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Nonperturbative Coulomb correlations generated by simultaneous excitation of excitonic and band-to-band continuum transitions

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We investigate theoretically the nonlinear optical response of a semiconductor for excitation conditions where simultaneously all kinds of correlated two-pair transitions contribute to the dynamics. This includes transitions to biexcitons, exciton-exciton scattering states, two free electron-hole pairs as well as two-pair states involving an exciton and a free electron-hole pair. For certain excitation conditions two-pair correlations give rise to a complex line shape of four-wave-mixing spectra with an emission spread over the whole range between the exciton line and the band-edge. Even a strong suppression of the signal at the exciton line can be achieved while the emission is still concentrated between the exciton and the band-edge. The dependence of these features on the excitation conditions and on the strength of the Coulomb interaction is discussed. Comparing a nonperturbative treatment of the Coulomb interaction with the Born approximation and the mean-field theory clearly reveals the importance of nonperturbative Coulomb correlations even for excitations involving the continuum of free electron-hole pairs.

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I. INTRODUCTION

A wealth of evidence has accumulated over recent years indicating that the nonlinear optics of near band-edge excitations in semiconductors is dominated by Coulomb correlations.[1,2] To a large extent this dominance is due to the prominent role played by excitonic and biexcitonic resonances for excitations in the vicinity of the band-edge. Clearly, the occurrence of bound states with discrete resonances can only be understood when the Coulomb interaction is accounted for in a nonperturbative way. For continuum excitations, on the other hand, it is often argued that the Coulomb interaction mainly provides for an additional scattering channel which can be treated on the level of the second Born approximation[3–7] (BA), i.e., by a perturbative procedure concentrating on the leading order contributions. This point of view has been supported by a number of corresponding investigations where a good qualitative agreement between BA calcultions and experiments has been found.[3–5,8] In these studies, usually the statically screened potential is used as the perturbative parameter in order to avoid known divergences that occur when the BA is combined with the Markov approximation and then applied to the scattering due to the bare Coulomb potential.[9] Obviously, this procedure is most adequate when the experiments are performed at high excitation densities where the effective strength of the Coulomb interaction is substantially reduced by screening. In contrast, at low excitation densities screening is not effective and thus the Coulomb potential is essentially unscreened. In this limit the BA can only be applied without invoking the Markov approximation, i.e. on the quantum kinetic level.[10–12] But even then the BA description of the scattering between excitons turned out to deviate strongly from experimental findings.[13,14] In Refs. 13 and 14 a selective excitation at the 1 *s* exciton line of a quantum well in a microcavity has been considered. In this case, no free electron-hole pairs are excited and the failure of the BA could be traced back to a divergence of the exciton-exciton scattering amplitude in the limit of zero center-of-mass energy for the relative motion between the two excitons. This type of divergence occurs quite generally in two-dimensional systems as a result of applying the BA.[13,14] These deficiencies of the BA have been overcome by accounting nonperturbatively for two-pair Coulomb correlations, demonstrating that the continuum of exciton-exciton scattering states is strongly correlated by the Coulomb interaction in a way that is beyond the limits of validity of perturbative treatments.[13,14] Indeed, transitions to the correlated exciton-exciton continuum have been the focus of many recent studies indicating that these continuum correlations change the behavior of near band-edge excitations qualitatively and quantitatively by large amounts.[15–29] For example, the excitonic emission in four-wave-mixing (FWM) signals is overestimated by more than an order of magnitude in comparison to the biexcitonic emission when exciton-exciton correlations are neglected.[24] The presence of these correlations changes the sign of the optical Stark effect[23] and contributes to a delay time dependent change of the sense of rotation observed in the FWM emission from transient polarization states.[20] In addition they give rise to further important properties of nonlinear optical emissions that can be exploited for profound signal manipulations. An example for the latter is the huge increase of the gain up to 5000 detected in semiconductor microcavities after the insertion of large numbers of quantum wells[30] which according to the analysis in Ref. 29 is caused by exciton-exciton scattering correlations. The above results clearly highlight the pertinent role of two-pair continuum correlations caused by the Coulomb interaction. However, in most previous studies of two-pair correlations selective excitations below the band-edge, mostly in resonance with the 1 *s* exciton line, have been investigated. In this case, transitions to exciton-exciton scattering states are the only relevant type of two-pair continuum correlations. In contrast, a simultaneous excitation of excitons and free electron-hole pairs with ultrafast laser pulses could potentially establish further types of two-pair correlations including correlations between an exciton and a free electron-hole pair or among two free pairs. Experimentally such excitation conditions have been studied for a variety of materials, in different density regimes and with varying pulse characteristics.[3–5,8,31–42] But up until now, in almost all corresponding theoretical investigations two-pair correlations have been either completely neglected by concentrating only on the mean-field (MF) dynamics[31–34] or they have been taken into account perturbatively on the BA level.[3–5,8] In some cases effects of Coulomb scattering were accounted for within phenomenological models, e.g., by introducing by hand a density dependent decay time to simulate the excitation induced dephasing (EID).[35,36,39,43] Without any doubt, all of these theoretical models have their merits and are able to reproduce quite a number of features of corresponding experiments. Nevertheless, not much can be learned about the role of genuine two-pair correlations within these approaches. In particular, it is still an open question whether for excitation conditions involving noticeably the free electron-hole continuum a proper inclusion of two-pair correlations in the theory will merely provide for a microscopic justification of less rigorous approaches or whether there are observable features that cannot be modeled neglecting these correlations. The few existing studies that account for all types of two-pair correlations when both excitons and free pairs are excited have given only preliminary insight with regard to this question.[44,45] An early finding was, e.g., that a delay time decay of FWM signals which is not governed by the intrinsic excitonic dephasing rate can be modeled by accounting for all types of two-pair coherences;[44] a feature found in many experiments.[35–39] These calculations can thus be regarded as a microscopic support for interpretations of the observed delay time behavior in terms of phenomenological EID models.[35,36,43] But already in these early studies the crucial role of nonperturbative Coulomb correlations became apparent from a comparison with corresponding BA calculations. Although the BA theory yields results that are qualitatively similar to the outcome of nonperturbative calculations, substantial quantitative differences were found between the two.[44] Finally, in Ref. 45 it was shown that for certain excitation conditions—again involving excitonic and band-to-band continuum transitions—the shapes of FWM spectra calculated including two-pair correlations can qualitatively deviate from the corresponding MF result.

