General formulation for quantum macroscopic nonlinear optics

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We present a general formulation for quantum macroscopic nonlinear optics, which can be considered as a fully quantized version of its semiclassical counterpart in which the electric field is treated as the classical variable. Our formulation begins with the fundamental minimal-coupling Lagrangian, which is then transformed into the multipolar Lagrangian. After a quantum preservative expansion by using a Hamiltonian decomposition proposed in this paper, we have found the formal relations between the Heisenberg operators of macroscopic polarization density and macroscopic electric field. Finally, the linearized quantum effects for nonlinear optics are also discussed. © 2009 Optical Society of America

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1. INTRODUCTION

The quantum theory of light has a central place in modern optics. Although the standard theories of quantum electrodynamics have been well established, there are still certain application issues for one who wishes to use an effective macroscopic quantum model to describe light in bulk materials. Just like their classical counterparts, the effective quantum models should enable one to describe the macroscopic optical phenomena with the pregiven macroscopic quantities, such as linear and nonlinear susceptibilities, without being involved in the *ab initio* calculations at a microscopic level. Many research works have been carried out in the past. Nowadays, these kinds of effective quantum theories have been well established for linear optics [1–6]. For nonlinear optics, however, some ambiguities persist because of some important restrictive approximations made in previous works [7–11].

In this paper, we present a formal theory for macroscopic quantum optics, which relates the macroscopic polarization density to the macroscopic electric field. In Sec. 2, we begin our study with the fundamental minimal-coupling Lagrangian [12–14]. Following the procedure presented in [12], we will explicitly construct a multipolar matter-field Hamiltonian, which will then be quantized. In Sec. 3, we will decompose this Hamiltonian into the microscopic and the macroscopic parts defined in this paper. After a quantum perturbative expansion by using the explicit expression of macroscopic interaction Hamiltonian, we will be able to find the quantized relation between polarization density field and electric field. Finally, in Sec. 4, the linearized quantum effects for nonlinear optics will be discussed.

2. QUANTUM MULTIPOLAR MATTER-FIELD HAMILTONIAN

Neglecting spin, we can use the following minimal-coupling Lagrangian [12] to describe the nonrelativist dynamics of a material made up of charged particles interacting with the electromagnetic (EM) field:

$$L_0 = \frac{1}{2}\int (\varepsilon_0|\dot{\mathbf{A}} + \nabla\varphi|^2 - \mu_0^{-1}|\nabla \times \mathbf{A}|^2)\mathrm{d}^3\mathbf{r} + \frac{1}{2}\sum_{s,\alpha} m_{s\alpha}\dot{\mathbf{x}}_{s\alpha}^2 + \int (\mathbf{A}\cdot\mathbf{J} - \rho\varphi)\mathrm{d}^3\mathbf{r}, \tag{1}$$

with the charge density and the current density given by

$$\mathbf{J} = \sum_{s,\alpha} e_{s\alpha}\dot{\mathbf{x}}_{s\alpha}\delta(\mathbf{r} - \mathbf{x}_{s\alpha}), \quad \rho = \sum_{s,\alpha} e_{s\alpha}\delta(\mathbf{r} - \mathbf{x}_{s\alpha}), \tag{2}$$

where the point-headed variables stand for the total time derivative, e.g., $\dot{\mathbf{A}} = \mathrm{d}\mathbf{A}/\mathrm{d}t$; $\mathbf{x}_{s\alpha}$, $e_{s\alpha}$, and $m_{s\alpha}$ are, respectively, the coordinate (Cartesian vector), the electric charge, and the mass of a particle numerated by α in an assembly s, e.g., atom, molecule, etc; and the field variables $\mathbf{A}$ and φ are, respectively, the vector and the scalar potentials, which are related to the electric field $\mathbf{E}$ and the magnetic field $\mathbf{B}$ by the following familiar relations with an arbitrary gauge:

$$\mathbf{B} = \nabla \times \mathbf{A}, \quad \mathbf{E} = -\nabla\varphi - \dot{\mathbf{A}}. \tag{3}$$

Equation (3) is equivalent to the following two Maxwell's equations:

$$\nabla \cdot \mathbf{B} = 0, \quad \nabla \times \mathbf{E} + \frac{\partial \mathbf{B}}{\partial t} = 0. \tag{4}$$

Appling the Euler-Lagrange Eqs. (3) and (14) on Eqs. (1) and (2), we can find the other two Maxwell's equations,

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$$\nabla \cdot \mathbf{E} = \rho/\varepsilon_0, \qquad \nabla \times \mathbf{B} - \varepsilon_0\mu_0 \frac{\partial \mathbf{E}}{\partial t} = \mu_0 \mathbf{J} \tag{5}$$

and the Newtonian equation of motion for the charged particulars, i.e., the Lorentz force equation $m_{s\alpha}\ddot{\mathbf{x}}_{s\alpha} = e_{s\alpha}[\mathbf{E}(\mathbf{x}_{s\alpha}) + \dot{\mathbf{x}}_{s\alpha} \times \mathbf{B}(\mathbf{x}_{s\alpha})]$.

Now, consider an assembly whose mass center, total mass, and total charge are given by

$$\mathbf{R}_s = M_s^{-1} \sum_{\alpha} m_{s\alpha}\mathbf{x}_{s\alpha}, \quad M_s = \sum_{\alpha} m_{s\alpha}, \quad Q_s = \sum_{\alpha} e_{s\alpha}. \tag{6}$$

For the sake of simplicity, we assume all assemblies constitute a neutral system, i.e., $\Sigma_s Q_s = 0$. Then, we can introduce two auxiliary field for the assembly s: the polarization density $\mathbf{P}_s(\mathbf{r})$ and the magnetization density $\mathbf{M}_s(\mathbf{r})$, under the following forms:

$$\mathbf{P}_s(\mathbf{r}) = \sum_{\alpha} e_{s\alpha}(\mathbf{x}_{s\alpha} - \mathbf{R}_s) \int_0^1 \delta(\mathbf{r} - \mathbf{R}_s - \mu(\mathbf{x}_{s\alpha} - \mathbf{R}_s))\mathrm{d}\mu + Q_s \mathbf{R}_s \int_0^1 \delta(\mathbf{r} - \mu \mathbf{R}_s)\mathrm{d}\mu, \tag{7}$$

and

$$\mathbf{M}_s = \sum_{\alpha} \dot{\mathbf{x}}_{s\alpha} \times \mathbf{N}_{s\alpha} \tag{8}$$

with

$$\mathbf{N}_{s\alpha}(\mathbf{r}) = -e_{s\alpha}(\mathbf{x}_{s\alpha} - \mathbf{R}_s) \int_0^1 \frac{m_{s\alpha} + (M_s - m_{s\alpha})\mu}{M_s} \delta[(\mathbf{r} - \mathbf{R}_s) - \mu(\mathbf{x}_{s\alpha} - \mathbf{R}_s)]\mathrm{d}\mu - \frac{Q_s}{N_s}\mathbf{R}_s \int_0^1 \mu\delta(\mathbf{r} - \mu\mathbf{R}_m)\mathrm{d}\mu, \tag{9}$$

where N_s is the total number of particles in assembly s. The total polarization and magnetization densities are then given by

$$\mathbf{P}(\mathbf{r}) = \sum_s \mathbf{P}_s(\mathbf{r}), \quad \mathbf{M}(\mathbf{r}) = \sum_s \mathbf{M}_s(\mathbf{r}). \tag{10}$$

Thus, the charge density and the current density defined in Eq. (2) can be rewritten under the forms

$$\nabla \cdot \mathbf{P}(\mathbf{r}) = -\rho(\mathbf{r}), \quad \dot{\mathbf{P}}(\mathbf{r}) + \nabla \times \mathbf{M}(\mathbf{r}) = \mathbf{J}(\mathbf{r}), \tag{11}$$

and, therefore, Eq. (5) becomes

$$\nabla \cdot \mathbf{D} = 0, \qquad \nabla \times \mathbf{H} - \frac{\partial \mathbf{D}}{\partial t} = 0, \tag{12}$$

where the two new field variables are, as usual, given by

$$\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M}), \quad \mathbf{D} = \varepsilon_0\mathbf{E} + \mathbf{P}. \tag{13}$$

