Excitons in Cu\textsubscript{2}O - from Quantum Wells to Bulk Crystals and Additional Boundary Conditions for Rydberg Exciton - Polaritons

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(Dated: December 2, 2019)

We propose a scheme for calculation of optical functions of a semiconductor with Rydberg excitons, for a wide interval of dimensions. We start with 2-dimensional structure, then going to thin films and ending on 3-dimensional bulk crystals. The calculations including the polaritons are performed, the case of large number of polariton branches is discussed and obtained theoretical absorption spectra show good agreement with experimental data.

PACS numbers: 71.35.-y,78.20.-e,78.40.-q

I. INTRODUCTION

Since 2014 Rydberg excitons (RE) in cuprous oxide observed by Kazimierczuk et al.\textsuperscript{11} have been subject of extensive research. Unusual properties of RE manifested in their interaction with external fields below and above the gap energy in linear and nonlinear regime have been studied, both experimentally and theoretically.\textsuperscript{12-15} The list being far from completeness.

The theoretical description of the optical properties of RE can be done in several ways. One manner is to apply the mesoscopic Real Density Matrix Approach (RDMA), which allows one to obtain analytical expressions for the optical functions of semiconductor crystals, including RE with a high principal quantum number, also for the case of indirect interband transitions, as it was done in the series of papers by S. Zielińska-Raczyńska et al.\textsuperscript{16,17}. In these papers the bulk crystals, in the form of slabs of thickness \(L\), much larger than the excitonic Bohr radius, were considered. This approach has turned out to be very useful and allows one to obtain detailed description of RE resonances in various external fields configurations. More recently this allows extend subject of our interest to potential applications of RE in cuprous oxide; the proposals have been put forward to use inter-series transitions between RE levels for the implementation of tunable excitonic masers\textsuperscript{18,20} and to apply RE for designing a tunable electro-modulator.\textsuperscript{19} Generally speaking the majority of papers on RE in Cu\textsubscript{2}O considered RE in bulk crystals or in plane-parallel slabs with dimensions much greater than the incident wave length, and the effective Bohr radius.

Recently one can observe a growing interest on optical properties of low dimensional systems (LDS) (Quantum Wells, Wires, and Dots) with Rydberg excitons.\textsuperscript{21,22} Takahata et al.\textsuperscript{22} have begun the studies on RE in low dimension structures performing the observations of non-local response of weakly confined RE in plane-parallel Cu\textsubscript{2}O films, the thickness of which ranging from 16 nm to 2000 nm, which are much smaller than those from first experiments i.e., in Ref.\textsuperscript{16,17} where the bulk dimension was around 30-50 \(\mu\)m. Konzelmann et al.\textsuperscript{22} has studied theoretically the optical properties of LDS with Rydberg excitons, focusing their attention on the impact of confinement potentials on the energy shifts of Rydberg excitons in Cu\textsubscript{2}O Quantum Wells, wires, and dots. Inspired by results of Takahata et al\textsuperscript{22}, we aim to overcome such a limitation, by extending the RDMA to thinner slabs, reaching the Quantum Well (QW) limit, still taking into account multiple Rydberg states. Quantum size effects become important when the thickness of the layer becomes comparable with the de Broglie wavelength of the electrons or holes. Regarding the dimension of structures with quantum-confinement effects one can distinguish between Quantum Wells, Wide Quantum Wells (WQW), ending with dimensions which can be called exciton-polariton regime. In each situations the theoretical description should be different, since the various relations between the optical confinement (characterized by the ratio between wave lengths \(\lambda\) and dimension \(L\)), the quantum-mechanical confinement (the ratio of a size in the growth direction to the effective exciton Bohr radius) and the coherence length, have to be taken into account. In the present paper we will discuss all these situations. With the help of RDMA we will consider the RE states in such quantum-confined structures and the optical properties which characterized such systems. Moreover, the role of polaritons, being the superpositions of electromagnetic field and quantum coherences modes, will be considered and the influence of their relative contribution on matching the experimental and calculated resonances positions will be presented. It should be mentioned that quantum-confined structures with RE may be of interest both to research scientists who would be able to explore uncharted areas of fundamental physics of RE in semiconductors in confined geometry and to engineers who might use their unique properties for device applications in the future. This insight may paved the way for a whole new breed of apparatus such as detectors and optoelectronical switches.