In the present paper we shall demonstrate nonperturbative two-pair Coulomb correlations after a simultaneous excitation of excitons and free electron hole pairs by ultrafast laser pulses. To this end we compare nonperturbative calculations of FWM spectra emitted from a quantum wire with corresponding results obtained on the MF and BA levels of theory. The MF theory marks the limit where two-pair correlations are absent while by comparing with the BA results, which deal perturbatively with Coulomb scattering, it becomes possible to evaluate the importance of a nonperturbative treatment of the Coulomb interaction. The full theory yields under certain excitation conditions complex FWM line shapes that are reproduced neither by the MF nor by the BA theory. We discuss systematically the dependences of these features on the characteristics of the exciting laser pulses such as the central frequency, the spectral width, and the polarization. For strongly correlated signals, it has to be expected that the strength of the interaction that mediates the pertinent correlations, i.e. the Coulomb interaction in our case, has a decisive impact. It should be noted that the effective strength of the Coulomb interaction in a solid state environment is not a fundamental constant but can vary due to different dielectric constants and in confined systems also due to different confinement lengths. In order to get more insight into the role of the interaction strength we used the dielectric constant as an adjustable parameter and compared the shapes of corresponding FWM spectra. It turns out that changing the strength of the Coulomb interaction not only induces the expected change of the exciton binding energy, it also results in considerable changes of the overall spectral shape of the continuous FWM emission located between the exciton line and the band-edge.

II. THEORETICAL APPROACH

As the main focus of the present paper is the role of two-pair correlations under broadband excitation conditions, a theoretical approach is required that is able to deal with biexcitons, exciton-exciton scattering states, and two-pair correlations involving free electron hole pairs on an equal footing. We shall restrict our discussion to the low intensity regime where the strongest correlation effects are expected.[1,2] In this regime, a convenient way to account for all types of correlated two-pair transitions is provided by the dynamics controlled truncation (DCT) scheme.[46,47] In recent studies, DCT has become the most widely used method for dealing with two-pair correlations,[19–29,48–50] mainly because it constitutes a very compact formulation of the dynamics which becomes asymptotically exact for low density excitations. In the present paper we shall use the DCT equations valid in the so called coherent limit (CL),[51] i.e., we shall assume that incoherent couplings, e.g. with phonons, are of minor importance for the dynamics. Scatterings other than those provided by the Coulomb interaction can thus be accounted for by phenomenological dephasing rates. With these assumptions there are two relevant dynamical variables, namely the amplitudes for single pair interband transitions:[46,47,51]

$$Y_2^1 := \langle \hat{Y}_2^1 \rangle := \langle \hat{d}_1 \hat{c}_2 \rangle, \tag{1}$$

and for correlated two-pair transitions,

$$\overline{B}_{24}^{13} := \langle \hat{Y}_2^1 \hat{Y}_4^3 \rangle - Y_2^1 Y_4^3 + Y_4^1 Y_2^3. \tag{2}$$

Here, we have used the real-space representation where $\hat{c}_j$ ($\hat{d}_j$) destroys an electron (hole) in the Wannier state at site j in the band σ_j. We consider a two-band model with two-fold degenerate bands (the valence band refers to heavy holes) corresponding to the lowest subbands of a cylindrical quantum wire with a 100 nm^2 cross-section confined by infinite barrier potentials. The space dependence of the Coulomb interaction in the wire is obtained in the standard way by projecting the 3D Coulomb potential onto the lowest wire sublevels. The transition density Y is directly related to the optical polarization[47] which is the main observable in optical measurements. The amplitude $\bar{B}$, on the other hand, represents the correlated part of two-pair coherences. In the Wannier representation the coupled nonlinear equations of motion for Y and $\bar{B}$ can be written in the compact form

$$\begin{aligned}[-i\hbar(\partial_t+\gamma_Y)+\hbar\hat{\Omega}_{Y_2^1}]Y_2^1 &= \mathbf{E}\cdot[\mathbf{M}_2^1-\sum_{jl}(\mathbf{M}_l^1 Y_l^{j*}Y_2^j+\mathbf{M}_2^j Y_l^{j*}Y_l^1)] \\ &\quad + \sum_{jl} V\left(\begin{smallmatrix}1\\2\end{smallmatrix}\middle|\begin{smallmatrix}j\\l\end{smallmatrix}\right) Y_l^{j*}(Y_l^j Y_2^1 - Y_2^j Y_l^1 + \bar{B}_{l2}^{j1}),\end{aligned} \tag{3}$$

