account the exchange effects among electrons and the characteristics of collisional decay due to the electron-phonon (and/or impurity) interaction(s) from first principles. In order to obtain more exact information about electron scattering and/or optical properties of solids from conductivities, we will develop a global formalism that enables us to include the relaxation mechanism due to, e.g., the electron-phonon interaction in linear and nonlinear optical conductivities. We will show the general method to evaluate those relaxation (damping) terms due to an electron-phonon interactions and obtain the rigorous explicit expressions for frequency-dependent damping matrices incorporated in the linear and the second-order nonlinear conductivities for an electron-phonon system. Those conductivity formulas, which include the damping effects, would be particularly useful for analyzing nonlinear effects such as harmonic generation, sum- and difference-frequency mixing, and stimulated Raman scattering in solids.

II. FORMULATION OF QUANTUM TRANSPORT

A. Hamiltonian

We consider an electron-phonon system characterized by the time-independent Hamiltonian H,

$$H = H_{\rm e} + H_{\rm p} + H_{\rm ep}, \tag{2.1}$$

$$H_{\rm e} = \sum_{\nu} \langle \nu | h_{\rm e} | \nu \rangle a_\nu^\dagger a_\nu = \sum_\nu \varepsilon_\nu a_\nu^\dagger a_\nu, \tag{2.2}$$

$$H_{\rm p} = \sum_{\mathbf{q}} (b_{\mathbf{q}}^\dagger b_{\mathbf{q}} + \tfrac{1}{2}) \hbar \omega_{\mathbf{q}}, \tag{2.3}$$

$$H_{\rm ep} = \sum_{\mu,\nu} \sum_{\mathbf{q}} \langle \mu | \gamma_{\mathbf{q}} | \nu \rangle (b_{\mathbf{q}} + b_{-\mathbf{q}}^\dagger) a_\mu^\dagger a_\nu, \tag{2.4}$$

where $H_{\rm e}$ stands for the Hamiltonian of dynamically independent electrons, $H_{\rm p}$ for the Hamiltonian for phonons, and $H_{\rm ep}$ for the interaction Hamiltonian between those electrons and phonons. $a_\nu^\dagger$ (a_ν) is the creation (annihilation) operator for the electrons in a state $|\nu\rangle$, obeying the fermion anticommutation relations $\{a_\mu, a_\nu\} = \{a_\mu^\dagger, a_\nu^\dagger\} = 0$ and $\{a_\mu, a_\nu^\dagger\} = \delta_{\mu,\nu}$. $b_{\mathbf{q}}$ ($b_{\mathbf{q}}^\dagger$) is the annihilation (creation) operator for the phonons with wave vector $\mathbf{q}$ and energy $\hbar\omega_{\mathbf{q}}$, obeying the boson commutation relations $[b_{\mathbf{q}}, b_{\mathbf{q}'}] = [b_{\mathbf{q}}^\dagger, b_{\mathbf{q}'}^\dagger] = 0$ and $[b_{\mathbf{q}}, b_{\mathbf{q}'}^\dagger] = \delta_{\mathbf{q},\mathbf{q}'}$. The coupling function $\gamma_{\mathbf{q}}$ $[= D(\mathbf{q})\exp(i\mathbf{q}\cdot\mathbf{r})]$ denotes a one-body interaction operator, which should be defined in terms of the matrix elements referring to electron states. Here $D(\mathbf{q})$ describes in a self-consistent scheme the interaction of an electron with the vibrating lattices (phonons) and characterizes the nature and the strength of the electron-phonon coupling potential. For convenience, we have chosen the single-particle representation that diagonalizes the one-electron energy operator $h_{\rm e}$ with an allowance for a static magnetic field $\mathbf{B}_0$ $(= \nabla \times \mathbf{A}_0)$ (i.e., $h_{\rm e}|\nu\rangle = [\mathbf{p} + e\mathbf{A}_0(\mathbf{r})]^2/2m|\nu\rangle = \epsilon_\nu|\nu\rangle$).

To derive a closed-form expression for the electric current, let us consider the case where those electrons in a phonon field are driven by effective (internal) electric and magnetic fields

$$\mathbf{E}(\mathbf{r},t) = -\frac{\partial}{\partial t}\mathbf{A}(\mathbf{r},t),$$
$$\mathbf{B}(\mathbf{r},t) = \nabla \times \{\mathbf{A}_0(\mathbf{r}) + \mathbf{A}(\mathbf{r},t)\}, \tag{2.5}$$

where $\mathbf{A}(\mathbf{r},t)$ is a time-dependent Maxwell field (vector potential), the gauge being chosen so that the scalar potential is zero. Although in this model the interaction between electrons is not explicitly included in the Hamiltonian H, the effects of electron-electron interaction could, however, be taken into account implicitly through the interaction potential $D(\mathbf{q})$ as a screening effect of those electrons via the dielectric constant. The effective electric field $\mathbf{E}(\mathbf{r},t)$ therefore takes into account possible polarization effects when the system is exposed to an external electric field $\mathbf{E}_{\rm ext}(\mathbf{r},t)$. In such a case, the electrons are subject directly to the probing (external) electric field $\mathbf{E}_{\rm ext}(\mathbf{r},t) = -\partial_t \mathbf{A}(\mathbf{r},t) = \mathbf{E}(\mathbf{r},t)$ [which is equal to an effective (internal) electric field]. Therefore, no distinction need be made between the acting (effective) field and the probing (external) field in the present model system. The probing electric field (and hence the effective electric field) can be derived from a time-dependent Maxwell field, which is assumed to be of the form

$$\mathbf{A}(\mathbf{r},t) = \sum_\alpha \{\mathbf{A}^\alpha \exp[i(\mathbf{q}_\alpha \cdot \mathbf{r} - \omega_\alpha t)] + \text{c.c.}\}, \tag{2.6}$$

where $\mathbf{q}_\alpha$ and ω_α represent the wave vector and the angular frequency of the Maxwell field with a mode α, respectively. The summation runs over all wave modes $\{\alpha\}$.

The expectation value of the induced electric current at some point $\mathbf{r}_0$ after the external (Maxwell) field has been turned on can be generally evaluated from

$$\langle \mathbf{J}(\mathbf{r}_0,t)\rangle = \text{Tr}\{\mathbf{J}(\mathbf{r}_0,t)\rho(t)\}, \tag{2.7}$$

where $\rho(t)$ is the density operator and the symbol Tr denotes a many-body trace with respect to electrons and phonons. The electric current operator $\mathbf{J}$ is given by a sum of one-electron current operator $\mathbf{j}(\mathbf{r}_0,t)$. Thus it can be expressed in the second-quantized form as

$$\mathbf{J}(\mathbf{r}_0,t)=\sum_{\mu,\nu}\langle\mu|\mathbf{j}(\mathbf{r}_0,t)|\nu\rangle a_\mu^\dagger a_\nu, \tag{2.8}$$

where

$$\mathbf{j}(\mathbf{r}_0,t)=-\frac{e}{2m}[\{\mathbf{p}+e\mathbf{A}_0(\mathbf{r})+e\mathbf{A}(\mathbf{r},t)\}\delta^{(3)}(\mathbf{r}-\mathbf{r}_0) + \delta^{(3)}(\mathbf{r}-\mathbf{r}_0)\{\mathbf{p}+e\mathbf{A}_0(\mathbf{r})+e\mathbf{A}(\mathbf{r},t)\}]. \tag{2.9}$$

The density operator $\rho(t)$ of the system of electrons plus phonons under the influence of the external Maxwell field changes with time, obeying the Liouville equation of motion

$$i\hbar\frac{\partial}{\partial t}\rho(t)=[H+H_{\mathrm{ef}}(t),\rho(t)], \tag{2.10}$$

where [,] denotes the commutator, H is the Hamiltonian of the system (electrons plus phonons) given by Eq. (2.1), and $H_{\mathrm{ef}}(t)$ is the Hamiltonian representing the external disturbance due to the application of the time-dependent Maxwell field given by Eq. (2.6). This perturbation Hamiltonian H_{ef}, which represents the interaction between conduction electrons (charge $-e$) and the time-dependent Maxwell field, can be expressed semiclassically in the second-quantized form with respect to the electrons:

$$H_{\mathrm{ef}}(t)=\sum_{\mu,\nu}\langle\mu|h_{\mathrm{ef}}(t)|\nu\rangle a_\mu^\dagger a_\nu, \tag{2.11}$$

where the single-electron–Maxwell-field interaction operator $h_{\mathrm{ef}}(t)$ is explicitly given by

$$h_{\mathrm{ef}}(t)=\frac{e}{2m}\{[\mathbf{p}+e\mathbf{A}_0(\mathbf{r})]\cdot\mathbf{A}(\mathbf{r},t) +\mathbf{A}(\mathbf{r},t)\cdot[\mathbf{p}+e\mathbf{A}_0(\mathbf{r})]\}+\frac{e^2}{2m}\mathbf{A}^2(\mathbf{r},t). \tag{2.12}$$

Thus the perturbation $H_{\mathrm{ef}}(t)$ induced in the medium can be connected to the applied field $\mathbf{E}_{\mathrm{ext}}(\mathbf{r},t)$ through the Maxwell field $\mathbf{A}(\mathbf{r},t)$ defined by Eq. (2.6). It should be noted that the radiation (i.e., electromagnetic) fields are treated as classical fields.

B. Formal solution of the Liouville equation

The formal solution of Eq. (2.10) can be easily obtained by introducing the operator function K defined by [2]

$$K\equiv\sum_\alpha \hbar\omega_\alpha c_\alpha^\dagger c_\alpha, \tag{2.13}$$

where c_α and $c_\alpha^\dagger$ are bosonic annihilation and creation operators satisfying

$$[c_\alpha,c_\beta^\dagger]\equiv c_\alpha c_\beta^\dagger-c_\beta^\dagger c_\alpha=\delta_{\alpha,\beta}, \tag{2.14}$$

$$[c_\alpha,c_\beta]=[c_\alpha^\dagger,c_\beta^\dagger]=0. \tag{2.15}$$

It is then easy to verify that

$$\exp[iKt/\hbar]c_\alpha\exp[-iKt/\hbar]=c_\alpha\exp[-i\omega_\alpha t], \tag{2.16}$$

$$\exp[iKt/\hbar]c_\alpha^\dagger\exp[-iKt/\hbar]=c_\alpha^\dagger\exp[+i\omega_\alpha t]. \tag{2.17}$$

If we define the time-independent operator $\hat{\mathbf{A}}(\mathbf{r})$ associated with $\mathbf{A}(\mathbf{r},t)$ as

$$\hat{\mathbf{A}}(\mathbf{r})\equiv\sum_\alpha\{\mathbf{A}^\alpha c_\alpha\exp[i\mathbf{q}_\alpha\cdot\mathbf{r}]+\mathrm{H.c.}\}, \tag{2.18}$$

we find from Eqs. (2.16)–(2.18) that

$$\exp[iKt/\hbar]\hat{\mathbf{A}}(\mathbf{r})\exp[-iKt/\hbar] =\sum_\alpha\{\mathbf{A}^\alpha c_\alpha\exp[i(\mathbf{q}_\alpha\cdot\mathbf{r}-\omega_\alpha t)]+\mathrm{H.c.}\}. \tag{2.19}$$

This expression is identical to the defining expression for the Maxwell field $\mathbf{A}(\mathbf{r},t)$ [see Eq. (2.6)] except for the factors c_α and $c_\alpha^\dagger$. If we agree to a convention that *after the operator K is eliminated completely, every c_α and $c_\alpha^\dagger$ are to be equated with unity*, we may equate $\exp[iKt/\hbar]\hat{\mathbf{A}}(\mathbf{r})\exp[-iKt/\hbar]$ with $\mathbf{A}(\mathbf{r},t)$. We adopt this convention (i.e., $c_\alpha,c_\alpha^\dagger\to1$) after applying the K operator not only to the Maxwell field $\mathbf{A}(\mathbf{r},t)$ but also to any function of $\mathbf{A}(\mathbf{r},t)$. It should be noted that upon acting on the $\hat{\mathbf{A}}(\mathbf{r})$, the K operator produces the correct form of Eq. (2.19) associated with the classical Maxwell field $\mathbf{A}(\mathbf{r},t)$. This purely mathematical technique introduced in Ref. [2] turns out to be very convenient in the subsequent development of the theory of nonlinear conductivity (see below) and especially in the calculation of nonlinear conductivity of higher rank (see Sec. III). Thus, in particular, by defining the time-independent operator $\hat{H}_{\mathrm{ef}}$ as

$$\hat{H}_{\mathrm{ef}}\equiv\sum_{\mu,\nu}\langle\mu|\hat{h}_{\mathrm{ef}}|\nu\rangle a_\mu^\dagger a_\nu, \tag{2.20}$$

we can express $H_{\mathrm{ef}}(t)$ [Eq. (2.11)] in terms of the operator K and the time-independent operator $\hat{H}_{\mathrm{ef}}$,

$$H_{\mathrm{ef}}(t)\doteq\exp[iKt/\hbar]\hat{H}_{\mathrm{ef}}\exp[-iKt/\hbar] =\exp[iK^\times t/\hbar]\hat{H}_{\mathrm{ef}}. \tag{2.21}$$

