Nonlinear Optical Properties and Self-Kerr Effect of Rydberg Excitons in Cu$_2$O

Sylwia Zielinska-Raczyńska, Gerard Czajkowski, Karol Karpinski, and David Ziemkiewicz

Institute of Mathematics and Physics, UTP University of Science and Technology, Al. Prof. S. Kaliskiego 7, PL 85-789 Bydgoszcz, Poland
(Dated: April 8, 2019)

We show how to compute the nonlinear optical functions (absorption, reflection, and transmission) for a medium with Rydberg excitons, including the effect of the coherence between the electron-hole pair and the electromagnetic field. Using the Real Density Matrix Approach the analytical expressions for nonlinear optical functions are obtained and numerical calculations for Cu$_2$O crystal are performed. We report a good agreement with recently published experimental data. Propagation of the electromagnetic waves in Rydberg excitons media with nonlinear effect is also discussed and the possibility of obtaining self-phase modulation due to Kerr nonlinearity is investigated.

PACS numbers: 78.20.e, 71.35.Cc, 71.36.+c

I. INTRODUCTION

Recently, a lot of attention has been drawn back to the subject of excitons in bulk crystals due to an experimental observation of the so-called yellow exciton series in Cu$_2$O up to a large principal quantum number of $n = 25$. Such excitons in copper oxide, in analogy to atomic physics, have been named Rydberg excitons (RE). By virtue of their special properties Rydberg excitons have become widely explored in solid and optical physics. These objects whose size scales as the square of the principal quantum number $n$, are ideally suited for fundamental quantum interogations, as well as detailed classical analysis. Due to their exaggerated properties, including long lifetimes, large electric dipole moments, and strong exciton-exciton interactions controlled by so-called Rydberg blockade, REs could have promising applications in, among many areas, quantum calculating and quantum information.

Several theoretical approaches to calculate optical properties of REs have been presented (see, for example, Ref. for a review). As was observed just in the first experiment the optical line shapes of RE are very sensitive to laser power of the exciting electromagnetic wave, which could be connected with nonlinear effects. However, almost all efforts in the area of RE have been mainly devoted to the linear optical properties of Rydberg excitons. The nonlinear phenomena with RE were first discussed by Walther et al. regarding coupling between strong interaction of RE and optical photons in semiconductor microcavities. Also the recent experiments by Hecktöter et al. has touched the problem of nonlinear properties of RE in the presence of electron and hole plasma and paved the way to extend the discussion of the optical properties of RE to include the nonlinear effects.

In this paper we discuss the role of the exciting light intensity on the RE spectra, considering the impact of simultaneous inter-band and intra-band excitations. As in our previous paper we will use the method based on the Real Density Matrix Approach (RDMA). While the experiments with REs were performed at helium temperatures there are in principle no obstacles for observations in temperatures reaching 100 K. By taking into account density matrices for electrons and holes we are able to include additional effects regarding temperature, which influences the gap energy as well as intrinsic damping parameter. We derive expressions for the third order susceptibility which enable us to obtain formula for the nonlinear optical functions. The calculation are performed to a Cu$_2$O crystal for which the nonlinear optical functions in the case of quasi-stationary excitation are analytically calculated.

Rydberg excitons in copper oxide might be of great potential for future application in photonic quantum information processing, where nonlinear interaction plays the crucial role, so we have directed our interest to light propagation in this medium. The electromagnetic waves propagation in nonlinear regime discussed in the present paper, is connected with Kerr effect, which manifests itself as a self-induced phase of a pulse of light as it travels through the medium. Self-phase modulation (SPM) is a nonlinear optical effect of light-matter interaction; it is induced by a varying refractive index of the medium. This produces a phase shift in the pulse, leading to a change of the pulse’s frequency spectrum. It might be interesting to examine the intensity dependence of the index of refraction in REs media. Such approach might be the first step to develop the new branch of investigations and applications in media with RE; the phenomenon of self-focusing is the promising example SPM steered on demand by light intensity can also find interesting applications in optoelectronic devices working with low-light intensity, such as all-optical switching and logic gates. In quantum information context two-photon self-Kerr nonlinearities may be used in quantum computing.

The paper is organized as follows. In Sec. I we recall the basic equations of the RDMA and formulate the equations for the case when the inter-band and intra-band electronic transitions are accounted for. In Sec. III we describe an iteration procedure, which will be applied to solve a system of coupled integro-differential equations. The second iteration step, from which the nonlinear optical functions will be calculated, is given in Sec. IV. The formulas, derived in this Section, are than applied in
Sec. IV, which is devoted to presentation and discussion of the nonlinear optical functions for a Cu$_2$O crystal. Self-phase modulation in such a system regarding intensity and transmission dependence is discussed in Sec. IV. Finally, in Sec. V we draw conclusions of nonlinear studies presented in this paper.

