Exciton-polaritons in cuprous oxide: I. Theory

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The observation of giant Rydberg excitons in cuprous oxide (Cu_2O) up to a principal quantum number of $n = 25$ by T. Kazimierczuk *et al.* [Nature **514**, 343, (2014)] inevitably raises the question whether these quasi-particles must be described within a multi-polariton framework since excitons and photons are always coupled in the solid. In this paper we present the theory of exciton-polaritons in Cu_2O, accounting for the complete valence band structure, the exchange interaction, and the central-cell corrections. To this end we extend the Hamiltonian which includes all these effects, and which has been recently deduced by F. Schweiner *et al.* [Phys. Rev. B **95**, 195201, (2017)], for finite values of the exciton momentum $\hbar K$. Furthermore, we derive formulas to calculate dipole and quadrupole oscillator strengths and to calculate the nonanalytic exchange interaction. The latter is required to ensure the correct treatment of the complete problem since the splitting at $K = 0$ due to the nonanalytic exchange interaction is identical to the longitudinal-transverse splitting when treating polaritons. As regards the $1S$ ortho exciton-polariton we set up a 5×5 matrix model which allows us to treat its dispersion for any direction of K. The theory presented here will be applied in the subsequent paper by F. Schweiner *et al.* [submitted to Phys. Rev. B].

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I. INTRODUCTION

Excitons are Coulomb-bound pairs of a positively charged hole in the valence band and a negatively charged electron in the conduction band of a semiconductor. Hence, these elementary excitations of a semiconductor are often regarded as the hydrogen analog of the solid state. It is now more than 80 years since Frenkel [1–3], Peierls [4], and Wannier [5] formulated the concept of excitons. After the experimental discovery of these quasi-particles in cuprous oxide (Cu_2O) by Gross and Karryjew in 1952 [6], excitons in bulk semiconductors became an important topic in solid-state physics from the late 1950s to the 1970s (see, e.g., Refs. [7–12] and further references therein).

Very recently, new attention has been drawn to the field of excitons by an experimental observation of the yellow exciton series in Cu_2O up to a large principal quantum number of $n = 25$ [13]. This discovery has opened up the research field of giant Rydberg excitons and led to a variety of new experimental and theoretical investigations [13–35]. Furthermore, it may pave the way, e.g., to a deeper understanding of inter-particle interactions in the solid [13] and to applications in quantum information technology [27].

Even though the spectrum of Rydberg excitons in Cu_2O can be described quite well in a first approximation by the hydrogen-like model of Wannier, one must keep in mind that excitons are complex many-body states of the solid and, hence, that there are significant limitations to the hydrogen-like model and to the atom-like description of these quasi-particles [36].

Some essential corrections to the hydrogen-like model comprise, e.g., the inclusion of the complete cubic valence band structure [37–42], which leads to a complicated fine-structure splitting, the central-cell corrections, which account for deviations from the hydrogen-like model in the limit of a small exciton radius [7, 43–49], and the exchange interaction [7, 46, 47, 50, 51]. Furthermore, interactions with other quasi-particles, like, e.g., phonons have to be considered [52–54]. All of these effects have already been discussed recently for the excitons in Cu_2O [15, 18, 20, 21, 25, 28].

Above all, there is another fundamental difference between atoms and excitons as regards their interaction with light. By analogy with the interaction of atoms with light one may suppose that absorption of light in a crystal can be described as the excitation of an exciton with the simultaneous disappearance of a photon [7]. Indeed, in the weak-coupling limit, the incident light acts only as a perturbation on the different energy states or excitations of the solid like, e.g., excitons [46]. However, since the excited states in the solid are connected with a polarization and since an oscillating polarization emits again an electromagnetic wave acting back onto the incident wave, there is an interplay between light and matter. If the frequency of light is within the range of the resonance frequency of an excitation, the coupling is strong and thus anomalous dispersion can be observed [7]. Due to this coupling, excitons and photons cannot be treated as independent entities or good eigenstates, but new quasi-particles must be introduced, which are called polaritons and which represent the quanta of the mixed state of polarization and electromagnetic wave [55–63].

In this paper we present the theory of exciton-polaritons in Cu_2O. We extend the Hamiltonian of

Ref. [28], which accounts for the complete valence band structure, the exchange interaction, and the central-cell corrections, for a finite momentum $\hbar K$ of the center of mass. The corresponding Schrödinger equation can then be solved using a complete basis. This method allows us not only to calculate dipole and quadrupole oscillator strengths but also the size of the nonanalytic exchange interaction. As the splitting due to the nonanalytic exchange interaction at $K = 0$ is identical to the longitudinal-transverse splitting (LT-splitting) when treating polaritons, this interaction needs to be considered for a correct treatment of the complete problem. We show how to calculate the polariton dispersion for the complete exciton spectrum. In particular, several properties of the $1S$ ortho exciton-polariton have been investigated thoroughly in the literature [64–66]. As this exciton state lies energetically clearly below the other states, it can be treated separately. We present a 5×5 matrix model, which allows us to calculate the dispersion of the $1S$ ortho exciton-polariton and to investigate its properties theoretically for any direction of $\boldsymbol{K}$. We shortly discuss criteria for spatial or temporal coherence, by which statements about the observability of polariton effects for Cu_2O can be made. For the application of the theory and the discussion of the exciton-polariton dispersion in Cu_2O we refer the reader to Ref. [67].

The paper is organized as follows: In Sec. II we present the Hamiltonian of excitons in Cu_2O when considering a finite momentum $\hbar K$ of the center of mass and show how to solve the corresponding Schrödinger equation in a complete basis. In Sec. III we present formulas to calculate dipole and quadrupole oscillator oscillator strengths for the three cases where $\boldsymbol{K}$ coincides with one of the high-symmetry axes of the crystal lattice. Having introduced the multi-polariton concept of exciton-polartions in Sec. IV A, we discuss the rotating wave approximation, the nonanalytic exchange interaction and criteria for the observability of polariton effects in Secs. IV B, IV C, and IV D, respectively. In Sec. V the 5×5 matrix model for the $1S$ ortho exciton polariton is introduced. We finally give a summary and outlook in Sec. VI.

II. HAMILTONIAN

In this section we shortly present the theory of excitons with a finite momentum of the center of mass in Cu_2O, where the cubic valence band structure, the exchange interaction and the central-cell corrections need to be considered.

The Hamiltonian of the exciton is given by

$$\begin{aligned} H &= E_\mathrm{g} + V\left(\boldsymbol{r}_e - \boldsymbol{r}_h\right) + H_\mathrm{e}\left(\boldsymbol{p}_\mathrm{e}\right) + H_\mathrm{h}\left(\boldsymbol{p}_\mathrm{h}\right) \\ &+ H_\mathrm{CCC}\left(\boldsymbol{r}_e - \boldsymbol{r}_h\right) + H_\mathrm{exch}\left(\boldsymbol{r}_e - \boldsymbol{r}_h\right) \end{aligned} \tag{1}$$

with the energy E_g of the band gap, the screened Coulomb interaction V, the central cell corrections H_CCC, the analytic exchange exchange interaction H_exch and the kinetic energies $H_\mathrm{e}\left(\boldsymbol{p}_\mathrm{e}\right)$ and $H_\mathrm{h}\left(\boldsymbol{p}_\mathrm{h}\right)$ of the electron and the hole are given in Ref. [28].

We now introduce relative and center-of-mass coordinates

$$\boldsymbol{r} = \boldsymbol{r}_\mathrm{e} - \boldsymbol{r}_\mathrm{h}, \tag{2a}$$

$$\boldsymbol{R} = \boldsymbol{\alpha}\boldsymbol{r}_\mathrm{e} + \boldsymbol{\gamma}\boldsymbol{r}_\mathrm{h}. \tag{2b}$$

The factors $\boldsymbol{\alpha}$ and $\boldsymbol{\gamma}$ are in general 3×3 matrices with $\left|\det\left(\boldsymbol{\alpha} + \boldsymbol{\gamma}\right)\right| = 1$ [41]. As the Hamiltonian (1) depends only on the relative coordinate $\boldsymbol{r} = \boldsymbol{r}_\mathrm{e} - \boldsymbol{r}_\mathrm{h}$ of electron and hole, the momentum of the center of mass

$$\boldsymbol{P} = \boldsymbol{p}_\mathrm{e} + \boldsymbol{p}_\mathrm{h} = -i\hbar\left(\boldsymbol{\alpha} + \boldsymbol{\gamma}\right)\nabla_{\boldsymbol{R}} \tag{3}$$

with

$$\nabla_{\boldsymbol{r}_\mathrm{e}} = \boldsymbol{\alpha}\nabla_{\boldsymbol{R}} + \nabla_{\boldsymbol{r}}, \tag{4a}$$

$$\nabla_{\boldsymbol{r}_\mathrm{h}} = \boldsymbol{\gamma}\nabla_{\boldsymbol{R}} - \nabla_{\boldsymbol{r}}, \tag{4b}$$

is a constant of motion, i.e., we can set $\boldsymbol{P} = \hbar\boldsymbol{K}$ [41, 68]. According to Ref. [41], the matrices $\boldsymbol{\alpha}$ and $\boldsymbol{\gamma}$ can be chosen arbitrarily, as long as $\left|\det\left(\boldsymbol{\alpha} + \boldsymbol{\gamma}\right)\right| = 1$ holds, but should be adapted to the problem. Note that if we insert Eqs. (2) and (4) into the Hamiltonian (1) in general a coupling term between the relative motion and the motion of center of mass appears. Only for a specific choice of $\boldsymbol{\alpha}$ and $\boldsymbol{\gamma}$ this coupling term vanishes. However, the correct values of $\boldsymbol{\alpha}$ and $\boldsymbol{\gamma}$ are difficult to find [20, 68]. In particular, the generalized relative and center of mass coordinate transformation of Ref. [20] holds only if the parameters η_i in the kinetic energy of the hole are set to zero (cf. Ref. [20]). When assuming isotropic coefficients $\boldsymbol{\alpha} = \alpha\mathbf{1}$ and $\boldsymbol{\gamma} = (1 - \alpha)\mathbf{1}$ it is not possible to find a constant value of α for which the relative motion and the motion of the center of mass are decoupled. This is connected to the fact that the exciton mass in Cu_2O is not isotropic [20]. Hence, the more complicated generalized transformation with 3×3 matrices would be needed.

Here we will use the coordinates and momenta of relative and center of mass motion with $\boldsymbol{\alpha} = m_\mathrm{e}/\left(m_\mathrm{e} + m_\mathrm{h}\right)\mathbf{1}$ and $\boldsymbol{\gamma} = m_\mathrm{h}/\left(m_\mathrm{e} + m_\mathrm{h}\right)\mathbf{1}$ known from the hydrogen atom in the following:

$$\boldsymbol{r} = \boldsymbol{r}_\mathrm{e} - \boldsymbol{r}_\mathrm{h}, \tag{5a}$$

$$\boldsymbol{R} = \left(m_\mathrm{e}\boldsymbol{r}_\mathrm{e} + m_\mathrm{h}\boldsymbol{r}_\mathrm{h}\right)/\left(m_\mathrm{e} + m_\mathrm{h}\right), \tag{5b}$$

$$\boldsymbol{p} = \left(m_\mathrm{h}\boldsymbol{p}_\mathrm{e} - m_\mathrm{e}\boldsymbol{p}_\mathrm{h}\right)/\left(m_\mathrm{e} + m_\mathrm{h}\right), \tag{5c}$$

$$\boldsymbol{P} = \boldsymbol{p}_\mathrm{e} + \boldsymbol{p}_\mathrm{h} = \hbar\boldsymbol{K}. \tag{5d}$$

We can then write the Hamiltonian in the form

$$H = H_0 + \left(\hbar K\right)H_1 + \left(\hbar K\right)^2 H_2. \tag{6}$$

The first part H_0 is exactly the Hamiltonian of relative motion presented and discussed in Ref. [28], while the last part H_2 describes the motion of the center of mass in the degenerate band case. The term H_1 depends on the relative momentum $\boldsymbol{p}$ and thus couples the relative motion and the motion of the center of mass.

For the case that the wave vector $\boldsymbol{K}$ is oriented along one of the directions of high symmetry, i.e., along [001], [110] or [111], one can rotate the coordinate system to make the quantization axis coincide with the direction of $\boldsymbol{K}$ and then express the Hamiltonian (6) in terms of irreducible tensors [39, 69, 70]. Explicit expressions for H_0, H_1, and H_2 for these special orientations of the wave vector $\boldsymbol{K}$ are given in Appendix A.

The Schrödinger equation corresponding to the Hamiltonian (6) is then solved using the method presented in Refs. [20, 21, 28] with a complete basis. The ansatz for the exciton wave function now reads

$$|\Psi_{\nu\boldsymbol{K}}\rangle = \sum_{NLJFF_tM_{F_t}} c^{\nu\boldsymbol{K}}_{NLJFF_tM_{F_t}} |\Pi\rangle , \tag{7a}$$

$$|\Pi\rangle = |N,\, L;\, (I,\, S_\mathrm{h})\; J;\, F,\, S_\mathrm{e};\, F_t,\, M_{F_t}\rangle \tag{7b}$$

with complex coefficients c and the quantum numbers explained in Refs. [20, 21, 28]. Note that the coefficients here will depend on the wave vector $\boldsymbol{K}$, which enters the Hamiltonian (6). The index ν is a number to distinguish the different exciton states.

Inserting the ansatz (7) in the Schrödinger equation $H\Psi = E\Psi$ and multiplying from the left with another basis state $\langle\Pi'|$, we obtain a matrix representation of the Schrödinger equation of the form

$$\boldsymbol{D}\boldsymbol{c} = E\boldsymbol{M}\boldsymbol{c}. \tag{8}$$

The vector $\boldsymbol{c}$ contains the coefficients of the ansatz (7). All matrix elements of H_1 and H_2, which enter the symmetric matrices $\boldsymbol{D}$ and $\boldsymbol{M}$ are given in the Appendices B and C. The matrix elements of H_0 are already given in the Appendices of Refs. [20] and [28]. The generalized eigenvalue problem (8) can finally be solved using an appropriate LAPACK routine [71].

III. OSCILLATOR STRENGTHS

Having solved the generalized eigenvalue problem (8), one can directly calculate the relative oscillator strengths for the transitions from the ground state of the solid to the exciton states. In doing so, four important points need to be considered (cf. Refs. [20, 21]):

(i) Dipole transitions in Cu_2O are parity forbidden. Hence, the transition matrix element is proportional to the gradient of the envelope function at $r = |\boldsymbol{r}| = 0$ and the exciton state must have a component with angular momentum $L = 1$. For quadrupole transitions the transition matrix element is proportional to the envelope function at $r = 0$, for which reason it must have a component with angular momentum $L = 0$.

(ii) As the dipole and quadrupole operator do not change the total spin $S = S_\mathrm{e} + S_\mathrm{h}$ of the electron and the hole, the exciton state must have a component with $S = 0$.

(iii) The total symmetry of the exciton state must be identical to the symmetry Γ_4^- of the dipole operator or Γ_5^+ of the quadrupole operator [7].

(iv) The quasispin I transforms according to Γ_5^+. Since a normal spin one transforms in O_h according to Γ_4^+ and since $\Gamma_5^+ = \Gamma_2^+ \otimes \Gamma_4^+$ holds for the cubic group [72], one has to multiply all symmetries by Γ_2^+ [18].

