Path integral formulation of retardation effects in nonlinear optics

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The signatures of retardation in nonlinear optical susceptibilities are studied by starting with the multipolar Hamiltonian and using path integral techniques to develop a perturbative scheme for incorporating the retarded interaction with the electromagnetic field. The present approach accounts for cooperative radiative decay and polariton transport which show up in resonant spectroscopies of nanostructures. These effects, which require a quantum electrodynamical description of the field, are missed by conventional nonretarded theories. Application is made to the enhanced spontaneous emission rate of biexcitons, which may show up in the nonlinear reflection off molecular superlattices.

I. INTRODUCTION

Nonlinear optical signals are usually calculated by first calculating a nonlinear susceptibility defined by expanding the optical polarization in powers of the transverse electric field, and then solving the Maxwell equations for the field, using the susceptibilities as input.[1] Normally the susceptibilities are calculated using a semiclassical procedure whereby the material degrees of freedom are treated quantum mechanically whereas the Maxwell field is assumed classical. In this approximation, the optical susceptibilities are purely material quantities which contain no signatures of retardation, and can therefore be calculated using the eigenvalues and dipole matrix elements of the purely material Hamiltonian. Retardation effects in the optical signal show up in this procedure only in the second step, when the Maxwell equations are solved and the signal is related to the applied (external) field.[2-4] For example, radiative linewidth in linear optical measurements which is absent in the linear susceptibilities $\chi^{(1)}(\mathbf{k},\omega)$ [and the dielectric function $\epsilon(\mathbf{k},\omega)$] will show up in linear optical signals such as reflection of light off an interface or a thin layer (quantum well). (Note that radiative linewidth is included in linear susceptibilities defined with respect to total Maxwell field.[3-5]) Since retardation effects appear only in the connection of the Maxwell and the external fields, and since the Maxwell field is expressed in terms of the external field in the framework of linear optics, all effects of retardation for the nonlinear signal in this approach are associated with linear optics.

Resonant nonlinear measurements, show effects that are missed by this procedure. These include cooperative radiative decay of excitons,[6-12] and polariton dephasing and transport,[2,13-17] which were probed in transient grating measurements[18] and two photon absorption[19] in anthracene and napththalene crystals. These effects are particularly interesting and significant in nanostructures such as molecular multilayers (superlattices),[6,7,20-22] chains,[4,9,10,22,23] and clusters.[24-26] For example, spontaneous emission which is absent in three-dimensional crystals[13] does show up in restricted geometries where spontaneous photons can leave the system.[8-10] The enhanced optical nonlinearities induced by exciton confinement and the existence of surface modes may lead to dramatic effects whose systematic incorporation in the formalism remains an open question.

In this paper we address this problem by abandoning the semiclassical approximation and formulating it using a microscopic quantum electrodynamical description of the material system and the radiation field. A Green's function perturbative technique is developed for incorporating radiative corrections in nonlinear susceptibilities. We first express the expectation value of the transverse Maxwell field in terms of correlation functions of electric field operators in the joint matter and field system, calculated in the absence of external sources. We then recast the correlation functions in the form of path integrals over material and electromagnetic field variables. This allows us to eliminate the material variables and express the correlation functions in the form of path integrals over the vector potential alone, using an effective action for the field. The necessary correlation functions of the electromagnetic field are then calculated in a reduced space containing the electromagnetic field alone. We then construct a perturbation theory and a diagrammatic technique, and expand the effective action in powers of the vector potential; the expansion coefficients turn out to be material correlation functions calculated in the material space, in the absence of the electromagnetic field. The standard nonretarded results obtained by treating the field classically are recovered when the correlation functions are calculated using classical equations of motion for the effective actions. Radiative corrections can then be systematically introduced by incorporating higher order terms in the perturbation expansion of the effective action. Adopting a diagrammatic terminology, the nonretarded limit is known as the tree approximation (i.e., neglecting all diagrams containing loops) and the expansion is in the number of loops.

The present expansion provides a clear physical picture for optical nonlinearities by viewing the material and the field degrees of freedom as weakly coupled anharmonic oscillators. Anharmonities in the material system result in the nonlinearities whereas anharmonities in the field result

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in radiative corrections and retardation. It also provides a unified approach which is applicable to systems of arbitrary size all the way from small microscopic particles to macroscopic nanostructures such as superlattices.[20]

In the following section we present the multipolar Hamiltonian describing the field and the material degrees of freedom interacting with an external polarization, which is the source for the optical response. In Sec. III we derive expressions for the nonlinear signal and susceptibilities in terms of Green's functions of the electromagnetic field. In Sec. IV we calculate the action corresponding to this Hamiltonian and represent these Green's functions in a path integral form. In Sec. V we express the effective action in terms of Green's functions of the material system, and develop the perturbation theory for its evaluation. In Sec. VI we apply these results to calculate the third order response of an assembly of two level molecules and explore radiative corrections to the susceptibilities and to the signal. As an application, we examine in Sec. VII the radiative decay of biexcitons in molecular monolayers which can be probed by two photon resonances in the third order response.

II. THE MULTIPOLAR HAMILTONIAN

The dynamics of a material system interacting with the radiation field can be most conveniently calculated by starting with the multipolar Hamiltonian[3,27,28]

$$\hat{H}_{\text{mult}}=\hat{H}_{\text{mat}}+\hat{H}_{\text{rad}}-\int d\mathbf{r}\,\hat{P}(\mathbf{r})\cdot\hat{D}^{\perp}(\mathbf{r})+2\pi\int|\hat{P}^{\perp}(\mathbf{r})|^{2}\,d\mathbf{r}. \tag{2.1}$$

This Hamiltonian, which may be obtained from the minimal coupling Hamiltonian by a canonical transformation,[27] describes a material system interacting with a transverse electromagnetic field $D^{\perp}$. The longitudinal part of electromagnetic field is taken into account by the Coulomb interaction in the material system Hamiltonian $\hat{H}_{\text{mat}}$ (the Coulomb gauge). We have further neglected magnetic terms. We denote an operator by a caret, $\hat{O}$, and set $\hbar=1$.

$\hat{H}_{\text{rad}}$ is the free-field Hamiltonian

$$\hat{H}_{\text{rad}}=\frac{1}{8\pi}\int d\mathbf{r}\{\hat{D}^{\perp}(\mathbf{r})^{2}+[\nabla\times\hat{A}(\mathbf{r})]^{2}\}, \tag{2.2}$$

where $\hat{A}(\mathbf{r})$ is the vector potential in the Coulomb gauge. $\hat{D}^{\perp}(\mathbf{r})$ is the operator representing the transverse part of electric displacement, $\nabla\cdot\hat{D}^{\perp}(\mathbf{r})=0$. In the multipolar form of the Hamiltonian $(1/4\pi)\hat{D}(\mathbf{r})$ is the momentum conjugate to $\hat{A}(\mathbf{r})$, i.e., it commutes with all material operators and

$$[\hat{D}_{i}^{\perp}(\mathbf{r}),\hat{A}_{j}(\mathbf{r}')]=4\pi i\delta_{ij}^{\perp}(\mathbf{r}-\mathbf{r}'), \tag{2.3a}$$

$\delta_{ij}^{\perp}(\mathbf{r}-\mathbf{r}')$ being the transverse δ function (i.e., the projection of the function $\delta_{ij}\delta(\mathbf{r}-\mathbf{r}')$ onto the space of transverse functions). The commutation relations (2.3a) can be alternatively recast in the form

$$\{\hat{D}_{i}^{\perp}(\mathbf{r}),[\nabla\times A(\mathbf{r}')]_{j}\}=4\pi i\sum_{m}\epsilon_{ijm}\frac{\partial}{\partial r'_{m}}\delta_{ij}^{\perp}(\mathbf{r}-\mathbf{r}'), \tag{2.3b}$$

where ϵ_{ijm} is the antisymmetric tensor (Levi-Civita tensor).

The transverse electromagnetic field $\hat{E}^{\perp}(r)$ is related to the electric displacement $\hat{D}^{\perp}(r)$ by

$$\hat{E}^{\perp}(\mathbf{r})\equiv\hat{D}^{\perp}(\mathbf{r})-4\pi\hat{P}^{\perp}(\mathbf{r}), \tag{2.4}$$

where $\hat{P}^{\perp}(\mathbf{r})$ is the operator of the transverse part of polarization. Since $\hat{P}^{\perp}(\mathbf{r})$ is a purely material operator, it commutes with all field operators $\hat{D}^{\perp}(\mathbf{r}')$ and $\hat{A}^{\perp}(\mathbf{r}')$.

The Hamiltonian of the system in the presence of external sources can be obtained by substituting $\hat{P}+P_{\text{ext}}$ for the polarization $\hat{P}$ in the Hamiltonian (2.1). P_{ext} stands for the external polarization coming from external sources. Thus the total Hamiltonian of the system, including the external polarization, has the form

$$\hat{H}(t)=\hat{H}_{\text{mult}}-\int d\mathbf{r}\,P_{\text{ext}}(\mathbf{r},t)\cdot\hat{E}^{\perp}(\mathbf{r}). \tag{2.5}$$

The Hamiltonian (2.5) provides a convenient starting point for calculating the optical response. The coupling of the field and the material degrees of freedom to the external polarization is represented by the second term which has a simple form of a product of P_{ext} and the Maxwell field $\hat{E}^{\perp}$. Strictly speaking, $\hat{H}(t)$ should contain an additional term

$$2\pi\int d\mathbf{r}|P_{\text{ext}}^{\perp}(\mathbf{r},t)|^{2},$$

however, since P_{ext} is a given classical function, this term does not depend on the dynamical variables of the system and has no effect on its time evolution, it can therefore be ignored.

III. GREEN'S FUNCTION EXPRESSIONS FOR THE OPTICAL FIELD

The Hamiltonian $\hat{H}(t)$ describes the coupled dynamics of the material and the field degrees of freedom in their joint space. We shall denote this space as "the system." The system's evolution operator is

$$\frac{d\hat{U}(t,t')}{dt}=-i\hat{H}(t)\hat{U}(t,t'), \tag{3.1a}$$

with $\hat{U}(t',t')=\hat{I}$ where $\hat{I}$ is the system's unit operator. We further introduce the time evolution operator for the isolated system (with $P_{\text{ext}}=0$), i.e.,

$$\frac{d\hat{U}_{\text{mult}}}{dt}(t,t')=-i\hat{H}_{\text{mult}}\hat{U}_{\text{mult}}(t,t'), \tag{3.1b}$$

again $\hat{U}_{\text{mult}}(t',t')=\hat{I}$.

In the following derivation we are going to work primarily in the *interaction picture* where we define operators evolving in time with $\hat{U}_{\text{mult}}$ [see Eq. (3.5)]. To avoid confusion we shall label quantities evaluated at time t using the full evolution operator $\hat{U}$ by a tilde $\tilde{O}(t)$, whereas $\hat{O}(t)$ will stand for operators in the interaction picture. The expectation value of the electric field in the presence of external sources is[29]

$$\tilde{E}^{\perp}(\mathbf{r},t)=\langle\Omega|\hat{U}^{\dagger}(t,-\infty)\hat{E}^{\perp}(\mathbf{r})\hat{U}(t,-\infty)|\Omega\rangle, \quad (3.2)$$

where $|\Omega\rangle$ is the state of the system at $t=-\infty$, when the external polarization vanishes.

Equations (3.2) can also be written as

$$\tilde{E}^{\perp}(\mathbf{r},t)=\mathrm{Tr}[\hat{E}^{\perp}(\mathbf{r})\tilde{\rho}(t)], \quad (3.3a)$$

with $\tilde{\rho}(t)$ being the density matrix of the system

$$\tilde{\rho}(t)=\hat{U}(t,-\infty)|\Omega\rangle\langle\Omega|\hat{U}^{\dagger}(t,-\infty). \quad (3.3b)$$

In the conventional semiclassical (nonretarded) theory, the interaction of the material and the external field E_{ext} is given by

$$-\int d\mathbf{r}\, P(\mathbf{r})\cdot E_{\mathrm{ext}}(\mathbf{r},t).$$

In this case E_{ext} is the source which is coupled to the dynamical variable $\hat{P}$. In the present formulation [Eq. (2.5)] the roles of the field and the polarization are thus interchanged! P_{ext} is the source and $\hat{E}^{\perp}$ is the dynamical variable coupled to the source. Nevertheless, the expansion of $E^{\perp}(\mathbf{r},t)$ in powers of P_{ext} can be made using the standard perturbation theory for the density matrix. We thus write

$$\tilde{E}^{\perp}(\mathbf{r},t)=\sum_{n=1}^{\infty} i^{n}\int d\mathbf{r}_1\cdots d\mathbf{r}_n\int_{-\infty}^{t} d\tau_n\cdots\int_{-\infty}^{\tau_3} d\tau_2\int_{-\infty}^{\tau_2} d\tau_1 P_{\mathrm{ext}}(\mathbf{r}_1,\tau_1)\cdots P_{\mathrm{ext}}(\mathbf{r}_n\tau_n)$$
$$\times\langle\hat{E}^{\perp}(\mathbf{r},t)[\hat{E}^{\perp}(\mathbf{r}_n,\tau_n)\cdots[\hat{E}^{\perp}(\mathbf{r}_2,\tau_2)[\hat{E}^{\perp}(\mathbf{r}_1,\tau_1),|\Omega\rangle\langle\Omega|]]\cdots]\rangle. \quad (3.4)$$

This expansion is fully time ordered $\tau_1\leqslant\tau_2\cdots\leqslant\tau_n$ and contains commutators, which act from the left as well as from the right. $\hat{E}^{\perp}(\mathbf{r},t)$ is the transverse field operator in the *interaction picture*

$$\hat{E}^{\perp}(\mathbf{r},t)\equiv\hat{U}^{\perp}_{\mathrm{mult}}(-\infty,t)\hat{E}^{\perp}(\mathbf{r})\hat{U}_{\mathrm{mult}}(t,-\infty) \quad (3.5)$$

[$\hat{O}(\mathbf{r},t)$ is an operator in the interaction picture and $O(\mathbf{r})$ is the corresponding expectation value].

We next introduce the following notation for correlation functions:

$$G_{i_1,\ldots,i_n}(\mathbf{r}_1,t_1,\ldots,\mathbf{r}_n,t_n)\equiv\langle O_{i_1}(\mathbf{r}_1,t_1)\cdots O_{i_n}(\mathbf{r}_n,t_n)\rangle\equiv\langle\Omega|\hat{T}_{i_1,\ldots,i_n}(\hat{O}(\mathbf{r}_1,t_1)\cdots\hat{O}(\mathbf{r}_n,t_n))|\Omega\rangle. \quad (3.6)$$

The indices $i_1,\ldots,i_n$ take the values L and R to denote action from the left ($\hat{U}$) and the right ($\hat{U}^{\dagger}$), respectively, in the expansion of the density matrix [Eq. (3.3b)]. $\hat{T}_{i_1,\ldots,i_n}$ denotes an ordering operator that acts in the following manner: all operators with the index R are placed to the left of all operators labeled L; the former being chronologically ordered, the latter antichronologically ordered. Equation (3.6) defines the expression $\langle O_{i_1}(\mathbf{r}_1,t_1)\cdots O_{i_n}(\mathbf{r}_n,t_n)\rangle$ as the expectation value of the product of operators on the right-hand side. The utility of this notation will be clarified in Sec. IV where we introduce a path integral representation for expectation values [Eqs. (4.6)]. Below we will use an abbreviated notation $1,\ldots,n$ instead of $\mathbf{r}_1$, $t_1,\ldots,\mathbf{r}_n$, t_n where possible and leave out indices where unnecessary.

Using this notation we can recast Eq. (3.4) in the form

$$\tilde{E}^{\perp}(\mathbf{r},t)=\sum_{n=0}^{\infty}\frac{1}{n!}\int d\mathbf{r}_1\, dt_1\cdots\int d\mathbf{r}_n\, dt_n\, P_{\mathrm{ext}}(\mathbf{r}_1t_1)\, P_{\mathrm{ext}}(\mathbf{r}_2t_2)\cdots P_{\mathrm{ext}}(\mathbf{r}_nt_n)\mathscr{R}^{(n)}(\mathbf{r}t;\mathbf{r}_1t_1,\mathbf{r}_2t_2,\ldots,\mathbf{r}_nt_n), \quad (3.7a)$$

with the *signal response function*

$$\mathscr{R}^{(n)}(\mathbf{r}\, t;\mathbf{r}_1t_1,\mathbf{r}_2t_2,\ldots,\mathbf{r}_nt_n)=i^{n}\sum_{i_1,\ldots,i_n}\langle E^{\perp}_{L}(\mathbf{r},t)E^{\perp}_{i_1}(\mathbf{r}_1t_1)E^{\perp}_{i_2}(\mathbf{r}_2t_2)\cdots E^{\perp}_{i_n}(\mathbf{r}_nt_n)\rangle s(i_1,\ldots,i_n). \quad (3.7b)$$

Here, $s=1$ if the number of R variables $i_1,\ldots,i_n$ is even, and $s=-1$ otherwise. Alternatively, we can change variables and define

$$O_{+}\equiv\tfrac{1}{2}(O_L+O_R),$$
$$O_{-}\equiv O_L-O_R. \quad (3.8a)$$

We shall label these variables O_α, where α assumes the values + and −. The Greek indices are related to the latin indices by the linear transformation.

$$O_\alpha=V_{\alpha i}O_i, \quad (3.8b)$$

where

$$V_{+,R}=V_{+,L}=\tfrac{1}{2};\quad V_{-,R}=1, V_{-,L}=-1, \quad (3.8c)$$

and summation over repeating indices is assumed. From the definitions (3.6) and (3.8a) we immediately get

$$G_{\alpha_1,\ldots,\alpha_n}(1,\ldots,n)=V_{\alpha_1 i_1}\cdots V_{\alpha_n i_n}G_{i_1,\ldots,i_n}(1,\ldots,n). \quad (3.9)$$

In Eq. (3.7b), the last $E^{\perp}_{L}(\mathbf{r},t)$ factor acts from the left. This is because we chose to multiply the density matrix by $\hat{E}^{\perp}$ from the left before taking the trace. This choice, however, is arbitrary. Using the cyclic invariance of the trace, this result would not change if we choose to act from the right instead, $E^\perp_R$. Hereafter, we use this freedom to act with the more symmetric combination $\hat{E}^\perp_+ = (\hat{E}^\perp_L + \hat{E}^\perp_R)/2$. We then write

$$\mathscr{R}^{(n)}(\mathbf{r}t;\mathbf{r}_1t_1,\mathbf{r}_2t_2,\ldots,\mathbf{r}_nt_n) \equiv i^n\langle \hat{E}^\perp_+(\mathbf{r},t)\hat{E}^\perp_-(\mathbf{r}_1t_1)\cdots\hat{E}^\perp_-(\mathbf{r}_nt_n)\rangle. \tag{3.10}$$

Equation (3.10) is an exact formal expression for the signal field in terms of equilibrium correlation functions of the isolated (material and radiation field) system with no external sources. In the coming sections, we shall separate the calculation into parts carried out separately in the material or the field spaces.