II. EXCITONIC NONLINEARITIES IN RYDBERG EXCITON MEDIA: DENSITY MATRIX FORMULATION

In what follows we adapt the real density matrix approach to the case of semiconductors under high excitation, and show how to calculate the nonlinear optical functions.

We discuss the nonlinear response of a semiconductorslab to an electromagnetic wave characterized by the electric field vector,

\[ \mathbf{E} = E_{00} \exp(ik_0 \mathbf{R} - i \omega t), \quad k_0 = \omega/c, \]

\( R \) being the excitonic center-of-mass coordinate (see Eq. 8 below).

In the RDMA approach the bulk nonlinear response will be described by a closed set of differential equations (“constitutive equations”): one for the coherent amplitude \( Y(r_1, r_2) \) representing the exciton density related to the interband transition, one for the density matrix for electrons \( C(r_1, r_2) \) (assuming a non-degenerate conduction band), and one for the density matrix for the holes in the valence band, \( D(r_1, r_2) \). Below we will use the notation

\[ Y(r_1, r_2) = Y_{12}, \quad \text{etc.} \]

The constitutive equations have the form: the interband equation

\[ i\hbar \partial_t Y_{12} - H_{eh} Y_{12} = -\mathbf{M} \mathbf{E}(R_{12}) + \mathbf{E}_1 \mathbf{M}_0 C_{12} + \mathbf{E}_2 \mathbf{M}_0 D_{12} + i\hbar \left( \frac{\partial Y_{12}}{\partial t} \right)_{\text{irrev}}, \]

conduction band equation

\[ i\hbar \partial_t C_{12} + H_{ee} C_{12} = \mathbf{M}_0 (\mathbf{E}_1 Y_{12} - \mathbf{E}_2 Y_{21}^*), \]

\[ +i\hbar \left( \frac{\partial C_{12}}{\partial t} \right)_{\text{irrev}}, \]

valence band equation

\[ i\hbar \partial_t D_{21} - H_{hh} D_{21} = \mathbf{M}_0 (\mathbf{E}_2 Y_{12} - \mathbf{E}_1 Y_{21}^*) \]

\[ +i\hbar \left( \frac{\partial D_{21}}{\partial t} \right)_{\text{irrev}}, \]

where the operator \( H_{eh} \) is the effective mass Hamiltonian

\[ H_{eh} = E_y - \frac{\hbar^2}{2 M_{tot}} \partial^2 \mathbf{R}_\parallel - \frac{\hbar^2}{2 \mu} \partial^2 Z - \frac{\hbar^2}{2 \mu} \nabla^2 \mathbf{\rho} + V_{eh}, \]

with the separation of the center-of-mass coordinate \( \mathbf{R}_\parallel \) from the relative coordinate \( \mathbf{\rho} \) on the plane \( x - y \),

\[ H_{ee} = - \frac{\hbar^2}{2 m_e} (\nabla^2_x - \nabla^2_y), \]

\[ H_{hh} = - \frac{\hbar^2}{2 m_h} (\nabla^2_x - \nabla^2_y), \]

and \( \mathbf{E}_{12} \) means that the wave electric field in the medium is taken in a middle point between \( r_1 \) and \( r_2 \): we take them at the center-of-mass

\[ \mathbf{R} = \mathbf{R}_{12} = m_h \mathbf{r}_1 + m_e \mathbf{r}_2. \]

In the above formulas \( m_e, m_h \) are the electron and the hole effective masses (more generally, the effective mass tensors), \( M_{tot} \) is the total exciton mass, and \( \mu \) the reduced mass of electron-hole pair. The smeared-out transition dipole density \( \mathbf{M}(r) \) is related to the bilocality of the amplitude \( Y \) and describes the quantum coherence between the macroscopic electromagnetic field and the inter-band transitions. The resulting coherent amplitude \( Y_{12} \) determines the excitonic part of the polarization of the medium

\[ \mathbf{P}(\mathbf{R}, t) = 2 \int d^3 r \mathbf{M}^*(\mathbf{r}) \text{Re} \mathbf{Y}(\mathbf{R}, \mathbf{r}, t) \]

\[ = \int d^3 r \mathbf{M}^*(\mathbf{r})[\mathbf{Y}(\mathbf{R}, \mathbf{r}, t) + c.c.], \]

where \( \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2 \) is the electron-hole relative coordinate.

The linear optical properties are obtained by solving the interband equation [3], supplemented by the corresponding Maxwell equation, where the polarization acts as a source. For computing the nonlinear optical properties we use the entire set of constitutive equations [3]-[5]. At the moment a general solution of the equations seems to be inaccessible. Only in special situations a solution can be found. For example, if one assumes that the matrices \( Y, C \) and \( D \) can be expanded in powers of the electric field \( \mathbf{E} \), an iteration scheme can be used.