In this section we will derive the formula for the relative oscillator strength of an exciton state. The oscillator strength is strongly connected to the interaction between the excitons and photons. According to Ref. [7] the probability per unit time for a transition from the ground state Φ_0 of the semiconductor to an exciton state $\Psi^{\sigma\tau}_{vc,\,\nu\boldsymbol{K}}$ is proportional to $|M|^2$ with

$$M = \int \Psi^{\sigma\tau *}_{vc,\,\nu\boldsymbol{K}} \left[\frac{-e}{m_0}\boldsymbol{A}_0\left(\boldsymbol{\kappa},\xi\right)\sum_{l=1}^{N} e^{i\boldsymbol{\kappa}\boldsymbol{r}_l}\boldsymbol{p}_l\right]\Phi_0 \mathrm{d}\boldsymbol{r}_1\cdots\mathrm{d}\boldsymbol{r}_N. \tag{9}$$

Here $\boldsymbol{A}_0\left(\boldsymbol{\kappa},\xi\right)$ denotes the amplitude of the vector potential of the radiation field with the wave vector $\boldsymbol{\kappa}$ and the polarization ξ. N denotes the number of electrons with the coordinates $\boldsymbol{r}_l$.

Within the scope of the simple band model the wave function of an exciton is given by

$$\Psi^{\sigma\tau}_{vc,\,\nu\boldsymbol{K}} = \sum_{\boldsymbol{q}} f_{vc\,\nu}\left(\boldsymbol{q}\right)\Phi^{\sigma\tau}_{vc}\left(\boldsymbol{q}-\gamma\boldsymbol{K},\,\boldsymbol{q}+\alpha\boldsymbol{K}\right), \tag{10}$$

where τ and $-\sigma$ denote the spins of the electron and the hole, respectively. As we will discuss below, the spin orbit splitting in Cu_2O does not have a perceptible effect on the oscillator strength. Hence, we will keep the derivation of the formula for the oscillator strength more simple by assuming a threefold degenerate Γ_5^+ valence band and treating the electron spin and the hole spin separately.

The envelope function $f_{vc\,\nu}\left(\boldsymbol{q}\right)$ in Eq. (10) is the Fourier transform of the solution $F_{vc\,\nu}\left(\boldsymbol{\beta}\right)$ of the Wannier equation [5, 7],

$$f_{vc\,\nu}\left(\boldsymbol{q}\right) = \frac{1}{\sqrt{N}}\sum_{\boldsymbol{\beta}} F_{vc\,\nu}\left(\boldsymbol{\beta}\right)e^{-i\boldsymbol{q}\boldsymbol{\beta}}, \tag{11}$$

with ν denoting the different exciton states. Note that the coordinate $\boldsymbol{\beta}$ is a lattice vector which in general takes only discrete values [47]. This coordinate is identical to the relative coordinate $\boldsymbol{r}$ used in Sec. II in the continuum approximation. The constant factors $\alpha = m_\mathrm{e}/(m_\mathrm{e}+m_\mathrm{h})$ and $\gamma = 1-\alpha$ depend on the effective masses of the electron and the hole.

The wave function (10) contains a Slater determinant of Bloch functions with one electron being in a Bloch state of the conduction band and $N-1$ electrons in Bloch states of the valence bands:

$$\Phi^{\sigma\tau}_{vc}\left(\boldsymbol{k}_\mathrm{h},\,\boldsymbol{k}_\mathrm{e}\right) = \mathcal{A}\psi_{v\boldsymbol{k}_1\alpha}\psi_{v\boldsymbol{k}_1\beta}\cdots\psi_{v\boldsymbol{k}_\mathrm{h}\sigma}\psi_{c\boldsymbol{k}_\mathrm{e}\tau}\cdots\psi_{v\boldsymbol{k}_N\beta}. \tag{12}$$

Here $\mathcal{A}$ denotes the antisymmetrization operator. With the ground state of the semiconductor

$$\Phi_0 = \mathcal{A}\psi_{v\boldsymbol{k}_1\alpha}\psi_{v\boldsymbol{k}_1\beta}\cdots\psi_{v\boldsymbol{k}_i\alpha}\psi_{v\boldsymbol{k}_i\beta}\cdots\psi_{v\boldsymbol{k}_N\beta} \tag{13}$$

we can express the exciton state (10) as

$$\left|\Psi^{\sigma\tau}_{vc,\,\nu\boldsymbol{K}}\right\rangle = \sum_{\boldsymbol{q}} f_{vc\,\nu}\left(\boldsymbol{q}\right) c^{\dagger}_{c(\boldsymbol{q}+\alpha\boldsymbol{K})\tau} c_{v(\boldsymbol{q}-\gamma\boldsymbol{K})\sigma}\left|\Phi_0\right\rangle, \quad (14)$$

using creation and annihilation operators. The operator in square brackets in Eq. (9) can be written in second quantization as

$$\sum_{nn'}\sum_{\boldsymbol{k}\boldsymbol{k}'}\sum_{\sigma'\tau'} -\frac{e}{m_0}\boldsymbol{A}_0\left(\boldsymbol{\kappa},\xi\right) \times \left\langle \psi_{n'\boldsymbol{k}'\tau'}\left|e^{i\boldsymbol{\kappa}\boldsymbol{r}}\boldsymbol{p}\right|\psi_{n\boldsymbol{k}\sigma'}\right\rangle c^{\dagger}_{n'\boldsymbol{k}'\tau'} c_{n\boldsymbol{k}\sigma'}. \quad (15)$$

After some transformations, using $\boldsymbol{A}_0\left(\boldsymbol{\kappa},\xi\right) = A_0\left(\boldsymbol{\kappa},\xi\right)\hat{\boldsymbol{e}}_{\xi\boldsymbol{\kappa}}$ as well as the relation

$$\sum_{\boldsymbol{R}} e^{i(\boldsymbol{\kappa}-\boldsymbol{K})\cdot\boldsymbol{R}} = N\sum_{\boldsymbol{G}}\delta_{\boldsymbol{\kappa},\boldsymbol{K}+\boldsymbol{G}} \quad (16)$$

and neglecting Umklapp processes, we arrive at

$$\begin{aligned} M &= -\frac{e}{m_0}A_0\left(\boldsymbol{\kappa},\xi\right)N\delta_{\tau\sigma}\delta_{\boldsymbol{\kappa},\boldsymbol{K}}\sum_{\boldsymbol{q}} f^{*}_{vc\,\nu}\left(\boldsymbol{q}\right) \\ &\times \int_{\mathrm{WSC}} \mathrm{d}\boldsymbol{r}\, u^{*}_{c(\boldsymbol{q}+\alpha\boldsymbol{K})}\left(\boldsymbol{r}\right)\hat{\boldsymbol{e}}_{\xi\boldsymbol{\kappa}} \\ &\times \left(\hbar\left(\boldsymbol{q}-\gamma\boldsymbol{K}\right)u_{v(\boldsymbol{q}-\gamma\boldsymbol{K})}\left(\boldsymbol{r}\right) + \frac{\hbar}{i}\nabla u_{v(\boldsymbol{q}-\gamma\boldsymbol{K})}\left(\boldsymbol{r}\right)\right) \end{aligned} \quad (17)$$

with an integral over the Wigner-Seitz cell (WSC) [73].

To obtain expressions for the dipole and quadrupole oscillator strength, we use $\boldsymbol{k}\cdot\boldsymbol{p}$ perturbation theory and keep all terms up to first order in $\boldsymbol{q}$ and $\boldsymbol{K}$. It is [47, 73]

$$u_{m\boldsymbol{k}}\left(\boldsymbol{r}\right) \approx u_{m\boldsymbol{0}}\left(\boldsymbol{r}\right) + \frac{\hbar}{m_0}\sum_{n\neq m}\frac{\boldsymbol{k}\cdot\boldsymbol{p}_{nm}}{\left(E_m - E_n\right)}u_{n\boldsymbol{0}}\left(\boldsymbol{r}\right) + \ldots \quad (18)$$

with

$$\boldsymbol{p}_{mn} = \left\langle u_{m\boldsymbol{0}}\left|\boldsymbol{p}\right|u_{n\boldsymbol{0}}\right\rangle \quad (19)$$

and the energy $E_n = E_n\left(\boldsymbol{k}=\boldsymbol{0}\right)$ of the band n at the Γ point. Due to the orthogonality relation of the Bloch functions

$$\int \mathrm{d}\boldsymbol{r}\psi^{*}_{n\boldsymbol{k}\sigma}\left(\boldsymbol{r}\right)\psi^{*}_{n'\boldsymbol{k}'\sigma'}\left(\boldsymbol{r}\right) = \delta_{n,n'}\delta_{\boldsymbol{k},\boldsymbol{k}'}\delta_{\sigma,\sigma'} \quad (20)$$

the first summand in the integral of Eq. (17) vanishes up to first order in $\boldsymbol{q}$ and $\boldsymbol{K}$. We obtain

$$\begin{aligned} M = &-\frac{e\hbar}{m_0^2}A_0\left(\boldsymbol{\kappa},\xi\right)\delta_{\tau\sigma}\delta_{\boldsymbol{\kappa},\boldsymbol{K}}\sum_{\boldsymbol{q}} f^{*}_{vc\,\nu}\left(\boldsymbol{q}\right) \\ &\times\left[\left\langle u_{c\boldsymbol{0}}\right|\hat{\boldsymbol{e}}_{\xi\boldsymbol{\kappa}}\cdot\boldsymbol{p}\left|u_{v\boldsymbol{0}}\right\rangle\right. \\ &+\left\langle u_{c\boldsymbol{0}}\right|\left(\hat{\boldsymbol{e}}_{\xi\boldsymbol{\kappa}}\cdot\boldsymbol{p}\right)M_v\left(\boldsymbol{p}\cdot\left(\boldsymbol{q}-\gamma\boldsymbol{K}\right)\right)\left|u_{v\boldsymbol{0}}\right\rangle \\ &+\left.\left\langle u_{c\boldsymbol{0}}\right|\left(\left(\boldsymbol{q}+\alpha\boldsymbol{K}\right)\cdot\boldsymbol{p}\right)M_c\left(\boldsymbol{p}\cdot\hat{\boldsymbol{e}}_{\xi\boldsymbol{\kappa}}\right)\left|u_{v\boldsymbol{0}}\right\rangle\right], \end{aligned} \quad (21)$$

where we used

$$N\left\langle u_{c\boldsymbol{q}}\left|\hat{\boldsymbol{e}}_{\xi\boldsymbol{\kappa}}\cdot\boldsymbol{p}\right|u_{v\boldsymbol{q}}\right\rangle_{\mathrm{WSC}} = \left\langle u_{c\boldsymbol{q}}\left|\hat{\boldsymbol{e}}_{\xi\boldsymbol{\kappa}}\cdot\boldsymbol{p}\right|u_{v\boldsymbol{q}}\right\rangle \quad (22)$$

and defined

$$M_m = \sum_{n\neq m}\frac{\left|u_{n\boldsymbol{0}}\right\rangle\left\langle u_{n\boldsymbol{0}}\right|}{\left(E_m - E_n\right)}. \quad (23)$$

The sum over $\boldsymbol{q}$ can be evaluated using

$$\frac{1}{\sqrt{N}}\sum_{\boldsymbol{q}} q_i^{\chi} f_{vc\,\nu}\left(\boldsymbol{q}\right) = \left(-i\right)^{\chi}\frac{\partial^{\chi}}{\partial\beta_i^{\chi}}F_{vc\,\nu}\left(\boldsymbol{\beta}\right)\Big|_{\boldsymbol{\beta}=\boldsymbol{0}} \quad (24)$$

and we arrive at

$$\begin{aligned} M &= -\frac{e\hbar}{m_0^2}A_0\left(\boldsymbol{\kappa},\xi\right)\sqrt{N}\delta_{\tau\sigma}\delta_{\boldsymbol{\kappa},\boldsymbol{K}} \\ &\times \lim_{\boldsymbol{r}\to\boldsymbol{0}}\left[\hat{\boldsymbol{e}}_{\xi\boldsymbol{\kappa}}\cdot\boldsymbol{p}_{cv}\,F^{*}_{vc\,\nu}\left(\boldsymbol{r}\right)\right. \\ &+ \hat{\boldsymbol{e}}_{\xi\boldsymbol{\kappa}}\cdot\left(\tilde{\boldsymbol{M}}_v + \tilde{\boldsymbol{M}}_c\right)\cdot\left(i\nabla_{\boldsymbol{\beta}}F^{*}_{vc\,\nu}\left(\boldsymbol{r}\right)\right) \\ &+ \left.\hat{\boldsymbol{e}}_{\xi\boldsymbol{\kappa}}\cdot\left(-\gamma\tilde{\boldsymbol{M}}_v + \alpha\tilde{\boldsymbol{M}}_c\right)\cdot\left(F^{*}_{vc\,\nu}\left(\boldsymbol{r}\right)\boldsymbol{K}\right)\right], \end{aligned} \quad (25)$$

where we replaced $\boldsymbol{\beta}$ with $\boldsymbol{r}$ and defined the matrices $\tilde{\boldsymbol{M}}_v$, $\tilde{\boldsymbol{M}}_c$ with the components

$$\left(\tilde{\boldsymbol{M}}_v\right)_{ij} = \left\langle u_{c\boldsymbol{0}}\right|p_i M_v p_j\left|u_{v\boldsymbol{0}}\right\rangle, \quad (26a)$$

$$\left(\tilde{\boldsymbol{M}}_c\right)_{ij} = \left\langle u_{c\boldsymbol{0}}\right|p_i M_c p_j\left|u_{v\boldsymbol{0}}\right\rangle. \quad (26b)$$

In Cu_2O the first term or $\boldsymbol{p}_{cv}$ vanishes since valence and conduction band have the same parity. The term $\delta_{\tau\sigma}$ has to be replaced by $\sqrt{2}\delta_{S,0}$ when using the eigenstates of the total spin $S = S_{\mathrm{e}} + S_{\mathrm{h}} = \tau - \sigma$ [74].

The operators M_c and M_v are projection operators. For reasons of symmetry these operators have to transform according to the irreducible representation Γ_1^+ of O_{h}. On the other hand, the operator $\boldsymbol{p}$ transforms according to Γ_4^-. The symmetry of the operator between the Bloch functions in Eq. (26) is therefore

$$\Gamma_4^- \otimes \Gamma_1^+ \otimes \Gamma_4^- = \Gamma_1^+ \oplus \Gamma_3^+ \oplus \Gamma_4^+ \oplus \Gamma_5^+. \quad (27)$$

The symmetry of the Bloch functions (without spin) is

$$\Gamma_5^+ \otimes \Gamma_1^+ = \Gamma_5^+. \quad (28)$$

Consequently, the expression (26) does not vanish only if the operator has the symmetry Γ_5^+ [72].

The same argument would also hold if we had considered the spin-orbit coupling in Cu_2O and if the spin still appeared in the Bloch functions: The momentum operator in Eq. (26) acts only on the orbital part of the Bloch functions. The Γ_6^+ conduction band in Cu_2O results from a product of a Γ_1^+ orbital function and the electron spin function while the Γ_7^+ and Γ_8^+ valence bands result from the spin-orbit splitting of a Γ_5^+ orbital function with the function of the hole spin. One can write the product of the Γ_6^+ band with the Γ_7^+ or the Γ_8^+ band as a linear

combination of the product of the Γ_1^+ with the Γ_5^+ band and the total spin $S = S_\mathrm{e} + S_\mathrm{h}$, which can take the values $S = 0$ (singlet, Γ_1^+) or $S = 1$ (triplet, Γ_4^+). Hence, only linear combinations of the conduction band and the valence band Bloch functions which transform according to Γ_5^+ have a spin-singlet component. All other states are not relevant for optical excitations.