$$[-i\hbar(\partial_t+\gamma_B)+\hbar\hat{\Omega}_{B_{24}^{13}}]\bar{B}_{24}^{13} = V\left(\begin{smallmatrix}1\\2\end{smallmatrix}\middle|\begin{smallmatrix}3\\4\end{smallmatrix}\right) Y_2^1 Y_4^3 - V\left(\begin{smallmatrix}1\\4\end{smallmatrix}\middle|\begin{smallmatrix}3\\2\end{smallmatrix}\right) Y_4^1 Y_2^3, \tag{4}$$

with

$$\hbar\hat{\Omega}_{Y_2^1} \equiv \hbar\omega_g - \frac{\hbar^2}{2m_h}\Delta_1 - \frac{\hbar^2}{2m_e}\Delta_2 - V_{12}, \tag{5}$$

$$\begin{aligned}\hbar\hat{\Omega}_{B_{24}^{13}} \equiv 2\hbar\omega_g &- \frac{\hbar^2}{2m_h}(\Delta_1+\Delta_3) - \frac{\hbar^2}{2m_e}(\Delta_2+\Delta_4) \\ &+ V_{13}+V_{24}-V_{34}-V_{12}-V_{14}-V_{23}.\end{aligned} \tag{6}$$

Here, for simplicity a spatially homogeneous excitation by a laser field $\mathbf{E}$ is assumed. $\mathbf{M}_2^1 \approx \delta_{\mathbf{r}_1,\mathbf{r}_2}\mathbf{m}_{c_2}^{v_1}$ are dipole matrix elements where $\mathbf{m}_{c_2}^{v_1}$ through its dependence on the valence (v_1) and conduction (c_2) band indices comprises the usual band selection rules for heavy-hole transitions. We shall account only for the interband dipole coupling, because intraband dipole couplings are considered to be of minor importance for the present discussion. γ_Y and γ_B describe the residual damping provided by interactions with the environment. The optical gap of our two-band model is denoted by $\hbar\omega_g$ while m_e and m_h are the effective masses for electrons and holes, respectively. We have defined, for convenience,

$$V\left(\begin{smallmatrix}1\\2\end{smallmatrix}\middle|\begin{smallmatrix}3\\4\end{smallmatrix}\right) \equiv V_{14}+V_{23}-V_{13}-V_{24}, \tag{7}$$

where V_{12} is the Coulomb potential between sites 1 and 2 projected onto the lowest quantum wire confinement modes. Finally, the sums in Eq. (3) comprise a sum over band indices as well as an integration over the space variables along the wire.

The equations of motion for Y and $\bar{B}$ have the structure of driven Schrödinger equations. The free propagation of the single-pair transition amplitude Y is determined by the operator $\hbar\hat{\Omega}_Y$ which is in fact the Hamiltonian for the exciton-problem in a quantum wire. The eigenenergies of $\hbar\hat{\Omega}_Y$ comprise discrete lines corresponding to bound exciton states as well as a continuum which belongs to unbound electron hole pairs. These eigenenergies show up as resonances of the transition density Y. This is most clearly seen in the linear absorption spectrum derived from Eq. (3) and plotted in the inset of Fig. 1(c). Analogously, the operator $\hbar\hat{\Omega}_B$, which is responsible for the free propagation of $\bar{B}$, is the Hamiltonian for the biexciton-problem in a quantum wire. It has a spectrum composed of a discrete line representing the bound exciton molecule (biexciton) and a continuum which can be roughly subdivided into parts corresponding to exciton-exciton scattering states and two-pair scattering states involving free electon-hole pairs. These spectral features are reflected as resonances in the dynamics of $\bar{B}$.

