

Nonlinear optical properties and self-Kerr effect of Rydberg excitons

Sylvia Zielińska-Raczyńska, Gerard Czajkowski, Karol Karpiński, and David Ziemkiewicz*

Institute of Mathematics and Physics, UTP University of Science and Technology, Aleje Profesora Sylwestra Kaliskiego 7, PL 85-789 Bydgoszcz, Poland

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We show how to compute the nonlinear optical functions (absorption, reflection, and transmission) for a medium with Rydberg excitons (REs), 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 are performed for Cu_2O crystal where REs have been observed. We report a good agreement with recently published experimental data. Propagation of the electromagnetic waves in Rydberg exciton media with nonlinear effect is also discussed and the possibility of obtaining self-phase modulation due to Kerr nonlinearity is investigated.

DOI: [10.1103/PhysRevB.99.245206](https://doi.org/10.1103/PhysRevB.99.245206)**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_2O up to a large principal quantum number of $n = 25$ [1]. Such excitons in copper oxide, in analogy to atomic physics, have been named Rydberg excitons (REs). By virtue of their special properties Rydberg excitons have become widely explored in solid and optical physics. These objects, the sizes of which scale as the square of the principal quantum number n , are ideally suited for fundamental quantum interrogations, 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 the 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. [2] for a review). As was observed just in the first experiment [1], the optical line shapes of REs 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 REs have been mainly devoted to the linear optical properties of Rydberg excitons. The nonlinear phenomena with REs were first discussed by Walther *et al.* regarding coupling in the strong interaction of REs and optical photons in a semiconductor microcavity [3]. Also the recent experiment by Heckötter *et al.* [4] has touched on the problem of nonlinear properties of REs in the presence of electron and hole plasma and paved the way to extend the discussion of the optical properties of REs to include nonlinear effects.

In this paper we discuss the role of the exciting light intensity on the RE spectra, considering the impact of simultaneous interband and intraband excitations. As in our previous paper [5], we will use a method based on the real

density-matrix approach (RDMA). This method is an alternative to the many-body approach, which can be used also for explaining Mott transition effects (see, for example, Ref. [6] and references therein). While the experiments with REs were performed at helium temperatures there are in principle no obstacles for observations at temperatures reaching 100 K [7,8]. 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 [7,9]. We derive expressions for the third-order susceptibility $\chi^{(3)}$ which enable us to obtain the formula for the nonlinear optical functions. The calculations are performed for a Cu_2O crystal for which the nonlinear optical functions in the case of quasistationary excitation are analytically calculated.

Rydberg excitons in cuprous 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 wave propagation in the nonlinear regime discussed in the present paper is connected with the 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 RE media. Such an approach might be the first step to develop a new branch of investigations and applications in media with REs; the phenomenon of self-focusing is a promising example [10]. 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 the quantum information context two-photon self-Kerr nonlinearities may be used in quantum computing [11].

The paper is organized as follows. In Sec. II we recall the basic equations of the RDMA and formulate the equations for the case when the interband and intraband electronic

*david.ziemkiewicz@utp.edu.pl

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 then applied in Sec. V, which is devoted to presentation and discussion of the nonlinear optical functions for a Cu₂O crystal. Self-phase modulation in such a system regarding intensity and transmission dependence is discussed in Sec. VI. Finally, in Sec. VII we draw conclusions of nonlinear studies presented in this paper.

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

In the following 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 semiconductor slab to an electromagnetic wave characterized by the electric-field vector:

$$\mathbf{E} = \mathbf{E}_{i0} \exp(i\mathbf{k}_0 \mathbf{R} - i\omega t), \quad k_0 = \omega/c, \quad (1)$$

\mathbf{R} being the excitonic center-of-mass coordinate [see Eq. (8)].

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 $Y(\mathbf{r}_1, \mathbf{r}_2)$ representing the exciton density related to the interband transition, one for the density matrix for electrons $C(\mathbf{r}_1, \mathbf{r}_2)$ (assuming a nondegenerate conduction band), and one for the density matrix for the holes in the valence band, $D(\mathbf{r}_1, \mathbf{r}_2)$. Below we will use the notation

$$Y(\mathbf{r}_1, \mathbf{r}_2) = Y_{12}, \quad \text{etc.} \quad (2)$$

The constitutive equations have the forms of the interband equation

$$i\hbar \partial_t Y_{12} - H_{eh} Y_{12} = -\mathbf{M}\mathbf{E}(\mathbf{R}_{12}) + \mathbf{E}_1 \mathbf{M}_0 C_{12} + \mathbf{E}_2 \mathbf{M}_0 D_{12} + i\hbar \left(\frac{\partial Y_{12}}{\partial t} \right)_{\text{irrev}}, \quad (3)$$

conduction-band equation

$$i\hbar \partial_t C_{12} + H_{ee} C_{12} = \mathbf{M}_0 (\mathbf{E}_1 Y_{12} - \mathbf{E}_2 Y_{21}^*) + i\hbar \left(\frac{\partial C_{12}}{\partial t} \right)_{\text{irrev}}, \quad (4)$$

and valence-band equation

$$i\hbar \partial_t D_{21} - H_{hh} D_{21} = \mathbf{M}_0 (\mathbf{E}_2 Y_{12} - \mathbf{E}_1 Y_{21}^*) + i\hbar \left(\frac{\partial D_{21}}{\partial t} \right)_{\text{irrev}}. \quad (5)$$