Since there are three Γ_5^+ orbital Bloch functions, one obtains three different matrices from Eq. (26) connected with the basis functions $|\tilde{X}\rangle = |YZ\rangle$, $|\tilde{Y}\rangle = |ZX\rangle$, and $|\tilde{Z}\rangle = |XY\rangle$ of Γ_5^+ when considering the coupling coefficients for the case $\Gamma_4^- \otimes \Gamma_4^- \to \Gamma_5^+$:

$$|\tilde{X}\rangle : \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \tilde{M}_{v,c} \tag{29a}$$

$$|\tilde{Y}\rangle : \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix} \tilde{M}_{v,c} \tag{29b}$$

$$|\tilde{Z}\rangle : \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tilde{M}_{v,c} \tag{29c}$$

In Sec. II we have introduced the quasi spin $I = 1$. If we compare the states $|I,\, M_I\rangle$ with the three functions $|u_{v\mathbf{0}}^{xy}\rangle$, $|u_{v\mathbf{0}}^{yz}\rangle$, and $|u_{v\mathbf{0}}^{zx}\rangle$ transforming according to Γ_5^+, it is [75]

$$|1, +1\rangle_I = -\frac{1}{\sqrt{2}} \left(|u_{v\mathbf{0}}^{yz}\rangle + i\, |u_{v\mathbf{0}}^{zx}\rangle \right), \tag{30a}$$

$$|1, 0\rangle_I = |u_{v\mathbf{0}}^{xy}\rangle, \tag{30b}$$

$$|1, -1\rangle_I = \frac{1}{\sqrt{2}} \left(|u_{v\mathbf{0}}^{yz}\rangle - i\, |u_{v\mathbf{0}}^{zx}\rangle \right). \tag{30c}$$

Let us write the function $|\Psi_{\nu \boldsymbol{K}}\rangle$ of the exciton in the form of Eq. (7), where the spins, the envelope with the angular momentum L and the function of the hole with the quasi spin I enter. The dipole term in Eq. (25) is then proportional to

$$-i(\tilde{M}_v^* + \tilde{M}_c^*) \left[(\hat{\boldsymbol{e}}_{\xi\boldsymbol{\kappa}})_x M_x^D + (\hat{\boldsymbol{e}}_{\xi\boldsymbol{\kappa}})_y M_y^D + (\hat{\boldsymbol{e}}_{\xi\boldsymbol{\kappa}})_z M_z^D \right] \tag{31}$$

with

$$M_x^D = \lim_{\boldsymbol{r}\to\mathbf{0}} \langle S = 0,\, M_S = 0| \left(\langle u_{v\mathbf{0}}^{xy}| \frac{\partial}{\partial y} + \langle u_{v\mathbf{0}}^{zx}| \frac{\partial}{\partial z} \right) |\Psi_{\nu \boldsymbol{K}}\rangle \tag{32}$$

and the y, z expressions obtained via cyclic permutation. The quadrupole term in Eq. (25) is proportional to

$$(-\gamma \tilde{M}_v^* + \alpha \tilde{M}_c^*) \left[(\hat{\boldsymbol{e}}_{\xi\boldsymbol{\kappa}})_x M_x^Q + (\hat{\boldsymbol{e}}_{\xi\boldsymbol{\kappa}})_y M_y^Q + (\hat{\boldsymbol{e}}_{\xi\boldsymbol{\kappa}})_z M_z^Q \right] \tag{33}$$

with

$$M_x^Q = \lim_{\boldsymbol{r}\to\mathbf{0}} \langle S = 0,\, M_S = 0| \left(\langle u_{v\mathbf{0}}^{xy}|\, K_y + \langle u_{v\mathbf{0}}^{zx}|\, K_z \right) |\Psi_{\nu \boldsymbol{K}}\rangle \tag{34}$$

and the y, z expressions again obtained via cyclic permutation.

In the envelope function of the exciton the angular dependence is given by the spherical harmonics Y_{LM}. We know that in Eq. (25) the gradient of the envelope function at $\boldsymbol{r} = \mathbf{0}$ is non-zero only if $L = 1$ holds. Furthermore, the envelope function itself vanishes at $\boldsymbol{r} = \mathbf{0}$ if $L \neq 0$ holds. Hence, we can rewrite the expressions (32) and (34) in the following way:

$$\begin{aligned}
&\lim_{\boldsymbol{r}\to\mathbf{0}} \langle S = 0,\, M_S = 0| \left(\langle u_{v\mathbf{0}}^{xy}| \frac{\partial}{\partial y} + \langle u_{v\mathbf{0}}^{zx}| \frac{\partial}{\partial z} \right) |\Psi_{\nu \boldsymbol{K}}\rangle \\
&= \lim_{r\to 0} \langle S = 0,\, M_S = 0| \frac{\partial}{\partial r} \Bigg(\langle I = 1,\, M_I = 0|\, (-i) \sqrt{\frac{3}{8\pi}} \left(\langle L = 1,\, M_L = 1| + \langle L = 1,\, M_L = -1| \right) \\
&\qquad\qquad - \frac{i}{\sqrt{2}} \left(\langle I = 1,\, M_I = -1| + \langle I = 1,\, M_I = 1| \right) \sqrt{\frac{3}{4\pi}}\, \langle L = 1,\, M_L = 0| \Bigg) |\Psi_{\nu \boldsymbol{K}}\rangle \\
&= -i \sqrt{\frac{3}{4\pi}} \lim_{r\to 0} \frac{\partial}{\partial r} \left({}_D\langle 2,\, 1| + {}_D\langle 2,\, -1| \right) |\Psi_{\nu \boldsymbol{K}}\rangle
\end{aligned} \tag{35}$$

Here the state $|F_t,\, M_{F_t}\rangle_D$ for the dipole transition (D) is a short notation for

$$\begin{aligned}
&|(S_\mathrm{e},\, S_\mathrm{h})\; S,\, I;\, I + S,\, L;\, F_t,\, M_{F_t}\rangle \\
&= |(1/2,\, 1/2)\; 0,\, 1;\, 1,\, 1;\, F_t,\, M_{F_t}\rangle,
\end{aligned} \tag{36}$$

in which the coupling scheme of the spins and angular momenta is different from the one of Eq. (7b) due to the requirement that S must be a good quantum number:

$$S_\mathrm{e} + S_\mathrm{h} = S \quad \to \quad (I + S) + L = F_t. \tag{37}$$

As the quantization axis we choose the z-axis, which is parallel to one of the principal axes of the crystal lattice.

In an analogous way, the quadrupole term can be written as

$$\begin{aligned}
&\lim_{\boldsymbol{r}\to\boldsymbol{0}} \langle S=0,\, M_S=0|\left(\langle u^{xy}_{v\boldsymbol{0}}|\, K_y + \langle u^{zx}_{v\boldsymbol{0}}|\, K_z\right)|\Psi_{\nu\boldsymbol{K}}\rangle \\
&= \lim_{r\to 0} \langle S=0,\, M_S=0|\,\frac{1}{\sqrt{4\pi}}\,\langle L=0,\, M_L=0|\left(\langle I=1,\, M_I=0|\, K_y\right. \\
&\qquad\qquad \left. -\frac{i}{\sqrt{2}}\left(\langle I=1,\, M_I=-1| + \langle I=1,\, M_I=1|\right) K_z\right)|\Psi_{\nu\boldsymbol{K}}\rangle \\
&= \lim_{r\to 0} \frac{1}{\sqrt{4\pi}}\left({}_Q\langle 1,\, 0|\, K_y - \frac{i}{\sqrt{2}}\left({}_Q\langle 1,\, -1| + {}_Q\langle 1,\, 1|\right) K_z\right)|\Psi_{\nu\boldsymbol{K}}\rangle
\end{aligned} \tag{38}$$

with the state $|F_t,\, M_{F_t}\rangle_Q$ for the quadrupole transition (Q) being a short notation for

$$\begin{aligned}
&|(S_\mathrm{e},\, S_\mathrm{h})\; S,\, I;\, I+S,\, L;\, F_t,\, M_{F_t}\rangle \\
&= |(1/2,\, 1/2)\; 0,\, 1;\, 1,\, 0;\, F_t,\, M_{F_t}\rangle\,.
\end{aligned} \tag{39}$$

Note that this state is similar to the one of Eq. (36) but only L is set to zero.

We finally arrive at the following expression for the relative oscillator strength:

$$f^{\mathrm{rel}}_{\xi\nu\boldsymbol{K}} = \left|\lim_{r\to 0}\left[-i\left(\tilde{M}^*_v + \tilde{M}^*_c\right)\frac{\partial}{\partial r}\langle T^D_{\xi\boldsymbol{K}}|\Psi_{\nu\boldsymbol{K}}\rangle + \left(-\gamma\tilde{M}^*_v + \alpha\tilde{M}^*_c\right)\frac{K}{\sqrt{6}}\langle T^Q_{\xi\boldsymbol{K}}|\Psi_{\nu\boldsymbol{K}}\rangle\right]\right|^2. \tag{40}$$

For the dipole term in Eq. (40) the two transverse states $|T^D_{\xi\boldsymbol{K}}\rangle$ are given by

$$|T^D_{\xi\boldsymbol{K}}\rangle = \sum_{i=1}^{3}\hat{e}_{\xi\boldsymbol{K}i}|\pi^D_i\rangle, \qquad \xi = 1,\, 2 \tag{41}$$

with the three components of the polarization vector $\hat{\boldsymbol{e}}_{\xi\boldsymbol{K}}$ and three states which transform according to Γ_4^- [21]:

$$|\pi^D_x\rangle = \frac{i}{\sqrt{2}}\left[|2,\, -1\rangle_D + |2,\, 1\rangle_D\right], \tag{42a}$$

$$|\pi^D_y\rangle = \frac{1}{\sqrt{2}}\left[|2,\, -1\rangle_D - |2,\, 1\rangle_D\right], \tag{42b}$$

$$|\pi^D_z\rangle = \frac{i}{\sqrt{2}}\left[|2,\, -2\rangle_D - |2,\, 2\rangle_D\right]. \tag{42c}$$

Note that there is a third linear combination of the states in Eq. (42), which is connected with a longitudinal polarization:

$$|L^D_{\boldsymbol{K}}\rangle = \sum_{i=1}^{3}\hat{K}_i|\pi^D_i\rangle. \tag{43}$$

Here we have introduced $\hat{\boldsymbol{K}} = \boldsymbol{K}/K$. The state $|T^Q_{\xi\boldsymbol{K}}\rangle$ in the quadrupole term of Eq. (40) reads

$$|T^Q_{\xi\boldsymbol{K}}\rangle = \sum_{i=1}^{3}\hat{e}_{\xi\boldsymbol{K}i}|\pi^Q_i\rangle, \qquad \xi = 1,\, 2 \tag{44}$$

with the three states which transform according to Γ_5^+ [21]:

$$\begin{aligned}
|\pi^Q_x\rangle &= \hat{K}_y\,|1,\, 0\rangle_Q \\
&\quad + \hat{K}_z\frac{i}{\sqrt{2}}\left[|1,\, -1\rangle_Q + |1,\, 1\rangle_Q\right],
\end{aligned} \tag{45a}$$

$$\begin{aligned}
|\pi^Q_y\rangle &= \hat{K}_x\,|1,\, 0\rangle_Q \\
&\quad + \hat{K}_z\frac{1}{\sqrt{2}}\left[|1,\, -1\rangle_Q - |1,\, 1\rangle_Q\right],
\end{aligned} \tag{45b}$$

$$\begin{aligned}
|\pi^Q_z\rangle &= \hat{K}_y\frac{1}{\sqrt{2}}\left[|1,\, -1\rangle_Q - |1,\, 1\rangle_Q\right] \\
&\quad + \hat{K}_x\frac{i}{\sqrt{2}}\left[|1,\, -1\rangle_Q + |1,\, 1\rangle_Q\right].
\end{aligned} \tag{45c}$$

The quadrupole interaction appears due to a finite wave vector. The exciton states, which have the symmetry Γ_5^+ at $K=0$, couple with the finite wave vector leading to a finite polarization proportional to K. If we now set $K=0$ in Eq. (40), we see that we have derived the expression for the relative oscillator strength, which has already been used in Refs. [20, 21].

We can finally make an assumption as regards the size of the parameters $\tilde{M}_v$ and $\tilde{M}_c$. Since in Cu_2O the uppermost valence bands as well as the lowermost conduction band have positive parity, we see from Eq. (26) that only bands with negative parity will contribute to the

TABLE I: Reduction of the irreducible representations of the cubic group O_h by the groups $C_{4\mathrm{v}}$ ($\boldsymbol{K} \parallel [001]$), $C_{2\mathrm{v}}$ ($\boldsymbol{K} \parallel [110]$), and $C_{3\mathrm{v}}$ ($\boldsymbol{K} \parallel [111]$) [76]. Note that only the irreducible representation Γ_5 of $C_{4\mathrm{v}}$ and the irreducible representation Γ_3 of $C_{3\mathrm{v}}$ are two-dimensional. Hence, almost all degeneracies in the exciton spectrum are lifted for $K \neq 0$.

O_h	$C_{4\mathrm{v}}$	$C_{2\mathrm{v}}$	$C_{3\mathrm{v}}$
Γ_1^+	Γ_1	Γ_1	Γ_1
Γ_2^+	Γ_3	Γ_2	Γ_2
Γ_3^+	$\Gamma_1 \oplus \Gamma_3$	$\Gamma_1 \oplus \Gamma_2$	Γ_3
Γ_4^+	$\Gamma_2 \oplus \Gamma_5$	$\Gamma_2 \oplus \Gamma_3 \oplus \Gamma_4$	$\Gamma_2 \oplus \Gamma_3$
Γ_5^+	$\Gamma_4 \oplus \Gamma_5$	$\Gamma_1 \oplus \Gamma_3 \oplus \Gamma_4$	$\Gamma_1 \oplus \Gamma_3$
Γ_1^-	Γ_2	Γ_3	Γ_2
Γ_2^-	Γ_4	Γ_4	Γ_1
Γ_3^-	$\Gamma_2 \oplus \Gamma_4$	$\Gamma_3 \oplus \Gamma_4$	Γ_3
Γ_4^-	$\Gamma_1 \oplus \Gamma_5$	$\Gamma_1 \oplus \Gamma_2 \oplus \Gamma_4$	$\Gamma_1 \oplus \Gamma_3$
Γ_5^-	$\Gamma_3 \oplus \Gamma_5$	$\Gamma_1 \oplus \Gamma_2 \oplus \Gamma_3$	$\Gamma_2 \oplus \Gamma_3$

sums in Eq. (23). In Cu_2O there are only two bands of negative parity, which lie 449 meV above the lowest conduction band and 5.6 eV below the highest conduction band [47]. Hence, as regards the denominators of the form $(E_m - E_n)$ in M_c and M_v the small energy difference between the Γ_7^+ and the Γ_8^+ valence band due to the spin-orbit coupling plays a minimal role. Furthermore, the denominator $(E_c - E_n)$ in M_c is much smaller than the denominator $(E_v - E_n)$ in M_v and it is $M_c \gg M_v$. We therefore neglect M_v in this paper. As a consequence, to obtain absolute oscillator strengths, only one parameter η in the final expression

$$f_{\xi\nu\boldsymbol{K}} = \eta \left| \lim_{r\to 0} \left[-i \frac{\partial}{\partial r} \langle T^D_{\xi\boldsymbol{K}} | \Psi_{\nu\boldsymbol{K}} \rangle + \frac{\alpha K}{\sqrt{6}} \langle T^Q_{\xi\boldsymbol{K}} | \Psi_{\nu\boldsymbol{K}} \rangle \right] \right|^2 \tag{46}$$

has to be determined via a comparison with experimental values. Note that when evaluating the oscillator strength a mixing term between the dipole and the quadrupole term appears. This is due to the fact that parity is no longer a good quantum number for finite values of K.