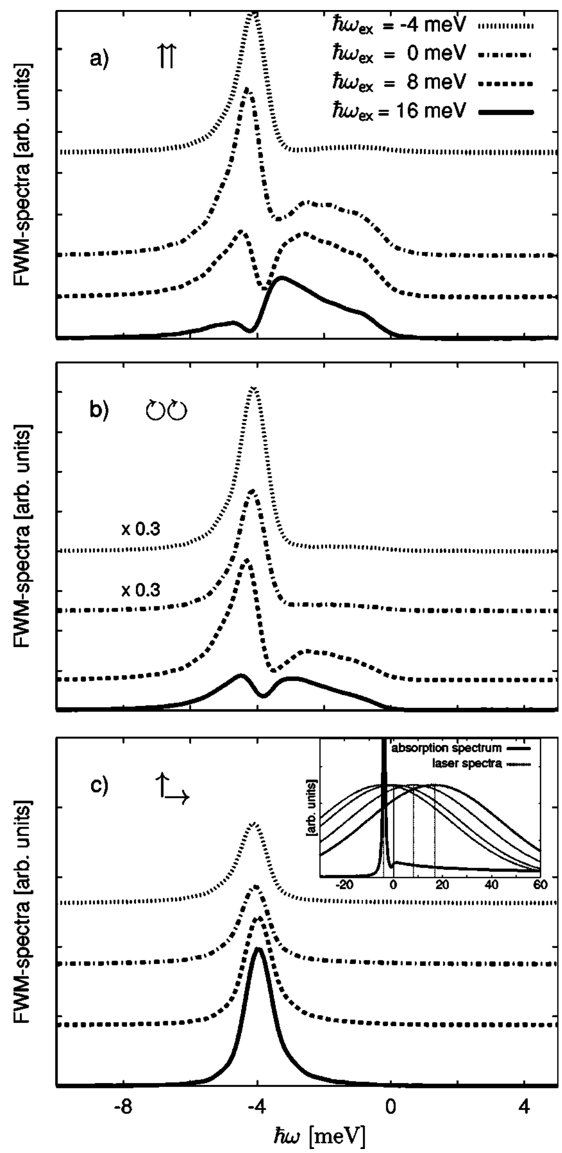

FIG. 1. FWM spectra at zero delay time, calculated accounting nonperturbatively for Coulomb correlations within the full CL theory. Spectra are plotted for different excess energies $\hbar\omega_{\text{ex}}$ (as indicated) and different polarizations of the exciting pulses: (a) colinear, (b) cocircular, (c) cross-linear. The inset shows the linear absorption spectrum of our quantum wire model together with the spectra of the laser pulses used. The pulses had a duration of 40 fs full width at half maximum of the field amplitude. The zero of energy is set to the band-edge.

The sources on the right hand side of Eq. (3) and Eq. (4) all have simple physical meanings: the terms proportional to the laser field $\mathbf{E}$ have the structure of a saturable driving force. They describe an excitation process which is saturated due to phase space filling. The terms proportional to $Y^{*}YY$ are MF Coulomb nonlinearities which account for the average action of all particles on an interband transition that promotes an electron from site 1 in the valance band to site 2 in the conduction band. Calculations, where Eq. (3) is solved including all contributions except for the terms proportional to $Y^{*}\bar{B}$, will be referred to as MF calculations. The terms $\sim Y^{*}\bar{B}$ represent the influence of two-pair correlations on interband transitions. Here, the variable $\bar{B}$ accounts for the time evolution of scattering processes involving two electron-hole pairs. In fact, one can think of $\bar{B}$ as a kind of reservoir where part of the excitation is stored. Then this reservoir can act back on the optically visible polarizations as long as it prevails.[1,2] From the point of view of single particle density matrices, like Y, the storing of parts of the excitation combined with a later back action provides for a memory structure which reflects the finite duration of two-pair scattering processes. Within the coherent limit DCT theory, correlated two-pair transitions $\bar{B}$ are generated by sources of the form $\sim VYY$ [cf. Eq. (4)]. The occurrence of a quadratic dependence on Y reflects the fact that two-pair transitions cannot be generated by an absorption of a single photon. Instead, at least a two-photon process is needed. Moreover, the sources are proportional to the Coulomb interaction V, because $\bar{B}$ respresents the correlated part of the two-pair transition density matrix and the correlation is mediated by the Coulomb interaction. Thus, it is natural that the sources for $\bar{B}$ do vanish in the limit of vanishing Coulomb interaction. It should be noted, however, that the Coulomb interaction enters the $\bar{B}$ equation not only via the sources on the right hand side of Eq. (4). Instead, the operator $\hbar\hat{\Omega}_B$, which determines the free propagation of $\bar{B}$, also contains the Coulomb potential [cf. Eq. (6)]. In fact, the Coulomb potentials contained in $\hbar\hat{\Omega}_B$ are responsible for the occurrence of the discrete biexciton resonance. In addition, even when two pairs are not bound into a molecule the way they are correlated can be strongly affected by the potentials in Eq. (6) due to changes of the density of states in the two-pair continuum. However, when $\bar{B}$ is expanded in powers of the Coulomb interaction, the lowest order contribution is provided exclusively by the source terms on the right hand side of Eq. (4) while the potentials in Eq. (6) yield higher order contributions. It has been shown previously[52] that, by neglecting the Coulomb potentials in the propagating operator of Eq. (6) and then formally inverting Eq. (4), one recovers the usual second order Coulomb scattering terms in the low density limit when the result is inserted on the right hand side of Eq. (3). This type of scattering theory is usually referred to as the second Born approximation. Technically, we have obtained the BA results discussed below not by this inversion procedure, but by solving the coupled equations of motion for Y and $\bar{B}$ for the case where the Coulomb potentials in the propagation operator $\hbar\hat{\Omega}_B$ are neglected. Both procedures are mathematically equivalent and thus our BA calculations represent indeed the standard BA scattering theory on the quantum kinetic level.[10–12]

For the numerical treatment it turned out to be convenient to transform Eqs. (3) and (4) to the momentum space by performing Fourier transformations with respect to all space arguments. Then, in order to take advantage of the spatial homogeneity of the system, we introduced relative and center of mass coordinates. Because there are many ways to introduce relative coordinates between the four arguments of $\bar{B}$ one has to make a choice. Here, we have followed the construction described in Ref. 53. In a homogeneous system, the dynamical variables depend only on relative coordinates and thus we end up with a k-space representation of Y and $\bar{B}$ where the former depends on one and the latter on three one-dimensional arguments. Of course, both Y and $\bar{B}$ depend in addition on the discrete band indices. Convergent numerical results were obtained by using equidistant k-space grids for all momentum arguments with 140 points in each dimension, i.e., $\bar{B}$ has been represented by a total of 2.744×10^{6} different k-space points. The discretized coupled equations of motion have then been integrated numerically in time without further approximation. We are interested in a standard two-pulse FWM setup where the pulses approach the sample from the directions $\mathbf{k}_1$ and $\mathbf{k}_2$ and the signal is recorded in the $2\mathbf{k}_2-\mathbf{k}_1$ direction. In order to extract the FWM signals from our calculation we have used a method proposed by Bányai,[11,54] where the nonlinear polarization is first determined for different relative phases between the two exciting pulses. The FWM contribution of the signal is then obtained by a Fourier transformation with respect to these phases. For all material parameters we have used standard values typical for GaAs, except for the dielectric constant which has been used as a variable parameter in order to be able to systematically change the strength of the Coulomb interaction. The phenomenological dephasing constants have been set to $\gamma_Y = 1/(1.34\ \text{ps})$ and $\gamma_B = 2\gamma_Y$, respectively. In Ref. 44 it has been shown that for our broadband excitation conditions the dephasing properties of $\bar{B}$ are clearly dominated by the destructive interference of the excitations in the two-pair continuum. The precise value of γ_B has therefore only little influence on our results.

