Demonstration of Sixth-Order Coulomb Correlations in a Semiconductor Single Quantum Well

S. R. Bolton,* U. Neukirch,† L. J. Sham,‡ and D. S. Chemla

Department of Physics, University of California and Materials Sciences Division, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, MS 2-346, Berkeley, California 94720

V. M. Axt

Institut für Theoretische Physik, Westfälische Wilhelms Universität Münster, Wilhelm-Klemm-Strasse 10, D-48149, Münster, Germany

(Received 9 March 2000)

Six-wave mixing in a ZnSe quantum well is investigated and compared with microscopic theory. We demonstrate that sixth-order Coulomb correlations have a significant qualitative impact on the nonlinear optical response. Six-wave mixing is shown to be a uniquely sensitive tool for investigation of correlations beyond the four-point level.

PACS numbers: 78.66.Hf, 42.65.–k, 71.35.Gg

One of the most striking differences between classical and quantum systems is that the latter are capable of being in a correlated state, i.e., in a superposition of states with well-defined relative phases. The entanglement in such a coherent state gives rise to properties that are required for applications such as quantum computation. In condensed matter, the Coulomb force induces both correlation and decoherence. The resulting dephasing processes turn coherent excitations into incoherent occupations and lead to qualitative changes in the behavior of initially coherent systems.

Optically excited semiconductor heterostructures are an ideal laboratory for investigating such correlated many-body quantum kinetics [1–13]. Almost perfect samples and quantum structures are available. This, combined with the recent experimental advances in ultrafast laser techniques and the development of novel many-particle theories [14–20], allows for very explicit comparison between experiments and theory. Although the semiconductor in its ground state is a true many-body system with correlation, the single particle excitations near the band gap provide a well-defined and completely uncorrelated starting point for the dynamics [21]. Once the system is excited strong correlations build up due to the Coulomb interaction between photocarriers. Because these correlations are induced by the laser field they are to some extent controllable, in contrast with the strong ground state correlations present in other systems. In the limit of medium-to-high particle densities the random-phase approximation, in which many-particle correlations are accounted for at a mean-field level and reduced to products of two-particle correlations by factorization, provides an adequate description of laser excited semiconductors. This approach results in the well-known semiconductor Bloch equation (SBE) formalism and works well for many experimental conditions [22]. However, as the density of interacting particles decreases the system becomes increasingly "strongly correlated" [1]. Then interactions between particles cannot be treated as local scattering events; they are essentially *nonlocal in space and time* and produce new quantum mechanical memory phenomena in the dynamics [2–7]. SBE-type approaches fail to describe experiments where two-exciton correlations play a prominent role and thus four-point correlations must be included in a microscopic theory. A growing body of recent experiments has demonstrated the importance of these correlations for the nonlinear optical response of semiconductor structures [5,6,8,23]. The theoretical description of such correlations has been approached with several different techniques and is at the center of much current interest. The dynamics controlled truncation (DCT) approach developed in [14,15], where the field of the exciting laser is used as the controllable truncation criterion, has been very successfully applied to interpret data obtained from four-wave mixing (FWM) and pump/probe experiments [5–8,11–13]. These experiments, however, are quite insensitive to high order correlations represented by six-point density matrices. Six-wave-mixing (SWM) experiments [24], in contrast, provide a sensitive monitor of such correlations beyond the four-point level.

In this Letter we demonstrate that high order Coulomb correlations have a significant qualitative impact on the optical response of semiconductor quantum wells (QW). In particular, we discuss the influence of the correlated part of the six-point density matrix describing transitions from incoherent excitons to correlated two-pair states. To probe the role of six-point correlations we have performed SWM experiments on a sample with very pure and well-characterized optical response. We perform a quantitative comparison between experiment and a microscopic DCT theory at three levels of approximation: (a) a fully coherent description accounting only for the dynamics of coherent single-pair and two-pair transition amplitudes; (b) a treatment that in addition accounts for incoherent densities; (c) a treatment where correlated six-point density matrices, representing transitions from incoherent excitons to bound or unbound two-pair states, are also taken into account. Our results show that the six-point correlation is crucial to correctly describe the optical response of this system.