Separating the vector fields into the transverse and longitudinal parts that we denote, respectively, with "⊥" and "∥," and following the gauge-independent Lagrange-transformation procedure of [12], we can obtain the following multipolar Lagrangian from the minimal-coupling Lagrangian (1), by using Eq. (11):

$$L_R = \int \left(\frac{\varepsilon_0}{2}|\dot{\mathbf{A}}^{\perp}|^2 - \frac{1}{2\mu_0}|\nabla \times \mathbf{A}^{\perp}|^2 + \mathbf{M} \cdot \nabla \times \mathbf{A}^{\perp} - \dot{\mathbf{A}}^{\perp} \cdot \mathbf{P}^{\perp} \right)\mathrm{d}^3\mathbf{r} + \frac{1}{2}\sum_{s,\alpha} m_{s\alpha}\dot{\mathbf{x}}_{s\alpha}^2 - V_{\mathrm{Coulomb}}, \tag{14}$$

where

$$V_{\mathrm{Coulomb}} = \frac{1}{2\varepsilon_0}\int |\mathbf{P}^{\parallel}|^2 \mathrm{d}^3\mathbf{r} \tag{15}$$

is the total Coulomb interaction among all charges [12]. It is worth noting that the effective multipolar Lagrangian (14), equivalent to the minimal-coupling Lagrangian (1) in the absence of the external charged particles [13,14], contains only the transverse part of the vector potential. The construction of the Hamiltonian is then straightforward. The canonical momentum conjugates to the transverse vector potential $\mathbf{A}^{\perp}$ can be found as follows:

$$\mathbf{\Pi} = \frac{\delta L_R}{\delta \dot{\mathbf{A}}^{\perp}} = \varepsilon_0 \dot{\mathbf{A}}^{\perp} - \mathbf{P}^{\perp} = -\varepsilon_0\mathbf{E}^{\perp} - \mathbf{P}^{\perp} = -\mathbf{D}^{\perp} = -\mathbf{D}, \tag{16}$$

where we have used the relation $\mathbf{E}^{\perp} = -\dot{\mathbf{A}}^{\perp}$, and the momentum conjugates to the particle's coordinate $\mathbf{x}_{s\alpha}$ is

$$\mathbf{p}_{s\alpha} = \frac{\partial L_R}{\partial \dot{\mathbf{x}}_{s\alpha}} = m_{s\alpha}\dot{\mathbf{x}}_{s\alpha} + \int \mathbf{N}_{s\alpha} \times \mathbf{B}\mathrm{d}^3\mathbf{r}. \tag{17}$$

Then, with Eqs. (16) and (17), we can find the following Hamiltonian:

$$\begin{aligned} H &= \int \mathbf{\Pi} \cdot \dot{\mathbf{A}}^{\perp}\mathrm{d}^3\mathbf{r} + \sum_{s,\alpha} \mathbf{p}_{s\alpha} \cdot \dot{\mathbf{x}}_{s\alpha} - L_R \\ &= \frac{1}{2}\int (\varepsilon_0^{-1}|\mathbf{\Pi}|^2 + \mu_0^{-1}|\mathbf{B}|^2)\mathrm{d}^3\mathbf{r} + \sum_{s,\alpha} \frac{p_{s\alpha}^2}{2m_{s\alpha}} + \int \frac{|\mathbf{P}|^2}{2\varepsilon_0}\mathrm{d}^3\mathbf{r} \\ &\quad + \int \left(\frac{\mathbf{\Pi} \cdot \mathbf{P}}{\varepsilon_0} + \mathbf{B} \cdot \sum_{s,\alpha} \frac{\mathbf{p}_{s\alpha}}{m_{s\alpha}} \times \mathbf{N}_{s\alpha} \right)\mathrm{d}^3\mathbf{r} \\ &\quad + \sum_{s,\alpha} \frac{1}{2m_{s\alpha}} \left| \int \mathbf{N}_{s\alpha} \times \mathbf{B}\mathrm{d}^3\mathbf{r} \right|^2, \end{aligned} \tag{18}$$

where the terms of the second line are the free energies of the transverse EM field and the system of charged particles, and the terms of the third line are the interaction energies between the charged particles and the transverse EM field. It is worth noting that this Hamiltonian only contains the EM field's transverse degree of freedom. This is because, from Eqs. (11) and (12), we have $\mathbf{E}^{\parallel} = -\mathbf{P}^{\parallel}/\varepsilon_0$, which means the longitudinal electric field can be expressed in terms of the charged coordinates and hence belongs to the material's degrees of freedom [13].

Now, we can quantize the system by replacing dynamic variables with quantum operators that we denote with a caret "∧" and imposing the following canonical commutation relations:

$$[\hat{x}_{r\alpha,j},\hat{p}_{s\beta,k}]=i\hbar\delta_{r\alpha,s\beta}\delta_{jk},\quad [\hat{A}_j^{\perp}(\mathbf{r}),\hat{\Pi}_k(\mathbf{r}')]=i\hbar\delta_{jk}^{\perp}(\mathbf{r}-\mathbf{r}'), \tag{19}$$

where $\delta_{jk}^{\perp}(\mathbf{r}-\mathbf{r}')$ is the transverse Dirac tensor defined as follows:

$$\delta_{jk}^{\perp}(\mathbf{r}-\mathbf{r}')=(\partial_j^r\partial_k^r-\delta_{jk}\Delta^r)\frac{1}{4\pi|\mathbf{r}-\mathbf{r}'|}, \tag{20}$$

with $\partial_k^r=\partial/\partial x_k$. In the Heisenberg picture, using the equation of motion for Heisenberg operators, i.e., $\partial_t\hat{O}(t)=i\hbar^{-1}[\hat{H},\hat{O}(t)]$, one can find the following equations of motion with Hamiltonian (18):

$$\partial_t\hat{\mathbf{A}}^{\perp}=\varepsilon_0^{-1}(\hat{\mathbf{\Pi}}+\hat{\mathbf{P}}^{\perp}),$$

$$\partial_t\hat{\mathbf{\Pi}}=-\mu_0^{-1}\nabla\times\nabla\times\hat{\mathbf{A}}^{\perp}. \tag{21}$$

Thus, using $\hat{\mathbf{E}}^{\perp}=-\partial_t\hat{\mathbf{A}}^{\perp}$ and $\hat{\mathbf{D}}^{\parallel}=\varepsilon_0\hat{\mathbf{E}}^{\parallel}+\hat{\mathbf{P}}^{\parallel}=0$, we find the equation of motion for the electric field,

$$\nabla\times\nabla\times\hat{\mathbf{E}}+\varepsilon_0\mu_0\partial_t^2\hat{\mathbf{E}}=-\mu_0\partial_t^2\hat{\mathbf{P}}. \tag{22}$$

