The propagation of light pulses which are coupled to the excitonic resonances is a fundamental problem in semiconductor optics that has been the subject of intense experimental and theoretical research. The observations are dominated by the strong light-matter interaction and its interplay with the inherent many-particle Coulomb interaction of the electronic system. In the linear optical regime, exciton polaritons give rise to effects like polariton beating in the time-resolved pulse transmission [1] or yield strong modifications of excitonic transmission spectra, see e.g. [2, 3, 4]. In the nonlinear optical regime, incoherent saturation of the polariton resonances in transmission spectra [5, 6] and in the amplitude and phase of the time-resolved transmission [7] as well as transmission changes in pump-probe experiments [8] have been studied.

The above investigations are focused on samples where the thickness corresponds to a few exciton Bohr radii where polariton effects are most pronounced in the optical spectra. In this case the interplay of the induced excitonic polarization in the medium with the propagating light field is strongly influenced by sample surfaces which considerably complicates the theoretical description. In a frequently used phenomenological approach [9] the coupling of the exciton relative and center-of-mass (COM) motion at the sample boundaries is neglected. Then the exciton COM motion is subject to quantization effects in the confinement geometry while the exciton relative motion is approximated by the result of the infinitely extended medium. As a result of this approach, the solution of the wave equation for the electromagnetic field requires additional boundary conditions (ABCs) [9, 10] which are, however, not uniquely defined. Unfortunately, in many situations the choice of ABCs can influence the theoretical predictions [11]. To avoid these ambiguities, the use of microscopic boundary conditions within a non-local semiconductor response has been discussed in Refs. [12, 13] and recently applied to the linear optical regime [3, 4, 14]. The description of optical nonlinearities combined with a microscopic treatment of boundary conditions has been restricted so far to the quantum-well (QW) limit where propagation effects lead to radiative exciton broadening, which can be modified in radiatively coupled QWs. Furthermore, excitonic nonlinearities in QWs have been studied in connection with microcavity polaritons; for a review see [15]. In the opposite limit of the sample thickness approaching the bulk limit nonlinear pulse propagation effects [16, 17] have been analyzed successfully within a local approach for the semiconductor response. The decoupling of relative and COM exciton motion has also been used in an earlier approach to study the influence of propagation effects on four-wave mixing signals [18].

In this letter we present a novel approach that describes the combined influence of polariton propagation effects and coherent excitonic and bie excitonic nonlinearities. While the theoretical understanding of the coherent nonlinear excitation dynamics in QW or bulk systems is well developed, the additional influence of propagation effects is missing especially in a regime where the sample thickness exceeds the QW limit but the heterostructure interfaces prevent bulk-like behavior. In this case typically several well-resolved bulk-like behavior. In this case typically several well-resolved excitonic states modifies optical nonlinearities.

Our approach is based on a direct solution of the two- and four-particle Schrödinger equations for the exciton and biexciton motion together with Maxwell’s equations. We apply microscopic boundary conditions to avoid ambiguities due to ABCs in situations where both material polarization as well as optical fields are strongly influ-
enced by the boundaries of the system. A direct comparison of nonlinear transmission spectra for a ZnSe/ZnSSe heterostructure shows excellent agreement between theory and experiment and supports the detailed analysis of the microscopic model. As another application, calculated pump-probe spectra for a GaAs/AlGaAs heterostructure are presented.

In the coherent regime, excitonic and biexcitonic nonlinearities up to third order in the optical field can be consistently described in terms of the dynamical-controlled truncation (DCT) formalism which has been successfully applied in the past to QW systems. We extend this formalism to layers with a finite thickness where the sample boundaries still provide a confinement potential for the electrons and holes. To account for the coupling of the exciton relative and COM motion, independent coordinates for the electron and hole motion in propagation direction are used while these carriers are subject to Coulomb interaction (treated on the level of DCT) and to the optical field.