III. RESULTS

Figure 1 shows FWM spectra calculated by numerically solving the full CL equations (3) and (4) for zero delay time between the pulses. The strength of the Coulomb interaction has been tuned by adjusting the dielectric constant to yield an exciton binding energy of 4 meV. Thus, the energetic situation resembles bulk GaAs in this case. We consider ultra-short-pulse excitations with a pulse duration of 40 fs full width at half maximum (FWHM) of the field amplitude. The calculations have been performed for four different central frequencies of the laser pulses. The corresponding pulse spectra are plotted in the inset of Fig. 1(c) together with the linear absorption spectrum of our quantum wire model. As seen from these plots, the excitation is spectrally broad and has in all cases a considerable overlap with the continuum of free electron-hole pairs as well as with the exciton line. Thus, for all excitation conditions considered here, all types of correlated two-pair transitions are simultaneously excited. By changing the excess energy we can control the relative weights of excitonic and continuum excitations. Figure 1(a) displays FWM spectra calculated for colinear polarized pulses. To facilitate the comparison, results corresponding to different excess energies are shifted vertically. For all four excess energies there is only a negligible FWM emission above the band-edge. This behavior has been reported for many experiments in the low intensity regime[3,31,39,42] and is also reproduced by corresponding MF calculations.[31,43,45] Clearly, the shape of the spectra depends crucially on the excess energy. For an excitation centered at the spectral position of the 1*s* exciton also the FWM emission is concentrated at the exciton line. Shifting the excess energy towards the band-edge broadens the exciton line and additional emissions emerge which are continuously spread over the whole region between the exciton and the band-edge, i.e., an emission occurs at frequencies where the linear absorption has a gap. A further increase of the excess energy leads to a decrease of the emission at the 1*s*-resonance while the continuous emission between the exciton and the band-edge is amplified. The spectra exhibit quite complex shapes under these excitation conditions. A pronounced feature is a marked dip which splits the spectra roughly into two parts. The dip appears close to but not exactly at the spectral position of the exciton. The complex continuous line shapes obviously reflect an interference of discrete and continuous parts of the excitation. According to this interpretation, the strong suppression of the emission at the exciton line, as manifested by the dip, occurs because different quantum mechanical pathways involving discrete as well as continuous excitations contribute to the signal at the exciton line and cancel due to destructive interference. The destructive superposition of different quantum mechanical pathways is a rather general feature which is at the heart of many interesting effects such as, e.g., excitation induced transparency (EIT). EIT has recently been demonstrated in a solid state system by using excitonic and biexcitonic transitions for representing the competing pathways.[50] Our case is, of course, different from EIT because the superposition suppresses the FWM emission at the exciton line instead of the absorption. The interesting point here is, however, that a strong suppression of a discrete line can be achieved not only by superpositions of discrete pathways, as is the case for EIT, but it can occur also as the result of combining discrete and continuous paths. It shall be demonstrated below that indeed nonperturbative Coulomb correlations determine the way in which discrete and continuum pathways are mixed such that the complex line shapes with the suppression of the exciton line, seen in Fig. 1(a), emerges.

Plotted in Fig. 1(b) are results for the same conditions as in Fig. 1(a) but calculated for cocircular polarizations of the laser pulses. As for the colinear case in Fig. 1(a), also for the cocircular excitation there is practically no emission above the band-edge. Also similar is the behavior for resonant excitation at the exciton, where the emission is concentrated at the 1 *s* line. A broad continuous emission between exciton and band-edge is, however, not yet present for excitations at the band-edge, it emerges in Fig. 1(b) only for higher excess energies. But, once the continuous emission has built up, also for cocircular excitation a dip appears close to the exciton resonance. Thus, apart from some quantitative differences, the shapes of the FWM spectra follow the same overall trends with increasing excess energy as in the colinear case. We therefore conclude that biexcitons play no decisive role for the occurrence of the complex line shapes and in particular of the dip structure near the exciton line, because due to well known selection rules biexcitons do not contribute for cocircular excitations.

FWM spectra calculated for cross-linear polarizations are depicted in Fig. 1(c) again for otherwise the same conditions as in Figs. 1(a) and 1(b). In this case, a rather narrow line approximately at the exciton position is obtained for all excess energies. In sharp contrast to Figs. 1(a) and 1(b), apart from small shifts of the position of the line and minor changes in its width and height, the signal in Fig. 1(c) is not much affected by changing the excess energy. Thus, the FWM emission is qualitatively different for different polarization configurations. While a pronounced dependence on the polarizations is well known from selective excitations at the exciton resonance,[23,24,55–59] such features are studied so far in much less detail when band-to-band excitations are involved.