3. QUANTIZED MACROSCOPIC RELATIONS BETWEEN THE POLARIZATION DENSITY AND THE ELECTRIC-FIELD

A. Interaction picture and the decomposition of Hamiltonian

The polarization density should be a functional of the electric field. In order to find the relation between them, it is convenient to work with the interaction picture, in which the total Hamiltonian of the system can be decomposed into two parts: $\hat{H}=\hat{H}_0+\hat{H}_{\text{int}}$, with $\hat{H}_0$ and $\hat{H}_{\text{int}}$ being the Hamiltonians of the unperturbed system and the perturbation. In this picture, if $\hat{H}_0$ is time-independent, the operators are transformed as follows:

$$\hat{\mathbf{P}}^I(t)=\exp\left(\frac{i}{\hbar}\hat{H}_0t\right)\hat{\mathbf{P}}\exp\left(-\frac{i}{\hbar}\hat{H}_0t\right), \tag{23}$$

where the index "**I**" stands for the interaction picture. Heisenberg operators are related to interaction operators by [15]

$$\hat{\mathbf{P}}(t)=\hat{U}(t_0,t)\hat{\mathbf{P}}^I(t)\hat{U}(t,t_0) \tag{24}$$

where $\hat{U}(t,t_0)$ is a unitary evolution operator given by

$$\begin{aligned}\hat{U}(t,t_0)&=T\left(\exp\left[-\frac{i}{\hbar}\int_{t_0}^{t}\mathrm{d}s\hat{H}_{\text{int}}^I(s)\right]\right)\\&=1+\frac{1}{i\hbar}\int_{t_0}^{t}\mathrm{d}s_1\hat{H}_{int}^I(s_1)+\left(\frac{1}{i\hbar}\right)^2\int_{t_0}^{t}\mathrm{d}s_1\\&\quad\times\int_{t_0}^{s_1}\mathrm{d}s_2\hat{H}_{\text{int}}^I(s_1)\hat{H}_{\text{int}}^I(s_2)+\left(\frac{1}{i\hbar}\right)^3\int_{t_0}^{t}\mathrm{d}s_1\\&\quad\times\int_{t_0}^{s_1}\mathrm{d}s_2\int_{t_0}^{s_2}\mathrm{d}s_3\hat{H}_{\text{int}}^I(s_1)\hat{H}_{\text{int}}^I(s_2)\hat{H}_{\text{int}}^I(s_3)+\cdots,\end{aligned} \tag{25}$$

with $T(\bullet)$ being the time-ordering operator and $\hat{H}_{\text{int}}^I(t)$ defined as follows:

$$\hat{H}_{\text{int}}^I(t)=\exp\left(\frac{i}{\hbar}\hat{H}_0t\right)\hat{H}_{\text{int}}\exp\left(-\frac{i}{\hbar}\hat{H}_0t\right). \tag{26}$$

To decompose our system (18) into the unperturbed part and the perturbation, we note first that we can rewrite the spatial integrals in Eq. (18) as the integrals in reciprocal space because of Parseval's theorem. For example, we have

$$\int\hat{\mathbf{\Pi}}(\mathbf{r})\cdot\hat{\mathbf{P}}(\mathbf{r})\mathrm{d}^3\mathbf{r}=\int\underline{\hat{\mathbf{\Pi}}}(\mathbf{k})\cdot\underline{\hat{\mathbf{P}}}(-\mathbf{k})\mathrm{d}^3\mathbf{k}. \tag{27}$$

This implies that we can decompose these integrals in microscopic and macroscopic parts as follows:

$$\int\mathrm{d}^3\mathbf{r}\hat{\mathbf{\Pi}}(\mathbf{r})\cdot\hat{\mathbf{P}}(\mathbf{r})=\int_{\text{mac}}\mathrm{d}^3\mathbf{r}\hat{\mathbf{\Pi}}(\mathbf{r})\cdot\hat{\mathbf{P}}(\mathbf{r})+\int_{\text{mic}}\mathrm{d}^3\mathbf{r}\hat{\mathbf{\Pi}}(\mathbf{r})\cdot\hat{\mathbf{P}}(\mathbf{r}), \tag{28}$$

with

$$\int_{\text{mac}}\mathrm{d}^3\mathbf{r}\hat{\mathbf{\Pi}}(\mathbf{r})\cdot\hat{\mathbf{P}}(\mathbf{r})=\int_{|\mathbf{k}|<\frac{2\pi}{\Lambda_c}}\mathrm{d}^3\mathbf{k}\underline{\hat{\mathbf{\Pi}}}(\mathbf{k})\cdot\underline{\hat{\mathbf{P}}}(-\mathbf{k}) \tag{29}$$

and

$$\int_{\text{mic}}\mathrm{d}^3\mathbf{r}\hat{\mathbf{\Pi}}(\mathbf{r})\cdot\hat{\mathbf{P}}(\mathbf{r})=\int_{|\mathbf{k}|\geq\frac{2\pi}{\Lambda_c}}\mathrm{d}^3\mathbf{k}\underline{\hat{\mathbf{\Pi}}}(\mathbf{k})\cdot\underline{\hat{\mathbf{P}}}(-\mathbf{k}), \tag{30}$$

where Λ_c is a characteristic length much larger than the molecular size Λ_a and much smaller than the optical wavelengths λ, i.e., $\Lambda_a\ll\Lambda_c\ll\lambda$. Thus, we can decompose the Hamiltonian (18) as follows:

$$\hat{H}=\hat{H}_0+\hat{H}_{\text{int}}, \tag{31}$$

with $\hat{H}_0=\hat{H}_{\text{em}}^{\text{mac}}+\hat{H}_{\text{mic}}$, where

$$\begin{aligned}\hat{H}_{\text{mic}}&=\int_{\text{mic}}\frac{\varepsilon_0^{-1}|\hat{\mathbf{\Pi}}|^2+\mu_0^{-1}|\hat{\mathbf{B}}|^2}{2}\mathrm{d}^3\mathbf{r}+\sum_{s,\alpha}\frac{\hat{p}_{s\alpha}^2}{2m_{s\alpha}}+\int_{\text{mic}}\frac{|\hat{\mathbf{P}}|^2}{2\varepsilon_0}\mathrm{d}^3\mathbf{r}\\&\quad+\int_{\text{mic}}\left(\frac{\hat{\mathbf{\Pi}}\cdot\hat{\mathbf{P}}}{\varepsilon_0}+\hat{\mathbf{B}}\cdot\sum_{s,\alpha}\frac{\hat{\mathbf{p}}_{s\alpha}}{m_{s\alpha}}\times\hat{\mathbf{N}}_{s\alpha}\right)\mathrm{d}^3\mathbf{r}\\&\quad+\sum_{s,\alpha}\frac{1}{2m_{s\alpha}}\left|\int_{\text{mic}}\hat{\mathbf{N}}_{s\alpha}\times\hat{\mathbf{B}}\mathrm{d}^3\mathbf{r}\right|^2\end{aligned} \tag{32}$$

is the Hamiltonian for the microscopic dynamics and formally equivalent to Eq. (18), with all full-space integrals replaced by the corresponding microscopic integrals defined by Eq. (30),

$$\hat{H}_{\text{em}}^{\text{mac}} = \int_{\text{mac}} \frac{\varepsilon_0^{-1}|\hat{\mathbf{\Pi}}|^2 + \mu_0^{-1}|\hat{\mathbf{B}}|^2}{2}\mathrm{d}^3\mathbf{r} \tag{33}$$

is the Hamiltonian of the free macroscopic (long wevelength) transverse EM field, and

$$\hat{H}_{\text{int}} = \frac{1}{\varepsilon_0}\int_{\text{mac}} \hat{\mathbf{\Pi}}\cdot\hat{\mathbf{P}}\mathrm{d}^3\mathbf{r} + \frac{1}{2\varepsilon_0}\int_{\text{mac}} |\hat{\mathbf{P}}|^2\mathrm{d}^3\mathbf{r} \tag{34}$$

is the interaction Hamiltonian between the macroscopic transverse EM field and the material. In Eq. (34), the magnetic interaction has been neglected. Because Eq. (19) can be rewritten in reciprocal space under the form,

$$[\hat{\underline{A}}_m^{\perp}(\mathbf{k}),\hat{\underline{\Pi}}_n(\mathbf{k}')] = i\hbar\left(\delta_{mn} - \frac{k_m k_n}{k^2}\right)\delta(\mathbf{k}+\mathbf{k}'), \tag{35}$$

we have

$$[\hat{H}_{\text{em}}^{\text{mac}},\hat{H}_{mic}] = 0. \tag{36}$$

As a result, we see that the unperturbed system, i.e., $\hat{H}_0 = \hat{H}_{\text{em}}^{\text{mac}} + \hat{H}_{mic}$, consists of two systems independent of each other.