The ± notation introduced here allows a compact representation of the response functions [compare Eq. (3.10) with Eq. (3.4)]. Let us consider, for example, all possible two-point Green's functions. First, we have

$$G_{--}(1,2)=0, \tag{3.11a}$$

G_{++} represents the symmetrized correlation function

$$G_{++}(1,2)=\tfrac{1}{2}\langle\Omega|\hat{O}(1)\hat{O}(2)+\hat{O}(2)\hat{O}(1)|\Omega\rangle, \tag{3.11b}$$

G_{-+} represents the *advanced* Green's function

$$G_{-+}(1,2)=G^{\text{adv}}(1,2),$$

$$G^{\text{adv}}(1,2)\equiv\begin{cases}0, & t_1>t_2,\\ \langle\Omega|\hat{O}(2)\hat{O}(1)-\hat{O}(1)\hat{O}(2)|\Omega\rangle, & t_1<t_2,\end{cases} \tag{3.11c}$$

and G_{+-} represents the *retarded* Green's function

$$G_{+-}(1,2)=G^{\text{ret}}(1,2),$$

$$G^{\text{ret}}(1,2)\equiv\begin{cases}\langle\Omega|\hat{O}(1)\hat{O}(2)-\hat{O}(2)\hat{O}(1)|\Omega\rangle, & t_1>t_2\\ 0, & t_1<t_2\end{cases}. \tag{3.11d}$$

Relations (3.11) will be used in the perturbation theory to be developed in Sec. V.

IV. PATH INTEGRAL REPRESENTATION FOR THE OPTICAL FIELD

In the present section we develop a path integral representation for the signal response function $\mathscr{R}^{(n)}$ which relates the expectation value of the electric field to the external polarization. The optical signal needs eventually to be expanded in powers of the external electric field, and the susceptibilities are coefficients in the expansion of the nonlinear polarization in powers of the Maxwell transverse electric field. In the coming sections we shall show how both quantities may be related to $\mathscr{R}^{(n)}$.

Equations (3.10) and (3.5) are suitable for deriving the path integral representation for the expectation value of the Maxwell field $E(t)$. To that end we represent the matrix elements of the evolution operator $\hat{U}(t'',t')$ in the form of an integral of $\exp(iS)$, over all paths beginning at some fixed point in configuration space at $t=t'$ and ending at another fixed point at $t=t''$; S is the classical action corresponding to the path.[30,31] The first step is to calculate the action corresponding to the Hamiltonian (2.5). This will be accomplished by calculating the action corresponding to the Hamiltonian (2.1) and then substituting everywhere $P+P_{\text{ext}}$ for P (where P is the polarization).

Hereafter, we delete the carets since the classical action is calculated using the classical form of the Hamiltonian (2.1), and we do not deal with operators. Using the canonical procedure[32] we get

$$S_{\text{mult}}[A,D^\perp,B]=S_{\text{mat}}[B]+\frac{1}{4\pi}\int d\mathbf{r}\,dt\,D^\perp(\mathbf{r},t)\dot{A}(\mathbf{r},t) - \int dt\,H_{\text{rad}}+\int d\mathbf{r}\,dt\,P(\mathbf{r},t)\,D^\perp(\mathbf{r},t) - 2\pi\int|P^\perp(\mathbf{r},t)|^2 d\mathbf{r}\,dt. \tag{4.1}$$

Here B stands for material variables. The classical action corresponding to the Hamiltonian of the material system, $S_{\text{mat}}[B]$, can be kept completely general and need not be specified at this stage. Here and below we use square brackets for listing functional arguments of the actions. Using the Heisenberg equations of motion, together with the Hamiltonians (2.1) and (2.3) we obtain

$$\dot{A}(\mathbf{r})=D^\perp(\mathbf{r})-4\pi P^\perp(\mathbf{r}). \tag{4.2a}$$

Comparing (4.2a) and (2.4) we see that

$$E^\perp(\mathbf{r},t)=\dot{A}(\mathbf{r},t). \tag{4.2b}$$

Expressing the variable $D^\perp(\mathbf{r})$ in Eq. (4.1) in terms of $\dot{A}(\mathbf{r})$ by means of Eq. (4.2a) we finally get

$$S_{\text{mult}}[A,B]=S_{\text{mat}}[B]+S_{\text{rad}}[A]+S_{\text{int}}[A,B], \tag{4.3a}$$

where

$$S_{\text{rad}}[A]=\frac{1}{8\pi}\int d\mathbf{r}\,dt[(\dot{A}(\mathbf{r},t))^2-(\nabla\times A(\mathbf{r},t))^2], \tag{4.3b}$$

and

$$S_{\text{int}}[A,B]=\int d\mathbf{r}\,dt\,P(\mathbf{r},t)\dot{A}(\mathbf{r},t). \tag{4.3c}$$

In Eq. (4.3c) P is the polarization which depends on the material variables B. We will not need an explicit expression for the action $S_{\text{mat}}[B]$ since we will eventually express all the path integrals over material variables in terms of Green's functions and will not use path integral methods for their evaluation. The main motivation for expressing Eq. (3.10) in the path integral form is to obtain an effective action which separates the material system and the dynamics of the electromagnetic field. The optical signal can then be expressed in terms of expectation values of products of material operators in the purely material system without the electromagnetic field.

The action $S[A,B]$ corresponding to the Hamiltonian (2.5) is finally given by

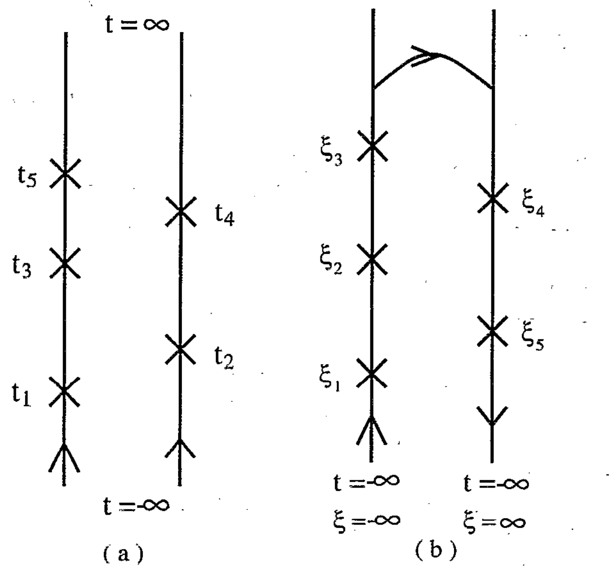

FIG. 1. Left and right operators and the Keldysh time loop. Using the loop time variable ξ, all operators are time ordered.

$$S[A,B]=S_{\rm mult}[A,B]+\int dt\,d\mathbf{r}\,P_{\rm ext}(\mathbf{r},t)\dot{A}(\mathbf{r},t), \tag{4.4a}$$

and the time evolution operator is

$$U(t_1,t_2)=\int \mathscr{D}[A]\mathscr{D}[B]\exp(iS[A,B]). \tag{4.4b}$$

We shall now derive the path integral representation for the response functions (3.10). Using the unitarity of the evolution operator, we rewrite Eq. (3.2) in the form

$$\tilde{E}^{\perp}(\mathbf{r},t)=\langle\Omega|\hat{U}(-\infty,t)\hat{E}^{\perp}(\mathbf{r})\hat{U}(t,-\infty)|\Omega\rangle. \tag{4.5a}$$

The expectation value $\tilde{E}^{\perp}(\mathbf{r},t)$ can be also presented as

$$\tilde{E}^{\perp}(\mathbf{r},t)=\langle\Omega|\hat{U}(-\infty,+\infty)\hat{U}(+\infty,t)\hat{E}^{\perp}(\mathbf{r})\hat{U}(t,-\infty)|\Omega\rangle \tag{4.5b}$$

or

$$\tilde{E}^{\perp}(\mathbf{r},t)=\langle\Omega|\hat{U}(-\infty,t)\hat{E}^{\perp}(\mathbf{r})\hat{U}(t,+\infty)\hat{U}(+\infty,-\infty)|\Omega\rangle. \tag{4.5c}$$

The path integral representation can only be derived for time-ordered Green's functions. On the other hand, the correlation functions obtained in Sec. III are expectation values of products of two types of terms: chronologically ordered "left" operators, and antichronologically ordered "right" operators. To overcome this difficulty we use the Keldysh time loop representation[33] as shown in Fig. 1. We consider the time loop from $t=-\infty$ to $t=+\infty$ and then from $t=+\infty$ to $t=-\infty$, placing the time ordered (L) operators on the first part of the loop and the (R) operators on the second part. Using a new time variable (ξ), all operators become time ordered, and we can use the path integral representation.

Using the path integral form[30,31] for the evolution operators we get

$$\begin{aligned}G(1,\dots,n)&=\langle O(1)\cdots O(n)\rangle\\&=\int \mathscr{D}[A(t)]\mathscr{D}[B(t)]O(\mathbf{r}_1,t_1)\cdots O(\mathbf{r}_n,t_n)\\&\quad\times\exp(iS^{(K)}[A(t),B(t)]),\end{aligned} \tag{4.6}$$

where the superscript K stands for the Keldysh time loop and we will use the indices $i=L$, R to denote variables on the first and the second parts of the time loop, $A(t)=[A_L(t),A_R(t)]$, $B(t)=[B_L(t),B_R(t)]$ with t changing from $t=-\infty$ to $t=+\infty$; $A_L(+\infty)=A_R(+\infty)$, $B_L(+\infty)=B_R(+\infty)$ and

$$S^{(K)}[A(t),B(t)]=S[A_L(t),B_L(t)]-S[A_R(t),B_R(t)]. \tag{4.7}$$

In particular the path integral representation of Eqs. (4.5b) and (4.5c) takes the form

$$\begin{aligned}E^{\perp}(t)=&\int \mathscr{D}[A_L,A_R]\mathscr{D}[B_L,B_R]\\&\times\dot{A}_i(t)e^{iS[A_L,B_L]-iS[A_R,B_R]},\end{aligned} \tag{4.8a}$$

with

$$\begin{aligned}&A_L(t=+\infty)=A_R(t=+\infty),\\&B_L(t=+\infty)=B_R(t=+\infty),\end{aligned} \tag{4.8b}$$

where $i=L$ and $i=R$ correspond to Eqs. (4.5b) and (4.5c), respectively.

Introducing variables A_α, P_α with $\alpha=+,-$ [see Eq. (3.8)] and taking Eq. (4.4a) into account, we get from Eq. (4.8) [since Eq. (4.8a) is valid for both $i=L$ and $i=R$]

$$\begin{aligned}E^{\perp}(\mathbf{r},t)=&\int D[A]D[B]\dot{A}_+(\mathbf{r},t)\\&\times\exp\left[i\int d\mathbf{r}\,dt\,P_{\rm ext}(\mathbf{r},t)\dot{A}_-(\mathbf{r},t)\right]\\&\times\exp(iS^{(K)}_{\rm mult}[A,B]).\end{aligned} \tag{4.9a}$$

Here,

$$\begin{aligned}&S^{(K)}_{\rm mult}[A,B]\\&\quad=S_{\rm mult}[A_L,B_L]-S_{\rm mult}[A_R,B_R]\\&\quad=S^{(K)}_{\rm mat}[B]+S^{(K)}_{\rm rad}[A]+\int dt\,d\mathbf{r}(P_+\dot{A}_-+P_-\dot{A}_+).\end{aligned} \tag{4.9b}$$

Performing the expansion of Eq. (4.9a) in powers of $P_{\rm ext}$, we get

$$\begin{aligned}&\mathscr{R}^{(n)}(\mathbf{r}t;\mathbf{r}_1t_1,\mathbf{r}_2t_2,\dots,\mathbf{r}_nt_n)\\&\quad=i^n\langle\dot{A}_-(\mathbf{r}_1,t_1)\cdots\dot{A}_-(\mathbf{r}_n,t_n)\dot{A}_+(\mathbf{r},t)\rangle.\end{aligned} \tag{4.9c}$$

Note that Eq. (4.9c) vanishes if we substitute $\dot{A}_-$ for $\dot{A}_+$

$$\langle \dot{A}_-(1)\cdots\dot{A}_-(n)\rangle=0. \tag{4.9d}$$

In Eq. (4.9c) we used the following notation for expectation values:

$$\langle \dot{A}(1)\cdots\dot{A}(n)\rangle=\int \mathscr{D}[A]\mathscr{D}[B]\dot{A}(1)\cdots\dot{A}(n)\times\exp(iS^{(K)}_{\text{mult}}[A,B]). \tag{4.10}$$

We shall use the notation (4.10) for correlation functions of arbitrary variables, not necessarily products of $\dot{A}_\alpha(r,t)$. Equations (3.6) and (3.9) express the path integrals (4.6a) and (4.6b) in terms of expectation values of quantum operators, ordered in a specific way. Note that we can get Eq. (4.9c) directly from Eq. (3.10) using the path integral representation (4.6a) for the right-hand side of Eq. (3.10). The introduction of the ± variables in this section provides a compact and extremely simple formal expression for the nonlinear response functions.

At this point, we should comment on the initial state of the system. The path integral (4.10) expresses the correlation function as an expectation value of a product of operators with respect to the initial state $|\Omega\rangle$ [see, for example, Eq. (3.6)]. Therefore, the correlation function (4.10) depends on this state $|\Omega\rangle$. In Eq. (4.10) this dependence is hidden in the integration measure. We will choose $|\Omega\rangle$ as the ground state of the entire material and field system with $P_{\text{ext}}=0$. We can adiabatically switch the interaction of the material system with the transverse electromagnetic field.[29] Therefore, we can take the state of the system $|\Omega\rangle$ at $t=-\infty$ to be a direct product of the ground state of the material system and the ground state of the electromagnetic field. The path integral (4.10) will be evaluated in two steps. First we integrate the material variables B to get the effective action. This will be reduced to the problem of evaluating correlation functions in the material system alone, and due to our assumption regarding the state $|\Omega\rangle$, we have to treat them as expectation values of products of operators with respect to the ground state of the material system. The second step is the integration over the vector potential which will be performed perturbatively. To that end we introduce the bare Green's function of the electromagnetic field, calculated using only the quadratic part of the effective action [Eq. (5.15)]. We can obtain this Green's function by adding the proper self energy to the inverse Green's function of the electromagnetic field in vacuum. This gives the complete prescription for evaluating (4.10). This prescription can be easily extended for more general cases by starting with an arbitrary initial state $|\Omega\rangle$. For example, in defining the bare Green's function for the effective action at finite temperatures we should add the proper temperature dependent self energy to the inverse temperature dependent Green's function of the electromagnetic field (without the material degrees of freedom).

V. PERTURBATION THEORY FOR THE EFFECTIVE ACTION

So far we derived a representation for path integrals of the type (4.10) in the form of expectation values of products of operators. This representation enables us to express the nonlinear signal in terms of Green's functions of the transverse electric field in the (joint material and field) system space. A tremendous advantage of the semiclassical procedure is that it divides the calculation into two separate steps, the first involving the material system alone, and the second involving the field alone. The path integral representation [Eqs. (4.9) and (4.10)] allows the development of a perturbative procedure in which, term by term, we work in either the field or the material spaces. We shall express the effective action in terms of purely material correlation functions. These in turn may be evaluated using standard Green's function techniques. Introducing the notation

$$D(1,\ldots,n)\equiv\langle \dot{A}(1)\cdots\dot{A}(n)\rangle, \tag{5.1}$$

we can then rewrite Eq. (4.10) in the form

$$D(1,\ldots,n)=\int \mathscr{D}[A]\dot{A}(1)\cdots\dot{A}(n)\exp(iS_{\text{eff}}[A]), \tag{5.2}$$

where

$$\exp(iS_{\text{eff}}[A])=\int \mathscr{D}[B]\exp(iS^{(K)}_{\text{mult}}[A,B]). \tag{5.3}$$

Formally our goal has been accomplished by these equations. Equation (5.3) defines the effective action $S_{\text{eff}}[A]$, which depends on the vector potential alone. Thus when evaluating the expectation values (5.1) we work in the electromagnetic field space, and when calculating the effective action we perform path integration over material variables only, i.e., we work with the material system treating the vector potential as an external classical field.

We shall now demonstrate how this scheme works in practice. We first evaluate the effective action. Using the general notation for the expectation values (4.6) and the action $\hat{S}_{\text{mult}}$, we obtain from Eq. (5.3)

$$S_{\text{eff}}[A]=S^{(K)}_{\text{rad}}[A]+\frac{1}{i}\ln\left[\left\langle\exp\left(i\int dt\,d\mathbf{r}(P_+\dot{A}_-+P_-\dot{A}_+)\right)\right\rangle_M\right], \tag{5.4}$$

where the subscript M signifies that the trace is taken only over the material degrees of freedom, keeping the field variables alive. Expanding the exponent on the right-hand side of Eq. (5.4), we express the effective action in terms of material Green's functions

$$S_{\mathrm{eff}}[A]=S^{(K)}_{\mathrm{rad}}[A]+i^{-1}\ln\left\{1+\sum_{n=1}^{\infty}\frac{i^n}{n!}\int dt_1\,d\mathbf{r}_1\cdots dt_n\,d\mathbf{r}_n\,\dot{A}_{\alpha_1}(1)\cdots\dot{A}_{\alpha_n}(n)\langle P_{-\alpha_1}(1)\cdots P_{-\alpha_n}(n)\rangle_M\right\}, \tag{5.5}$$

where

$$\langle P(1)\cdots P(n)\rangle_M$$

$$=\int\mathscr{D}[B]P(1)\cdots P(n)\exp(iS^{(K)}_{\mathrm{mat}}[B]), \tag{5.6}$$

are the ordered Green's functions in the sense of Sec. IV. Thus evaluating the effective action reduces to calculating the material Green's functions. This can be accomplished using methods other than path integrals when appropriate (see Sec. VI). Equation (5.6) can be expressed in terms of ordinary material correlation functions.

$$\langle P_{\beta_1}(\mathbf{r}_1,t_1)\cdots P_{\beta_n}(\mathbf{r}_n,t_n)\rangle_M$$

$$=\mathrm{Tr}[\hat{P}^M_{\beta_1}(\mathbf{r}_1,t_1)\cdots\hat{P}^M_{\beta_n}(\mathbf{r}_n,t_n)\rho_M(-\infty)]$$

with

$$\hat{P}^M(\mathbf{r},t)\equiv\exp(i\hat{H}_{\mathrm{mat}}t)\hat{P}(\mathbf{r})\exp(-i\hat{H}_{\mathrm{mat}}t),$$

This is completely analogous to Eq. (4.6). The only difference is that the time evolution of $\hat{P}$ is determined by the purely material Hamiltonian. When the logarithm on the right-hand side of Eq. (5.5) is expanded in a Taylor series, we obtain an expansion of the effective action in powers of the vector potential.