The relevant expansion of the polarization in powers of the field has the form

\[ P(\mathbf{k}, \omega) = \epsilon_0 \left[ \chi^{(1)} E(\mathbf{k}, \omega) + \chi^{(3)}(\omega, -\omega, \omega) |E(\mathbf{k}, \omega)|^2 + \ldots \right], \]

where \( \chi^{(1)} \) is the linear and \( \chi^{(3)} \) is a nonlinear susceptibility.

III. THE ITERATION PROCEDURE

Following the calculation scheme proposed in Refs. [3]-[5], we calculate the susceptibility \( \chi^{(3)} \) iteratively from the dynamic equations [3]-[5]. The first step in the iteration consists of solving the equation [3], which we take in the form

\[ i\hbar \partial_t Y_{12}^{(1)} - H_{eh} Y_{12}^{(1)} = -\mathbf{M} E + i\hbar \left( \frac{\partial Y_{12}^{(1)}}{\partial t} \right)_{\text{irrev}}. \]
For the irreversible part we assume, as usually, a relaxation time approximation

$$\left( \frac{\partial Y_{12}(t)}{\partial t} \right)_{irrev} = -\frac{1}{T_2} Y_{12} = -\Gamma Y_{12},$$

where $\Gamma$ is a dissipation constant and $T_2 = \hbar/\Gamma$. In the discussion of nonlinear effects we take also into account the non-resonant parts of the amplitude $Y$, and consider the electric field $E$ in the medium in the form

$$E_{12} = E(R(t)) + E^*(R(t)) = E_0 e^{i(kR - \omega t)} + E_0 e^{-i(kR - \omega t)}.$$ 

Therefore the equations (11) generate two equations: one for an amplitude $Y_{12}^{(1)} \propto \exp(-i\omega t)$, and the second for the non resonant part $Y_{12}^{(1)} \propto \exp(i\omega t)$,

$$\hbar \left( i\omega + \frac{1}{T_2} \right) Y_{12}^{(1)} - H_{ch} Y_{12}^{(1)} = -\mathbf{M} \mathbf{E}^*(R(t)), \quad \text{(14)}$$

$$\hbar \left( -i\omega + \frac{1}{T_2} \right) Y_{12}^{(1)} - H_{ch} Y_{12}^{(1)} = -\mathbf{M} \mathbf{E}(R(t)).$$

We will consider only one component of $\mathbf{E}$ and $\mathbf{M}$. As in our previous papers, we look for a solution in terms of eigenfunctions of the Hamiltonian $H_{ch}$, which we use in the form $\varphi_{n\ell m} = R_{n\ell}(r)Y_{\ell m}(\theta, \phi)$, where $R_{n\ell}$ are the hydrogen radial functions, and $E_n$ the corresponding values. So we obtain

$$Y_{12}^- = \frac{1}{\hbar} \sum_n \frac{c_{n\ell m} \varphi_{n\ell m}(r)}{E_n - \omega - i/T_2},$$

$$Y_{12}^+ = \frac{1}{\hbar} \sum_n \frac{c_{n\ell m} \varphi_{n\ell m}(r)}{E_n + \omega - i/T_2}.$$ 

where

$$c_{n\ell m} = \int d^3r M(r) \varphi_{n\ell m}(r),$$

$$\hbar \Omega_{n\ell m} = E_{g\ell m} + E_n + \frac{\hbar^2}{2M_{tot}} k^2,$$

$$r = \sqrt{x^2 + y^2 + z^2},$$

and, in the case of Cu$_2$O, $E_{g\ell m}$ are the gap energies appropriate for $p$ and $f$ excitons. For the sake of simplicity, we consider only the $p$ excitons contribution. The solutions $Y_{12}^{(1)}$ determine the linear susceptibility

$$\chi^{(1)}(\omega, k_z^{(1)}) = \frac{1}{\epsilon_0 E_0} \int d^3r \left( Y_{12}^{(1)} + Y_{12}^{(1)} \right) M^*(r)$$

$$= \frac{1}{\epsilon_0 \hbar} \sum_{n\ell m} \frac{b_{n\ell m} \Omega_{n\ell m}}{\Omega_{n\ell m} - (\omega - i/T_2)^2},$$

with the coefficients

$$b_{n\ell m} = \left| c_{n\ell m} \right|^2 = \frac{8\pi}{3} \left( \int_0^\infty r^2 dr M(r) R_{n\ell}(r) \right)^2.$$ 

The so obtained susceptibility defines the linear dispersion rule for the polariton modes

$$\frac{c^2}{\omega^2} \left( k_z^{(1)} \right)^2 = \epsilon_b + \chi^{(1)}(\omega, k_z^{(1)}).$$

