

K -dependent exchange interaction of the 1S orthoexciton in Cu₂O

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When treating the exchange interaction of Wannier excitons, usually only the leading terms of the analytic and the nonanalytic exchange interaction are considered. However, higher-order terms can lead to a splitting of exciton states, for which reason a splitting of the 1S exciton in cuprous oxide (Cu₂O) depending on its total momentum $\hbar K$ has been attributed to a K -dependent analytic exchange interaction by Dasbach *et al.* [*Phys. Rev. Lett.* **91**, 107401 (2003)]. Going beyond the common treatment of the exchange interaction, we derive the correct expressions for these K -dependent higher-order terms using $\mathbf{k} \cdot \mathbf{p}$ perturbation theory. We prove that the appearance of a K -dependent exchange interaction is inseparably connected with a K -independent exchange interaction of P and D excitons. We estimate the magnitude of these terms for Cu₂O from microscopic calculations and show that they are far too small to explain the observed K -dependent splitting. Instead, this splitting has to be treated in terms of the dispersion of the excitons. Furthermore, we prove the occurrence of a coupling between longitudinal and transverse excitons in Cu₂O due to the K -dependent nonanalytic exchange interaction.

DOI: [10.1103/PhysRevB.94.115201](https://doi.org/10.1103/PhysRevB.94.115201)**I. INTRODUCTION**

Excitons are the quanta of the fundamental optical excitations in both insulators and semiconductors in the visible and ultraviolet spectrum of light. They consist of a negatively charged electron in the conduction band and a positively charged hole in the valence band. Wannier excitons extend over a huge number of unit cells and can be described within the simple band model as hydrogenlike particles [1]. Recently, the corresponding hydrogenlike exciton absorption spectrum could be followed up to a principal quantum number of $n = 25$ in cuprous oxide (Cu₂O) [2]. This recent experiment led to a variety of new theoretical and experimental investigations on the topic of excitons in Cu₂O [3–11].

When investigating exciton spectra of Cu₂O using high-resolution spectroscopy and crystals of high quality, two of the most striking experimental findings are the observation of F excitons and a splitting of the 1S exciton depending on its total momentum $\hbar K$. Both effects cannot be understood within a simple effective mass model. Therefore, the K -dependent splitting of the 1S exciton was attributed by Dasbach *et al.* [12–14] to a K -dependent exchange interaction. This is beyond the scope of the common treatment of the exchange interaction for Cu₂O, where only a K -independent analytic exchange and a vanishing nonanalytic exchange interaction are considered.

Since we have recently shown that the observed splitting could also be explained by taking full account of the anisotropic dispersion of the Γ_5^+ orbital Bloch states [10], we believe that the influence of a K -dependent exchange interaction on the 1S orthoexciton in Cu₂O deserves a closer investigation as it is *a priori* unknown whether dispersion and exchange interaction are of the same size.

Although a preliminary investigation as regards the presence of a K -dependent exchange interaction was undertaken by Kavoulakis *et al.* [15], their treatment was limited to the nonanalytic part of the exchange interaction only and lacking a

consideration of the complete valence band structure of Cu₂O. Using $\mathbf{k} \cdot \mathbf{p}$ perturbation theory, we derive general expressions for both the analytic and nonanalytic part of the exchange interaction for all direct excitons up to basically arbitrary order in K . This allows us not only to show the unknown fact that the appearance of a K -dependent exchange interaction is inseparably connected to a K -independent exchange interaction of P and D excitons but also to estimate the magnitude of the K -dependent terms from microscopic calculations for both parts of the interaction. This is furthermore in contrast to the simple group theoretical treatment of the exchange interaction of Refs. [12–14], which leads to K -dependent terms of the correct form but does not yield their prefactors. Since every K -dependent energy as regards states of the symmetry Γ_5^+ must lead to matrices of the form presented in Ref. [13], the unambiguous assignment of the experimentally observed K -dependent splitting to the exchange interaction is not possible by these means.

Moreover, as regards the nonanalytic exchange interaction, we go beyond the treatment of Kavoulakis *et al.* [15] and pay special attention to its angular dependency. This allows us to prove the occurrence of a coupling between longitudinal and transverse excitons in Cu₂O due to the K -dependent terms of this part of the exchange interaction. Hence, we show that all three orthoexciton states couple to light if the wave vector is not oriented in a direction of high symmetry.

