Probing many-body interactions in a disordered semiconductor quantum well with electronic two-dimensional Fourier transform spectroscopy

Zheng Sun, Thomas W. Jarvis, Xiaoqin Li, Mikhail Erementchouk, Michael N. Leuenberger

Physics Department, University of Texas-Austin, Austin, TX, U.S.A. 78712;
Texas Materials Institute, the University of Texas at Austin, Austin, TX 78712, USA
NanoScience Technology Center and Department of Physics, University of Central Florida, Orlando, Florida 32826, USA

ABSTRACT

The interplay between disorder and Coulomb interactions ubiquitously affects the properties of condensed matter systems. We examine its role in the nonlinear optical response of semiconductor quantum wells. In particular, we investigate the coherent coupling strength between exciton resonances that are spectrally split by interface fluctuations. Previous studies yielded conflicting results. In light of rising interest in semiconductor devices that rely on spatial and/or temporal coherence, we revisit this problem by applying a newly developed spectroscopy method: electronic two-dimensional Fourier transform spectroscopy (2DFTS). 2DFTS is a powerful technique for revealing the presence of coupling and for distinguishing the (coherent or incoherent) nature of such coupling, especially in complex systems with several spectrally overlapping resonances. Even the most basic information about such complex systems, including the homogeneous and inhomogeneous linewidths of various resonances, cannot be extracted reliably using conventional spectroscopic tools. In these new 2DFTS measurements, we did not observe any clear cross peaks corresponding to coherent couplings between either heavy-hole or light-hole excitons. These measurements allow us to place a quantitative upper bound on the possible coupling strength in this prototypical system. A modified mean-field theory reveals a simple yet important relation that determines how the coherent coupling strength depends on the disorder correlation length and Coulomb interaction length.

Keywords: disorder, Coulomb interaction, semiconductor quantum wells, spectroscopy

1. INTRODUCTION

The band theory of condensed matter systems emphasizes the periodicity of crystal potentials. Disorder, however, inevitably exists in real materials to various degrees. In the presence of disorder, the fundamental nature of electron wave functions changes from spatially extended Bloch waves to localized wave functions. Coulomb interactions among electrons critically depend on the characteristics of the electron wave functions. The interplay between disorder and Coulomb correlations, therefore, affects the transport and optical properties of various materials, leading to well-known phenomena, such as metal-to-insulator transitions and the fractional quantum Hall effect.

An ideal model system for investigating the interplay of Coulomb correlation and disorder is an optically excited semiconductor. In direct-gap semiconductors, excitons (bound electron-hole pairs) dominate the optical properties near the fundamental band gap[1, 2]. Excitons are charge-neutral quasi-particles. The residual Coulomb forces not accounted for in the formation of excitons lead to weak interactions among the excitons. Coulomb correlation among excitons is most evident in the nonlinear optical response, leading to a host of phenomena, including four-wave-mixing (FWM) at
the “wrong” time delays[3], excitation-induced dephasing[4], excitation-induced shift[5], biexciton formation[6], and local field effects[3]. Coulomb correlation as well as exciton-phonon interactions affect the homogeneous linewidth of exciton resonances. Disorder, on the other hand, leads to inhomogeneous broadening. An important type of disorder present in semiconductor quantum wells is interface fluctuation, as illustrated in Fig 1. Even in samples of the highest quality, monolayer fluctuations in the well width lead to islands of local potential minima. Excitons localized in different regions of the sample are subject to different confinement potentials. As a result, these exciton resonances are inhomogeneously broadened. While it is clear that static disorder broadens the inhomogeneous linewidth, whether or not disorder influences the homogeneous linewidth (i.e., dephasing time) is a more subtle matter that is not yet understood[7, 8].

![Fig. 1: Monolayer fluctuations in quantum well thickness are inevitable. Excitons localized in narrower regions of the quantum wells are referred to as island excitons (A) and excitons localized in wider regions of the quantum wells are referred to as plateau excitons.](image)

Although it has been well established that both many-body correlations and disorder manifest themselves in the nonlinear coherent response of semiconductors, quantifying their effects has been difficult with conventional transient nonlinear spectroscopy, especially in complex systems that exhibit several spectrally overlapped resonances. Even the most basic information about such complex systems, including homogeneous and inhomogeneous linewidths of various resonances, cannot be extracted reliably using such conventional methods[9].

