Effective nonlinear Hamiltonians in dielectric media

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We derive an effective Hamiltonian for the nonlinear process of parametric down conversion in the presence of absorption. Based upon the Green function method for quantizing the electromagnetic field, we first set up Heisenberg’s equations of motion for a single atom driven by an external electric field and in the presence of an absorbing dielectric material. The equations of motion are then solved to second order in perturbation theory which, in rotating-wave approximation, yields the standard effective interaction Hamiltonian known from free-space nonlinear optics. In a second step, we derive the local-field corrected Hamiltonian for an atom embedded in a dielectric host medium, i.e. a nonlinear crystal. Here we show that the resulting effective Hamiltonian is found to be trilinear in the electric and noise polarization fields, and is thus capable of describing nonlinear noise processes. Furthermore, it reduces to the phenomenological nonlinear Hamiltonian for the cases where absorption, and hence the noise polarization field, vanishes.

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I. INTRODUCTION

Ever since the discovery of second harmonic generation by Franken in 1961 [1], nonlinear optical process have been the subject of great interest. Uses of such processes cover the full spectrum of possible applications from optical communications [2] at one end to fundamental tests of quantum mechanics [3, 4] at the other. The strongly correlated photons that are created in these processes are regularly used in many quantum cryptographic protocols [5, 6], and in the areas of quantum information processing and quantum computing [7]. As a result, these process have been the subject of much study (for a necessarily incomplete selection, see e.g. Refs. [8–11]).

The fundamental theory that describes the interaction of light and matter is quantum electrodynamics (QED). This theory has proven to be highly successful over the past sixty years, and has accurately described a disparate range of physical phenomena over a wide range of energies, from scattering of charged particles in high energy colliders to the low energy dynamics of atoms in electromagnetic fields. The theory which, in its microscopic form, describes the interaction of electromagnetic fields with charged particles, predicts the appearance of nonlinear processes when high intensity fields interact with certain types of matter. However, owing to the complexities associated with the microscopic structure of matter, the calculation of such properties are highly involved and often neglect some of the more complicated features. For example, in such calculations absorption is almost always neglected. As a result the standard approach to nonlinear optical processes is, in the main, phenomenological and, although it provides a good approximation at high intensities [12], does not necessarily hold for all situations. Furthermore, there are several circumstances where nonlinear absorption is thought to be a critical factor [13, 14] and hence the standard approach is insufficient in these cases.

It is certainly the case that absorption plays an important role in many physical processes. Recently, a method for consistently quantizing the electromagnetic field in absorbing linear electric and magnetic materials has been developed (for reviews, see e.g. Refs. [15, 16]). There have been some attempts to extend this theory to nonlinear materials [17–19], however, as yet a full theory has proven to be elusive.

In this article we present an extension of the linear quantum theory of light in absorbing media to nonlinear processes. In the following we will consider, as an example, the second order process of parametric down conversion, where an input (pump) photon is converted by a nonlinear medium to give two output photons (signal and idler) whose frequencies sum to that of the input photon. We will begin, in Sec. [I] by briefly reviewing the quantization scheme for linear absorbing dielectric materials. In Sec. [III] we consider the interaction of photons with a single atom to second order in perturbation theory and derive an effective interaction Hamiltonian for this process. In Sec. [IV] in order to find the nonlinear response for a bulk material, we apply local field corrections to the Green functions of the interacting electric fields by considering the effect of placing the interacting atom in a cavity within a bulk material. This method produces an effective interaction Hamiltonian for the second order nonlinear process that includes the sought nonlinear noise processes. Concluding remarks are given in Sec. [V]. Some useful expressions and lengthy derivations can be found in the Appendices.
II. ELECTROMAGNETIC FIELD QUANTIZATION IN LINEAR MEDIA

Before we outline the theory of electromagnetic field quantization in nonlinear dielectric media we shall briefly review the quantization of the electromagnetic field in a linearly responding medium \[15, 16\]. We begin with the classical Maxwell equations in frequency space. In the absence of free currents and charges these equations take the form

\[
\nabla \cdot B(r, \omega) = 0, \\
\nabla \times E(r, \omega) - i \omega B(r, \omega) = 0, \\
\nabla \cdot D(r, \omega) = 0, \\
\nabla \times B(r, \omega) + i \omega \mu_0 D(r, \omega) = 0,
\]

with

\[
D(r, \omega) = \varepsilon_0 E(r, \omega) + P(r, \omega).
\]

Although magnetoelectric media can be treated along the same lines, for simplicity we assume that there are no magnetic responses present. For spatially local isotropic media, the general form of the linear polarization field is

\[
P(r, \omega) = \varepsilon_0 \chi^{(1)}(r, \omega) E(r, \omega) + P_N(r, \omega).
\]

The first term in Eq. (6) is the linear response of the medium to an external electric field with a linear susceptibility \(\chi^{(1)}(r, \omega)\). The second term is the linear noise polarization field which describes Langevin noise that is associated with absorption, and is required for the theory to be consistent with the fluctuation-dissipation theorem. As a result the frequency components of the electric field obey the inhomogeneous Helmholtz equation

\[
\nabla \times \nabla \times \mathbf{E}(r, \omega) - \omega^2 \varepsilon(r, \omega) \mathbf{E}(r, \omega) = \omega^2 \mu_0 \mathbf{P}_N(r, \omega),
\]

where \(\varepsilon(r, \omega) = 1 + \chi^{(1)}(r, \omega)\) is the complex permittivity of the medium. This equation can be formally solved using the Green tensor for the Helmholtz operator

\[
\mathbf{E}(r, \omega) = \omega^2 \mu_0 \int d^3s \mathbf{G}(r, s, \omega) \cdot \mathbf{P}_N(s, \omega).
\]

The Green tensor \(\mathbf{G}(r, s, \omega)\) solves the Helmholtz equation with a point source

\[
\nabla \times \nabla \times \mathbf{G}(r, s, \omega) - \omega^2 \varepsilon(r, \omega) \mathbf{G}(r, s, \omega) = \delta(r - s).
\]

Quantization is then performed by relating the noise polarization field to a set of bosonic field operators

\[
\hat{P}_N(r, \omega) = i \sqrt{\frac{\hbar \varepsilon_0}{\pi \varepsilon''(r, \omega)}} \hat{f}(r, \omega)
\]

and imposing canonical commutation relations for them,

\[
\left[ \hat{f}(r, \omega), \hat{f}^\dagger(s, \omega') \right] = \delta(r - s) \delta(\omega - \omega').
\]

Thus the frequency components of the quantized electric field can be written as

\[
\hat{E}(r, \omega) = i \sqrt{\frac{\hbar \varepsilon_0}{\pi \varepsilon''(r, \omega)}} \int d^3s \sqrt{\varepsilon''(s, \omega)} \mathbf{G}(r, s, \omega) \cdot \hat{f}(s, \omega)
\]

and the total field operator reads

\[
\hat{E}(r) = \int_0^\infty d\omega \hat{E}(r, \omega) + \text{h.c.}.
\]

The bosonic operators \(\hat{f}(s, \omega)\) and \(\hat{f}^\dagger(s, \omega)\) describe collective excitations of the electromagnetic field and the absorbing dielectric material and can be viewed as the generalization of the free space photonic mode operators to arbitrary media. The bilinear Hamiltonian

\[
\hat{H}_F = \int d^3r \int_0^\infty d\omega \hbar \omega \hat{f}^\dagger(r, \omega) \cdot \hat{f}(r, \omega),
\]

generates the time-dependent Maxwell equations from Heisenberg’s equations of motion for the electromagnetic field operators.

This quantization scheme has already been successfully applied to a wide range of linear media including magnetic and magnetodielectric materials and has been used to study many physical effects including spontaneous relaxation rates, atom surface interactions and various cavity QED processes \[16\].