The diagonal elements of matrices C and D describe the densities of electrons and holes, respectively. The operator H_{eh} is the effective mass Hamiltonian:

$$\begin{aligned} H_{eh} &= H_{\text{c.m.}} + H_r, \\ H_{\text{c.m.}} &= (-\hbar^2/2) \nabla_R (\underline{M}_{\text{tot}})^{-1} \nabla_R + E_g, \\ H_r &= (-\hbar^2/2) \nabla_r (\underline{\mu}^\lambda)^{-1} \nabla_r + V_{eh}(r), \end{aligned} \quad (6)$$

where $\underline{\mu}$ and $\underline{M}_{\text{tot}}$ are the exciton reduced and total mass tensors, respectively; E_g is the energy gap for the considered pair of energy levels; $H_{\text{c.m.}}$ and H_r are Hamiltonian parts for center-of-mass motion and relative motion, respectively,

$$\begin{aligned} H_{ee} &= -\frac{\hbar^2}{2m_e} (\nabla_1^2 - \nabla_2^2), \\ H_{hh} &= -\frac{\hbar^2}{2m_h} (\nabla_1^2 - \nabla_2^2); \end{aligned} \quad (7)$$

and \mathbf{E}_{12} means that the wave electric field in the medium is taken in a middle point between \mathbf{r}_1 and \mathbf{r}_2 : we take them at the center of mass:

$$\mathbf{R} = \mathbf{R}_{12} = \frac{m_h \mathbf{r}_1 + m_e \mathbf{r}_2}{m_h + m_e}. \quad (8)$$

In the above formulas m_e and m_h are the electron and the hole effective masses (more generally, the effective mass tensors), M_{tot} is the total exciton mass, and μ is the reduced mass of the electron-hole pair. The smeared-out transition dipole density $\mathbf{M}(\mathbf{r})$ is related to the bilocality of the amplitude Y and describes the quantum coherence between the macroscopic electromagnetic field and the interband transitions [12]. The band structure of Cu₂O is included in the form of the transition dipole density \mathbf{M} . The coherent amplitude Y_{12} determines the excitonic part of the polarization of the medium [13]:

$$\begin{aligned} \mathbf{P}(\mathbf{R}, t) &= 2 \int d^3 r \mathbf{M}^*(\mathbf{r}) \text{Re} Y(\mathbf{R}, \mathbf{r}, t) \\ &= \int d^3 r \mathbf{M}^*(\mathbf{r}) [Y(\mathbf{R}, \mathbf{r}, t) + \text{c.c.}], \end{aligned} \quad (9)$$

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 (9) 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

$$\mathbf{P}^{(2)}(\omega_j) = \sum_k \chi^{(2)}(\omega_j, \omega_k) : \mathbf{E}(\omega_k) \mathbf{E}(\omega_j - \omega_k), \quad (10)$$

with the second-order susceptibility

$$\chi^{(2)}(\omega_j, \omega_k) = \int_0^\infty d\tau \int_0^\infty d\tau' \chi^{(2)}(\tau, \tau') e^{-i\omega_j \tau - i\omega_k \tau'}, \quad (11)$$

and for the third-order polarization

$$\begin{aligned} \mathbf{P}^{(3)}(\omega_j) &= \sum_{k,\ell} \chi^{(3)}(\omega_j, \omega_k, \omega_\ell) : \mathbf{E}(\omega_\ell) \\ &\quad \times \mathbf{E}(\omega_k - \omega_\ell) \mathbf{E}(\omega_j - \omega_k), \end{aligned} \quad (12)$$

with the third-order polarization

$$\chi^{(3)}(\omega_j, \omega_k, \omega_\ell) = \int_0^\infty d\tau \int_0^\infty d\tau' \int_0^\infty d\tau'' \chi^{(3)}(\tau, \tau', \tau'') e^{-i\omega_j\tau - i\omega_k\tau' - i\omega_\ell\tau''}. \quad (13)$$

The expressions $\chi^{(2)}(\omega_j, \omega_k) : \mathbf{E}(\omega_k)\mathbf{E}(\omega_j - \omega_k)$ and $\chi^{(3)}(\omega_j, \omega_k, \omega_\ell) : \mathbf{E}(\omega_\ell)\mathbf{E}(\omega_k - \omega_\ell)\mathbf{E}(\omega_j - \omega_k)$ represent vectors with components

$$P_m^{(2)} = \sum_{s,p} \chi_{msp}^{(2)}(\omega_j, \omega_k) E_s(\omega_k) E_p(\omega_j - \omega_k),$$

$$P_m^{(3)} = \sum_{s,p,r} \chi_{mspr}^{(3)}(\omega_j, \omega_k, \omega_\ell) E_s(\omega_\ell) \times E_p(\omega_k - \omega_\ell) E_r(\omega_j - \omega_k). \quad (14)$$

Below we consider the situation with $\omega_j = \omega = -\omega_k = \omega_\ell$ and assume that the incoming field is polarized along the \mathbf{e}_m axis. Then the nonlinear optical response is due to $\chi_{mmmm}^{(3)}(\omega) = \chi^{(3)}(\omega)$, and the third-order polarization will have a \mathbf{e}_m component only, so we can write

$$P_m(\mathbf{k}, \omega) = \epsilon_0 [\chi^{(1)} E_m(\mathbf{k}, \omega) + \chi^{(3)}(\omega, -\omega, \omega) |E_m(\mathbf{k}, \omega)|^2 E_m(\mathbf{k}, \omega)]. \quad (15)$$

We will assume that the transition density vector \mathbf{M} has a component in the direction \mathbf{e}_m and the interband transition is allowed for the given polarization. Once the polarization \mathbf{e}_m is chosen, we will omit the index in further considerations.