The paper is organized as follows. In Sec. II we recall the basic equations of the RDMA and formulate the equations for the case of Quantum Wells with Rydberg
excitons. In Sec. II the equations of Sec. II are adapted for the case of Wide Quantum Wells. In Sec. IV we discuss the case of bulk crystals, where the optical properties for exciting energies near the fundamental gap are dominated by exciton-polaritons. Using a generalization of Pekar’s ABCs we show how to obtain the amplitudes of polariton waves and optical properties from them. The formulas, derived in Sections II-IV, are then applied in Sec. V, which is devoted to presentation and discussion of optical properties for Cu2O QWs, QWWs, and bulk crystals. Sec. VI contains conclusions of the studies presented in the paper.

II. QUANTUM WELL REGIME

We study the optical properties of RE having in mind the experiments where Cu2O is the medium interacting with the electromagnetic waves. Due to properties of this crystal, the lowest exciton state has the p symmetry with the extension of about 4 nm. Therefore a slab with the thicknesses, e.g., 10-20 nm, can be considered as a Quantum Well, and the methods, developed for the optical properties of QWs, can be applied. Optical properties of semiconducting quantum wells have attracted much interest in the recent decades. The main stream of investigations, both experimental and theoretical, was devoted to purely electronic excitations (excitons), see, for instance, refs. [23-27] and to basic optical features, like photoabsorption, reflectivity and photoluminescence. Here we will use the Real Density Matrix Approach, applied to systems with reduced dimensionality, showing the phenomenon of Rydberg states. In this approach the optical properties are described by equations for the coherent amplitudes $Y_{ab}^{\alpha b}$ of the electron-hole pair of coordinates $\mathbf{r}_1 = \mathbf{r}_h$ and $\mathbf{r}_2 = \mathbf{r}_e$ which for any pair of conduction and valence $\alpha$ and $b$ read:

$$-i\hbar \partial_t + \Gamma_{ab} Y_{ab}^{\alpha b} + H_{ehab} Y_{ab}^{\alpha b} = M_{ab} E,$$  \hspace{1cm} (1)

where $\Gamma_{ab} = \hbar / T_{ab}^{\alpha b}$ is a phenomenological damping coefficient. As we have stated in previous papers[23,24] RDMA is a mesoscopic approach which, in the lowest order, neglects all effects from the multiband semiconductor structure, so that the exciton Hamiltonian becomes identical to that of the two-band effective mass Hamiltonian $H_{ch}$, which includes the electron and hole kinetic energy, the electron-hole interaction potential and the confinement potentials (see also Ref[25]). In consequence, the two-band Hamiltonian $H_{ehab}$ with gap $E_{ghab}$ for any pair of bands is

$$H_{ehab} = E_{ghab} + \frac{p_{2\alpha}^2}{2m_{\alpha}} + \frac{p_{2b}^2}{2m_{b}} + V_{eh}(1,2) + V_h(1) + V_e(2),$$  \hspace{1cm} (2)

where the second and the third term on the r.h.s. give the electron and the hole kinetic energy operators with band effective masses, the fourth term is the electron-hole attraction, and the two last terms are the surface confinement potentials on electron and hole. The total polarization of the medium is related to the coherent amplitudes by

$$\mathbf{P}(\mathbf{R}) = 2 \sum_{\alpha,...} \text{Re} \int d^3\mathbf{r} M_{\alpha}(\mathbf{r}) Y^{\alpha}(\mathbf{R}, \mathbf{r}),$$  \hspace{1cm} (3)

where the summation includes all allowed excitonic transitions between the valence ($v = \alpha, \beta, \ldots$) and conduction $c = a, b, \ldots$ bands. The above equations are the constitutive equations which connect linearly the polarization to the electric field, which in addition must obey Maxwell’s equations. The constitutive equation for a QW with one valence and one conduction band takes the form

$$\begin{bmatrix}
E_g - \hbar \omega - i G + \frac{p_2^2}{2m_e} + \frac{p_2^2}{2m_h} + \frac{p_2^2}{2M} + \frac{P^2||}{2M||} \\
+ V_{ch}(z_e - z_h, \rho) + V_e(z_e) + V_h(z_h)
\end{bmatrix} Y(\rho, z_e, z_h) = M(\rho, z_e, z_h) E(R||, Z),$$  \hspace{1cm} (4)

where we have separated the center-of-mass coordinate $\mathbf{R}$ from the relative coordinate $\rho$ on the plane $x - y$. In the above equations $V_{ch}(z_e, z_h)$ are the confining potentials in the $z$-direction, while $V_{eh}$ is the electron-hole interaction potential. The harmonic-type time dependence is considered, $\omega$ being the frequency of the driving electric field.