III. EQUATIONS OF MOTION OF THE LIGHT-ATOM SYSTEM

Starting with this theory, it is possible to study nonlinear interactions of light with an atom in the presence of dielectric bodies. Here, one solves the coupled equations of motion recursively to obtain an expansion in powers of the electric field operator. Each of these higher-order terms corresponds to a specific nonlinear process. From these interaction terms effective nonlinear Hamiltonians can be derived which characterise each of these processes. In this section we will look at the derivation of the effective Hamiltonian for the second order nonlinear process of parametric down conversion, where an input (pump) photon with frequency \(\omega_p\) is converted by a nonlinear crystal to give two output photons (a signal photon with frequency \(\omega_s\) and an idler photon with frequency \(\omega_i\)) such that \(\omega_p = \omega_s + \omega_i\).

The interaction between light and a single atom can be described using the multipolar coupling in the dipole approximation. Here the electromagnetic field couples linearly to the dipole moment of the atom. The multipolar coupling Hamiltonian can be written as

\[
\hat{H} = \hat{H}_F + \hat{H}_A + \hat{H}_{\text{int}}
\]
The differential equations (17) and (18) completely describe the dynamics of the coupled light-atom system. As we are primarily interested in the dynamics of the radiation field, the next step will be to remove the atomic degrees of freedom. This is done by formally solving for the atomic operators and resubstituting the result into the equation for the field operators. The result will be a single dynamic equation for the radiation field in the presence of the atom. The formal solution of Eq. (18) is

\[
\hat{\sigma}_{ij}(t) = \hat{\sigma}_{ij}(0)e^{i\omega_{ij}t} - i \int_{0}^{t} dt' \int d^3s \int d\omega \sum_{k} e^{i\omega_{ij}(t-t')} \times \left\{ \left[ g_{\lambda,ij}(r,\lambda,\sigma)(\hat{\sigma}_{ik}(t') - g_{\lambda,ki}(r,\lambda,\sigma)\hat{\sigma}_{kj}(t')) \hat{f}_{\lambda}(s,\omega) \right] \right. \\
\left. + \left[ g_{\lambda,ik}(r,\lambda,\sigma)\hat{\sigma}_{ik}(t') - g_{\lambda,ki}^{*}(r,\lambda,\sigma)\hat{\sigma}_{kj}(t') \right] \hat{f}_{\lambda}^{\dagger}(s,\omega) \right\}
\]

where \( \hat{\sigma}_{ij}(0) \) is the atomic operator at \( t = 0 \). This is a recursive expression for \( \hat{\sigma}_{ij} \). The full solution can be obtained by substituting Eq. (20) back into itself. The result is an infinite series in increasing powers of the field operators \( \hat{f}_{\lambda}(s,\omega) \) and \( \hat{f}_{\lambda}^{\dagger}(s,\omega) \). Each of these higher order terms corresponds to a specific nonlinear process that can occur when the radiation field interacts with the atom. We are interested in parametric down conversion and hence are interested in the term that is quadratic in the field operators. In fact, since the parametric down conversion process creates two photons we will be interested in terms quadratic in field creation operators. It transpires that terms containing the annihilation operator will average to zero when we apply the rotating wave approximation. In the light of this, for notational clarity, we will henceforth not display in detail terms that contain either \( \hat{f}_{\lambda}(s,\omega) \) and/or \( \hat{f}_{\lambda}^{\dagger}(s,\omega) \). Resubstituting Eq. (20) twice and then inserting it back into Eq. (17) gives

\[
\hat{f}_{\lambda}^{\dagger}(r,\lambda,\omega') = \hat{f}_{\lambda}^{\dagger}(r,\lambda,\omega') - \int_{ij} g_{\mu,ij}(r,\lambda,\sigma) \left[ \hat{\sigma}_{ij}(0)e^{i\omega_{ij}t} - i \int_{0}^{t} dt' \int d^3s \int d\omega \int d\omega'' e^{i\omega_{ij}(t-t')} \times \left\{ \left[ g_{\lambda,ij}(r,\lambda,\sigma)\hat{\sigma}_{ik}(t') - g_{\lambda,ki}(r,\lambda,\sigma)\hat{\sigma}_{kj}(t') \right] \hat{f}_{\lambda}(s,\omega) \right\} \\
\left. + \left[ g_{\lambda,ik}(r,\lambda,\sigma)\hat{\sigma}_{ik}(t') - g_{\lambda,ki}^{*}(r,\lambda,\sigma)\hat{\sigma}_{kj}(t') \right] \hat{f}_{\lambda}^{\dagger}(s,\omega) \right\} \right]
\]

(21)
It is worth momentarily digressing from the derivation to consider the consistency of Eq. (21) with the coupled Eqs. (17) and (18). Here we have formally solved the atomic equations of motion and substituted the result into the equation of motion for the electromagnetic field, thereby describing the effect of the atom on the field. In order to complete the analysis, one also has to study the backreaction of the field on the atom. As a result of this backreaction, the bare atomic transition frequencies \( \omega_{ij} \) become complex-valued quantities, gaining a line width \( \Gamma_{ij} \) and a level shift \( \delta \omega_{ij} \)

\[
\omega_{ij} = \tilde{\omega}_{ij} + \delta \omega_{ij} + i \Gamma_{ij}.
\]  

The derivation of this result and the explicit expressions for the line shifts \( \delta \omega_{ij} \) and the line widths \( \Gamma_{ij} \), in terms of the dyadic Green function, is well documented in the literature (see, e.g. Refs. [16, 20] for reviews). In reality this feature will not be critical in the following derivation, but it is important when considering the consistency of Eq. (21) with the coupled equations of motion, the modified transition frequencies \( \omega_{ij} \) in Eq. (22) must be used in place of their bare counterparts.

We now return to Eq. (21). In order to solve the integrals a number of approximations need to be made. Firstly we write the bosonic field operators as the product of a rapidly oscillating function and a slowly varying envelope function,

\[
\hat{f}_\lambda(s, \omega, t) = \tilde{f}_\lambda(s, \omega, t) e^{-i \omega t}.
\]  

Secondly we assume that the radiation is off-resonant with any of the atomic transitions and hence the frequency of the radiation field and those associated with the atomic transitions are significantly different.

We now apply the rotating-wave approximation. The l.h.s of Eq. (21) evolves at a frequency \( \omega'' \). Terms on the r.h.s of Eq. (21) contain contributions from the two field modes evolving at \( \omega \) and \( \omega'' \) and contributions from the atomic operators. We are interested in the process of parametric down conversion where the frequencies of the incoming and outgoing photons combine such that \( \omega'' = \omega' + \omega \). Terms on the r.h.s whose frequencies of evolution deviate significantly from the above condition will oscillate rapidly in comparison to the resonant terms. Hence, over long time periods these non-resonant terms average to zero. Thus, we keep all terms on the r.h.s of Eq. (21) that satisfy \( \omega'' = \omega' + \omega \). As a result we neglect terms which contain the annihilation operator \( \tilde{f}_\lambda(s, \omega) \).

Furthermore, in order to obey \( \omega'' = \omega' + \omega \), none of the (far off-resonant) atomic transition frequencies \( \omega_{ij} \) can appear on the r.h.s. Hence, we drop all off-diagonal atomic operators and retain only those terms that contain diagonal atomic projection operators \( \hat{\sigma}_{ij} \). Lastly terms with \( \hat{\sigma}_{ij}(0) \) represent the free (undriven) motion of the atom in the background field and hence are not of interest here.

The physical motivation for these approximations comes from the nature of the parametric down conversion process itself. The condition \( \omega'' = \omega' + \omega \) is a statement of energy conservation. Hence there is no energy available to drive atomic transitions and thus the atom must stay in its initial state. Therefore, the off diagonal atomic operators, which describe atomic transitions, cannot contribute.