The last equality can be easily verified by expanding both sides with respect to *t*. It should be noted that the cross superscript denotes the commutator-generating superoperator (or the Liouville operator). In Eq. (2.20) the time-independent single-electron–Maxwell-field interaction operator $\hat{h}_{\rm ef}$ associated with $h_{\rm ef}(t)$ [Eq. (2.12)] is given by

$$\hat{h}_{\rm ef}\equiv \frac{e}{2m}\{[\mathbf{p}+e\mathbf{A}_0(\mathbf{r})]\cdot\hat{\mathbf{A}}(\mathbf{r})+\hat{\mathbf{A}}(\mathbf{r})\cdot[\mathbf{p}+e\mathbf{A}_0(\mathbf{r})]\}+\frac{e^2}{2m}\hat{\mathbf{A}}^2(\mathbf{r}). \quad (2.22)$$

In order to obtain the solution of Eq. (2.10), let us introduce a transformed density operator $\rho'(t)$ defined by

$$\rho'(t)\equiv \exp[-iK^{\times}t/\hbar]\rho(t). \quad (2.23)$$

From Eqs. (2.10), (2.21), and (2.23), we obtain the equation of motion for $\rho'(t)$ as

$$i\hbar\frac{\partial}{\partial t}\rho'(t)=(H^{\times}+\hat{H}^{\times}_{\rm ef}+K^{\times})\rho'(t). \quad (2.24)$$

This equation can be easily solved for $\rho'(t)$ since the Liouville operators $H^{\times}$ $(=H^{\times}_{\rm e}+H^{\times}_{\rm p}+H^{\times}_{\rm ep})$, $\hat{H}^{\times}_{\rm ef}$, and $K^{\times}$ do *not* contain t explicitly. The formal solution of Eq. (2.24) is given by

$$\rho'(t)=\exp[-i(H^{\times}+\hat{H}^{\times}_{\rm ef}+K^{\times})t/\hbar]\rho_0, \quad (2.25)$$

where ρ_0 $[=\rho(0)=\rho'(0)]$ is the density operator at the initial time $t=0$. From Eqs. (2.23) and (2.25) we can thus formally express the solution of Eq. (2.10) in a simple form

$$\rho(t)\doteq \exp[iK^{\times}t/\hbar]\exp[-i(H^{\times}+\hat{H}^{\times}_{\rm ef}+K^{\times})t/\hbar]\rho_0. \quad (2.26)$$

It should be understood that the symbol $\doteq$ stands for "is represented by the K operator" and that the convention with regard to the K operator along with the bosonic operators $(c^{\dagger}_{\alpha},c_{\alpha})$ *must* be applied to the evaluation of $\langle \mathbf{J}(\mathbf{r}_0,t)\rangle$. Substituting this in Eq. (2.7) and noting that the current operator $\mathbf{J}(\mathbf{r}_0,t)$ [Eq. (2.8)] is expressed by

$$\mathbf{J}(\mathbf{r}_0,t)\doteq \exp[iK^{\times}t/\hbar]\hat{\mathbf{J}}(\mathbf{r}_0), \quad (2.27)$$

the electronic current at $\mathbf{r}_0$ at a time t can be exactly prescribed by

$$\langle \mathbf{J}(\mathbf{r}_0,t)\rangle = {\rm Tr}\{\mathbf{J}(\mathbf{r}_0,t)\rho(t)\}$$
$$\doteq {\rm Tr}\{\exp[iK^{\times}t/\hbar]\hat{\mathbf{J}}(\mathbf{r}_0)\times\exp[-i(H^{\times}+\hat{H}^{\times}_{\rm ef}+K^{\times})t/\hbar]\rho_0\}. \quad (2.28)$$

Here the time-independent current operator $\hat{\mathbf{J}}(\mathbf{r}_0)$ associated with $\mathbf{J}(\mathbf{r}_0,t)$ is given by

$$\hat{\mathbf{J}}(\mathbf{r}_0)\equiv\sum_{\mu,\nu}\langle\mu|\hat{\mathbf{j}}(\mathbf{r}_0)|\nu\rangle a^{\dagger}_{\mu}a_{\nu}, \quad (2.29)$$

where the time-independent single-electron current operator $\hat{\mathbf{j}}$ is given by

$$\hat{\mathbf{j}}(\mathbf{r}_0)\equiv -\frac{e}{2m}\{[\mathbf{p}+e\mathbf{A}_0(\mathbf{r})+e\hat{\mathbf{A}}(\mathbf{r})]\delta^{(3)}(\mathbf{r}-\mathbf{r}_0)+\delta^{(3)}(\mathbf{r}-\mathbf{r}_0)[\mathbf{p}+e\mathbf{A}_0(\mathbf{r})+e\hat{\mathbf{A}}(\mathbf{r})]\}. \quad (2.30)$$

In Eq. (2.29), $|\mu\rangle,|\nu\rangle$ are the eigenstates of the single-electron Hamiltonian $h_{\rm e}$. It should be noted that the many-body trace in Eq. (2.28) is taken over the electron and the phonon coordinates.

C. Asymptotic behavior of $\langle \mathbf{J}(\mathbf{r}_0,t)\rangle$ and the conductivity tensors

It is expected that a sufficiently long time after the steady electromagnetic field characterized by $\mathbf{A}(\mathbf{r},t)$ [see Eq. (2.6)] is switched on, the system should approach a stationary state in which the generalized Ohm law holds between the current density $\langle \mathbf{J}(\mathbf{r}_0,t)\rangle/\Omega$ (Ω is a volume of the sample) and the effective electric field $\mathbf{E}(\mathbf{r}_0,t)$. Responding to the applied Maxwell (or electric) field with a set of modes $\{\omega_{\alpha}\}$ $=(\omega_1,\omega_2,\ldots,\omega_m)$ and $\{\mathbf{q}_{\alpha}\}=(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_m)$, a component of the nth-order electric current characterized by the set of combination frequencies and wave vectors $\{\omega_{\alpha_j}\}$ $=(\omega_{\alpha_1},\omega_{\alpha_2},\ldots,\omega_{\alpha_n})$ and $\{\mathbf{q}_{\alpha_j}\}=(\mathbf{q}_{\alpha_1},\mathbf{q}_{\alpha_2},\ldots,\mathbf{q}_{\alpha_n})$ will be induced. Here $\alpha_1,\alpha_2,\ldots,\alpha_n=1,2,\ldots,m$.

Let us consider the case where the probing time-dependent electric field $\mathbf{E}_{\rm ext}(\mathbf{r},t)$ $[=\mathbf{E}(\mathbf{r},t)]$, which is derived from the Maxwell field $\mathbf{A}(\mathbf{r},t)$ [Eq. (2.6)], is sinusoidal and is characterized by the set of wave vectors $\{\mathbf{q}_{\alpha}\}$ and angular frequencies $\{\omega_{\alpha}\}$. It is then convenient to introduce a time-dependent complex electric field $\mathbf{E}(\mathbf{r},t)$ defined by

$$\mathbf{E}(\mathbf{r},t)\equiv\sum_{\alpha=1}^{m}\mathbf{E}^{\alpha}\exp[i(\mathbf{q}_{\alpha}\cdot\mathbf{r}-\omega_{\alpha}t)]\equiv\sum_{\alpha=1}^{m}\mathbf{E}^{\alpha}(\mathbf{r},t), \quad (2.31)$$

where the sum is taken over all wave modes $\{\alpha\}$. The amplitudes and phases of these modes are generally related to the nth-order nonlinear (complex) conductivity tensor $\boldsymbol{\sigma}^{(n)}$ such that, as $t\to\infty$,

$$\langle \mathbf{J}(\mathbf{r}_0,t)\rangle=\sum_{n=1}^{\infty}\langle \mathbf{J}^{(n)}(\mathbf{r}_0,t)\rangle, \quad (2.32)$$

where the nth-order contribution to the current density $\langle \mathbf{J}^{(n)}(\mathbf{r}_0,t)\rangle/\Omega$ in the stationary state may be expressed in terms of $\mathbf{E}^{\alpha}(\mathbf{r},t)$'s as

$$\langle \mathbf{J}^{(n)}(\mathbf{r}_0,t)\rangle/\Omega=\sum_{\alpha_1}\cdots\sum_{\alpha_n}\boldsymbol{\sigma}^{(n)}(\{\mathbf{q}_{\alpha_j}\},\{\omega_{\alpha_j}\}):\mathbf{E}^{\alpha_1}(\mathbf{r},t)\cdots\mathbf{E}^{\alpha_n}(\mathbf{r},t), \quad (2.33)$$

$$\mathbf{E}^{\alpha_1}(\mathbf{r},t)\cdots\mathbf{E}^{\alpha_n}(\mathbf{r},t)=\mathbf{E}^{\alpha_1}\cdots\mathbf{E}^{\alpha_n}\exp[i(\tilde{\mathbf{q}}\cdot\mathbf{r}-\tilde{\omega}t)], \quad (2.34)$$

$$\tilde{\omega}\equiv\sum_{j=1}^{n}\omega_{\alpha_j},\quad \tilde{\mathbf{q}}\equiv\sum_{j=1}^{n}\mathbf{q}_{\alpha_j}. \quad (2.35)$$

Here ω_{α_j}, $\mathbf{q}_{\alpha_j}$, and $\mathbf{E}^{\alpha_j}$ are frequencies, wave vectors, and amplitudes of the contributing fields, respectively, with the resulting (generated) frequency $\tilde{\omega}$ and wave vector $\tilde{\mathbf{q}}$. This asymptotic constitutive relation (2.33) between the current density and the effective (internal) electric fields *defines* a generalized complex conductivity tensor $\boldsymbol{\sigma}^{(n)}$, which in general depends on the set of combination frequencies $\{\omega_{\alpha_j}\}$ and wave vectors $\{\mathbf{q}_{\alpha_j}\}$ of the contributing applied fields. In order to obtain the general expression for $\boldsymbol{\sigma}^{(n)}$, it is convenient to formulate $\langle \mathbf{J}(\mathbf{r}_0,t)\rangle$ in the wave-vector–frequency representation rather than in the ordinary space $\mathbf{r}_0$ and time t since a local, asymptotic behavior of the current is more appropriately characterized by the contributing electromagnetic modes $(\{\mathbf{q}_{\alpha_j}\},\{\omega_{\alpha_j})\}$. In order to obtain the expression of $\langle \mathbf{J}(\mathbf{r}_0,t)\rangle$ in the wave-vector–frequency representation, let us define the Fourier-Laplace transform of a space-time function $f(\mathbf{r},t)$ by

$$f(\mathbf{q},z)\equiv i\int_0^{\infty}dt\ \exp[izt]\int_{\Omega}\frac{d^3r}{\Omega}\exp[-i\mathbf{q}\cdot\mathbf{r}]f(\mathbf{r},t). \tag{2.36}$$

The inverse Fourier-Laplace transform of $f(\mathbf{q},z)$ is then given by

$$f(\mathbf{r},t)=\frac{1}{2\pi i}\int_{ic-\infty}^{ic+\infty}dz\ \exp[-izt]\sum_{\mathbf{q}}\ \exp[i\mathbf{q}\cdot\mathbf{r}]f(\mathbf{q},z), \tag{2.37}$$

where c is a positive number chosen such that $f(z)$ should be analytic above the infinite line from $ic-\infty$ to $ic+\infty$ in the complex z plane except at a finite number of poles. Accordingly, the relation (2.33) can be expressed alternatively and more precisely expressed as (Res denotes the residue of)

$$\mathrm{Res}\langle \mathbf{J}^{(n)}(\tilde{\mathbf{q}},z)\rangle/\Omega|_{z=\bar{\omega}-i\delta}$$

$$=-\sum_{\alpha_1}\cdots\sum_{\alpha_n}\boldsymbol{\sigma}^{(n)}(\{\mathbf{q}_{\alpha_j}\},\{\omega_{\alpha_j}\}):\mathbf{E}^{\alpha_1}(\mathbf{r},t)\cdots\mathbf{E}^{\alpha_n}(\mathbf{r},t), \tag{2.38}$$

where $\tilde{\omega}$ and $\tilde{\mathbf{q}}$ are respectively given by Eq. (2.35). This means that *the generalized* n*th-order conductivity* $\boldsymbol{\sigma}^{(n)}$, *being the coefficient in the term with the products of the contributing electric fields* $\mathbf{E}^{\alpha_1}(\mathbf{r},t)\cdots\mathbf{E}^{\alpha_n}(\mathbf{r},t)$ *can be obtained by finding the residue of the Laplace(-Fourier) transform of the current density at a prescribed pole* (i.e., $z=\tilde{\omega}-i\delta$ in the present case) since the current density $\langle \mathbf{J}^{(n)}(\mathbf{r}_0,t)\rangle/\Omega$ expanded in terms of the n products of the contributing fields $\mathbf{E}^{\alpha_j}$ $(j=1,2,3,...,m)$ can be evaluated from the complex inversion integral and may be expressed as in the right-hand side of Eq. (2.38). This fact tremendously simplifies the mathematical treatment of the conductivity tensor of any rank since the study of the residue is much simpler than that of the full analytic behavior of $\langle \mathbf{J}^{(n)}(\tilde{\mathbf{q}},z)\rangle$ in the complex z plane. It should be noted that a small imaginary part $-i\delta$ (δ is a vanishingly small positive number) added to the frequency $\tilde{\omega}$ implies adiabatic switching of an external electric field and ensures convergence of the integral at $t=\infty$. The study of the residue is sufficient for the description of the nonlinear conductivity of any rank [2].