When one aims to consider the effects of Rydberg excitons the excitonic states of an arbitrary order $j$ have to be included. In the cases of Quantum Wells and Wide Quantum Wells the higher order states are easily obtained when we consider a "2-dimensional" form of the electron-hole potential,

$$V_{eh}(\rho) = \frac{-e^2}{4\pi\epsilon_0\epsilon_b\rho},$$  \hspace{1cm} (5)

where $\rho = \sqrt{x^2 + y^2}$ and $\epsilon_b$ is the background dielectric function of the QW material. For any confinement functions $u_{N_e}, u_{N_h}$ (which may be due to step-like or parabolic type potentials), we obtain the amplitudes $Y$ in the form

$$Y(\rho, z_e, z_h, \phi) = \sum_{j,m} \sum_{N_e, N_h} C_{jm} N_e N_h u_{N_e}(z_e) u_{N_h}(z_h) \times \frac{e^{im\phi}}{\sqrt{2\pi}} \psi_{j}^{(2D)}(\rho),$$  \hspace{1cm} (6)

where $\psi_{j}^{(2D)}(\rho)$ are the eigenfunctions of the Schrödinger
equation with the potential \[5\] which have the form
\[
\psi_{jm} = \frac{1}{a^* \sqrt{2\pi}} e^{im\phi} e^{-2\lambda\rho/a^*} (4\lambda\rho)^m 4\lambda^{3/2} \frac{1}{(2m)!} \frac{[(j + 2m)!]^{1/2}}{[j!]^{1/2}}
\]
\[
\times e^{-2\pi a^*/\lambda\rho} \lambda\rho (j + 1, 4\lambda\rho),
\]
\[
\times M (-j, 2|m| + 1, 4\lambda\rho),
\]
\[
\lambda = \frac{1}{1 + 2(j + |m|)},
\]
corresponding to the eigenvalues
\[
\frac{E_{jm}}{R^*} = \varepsilon_{jm} = - \frac{4}{1 + 2(j + |m|)^2},
\]
where \(M(a, b, z)\) is the Kummer’s function in the notation of Ref.\[22\] and \(a^*, R^*\) are the excitonic Bohr radius and Rydberg energy, respectively. Note that the energy \(E_{jm}\) is usually modified with a quantum defect \(\delta\), which replaces \(j \) with \(j - \delta\), shifting mostly low-\(j\) states in a manner better reflecting the experimental data. With the help of the amplitude \(Y\) we can calculate the polarization from Eq. \(3\) and by an appropriate assumption on the wave electric vector \(E\) (regarding the dimension), we obtain the effective QW susceptibility and other optical functions. For further considerations we must define the transition dipole density \(M\). We assume that the wave propagating in QW is linearly polarized in \(y\) direction and the transition dipole has a component in the same direction, having the form\[13\]
\[
M(\rho, z_e, z_h, \phi) = \frac{M_0}{2\rho_0} \rho e^{-\rho/\rho_0} \frac{e^{i\phi}}{\sqrt{2\pi}} \delta(z_e - z_h),
\]
with the integrated strength \(M_0\) and the coherence radius \(\rho_0\). The coherence radius and the strength \(M_0\) are related to the longitudinal-transverse energy \(\Delta_{LT}\) in the considered QW regime the typical wavelength of the input electromagnetic wave is much larger than the QW dimension, so one usually uses the long wave approximation. With this approximation, inserting the formulas \(7\) into the constitutive equation \(4\) and the polarization \(9\), we obtain the effective susceptibility in the form
\[
\chi^{(2D)}(\omega) = \frac{\varepsilon_b \Delta_{LT} a^* f_j^{(2D)} a_{N_e, N_h}}{jN_{jN_e, N_h}} (E_g - \hbar\omega + E_j + W_{N_e} + W_{N_h} - i\Gamma_{jN_e, N_h}),
\]
\[
= 48 \frac{(j + 1)(j + 2)}{(j + 3)\lambda^{3/2}} \frac{1}{1 + 2\lambda\rho_0^2} \left[F\left(-j, 4; 3; \frac{4\lambda\rho_0}{1 + 2\lambda\rho_0}\right)^2\right],
\]
\[
E_j = - \frac{4}{(2j + 3)^2} R^*,
\]
\[
a_{N_e, N_h} = \int_{-\infty}^{\infty} u_{N_e}(z) u_{N_h}(z) dz,
\]
where \(W_{N_e}, W_{N_h}\) are the eigenvalues of the confinement eigenfunctions, \(F(a; b; c; z)\) is the Gauss hypergeometric series,\[23\] and the damping coefficients \(\Gamma_{jN_e, N_h}\) should be specified for any set of quantum numbers. For the sake of simplicity, we assume the infinite step-like confinement potentials for the electrons and the holes, so the eigenvalues have the following form
\[
u_{N_e, h}(z) = \sqrt{\frac{2}{L}} \sin \left(\frac{N_{e, h} \pi z}{L}\right),
\]
\[
W_{N_e} = \frac{\mu}{m_e} \left(\frac{\pi a^*}{L}\right)^2 N_e^2 R^*,
\]
\[
W_{N_h} = \frac{\mu}{m_h} \left(\frac{\pi a^*}{L}\right)^2 N_h^2 R^*.
\]
Using the above expressions \(11\) we obtain the final form of the QW effective susceptibility
\[
\chi^{(2D)} = \frac{(a^* L)}{\lambda} \sum_{j, N_e, N_h} \varepsilon_b \Delta_{LT} f_j^{(2D)} \frac{e^{-\rho/\rho_0}}{\sqrt{2\pi}} \delta(z_e - z_h),
\]
\[
\approx \frac{\varepsilon_b \Delta_{LT} f_{jN_e, N_h}}{\sqrt{\varepsilon_b}},
\]
where \(\delta = \varepsilon_b + \chi^{(2D)}\) is the effective dielectric function. Assuming that the electromagnetic wave enters normally from the medium I (barrier) to the medium II (QW), we can calculate other optical functions, the reflectivity \(R\) and transmissivity \(T\), by the known formulas (for example, Ref.\[24\])
\[
\hat{T} = \frac{A}{1 + F \sin^2 \delta},
\]
\[
\hat{R} = \frac{B + F \sin^2 \delta}{1 + F \sin^2 \delta},
\]
\[
F = \frac{4R_a}{(1 - R_a)^2},
\]
\[
A = \frac{e^{-\alpha L}(1 - R)^2}{(1 - R_a)^2},
\]
\[
B = \frac{R(1 - R_a)}{(1 - R_a)^2},
\]
where \(R = RF = RB\) is the reflectivity of a front or a back surface of the slab
\[
R = \left(\frac{n_1 - n_2}{n_1 + n_2}\right)^2,
\]
\[
R_a = Re^{-\alpha L},
\]
\[
\delta = Re\sqrt{\varepsilon_b + \chi^{(2D)}k_0L} = L \frac{\hbar\omega}{hc} \Re \sqrt{\varepsilon_b + \chi^{(2D)}}.
\]
III. WIDE QUANTUM WELL REGIME

