Exciton-Exciton Correlation in the Nonlinear Optical Regime

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We present a theory of the time development of the nonlinear optical excitations in a semiconductor in which the correlated part of the many-body problem is expressed in terms of the exact N-exciton eigenstates and is decoupled from the optical excitation process. A first-principles exact numerical solution for the four-wave mixing in a one-dimensional model demonstrates the role of two-exciton correlation in polarization mixing and, in particular, shows a ringing of the polarization with the frequency given by the binding energy of the biexciton.

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Recent four-wave mixing (FWM) experiments in semiconductors have shown the importance of the biexciton effects in the nonlinear response. The inclusion of biexcitonic effects as well as the effects of polarization mixing in the description of optical excitations in semiconductors was discussed in terms of an effective phenomenological few-level model [1–3] to explain the temporal dependence of the FWM signal as well as beating phenomena between bound and unbound biexciton states observed for cross-polarized excitations near the fundamental exciton resonance. By the equation of motion approach, Axt and Stahl [4] show that the semiconductor Bloch equations form a closed set for the density matrix elements to any given order of the external field. A diagrammatic approach by Maialle and Sham [5] shows the structures of the excitons and biexcitons involved in the third-order susceptibility and the relation of the particle loops to the polarization mixing. The truncation scheme provides a starting point for a study of polarization effects from a microscopic point of view. This Letter addresses the problem of separation of the static problem of the exciton and biexciton eigenstates and of the dynamical optical processes. By expressing the nonlinear response in terms of exact eigenstates of the system involving a given number of electron-hole (eh) pairs, it follows that the third-order polarization depends only on the one eh-pair subspace (excitons) and the two eh-pair subspace (biexcitons). The correlated part of the biexciton which appears in the third-order polarization is further expressed succinctly in terms of an exciton-exciton correlation function. Our formulation offers the alternatives of (1) solving the exciton and biexciton eigenstates to a desired numerical accuracy and then using them to obtain the correlation functions, and (2) using the standard many-body techniques to solve approximately for the dynamical two-exciton correlation functions. We present a first-principles exact numerical solution for the correlation function in a one-dimensional semiconductor model. The solution offers a physical picture of the two-exciton correlation which does not always correspond to the existing phenomenological models but which we believe represents more closely the underlying physical processes in the experimental observations.

In the absence of the light-matter interaction the eigenstates $|E_{N,\alpha}\rangle$ of the Hamiltonian of the usual semiconductor model can be labeled according to the number N of eh pairs [6]. For $N = 0$ there are no additional quantum numbers α and we denote this semiconductor ground state by $|0\rangle$ and choose its energy to be zero. The $N = 1$ subspace is the exciton subspace with the additional quantum numbers $\alpha = (n, \sigma)$ where σ denotes the polarization. We consider only the heavy valence subbands with angular momentum $\pm 3/2$ and a conduction band with spin $\pm 1/2$. The selection rules dictate that for light along the growth axis the $+3/2$ $(-3/2)$ electrons in the heavy-hole band are coupled via an optical transition with $-$ $(+)$ polarized photons to the $+1/2$ $(-1/2)$ spin states in the conduction band. The next relevant subspace is the biexciton Hilbert space with a complete set $|E_{2,\alpha}\rangle$ of bound and unbound states. The interband matrix element between the Bloch states of the bands is denoted by μ_σ. It is convenient to express the total σ polarization in terms of exciton operators [7]

$$P_\sigma = \mu_\sigma^* \sum_{\mathbf{k},n} \Phi^*_{\mathbf{k},n,\sigma} B_{n,\sigma} = \mu_\sigma^* \sum_n \alpha^*_{n,\sigma} B_{n,\sigma} . \quad (1)$$