The paper is organized as follows. In Sec. II we discuss the exchange interaction of Wannier excitons and derive the expressions for the K -dependent terms of the analytic and the nonanalytic exchange energy. Having pointed out the specific properties of excitons in Cu₂O in Sec. III, we investigate in Sec. IV A the analytic and in Sec. IV B the nonanalytic exchange interaction for the 1S exciton of cuprous oxide as well as the coupling between longitudinal and transverse excitons. Finally, we give a short summary and outlook in Sec. V.

II. EXCHANGE INTERACTION

In this section we derive the K -dependent terms of the analytic and the nonanalytic exchange interaction based on the main expressions of the exchange interaction given in Refs. [1,15–18]. Within the scope of the simple band model the wave function of an exciton is given by

$$\Psi_{vc\nu\mathbf{K}} = \sum_{\mathbf{q}} f_{vc\nu}(\mathbf{q}) \Phi_{vc}^{\sigma\tau}(\mathbf{q} - \gamma\mathbf{K}, \mathbf{q} + \alpha\mathbf{K}). \quad (1)$$

The envelope function $f_{vc\nu}(\mathbf{q})$ is the Fourier transform of the hydrogenlike solution $F_{vc\nu}(\boldsymbol{\beta})$ of the Wannier equation [1,19],

$$f_{vc\nu}(\mathbf{q}) = \frac{1}{\sqrt{N}} \sum_{\boldsymbol{\beta}} F_{vc\nu}(\boldsymbol{\beta}) e^{-i\mathbf{q}\boldsymbol{\beta}}, \quad (2)$$

with ν being a short notation for the three quantum numbers n , L , and M . Note that the coordinate $\boldsymbol{\beta}$ is a lattice vector, which takes in general only discrete values. The constant factors $\alpha = m_e/(m_e + m_h)$ and $\gamma = 1 - \alpha$ depend on the effective masses of electron and hole. Additionally, the wave function (1) 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,

$$\Phi_{vc}^{\sigma\tau}(\mathbf{k}_h, \mathbf{k}_e) = \mathcal{A} \psi_{vk_1\alpha} \psi_{vk_1\beta} \cdots \psi_{vk_h\sigma} \psi_{ck_e\tau} \cdots \psi_{vk_N\beta}. \quad (3)$$

Here \mathcal{A} denotes the antisymmetrization operator.

In the Wannier equation the exchange energy is missing since it is often treated as a correction to the hydrogenlike solution [1]. In general, the exchange energy between two exciton states $\Psi_{vc\nu\mathbf{K}}$ and $\Psi_{v'c'\nu'\mathbf{K}'}$ reads [1,16]

$$\begin{aligned} E_{\text{exch}}(vc\nu\mathbf{K}, v'c'\nu'\mathbf{K}') \\ = \delta_{\sigma\tau} \delta_{\sigma'\tau'} \delta_{\mathbf{K},\mathbf{K}'} \sum_{\mathbf{q},\mathbf{q}'} f_{vc\nu}^*(\mathbf{q}) f_{v'c'\nu'}(\mathbf{q}') \int d\mathbf{r}_1 \int d\mathbf{r}_2 \psi_{c\mathbf{q}}^*(\mathbf{r}_1) \\ \times \psi_{v\mathbf{q}-\mathbf{K}}(\mathbf{r}_1) \frac{e^2}{4\pi\epsilon_0\epsilon|\mathbf{r}_1 - \mathbf{r}_2|} \psi_{c'\mathbf{q}'}(\mathbf{r}_2) \psi_{v'\mathbf{q}'-\mathbf{K}'}^*(\mathbf{r}_2). \end{aligned} \quad (4)$$

The exchange energy includes the term $\delta_{\sigma\tau} \delta_{\sigma'\tau'}$. Introducing the total spin $S = S_e + S_h = \tau - \sigma$ of electron and hole, this term can be written with singlet and triplet states as $2\delta_{S,0}$ [20].