When the thickness of the considered QW increases, one arrives at the situation where the thickness is larger than the wavelength of the propagating wave. When Cu$_2$O is the QW medium, it corresponds to the width of about 300 nm. This is the Wide Quantum Well regime. On the other hand, such thickness is to small for formation of exciton-polaritons, particularly these corresponding to higher states with $j > 5$. The long wave approximation cannot be maintained, but we can assume that the electric field of the wave is varying slowly, and use the so-called slow field approximation for solving the QW Maxwell equation (see, for example, Refs. 24-26). For the slow varying field the Maxwell equation for the relevant electric vector component inside the QW satisfies the equation

$$\frac{d^2 E}{dz^2} + f(z)E = 0,$$  \hspace{1cm} (16)

with

$$f(z) = \frac{\omega^2}{c^2} [\epsilon_b + \chi(z)].$$  \hspace{1cm} (17)

The non-local susceptibility $\chi(z)$ will be obtained from the constitutive equation \hspace{1cm} (4). In the conditions of slow-varying field the solution of the Maxwell equation reads

$$E(z) = A_1(z)e^{i\beta(z)} + A_2(z)e^{-i\beta(z)},$$ \hspace{1cm} (18)

where

$$\beta(z) = \int [f(z)]^{1/2} dz, \quad A_i = a_i [f(z)]^{-1/4}.$$ \hspace{1cm} (19)

The coefficients $a_i$ are obtained with the help of the Maxwell boundary conditions for the electric field. Thus, the field $E$ within the QW allows one to calculate the optical functions in the analytical form manifesting their dependence on the confinement shape.