We confine ourselves to material systems for which the Green's functions (5.6) are nonzero only for even values of n (as is the case in systems with inversion symmetry). Expanding the logarithm on the right-hand side of Eq. (5.5) and collecting terms order by order in the vector potential, the effective action finally takes the form

$$S_{\mathrm{eff}}[A]=S^{(K)}_{\mathrm{rad}}[A]+i^{-1}\sum_{n=1}^{\infty}\frac{i^{2n}}{(2n)!}\int dt_1\,d\mathbf{r}_1\cdots dt_{2n}\,d\mathbf{r}_{2n}$$

$$\times\langle\langle P_{-\alpha_1}(1)\cdots P_{-\alpha_{2n}}(2n)\rangle\rangle_M$$

$$\times\dot{A}_{\alpha_1}(1)\cdots\dot{A}_{\alpha_{2n}}(2n), \tag{5.7}$$

where we have introduced the irreducible correlation functions

$$\langle\langle P(1)P(2)\rangle\rangle_M\equiv\langle P(1)P(2)\rangle_M,$$

$$\langle\langle P(1)P(2)P(3)P(4)\rangle\rangle_M$$

$$\equiv\langle P(1)P(2)P(3)P(4)\rangle_M$$

$$-\langle P(1)P(2)\rangle_M\langle P(3)P(4)\rangle_M$$

$$-\langle P(1)P(3)\rangle_M\langle P(2)P(4)\rangle_M$$

$$-\langle P(1)P(4)\rangle_M\langle P(2)P(3)\rangle_M. \tag{5.8}$$

The higher order irreducible correlation functions are defined similarly. The expectation value of a product of operators is the sum over all partitions of the operators in subgroups of products of irreducible expectations values of products of operators. In other words, the irreducible correlation function is the difference between the ordinary correlation function and the sum over all the possible factorizations into products of lower order correlation functions.

The perturbation theory for the path integrals on the right-hand side of Eq. (5.2) is formulated as follows.[31] We partition the effective action $S_{\mathrm{eff}}[A]$ in the form

$$S_{\mathrm{eff}}[A]=S^{(0)}_{\mathrm{eff}}[A]+S'_{\mathrm{eff}}[A], \tag{5.9a}$$

where $S^{(0)}_{\mathrm{eff}}$ contains the quadratic in the vector potential terms,

$$S^{(0)}_{\mathrm{eff}}\equiv S^{(K)}_{\mathrm{rad}}[A]+\frac{i}{2}\int dt_1\,d\mathbf{r}_1\,dt_2\,d\mathbf{r}_2\langle\langle P_{-\alpha_1}(\mathbf{r}_1,t_1)$$

$$\times P_{-\alpha_2}(\mathbf{r}_2,t_2)\rangle\rangle_M\dot{A}(\mathbf{r}_1,t_1)\dot{A}(\mathbf{r}_2,t_2), \tag{5.9b}$$

and $S'_{\mathrm{eff}}[A]$ contains the higher order terms. We then expand $\exp[iS'_{\mathrm{eff}}]$ in powers of A and evaluate the expectation values of products of the vector potential with the quadratic action $S^{(0)}_{\mathrm{eff}}[A]$, using Wick's theorem. This enables us to formulate the perturbation theory in the form of Feynmann diagrammatic techniques.[29–31,33] This procedure defines a natural reference harmonic oscillator model for the field, with anharmonities included perturbatively.

We shall now specialize to the third order response. In Appendix A we recast the corresponding field correlation functions in the form

$$\langle\dot{A}_-(\mathbf{r}_1,t_1)\dot{A}_-(\mathbf{r}_2,t_2)\dot{A}_-(\mathbf{r}_3,t_3)\dot{A}_+(\mathbf{r},t)\rangle=i\int d\mathbf{r}'_1\,dt'_1\,d\mathbf{r}'_2\,dt'_2\,d\mathbf{r}'_3\,dt'_3\,d\mathbf{r}'\,dt'\,\bar{D}^{\mathrm{ret}}(\mathbf{r}'_1,t'_1,\mathbf{r}_1,t_1)\,\bar{D}^{\mathrm{ret}}(\mathbf{r}'_2,t'_2,\mathbf{r}_2,t_2)$$

$$\times\bar{D}^{\mathrm{ret}}(\mathbf{r}'_3,t'_3,\mathbf{r}_3,t_3)\,\bar{D}^{\mathrm{ret}}(\mathbf{r},t,\mathbf{r}',t')\Gamma^{A}_{---+}(\mathbf{r}'_1,t'_1,\mathbf{r}'_2,t'_2,\mathbf{r}'_3,t'_3,\mathbf{r}',t'), \tag{5.10a}$$

where

$$\bar{D}^{\mathrm{ret}}(\mathbf{r}',t',\mathbf{r},t) \equiv i^{-1}\langle \dot{A}_{+}(\mathbf{r}',t')\dot{A}_{-}(\mathbf{r},t)\rangle, \tag{5.10b}$$

is the retarded Green's function of the transverse electric field, and Γ_{---+} is the one-particle irreducible four point Green's function, which can be calculated perturbatively using the expansion given in Appendix A. Γ_{---+} will be analyzed and calculated for a specific model of the material system in the coming section.

At this point, we turn our attention to the conventional nonlinear response functions. These are normally defined by expanding the material polarization in powers of the transverse field

$$P = \mathscr{S}^{(1)}E^{\perp} + \frac{1}{3!}\mathscr{S}^{(3)}(E^{\perp})^{3}\cdots, \tag{5.11}$$

$\mathscr{S}^{(n)}$ being the nth order response function. In Appendix B we show that

$$\mathscr{S}^{(1)}(\mathbf{r},t;\mathbf{r}_1,t_1) = \mathscr{G}^{1}(\mathbf{r},t;\mathbf{r}_1,t_1) - (\bar{D}^{\mathrm{ret}})^{-1}(\mathbf{r},t,\mathbf{r}_1,t_1). \tag{5.12a}$$

Here $\mathscr{G}$ is the Green's function of electromagnetic field in vacuum given by Eq. (6.12),

$$\mathscr{S}^{(3)}(\mathbf{r},t;\mathbf{r}_1,t_1,\mathbf{r}_2,t_2,\mathbf{r}_3,t_3) = \Gamma^{A}_{---+}(\mathbf{r}_1,t_1,\mathbf{r}_2,t_2,\mathbf{r}_3,t_3,\mathbf{r},t), \tag{5.12b}$$

and more generally

$$\mathscr{S}^{(n)}(\mathbf{r},t;\mathbf{r}_1,t_1,\ldots,\mathbf{r}_n,t_n) = \Gamma^{A}_{+-\cdots-}(\mathbf{r},t,\mathbf{r}_1,t_1,\ldots,\mathbf{r}_n,t_n). \tag{5.12c}$$

We have thus shown that the linear response function is equal to the self-energy of the two-point Green's function of the transverse electromagnetic field, and that the nth order response function is equal to the one particle irreducible four point Green's function of the transverse electric field with a specific choice of indices (all indices are — and one index is +).

The perturbation theory developed in this section enables us to evaluate the irreducible Green's functions Γ order by order. In Appendix A we carry out the expansion for the third order response function. We then have

$$\mathscr{S}^{(3)}(\mathbf{r},t;\mathbf{r}_1,t_1,\mathbf{r}_2,t_2,\mathbf{r}_3,t_3) = \bar{\mathscr{S}} + \mathscr{S}_{\mathrm{I}} + \mathscr{S}_{\mathrm{II}} + \cdots. \tag{5.13}$$

The leading term results from the harmonic (tree) approximation and is given by the purely material correlation function

$$\bar{\mathscr{S}} = -i\langle\langle P_{-}(\mathbf{r}_1,t_1)P_{-}(\mathbf{r}_2,t_2)P_{-}(\mathbf{r}_3,t_3)P_{+}(\mathbf{r},t)\rangle\rangle_{M}. \tag{5.14}$$

The other terms require the introduction of the zeroth field Green's function

$$D^{(0)}_{\alpha_1\alpha_2}(\mathbf{r}_1,t_1,\mathbf{r}_2,t_2) = i^{-1}\int \mathscr{D}[A]\dot{A}_{\alpha_1}(\mathbf{r}_1,t_1)\dot{A}_{\alpha_2}(\mathbf{r}_2,t_2)\exp(iS^{(0)}_{\mathrm{eff}}[A]). \tag{5.15}$$

Since the interaction of electromagnetic fields with the material polarization is proportional to the electronic charge, each additional Green's function $D^{(0)}_{\alpha_1\alpha_2}$ in the perturbative expressions for Γ gives an additional power of the square of the electronic charge. In fact, the expansion parameter for this perturbation theory is the fine structure constant $\alpha \equiv e^2/\hbar c$. In models like the one described by Eq. (6.1), one can use alternatively the square of the molecular dipole moment $|\mu|^2$ as the formal expansion parameter. The second term is

$$\mathscr{S}_{\mathrm{I}}(\mathbf{r},t;\mathbf{r}_1,t_1,\mathbf{r}_2,t_2,\mathbf{r}_3,t_3) = -\frac{1}{2}\int d\mathbf{r}'_1\, dt'_1\, d\mathbf{r}'_2\, dt'_2 \sum_{\alpha_1,\alpha_2} \langle\langle P_{-}(\mathbf{r}_1,t_1)P_{-}(\mathbf{r}_2,t_2)P_{-}(\mathbf{r}_3,t_3)P_{+}(\mathbf{r},t) \times P_{-\alpha_1}(\mathbf{r}'_1,t'_1)P_{-\alpha_2}(\mathbf{r}'_2,t'_2)\rangle\rangle_{M} D^{(0)}_{\alpha_1\alpha_2}(\mathbf{r}'_1,t'_1,\mathbf{r}'_2,t'_2). \tag{5.16a}$$

The third term (second order in the expansion parameter) is

$$\begin{aligned}\mathscr{S}_{\mathrm{II}}(\mathbf{r},t;\mathbf{r}_1,t_1,\mathbf{r}_2,t_2,\mathbf{r}_3,t_3) = {} & \frac{i}{8}\int d\mathbf{r}'_1\, dt'_1\, d\mathbf{r}'_2\, dt'_2\, d\mathbf{r}'_3\, dt'_3\, d\mathbf{r}'_4\, dt'_4 \sum_{\alpha_1,\ldots,\alpha_4} \\ & \times\langle\langle P_{-}(\mathbf{r}_1,t_1)P_{-}(\mathbf{r}_2,t_2)P_{-}(\mathbf{r}_3,t_3)P_{+}(\mathbf{r},t)P_{-\alpha_1}(\mathbf{r}'_1,t'_1)P_{-\alpha_2}(\mathbf{r}'_2,t'_2)P_{-\alpha_3}(\mathbf{r}'_3,t'_3)P_{-\alpha_4}(\mathbf{r}'_4,t'_4)\rangle\rangle_{M} \\ & \times D^{(0)}_{\alpha_1\alpha_2}(\mathbf{r}'_1,t'_1,\mathbf{r}'_2,t'_2)\, D^{(0)}_{\alpha_3\alpha_4}(\mathbf{r}'_3,t'_3,\mathbf{r}'_4,t'_4) + \frac{3i}{2}\int d\mathbf{r}'_1\, dt'_1\, d\mathbf{r}'_2\, dt'_2\, d\mathbf{r}'_3\, dt'_3\, d\mathbf{r}'_4\, dt'_4 \sum_{\alpha_1,\ldots,\alpha_4} \\ & \times\langle\langle P_{-}(\mathbf{r}_1,t_1)P_{-}(\mathbf{r}_2,t_2)P_{-\alpha_1}(\mathbf{r}'_1,t'_1)P_{-\alpha_2}(\mathbf{r}'_2,t'_2)\rangle\rangle_{M}\langle\langle P_{-}(\mathbf{r}_3,t_3)P_{+}(\mathbf{r},t)P_{-\alpha_3}(\mathbf{r}'_3,t'_3)P_{-\alpha_4}(\mathbf{r}'_4,t'_4)\rangle\rangle_{M} \\ & \times D^{(0)}_{\alpha_1\alpha_3}(\mathbf{r}'_1,t'_1,\mathbf{r}'_3,t'_3)\, D^{(0)}_{\alpha_2\alpha_4}(\mathbf{r}'_2,t'_2,\mathbf{r}'_4,t'_4).\end{aligned} \tag{5.16b}$$

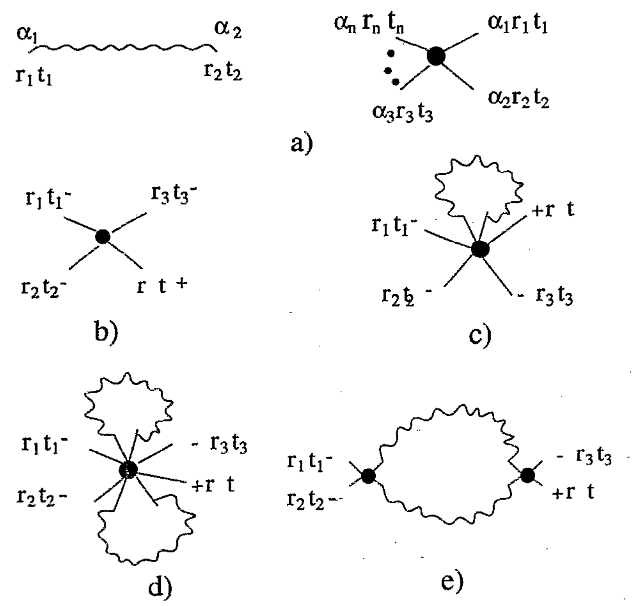

FIG. 2. Diagrammatic representation of the radiative corrections to the nonlinear response function $\mathscr{S}^{(3)}$. (a) The wavy line stands for the bare Green's function $D^{(0)}_{\alpha_1\alpha_2}(\mathbf{r}_1,t_1,\mathbf{r}_2,t_2)$ from Eq. (5.15), the circle stands for the bare vertex $\langle\langle P_{\alpha_1}(\mathbf{r}_1,t_1)P_{\alpha_2}(\mathbf{r}_2,t_2)\cdots P_{\alpha_n}(\mathbf{r}_n,t_n)\rangle\rangle_M$. (b) The tree approximation contribution $\bar{\mathscr{S}}$. (c) The first order correction $\mathscr{S}_{\mathrm{I}}$ by Eq. (5.16a). (d) and (e) The second order correction $\mathscr{S}_{\mathrm{II}}$ two terms in Eq. (5.16b).

The diagrams corresponding to Eqs. (5.16) are presented in Fig. 2.

VI. APPLICATION TO THE NONLINEAR RESPONSE OF CONFINED FRENKEL EXCITONS IN MOLECULAR ASSEMBLIES

We consider an assembly of molecules with nonoverlapping charge distributions and an arbitrary geometry, described by the material Hamiltonian[34]

$$\hat{H}_{\mathrm{mat}}=\sum_m \Omega_m \hat{C}_m^+\hat{C}_m+\sum_{m\neq n} J_{mn}\hat{C}_m^+\hat{C}_n+\frac{g}{2}\sum_m(\hat{C}_m^+)^2\hat{C}_m^2. \tag{6.1a}$$

$\hat{C}_m^+$ which creates an excitation on the mth molecule, satisfies the bosonic commutation relations

$$[\hat{C}_m,\hat{C}_n^+]=\delta_{mn}, \tag{6.1b}$$

and the polarization operator $\hat{P}(\mathbf{r})$ is

$$\hat{P}(\mathbf{r})=\sum_m \hat{P}_m(\mathbf{r}),P_m(\mathbf{r})=|\mu|\rho(\mathbf{r}-\mathbf{R}_m)(\hat{C}_m+\hat{C}_m^+), \tag{6.1c}$$

with $|\int\rho(\mathbf{r})d\mathbf{r}|=1$.

Here $\mathbf{R}_m$ is the position of the mth molecule. $\rho(\mathbf{r}-\mathbf{R}_m)$ its transition dipole density. In the dipole approximation we simply set $\rho(\mathbf{r}-\mathbf{R}_m)=\delta(\mathbf{r}-\mathbf{R}_m)$.

Equation (6.1a) describes a set of anharmonic oscillators in the Heitler–London approximation. When the anharmonicity constant $g\rightarrow+\infty$, the Hamiltonian excludes two excitations on the same molecule and thus describes an assembly of two-level molecules. For $g<0$, the system can have two particle bound states known as biexcitons,[22,34] which may lead to new resonances in the nonlinear response.[35] When the molecules form a 3D lattice, bound states exist when $|g|>g_c\sim J$. In the case of a 2D lattice, bound states are formed for arbitrary value of $g<0$.