The coefficients $b_{n\ell m}$ can be expressed in terms of the band parameters and, for energies below the gap, one obtains

$$\frac{k_z^{(1)^2}}{\xi_0^2} - \epsilon_b = \epsilon_b \sum_{n=1}^N \left( E_{irn} - E - i\Gamma_n / R^* + (\mu/M_{tot})(k_z^{(1)} + \xi_0) \right)^2,$$

where $\xi_0 = \omega/c$, $\Gamma_n = \hbar / T_{2n}$, $E_{irn}$ are energies of the exciton resonances, and the oscillator strengths are given by

$$f_{n\ell} = \frac{32(n^2 - 1)}{3n^3} \left[ n(r_0 + 2\xi_0) \right]^6.$$ 

For the wave propagating in the medium, we choose the appropriate component of the dipole density. For $p$ excitons ($\ell = 1$) the $z$-component of the dipole density vector, which will be used below, has the form

$$M_z(r) = M_{10} r + r_0 \sqrt{\frac{4\pi}{3}} Y_{10} e^{-r/r_0},$$

with the coherence radius $r_0$.

$$r_0^{-1} = \sqrt{\frac{2\mu \hbar}{\hbar E_g}}.$$ 

IV. ITERATION PROCEDURE: SECOND STEP

Let us consider a wave linearly polarized in the $z$ direction. Then $Y_1^{(1)}$ are inserted into the source terms of the conduction-band and valence band equation (4 - 5). Solving for stationary solutions, we have

$$J_C = M_{10} \left( E_1 Y_{12}^{(1)} - E_2 Y_{21}^{(1)} \right)$$

$$= \frac{2iM_{10} E_0^2}{\hbar} \left[ \exp \left( ik_z^{(1)} z \frac{m_n}{M_{tot}} \right) \Im g(-\omega, r) \right.$$

$$\left. + \exp \left( -ik_z^{(1)} z \frac{m_n}{M_{tot}} \right) \Im g(\omega, r) \right],$$

where

$$g(\pm\omega, r) = \sum_j \frac{c_{j10} \varphi_{j10}(r)}{\Omega_{j10} + \omega - i/T_2}.$$
For the source terms of the valence band equations we obtain
\[ J_V = M_{01}(E_2 Y_{12}^{(1)} - E_1 Y_{21}^{(1)*}) \]
\[ = \frac{2iM_{01}e^2}{\hbar} \left[ \exp \left( \frac{i \hbar z m_h}{M_{tot}} \right) \eta g(\omega, r) \right] \]
\[ + \exp \left( -i \frac{\hbar z m_h}{M_{tot}} \right) \eta g(-\omega, r) . \]

If irreversible terms are well defined, the equations can be solved and their solutions are then used in the saturating terms on the r.h.s. of the equations. Assuming relaxation time approximation the time dependence of density matrices \( C \) and \( D \) is described as
\[
\frac{\partial C}{\partial t}_{\text{irrev}} = -\frac{1}{\tau} [C(X, r, t) - f_{oe}(r)C(X, r = r_0, t)] - \frac{C(r_0)}{T_1},
\]
\[
\frac{\partial D}{\partial t}_{\text{irrev}} = -\frac{1}{\tau} [D(X, r, t) - f_{oh}(r)D(X, r = r_0, t)] - \frac{D(r_0)}{T_1},
\]
where
\[ X = \frac{1}{2} (r_e + r_h), \]
and \( f_{oe}, f_{oh} \) are normalized Boltzmann distributions for electrons and holes, respectively and \( \tau \) denotes the relaxation time. The relaxation \( T_1 \) stands for interband recombination and \( f_{oe} \) is defined as
\[ f_{oe}(r) = \int d^3 q f_{oe}(q)e^{-iqr} = \exp \left[ -\frac{m_e k_B T}{\hbar^2} r^2 \right] \]
with
\[ f_{oe}(q) = \left( \frac{\hbar^2}{2\pi k_B T} \right)^{3/2} \frac{1}{m_e^{3/2}} \exp \left( -\frac{\hbar^2 q^2}{2m_e k_B T} \right) . \]
where \( T \) is the temperature and \( k_B \) is the Boltzmann constant. Similarly, for the hole equilibrium distribution, we have
\[ f_{oh}(r) = \exp \left( -\frac{m_h k_B T}{\hbar^2} r^2 \right) . \]