## 2. COUPLING BETWEEN EXCITONS RESONANCES IN DISORDERED QUANTUM WELLS

Interface fluctuations in quantum wells are known to have a significant effect on a sample’s linear optical spectrum. Two parameters, confinement length ($\xi_0$) and disorder correlation length ($r_c$), play critical roles in determining the qualitative features of the linear spectrum[10, 11]. The confinement length is defined as:

$$\xi_0 = \frac{\pi h}{\sqrt{2M_\sigma V_\sigma}}$$

Where the $M_\sigma$ is the exciton mass and the $V_\sigma$ is the potential energy step in regions of the quantum well with a difference in width of one atomic layer. Physically, the confinement length describes a critical island size above which an exciton localized inside that island will have a kinetic energy less than its potential energy. The confinement length $\xi_0$ increases with the quantum well thickness. Disorder correlation length can be understood as the typical size of an island for the disordered quantum wells. As the typical island size becomes larger, the disorder correlation length $r_c$ correspondingly increases.
Under the condition that $\xi < r_c$, the linear spectrum of an exciton resonance evolves from a single inhomogeneously broadened feature into a doublet with narrower individual linewidths. Similar situations arise in molecular aggregates. The emergence of sharp resonances in the optical spectrum of a molecular aggregate is often referred to as “motion narrowing”, where the sharp features emerge as delocalized electronic states average over disordered local potential energies.

The lower energy exciton resonances correspond to excitons mostly localized in the wider regions of the quantum well. We will refer them as the “island excitons” (or type A excitons as shown in Fig. 1). The higher energy exciton resonances correspond to excitons that reside mostly in the narrower regions of the quantum well. We will refer to these as the “plateau excitons” (or type B excitons as shown in Fig. 1). Previous studies have shown that the island exciton regions are bright luminescence centers. These islands can also be modeled as quantum dots in the weak confinement regime. These “natural quantum dots” have been studied extensively, particularly on the single dot level. Studies focused on the plateau excitons, however, are rare.

One outstanding question highlights the interplay between disorder and Coulomb interactions: are these two types of excitons coupled via Coulomb interactions? Previous experiments based on conventional spectroscopy methods yielded conflicting results. Whether or not these excitons are coupled will impact the statistics of photons emitted from the quantum well. Such coupling may also induce mediated coupling among localized island excitons.

Some prior work suggests that coherent coupling exists[12]. In a time-resolved FWM experiment, an oscillatory signal with a period corresponding to the energy splitting between different types of excitons was observed, as shown in Fig. 2. Time-resolved FWM experiments permit one to distinguish between quantum beating and classical polarization interference; the oscillatory signal in this experiment was therefore considered to be a signature of coherent coupling. Another FWM experiment conducted in the spectrally resolved geometry upholds the view that coherent coupling exists between different types of excitons, although the authors did not discuss this aspect of their experiments explicitly[13].

Others believe that there is no coherent coupling, but that there may be incoherent transfer among localization sites[14]. In another transient FWM experiment, a two-color technique was employed to investigate this problem. A broadband, 100 fs pulse simultaneously illuminated several exciton
resonances, while a narrow-band, picosecond pulse was tuned across the individual spectral features. The nonlinear polarization field in the self-diffracted FWM direction was spectrally resolved. A 2D spectrum was obtained as a function of the emission energy and the excitation energy of the tunable laser. No coherent coupling between island and plateau excitons was observed, as shown in Fig.3.

![Fig. 3: Another previous experiment reached opposite conclusion. The experiment is based on a two-color FWM technique. One narrow-band pulse was tuned in energy and yielded the excitation energy axis. Another pulse was broad band and probed all resonances simultaneously. The FWM signal was spectrally resolved and yielded the detection energy. No cross peak was observed, indicating that no coupling was observed in this experiment. Data reproduced from Ref [14].](image)

In light of rising interest in semiconductor devices that rely on spatial and/or temporal coherence[15, 16], we revisit the problem of coupling among exciton resonances spectrally resolved by interface fluctuations via a newly developed spectroscopy method: electronic two-dimensional Fourier transform spectroscopy (2DFTS). 2DFTS is a powerful technique for revealing the presence of coupling and for distinguishing the (coherent or incoherent) nature of such coupling, especially in complex systems with several spectrally overlapping resonances[17].