By applying the Fourier-Laplace transform formula (2.36) to the formal expression for the electronic current $\langle \mathbf{J}(\mathbf{r}_0,t)\rangle$ [Eq. (2.28)], we obtain the exact expression for the Fourier-Laplace transformed electronic current $\langle \mathbf{J}(\mathbf{q},z)\rangle$ as

$$\langle \mathbf{J}(\mathbf{q},z)\rangle \doteq -\frac{\hbar^2}{2\pi i}\int_{ic-\infty}^{ic+\infty}dz_1(K^{\times}+\hbar z_1)^{-1}$$

$$\times\mathrm{Tr}\{\hat{\mathbf{J}}(\mathbf{q})\Psi(z-z_1)\rho_0\}, \tag{2.39}$$

where $\Psi(z)$ is given by

$$\Psi(z)\equiv(H^{\times}+\hat{H}_{\mathrm{ef}}^{\times}+K^{\times}-\hbar z)^{-1} \tag{2.40}$$

and the Fourier components of the time-independent electric current $\hat{\mathbf{J}}(\mathbf{q})$ in wave-vector space are given by Fourier transforming Eq. (2.29) as

$$\hat{\mathbf{J}}(\mathbf{q})=\sum_{\mu,\nu}\langle\mu|\hat{\mathbf{j}}(\mathbf{q})|\nu\rangle a_{\mu}^{\dagger}a_{\nu}, \tag{2.41}$$

with

$$\hat{\mathbf{j}}(\mathbf{q})\equiv\int_{\Omega}\frac{d^3r_0}{\Omega}\exp[-i\mathbf{q}\cdot\mathbf{r}_0]\hat{\mathbf{j}}(\mathbf{r}_0)$$

$$=-\frac{e}{2m\Omega}[\{\mathbf{p}+e\mathbf{A}_0(\mathbf{r})+e\hat{\mathbf{A}}(\mathbf{r})\}\exp[-i\mathbf{q}\cdot\mathbf{r}]$$

$$+\exp[-i\mathbf{q}\cdot\mathbf{r}]\{\mathbf{p}+e\mathbf{A}_0(\mathbf{r})+e\hat{\mathbf{A}}(\mathbf{r})\}]. \tag{2.42}$$

This compact expression (2.39) along with Eqs. (2.40)–(2.42) contains full information about linear or nonlinear conductivity tensor of an arbitrary rank, which can be obtained by the study of the residue of $\langle \mathbf{J}^{(n)}(\tilde{\mathbf{q}},z)\rangle$ $(n=1,2,3,...)$ at a prescribed pole.

D. Choice of an initial condition

The evaluations of the Fourier-Laplace transformed electric current $\langle \mathbf{J}(\tilde{\mathbf{q}},z)\rangle$ involve the operator Ψ defined by Eq. (2.40) and the initial density operator ρ_0. In general, we may assume that the initial state of the system is uncorrelated with the probing Maxwell (or electric) fields. This can be mathematically expressed by

$$K^{\times}\rho_0\equiv K\rho_0-\rho_0K=0 \tag{2.43}$$

at $t=0$. In fact, in the absence of the probing Maxwell field, the density operator $\rho(t)$ is given by [see Eq. (2.26)]

$$\rho(t)=\exp[-iH^{\times}t/\hbar]\rho_0. \tag{2.44}$$

As $t\to\infty$, the system would approach a stationary state. This means that all intensive properties of an observable $\langle \mathbf{A}\rangle$, which can be described in the form of $\mathrm{Tr}\{\mathbf{A}\rho(t)\}$, would also attain their stationary values for very large t. (Here $\mathbf{A}$ is the operator of an arbitrary physical quantity.) Symbolically, this may be stated as

$$\rho(t)\rightarrow\rho_{\text{stationary}} \quad \text{for} \quad t\rightarrow\infty. \tag{2.45}$$

In the Laplace space this asymptotic relation should take the form [2]

$$\rho(z)=\frac{\rho_{\text{stationary}}}{z-i\delta}+(\text{nonsingular terms}) \tag{2.46}$$

and hence this can be alternatively expressed as

$$\rho_{\text{stationary}}=-\text{Res}\,\rho(z)|_{z=i\delta}=-\text{Res}(H^{\times}-\hbar z)^{-1}\rho_0. \tag{2.47}$$

Therefore, we may replace $\Psi(z)\rho_0$ in Eq. (2.39) by

$$\Psi(z)\rho_0=-\frac{1}{\hbar z}\rho_{\text{stationary}}+\frac{1}{\hbar z}\Psi(z)\hat{H}_{\text{ef}}^{\times}\rho_{\text{stationary}}, \tag{2.48}$$

where we have used the identity

$$\Psi(z)\equiv R_z-\Psi(z)\hat{H}_{\text{ef}}^{\times}R_z. \tag{2.49}$$

Here the resolvent operator R_z is defined by

$$R_z\equiv(H^{\times}+K^{\times}-\hbar z)^{-1}. \tag{2.50}$$

If we assume that the asymptotic state of the system characterized by the system Hamiltonian H is close to the equilibrium state, we can then replace $(H^{\times}+K^{\times}-\hbar z)^{-1}\rho_0$ by $-\rho_{\text{stationary}}/\hbar z\approx-\rho_{\text{eq}}/\hbar z$, where ρ_{eq} denotes an equilibrium density operator. The density operator $\rho_{\text{stationary}}$ corresponding to the stationary state can in practice be chosen to be the grand-canonical density operator $\rho_{\text{eq}}(\tilde{H})$:

$$\rho_{\text{stationary}}=\rho_{\text{eq}}(\tilde{H})=\frac{\exp[-\beta\tilde{H}]}{\text{Tr}\{\exp[-\beta\tilde{H}]\}}, \tag{2.51}$$

where β is the reciprocal temperature defined by $1/k_{\text{B}}T$ and $\tilde{H}\equiv H-\zeta N$. Here $H=H_{\text{e}}+H_{\text{p}}+H_{\text{ep}}$, $N=\Sigma_{\nu}a_{\nu}^{\dagger}a_{\nu}$, and ζ is the Fermi energy in the presence of the electron-phonon interaction and is determined from $\text{Tr}[N\rho_{\text{eq}}]=N_{\text{e}}$, the total number of electrons in the system. It should be noted that the argument of ρ_{eq} excludes H_{ef} (i.e., the interaction energy between the external probing Maxwell field and electrons). This choice would be valid for the case where the conductivities of lower rank is discussed. It is noted that our requirement (2.45), which is imposed on the nature of initial density operator, is less restrictive than the choice of $\rho_0=\rho_{\text{eq}}$ selected by Kubo [8]. We can see that this latter choice surely satisfies the requirement (2.45) since $(H^{\times}-\hbar z)^{-1}\rho_{\text{eq}}=-(\hbar z)^{-1}\rho_{\text{eq}}$ and $[H,N]=0$ for a weak electron-radiation interaction.

Utilizing Eq. (2.48) along with Eq. (2.51), we can express Eq. (2.39) as

$$\begin{aligned}\langle\mathbf{J}(\mathbf{q},z)\rangle\doteq&-\frac{\hbar}{2\pi i}\int_{ic-\infty}^{ic+\infty}dz_1(z_1-z)^{-1}\\&\times(K^{\times}+\hbar z_1)^{-1}\text{Tr}\{\hat{\mathbf{J}}(\mathbf{q})\rho_{\text{eq}}\}\\&+\frac{\hbar}{2\pi i}\int_{ic-\infty}^{ic+\infty}dz_1(z_1-z)^{-1}(K^{\times}+\hbar z_1)^{-1}\\&\times\text{Tr}\{\hat{\mathbf{J}}(\mathbf{q})\Psi(z-z_1)\hat{H}_{\text{ef}}^{\times}\rho_{\text{eq}}\},\end{aligned} \tag{2.52}$$

where $\Psi(z-z_1)$ is given by Eq. (2.40) and $\hat{\mathbf{J}}(\mathbf{q})$ by Eq. (2.41). This is the basic equation for the current, from which we can extract a conductivity formula of any rank. In the next section we will show the method of obtaining the formulas for linear and nonlinear conductivities ($\boldsymbol{\sigma}^{(1)}$ and $\boldsymbol{\sigma}^{(2)}$) and derive explicitly their rigorous expressions including the associated damping matrices due to an electron-phonon interaction.

III. RESOLVENT EXPANSION METHOD

A. Derivation of linear conductivity

Let us proceed to the calculation of Eq. (2.52) to derive the general expressions for linear and nonlinear conductivity tensors. Since $\Psi(z)$ and $\hat{\mathbf{J}}(\mathbf{q})$ contain the field strengths $\hat{\mathbf{A}}$ associated with $\mathbf{E}$'s, in order to obtain the expressions for linear and nonlinear conductivity tensors, we expand $\Psi(z)$ and $\hat{\mathbf{J}}(\mathbf{q})$ in terms of $\hat{\mathbf{A}}$ or $\hat{H}_{\text{ef}}$. From Eq. (2.49) we obtain

$$\Psi(z)\approx R_z-\lambda R_z\hat{H}_{\text{ef}}^{\times}R_z+\lambda^2R_z\hat{H}_{\text{ef}}^{\times}R_z\hat{H}_{\text{ef}}^{\times}R_z-\cdots. \tag{3.1}$$

In this equation we have introduced the dimensionless parameter λ in order to indicate the order of expansion in the field strengths and may set $\lambda=1$ later on. We shall use such a convention in this and other similar expansions. Using this in Eq. (2.52), the first order of $\langle\mathbf{J}(\mathbf{q},z)\rangle$ is given by

$$\begin{aligned}\langle\mathbf{J}^{(1)}(\mathbf{q},z)\rangle=&-\frac{\hbar}{2\pi i}\int_{ic-\infty}^{ic+\infty}dz_1(z_1-z)^{-1}\\&\times(K^{\times}+\hbar z_1)^{-1}\text{Tr}\{\hat{\mathbf{J}}^{(1)}(\mathbf{q})\rho_{\text{eq}}\}\\&+\frac{\hbar}{2\pi i}\int_{ic-\infty}^{ic+\infty}dz_1(z_1-z)^{-1}\\&\times(K^{\times}+\hbar z_1)^{-1}\text{Tr}\{\hat{\mathbf{J}}^{(0)}(\mathbf{q})R_{z-z_1}\hat{H}_{\text{ef}}^{\times}\rho_{\text{eq}}\},\end{aligned} \tag{3.2}$$

where the superscript (n) $(n=0,1,2,\dots)$ denotes the order in the field strength parameter.

When the wavelength $2\pi/q$ of an applied electromagnetic wave, characterized by $(\mathbf{q},\omega)$, is large compared to the mean free path of electrons and therefore the spatial variation of the field is negligible, the Hamiltonian $H_{\text{ef}}(t)$ describing the electromagnetic interaction with electrons can be approximated by

$$H_{\rm ef}(t)=e\mathbf{R}\cdot\mathbf{E}\{\exp[i\omega t]+\exp[-i\omega t]\}, \tag{3.3}$$

where $\mathbf{R}$ $(=\Sigma_i\mathbf{r}_i)$ is the sum of a position operator for each electron and is expressed in the second quantized form

$$\mathbf{R}=\sum_{\mu,\nu}\langle\mu|\mathbf{r}|\nu\rangle a_\mu^\dagger a_\nu. \tag{3.4}$$

We shall employ this so-called dipole approximation hereinafter. The theory developed in Sec. II for solving the Liouville equation can be simply extended to the case of Eq. (3.3) with Eq. (3.4) by the adaptation

$$\hat{H}_{\rm ef}=e\mathbf{R}\cdot\mathbf{E}[c_\omega+c_\omega^\dagger], \tag{3.5}$$

where c_ω and $c_\omega^\dagger$ are for the mode $\mathbf{q}_\alpha=0$, $\omega_\alpha=\omega$.