Matrices \( C \) and \( D \) are related to charge densities
\[ \rho_e = -eC(r, r), \quad \rho_h = eD(r, r), \]
which are conserved quantities. We therefore have assumed that they relax to an equilibrium normalized to the actual number of carriers. It should be noticed that matrices \( C \) and \( D \) are temperature-dependent and they give an additional contribution for interpretation of temperature variations of excitonic optical spectra. However, the temperature dependence of relaxation constants \( \Gamma_n \) remains a dominant mechanism influencing the spectra. Further, we will assume that our medium is excited homogeneously in \( X \)-space. For \( p \) excitons the matrices \( C \) and \( D \) relax to their values at \( r = r_0 \). In CuQ, the dipole density can be approximated by \( M(r) \propto r \delta(r - r_0) \), which leads to the following expressions for the matrices \( C \), \( D \)
\[ C(r) = -\frac{i}{\hbar} \left[ \tau J_C(r) - \tau J_C(r_0) + T_1 f_{oh}(r)f_{oh}(r_0) \right] , \]
\[ D(r) = -\frac{i}{\hbar} \left[ \tau J_V(r) - \tau J_V(r_0) + T_1 f_{oh}(r)f_{oh}(r_0) \right] . \]

With above expressions the equation for the third order coherent amplitude \( Y_{12}^{(3)} \) takes the form
\[ \hbar \left( \omega + \frac{1}{T_2} \right) Y_{12}^{(3)} - H_{eh} Y_{12}^{(3)} \]
\[ = M_{10}(E_1 C_{12} + E_2 D_{21}) = E(r, t) \tilde{J}_-, \]
\[ \hbar \left( -\omega + \frac{1}{T_2} \right) Y_{12}^{(3)} - H_{eh} Y_{12}^{(3)} \]
\[ = M_{10}(E_1 C_{12} + E_2 D_{21}) = E^*(r, t) \tilde{J}_+, \]
where
\[ \tilde{J}_- = -\frac{i}{\hbar} M_{10} \left\{ \tau \left[ J_C(r)e^{ik_z z_m_e/M_e} \right. \right. \]
\[ + J_V(r)e^{-ik_z z_m_h/M_{tot}} \right. \]
\[ - \tau J_C(r_0)e^{ik_z z_m_e/M_e} - \tau J_V(r_0)e^{-ik_z z_m_h/M_{tot}} \right. \]
\[ + T_1 J_C(r_0)f_{oh}(r)e^{ik_z z_m_h/M_{tot}} \]
\[ + T_1 J_V(r_0)f_{oh}(r)e^{-ik_z z_m_h/M_{tot}} \right\} , \]
\[ \tilde{J}_+ = -\frac{i}{\hbar} M_{10} \left\{ \tau \left[ J_C(r)e^{-ik_z z_m_e/M_{tot}} \right. \right. \]
\[ + J_V(r)e^{ik_z z_m_h/M_{tot}} \right. \]
\[ - \tau J_C(r_0)e^{-ik_z z_m_e/M_{tot}} - \tau J_V(r_0)e^{ik_z z_m_h/M_{tot}} \right. \]
\[ + T_1 J_C(r_0)f_{oh}(r)e^{ik_z z_m_h/M_{tot}} \]
\[ + T_1 J_V(r_0)f_{oh}(r)e^{-ik_z z_m_h/M_{tot}} \right\} . \]

From \( Y_{12}^{(3)} \) one finds the third order polarization according to
\[ P^{(3)}(R) = 2 \int d^3 r \text{Re} M(r) Y_{12}^{(3)}(R, r) \]
\[ = \int d^3 r M(r) \left( Y_{12}^{(3)} + Y_{12}^{(3*)} \right) . \]
The fact that the source terms \( \tilde{J}_\pm \) contain terms proportional either to the relaxation time \( \tau \) or to the interband
recombination time $T_1$ allows a further approximation. For most semiconductors $T_1 \gg \tau$, so the terms proportional to $\tau$ can be neglected. As in the case of linear amplitudes $Y^{(1)}$, we expand the nonlinear amplitudes in terms of the eigenfunctions $\varphi_{nm}(r)$ obtaining

$$
\chi^{(3)}(\omega, k_z^{(1)}) = -\frac{M_1^2}{\epsilon_0 \hbar^2} \sum_n \frac{c_{n10} \Omega_{n0}}{\Omega_{n10}^2 - (\omega + i T_1^{-1})^2} \times \left\{ \text{Im} g(\omega, r_0) + \text{Im} g(-\omega, r_0) \right\} \times \left\langle \varphi_{n10} e^{i k_z^{(1)} z} \frac{m_e}{m_c} f_{0c}(r) + e^{-i k_z^{(1)} z} \frac{m_h}{m_c} f_{0h}(r) \right\}.
$$

where

$$
\left\langle \varphi_{n10} f \right\rangle = \int d^3 r \varphi_{n10}(r) f(r).
$$