Our aim of the present paper is to systematically analyze the role of two-pair correlations under conditions where excitonic and band-to-band continuum contributions are simultaneously excited. Choosing a quantum wire as our model system has the advantage of providing for a numerically tractable, well defined theoretical model which at the same time corresponds to a realizable physical system. However, to the best of our knowledge, there are no measurements available performed on quantum wire systems that are directly comparable with our calculations. Nevertheless, it is worthwhile to note that broad FWM spectra that are spread over the gap region between the exciton position and the band-edge have been observed in multiple quantum well systems for excitation conditions similar to ours.[42] Even a pronounced dip close to the exciton position has been reported.[42] A microscopic modeling of the experiments in Ref. 42, which would require us to deal with a multiple quantum well system, is definitely not our goal in the present paper. Thus, no final statement should be made at this point as to whether or not the results of Ref. 42 can be regarded as evidence for the nonperturbative Coulomb correlations described by our theory. Nevertheless, we find it encouraging that complex line shapes very similar to the ones predicted by our theory have indeed been observed under comparable excitation conditions.

In order to clarify the role of two-pair correlations for the results presented so far, we have repeated all calculations of Fig. 1 for the MF as well as the BA level of theory. The corresponding FWM spectra are shown in Fig. 2. The MF results are plotted in Figs. 2(a)–2(c) (left panels) while the BA spectra can be seen in Figs. 2(d)–2(f) (right panels). From the difference between the full CL calculations in Fig. 1 and the MF results we can infer the effects brought forth by two-pair correlations while the comparison with the BA theory reveals which features of the full results require a nonperturbative treatment of the Coulomb interaction. Let us first concentrate on the MF results. The MF spectra are al-

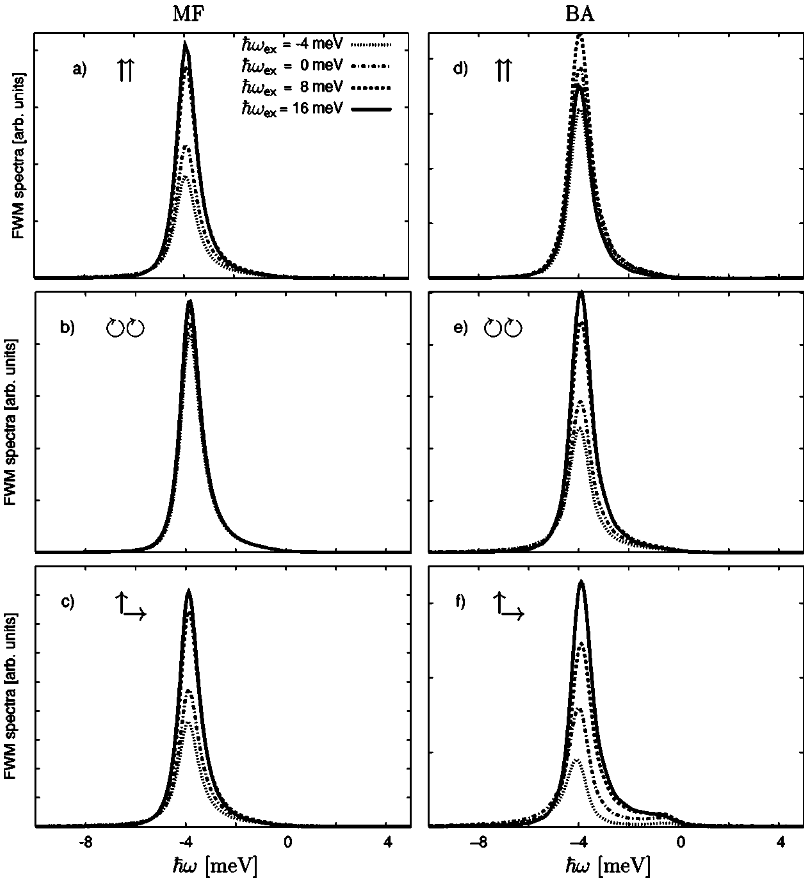

FIG. 2. FWM spectra at zero delay time, calculated for the same excitation conditions as in Fig. 1 but using the MF (left) or the BA (right) level of the theory.

ways concentrated at the exciton resonance. The shape is almost independent of the excess energies and the polarization configurations. Neither a sizeable broadening nor shifts occur. Only the total signal height decreases monotonously the closer the excitation is to the exciton line. For cocircular excitation even the latter effect is small. The BA spectra differ noticeably from the MF theory, though also here the emission is for all excitation conditions mostly concentrated near the exciton. For colinear excitation the BA theory predicts a nonmonotonous dependence of the peak height on the excess energy, while for cocircular and cross-linear polarizations the BA curves follow the trend of the MF theory. For cross-linear polarizations the width and the position of the emitted peak depends noticeably on the excess energy in contrast to the MF result. In particular, an increase of the excess energy leads in the BA theory to a shift of the FWM emission towards higher energies [cf. Fig. 2(f)] which is even quantitatively almost comparable with the full results for the cross-linear configuration in Fig. 1(c). But the BA curves in Fig. 2(f) also exhibit an enhanced emission spread between the exciton line and the band-edge which is absent in the full calculation for cross-linear polarizations. Comparing Fig. 1 with Fig. 2 by far the most striking feature is, however, that neither the MF nor the BA theory is able to account for the complex line shapes found in the full theory for the colinear and cocircular polarization configurations. Neither the strong dependence on the excess energy of the shape of the continuous emission between 1*s* resonance and band-edge nor the dip near the exciton position is reproduced. In addition, the MF and BA spectra for cross-linear excitation differ only quantitatively from the other polarization configurations. A large qualitative change of the behavior, as found in the full theory, is not obtained from the MF or BA theory. Altogether, one has to conclude that two-pair correlations indeed determine the way in which continuum and discrete excitations are mixed in the nonlinear response. Furthermore, the comparison between the MF, the BA, and the full CL theory clearly demonstrates that the complex line shapes in Fig. 1 reflect correlations that can only be understood when the Coulomb interaction is treated nonperturbatively during the scattering process.