For the infinite confinement potential, using the eigenfunctions \hspace{1cm} (11), the nonlocal susceptibility has the form

$$\chi(z) =$$ \hspace{1cm} 

$$= \frac{2a^*}{L} \sum_{j,N} \frac{\epsilon_b \Delta_{LT} f^{(2D)}_{j}}{E_g - \hbar \omega + E_j + W_N - i\Gamma_{jN}} \sin^2 \frac{N \pi z}{L}.$$ \hspace{1cm} (20)

Inserting the above susceptibility into Eq. \hspace{1cm} (19) one obtains

$$\beta(z) \approx$$ \hspace{1cm} 

$$= q(z)z,$$ \hspace{1cm} (21)

With the help of $\beta(z)$ one is able to calculate the electric field and finally the QW reflectivity, which has the following form

$$\hat{R} = \left| \frac{r_{\infty} (1 - e^{i\Theta})}{1 - r_{\infty} e^{i\Theta}} \right|^2, \quad \Theta = 2q(0)L,$$ \hspace{1cm} (22)

where

$$r_{\infty} = \frac{k_0 - q(0)}{k_0 + q(0)} = 1 - \frac{\sqrt{\epsilon_b} [1 + \chi^{(2D)} / \epsilon_b]}{1 + \sqrt{\epsilon_b} [1 + \chi^{(2D)} / \epsilon_b]}.$$ \hspace{1cm} (23)

In a similar way we compute the WQW transmission coefficient

$$\hat{T} = \left| \frac{1 - n_{WQW}^2}{1 + n_{WQW}^2} \right|^2.$$ \hspace{1cm} (24)

The equation \hspace{1cm} (22) can be put into an equivalent form

$$\hat{R} = \left[ 1 - \frac{n_{WQW}}{1 + n_{WQW}} \right]^2,$$ \hspace{1cm} (25)

by means of an effective refraction index $n_{WQW}$

$$n_{WQW} = \frac{1 - r_{\infty}^2 e^{i\Theta}}{1 - r_{\infty}^2 e^{i\Theta} + r_{\infty} (1 - e^{i\Theta})}.$$ \hspace{1cm} (26)

IV. THE EXCITON-POLARITON REGIME. GENERALIZED ABC CONDITIONS

When the thickness of the slab exceeds largely the exciton Bohr radius, the mixed exciton-polaritons modes, play an important role. In macroscopic approach one uses the excitonic susceptibility of the spatially homogeneous (infinitely extended) medium. In this case the inclusion of sample surfaces requires considerations of propagation effects with microscopic boundary conditions for the induced material polarization. The problem called the Additional Boundary Conditions (ABC) has appeared with the discovery of polaritons - joint electromagnetic-field-matter quasiparticles, which move in a medium as a superposition of the field and quantum coherence. The simplest version of ABC relay on two polariton waves propagating in the half space geometry. When two polariton waves propagate in the crystal and one of them is reflected in order to solve the problem of complete description of for example, reflectivity, one has to determine three amplitudes. The classical electrodynamics yield in this case only two boundary conditions for the electric and magnetic field. So it was the idea for additional a certain condition (an additional boundary condition) to obtain a sufficient number of equations.
The first proposal came from Pekar (Pekar’s ABC)\textsuperscript{20} which assumed the polarization to be zero at the crystal surface. His ABC was then improved by Hopfield and Thomas\textsuperscript{31} who assumed that the polarization vanishes at a certain surface inside the crystal. The ABC problem became more complicated when, in certain semiconductors and in the cases it is necessary to take into account higher excitons states, more than 2 polaritons can propagate (for example, in GaAs and GaAs based superlattices). So various ABC models, going beyond the above mentioned, have been proposed\textsuperscript{21,22,23,27} see also\textsuperscript{24} for further details on ABC. The Rydberg excitons and polaritons are an exceptional example, in which a huge number of polariton waves can appear. The polariton dispersion relation has been discussed in\textsuperscript{31}4. This problem consists in the fact that, for RE in Cu$_2$O in a certain interval of exciting energy, one has 25 polariton waves propagating and 25 reflected, so for a correct description of the optical response 50 amplitudes are to be established. It is well-known that Pekar’s ABC are applied for an arbitrary surface (0, L = z), but it is assumed that excitons-polaritons appear at the distance of several Bohr radius from the surface. In the case of j = 25, the critical distance is less then 1μm, while for states characterized by smaller j these distances are considerably smaller. Therefore the excitons-polaritons fallout might be observed in structures with the quantum confinement effects providing fine spectral resolution. Here we propose a certain modification of the Pekar-Hopfield-Thomas model (PHT) which is applied for the case of Rydberg exciton-polaritons. Since we will assume that the polarization vanishes at the surface, this will correspond to the „no escape” conditions for electrons and holes, defined by equations (11), and, in consequence, the same boundary conditions will be used in all three dimension regimes considered in the paper. We start with the polariton dispersion relation (taking into account only P excitons)\textsuperscript{32}.