III. THE ITERATION PROCEDURE

Following the calculation scheme proposed in Refs. [12,14,15], we calculate the susceptibility $\chi^{(3)}$ iteratively from the dynamic equations (3)–(5). The first step in the iteration consists of solving Eq. (3), which we take in the form

$$i\hbar\partial_t Y_{12H}^{(1)} - H_{eh} Y_{12}^{(1)} = -\mathbf{M}\mathbf{E} + i\hbar \left(\frac{\partial Y_{12}^{(1)}}{\partial t} \right)_{\text{irrev}}. \quad (16)$$

For the irreversible part we assume, as usual, a relaxation-time approximation:

$$\left(\frac{\partial Y_{12}^{(1)}}{\partial t} \right)_{\text{irrev}} = -\frac{1}{T_2} Y_{12} = \frac{-\Gamma}{\hbar} Y_{12}, \quad (17)$$

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

$$\mathbf{E}_{12} = \mathbf{E}(\mathbf{R}, t) + \mathbf{E}^*(\mathbf{R}, t) = \mathbf{E}_0 e^{i(\mathbf{k}\mathbf{R} - \omega t)} + \mathbf{E}_0 e^{-i(\mathbf{k}\mathbf{R} - \omega t)}. \quad (18)$$

Therefore Eq. (16) generate two equations: one for an amplitude $Y_-^{(1)} \propto \exp(-i\omega t)$ and the second for the nonresonant

part $Y_+^{(1)} \propto \exp(i\omega t)$:

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

$$i\hbar \left(-i\omega + \frac{1}{T_2} \right) Y_{12-}^{(1)} - H_{eh} Y_{12-}^{(1)} = -\mathbf{M}\mathbf{E}(\mathbf{R}, t). \quad (19)$$

We will consider only one component of \mathbf{E} and \mathbf{M} . As in our previous papers [5,16] we look for a solution in terms of eigenfunctions of the Hamiltonian H_{eh} , 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 are the corresponding eigenvalues. So we obtain

$$Y_{12-} = E(\mathbf{R}, t) \sum_n \frac{c_{n\ell m} \varphi_{n\ell m}(\mathbf{r})}{\hbar(\Omega_{n\ell m} - \omega - i/T_{2n})},$$

$$Y_{12+} = E^*(\mathbf{R}, t) \sum_n \frac{c_{n\ell m} \varphi_{n\ell m}(\mathbf{r})}{\hbar(\Omega_{n\ell m} + \omega - i/T_{2n})}, \quad (20)$$

where

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

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

$$r = \sqrt{x^2 + y^2 + z^2}, \quad (21)$$

and, in the case of Cu_2O , $E_{g\ell m}$ are the gap energies appropriate for p and f excitons. For the sake of simplicity, we consider only the p exciton contribution. The solutions $Y_{12\pm}^{(1)}$ determine the linear susceptibility

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

$$= \frac{1}{\epsilon_0 \hbar} \sum_{n\ell m} \frac{b_{n1} \Omega_{n\ell m}}{\Omega_{n\ell m}^2 - (\omega + i/T_{2n})^2}, \quad (22)$$

with the coefficients [5]

$$b_{n1} = 2|c_{n10}|^2$$

$$= \frac{8\pi}{3} \left(\int_0^\infty r^2 dr M(r) R_{n1}(r) \right)^2. \quad (23)$$

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

$$\frac{c^2 (k_z^{(1)})^2}{\omega^2} = \epsilon_b + \chi^{(1)}(\omega, k_z^{(1)}). \quad (24)$$

The coefficients b_{n1} can be expressed in terms of the band parameters and, for energies below the gap, one obtains

$$\frac{k_z^{(1)2}}{k_0^2} - \epsilon_b$$

$$= \epsilon_b \sum_{n=2}^N \frac{f_{n1} \Delta_{LT}/R^*}{(E_{Tn} - E - i\Gamma_n)/R^* + (\mu/M_{\text{tot}})(k_z^{(1)} a^*)^2} \quad (25)$$

where $k_0 = \omega/c$, $\Gamma_n = \hbar/T_{2n}$, and E_{Tn} are energies of the exciton resonances, and the oscillator strengths are given

by [5]

$$f_{n1} = \frac{32(n^2 - 1)}{3n^5} \left[\frac{n(r_0 + 2a^*)}{2(r_0 + na^*)} \right]^6. \quad (26)$$

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 [5]

$$M_z(\mathbf{r}) = M_{10} \frac{r + r_0}{2r^2 r_0^2} \sqrt{\frac{4\pi}{3}} Y_{10} e^{-r/r_0}, \quad (27)$$

with the coherence radius r_0 [5,12]:

$$r_0^{-1} = \sqrt{\frac{2\mu_{\parallel}}{\hbar^2} E_g}. \quad (28)$$

IV. ITERATION PROCEDURE: SECOND STEP

Let us consider a wave linearly polarized in the z direction. Then $Y_{\pm}^{(1)}$ [Eq. (20)] are inserted into the source terms of the conduction-band and valence-band equations (4) and (5), respectively. Solving for stationary solutions, we have

$$\begin{aligned} J_C &= M_{10} (E_1 Y_{12}^{(1)} - E_2 Y_{21}^{(1)*}) \\ &= \frac{2iM_{10}E_0^2}{\hbar} \left[\exp\left(ik_z^{(1)}z \frac{m_e}{M_{\text{tot}}}\right) \text{Im} g(-\omega, \mathbf{r}) \right. \\ &\quad \left. + \exp\left(-ik_z^{(1)}z \frac{m_e}{M_{\text{tot}}}\right) \text{Im} g(\omega, \mathbf{r}) \right], \end{aligned} \quad (29)$$

where

$$g(\pm\omega, \mathbf{r}) = \sum_j \frac{c_{j10} \varphi_{j10}(\mathbf{r})}{\Omega_{j10} \mp \omega - i/T_{2j1}}. \quad (30)$$