The first term of the right-hand side of Eq. (3.2) vanishes identically because

$$\mathbf{j}^{(1)}(\mathbf{q})\equiv\frac{ie}{\hbar}[\mathbf{r},H_{\rm ef}]=\frac{e^2}{i\hbar}[\mathbf{r},\mathbf{r}\cdot\mathbf{E}]=0. \tag{3.6}$$

By a straightforward calculation along with Eqs. (2.13)–(2.15) and (3.5), the part of the integrand in the second term in Eq. (3.2), which contains c_ω and $c_\omega^\dagger$, is finally given by

$$\begin{aligned}&(K^\times+\hbar z_1)^{-1}{\rm Tr}\{\hat{\mathbf{J}}^{(0)}(\mathbf{q})R_{z-z_1}\hat{H}_{\rm ef}^\times\rho_{\rm eq}\}\\&=\{\hbar(\omega+z_1)\}^{-1}{\rm Tr}\{\hat{\mathbf{J}}^{(0)}(\mathbf{q})(H^\times+\hbar\omega-\hbar z+\hbar z_1)^{-1}\\&\quad\times[e\mathbf{R}\cdot\mathbf{E},\rho_{\rm eq}]\}+\{\hbar(-\omega+z_1)\}^{-1}{\rm Tr}\{\hat{\mathbf{J}}^{(0)}(\mathbf{q})\\&\quad\times(H^\times-\hbar\omega-\hbar z+\hbar z_1)^{-1}[e\mathbf{R}\cdot\mathbf{E},\rho_{\rm eq}]\}.\end{aligned} \tag{3.7}$$

Substituting this equation and performing the integral in Eq. (3.2), we obtain

$$\begin{aligned}\langle\mathbf{J}^{(1)}(\mathbf{q},z)\rangle=&\{(z+\omega)^{-1}+(z-\omega)^{-1}\}\\&\times{\rm Tr}\{\hat{\mathbf{J}}^{(0)}(\mathbf{q})G_z[e\mathbf{R}\cdot\mathbf{E},\rho_{\rm eq}]\},\end{aligned} \tag{3.8}$$

where G_z is given by

$$G_z\equiv(H^\times-\hbar z)^{-1}. \tag{3.9}$$

Since we are interested in $\boldsymbol{\sigma}(\omega)$, we only need to find the residue at $z=-\omega+i\delta$. Thus the relation (2.38) in Sec. II C should be expressed by

$$\begin{aligned}&{\rm Res}\langle\mathbf{J}^{(1)}(\mathbf{q},z)\rangle/\Omega|_{z=-\omega+i\delta}\\&=\frac{e}{\Omega}{\rm Tr}\{\hat{\mathbf{J}}^{(0)}(\mathbf{q})[H^\times+\hbar(\omega-i\delta)]^{-1}[\mathbf{R}\cdot\mathbf{E},\rho_{\rm eq}]\}\\&=-\boldsymbol{\sigma}(\omega)\cdot\mathbf{E}.\end{aligned} \tag{3.10}$$

From this, the linear (complex) conductivity reads

$$\sigma_{ij}(\omega)=-\frac{e}{\Omega}{\rm Tr}\{J_iG(-\omega^-)[R_j,\rho_{\rm eq}]\}\quad(i,j=x,y,z), \tag{3.11}$$

where J_i and $G(\omega^-)$ are, respectively, given by

$$J_i=-e\dot{R}_i=\frac{ie}{\hbar}[R_i,H], \tag{3.12}$$

$$G(\omega^-)\equiv(H^\times-\hbar\omega^-)^{-1}=(H_{\rm e}^\times+H_{\rm p}^\times+H_{\rm ep}^\times-\hbar\omega^-)^{-1}. \tag{3.13}$$

The overdot in Eq. (3.12) is $\partial/\partial t$. It should be noted that ω^- is a complex external frequency and will be set equal to $\omega-i\delta$, where ω is real and δ is a positive infinitesimal. To get rid of the commutator in Eq. (3.11), we apply the Kubo identity [8]

$$[-e\mathbf{R},\rho_{\rm eq}]=-i\hbar\rho_{\rm eq}\int_0^{\beta=1/k_{\rm B}T}d\beta'\,\mathbf{J}(-i\hbar\beta'), \tag{3.14}$$

where

$$\mathbf{J}(-i\hbar\beta')\equiv\exp[\beta'H]\mathbf{J}\exp[-\beta'H]. \tag{3.15}$$

Accordingly, Eq. (3.11) can be written as

$$\begin{aligned}\sigma_{ij}(\omega)=&\frac{\hbar}{i\Omega}{\rm Tr}\left\{J_i(H^\times+\hbar\omega-i\hbar\delta)^{-1}\rho_{\rm eq}\right.\\&\left.\times\int_0^\beta d\beta'J_j(-i\hbar\beta')\right\}\\\equiv&\lim_{\delta\to0^+}\int_0^\infty dt\,\exp[-i(\omega-i\delta)t]\\&\times\int_0^\beta d\beta'\,\Omega^{-1}{\rm Tr}\{\rho_{\rm eq}J_j(-i\hbar\beta')J_i(t)\},\end{aligned} \tag{3.16}$$

where

$$J_i(t)=\exp[iH^\times t/\hbar]J_i \tag{3.17}$$

is the total current operator in the Heisenberg picture; $\rho_{\rm eq}$ is the normalized grand canonical density operator (2.51). It should be noted that the limit $\delta\to0^+$ should be taken last in Eqs. (3.11) and (3.16), in particular after the bulk limit ($\Omega\to\infty$, $N_{\rm e}\to\infty$ while $N_{\rm e}/\Omega=n_{\rm e}$, which is finite). This expression is identically equal to the well-known Kubo formula [8].

B. Evaluation of linear conductivity

We start with the linear conductivity formula (3.11):

$$\sigma_{ij}(\omega) = -\frac{e}{\Omega}\,\mathrm{Tr}\{J_i G(-\omega^-)[R_j,\rho_{\mathrm{eq}}(\tilde{H})]\}$$
$$\simeq -\frac{e}{\Omega}\,\mathrm{Tr}\{J_i G(-\omega^-)[R_j,\rho_{\mathrm{eq}}(\tilde{H}_0)]\}$$
$$= -\frac{e}{\Omega}\,\mathrm{Tr}\{\rho_{\mathrm{eq}}(\tilde{H}_0)[R_j,K(\omega^-)]\}. \tag{3.18}$$

In the last equality we have made use of the invariance property of the trace under cyclic permutation. Here we have assumed that ρ_{eq} for the electron-phonon system [Eq. (2.51)] can be factorized as

$$\rho_{\mathrm{eq}}(\tilde{H}) \simeq \rho_{\mathrm{eq}}(\tilde{H}_0) = \rho_{\mathrm{e}}(\tilde{H}_{\mathrm{e}}) \otimes \rho_{\mathrm{p}}(H_{\mathrm{p}}), \tag{3.19}$$

where $\tilde{H}_0 \equiv H_{\mathrm{e}} + H_{\mathrm{p}} - \zeta N \equiv H_0 - \zeta N$, $\tilde{H}_{\mathrm{e}} \equiv H_{\mathrm{e}} - \zeta N$, and a many-body electron-phonon operator $K(\omega^-)$ is defined as

$$K(\omega^-) \equiv G(\omega^-) J_i. \tag{3.20}$$

The resolvent operator $G(\omega^-)$ is given by Eq. (3.13). The approximation for ρ_{eq} is justified in our weak coupling calculation. Using Eq. (3.4), Eq. (3.18) can be expressed in the matrix form as

$$\sigma_{ij}(\omega) = -\frac{e}{\Omega}\sum_{\mu,\nu}\langle\mu|r_j|\nu\rangle\langle K(\omega^-)\rangle_{\mu\nu}, \tag{3.21}$$

where we have introduced the notation

$$\langle\cdots\rangle_{\mu\nu} \equiv \mathrm{Tr}\{\rho_{\mathrm{eq}}(\tilde{H}_0)(a_\mu^\dagger a_\nu)^\times\cdots\}. \tag{3.22}$$

Our problem is now to evaluate the quantity $\langle K(\omega^-)\rangle_{\mu\nu}$ in Eq. (3.21). To do this, we introduce the projection operators $\mathcal{P},\mathcal{P}'$ defined by [4–7]

$$\mathcal{P}\cdots \equiv \langle\cdots\rangle_{\mu\nu} J_i/\langle J_i\rangle_{\mu\nu}, \tag{3.23}$$

$$\mathcal{P}' \equiv 1 - \mathcal{P}. \tag{3.24}$$

It is clear from these definitions that

$$\mathcal{P}J_i = \langle J_i\rangle_{\mu\nu} J_i/\langle J_i\rangle_{\mu\nu} = J_i, \tag{3.25}$$

$$\mathcal{P}' J_i = J_i - \mathcal{P}J_i = J_i - J_i = 0, \tag{3.26}$$

$$\mathcal{P}^2 = \mathcal{P}, \quad \mathcal{P}'^2 = \mathcal{P}'. \tag{3.27}$$

From Eq. (3.20), $K(\omega^-)$ should obey the equation

$$J_i = (H^\times - \hbar\omega^-)K(\omega^-)$$
$$= (H^\times - \hbar\omega^-)[\mathcal{P}K(\omega^-) + \mathcal{P}'K(\omega^-)]. \tag{3.28}$$

Letting $\mathcal{P}$ and $\mathcal{P}'$ operate separately on Eq. (3.28), we obtain the equations

$$J_i = \mathcal{P}J_i = (\mathcal{P}H^\times - \hbar\omega^-)\mathcal{P}K(\omega^-) + \mathcal{P}H^\times\mathcal{P}'K(\omega^-), \tag{3.29}$$

$$0 = \mathcal{P}'J_i = (\mathcal{P}'H^\times - \hbar\omega^-)\mathcal{P}'K(\omega^-) + \mathcal{P}'H^\times\mathcal{P}K(\omega^-). \tag{3.30}$$

Here we have used the identity

$$\mathcal{P}\mathcal{P}' = \mathcal{P}'\mathcal{P} = 0, \tag{3.31}$$

which can be easily verified from Eqs. (3.24) and (3.27). Solving Eq. (3.30) for $\mathcal{P}'K(\omega^-)$, we obtain the equation

$$\mathcal{P}'K(\omega^-) = -(\mathcal{P}'H^\times - \hbar\omega^-)^{-1}\mathcal{P}'H^\times\mathcal{P}K(\omega^-). \tag{3.32}$$

Substituting Eq. (3.32) into Eq. (3.29), we obtain the relevant term J_i:

$$J_i = \mathcal{P}[H^\times - H^\times G'(\omega^-)\mathcal{P}'H^\times - \hbar\omega^-]\mathcal{P}K(\omega^-)$$
$$= \frac{\langle K(\omega^-)\rangle_{\mu\nu}}{\langle J_i\rangle_{\mu\nu}}\,\frac{\langle(H^\times - H^\times G'(\omega^-)\mathcal{P}'H^\times - \hbar\omega^-)J_i\rangle_{\mu\nu}J_i}{\langle J_i\rangle_{\mu\nu}}, \tag{3.33}$$

where we have defined a resolvent operator $G'(\omega^-)$ as

$$G'(\omega^-) \equiv (\mathcal{P}'H^\times - \hbar\omega^-)^{-1}. \tag{3.34}$$

Thus the quantity $\langle K(\omega^-)\rangle_{\mu\nu}$ can be exactly expressed by

$$\langle K(\omega^-)\rangle_{\mu\nu} = \frac{\langle J_i\rangle_{\mu\nu}}{\langle[H^\times - H^\times G'(\omega^-)\mathcal{P}'H^\times]J_i\rangle_{\mu\nu}\langle J_i\rangle_{\mu\nu}^{-1} - \hbar\omega^-}. \tag{3.35}$$

Noting that $\langle J_i\rangle_{\mu\nu} = -\langle\nu|j_i|\mu\rangle(f_\nu - f_\mu)$ and $\langle(H_{\mathrm{e}}^\times + H_{\mathrm{p}}^\times)J_i\rangle_{\mu\nu} = -\varepsilon_{\nu\mu}\langle\nu|j_i|\mu\rangle(f_\nu - f_\mu)$ ($\varepsilon_{\nu\mu} \equiv \varepsilon_\nu - \varepsilon_\mu$) in Eq. (3.35), an expression for a dynamic complex conductivity (3.18) can be expressed as

$$\sigma_{ij}(\omega) = -\frac{e}{\Omega}\sum_{\mu,\nu}(f_\nu - f_\mu)\,\frac{\langle\mu|r_j|\nu\rangle\langle\nu|j_i|\mu\rangle}{\hbar\omega^- - \varepsilon_{\nu\mu} - i\Gamma_{\mu\nu}(\omega^-)}, \tag{3.36}$$

where the damping matrix (self-energy) $\Gamma_{\mu\nu}(\omega^-)$ is given by

$$i\Gamma_{\mu\nu}(\omega^-) = \frac{\langle[H_{\mathrm{ep}}^\times - H_{\mathrm{ep}}^\times G'(\omega^-)\mathcal{P}'H_{\mathrm{ep}}^\times]J_i\rangle_{\mu\nu}}{\langle J_i\rangle_{\mu\nu}}. \tag{3.37}$$

Equation (3.36) along with Eq. (3.37) is the exact formal expression for the linear optical conductivity $\sigma_{ij}(\omega)$ valid for an arbitrarily strong electron-phonon interaction H_{ep} except for the approximation (3.19) introduced in the exact conductivity formula (3.11). This expression (3.36) provides a rigorous basis for the evaluation of optical properties of conduction electrons in solids. The quantity $\Gamma_{\mu\nu}(\omega^-)$ clearly determines the spectral line shape (phonon-induced broadening) of the dynamic (optical) conductivity of solids.