In order to get a more detailed picture on how these spectral features depend on the excitation conditions, we have performed further calculations. For the plots in Fig. 3 we have reduced the pulse duration to 20 fs FWHM. The curves are the result of the full theory for colinear polarized pulses. Taking shorter pulses implies that now the pulse spectra are much broader and thus cover a much larger portion of the continuum. Based on the assumption that the BA treatment should give better results for excitations in the continuum one might expect that the spectra should show a tendency to become more similar to the BA results. However, the emission has now a complex shape with a pronounced dip for all excess energies, while the shapes of the corresponding BA spectra (not shown) closely resemble the results in Fig. 2. The overall shape of the spectra in Fig. 3 is similar for all excess energies although some dependencies are still visible. Even for resonant excitation at the exciton in Fig. 3 only a weak enhancement is found in the low frequency component of the emission which is reminiscent of the strong excitonic

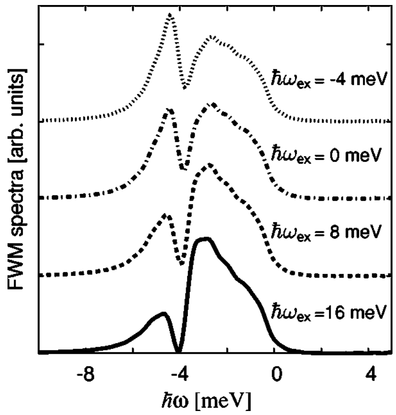

FIG. 3. FWM spectra at zero delay time for colinear polarized pulses, calculated accounting nonperturbatively for Coulomb correlation within the full CL theory. The calculations are performed for the same excitation condictions as in Fig. 1 except that the pulses had a duration of 20 fs full width at half maximum of the field amplitude.

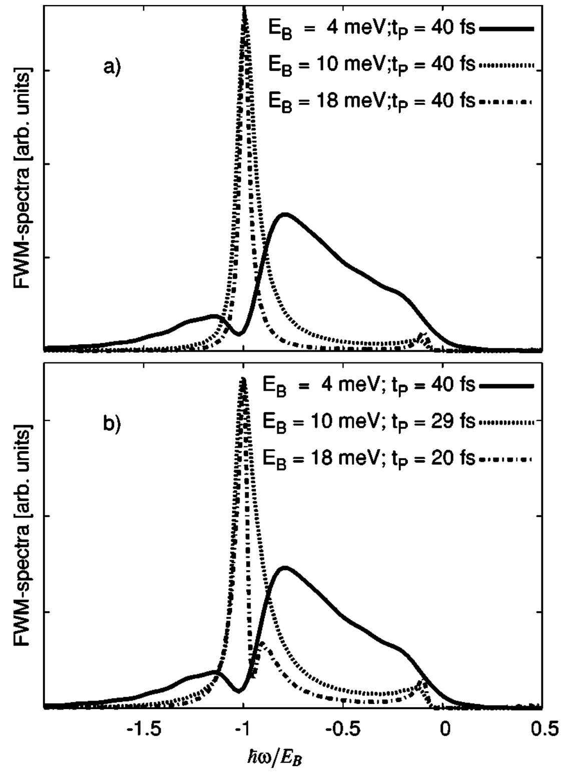

FIG. 4. FWM spectra according to the full CL theory for different strengths of the Coulomb interaction (indicated is the resulting exciton binding energy E_{B}). The central frequency was kept fixed 16 meV above the band-edge and colinear polarized pulses have been used throughout. (a) for a fixed pulse duration of 40 fs, (b) for pulse durations as indicated. The pulse durations in (b) have been chosen such that the linear absorptions at the exciton and in the continuum have a constant ratio for calculations with different interaction strengths.

emission found in Fig. 1. Here, we have almost reached the limit where the excitation is flat in all relevant parts of the spectrum for all central frequencies that have been considered. It is, of course, expected that in this limit there should be only minor dependences of the FWM emission on the excess energy. The most interesting finding of Fig. 3 is therefore not the weak dependence on the central frequency, but the fact that by reaching this ultra short pulse limit, the MF or BA prediction of an emission that is strongly peaked near the exciton line and otherwise unstructured, is not restored.