Inserting the Fourier transform [17,21]

$$\frac{1}{r} = \frac{4\pi}{NV_{\text{uc}}} \sum_{\mathbf{G}} \sum_{\mathbf{k} \in \text{BZ}} \frac{1}{(\mathbf{k} + \mathbf{G})^2} e^{i(\mathbf{k} + \mathbf{G})\mathbf{r}} \quad (5)$$

with the volume of one unit cell of the lattice V_{uc} and reciprocal lattice vectors \mathbf{G} in Eq. (4), we can write the exchange energy as

$$E_{\text{exch}} = 2\delta_{S,0} \delta_{\mathbf{K},\mathbf{K}'} \sum_{\mathbf{G}} \frac{m_{vc\nu}^*(\mathbf{K}, \mathbf{G}) m_{v'c'\nu'}(\mathbf{K}, \mathbf{G})}{\epsilon_0\epsilon V_{\text{uc}}(\mathbf{K} + \mathbf{G})^2} \quad (6)$$

with

$$m_{vc\nu}(\mathbf{K}, \mathbf{G}) = \frac{e}{\sqrt{N}} \sum_{\mathbf{q}} f_{vc\nu}(\mathbf{q}) \langle u_{v\mathbf{q}-\gamma\mathbf{K}} | e^{-i\mathbf{G}\mathbf{r}} | u_{c\mathbf{q}+\alpha\mathbf{K}} \rangle. \quad (7)$$

The functions $u_{nk}(\mathbf{r})$ denote the lattice-periodic part of the Bloch functions $\psi_{nk}(\mathbf{k}) = e^{i\mathbf{k}\mathbf{r}} u_{nk}(\mathbf{r})$ [21]. In the representa-

tion of Eq. (6) the exchange energy can be divided into the nonanalytic part $E_{\text{exch}}^{\text{NA}}$, which is the summand with $\mathbf{G} = \mathbf{0}$, and the analytic part $E_{\text{exch}}^{\text{A}}$, which is the sum of the remaining terms. Note that if the exchange energy is formulated in the Wannier representation [1] instead of the representation with Bloch functions, it is generally separated into a long-range and a short-range part. However, according to Refs. [16,17,22] there is no identity between the nonanalytic exchange and the long-range part or between the analytic exchange and the short-range part but only a close correspondence.

In the limit $Ka \ll 1$ one obtains the simple expression [1,16]

$$\begin{aligned} E_{\text{exch}}^{\text{NA}} = 2\delta_{S,0} \delta_{\mathbf{K},\mathbf{K}'} \frac{1}{\epsilon_0\epsilon V_{\text{uc}} K^2} (\boldsymbol{\mu}_{vc\nu\mathbf{K}}^* \mathbf{K})(\boldsymbol{\mu}_{v'c'\nu'\mathbf{K}'} \mathbf{K}) \\ + O(K^2 a^2) \end{aligned} \quad (8)$$

for the nonanalytic exchange energy of excitons in a cubic crystal. By a we denote the lattice constant of the solid. The expression (8) depends only on the two angles between \mathbf{K} and the dipole moments $\boldsymbol{\mu}_{vc\nu\mathbf{K}}^*$ or $\boldsymbol{\mu}_{v'c'\nu'\mathbf{K}'}$ with

$$\boldsymbol{\mu}_{vc\nu\mathbf{K}} = \int d\mathbf{r} \mathbf{r} \rho_{vc\nu\mathbf{K}}(\mathbf{r}). \quad (9)$$

The localized charge density or transition density [1,16]

$$\rho_{vc\nu\mathbf{K}}(\mathbf{r}) = e \sum_{\boldsymbol{\beta}} U_{vc\nu\mathbf{K}}(\boldsymbol{\beta}) a_c \boldsymbol{\beta} a_v^*(\mathbf{r}), \quad (10)$$

with $U_{vc\nu\mathbf{K}}(\boldsymbol{\beta}) = F_{vc\nu}(\boldsymbol{\beta}) e^{i\alpha\mathbf{K}\boldsymbol{\beta}}$ is often given in terms of Wannier functions

$$a_{n\mathbf{R}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{-i\mathbf{k}\mathbf{R}} \psi_{n\mathbf{k}}(\mathbf{r}). \quad (11)$$

If $\boldsymbol{\mu}$ is parallel or perpendicular to \mathbf{K} , one speaks of longitudinal or transversal excitons, respectively [1]. The nonanalytic exchange energy therefore causes a longitudinal-transverse splitting (LT splitting) of spin singlet states near $K = 0$. It is obvious that the nonanalytic exchange energy is nonzero only for longitudinal excitons and that it is therefore connected to a macroscopic polarization. Thus, the effect can be compared to the LT splitting of phonons. Since the splitting between transverse and longitudinal excitons depends on $|\boldsymbol{\mu}_{vc\nu\mathbf{K}}|^2$ for $vc\nu = v'c'\nu'$, it is proportional to the oscillator strength $f_{v\mathbf{0}}$ for exciting one exciton from the ground state of the solid by light. This oscillator strength reads for $Ka \ll 1$ [1]