The next step is to evaluate the damping matrix $\Gamma_{\mu\nu}(\omega^-)$ [Eq. (3.37)]. To do this, we expand Eq. (3.34) in terms of the electron-phonon coupling parameter η [3],

$$G'(\omega^-)\mathcal{P}'=(H_0^\times+\mathcal{P}'H_{\rm ep}^\times-\hbar\omega^-)^{-1}\mathcal{P}'$$
$$=G^0(\omega^-)\sum_{n=0}^{\infty}[-\eta\mathcal{P}'H_{\rm ep}^\times G^0(\omega^-)]^n\mathcal{P}', \tag{3.38}$$

where $G^0(\omega^-)$ is an unperturbed resolvent operator defined by

$$G^0(\omega^-)\equiv(H_0^\times-\hbar\omega^-)^{-1}. \tag{3.39}$$

Using Eq. (3.38) in Eq. (3.37), we can formally expand Eq. (3.37) in terms of η,

$$i\Gamma_{\mu\nu}(\omega^-)=\frac{1}{\langle J_i\rangle_{\mu\nu}}\sum_{n=1}^{\infty}\langle H_{\rm ep}^\times[-G^0(\omega^-)\mathcal{P}'H_{\rm ep}^\times]^nJ_i\rangle_{\mu\nu}$$
$$=i\sum_{n=1}^{\infty}\Gamma_{\mu\nu}^{(n)}(\omega^-). \tag{3.40}$$

Since $\Gamma_{\mu\nu}(\omega^-)$ has already been expanded in powers of η, the lowest-order nonvanishing term $\Gamma^{(2)}$ can be expressed, after some algebraic manipulations, by

$$i\Gamma_{\mu\nu}^{(2)}(\omega^-)=-\frac{\langle H_{\rm ep}^\times G^0(\omega^-)H_{\rm ep}^\times J_i\rangle_{\mu\nu}}{\langle J_i\rangle_{\mu\nu}}=\sum_{\alpha,\beta}\sum_{\mathbf{q}}[\langle\nu|\gamma_{\mathbf{q}}|\alpha\rangle\langle\alpha|j_i|\beta\rangle-\langle\nu|j_i|\alpha\rangle\langle\alpha|\gamma_{\mathbf{q}}|\beta\rangle]\frac{\langle\beta|\gamma_{-\mathbf{q}}|\mu\rangle}{\langle\nu|j_i|\mu\rangle}$$
$$\times\left[\frac{N_{\mathbf{q}}+1-f_\beta}{\epsilon_{\nu\beta}-\hbar\omega_{\mathbf{q}}-\hbar\omega^-}+\frac{N_{\mathbf{q}}+f_\beta}{\epsilon_{\nu\beta}+\hbar\omega_{\mathbf{q}}-\hbar\omega^-}\right]$$
$$+\sum_{\alpha,\beta}\sum_{\mathbf{q}}[\langle\nu|\gamma_{\mathbf{q}}|\alpha\rangle\langle\alpha|j_i|\mu\rangle-\langle\nu|j_i|\alpha\rangle\langle\alpha|\gamma_{\mathbf{q}}|\mu\rangle]\frac{\langle\beta|\gamma_{-\mathbf{q}}|\beta\rangle}{\langle\nu|j_i|\mu\rangle}$$
$$\times\left[\frac{f_\beta}{\varepsilon_{\nu\mu}-\hbar\omega_{\mathbf{q}}-\hbar\omega^-}-\frac{f_\beta}{\varepsilon_{\nu\mu}+\hbar\omega_{\mathbf{q}}-\hbar\omega^-}\right]$$
$$+\sum_{\alpha,\beta}\sum_{\mathbf{q}}\frac{\langle\nu|\gamma_{-\mathbf{q}}|\alpha\rangle}{\langle\nu|j_i|\mu\rangle}[\langle\alpha|j_i|\beta\rangle\langle\beta|\gamma_{\mathbf{q}}|\mu\rangle-\langle\alpha|\gamma_{\mathbf{q}}|\beta\rangle\langle\beta|j_i|\mu\rangle]$$
$$\times\left[\frac{N_{\mathbf{q}}+f_\beta}{\varepsilon_{\alpha\mu}-\hbar\omega_{\mathbf{q}}-\hbar\omega^-}+\frac{N_{\mathbf{q}}+1-f_\beta}{\varepsilon_{\alpha\mu}+\hbar\omega_{\mathbf{q}}-\hbar\omega^-}\right], \tag{3.41}$$

where $N_{\mathbf{q}}={\rm Tr}\{\rho_{\rm p}b_{\mathbf{q}}^\dagger b_{\mathbf{q}}\}$ and $f_\beta={\rm Tr}\{\rho_{\rm e}a_\beta^\dagger a_\beta\}$ denote the Planck distribution function for phonons with energy $\hbar\omega_{\mathbf{q}}$ and the Fermi-Dirac distribution function for electrons with energy ϵ_β, at equilibrium temperature $T=1/k_{\rm B}\beta$, respectively. It should be noted that the above expression for the damping matrix (self-energy) is exact to second order in η for an electron-phonon interaction and determines the spectral line shape of the optical conductivity (3.36) [or (3.18)]. The terms associated with the Fermi-Dirac distribution function f_β describe the effects of exchange among electrons and play an important role in the determination of the temperature dependence on the optical conductivity for low temperatures. In the usual transport theory of conductivity in solids [9,10], the exchange effects of electrons in their collisions with phonons enter through the exclusion factors. If we ignore the exchange effects among electrons by setting $f_\beta=0$, we recover the expression for the same quantity obtained by assuming a system of one electron moving in a phonon field. Badjou and Argyres [7] showed that these effects play an important role in the case of the cyclotron resonance line shape. In fact, our expression $\Gamma_{\mu\nu}^{(2)}(\omega^-)$ [Eq. (3.41)] reduces to the corresponding expressions [7,11] obtained for a cyclotron resonance linewidth by replacing the electron states by Landau states and the current operator j_i by j_+ $(\equiv j_x+ij_y)$.

C. Evaluation of nonlinear conductivity

From Eq. (2.52) along with Eq. (3.1), $\langle\mathbf{J}(\mathbf{q},z)\rangle$ in the second order of the field-strength parameter (λ^2) is given by

$$\langle\mathbf{J}^{(2)}(\mathbf{q},z)\rangle=-\frac{\hbar}{2\pi i}\int_{ic-\infty}^{ic+\infty}dz_1(z_1-z)^{-1}(K^\times+\hbar z_1)^{-1}$$
$$\times{\rm Tr}\{\mathbf{J}^{(0)}(\mathbf{q})R_{z-z_1}\hat{H}_{\rm ef}^\times R_{z-z_1}\hat{H}_{\rm ef}^\times\rho_{\rm eq}\}. \tag{3.42}$$

We will apply the dipole approximation to the present nonlinear case and assume that the time-dependent electric field consists of a set of frequency modes $\{\omega_\alpha\}$ $(\alpha=1,2,3,...,m)$, where the component field is sinusoidal with a frequency ω_α. In this case, $H_{\rm ef}$ is given by

$$H_{\rm ef}(t)=e\sum_{\alpha=1}^{m}\mathbf{E}^{\alpha}\cdot\mathbf{R}\{\exp[i\omega_\alpha t]+\exp[-i\omega_\alpha t]\}. \tag{3.43}$$

The time-independent interaction Hamiltonian $\hat{H}_{\rm ef}$ associated with $H_{\rm ef}(t)$ [Eq. (3.43)] is then given by

$$\hat{H}_{\rm ef}=e\sum_{\alpha=1}^{m}\mathbf{E}^{\alpha}\cdot\mathbf{R}\{c_\alpha+c_\alpha^\dagger\}. \tag{3.44}$$

By a straightforward calculation along with Eqs. (2.14), (2.15), and (3.44), we obtain the part of the right-hand side of Eq. (3.42) that contains the operators $c_\alpha, c_\alpha^\dagger$ as

$$\begin{aligned}(K^\times+\hbar z_1)^{-1}R_{z-z_1}\hat{H}_{\rm ef}^\times R_{z-z_1}\hat{H}_{\rm ef}^\times\rho_{\rm eq}=&\sum_{\alpha,\beta}\frac{1}{\hbar}\{(\omega_\alpha-\omega_\beta+z_1)^{-1}G_{-\omega_\alpha+\omega_\beta+z-z_1}[e\mathbf{R}\cdot\mathbf{E}^\beta,G_{-\omega_\alpha+z-z_1}[e\mathbf{R}\cdot\mathbf{E}^\alpha,\rho_{\rm eq}]]\}\\&+\sum_{\alpha,\beta}\frac{1}{\hbar}\{(\omega_\alpha+\omega_\beta+z_1)^{-1}G_{-\omega_\alpha-\omega_\beta+z-z_1}[e\mathbf{R}\cdot\mathbf{E}^\beta,G_{-\omega_\alpha+z-z_1}[e\mathbf{R}\cdot\mathbf{E}^\alpha,\rho_{\rm eq}]]\}\\&+\sum_{\alpha,\beta}\frac{1}{\hbar}\{(-\omega_\alpha-\omega_\beta+z_1)^{-1}G_{\omega_\alpha+\omega_\beta+z-z_1}[e\mathbf{R}\cdot\mathbf{E}^\beta,G_{\omega_\alpha+z-z_1}[e\mathbf{R}\cdot\mathbf{E}^\alpha,\rho_{\rm eq}]]\}\\&+\sum_{\alpha,\beta}\frac{1}{\hbar}\{(-\omega_\alpha+\omega_\beta+z_1)^{-1}G_{\omega_\alpha-\omega_\beta+z-z_1}[e\mathbf{R}\cdot\mathbf{E}^\beta,G_{\omega_\alpha+z-z_1}[e\mathbf{R}\cdot\mathbf{E}^\alpha,\rho_{\rm eq}]]\},\end{aligned} \tag{3.45}$$

where the resolvent operator G_z is defined by Eq. (3.9). Substituting Eq. (3.45) into Eq. (3.42) and performing the z_1 integration, we can recast Eq. (3.42) to the form

$$\begin{aligned}\langle\mathbf{J}^{(2)}(\mathbf{q},z)\rangle=&e^2\sum_{\alpha,\beta}((-\omega_\alpha+\omega_\beta-z)^{-1}{\rm Tr}\{\mathbf{J}^{(0)}(\mathbf{q})G_z[\mathbf{R}\cdot\mathbf{E}^\beta,G_{z-\omega_\beta}[\mathbf{R}\cdot\mathbf{E}^\alpha,\rho_{\rm eq}]]\})\\&+e^2\sum_{\alpha,\beta}((-\omega_\alpha-\omega_\beta-z)^{-1}{\rm Tr}\{\mathbf{J}^{(0)}(\mathbf{q})G_z[\mathbf{R}\cdot\mathbf{E}^\beta,G_{z+\omega_\beta}[\mathbf{R}\cdot\mathbf{E}^\alpha,\rho_{\rm eq}]]\})\\&+e^2\sum_{\alpha,\beta}((\omega_\alpha+\omega_\beta-z)^{-1}{\rm Tr}\{\mathbf{J}^{(0)}(\mathbf{q})G_z[\mathbf{R}\cdot\mathbf{E}^\beta,G_{z-\omega_\beta}[\mathbf{R}\cdot\mathbf{E}^\alpha,\rho_{\rm eq}]]\})\\&+e^2\sum_{\alpha,\beta}((\omega_\alpha-\omega_\beta-z)^{-1}{\rm Tr}\{\mathbf{J}^{(0)}(\mathbf{q})G_z[\mathbf{R}\cdot\mathbf{E}^\beta,G_{z+\omega_\beta}[\mathbf{R}\cdot\mathbf{E}^\alpha,\rho_{\rm eq}]]\}).\end{aligned} \tag{3.46}$$