 0031-9007/00/85(9)/2002(4)$15.00

Spectrally resolved, degenerate SWM experiments were performed on a 5 nm ZnSe/ZnMgSSe single QW. This ZnSe-QW combines large exciton, X, and biexciton, X_2, binding energies, $E_X^b = 25$ meV and $E_{X_2}^b = 6.6$ meV with narrow X linewidth and provides an optimal system for quantitative comparisons of theory and experiment. It allows for exclusive excitation of heavy-hole (hh) X and X_2 and yields a well-resolved spectral response. The sample was held at $T = 10$ K, where the hh-X peak is centered at $\omega_X = 2.825$ eV. 70 fs transform-limited pulses from a frequency-doubled Ti:sapphire laser were used for excitation and were tuned to excite exclusively the $1S$ hh-X. The excitation areal density was $N \approx 4 \times 10^{10}$ cm^{-2}. Two laser pulses with wave vectors $\vec{k}_1$ and $\vec{k}_2$ separated by the time delay, Δt, excite the sample, and the SWM signal is measured in the momentum-conserving direction $\vec{k}_s = 3\vec{k}_2 - 2\vec{k}_1$. ($\Delta t > 0$ if pulse 1 precedes pulse 2.) The polarizations $\sigma_{1,2}$ of the exciting pulses were varied among all significant combinations of circular and linear, and the SWM emission was projected onto each of the $\sigma_s = X, Y$, σ^+, and σ^- polarizations. The spectrum of each σ_s was recorded as a function of Δt. To label the various polarization configurations we use the notation $\{\sigma_1, \sigma_2, \sigma_s\}$. For all excitation configurations the measured polarization of the SWM emission is consistent with selection rules based on momentum conservation. In this Letter we discuss a limited set of our data, which demonstrates most clearly the role of six-point correlations. Novel results from other polarization configurations will be presented in a longer paper elsewhere [25].

Figure 1 presents SWM emission measured in the $\{X, Y, Y\}$ configuration. The X emission decays smoothly without temporal or spectral beats. At $\approx$2.818 eV $= \omega_{X_2} - \omega_X = \Delta\omega_{X_2-X}$, a second feature is seen. It corresponds to a X_2-X transition and shows no beats.

The starting point for our model is the hierarchy of density matrices truncated according to DCT [14,15]. We

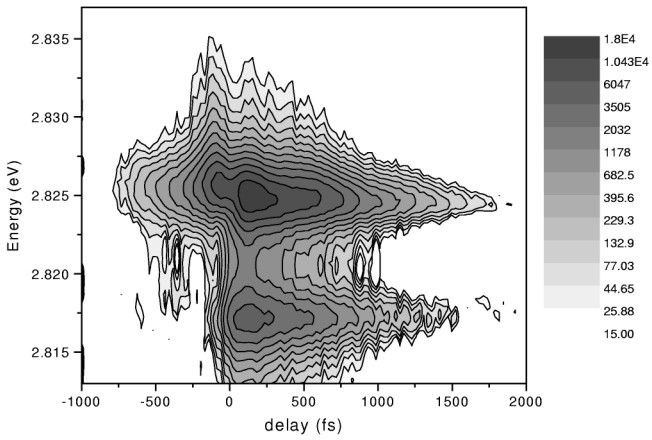

FIG. 1. Six-wave mixing emission measured in the $\{X, Y, Y\}$ configuration, shown over 3 orders of magnitude in emission intensity.

follow the dynamics of four density matrices: Y, B, N, and Z. In the electron hole representation these are given by $Y = \langle h_1 e_2 \rangle$, $B = \langle h_1 e_2 h_3 e_4 \rangle$, $N = \langle e_1^\dagger h_2^\dagger h_3 e_4 \rangle$, $Z = \langle e_1^\dagger h_2^\dagger h_3 e_4 h_5 e_6 \rangle$. To clarify the role of correlations, we focus on the correlated parts of the four- and six-particle operators, given in the notation of [11,15] by $\bar{B}$, $\bar{N}$, and $\bar{Z}$. Y and $\bar{B}$ represent, respectively, single-pair transition densities and the correlated part of two-pair transition densities, i.e., two-photon coherence. These are phase-sensitive, rapidly oscillating quantities around ω_X and ω_{X_2}, respectively. We note that Y is directly connected to the polarization of the sample and that $\bar{B}$ contains contributions from both the bound biexcitonic states, X_2, and the unbound two-exciton continuum, X-X. Accounting only for the contributions of Y and $\bar{B}$ corresponds to a system evolving fully coherently. We call this case the coherent limit (CL). $\bar{N}$ contains the incoherent densities. It can be interpreted in different ways including (i) coherences between different pair states involved in intersubband and intraband transitions and (ii) fluctuations of the one-pair amplitude Y, $\bar{N} = \langle (\hat{Y} - \langle \hat{Y} \rangle)^\dagger (\hat{Y} - \langle \hat{Y} \rangle) \rangle$. In the following we refer to a level of theory that in addition to the CL parts accounts for the $\bar{N}$ contributions as the incoherent density (ID) level. Finally $\bar{Z}$ describes transitions from incoherent exciton densities to two-pair states. We call the theory that accounts for the contributions of $\bar{Z}$ as well as ID the incoherent density assisted transition (IDAT) level. Note that of the density matrices included in our calculation *only* $\bar{Z}$ includes six-particle correlations; thus only the IDAT theory goes beyond four-particle approximations. The SWM signal can also be influenced at the fifth order in the laser field, $\mathcal{O}(E^5)$, by other high order correlation functions such as the correlated part of three-pair transition amplitudes or the incoherent two-pair occupation densities. However, we show below that a description based on Y, $\bar{B}$, $\bar{N}$, and $\bar{Z}$ gives very good overall agreement with our experiments. We take this as an indication that we have identified the dominant contributions to the SWM emission for our excitation conditions.