After applying these simplifications and permutating some indices we find

\[
\tilde{f}_\lambda(s, \omega', t) = i \omega'' \tilde{f}_\lambda(s, \omega', t) + i \int_0^t dt' \int_0^t dt'' \int d^3 s \int d^3 s' \int d \omega \int d \omega' \sum_{ij \kappa} \hat{\sigma}_{ij} \times \left\{ e^{i \omega_{ij} t} e^{i(\omega - \omega_{ij}) t'} e^{i(\omega' - \omega_{ij}) t''} g_{\lambda, kj}(r_A, s, \omega) g_{\sigma, ik}(r_A, s', \omega') g_{\mu, ij}(r_A, r, \omega'') 
\right.
\]

\[
- e^{i \omega_{ij} t} e^{i(\omega - \omega_{ij}) t'} e^{i(\omega' - \omega_{ij}) t''} g_{\lambda, ij}(r_A, s, \omega) g_{\sigma, k\kappa}(r_A, s', \omega') g_{\mu, ij}(r_A, r, \omega'') 
\]

\[
- e^{i \omega_{ij} t} e^{i(\omega - \omega_{ij}) t'} e^{i(\omega' - \omega_{ij}) t''} g_{\lambda, k\kappa}(r_A, s, \omega) g_{\sigma, ij}(r_A, s', \omega') g_{\mu, ij}(r_A, r, \omega'') 
\]

\[
+ e^{i \omega_{ij} t} e^{i(\omega - \omega_{ij}) t'} e^{i(\omega' - \omega_{ij}) t''} g_{\lambda, j\kappa}(r_A, s, \omega) g_{\sigma, ij}(r_A, s', \omega') g_{\mu, ij}(r_A, r, \omega'') \right\} \tilde{f}_\lambda(s, \omega) \tilde{f}_\lambda(s', \omega').
\]  

We would now like to perform the time integrals. Note here that the coupling constants \( g_{\lambda, ij}(r, s, \omega) \) are not functions of time and hence can be taken out of the integral. Since the slowly varying envelope of the field operator \( \tilde{f}_\lambda(s, \omega) \) is approximately constant over the time periods of interest, it can also be taken out of the integral. Lastly the atomic operators \( \hat{\sigma}_{ij} \) are the projection operators on to the energy eigenstates of the atomic Hamiltonian and hence stationary under evolution by the atomic Hamiltonian. Thus, the first term in Eq. (24) integrates
where we defined the nonlinear coupling tensor operator
\[ \lambda_{\alpha\beta\gamma}(\omega, \omega') = \frac{1}{(\hbar i)^2 \varepsilon_0} \sum_{ij} \rho_{ij}^{(0)} \]
where \( i \) is the field index, \( \omega \) is the frequency, and \( \omega' \) is the frequency of the field. Integrating the other terms in Eq. (24) in a similar way gives
\begin{equation}
\hat{f}_j^\dagger(s, \omega) \hat{f}_j'(s', \omega') = \sum_{ij} \hat{\sigma}_{ii} \times \hat{K}_{\lambda\mu\nu}(r_A; s, s', r; \omega, \omega', \omega'') \times \hat{K}_{\lambda\mu\nu}(r_A; s, s', r; \omega, \omega', \omega''), \end{equation}
where we have neglected the rapidly oscillating terms since these will again average to zero over long time periods. Integrating the other terms in Eq. (24) in a similar way gives
\begin{equation}
\hat{f}_j^\dagger(s, \omega) = i \nu \hat{f}_j'(s, \omega') - i \int d^3 s \int d^3 s' \int d\omega \int d\omega' \times \hat{K}_{\lambda\mu\nu}(r_A; s, s', r; \omega, \omega', \omega''), \end{equation}
where we defined the nonlinear coupling tensor operator
\begin{equation}
\hat{K}_{\lambda\mu\nu}(r_A; s, s', r; \omega, \omega', \omega'') = \sum_{ij} \hat{\sigma}_{ii} \times \left\{ \begin{array}{l}
g_{\lambda, ij}(r_A; s, s', r; \omega, \omega', \omega'') \\
g_{\lambda, ij}(r_A; s, s', r; \omega, \omega', \omega'') g_{\nu, kl}(r_A; s, s', r; \omega, \omega', \omega'') \\
g_{\alpha, ij}(r_A; s, s', r; \omega, \omega', \omega'') g_{\beta, kl}(r_A; s, s', r; \omega, \omega', \omega'') \\
g_{\alpha, ij}(r_A; s, s', r; \omega, \omega', \omega'') g_{\beta, kl}(r_A; s, s', r; \omega, \omega', \omega'') \\
\end{array} \right\}. \end{equation}

It is now straightforward to write down an effective interaction Hamiltonian that, via Heisenberg’s equations of motion, generates the correct dynamical equation for the bosonic field operators:
\begin{equation}
\hat{H}_{\text{int}} = -\hbar \int d^3 r \int d^3 s \int d^3 s' \int d\omega \int d\omega' \int d\omega'' + \text{h.c.} \end{equation}

It is evident that the dynamical evolution of the atomic quantities is frozen out in this approximation. The nonlinear coupling tensor operator depends solely on the projection operators \( \hat{\sigma}_{ii} \) on to the atomic eigenstates. Since their evolution is now static, \( \hat{\sigma}_{ii} = 0 \), we can replace them by their expectation values \( \rho_{ii}^{(0)} \). Hence, the effective interaction Hamiltonian (29) becomes a functional of the dynamical variables of the quantized electromagnetic field alone.

Although the interaction part of the Hamiltonian in (29) correctly describes this process at a microscopic level in terms of bosonic operators, it is the macroscopic description, in terms of electric fields, that is of practical interest. The response of an atom to an applied electric field is described in terms of a single atom susceptibility or polarizability. Although an essential part of the macroscopic description, the polarizability is, in fact, a function of the microscopic properties of the atom. Hence we can use this to relate the microscopic effective Hamiltonian to an equivalent macroscopic effective Hamiltonian. It can be shown (see Appendices A and B) that the causal second order nonlinear polarizability can be written as
\begin{equation}
\lambda_{\alpha\beta\gamma}(\omega, \omega') = \frac{1}{(\hbar i)^2 \varepsilon_0} \sum_{ij} \rho_{ij}^{(0)} \times \left\{ \begin{array}{l}
d_{\alpha, ij} d_{\beta, kl} d_{\gamma, mn} \\
d_{\alpha, ij} d_{\beta, kl} d_{\gamma, mn} d_{\delta, ok} \\
d_{\alpha, ij} d_{\beta, kl} d_{\gamma, mn} d_{\delta, ok} d_{\epsilon, pq} \\
\end{array} \right\}. \end{equation}

One should also note that in using this form of the polarizability requires the condition \( \omega'' = \omega + \omega' \). Using this we can write Eq. (28) in terms of the second order nonlinear polarizability
\begin{equation}
K_{\lambda\mu\nu}(r_A; s, s', r; \omega, \omega', \omega'') = \frac{i}{\hbar} \lambda_{\alpha\beta\gamma}(\omega, \omega') \left( \frac{\hbar \varepsilon_0}{\pi} \right)^{\frac{1}{2}} \times \hat{K}_{\lambda\mu\nu}(r_A; s, s', r; \omega, \omega', \omega'') \end{equation}

Hence the interaction term of the effective Hamiltonian becomes
\begin{equation}
\hat{H}_{\text{int}} = -\hbar \int d^3 r \int d^3 s \int d^3 s' \int d\omega \int d\omega' \int d\omega'' + \text{h.c.} \end{equation}

Finally, we can combine the Green functions with the various factors to re-form electric field operators
\begin{equation}
\hat{H}_{\text{int}} = \varepsilon_0 \int d\omega \int d\omega' \int d\omega'' \chi_{\alpha\beta\gamma}^{(2)}(\omega, \omega') \times \hat{E}_{\alpha}^\dagger(r_A, \omega) \hat{E}_{\beta}^\dagger(r_A, \omega') \hat{E}_{\gamma}(r_A, \omega'') + \text{h.c.} \end{equation}
The Hamiltonian [23] describes a second order nonlinear interaction between the quantized electromagnetic field and a single atom in free space, possibly near (but outside) a dielectric body. In order to describe the situation in which the nonlinearly responding atom is located inside a dielectric or even part of the dielectric medium itself, an additional ingredient is necessary.