We can see from this expression the frequency mixing of modes, e.g., α and β. For the sum frequency $\omega_\alpha+\omega_\beta$, the relation (2.38) in Sec. II C can be expressed in the present case by taking the residue at $z=-\omega_\alpha-\omega_\beta+i\delta$ (see the Appendix):

$$\begin{aligned}&{\rm Res}\langle\mathbf{J}^{(2)}(\mathbf{q},z)\rangle/\Omega|_{z=-\omega_\alpha-\omega_\beta+i\delta}\\&=\frac{e^2}{\Omega}{\rm Tr}\{\mathbf{J}^{(0)}(\mathbf{q})G(-\omega_\alpha-\omega_\beta+i\delta)\\&\quad\times[\mathbf{R}\cdot\mathbf{E}^\beta,G(-\omega_\alpha+i\delta)[\mathbf{R}\cdot\mathbf{E}^\alpha,\rho_{\rm eq}]]\}\\&=-\boldsymbol{\sigma}^{(2)}(\omega_\alpha,\omega_\beta;\omega_\alpha+\omega_\beta):\mathbf{E}^\alpha\mathbf{E}^\beta\end{aligned} \tag{3.47}$$

for the lowest-order nonlinear case. Another combination of frequency mixing in $\boldsymbol{\sigma}^{(2)}$ is similarly extracted from taking a residue of $\langle\mathbf{J}^{(2)}(\mathbf{q},z)\rangle/\Omega$ at an appropriate pole. From Eq. (3.47) we can obtain a general expression for the sum-frequency second-order conductivity as

$$\begin{aligned}&\sigma_{ijk}^{(2)}(\omega_\alpha,\omega_\beta;\omega_\alpha+\omega_\beta)\\&=-\frac{e^2}{\Omega}{\rm Tr}\{J_iG(-\omega_\alpha-\omega_\beta+i\delta)\\&\quad\times R_j^\times G(-\omega_\alpha+i\delta)R_k^\times\rho_{\rm eq}\}\\&=-\frac{e^2}{\Omega}{\rm Tr}\{\rho_{\rm eq}R_k^\times G(\omega_\alpha-i\delta)\\&\quad\times R_j^\times G(\omega_\alpha+\omega_\beta-i\delta)J_i\}\quad(i,j,k=x,y,z),\end{aligned} \tag{3.48}$$

where the last equality is due to the cyclicity of the trace. It is noted that α,β take any combination of a frequency mode among α,β $(=1,2,3,...,m)$ applied to the system.

In order to obtain $\boldsymbol{\sigma}^{(2)}$ in the matrix representation, let us introduce a notation for the right-hand side of Eq. (3.48):

$$\langle\langle K(\omega_{\alpha\beta}^{-})\rangle\rangle \equiv \mathrm{Tr}\{\rho_{\mathrm{eq}}(a_{\epsilon}^{\dagger}a_{\xi})^{\times}G(\omega_{\alpha}^{-})(a_{\gamma}^{\dagger}a_{\delta})^{\times}K(\omega_{\alpha\beta}^{-})\}, \tag{3.49}$$

where $\omega_{\alpha}^{-}\equiv\omega_{\alpha}-i\delta$, $\omega_{\alpha\beta}^{-}\equiv\omega_{\alpha}+\omega_{\beta}-i\delta$, and $\langle\langle\cdots\rangle\rangle$ is defined by

$$\langle\langle\cdots\rangle\rangle \equiv \mathrm{Tr}\{\rho_{\mathrm{eq}}(a_{\epsilon}^{\dagger}a_{\xi})^{\times}G(\omega_{\alpha}^{-})(a_{\gamma}^{\dagger}a_{\delta})^{\times}\cdots\}, \tag{3.50}$$

$$K(\omega_{\alpha\beta}^{-})\equiv G(\omega_{\alpha\beta}^{-})J_i . \tag{3.51}$$

From Eqs. (3.48) and (3.49), the second-order conductivity (3.48) can be expressed in terms of $\langle\langle K(\omega_{\alpha\beta}^{-})\rangle\rangle$ as

$$\sigma_{ijk}^{(2)}(\omega_{\alpha},\omega_{\beta};\omega_{\alpha}+\omega_{\beta}) = -\frac{e^2}{\Omega}\sum_{\varepsilon,\xi}\sum_{\gamma,\delta}\langle\varepsilon|r_k|\xi\rangle\langle\gamma|r_j|\delta\rangle\langle\langle K(\omega_{\alpha\beta}^{-})\rangle\rangle. \tag{3.52}$$

Here we have adopted the approximation (3.19) for the equilibrium density operator as is used for the evaluation of a linear conductivity. Our problem is thus reduced to the evaluation of the quantity $\langle\langle K(\omega_{\alpha\beta}^{-})\rangle\rangle$ to obtain the explicit expression of the second-order conductivity. To carry it out we apply the projection operator technique introduced in Sec. III B. We again define the projection operators $\mathcal{P},\mathcal{P}'$ by

$$\mathcal{P}\cdots\equiv\langle\langle\cdots\rangle\rangle J_i/\langle\langle J_i\rangle\rangle, \tag{3.53}$$

$$\mathcal{P}'\equiv 1-\mathcal{P}. \tag{3.54}$$

In a similar manner as we did in Sec. III B, the expression for the quantity $\langle\langle K(\omega_{\alpha\beta}^{-})\rangle\rangle$ may be expressed in the form

$$\langle\langle K(\omega_{\alpha\beta}^{-})\rangle\rangle = \frac{\langle\langle J_i\rangle\rangle}{\langle\langle[H^{\times}-H^{\times}G'(\omega_{\alpha\beta}^{-})\mathcal{P}'H^{\times}]J_i\rangle\rangle\langle\langle J_i\rangle\rangle^{-1}-\hbar\omega_{\alpha\beta}^{-}}, \tag{3.55}$$

where the resolvent operator $G'(\omega_{\alpha\beta}^{-})$ is defined by $G'(\omega_{\alpha\beta}^{-})\equiv(\mathcal{P}'H^{\times}-\hbar\omega_{\alpha\beta}^{-})^{-1}$. To evaluate the quantity $\langle\langle J_i\rangle\rangle$ in Eq. (3.55), let us rewrite the quantity $\langle\langle J_i\rangle\rangle$ as

$$\langle\langle J_i\rangle\rangle = \mathrm{Tr}\{\rho_{\mathrm{eq}}(a_{\varepsilon}^{\dagger}a_{\xi})^{\times}G(\omega_{\alpha}^{-})(a_{\gamma}^{\dagger}a_{\delta})^{\times}J_i\} = \langle Y(\omega_{\alpha}^{-})\rangle_{\varepsilon\xi}, \tag{3.56}$$

$$\langle\cdots\rangle_{\varepsilon\xi}\equiv\mathrm{Tr}\{\rho_{\mathrm{eq}}(a_{\varepsilon}^{\dagger}a_{\xi})^{\times}\cdots\}, \tag{3.57}$$

$$Y(\omega_{\alpha}^{-})\equiv G(\omega_{\alpha}^{-})(a_{\gamma}^{\dagger}a_{\delta})^{\times}J_i\equiv G(\omega_{\alpha}^{-})Z. \tag{3.58}$$

We define the projection operators $\mathcal{Q},\mathcal{Q}'$ by

$$\mathcal{Q}\cdots\equiv\langle\cdots\rangle_{\varepsilon\xi}Z/\langle Z\rangle_{\varepsilon\xi}, \tag{3.59}$$

$$\mathcal{Q}'\equiv 1-\mathcal{Q}. \tag{3.60}$$

Thus the quantity $\langle Y(\omega_{\alpha}^{-})\rangle_{\varepsilon\xi}$ can be exactly expressed as

$$\langle Y(\omega_{\alpha}^{-})\rangle_{\varepsilon\xi} = \frac{\langle Z\rangle_{\varepsilon\xi}}{\langle[H^{\times}-H^{\times}G''(\omega_{\alpha}^{-})\mathcal{Q}'H^{\times}]Z\rangle_{\varepsilon\xi}\langle Z\rangle_{\varepsilon\xi}^{-1}-\hbar\omega_{\alpha}^{-}}, \tag{3.61}$$

where the resolvent operator $G''(\omega_{\alpha}^{-})$ is given by $G''(\omega_{\alpha}^{-})\equiv(\mathcal{Q}'H^{\times}-\hbar\omega_{\alpha}^{-})^{-1}$. From Eqs. (3.55), (3.56), and (3.61) we can write the expression for the quantity $\langle\langle K(\omega_{\alpha\beta}^{-})\rangle\rangle$ [Eq. (3.55)] as

$$\langle\langle K(\omega_{\alpha\beta}^{-})\rangle\rangle = \frac{\langle Z\rangle_{\epsilon\xi}}{[\hbar\omega_{\alpha}^{-}-i\Gamma(\omega_{\alpha}^{-})][\hbar\omega_{\alpha\beta}^{-}-i\Gamma(\omega_{\alpha}^{-},\omega_{\alpha\beta}^{-})]}, \tag{3.62}$$

where $\Gamma(\omega_{\alpha}^{-})$ and $\Gamma(\omega_{\alpha}^{-},\omega_{\alpha\beta}^{-})$ are the quantities associated with damping due to the electron-phonon interaction and are given by

$$i\Gamma(\omega_{\alpha}^{-})\equiv\mathrm{Tr}\{\rho_{\mathrm{eq}}(a_{\varepsilon}^{\dagger}a_{\xi})^{\times}\times[H^{\times}-H^{\times}G''(\omega_{\alpha}^{-})\mathcal{Q}'H^{\times}]Z\}/\langle Z\rangle_{\varepsilon\xi}, \tag{3.63}$$

$$\begin{aligned}i\Gamma(\omega_{\alpha}^{-},\omega_{\alpha\beta}^{-})\equiv{}&\mathrm{Tr}\{\rho_{\mathrm{eq}}(a_{\varepsilon}^{\dagger}a_{\xi})^{\times}G(\omega_{\alpha}^{-})(a_{\gamma}^{\dagger}a_{\delta})^{\times}\\&\times[H^{\times}-H^{\times}G'(\omega_{\alpha\beta}^{-})\mathcal{P}'H^{\times}]J_i\}/\langle Z\rangle_{\varepsilon\xi}\\&\times\mathrm{Tr}\{\rho_{\mathrm{eq}}(a_{\varepsilon}^{\dagger}a_{\xi})^{\times}[H^{\times}-H^{\times}G''(\omega_{\alpha}^{-})\\&\times\mathcal{Q}'H^{\times}-\hbar\omega_{\alpha}^{-}]Z\}/\langle Z\rangle_{\varepsilon\xi},\end{aligned} \tag{3.64}$$

respectively. The quantity $\langle Z\rangle_{\varepsilon\xi}$ is easily evaluated and is given by

$$\begin{aligned}\langle Z\rangle_{\varepsilon\xi}&=\mathrm{Tr}\{\rho_{\mathrm{eq}}(a_{\varepsilon}^{\dagger}a_{\xi})^{\times}(a_{\gamma}^{\dagger}a_{\delta})^{\times}J_i\}\\&=[\langle\xi|j_i|\gamma\rangle\delta_{\varepsilon\delta}-\langle\delta|j_i|\varepsilon\rangle\delta_{\xi\gamma}](f_{\xi}-f_{\varepsilon}).\end{aligned} \tag{3.65}$$