To evaluate the nonlinear response function $\bar{\mathscr{S}}^{(3)}$ for this model in the tree approximation we use the path integral representation for Eq. (5.14) to get

$$\bar{\mathscr{S}}^{(3)}(\mathbf{r},t;\mathbf{r}_1,t_1,\mathbf{r}_2,t_2,\mathbf{r}_3,t_3)=|\mu|^4\sum_{nm_1m_2m_3}\rho(\mathbf{r}-\mathbf{R}_n)\rho(\mathbf{r}_1-\mathbf{R}_{m_1})\rho(\mathbf{r}_1-\mathbf{R}_{m_2})\times\rho(\mathbf{r}_3-\mathbf{R}_{m_3})\hat{\mathscr{S}}^{(3)}_{nm_1m_2m_3}, \tag{6.2a}$$

with

$$\hat{\mathscr{S}}^{(3)}_{nm_1m_2m_3}(t;t_1,t_2,t_3)=-i\langle(C_n(t)_++\bar{C}_n(t)_+)(C_{m_1}(t_1)_-+\bar{C}_{m_1}(t_1)_-)(C_{m_2}(t_2)_-+\bar{C}_{m_2}(t_2)_-)(C_{m_3}(t_3)_-+\bar{C}_{m_3}(t_3)_-)\rangle_M. \tag{6.2b}$$

Expectation values on the right-hand side of (6.2b) are taken with respect to the action given by Eqs. (C1) corresponding to the Hamiltonian (6.1a) with the commutation relations (6.1b). The variables C_n and $\bar{C}_n$ stand for the operators $\hat{C}_n$ and $\hat{C}_n^+$. When the expectation values are evaluated, we find only two surviving contributions

$$\hat{\mathscr{S}}^{(3)}=\bar{\mathscr{S}}^{(a)}+\bar{\mathscr{S}}^{(b)}, \tag{6.3a}$$

with

$$\bar{\mathscr{S}}^{(a)}_{nm_1m_2m_3}(t,t_1,t_2,t_3)=-i\langle\bar{C}_{m_1}(t_1)_-\bar{C}_{m_2}(t_2)_-C_{m_3}(t_3)_-C_n(t)_+\rangle_M, \tag{6.3b}$$

and

$$\bar{\mathscr{S}}^{(b)}_{nm_1m_2m_3}(t,t_1,t_2,t_3)=-i\langle C_{m_1}(t_1)_-C_{m_2}(t_2)_-\bar{C}_{m_3}(t_3)_-\bar{C}_n(t)_+\rangle_M. \tag{6.3c}$$

The correlation functions [Eq. (6.3)] are evaluated in Appendix C. The result, in the frequency domain, has the form

$$P^{(3)}(\mathbf{r},\omega_s)=\frac{1}{(2\pi)^2 6}\iiint d\omega_1\, d\omega_2\, d\omega_3 \iiint d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{r}_3\, \delta(\omega_s-\omega_1-\omega_2-\omega_3)$$
$$\times \mathscr{T}^{(3)}(\mathbf{r}\omega_s;\mathbf{r}_1\omega_1,\mathbf{r}_2\omega_2,\mathbf{r}_3\omega_3)E^{\perp}(\mathbf{r}_1,\omega_1)E^{\perp}(\mathbf{r}_2,\omega_2)E^{\perp}(\mathbf{r}_3,\omega_3), \tag{6.4}$$

with

$$\mathscr{T}^{(3)}(\mathbf{r},\omega_s;\mathbf{r}_1,\omega_1,\mathbf{r}_2,\omega_2,\mathbf{r}_3;\omega_3)=\sum_{n,m_1,m_2,m_3} \rho(\mathbf{r}-\mathbf{R}_n)\rho(\mathbf{r}_1-\mathbf{R}_{m_1})\rho(\mathbf{r}_2-\mathbf{R}_{m_2})\rho(\mathbf{r}_3-\mathbf{R}_{m_3})\hat{\mathscr{T}}^{(3)}_{nm_1m_2m_3}(\omega_s;\omega_1,\omega_2,\omega_3), \tag{6.5a}$$

and

$$\hat{\mathscr{T}}^{(3)}_{nm_1m_2m_3}(\omega;_s,\omega_1,\omega_2,\omega_3)=|\mu|^4 \sum_{\substack{\text{perm}\\(m_j,\omega_j)}} \sum_{n',n''} \{G_{nn'}(\omega_s)G^*_{n'm_3}(-\omega_3)G_{n''m_2}(\omega_2)G_{n''m_1}(\omega_1)\bar{\Gamma}_{n'n''}(\omega_1+\omega_2)$$
$$+G^*_{nn'}(-\omega_s)G_{n'm_3}(\omega_3)G^*_{n''m_2}(-\omega_2)G^*_{n''m_1}(-\omega_1)\bar{\Gamma}^*_{n'n''}(-\omega_1-\omega_2)\}. \tag{6.5b}$$

Here, G is one particle Green's function. The symbol $\Sigma_{\substack{\text{perm}\\(m_j,\omega_j)}}$ implies the sum over six permutations of three pairs (m_1,ω_1), (m_2,ω_2), (m_3,ω_3). To get Eq. (6.5) we used the material correlation function

$$\langle \bar{C}_m(\tau_1)_+ \bar{C}_n(\tau_2)_+\rangle = \tfrac{1}{2}\langle \bar{C}_m(\tau_1)_- C_n(\tau_2)_+\rangle, \quad \text{for } \tau_2>\tau_1 \tag{6.6a}$$

and

$$G_{mn}(\omega)\equiv \int d\tau_2\, e^{i\omega(\tau_2-\tau_1)} i\langle \bar{C}_m(\tau_1)_- C_n(\tau_2)_+\rangle. \tag{6.6b}$$

The Green's function can be easily evaluated using the one particle eigenstates Ψ_α with eigenvalues $\epsilon_\alpha \hat{H}_{\text{mat}}\Psi_\alpha=\epsilon_\alpha\Psi_\alpha$. Here,

$$\Psi_\alpha=\sum_n \Psi_\alpha(n)\hat{C}^\dagger_n|\Omega_M\rangle, \tag{6.7}$$

where $|\Omega_M\rangle$ is the ground state of the material system. We then have

$$G_{mn}(\omega)=\sum_\alpha \frac{\Psi^*_\alpha(m)\Psi_\alpha(n)}{\omega-\epsilon_\alpha+i0}. \tag{6.8a}$$

$\bar{\Gamma}$ is a two particle scattering matrix

$$\bar{\Gamma}_{mn}(\omega)=2g\{[1-gF(\omega)]^{-1}\}_{mn}, \tag{6.8b}$$

$$F_{mn}(\omega)=\int \frac{d\omega'}{2\pi i} G_{mn}(\omega')G_{mn}(\omega-\omega'). \tag{6.8c}$$

In Appendix D we extend this result beyond the tree approximation, introducing radiative corrections to $\mathscr{T}^{(3)}$ by a partial resummation of the infinite series (5.13). The result is identical to Eq. (6.5b) except that the scattering matrix $\bar{\Gamma}$ is replaced by a renormalized matrix $\hat{\Gamma}$. The expression for $\hat{\Gamma}_{n'n''}(\omega)$ in matrix notation is

$$\hat{\Gamma}(\omega)=\bar{\Gamma}(\omega)\{1-V(\omega)\bar{\Gamma}(\omega)\}^{-1}, \tag{6.9a}$$

with

$$V_{n'n''}(\omega)=(2\pi)^{-3}|\mu|^2 \sum_{m_1,m_1',m_2,m_2'} \int d\omega_1\, d\omega_2\, d\omega_3 \int d\mathbf{r}_1\, d\mathbf{r}_2\, G_{n'm_1}(\omega_1)G_{n'm_1'}(\omega-\omega_1)G_{m_2n''}(\omega_2)G_{m_2'n''}(\omega-\omega_2)$$
$$\times \rho(\mathbf{r}_1-\mathbf{R}_{m_1})\bar{D}^c(\omega',\mathbf{r}_1,\mathbf{r}_2)\rho(\mathbf{r}_2-\mathbf{R}_{m_2})G_{m_1'm_2'}(\omega-\omega'). \tag{6.9b}$$

Here, $\bar{D}^c$ is the chronologically ordered Green's function of the electromagnetic field in the tree approximation, i.e.,

$$\bar{D}^c(\omega,\mathbf{r}_1,\mathbf{r}_2)\equiv \int dt_1\, e^{i\omega(t_1-t_2)} i^{-1}\langle \dot{A}_L(\mathbf{r}_1,t_1)\dot{A}_L(\mathbf{r}_2,t_2)\rangle, \tag{6.9c}$$

where the evolution on the right-hand side of Eq. (6.9c) is performed with respect to $S_{\rm eff}^{(0)}$. $\hat{\Gamma}$ can alternatively be calculated by simply replacing $G(\omega)$ in Eq. (6.8c) with the renormalized Green's function $\hat{G}(\omega)$ [see Eq. (6.15a)] (the derivation is presented in Appendix F)

$$\hat{\Gamma}_{mn}(\omega)=2g\{[1-g\hat{F}(\omega)]^{-1}\}_{mn}, \tag{6.10a}$$

$$\hat{F}_{mn}(\omega)=\int\frac{d\omega'}{2\pi i}\,\hat{G}_{mn}(\omega')\hat{G}_{mn}(\omega-\omega'). \tag{6.10b}$$

Finally, we express the nonlinear signal in terms of the external field. Following Ref. 28, we introduce the external electric field $E_{\rm ext}$ and the polarization of the signal P_n^s which is related to the external polarization $P_{\rm ext}$ and to the electric field in the nonlinear signal E^s by means of the vacuum Green's function $\mathscr{G}$

$$E_{\rm ext}(\mathbf{r},\omega)=\int dr'\,\mathscr{G}(\mathbf{r}-\mathbf{r}',\omega)P_{\rm ext}(\mathbf{r}',\omega), \tag{6.11a}$$

and

$$E^s(\mathbf{r},\omega)=\sum_n\mathscr{G}(\mathbf{r}-\mathbf{R}_n,\omega)P_n^s(\omega), \tag{6.11b}$$

$$P^s(\mathbf{r},\omega)=\sum_n\rho(\mathbf{r}-\mathbf{R}_n)P_n^s \tag{6.11c}$$

with

$$\mathscr{G}(\mathbf{r},\mathbf{r}';\omega)=(2\pi)^{-3}\int_{-\infty}^{\infty}d^3q\,e^{i\mathbf{q}(\mathbf{r}-\mathbf{r}')}\mathscr{G}(\mathbf{q},\omega), \tag{6.12a}$$

$$\mathscr{G}_{ij}(\mathbf{q},\omega)=\frac{4\pi\omega^2}{\omega^2-\mathbf{q}^2c^2}\left(\delta_{ij}-\frac{q_iq_j}{\mathbf{q}^2}\right). \tag{6.12b}$$

Using Eq. (4.9c) and (5.10a) for the nonlinear response function $\mathscr{R}^{(3)}$, calculating the Green functions $\bar{D}^{\rm ret}$ in Eq. (5.10a) using the zeroth order effective action [Eq. (5.9b)] and combining with Eq. (5.12b) and definitions (6.11) we finally obtain after some straightforward calculations

$$\begin{aligned}P^s(\mathbf{r},\omega_s)=&\frac{1}{6(2\pi)^2}\iiint d\omega_1\,d\omega_2\,d\omega_3\iiint d\mathbf{r}_1\,d\mathbf{r}_2\,d\mathbf{r}_3\,\delta(\omega_s-\omega_1-\omega_2-\omega_3)\\&\times R^{(3)}(\mathbf{r}\omega_s;\mathbf{r}_1\omega_1,\mathbf{r}_2\omega_2,\mathbf{r}_3\omega_3)E_{\rm ext}(\mathbf{r}_1,\omega_1)E_{\rm ext}(\mathbf{r}_2,\omega_2)E_{\rm ext}(\mathbf{r}_3,\omega_3),\end{aligned} \tag{6.13a}$$

where

$$R^{(3)}(\mathbf{r}\omega_s;\mathbf{r}_1\omega_1,\mathbf{r}_2\omega_2,\mathbf{r}_3\omega_3)=\sum_{n,m_1,m_2,m_3}\rho(\mathbf{r}-\mathbf{R}_n)\rho(\mathbf{r}_1-\mathbf{R}_{m_1})\rho(\mathbf{r}_2-\mathbf{R}_{m_2})\rho(\mathbf{r}_3-\mathbf{R}_{m_3})\hat{R}^{(3)}_{nm_1m_2m_3}(\omega_s,\omega_1,\omega_2,\omega_3), \tag{6.13b}$$

and

$$\begin{aligned}\hat{R}_{nm_1m_2m_3}(\omega_s;\omega_1,\omega_2,\omega_3)=|\mu|^4\sum_{\substack{\rm perm\\ m_j,\omega_j}}\sum_{n',n''}&\{\hat{G}_{nn'}(\omega_s)\hat{G}^*_{n'm_3}(-\omega_3)\hat{G}_{n''m_2}(\omega_2)\hat{G}_{n''m_1}(\omega_1)\hat{\Gamma}_{n'n''}(\omega_1+\omega_2)\\&+\hat{G}^*_{nn'}(\omega_s)\hat{G}_{n'm_3}(\omega_3)\hat{G}^*_{n''m_2}(-\omega_2)\hat{G}^*_{n''m_1}(-\omega_1)\hat{\Gamma}^*_{n'n''}(-\omega_1-\omega_2)\}.\end{aligned} \tag{6.14}$$

The renormalized Green's function is

$$\hat{G}_{mn}(\omega)\equiv\{G(\omega)\{1-|\mu|^2\phi(\omega)[G(\omega)+G^*(-\omega)]\}^{-1}\}_{mn}, \tag{6.15a}$$

where the self-energy ϕ has the form

$$\phi(\omega)=\phi^{\rm mol}(\omega)+\phi^c(\omega), \tag{6.15b}$$

$\phi^{\rm mol}(\omega)$ and $\phi^c(\omega)$ are the single molecule and cooperative contributions to the self-energy, i.e.,

$$\phi^{\rm mol}_{mn}(\omega)=\delta_{mn}\int d\mathbf{r}\,d\mathbf{r}'\,\rho(\mathbf{r})\cdot\mathscr{G}(\mathbf{r}-\mathbf{r}',\omega)\cdot\rho(\mathbf{r}'), \tag{6.15c}$$

$$\phi^c_{mn}(\omega)=|\mu|^{-2}\mu_m\cdot\mathscr{G}(\mathbf{R}_m-\mathbf{R}_n,\omega)\cdot\mu_n[1-\delta_{nm}]. \tag{6.15d}$$

This expression contains the effects of retardation, which enter in two ways. First, the matrix $\phi(\omega)$ changes $G(\omega)$ to $\hat{G}(\omega)$. This reflects retardation of the one particle states which appears at the stage of solving Maxwell equations for the signal, but not in $\mathcal{S}^{(3)}$ itself, which only depends on $G(\omega)$. Second, the matrix $V(\omega)$ which renormalizes $\bar{\Gamma}$. This reflects the radiative decay and energy shift of two-exciton states which appear in $\mathcal{S}^{(3)}$ itself. This is the only place where retardation corrections to $\mathcal{S}^{(3)}$ appear in the present theory.

VII. RADIATIVE CORRECTIONS TO THE THIRD ORDER RESPONSE OF MOLECULAR NANOSTRUCTURES IN *k* SPACE: BIEXCITONS AND POLARITON DYNAMICS

We consider a 2D lattice (monolayer) with the lattice parameter a. All lattice sites are occupied by two level molecules which have the same transition frequency Ω, and their transition dipole moment is taken to be perpendicular to the monolayer.

For this geometry, we have a good quantum number, namely, the momentum in the plane of the monolayer in the first Brillouin zone (with components $\mathbf{k}_x$, $\mathbf{k}_y$ taking values from $-\pi/a$ to π/a). The one exciton eigenstates are

$$\psi_{\mathbf{k}}(n)=e^{i\mathbf{k}\cdot\mathbf{R}_n}, \tag{7.1a}$$

with eigenvalues

$$\epsilon_{\mathbf{k}}=\Omega_{\mathbf{k}}\equiv\omega_0+J(\mathbf{k}), \tag{7.1b}$$

and

$$J(\mathbf{k})=\sum_m J_{m0}e^{i\mathbf{k}\cdot\mathbf{R}_m}. \tag{7.1c}$$

We can also neglect in Eq. (6.9b) the self-energy of the Green's function (6.9c). This can be rationalized as follows: Strictly speaking, the biexciton decays to form two polaritons, but for the most part, these two polaritons are either excitonlike or photonlike and only a small fraction of the polariton phase space has a significant mixing. The decay to two excitons is impossible as the biexciton is an eigenstate of the material Hamiltonian. Therefore, the decay of biexcitons is determined to first order in the fine structure constant and results in an exciton and a photon. Eq. (6.9b) with $\bar{D}^c$ given by (6.9c) describes the decay of biexcitons to form an exciton and a polariton. This implies that we have already neglected polariton effects for one of the particles. Neglecting polariton effects for the second particle, we substitute in (6.9b) for $\bar{D}^c$

$$\bar{D}^c_{kj}(\omega,\mathbf{r}_1,\mathbf{r}_2)=\int\frac{d^3q}{(2\pi)^3}e^{i\mathbf{q}(\mathbf{r}_1-\mathbf{r}_2)}\bar{D}^c_{kj}(\omega,\mathbf{q}), \tag{7.2a}$$

$$\bar{D}^c_{kj}(\omega,\mathbf{q})=4\pi\omega^2\frac{\delta_{kj}-q_kq_j/\mathbf{q}^2}{\omega^2-\mathbf{q}^2+i0}, \tag{7.2b}$$

where the indices *i, j* denote spatial components taking the values *x, y*, and *z*. We shall adopt the following definition of the spatial Fourier transform of an arbitrary function $\mathcal{f}$:

$$\mathcal{f}(n)=\frac{1}{(2\pi)^2}\int a^2\,d^2k\,f(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{R}_n}. \tag{7.3}$$