We now have to note that light is always transversely polarized and that the vector $\boldsymbol{K}$ of the exciton is identical to the wave vector of the incident light [7]. Here we choose $\boldsymbol{K}$ to be oriented in [001], [110], or [111] direction and, as in Ref. [21], we also rotate the coordinate system to make the z axis of the new coordinate system coincide with the direction of $\boldsymbol{K}$. The formulas for the oscillator strengths for the three orientations of $\boldsymbol{K}$ will be given in the following.

A. Wave vector $\boldsymbol{K} \parallel [001]$

For $\boldsymbol{K} \parallel [001]$, the symmetry O_h of the system is reduced to $C_{4\mathrm{v}}$ and we have to consider the reduction of the irreducible representations of O_h by the group $C_{4\mathrm{v}}$ (see Table I). Especially for Γ_4^- it is

$$\Gamma_4^- \to \Gamma_1 \oplus \Gamma_5. \tag{47}$$

Using the method of projection operators [72], we can determine the correct linear combinations of the states in Eqs. (42) and (45) which transform according to the irreducible representations of $C_{4\mathrm{v}}$. On the other hand, it is instructive that the correct linear combinations are given according to the direction of $\boldsymbol{K}$ and the polarization vectors $\hat{\boldsymbol{e}}_{\xi\boldsymbol{K}}$ transverse to $\boldsymbol{K}$:

$$\hat{\boldsymbol{K}} = (0,\, 0,\, 1)^\mathrm{T}, \tag{48a}$$

$$\hat{\boldsymbol{e}}_{1\boldsymbol{K}} = (1,\, 0,\, 0)^\mathrm{T}, \tag{48b}$$

$$\hat{\boldsymbol{e}}_{2\boldsymbol{K}} = (0,\, 1,\, 0)^\mathrm{T}. \tag{48c}$$

Since light is always transversely polarized, only states of symmetry Γ_5 are allowed. The correct linear combinations of the states (42) are

$$\Gamma_1 : |L^D_{\boldsymbol{K}}\rangle = |\pi^D_z\rangle, \tag{49a}$$

$$\Gamma_5 : |T^D_{1\boldsymbol{K}}\rangle = |\pi^D_x\rangle \text{ and} \tag{49b}$$

$$|T^D_{2\boldsymbol{K}}\rangle = |\pi^D_y\rangle, \tag{49c}$$

and likewise for the states of Eq. (45). If we assume the incident light to be circularly polarized, the oscillator strength is given by

$$f_{\xi\nu\boldsymbol{K}} = \eta \left| \lim_{r\to 0} \left[-i \frac{\partial}{\partial r} \langle T^D_{\pm\boldsymbol{K}} | \Psi_{\nu\boldsymbol{K}} \rangle + \frac{\alpha K}{\sqrt{6}} \langle T^Q_{\pm\boldsymbol{K}} | \Psi_{\nu\boldsymbol{K}} \rangle \right] \right|^2 \tag{50}$$

with

$$|T^D_{+\boldsymbol{K}}\rangle = \frac{-i}{\sqrt{2}} \left[|T^D_{1\boldsymbol{K}}\rangle + i |T^D_{2\boldsymbol{K}}\rangle \right] = |2,\, -1\rangle_D\,, \tag{51a}$$

$$|T^D_{-\boldsymbol{K}}\rangle = \frac{i}{\sqrt{2}} \left[|T^D_{1\boldsymbol{K}}\rangle - i |T^D_{2\boldsymbol{K}}\rangle \right] = -\,|2,\, 1\rangle_D \tag{51b}$$

and

$$|T^Q_{+\boldsymbol{K}}\rangle = \frac{-i}{\sqrt{2}} \left[|T^Q_{1\boldsymbol{K}}\rangle + i |T^Q_{2\boldsymbol{K}}\rangle \right] = |1,\, -1\rangle_Q\,, \tag{52a}$$

$$|T^Q_{-\boldsymbol{K}}\rangle = \frac{i}{\sqrt{2}} \left[|T^Q_{1\boldsymbol{K}}\rangle - i |T^Q_{2\boldsymbol{K}}\rangle \right] = -\,|1,\, 1\rangle_Q\,. \tag{52b}$$

Note that the sign $\pm$ is defined by the direction of rotation of the polarization with respect to $\boldsymbol{K}$.

B. Wave vector $\boldsymbol{K} \parallel [110]$

For $\boldsymbol{K} \parallel [110]$ the symmetry is reduced to $C_{2\mathrm{v}}$ and it is

$$\Gamma_4^- \to \Gamma_1 \oplus \Gamma_2 \oplus \Gamma_4. \tag{53}$$

The corresponding vectors are

$$\hat{\boldsymbol{K}} = (1,\,1,\,0)^{\mathrm{T}}/\sqrt{2}, \tag{54a}$$
$$\hat{\boldsymbol{e}}_{1\boldsymbol{K}} = (1,\,-1,\,0)^{\mathrm{T}}/\sqrt{2}, \tag{54b}$$
$$\hat{\boldsymbol{e}}_{2\boldsymbol{K}} = (0,\,0,\,1)^{\mathrm{T}}, \tag{54c}$$

so that the correct linear combinations of the states (42) read

$$\Gamma_1 : |L^D_{\boldsymbol{K}}\rangle = \frac{1}{\sqrt{2}}\left[\left|\pi^D_x\right\rangle + \left|\pi^D_y\right\rangle\right], \tag{55a}$$

$$\Gamma_2 : |T^D_{1\boldsymbol{K}}\rangle = \frac{1}{\sqrt{2}}\left[\left|\pi^D_x\right\rangle - \left|\pi^D_y\right\rangle\right], \tag{55b}$$

$$\Gamma_4 : |T^D_{2\boldsymbol{K}}\rangle = \left|\pi^D_z\right\rangle. \tag{55c}$$

We now choose the quantization axis parallel to $\boldsymbol{K}$, i.e., we rotate the coordinate system by the Euler angles $(\alpha,\,\beta,\,\gamma) = (\pi,\,\pi/2,\,\pi/4)$. Rotating the states $|L^i_{\boldsymbol{K}}\rangle$ and $|T^i_{\xi\boldsymbol{K}}\rangle$ as well yields

$$|L'^D_{\boldsymbol{K}}\rangle = |\pi^D_{z'}\rangle = \frac{1}{\sqrt{2}}\left[|2,\,-1\rangle_D - |2,\,1\rangle_D\right], \tag{56a}$$

$$|T'^D_{1\boldsymbol{K}}\rangle = |\pi^D_{y'}\rangle = \frac{i}{\sqrt{2}}\left[|2,\,2\rangle_D - |2,\,-2\rangle_D\right], \tag{56b}$$

$$|T'^D_{2\boldsymbol{K}}\rangle = |\pi^D_{x'}\rangle = \frac{\sqrt{3}}{2}|2,\,0\rangle_D + \frac{1}{\sqrt{8}}\left[|2,\,-2\rangle_D + |2,\,2\rangle_D\right], \tag{56c}$$

and

$$|L'^Q_{\boldsymbol{K}}\rangle = |\pi^Q_{z'}\rangle = \frac{1}{\sqrt{2}}\Big[|1,\,-1\rangle_Q - |1,\,1\rangle_Q\Big], \tag{57a}$$

$$|T'^Q_{1\boldsymbol{K}}\rangle = |\pi^Q_{y'}\rangle = 0, \tag{57b}$$

$$|T'^Q_{2\boldsymbol{K}}\rangle = |\pi^Q_{x'}\rangle = |1,\,0\rangle_Q. \tag{57c}$$

The labels x', y' and z' are meant to indicate that the states are given in the rotated coordinate system. Finally, we calculate the oscillator strengths by evaluating

$$f_{\nu\xi\boldsymbol{K}} = \eta\left|\lim_{r\to 0}\left[-i\frac{\partial}{\partial r}\langle T'^D_{\xi\boldsymbol{K}}|\Psi_{\nu\boldsymbol{K}}\rangle + \frac{\alpha K}{\sqrt{6}}\langle T'^Q_{\xi\boldsymbol{K}}|\Psi_{\nu\boldsymbol{K}}\rangle\right]\right|^2 \tag{58}$$

for light which is polarized in [001] or in $[1\bar{1}0]$ direction.

C. Wave vector $\boldsymbol{K} \parallel [111]$

For $\boldsymbol{K} \parallel [111]$ the symmetry is reduced to $C_{3\mathrm{v}}$ and we have

$$\Gamma_4^- \to \Gamma_1 \oplus \Gamma_3 \tag{59}$$

with the vectors

$$\hat{\boldsymbol{K}} = (1,\,1,\,1)^{\mathrm{T}}/\sqrt{3}, \tag{60a}$$
$$\hat{\boldsymbol{e}}_{1\boldsymbol{K}} = (1,\,1,\,-2)^{\mathrm{T}}/\sqrt{6}, \tag{60b}$$
$$\hat{\boldsymbol{e}}_{2\boldsymbol{K}} = (-1,\,1,\,0)^{\mathrm{T}}/\sqrt{2}. \tag{60c}$$

The correct linear combinations of the states in Eqs. (42) are therefore

$$\Gamma_1 : |L^D_{\boldsymbol{K}}\rangle = \frac{1}{\sqrt{3}}\left[\left|\pi^D_x\right\rangle + \left|\pi^D_y\right\rangle + \left|\pi^D_z\right\rangle\right], \tag{61a}$$

$$\Gamma_3 : |T^D_{1\boldsymbol{K}}\rangle = \frac{1}{\sqrt{6}}\left[\left|\pi^D_x\right\rangle + \left|\pi^D_y\right\rangle - 2\left|\pi^D_z\right\rangle\right] \text{ and} \tag{61b}$$
$$|T^D_{2\boldsymbol{K}}\rangle = \frac{1}{\sqrt{2}}\left[-\left|\pi^D_x\right\rangle + \left|\pi^D_y\right\rangle\right] \tag{61c}$$

Here we rotate the coordinate system by the Euler angles $(\alpha,\,\beta,\,\gamma) = \big(0,\,\arccos(1/\sqrt{3}),\,\pi/4\big)$. Rotating the states of Eq. (61) and assuming circularly polarized light yields

$$|L''^D_{\boldsymbol{K}}\rangle = |2,\,0\rangle_D, \tag{62a}$$

$$|T''^D_{+\boldsymbol{K}}\rangle = \frac{i}{\sqrt{3}}\left[\sqrt{2}\,|2,\,-2\rangle_D - |2,\,1\rangle_D\right] \text{ and} \tag{62b}$$
$$|T''^D_{-\boldsymbol{K}}\rangle = \frac{-i}{\sqrt{3}}\left[\sqrt{2}\,|2,\,2\rangle_D + |2,\,-1\rangle_D\right], \tag{62c}$$

and

$$|L''^Q_{\boldsymbol{K}}\rangle = \frac{2}{\sqrt{3}}|1,\,0\rangle_Q, \tag{63a}$$

$$|T''^Q_{+\boldsymbol{K}}\rangle = \frac{-i}{\sqrt{3}}|1,\,1\rangle_Q \text{ and} \tag{63b}$$
$$|T''^Q_{-\boldsymbol{K}}\rangle = \frac{-i}{\sqrt{3}}|1,\,-1\rangle_Q. \tag{63c}$$

We finally calculate the oscillator strengths by evaluating

$$f_{\xi\nu\boldsymbol{K}} = \eta\left|\lim_{r\to 0}\left[-i\frac{\partial}{\partial r}\langle T''^D_{\pm\boldsymbol{K}}|\Psi_{\nu\boldsymbol{K}}\rangle + \frac{\alpha K}{\sqrt{6}}\langle T''^Q_{\pm\boldsymbol{K}}|\Psi_{\nu\boldsymbol{K}}\rangle\right]\right|^2. \tag{64}$$

IV. EXCITON-POLARITONS

In this section we recapitulate the quantum mechanical theory of exciton-polaritons in Sec. IV A and discuss the

rotating-wave approximation in Sec. IV B. To obtain the correct treatment of the K-dependent problem, we consider the nonanalytic exchange interaction in Sec. IV C. In Sec. IV D we shortly present the criteria for the observability of polariton effects.

A. Polariton transformation

The quantum mechanical theory of polaritons was first developed by Hopfield, Fano, and Agranovich [55–57]. According to Refs. [55, 77, 78], the second-quantized Hamiltonian for the interaction of excitons and photons

$$\begin{aligned} H &= \sum_{\xi\boldsymbol{K}} \Bigg[\hbar\omega_{\xi\boldsymbol{K}} \left(a^\dagger_{\xi\boldsymbol{K}} a_{\xi\boldsymbol{K}} + \frac{1}{2} \right) \\ &+ \sum_{\nu} E_{\nu\boldsymbol{K}} \left(B^\dagger_{\nu\boldsymbol{K}} B_{\nu\boldsymbol{K}} + \frac{1}{2} \right) \\ &+ i \sum_{\nu} C_{\xi\,\nu\boldsymbol{K}} \left(a^\dagger_{\xi\boldsymbol{K}} + a_{\xi-\boldsymbol{K}} \right) \left(B_{\nu\boldsymbol{K}} - B^\dagger_{\nu-\boldsymbol{K}} \right) \\ &+ \sum_{\nu} D_{\xi\,\nu\boldsymbol{K}} \left(a^\dagger_{\xi\boldsymbol{K}} + a_{\xi-\boldsymbol{K}} \right) \left(a_{\xi\boldsymbol{K}} + a^\dagger_{\xi-\boldsymbol{K}} \right) \Bigg] \end{aligned} \tag{65}$$

can be derived either from a microscopic model of excitons with the Hamiltonian describing the interaction between radiation and matter or from the equation of motion for the exciton polarization. In the Hamiltonian (65) the operator $B^\dagger_{\nu\boldsymbol{K}}$ ($B_{\nu\boldsymbol{K}}$) creates (annihilates) an exciton with energy $E_{\nu\boldsymbol{K}}$. Likewise, the operator $a^\dagger_{\xi\boldsymbol{K}}$ ($a_{\xi\boldsymbol{K}}$) creates (annihilates) a photon with polarization ξ and energy $\hbar\omega_{\xi\boldsymbol{K}} = \hbar cK/\sqrt{\varepsilon_{\mathrm{b}2}}$. The coupling coefficients in the exciton-photon and the photon-photon interaction terms of Eq. (65) are given by

$$C_{\xi\,\nu\boldsymbol{K}} = \left[\frac{\kappa_{\mathrm{SI}} \pi \beta_{\xi\nu\boldsymbol{K}} E^3_{\nu\boldsymbol{K}}}{\varepsilon_{\mathrm{b}2} \hbar\omega_{\xi\boldsymbol{K}}} \right]^{\frac{1}{2}} \tag{66}$$

with

$$\kappa_{\mathrm{SI}} = \frac{1}{4\pi\varepsilon_0} \tag{67}$$

and

$$D_{\xi\,\nu\boldsymbol{K}} = \frac{C^2_{\xi\,\nu\boldsymbol{K}}}{E_{\nu\boldsymbol{K}}}. \tag{68}$$