The SWM signal is derived from the equation of motion for the single-pair amplitude Y with a nonlinear source term which can be decomposed as follows:

$$\mathcal{Q}_{\text{nonlinear}} = \mathcal{Q}_{\text{CL}} + \mathcal{Q}_{\text{ID}} + \mathcal{Q}_{\text{IDAT}}. \qquad (1)$$

In the CL the source can be written as a sum of a coherent mean-field contribution (CMF) and a correlated part representing two-pair transitions (TPT) $\mathcal{Q}_{\text{CL}} = \mathcal{Q}_{\text{CMF}} + \mathcal{Q}_{\text{TPT}}$. The CMF part comprises the contributions known from the SBE which can be classified as Pauli blocking and coherent mean-field Coulomb nonlinearities. Following [5,7,26] we have accounted for TPT by using a memory kernel representation. The ID contributions are proportional to either $\bar{N}Y$ or $\bar{N}E$ and may therefore influence the single pair transitions Y [5]. Thus the ID terms couple Y and $\bar{B}$ to incoherent densities. Finally, the IDAT nonlinear source is driven by $\bar{Z}$ [11,15]. To the best of our knowledge

the $\bar{Z}$ contribution has previously been taken into account only in 1D models [11,12]. In order to deal with the 2D QW case, we have derived a memory kernel representation for $\mathcal{Q}_{\mathrm{IDAT}}$ starting from the equation of motion for $\bar{Z}$ with source terms $\propto Y\bar{N}$ (details will be presented in [25]). The oscillation frequency of $\bar{Z}$ is $\Delta\omega_{X_2-X}$, the difference between two-pair and one-pair transition energies. Note that in the absence of incoherent densities $\propto \bar{N}$ these transitions are absent.

In order to identify the contribution of the four dynamical variables to the SWM response, we compare our experimental results to calculations of the SWM signal with nonlinear source terms: (a) $\mathcal{Q}_{\mathrm{CL}}$ only; (b) $\mathcal{Q}_{\mathrm{CL}} + \mathcal{Q}_{\mathrm{ID}}$; (c) all contributions in Eq. (1). The calculations include all states on the $1S$ exciton parabola, and following the results of [27] we have set the low density exciton and biexciton dephasing times equal. As some dephasing processes originate in Coulomb interactions among particles, our theory automatically includes density induced dephasing. In all cases the coupled equations of motion are solved numerically to infinite order, and thus the results include contributions of all orders in the exciting laser field.

We note that FWM experiments performed on this and similar samples have been analyzed using CL and ID level DCT theories [5,6,28]. It was found that under many conditions the CL theory is sufficient to give qualitative agreement with the data. In particular, the ratio between FWM signals at the exciton and the biexciton is well reproduced for all polarizations [28]. CL theory fails to describe correctly the transient polarization state of FWM emission, but calculations at the ID level give an almost perfect agreement with these data. Even at densities for which $\mathcal{O}(E^5)$ contributions become important the ID-level theory continues to be in excellent agreement with the FWM experiment. We have verified that this agreement is not modified when the FWM calculation is performed on the IDAT level. These investigations thus confirm that FWM measurements are insensitive to six-point correlations.