The operator $B^\dagger_{n,\sigma} = \sum_{\mathbf{k}} \Phi^*_{\mathbf{k},n,\sigma} c^\dagger_{2,\mathbf{k},\sigma} c_{1,\mathbf{k},\sigma}$ creates an exciton state with zero total momentum and wave function $\Phi_{\mathbf{k},n,\sigma}$ with energy $\omega_{1,n,\sigma}$. These states are the solution of the Wannier equation [7] for the semiconductor. The dynamical evolution of the polarization in an applied external field is governed by the expectation values of the following relevant Hubbard operators:

$$\hat{X}_{N,\alpha;M,\beta} = |E_{N,\alpha}\rangle\langle E_{M,\beta}| , \quad (2)$$

which can be used to express the exciton operator

$$B_{n,\sigma} = \hat{X}_{0;1,n,\sigma} + \sum_{N\geq 1,\alpha,\beta} \langle E_{N,\alpha}|B_{n,\sigma}|E_{N+1,\beta}\rangle \hat{X}_{N,\alpha;N+1,\beta} .$$

The interaction of the semiconductor with a classical external laser field with central frequency ω_p and $\mathbf{E}(t) =$

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$\sum_\sigma E_\sigma(t)e^{-i\omega_p t}\mathbf{e}_\sigma$ + c.c. is given in the usual rotating wave approximation [7,8] by

$$H_I = -\sum_{n,\sigma}\left(\frac{\Omega^*_{n,\sigma}}{2} B_{n,\sigma} + \text{H.c.}\right), \tag{3}$$

with the time-dependent Rabi frequency of a given polarization ($\hbar \equiv 1$) and a renormalized Rabi frequency given by $\Omega_\sigma = 2(\mu_\sigma E_\sigma)$ and $\Omega_{n,\sigma} = \alpha_{n,\sigma}\Omega_\sigma$. From the form of the interaction H_I it follows that the expectation values $\langle \hat{X}_{0;N,\alpha}\rangle_t$ can be expressed as a power series in the external field

$$\langle \hat{X}_{0;N,\alpha}\rangle_t = \sum_{m=0}^{m_0} X^{(N+2m)}_{N,\alpha}(t) + O(E^{N+2m_0+2}). \tag{4}$$

The general expectation values follow from the relation

$$\langle \hat{X}_{N,\alpha;M,\beta}\rangle_t = \langle \hat{X}_{0;N,\alpha}\rangle^*_t \langle \hat{X}_{0;M,\beta}\rangle_t / \langle \hat{X}_{0;0}\rangle_t, \tag{5}$$

with $\hat{X}^{(0)}_0(t) = 1$ from the initial condition of the semiconductor in its ground state. In order to calculate the σ polarization we consider the equation of motion for $\langle B_{n,\sigma}\rangle_t$. Using the Hubbard operators it reads

$$i\frac{\partial}{\partial t}\langle B_{n,\sigma}\rangle_t = (\omega_{1,n,\sigma} - i\Gamma)\langle B_{n,\sigma}\rangle_t + \sum_{N\geq 1}\sum_{\alpha,\beta} c^{(N)}_{n,\sigma;\alpha,\beta}\langle \hat{X}_{N,\alpha;N+1,\beta}\rangle_t - \frac{\Omega_{n,\sigma}}{2} + \sum_{N\geq 1}\sum_{\alpha,\beta}\frac{\Omega^{(N)}_{n,\sigma;\alpha,\beta}}{2}\langle \hat{X}_{N,\alpha;N,\beta}\rangle_t, \tag{6}$$

with

$$c^{(N)}_{n,\sigma;\alpha,\beta} = (\omega_{N+1,\beta} - \omega_{N,\alpha} - \omega_{1,n,\sigma})\langle E_{N,\alpha}|B_{n,\sigma}|E_{N+1,\beta}\rangle,$$

$$\Omega^{(N)}_{n,\sigma;\alpha,\beta} = \sum_{\mathbf{q}} \Omega_\sigma \Phi_{\mathbf{q},n,\sigma}\langle E_{N,\alpha}|1 - n_{1,\mathbf{q},\sigma} + n_{2,\mathbf{q},\sigma}|E_{N,\beta}\rangle. \tag{7}$$