\[
\frac{k^2}{k_0^2} - \epsilon_b = \epsilon_b \sum_{j=1}^{2} \frac{f_j^{(3D)} \Delta_{LT}/R^*}{(E - E_{Tj10} - E - i\Gamma_j)/R^* + (\mu/M_{tot})(k\alpha^*)^2},
\]

\[
f_j^{(3D)} = \frac{32}{3} \left( \frac{\vec{j}^2 - 1}{\vec{j}^6} \right) \frac{g_j(\rho_0)}{g_2(\rho_0)},
\]

\[
g_j(\rho_0) = \exp \left[ \rho_0^2 \left( \frac{4}{j^2 - 1} \right) \right],
\]

\[
k_0 = \frac{\hbar \omega}{\hbar c},
\]

where $M_{tot}$ is the total exciton mass, and the energies of exciton resonances $E_{Tj10}$ are assumed to be known. In order to apply the PHT model we assume, that for exciting energy near a certain exciton resonance $E_{Tj10}$ the biggest contribution to the optical functions comes from two polariton waves with wave vectors $k_1^{(j)}$, $k_2^{(j)}$, which are the nearest to the axis $E = k_0 \hbar \omega / \sqrt{\epsilon_b}$. These wave vectors are solutions of the following equation

\[
k^2 - \epsilon_b = \epsilon_b \left( E - E_{Tj10} - E - i\Gamma_j \right)/R^* + (\mu/M_{tot})(k\alpha^*)^2,
\]

\[
\left( \frac{k_{1,2}^{(j)}}{k_0} \right)^2 = \frac{\epsilon_b - E_{j} \pm \sqrt{\Delta}}{2b},
\]

\[
\Delta = \left( \epsilon_b + \tilde{E}_j \right)^2 + 4\epsilon_b f_j^{(3D)} \Delta_{LT}/R^*.
\]

In further considerations we use the notation by Hopfield et al\textsuperscript{31}.

\[
k_1^{(j)} = k_0 n_1^{(j)}, \quad k_2^{(j)} = k_0 n_2^{(j)},
\]

\[
\chi_1^{(j)} = n_1^{(j)} - \epsilon_b, \quad \chi_2^{(j)} = n_2^{(j)} - \epsilon_b,
\]

\[
\chi_1^{(j)} - \chi_1^{(j)} = \left[ n_2^{(j)} - n_1^{(j)} \right]^2,
\]

\[
k_1^{(j)} \chi_1^{(j)} = k_0 n_1^{(j)} \left[ \left( n_2^{(j)} - n_1^{(j)} \right)^2 - \epsilon_b \right],
\]

\[
k_1^{(j)} \chi_2^{(j)} - k_2^{(j)} \chi_1^{(j)} = k_0 \left[ n_2^{(j)} - n_1^{(j)} \right] \left[ n_2^{(j)} + n_1^{(j)} + \epsilon_b \right].
\]

Using Pekar’s model\textsuperscript{20} for two polariton waves with wave vectors $k_1^{(j)}$, $k_2^{(j)}$ we assume that the contribution to the exciton polarization coming from these waves with amplitudes $E_1^{(j)}$, $E_2^{(j)}$ vanishes at the crystal surface

\[
\chi_1^{(j)} E_1^{(j)} + \chi_2^{(j)} E_2^{(j)} = 0. \tag{29}
\]

The above equation, supplemented with Maxwell’s boundary conditions for the electric field of the propagating wave, gives the polariton amplitudes

\[
E_1^{(j)} = \frac{2 \left( n_2^{(j)} - \epsilon_b \right)}{\left[ n_2^{(j)} - n_1^{(j)} \right] \left[ n_1^{(j)} + n_2^{(j)} + n_1^{(j)} n_2^{(j)} + \epsilon_b \right]} E_i,
\]

\[
E_2 = -\frac{2 \left( n_1^{(j)} - \epsilon_b \right)}{\left[ n_2^{(j)} - n_1^{(j)} \right] \left[ n_1^{(j)} + n_2^{(j)} + n_1^{(j)} n_2^{(j)} + \epsilon_b \right]} E_i,
\]

where $E_i$ is the electric field amplitude of the incoming wave. For any pair of polaritons with wave vectors $k_1^{(j)}$, $k_2^{(j)}$ we define a partial complex refraction index

\[
n^{(j)} = \frac{n_2^{(j)} + \epsilon_b}{n_1^{(j)} + n_2^{(j)}}. \tag{31}
\]

