Biexcitonic effects in transient nonlinear optical experiments in quantum wells

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We present a model for the nonlinear optical response of quantum wells, which includes biexcitons. We show that within this model, the interaction of two laser pulses, mediated by the nonlinear susceptibility, results in oscillations and in coupling between σ^+ and σ^- excitons. This explains the temporal behavior of the differential absorption and four-wave mixing in recent experiments [Phys. Rev. Lett. **68**, 349 (1992); **68**, 1880 (1992)]. The oscillations have a frequency equal to the biexciton binding energy, and are different from known interference and quantum beat phenomena.

The nonlinear optical properties of III-V semiconductors at energies close to the band gap are dominated by excitons. These properties have been intensively investigated during the past decade, especially in quantum wells (QW's), in which the confinement of the excitons to two dimensions increases the binding energy and oscillator strength.[1] The nonlinear properties of more complex excitations, in which a number of excitons are involved, have been investigated to a lesser extent. The simplest form of such an excitation is the biexciton. The binding energy of the biexciton in these structures is relatively small,[2,3] hence it is unstable even at low temperatures, and therefore considered unimportant.

Time-resolved differential absorption (DA) and four-wave mixing (FWM) are two nonlinear experimental techniques which are often used in investigating the nonlinear response of QW's.[4,5] In these techniques two pulses, delayed by t_D with respect to each other, are incident on a sample. In a DA experiment the change of absorption of the second pulse (probe) due to the first pulse (pump) is measured as a function of t_D. In a FWM experiment the two pulses have wave vectors $\mathbf{k}_1$ and $\mathbf{k}_2$ with a small angle between them. The integrated light intensity in direction $2\mathbf{k}_1 - \mathbf{k}_2$ is measured as a function of t_D.

Biexcitonic nonlinearity in a GaAs QW was directly observed in a FWM experiment.[6] Very recently, there were several reports on oscillatory behavior in DA (Ref. 7) and FWM (Ref. 8) experiments in GaAs QW's. In the DA experiment, deep oscillations of the transmitted probe intensity were observed for oppositely handed circularly polarized pump and probe. In the FWM experiment, the intensity of the emitted signal was shown to oscillate with the delay between the two cross-linearly polarized exciting pulses. These oscillations were interpreted as quantum beats between excitonic and biexcitonic states, and their frequency was used to deduce the biexciton binding energy. However, the theory of quantum beats accounts for oscillatory behavior of states which are very close in energy and are coherently driven by the same laser field.[9,10] This is clearly not the case here, since the biexciton energy is almost twice that of the exciton.

In this paper we present a model which takes into account the biexcitonic state, and calculate the resulting nonlinear optical behavior. We show that the biexcitonic state introduces a channel for coupling between the σ^+ and the σ^- exciton states, and that a manifestation of this coupling is the appearance of oscillations whose frequency is the binding energy of the biexciton. These oscillations are of a special type, as they originate from interference of two laser pulses, mediated by the oscillating time-dependent nonlinear susceptibility $\chi^{(3)}$. In contrast with known beating phenomena, these oscillations appear only as long as the two pulses overlap in time.

Assuming that two excitons may bind to form a biexciton only if the $\hat{z}$ projections m of their angular momentum are $m = \pm 1$; that is, if they are created by circularly polarized light of opposite handedness, we describe the system as a four-level system (Fig. 1). The ground state $|g\rangle$, with $m = 0$, corresponds to the state of no excitons

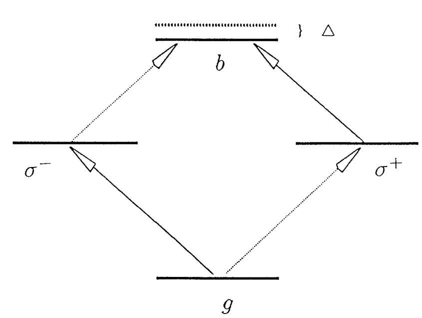

FIG. 1. The four-level system consisting of a ground state g, two exciton states $\sigma^{\pm}$, and a biexciton state b with a binding energy Δ.