The polarizability $\beta_{\xi\nu\boldsymbol{K}}$ is proportional to the oscillator strength of the exciton state. With our definition of the oscillator strength $f_{\xi\nu\boldsymbol{K}}$ (cf. Refs. [64–67]) this proportionality is given by [77, 79, 80]

$$\beta_{\xi\nu\boldsymbol{K}} = \varepsilon_0 \varepsilon_{\mathrm{b}2} f_{\xi\nu\boldsymbol{K}}. \tag{69}$$

The Hamiltonian (65) can be diagonalized by the Hopfield transformation [55, 56], which is similar to the Bogolyubov's uv transformation [81, 82]: New creation and annihilation operators $p^\dagger_{\mu\xi\boldsymbol{K}}$ and $p_{\mu\xi\boldsymbol{K}}$ are introduced via

$$a_{\xi\boldsymbol{K}} = \sum_{\mu} \left[u_{\mu\xi\boldsymbol{K}} p_{\mu\xi\boldsymbol{K}} + v^*_{\mu\xi-\boldsymbol{K}} p^\dagger_{\mu\xi-\boldsymbol{K}} \right], \tag{70a}$$

$$B_{\nu\boldsymbol{K}} = \sum_{\mu} \left[u_{\mu\xi\nu\boldsymbol{K}} p_{\mu\xi\boldsymbol{K}} + v^*_{\mu\xi\nu-\boldsymbol{K}} p^\dagger_{\mu\xi-\boldsymbol{K}} \right], \tag{70b}$$

to obtain the polariton Hamiltonian

$$H = \sum_{\mu\xi\boldsymbol{K}} E_{\mu\xi\boldsymbol{K}} p^\dagger_{\mu\xi\boldsymbol{K}} p_{\mu\xi\boldsymbol{K}} + \text{const.} \tag{71}$$

with μ and $E_{\mu\xi\boldsymbol{K}}$ denoting the polariton branches and the polariton energies, respectively. The new operators must obey Bose commutation relations and the Hamiltonian shall be diagonal, i.e.,

$$[p_{\mu\xi\boldsymbol{K}}, H] = E_{\mu\xi\boldsymbol{K}} p_{\mu\xi\boldsymbol{K}} \tag{72}$$

must hold. This provides the following conditional equation for the polariton energies [57, 78, 83]:

$$\frac{\hbar^2 c^2 K^2}{E^2_{\mu\xi\boldsymbol{K}}} = \varepsilon_{\mathrm{b}2} + \sum_{\nu} \frac{4\pi\kappa_{\mathrm{SI}} \beta_{\xi\nu\boldsymbol{K}}}{1 - \left(E_{\mu\xi\boldsymbol{K}} / E_{\nu\boldsymbol{K}} \right)^2}. \tag{73}$$

Using the phase convention of Hopfield [55], one obtains the following solution for the coefficients of the polariton transformation [78]:

$$u_{\mu\xi\boldsymbol{K}} = \frac{\hbar\omega_{\xi\boldsymbol{K}} + E_{\mu\xi\boldsymbol{K}}}{2\sqrt{\hbar\omega_{\xi\boldsymbol{K}} E_{\mu\xi\boldsymbol{K}} g_{\mu\xi\boldsymbol{K}}}}, \tag{74a}$$

$$\begin{aligned} u_{\mu\xi\nu\boldsymbol{K}} &= i \sqrt{\frac{\pi\kappa_{\mathrm{SI}} \beta_{\xi\nu\boldsymbol{K}}}{\varepsilon_{\mathrm{s}1} E_{\mu\xi\boldsymbol{K}} E_{\nu\boldsymbol{K}} g_{\mu\xi\boldsymbol{K}}}} \\ &\times \frac{E_{\nu\boldsymbol{K}} + E_{\mu\xi\boldsymbol{K}}}{1 - \left(E_{\mu\xi\boldsymbol{K}} / E_{\nu\boldsymbol{K}} \right)^2}, \end{aligned} \tag{74b}$$

$$v_{\mu\xi-\boldsymbol{K}} = \frac{\hbar\omega_{\xi\boldsymbol{K}} - E_{\mu\xi\boldsymbol{K}}}{\hbar\omega_{\xi\boldsymbol{K}} + E_{\mu\xi\boldsymbol{K}}} u_{\mu\xi\boldsymbol{K}}, \tag{74c}$$

$$v_{\mu\xi\nu-\boldsymbol{K}} = -\frac{E_{\nu\boldsymbol{K}} - E_{\mu\xi\boldsymbol{K}}}{E_{\nu\boldsymbol{K}} + E_{\mu\xi\boldsymbol{K}}} u_{\mu\xi\nu\boldsymbol{K}}, \tag{74d}$$

with

$$g_{\mu\xi\boldsymbol{K}} = 1 + \sum_{\nu} \frac{4\pi\kappa_{\mathrm{SI}} \beta_{\xi\nu\boldsymbol{K}}}{\varepsilon_{\mathrm{b}2} \left[1 - \left(E_{\mu\xi\boldsymbol{K}} / E_{\nu\boldsymbol{K}} \right)^2 \right]^2}. \tag{74e}$$

The polariton operators can also be expressed in terms of exciton and photon operators:

$$\begin{aligned} p_{\mu\xi\boldsymbol{K}} &= w^{(1)}_{\mu\xi\boldsymbol{K}} a_{\xi\boldsymbol{K}} + w^{(2)*}_{\mu\xi-\boldsymbol{K}} a^\dagger_{\xi-\boldsymbol{K}} \\ &+ \sum_{\nu} \left[z^{(1)}_{\mu\xi\nu\boldsymbol{K}} B_{\nu\boldsymbol{K}} + z^{(2)*}_{\mu\xi\nu-\boldsymbol{K}} B^\dagger_{\nu-\boldsymbol{K}} \right]. \end{aligned} \tag{75}$$

Since all creation and annihilation operators of the three (quasi-) particles obey Bose commutation relations, we can determine the coefficients w and z by evaluating

$$\left[p_{\mu\xi\boldsymbol{K}},\, a^\dagger_{\xi\boldsymbol{K}}\right] = +w^{(1)}_{\mu\xi\boldsymbol{K}} = u^*_{\mu\xi\boldsymbol{K}}, \tag{76a}$$

$$\left[p_{\mu\xi\boldsymbol{K}},\, a_{\xi-\boldsymbol{K}}\right] = -w^{(2)*}_{\mu\xi\boldsymbol{K}} = v^*_{\mu\xi\boldsymbol{K}} \tag{76b}$$

and

$$\left[p_{\mu\xi\boldsymbol{K}},\, B^\dagger_{\nu-\boldsymbol{K}}\right] = +z^{(1)}_{\mu\xi\nu\boldsymbol{K}} = u^*_{\mu\xi\nu\boldsymbol{K}}, \tag{77a}$$

$$\left[p_{\mu\xi\boldsymbol{K}},\, B_{\nu\boldsymbol{K}}\right] = -z^{(2)*}_{\mu\xi\nu\boldsymbol{K}} = v^*_{\mu\xi\nu\boldsymbol{K}}. \tag{77b}$$

The coefficients $w^{(i)}_{\mu\xi\boldsymbol{K}}$ or the sum

$$W_{\mu\xi\boldsymbol{K}} = \sum_{i=1}^{2} |w^{(i)}_{\mu\xi\boldsymbol{K}}|^2 \tag{78}$$

then allow one to determine whether the polariton is more photon-like ($W_{\mu\xi\boldsymbol{K}} \to 1$) or more exciton-like ($W_{\mu\xi\boldsymbol{K}} \to 0$).

B. Rotating-wave approximation

In the literature polaritons are often treated within the so-called rotating-wave approximation [77]. In this case the term with the coefficient D and the anti-resonant terms of the form aB and $a^\dagger B^\dagger$ are neglected in the Hamiltonian (65). The resulting Hamiltonian

$$H = \sum_{\xi\boldsymbol{K}} \Bigg[\hbar\omega_{\xi\boldsymbol{K}} a^\dagger_{\xi\boldsymbol{K}} a_{\xi\boldsymbol{K}} + \sum_\nu E_{\nu\boldsymbol{K}} B^\dagger_{\nu\boldsymbol{K}} B_{\nu\boldsymbol{K}} + \sum_\nu C_{\xi\,\nu\boldsymbol{K}} \left(a^\dagger_{\xi\boldsymbol{K}} B_{\nu\boldsymbol{K}} + a_{\xi\boldsymbol{K}} B^\dagger_{\nu\boldsymbol{K}} \right) \Bigg] \tag{79}$$

is then called the Jaynes-Cummings Hamiltonian [84], where the vacuum energy of the photons has also been neglected [77] and where the operators $a_{\xi\boldsymbol{K}}$ have been replaced with $ia_{\xi\boldsymbol{K}}$. Note that this replacement does not change the physics of the problem since it only adds global phases to the occupation-number states. The occupation-number operator and the commutation relations remain unchanged.

The coefficient $C_{\xi\,\nu\boldsymbol{K}}$ can be written as [77, 80]

$$C_{\xi\,\nu\boldsymbol{K}} = \left[\frac{\kappa_{\mathrm{SI}} \pi \beta_{\xi\nu\boldsymbol{K}} E^3_{\nu\boldsymbol{K}}}{\varepsilon\hbar\omega_{\xi\boldsymbol{K}}} \right]^{\frac{1}{2}} \approx \frac{1}{2} \left(\frac{K_0}{K} \right)^{\frac{1}{2}} \hbar\Omega_{\mathrm{R}} \tag{80}$$

with the wave vector at the exciton-photon resonance $K_0 = E_{\nu\boldsymbol{K}_0}\sqrt{\varepsilon_{\mathrm{b2}}}/\hbar c$ and the Rabi frequency

$$\Omega_{\mathrm{R}} = E_{\nu\boldsymbol{K}_0} \sqrt{\frac{4\pi\kappa_{\mathrm{SI}}\beta_{\xi\nu\boldsymbol{K}}}{\varepsilon\hbar^2}}. \tag{81}$$

The rotating wave approximation is generally valid if $\hbar\Omega_{\mathrm{R}} \ll E_{\nu\boldsymbol{K}_0}$ holds. This is, e.g., the case for anorganic semiconductors and especially for Cu_2O [80].

Close to the resonance ($K \approx K_0$) one can assume $C_{\xi\,\nu\boldsymbol{K}} \approx \hbar\Omega_{\mathrm{R}}/2$. Note that for $K \to 0$ the coupling constant (80) diverges, which is *a manifestation of the infrared catastrophe in quantum electrodynamics* [77]. Hence, the simplifications made above are valid only in the vicinity of the exciton-photon resonance. Otherwise, the full Hamiltonian (65) has to be diagonalized.

In the rotating-wave approximation the polariton transformation is more simple as there is no interaction between states with different values of $\boldsymbol{K}$. Using the ansatz

$$p_{\mu\xi\boldsymbol{K}} = w_{\mu\xi\boldsymbol{K}} a_{\xi\boldsymbol{K}} + \sum_i z_{\mu\xi\nu_i\boldsymbol{K}} B_{\nu_i\boldsymbol{K}}, \tag{82}$$

the Bose commutation relations of the creation and annihilation operators, and the condition (72) for the polariton operator, one ends up with the eigenvalue problem

$$\boldsymbol{P}_{\xi\{\nu\}\boldsymbol{K}} \boldsymbol{z}_{\mu\xi\{\nu\}\boldsymbol{K}} = E_{\mu\xi\boldsymbol{K}} \boldsymbol{z}_{\mu\xi\{\nu\}\boldsymbol{K}} \tag{83}$$

with

$$\boldsymbol{P}_{\xi\{\nu\}\boldsymbol{K}} = \begin{pmatrix} \hbar\omega_{\xi\boldsymbol{K}} & \frac{1}{2}\hbar\Omega_{\mathrm{R},\,\nu_1} & \frac{1}{2}\hbar\Omega_{\mathrm{R},\,\nu_2} & \cdots & \frac{1}{2}\hbar\Omega_{\mathrm{R},\,\nu_n} & \cdots \\ \frac{1}{2}\hbar\Omega_{\mathrm{R},\,\nu_1} & E_{\nu_1\boldsymbol{K}} & 0 & \cdots & 0 & \cdots \\ \frac{1}{2}\hbar\Omega_{\mathrm{R},\,\nu_2} & 0 & E_{\nu_2\boldsymbol{K}} & & \vdots & \\ \vdots & \vdots & & \ddots & 0 & \cdots \\ \frac{1}{2}\hbar\Omega_{\mathrm{R},\,\nu_n} & 0 & \cdots & 0 & E_{\nu_n\boldsymbol{K}} & \\ \vdots & \vdots & & \vdots & & \ddots \end{pmatrix} \quad \text{and} \quad \boldsymbol{z}_{\mu\xi\{\nu\}\boldsymbol{K}} = \begin{pmatrix} w_{\mu\xi\boldsymbol{K}} \\ z_{\mu\xi\nu_1\boldsymbol{K}} \\ z_{\mu\xi\nu_2\boldsymbol{K}} \\ \vdots \\ z_{\mu\xi\nu_n\boldsymbol{K}} \\ \vdots \end{pmatrix}. \tag{84}$$

Knowing the energies $E_{\nu\boldsymbol{K}}$ and the Rabi frequencies $\Omega_{\mathrm{R},\,\nu}$ of the exciton states, one can directly obtain the corre-

sponding polariton energies by determining the eigenvalues of Eq. (83). Note that the characteristic polynomial for the eigenvalue problem (83) is of a similar form than Eq. (73) [85–87],

$$\hbar\omega_{\xi\boldsymbol{K}} = E_{\mu\xi\boldsymbol{K}} + \sum_{j=2}^{n} \frac{\left(\frac{\hbar}{2}\Omega_{\mathrm{R},\,j}\right)^2}{E_{j\boldsymbol{K}} - E_{\mu\xi\boldsymbol{K}}}, \tag{85}$$

but due to the approximations made in the rotating wave approximation, both equations are not identical.

Finally, as the polariton is a mixed state of a photon and excitons, one can again determine the photon-like part

$$W_{\mu\xi\boldsymbol{K}} = |w_{\mu\xi\boldsymbol{K}}|^2 \tag{86}$$

of the polariton or the contribution of the exciton with the energy $E_{\nu\boldsymbol{K}}$ to the polariton

$$Z_{\mu\xi\nu\boldsymbol{K}} = |z_{\mu\xi\nu\boldsymbol{K}}|^2. \tag{87}$$

C. Nonanalytic exchange interaction

From the formula (46) for the oscillator strength one can see that the exciton-photon coupling affects only the transverse exciton states. However, there is another interaction affecting the longitudinal exciton states: the nonanalytic (NA) exchange interaction. It is well known that the splitting caused by $H_{\mathrm{exch}}^{\mathrm{NA}}$ is identical to the longitudinal-transverse splitting (LT-splitting) when treating polaritons [88]. Hence, it is indispensable to include the nonanalytic exchange interaction in the theory to obtain a correct treatment of the complete problem.