For the source terms of the valence-band equations (5) we obtain

$$\begin{aligned} J_V &= M_{01} (E_2 Y_{12}^{(1)} - E_1 Y_{21}^{(1)*}) \\ &= \frac{2iM_{10}E_0^2}{\hbar} \left[\exp\left(ik_z^{(1)}z \frac{m_h}{M_{\text{tot}}}\right) \text{Im} g(\omega, \mathbf{r}) \right. \\ &\quad \left. + \exp\left(-ik_z^{(1)}z \frac{m_h}{M_{\text{tot}}}\right) \text{Im} g(-\omega, \mathbf{r}) \right]. \end{aligned} \quad (31)$$

If irreversible terms are well defined, Eq. (5) can be solved and their solutions are then used in the saturating terms on the right-hand side of Eq. (3). Assuming relaxation-time approximation the time dependence of density matrices C and D is described as

$$\begin{aligned} \left(\frac{\partial C}{\partial t}\right)_{\text{irrev}} &= -\frac{1}{\tau} [C(\mathbf{X}, \mathbf{r}, t) - f_{0e}(\mathbf{r}) \\ &\quad \times C(\mathbf{X}, \mathbf{r} = \mathbf{r}_0, t)] - \frac{C(r_0)}{T_1}, \\ \left(\frac{\partial D}{\partial t}\right)_{\text{irrev}} &= -\frac{1}{\tau} [D(\mathbf{X}, \mathbf{r}, t) - f_{0h}(\mathbf{r}) \\ &\quad \times D(\mathbf{X}, \mathbf{r} = \mathbf{r}_0, t)] - \frac{D(r_0)}{T_1}, \end{aligned} \quad (32)$$

where

$$\mathbf{X} = \frac{1}{2}(\mathbf{r}_e + \mathbf{r}_h), \quad (33)$$

and f_{0e} and f_{0h} are normalized Boltzmann distributions for electrons and holes, respectively, and τ denotes the relaxation time. For the considered temperatures $T \sim 10$ K, the use of the Boltzmann distribution is justified because $R^*/k_B T \gg 1$, k_B being the Boltzmann constant [17,18]. The relaxation T_1 stands for interband recombination [14] and f_{0e} is defined as

$$f_{0e}(\mathbf{r}) = \int d^3q f_{0e}(\mathbf{q}) e^{-i\mathbf{q}\mathbf{r}} = \exp\left[-\frac{m_e k_B T}{2\hbar^2} r^2\right]$$

with

$$f_{0e}(\mathbf{q}) = \left(\frac{\hbar^3}{2\pi k_B T}\right)^{3/2} \frac{1}{m_e^{3/2}} \exp\left(-\frac{\hbar^2 q^2}{2m_e k_B T}\right), \quad (34)$$

where T is the temperature. Similarly, for the hole equilibrium distribution, we have

$$f_{0h}(\mathbf{r}) = \exp\left(-\frac{m_h k_B T}{2\hbar^2} r^2\right). \quad (35)$$

Matrices C and D are related to charge densities

$$\rho_e = -eC(\mathbf{r}, \mathbf{r}), \quad \rho_h = eD(\mathbf{r}, \mathbf{r}), \quad (36)$$

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 Γ_n remains a dominant mechanism influencing the spectra. Moreover, for sufficient temperature and optical power, the density matrices C and D inherently include the effect of the Mott transition. Due to the value of the exciton radius in Cu_2O , the Mott density is relatively large, so at least at low temperatures and moderate power density one is below the Mott transition. We remain in this regime, where both excitons and holes define the optical properties. Further, we will assume that our medium is excited homogeneously in \mathbf{X} space. For p excitons the matrices C and D relax to their values at $r = r_0$. In Cu_2O , the dipole density can be approximated by [12] $\mathbf{M}(\mathbf{r}) \propto \mathbf{r}\delta(r - r_0)$, which leads to the following expressions for the matrices C and D :

$$\begin{aligned} C(\mathbf{r}) &= -\frac{i}{\hbar} [\tau J_C(\mathbf{r}) - \tau J_C(r_0) + T_1 f_{0e}(\mathbf{r}) J_C(r_0)], \\ D(\mathbf{r}) &= -\frac{i}{\hbar} [\tau J_V(\mathbf{r}) - \tau J_V(r_0) + T_1 f_{0h}(\mathbf{r}) J_V(r_0)]. \end{aligned} \quad (37)$$

With the above expressions the equation for the third-order coherent amplitude $Y_{12}^{(3)}$ takes the form

$$\begin{aligned} \hbar \left(\omega + \frac{i}{T_2}\right) Y_{12-}^{(3)} - H_{eh} Y_{12-}^{(3)} \\ &= M_{10} (E_1 C_{12} + E_2 D_{21}) = E(\mathbf{R}, t) \tilde{J}_-, \\ \hbar \left(-\omega + \frac{i}{T_2}\right) Y_{12+}^{(3)} - H_{eh} Y_{12+}^{(3)} \\ &= M_{10} (E_1^* C_{12} + E_2^* D_{21}) = E^*(\mathbf{R}, t) \tilde{J}_+, \end{aligned} \quad (38)$$

where

$$\begin{aligned} \tilde{J}_- = & -\frac{i}{\hbar}M_{10}\{\tau[J_C(\mathbf{r})e^{ik_z z m_e/M_z} + J_V(\mathbf{r})e^{-ik_z z m_h/M_{\text{tot}}}] \\ & - \tau J_C(r_0)e^{ik_z z m_e/M_z} - \tau J_V(r_0)e^{-ik_z^{(1)} z m_h/M_{\text{tot}}} \\ & + T_1 J_C(r_0)f_{0e}(\mathbf{r})e^{ik_z^{(1)} z m_e/M_{\text{tot}}} \\ & + T_1 J_V(r_0)f_{0h}(\mathbf{r})e^{-ik_z^{(1)} z m_h/M_{\text{tot}}}\}, \end{aligned} \quad (39)$$

