

SUSCEPTIBILITIES, LOCAL FIELD, AND POLARITONS IN NONLINEAR OPTICS: A UNIFYING THEORY

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A general scheme is presented for calculating the nonlinear optical response in condensed phases which provides a unified picture of excitons, polaritons, retardation and local field effects in crystals and in disordered systems. From a fully microscopic starting point we show that the traditional approach of applying response theory to the material system perturbed by the external field, is justified if retardation is neglected. For the case of strong retardation effects, we propose a new procedure to evaluate optical response, based on a hierarchy of equations of motion for polaritons.

The traditional approach to calculate (nonlinear) optical signals is based on performing response theory of the material system with instantaneous intermolecular interactions with respect to the external laser fields [1,2]. From this, one may, for instance, obtain the nonlinear optical susceptibilities as equilibrium correlation functions of the polarization field of the material system. For dense systems the application of response theory requires the solution of a many-body problem, as a result of the intermolecular interactions. One therefore often invokes the local field approximation [1], in which every molecule is considered to interact only with an effective (local) electric field which incorporates the interactions with the environment. A more fundamental problem than the proper inclusion of the instantaneous Coulomb interactions, is that the radiation field itself is a degree of freedom. In condensed phases with a large density of oscillator strength, this may lead to the formation of coupled material–radiation eigenmodes (polaritons). In recent years, many nonlinear optical experiments were performed in which polariton properties played an important role [3]. The traditional approach of calculating the response of the material system with instantaneous interactions to the external field cannot account for these effects. A complete theory of optical response should be derived from a microscopic basis in which the coupled evolution of the radiation field and the molecular system is considered. Only then is it possible to address the response of systems in which polaritons are important and, moreover, it can be shown in what approximations the susceptibilities may be used and defined as done traditionally. In this paper,

we present exact equations of motion for the radiation fields and the material variables which serve as such a general starting point and we discuss their practical implementation.

We consider an arbitrary system (lattice, disordered system, monolayer, cluster, etc.) of multilevel molecules with localized electronic states coupled to the radiation field. The multipolar Hamiltonian for this system reads in the dipole approximation (a caret denotes an operator) [4]:

$$\hat{H} = \sum_m \hat{H}_m + \hat{H}_{\text{rad}} - \int \hat{\mathbf{P}}(\mathbf{r}) \cdot \hat{\mathbf{D}}^\perp(\mathbf{r}) d\mathbf{r} + 2\pi \sum_m \int |\hat{\mathbf{P}}_m^\perp(\mathbf{r})|^2 d\mathbf{r}, \quad (1)$$

where \hat{H}_m is the Hamiltonian of the isolated molecule m and \hat{H}_{rad} is the contribution from the free radiation field. The third term is the coupling between the radiation and the molecules; $\hat{\mathbf{P}}(\mathbf{r})$ is the polarization field in the medium and $\hat{\mathbf{D}}^\perp(\mathbf{r})$ is the transverse electric displacement field, which is related to the Maxwell field operator $\hat{\mathbf{E}}(\mathbf{r})$ by $\hat{\mathbf{D}}^\perp(\mathbf{r}) = \hat{\mathbf{E}}^\perp(\mathbf{r}) + 4\pi\hat{\mathbf{P}}^\perp(\mathbf{r})$. Finally, the last term in eq. (1) is a self-energy, in which $\hat{\mathbf{P}}_m^\perp(\mathbf{r})$ is the transverse polarization field caused by molecule m only. In the multipolar Hamiltonian, $\hat{\mathbf{D}}^\perp(\mathbf{r})$ is the conjugate momentum of the vector potential $\hat{\mathbf{A}}(\mathbf{r})$ [4], so that in second quantization it is totally expressed in terms of radiation creation and annihilation operators only, and commutes with all material operators.

The basis for the calculation of optical response is the time evolution for the coupled radiation–matter system, which can be described by the Heisenberg equations of motion. For the radiation operators, these equations can be shown to be equivalent to the Maxwell equations in the dipole approximation [5]. To describe the material evolution, we have to face the problem of total absence of explicit intermolecular interactions in