In this section we will derive an expression for the nonanalytic exchange interaction. We start with the formula of Ref. [25] for the nonanalytic exchange energy between two exciton states $\Psi^{\sigma\tau}_{vc,\,\nu\boldsymbol{K}}$ and $\Psi^{\sigma'\tau'}_{vc,\,\nu'\boldsymbol{K}'}$ in second quantization

$$H_{\mathrm{exch}}^{\mathrm{NA}} = \sum_{\nu\nu'\boldsymbol{K}} \frac{m^*_{\nu\boldsymbol{K}} m_{\nu'\boldsymbol{K}}}{\varepsilon_0\varepsilon_{\mathrm{b}2} V_{\mathrm{uc}} K^2} B^\dagger_{\nu\boldsymbol{K}} B_{\nu'\boldsymbol{K}} \tag{88}$$

with the volume V_{uc} of one unit cell and

$$m_{\nu\boldsymbol{K}} = \delta_{\sigma\tau}\frac{e}{\sqrt{N}}\sum_{\boldsymbol{q}} f_{vc\,\nu}(\boldsymbol{q}) \left\{ -\frac{\hbar}{m_0}\frac{\boldsymbol{K}\boldsymbol{p}_{vc}}{E_v - E_c} + \frac{\hbar^2}{m_0^2}\sum_{n\neq v,c}\left[\frac{(\boldsymbol{q}-\gamma\boldsymbol{K})\,\boldsymbol{p}_{vn}\;(\boldsymbol{q}+\alpha\boldsymbol{K})\,\boldsymbol{p}_{nc}}{(E_v - E_n)\,(E_c - E_n)} \right.\right.$$
$$\left.\left. + \frac{(\boldsymbol{q}+\alpha\boldsymbol{K})\,\boldsymbol{p}_{vn}\;(\boldsymbol{q}+\alpha\boldsymbol{K})\,\boldsymbol{p}_{nc}}{(E_c - E_v)\,(E_c - E_n)} + \frac{(\boldsymbol{q}-\gamma\boldsymbol{K})\,\boldsymbol{p}_{nc}\;(\boldsymbol{q}-\gamma\boldsymbol{K})\,\boldsymbol{p}_{vn}}{(E_v - E_c)\,(E_v - E_n)} \right] \right\}. \tag{89}$$

Here $m_{\nu\boldsymbol{K}}$ is a short notation for the function $m_{vc\,\nu}(\boldsymbol{K}, \boldsymbol{0})$ of Ref. [25]. For the definitions of $\Psi^{\sigma\tau}_{vc,\,\nu\boldsymbol{K}}$, $f_{vc\,\nu}(\boldsymbol{q})$, and $\boldsymbol{p}_{mn}$ see Sec. III. The exchange energy includes the term $\delta_{\sigma\tau}\delta_{\sigma'\tau'}$. Introducing the total spin $S = S_{\mathrm{e}} + S_{\mathrm{h}} = \tau - \sigma$ of electron and hole, this term can be written for singlet and triplet states as $2\delta_{S,0}$ [74].

Using Eq. (24) and rearranging the different terms in Eq. (89) yields

$$\begin{aligned} m_{\nu\boldsymbol{K}} &= \delta_{\sigma\tau}\frac{e\hbar^2}{m_0^2}\frac{K}{(E_c - E_v)} \\ &\times \lim_{\boldsymbol{r}\to\boldsymbol{0}}\Big[\left(\tilde{\boldsymbol{N}}_v + \tilde{\boldsymbol{N}}_c\right)\cdot\left(-i\nabla_{\boldsymbol{r}} F_{vc\,\nu}(\boldsymbol{r})\right) \\ &+ \left(-\gamma\tilde{\boldsymbol{N}}_v + \alpha\tilde{\boldsymbol{N}}_c\right)\cdot\left(F_{vc\,\nu}(\boldsymbol{r})\,\boldsymbol{K}\right)\Big] \end{aligned} \tag{90}$$

with the matrices

$$\tilde{\boldsymbol{N}}_v = \langle u_{v\boldsymbol{0}}|\,\boldsymbol{p} M_v(\hat{\boldsymbol{K}}\cdot\boldsymbol{p})\,|u_{c\boldsymbol{0}}\rangle\,, \tag{91a}$$
$$\tilde{\boldsymbol{N}}_c = \langle u_{v\boldsymbol{0}}|\,(\hat{\boldsymbol{K}}\cdot\boldsymbol{p}) M_c \boldsymbol{p}\,|u_{c\boldsymbol{0}}\rangle\,. \tag{91b}$$

and $\hat{\boldsymbol{K}} = \boldsymbol{K}/K$.

Due to the similarity between Eq. (25) and Eq. (90), we can perform the same calculation as in Sec. III to obtain

$$m_{\nu\boldsymbol{K}} \sim K \lim_{r\to 0}\left[-i\left(\tilde{M}_v+\tilde{M}_c\right)\frac{\partial}{\partial r}\langle L^D_{\boldsymbol{K}}|\Psi_{\nu\boldsymbol{K}}\rangle+\left(-\gamma\tilde{M}_v+\alpha\tilde{M}_c\right)\frac{K}{\sqrt{6}}\langle L^Q_{\boldsymbol{K}}|\Psi_{\nu\boldsymbol{K}}\rangle\right]. \tag{92}$$

with the longitudinal states

$$|L^D_{\boldsymbol{K}}\rangle = \sum_{i=1}^{3}\hat{K}_i|\pi_i^D\rangle, \tag{93a}$$

$$|L^Q_{\boldsymbol{K}}\rangle = \sum_{i=1}^{3}\hat{K}_i|\pi_i^Q\rangle, \tag{93b}$$

where $|\pi_i^D\rangle$ and $|\pi_i^Q\rangle$ were defined in Eqs. (42) and (45). As in Sec. III we will assume $M_c \gg M_v$ so that we can finally state that $m_{\nu\boldsymbol{K}}$ is proportional to

$$K\lim_{r\to 0}\left[-i\frac{\partial}{\partial r}\langle L^D_{\boldsymbol{K}}|\Psi_{\nu\boldsymbol{K}}\rangle+\frac{\alpha K}{\sqrt{6}}\langle L^Q_{\boldsymbol{K}}|\Psi_{\nu\boldsymbol{K}}\rangle\right]. \tag{94}$$

We can see that from Eq. (88) that there is no interaction between states with different values of $\boldsymbol{K}$, which is the same case as for the Hamiltonian (79) of the polariton interaction in the rotating-wave approximation. Knowing the exciton energies $E_{\nu\boldsymbol{K}}$ and the corresponding wave functions $|\Psi_{\nu\boldsymbol{K}}\rangle$, we can simultaneously diagonalize the polariton Hamiltonian and the NA-exchange Hamiltonian by solving the eigenvalue problem

$$\left(\boldsymbol{P}_{\xi\{\nu\}\boldsymbol{K}}+\boldsymbol{N}_{\{\nu\}\boldsymbol{K}}\right)\boldsymbol{z}_{\mu\xi\{\nu\}\boldsymbol{K}} = E_{\mu\xi\boldsymbol{K}}\boldsymbol{z}_{\mu\xi\{\nu\}\boldsymbol{K}} \tag{95}$$

with the matrix

$$\boldsymbol{N}_{\{\nu\}\boldsymbol{K}} = \frac{\zeta}{\varepsilon_{\mathrm{b}2}K^2}\begin{pmatrix} 0 & 0 & 0 & \cdots & 0 & \cdots \\ 0 & m^*_{\nu_1\boldsymbol{K}}m_{\nu_1\boldsymbol{K}} & m^*_{\nu_1\boldsymbol{K}}m_{\nu_2\boldsymbol{K}} & \cdots & m^*_{\nu_1\boldsymbol{K}}m_{\nu_n\boldsymbol{K}} & \cdots \\ 0 & m^*_{\nu_2\boldsymbol{K}}m_{\nu_1\boldsymbol{K}} & m^*_{\nu_2\boldsymbol{K}}m_{\nu_2\boldsymbol{K}} & & \vdots & \\ \vdots & \vdots & & \ddots & & \cdots \\ 0 & m^*_{\nu_n\boldsymbol{K}}m_{\nu_1\boldsymbol{K}} & \cdots & & m^*_{\nu_n\boldsymbol{K}}m_{\nu_n\boldsymbol{K}} & \\ \vdots & \vdots & & \vdots & & \ddots \end{pmatrix}, \tag{96}$$

and the matrix $\boldsymbol{P}_{\xi\{\nu\}\boldsymbol{K}}$ and vector $\boldsymbol{z}_{\mu\xi\{\nu\}\boldsymbol{K}}$ defined in Eq. (84). The constant parameter ζ can be determined by the fact that the splitting caused by $H^{\mathrm{NA}}_{\mathrm{exch}}$ is identical to the LT-splitting.

D. Observability of polariton effects

We now shortly discuss the criteria for the observability of polariton effects, which were derived by Tait in Ref. [89]. To obtain these criteria, he included a damping term Γ in the model of polaritons since damping is always present in the solid due to the interaction between excitons and phonons or the leakage of photons out of the solid [80]:

$$\frac{\hbar^2c^2K^2}{E^2_{\mu\xi\boldsymbol{K}}} = \varepsilon_{\mathrm{b}2}+\sum_{\nu}\frac{4\pi\kappa_{\mathrm{SI}}\beta_{\xi\nu\boldsymbol{K}}E^2_{\nu\boldsymbol{K}}}{E^2_{\nu\boldsymbol{K}}-E^2_{\mu\xi\boldsymbol{K}}-i\Gamma E_{\mu\xi\boldsymbol{K}}}. \tag{97}$$

This equation can either be solved for a fixed wave vector K or for a fixed frequency $\omega = E_{\mu\xi\boldsymbol{K}}/\hbar$.

The first case corresponds to nonlinear optical experiments like, e.g., two-photon absorption. For this case a criterion of temporal coherence between the photon and the exciton can be derived [77, 89]. As long as

$$\hbar\Gamma < \hbar\sqrt{\kappa_{\mathrm{SI}}\frac{\pi}{\varepsilon_{\mathrm{b}2}}\beta_{\xi\nu\boldsymbol{K}}E^2_{\nu\boldsymbol{K}_0}} = \frac{\hbar}{2}\Omega_{\mathrm{R}} \tag{98}$$

holds, where $\hbar\Gamma$ is the broadening of the linewidth due to damping, the polariton splitting is observable. This criterion can be interpreted in terms of Rabi oscillations, i.e., polariton effects are observable if a coherent energy transfer between an exciton and a photon is possible at least once [80]. Spatial coherence is already provided here by keeping K fixed [77].

The second case corresponds to reflectivity or absorption experiments. Here the coupling between the photon and the exciton must remain coherent during the propagation of the polariton through the solid in the presence of damping [77]. The criterion of spatial coherence reads [77, 80, 90]

$$\hbar\Gamma < \sqrt{\frac{16\pi}{Mc^2}\kappa_{\mathrm{SI}}E^3_{\nu\boldsymbol{K}_0}\beta_{\xi\nu\boldsymbol{K}}} = \frac{\hbar}{2}\Omega_{\mathrm{R}}\sqrt{\frac{16\varepsilon_{\mathrm{b}2}}{Mc^2}E_{\nu\boldsymbol{K}_0}}, \tag{99}$$

and it is generally more difficult to satisfy than

Eq. (98) [80, 91] since $\sqrt{16\varepsilon_{\mathrm{b}2}E_{\nu\boldsymbol{K}_0}/Mc^2} \ll 1$ holds for an exciton mass M on the order of m_0 and an exciton energy on the order of a few eV. The criterion (99) is equivalent to $l \gg \lambda$ with λ denoting the light wavelength and $l = v_g/\Gamma$ the mean free path of the exciton [77]. Hence, polariton effects can hardly be observed in semiconductors with very shallow excitons, e.g., in GaAs [77], when using linear optical techniques. Therefore, polariton effects are often investigated using nonlinear optical spectroscopic techniques due to the much less stringent criterion (98) [92, 93].

V. 5×5 MATRIX MODEL FOR THE $1S$ ORTHO EXCITON POLARITON

The yellow $1S$ ortho exciton is well separated from the other exciton states regarding its energy. Hence, it can be treated separately. In this section we set up a model with a 5×5 matrix, which allows calculating the dispersion of the $1S$ ortho exciton polariton for any direction of $\boldsymbol{K}$ close to the resonance ($K \approx K_0$). This model includes the two photon states with the polarization vectors $\hat{\boldsymbol{e}}_{\xi\boldsymbol{K}}$ and the three ortho exciton states Ψ_i, which transform according to yz, zx and xy.

First we will treat the oscillator strength and the Rabi frequency. Let us consider the most simple case with $\boldsymbol{K} \parallel [001]$. Due to group theoretical reasons, the three states Ψ_{yz}, Ψ_{zx}, and Ψ_{xy} are good eigenstates of the Hamiltonian. The Ψ_{zx} exciton interacts with the photon in x polarization and the Ψ_{yz} exciton interacts with the photon in y polarization. Let us denote the oscillator strength of these exciton states at the exciton-photon resonance by f_0.

For other orientations of $\boldsymbol{K}$ superpositions of the form $\sum_i a_i\Psi_i$ are eigenstates of the Hamiltonian. From the expression (46) or especially from the form of the states $|T^Q_{\xi\boldsymbol{K}}\rangle$ (44) we can see that the K-dependent oscillator strength of these exciton states is given by

$$f_{1S\,\xi\boldsymbol{K}} = f_0 \left| \begin{pmatrix} \hat{e}_{\xi\boldsymbol{K},y}K_z + \hat{e}_{\xi\boldsymbol{K},z}K_y \\ \hat{e}_{\xi\boldsymbol{K},z}K_x + \hat{e}_{\xi\boldsymbol{K},x}K_z \\ \hat{e}_{\xi\boldsymbol{K},x}K_y + \hat{e}_{\xi\boldsymbol{K},y}K_x \end{pmatrix} \cdot \begin{pmatrix} a_{yz} \\ a_{zx} \\ a_{xy} \end{pmatrix} \right|^2 \tag{100}$$

with the components $\hat{e}_{\xi\boldsymbol{K},i}$ of the polarization vector $\hat{\boldsymbol{e}}_{\xi\boldsymbol{K}}$.

For the $1S$ ortho exciton a K-dependent splitting was observed experimentally in Refs. [75, 94, 95] and originally discussed in terms of a K-dependent exchange interaction. However, a closer examination of this interaction revealed that it is far too weak in Cu_2O to describe the observed splitting [25]. Instead, it could be shown that the effects due to the cubic valence band structure lead to a K-dependent effective mass and a K-dependent splitting of the $1S$ ortho exciton [20]. Hence, the directional dispersion is the true cause of the experimentally observed splitting. However, in Ref. [20] the splitting was treated within a perturbation approach and it was already emphasized that the complete K-dependent Schrödinger equation including the central cell corrections would have to be solved to obtain correct results. This can now be done with the help of the theory of Sec. II.

We have already stated in Ref. [25] that a K-dependent splitting of a state with the symmetry Γ_5^+ must always have the form

$$\begin{aligned} \boldsymbol{H}_{\mathrm{disp}}(\boldsymbol{K}) =& \Delta_1 \begin{pmatrix} K^2 & 0 & 0 \\ 0 & K^2 & 0 \\ 0 & 0 & K^2 \end{pmatrix} \\ &+ \Delta_3 \begin{pmatrix} 3K_x^2 - K^2 & 0 & 0 \\ 0 & 3K_y^2 - K^2 & 0 \\ 0 & 0 & 3K_z^2 - K^2 \end{pmatrix} \\ &+ \Delta_5 \begin{pmatrix} 0 & K_xK_y & K_xK_z \\ K_xK_y & 0 & K_yK_z \\ K_xK_z & K_yK_z & 0 \end{pmatrix} \end{aligned} \tag{101}$$

for group theoretical reasons. We will prove the consistency with this formula in Ref. [67] by diagonalizing the Hamiltonian (101) for $\boldsymbol{K} \parallel [001]$, $\boldsymbol{K} \parallel [110]$, and $\boldsymbol{K} \parallel [111]$ and fitting the resulting eigenvalues to the numerical results of the complete problem (6). This will yield the values of the parameters Δ_1, Δ_3 and Δ_5.