$$\begin{aligned} \tilde{J}_+ = & -\frac{i}{\hbar}M_{10}\{\tau[J_C(\mathbf{r})e^{-ik_z^{(1)} z m_e/M_{\text{tot}}} + J_V(\mathbf{r})e^{ik_z^{(1)} z m_h/M_{\text{tot}}}] \\ & - \tau J_C(r_0)e^{-ik_z^{(1)} z m_e/M_{\text{tot}}} - \tau J_V(r_0)e^{ik_z^{(1)} z m_h/M_{\text{tot}}} \\ & + T_1 J_C(r_0)f_{0e}(\mathbf{r})e^{-ik_z^{(1)} z m_e/M_{\text{tot}}} \\ & + T_1 J_V(r_0)f_{0h}(\mathbf{r})e^{ik_z^{(1)} z m_h/M_{\text{tot}}}\}. \end{aligned} \quad (40)$$

From $Y^{(3)}$ one finds the third-order polarization according to

$$\begin{aligned} P^{(3)}(\mathbf{R}) &= 2 \int d^3 r \text{Re} M(\mathbf{r}) Y^{(3)}(\mathbf{R}, \mathbf{r}) \\ &= \int d^3 r M(\mathbf{r})(Y_{12-}^{(3)} + Y_{12+}^{(3)*}). \end{aligned} \quad (41)$$

The fact that the source terms \tilde{J}_{\pm} contain terms proportional either to the relaxation time τ or to the interband recombination time T_1 allows a further approximation. For most semiconductors $T_1 \gg \tau$, so the terms proportional to τ can be neglected. As in the case of linear amplitudes $Y^{(1)}$, we expand the nonlinear amplitudes in terms of the eigenfunctions $\varphi_{n\ell m}(\mathbf{r})$, obtaining

$$\begin{aligned} \chi^{(3)}(\omega, k_z^{(1)}) &= -\frac{M_{10}^2 T_1}{\epsilon_0 \hbar^3} \sum_n \frac{c_{n10} \Omega_{n10}}{\Omega_{n10}^2 - (\omega + iT_2^{-1})^2} \\ &\times \{[\text{Im} g(\omega, r_0) + \text{Im} g(-\omega, r_0)] \\ &\times \langle \varphi_{n10} | e^{ik_z^{(1)} z \frac{m_e}{M_{\text{tot}}}} f_{0e}(\mathbf{r}) + e^{-ik_z^{(1)} z \frac{m_h}{M_{\text{tot}}}} f_{0h}(\mathbf{r}) \rangle\}, \end{aligned} \quad (42)$$

where

$$\langle \varphi_{n10} | f \rangle = \int d^3 r \varphi_{n10}(\mathbf{r}) f(\mathbf{r}). \quad (43)$$

Assuming further that $\hbar\omega$ is just below the band edge, with regard to the relation (23), and

$$\begin{aligned} \Delta_{\text{LT}} &= \frac{\pi}{\epsilon_0 \epsilon_b a^{*3}} M_{10}^2 \left(\frac{a^*}{r_0}\right)^4 \left(\frac{2r_0}{r_0 + 2a^*}\right)^6 \\ &= R^* \times 2 \frac{2\mu}{\hbar^2} \frac{M_{01}^2}{\pi \epsilon_0 \epsilon_b a^*} f(r_0, a^*), \end{aligned} \quad (44)$$

one obtains

$$\begin{aligned} \chi^{(3)} &= -\frac{8\pi \epsilon_0 (\epsilon_b \Delta_{\text{LT}})^2 a^{*3}}{g_2(r_0)} \sum_{jn} \left(\frac{\Gamma_j}{\Gamma_{01}}\right) \\ &\times \frac{\varphi_{j10}(\rho_0) \sqrt{f_{j1} f_{n1}} E_{Tn1} (A_{n10} + B_{n10})}{[(E_{Tj1} - E)^2 + \Gamma_j^2][E_{Tn1}^2 - (E + i\Gamma_n)^2]}, \end{aligned} \quad (45)$$

TABLE I. Band parameter values for Cu_2O , masses in free-electron mass m_0 .

Parameter	Value	Unit	Reference
E_g	2172.08	meV	[1]
R^a	87.78	meV	[2] ^a
Δ_{LT}	1.25×10^{-3}	meV	[7]
m_e	0.99	m_0	[19]
m_h	0.58	m_0	[19]
μ	0.363	m_0	
μ'	-2.33	m_0	
M_{tot}	1.56	m_0	
a^3	1.1	nm	[2]
r_0	0.22	nm	[5]
ϵ_b	7.5		[1]
T_1	500	ns	

$$^a \frac{2\mu}{\hbar^2} = \frac{1}{R^* (a^*)^2}.$$

with coefficients

$$\begin{aligned} A_{n10} &= \langle \varphi_{n10} | e^{ik_{ez} z} f_{0e}(\mathbf{r}) \rangle, \\ B_{n10} &= \langle \varphi_{n10} | e^{-ik_{hz} z} f_{0h}(\mathbf{r}) \rangle, \end{aligned} \quad (46)$$

where

$$\begin{aligned} k_{ez} &= k_{jz}^{(1)} \frac{m_e}{M_{\text{tot}}}, \quad k_{hz} = k_{jz}^{(1)} \frac{m_h}{M_{\text{tot}}}, \\ \Gamma_j &= \frac{\hbar}{T_{2j}}, \quad \Gamma_{01} = \frac{\hbar}{T_1}, \\ \varphi_{j10}(\rho_0) &= \sqrt{\frac{3}{4\pi}} R_{j1}(\rho_0), \quad \rho_0 = \frac{r_0}{a^*}, \\ E_{Tn1} &= \hbar \Omega_n(k_z = 0), \quad E = \hbar \omega. \end{aligned} \quad (47)$$