We consider a two-band model with spin-degenerate conduction and valence bands to describe the spectrally lowest interband transitions for a semiconductor layer in a slab geometry with strain-split light- and heavy-hole valence bands. The resonant contribution to the spatially inhomogeneous polarization in the semiconductor,

\[ P(z, t) = d_{eh}^* \sum_{k} \left( p^{eh}_{(k,z,z_0)} e_+ + p^{eh}_{(k,z,z_0)} e_- \right), \]

is given in terms of the non-local excitonic transition amplitude \( p^{eh}_{(k,z,z_0)}(t) = \langle h_k(z_0) e_k(z_0) \rangle \) with the electron \( e_k(z_0) \) and hole \( h_k(z_0) \) operators, respectively. According to the dipole selection rules, the \((-\frac{\pi}{3}, \frac{-\pi}{3})\) and \((+\frac{\pi}{3}, +\frac{\pi}{3})\) transitions are independently driven by circular optical polarization with unit vectors \( e_+ \) and \( e_- \), respectively, \( k \) is the in-plane carrier momentum (for the directions possessing translational invariance) and \( e, h \) are quantum numbers that simultaneously denote the directions possessing translational invariance and the \( z \)-component of the corresponding total angular momenta. A local dipole-interaction \( d_{eh}(k, z - z_0) = d_{eh}(z - z_0) \) is used. Applying the DCT scheme, an equation of motion for the excitonic transition amplitude \( p^{eh}_{(k,z,z_0)} \) is obtained which is coupled to the biexcitonic correlation function,

\[ b^{eh'\lambda}_{(k_2,z_2,k_1,z_1)}(t) = \langle h_{k_1}(z_1) e_{k_2}(z_2) h_{k_2}(z_3) e_{k_3}(z_4) \rangle, \]

(2)

that itself obeys a four-particle Schrödinger equation with coherent source terms. The resulting closed set of equations contains all mean-field (Hartree-Fock) as well as biexcitonic contributions to the semiconductor response up to third order in the optical field. The evaluation of these material equations is performed in the exciton eigenbasis. As an important ingredient of our approach, exciton eigenfunctions \( \phi_{m}(k, z_e, z_h) \) are determined for the given confinement geometry to include the additional non-local space dependence. In contrast to Ref. [14] we use eigenfunctions that individually fulfill the boundary conditions of the inhomogeneous system. Then every eigenfunction corresponds to a polariton resonance in the linear optical spectrum and a truncation of the expansion can be justified with the considered spectral range while the boundary conditions of the inhomogeneous system remain fully satisfied. The excitonic transition amplitude and the singlet \( (\lambda = -1) \) and triplet \( (\lambda = +1) \) contributions to the biexcitonic correlation function are expressed as

\[ P^{eh}_{(k,z,z_0)}(t) = \sum_{m} p^{eh}_{m}(t) \phi_{m}(k, z_e, z_h), \]

(3)

where \( p^{eh}_{m}(t) \) and \( b^{eh'\lambda}_{nm}(q, t) \) are the time-dependent expansion coefficients. \( \alpha = m_n^*/M^* \) and \( \beta = m_e^*/M^* \) are the ratio of the hole and the electron masses to the total exciton mass \( M^* = m_n^* + m_h^* \), respectively. This treatment generalizes the eigenfunction expansion in the QW limit discussed in [27]. For a self-consistent description of the light propagation in a semiconductor material, Maxwell’s equations are solved directly together with the excitonic and the biexcitonic dynamics.

In Fig. [1] the theoretical and experimental results are shown for the transmission of a single light pulse through a high-quality 20 nm ZnSe layer sandwiched between two ZnSSe cladding layers. The sample was pseudomorphically grown by molecular-beam epitaxy on a (001)GaAs substrate. Further details on growth and sample characterization as well as on modeling of the finite-height confinement potentials at the ZnSe/ZnSSe interfaces are described in [4]. The opaque GaAs substrate was carefully removed by grinding and subsequent chemical etching to permit measurements in transmission geometry. The sample was mounted onto a glass plate and kept on a cold finger in a cryocryostat at a temperature of 4 K. A frequency-doubled self-mode-locked Ti-sapphire laser with 110 fs (FWHM) pulse duration and 83 MHz repetition rate was used as excitation source for the spectrally resolved but time integrated transmission experiments. The maximum of the spectral pulse profile was set close to the spectral position of the first heavy-hole (hh1) polariton mode to excite the whole spectral region from the
Pockels cell. The transmitted signal was analyzed with a spectrometer and was recorded with a CCD camera.