For states of symmetry Γ_5^+ it has been shown in Ref. [25] that the nonanalytic exchange interaction can be written as

$$\boldsymbol{H}^{\mathrm{NA}}_{\mathrm{exch}}(\boldsymbol{K}) = \frac{\Delta_Q}{K^2} \begin{pmatrix} K_y^2K_z^2 & K_z^2K_yK_x & K_y^2K_xK_z \\ K_z^2K_yK_x & K_z^2K_x^2 & K_x^2K_yK_z \\ K_y^2K_xK_z & K_x^2K_yK_z & K_x^2K_y^2 \end{pmatrix}. \tag{102}$$

Contrary to dipole allowed excitons, the nonanalytic exchange energy depends on the fourth power of the angular coordinates of $\boldsymbol{K}$. The prefactor Δ_Q is connected to the oscillator strength and can be determined for the $1S$ state in the following way: For the special case of $\boldsymbol{K}$ being oriented in [111] direction, the Γ_5^+ state splits into one longitudinal Γ_1 and two transverse Γ_5 states. The longitudinal state is an eigenstate of the operator (102) with the eigenvalue $\Delta_Q/3$. An excitation of the longitudinal exciton leads to an oscillating longitudinal polarization. Due to the Maxwell equation $\nabla \cdot \boldsymbol{D} = 0$, the dielectric function must be zero. Hence, we have

$$\varepsilon(\omega,\, K_0)\,[\Gamma_1] = \varepsilon_{\mathrm{b}2} + \frac{\frac{4}{3}f_0\varepsilon_{\mathrm{b}2}}{1 - \left(E_0 + \frac{1}{3}\Delta_Q K_0^2\right)^2 / (E_0)^2} \tag{103}$$

with the energy $E_0 = \hbar c K_0/\sqrt{\varepsilon_{\mathrm{b}2}}$ of the Γ_1 exciton at $K = K_0$ without the nonanalytic exchange interaction [cf. also Eq. (73)]. This relation can be solved for Δ_Q. Using $f_0 \ll 1$ [64–66], we obtain

$$\Delta_Q = 2f_0E_0/K_0^2 = 2f_0\hbar^2c^2/\varepsilon_{\mathrm{b}2}. \tag{104}$$

Combining all the K dependent effects for the $1S$ ortho exciton, we arrive at the Hamiltonian for the $1S$ ortho exciton-polariton in the rotating-wave approximation:

$$\boldsymbol{H} = \begin{pmatrix} \boldsymbol{H}_{\mathrm{ph}} & \boldsymbol{H}_{\mathrm{exc-ph}} \\ \boldsymbol{H}_{\mathrm{exc-ph}}^{\mathrm{T}} & \boldsymbol{H}_{\mathrm{exc}} \end{pmatrix} \tag{105}$$

with the 2×2 matrix $\boldsymbol{H}_{\mathrm{ph}}$ containing the photon dispersion,

$$\boldsymbol{H}_{\mathrm{ph}} = \frac{\hbar c K}{\sqrt{\varepsilon_{\mathrm{b2}}}} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = E_0 \frac{K}{K_0} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \tag{106}$$

a 2×3 matrix $\boldsymbol{H}_{\mathrm{exc-ph}}$ with the Rabi energies $\hbar\Omega_{\mathrm{R}} = E_0\sqrt{f_0}$,

$$\boldsymbol{H}_{\mathrm{exc-ph}} = \frac{1}{2}\hbar\Omega_{\mathrm{R}} \frac{1}{K_0} \begin{pmatrix} (\hat{e}_{1\boldsymbol{K},y} K_z + \hat{e}_{1\boldsymbol{K},z} K_y) & (\hat{e}_{1\boldsymbol{K},z} K_x + \hat{e}_{1\boldsymbol{K},x} K_z) & (\hat{e}_{1\boldsymbol{K},x} K_y + \hat{e}_{1\boldsymbol{K},y} K_x) \\ (\hat{e}_{2\boldsymbol{K},y} K_z + \hat{e}_{2\boldsymbol{K},z} K_y) & (\hat{e}_{2\boldsymbol{K},z} K_x + \hat{e}_{2\boldsymbol{K},x} K_z) & (\hat{e}_{2\boldsymbol{K},x} K_y + \hat{e}_{2\boldsymbol{K},y} K_x) \end{pmatrix}, \tag{107}$$

and

$$\boldsymbol{H}_{\mathrm{exc}} = E_0\, \mathbf{1} + \boldsymbol{H}_{\mathrm{disp}}(\boldsymbol{K}) + \boldsymbol{H}_{\mathrm{exch}}^{\mathrm{NA}}(\boldsymbol{K}), \tag{108}$$

where $\mathbf{1}$ is the 3×3 identity matrix.

Note that the Rabi energy depends on the square root of the oscillator strength [cf. Eq. (81)]. Hence, questions about the sign of the terms $(\hat{e}_{1\boldsymbol{K},y} K_z + \hat{e}_{1\boldsymbol{K},z} K_y)$ in Eq. (107) may arise. However, for reasons of symmetry the terms must be linear in $\boldsymbol{K}$. As the photon has negative parity, i.e., since it transforms according to Γ_4^- in O_{h}, the terms have to change the sign if the direction of $\boldsymbol{K}$ is reversed.

The eigenstates of the Hamiltonian (105) can be calculated using an appropriate LAPACK routine [71]. The values of f_0 and E_0 as well as the parameters Δ_i can be determined from the solutions of the complete Hamiltonian (6) in Ref. [67].

VI. SUMMARY AND OUTLOOK

We presented the theory of exciton-polaritons in Cu_2O. In the derivation of the formulas we accounted for all relevant effects which are needed to describe the spectra theoretically in an appropriate way, i.e., the complete valence-band structure, the exchange interaction, and the central-cell corrections [28]. This leads to a likewise complicated expression for the momentum-dependent Hamiltonian of excitons. Our method of solving the corresponding Schrödinger equation allows calculating dipole and quadrupole oscillator strengths, for which general formulas have been derived. The subsequent polariton transformation can be performed within the so-called rotating-wave approximation. Within this approximation it is straightforward to additionally account for the nonanalytic exchange interaction.

As the exciton ground state is well separated from the other exciton states, it can be treated separately. Exploiting the symmetry properties of the $1S$ ortho exciton, we were able to set up a 5×5 matrix model, which allows for the calculation of the corresponding polariton dispersion for any direction of $\boldsymbol{K}$.

In the next paper [67] we will investigate the complete exciton spectrum for Cu_2O. We will show that a strong mixing of states occurs and, hence, that the states with $n \geq 2$ can be described appropriately only within the multi-polariton concept presented here. Using criteria for spatial or temporal coherence, we discuss the observability of polariton effects as regards absorption experiments in Cu_2O. The dispersion of the $1S$ ortho exciton will be discussed in detail using the 5×5 matrix model. In particular, we will compare our results with experimental values of the K-dependent splitting, the group velocity and the oscillator strengths of this polariton.

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Appendix A: Hamiltonian

In this section we give the expressions for H_0, H_1 and H_2 [see Eq. (6)] in terms of irreducible tensors for the case that the wave vector $\boldsymbol{K}$ is oriented in [001], [110] or [111] direction [20, 39, 69, 70]. Note that we rotate the coordinate system to make the quantization axis or z axis coincide with the direction of $\boldsymbol{K}$. Hence, we rotate the coordinate system by the Euler angles $(\alpha, \beta, \gamma) = (\pi, \pi/2, \pi/4)$ for $\boldsymbol{K} \parallel [110]$ and by $(\alpha, \beta, \gamma) = \big(0, \arccos(1/\sqrt{3}), \pi/4\big)$ for $\boldsymbol{K} \parallel [111]$.

The first-order and second-order tensor operators used in the following correspond, as in Ref. [70], to the vector operators $\boldsymbol{r}$, $\boldsymbol{p}$, $\boldsymbol{I}$, $\boldsymbol{S}_{\mathrm{h}}$ and to the second-rank Cartesian operators

$$I_{mn} = 3\{I_m, I_n\} - \delta_{mn} I^2, \tag{A1a}$$

$$P_{mn} = 3\{p_m, p_n\} - \delta_{mn} p^2, \tag{A1b}$$

respectively. We also use the abbreviation

$$D_k^{(2)} = \left[I^{(1)} \times S_{\rm h}^{(1)}\right]_k^{(2)}. \tag{A2}$$

The coefficients γ_1', μ' and δ' are given by [39, 96]

$$\gamma_1' = \gamma_1 + \frac{m_0}{m_{\rm e}}, \quad \mu' = \frac{6\gamma_3 + 4\gamma_2}{5\gamma_1'}, \quad \delta' = \frac{\gamma_3 - \gamma_2}{\gamma_1'}, \tag{A3}$$

and we define by analogy [20]

$$\nu = \frac{6\eta_3 + 4\eta_2}{5\eta_1}, \quad \tau = \frac{\eta_3 - \eta_2}{\eta_1}. \tag{A4}$$

1. Wave vector in [001] direction

$$\begin{aligned}
H_0 = {} & E_{\rm g} - \frac{e^2}{4\pi\varepsilon_0\varepsilon}\frac{1}{r} - \frac{e^2}{4\pi\varepsilon_0 r}\left[\frac{1}{2\varepsilon_1^*}\left(e^{-r/\rho_{\rm h1}} + e^{-r/\rho_{\rm e1}}\right) + \frac{1}{2\varepsilon_2^*}\left(e^{-r/\rho_{\rm h2}} + e^{-r/\rho_{\rm e2}}\right)\right] \\
& + \frac{2}{3}\Delta\left(1 + \frac{1}{\hbar^2} I^{(1)} \cdot S_{\rm h}^{(1)}\right) + \left[-V_0 + J_0\left(\frac{1}{4} - \frac{1}{\hbar^2} S_{\rm e}^{(1)} \cdot S_{\rm h}^{(1)}\right)\right] V_{\rm uc}\delta(\boldsymbol{r}) \\
& + \frac{\gamma_1'}{2\hbar^2 m_0}\left\{\hbar^2 p^2 - \frac{\mu'}{3}\left(P^{(2)} \cdot I^{(2)}\right)\right. \\
& \qquad \left. + \frac{\delta'}{3}\left(\sum_{k=\pm 4}\left[P^{(2)} \times I^{(2)}\right]_k^{(4)} + \frac{\sqrt{70}}{5}\left[P^{(2)} \times I^{(2)}\right]_0^{(4)}\right)\right\} \\
& + \frac{3\eta_1}{\hbar^2 m_0}\left\{\frac{1}{3}p^2\left(I^{(1)} \cdot S_{\rm h}^{(1)}\right) - \frac{\nu}{3}\left(P^{(2)} \cdot D^{(2)}\right)\right. \\
& \qquad \left. + \frac{\tau}{3}\left(\sum_{k=\pm 4}\left[P^{(2)} \times D^{(2)}\right]_k^{(4)} + \frac{\sqrt{70}}{5}\left[P^{(2)} \times D^{(2)}\right]_0^{(4)}\right)\right\},
\end{aligned} \tag{A5a}$$

$$\begin{aligned}
H_1 = {} & \frac{1}{2\hbar^2 m_{\rm e}}\left\{-2\sqrt{\frac{5}{3}}\mu'\left[P^{(1)} \times I^{(2)}\right]_0^{(1)} - 4\sqrt{\frac{2}{5}}\delta'\left[P^{(1)} \times I^{(2)}\right]_0^{(3)}\right\} \\
& + \frac{3\eta_1}{\gamma_1'\hbar^2 m_{\rm e}}\left\{-\frac{2}{3}P_0^{(1)}\left(I^{(1)} \cdot S_{\rm h}^{(1)}\right) - 2\sqrt{\frac{5}{3}}\nu\left[P^{(1)} \times D^{(2)}\right]_0^{(1)} - 4\sqrt{\frac{2}{5}}\tau\left[P^{(1)} \times D^{(2)}\right]_0^{(3)}\right\},
\end{aligned} \tag{A5b}$$

$$\begin{aligned}
H_2 = {} & \frac{\gamma_1' m_{\rm e} - m_0}{2\gamma_1' m_{\rm e}^2} + \frac{m_0}{2\gamma_1'\hbar^2 m_{\rm e}^2}\left\{\left(-\sqrt{\frac{2}{3}}\mu' + \frac{2}{5}\sqrt{6}\delta'\right) I_0^{(2)}\right\} \\
& + \frac{3\eta_1 m_0}{\gamma_1'^2\hbar^2 m_{\rm e}^2}\left\{\frac{1}{3}\left(I^{(1)} \cdot S_{\rm h}^{(1)}\right) + \left(-\sqrt{\frac{2}{3}}\nu + \frac{2}{5}\sqrt{6}\tau\right) D_0^{(2)}\right\}.
\end{aligned} \tag{A5c}$$