We have introduced the dephasing due to degrees of freedom not included (e.g., phonons) in a phenomenological way with the effective parameter Γ. Using Eqs. (4) and (5) we see that Eq. (6) can be considered as a linear differential equation with a (trivial) first-order source and nontrivial source terms of third and higher order. In the following we restrict ourselves to the contributions up to *third* order. Then using Eqs. (4) and (5) we see that only $X^{(1)}_{1,n,\sigma}$ and $X^{(2)}_{2,\alpha}$ have to be determined. As $X^{(1)}_{1,n,\sigma}(t)$ obeys Eq. (6) without the terms involving the summations one obtains

$$X^{(1)}_{1,n,\sigma}(t) = \frac{i}{2}\int_{-\infty}^{t} e^{-i(\omega_{1,n,\sigma} - i\Gamma)(t-t')}\Omega_{n,\sigma}(t')\,dt'. \tag{8}$$

The equation of motion for $X^{(2)}_{2,\beta}$ reads

$$i\frac{\partial}{\partial t}X^{(2)}_{2,\beta} = (\omega_{2,\beta} - i\Gamma_{xx})X^{(2)}_{2,\beta} - \sum_{n',\sigma';n'',\sigma''}\frac{\Omega_{n'',\sigma''}}{2}\langle E_{2,\beta}|B^\dagger_{n'',\sigma''}|E_{1,n',\sigma'}\rangle X^{(1)}_{1,n',\sigma'}, \tag{9}$$

where the biexciton phenomenological dephasing constant Γ_{xx} is taken in the following as 2Γ. In order to write the second term on the right-hand side of Eq. (6) in a compact form we use the explicit result (9) for $X^{(2)}_{2,\beta}(t)$ in order to perform the summation of the biexciton quantum numbers β. Then we obtain after a partial integration

$$\sum_\beta c^{(1)}_{n,\sigma;\tilde{n},\tilde{\sigma},\beta}X^{(2)}_{2,\beta}(t) = \frac{1}{2}\sum_{n',\sigma',n'',\sigma''}\Big\{\langle 0|D_{\tilde{n},\tilde{\sigma};n,\sigma}B^\dagger_{n',\sigma'}B^\dagger_{n'',\sigma''}|0\rangle X^{(1)}_{1,n',\sigma'}(t)X^{(1)}_{1,n'',\sigma''}(t)$$
$$- i\int_{-\infty}^{t} e^{-2\Gamma(t-t')}F^{n',\sigma';n'',\sigma''}_{\tilde{n},\tilde{\sigma};n,\sigma}(t-t')X^{(1)}_{1,n',\sigma'}(t')X^{(1)}_{1,n'',\sigma''}(t')\,dt'\Big\}. \tag{10}$$

Here we have introduced the operators $D_{\tilde{n},\tilde{\sigma};n,\sigma} = [B_{\tilde{n},\tilde{\sigma}},[B_{n,\sigma},H]]$ and the memory kernel

$$F^{n',\sigma';n'',\sigma''}_{\tilde{n},\tilde{\sigma};n,\sigma}(\tau) = \langle 0|D_{\tilde{n},\tilde{\sigma};n,\sigma}(\tau)D^\dagger_{n',\sigma';n'',\sigma''}|0\rangle. \tag{11}$$