IV. LOCAL FIELD CORRECTIONS

Previously, we have considered the nonlinear interaction of an electric field and a single atom in free space. In this case the applied fields act directly on the atom, and thus the local field at the atom $E_{\text{loc}}(r_A)$ is equal to the applied field $E_{\alpha}(r_A)$. In the case where the interacting atom is part of a larger body, the electric field at the position the atom is different from the applied external field. The surrounding material modifies the applied field such that

$$E_{\text{loc}}(r_A) = L[\varepsilon(\omega)] E_{\alpha}(r_A).$$

(34)

The local field correction method involves calculating the prefactor $L[\varepsilon(\omega)]$ so that the local interaction can be related to the applied fields. This is a common technique in linear optics and has even been applied to nonlinear processes [21]. There are a number of ways to perform these corrections. Here we shall consider the real cavity model, which was first discussed in the framework of quantum optics in Ref. [22] and in its present form in Ref. [23]. This technique is well known and has already been used to calculate a number of atomic properties such as modified spontaneous decay rates [24] and one and two atom van der Waals interactions [25].

In this model the interacting atom is placed inside an empty spherical cavity of radius $R_c$, which itself is embedded in the host medium. The local field correction is performed by replacing the Green function found in the expansion of the electric field with that of the spherical cavity. The Green function for the spherical cavity can be found by considering wave propagation from the cavity centred at $r_A$ to a point $r$ located in the host medium. This is similar to the Onsager model [26, 27] for local field corrections (Appendix C), a technique that is more common in classical nonlinear optics, where the corrections to the classical fields are calculated using similar concepts. The Green function method, however, is more general as it takes into account the absorptive properties of the surrounding medium whereas the Onsager model does not.

Consider an atom at the centre of an empty spherical cavity of radius $R_c$ embedded in an infinite medium of permittivity $\varepsilon(\omega)$ such that

$$\varepsilon(r, \omega) = \begin{cases} 
1 & \text{if } |r - r_A| < R_c \\
\varepsilon(\omega) & \text{if } |r - r_A| \geq R_c
\end{cases}$$

(35)

with $R_c$ on the order of the interatomic distance. The Green function for the spherical cavity can be split up into two parts

$$G_{\alpha\beta}(r_A, r, \omega) = G^C_{\alpha\beta}(r_A, r, \omega) + G^S_{\alpha\beta}(r_A, r, \omega),$$

(36)

where $G^C_{\alpha\beta}(r_A, r, \omega)$ is the part which describes transmission within the cavity medium (i.e. free space) and $G^S_{\alpha\beta}(r_A, r, \omega)$ is the part which describes scattering off the cavity wall. Furthermore, we use the decomposition

$$G_{\alpha\beta}(r_A, r, \omega) = R_{\alpha\beta}(r_A, r, \omega) + T_{\alpha\beta}(r_A, r, \omega)$$

(37)

where $R_{\alpha\beta}(r_A, r, \omega)$ is the contribution from reflection off the cavity wall and $T_{\alpha\beta}(r_A, r, \omega)$ is the contribution from transmission through the cavity wall. We shall consider a coarse-grained model with the characteristic length scale much greater than $R_c$, the interatomic distance. Thus the individual atoms cannot be resolved and so the medium can be considered to be a uniform and continuous. Furthermore, since the cavity is of radius $R_c$ there is only one resolvable point within the cavity, the location of the atom, $r_A$. As a result there can be no propagation within the cavity and thus $G^C_{\alpha\beta}(r_A, r, \omega)$ can be neglected.

The reflective part of the Green function is

$$R_{\alpha\beta}(r_A, r, \omega) = \frac{i\omega}{6\pi} C(\omega) \frac{4}{3} \pi R_c^3 \delta(r_A - r) \delta_{\alpha\beta}$$

(38)

with the Mie reflection coefficient

$$C(\omega) = \frac{h_1^{(1)}(z_0) \left[z h_1^{(1)}(z)\right]'}{\varepsilon(\omega) h_1^{(1)}(z) \left[z h_1^{(1)}(z)\right]'}$$

(39)

where $z_0 = \omega R_c / c$ and $z = \sqrt{\varepsilon(\omega) / \omega} R_c / c$ and $j_1^{(1)}(z)$ and $h_1^{(1)}(z)$ are, respectively, the first spherical Bessel and
Hankel functions of the first kind,
\[ j_1^{(1)}(z) = \frac{\sin(z)}{z^2} - \frac{\cos(z)}{z}, \quad h_1^{(1)}(z) = \left( \frac{1}{z} + \frac{i}{z^2} \right) e^{iz}. \]

(40)

As \( R_c \) is small compared to the optical wavelengths associated with the process (i.e. \( R_c \ll c/\omega \)) we can expand \( C(\omega) \) in powers of \( \omega R_c/c \)
\[ C(\omega) = \frac{3}{2} \frac{\varepsilon(\omega) - 1}{\varepsilon(\omega) + 1} \frac{\varepsilon}{\varepsilon R_c^2} + \frac{9}{5} \frac{\varepsilon(\omega)}{\varepsilon(\omega) + 1} \frac{\varepsilon}{\varepsilon R_c^2} + O\left(\frac{\omega R_c}{c}\right). \]

(41)

Substituting these expressions into \( R_{\alpha\beta}(r_A, r, \omega) \) and taking the cavity radius to zero (\( \omega R_c/c \to 0 \)) gives
\[ R_{\alpha\beta}(r_A, r, \omega) = \frac{2}{3} \frac{\varepsilon(\omega) - 1}{\varepsilon(\omega) + 1} \frac{\varepsilon}{\varepsilon R_c^2} \delta(r_A - r) \delta_{\alpha\beta}. \]

(42)

The transmission part of the Green function is [24][25]
\[ T_{\alpha\beta}(r_A, r, \omega) = D(\omega) G_{\alpha\beta}^B(r_A, r, \omega) \]
with the Mie transmission coefficient
\[ D(\omega) = \frac{3}{2} \frac{\varepsilon(\omega)}{\varepsilon(\omega) + 1} + O\left(\frac{\omega R_c}{c}\right) \]

(43)

which, in the limit \( \omega R_c/c \to 0 \), leads to
\[ T_{\alpha\beta}(r_A, r, \omega) = \frac{3}{2} \frac{\varepsilon(\omega)}{\varepsilon(\omega) + 1} G_{\alpha\beta}^B(r_A, r, \omega) \]

(44)

for the transmission part of the Green function. Collecting all the results yields
\[ G_{\alpha\beta}(r_A, r, \omega) = \frac{2}{3} \frac{\varepsilon(\omega)}{\varepsilon(\omega) + 1} \frac{\varepsilon}{\varepsilon R_c^2} \delta(r_A - r) \delta_{\alpha\beta} \]
\[ + \frac{3}{2} \frac{\varepsilon(\omega)}{\varepsilon(\omega) + 1} G_{\alpha\beta}^B(r_A, r, \omega) \]

(45)

for the local-field corrected Green function including the cavity. One should note that the \( \delta \)-function in Eq. (47) is the contribution from the reflective part of the scattering Green function. The intrinsic singularity present in the bulk Green function is still contained within \( G_{\alpha\beta}^B(r_A, r, \omega) \).