Assuming further that $\hbar \omega$ is just below the band edge, with regard to the relation (18), and

$$
\Delta_L T = \frac{\pi}{\epsilon_0 \epsilon_r a^*} M_1^2 \left( \frac{a^*}{r_0} \right)^4 \left( \frac{2 r_0}{r_0 + 2 a^*} \right)^6 = R^* \frac{2 \mu_0 M_1^2}{\pi \epsilon_0 \epsilon_r a^*} f(r_0, a^*),
$$

one obtains

$$
\chi^{(3)} = -\frac{8 \pi \epsilon_0 (\epsilon_0 \Delta_L T)^2 a^*^3}{g_2 r_0} \times \sum_{jn} \left( \frac{\Gamma_j}{\Gamma_{01}} \right) \varphi_{j10}(\rho_0) \sqrt{f_{j1} f_{j1}} E_{Tn1} (A_{n10} + B_{n10}) \left( (E_{Tj1} - E)^2 + \Gamma_j^2 \right) \left[ (E_{Tn1}^2 - (E + i \Gamma_n)^2) \right]^{1/2},
$$

with coefficients

$$
A_{n10} = \left( \varphi_{n10} e^{i k_z z} f_{0c}(r) \right),
B_{n10} = \left( \varphi_{n10} e^{-i k_z z} f_{0h}(r) \right),
$$

where

$$
k_{cz} = k_{cz}^{(1)} \frac{m_e}{M_{tot}},
k_{hz} = k_{hz}^{(1)} \frac{m_h}{M_{tot}},
\Gamma_j = \frac{\hbar}{T_2}, \quad \Gamma_{01} = \frac{\hbar}{T_1},
\varphi_{j10}(\rho_0) = \sqrt{\frac{3}{4 \pi}} P_{j1}(\rho_0), \quad \rho_0 = \frac{r_0}{a^*},
E_{Tn1} = \hbar \Omega_n (k_z = 0), \quad E = \hbar \omega.
$$

V. NONLINEAR OPTICAL FUNCTIONS

Basing on the nonlinear susceptibility $\chi^{(3)}$, one obtains the total index of refraction

$$
\left[ n^{(3)} \right]^2 = \epsilon_b \left[ 1 + \frac{\chi^{(1)}}{\epsilon_b} + \left| E_{prop} \right|^2 \frac{\chi^{(3)}}{\epsilon_b} \right],
$$

where $E_{prop}$ is the amplitude of the wave propagating in the crystal. It is obtained from the equation

$$
\left| E_{prop} \right|^2 = \frac{2}{1 + \sqrt{\epsilon_b}} \zeta P,
$$

where $P$ is the laser power, and $\zeta \approx 377 \Omega$ is the impedance of free space.

Regarding the experiment by Hecktotter et al.\cite{22} carried out at the temperature 1.35 K, we performed the calculations for a Cu$_2$O crystal of thickness 40 $\mu$m, for various powers of the impinging light. The band parameters of cuprous oxide used in the calculations are collected in Table I. We used the damping parameters $\Gamma_n$ obtained by fitting of the experimental curves by Kazimierczuk et al.\cite{31} and Hecktotter et al.\cite{22}.

We start the iteration procedure with the linear polariton problem, taking in the bulk dispersion the antiresonant terms as in the Eq. (18). We obtain the polariton wave vector $k_z^{(1)}$ from Eq. (20) and the bulk polariton amplitude $E_{prop}$. The real and imaginary part of the wave vector are presented in Fig. 2. The relation has been calculated without accounting the spatial dispersion, so we obtained $k_z^{(1)}$ as a one-valued function of the wave energy. The spatial dispersion gives a set of polariton branches and distinct polariton waves. The calculations require the value of amplitudes of the polariton waves. This would lead to the problem of Additional Boundary Conditions (ABC) in the case of a large number of polaritons (as appears in Cu$_2$O) which goes beyond the scope of the present paper.

When the spatial dispersion effects are neglected, the amplitude of the propagating wave results from the standard relation for the half-space geometry (44).

In the second step we compute the third order susceptibility and the total excitonic bulk polarization using as input the linear polariton characteristics.

From the imaginary part one obtains the absorption coefficient

$$
\alpha^{(3)} = 2 \frac{\hbar \omega}{hc} \text{Im} \left[ n^{(3)} \right].
$$

It has been calculated for various laser intensities, in the energetic region of the $n = 10, \ldots 20$ excitonic states (Fig 2). The results are in excellent agreement with the experimental data by Hecktotter et al.\cite{22} the maxima of absorption are vanishing for higher excitonic states, especially for larger laser power. Additionally, the optical bleaching is noticeable, e. g. the overall absorption is decreasing with power. An intensity dependent shift of the positions of the excitonic resonances can be attributed to the interplay between the real and imaginary part of the susceptibility. Here one can notice the advantage of using RDMA which gives simultaneously (without use of Kramers-Kronig relations) both parts of the susceptibility.