Switching to the momentum domain, performing the integrations and summations in Eq. (6.14) and neglecting the real part of $V(\omega)$, we finally obtain for $\hat{R}^{(3)}$

$$\hat{R}^{(3)}(\omega_s\mathbf{k}_s;\omega_1\mathbf{k}_1,\omega_2\mathbf{k}_2,\omega_3\mathbf{k}_3)=|\mu|^4\sum_{\substack{\text{perm}\\(\omega_j,\mathbf{k}_j)}}\{\hat{G}(\omega_s,\mathbf{k}_s)\hat{G}^*(-\omega_3,\mathbf{k}_3)\hat{G}(\omega_1,\mathbf{k}_1)\hat{G}(\omega_2,\mathbf{k}_2)\hat{\Gamma}(\omega_1+\omega_2,\mathbf{k}_1+\mathbf{k}_2)$$
$$+\hat{G}^*(-\omega_s,-\mathbf{k}_s)\hat{G}(\omega_3,\mathbf{k}_3)\hat{G}^*(-\omega_1,-\mathbf{k}_1)\hat{G}^*(-\omega_2,-\mathbf{k}_2)\hat{\Gamma}^*(-\omega_1-\omega_2,-\mathbf{k}_1-\mathbf{k}_2)\}, \tag{7.4a}$$

$$\hat{\Gamma}(\omega,\mathbf{k})=\frac{\bar{\Gamma}(\omega,\mathbf{k})}{1-V(\omega,\mathbf{k})\bar{\Gamma}(\omega,\mathbf{k})}, \tag{7.4b}$$

$$\hat{G}(\omega,\mathbf{k})=\frac{\omega+\Omega_k}{\omega^2-\Omega_{\mathbf{k}}^2+2|\mu|^2\Omega_{\mathbf{k}}\phi(\omega,\mathbf{k})}, \tag{7.4c}$$

$$\bar{\Gamma}(\omega,\mathbf{k})=2g\left\{1-g\int\frac{a^2}{(2\pi)^2}d^2q\frac{1}{\omega-\Omega_{\mathbf{q}}-\Omega_{\mathbf{k}-\mathbf{q}}}\right\}^{-1}, \tag{7.4d}$$

$$\phi(\omega,\mathbf{k})=\phi^{\mathrm{mol}}(\omega)+\phi^c(\omega,\mathbf{k}), \tag{7.4e}$$

$$\phi^{\mathrm{mol}}(\omega)=\frac{2}{(2\pi)^2}\pi|\mu|^2\int_{-\infty}^{\infty}d^3q\left[\frac{(\omega^2/c^2)\bar{\rho}(\mathbf{q})\cdot\rho(\mathbf{q})-|\mathbf{q}\cdot\rho(\mathbf{q})|^2}{\omega^2/c^2-\mathbf{q}^2}-\frac{|\mathbf{q}\cdot\rho(\mathbf{q})|^2}{\mathbf{q}^2}\right], \tag{7.4f}$$

$$\phi^c(\omega,\mathbf{k})=|\mu|^2\Bigg\{\frac{2\pi}{a^2}\sum_{G_1,G_2}\left[i\frac{(k_1+G_1)^2+(k_2+G_2)^2}{\sqrt{\omega^2/c^2-(k_1+G_1)^2-(k_2+G_2)^2}}-\sqrt{(k_1+G_1)^2+(k_2+G_2)^2}\right]$$
$$-\frac{1}{2\pi}\int_{-\infty}^{\infty}d^2q\left(i\frac{\mathbf{q}^2}{\sqrt{\omega^2/c^2-\mathbf{q}^2}}-|\mathbf{q}|\right)\Bigg\}\quad\text{for } \omega>0. \tag{7.4g}$$

Note that

$$\phi^c(-\omega,\mathbf{k})=\phi^{c*}(\omega,\mathbf{k}). \tag{7.4h}$$

$G_1\equiv2\pi m_1/a$ and $G_2\equiv2\pi m_2/a$ are reciprocal lattice vectors, m_1, m_2 are integer numbers. k_1 and k_2 are the components of the momentum $\mathbf{k}$ in the first Brillouin zone, and $\rho(\mathbf{q})$ is the continuous Fourier transform of $\rho(\mathbf{r})$ [see Eq. (6.12a)]

$$V(\omega,\mathbf{k})=i(2\pi)^{-2}|\mu|^2\int d^2q\,dq_z\,\delta(\omega-\sqrt{\mathbf{q}^2+q_z^2}-\Omega_{\mathbf{k}-\mathbf{q}})$$
$$\times\frac{2\pi\mathbf{q}^2}{\sqrt{\mathbf{q}^2+q_z^2}}\frac{1}{(\omega-\Omega_{\mathbf{q}}-\Omega_{\mathbf{k}-\mathbf{q}})^2}. \tag{7.4i}$$

The integral on the right-hand side of Eq. (7.4i) is over all possible final states. The decay of the biexciton with energy ω and momentum $\mathbf{k}$ results in a photon with energy $\sqrt{\mathbf{q}^2+q_z^2}$ and momentum $(\mathbf{q},q_z)$, and an exciton with energy $\Omega_{\mathbf{k}-\mathbf{q}}$ and momentum $\mathbf{k}-\mathbf{q}$. The δ function on the right-hand side of Eq. (7.4i) represents the energy conservation.

The biexciton energy ω_B is determined from the equation

$$\bar{\Gamma}^{-1}(\omega_B,\mathbf{k})=0. \tag{7.5}$$

Effects of radiative decay of two exciton states (in particular biexcitons) in the nonlinear signal are contained in the function $\hat{\Gamma}(\omega,\mathbf{k})$ [Eq. (7.4b)]. These effects are important for two-photon resonant measurements. Consider an example of a two photon nonlinear reflection in which a single monochromatic field with frequency ω_p, tangent component of the wave vector $\mathbf{k}_p$, and amplitude E_p is reflected off the surface. The relevant polarization is

$$P(\omega_p\mathbf{k}_p)=\hat{R}^{(1)}(\omega_p\mathbf{k}_p)E_p$$
$$+\hat{R}^{(3)}(\omega_p\mathbf{k}_p;\omega_p\mathbf{k}_p,-\omega_p-\mathbf{k}_p,\omega_p\mathbf{k}_p)|E_p|^2E_p. \tag{7.6a}$$

The reflected signal I is proportional to $|P(\omega_p\mathbf{k}_p)|^2$. Since typically the linear contribution $\hat{R}^{(1)}$ is much stronger than $\hat{R}^{(3)}$, we have an intrinsic heterodyne detection. Omitting geometrical factors we obtain

$$I\sim\mathrm{Re}\{\hat{R}^{(3)}(\omega_p\mathbf{k}_p;\omega_p\mathbf{k}_p,-\omega_p-\mathbf{k}_p,\omega_p\mathbf{k}_p)$$
$$\times\hat{R}^{(1)*}(\omega_p\mathbf{k}_p)\}|E_p|^4. \tag{7.6b}$$

In the vicinity of the biexciton energy, $2\omega_p\approx\omega_B$, and when the biexciton resonance is well separated, i.e., $|\omega_B-2\omega_0|$ is much larger than the radiative width of one-exciton and two-exciton states, both $\hat{G}$ from Eq. (7.4a) and $\hat{R}^{(1)}$ are off-resonant and real, and we get for the signal in the vicinity of the biexciton resonance

$$I\sim|E_p|^4\,\mathrm{Re}\{\hat{\Gamma}(2\omega_p,2\mathbf{k}_p)\}. \tag{7.6c}$$

To calculate the expression for $\hat{\Gamma}$ in this particular case we set $\omega=2\omega_p$, $\mathbf{k}=2\mathbf{k}_p$ ($\mathbf{k}_p$ is the in-plane component of the incident wave vector in Eq. (7.4b) and recast it in the form

$$\hat{\Gamma}(\omega,\mathbf{k})=\frac{1}{\bar{\Gamma}^{-1}(2\omega_p,2\mathbf{k}_p)-V(2\omega_p,2\mathbf{k}_p)}. \tag{7.7a}$$

Expanding the real part of the denominator of Eq. (7.7a) up to linear terms in $2\omega_p-\omega_B$ and making use of Eq. (7.5), we obtain the following expression for $\hat{\Gamma}(\omega,\mathbf{k})$ in the vicinity of the biexciton resonance:

$$\hat{\Gamma}(2\omega_p,2\mathbf{k}_p)=\left[\frac{\partial\bar{\Gamma}^{-1}(\omega,2\mathbf{k}_p)}{\partial\omega}\bigg|_{\omega=\omega_B}\right]^{-1}$$
$$\times(2\omega_p-\omega_B+i\tau_B^{-1})^{-1}, \tag{7.7b}$$

with the biexciton lifetime τ_B

$$\tau_B=\frac{\partial\bar{\Gamma}^{-1}(\omega,2\mathbf{k}_p)}{\partial\omega}\bigg|_{\omega=\omega_B}|V(\omega_B,2\mathbf{k}_p)|^{-1}, \tag{7.8a}$$

or taking into account (7.4d) and (7.4e)

$$\tau_B=\int\frac{a^2}{2(2\pi)^2}\frac{d^2q}{(\omega_B-\Omega_{\mathbf{q}}-\Omega_{2\mathbf{k}_p-\mathbf{q}})^2}\left\{\frac{|\mu|^2}{(2\pi)^3}\int d^2p\,dp_z 2\pi\delta(\omega_B-\sqrt{\mathbf{p}^2+p_z^2}-\Omega_{2\mathbf{k}_p-\mathbf{p}})\frac{2\pi\mathbf{p}^2}{\sqrt{\mathbf{p}^2+p_z^2}}\frac{1}{(\omega_B-\Omega_{\mathbf{p}}-\Omega_{2\mathbf{k}_p-\mathbf{p}})^2}\right\}^{-1}. \tag{7.8b}$$

Substituting Eq. (7.7b) into (7.6c) we get for the nonlinear signal in the resonant case

$$I \sim \frac{2\omega_p-\omega_B}{(2\omega_p-\omega_B)^2+\tau_B^{-2}}. \tag{7.9}$$

We had derived Eq. (7.8b) for the biexciton radiative lifetime from the near resonance expression for the third order nonlinear response function. The same result can be obtained using the Fermi golden rule. Expressions for this lifetime for two dimensional structures were discussed in Ref. 36 for Hamiltonians depending on more parameters than Eq. (6.1a). In the particular case of the Hamiltonian (6.1a) the radiative lifetime of the biexciton $\tau_b \sim \tau_m(\Gamma_b/a)^2$, where Γ_b is the biexciton size and τ_m is the single molecule radiative lifetime. This implies that the biexciton superradiant coherent size is Γ_b, and the one exciton coherence size is its wavelength λ.

In conclusion, we note that transient grating experiments as well as two photon absorption measurements in molecular crystals have shown evidence for polariton, rather than exciton, transport.[2,18,19] This is another signature of retardation in the nonlinear susceptibilities. We can naturally account for polariton transport if we add some other degrees of freedom such as phonons or disorder. In the conventional approach we average $\mathscr{S}^{(3)}$ over these degrees of freedom, and then calculate the field. By doing so, $\mathscr{S}^{(3)}$ will depend on averages of products of G factors which contain no retardation effects and will represent exciton (rather than polariton) transport and diffusion. We can naturally account for polariton transport if we abandon the conventional two-step procedure (first susceptibilities, then signals) and calculate the signal in one step, including retardation and material interactions simultaneously in the joint space, we shall then average our products of $\hat{G}$ Green functions which contain the polariton dispersion. In order to recover these effects through $\mathscr{S}^{(3)}$ we need to incorporate retardation effects in $\mathscr{S}^{(3)}$ which, in this case, will be a tedious procedure. The expansion parameter for polariton effects was discussed by Knoester and Mukamel.[2]

We further note that in this article we did not need or use the explicit form for the action of the material system $S_{\mathrm{mat}}[B]$. We have used path integrals primarily for bookkeeping and for the systematic treatment of material and field interactions. Other applications may require a path integral approximation for the material evolution as well. This may be accomplished using geometric quantization as outlined in Appendix E.

Another issue not addressed here is that, in general, the signal is related to the field density matrix $E^\dagger E$ rather than the field itself. Throughout this article, we have factorized the expectation values of products of field operators as

$$\langle E^\dagger E\rangle = |\langle E\rangle|^2.$$

This factorization is expected to hold for strong coherent fields with a large number of photons. Otherwise, photon statistics may become important, and the present approach needs to be extended.

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APPENDIX A: EXPANSION OF THE FIELD CORRELATION FUNCTIONS

In this Appendix, we derive the expression for the nonlinear response function $\mathscr{S}^{(3)}$ [Eqs. (5.10a) and (5.12b)] and show how to expand it in powers of the fine structure constant [Eqs. (5.13), (5.14), and (5.16)].

We first introduce the one-particle irreducible Green's function $\Gamma^A_{\alpha_1,\ldots,\alpha_4}(\mathbf{r}_1,t_1,\ldots,\mathbf{r}_4,t_4)$ by

$$\begin{aligned}\langle\langle \dot{A}_{\alpha_1}(\mathbf{r}_1,t_1)\cdots\dot{A}_{\alpha_4}(\mathbf{r}_4,t_4)\rangle\rangle\\ &= i\int d\mathbf{r}_1'\,dt_1'\cdots d\mathbf{r}_4'\,dt_4'\\ &\times\langle \dot{A}_{\alpha_1}(\mathbf{r}_1,t_1)\dot{A}_{-\alpha_1'}(\mathbf{r}_1',t_1')\rangle\cdots\langle\dot{A}_{\alpha_4}(\mathbf{r}_4,t_4)\\ &\times\dot{A}_{-\alpha_4'}(\mathbf{r}_4',t_4')\rangle\Gamma^A_{\alpha_1',\ldots,\alpha_4'}(\mathbf{r}_1',t_1',\ldots,\mathbf{r}_4',t_4').\end{aligned} \tag{A1}$$

To express the signal to third order in the external polarization we have due to Eq. (4.9c) to evaluate the expectation value $\langle\dot{A}_-(\mathbf{r}_1,t_1)\dot{A}_-(\mathbf{r}_2,t_2)\dot{A}_-(\mathbf{r}_3,t_3)\dot{A}_+(\mathbf{r},t)\rangle$. From the definition of the irreducible Green's function and taking into account Eq. (3.11a) for $n=2$, we get

$$\begin{aligned}\langle\dot{A}_-(\mathbf{r}_1,t_1)\dot{A}_-(\mathbf{r}_2,t_2)\dot{A}_-(\mathbf{r}_3,t_3)\dot{A}_+(\mathbf{r},t)\rangle\\ &=\langle\langle\dot{A}_-(\mathbf{r}_1,t_1)\dot{A}_-(\mathbf{r}_2,t_2)\dot{A}_-(\mathbf{r}_3,t_3)\dot{A}_+(\mathbf{r},t)\rangle\rangle.\end{aligned} \tag{A2}$$

Combining Eqs. (A1) and (A2) and taking into account Eq. (4.9d), we obtain

$$\begin{aligned}\langle \dot{A}_-(\mathbf{r}_1,t_1)\dot{A}_-(\mathbf{r}_2,t_2)\dot{A}_-(\mathbf{r}_3,t_3)\dot{A}_+(\mathbf{r},t)\rangle = i\int & d\mathbf{r}_1'\, dt_1'\, d\mathbf{r}_2'\, dt_2'\, d\mathbf{r}_3'\, dt_3'\, d\mathbf{r}'\, dt' \{\langle \dot{A}_-(\mathbf{r}_1,t_1)\dot{A}_+(\mathbf{r}_1',t_1')\rangle \\ & \times\langle \dot{A}_-(\mathbf{r}_2,t_2)\dot{A}_+(\mathbf{r}_2',t_2')\rangle\langle \dot{A}_-(\mathbf{r}_3,t_3)\dot{A}_+(\mathbf{r}_3',t_3')\rangle \\ & \times\langle \dot{A}_-(\mathbf{r}',t')\dot{A}_+(\mathbf{r},t)\rangle\Gamma^{A}_{---+}(\mathbf{r}_1',t_1',\mathbf{r}_2',t_2',\mathbf{r}_3',t_3',\mathbf{r}',t') \\ & +\langle \dot{A}_-(\mathbf{r}_1,t_1)\dot{A}_+(\mathbf{r}_1',t_1')\rangle\langle \dot{A}_-(\mathbf{r}_2,t_2)\dot{A}_+(\mathbf{r}_2',t_2')\rangle\langle \dot{A}_-(\mathbf{r}_3,t_3)\dot{A}_+(\mathbf{r}_3',t_3')\rangle \\ & \times\langle \dot{A}_+(\mathbf{r}',t')\dot{A}_+(\mathbf{r},t)\rangle\Gamma^{A}_{----}(\mathbf{r}_1',t_1',\mathbf{r}_2',t_2',\mathbf{r}_3',t_3',\mathbf{r}',t')\}. \end{aligned} \tag{A3}$$

From the analogous representation for the expectation value $\langle \dot{A}_-(\mathbf{r}_1,t_1)\dot{A}_-(\mathbf{r}_2,t_2)\dot{A}_-(\mathbf{r}_3,t_3)\dot{A}_-(\mathbf{r},t)\rangle$ that is equal to zero due to Eq. (4.9d), we get

$$\begin{aligned}\langle \dot{A}_-(\mathbf{r}_1,t_1)\dot{A}_-(\mathbf{r}_2,t_2)\dot{A}_-(\mathbf{r}_3,t_3)\dot{A}_-(\mathbf{r},t)\rangle = i\int & dt_1'\, d\mathbf{r}_1'\, dt_2'\, d\mathbf{r}_2'\, dt_3'\, d\mathbf{r}_3'\, dt'\, d\mathbf{r}'\langle \dot{A}_-(\mathbf{r}_1,t_1)\dot{A}_+(\mathbf{r}_1',t_1')\rangle \\ & \times\langle \dot{A}_-(\mathbf{r}_2,t_2)\dot{A}_+(\mathbf{r}_2',t_2')\rangle\langle \dot{A}_-(\mathbf{r}_3,t_3)\dot{A}_+(\mathbf{r}_3',t_3')\rangle \\ & \times\langle \dot{A}_+(\mathbf{r}',t')\dot{A}_-(\mathbf{r},t)\rangle\Gamma^{A}_{----}(\mathbf{r}_1',t_1',\mathbf{r}_2',t_2',\mathbf{r}_3',t_3',\mathbf{r}',t'). \end{aligned} \tag{A4}$$

We thus get

$$\Gamma^{A}_{----}(\mathbf{r}_1',t_1',\mathbf{r}_2',t_2',\mathbf{r}_3',t_3',\mathbf{r}',t')=0. \tag{A5}$$

Substituting Eq. (A5) into Eq. (A3) and using the notation for the Green's functions (5.10b) we finally get Eq. (5.10a).