The explicit form of the D operators is

$$D_{\tilde{n},\tilde{\sigma};n,\sigma} = \sum_{\mathbf{q}\neq 0}\tilde{U}_{\mathbf{q}}A_{\tilde{n},\tilde{\sigma}}(\mathbf{q})A_{n,\sigma}(-\mathbf{q}), \tag{12}$$

$$A_{n,\sigma}(\mathbf{q}) = \sum_{\mathbf{k}}(\Phi_{\mathbf{k}-\mathbf{q}/2,n,\sigma} - \Phi_{\mathbf{k}+\mathbf{q}/2,n,\sigma})c^\dagger_{1,\mathbf{k}-\mathbf{q}/2,\sigma}c_{2,\mathbf{k}+\mathbf{q}/2,\sigma}, \tag{13}$$

where $\tilde{U}_{\mathbf{q}}$ denotes the Fourier transform of the Coulomb interaction between the electrons. The first term on the right-hand side of Eq. (10) describes the correlations between excitons as in the usual mean-field semiconductor Bloch equations (MFA) [9–12]. It is only nonzero for excitons with *identical polarization* and does not produce polarization mixing. As $D_{\tilde{n},\tilde{\sigma};n,\sigma}(\tau)|0\rangle = 0$ the correlation function $F(\tau)$ can be written as a time-ordered product and standard Feynman diagrams can be used, e.g., to set up approximation schemes. From a diagrammatic analysis to all orders the rigorous polarization selection rule $\sigma + \tilde{\sigma} = \sigma' + \sigma''$ can easily be read off. As the operators $A_{n,\sigma}(\mathbf{q})$ can be expressed in terms of *finite* center of mass exciton operators $B_{n,\sigma}(\mathbf{q})$, $F(\tau)$ can be considered a two-exciton correlation function. The fact that the third-order polarizability can be expressed in terms of this correlation function depending on a *single* time difference is due to the simplicity of the semiconductor ground state

approximated by the vacuum state of the bound and unbound excitons [4,7].

In the limit of *large dephasing* a short-time approximation $B_{n,\sigma}(\mathbf{q},\tau) \approx B_{n,\sigma}(\mathbf{q})e^{-i\omega_{1,n,\sigma}(\mathbf{q})\tau}$ in the calculation of F can be considered, which neglects the residual interaction between the two excitons. This approximation, which only involves simple equal-time ground-state expectation values, already leads to polarization mixing. It does not require the existence of a real *bound* biexciton.

For $N = 1$ the last term on the right-hand side of Eq. (6) provides the other third-order source term, which, from Eq. (5), is bilinear in $X^{(1)}$ and is usually called the state-filling term [9–12]. Its strength is determined by

$$\Omega^{(1)}_{n,\sigma;n',\sigma',n'',\sigma''} = 2\delta_{\sigma,\sigma'}\delta_{\sigma,\sigma''}\sum_{\mathbf{q}}\Phi_{\mathbf{q},n,\sigma}\Phi_{\mathbf{q},n',\sigma'}\Phi^{*}_{\mathbf{q},n'',\sigma''}\Omega_{\sigma}\,.$$

We have applied our theory above to a one-dimensional Hubbard model of n sites, extended to two bands for a semiconductor and to include a long-range interaction between electrons from both bands on different sites inversely proportional to the distance. The correlation function was calculated by numerically solving for the time evolution of the wave function $D^{\dagger}|0\rangle$ in the site representation [13,14]. The number of sites $n = 60-160$ used was much larger than the ground-state spatial extent of the biexciton molecule. The dimension of the matrices involved, $2n^3$, was manageable because of the sparseness of the Hamiltonian matrix. Figure 1 shows the time dependence of $F^{+,-}_{+,-}(\tau)/F^{+,-}_{+,-}(0)$ on the fundamental time scale for the ground-state excitons. The ultrafast *intrinsic* decay is due to the superposition of the continuum of *unbound* biexciton states, whereas for longer times only the bound-state contribution remains. The binding energy of the bound biexciton molecule is $\approx 0.1\omega_x$, where ω_x denotes the binding energy of the fundamental exciton resonance. The corresponding normalized spectral distribution of the correlation function is plotted in Fig. 2 with a dephasing of $\Gamma = 0.1\omega_x$. The relative weight of the bound biexciton peak is ≈ 0.04. The spectrum has a maximum at $\omega \approx 4\omega_x$