The measured linear transmission spectrum in the vicinity of the heavy-hole (hh) exciton resonance, depicted as dashed-dotted line in Fig. 1a, exhibits three pronounced polariton resonances denoted by hh1-hh3. With the microscopic treatment of boundary conditions, these polariton modes are perfectly reproduced in Fig. 1a (without adjustable parameters like a dead-layer thickness, the sample thickness has been independently determined using x-ray diffraction \[4\]). Results for nonlinear transmission spectra are shown in Figs. 1b, (experiment) and c (theory) where linear and circular light polarization are shown in Figs. 1a (experiment) and c (theory) with spin-singlet symmetry, is clearly identified in the theory-experiment comparison. The spectral changes at the polariton resonances result from mean-field (Hartree-Fock) barriers in the GaAs layer are confined by infinitely high potential electronic triplet configuration are excited whereas for linear light polarization both singlet and triplet biexcitonic states contribute to the transmitted signal. In particular, an advantage of the theoretical approach applied here is the simultaneous inclusion of the bound biexciton state and the exciton-exciton scattering continuum. The latter one is essential to reproduce the broad background on the high-energy side of the polariton resonances in the nonlinear transmission spectra. As a minor aspect, the biexciton binding energy is slightly underestimated by the truncation of the exciton basis, similar to the result in \[26\] for a QW system.

To provide further insight into the nature of coherent nonlinear polariton saturation, we also studied the pump-probe excitation for a GaAs layer embedded between Al-GaAs barriers \[30\]. This part of the paper is intended to demonstrate the potential of our theory within another application and to stimulate further experiments for this material system. In a good approximation, the carriers in the GaAs layer are confined by infinitely high potential barriers in the z-direction \[11\]. The solid line in Fig. 2a shows the linear optical transmission \(T\) through a GaAs layer of 5 exciton Bohr radii thickness. The energy \(\hbar \omega\) is given relative to the bulk band-gap energy \(E_G\) and normalized to the corresponding exciton binding energy \(E_B^{XX}\). For the chosen layer thickness, the confinement of carriers in the z-direction yields three polariton resonances of the 1s exciton in the displayed part of the spectrum which are labeled by consecutive numbers.

For the pump-probe excitation, two 120 fs laser pulses (from slightly different directions) without time-delay are considered. The dashed line in Fig. 2a corresponds to the pulse spectrum. Figure 2b shows changes in the probe-pulse transmission that are induced by the pump pulse for opposite circular (solid line) and co-circular (dashed-dotted line) polarization of pump and probe pulses. The probe pulse enters the excitonic polarization in linear order only. For the pump pulse a Rabi energy \(\hbar |E_{\text{pump}}| = 0.01 E_B^{XX}\) is used which ensures a consistent description within our \(\chi^{(3)}\) theory. The transmission changes around the higher (1s,2 and 1s,3) polariton re-
FIG. 2: (a) Solid line: Calculated linear transmission spectrum $T$ (depicted as $1 - T$) for a GaAs layer with 5 exciton Bohr radii thickness. Dashed line: Spectral shape of a 120 fs laser pulse. (b) Differential probe transmission $\Delta T$ for opposite circular (solid line), and co-circular (dashed-dotted line) polarization of pump and probe pulses. (c) Differential probe transmission $\Delta T$ for opposite circular polarization including all Coulomb terms (solid line) and without Coulomb interaction of different polaritons (dashed line).

sonances in Fig. 2 are similar to those around the lowest one (1s,1) but with a decreased amplitude. A similar dependence on the light polarization has been reported for the differential probe absorption around the 1s exciton resonance in a QW system [22]. For opposite-circular polarization, the pump-induced changes in the probe transmission are exclusively determined by biexcitonic correlations [22]; no mean-field effects contribute. This configuration is chosen for the analysis of the Coulomb interaction between polaritons in states with different spatial distribution. The dashed line in Fig. 2 shows the result where Coulomb interaction that couples different eigenfunctions in the two-exciton product basis of Eq. 11 is artificially switched off. We encounter only a slight change of the nonlinearities around the lowest polariton resonance (1s,1) whereas for higher peaks (1s,2 and 1s,3) the influence of the pump pulse almost vanishes. Therefore, Coulomb interaction between exciton states with different spatial distribution (corresponding to different polariton resonances) turns out to be the main source for transmission changes of higher polariton states.