Figure 2 shows the theoretical results for calculations of SWM in the $\{X, Y, Y\}$ configuration. First, note that the mere presence of a SWM signal does not constitute evidence of six-particle correlations. As shown in Figs. 2a and 2b, a significant SWM signal is predicted by theories including only four-particle correlations. However, Figs. 2a and 2b also show that the spectral and temporal shape of the SWM signal is not correctly predicted by theories including only four-particle correlations—both the CL and ID theories show major disagreements with experiment. Although it correctly predicts the polarization of the SWM emission, the CL theory essentially misses the X_2-X contributions, underestimating the strength of that emission by at least 2 orders of magnitude, which is surprising in view of the FWM results [28]. Furthermore, and in contrast to the FWM case, the addition of the ID level terms actually degrades the agreement with experiment. The X_2-X emission continues to be greatly underestimated. Furthermore, the ID theory predicts strong beating in both the X emission and the X_2-X emission contrary to experiment which essentially shows a smooth decay. Thus, the ID-level theory, although able to give excellent agreement with FWM experiments, fails to reproduce the spectral and temporal profile of the SWM emission. Adding the six-point correlation, $\bar{Z}$, strongly alters these results as shown in Fig. 2c. The $\bar{Z}$ contribution increases the relative strength of the X_2-X emission by more than an order of magnitude and brings it into excellent agreement with experiment. Furthermore, the temporal beats introduced by the $\bar{N}$ contributions in the ID calculation are strongly suppressed. Thus, the six-point correlation $\bar{Z}$ is absolutely necessary to describe accurately the SWM experiments, and the DCT theory including this term captures very well the major contributions to the emission.

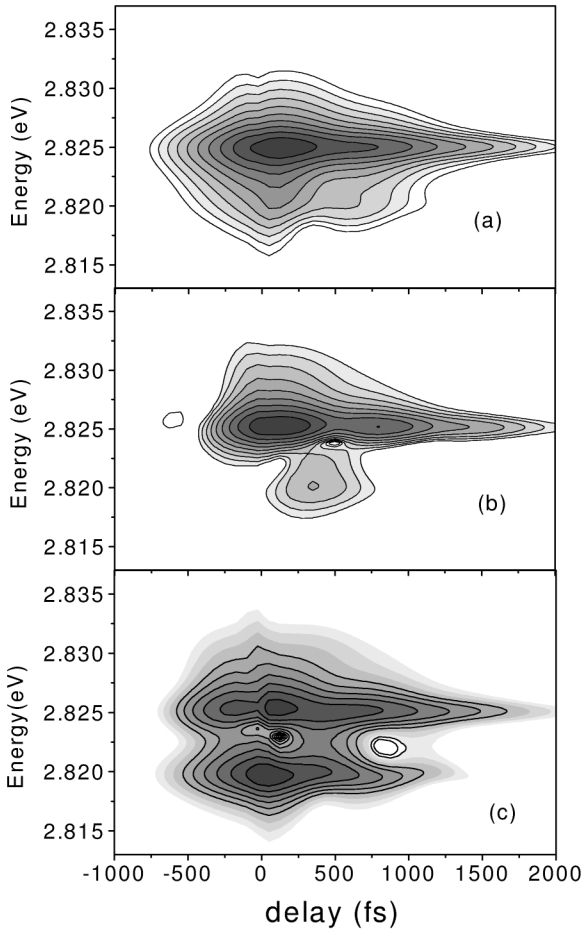

FIG. 2. Theoretical calculations of SWM emission in the $\{X, Y, Y\}$ configuration, shown over 3 orders of magnitude in emission intensity: (a) calculation in the coherent limit CL including Y and $\bar{B}$; (b) calculation including contributions of Y, $\bar{B}$, and $\bar{N}$, i.e., the ID level; (c) calculation on the IDAT level including the four- and six-point contributions Y, $\bar{B}$, $\bar{N}$, and $\bar{Z}$.

Although the theory described here gives good general agreement with the experimental results, a number of details of the SWM spectra remain to be understood. For

example, the small (1 meV) redshift of the exciton with increasing time delay and the very rapid temporal rise of the biexciton emission are not explained even within the IDAT framework. As mentioned in the introduction, there are a number of potential contributions to SWM signals which have yet to be explored. These include correlated three-pair transitions and incoherent two-pair occupations. At present it is not possible to discriminate between these possible explanations for the experimental features. However, work on including such terms in the theory is currently in progress.

Although there have been previous observations of biexcitonic scattering in other materials [29], these have all been in the incoherent, long time (20 ps) relaxation regime, and interpreted phenomenologically. Here, we have demonstrated that careful measurement of SWM emission combined with microscopic theory yields unambiguous signatures of six-point correlations not accessible in any previous measurements.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Division of Material Sciences of the U.S. Department of Energy, under Contract No. DE-AC03-76SF00098 and by the Deutsche Forschungsgemeinschaft through the program *Quantenkohärenz in Halbleitern*. U. N. was supported by the Max-Kade foundation. The authors thank J. Nürnberger and W. Faschinger (Universitat Würzburg) for providing the ZnSe heterostructure, as well as T. Kuhn for many inspiring discussions.