2. Wave vector in [110] direction

$$
\begin{aligned}
H_0 = {} & E_{\mathrm{g}} - \frac{e^2}{4\pi\varepsilon_0\varepsilon}\frac{1}{r} - \frac{e^2}{4\pi\varepsilon_0 r}\left[\frac{1}{2\varepsilon_1^*}\left(e^{-r/\rho_{\mathrm{h}1}} + e^{-r/\rho_{\mathrm{e}1}}\right) + \frac{1}{2\varepsilon_2^*}\left(e^{-r/\rho_{\mathrm{h}2}} + e^{-r/\rho_{\mathrm{e}2}}\right)\right] \\
& + \frac{2}{3}\Delta\left(1 + \frac{1}{\hbar^2} I^{(1)}\cdot S_{\mathrm{h}}^{(1)}\right) + \left[-V_0 + J_0\left(\frac{1}{4} - \frac{1}{\hbar^2} S_{\mathrm{e}}^{(1)}\cdot S_{\mathrm{h}}^{(1)}\right)\right] V_{\mathrm{uc}}\delta(\boldsymbol{r}) \\
& + \frac{\gamma_1'}{2\hbar^2 m_0}\left\{\hbar^2 p^2 - \frac{\mu'}{3}\left(P^{(2)}\cdot I^{(2)}\right) + \frac{\delta'}{4}\left(\sum_{k=\pm 4}\left[P^{(2)}\times I^{(2)}\right]_k^{(4)}\right)\right. \\
& \qquad \left. - \frac{\sqrt{7}}{6}\delta'\left(\sum_{k=\pm 2}\left[P^{(2)}\times I^{(2)}\right]_2^{(4)} + \sqrt{\frac{1}{10}}\left[P^{(2)}\times I^{(2)}\right]_0^{(4)}\right)\right\} \\
& + \frac{3\eta_1}{\hbar^2 m_0}\left\{\frac{1}{3}p^2\left(I^{(1)}\cdot S_{\mathrm{h}}^{(1)}\right) - \frac{\nu}{3}\left(P^{(2)}\cdot D^{(2)}\right) + \frac{\tau}{4}\left(\sum_{k=\pm 4}\left[P^{(2)}\times D^{(2)}\right]_k^{(4)}\right)\right. \\
& \qquad \left. - \frac{\sqrt{7}}{6}\tau\left(\sum_{k=\pm 2}\left[P^{(2)}\times D^{(2)}\right]_k^{(4)} + \sqrt{\frac{1}{10}}\left[P^{(2)}\times D^{(2)}\right]_0^{(4)}\right)\right\},
\end{aligned}
\tag{A6a}
$$

$$
\begin{aligned}
H_1 = {} & \frac{1}{2\hbar^2 m_{\mathrm{e}}}\left\{-2\sqrt{\frac{5}{3}}\mu'\left[P^{(1)}\times I^{(2)}\right]_0^{(1)} + \sqrt{3}\delta'\left(\sum_{k=\pm 2}\left[P^{(1)}\times I^{(2)}\right]_k^{(3)} + \sqrt{\frac{2}{15}}\left[P^{(1)}\times I^{(2)}\right]_0^{(3)}\right)\right\} \\
& + \frac{3\eta_1}{\gamma_1'\hbar^2 m_{\mathrm{e}}}\left\{-\frac{2}{3}P_0^{(1)}\left(I^{(1)}\cdot S_{\mathrm{h}}^{(1)}\right) - 2\sqrt{\frac{5}{3}}\nu\left[P^{(1)}\times D^{(2)}\right]_0^{(1)}\right. \\
& \qquad \left. + \sqrt{3}\tau\left(\sum_{k=\pm 2}\left[P^{(1)}\times D^{(2)}\right]_k^{(3)} + \sqrt{\frac{2}{15}}\left[P^{(1)}\times D^{(2)}\right]_0^{(3)}\right)\right\},
\end{aligned}
\tag{A6b}
$$

$$
\begin{aligned}
H_2 = {} & \frac{\gamma_1' m_{\mathrm{e}} - m_0}{2\gamma_1' m_{\mathrm{e}}^2} + \frac{m_0}{2\gamma_1'\hbar^2 m_{\mathrm{e}}^2}\left\{-\frac{1}{2}\delta'\left(I_{-2}^{(2)} + I_2^{(2)}\right) + \left(-\sqrt{\frac{2}{3}}\mu' - \frac{1}{5}\sqrt{\frac{3}{2}}\delta'\right) I_0^{(2)}\right\} \\
& + \frac{3\eta_1 m_0}{\gamma_1'^2\hbar^2 m_{\mathrm{e}}^2}\left\{\frac{1}{3}\left(I^{(1)}\cdot S_{\mathrm{h}}^{(1)}\right) - \frac{1}{2}\tau\left(D_{-2}^{(2)} + D_2^{(2)}\right) + \left(-\sqrt{\frac{2}{3}}\nu - \frac{1}{5}\sqrt{\frac{3}{2}}\tau\right) D_0^{(2)}\right\}.
\end{aligned}
\tag{A6c}
$$

3. Wave vector in [111] direction

$$
H_0 = E_{\mathrm{g}} - \frac{e^2}{4\pi\varepsilon_0\varepsilon}\frac{1}{r} - \frac{e^2}{4\pi\varepsilon_0 r}\left[\frac{1}{2\varepsilon_1^*}\left(e^{-r/\rho_{\mathrm{h}1}} + e^{-r/\rho_{\mathrm{e}1}}\right) + \frac{1}{2\varepsilon_2^*}\left(e^{-r/\rho_{\mathrm{h}2}} + e^{-r/\rho_{\mathrm{e}2}}\right)\right]
$$

$$+\frac{2}{3}\Delta\left(1+\frac{1}{\hbar^2}I^{(1)}\cdot S_{\rm h}^{(1)}\right)+\left[-V_0+J_0\left(\frac{1}{4}-\frac{1}{\hbar^2}S_{\rm e}^{(1)}\cdot S_{\rm h}^{(1)}\right)\right]V_{\rm uc}\delta(\boldsymbol{r})$$

$$+\frac{\gamma_1'}{2\hbar^2 m_0}\left\{\hbar^2p^2-\frac{\mu'}{3}\left(P^{(2)}\cdot I^{(2)}\right)\right.$$

$$\left.+\frac{4}{27}\delta'\left(\sum_{k=\pm3}k\left[P^{(2)}\times I^{(2)}\right]_k^{(4)}-3\sqrt{\frac{7}{10}}\left[P^{(2)}\times I^{(2)}\right]_0^{(4)}\right)\right\}$$

$$+\frac{3\eta_1}{\hbar^2 m_0}\left\{\frac{1}{3}p^2\left(I^{(1)}\cdot S_{\rm h}^{(1)}\right)-\frac{\nu}{3}\left(P^{(2)}\cdot D^{(2)}\right)\right.$$

$$\left.+\frac{4}{27}\tau\left(\sum_{k=\pm3}k\left[P^{(2)}\times D^{(2)}\right]_3^{(4)}-3\sqrt{\frac{7}{10}}\left[P^{(2)}\times D^{(2)}\right]_0^{(4)}\right)\right\},\tag{A7a}$$

$$H_1=\frac{1}{2\hbar^2 m_{\rm e}}\left\{-2\sqrt{\frac{5}{3}}\mu'\left[P^{(1)}\times I^{(2)}\right]_0^{(1)}-\frac{4}{9}\delta'\left(\sum_{k=\pm3}k\left[P^{(1)}\times I^{(2)}\right]_k^{(3)}-6\sqrt{\frac{2}{5}}\left[P^{(1)}\times I^{(2)}\right]_0^{(3)}\right)\right\}$$

$$+\frac{3\eta_1}{\gamma_1'\hbar^2 m_{\rm e}}\left\{-\frac{2}{3}P_0^{(1)}\left(I^{(1)}\cdot S_{\rm h}^{(1)}\right)-2\sqrt{\frac{5}{3}}\nu\left[P^{(1)}\times D^{(2)}\right]_0^{(1)}\right.$$

$$\left.-\frac{4}{9}\tau\left(\sum_{k=\pm3}k\left[P^{(1)}\times D^{(2)}\right]_k^{(3)}-6\sqrt{\frac{2}{5}}\left[P^{(1)}\times D^{(2)}\right]_0^{(3)}\right)\right\},\tag{A7b}$$

$$H_2=\frac{\gamma_1' m_{\rm e}-m_0}{2\gamma_1' m_{\rm e}^2}+\frac{m_0}{2\gamma_1'\hbar^2 m_{\rm e}^2}\left\{-\sqrt{\frac{2}{3}}\left(\mu'+\frac{4}{5}\delta'\right)I_0^{(2)}\right\}$$

$$+\frac{3\eta_1 m_0}{\gamma_1'^2\hbar^2 m_{\rm e}^2}\left\{\frac{1}{3}\left(I^{(1)}\cdot S_{\rm h}^{(1)}\right)-\sqrt{\frac{2}{3}}\left(\nu+\frac{4}{5}\tau\right)D_0^{(2)}\right\}.\tag{A7c}$$

Appendix B: Matrix elements

In this section we give the matrix elements of the terms of the Hamiltonian H [Eq. (6)] in the basis of Eq. (7) in Hartree units using the formalism of irreducible tensors [69]. The matrix elements of the first part H_0 of the Hamiltonian are given in the Appendices of Refs. [20, 28]. The function $(R_1)_{nL}^{j}$ was defined in the Appendix of Ref. [20].

$$\left\langle\Pi'\left|I_q^{(2)}\right|\Pi\right\rangle=\delta_{LL'}3\sqrt{5}\,(-1)^{F_t'+F_t-M_{F_t}'+2F'+2J+L}$$

$$\times\left[(2F_t+1)\,(2F_t'+1)\,(2F+1)\,(2F'+1)\,(2J+1)\,(2J'+1)\right]^{\frac{1}{2}}$$

$$\times \begin{pmatrix} F_t' & 2 & F_t \\ -M'_{F_t} & q & M_{F_t} \end{pmatrix} \begin{Bmatrix} F' & F_t' & \frac{1}{2} \\ F_t & F & 2 \end{Bmatrix} \begin{Bmatrix} J' & F' & L \\ F & J & 2 \end{Bmatrix} \begin{Bmatrix} 1 & J' & \frac{1}{2} \\ J & 1 & 2 \end{Bmatrix}$$

$$\times \sum_{j=-1}^{1} (R_1)^j_{NL} \left[N+L+j+1\right]^{-1} \delta_{N',N+j}, \tag{B1}$$

$$\left\langle \Pi' \left| D^{(2)}_q \right| \Pi \right\rangle = \delta_{LL'} 3\sqrt{5} \, (-1)^{F_t'+F_t-M'_{F_t}+2F'+L+J+\frac{1}{2}}$$

$$\times \left[(2F_t+1)\,(2F_t'+1)\,(2F+1)\,(2F'+1)\,(2J+1)\,(2J'+1)\right]^{\frac{1}{2}}$$

$$\times \begin{pmatrix} F_t' & 2 & F_t \\ -M'_{F_t} & q & M_{F_t} \end{pmatrix} \begin{Bmatrix} F' & F_t' & \frac{1}{2} \\ F_t & F & 2 \end{Bmatrix} \begin{Bmatrix} J' & F' & L \\ F & J & 2 \end{Bmatrix} \begin{Bmatrix} 1 & 1 & 1 \\ \frac{1}{2} & \frac{1}{2} & 1 \\ J' & J & 2 \end{Bmatrix}$$

$$\times \sum_{j=-1}^{1} (R_1)^j_{NL} \left[N+L+j+1\right]^{-1} \delta_{N',N+j}, \tag{B2}$$

$$\left\langle \Pi' \left| \left(I^{(1)} \cdot S^{(1)}_{\mathrm{h}} \right) \right| \Pi \right\rangle = \delta_{LL'} \delta_{M_{F_t} M'_{F_t}} \delta_{F_t F_t'} 3\sqrt{3} \, (-1)^{F_t+2F'+L+J+\frac{3}{2}}$$

$$\times \left[(2F_t+1)\,(2F+1)\,(2F'+1)\,(2J+1)\,(2J'+1)\right]^{\frac{1}{2}}$$

$$\times \begin{Bmatrix} F' & F_t & \frac{1}{2} \\ F_t & F & 0 \end{Bmatrix} \begin{Bmatrix} J' & F' & L \\ F & J & 0 \end{Bmatrix} \begin{Bmatrix} 1 & 1 & 1 \\ \frac{1}{2} & \frac{1}{2} & 1 \\ J' & J & 0 \end{Bmatrix}$$

$$\times \sum_{j=-1}^{1} (R_1)^j_{NL} \left[N+L+j+1\right]^{-1} \delta_{N',N+j}, \tag{B3}$$

$$\left\langle \Pi' \left| \left[P^{(1)} \times I^{(2)} \right]^{(K)}_q \right| \Pi \right\rangle = 3\sqrt{5} \, (-1)^{F_t'+F_t-M'_{F_t}+F'+J+K} \left\langle N' \, L' \left\| P^{(1)} \right\| N \, L \right\rangle$$

$$\times \left[(2F_t+1)\,(2F_t'+1)\,(2F+1)\,(2F'+1)\,(2J+1)\,(2J'+1)\,(2K+1)\right]^{\frac{1}{2}}$$

$$\times \begin{pmatrix} F_t' & K & F_t \\ -M'_{F_t} & q & M_{F_t} \end{pmatrix} \begin{Bmatrix} F' & F_t' & \frac{1}{2} \\ F_t & F & K \end{Bmatrix} \begin{Bmatrix} L' & L & 1 \\ J' & J & 2 \\ F' & F & K \end{Bmatrix} \begin{Bmatrix} 1 & J' & \frac{1}{2} \\ J & 1 & 2 \end{Bmatrix}, \tag{B4}$$

$$\left\langle \Pi' \left| \left[P^{(1)} \times D^{(2)} \right]^{(K)}_q \right| \Pi \right\rangle = 3\sqrt{5} \, (-1)^{F_t'+F_t-M'_{F_t}+F'+\frac{1}{2}+K} \left\langle N' \, L' \left\| P^{(1)} \right\| N \, L \right\rangle$$

$$\times \left[(2F_t+1)\,(2F_t'+1)\,(2F+1)\,(2F'+1)\,(2J+1)\,(2J'+1)\,(2K+1)\right]^{\frac{1}{2}}$$

$$\times \begin{pmatrix} F_t' & K & F_t \\ -M_{F_t}' & q & M_{F_t} \end{pmatrix} \begin{Bmatrix} F' & F_t' & \frac{1}{2} \\ F_t & F & K \end{Bmatrix} \begin{Bmatrix} L' & L & 1 \\ J' & J & 2 \\ F' & F & K \end{Bmatrix} \begin{Bmatrix} 1 & 1 & 1 \\ \frac{1}{2} & \frac{1}{2} & 1 \\ J' & J & 2 \end{Bmatrix}, \tag{B5}$$

$$\left\langle \Pi' \left| P_0^{(1)} \left(I^{(1)} \cdot S_{\rm h}^{(1)} \right) \right| \Pi \right\rangle = \delta_{M_{F_t} M_{F_t}'}\, 9\, (-1)^{F_t'+F_t-M_{F_t}+F'+\frac{1}{2}} \left\langle N'\, L' \left\| P^{(1)} \right\| N\, L \right\rangle$$

$$\times \left[(2F_t+1)\,(2F_t'+1)\,(2F+1)\,(2F'+1)\,(2J+1)\,(2J'+1)\right]^{\frac{1}{2}}$$

$$\times \begin{pmatrix} F_t' & 1 & F_t \\ -M_{F_t} & 0 & M_{F_t} \end{pmatrix} \begin{Bmatrix} F' & F_t' & \frac{1}{2} \\ F_t & F & 1 \end{Bmatrix} \begin{Bmatrix} L' & L & 1 \\ J' & J & 0 \\ F' & F & 1 \end{Bmatrix} \begin{Bmatrix} 1 & 1 & 1 \\ \frac{1}{2} & \frac{1}{2} & 1 \\ J' & J & 0 \end{Bmatrix}. \tag{B6}$$

Appendix C: Reduced matrix elements

We now give the value of the reduced matrix element $\left\langle N'\, L' \left\| P^{(1)} \right\| N\, L \right\rangle$. The functions of the form $(R_1)_{NL}^{j}$ and the quantities $I_{N'\,L';N\,L}$ are taken from the Appendix of Ref. [20].

$$\left\langle N'\, L' \left\| P^{(1)} \right\| N\, L \right\rangle = \delta_{L',L+1}\ (-i) \left[\frac{(2L+3)\,(2L+1)}{L+1}\right]^{\frac{1}{2}}$$

$$\times \left[\sum_{j=-1}^{1} \sum_{k=-2}^{0} (L_1)_{N',L+1}^{k,1} \left\{ (RP_1)_{N,L}^{j}\, (N_1)_{L,0}^{1} + \delta_{0j}\, (D_1)_{L,0}^{1} \right\} I_{N'+k\,L+2;\,N+j\,L} \right]$$

$$+ \delta_{L',L-1}\ (+i) \left[\frac{(2L+1)\,(2L-1)}{L}\right]^{\frac{1}{2}}$$

$$\times \left[\sum_{j=-1}^{1} \sum_{k=-2}^{0} (L_1)_{N+j,L}^{k,1} \left\{ (RP_1)_{N,L}^{j}\, (N_1)_{L,0}^{-1} + \delta_{0j}\, (D_1)_{L,0}^{-1} \right\} I_{N'\,L-1;\,N+j+k\,L+1} \right]. \tag{C1}$$

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