B. Perturbative expansion of the polarization density

To find the explicit relation between the polarization density $\hat{\mathbf{P}}$ and the electric field $\hat{\mathbf{E}}$, we shall use the following important relation:

$$\begin{aligned}
&\hat{U}(t_0,t)\hat{O}^I(t)\hat{U}(t,t_0)\\
&= \hat{O}^I(t) + \int_{t_0}^{t}\mathrm{d}t_1\frac{\partial}{\partial t_1}[\hat{U}(t_0,t_1)\hat{O}^I(t)\hat{U}(t_1,t_0)]\\
&= \hat{O}^I(t) + \int_{t_0}^{t}\mathrm{d}t_1\Bigg[\frac{\partial}{\partial t_1}\\
&\times\hat{U}(t_0,t_1)\hat{O}^I(t)\hat{U}(t_1,t_0) + \hat{U}(t_0,t_1)\hat{O}^I(t)\frac{\partial}{\partial t_1}\hat{U}(t_1,t_0)\Bigg]\\
&= \hat{O}^I(t) + \frac{i}{\hbar}\int_{t_0}^{t}\mathrm{d}t_1\hat{U}(t_0,t_1[\hat{H}_{\text{int}}^I(t_1),\hat{O}^I(t)])\hat{U}(t_1,t_0),
\end{aligned} \tag{37}$$

where we have used the following relations:

$$\frac{\partial\hat{U}}{\partial t}(t,t_0) = -\frac{i}{\hbar}\hat{H}_{\text{int}}^I(t)\hat{U}(t,t_0),$$

$$\frac{\partial\hat{U}}{\partial t}(t_0,t) = \frac{i}{\hbar}\hat{U}(t_0,t)\hat{H}_{\text{int}}^I(t). \tag{38}$$

Now, we set t_0 to $-\infty$ where we adiabatically launch the interaction. The interaction Hamiltonian in the interaction picture is given by

$$\hat{H}_{\text{int}}^I(t) = \frac{1}{\varepsilon_0}\int_{\text{mac}} \hat{\mathbf{\Pi}}^I(\mathbf{r},t)\cdot\hat{\mathbf{P}}^I(\mathbf{r},t)\mathrm{d}^3\mathbf{r} + \frac{1}{2\varepsilon_0}\int_{\text{mac}} |\hat{\mathbf{P}}^I(\mathbf{r},t)|^2\mathrm{d}^3\mathbf{r}. \tag{39}$$

In what follows, keeping in mind that we are treating the macroscopic phenomenon, we will omit the macroscopic indication under the integral symbol. To avoid the divergence of temporal integrals, we can conventionally multiply $\hat{H}_{\text{int}}^I$ by a time factor such that

$$\hat{H}_{\text{int}}^I(t) \to \hat{H}_{\text{int}}^I(t)\exp(-\epsilon|t|), \quad \text{with} \quad \epsilon \to 0_+. \tag{40}$$

Thus, using Eqs. (24), (37), and (39), we find

$$\begin{aligned}
\hat{P}_\mu(\mathbf{r},t) &= \hat{P}_\mu^I(\mathbf{r},t) + \frac{i}{\hbar}\int_{-\infty}^{t}\mathrm{d}t_1\hat{U}(-\infty,t_1)\\
&\quad\times[\hat{H}_{\text{int}}^I(t_1),\hat{P}_\mu^I(\mathbf{r},t)]\hat{U}(t_1,-\infty)\\
&= \hat{P}_\mu^I(\mathbf{r},t) + \frac{1}{i\hbar}\sum_{\alpha_1}\int\mathrm{d}^3\mathbf{r}_1\int_{-\infty}^{t}\mathrm{d}t_1\frac{1}{2}\hat{E}_{\alpha_1}(\mathbf{r}_1,t_1)\\
&\quad\times\hat{U}(-\infty,t_1)[\hat{P}_{\alpha_1}^I(\mathbf{r}_1,t_1),\hat{P}_\mu^I(\mathbf{r},t)]\hat{U}(t_1,-\infty)\\
&\quad+\frac{1}{i\hbar}\sum_{\alpha_1}\int\mathrm{d}^3\mathbf{r}_1\int_{-\infty}^{t}\mathrm{d}t_1\frac{1}{2}\hat{U}(-\infty,t_1)\\
&\quad\times[\hat{P}_{\alpha_1}^I(\mathbf{r}_1,t_1),\hat{P}_\mu^I(\mathbf{r},t)]\hat{U}(t_1,-\infty)\hat{E}_{\alpha_1}(\mathbf{r}_1,t_1),
\end{aligned} \tag{41}$$

where we have used $[\hat{\Pi}_{\alpha_1}^I(\mathbf{r}_1,t_1),\hat{P}_\mu^I(\mathbf{r},t)]=0$, $\hat{E}_{\alpha_1}^I = -\varepsilon_0^{-1}(\hat{\Pi}_{\alpha_1}^I + \hat{P}_{\alpha_1}^I)$, and the following identities:

$$\hat{U}(-\infty,t_1)\hat{E}_{\alpha_1}^I(\mathbf{r}_1,t_1) = \hat{E}_{\alpha_1}(\mathbf{r}_1,t_1)\hat{U}(-\infty,t_1),$$

$$\hat{E}_{\alpha_1}^I(\mathbf{r}_1,t_1)\hat{U}(t_1,-\infty) = \hat{U}(t_1,-\infty)\hat{E}_{\alpha_1}(\mathbf{r}_1,t_1). \tag{42}$$

For the sake of abbreviation, we define a symmetric Liouville superoperator for each operator $\hat{C}$ in Hilbert space denoted by "+" such that

$$\hat{C}_+\hat{O} = \frac{1}{2}(\hat{C}\hat{O} + \hat{O}\hat{C}). \tag{43}$$

So, we can rewrite Eq. (41) as follows:

$$\begin{aligned}
\hat{P}_\mu(\mathbf{r},t) &= \hat{P}_\mu^I(\mathbf{r},t) + \frac{1}{i\hbar}\sum_{\alpha_1}\int\mathrm{d}^3\mathbf{r}_1\int_{-\infty}^{t}\mathrm{d}t_1\hat{E}_{\alpha_1,+}(\mathbf{r}_1,t_1)\hat{U}(-\infty,t_1)\\
&\quad\times[\hat{P}_{\alpha_1}^I(\mathbf{r}_1,t_1),\hat{P}_\mu^I(\mathbf{r},t)]\hat{U}(t_1,-\infty).
\end{aligned} \tag{44}$$