and no biexcitons, and the states $|\sigma^{\pm}\rangle$, with degenerate energy ϵ and $m=\pm 1$, correspond to one exciton with either a right or a left polarization. The state $|b\rangle$ with energy $2\epsilon-\Delta$ and $m=0$ corresponds to the singlet biexciton, Δ being the binding energy. The Hamiltonian of this four-level system (4LS) is

$$H_0=\epsilon\, a^\dagger a+\epsilon\, c^\dagger c-\Delta\, a^\dagger a c^\dagger c, \tag{1}$$

where $a^\dagger$ (a) and $c^\dagger$ (c) are creation (annihilation) operators of right and left excitons, respectively. Note that this model neglects the continuous spectrum of the biexciton and is valid only at low excitation densities, where the average distance between excitons is larger than the biexciton area.

The coupling of the 4LS with light is given by

$$V=-\hat{d}_\alpha E_\alpha-\hat{d}_\beta E_\beta, \tag{2}$$

where $E_{\alpha,\beta}$ are the right and left components of the total electric field (of both pulses), and $\hat{d}_{\alpha,\beta}$ are the corresponding components of the dipole moment operator. The nonvanishing matrix elements of these operators are

$$\begin{aligned}&\langle g|\hat{d}_\alpha|\sigma^+\rangle=\langle\sigma^-|\hat{d}_\beta|g\rangle=d_{\rm ex},\\ &\langle\sigma^-|\hat{d}_\alpha|b\rangle=\langle b|\hat{d}_\beta|\sigma^+\rangle=d_{\rm bx},\end{aligned} \tag{3}$$

and their complex conjugates. Here $d_{\rm ex}$ is the dipole moment of the exciton transition, while $d_{\rm bx}$ corresponds to the transition from an already existing exciton to the biexciton state.

To calculate the nonlinear response in a DA or FWM experiments it is necessary to evaluate the third-order dipole moment, which is proportional to the third power of the electric field. The change of absorption $Q^{(3)}$ in a DA experiment with two oppositely handed circularly polarized pulses, $E_\alpha(t)$ (pump) and $E_\beta(t)$ (probe), is given by

$$Q^{(3)}=\int_{-\infty}^{+\infty}dt\,E_\beta(t)\frac{\partial}{\partial t}d_\beta^{(3)}(t), \tag{4}$$

where $d_\beta^{(3)}$ is the β polarization component of the third-order dipole moment, proportional to $E_\beta E_\alpha^2$. Similarly, the signal in a FWM experiment with two linear cross-polarized pulses $E_x(t)$ and $E_y(t)$ is proportional to $|P|^2$, where P is given by

$$P\sim\int_{-\infty}^{+\infty}dt\,|d^{(3)}(t)|^2 \tag{5}$$

and $d^{(3)}(t)$ is the relevant contribution to the third-order dipole moment proportional to $E_x^2E_y$.

To find $d^{(3)}$ we solve the equation for the time evolution of the density matrix $\hat{\rho}$ iteratively,[11,12] with the Hamiltonian H_0+V, expanding it in powers of E and collecting terms of the order of E^3, which give $\hat{\rho}^{(3)}$. Next, the dipole moment is calculated from

$$d_\sigma^{(3)}(t)=\mathrm{Tr}\{\hat{d}_\sigma\hat{\rho}^{(3)}(t)\}. \tag{6}$$

Let us consider first a DA experiment with two oppositely handed circularly polarized pulses. Calculating $Q^{(3)}$ for our system and taking the detuning $\nu=\epsilon-\omega_0$ of the center laser frequency ω_0 from the excitonic transition as a parameter, we find out that $Q^{(3)}$ oscillates in the delay t_D between the pump and probe pulses, with a period which depends on both Δ and ν. The pattern of the oscillations, a dip at the beginning and then damped oscillations, is in a very good agreement with the experimental observation in Ref. 7, but no dependence on the laser energy was observed in the experiment. We therefore consider the role of inhomogeneous broadening of the exciton line, which occurs in many QW samples, and in particular in the samples in which oscillations of the differential absorption were reported.[7]