From the foregoing analysis it has become clear that the specific mixture of discrete and continuum contributions which manifests itself in complex FWM line shapes is governed by the Coulomb interaction. For such a situation where obviously strong nonperturbative Coulomb correlations dominate the dynamics it is evident that the interaction strength is a critical parameter of the system. In order to get more insight into the role of the interaction strength we have systematically varied the dielectric constant which scales the Coulomb potential. In a first set of calculations we have kept fixed the characteristics of the pulses and considered colinearly polarized 40 fs pulses with an excess energy 16 meV above the band-edge. Changing the interaction strength, first of all, has the more or less trivial consequence of changing the exciton binding energy. In Fig. 4(a) we compare FWM spectra calculated for fixed pulse characteristics for three different cases corresponding to exciton binding energies of 4, 10, and 18 meV, respectively. To facilitate the comparison we have plotted the spectra in units of the exciton binding energy E_{B}. As seen from Fig. 4(a), for a stronger Coulomb interaction the complex line shape disappears. Already, in the $E_{\mathrm{B}}=10$ meV case the emission is concentrated at the exciton resonance. Here, the influence of two-pair correlations merely leads to some broadening which is even further reduced when the binding energy is increased to $E_{\mathrm{B}}=18$ meV. In the gap region between the exiton and the band-edge we find for the stronger interactions no longer a broad continuous emission, instead a well resolved second resonance emerges which corresponds to the 2*s* exciton transition. Exciting the wire above the band-edge with a fixed pulse width and then increasing the exciton binding energy implies that the relative weight of the excitonic excitation is decreased compared with the excitation above the band-edge. In contrast, increasing the excess energy for a fixed binding energy, as studied in Fig. 1, reduces also the excitonic contribution but at the same time substantially increases the continuum absorption. Moreover, keeping the central frequency as well as the pulse width fixed implies that in Fig. 4(a) we cover the same energy region of the continuum in all cases, while the increasing excess energy used in Fig. 1 increases the continuum absoption mostly by covering a larger energy range in the band-to-band continuum. It is often argued that continuum excitations are reasonably well approximated by free electron hole pairs that are represented by plane waves. Within this simplified model, the three cases studied in Fig. 4(a) correspond to identical continuum excitations. From this point of view it is rather surprising to find that a *reduction* of the excitation at the exciton results in an almost complete concentration of the emission at the exciton line and removes practically all continuous parts from the FWM spectra. Thus, the trends obtained in Fig. 4(a) indicate that the uncorrelated free-particle picture is inadequate for near band-edge excitations. Indeed, it is well known that the effect of changing the interaction strength is not limited to a change of the exciton binding energy and thus for fixed pulse characteristics, to a change of the weight of the excitonic contribution. Instead, there are further modifications such as changes of the pertinent densities of states which may affect all possible scattering processes.[60] The best known consequence of this effect is the Coulomb enhancement of the near band-edge absorption in bulk systems. In quantum wire systems the corresponding effect is a Coulomb induced reduction of the band-edge absorption.[61,62] It should be noted, however, that in order to understand the spectral shapes discussed in the present paper it is not enough to account for the Coulomb induced changes of the linear absorption. These are fully included on the same level of sophistication in the MF and BA level of theory just as in the CL treatment. Having noted that we are dealing with nonperturbative Coulomb correlations that result from the Coulomb potentials in the propagation operator $\hbar\hat{\Omega}_B$ [cf. Eq. (6)], it becomes evident that what really matters here are the modifications of the scattering process itself which in turn determine the way discrete and continuum parts of the excitation are combined in the nonlinear dynamics. From this discussion it has to be concluded that the trends in Fig. 4 indeed provide further evidence for the decisive role of nonperturbative Coulomb correlations which obviously result in the most pronounced mixing of discrete and continuum excitations for not too strong interactions.

Finally, we would like to show that the actual superposition of discrete and continuum excitations that eventually is reflected in the FWM spectra is not determined alone by the relative weigths of excitonic and continuum excitations. To this end we have performed calculations for the three different quantum wires that were already considered in Fig. 4(a). Again, we have used a fixed excess energy 16 meV above the band-edge. But this time, by changing the pulse durations we have adjusted the pulse width in such a way that the ratio of the total absorptions at the exciton line and above the band-edge is exactly the same for all three calculations. The corresponding results displayed in Fig. 4(b) show essentially the same trends as the curves in Fig. 4(a). The complex line shape disappears with an increasing interaction strength in favor of an emission which is located at the 1*s* resonance. Compared with Fig. 4(a) there are some noteworthy differences: the emission in the gap region is now slightly higher and the curve for $E_{\mathrm{B}}=18$ meV exhibits a dip-like structure close to the exciton line. Apart from these details the curves in Fig. 4(b) are evidently very similar to the corresponding curves in Fig. 4(a). Thus, even when the total amount of excitation as measured by the linear absroption is kept at a constant ratio for excitonic and band-to-band transitions, we find a strong mixing of discrete and continuum excitations only when the interaction is not too strong.

IV. CONCLUSIONS

We have analyzed FWM spectra in the low density regime within a quantum wire model under excitation conditions where transitions to excitonic states and to the band-to-band continuum are simultaneously excited. We have accounted for all types of correlated two-pair transitions comprising biexcitons, exciton-exciton scattering states, two free electron-hole pairs as well as two-pair states involving an exciton and a free electron-hole pair within the framework of the coherent limit DCT scheme. For the broadband excitation considered here, all of these correlations contribute actively to the dynamics. It turns out that even for broadband excitation the FWM spectra depend crucially on the excitation conditions such as the excess energy, the spectral width, and the polarization of the laser pulses. Under certain excitation conditions, two-pair correlations give rise to complex line shapes of the FWM spectra, where a continuous emission is obtained in the gap region between the exciton line and the band-edge. Typically, these spectra exhibit a dip-like structure near the exciton resonance and in some cases the emission at the exciton is strongly suppressed. The bound biexciton does not play a decisive role for the occurrence of these spectral features as is evidenced by calculations for cocircular polarizations which exhibit these features although no biexcitons are excited. By comparing calculations that account nonperturbatively for the Coulomb interaction, with results of the MF and the BA theories, it is conclusively demonstrated that the complex line shapes reflect nonperturbative Coulomb correlations which are present during the scattering process. The decisive role of the interaction is further highlighted by calculations performed for different strengths of the interaction, which clearly reveal that it is indeed the interaction which determines the combination of discrete and continuum excitations that is eventually seen in the spectra.

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