V. NONLINEAR OPTICAL FUNCTIONS

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

$$[n^{(3)}]^2 = \epsilon_b \left[1 + \frac{\chi^{(1)}}{\epsilon_b} + |E_{\text{prop}}|^2 \frac{\chi^{(3)}}{\epsilon_b} \right], \quad (48)$$

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

$$|E_{\text{prop}}|^2 = 2 \left| \frac{2}{1 + \sqrt{\epsilon_b}} \right|^2 \zeta P, \quad (49)$$

where P is the laser power, and $\zeta \approx 377 \Omega$ is the impedance of free space. Regarding the experiment by Heckötter *et al.* [4] carried out at the temperature 1.35 K, we performed the calculations for a Cu_2O crystal of thickness 40 μm , for various powers of the impinging light. For the lowest excitonic state considered in the paper ($n = 10$), the upper limit for exciton density, assuming that all the absorbed energy is used to create excitons and no Rydberg blockade is present, is $\rho_E \sim 10^{15} \text{ cm}^{-3}$. The band parameters of cuprous oxide used in the calculations are collected in Table I. Important parameters such as Bohr radius, effective masses, and longitudinal-transverse splitting are taken from the literature [7,19] and the Rydberg energy is calculated accordingly. We used the

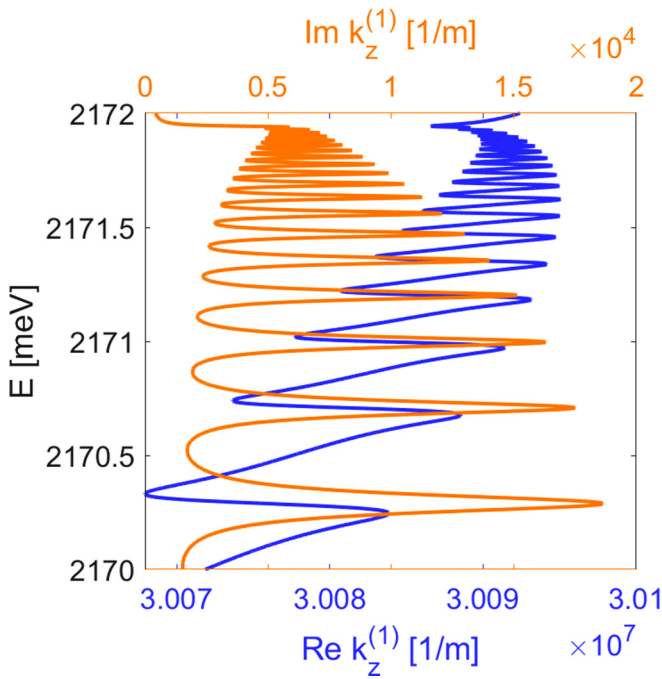


FIG. 1. The real and imaginary part of the wave vector $k_z^{(1)}$ of a Cu_2O crystal, in the energetic region of $n = 2$ – 20 excitonic states, calculated by Eq. (25).

damping parameters Γ_n obtained by fitting of the experimental curves by Kazimierczuk *et al.* [1] and Heckötter *et al.* [4]. The dependence on the temperature owing to the Boltzmann distribution is very weak, and a much larger impact of the temperature increase is dependent on the energy gap and the dissipation constants, as was noticed, for example, in Ref. [18].

We start the iteration procedure with the linear polariton problem, taking in the bulk dispersion the antiresonant terms as in Eq. (22). We obtain the polariton wave vector $k_z^{(1)}$ from Eq. (25) and the bulk polariton amplitude E_{prop} . The real and imaginary parts of the wave vector are presented in Fig. 1.

It is known that the separation of the center of exciton masses and electron-hole relative motion in excitons is not possible in a complex valence band. However, most of the authors dealing with the topic make this assumption, and the obtained theoretical shapes of the optical functions (for example, absorption) agree very well with the experimental data. We do not neglect the effect of the nonzero exciton center-of-mass wave vector. It is used in the calculation of the electron (hole) density matrices C and D [see Eq. (42)]. On the other hand, we neglect the c.m. vector in the denominator of the polariton dispersion relation [Eq. (25)]. As a consequence, we do not consider the separate polariton branches. In the calculations, detailed knowledge of the polariton amplitudes, corresponding to every branch, is needed. To calculate the amplitudes, one has to solve the boundary problem with at least $2n$ polariton waves (or $4n$, when including the reflected waves). This problem is related to the so-called additional boundary conditions (ABCs) problem, since the ordinary Maxwell boundary conditions are not sufficient. In semiconductors, where few excitonic states were considered, many

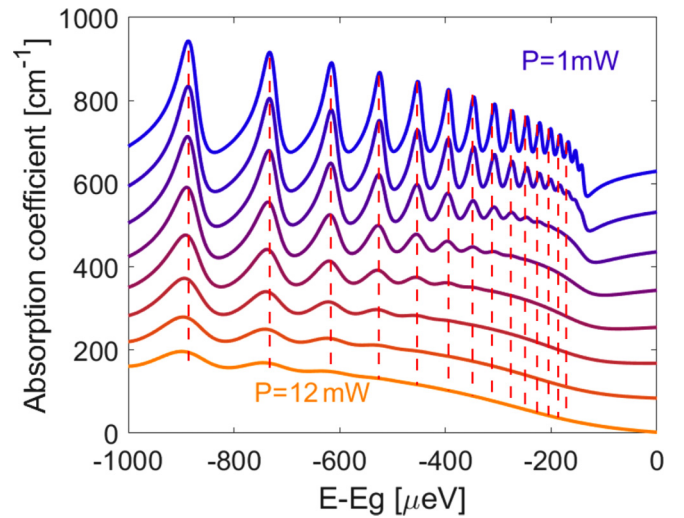


FIG. 2. The nonlinear absorption coefficient of a Cu_2O crystal, in the energetic region of $n = 10$ – 20 excitonic states. Dashed lines mark the resonance positions reported in Ref. [4]. For clarity, absorption spectra are separated vertically.

models for ABCs have been proposed, and the solution is possible. When considering REs, the number of ABCs should be at least $2n$ (for half-space geometry). To our best knowledge, the ABCs for RE polaritons in Cu_2O were not proposed. Therefore we did not consider this problem, as it is beyond the scope of this paper.