Repeating the procedure of Eq. (41) to unwrap the term $\hat{U}(-\infty,t_m)[\hat{P}_{\alpha_m}^I(\mathbf{r}_m,t_m),[\bullet]]\hat{U}(t_m,-\infty)$, we arrive at a series expansion as follows:

$$\hat{P}_\mu(\mathbf{r},t) = \hat{P}_\mu^{(0)}(\mathbf{r},t) + \hat{P}_\mu^{(1)}(\mathbf{r},t) + \hat{P}_\mu^{(2)}(\mathbf{r},t) + \hat{P}_\mu^{(3)}(\mathbf{r},t) + \cdots, \tag{45}$$

where $\hat{P}_\mu^{(0)}(\mathbf{r},t) = \hat{P}_\mu^I(\mathbf{r},t)$, and for $n>0$, $\hat{P}_\mu^{(n)}$ is the nth-order polarization density given by

$$\hat{P}_{\mu}^{(n)}(\mathbf{r},t) = \int \mathrm{d}^3\mathbf{r}_1 \cdots \mathrm{d}^3\mathbf{r}_n \int_{-\infty}^{+\infty} \mathrm{d}\tau_1 \cdots \int_{-\infty}^{+\infty} \mathrm{d}\tau_n \times \hat{E}_{\alpha_1,+}(\mathbf{r}_1,\tau_1)\hat{E}_{\alpha_2,+}(\mathbf{r}_2,\tau_2)\cdots\hat{E}_{\alpha_n,+}(\mathbf{r}_n,\tau_n) \times \hat{G}^{(n)}_{\alpha_n\alpha_{n-1}\cdots\alpha_1\mu} \times (\mathbf{r}_n,\mathbf{r}_{n-1},\cdots,\mathbf{r}_1;\tau_n,\tau_{n-1},\cdots,\tau_1;\mathbf{r},t)m, \tag{46}$$

with the n-points Green's operator

$$\hat{G}^{(n)}_{\alpha_n\alpha_{n-1}\cdots\alpha_1\mu}(\mathbf{r}_n,\mathbf{r}_{n-1},\cdots,\mathbf{r}_1;\tau_n,\tau_{n-1},\cdots,\tau_1;\mathbf{r},t) = \left(\frac{1}{i\hbar}\right)^n \theta(t-\tau_1)\theta(\tau_1-\tau_2)\cdots\theta(\tau_{n-1}-\tau_n) \times [\hat{P}^I_{\alpha_n}(\mathbf{r}_n,\tau_n),[\cdots,[\hat{P}^I_{\alpha_2}(\mathbf{r}_2,\tau_2),[\hat{P}^I_{\alpha_1}(\mathbf{r}_1,\tau_1),\hat{P}^I_{\mu}(\mathbf{r},t)]]]] \tag{47}$$

and $\theta(t)$ being the Heaviside step function,

$$\theta(t) = \begin{cases} 1, & t \geq 0 \\ 0, & t < 0. \end{cases} \tag{48}$$

In Eq. (46), the Einstein summation convention on repeated indexes has been used. In the frequency domain, Eq. (46) can be rewritten as

$$\hat{P}_{\mu}^{(n)}(\mathbf{r},t) = \frac{\varepsilon_0}{(2\pi)^n}\int \mathrm{d}^3\mathbf{r}_1 \cdots \mathrm{d}^3\mathbf{r}_n \int_{-\infty}^{+\infty} \mathrm{d}\omega_1 \cdots \int_{-\infty}^{+\infty} \mathrm{d}\omega_n \times \hat{\underline{E}}_{\alpha_1,+}(\mathbf{r}_1,\omega_1)\hat{\underline{E}}_{\alpha_2,+}(\mathbf{r}_2,\omega_2)\cdots\hat{\underline{E}}_{\alpha_n,+}(\mathbf{r}_n,\omega_n) \times \hat{\chi}^{(n)}_{\alpha_n\alpha_{n-1}\cdots\alpha_1\mu}(\mathbf{r}_n,\mathbf{r}_{n-1},\cdots,\mathbf{r}_1;\omega_n,\omega_{n-1},\cdots,\omega_1;\mathbf{r},t) \times \exp\left(-i\sum_{l=1}^{n}\omega_l t\right), \tag{49}$$

or more compactly as

$$\hat{\underline{P}}_{\mu}^{(n)}(\mathbf{r},t) = \frac{\varepsilon_0}{(2\pi)^n}\int \mathrm{d}^{4n}\sigma \hat{\underline{E}}_{\alpha_1,+}\hat{\underline{E}}_{\alpha_2,+}\cdots\hat{\underline{E}}_{\alpha_n,+}\hat{\chi}^{(n)}_{\alpha_n\alpha_{n-1}\cdots\alpha_1\mu} \times (\mathbf{r},t)\exp\left(-i\sum_{l=1}^{n-1}\omega_l t\right), \tag{50}$$

with the nth-order electric susceptibility operator given by

$$\hat{\chi}^{(n)}_{\alpha_n\cdots\alpha_1\mu}(\mathbf{r}_n,\cdots,\mathbf{r}_1;\omega_n,\cdots,\omega_1;\mathbf{r},t) = \varepsilon_0^{-1}\int_{-\infty}^{+\infty}\mathrm{d}\tau_1\cdots\int_{-\infty}^{+\infty}\mathrm{d}\tau_n \hat{G}^{(n)}_{\alpha_n\cdots\alpha_1\mu}(\mathbf{r}_n,\cdots,\mathbf{r}_1;\tau_n,\cdots,\tau_1;\mathbf{r},t) \times \exp\left(i\sum_{l=1}^{n}\omega_l(t-\tau_l)\right). \tag{51}$$

Notice that we have used the following relation:

$$\hat{\mathbf{E}}(\mathbf{r},t) = \frac{1}{2\pi}\int_0^{+\infty}\hat{\underline{\mathbf{E}}}(\mathbf{r},\omega)\exp(-i\omega t)\mathrm{d}\omega + \mathrm{H.c.} \tag{52}$$

Equations (45)–(51) are therefore a quantized version of the standard macroscopic nonlinear optics [16] to recover which we only need to replace quantum operators in these equations with their classical values. In fact, if we consider the electric field as classical and write the interaction Hamiltonian in interaction picture as

$$\hat{H}^I_{\mathrm{int}}(t) = -\int \mathrm{d}^3\mathbf{r}E_{\alpha}(\mathbf{r},t)\cdot\hat{P}^I_{\alpha}(\mathbf{r},t), \tag{53}$$

using the same technique as for Eq. (45), we can find

$$\hat{P}_{\mu}^{(n)}(\mathbf{r},t) = \int \mathrm{d}^{4n}\sigma E_{\alpha_1}E_{\alpha_2}\cdots E_{\alpha_n}\hat{G}^{(n)}_{\alpha_n\alpha_{n-1}\cdots\alpha_1\mu}(\mathbf{r},t), \tag{54}$$

where the Green's operator is the same as given by Eq. (47). This is the reason why we did not put the second term of interaction Hamiltonian (34) into the unperturbed system. Indeed, if we only kept the first term of Eq. (34), the polarization density would become the response to the displacement field instead of the electric field, which is in disaccord with the conventional nonlinear optics formalism.

C. Some discussions

In Sec. 3.A, we have decomposed our system into the microscopic and the macroscopic parts, and this last one is the sum of the macroscopic EM field and its interaction with the microscopic part. In what follows, we will assume that the characteristic distance Λ_c can be chosen short enough that the microscopic Hamiltonian $\hat{H}_{\mathrm{mic}}$ is approximately the Hamiltonian of the material. That is to say, without external perturbations, the impact of the intrinsic macroscopic optical radiation is negligible. This should be verified in the dielectrics in which the electrons are bounded, and the direct interactions between charged particles at a macroscopic scale ($\sim\Lambda_c$) are negligible. Indeed, without perturbations, the macroscopic fields originate from the material's spontaneous fluctuations, which are very weak at optical frequencies. Besides, it is of interest to note that in Eq. (32) we did not extract the microscopic matter-field interaction term of $\varepsilon_0^{-1}\int_{\mathrm{mic}}\hat{\mathbf{\Pi}}(\mathbf{r})\cdot\hat{\mathbf{P}}(\mathbf{r})\mathrm{d}^3\mathbf{r}$ from the material's unperturbed Hamiltonian, i.e., $\hat{H}_{\mathrm{mic}}$. This is because—as a matter of fact—for neutral assemblies, all the intermolecule interactions are mediated through the exchange of transverse photons [12,14]. Thus, a material's Hamiltonian should consist of the Hamiltonians of molecules, EM field, and the interactions between them, which are principally microscopic. In fact, this implies that our formalization above has already taken into account the local field correction [16], unlike in the classical calculations of nonlinear susceptibilities where we consider—at first—the molecules as independent to each other.