Here we have used the Green function for a cavity embedded in an infinite homogeneous medium to locally field correct the electric field at the location of the atom. However, it was shown in Ref. [24] that this result can be easily generalized to cavities embedded in arbitrary media. To obtain the expression for arbitrary media one merely needs to replace the bulk Green function and the homogeneous permittivity with the appropriate Green function and inhomogeneous permittivity for the new geometry. Hence the following results are, with the right substitutions, correct for any system.

We can now apply these local-field corrections to the nonlinear Hamiltonian. Inserting the local-field corrected Green function (47) into the effective nonlinear Hamiltonian (33) gives
\[ \hat{H}_{\text{int}} = i \int \frac{d^3 r}{d^3 r'} \int d^3 r'' \int d\omega \int d\omega' \int d\omega'' \left( \frac{\hbar}{c} \right)^2 \]
\[ \times \chi_{\alpha\beta\gamma}^{(2)}(\omega, \omega') \omega^2 \omega'^2 \omega''^2 \delta\left(\frac{\mathbf{r}_A - \mathbf{r}}{\omega} \right) \delta_{\beta\gamma} + \hat{D}^*(\omega) G_{\alpha\beta}^B(r_A, r, \omega) \]
\[ \times \left[ \hat{C}^*(\omega') \frac{c^2}{\omega''} \delta(r_A - r') \delta_{\alpha\gamma} + \hat{D}^*(\omega') G_{\alpha\beta}^B(r_A, r', \omega') \right] \]
\[ \times \left[ \hat{C}(\omega'') \frac{c^2}{\omega''^2} \delta(r_A - r'') \delta_{\beta\nu} + \hat{D}(\omega'') G_{\alpha\beta}^B(r_A, r'', \omega'') \right] \]
\[ \times \hat{f}_{\lambda}(r, \omega)(\mathbf{r}'') \text{h.c.} \]

(46)

where we abbreviated
\[ \hat{C}(\omega) = \frac{2}{3} \frac{\varepsilon(\omega)}{\varepsilon(\omega) + 1}, \quad \hat{D}(\omega) = \frac{3}{2} \frac{\varepsilon(\omega)}{\varepsilon(\omega) + 1}. \]

(47)

Recall that \( \chi_{\alpha\beta\gamma}^{(2)}(\omega, \omega') \) is the polarizability for an isolated atom in free space and that \( \omega'' = \omega + \omega' \). Inside a material body, the interpretation of the nonlinear polarizability has changed. We can thus define a local-field corrected polarizability (i.e. the polarizability of an atom embedded in an extended medium) as
\[ \chi_{\alpha\beta\gamma}^{(2)}(\omega, \omega') = \hat{D}^*(\omega) \hat{D}^*(\omega') \hat{D}(\omega'') \chi_{\alpha\beta\gamma}^{(2)}(\omega, \omega'). \]

(48)

Performing the integrations over the \( \delta \)-functions and recombining the various factors to form electric and linear noise polarization fields gives
\[ \hat{H}_{\text{int}} = \frac{\hbar}{c} \int d\omega \int d\omega' \int d\omega'' \chi_{\alpha\beta\gamma}^{(2)}(\omega, \omega') \]
\[ \times \left[ \hat{E}_{\lambda\alpha}(r_A, \omega) + \mathcal{L}[\varepsilon(\omega)] \hat{P}_{\lambda\alpha}(r_A, \omega) \right] \]
\[ \times \left[ \hat{E}_{\lambda\beta}(r_A, \omega') + \mathcal{L}[\varepsilon(\omega') \hat{P}_{\lambda\beta}(r_A, \omega') \right] \]
\[ \times \left[ \hat{E}_{\lambda\gamma}(r_A, \omega'') + \mathcal{L}[\varepsilon(\omega'') \hat{P}_{\lambda\gamma}(r_A, \omega'' \right] + \text{h.c.} \]

(49)

where
\[ \mathcal{L}[\varepsilon(\omega)] = \frac{2}{9 \varepsilon_0} \frac{\varepsilon(\omega) - 1}{\varepsilon(\omega)} \]

(50)
is the local correction factor for the noise polarization field.

The interaction Hamiltonian \( \hat{H}_{\alpha\beta\gamma}^{(2)} \) is trilinear in the electric field and the (local-field corrected) noise polarization field with the strength of the interaction characterised by the (local-field corrected) second order polarizability \( \chi_{\alpha\beta\gamma}^{(2)}(\omega, \omega') \). This can be viewed as the combination of several different types of interaction processes. The term trilinear in the electric field corresponds to the sought parametric down-conversion process. All other terms describe various nonlinear interactions between the electric field and noise polarization fields. They correspond to the absorption of one or both of the outgoing photons by the medium, the production of one or two outgoing photons from an excited noise field (e.g. by thermal excitation) and a pure nonlinear noise field interaction. These extra interaction terms are features of the absorptive properties of the medium and are in effect corrections to lower-order (nonlinear) processes.

On taking the limit of vanishing absorption the noise polarization fields vanish identically [recall Eq. (10)]. Hence, the interaction Hamiltonian \( \hat{H}_{\alpha\beta\gamma}^{(2)} \) reduces to the standard interaction Hamiltonian associated with parametric down conversion in non-absorbing media. It should be noted that computing higher-order nonlinear processes will similarly lead to corrections to second order processes. However, in view of the applied rotating-wave approximation, their effect remains negligible.

V. SUMMARY

Beginning with the total Hamiltonian for the medium-assisted electromagnetic field interaction with a single \( N \)-level atom \( \{15\} \), we derived Heisenberg’s equations of motion for the dynamical variables of both the atom and the medium-assisted field. By integrating out the atomic degrees of freedom and then focusing on one particular term in the nonlinear expansion of the field variables, we have found an effective equation of motion for one particular optical process. One can think of this equation of motion as the dynamical equation that is generated from an effective Hamiltonian which describes only the process of interest. This effective Hamiltonian does not refer to the \( N \)-level atom, consisting only of the dynamical variables relating to the medium-assisted field. All information about the effect of the atom is now contained in the coupling constant for the interaction terms.

Here, as a specific example, by studying the equations of motion to second order in perturbation theory we have derived an effective Hamiltonian for the second order nonlinear process of parametric down conversion in the presence of an absorbing host material. By applying local-field corrections to the Hamiltonian we have moved from considering the interaction of light with a single atom to considering the interaction of light with a bulk material. We found that the Hamiltonian can be expressed in terms of various products of electric and linear noise polarization fields.

The local-field corrections have two effects: to replace the free-space second order nonlinear polarizability \( \chi_{\alpha\beta\gamma}^{(2)}(\omega, \omega') \) by its bulk modified counterpart \( \tilde{\chi}_{\alpha\beta\gamma}^{(2)}(\omega, \omega') \), and to introduce additional contributions to the effective interaction Hamiltonian. These additional terms are related to nonlinear absorption processes inside the bulk material, similar to those found in the purely macroscopic approach pursued in \( \{18, 19\} \). In contrast to the macroscopic picture, in our present microscopic derivation we have gained a better understanding of the origins of the additional contributions to the effective Hamiltonian.

In the limit of vanishing absorption, where the noise polarization field disappears, one recovers the standard second order effective interaction Hamiltonian as used in classical nonlinear optics. In the generic situation when absorption cannot be disregarded, the effective Hamiltonian \( \{51\} \) will be the starting point for subsequent investigations into the role of absorption on the generation of down-converted photons and their propagation through nonlinear media.

VI. ACKNOWLEDGEMENTS

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Appendix A: Second order polarizability

Here we derive the second order susceptibility of a single atom (also known as the second order polarizability) in terms of the microscopic properties of the atom. A semi-classical approach with classical radiation and a quantized atom is used. This approach follows closely the derivation in Ref. \( \{29\} \).