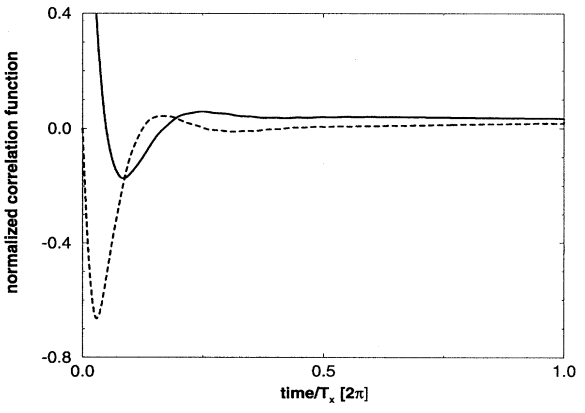

FIG. 1. Real (solid line) and imaginary (dashed line) parts of the normalized correlation function $F(\tau)/F(0)$ for the one-dimensional semiconductor model.

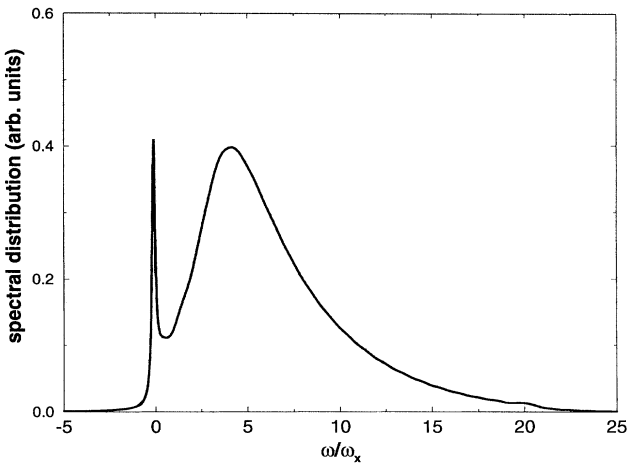

FIG. 2. Spectral distribution of the correlation function of Fig. 1. The sharp resonance is due to the bound biexciton molecule in the system.

which determines the fast time scale for the intrinsic decay. The complete information about the correlation function obtained for this model serves as the input for a three-pulse degenerate four-wave-mixing (DFWM) experiment [2]. We have used short Gaussian pulses with central frequency at the fundamental exciton resonance. With the direction and the polarization of the incident pulses given by $(\mathbf{k}_1, -)$, $(\mathbf{k}_2, +)$, and $(\mathbf{k}_3, -)$, the signal in the $(\mathbf{k}_f = \mathbf{k}_3 + \mathbf{k}_2 - \mathbf{k}_1, +)$ direction is then due to the correlations of excitons with *different* polarization; i.e., this signal vanishes in the MFA and space-filling effects are also absent at this order of the signal. Figure 3 shows the time-resolved intensity, which is given by the square of the nonlinear polarization of Eq. (6) of the signal with all three pulses interacting with the semiconductor at $t = 0$ (solid

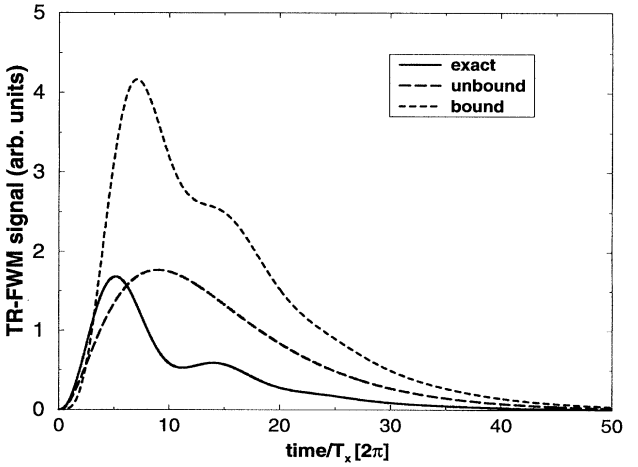

FIG. 3. Time-resolved DFWM signal ($\Gamma = 0.01\omega_x$) in the cross-polarized configuration. Destructive interference of bound and unbound biexciton states leads to a smaller effective signal (solid line).