Finally, having the intensity dependent index of refraction (43), we can calculate the optical functions (reflectivity, transmissivity, and absorption). We have chosen...
the reflectivity, resulting from the equation

\[ R = \left| \frac{1 - n^{(3)}(P)}{1 + n^{(3)}(P)} \right|^2. \]  

(46)

The results, for the same crystal as above, and in the same energetic region, are shown in Fig. 3. Both quantities, the absorption and the reflectivity, show the decreasing oscillator strengths, which is the main effect of the increasing applied laser power. We have estimated the relative oscillator strengths by integrating the peak area for \( n = 1 - 24 \) excitons, for various laser powers. The results are shown on the Fig. 4. At low power, one obtains the well-known \( n^{-3} \) dependence reported by Kazimierczuk et al.\(^{10} \) evident for the Rydberg states with \( n > 10 \). Our fit gives proper predictions for both \( n \) number and power dependence of the oscillator strengths; as the power increases, the highly excited states are suppressed due to the Urbach tail.\(^{4} \) We have approximated this effect by introducing additional relaxation term \( \Gamma^o = \frac{\Gamma^0}{(E - Eg)^{4/3}} \) which is added to the excitonic relaxation constants \( \Gamma_n \). The constant \( \Gamma^0 \) is obtained by fitting the data on the Fig. 2 to the experimental results by Hecktötter et al.\(^{13} \)

VI. SELF-KERR NONLINEARITY AND SELF-PHASE MODULATION

The self-Kerr interaction is a nonlinear self-interaction of electromagnetic wave which arises during its propagation in the medium that produces a phase shift proportional to the square of the field or, in quantum regime, number of photons in the field. The dependence of the medium polarization, or equivalently the index of refraction, on the intensity of the field, is the base of this effect. The consequences of the Kerr effect is self-phase modulation (SPM); this means that a light wave in the medium experiences a nonlinear phase change; an optical field modifies its own phase. The self-induced phase modulation of a pulse of light is useful measurable parameter and the engineering of self-Kerr interaction is of great interest for processing of optical spectrum of light beams propagating through the media.

In media which are characterized with a non-negligible nonlinear term of susceptibility, the phase of a wave traversing a distance \( L \) increases by \( \varphi = \Delta k_z L \), and increment in phase due to the power-dependent term is equal

\[ \varphi = \frac{\omega}{c} [n^{(3)}(P) - n^{(3)}(0)], \]  

(47)

where \( n^{(3)}(P) \) is the power-dependent part of the refractive index.

It seems that coprous oxide with Rydberg excitons is a superior material for solide-state quantum optics, so we have performed numerical calculations of phase dependence for this medium using results presented in Sec. IV and V. It can be seen from Fig. 5 that the self-Kerr nonlinear phase changes are observed even at relatively low light intensity. One can observe that the phase gets larger if the optical intensity increases and the phase modulation can reach several radians at readily available conditions \((P = 120 \text{ mW}, \text{crystal length } L = 100 \mu \text{m})\). As in the case of absorption, the medium exhibits bleaching; the refraction index and corresponding phase shift is decreasing with power throat the whole spectrum. The self-Kerr nonlinear optical properties of the system can be controlled by changing the crystal size. Due to the absorption, there is an interplay between transmissivity and field intensity. This is shown on the Fig. 6. For any desired phase change, there is a range of parameters for which such a value can be obtained. One can see that while the maximum value of 6 rad is acquired only for very low, practically negligible transmission, the phase change of \( \pi \) can be reached with 10% transmission and \( P \sim 100 \text{ mW} \).

VII. CONCLUSIONS

We have developed a simple mathematical procedure to calculate the nonlinear optical functions of a semiconductor crystal with Rydberg excitons. The experiments with Cu\(_2\)O have made it possible to observe the nonlinear absorption and dependence of oscillator strength on laser power, and our theoretical results show a good agreement with experimental data, facilitating the calculation of absorption spectra for any number of excitonic states in a wide range of conditions (laser power, temperature). Taking advantage of optical functions in nonlinear regime we have studied how SPM, which is a measurable evidence of self-Kerr interaction, can be controlled by laser intensity. Obtained results show that, depending on the length of the crystal, it is possible to reach a phase shift of \( \pi \) for selected excitonic states even for relatively low light intensities. We conclude that the Real Density Matrix Approach is well suited for describing the linear and nonlinear properties of various types of excitons.

ACKNOWLEDGMENTS

Support from National Science Centre, Poland (project OPUS, CIREL 2017/25/B/ST3/00817) is greatly acknowledged.
1. T. Kazimierczuk, D. Fröhlich, S. Scheel, H. Stolz, and M. Bayer, Giant Rydberg excitons in the copper oxide Cu$_2$O, Nature 514, 344 (2014).