To calculate absorption, one can use the partial wave vectors $k_\nu^{(j)}$, $\nu = 1, 2$ to write the polariton dispersion
relation (27) in the form
\[ \frac{k^2}{k_0^2} - \epsilon_b = \frac{\epsilon_b f_j^{(3D)} \Delta_{LT}/R^*}{\sum_{j=2}^{N} \sum_{\nu=1,2} (E_{Tj10} - E - i\Gamma_j)/R^* + (\mu/M_{tot})(k_{j0}^2a^*)^2} \]
\[ f_j^{(3D)} = \frac{32}{3} \left( \frac{j^2-1}{j^5} \right) \frac{g_j(\rho_0)}{g_2(\rho_0)}, \]
\[ g_j(\rho_0) = \exp \left[ \frac{\rho_0^2}{4} \left( \frac{j^2}{j^2 - 1} \right) \right], \]  
(32)

to obtain the effective exciton-polariton susceptibility and dielectric function as
\[ \chi^{(3D)}_{eff} = \frac{\sum_{j=2}^{N} \sum_{\nu=1,2} \epsilon_b f_j^{(3D)} \Delta_{LT}/R^*}{\sum_{j=2}^{N} \sum_{\nu=1,2} (E_{Tj10} - E - i\Gamma_j)/R^* + (\mu/M_{tot})(k_{j0}^2a^*)^2} \]
\[ \tilde{\epsilon} = \epsilon_b + \chi^{(3D)}_{eff}, \]
\[ n^{(3D)}_{eff} = \sqrt{\tilde{\epsilon}}. \]  
(33)

Finally, with the above quantities, following the presented scheme, we again calculate the absorption coefficient
\[ \alpha_{eff}^{(3D)} = \frac{2\hbar \omega}{\hbar c} \text{Im} n^{(3D)}_{eff}. \]  
(34)

V. RESULTS OF SPECIFIC CALCULATIONS

We have performed numerical calculations of optical functions (absorption, reflectivity, and transmissivity) for plan-parallel slabs of Cu2O. The dimensions in the z-direction varied from 20 nm to micrometer range, which corresponds to structures used in experiments by Takahata et al (lower limit) and by Kazimierczuk et al (upper limit). Such dimensions cover the regimes of QWs, Wide QWs, and exciton-polariton regime. For any regime the calculations were performed by methods appropriate to the given regime. The limits between regimes are not sharply defined. For example, the thickness \( L = 200 \) nm is large compared to the extension of the lowest exciton state (about 4 nm) but small compared to the extension of states with \( j > 10 \). Therefore we used the criterion of the relation between the slab thickness and the wavelength of the wave propagating in the crystal, which equals to about 200 nm. We consider the slabs with \( L < 200 \) nm as QWs and use the long-wave approximation, which, together with the assumption of infinite confinement potentials, leads to the expression (12) for the effective dielectric susceptibility and, in consequence, to the expression for the absorption coefficient. The parameters used in the calculations are collected in Table 1. The absorption line shape resulting from Eq. (15) is shown in the lowest part of Fig. 1. We observe the overlapping of exciton and confinement states. For small \( j \) and \( \Gamma \) the exciton effect prevails, whereas for large values of \( N \) the series of exciton resonances appears below every confinement state. These peaks exhibit a strong, roughly parabolic shift towards higher energy with decreasing \( L \). Eventually, the lines cross and mix together, creating a complicated spectrum, especially for \( E > E_g \). Interestingly, due to the large number of confinement states present only in a thin crystal, the absorption coefficient is decreasing with \( L \). However, the total absorption is still proportional to thickness, as shown in Fig. 2. One can also observe that the absorption discontinuity at the bandgap is smeared out and disappears completely at \( L < 200 \) nm. For \( L > 200 \) nm the long-wave approximation is not valid, and the methods of Sec. III are used. The effect of confinement decreases, and the maxima related to the exciton states with \( j = 2, 3, ... \) are visible. This effect is also observed in the central part of Fig. 1. When the considered crystal thickness is considerably larger that the wavelength inside the crystal, the reflection and transmission spectra will be strongly influenced by Fabry-Perot interference. This is shown on the Figs. 3 and 4. Due to the fact that the excitonic lines are spectrally narrow and up to 3 orders of magnitude weaker than F-P interference, the first derivative \( dR/dE \) is used to enhance these details. One can observe that the maxima closely follow the lines on the Fig. 1 and their strong mixing for \( L < 200 \) nm creates a very complicated reflection/transmission pattern. Fig. 5 shows the exciton dispersion relation (27), including polaritonic contribution, e. g. the spatial dispersion of N the series of exciton resonances appears below every regime. Overall, the inclusion the polaritons gives a nonlinear shift to the position of the resonances; the higher states, which are closer to \( E_g \) are more affected. It should be mentioned that such an effect could explain some discrepancies observed in fitting a simple \( j^{-2} \) model to the available experimental data; the Fig. 6 shows the comparison between absorption maxima positions measured by Kazimierczuk et al and our absorption spectrum calculated from (14). For our fit, we have used the Rydberg energy \( R = 91.5 \) meV and quantum defect \( \delta = 0.083 \). With these values, we have obtained almost perfect fit to all excitonic peaks for \( j = 2 \ldots 25 \). Note that the quantum defect affects mostly low-energy states but cannot explain the apparent deviation from \( j^{-2} \) relation for high states. This is easily visible in Fig. 7 even with proper fitting values, the standard relation, represented by straight line, cannot fit all the states. On the other hand, the nonlinear curve provided by polaritonic relation appears to be a much better fit.