In general media the susceptibility \( \chi \) is a tensorial function that relates the polarization of the medium to the strength of the applied electric field. In the time domain, for the case of second order processes, the polarization is related to the applied electric field by

\[
P^{(2)}(r, t) = \varepsilon_0 \int_0^\infty d\tau' \int_{\tau'}^{\infty} d\tau' \chi_{\alpha\beta\gamma}^{(2)}(\tau, \tau') E_{\alpha}(r, t - \tau) E_{\beta}(r, t - \tau'). \quad (A1)
\]

Here \( \chi_{\alpha\beta\gamma}^{(2)} \) is the second order susceptibility. If the medium consists of a single atom, Eq. \( \{A1\} \) still applies with the left hand side giving the polarization of the single atom. The susceptibility that appears in the single atom version of Eq. \( \{A1\} \) is often referred to as the second order polarizability of the atom.

Consider a single atom in state \( \hat{\rho} \) which evolves under the perturbed Hamiltonian \( \hat{H} = \hat{H}_A + \hat{H}_{\text{int}}. \) Since the operator \( \hat{\rho} \) can be written as a sum over the projection operators onto the energy eigenstates of the atomic
Hamiltonian, the state is time stationary under evolution of the unperturbed atomic Hamiltonian $H_A$. Hence the Heisenberg equation of motion for the atom is
\[ \frac{\partial \hat{\rho}(t)}{\partial t} = \frac{i}{\hbar} [\hat{\rho}(t), \hat{H}_{\text{int}}(t)]. \tag{A2} \]
This can be formally solved to give the recursive relation
\[ \hat{\rho}(t) = \frac{1}{i\hbar} \int_{t_0}^{t} dt_1 [\hat{\rho}(t_1), \hat{H}_{\text{int}}(t_1)] + \rho^{(0)} \tag{A3} \]
where $\rho^{(0)}$ is a constant of integration and is equal to the state of the system at $t = t_0$. Equation (A3) can be resubstituted into itself to give a series solution for $\hat{\rho}(t)$,
\[ \hat{\rho}(t) = \sum_{n=1}^{\infty} \frac{1}{(i\hbar)^n} \int_{t_0}^{t} dt_1 \cdots \int_{t_0}^{t_{n-1}} dt_n \]
\[ \times \left[ \cdots [\hat{\rho}^{(0)}, \hat{H}_{\text{int}}(t_n)], \cdots, \hat{H}_{\text{int}}(t_2), \hat{H}_{\text{int}}(t_1) \right] + \rho^{(0)}. \]
Given that we now have an expression for the quantum state of the atom, we can now write down the polarization of the system, which is defined as the expectation value of the dipole moment operator
\[ P_\gamma(t) = \langle \hat{d}_\gamma \rangle = \text{Tr} \left( \hat{\rho}(t) \hat{d}_\gamma(t) \right). \tag{A4} \]
As $\hat{\rho}(t)$ is an infinite expansion so $P_\gamma(t)$ will be an infinite expansion. Here second order processes are of interest so only the second order term is considered,
\[ P_\gamma^{(2)}(t) = \frac{1}{(i\hbar)^2} \int_{t_0}^{t} dt_1 \int_{t_0}^{t_2} \text{Tr} \left\{ [\hat{\rho}^{(0)}, \hat{H}_{\text{int}}(t_2)], \hat{H}_{\text{int}}(t_1) \right\} \hat{d}_\gamma(t). \tag{A5} \]
In the dipole approximation, $\hat{H}_{\text{int}}(t)$ is given by
\[ \hat{H}_{\text{int}}(t) = -\hat{d}_\alpha(t) E_\alpha(t). \tag{A6} \]
Hence (A3) becomes
\[ P_\gamma^{(2)}(t) = \frac{1}{(i\hbar)^2} \int_{t_0}^{t} dt_1 \int_{t_0}^{t_2} \text{Tr} \left\{ [\rho^{(0)}, \hat{d}_\beta(t_2) E_\beta(t_2)], -\hat{d}_\alpha(t_1) E_\alpha(t_1) \right\} \hat{d}_\gamma(t) \]
\[ = \frac{1}{(i\hbar)^2} \int_{t_0}^{t} dt_1 \int_{t_0}^{t_2} \text{Tr} \left\{ \rho^{(0)} [\hat{d}_\gamma(t), \hat{d}_\alpha(t_1)], \hat{d}_\beta(t_2) \right\} E_\alpha(t_1) E_\beta(t_2), \tag{A7} \]
where the cyclicity of the trace and the classical nature of the radiation have been used to arrive at the result. We now make the substitutions $t_1 = -\tau_1$ and $t_2 = -\tau_2$ and take $t_0 \to -\infty$ (and hence $\tau_{1,2} \to +\infty$). Hence Eq. (A7) becomes
\[ P_\gamma^{(2)}(t) = \frac{1}{(i\hbar)^2} \int_{0}^{\infty} d\tau_1 \int_{\tau_1}^{\infty} d\tau_2 \]
\[ \times \text{Tr} \left\{ \rho^{(0)} [\hat{d}_\gamma(t), \hat{d}_\alpha(-\tau_1)], \hat{d}_\beta(-\tau_2) \right\} E_\alpha(t - \tau_1) E_\beta(-\tau_2). \tag{A8} \]
The time dependence of quantum operators can be written as $\hat{O}(t) = \hat{U}(t) \hat{O}(0) \hat{U}^\dagger(t)$ where $\hat{U}$ is the unitary operator $\hat{U} = e^{-i\hat{H}t/\hbar}$ associated with the Hamiltonian $\hat{H}$. Hence, we can write
\[ \hat{d}_\alpha(t - \tau) = \hat{U}(t)^\dagger \hat{d}_\alpha(-\tau) \hat{U}(t). \tag{A9} \]
Noting that the dipole moment operator commutes with $\hat{H}_{\text{int}}$ and that $\rho^{(0)}$ commutes with $H_A$ and again using the cyclicity of the trace, Eq. (A8) becomes
\[ P_\gamma^{(2)}(t) = \frac{1}{(i\hbar)^2} \int_{0}^{\infty} d\tau_1 \int_{\tau_1}^{\infty} d\tau_2 \]
\[ \times \text{Tr} \left\{ \rho^{(0)} [\hat{d}_\gamma(0), \hat{d}_\alpha(-\tau_1)], \hat{d}_\beta(-\tau_2) \right\} E_\alpha(t - \tau_1) E_\beta(-\tau_2). \tag{A10} \]
Comparing Eq. (A10) with Eq. (A11) one can see that the second order nonlinear polarizability is given by
\[ \chi_{\alpha\beta\gamma}^{(2)}(\tau_1, \tau_2) = \frac{1}{(i\hbar)^2} \frac{1}{\varepsilon_0} \text{Tr} \left\{ \rho^{(0)} [\hat{d}_\gamma(0), \hat{d}_\alpha(-\tau_1)], \hat{d}_\beta(-\tau_2) \right\} \right. \]
\[ \times \left. E_\alpha(t - \tau_1) E_\beta(-\tau_2). \tag{A11} \right] \]
In the frequency domain, the Fourier transforms of the electric field and the polarization field are substituted into Eq. (A10), and we find that
\[ P_\gamma^{(2)}(\omega') = \frac{1}{(i\hbar)^2} \int_{0}^{\infty} d\tau_1 \int_{\tau_1}^{\infty} d\tau_2 e^{-i\omega\tau_1} e^{-i\omega'\tau_2} \]
\[ \times \text{Tr} \left\{ \rho^{(0)} [\hat{d}_\gamma(0), \hat{d}_\alpha(-\tau_1)], \hat{d}_\beta(-\tau_2) \right\} E_\alpha(\omega) E_\beta(\omega'), \tag{A12} \]
and hence
\[ \chi_{\alpha\beta\gamma}^{(2)}(\omega, \omega') = \frac{1}{(i\hbar)^2} \frac{1}{\varepsilon_0} \int_{0}^{\infty} d\tau_1 \int_{\tau_1}^{\infty} d\tau_2 e^{-i\omega\tau_1} e^{-i\omega'\tau_2} \]
\[ \times \text{Tr} \left\{ \rho^{(0)} [\hat{d}_\gamma(0), \hat{d}_\alpha(-\tau_1)], \hat{d}_\beta(-\tau_2) \right\}. \tag{A13} \]
Note here that, by performing the Fourier transform, we have imposed the condition \( \omega'' = \omega + \omega' \). The trace of the combination of dipole moment operators can be computed by inserting identity operators in terms of atomic energy eigenstates \( |\epsilon_i\rangle \). The matrix elements of the dipole moment operators are given by

\[
(\epsilon_i|\hat{d}_\alpha(t)|\epsilon_j\rangle = (\epsilon_i|\hat{U}^\dagger(t)|\hat{d}_\alpha\hat{U}(t)|\epsilon_j\rangle = (\epsilon_i|\hat{H}_A/\hbar\hat{d}_\alpha e^{-i\hat{H}_A t/\hbar}|\epsilon_j\rangle = d_{\alpha,i,j} e^{i\omega_{ij}t}\). \tag{A14}
\]