The electric susceptibility operator (51) depends on the absolute time t. This reflects the fact that the material's response functions are not stationary. Indeed, if adopting the conventional assumption that the unperturbed system is originally in thermal state, whose density matrix is given by

$$\hat{\rho}_{\mathrm{th}} = \frac{\exp(-\hat{H}_{\mathrm{mic}}/K_B T)}{\mathrm{tr}[\exp(-\hat{H}_{\mathrm{mic}}/K_B T)]}, \tag{55}$$

and hence commutes with the unperturbed Hamiltonian, i.e., $\hat{H}_{\mathrm{mic}}$, one can find that the quantum expectation of the Green's operators is independent on the absolute time t,

$$\begin{aligned}\langle \hat{G}^{(n)}_{\alpha_n\cdots\alpha_1\mu}(\tau_n, \ldots, \tau_1;\mathbf{r},t)\rangle &= \mathrm{tr}[\hat{\rho}_{\mathrm{th}}\hat{G}^{(n)}_{\alpha_n\cdots\alpha_1\mu}(\tau_n, \ldots, \tau_1;\mathbf{r},t)] \\ &= \mathrm{tr}[\hat{\rho}_{\mathrm{th}}\hat{G}^{(n)}_{\alpha_n\cdots\alpha_1\mu}(\tau_n - t, \ldots, \tau_1 \\ &\quad - t;\mathbf{r},0)] = G^{(n)}_{\alpha_n\cdots\alpha_1\mu}(\tau_n - t, \ldots, \tau_1 \\ &\quad - t;\mathbf{r})\end{aligned} \tag{56}$$

and, therefore, the susceptibilities or the quantum expectation of the susceptibility operators are time independent, i.e.,

$$\langle \hat{\chi}^{(n)}_{\alpha_n\cdots\alpha_1\mu}(\mathbf{r},t)\rangle = \chi^{(n)}_{\alpha_n\cdots\alpha_1\mu}(\mathbf{r}). \tag{57}$$

Thus, the susceptibility operators can be decomposed into the classical part and the time-dependent quantum fluctuations part,

$$\hat{\chi}^{(n)}_{\alpha_n\cdots\alpha_1\mu}(\mathbf{r},t) = \chi^{(n)}_{\alpha_n\cdots\alpha_1\mu}(\mathbf{r}) + \Delta\hat{\chi}^{(n)}_{\alpha_n\cdots\alpha_1\mu}(\mathbf{r},t), \tag{58}$$

and we can rewrite the nth-order polarization density operator under the form,

$$\hat{P}^{(n)}_{\mu}(\mathbf{r},t) = \hat{\mathcal{P}}^{(n)}_{\mu}(\mathbf{r},t) + \Delta\hat{P}^{(n)}_{\mu}(\mathbf{r},t), \tag{59}$$

with

$$\begin{aligned}\hat{\mathcal{P}}^{(n)}_{\mu}(\mathbf{r},t) &= \frac{\varepsilon_0}{(2\pi)^n}\int \mathrm{d}^{4n}\sigma\chi^{(n)}_{\alpha_n\alpha_{n-1}\cdots\alpha_1\mu} \\ &\quad \times(\mathbf{r})\hat{\underline{E}}_{\alpha_1,+}\cdots\hat{\underline{E}}_{\alpha_{n-1},+}\hat{\underline{E}}_{\alpha_n}\exp\left(-i\sum_{l=1}^{n}\omega_l t\right),\end{aligned} \tag{60}$$

representing the nth-order response of the material to the electric field, and

$$\begin{aligned}\Delta\hat{P}^{(n)}_{\mu}(\mathbf{r},t) &= \frac{\varepsilon_0}{(2\pi)^n}\int \mathrm{d}^{4n}\sigma\hat{\underline{E}}_{\alpha_1,+}\cdots\hat{\underline{E}}_{\alpha_{n-1},+}\hat{\underline{E}}_{\alpha_n}\Delta\hat{\chi}^{(n)}_{\alpha_n\alpha_{n-1}\cdots\alpha_1\mu} \\ &\quad \times(\mathbf{r},t)\exp\left(-i\sum_{l=1}^{n}\omega_l t\right),\end{aligned} \tag{61}$$

representing the nth-order mixing of material's spontaneous fluctuations and the electric field. The total polarization density is, therefore, the sum of the material's response to the electric field and the mixing of material's spontaneous fluctuations with the electric field.

4. FORMAL RELATION FOR LINEARIZED QUANTUM EFFECTS

Although Eqs. (60) and (61) are rather general, there are some calculus difficulties due to the noncommutative nature of quantum operators. This problem remains open for future research. In what follows, we will assume for further discussions that, over the wavelengths of interest, we can consider the macroscopic electric field as the sum of a classical intense coherent field and a small quantum one, i.e., $\hat{\mathbf{E}} = \mathbf{E} + \Delta\hat{\mathbf{E}}$. This later can be considered as the quantum fluctuations noise or a small nonclassical quantum field. In practice, this is usually the case, for example, in the parametric fluorescence [17], where the pump is generally coherent and intense and the created entangled photon-pairs number is small. Another example is the fiber Raman amplifiers [18] where the pump and the signal are both coherent and intense, and the quantum effect is related to a relatively small fluctuating quantum noise. Thus, we can linearize Eqs. (60) and (61) in terms of quantum fluctuations, by only retaining in Eq. (60) the terms linear in $\Delta\hat{\mathbf{E}}$ and replacing $\hat{\mathbf{E}}$ by $\mathbf{E}$ in Eq. (60). With this approximation, Eq. (60) becomes $\hat{\mathcal{P}}^{(n)}_{\mu} = P^{(n)}_{\mu} + \Delta\hat{\mathcal{P}}^{(n)}_{\mu}$, where $P^{(n)}_{\mu}$ is the classical nth-order polarization density, and

$$\Delta\hat{\mathcal{P}}^{(n)}_{\mu}(\mathbf{r},t) = n\int \mathrm{d}^{4n}\sigma\Delta\hat{E}_{\alpha_1}E_{\alpha_2}\cdots E_{\alpha_{n-1}}E_{\alpha_n}G^{(n)}_{\alpha_n\alpha_{n-1}\cdots\alpha_1\mu}(\mathbf{r}) \tag{62}$$

is the material's nth-order response to the quantum fluctuations of the electric field. Equation (61) becomes

$$\Delta\hat{P}^{(n)}_{\mu}(\mathbf{r},t) = \int \mathrm{d}^{4n}\sigma E_{\alpha_1}\cdots E_{\alpha_{n-1}}E_{\alpha_n}\Delta\hat{G}^{(n)}_{\alpha_n\alpha_{n-1}\cdots\alpha_1\mu}(\mathbf{r},t), \tag{63}$$

which is due to the material's nth-order spontaneous fluctuations. Notice that, when deriving Eq. (62), since there is no longer the operator-ordering problem, we used the fact that only the part having the following permutation symmetry property contributes to the integral of Eq. (62):

$$\begin{aligned}&G^{(n)}_{\alpha_n\cdots\alpha_p\cdots\alpha_q\cdots\alpha_1\mu} \\ &\quad \times(\mathbf{r}_n, \ldots, \mathbf{r}_p, \ldots, \mathbf{r}_q, \ldots, \mathbf{r}_1;t_n, \ldots, t_p, \ldots, t_q, \ldots, t_1;\mathbf{r}) \\ &= G^{(n)}_{\alpha_n\cdots\alpha_q\cdots\alpha_p\cdots\alpha_1\mu} \\ &\quad \times(\mathbf{r}_n, \ldots, \mathbf{r}_q, \ldots, \mathbf{r}_p, \ldots, \mathbf{r}_1;t_n, \ldots, t_q, \ldots, t_p, \ldots, t_1;\mathbf{r}).\end{aligned} \tag{64}$$