In Sec. V we described a perturbation theory for calculating optical susceptibilities and expressed them using multitime correlation functions of electromagnetic field in the joint field and material phase space. The bare (zero order) Green's functions corresponding to lines in diagrams of the perturbation theory are $D^{(0)}$, and the bare vertex of the $2n$th order is determined by the irreducible material Green's function $\langle\langle P_{\alpha_1}(\mathbf{r}_1,t_1)\cdots P_{\alpha_{2n}}(\mathbf{r}_{2n},t_{2n})\rangle\rangle_M$.

The classical limit of the electromagnetic field in this approach is obtained by using the tree approximation for the corresponding diagrammatic techniques, where we take into account only diagrams containing no loops. For the two point Green's function this means that we neglect nonlinear terms in the effective action. Thus using Eqs. (5.9) and the general relation Eq. (3.11a), the self-energy for the one particle Green's function $\langle \dot{A}_-(\mathbf{r}_1,t_1)\dot{A}_+(\mathbf{r}_2,t_2)\rangle$ is $i^{-1}\langle P_-(\mathbf{r}_1,t_1)P_+(\mathbf{r}_2,t_2)\rangle$, and we immediately get for this Green's function in the tree approximation the result of Ref. 28.

To get $\mathscr{S}^{(3)}$ we evaluate the right-hand side of Eq. (5.12b) in the tree approximation where Γ^{A}_{---+} coincides with bare vertex, i.e., [see Eq. (5.7)]

$$\begin{aligned}&\Gamma^{A}_{---+}(\mathbf{r}_1,t_1,\mathbf{r}_2,t_2,\mathbf{r}_3,t_3,\mathbf{r},t) \\ &\quad = -i\langle\langle P_-(\mathbf{r}_1,t_1)P_-(\mathbf{r}_2,t_2)P_-(\mathbf{r}_3,t_3)P_+(\mathbf{r},t)\rangle\rangle_M.\end{aligned} \tag{A6}$$

On the other hand, we can evaluate the $\bar{\mathscr{S}}^{(3)}$, the nonlinear response for a classical electromagnetic field, in a standard way, i.e., by introducing the interaction of the material system with the external transverse field E_{ext} and evaluating the polarization $P=\langle P\rangle$ using the action

$$S[B]=S_{\text{mat}}[B]+\int dt\, d\mathbf{r}\, P(\mathbf{r},t)E_{\text{ext}}(\mathbf{r},t). \tag{A7}$$

In analogy with Sec. III we get

$$\begin{aligned}P(\mathbf{r},t)=\sum_{n=0}^{\infty}\frac{i^n}{n!}\int & d\mathbf{r}_1\, dt_1\cdots d\mathbf{r}_n\, dt_n \\ & \times E_{\text{ext}}(\mathbf{r}_1,t_1)\cdots E_{\text{ext}}(\mathbf{r}_n,t_n) \\ & \times\langle P_-(\mathbf{r}_1,t_1)\cdots P_-(\mathbf{r}_n,t_n)P_+(\mathbf{r},t)\rangle_M,\end{aligned} \tag{A8a}$$

$$\langle P_-(\mathbf{r}_1,t_1)\cdots P_-(\mathbf{r}_n,t_n)\rangle_M=0. \tag{A8b}$$

Using Eq. (A8b) we have

$$\begin{aligned}&\langle P_-(\mathbf{r}_1,t_1)\cdots P_-(\mathbf{r}_n,t_n)P_+(\mathbf{r},t)\rangle_M \\ &\quad =\langle\langle P_-(\mathbf{r}_1,t_1)\cdots P_-(\mathbf{r}_n,t_n)P_+(\mathbf{r},t)\rangle\rangle_M.\end{aligned} \tag{A9}$$

From Eq. (A8a), and taking into account Eq. (A9) we obtain

$$\begin{aligned}&\bar{\mathscr{S}}^{(3)}(\mathbf{r},t;\mathbf{r}_1,t_1\mathbf{r}_2,t_2,\mathbf{r}_3,t_3) \\ &\quad =-i\langle\langle P_-(\mathbf{r}_1,t_1)P_-(\mathbf{r}_2,t_2)P_-(\mathbf{r}_3,t_3)P_+(\mathbf{r},t)\rangle\rangle_M.\end{aligned} \tag{A10}$$

Comparing Eqs. (A6) and (5.12b) with Eq. (A10) we see that in the tree approximation $\mathscr{S}^{(3)}=\bar{\mathscr{S}}^{(3)}$. It is easy to show that this result applies to higher order susceptibilities as well, and we have in the tree approximation $\mathscr{S}^{(n)}=\bar{\mathscr{S}}^{(n)}$. The susceptibilities $\bar{\mathscr{S}}^{(n)}$ thus become constants in a nonlinear theory of the electromagnetic field described by $S_{\text{eff}}[A]$. By including in the perturbation theory diagrams containing loops, we can systematically incorporate radiative corrections to the exact susceptibilities $\mathscr{S}^{(n)}$.

To get the first and the second order corrections to $\mathscr{S}^{(3)}$, we expand Eq. (5.2) in powers of $S'_{\text{eff}}[A]$, evaluating the expectation values of products of variables A by means of the Wick theorem keeping the terms with one or two internal lines (Green's functions $D^{(0)}_{\alpha_1\alpha_2}$). This procedure results in Eqs. (5.16). The diagrams corresponding to these terms are presented in Fig. 2.

APPENDIX B: NONLINEAR RESPONSE FUNCTIONS AND GREEN'S FUNCTIONS OF THE ELECTROMAGNETIC FIELD

In this appendix we derive Eqs. (5.12) which connect the nonlinear response functions $\mathscr{S}^{(n)}$ to one particle irreducible Green's functions of electromagnetic field.

A standard procedure for calculating the nonlinear optical properties of materials is by introducing nonlinear response functions. External sources which result in creation of electromagnetic waves in the system can be described by the external polarization P_{ext}. We can introduce another variable, namely, the external electric field E_{ext} related to P_{ext} linearly by means of vacuum Green's function of electromagnetic field $\mathscr{G}$ [see Eq. (6.12)] (all formulas in this Appendix will be written in an operator form)

$$E_{\text{ext}}=\mathscr{G}P_{\text{ext}}. \tag{B1}$$

Equation (B1) is linear and does not contain any information about the material. The only reason for introducing E_{ext} is that it is somewhat more convenient to express the optical signals in terms of E_{ext} (i.e., the electric field we would have had we created the wave with the same sources in vacuum) rather than in terms of the external polarization.

The expectation values of the transverse electric field $E^{\perp}$ and the polarization of the material are determined completely by P_{ext} [or due to Eq. (B1) by E_{ext}] and can be expanded in terms of the latter. These expansions lead to the response functions $\mathscr{R}^{(n)}$ introduced in Sec. IV and $R^{(n)}_{\text{ext}}$

$$E^{\perp}=\sum_{n=1}^{\infty}\frac{1}{n!}\mathscr{R}^{(n)}(P_{\text{ext}})^n, \tag{B2a}$$

$$E^{\perp}=\sum_{n=1}^{\infty}\frac{1}{n!}R^{(n)}_{\text{ext}}(E_{\text{ext}})^n. \tag{B2b}$$

On the other hand, the transverse electric field is related to the total polarization in the system, which consists of the external polarization P_{ext} and the polarization of the material, by means of the vacuum Green's function of the electromagnetic field $\mathscr{G}$ [see Eq. (6.12)]

$$E^{\perp}=\mathscr{G}(P+P_{\text{ext}}). \tag{B3}$$

Combining Eqs. (B2a) with (B3), we get the expansion of P in powers of P_{ext}

$$P=(\mathscr{G}^{-1}\mathscr{R}^{(1)}-I)P_{\text{ext}}+\sum_{n=1}^{\infty}\frac{1}{n!}\mathscr{G}^{-1}\mathscr{R}^{(n)}(P_{\text{ext}})^n. \tag{B4}$$

If we solve Eq. (B2a) iteratively, we get P_{ext} expanded in powers of $E^{\perp}$. Substituting this expansion into Eq. (B4) we obtain the expansion of the polarization in the material P in powers of transverse electric field $E^{\perp}$,[1]

$$P=\sum_{n=1}^{\infty}\frac{1}{n!}\mathscr{S}^{(n)}(E^{\perp})^n. \tag{B5}$$

Our goal is to derive Eqs. (5.12) connecting the response functions $\mathscr{S}^{(n)}$ to one particle irreducible Green function of the electromagnetic field Γ^{A} [we will confine ourselves to systems with an inversion symmetry center, i.e., $\mathscr{S}^{(2n)}=0$].

We begin with the direct derivation of Eqs. (5.12a) and (5.12b). To that end, we expand the expectation value of the transverse electric field in the system $E^{\perp}$, in powers of external polarization P_{ext} to third order in P_{ext}. Keeping the first and the third order in P_{ext} terms in the expansion (3.7a) and taking into account Eq. (4.9c) for $n=3$, Eqs. (5.10a), and (5.10b) we obtain the following expression in operator form:

$$E^{\perp}=\bar{D}^{\text{ret}}P_{\text{ext}}+\frac{1}{3!}\bar{D}^{\text{ret}}\Gamma^{A}_{+---}(\bar{D}^{\text{ret}}P_{\text{ext}})^3. \tag{B6}$$

We can easily get from Eqs. (B6) and (B3)

$$P=[\mathscr{G}^{1}-(\bar{D}^{\text{ret}})^{-1}]E^{\perp}+\frac{1}{3!}\Gamma^{A}_{+---}(\bar{D}^{\text{ret}}P_{\text{ext}})^3. \tag{B7}$$

Since we are keeping the terms up to the third order in P_{ext}, we can substitute $E^{\perp}$ instead of $\bar{D}^{\text{ret}}P_{\text{ext}}$ in the second term on the right-hand side of Eq. (B7) [this follows from Eq. (B6) after neglecting the nonlinear in P_{ext} term]. We get finally

$$P=(\mathscr{G}^{-1}-(\bar{D}^{\text{ret}})^{-1})E^{\perp}+\frac{1}{3!}\Gamma_{+---}(E^{\perp})^3. \tag{B8}$$

Comparing Eqs. (B8) and (B5) we get Eqs. (5.12a) and (5.12b). To prove Eq. (5.12c) we combine expansion (B5) with Eq. (B3) to get

$$(\mathscr{G}^{-1}-\mathscr{S}^{(1)})E^{\perp}=P_{\text{ext}}+\sum_{n=1}^{\infty}\frac{1}{(2n+1)!}\mathscr{S}^{(2n+1)}\times(E^{\perp})^{2n+1}. \tag{B9}$$

Making use of Eq. (5.12a) we recast Eq. (B9) in the form

$$(\bar{D}^{\text{ret}})^{-1}E^{\perp}=P_{\text{ext}}+\sum_{n=1}^{\infty}\frac{1}{(2n+1)!}\mathscr{S}^{(2n+1)}(E^{\perp})^{2n+1}. \tag{B10a}$$

Putting $\mathscr{S}^{(2n)}=0$ and using Eq. (4.9c) and the notation (5.2) and (5.10b) we recast Eq. (B2a) in the form

$$E^{\perp}=\bar{D}^{\text{ret}}P_{\text{ext}}+\sum_{n=1}^{\infty}\frac{i^{2n+1}}{(2n+1)!}D^{(2n+2)}_{+-\dots-}(P_{\text{ext}})^{2n+1}. \tag{B10b}$$

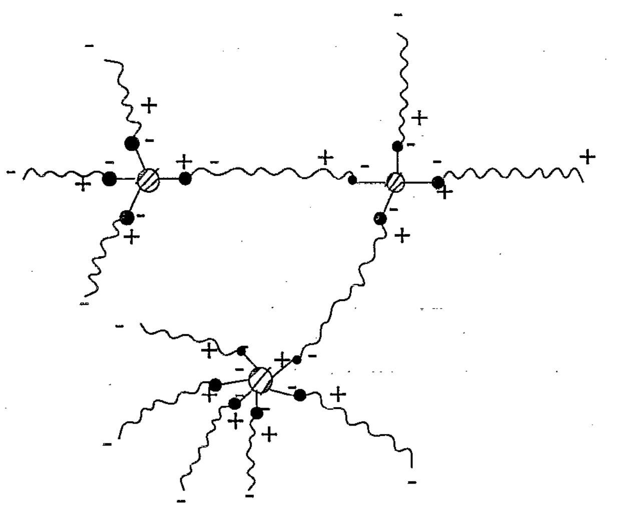

FIG. 3. Typical nonzero tree diagram for a higher order Green's function of the electromagnetic field Eq. (B10b). The lines stand for the exact two point Green's functions, the vertices (hatched circles) are the one-particle irreducible Green's functions Γ^A. This diagram contains ten free lines and these correspond to $D^{(2n+2)}$ with $n=4$.

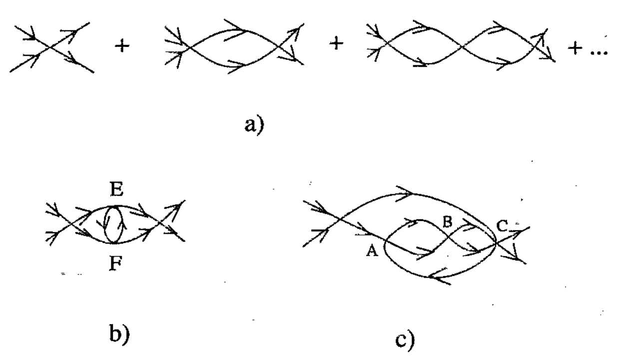

FIG. 4. Diagrammatic representation of contributions to the correlation functions (6.3). Lines with arrows stand for bare Green's functions $\langle CC^+\rangle$ [with respect to quadratic action Eq. (C.1b)]. Vertices represent the nonquadratic part of action $S^{\text{int}}_{\text{mat}}$ from Eq. (C.1c). The time ξ in the diagrams takes values on the Keldysh time loop (Ref. 33). (a) Ladder diagrams contributing to Eq. (6.3). (b) and (c) Diagrams containing loops and therefore equal to zero. Going along the paths *EFE* and *ABCA* along the directions of arrows we return to the beginning, to get zero.

To prove Eq. (5.12c) we shall compare Eqs. (B.10a) and (B.10b). First we observe that the coefficient $D^{(2n+2)}_{+-\cdots-}$ in the expansion (B.10b) is given by the sum of all diagrams with lines and vertices presented on Fig. 2, and with one external line with external index $+$ and $2n$ external lines with indices $-$. The one particle irreducible Green's functions $\Gamma^A_{\alpha_1,\ldots,\alpha_{2n}}$ are defined in the following manner: $i\Gamma^A_{\alpha_1,\ldots,\alpha_{2n}}$ is the sum of all diagrams which cannot be cut by one line into two disconnected diagrams. Introducing Γ^A we conclude that $D^{(2n+2)}_{+-\cdots-}$ is the sum of all tree diagrams (i.e., diagrams without loops), with $\Gamma^A_{\alpha_1,\ldots,\alpha_{2n}}$ as vertices, and exact Green's functions $D_{\alpha\beta}$ as lines. Note that we have to sum over all Greek indices corresponding to internal lines in the diagram. However, due to the fact that $D_{--}=0$ and $\Gamma^A_{\alpha_1,\ldots,\alpha_m}=0$ if $\alpha_1=\cdots=\alpha_m=-$, all the internal indices are fixed: for internal lines we have $D_{\alpha\beta}$ with $\alpha=-$, $\beta=+$, for vertices $\Gamma^A_{\alpha_1,\ldots,\alpha_{2m}}$ we have $\alpha_1=\cdots=\alpha_{m-1}=-$, $\alpha_m=+$. A typical diagram is presented in Fig. 3. In other words, all lines stand for Green's functions $\bar{D}^{\text{ret}}$ and vertices stand for $\Gamma^A_{-\cdots-+}$. On the other hand, if we solve Eq. (B10a) iteratively, and expand $E^\perp$ in powers P_{ext} we can present the expansion coefficients in the form of the sum of the same tree diagrams with the only difference that the vertices are the response functions $\mathscr{S}^{(2n+1)}$. Since expansion (B5) is unique, this completes the proof of Eq. (5.12). Equations (5.12) enable us to use a convenient Green's function perturbation technique for evaluating the nonlinear response functions $\mathscr{S}^{(n)}$.

The approach presented here shows clearly effects of cascading in the formation of higher order nonlinear optical signals. As mentioned above, the nonlinear signal expressed in terms of the external field or external polarization is given by the sum of all tree diagrams with nonlinear response functions $\mathscr{S}^{(n)}$ as vertices and one-particle Green's functions $\bar{D}^{\text{ret}}$ as lines. Physically this means that nonlinear polarization creates the electric field which in turn is involved in formation of the nonlinear polarization. Representation of the signal in terms of the tree diagrams in a convenient and clear way to classify all the contributions to the nonlinear signal to a given order in the external field, expressed in terms of response functions $\mathscr{S}^{(n)}$.

APPENDIX C: NONLINEAR RESPONSE OF MOLECULAR ASSEMBLIES

In this Appendix we evaluate the correlation functions (6.3) from Sec. VI.

The expectation values in Eq. (6.3) are taken with respect to the action of the form

$$S_{\text{mat}}[C,\bar{C}]=S^{(0)}_{\text{mat}}[C,\bar{C}]+S^{\text{int}}_{\text{mat}}[C,\bar{C}], \tag{C1a}$$

$$S^{(0)}_{\text{mat}}[C,\bar{C}]=\int d\xi\left\{i\sum_n \bar{C}_n(\xi)\frac{\partial C_n(\xi)}{\partial\xi}\right. \\ \left. -\sum_n \Omega_n\bar{C}_n(\xi)C_n(\xi)-\sum_{m\neq n} J_{mn}\bar{C}_m(\xi)C_n(\xi)\right\}, \tag{C1b}$$

$$S^{\text{int}}_{\text{mat}}[C,\bar{C}]=-\int d\xi\frac{g}{2}\sum_n \bar{C}^2_n(\xi)C^2_n(\xi). \tag{C1c}$$

Here ξ denotes the time variable on the Keldysh time loop with the natural time ordering. For each value of the original time variable we have two values of ξ corresponding to the two parts of the loop. The variables C and $\bar{C}$ stand for the quantum operators $\hat{C}$ and $\hat{C}^+$, and the first term in Eq. (C.1b) provides the commutation relations (6.1b).