The above indicated agreement can be understood as an indirect proof for existence of polariton waves. Another argument may come from experiment. Just at early stage of the research on Wannier-Mott excitons a number of experiments has been performed to manifest the existence of many transverse waves (polaritons) with fixed
frequency and polarization, distinguished by the index of refraction (for example, Broser et al.\textsuperscript{[39]}). In particular, for a CdS crystal, Lebedev et al.\textsuperscript{[39]} observed the simultaneous transmission of two polariton waves through a wedge-shaped crystal and spatially separated them. As we have shown above, a similar situation occurs in a Cu$_2$O crystal: near any exciton resonance energy there are two polariton waves with wave vectors $k_1$ and $k_2$ (and two refraction indices $n_1$ and $n_2$, respectively), propagating through the crystal. So we hope, that a similar experiment, as for the CdS crystal, can be performed for a Cu$_2$O crystal, to give an unambiguous proof for the existence of polariton waves.

VI. CONCLUSIONS

A theoretical solution to model absorption spectra of low dimensional systems with Rydberg excitons in a wide range of system dimensions is presented. The approach uses the Real Density Matrix Approach, where the confinement potential, the screened Coulomb interaction between electron and hole, and the effects of coherence with radiation field, are accounted for. We have chosen the example of cuprous dioxide planar systems, with dimensions corresponding to the range between QWs and bulk crystals. The unique method of calculating the optical properties ensured a smooth transition of optical functions by changing the dimensionality. For bulk crystals we have calculated the amplitudes of the polariton waves and have shown that the existence of polaritons can explain some properties of energies of exciton resonances. Presented calculations performed in terms of microscopic boundary conditions for the exciton motion inside the crystal of finite size are in well agreement with the measured absorption spectra. It should be mentioned that polaritons might play crucial role in explanation of nonlinear dependence of peaks positions observed in the generic experiment\textsuperscript{[4]}.

ACKNOWLEDGMENTS

Support from National Science Centre, Poland (project OPUS, CIREL 2017/25/B/ST3/00817) is greatly acknowledged.

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FIGURES

**FIG. 1:** The absorption coefficient $\alpha$ of Cu$_2$O crystal, calculated from (26), as a function of crystal thickness. The top and bottom panels show cross-sections for thickness $L = 900$ nm and $L = 100$ nm, respectively.

**FIG. 2:** The absorption coefficient from Fig. (1), for selected values of thickness.

**FIG. 3:** First derivative of reflectivity $R$ calculated from (15) with respect to energy $E$ for a Cu$_2$O crystal of thickness $L$.

**FIG. 4:** First derivative of transmissivity $\hat{T}$ calculated from (15) with respect to energy $E$ for a Cu$_2$O crystal of thickness $L$.
FIG. 5: Polariton dispersion relation calculated from (27).

FIG. 6: Excitonic absorption in Cu$_2$O crystal with polaritons calculated from (34). Black lines are peaks from experimental data by Kazimierczuk et al. Line $j^{-2}$ added for reference.

FIG. 7: Absorption peaks position comparison between theory with (27) or without polaritons to experimental data by Kazimierczuk et al. Line $j^{-2}$ added for reference.

TABLES

| Parameter  | Value       | Unit   | Reference |
|------------|-------------|--------|-----------|
| $E_g$      | 2172.08     | meV    | 11        |
| $R^*$      | 87.78       | meV    | 15        |
| $\Delta LT$ | $1.25 \times 10^{-3}$ | meV    | 14        |
| $m_e$      | 0.99        | $m_0$  | 15        |
| $m_h$      | 0.58        | $m_0$  | 15        |
| $\mu$      | 0.363       | $m_0$  | 15        |
| $M_{tot}$  | 1.56        | $m_0$  | 15        |
| $a^*$      | 1.1         | nm     | 3         |
| $r_0$      | 0.22        | nm     | 3         |
| $\epsilon_b$ | 7.5        |        | 3         |