Equation (62) implies that we can now write the total material's response to the quantum fluctuations of the electric field as follows:

$$\begin{aligned}\Delta\hat{\mathcal{P}}_{\mu}(\mathbf{r},t) &= \sum_n \Delta\hat{\mathcal{P}}^{(n)}_{\mu}(\mathbf{r},t) \\ &= \varepsilon_0\int \mathrm{d}^3\mathbf{r}_1\int_{-\infty}^{+\infty}\mathrm{d}t_1\Delta\hat{E}_{\alpha_1}(\mathbf{r}_1,t_1)R_{\alpha_1\mu}(\mathbf{r}_1,t_1,\mathbf{r},t),\end{aligned} \tag{65}$$

where

$$\begin{aligned}R_{\alpha_1\mu}(\mathbf{r}_1,t_1,\mathbf{r},t) &= \sum_n R^{(n)}_{\alpha_1\mu}(\mathbf{r}_1,t_1,\mathbf{r},t) \\ &= \theta(t - t_1)\sum_n \frac{n}{\varepsilon_0}\int \mathrm{d}^{4(n-1)} \\ &\quad \times\sigma G^{(n)}_{\alpha_n\cdots\alpha_2\alpha_1\mu}E_{\alpha_2}\cdots E_{\alpha_n}\end{aligned} \tag{66}$$

is the total response function, which explicitly depends on the classical electric field and is generally nonstationary. For the sake of simplicity, we assume that the response is spatially local, which means we have in frequency domain

$$\underline{\underline{R}}_{\alpha_1\mu}(\mathbf{r}_1,\omega_1,\mathbf{r},\omega)=2\pi\delta(\mathbf{r}-\mathbf{r}_1)\chi_{\alpha_1\mu}(\mathbf{r},\omega_1,\omega), \tag{67}$$

where the effective electric susceptibility can be found under the form,

$$\begin{aligned}\chi_{\alpha\beta}(\mathbf{r},-\omega_1,\omega)=\chi^{(1)}_{\alpha\beta}(\omega)\,\delta(\omega-\omega_1)&\\ +\frac{1}{\pi}\underline{E}_{\alpha_2}(\omega-\omega_1)\chi^{(2)}_{\alpha_2\alpha\beta}(\omega-\omega_1,\omega_1)&\\ +\frac{3}{(2\pi)^2}\int_{-\infty}^{+\infty}\mathrm{d}\omega_2\underline{E}_{\alpha_2}(\omega-\omega_2)\underline{E}_{\alpha_3}(\omega_2-\omega_1)&\\ \times\chi^{(3)}_{\alpha_3\alpha_2\alpha\beta}(\omega_2-\omega_1,\omega-\omega_2,\omega_1)+\cdots&\end{aligned} \tag{68}$$

Thus, from Eqs. (65)–(67), we have

$$\Delta\hat{\underline{P}}_{\mu}(\mathbf{r},\omega)=\varepsilon_0\int_{-\infty}^{+\infty}\mathrm{d}\omega_1\Delta\hat{\underline{E}}_{\alpha_1}(\mathbf{r},\omega_1)\chi_{\alpha_1\mu}(\mathbf{r},-\omega_1,\omega). \tag{69}$$

From Eq. (22), the quasilinearized equation of propagation for the electric field's quantum fluctuations is therefore written as

$$\begin{aligned}\nabla\times\nabla\times\Delta\hat{\underline{\mathbf{E}}}(\mathbf{r},\omega)-\frac{\omega^2}{c^2}\int_{-\infty}^{+\infty}\mathrm{d}\omega_1\boldsymbol{\varepsilon}(\mathbf{r},\omega,\omega_1)\Delta\hat{\underline{\mathbf{E}}}(\mathbf{r},\omega_1)&\\ =-\omega^2\mu_0\Delta\hat{\underline{\mathbf{P}}}(\mathbf{r},\omega),&\end{aligned} \tag{70}$$

where $\varepsilon_{\alpha\beta}(\mathbf{r},\omega,\omega_1)=\delta_{\alpha\beta}\delta(\omega-\omega_1)+\chi_{\beta\alpha}(\mathbf{r},-\omega_1,\omega)$ is the effective relative permittivity. It is worth noting that the frequency integral of Eq. (70) is over the entire real axis, and, thus, the positive and negative frequency components are coupled.

Since Eq. (70) is linear, its solution can be represented under the form

$$\Delta\hat{\underline{\mathbf{E}}}(\mathbf{r},\omega)=-\mu_0\int\omega\omega_1\mathbf{G}(\mathbf{r},\omega,\mathbf{r}_1,\omega_1)\Delta\hat{\underline{\mathbf{P}}}(\mathbf{r}_1,\omega_1)\mathrm{d}^3\mathbf{r}_1\mathrm{d}\omega_1, \tag{71}$$

where the two-dimensional (2D) Green's tensor is defined as the solution of the following equation:

$$\begin{aligned}\nabla\times\nabla\times\mathbf{G}(\mathbf{r},\omega,\mathbf{r}_1,\omega_1)-\int\mathrm{d}\omega_2\frac{\omega}{c}\boldsymbol{\varepsilon}(\mathbf{r},\omega,\omega_2)\frac{\omega_2}{c}\mathbf{G}(\mathbf{r},\omega_2,\mathbf{r}_1,\omega_1)&\\ =\mathbf{I}\delta(\mathbf{r}-\mathbf{r}_1)\delta(\omega-\omega_1).&\end{aligned} \tag{72}$$

It is easy to verify that the following relations hold:

$$\mathbf{G}(\mathbf{r},\omega,\mathbf{r}_1,\omega_1)=\mathbf{G}^T(\mathbf{r}_1,\omega_1,\mathbf{r},\omega), \tag{73}$$

$$\mathbf{G}^*(\mathbf{r},\omega,\mathbf{r}_1,\omega_1)=\mathbf{G}(\mathbf{r}_1,-\omega_1,\mathbf{r},-\omega), \tag{74}$$

and

$$\begin{aligned}\mathrm{Im}\,\mathbf{G}(\mathbf{r}_2,\omega_2,\mathbf{r}_1,\omega_1)&=\frac{1}{2i}[\mathbf{G}(\mathbf{r}_2,\omega_2,\mathbf{r}_1,\omega_1)-\mathbf{G}^{\dagger}(\mathbf{r}_1,\omega_1,\mathbf{r}_2,\omega_2)]\\ &=\int\mathbf{G}^{\dagger}(\mathbf{r},\omega,\mathbf{r}_2,\omega_2)\frac{\omega}{c}\boldsymbol{\varepsilon}_A(\mathbf{r},\omega,\omega_3)\frac{\omega_3}{c}\\ &\quad\times\mathbf{G}(\mathbf{r},\omega_3,\mathbf{r}_1,\omega_1)\mathrm{d}^3\mathbf{r}\mathrm{d}\omega\mathrm{d}\omega_3,\end{aligned} \tag{75}$$

with $\boldsymbol{\varepsilon}_A(\mathbf{r},\omega,\omega_1)=[\boldsymbol{\varepsilon}(\mathbf{r},\omega,\omega_1)-\boldsymbol{\varepsilon}^{\dagger}(\mathbf{r},\omega_1,\omega)]/2i$, whose explicit expression can be found by simply replacing $\chi^{(n)}_{\cdots\alpha\beta}\times(\cdots,\omega_1)$ of Eq. (68) by $[\chi^{(n)}_{\cdots\alpha\beta}(\cdots,\omega_1)-\chi^{(n)}_{\cdots\beta\alpha}(\cdots,-\omega)]/2i$. In the Appendix, we have proven that the following relation holds:

$$\begin{aligned}R^{(n)}_{\alpha_1\mu}(\mathbf{r}_1,t_1,\mathbf{r},t)&=\frac{\theta(t-t_1)}{i\hbar\varepsilon_0}\langle[\Delta\hat{P}_{\alpha_1}(\mathbf{r}_1,t_1),\Delta\hat{P}_{\mu}(\mathbf{r},t)]\rangle^{(n-1)}\\ &=\frac{\theta(t-t_1)}{i\hbar\varepsilon_0}\sum_{m=0}^{n-1}\langle[\Delta\hat{P}^{(m)}_{\alpha_1}(\mathbf{r}_1,t_1),\Delta\hat{P}^{(n-m-1)}_{\mu}(\mathbf{r},t)]\rangle.\end{aligned} \tag{76}$$