We will concentrate on evaluating $\mathscr{S}^{(a)}$; the procedure of evaluating $\mathscr{S}^{(b)}$ is identical. To evaluate the right-hand side of Eq. (6.3b) we expand the $\exp(iS^{\text{int}}_{\text{mat}})$ factor in powers of C and $\bar{C}$, calculating the resulting expectation values with respect to $S^{(0)}_{\text{mat}}$ using the Wick theorem. We first observe that nonzero contributions cannot contain loops, i.e., products of the type $\langle C(\xi_1)\bar{C}(\xi_n)\rangle\langle C(\xi_n)\bar{C}(\xi_{n-1})\rangle\cdots\langle C(\xi_2)\bar{C}(\xi_1)\rangle$ as the condition of all the correlators in the product being nonzero $\xi_1\langle\xi_2\langle\cdots\langle\xi_{n-1}\langle\xi_n\langle\xi_1$ cannot be satisfied. Therefore, the nonzero contributions can have only the following types of coupling: the variables $\bar{C}$ in Eq. (6.3b) are coupled to the variable C belonging to the same vertex given by Eq. (C.1c), the variables C belonging to the vertex considered can be coupled to the variables C belonging to some other (but the same) vertex, etc. In diagrammatic techniques such contributions are usually denoted the ladder diagrams. Ladder diagrams and examples of diagrams containing loops are presented in Fig. 4. After making this important observation we can switch to the ± variables using ordinary time variables, and rewriting the $S_{\text{mat}}^{\text{int}}$ in the form

$$S_{\text{mat}}^{\text{int}}[C,\bar{C}]=-g\int_{-\infty}^{\infty}d\tau\sum_n[C_+^2(\tau)-\tfrac{1}{4}C_-^2(\tau)]\times\bar{C}_+(\tau)\bar{C}_-(\tau)-g\int_{-\infty}^{\infty}d\tau\sum_n[\bar{C}_+^2(\tau)-\tfrac{1}{4}\bar{C}_-^2(\tau)]C_+(\tau)C_-(\tau). \qquad \text{(C2)}$$

We note that nonzero contributions do not contain the second term of Eq. (C.2). Actually, the $\bar{C}$ variables in Eq. (6.3b) can be coupled only to the C variables of the first term of Eq. (C.2) [due to Eq. (3.11)]. The $\bar{C}$ variables of this vertex can be coupled only to the C variables of the vertex of the same type, etc. We thus obtain the following expression for $\mathscr{S}^{(a)}$:

$$\begin{aligned}\mathscr{S}^{(a)}_{nm_1m_2m_3}(t,t_1,t_2,t_3)={}&-i\sum_{N=1}^{\infty}\int_{-\infty}^{\infty}d\tau_1\cdots d\tau_N\sum_{j_1,\ldots,j_N}(-2ig)^N\langle\bar{C}_{m_1}(t_1)_-C_{j_1}(\tau_1)_+\rangle\langle\bar{C}_{m_2}(t_2)_-C_{j_1}(\tau_1)_+\rangle\\&\times\langle\bar{C}_{j_1}(\tau_1)_-C_{j_2}(\tau_2)_+\rangle\langle\bar{C}_{j_1}(\tau_1)_+C_{j_2}(\tau_2)_+\rangle\cdots\langle\bar{C}_{j_{N-1}}(\tau_{N-1})_-C_{j_N}(\tau_N)_+\rangle\\&\times\langle\bar{C}_{j_{N-1}}(\tau_{N-1})_+C_{j_N}(\tau_N)_+\rangle\langle\bar{C}_{j_N}(\tau_N)_-C_n(\tau)_+\rangle\langle\bar{C}_{j_N}(\tau_N)_+C_{m_3}(\tau_3)_-\rangle.\end{aligned} \qquad \text{(C3)}$$

Since the time integration in Eq. (C.3) is performed from $-\infty$ to $+\infty$, we can easily switch to the frequency domain. The free correlation function is on the right-hand side of Eq. (C.3) can be evaluated directly using the quantum mechanical representation of Sec. IV. Evaluating $\mathscr{S}^{(b)}$ in the same manner, and combining all the contributions we finally obtain the expression for $\mathscr{S}^{(3)}$ in the frequency domain [see Eq. (6.5)].

APPENDIX D: BEYOND THE TREE APPROXIMATION

In this appendix we derive the expression for the third order nonlinear response function near the biexciton resonance [Eqs. (6.9)].

As indicated in Sec. I, we cannot describe the effects of radiative decay of two exciton states in the nonlinear signal without taking into account the quantum nature of electromagnetic field. The effects of radiative decay of two-exciton states are important near the two-photon resonance especially in the case when the spectrum of two-exciton states contains bound states (biexcitons). To see this we will use the simple model of interacting bosons introduced in Sec. VI and calculate the nonlinear susceptibility near the resonance with the bound two-particle state using the techniques developed in the previous sections.

To evaluate the susceptibility $\mathscr{S}^{(3)}$ near the biexciton resonance we use the path integral representation (5.2) for the Green's function [Eq. (5.10a)] and perform the expansion of $\exp[iS'_{\text{eff}}]$ [see Eq. (5.9a)] in powers of $\dot{A}$. Note that due to Eq. (6.1c) and (5.7), each couple of variables $\dot{A}$ in the effective action gives an additional power of the parameter $|\mu|^2$ which is proportional to the fine structure constant. Thus, the only reason we cannot confine ourselves to taking into account only the lowest order terms is that the coefficients in the expansion [Eq. (5.7)] which are the material correlation functions can contain large resonant factors. Each of these factors is due to some two exciton (i.e., biexciton) intermediate states in the spectral decomposition of the material correlation functions in Eq. (5.7). Thus to first order in the fine structure constant we have to use only those terms in the expansion (5.7) that contain the maximum number of resonant factors or, in other words, the maximum number of two-exciton states in the spectral decomposition of material correlation functions (for the given number of the variables $\dot{A}$). It is easy to see that these terms are given only by terms linear in S'_{eff} in the expansion of $\exp(iS'_{\text{eff}})$. Near resonance we get

$$D_{---+}(\mathbf{r}_1,t_1,\mathbf{r}_2,t_2,\mathbf{r}_3,t_3,\mathbf{r},t)=i\langle\dot{A}_-(\mathbf{r}_1,t_1)\dot{A}_-(\mathbf{r}_2,t_2)\dot{A}_-(\mathbf{r}_3,t_3)\dot{A}_+(\mathbf{r},t)S'_{\text{eff}}[A]\rangle, \qquad \text{(D1)}$$

where the average of A variables in Eq. (D.1) and below is with the zero-order effective action $S_{\text{eff}}^{(0)}[A]$ [see Eqs. (5.9)]. Near resonance, substituting $S_{\text{eff}}^{(\text{int})}[A]$ from Eqs. (5.7) and (5.9) to (D.1), we can also replace the irreducible material correlation functions in Eq. (5.7) by ordinary ones [Eq. (3.6)] since the difference between them is of higher order in the fine structure constant. We can make further simplifications. On the one hand, we are interested in getting the maximum number of two exciton intermediate states in the spectral decomposition of material correlators in Eq.

(5.7). On the other hand, as we are interested in the effects of biexciton decay in $\mathscr{S}^{(3)}$ but not the energy shift, we would not take into account intermediate states containing more than two excitons, as the energy of these states is higher than that of the biexciton. Consequently, we consider only one and two exciton states in the spectral decomposition of the material correlation functions. The next simplification comes since there are two kinds of two-photon resonant terms in the Green's function (D.1): Terms resonant when a sum of two frequencies corresponding to incoming fields is close to the biexciton energy, and the resonant terms with this sum close to the biexciton energy taken with the opposite sign. This leads to the following representation of D_{---+} from Eq. (D1):

$$D_{---+}=D^{(+)}_{---+}+D^{(-)}_{---+}, \tag{D2}$$

where $D^{(+)}$ and $D^{(-)}$ stand for the terms of the first and the second kind.

We will concentrate on evaluating the Green's function $D^{(+)}_{---+}$, $D^{(-)}_{---+}$ can be evaluated in a completely analogous manner. It is convenient to switch back from summation over Greek to latin indices in Eq. (5.7). Taking into account all the simplifications mentioned above, substituting the expression for polarization [Eq. (6.1c)] into Eq. (5.7) we then use Wick's theorem to calculate the expectation values of products of variables $\dot{A}$ in Eq. (D1). Keeping only terms containing the highest possible power of the resonant factor we get the following expression for $D^{(+)}_{---+}$ (see Fig. 5):

$$
\begin{aligned}
&D^{(+)}_{---+}(\mathbf{r}_1,t_1,\mathbf{r}_2,t_2,\mathbf{r}_3,t_3,\mathbf{r},t)=D_{\mathrm{I}}+D_{\mathrm{II}},\\
&D_{\mathrm{I}}=\sum_{n=2}^{\infty} i^{2n}|\mu|^{2n}\sum_{m_1,\ldots,m_{2n}}\int d\mathbf{r}_1'\cdots d\mathbf{r}_{2n}'\int_{-\infty}^{t}d\tau_{2n}\int_{-\infty}^{\tau_{2n}}d\tau_{2n-1}\cdots\int_{-\infty}^{\tau_2}d\tau_1\langle\Omega_M|\hat{C}_{m_{2n}}(\tau_{2n})\\
&\quad\times\hat{C}_{m_{2n-1}}(\tau_{2n-1})\hat{C}^{+}_{m_{2n-2}}(\tau_{2n-2})\hat{C}_{m_{2n-3}}(\tau_{2n-3})\cdots\hat{C}^{+}_{m_4}(\tau_4)\hat{C}_{m_3}(\tau_3)\hat{C}^{+}_{m_2}(\tau_2)\hat{C}^{+}_{m_1}(\tau_1)\\
&\quad\times|\Omega_M\rangle\rho(\mathbf{r}_1'-\mathbf{R}_{m_1})\rho(\mathbf{r}_2'-\mathbf{R}_{m_2})\cdots\rho(\mathbf{r}_{2n}'-\mathbf{R}_{m_{2n}})\langle\dot{A}_-(\mathbf{r}_{2n}',\tau_{2n})\dot{A}_+(\mathbf{r},t)\rangle\\
&\quad\times\sum_{\substack{\text{perm}\\(\mathbf{r}_j,t_j)}}\{\langle\dot{A}_-(\mathbf{r}_1,t_1)\dot{A}_+(\mathbf{r}_1',\tau_1)\rangle\langle\dot{A}_-(\mathbf{r}_2,t_2)\dot{A}_+(\mathbf{r}_2',\tau_2)\rangle\\
&\quad\times\langle\dot{A}_-(\mathbf{r}_3,t_3)\dot{A}_+(\mathbf{r}_{2n-1}',\tau_{2n-1})\rangle\}\langle\dot{A}_1(\mathbf{r}_3',\tau_3)\dot{A}_1(\mathbf{r}_4',\tau_4)\rangle\\
&\quad\times\langle\dot{A}_L(\mathbf{r}_5',\tau_5)\dot{A}_L(\mathbf{r}_6',\tau_6)\rangle\cdots\langle\dot{A}_L(\mathbf{r}_{2n-3}',\tau_{2n-3})\dot{A}_L(\mathbf{r}_{2n-2}',\tau_{2n-2})\rangle,\\
&D_{\mathrm{II}}=-\sum_{n=2}^{\infty} i^{2n}|\mu|^{2n}\sum_{m_1,\ldots,m_{2n}}\int d\mathbf{r}_1'\cdots d\mathbf{r}_{2n}'\int_{-\infty}^{t}d\tau_{2n}\int_{-\infty}^{\tau_{2n}}d\tau_{2n-2}\int_{-\infty}^{\tau_{2n-2}}d\tau_{2n-3}\cdots\int_{-\infty}^{\tau_2}d\tau_1\\
&\quad\times\int_{-\infty}^{\tau_{2n}}d\tau_{2n-1}\langle\Omega_M|\hat{C}_{m_{2n-1}}(\tau_{2n-1})\hat{C}_{m_{2n}}(\tau_{2n})\hat{C}^{+}_{m_{2n-2}}(\tau_{2n-2})\hat{C}_{m_{2n-3}}(\tau_{2n-3})\cdots\hat{C}^{+}_{m_4}(\tau_4)\hat{C}_{m_3}(\tau_3)\hat{C}^{+}_{m_2}(\tau_2)\\
&\quad\times\hat{C}^{+}_{m_1}(\tau_1)|\Omega_M\rangle\rho(\mathbf{r}_1'-\mathbf{R}_{m_1})\cdots\rho(\mathbf{r}_{2n}'-\mathbf{R}_{m_{2n}})\langle\dot{A}_-(\mathbf{r}_{2n}',\tau_{2n})\dot{A}_+(\mathbf{r},t)\rangle\sum_{\substack{\text{perm}\\(\mathbf{r}_j,t_j)}}\{\langle\dot{A}_-(\mathbf{r}_1,t_1)\dot{A}_+(\mathbf{r}_1',\tau_1)\rangle\\
&\quad\times\langle\dot{A}_-(\mathbf{r}_2,t_2)\dot{A}_+(\mathbf{r}_2',\tau_2)\rangle\langle\dot{A}_-(\mathbf{r}_3,t_3)\dot{A}_+(\mathbf{r}_{2n-1},\tau_{2n-1})\rangle\}\langle\dot{A}_L(\mathbf{r}_3',\tau_3)\dot{A}_L(\mathbf{r}_4,\tau_4)\rangle\\
&\quad\times\langle\dot{A}_L(\mathbf{r}_5',\tau_5)\dot{A}_L(\mathbf{r}_6',\tau_6)\rangle\cdots\langle\dot{A}_L(\mathbf{r}_{2n-3}',\tau_{2n-3})\dot{A}_L(\mathbf{r}_{2n-2}',\tau_{2n-2})\rangle.
\end{aligned}
\tag{D3}
$$

Here $\mathbf{R}_m$ is the position of the mth molecule. The following procedure is straightforward. Making use of Eqs. (5.10a) and (5.10b) we can get from Eq. (D3) an expression for $\mathscr{S}^{(3)}$ near the biexcitonic resonance. The material correlation functions on the right-hand side of Eq. (D3) involve only one particle and two particle states and hence can be expressed in terms of one particle scattering matrix $\bar{\Gamma}$. Switching to the frequency domain and using the similar to Eq. (D3) expression for the Green's function $D^{(-)}_{---+}$, we get after straightforward calculations the resonant expression for the nonlinear response of $\mathscr{S}^{(3)}$ [see Eq. (6.5) with $\hat{\Gamma}$ given by Eq. (6.9) instead of $\bar{\Gamma}$].

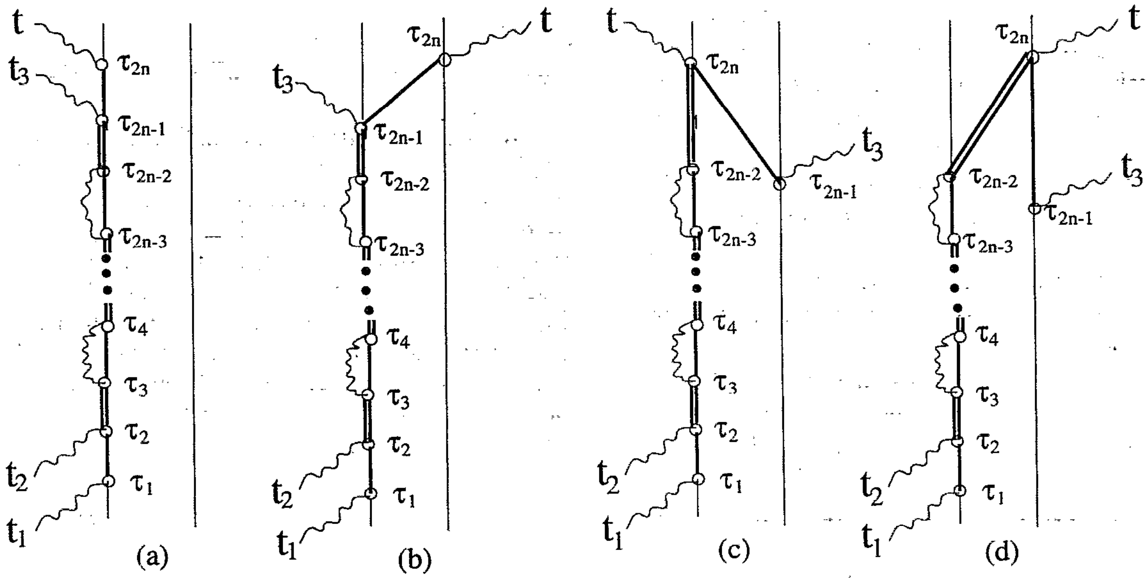

FIG. 5. Double sided Feynman diagram representation of contributions to Eq. (D3). $D_{\rm I}$ is represented by diagrams (a) and (b), whereas $D_{\rm II}$ is given by (c) and (d). The left and the right lines denote the first and the second parts of the Keldysh loop. The wavy lines denote the $\langle \hat{A}\hat{A}\rangle$ correlation function. The solid lines stand for the material correlation function, the single and the double lines stand for one-exciton and two-exciton intermediate states.