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the multipolar Hamiltonian. Interactions are instead carried by exchange of photons between the molecules. Consequently, it seems that even to describe the intuitively simple notion of instantaneous interactions, we are forced to include the radiation field in our description. We present an *exact* representation of the Heisenberg equations of motion in which instantaneous intermolecular interactions are explicitly recovered, without addressing the dynamics of the radiation field. For an arbitrary material operator \hat{Q} , this equation is derived by formally writing the commutator of the Hamiltonian eq. (1) with \hat{Q} , while realizing that $\hat{D}^\perp(\mathbf{r})$ commutes with all material operators. Substituting the relation $\hat{D}^\perp(\mathbf{r}) = \hat{E}^\perp(\mathbf{r}) + 4\pi\hat{P}^\perp(\mathbf{r})$ and explicitly writing the transverse polarization field in terms of the molecular dipole operators $\hat{\mu}_m$, we arrive at [5]

$$\frac{\hbar}{i} \frac{d\hat{Q}}{dt} = [\hat{H}_0, \hat{Q}] - \frac{1}{2} \sum_m \{ [\hat{\mu}_m, \hat{Q}] \cdot \hat{E}^\perp(\mathbf{r}_m) + \hat{E}^\perp(\mathbf{r}_m) \cdot [\hat{\mu}_m, \hat{Q}] \}, \quad (2)$$

where all operators are taken at time t , \mathbf{r}_m is the position of molecule m , and

$$\hat{H}_0 = \sum_m \hat{H}_m + \frac{1}{2} \sum'_{m,n} \hat{\mu}_m \cdot (\mathbf{r}_{mn}^2 - 3\mathbf{r}_{mn}\mathbf{r}_{mn}) \cdot \hat{\mu}_n / r_{mn}^5. \quad (3)$$

Here $\mathbf{r}_{mn} \equiv \mathbf{r}_m - \mathbf{r}_n$ and the prime on the summation excludes terms with $m = n$. The last term in \hat{H}_0 is the instantaneous dipole–dipole interaction. The great merit of this equation is that it separates the contribution from the material Hamiltonian \hat{H}_0 , which is the common basis for optical response theories and the calculation of susceptibilities. Furthermore, the interaction with the Maxwell electric field is obtained in the familiar $\hat{\mu} \cdot \hat{E}^\perp$ form. Because in eq. (2) the electric field appears as an operator, it is possible to define coupled matter–radiation eigenmodes (polaritons); on the other hand, this prevents us from directly applying response theory and obtaining susceptibilities.

In order to define susceptibilities, the expectation value of the polarization field must be expanded in the average Maxwell electric field. If in eq. (2) the electric field would appear as the expectation value $\langle \hat{E}^\perp \rangle$, we could use the expectation value of this equation to generate a hierarchy of equations of motion, coupling material variables to each other and to $\langle \hat{E}^\perp \rangle$. The susceptibilities could be obtained from this by truncating the hierarchy at some point, substituting for all introduced material variables expansions in terms of $\langle \hat{E}^\perp \rangle$, and iteratively solving for the expansion coefficients [6]. In reality, however, the expectation value of eq. (2) involves averages of products of material operators and the electric field, so that such a hierarchy can only be built if we factorize these products. Instead of introducing an ad hoc factorization approximation, we will use an approach which gives a more physical mean-

ing to this approximation. Consider the formal solution to the Maxwell equations in Fourier space [7]:

$$\hat{E}(\mathbf{k}, \omega) = \mathbf{E}_{\text{ext}}(\mathbf{k}, \omega) - 4\pi \frac{\mathbf{k}\mathbf{k} - (\omega/c)^2}{k^2 - (\omega/c + i0^+)^2} \cdot \hat{P}(\mathbf{k}, \omega), \quad (4)$$

where \mathbf{E}_{ext} denotes the external electric field, which is a c number. Subtracting from eq. (4) its expectation value, we obtain

$$\hat{E}(\mathbf{k}, \omega) = \langle \hat{E}(\mathbf{k}, \omega) \rangle - 4\pi \frac{\mathbf{k}\mathbf{k} - (\omega/c)^2}{k^2 - (\omega/c + i0^+)^2} \cdot (\hat{P}(\mathbf{k}, \omega) - \langle \hat{P}(\mathbf{k}, \omega) \rangle). \quad (5)$$

From this, we find that the transverse Maxwell field equals its expectation value up to a contribution of the order $(\omega/c)^2$. Thus, if we totally neglect retardation ($\omega/c = 0$), we may replace the operator \hat{E}^\perp in eq. (2) by $\langle \hat{E}^\perp \rangle$, and susceptibilities can be obtained in the way described above. In this approximation, the material evolution can be described by a time-dependent effective Hamiltonian

$$\hat{H}_{\text{eff}}(t) = \hat{H}_0 - \sum_m \hat{\mu}_m \cdot \langle \hat{E}^\perp(\mathbf{r}_m, t) \rangle. \quad (6)$$