To take into account the inhomogeneous broadening of the excitonic transition we assume that there is a distribution of 4LS with different energies ϵ (but with the same Δ), and average $d^{(3)}$ over ϵ. The width of the inhomogeneously broadened line $\Delta\epsilon$ is taken to infinity, which is appropriate for $\Delta\epsilon\gg\Delta,\nu,\Delta\omega_0$, where $\Delta\omega_0$ is the spectral width of the laser. For such an inhomogeneously broadened 4LS the DA signal is

$$Q^{(3)}\sim\int_0^\infty ds(G\,e^{-i\Delta s}-1)\int_{-\infty}^{+\infty}dt\int_{-\infty}^{t-s}dt'\{[B(t)B^*(t-s)A^*(t')A(t'-s)+B(t)A^*(t-s)B^*(t')A^*(t'-s)]\}+\text{c.c.} \tag{7}$$

Here $A(t)$ and $B(t)$ are the slowly varying envelopes of the pulses $E_\alpha(t)$ and $E_\beta(t)$, and $G=|d_{\rm bx}|^2/|d_{\rm ex}|^2$. All the omitted prefactors are positive. Calculating $Q^{(3)}$ for a probe pulse $B(t)$ delayed relative to the pump pulse $A(t)$, namely $B(t)=A(t-t_D)$, we find out that $Q^{(3)}$ oscillates in t_D with frequency Δ. Note that ν does not appear in Eq. (7), and there is no dependence of the oscillation frequency on the detuning. The result of a calculation with single-sided exponential pulses is shown in Fig. 2, where the value of G was taken to be 5. As will be discussed later this value agrees with theoretical estimates for the oscillator strength of the biexciton transition.[13] One can clearly see that the oscillations persist only as long as there is overlap between the pump and probe pulses. The inset of Fig. 2 shows the experimental data from Ref. 7. It can be seen that there is good qualitative agreement between the calculations and the measured signal.

For delays which are much larger than the pulse width one can easily show that

$$Q_\infty^{(3)}\sim-2\int_0^\infty ds(1-G\cos\Delta s)|K(s)|^2, \tag{8}$$

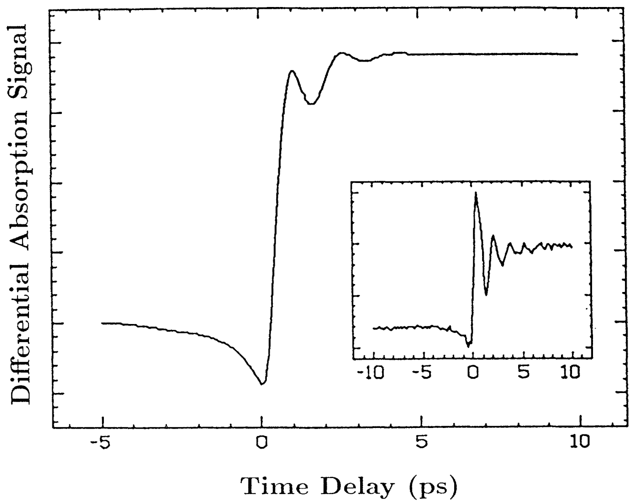

FIG. 2. The calculated differential absorption signal $-Q^{(3)}$ as a function of the time delay for single-sided exponential pulses with an autocorrelation width of 1.8 ps and assuming $G=5$. The inset shows the experimental results of Ref. 7.

where $K(s)$ is the pulse autocorrelation function. Equation (8) clearly shows that, due to the biexcitonic coupling, a differential absorption signal is obtained at large delays. This signal reflects the transfer of oscillator strength from the excitonic transition to the biexcitonic transition due to the redistribution by the pump pulse of the population in the 4LS. As some of the 4LS's are excited by the pump to an excitonic state, the probe pulse detects a decreased absorption at the ground state to exciton transition, and an increased absorption at the exciton-biexciton transition. It can be seen from Eq. (8) that depending on the value of G and the relative size of Δ and $\Delta\omega_0$, which defines the time scale of $K(s)$, the sign of $Q^{(3)}$ can be either positive or negative. In general, large G values would tend to make $Q^{(3)}$ positive, while a large Δ would tend to make it negative.