APPENDIX E: NONRETARDED RESPONSE FUNCTION OF AN ASSEMBLY OF TWO-LEVEL SYSTEMS

We will apply the general results of this paper to the case when the material system is a set of neutral nonoverlapping two-level molecules.[28] For this case we take the material Hamiltonian in the Heitler–London form

$$\hat{H}_{\rm mat}=\sum_m \Omega_m B_m^\dagger B_m+\sum_{m\neq n} J_{mn}B_m^\dagger B_n. \tag{E1}$$

The first term in Eq. (E1) is the Hamiltonian of noninteracting two-level systems, the second term describes the Coulomb (dipole–dipole) interaction in the Heitler–London approximation. The operators $\hat{B}_m$ are the transition operator of the mth two-level system, changing its excited state to the ground state. They satisfy the commutation relations

$$[B_m,B_{m'}^\dagger]=(1-2B_m^\dagger B_m)\delta_{mm'}. \tag{E2}$$

The polarization operator $\hat{P}(r)$ can be represented in the following form:

$$\hat{P}(\mathbf{r})=\sum_m \hat{P}_m(\mathbf{r}),$$

$$\hat{P}_m(\mathbf{r})=|\mu|\rho(\mathbf{r}-\mathbf{R}_m)(\hat{B}_m+\hat{B}_m^\dagger),\qquad \left|\int \rho(\mathbf{r})d\mathbf{r}\right|. \tag{E3}$$

The classical phase space of a two-level system is the two dimensional sphere S^2 (it can be regarded also as one dimensional complex projective space CP^1). The space of states is the two dimensional space of holomorphic sections of the twisted bundle $\mathcal{O}(1)$ on CP^1 (see Ref. 37). The classical variables corresponding to operators $\hat{B}$ and $\hat{B}^\dagger$ are B^x-iB^y and B^x+iB^y, respectively, where $\mathbf{B}=(B^x,B^y,B^z)$ is a unit three dimensional vector on the phase space S^2. The action $S_{\rm mat}[B]$ has the form

$$S_{\rm mat}[B]=\sum_m S_m^{(0)}-\sum_m \int dt\,\Omega_m \frac{1+B_m^z}{2} \times \sum_{m\neq n}\int dt\, J_{mn}B_m^\perp\cdot B_n^\perp, \qquad B^\perp=(B^x,B^y,0) \tag{E4}$$

where $S_m^{(0)}$ is the multilevel action (for the mth two-level system), $e^{iS_m^{(0)}}$ being the parallel transition along the canonical connection on the bundle $O(1)$ with the curvature ω—the canonical simplectic structure on S^2 for spin 1/2

$$\omega=\tfrac{1}{2}\epsilon_{ijk}\,dB_j\wedge dB_kB_i, \tag{E5}$$

where $|\mu|\rho(r)$ is the polarization operator between the excited and the ground states of a molecule (see Ref. 3 for the microscopic expression).

$\mathcal{P}^{(3)}$ were calculated in Ref. 28 using a different method (solving the equations of motion for material operators in the external transverse field). Thus, in the tree approximation we can use the results of Ref. 28.

APPENDIX F: GREEN'S FUNCTION EXPRESSIONS (GFE) FOR THE NONLINEAR RESPONSE OF THE SYSTEM OF INTERACTING BOSONS

In this appendix we derive Eqs. (6.10) for the two-exciton scattering matrix $\hat{\Gamma}_{mn}(\omega)$ which is affected by the quantum electromagnetic field. Together with Eq. (6.14) it provides an expression for the nonlinear response function $\hat{R}$ with respect to the external field.

In Sec. V we obtained a general procedure of evaluating radiative corrections to the nonlinear response functions by integrating first over the material variables B to get the effective action which depends only on the field variables A. In this appendix we adopt a different approach based on integrating over the vector potential first to get the effective action for the material variables. This approach seems to be more appropriate for the material system described by Eqs. (6.1) due to the following reasons. Correlation functions of the material system can be evaluated exactly since the Hamiltonian (6.1a) conserves the number of particles. If we neglect the terms in the effective material action which do not conserve the number of particles (these terms are induced by interaction with transverse electromagnetic field), we can still obtain exact expressions for the correlation functions of material variables, when the material system is described by the effective action. To perform the integration over the vector potential in Eq. (4.9a) it is convenient to introduce a function $W[P_{\text{ext}},Q]$ which depends on the generating function $Q(r,t)$,

$$W[P_{\text{ext}},Q]=\int \mathscr{D}[A]\mathscr{D}[B]\exp\left\{i\int d\mathbf{r}\,dt[P_{\text{ext}}(\mathbf{r},t)\dot{A}_{-}(\mathbf{r},t)+Q(\mathbf{r},t)\dot{A}_{+}(\mathbf{r},t)]\right\}$$
$$\times\exp\left\{i\left(S^{(K)}_{\text{mat}}[B]+S^{(K)}_{\text{rad}}[a]+\int dt\,d\mathbf{r}(P_{+}\dot{A}_{-}+P_{-}\dot{A}_{+})\right)\right\}. \tag{F1}$$

Combining Eq. (4.9a) with Eq. (F1) we get

$$E^{\perp}(\mathbf{r},t)=-i\frac{\delta W[P_{\text{ext}},Q]}{\delta Q(\mathbf{r},t)}\bigg|_{Q=0}. \tag{F2}$$

The integration over the vector potential in Eq. (F1) can be performed exactly, and yields

$$W[P_{\text{ext}},Q]=\bigg\langle\exp\bigg[i\int dt'\,dt''\,d\mathbf{r}'\,d\mathbf{r}''(\mathscr{G}_{+-}(\mathbf{r}'',t'';\mathbf{r}',t')P_{-}(\mathbf{r}'',t'')P_{\text{ext}}(\mathbf{r}',t')+\mathscr{G}_{+-}(\mathbf{r}'',t'';\mathbf{r}',t')Q(\mathbf{r}'',t'')P_{+}(\mathbf{r}',t')$$
$$+\mathscr{G}_{++}(\mathbf{r}'',t'';\mathbf{r}',t')Q(\mathbf{r}'',t'')P_{-}(\mathbf{r}',t'))\bigg]\bigg\rangle_{S^{(m)}_{\text{eff}}}\exp\bigg[i\int dt'\,dt''\,d\mathbf{r}'\,d\mathbf{r}''(\mathscr{G}_{+-}(\mathbf{r}'',t'';\mathbf{r}',t')Q(\mathbf{r}'',t'')$$
$$\times P_{\text{ext}}(\mathbf{r}',t')+\frac{1}{2}\mathscr{G}_{++}(\mathbf{r}'',t'';\mathbf{r}',t')Q(\mathbf{r}'',t'')Q(\mathbf{r}',t'))\bigg]. \tag{F3}$$

We used in Eq. (F3) the following notation:

$$\langle f[B]\rangle_{S^{(m)}_{\text{eff}}}=\int \mathscr{D}[B]f[B]\exp(iS^{(m)}_{\text{eff}}[B]), \tag{F4}$$

for an arbitrary function $f[B]$ of material variables. $S^{(m)}_{\text{eff}}[B]$ has the form

$$S^{(m)}_{\text{eff}}[B]=S^{(K)}_{\text{mat}}+\int dt'\,dt''\,d\mathbf{r}'\,d\mathbf{r}''[\mathscr{G}_{+-}(\mathbf{r}'',t'';\mathbf{r}',t')$$
$$\times P_{-}(\mathbf{r}'',t'')P_{+}(\mathbf{r}',t')$$
$$+\tfrac{1}{2}\mathscr{G}_{++}(\mathbf{r}'',t'';\mathbf{r}',t')P_{-}(\mathbf{r}'',t'')P_{-}(\mathbf{r}',t')], \tag{F5}$$

and the Green's functions of the transverse field $\mathscr{G}_{\alpha\beta}$ have the form

$$\mathscr{G}_{\alpha\beta}(\mathbf{r}'',t'';\mathbf{r}',t')=\langle A_{\alpha}(\mathbf{r}'',t'')A_{\beta}(\mathbf{r}',t')\rangle_{S_{\text{rad}}}$$
$$=\int \mathscr{D}[A]A_{\alpha}(\mathbf{r}'',t'')A_{\beta}(\mathbf{r}',t')$$
$$\times\exp(iS^{(K)}_{\text{rad}}[A]), \tag{F6}$$

and

$$\mathscr{G}_{+-}(\mathbf{r}'',t'';\mathbf{r}',t')=\int\frac{d\omega}{2\pi}\mathscr{G}(\mathbf{r}'',\mathbf{r}';\omega)e^{-i\omega(t''-t')}, \tag{F7}$$

with $\mathscr{G}(\mathbf{r}'',\mathbf{r}';\omega)$ given by Eq. (6.12). Substituting Eq. (F3) into Eq. (F2) we obtain

$$P^{s}(\mathbf{r},t)=\bigg\langle P_{+}(\mathbf{r},t)\exp\bigg[i\int dt'\,d\mathbf{r}'\,E_{\text{ext}}(\mathbf{r}',t')$$
$$\times P_{-}(\mathbf{r}',t')\bigg]\bigg\rangle_{S^{(m)}_{\text{eff}}}, \tag{F8}$$

where the external electric field E_{ext} and the polarization P^{s} which generates the signal are given by Eqs. (6.11). In the derivation of Eq. (F8) we made use of the relation

$$\bigg\langle P_{-}(\mathbf{r},t)\exp\bigg[i\int dt'\,d\mathbf{r}'\,E_{\text{ext}}(\mathbf{r}',t')P_{-}(\mathbf{r}',t')\bigg]\bigg\rangle_{S^{(m)}_{\text{eff}}}=0. \tag{F9}$$

The expansion of Eq. (F8) in powers of external field E^{ext} has the form

$$P^s(\mathbf{r},t)=\sum_{n=0}\frac{1}{n!}\int d\mathbf{r}_1\,dt_1\cdots d\mathbf{r}_n\,dt_n\,R^{(n)}$$
$$\times(\mathbf{r}t;\mathbf{r}_1t_1,\ldots,\mathbf{r}_nt_n)E_{\text{ext}}(\mathbf{r}_1t_1)E_{\text{ext}}(\mathbf{r}_nt_n), \qquad \text{(F10a)}$$

$$R^{(n)}(\mathbf{r}t;\mathbf{r}_1t_1,\ldots,\mathbf{r}_nt_n)=i^n\langle P_+(\mathbf{r},t)P_-(\mathbf{r}_1,t_1)\cdots$$
$$\times P_-(\mathbf{r}_n,t_n)\rangle_{S_{\text{eff}}^{(m)}}. \qquad \text{(F10b)}$$

This result can be derived alternatively by adding a term

$$-\int dr\,P(\mathbf{r},t)\cdot E_{\text{ext}}(\mathbf{r},t)$$

to the Hamiltonian, and expanding the density matrix in powers of E_{ext}.

We next apply the general formula (F10b) for $n=3$ to the case of the material system described by Eqs. (6.1) with the corresponding action given by Eqs. (C1).

It follows from Eq. (F5) and Eq. (6.1c) that the effective action has corrections only in its quadratic part, $S_{\text{eff}}^{(0)}$ i.e.,

$$S_{\text{eff}}^{(m)}=S_{\text{eff}}^{(0)}+S_{\text{mat}}^{\text{int}(K)}. \qquad \text{(F11)}$$

In Appendix C, the correlation function Eq. (F10b) for $n=3$ was evaluated but the expectation value on the right-hand side of Eq. (F10b) was taken with respect to $S_{\text{mat}}^{(K)}$ [see Eq. (6.2b)]. The response function $\mathscr{S}^{(3)}$ was expressed in terms of the one-exciton Green's function

$$G_{mn}(t'',t')=\langle C_m(t'')_+\bar{C}_n(t')_-\rangle_{S_{\text{mat}}^{(0)}}. \qquad \text{(F12)}$$

If we neglect in $S_{\text{eff}}^{(0)}$ the terms which do not conserve the number of excitons [namely, the terms of the type $C_n(t')C_m(t'')$, $\bar{C}_n(t')\bar{C}_m(t'')$ and the terms $C_n(t')\bar{C}_m(t'')$ for $t'>t''$] we get for Eq. (F10) with $j=3$ the same expression in terms of the Green's function G. However the expectation value in Eq. (B7) should be taken with respect to the action $S_{\text{eff}}^{(0)}$, i.e., we define a new Green's function $\hat{G}$ by

$$\hat{G}_{mn}(t'',t')\equiv\langle C_m(t'')_+\bar{C}_n(t')_-\rangle_{S_{\text{eff}}^{(0)}}. \qquad \text{(F13)}$$

Evaluating the Green function Eq. (F13) using Eq. (F5), and making use of the results of Appendix C we obtain in the frequency domain

$$R(\mathbf{r}\omega;\mathbf{r}_1\omega_1,\mathbf{r}_2\omega_2,\mathbf{r}_3\omega_3)$$
$$=\sum_{nm_1m_2m_3}\rho(\mathbf{r}-\mathbf{R}_n)\rho(\mathbf{r}_1-\mathbf{R}_{m_1})\rho(\mathbf{r}_2-\mathbf{R}_{m_2})$$
$$\times\rho(\mathbf{r}_3-\mathbf{R}_{m_3})\hat{R}_{nm_1m_2m_3}(\omega_s;\omega_1,\omega_2,\omega_3), \qquad \text{(F14)}$$

where $\hat{R}_{nm_1m_2m_3}(\omega_s;\omega_1,\omega_2,\omega_3)$ is given in Eq. (6.14) with $\hat{\Gamma}$ defined in Eq. (6.10).

[1] N. Bloembergen, *Nonlinear Optics* (Benjamin, New York, 1965).

[2] J. Knoester and S. Mukamel, Phys. Rep. **205**, 1 (1991).

[3] J. Jenkins and S. Mukamel, J. Chem. Phys. **98**, 7046 (1993).

[4] K. Cho, in *Excitons in Confined Systems*, edited by A. Andrea, R. Del Sole, and R. Girlanda (The Institute of Physics, Bristol, 1992).

[5] V. M. Agranovich in Excitons in Confined Systems, edited by A. Andrea, R. Del Sole, and R. Girlanda (The Institute of Physics, Bristol, 1992).

[6] D. Möbius and H. Kuhn, J. Appl. Phys. **64**, 5138 (1988); Isr. J. Chem. **18**, 375 (1979).

[7] M. Orrit and Ph. Kottis, Adv. Chem. Phys. **74**, 1 (1988).

[8] V. M. Agranovich and O. Dubovsky, Soviet Phys. JETP Lett. **3** 223 (1966).

[9] F. C. Spano, J. R. Kuklinski, and S. Mukamel, Phys. Rev. Lett. **65**, 211 (1990); A. A. Muenter, D. V. Brumbaugh, J. Apolito, L. A. Horn, F. C. Spano and S. Mukamel, J. Phys. Chem. **92**, 2783 (1992); S. Mukamel, in *Molecular Nonlinear Optics*, edited by J. Zyss (Academic, New York, 1994), p. 1.

[10] H. Fidder, J. Knoester, and D. A. Wiersma, Chem. Phys. Lett. **171**, 529 (1990).

[11] B. Deveaud, F. Clerot, N. Roy, K. Satzke, B. Sermage, and D. S. Katzer, Phys. Rev. Lett. **67**, 2355 (1991); L. Claudio Andreani, Solid State Commun. **77**, 641 (1991).

[12] R. Eccleston, B. F. Feuerbacher, J. Kuhl, W. W. Rühle, and K. Ploog, Phys. Rev. B **45**, 11403 (1992); D. S. Citrin, Solid State Commun. **84**, 281 (1992).

[13] J. J. Hopfield, Phys. Rev. **112**, 1555 (1958); M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University, London, 1954).

[14] D. Frölich, S. Kirchhoff, P. Köhler, and W. Nieswand, Phys. Rev. B **40**, 1976 (1989).

[15] G. M. Gale, F. Vallee, and C. Flytzanis, Phys. Rev. Lett. **57**, 1867 (1986).

[16] L. Claudio Andreani and F. Bassani, Phys. Rev. B **41**, 7536 (1990).

[17] M. Combescot and O. Betbeder-Matibet, Solid State Commun. **80**, 1011 (1991).

[18] T. S. Rose, R. Righini, and M. D. Fayer, Chem. Phys. Lett. **106**, 13 (1984).

[19] (a) G. J. Small, in *Excited States*, edited by E. C. Lim (Academic, New York, 1982); (b) S. H. Stevenson, M. A. Connolly, and G. J. Small, Chem. Phys. **128**, 157 (1988).

[20] F. F. So, S. R. Forrest, Y. Q. Shi, and W. H. Steier, Appl. Phys. Lett. **56**, 674 (1990); F. F. So and S. R. Forrest, Phys. Rev. Lett. **66**, 2649 (1991); F. F. So, Ph.D. thesis, University of Southern California, 1991.

[21] S. Chemla and J. Zyss, *Nonlinear Optical Properties of Organic Molecules and Crystals* (Academic, New York, 1987), Vols. I and II.

[22] O. Dubovsky and S. Mukamel, J. Chem. Phys. **95**, 7828 (1991); **96**, 9201 (1992).

[23] F. C. Spano and S. Mukamel, Phys. Rev. A **66**, 1197 (1991); **40**, 5783 (1989); S. Mukamel, in *Nonlinear Optical Properties of Organic Molecules and Crystals*, edited by J. Zyss (Academic, New York, 1993), Vol. III (in press).

[24] M. L. Steigerwald and L. E. Brus, Acc. Chem. Res. **23**, 183 (1990); M. Bawendi, M. L. Steigerwald, and L. E. Brus, Ann. Rev. Phys. Chem. **44**, 21 (1990).

[25] J. A. Leegwater and S. Mukamel, Phys. Rev. A **46**, 452 (1992).

[26] C. Flytzanis and J. Hutter, *Contemporary Nonlinear Optics* (Academic, New York, 1992), pp. 297–365.

[27] E. A. Power and T. Thirunamachandran. Phys. Rev. A **28**, 2649 (1983); E. A. Power and S. Zienau, Philos. Trans. R. Soc. London, Ser. A **251**, 427 (1959).

[28] V. Chernyak and S. Mukamel, Phys. Rev. B **48**, 2470 (1993).

[29] A. A. Abrikosov, L. P. Gorkov, and I. Ye. Dzyaloshinsky. *Quantum Field Theoretical Methods in Statistical Physics* (Pergamon, New York, 1965).

[30] R. P. Feynman and F. L. Vernon, *Ann. Phys.* **24**, 118 (1963).

[31] V. N. Popov. *Functional Integrals in Quantum Field Theory and Statistical Physics* (Reidel, Hingham, 1983).

[32] L. D. Landau and E. U. Lifshitz, *Mechanics* (Pergamon, New York, 1969).

[33] E. M. Lifshitz and L. P. Pitaevsky, *Physical Kinetics* (Pergamon, New York, 1981).

[34] V. M. Agranovich, *Theory of Excitons* (Nauka, Moscow [in Russian] 1968).

[35] V. M. Agranovich, Sov. Phys. Solid State **12**, 430 (1970); V. M. Agranovich, *Spectroscopy and Dynamics of Excitons in Molecular Systems*, edited by V. M. Agranovich and R. Hochstrasser (North-Holland, Amsterdam, 1983), p. 83.

[36] V. M. Agranovich and S. Mukamel, *Phys. Lett. A* **147**, 155 (1990).

[37] A. Perelomov, *Generalized Coherent States and Their Application* (Springer, Berlin, 1986).