Here \( \epsilon_i \) is the energy eigenvalue associated with the eigenstate \( |\epsilon_i\rangle \). Note also that \( \hat{\rho}^{(0)} \) is diagonal in the eigenbasis of the atomic Hamiltonian \( \hat{H}_A \),

\[
(\epsilon_i|\hat{\rho}^{(0)}|\epsilon_j\rangle = \rho_{ij}^{(0)} \delta_{ij}. \tag{A15}
\]

Using the relations \[A14\], \[A15\] and the completeness relation for the atomic eigenstates, the second order susceptibility becomes

\[
\chi^{(2)}_{\alpha\beta\gamma}(\omega,\omega') = \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \frac{1}{(i\hbar)^2} \sum_{ij} \rho_{ii}^{(0)} \times \left[ d_{\alpha,j,k} \bar{d}_{\beta,k,i} e^{-i(\omega - \omega_{ij})\tau_1} e^{-i(\omega' - \omega_{ik})\tau_2} - d_{\alpha,i,j} \bar{d}_{\beta,k,i} e^{-i(\omega - \omega_{ij})\tau_1} e^{-i(\omega' - \omega_{ik})\tau_2} - d_{\alpha,k,i} \bar{d}_{\beta,j,i} e^{-i(\omega - \omega_{ij})\tau_1} e^{-i(\omega' - \omega_{jk})\tau_2} + d_{\alpha,j,k} \bar{d}_{\beta,j,i} e^{-i(\omega - \omega_{ij})\tau_1} e^{-i(\omega' - \omega_{jk})\tau_2} \right].
\tag{A16}
\]

It is important to note that, in order for the expression to be consistent with the atom-field equations of motion, the transition frequencies \( \omega_{ij} \) must be complex variables

\[
\omega_{ij} = \omega_{ij}^0 + \delta\omega_{ij} + i\Gamma_{ij}. \tag{A17}
\]

As in Eq. (22), \( \omega_{ij}^0 \) is the bare atomic transition frequency, \( \delta\omega_{ij} \) is the level shift and \( \Gamma_{ij} \) is the transition linewidth. This results in a factor of \( e^{-\Gamma\tau} \) in the integrand which leads to convergence at the upper limit of the integral. Integrating both time integrals leads to

\[
\chi^{(2)}_{\alpha\beta\gamma}(\omega,\omega') = \frac{1}{(i\hbar)^2} \sum_{ij} \rho_{ii}^{(0)} \times \left[ \frac{d_{\alpha,j,k} \bar{d}_{\beta,k,i} d_{\gamma,l,j}}{(\omega' - \omega_{ij})(\omega + \omega' - \omega_{lj})} - \frac{d_{\alpha,i,j} \bar{d}_{\beta,k,i} d_{\gamma,l,j}}{(\omega' - \omega_{ij})(\omega + \omega' - \omega_{lk})} - \frac{d_{\alpha,k,i} \bar{d}_{\beta,j,i} d_{\gamma,l,j}}{(\omega' - \omega_{ij})(\omega + \omega' - \omega_{jk})} + \frac{d_{\alpha,j,k} \bar{d}_{\beta,j,i} d_{\gamma,l,i}}{(\omega' - \omega_{ij})(\omega + \omega' - \omega_{lk})} \right].
\tag{A18}\]

which is the expression for the polarizability of a single atom in frequency space.

**Appendix B: Causality and the Kramers-Kronig Relations**

The linear polarization field is a linear response to the applied electric field. As with any response theory the magnitude of the reaction is described by the response function. In the case of the linear polarization field the response function is the linear susceptibility

\[
P_{\alpha}(r,t) = \varepsilon_0 \int_0^\infty d\tau \chi^{(1)}_{\alpha\beta}(\tau) E_{\beta}(r,t - \tau). \tag{B1}
\]

By causality \( \chi^{(1)}_{\alpha\beta}(\tau) \) must vanish for \( \tau < 0 \); the polarization field at time \( t \) cannot depend on electric fields at times greater than \( t \). Thus

\[
\chi^{(1)}_{\alpha\beta}(\tau) = \Theta(\tau)\chi^{(1)}_{\alpha\beta}(\tau), \tag{B2}
\]

where \( \Theta(\tau) \) is the Heaviside step function. Fourier transforming both sides of the equation gives

\[
\chi^{(1)}_{\alpha\beta}(\omega) = \frac{1}{2\pi i} \int_{-\infty}^{\infty} d\omega' \frac{\chi^{(1)}_{\alpha\beta}(\omega')}{\omega - \omega'}. \tag{B3}
\]

The function \( 1/(\omega - \omega') \) has to be seen in its distributional sense and, by using Sochotzki’s formula, can be decomposed into \( 1/(\omega - \omega') = P/(\omega - \omega') + i\pi \delta/(\omega - \omega') \). Here \( P \) denotes the principal part. This results in

\[
\chi^{(1)}_{\alpha\beta}(\omega) = \frac{P}{\pi i} \int_{-\infty}^{\infty} d\omega' \chi^{(1)}_{\alpha\beta}(\omega') \frac{\chi^{(1)}_{\alpha\beta}(\omega')}{(\omega - \omega')}, \tag{B4}
\]

Decomposing Eq. (B4) into its real and imaginary parts gives

\[
\text{Re}\left[\chi^{(1)}_{\alpha\beta}(\omega)\right] = \frac{P}{\pi} \int_{-\infty}^{\infty} d\omega' \frac{\text{Im}\left[\chi^{(1)}_{\alpha\beta}(\omega')\right]}{(\omega - \omega')}, \tag{B5}
\]

\[
\text{Im}\left[\chi^{(1)}_{\alpha\beta}(\omega)\right] = -\frac{P}{\pi} \int_{-\infty}^{\infty} d\omega' \frac{\text{Re}\left[\chi^{(1)}_{\alpha\beta}(\omega')\right]}{(\omega - \omega')}. \tag{B6}
\]

These are the linear Kramers-Kronig relations. A causal linear response function must satisfy these relations. For more information about the linear Kramers-Kronig relations the reader is referred to Ref. [30].