With the use of the identity for the resolvent operator

$$G(\omega_{\alpha}^{-})=G^0(\omega_{\alpha}^{-})-G(\omega_{\alpha}^{-})H_{\mathrm{ep}}^{\times}G^0(\omega_{\alpha}^{-}), \tag{3.66}$$

$$G^0(\omega_{\alpha}^{-})\equiv(H_0^{\times}-\hbar\omega_{\alpha}^{-})^{-1}=(H_{\mathrm{e}}^{\times}+H_{\mathrm{p}}^{\times}-\hbar\omega_{\alpha}^{-})^{-1}, \tag{3.67}$$

we expand $i\Gamma(\omega_{\alpha}^{-})$ and $i\Gamma(\omega_{\alpha}^{-},\omega_{\alpha\beta}^{-})$ in terms of the electron-phonon coupling parameter η and keep the terms up to $O(\eta^2)$. Noting in the resultant expressions that $i\Gamma^{(0)}(\omega_{\alpha}^{-})=\varepsilon_{\xi\varepsilon}$, $i\Gamma^{(0)}(\omega_{\alpha}^{-},\omega_{\alpha\beta}^{-})=(\varepsilon_{\xi\gamma}\langle\xi|j_i|\gamma\rangle\delta_{\varepsilon\delta}-\varepsilon_{\delta\varepsilon}\langle\delta|j_i|\varepsilon\rangle\delta_{\xi\gamma})\,(\langle\xi|j_i|\gamma\rangle\delta_{\varepsilon\delta}-\langle\delta|j_i|\varepsilon\rangle\delta_{\xi\gamma})^{-1}$, and $i\Gamma^{(1)}(\omega_{\alpha}^{-})=i\Gamma^{(1)}(\omega_{\alpha}^{-},\omega_{\alpha\beta}^{-})=0$, $\langle\langle K(\omega_{\alpha\beta}^{-})\rangle\rangle$ in Eq. (3.62) can be written as

$$\langle\langle K(\omega_{\alpha\beta}^{-})\rangle\rangle=(f_{\xi}-f_{\varepsilon})\Bigg[\frac{\langle\xi|j_i|\gamma\rangle\delta_{\varepsilon\delta}}{[\hbar\omega_{\alpha}^{-}-\varepsilon_{\xi\varepsilon}-i\Gamma^{(2)}(\omega_{\alpha}^{-})][\hbar\omega_{\alpha\beta}^{-}-\varepsilon_{\xi\gamma}-i\Gamma^{(2)}(\omega_{\alpha}^{-},\omega_{\alpha\beta}^{-})]}-\frac{\langle\delta|j_i|\varepsilon\rangle\delta_{\xi\gamma}}{[\hbar\omega_{\alpha}^{-}-\varepsilon_{\xi\varepsilon}-i\Gamma^{(2)}(\omega_{\alpha}^{-})][\hbar\omega_{\alpha\beta}^{-}-\varepsilon_{\delta\varepsilon}-i\Gamma^{(2)}(\omega_{\alpha}^{-},\omega_{\alpha\beta}^{-})]}\Bigg]. \tag{3.68}$$

By utilizing Eq. (3.68) in Eq. (3.52), the rigorous expression of the second-order conductivity (3.52) is thus given by

$$\sigma_{ijk}^{(2)}(\omega_{\alpha},\omega_{\beta};\omega_{\alpha}+\omega_{\beta})=-\frac{e^2}{\Omega}\sum_{\varepsilon,\xi,\gamma,\delta}(f_{\xi}-f_{\varepsilon})\Bigg[\frac{\langle\gamma|r_j|\varepsilon\rangle\langle\varepsilon|r_k|\xi\rangle\langle\xi|j_i|\gamma\rangle\delta_{\varepsilon\delta}}{[\hbar\omega_{\alpha\beta}^{-}-\varepsilon_{\xi\gamma}-i\Gamma_{\varepsilon\xi\gamma\delta}^{(2)}(\omega_{\alpha}^{-},\omega_{\alpha\beta}^{-})][\hbar\omega_{\alpha}^{-}-\varepsilon_{\xi\varepsilon}-i\Gamma_{\varepsilon\xi\gamma\delta}^{(2)}(\omega_{\alpha}^{-})]}-\frac{\langle\varepsilon|r_k|\xi\rangle\langle\xi|r_j|\delta\rangle\langle\delta|j_i|\varepsilon\rangle\delta_{\xi\gamma}}{[\hbar\omega_{\alpha\beta}^{-}-\varepsilon_{\delta\varepsilon}-i\Gamma_{\varepsilon\xi\gamma\delta}^{(2)}(\omega_{\alpha}^{-},\omega_{\alpha\beta}^{-})][\hbar\omega_{\alpha}^{-}-\varepsilon_{\xi\varepsilon}-i\Gamma_{\varepsilon\xi\gamma\delta}^{(2)}(\omega_{\alpha}^{-})]}\Bigg], \tag{3.69}$$

where α,β take any frequency modes (i.e., $\alpha,\beta=1,2,3,\ldots,m$) and the damping matrices $\Gamma(\omega_{\alpha}^{-})$ and $\Gamma(\omega_{\alpha}^{-},\omega_{\alpha\beta}^{-})$ are, respectively, given by

$$\begin{aligned}
i\Gamma_{\varepsilon\xi\gamma\delta}^{(2)}(\omega_{\alpha}^{-})\simeq&\sum_{\alpha}\sum_{\mathbf{q}}\frac{\langle\alpha|\gamma_{-q}|\varepsilon\rangle}{\langle\delta|j_i|\varepsilon\rangle\delta_{\xi\gamma}-\langle\xi|j_i|\gamma\rangle\delta_{\varepsilon\delta}}[\langle\xi|\gamma_{\mathbf{q}}|\gamma\rangle\langle\delta|j_i|\alpha\rangle+\langle\delta|\gamma_{\mathbf{q}}|\alpha\rangle\langle\xi|j_i|\gamma\rangle]\\
&\times\left[\frac{N_{\mathbf{q}}+1-f_{\alpha}}{\varepsilon_{\xi\alpha}-\hbar\omega_{\mathbf{q}}-\hbar\omega_{\alpha}^{-}}+\frac{N_{\mathbf{q}}+f_{\alpha}}{\varepsilon_{\xi\alpha}+\hbar\omega_{\mathbf{q}}-\hbar\omega_{\alpha}^{-}}\right]\\
&-\sum_{\alpha,\beta}\sum_{\mathbf{q}}\frac{\langle\alpha|\gamma_{-\mathbf{q}}|\varepsilon\rangle\langle\beta|\gamma_{\mathbf{q}}|\alpha\rangle\langle\delta|j_i|\beta\rangle}{\langle\delta|j_i|\varepsilon\rangle\delta_{\xi\gamma}-\langle\xi|j_i|\gamma\rangle\delta_{\varepsilon\delta}}\left[\frac{N_{\mathbf{q}}+1-f_{\alpha}}{\varepsilon_{\xi\alpha}-\hbar\omega_{\mathbf{q}}-\hbar\omega_{\alpha}^{-}}+\frac{N_{\mathbf{q}}+f_{\alpha}}{\varepsilon_{\xi\alpha}+\hbar\omega_{\mathbf{q}}-\hbar\omega_{\alpha}^{-}}\right]\delta_{\gamma\xi}\\
&-\sum_{\alpha}\sum_{\mathbf{q}}\frac{\langle\delta|\gamma_{-\mathbf{q}}|\varepsilon\rangle\langle\xi|\gamma_{\mathbf{q}}|\alpha\rangle\langle\alpha|j_i|\gamma\rangle}{\langle\delta|j_i|\varepsilon\rangle\delta_{\xi\gamma}-\langle\xi|j_i|\gamma\rangle\delta_{\varepsilon\delta}}\left[\frac{N_{\mathbf{q}}+1-f_{\delta}}{\varepsilon_{\xi\delta}-\hbar\omega_{\mathbf{q}}-\hbar\omega_{\alpha}}+\frac{N_{\mathbf{q}}+f_{\delta}}{\varepsilon_{\xi\delta}+\hbar\omega_{\mathbf{q}}-\hbar\omega_{\alpha}}\right]\\
&-\sum_{\alpha}\sum_{\mathbf{q}}\frac{\langle\xi|\gamma_{-\mathbf{q}}|\alpha\rangle}{\langle\delta|j_i|\varepsilon\rangle\delta_{\xi\gamma}-\langle\xi|j_i|\gamma\rangle\delta_{\varepsilon\delta}}[\langle\alpha|\gamma_{\mathbf{q}}|\gamma\rangle\langle\delta|j_i|\varepsilon\rangle+\langle\delta|\gamma_{\mathbf{q}}|\varepsilon\rangle\langle\alpha|j_i|\gamma\rangle]\\
&\times\left[\frac{N_{\mathbf{q}}+f_{\alpha}}{\varepsilon_{\alpha\varepsilon}-\hbar\omega_{\mathbf{q}}-\hbar\omega_{\alpha}^{-}}+\frac{N_{\mathbf{q}}+1-f_{\alpha}}{\varepsilon_{\alpha\varepsilon}+\hbar\omega_{\mathbf{q}}-\hbar\omega_{\alpha}^{-}}\right]\\
&+\sum_{\alpha,\beta}\sum_{\mathbf{q}}\frac{\langle\xi|\gamma_{-\mathbf{q}}|\alpha\rangle\langle\alpha|\gamma_{\mathbf{q}}|\beta\rangle\langle\beta|j_i|\gamma\rangle}{\langle\delta|j_i|\varepsilon\rangle\delta_{\xi\gamma}-\langle\xi|j_i|\gamma\rangle\delta_{\varepsilon\delta}}\left[\frac{N_{\mathbf{q}}+f_{\alpha}}{\varepsilon_{\alpha\varepsilon}-\hbar\omega_{\mathbf{q}}-\hbar\omega_{\alpha}^{-}}+\frac{N_{\mathbf{q}}+1-f_{\alpha}}{\varepsilon_{\alpha\varepsilon}+\hbar\omega_{\mathbf{q}}-\hbar\omega_{\alpha}^{-}}\right]\delta_{\varepsilon\delta}\\
&+\sum_{\alpha}\sum_{\mathbf{q}}\frac{\langle\xi|\gamma_{-\mathbf{q}}|\gamma\rangle\langle\alpha|\gamma_{\mathbf{q}}|\varepsilon\rangle\langle\delta|j_i|\alpha\rangle}{\langle\delta|j_i|\varepsilon\rangle\delta_{\xi\gamma}-\langle\xi|j_i|\gamma\rangle\delta_{\varepsilon\delta}}\left[\frac{N_{\mathbf{q}}+f_{\gamma}}{\varepsilon_{\gamma\varepsilon}-\hbar\omega_{\mathbf{q}}-\hbar\omega_{\alpha}^{-}}+\frac{N_{\mathbf{q}}+1-f_{\gamma}}{\varepsilon_{\gamma\varepsilon}+\hbar\omega_{\mathbf{q}}-\hbar\omega_{\alpha}^{-}}\right],
\end{aligned} \tag{3.70}$$

$$\begin{aligned}
i\Gamma_{\varepsilon\xi\gamma\delta}^{(2)}(\omega_{\alpha}^{-},\omega_{\alpha\beta}^{-})\simeq&\sum_{\alpha,\beta}\sum_{\mathbf{q}}\frac{\langle\alpha|\gamma_{-\mathbf{q}}|\varepsilon\rangle}{\langle\delta|j_i|\varepsilon\rangle\delta_{\xi\gamma}-\langle\xi|j_i|\gamma\rangle\delta_{\varepsilon\delta}}[\langle\delta|\gamma_{\mathbf{q}}|\beta\rangle\langle\beta|j_i|\alpha\rangle-\langle\beta|\gamma_{\mathbf{q}}|\alpha\rangle\langle\delta|j_i|\beta\rangle]\\
&\times\left[\frac{N_{\mathbf{q}}+1-f_{\alpha}}{\varepsilon_{\xi\alpha}-\hbar\omega_{\mathbf{q}}-\hbar\omega_{\alpha}^{-}}+\frac{N_{\mathbf{q}}+f_{\alpha}}{\varepsilon_{\xi\alpha}+\hbar\omega_{\mathbf{q}}-\hbar\omega_{\alpha}^{-}}\right]\delta_{\gamma\xi}\\
&-\sum_{\alpha}\sum_{\mathbf{q}}\frac{\langle\delta|\gamma_{-\mathbf{q}}|\varepsilon\rangle}{\langle\delta|j_i|\varepsilon\rangle\delta_{\xi\gamma}-\langle\xi|j_i|\gamma\rangle\delta_{\varepsilon\delta}}[\langle\xi|\gamma_{\mathbf{q}}|\alpha\rangle\langle\alpha|j_i|\gamma\rangle-\langle\alpha|\gamma_{\mathbf{q}}|\gamma\rangle\langle\xi|j_i|\alpha\rangle]\\
&\times\left[\frac{N_{\mathbf{q}}+1-f_{\delta}}{\varepsilon_{\xi\delta}-\hbar\omega_{\mathbf{q}}-\hbar\omega_{\alpha}^{-}}+\frac{N_{\mathbf{q}}+f_{\delta}}{\varepsilon_{\xi\delta}+\hbar\omega_{\mathbf{q}}-\hbar\omega_{\alpha}^{-}}\right]\\
&-\sum_{\alpha,\beta}\sum_{\mathbf{q}}\frac{\langle\xi|\gamma_{-\mathbf{q}}|\alpha\rangle}{\langle\delta|j_i|\varepsilon\rangle\delta_{\xi\gamma}-\langle\xi|j_i|\gamma\rangle\delta_{\varepsilon\delta}}[\langle\alpha|\gamma_{\mathbf{q}}|\beta\rangle\langle\beta|j_i|\gamma\rangle-\langle\beta|\gamma_{\mathbf{q}}|\gamma\rangle\langle\alpha|j_i|\beta\rangle]\\
&\times\left[\frac{N_{\mathbf{q}}+f_{\alpha}}{\varepsilon_{\alpha\delta}-\hbar\omega_{\mathbf{q}}-\hbar\omega_{\alpha}^{-}}+\frac{N_{\mathbf{q}}+1-f_{\alpha}}{\varepsilon_{\alpha\delta}+\hbar\omega_{\mathbf{q}}-\hbar\omega_{\alpha}^{-}}\right]\delta_{\varepsilon\delta}
\end{aligned}$$