It follows from numerical calculations with different pulse shapes that the main features of $Q^{(3)}$ vs t_D, namely, zero signal for large negative delays, a dip for small negative delays (of the order of the pulse width), oscillations for positive delays within the overlap of the pulses, and, finally, a constant positive value for large positive delays, are all pulse shape independent.

We now apply our model to the calculation of the signal in FWM experiments in inhomogeneously broadened systems, where two pulses with wave vectors $\mathbf{k}_1$ and $\mathbf{k}_2$, and envelopes $X(t)$ and $Y(t)$, are polarized along x and y, respectively. The field emitted in the direction $2\mathbf{k}_1-\mathbf{k}_2$ is polarized along y and is given by Eq. (5), where the third-order dipole moment is

$$d_y^{(3)}(t) \sim |d_{\mathrm{ex}}|^2 d_{\mathrm{bx}} e^{i(\epsilon-\Delta)t} \times \int_{-\infty}^{t} dt'\, X^*(t') e^{i\Delta t'} \times \int_{-\infty}^{t'} dt''\, X^*(t'') Y(t'+t''-t) + \text{c.c.} \tag{9}$$

It should be emphasized that if one assumes a three-level system, consisting of a ground state and two $\sigma^\pm$ exciton states, the FWM signal in the cross-polarization configuration vanishes. On the other hand, it can be easily seen from Eq. (9) that in the 4LS system, for nonoverlapping pulses, there is an echo, centered around $t=2t_D$.

In the calculation of the FWM signal we must consider the decay and the dephasing of the biexciton. We describe the decay $b \to \sigma^+ + \sigma^-$ by a population relaxation rate Γ, while the dephasing of the nondiagonal matrix elements $\langle b|\hat{\rho}^{(3)}|\sigma^\pm\rangle$ is described by a phase relaxation rate γ. If we further assume that the relaxation rates for the excitonic states are much smaller than those associated with the biexcitonic state, we get that Γ does not enter $d^{(3)}$, while the dephasing rate γ appears in Eq. (9) through the substitution $\Delta \to \Delta - i\gamma$.

A numerical calculation of the FWM signal with single-sided exponential pulses and $1/\gamma = 8$ ps is presented in Fig. 3, where we plot P as a function of the delay between the two pulses. It can clearly be seen that oscillations with a frequency Δ appear as long as there is an overlap between the pulses. The overall decay of the FWM signal is governed by the biexciton dephasing rate γ. The inset of Fig. 3 shows the experimental data of Ref. 8. Again there is good qualitative agreement between our calculation and the experimental data.

The origin of the oscillations in the DA and FWM can be understood in terms of the time-dependent third-order susceptibility $\chi^{(3)}$, defined by the following general expression for the third-order dipole moment:

$$d_\sigma^{(3)}(t) = \sum_{\sigma_i} \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2 \int_{-\infty}^{t_2} dt_3\, \chi^{(3)}_{\sigma\sigma_1\sigma_2\sigma_3}(t,t_1,t_2,t_3)\, E_{\sigma_1}(t_1) E_{\sigma_2}(t_2) E_{\sigma_3}(t_3), \tag{10}$$

where the polarization σ can be α, β (when the beams are circularly polarized) or x, y (in the case of linear polarizations). The nonlinear response $\chi^{(3)}$ is a function of the time intervals $t_i - t$ (i=1,2,3), oscillating with the eigenfrequencies of the 4LS, namely ϵ and $\epsilon - \Delta$. An additional frequency in the system is obviously ω_0–the laser frequency. As a result, $d^{(3)}(t)$ oscillates in t with frequencies ϵ, $\epsilon-\Delta$, and ω_0, as well as with sums (and differences) of these. In the special case where $E(t)$ is a superposition of two laser pulses with delay t_D, $d^{(3)}$