$$f_{v\mathbf{0}} = \frac{4\delta_{S,0}}{\hbar^2 e^2 m_0} E_{v\mathbf{K}} |\hat{\boldsymbol{\epsilon}}_{\xi\mathbf{K}} \cdot \boldsymbol{\mu}_{vc\nu\mathbf{K}}|^2 \quad (12)$$

with the energy $E_{v\mathbf{K}}$ of the exciton state [5], the free electron mass m_0 , and the polarization vector $\hat{\boldsymbol{\epsilon}}_{\xi\mathbf{K}}$ perpendicular to \mathbf{K} . Thus, the splitting caused by $E_{\text{exch}}^{\text{NA}}$ is identical to the LT splitting when treating polaritons [23] and it is of appreciable size only if the exciton is dipole allowed.

It is now important to note that light is always transversely polarized and that only transverse excitons are produced in optical absorption [24] [cf. Eq. (12)]. Longitudinal excitons cannot be seen in optical absorption spectra. Thus, the LT splitting in the case of polaritons increases the transverse excitons by an energy Δ_{LT} . On the other hand, the LT splitting

connected to the nonanalytic exchange interaction increases the energy of the longitudinal excitons by the same amount Δ_{LT} . Finally, both states are again degenerate at $K = 0$, which is required for reasons of symmetry.

We can see from Eq. (8) that longitudinal and transverse exciton states are not coupled for $Ka \ll 1$. As has been stated in Ref. [1], this uncoupling is accidental since it is expected that these states are decoupled only if they transform according to different irreducible representations of the group

of \mathbf{K} [25,26]. However, the higher-order terms $O(K^2a^2)$ in Eq. (8) may lead to a coupling of longitudinal and transverse exciton states unless they transform according to different irreducible representations. This will be shown for Cu_2O in Sec. IV B. If a coupling occurs, the longitudinal states will become observable in experiments due to the admixture of transverse states [24].

We can now take a closer look at $m_{vcv}(\mathbf{K}, \mathbf{G})$ using $\mathbf{k} \cdot \mathbf{p}$ perturbation theory. It is [15,21]

$$u_{mk}(\mathbf{r}) \approx u_{m0}(\mathbf{r}) + \frac{\hbar}{m_0} \sum_{n \neq m} \frac{\mathbf{k} \mathbf{p}_{nm}}{(E_m - E_n)} u_{n0}(\mathbf{r}) + \frac{\hbar^2}{m_0^2} \left[\sum_{n \neq m, l \neq m} \frac{\mathbf{k} \mathbf{p}_{nl} \mathbf{k} \mathbf{p}_{lm}}{(E_m - E_n)(E_m - E_l)} u_{n0}(\mathbf{r}) - \sum_{n \neq m, l \neq m} \frac{\mathbf{k} \mathbf{p}_{mm} \mathbf{k} \mathbf{p}_{nm} \delta_{nl}}{(E_m - E_n)(E_m - E_l)} u_{n0}(\mathbf{r}) \right] \quad (13)$$

with $\mathbf{p}_{mn} = \langle u_{m0} | \mathbf{p} | u_{n0} \rangle$ and the energy $E_n = E_n(\mathbf{k} = \mathbf{0})$ of the band n at the Γ point. We assume that the point group of the solid contains inversion as a group element. Then the term \mathbf{p}_{mm} vanishes for reasons of parity. Using the expression (13), we obtain up to second order in \mathbf{K} and \mathbf{q} :