![Fig. 4: A congested 1D NMR spectrum is unraveled by spreading into 2D. The presence of “cross peaks” (peaks not on the red line) identifies coupling between corresponding resonances. Figure adapted from Ref [19].](image)
3. EXPERIMENTAL METHOD

We employ a new technique to probe electronic couplings and correlations, two-dimensional Fourier transform spectroscopy. Conceptually similar to multi-dimensional NMR spectroscopy, this technique offers several distinct advantages when compared to the 1D method [18-21]. First, congested 1D spectra are often impossible to interpret due to severe overlap between resonances. By expanding the spectra into a two-dimensional space, overlapped spectra are unraveled much like a window blind is opened, as illustrated in Fig. 4. Second, the phenomenon of coherence transfer can be used to identify couplings and energy/charge transfer without ambiguity by measuring the cross peaks in a 2D spectrum. Finally, excited states relax and dephase via many possible quantum mechanical pathways, all of which contribute to the observed signal in conventional spectroscopic measurements. Using 2DFTS, one can separate different quantum mechanical pathways and gain detailed information about relaxation and dephasing dynamics by detecting the amplitude and phase (not just the intensity) of the signal field.

![Image](image_url)

**Fig. 5:** The pulse sequence and time evolution of the polarization field in a FWM experiment, which is also the basis of 2DFTS.

2D Fourier transform spectroscopy is an enhanced four wave mixing (FWM) technique. In a typical three-pulse FWM experiment illustrated in Fig. 5, the first pulse excites a coherent polarization field that oscillates at the absorption frequency $\omega_\tau$. After a delay $\tau$, a second pulse enhances or suppresses that oscillation, depending on the phase between the second pulse and the oscillation induced by the first pulse. This second pulse transfers energy into the system by populating excited states. After a waiting period, $T$, the system is then perturbed by a third pulse and starts to oscillate at the emission frequency, $\omega_t$. In conventional experiments, the FWM signal satisfying phase-matching conditions is emitted along a background-free direction, $k_s = -k_a + k_b + k_c$, as illustrated in Fig. 6. The intensity of this weak nonlinear signal ($10^{-8}$ of the transmitted laser pulses) is then measured by a photo detector.

In 2D Fourier transform spectroscopy, that FWM signal field is instead completely characterized in amplitude and phase by heterodyne detection. Characterization of the signal field includes the measurement of the overall phase, not just the spectral phase, via comparison with a fixed-phase reference pulse using spectral interferometry [22], as illustrated in Fig. 6. By coherently tracking the overall phase of the FWM signal as a function of the phase delay between excitation pulses, 2D Fourier transform spectroscopy records and correlates the evolution of polarization coherence during two time periods, an initial evolution period, $\tau$, and a final signal detection period, $t$, separated by the waiting (or mixing) period, $T$, as shown in Fig. 5. A 2D Fourier transform with respect to $\tau$ and $t$ yields a spectrum that is a function of the absorption frequency $\omega_\tau$ and the emission frequency $\omega_t$. 

Proc. of SPIE Vol. 7600  76000U-5
The appearance of cross-peaks ($\omega_{t} \neq \omega_{t}$) in 2D spectra indicates oscillation frequency changes during or between the two time periods, proving that the participating resonances must be coupled. The imaginary part of the spectrum measures the transient change in the refractive index, while the real part approximates the resonant absorption of a probe field at frequency $\omega_{t}$, induced by the excitation frequency $\omega_{t}$.

Fig. 6: Experimental set-up for the 2D spectroscopy. The three incident pulses are arranged in a “box” geometry. The four mixing signal copropagating with the reference pulse is characterized via spectral interferometry, where both the electrical field amplitude and phase of the nonlinear signal are determined.

To better understand 2D spectroscopy, it is helpful to first consider the time domain picture of the measured FWM signal, as illustrated in Fig. 7. The nonlinear signal has an optical phase that varies as $\exp[-i(\omega_{t}\tau - \omega_{t}t)]$. If the delay between the first two pulses, $\tau$, is fixed at a certain value, the signal in the detection period oscillates at a frequency of $\omega_{t}$. If we detect such oscillations at a series of different $\tau$ positions, we obtain a set of data as a function of $t$ and $\tau$. We emphasize that the oscillation frequency $\omega_{t}$ is not necessarily the same as the oscillation frequency $\omega_{t}$. After taking the Fourier transform with respect to $\tau$ and $t$, one obtains a 2D spectrum in frequency space and establishes a correlation between the frequencies of absorption and emission events.