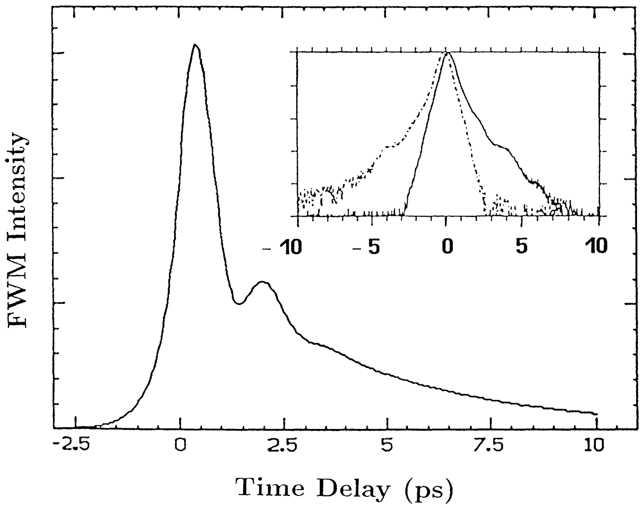

FIG. 3. The calculated four-wave mixing signal $|P|^2$ as a function of the time delay for single-sided exponential pulses with a width of 0.9 ps, and assuming $1/\gamma = 8$ ps. The inset shows the experimental results (on a logarithmic scale) of Ref. 8.

oscillates not only in real time but also in t_D. Since in time-resolved optical experiments one measures slow time variations of the signal (relative to the laser frequency), the only frequency which survives is Δ. The oscillations of $d^{(3)}(t)$ in two-pulse experiments like DA and FWM are thus a result of interference of the two pulses, mediated by the oscillating susceptibility $\chi^{(3)}(t)$.

For the estimation of the enhancement factor $G = |d_{\rm bx}|^2/|d_{\rm ex}|^2$ used in the calculation of the DA signal we refer to Ref. 13, according to which the ratio of the biexcitonic absorption (from an already existing exciton) to the excitonic absorption in two dimensions is $\alpha_{\rm bx}/\alpha_{\rm ex} \sim N_{\rm ex} a_{\rm bx}^2$, where $N_{\rm ex}$ is the sheet density of excitons and $a_{\rm bx}$ is the biexciton diameter. On the other hand, in our model we get an independent estimation $\alpha_{\rm bx}/\alpha_{\rm ex} \sim G n_e$, where n_e is the population of the excitonic levels $\sigma^{\pm}$, assuming $n_e \ll 1$ and a population of the ground state $n_g \approx 1$. In our model $N_{\rm ex} = n_e N_0$, where $N_0 \sim a_{\rm ex}^{-2}$ is the density of the 4LS. From these arguments it follows that $G \sim a_{\rm bx}^2/a_{\rm ex}^2 \sim E_{\rm ex}/\Delta$, where $E_{\rm ex}$ is the binding energy of the exciton. Taking $\Delta \sim 2$ meV and $E_{\rm ex} \sim 10$ meV for the binding energies,[2] we get an estimate of $G \sim 5$ for the enhancement factor, as used in the calculation of the DA signal.

In conclusion, we have shown that this simple 4LS model of the exciton-biexciton system explains the temporal oscillations and the coupling between σ^+ and σ^- excitons observed in nonlinear optical experiments in GaAs QW samples. Our work emphasizes the importance of biexcitons in nonlinear optical experiments in GaAs QW's, beyond their role in the optical Stark effect.[14] Since the essence of this work was to examine the effect of the biexcitonic interaction, we did not include in this simple model exciton-exciton interaction effects which are related to unbound excitons, and in particular the local-field effect.[15,16]

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