2. Zielińska-Raczyńska, D. Ziemkiewicz, and G. Czajkowski, Electro-optical properties of Cu$_2$O for $p$ excitons in the regime of Franz-Keldysh oscillations, Phys. Rev. B 97, 165205 (2018).

3. V. Walther, R. Johne, and T. Pohl, Giant optical nonlinearities from Rydberg excitons in semiconductor microcavities, Nature Communications, 9:1309, (2018).

4. J. Heckötter, M. Freitag, D. Fröhlich, M. Aßmann, M. Bayer, P. Grünwald, F. Schöne, D. Semkat, H. Stolz, and S. Scheel, Rydberg excitons in the presence of an ultralow-density electron-hole plasma, Phys. Rev. Lett. 121, 097401 (2018).

5. S. Zielińska-Raczyńska, G. Czajkowski, and D. Ziemkiewicz, Optical properties of Rydberg excitons and polaritons, Phys. Rev. B 93, 075206 (2016).

6. H. Stolz, F. Schöne, D. Semkat, Interaction of Rydberg Excitons in Cuprous Oxide with Phonons and Photons: Optical Linewidth and Polariton Effect, New. J. Phys. 20, 023019, (2018).

7. T. Kitamura, M. Takahata, and N. Naka, Quantum number dependence of the photoluminescence broadening of excitonic Rydberg states in cuprous oxide, J. Luminescence 192, 808 (2017).

8. C. Li, Optical Kerr Effect and Self-focusing, in: C. Li, Nonlinear Optics, Principlles and Applications (Shanghai and Springer Nature, Singapore, 2017, DOI: 10.1007/978-981-10-1488-8).

9. J. Combes and D. J. Brod, Two-photon self-Kerr nonlinearities for quantum computing and quantum optics, Phys. Rev. A 98, 062313 (2018).

10. A. Stahl and I. Balslev, Electrodynamics of the Semiconductor Band Edge (Springer-Verlag, Berlin-Heidelberg-New York, 1987).

11. D. Frank and A. Stahl, Solid State Commun. 52, 861 (1984).

12. S. Zielińska-Raczyńska, D. Ziemkiewicz, G. Czajkowski, and K. Karpiński, Towards highly-precise tunable electro-modulator based on Franz-Keldysh effect, Phys. Stat. Sol. B 1800502, 2019.

13. G. Czajkowski, F. Bassani, and L. Silvestri, Rivista del Nuovo Cimento 26, 1-150 (2003).

14. S. Zielińska-Raczyńska, D. Ziemkiewicz, and G. Czajkowski, Magneto-optical properties of Rydberg excitons: Center-of-mass quantization approach, Phys. Rev. B 95, 075204 (2017).

15. N. Naka, I. Akimoto, M. Shirai, and Ken-ichi Kan’no, Time-resolved cyclotron resonance in cuprous oxide, Phys. Rev. B 85, 035209 (2012).

FIGURES

FIG. 1: The real and imaginary part of the wave vector $k_z^{(1)}$ of a Cu$_2$O crystal, in the energetic region of $n = 2 - 20$ excitonic states, calculated by Eq. [20].

FIG. 2: The nonlinear absorption coefficient of a Cu$_2$O crystal, in the energetic region of $n = 10 - 20$ excitonic states.
FIG. 3: The nonlinear reflectivity of a Cu$_2$O crystal, in the energetic region of $n = 10$ – 20 excitonic states.

FIG. 4: Dependence of oscillator strength (peak area) on laser power for different $n$ resonances.

FIG. 5: The relative phase shift $\varphi(P) - \varphi(0)$, for various laser powers $P$ and crystal length $L = 100 \mu$m.

FIG. 6: The absolute value of phase shift as a function of absorption coefficient and laser power, for $E = 2171$ meV.

TABLES

| Parameter | Value | Unit | Reference |
|-----------|-------|------|-----------|
| $E_g$     | 2172.08 | meV | 11         |
| $R^*$     | 87.78    | meV | 2          |
| $\Delta_LT$ | $1.25 \times 10^{-3}$ | meV | 9          |
| $m_e$     | 0.99    | $m_0$ | 12         |
| $m_h$     | 0.58    | $m_0$ | 15         |
| $\mu$     | 0.363   | $m_0$ | 12         |
| $\mu'$    | -2.33   | $m_0$ | 12         |
| $M_{tot}$ | 1.56    | $m_0$ | 15         |
| $a^*$     | 1.1     | nm   | 2          |
| $r_0$     | 0.22    | nm   | 2          |
| $\epsilon_b$ | 7.5     |      | 2          |
| $T_1$     | 500     | ns   | 15         |