One can derive a second order nonlinear version of the Kramers-Kronig relations in a similar way. The second order nonlinear polarization is given by

\[
P^{(2)}_{\alpha}(r,t) = \varepsilon_0 \int_0^\infty d\tau \int_{-\infty}^{\infty} d\tau' \chi^{(2)}_{\alpha\beta\gamma}(\tau,\tau') E_{\beta}(r,t - \tau) E_{\gamma}(r,t - \tau'). \tag{B7}
\]

where \( \chi^{(2)}_{\alpha\beta\gamma}(\tau,\tau') \) is the second order response function. Owing to causality, \( \chi^{(2)}_{\alpha\beta\gamma}(\tau,\tau') \) must satisfy

\[
\chi^{(2)}_{\alpha\beta\gamma}(\tau,\tau') = \Theta(\tau')\Theta(\tau)\chi^{(2)}_{\alpha\beta\gamma}(\tau,\tau'). \tag{B8}
\]
By Fourier transforming Eq. (B8), we find that
\[
\chi_{\alpha\beta\gamma}^{(2)}(\omega, \omega') = -\frac{P}{3\pi^2} \int_{-\infty}^{\infty} d\tilde{\omega} d\tilde{\omega}' \frac{\chi_{\alpha\beta\gamma}^{(2)}(\tilde{\omega}, \tilde{\omega}')}{(\tilde{\omega} - \omega)(\tilde{\omega}' - \omega')}
- \frac{P}{3\pi^2} \int_{-\infty}^{\infty} d\omega' \frac{\chi_{\alpha\beta\gamma}^{(2)}(\tilde{\omega}, \omega')}{(\tilde{\omega} - \omega)(\omega' - \omega')},
\]

(B9)

Splitting up Eq. (B9) into its real and imaginary parts gives the nonlinear Kramers-Kronig relations of the form
\[
\text{Re} \left[ \chi_{\alpha\beta\gamma}^{(2)}(\omega, \omega') \right] + \frac{P}{3\pi^2} \int_{-\infty}^{\infty} d\omega d\omega' \frac{\text{Re} \left[ \chi_{\alpha\beta\gamma}^{(2)}(\tilde{\omega}, \tilde{\omega}') \right]}{(\tilde{\omega} - \omega)(\tilde{\omega}' - \omega')}
= -\frac{P}{3\pi} \int_{-\infty}^{\infty} d\omega \frac{\text{Im} \left[ \chi_{\alpha\beta\gamma}^{(2)}(\tilde{\omega}, \omega') \right]}{(\omega' - \omega)}
- \frac{P}{3\pi} \int_{-\infty}^{\infty} d\omega' \frac{\text{Im} \left[ \chi_{\alpha\beta\gamma}^{(2)}(\omega, \tilde{\omega}') \right]}{(\tilde{\omega}' - \omega')},
\]

(B10)
\[
\text{Im} \left[ \chi_{\alpha\beta\gamma}^{(2)}(\omega, \omega') \right] + \frac{P}{3\pi^2} \int_{-\infty}^{\infty} d\omega d\omega' \frac{\text{Im} \left[ \chi_{\alpha\beta\gamma}^{(2)}(\tilde{\omega}, \tilde{\omega}') \right]}{(\tilde{\omega} - \omega)(\tilde{\omega}' - \omega')}
= \frac{P}{3\pi} \int_{-\infty}^{\infty} d\omega \frac{\text{Re} \left[ \chi_{\alpha\beta\gamma}^{(2)}(\tilde{\omega}, \omega') \right]}{(\omega' - \omega)}
+ \frac{P}{3\pi} \int_{-\infty}^{\infty} d\omega' \frac{\text{Re} \left[ \chi_{\alpha\beta\gamma}^{(2)}(\omega, \tilde{\omega}') \right]}{(\tilde{\omega}' - \omega')},
\]

(B11)

As in the case of linear response functions, all causal second order response function must satisfy these relations.

The polarizability of an atom is a response function and hence must satisfy the relevant Kramers-Kronig relations. The full expression for the second order nonlinear polarizability in absorbing media is
\[
\chi_{\alpha\beta\gamma}^{(2)}(\omega, \omega') = \frac{1}{(i\hbar)^2} \frac{1}{\varepsilon_0} \sum_{ijkl} \rho_{ij}^{(0)}
\times \left[ (\omega' - \omega_{ik} - \delta\omega_{ik} - i\Gamma_{ik})/(\omega' - \omega_{ij} - \delta\omega_{ij} - i\Gamma_{ij})
- (\omega' - \omega_{ik} - \delta\omega_{ik} - i\Gamma_{ik})/(\omega' - \omega_{jk} - \delta\omega_{jk} - i\Gamma_{jk})
- (\omega' - \omega_{ij} - \delta\omega_{ij} - i\Gamma_{ji})/(\omega' - \omega_{jk} - \delta\omega_{jk} - i\Gamma_{jk})
+ (\omega' - \omega_{ij} - \delta\omega_{ij} - i\Gamma_{ji})/(\omega' - \omega_{ki} - \delta\omega_{ki} - i\Gamma_{ki}) \right]
\]

(B12)

which must obey Eq. (B9). Note that the response function is constructed from four terms of the general form
\[
T_{abd}(\omega, \omega') = \frac{A}{(\omega - \omega_{ab} - i\Gamma_{ab})(\omega' - \omega_{ad} - i\Gamma_{ad})}
\]

(B13)

where A is a constant. Applying Eq. (B9) to (B13) gives
\[
\begin{align*}
T_{abd}(\omega, \omega') &= -\frac{P}{3\pi^2} \int_{-\infty}^{\infty} d\omega d\omega' \frac{T_{abd}(\tilde{\omega}, \tilde{\omega}')}{(\tilde{\omega} - \omega)(\tilde{\omega}' - \omega')} + \frac{iP}{3\pi} \int_{-\infty}^{\infty} d\omega \frac{T_{abd}(\tilde{\omega}, \omega')}{(\tilde{\omega} - \omega)} + \frac{iP}{3\pi} \int_{-\infty}^{\infty} d\omega' \frac{T_{abd}(\omega, \tilde{\omega}')}{(\omega' - \omega')} \\
&= \frac{P}{3\pi^2} \int_{-\infty}^{\infty} d\omega d\omega' \frac{T_{abd}(\tilde{\omega}, \omega')}{(\tilde{\omega} - \omega)(\omega' - \omega)}
+ \frac{iP}{3\pi} \int_{-\infty}^{\infty} d\omega \frac{T_{abd}(\tilde{\omega}, \omega')}{(\tilde{\omega} - \omega)}(\omega' - \omega_{ab} - i\Gamma_{ab})(\tilde{\omega} - \omega_{ad} - i\Gamma_{ad})
+ \frac{iP}{3\pi} \int_{-\infty}^{\infty} d\omega' \frac{T_{abd}(\omega, \tilde{\omega}')}{(\omega - \omega')}(\omega - \omega_{ab} - i\Gamma_{ab})(\tilde{\omega}' - \omega_{ad} - i\Gamma_{ad})
\end{align*}
\]

(B14)

The integrals in (B14) can be solved by residue calculus to show that the rhs is indeed identically \( T_{abd}(\omega, \omega') \). Thus terms of this type, and hence the second order nonlinear polarizability, obey the relevant Kramers-Kronig relations. Therefore, the second order nonlinear polariz-
Appendix C: The Onsager Model

The Onsager model for local field corrections, as used in classical nonlinear optics, is the classical variant of the real cavity model [22, 23] and involves considering a point charge at the centre of an empty spherical cavity embedded within a dielectric medium. One then considers two cases: firstly, the field in the empty cavity when the dielectric is subjected to an external electric field and, secondly, the field in the cavity as a result of the polarization the point charge induces in the surrounding dielectric. By considering the Maxwell equations for the field on the boundary of the cavity, one can derive relations between the applied and local fields electric and polarization fields,

\[ E_{\text{loc}} = \frac{3\varepsilon(\omega)}{2\varepsilon(\omega) + 1} E, \quad (C1) \]

\[ P_{\text{loc}} = \frac{2}{3\varepsilon_0} \left[ \frac{\varepsilon(\omega) - 1}{2\varepsilon(\omega) + 1} \right] P. \quad (C2) \]

One should also note that since \( P_{\text{tot}} = P + P_N \), the noise polarization field can be assumed to be corrected in the same way as the reactive polarization field.

This method results in the same local field correction factors as the real cavity model used for quantum systems. For a more detailed description of the method readers are referred to Onsager’s original paper [26]. A good summary of the model can also be found in Ref. [27].

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