line). The signal shows a sharp rise and the observed temporal oscillation superposed on the decay of the signal has the frequency of the binding energy of the bound biexciton. This phenomenon can be explained by a *ringing* of the polarization due to the biexciton resonance, which is below the energy of the two-exciton continuum. These oscillations occur also in the time-integrated signal of Fig. 4 for negative delay; i.e., pulse 1 arrives last and the diffracted signal contains the information from delayed stages of the coherence decay only. In addition, the ringing does not need additional biexciton or unbound two-exciton states, which is demonstrated using the bound biexciton (short dashed line) and the continuum contributions (long dashed line) only in Fig. 3. The interference of bound and unbound states reduces the actual signal intensity due to destructive interference. This cannot be correctly described in a few-level model. From the derivation of Eq. (6) we conclude that these oscillations cannot be denoted as polarization interference because the source term responsible for this DFWM signal is due to correlations between the exciton states ($N = 1$) and biexciton states ($N = 2$). We expect a similar behavior of the signal for higher-dimensional semiconductor systems with a bound biexciton resonance, because of a partial cancellation of dimensionality effects in the expression of Eq. (12).

In conclusion, we have investigated the role of exciton-exciton correlations in the weak nonlinear regime of optical excitations in semiconductor systems, including spin-dependent effects. We have demonstrated how the correlated part of the many-body problem can be separated from the dynamics of the nonlinear polarization, which is different from recent approaches [4,5]. In addition to the well known mean-field corrections, a two-exciton correlation function has to be calculated to obtain the exact third-order nonlinear polarization. In contrast to phenomenological approaches, which stress the importance of real bound biexciton states in the common few-level models [1,3], we showed that second-order contributions in the exciton-exciton interaction can already lead to significant polarization mixing in the exciton polarization dynamics which is absent in a conventional mean-field approach.

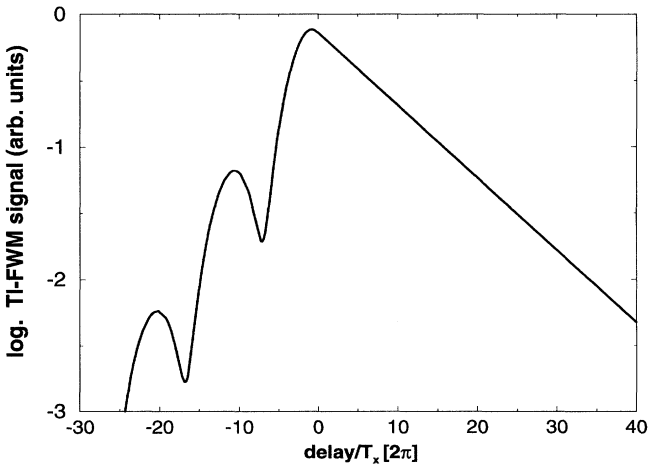

FIG. 4. Time-integrated DFWM signal in the cross-polarized configuration. The ringing with the biexciton binding frequency occurs only for negative delay, i.e., pulse 1 arriving after pulses 2 and 3.

In an application of the formalism, we have calculated the exact numerical DFWM signal in the cross circularly polarized configuration for a one-dimensional semiconductor. For resonant excitation of the fundamental exciton resonance the signal shows oscillations with the biexciton binding energy which are due to a ringing of the semiconductor polarization for short-pulse excitations. For ultrashort-pulse excitations, the nonlinear polarization is dominated by the continuum of unbound biexciton states, which shows a fast intrinsic dephasing in the correlation function.

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