*Permanent address: Physics Department, Williams College, Williamstown, MA 01267.

†Permanent address: Institut für Festkörperphysik, Universität Bremen, P.O. Box 330 440, D-28334, Bremen, Germany.

‡Permanent address: Department of Physics, University of California at San Diego, La Jolla, CA 92093-0319.

[1] P. Kner, W. Schäfer, R. Lövenich, and D. S. Chemla, Phys. Rev. Lett. **81**, 5386 (1998).

[2] S. Bar-Ad, P. Kner, M. V. Marquezini, D. S. Chemla, and K. El Sayed, Phys. Rev. Lett. **77**, 3177 (1996).

[3] Q. T. Vu, L. Banyai, P. I. Tamborenea, and H. Haug, Europhys. Lett. **40**, 323 (1997).

[4] L. Banyai, Q. T. Vu, B. Mieck, and H. Haug, Phys. Rev. Lett. **81**, 882 (1998).

[5] G. Bartels, A. Stahl, V. M. Axt, B. Haase, U. Neukirch, and J. Gutowski, Phys. Rev. Lett. **81**, 5880 (1998).

[6] B. Haase, U. Neukirch, J. Gutowski, G. Bartels, A. Stahl, V. M. Axt, J. Nürnberger, and W. Faschinger, Phys. Rev. B **59**, R7805 (1999).

[7] T. Östreich and L. J. Sham, Phys. Rev. Lett. **83**, 3510 (1999).

[8] P. Kner, S. Bar-Ad, M. V. Marquezini, D. S. Chemla, and W. Schäfer, Phys. Rev. Lett. **78**, 1319 (1997).

[9] U. Hohenester, F. Rossi, and E. Molinari, Solid State Commun. **111**, 187 (1999).

[10] U. Hohenester, F. Rossi, and E. Molinari, Physica (Amsterdam) **272B**, 1 (1999).

[11] V. M. Axt, K. Victor, and A. Stahl, Phys. Rev. B **53**, 7244 (1996).

[12] T. Meier and S. W. Koch, Phys. Rev. B **59**, 13 202 (1999).

[13] C. Sieh *et al.,* Phys. Rev. Lett. **82**, 3112 (1999).

[14] V. M. Axt and A. Stahl, Z. Phys. B **93**, 195 (1994).

[15] V. M. Axt and S. Mukamel, Rev. Mod. Phys. **70**, 145 (1998).

[16] A. L. Ivanov, H. Haug, and L. V. Keldysh, Phys. Rep. **296**, 237 (1998).

[17] M. Bonitz, J. W. Dufty, and C. S. Kim, Phys. Status Solidi B **206**, 181 (1998).

[18] U. Hohenester and W. Pötz, Phys. Rev. B **56**, 13 177 (1997).

[19] M. F. Pereira and K. Henneberger, Phys. Rev. B **58**, 2064 (1998).

[20] T. Kuhn, in *Theory of Transport Properties of Semiconductor Nanostructures,* edited by E. Schöll (Chapman and Hall, London, 1998), p. 173.

[21] L. J. Sham and T. M. Rice, Phys. Rev. **144**, 708 (1966).

[22] H. Haug and S. W. Koch, *Quantum Theory of Optical and Electronic Properties of Semiconductors* (World Scientific, Singapore, 1993), 2nd ed.

[23] U. Neukirch *et al.,* Phys. Rev. Lett. **84**, 2215 (2000).

[24] D. S. Chemla and A. Maruani, Prog. Quantum Electron. **8**, 1 (1982), and references therein.

[25] V. M. Axt, S. R. Bolton, U. Neukirch, L. J. Sham, and D. S. Chemla (to be published).

[26] V. M. Axt, K. Victor, and T. Kuhn, Phys. Status Solidi (b) **206**, 189 (1998).

[27] W. Langbein and J. M. Hvam, Phys. Rev. B **61**, 1692 (2000).

[28] B. Haase, U. Neukirch, J. Gutowski, G. Bartels, A. Stahl, J. Nürnberger, and W. Faschinger, Phys. Status Solidi B **206**, 363 (1998).

[29] Y. Masumoto and S. Shionoya, Solid State Commun. **41**, 147 (1982).