$$
\begin{aligned}
&-\sum_{\alpha}\sum_{\mathbf{q}} \frac{\langle\xi|\gamma_{-\mathbf{q}}|\gamma\rangle}{\langle\delta|j_i|\varepsilon\rangle\delta_{\xi\gamma}-\langle\xi|j_i|\gamma\rangle\delta_{\varepsilon\delta}}[\langle\delta|\gamma_{\mathbf{q}}|\alpha\rangle\langle\alpha|j_i|\varepsilon\rangle-\langle\alpha|\gamma_{\mathbf{q}}|\varepsilon\rangle\langle\delta|j_i|\alpha\rangle]\\
&\times\left[\frac{N_{\mathbf{q}}+f_\gamma}{\varepsilon_{\gamma\varepsilon}-\hbar\omega_{\mathbf{q}}-\hbar\omega_\alpha^-}+\frac{N_{\mathbf{q}}+1-f_\gamma}{\varepsilon_{\gamma\varepsilon}+\hbar\omega_{\mathbf{q}}-\hbar\omega_\alpha^-}\right]\\
&+\sum_{\alpha,\beta}\sum_{\mathbf{q}} \frac{\langle\xi|\gamma_{-\mathbf{q}}|\beta\rangle}{\langle\delta|j_i|\varepsilon\rangle\delta_{\xi\gamma}-\langle\xi|j_i|\gamma\rangle\delta_{\varepsilon\delta}}[\langle\beta|\gamma_{\mathbf{q}}|\alpha\rangle\langle\alpha|j_i|\gamma\rangle-\langle\alpha|\gamma_{\mathbf{q}}|\gamma\rangle\langle\beta|j_i|\alpha\rangle]\\
&\times\left[\frac{N_{\mathbf{q}}+f_\beta}{\varepsilon_{\beta\gamma}-\hbar\omega_{\mathbf{q}}-\hbar\omega_{\alpha\beta}^-}+\frac{N_{\mathbf{q}}+1-f_\beta}{\varepsilon_{\beta\gamma}+\hbar\omega_{\mathbf{q}}-\hbar\omega_{\alpha\beta}^-}\right]\delta_{\varepsilon\delta}\\
&+\sum_{\alpha,\beta}\sum_{\mathbf{q}} \frac{\langle\delta|\gamma_{-\mathbf{q}}|\beta\rangle}{\langle\delta|j_i|\varepsilon\rangle\delta_{\xi\gamma}-\langle\xi|j_i|\gamma\rangle\delta_{\varepsilon\delta}}[\langle\alpha|\gamma_{\mathbf{q}}|\varepsilon\rangle\langle\beta|j_i|\alpha\rangle-\langle\beta|\gamma_{\mathbf{q}}|\alpha\rangle\langle\alpha|j_i|\varepsilon\rangle]\\
&\times\left[\frac{N_{\mathbf{q}}+f_\beta}{\varepsilon_{\beta\gamma}-\hbar\omega_{\mathbf{q}}-\hbar\omega_{\alpha\beta}^-}+\frac{N_{\mathbf{q}}+1-f_\beta}{\varepsilon_{\beta\gamma}+\hbar\omega_{\mathbf{q}}-\hbar\omega_{\alpha\beta}^-}\right]\delta_{\gamma\xi}\\
&+\sum_{\alpha,\beta}\sum_{\mathbf{q}} \frac{\langle\beta|\gamma_{-\mathbf{q}}|\varepsilon\rangle}{\langle\delta|j_i|\varepsilon\rangle\delta_{\xi\gamma}-\langle\xi|j_i|\gamma\rangle\delta_{\varepsilon\beta}}[\langle\beta|\gamma_{\mathbf{q}}|\alpha\rangle\langle\alpha|j_i|\beta\rangle-\langle\alpha|\gamma_{\mathbf{q}}|\beta\rangle\langle\delta|j_i|\alpha\rangle]\\
&\times\left[\frac{N_{\mathbf{q}}+1-f_\beta}{\varepsilon_{\delta\beta}-\hbar\omega_{\mathbf{q}}-\hbar\omega_{\alpha\beta}^-}+\frac{N_{\mathbf{q}}+f_\beta}{\varepsilon_{\delta\beta}+\hbar\omega_{\mathbf{q}}-\hbar\omega_{\alpha\beta}^-}\right]\delta_{\gamma\xi}\\
&+\sum_{\alpha,\beta}\sum_{\mathbf{q}} \frac{\langle\beta|\gamma_{-\mathbf{q}}|\gamma\rangle}{\langle\delta|j_i|\varepsilon\rangle\delta_{\xi\gamma}-\langle\xi|j_i|\gamma\rangle\delta_{\varepsilon\delta}}[\langle\alpha|\gamma_{\mathbf{q}}|\beta\rangle\langle\xi|j_i|\alpha\rangle-\langle\xi|\gamma_{\mathbf{q}}|\alpha\rangle\langle\alpha|j_i|\beta\rangle]\\
&\times\left[\frac{N_{\mathbf{q}}+1-f_\beta}{\varepsilon_{\xi\beta}-\hbar\omega_{\mathbf{q}}-\hbar\omega_{\alpha\beta}^-}+\frac{N_{\mathbf{q}}+f_\beta}{\varepsilon_{\xi\beta}+\hbar\omega_{\mathbf{q}}-\hbar\omega_{\alpha\beta}^-}\right]\delta_{\varepsilon\delta}. \qquad (3.71)
\end{aligned}
$$

Here we have ignored the terms that are in proportion to the Fermi-Dirac distribution function $f_\alpha \equiv f(\varepsilon_\alpha)$ in $\Gamma(\omega_\alpha^-)$ and $\Gamma(\omega_\alpha^-,\omega_{\alpha\beta}^-)$.

IV. CONCLUSION

In the present paper we have given a formalism and a full account of the method of evaluation of linear and nonlinear conductivity tensors for an electron-phonon system. We relate the conductivity tensors to damping (relaxation) matrices, which reflect the effects of contributing frequencies of applied radiation fields as well as the collision processes between electrons and phonons. Thus the collisions between those phonons and electrons and those radiation field frequencies are responsible for the broadening of spectral line shape and can be studied theoretically by examining the real part of these conductivity tensors. The theory is developed independently of the single-particle representation (momentum, Landau, or other representation) and hence it can be applied irrespectively of the system studied. For the sake of demonstration, only the linear (in Sec. III B) and the lowest-order nonlinear (in Sec. III C) conductivities are calculated explicitly along with the rigorous expressions for the complex damping matrices $\Gamma^{(2)}_{\mu\nu}(\omega^-)$ in $\sigma_{ij}(\omega)$ and $\Gamma^{(2)}_{\varepsilon\xi\gamma\delta}(\omega_\alpha^-),\Gamma^{(2)}_{\varepsilon\xi\gamma\delta}(\omega_\alpha^-,\omega_{\alpha\beta}^-)$ in $\sigma^{(2)}_{ijk}(\omega_\alpha,\omega_\beta;\omega_\alpha+\omega_\beta)$ to order η^2 in an electron-phonon interaction. In these expressions for the damping matrices, the terms associated with the Fermi-Dirac distribution functions f_α and f_β describe the effects of exchange among electrons. If we ignore the effects of electron exchange by setting $f_\beta=0$, our result (3.14) reduces to the same quantity [9,10], which is obtained by assuming a system of one electron moving in a phonon field. We expect that the lowest-order nonlinear conductivity formula (3.69) along with Eqs. (3.70) and (3.71) can be applied to study nonlinear optical phenomena at finite temperatures such as sum-frequency generation [12,13] or second-harmonic generation [14–16] in solids. Finally, we have made the approximation (3.19), $\rho_{\rm eq}(\tilde{H})\simeq\rho_{\rm eq}(\tilde{H}_0)=\rho_{\rm e}(\tilde{H}_{\rm e})\otimes\rho_{\rm p}(H_{\rm p})$ to obtain the results. This approximation disregards initial correlations between electrons and phonons, which play a role of subtle interference effects between the applied fields and the scattering. However, in most cases of optical mixing problems in solids, the neglect of the electron-phonon interaction Hamiltonian in the initial density operator $\rho_{\rm eq}(\tilde{H})$ does not affect the features of the high-frequency optical conductivity for weakly interacting systems, which we have presented in this paper.

Although we have formulated the theory for an electron-phonon system, impurity effects on damping can be also included in the present theory; in the lowest-order approximation, the relaxation matrix due to phonons and static impurities is given by the sum of relaxations due to the phonon and the impurity scatterings. The formula for the relaxation matrix due to the impurity scattering can be obtained for a low impurity density case can be obtained simply by replacing H_{ep} by an electron-impurity interaction Hamiltonian H_{imp} in $\Gamma^{(2)}_{\mu\nu}$, which is written for an appropriate electron-impurity interaction potential in the second quantized form. We will leave the application of the present results to study the effect of the electron exchange and the effect of phonon (and/or) impurity scattering(s) on the optical mixing problems for future studies.

APPENDIX: DERIVATION OF THE SUM-FREQUENCY NONLINEAR CONDUCTIVITY FORMULA (3.48)

The sum-frequency second-order conductivity $\sigma^{(2)}_{ijk}\times(\omega_\alpha,\omega_\beta;\omega_\alpha+\omega_\beta)$ can be extracted from Eq. (3.46) by taking the residue of $\langle \mathbf{J}^{(2)}(\mathbf{q},z)\rangle/\Omega$ at $z=-\omega_\alpha-\omega_\beta+i\delta$:

$$\begin{aligned}
\mathrm{Res}\langle \mathbf{J}^{(2)}(\mathbf{q},z)\rangle/\Omega\big|_{z=-\omega_\alpha-\omega_\beta+i\delta} &= \frac{e^2}{\Omega}\,\mathrm{Tr}\{\mathbf{J}^{(0)}(\mathbf{q})G(-\omega_\alpha-\omega_\beta+i\delta)[\mathbf{R}\cdot\mathbf{E}^\beta,G(-\omega_\alpha+i\delta)[\mathbf{R}\cdot\mathbf{E}^\alpha,\rho_{\mathrm{eq}}]]\}\\
&= \frac{e^2}{\Omega}\sum_{j,k}\mathrm{Tr}\{\mathbf{J}^{(0)}(\mathbf{q})G(-\omega_\alpha-\omega_\beta+i\delta)[R_jE_j^\beta,G(-\omega_\alpha+i\delta)[R_kE_k^\alpha,\rho_{\mathrm{eq}}]]\}\\
&= \frac{e^2}{\Omega}\sum_{j,k}\mathrm{Tr}\{\mathbf{J}^{(0)}(\mathbf{q})G(-\omega_\alpha-\omega_\beta+i\delta)[R_j,G(-\omega_\alpha+i\delta)[R_k,\rho_{\mathrm{eq}}]]\}E_j^\beta E_k^\alpha\\
&= \frac{e^2}{\Omega}\sum_{j,k}\mathrm{Tr}\{\mathbf{J}^{(0)}(\mathbf{q})G(-\omega_\alpha-\omega_\beta+i\delta)R_j^\times G(-\omega_\alpha+i\delta)R_k^\times\rho_{\mathrm{eq}}\}E_j^\beta E_k^\alpha\\
&= -\boldsymbol{\sigma}^{(2)}(\omega_\alpha,\omega_\beta;\omega_\alpha+\omega_\beta):\mathbf{E}^\alpha\mathbf{E}^\beta,
\end{aligned}\tag{A1}$$

from which we can immediately write a general expression for the sum-frequency second-order conductivity as

$$\begin{aligned}
\sigma^{(2)}_{ijk}(\omega_\alpha,\omega_\beta;\omega_\alpha+\omega_\beta) &= -\frac{e^2}{\Omega}\,\mathrm{Tr}\{J_iG(-\omega_\alpha-\omega_\beta+i\delta)R_j^\times G(-\omega_\alpha+i\delta)R_k^\times\rho_{\mathrm{eq}}\}\\
&= -\frac{e^2}{\Omega}\,\mathrm{Tr}\{\rho_{\mathrm{eq}}R_k^\times G(\omega_\alpha-i\delta)R_j^\times G(\omega_\alpha+\omega_\beta-i\delta)J_i\}\quad (i,j,k=x,y,z),
\end{aligned}\tag{A2}$$

where $G(\omega_\alpha-i\delta)\equiv G(\omega_\alpha^-)$ and $G(\omega_\alpha+\omega_\beta-i\delta)\equiv G(\omega_{\alpha\beta}^-)$ are given by Eq. (3.13) and ρ_{eq} by Eq. (3.20). The many-body trace should be taken over the electron and the phonon coordinates.

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