$$S(\tau, t) \sim \exp[-i(\omega_{t}\tau - \omega_{t}t)]$$

Fig. 7: Two dimensional FWM data in the time domain. The FWM signal is a function of both the evolution time $\tau$ and detection time $t$. The phase of the signal depends on both time delays.
A variety of different electronic coupling and energy transfer processes can be identified using 2D Fourier transform spectroscopy. If the system under study consists of two independent 2-level systems, one only observes two diagonal peaks, as shown in Fig. 8 (a). If an energy relaxation process is allowed from the higher energy state to the lower energy state, a cross peak is observable as shown in Fig. 8 (b). Since it takes time for such an energy relaxation process to happen, the cross peak is only observable after a finite waiting time, i.e., for $T \neq 0$. If the two 2-level systems are coupled via a shared ground state, two cross peaks are observed that are symmetric about the diagonal direction, as shown in Fig. 8 (c). Since electronic coupling is coherent in nature, those cross peaks are present even at $T = 0$. Therefore, 2D Fourier transform spectroscopy can not only identify the presence of electronic coupling, but also reveal the nature of that coupling.

![Simulated 2D amplitude spectra for two 2-level systems that are (a) independent, (b) coupled via population relaxation processes, and (c) coupled via sharing common states or “Raman” coherence.](image)

In 2DFTS experiments, broadband, ultrafast pulses are used to excite all resonances of interest simultaneously. Significantly, the spectral resolution of 2DFTS is not determined by the bandwidth of the excitation pulses; rather, the spectral resolution of Fourier transform spectroscopy is mathematically limited only by the maximum time delay introduced between the excitation pulses. Physically, the spectral resolution within the pulse bandwidth is retained by keeping track of the phase evolution of individual oscillators. The trade-off between temporal and spectral resolutions is removed in the time interval that no Fourier Transform is performed (e.g. the waiting period $T$). Therefore, 2DFTS is often referred to as a “universal spectrometer”[20, 23].

Previous transient nonlinear spectroscopy experiments have explored the information embedded in the phase of nonlinear polarization fields [24-26]. These experiments, however, did not take the full advantages offered by multidimensional spectroscopy methods.

### 4. RESULTS AND DISCUSSION

We have investigated a multiple quantum well sample with eight periods of 13 nm $GaAs$ quantum wells separated by 15 nm $Al_{0.3}Ga_{0.7}As$ barriers. The sample was held at $\sim 8K$ and the excitation density was $\sim 10^{10}$ excitons/well/cm² for all measurements. Details of the experimental set-up can be found elsewhere[27]. A conventional FWM spectrum taken at $\tau=0$ and $T=200$ fs showed four
resonances. Strain may further shift the spectral positions of resonances, so we may only tentatively assign the four resonances as the hh in the wide region (A), the hh in the narrow region (B), the lh in the wide region (C), and the lh in the narrow region (D) respectively in the order of increasing energy.

In our initial 2D measurements (data not shown), we have observed coupling between two pairs of resonances, i.e., between A/C and B/D. These cross peaks are expected, since they arise from coupling between resonances that share common conduction band states under the collinear excitation condition[28]. The presence of these cross peaks also confirmed our assignment of the exciton resonances. We have also observed the signature of biexciton formation. Quantum coherence related to biexciton states has been investigated recently using the 2DFTS[29, 30]. Our measurement is consistent with these previous studies.

We did not observe any strong cross peaks that would correspond to coupling between island and plateau excitons. These measurements, however, allow us to place a quantitative upper bound on the possible coupling strength between exciton resonances. This observation is explained by our theoretical model[31]: strong coherent coupling may only be observed when the Coulomb correlation length is greater than the disorder correlation length, which itself must be greater than the exciton confinement length. We believe that the theoretical and experimental approach and findings reported here are relevant to a broad range of problems, such as configuration changes in biological molecules, energy transfer in natural/artificial photosynthetic systems, and charge transfer in semiconducting polymers.

The authors gratefully acknowledge M. Philips, Hailin Wang, and Steve Cundiff for enlightening discussions. This work is supported financially by the following agencies: ARO W911NF-07-100223, ARO W911NF-08-1-0348, NSF DMR-0747822, Welch Foundation F-1662, Texas-ARP 003658-0160-2007, ONR N00014-08-1-0745, and the Alfred P. Sloan Foundation. The work at the University of Central Florida is supported by NSF ECCS-0725514, DARPA/MTO HR0011-08-1-0059, and NSF ECCS-0901784.

*elaineli@physics.utexas.edu; phone 1 512-471-2063; fax 1 512-471-1005; http://www.ph.utexas.edu/~lilab/
REFERENCES