When the spatial dispersion effects are neglected, the amplitude of the propagating wave results from the standard relation for the half-space geometry (49). 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:

$$\alpha^{(3)} = 2 \frac{\hbar\omega}{\hbar c} \text{Im} n^{(3)}. \quad (50)$$

It has been calculated for various laser intensities, in the energetic region of the $n = 10, \dots, 20$ excitonic states (Fig. 2). The results are in excellent agreement with the experimental data by Heckötter *et al.* [4]; the maxima of absorption vanish for higher excitonic states, especially for larger laser power. Additionally, optical bleaching is noticeable, e.g., the overall absorption decreases with power. 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 (48), we can calculate the optical functions (reflectivity, transmissivity, and absorption). We have chosen the reflectivity, resulting from the equation [17]

$$R(\omega, L) = R_\infty(\omega) + \{1 - [R_\infty(\omega)]^2\} R_\infty(\omega) \times \exp[-2\alpha(\omega)L], \quad (51)$$

$$R_\infty = \left| \frac{1 - n^{(3)}}{1 + n^{(3)}} \right|^2.$$

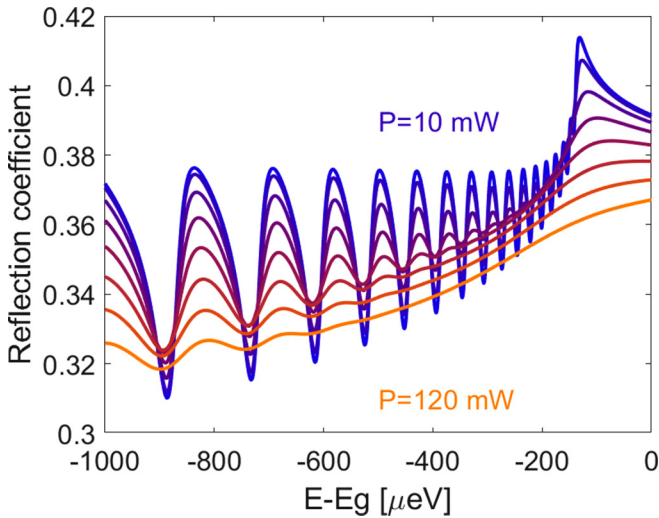


FIG. 3. The nonlinear reflectivity of a Cu_2O crystal, in the energetic region of $n = 10\text{--}20$ excitonic states.

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 $n = 1\text{--}24$ excitons, for various laser powers. The results are shown in Fig. 4. At low power, one obtains the well-known n^{-3} dependence reported by Kazimierczuk *et al.* [1] 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 $\Gamma' = \frac{\Gamma'_0}{(E-E_g)^{3/2}}$, which is added to the excitonic relaxation constants Γ_n . The constant Γ'_0 is obtained by fitting the data in Fig. 2 to the experimental results by Heckötter *et al.* [4].

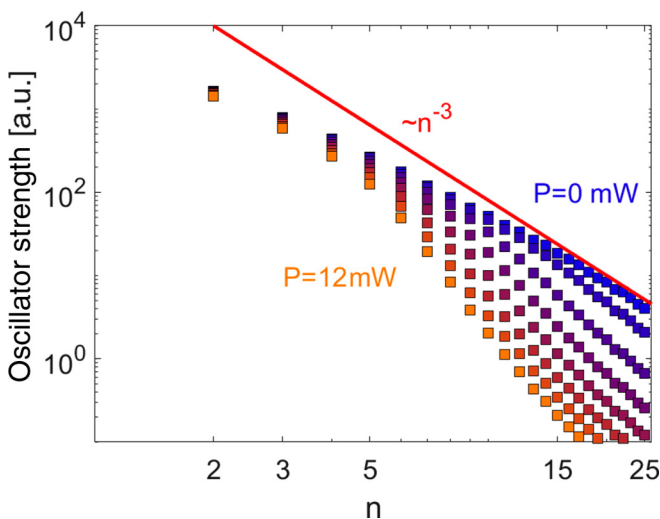


FIG. 4. Dependence of Oscillator strength (peak area) on laser power for different n resonances.

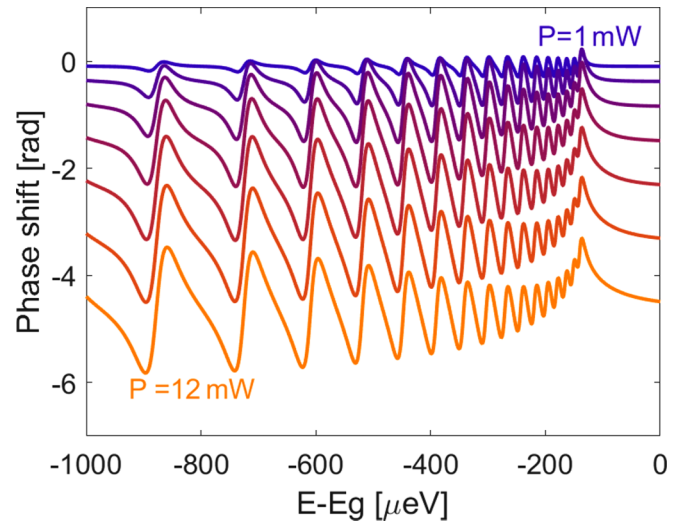


FIG. 5. The relative phase shift $\varphi(P) - \varphi(0)$, for various laser powers P and crystal length $L = 100 \mu\text{m}$.