Thus, since $\Delta\hat{\underline{P}}^{\dagger}_{\mu}(\omega)=\Delta\hat{\underline{P}}_{\mu}(-\omega)$, we can find the following relation for material's total spontaneous fluctuations:

$$\langle[\Delta\hat{\underline{P}}_{\alpha}(\mathbf{r},\omega),\Delta\hat{\underline{P}}^{\dagger}_{\beta}(\mathbf{r}_1,\omega_1)]\rangle=4\pi\hbar\varepsilon_0\varepsilon_{A,\alpha\beta}(\mathbf{r},\omega,\omega_1)\,\delta(\mathbf{r}-\mathbf{r}_1), \tag{77}$$

which can be considered as a fluctuation-dissipation relation [5,15,19]. Due to Eq. (77), the material's spontaneous fluctuations should be approximated to the $(n-1)$th order for an effective electric susceptibility approximated to the nth order. When an effective electric susceptibility is already given, however, we do not really need to write out the explicit expression for the spontaneous fluctuations. Finally, with Eq. (77) and using Eqs. (71) and (75), we can find

$$\langle[\Delta\hat{\underline{E}}_{\alpha}(\mathbf{r}_2,\omega_2),\Delta\hat{\underline{E}}^{\dagger}_{\beta}(\mathbf{r}_1,\omega_1)]\rangle=\frac{\hbar\omega_1\omega_2}{c^2\varepsilon_0}4\pi\,\mathrm{Im}\,G_{\alpha\beta}(\mathbf{r}_2,\omega_2,\mathbf{r}_1,\omega_1). \tag{78}$$

This result is in good agreement with the previous work for linear optics [5] in which the frequency dependence of the Green's tensor is $\delta(\omega_2-\omega_1)$. We see that it is in general not the case for nonlinear optics, since nonlinear effects can create new frequency components, which are, therefore, quantum entangled.

5. CONCLUSION

In this paper, we have presented a general formulation for quantum macroscopic nonlinear optics by decomposing the multipolar matter-field Hamiltonian (18) into the microscopic and the macroscopic parts. Equations (45)–(51) can be considered as a fully quantized version of standard nonlinear optics formalism. Our development is gauge independent and independent of the choice of the explicit expression of the material's Hamiltonian. To our knowledge, this is the first time that a general quantum relation between the Heisenberg operators of the macroscopic polarization density and the macroscopic electric field is discussed.

Moreover, we have discussed the quantum effects with the quasilinearization approximation, which enables us to study the quantum effects in a frame of the linear response theory. We have shown that the response function or the effective permittivity is generally nonstationary due to the nonlinear coupling. Equations (77) and (78) can be understood as the fluctuation-dissipation relations. Different from linear optics, the quantum fluctuations in nonlinear optics are generally nonstationary and hence correlated in frequency.

APPENDIX

To prove Eq. (76), we will first define the following evolution operator that depends on an extra parameter λ:

$$\hat{U}(t,t_0;\lambda) = T\left(\exp\frac{i\lambda}{\hbar}\int_{t_0}^{t} \mathrm{d}t_1 \hat{H}^{I}_{\mathrm{int}}(t_1)\right), \tag{A1}$$

where $\hat{H}^{I}_{\mathrm{int}}(t_1)$ is the semiclassical Hamiltonian given by Eq. (53). With this evolution operator, we can define the following λ-parametered polarization density operator:

$$\hat{P}_{\mu}(\mathbf{r},t;\lambda) = \hat{U}(-\infty,t;\lambda)\hat{P}^{I}_{\mu}(\mathbf{r},t)\hat{U}(t,-\infty;\lambda). \tag{A2}$$

Therefore, we have $\hat{P}_{\mu}(\mathbf{r},t)=\hat{P}_{\mu}(\mathbf{r},t;\lambda=1)$ and $\hat{P}^{I}_{\mu}(\mathbf{r},t)=\hat{P}_{\mu}(\mathbf{r},t;\lambda=0)$. Hence, the nth-order semiclassical polarization density operator given by Eq. (54) can also be regarded as the nth-order coefficient of the Taylor's expansion of Eq. (A2) about $\lambda=0$, that is to say

$$\hat{P}^{(n)}_{\mu}(\mathbf{r},t) = \left.\frac{1}{n!}\frac{\partial^n \hat{P}_{\mu}(\mathbf{r},t;\lambda)}{\partial \lambda^n}\right|_{\lambda=0}. \tag{A3}$$

Using the properties of the evolution operators expressed explicitly by Eq. (37), it is not difficult to prove

$$\frac{\partial \hat{U}(t,-\infty;\lambda)}{\partial\lambda} = \hat{U}(t,-\infty;\lambda)\frac{i}{\hbar}\int_{-\infty}^{t}\mathrm{d}t_1\int \mathrm{d}^3\mathbf{r}_1 E_{\alpha_1} \times(\mathbf{r}_1,t_1)\hat{P}_{\alpha_1}(\mathbf{r}_1,t_1;\lambda). \tag{A4}$$

Thus, using Eq. (A3), we have

$$\begin{aligned}\hat{P}^{(n)}_{\mu}(\mathbf{r},t) &= \frac{1}{n!\,i\hbar}\int_{-\infty}^{t}\mathrm{d}t_1\int \mathrm{d}^3\mathbf{r}_1 E_{\alpha_1}(\mathbf{r}_1,t_1) \times\left.\frac{\partial^{n-1}[\hat{P}_{\alpha_1}(\mathbf{r}_1,t_1;\lambda),\hat{P}_{\mu}(\mathbf{r},t;\lambda)]}{\partial\lambda^{n-1}}\right|_{\lambda=0}\\ &= \frac{1}{in\hbar}\int_{-\infty}^{t}\mathrm{d}t_1\int \mathrm{d}^3\mathbf{r}_1 E_{\alpha_1}(\mathbf{r}_1,t_1) \times[\hat{P}_{\alpha_1}(\mathbf{r}_1,t_1),\hat{P}_{\mu}(\mathbf{r},t)]^{(n-1)}\\ &= \frac{1}{in\hbar}\int_{-\infty}^{t}\mathrm{d}t_1\int \mathrm{d}^3\mathbf{r}_1 E_{\alpha_1}(\mathbf{r}_1,t_1) \times\sum_{m=0}^{n-1}[\hat{P}^{(m)}_{\alpha_1}(\mathbf{r}_1,t_1),\hat{P}^{(n-1-m)}_{\mu}(\mathbf{r},t)].\end{aligned} \tag{A5}$$

Now, since $[\hat{P}_{\alpha_1}(\mathbf{r}_1,t_1),\hat{P}_{\mu}(\mathbf{r},t)]=[\Delta\hat{P}_{\alpha_1}(\mathbf{r}_1,t_1),\Delta\hat{P}_{\mu}(\mathbf{r},t)]$, comparing Eq. (A5) with Eq. (54), we find

$$\int \mathrm{d}^{4(n-1)}\sigma E_{\alpha_2}\cdots E_{\alpha_n}\hat{G}^{(n)}_{\alpha_n\alpha_{n-1}\cdots\alpha_1\mu}(\mathbf{r},t) = \frac{\theta(t-t_1)}{in\hbar}[\Delta\hat{P}_{\alpha_1}(\mathbf{r}_1,t_1),\Delta\hat{P}_{\mu}(\mathbf{r},t)]^{(n-1)}. \tag{A6}$$

Thus, replacing Eq. (A6) in Eq. (66), we obtain Eq. (76).

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