We may alternatively describe the material evolution by transforming to the Schrödinger picture and giving the Liouville equation for the reduced material density operator

$$\frac{\hbar}{i} \frac{d\hat{\rho}^M(t)}{dt} = -[\hat{H}_{\text{eff}}(t), \hat{\rho}^M(t)], \quad (7)$$

where $\hat{\rho}^M(t)$ is the total density operator traced over the radiation field. This is the common starting point for performing response theory, yielding the expressions for the susceptibilities in terms of equilibrium correlation functions of the material polarization field in the standard way [1,2]. Because of the many-body character of the material evolution in condensed phases, susceptibilities are hard to evaluate for such systems. A common approximation is obtained by factoring in the expectation value of eq. (2) any product of operators acting on different molecules into the product of expectation values. This mean-field approximation allows us to consider the evolution of a single molecule responding to the well-known local field

$$\mathbf{E}_L(\mathbf{r}_m, t) = \langle \hat{E}(\mathbf{r}_m, t) \rangle + \frac{4\pi}{3} \langle \hat{P}(\mathbf{r}_m, t) \rangle, \quad (8)$$

and leads to susceptibilities given by the single molecule hyperpolarizabilities multiplied by local field correction factors [1].

Clearly, the above replacement of \hat{E}^\perp by its expectation value destroys the possibility to describe polaritons in crystals. To do this, the full operator nature of the radiation field should be maintained, so that we return to eq. (2). Combining this equation for the

material (exciton) creation and annihilation operators with the Maxwell equations, the polaritons are derived as eigenmodes of the coupled radiation–material Hamiltonian (cf. ref. [8], where this is done within the minimal coupling ($\mathbf{p} \cdot \mathbf{A}$) Hamiltonian). The explicit separation of the instantaneous interactions in eq. (2) proves advantageous in this derivation [5], because it allows us to neglect Umklapp processes (high wave vector modes) in the transverse electric field, which considerably simplifies the eigenvalue problem involved in the calculation of the polaritons. A similar approximation directly applied to the displacement field in eq. (1) leads to an incorrect polariton dispersion relation [5]. For systems in which polaritons play an important role (typically, low-temperature crystals with a high density of oscillator strength) the above theory of susceptibilities does not provide a solid basis to calculate optical response. Instead, a procedure which directly addresses the response of the polaritons to the laser fields is favorable. We propose to describe nonlinear optical response in terms of polaritons in the following way [5]: the expectation values of the creation and annihilation operators of the polaritons which are directly created by the external field can be found by matching the boundary conditions for the electromag-

netic fields. Call these polaritons the “first order” polaritons, because they describe the linear response of the crystal. We now build a hierarchy of equations of motion for polariton operators, which may be done using the Maxwell equations and eq. (2). In doing this, the Bose approximation for the commutation relations of the exciton operators should not be made, because this automatically leads to a truncation of the hierarchy at the lowest level and the absence of nonlinearities. In order to calculate the optical signal (which depends on the expectation value of the polarization field), we take expectation values of all the equations in the hierarchy and truncate by factorizing at a certain level into lower order variables and expectation values of single polariton creation and annihilation operators. The set of equations thus generated may be solved in terms of the expectation values of the “first order” polariton operators, so that the signal can be expressed in terms of the external field amplitudes. This procedure guarantees that the optical signal has resonances fully determined by the polariton dispersion relation.

In conclusion, we showed how both the traditional approaches to optical response and a new procedure which accounts for polariton effects can be obtained from a unified starting point. The relation between the different approaches is summarized in fig. 1.

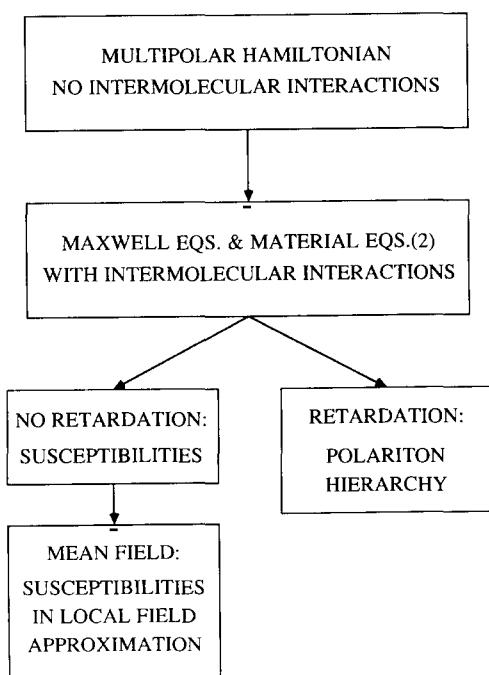


Fig. 1. Diagram illustrating how the different approaches to calculate nonlinear optical response discussed in the text derive from a common root.

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