VI. SELF-KERR NONLINEARITY AND SELF-PHASE MODULATION

The self-Kerr interaction is a nonlinear self-interaction of an electromagnetic wave which arises during its propagation in the medium that produces a phase shift proportional to the square of the field or, in the 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 basis of this effect. The consequence of the Kerr effect is self-phase modulation; 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 a useful measurable parameter and the engineering of self-Kerr interaction is of great interest for processing of the 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 the increment in phase due to the power-dependent term is equal to

$$\varphi = \frac{\omega}{c} [n^{(3)}(P) - n^{(3)}(0)], \quad (52)$$

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

It seems that cuprous oxide with Rydberg excitons is a superior material for solid-state quantum optics, so we have performed numerical calculations of phase dependence for this medium using results presented in Secs. 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 ($P = 12 \text{ mW}$, crystal length $L = 100 \mu\text{m}$). As in the case of absorption, the medium exhibits bleaching; the refraction index and corresponding phase shift decrease with power through the whole spectrum. The self-Kerr nonlinear optical properties of the system can be

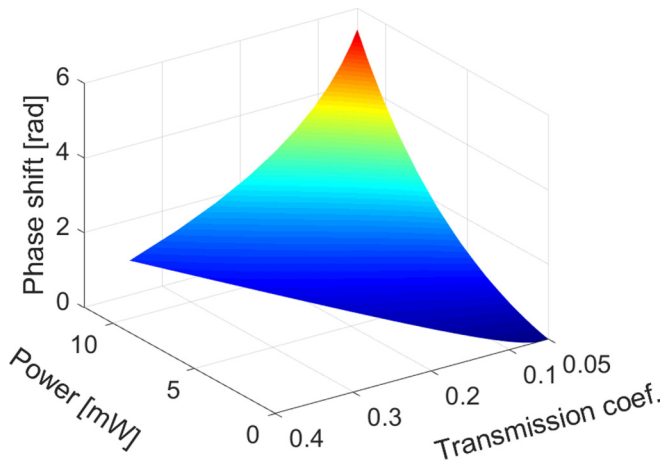


FIG. 6. The absolute value of phase shift as a function of absorption coefficient and laser power, for $E = 2171$ meV.

controlled by changing the crystal size. Due to the absorption, there is an interplay between transmission and field intensity. This is shown in 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 π can be reached with 10% transmission and $P \sim 10$ 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_2O 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, etc.). Taking advantage of optical functions in the 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 π 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

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- [1] T. Kazimierczuk, D. Fröhlich, S. Scheel, H. Stolz, and M. Bayer, Giant Rydberg excitons in the copper oxide Cu_2O , *Nature (London)* **514**, 343 (2014).
- [2] S. Zielińska-Raczyńska, D. Ziemkiewicz, and G. Czajkowski, Electro-optical properties of Cu_2O for p excitons in the regime of Franz-Keldysh oscillations, *Phys. Rev. B* **97**, 165205 (2018).
- [3] V. Walthers, R. Johnes, and T. Pohl, Giant optical nonlinearities from Rydberg excitons in semiconductor microcavities, *Nat. Commun.* **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] G. Manzke, D. Semkat, and H. Stolz, Mott transition of excitons in GaAs-GaAlAs quantum wells, *New J. Phys.* **14**, 095002 (2012).
- [7] H. Stolz, F. Schöne, and D. Semkat, Interaction of rydberg excitons in cuprous oxide with phonons and photons: Optical linewidth and polariton effect, *New J. Phys.* **20**, 023019 (2018).
- [8] 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).
- [9] S. Zielińska-Raczyńska, D. Ziemkiewicz, G. Czajkowski, and K. Karpiński, Towards highly-precise tunable electro-modulator based on Franz-Keldysh effect, *Phys. Status Solidi B* **256**, 1800502 (2019).
- [10] C. Li, Optical Kerr effect and self-focusing, in *Nonlinear Optics, Principles and Applications*, edited by C. Li (Springer, New York, 2017).
- [11] J. Combes and D. J. Brod, Two-photon self-Kerr nonlinearities for quantum computing and quantum optics, *Phys. Rev. A* **98**, 062313 (2018).
- [12] A. Stahl and I. Balslev, *Electrodynamics of the Semiconductor Band Edge* (Springer-Verlag, Berlin, 1987).
- [13] G. Czajkowski, F. Bassani, and A. Tredicucci, Polaritonic effects in superlattices, *Phys. Rev. B* **54**, 2035 (1996).
- [14] D. Frank and A. Stahl, Nonlinear susceptibility χ^3 in a direct gap semiconductor derived from coupled inter- and intraband equations of motion, *Solid State Commun.* **52**, 861 (1984).
- [15] G. Czajkowski, F. Bassani, and L. Silvestri, Excitonic optical properties of nanostructures: Real density matrix approach, *Rivista del Nuovo Cimento* **26**, 1 (2003).
- [16] 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).
- [17] C. F. Klingshirn, *Semiconductor Optics* (Springer, New York, 2012).
- [18] C. Malerba, F. Biccari, C. L. A. Ricardo, M. D’Incau, P. Scardi, and A. Mittiga, Absorption coefficient of bulk and thin film Cu_2O , *Solar Energy Mater. Solar Cells* **95**, 2848 (2011).
- [19] N. Naka, I. Akimoto, M. Shirai, and K.-i. Kan’no, Time-resolved cyclotron resonance in cuprous oxide, *Phys. Rev. B* **85**, 035209 (2012).