In summary, a theory for the nonlinear polariton dynamics in semiconductor heterostructures has been presented which consistently includes (i) propagation effects with microscopic boundary conditions for the induced material polarization as well as for the optical fields and (ii) excitonic and biexcitonic coherent nonlinearities previously studied only in QWs or one-dimensional model systems. The application to nonlinear transmission spectra for a ZnSe/ZnSSe heterostructure shows excellent agreement between theory and experiment. The influence of light-polarization dependent excitonic and biexcitonic nonlinearities has also been demonstrated for a pump-probe excitation of a GaAs heterostructure. Coulomb interaction of polariton states with different spatial distribution turns out to strongly influence the nonlinear optical transmission.

The authors acknowledge a grant for CPU time from the John von Neumann Institute for Computing at the Forschungszentrum Jülich. We thank G. Alexe for the sample characterization via x-ray diffraction.

[1] D. Fröhlich et al., Phys. Rev. Lett. 67, 2343 (1991).
[2] A. Tredicucci et al., Phys. Rev. B 47, 10348 (1993).
[3] J. Tignon et al., Phys. Rev. Lett. 84, 3382 (2000).
[4] S. Schumacher et al., Phys. Rev. B 70, 235340 (2004).
[5] U. Neukirch and K. Wundke, Phys. Rev. B 55, 15408 (1997).
[6] M. Betz et al., Phys. Rev. B 65, 085314 (2002).
[7] J. S. Nägerl et al., Phys. Rev. B 63, 235202 (2001).
[8] A. C. Schaefer and D. G. Steel, Phys. Rev. Lett. 79, 4870 (1997).
[9] S. I. Pekar, Sov. Phys. JETP 6, 785 (1958).
[10] C. S. Ting et al., Solid State Commun. 17, 1285 (1975).
[11] H. C. Schneider et al., Phys. Rev. B 63, 045202 (2001).
[12] A. D’Andrea and R. Del Sole, Phys. Rev. B 25, 3714 (1982).
[13] A. D’Andrea and R. Del Sole, Phys. Rev. B 41, 1413 (1990).
[14] E. A. Muljarov and R. Zimmermann, Phys. Rev. B 66, 235319 (2002).
[15] G. Khitrova et al., Rev. Mod. Phys. 71, 1591 (1999).
[16] H. Giessen et al., Phys. Rev. Lett. 81, 4260 (1998).
[17] J. Förstner et al., Phys. Rev. Lett. 86, 476 (2001).
[18] A. Schulze et al., Phys. Rev. B 51, 10601 (1995).
[19] V. M. Axt and A. Stahl, Z. Phys. B 93, 195 (1994).
[20] M. Lindberg et al., Phys. Rev. B 50, 18060 (1994).
[21] V. M. Axt et al., Z. Phys. B 188, 447 (1995).
[22] C. Sieh et al., Phys. Rev. Lett. 82, 3112 (1999).
[23] W. Schäfer et al., Phys. Rev. Lett. 86, 344 (2001).
[24] N. H. Kwong et al., Phys. Rev. B 64, 045316 (2001).
[25] M. E. Donovan et al., Phys. Rev. B 63, 476 (2001).
[26] M. Buck et al., Eur. Phys. J. B 42, 175 (2004).
[27] W. Schäfer and M. Wegener, Semiconductor Optics and Transport Phenomena (Springer Berlin, 2002).
[28] S. Schumacher et al., Phys. Stat. Sol. B 234, 172 (2002).
[29] R. Takayama et al., Eur. Phys. J. B 25, 445 (2002).
[30] Material parameters are: $m_e^* = 0.067 m_0$, $m_h^* = 0.457 m_0$ for effective electron and hole masses, with the bare electron mass $m_0$, the backgroud refractive index $n_0 = 3.71$, a dephasing constant $\gamma = 0.06$ meV, the bulk GaAs band-gap energy $E_G = 1.42$ eV, and a dipole coupling constant $d_{ab}/e_0 = 5$ Å.