$$m_{vcv}(\mathbf{K}, \mathbf{G}) \approx \frac{e}{\sqrt{N}} \sum_{\mathbf{q}} f_{vcv}(\mathbf{q}) \left[I_{vc}(\mathbf{G}) + \frac{\hbar}{m_0} \sum_{n \neq v} \frac{(\mathbf{q} - \gamma \mathbf{K}) \mathbf{p}_{vn}}{(E_v - E_n)} I_{nc}(\mathbf{G}) + \frac{\hbar}{m_0} \sum_{n \neq c} \frac{(\mathbf{q} + \alpha \mathbf{K}) \mathbf{p}_{nc}}{(E_c - E_n)} I_{vn}(\mathbf{G}) + \frac{\hbar^2}{m_0^2} \sum_{n \neq v, m \neq c} \frac{(\mathbf{q} - \gamma \mathbf{K}) \mathbf{p}_{vn} (\mathbf{q} + \alpha \mathbf{K}) \mathbf{p}_{mc}}{(E_v - E_n)(E_c - E_m)} I_{nm}(\mathbf{G}) + \frac{\hbar^2}{m_0^2} \sum_{n \neq c, m \neq v} \frac{(\mathbf{q} + \alpha \mathbf{K}) \mathbf{p}_{nm} (\mathbf{q} + \alpha \mathbf{K}) \mathbf{p}_{mc}}{(E_c - E_n)(E_c - E_m)} I_{vn}(\mathbf{G}) + \frac{\hbar^2}{m_0^2} \sum_{n \neq v, m \neq v} \frac{(\mathbf{q} - \gamma \mathbf{K}) \mathbf{p}_{mn} (\mathbf{q} - \gamma \mathbf{K}) \mathbf{p}_{vm}}{(E_v - E_n)(E_v - E_m)} I_{nc}(\mathbf{G}) \right]. \quad (14)$$

Here we have defined $I_{mn}(\mathbf{G}) = \langle u_{m0} | e^{-i\mathbf{G}\mathbf{r}} | u_{n0} \rangle$. The sum over \mathbf{q} can be evaluated using

$$\frac{1}{\sqrt{N}} \sum_{\mathbf{q}} q_i^\chi q_j^\varphi f_{vcv}(\mathbf{q}) = (-i)^{\chi+\varphi} \frac{\partial^\chi}{\partial \beta_i^\chi} \frac{\partial^\varphi}{\partial \beta_j^\varphi} F_{vcv}(\boldsymbol{\beta}) \Big|_{\boldsymbol{\beta}=\mathbf{0}} \quad (15)$$

with $\chi, \varphi = 0, 1, 2$.

It is evident that the derivatives of the function F_{vcv} at the origin must enter the exchange interaction since we could also treat the interaction in the Wannier representation [16] and obtain higher-order terms using a Taylor expansion at $\boldsymbol{\beta} = \mathbf{0}$.

Due to the special properties of the wave functions F_{vcv} , the expression (15) is nonzero only if $\varphi + \chi = L$ holds. Therefore, we see that the leading term in Eq. (14) describes the K -independent exchange interaction of S excitons. The terms of higher order show that the appearance of a K -dependent exchange interaction of S excitons is inseparably connected to a K -independent exchange interaction of P and D excitons. As the function $m_{vcv}(\mathbf{K}, \mathbf{G})$ enters quadratically the exchange energy (6), the relative size of the K -dependent exchange energy of S excitons and the K -independent exchange energy of P excitons can be estimated comparing

$$|F_{vcv}(\mathbf{0})|^2 K_0^2 = \frac{V_{uc}}{\pi a_{exc}^3} \frac{1}{n^3} K_0^2 \delta_{L,0} \quad (16)$$

with

$$\left| \frac{\partial}{\partial \boldsymbol{\beta}} F_{vcv}(\boldsymbol{\beta}) \Big|_{\boldsymbol{\beta}=\mathbf{0}} \right|^2 = \frac{V_{uc}}{3\pi a_{exc}^5} \frac{n^2 - 1}{n^5} \delta_{L,1}. \quad (17)$$

Here we have introduced the exciton Bohr radius a_{exc} and the value K_0 of K at the exciton photon resonance [1,18]. Note that there are always polaritons and no excitons in bulk semiconductors due to the coupling between excitons and photons. However, if this coupling is weak, it is common to speak of excitons and treat the interaction within perturbation theory [1].

For the nonanalytic exchange interaction, the expression (14) simplifies due to $I_{mn}(\mathbf{0}) = \delta_{mn}$:

$$m_{vcv}(\mathbf{K}, \mathbf{0}) \approx \frac{e}{\sqrt{N}} \sum_{\mathbf{q}} f_{vcv}(\mathbf{q}) \left\{ -\frac{\hbar}{m_0} \frac{\mathbf{K} \mathbf{p}_{vc}}{E_v - E_c} + \frac{\hbar^2}{m_0^2} \sum_{n \neq v,c} \left[\frac{(\mathbf{q} - \gamma \mathbf{K}) \mathbf{p}_{vn} (\mathbf{q} + \alpha \mathbf{K}) \mathbf{p}_{nc}}{(E_v - E_n)(E_c - E_n)} \right. \right. \\ \left. \left. + \frac{(\mathbf{q} + \alpha \mathbf{K}) \mathbf{p}_{vn} (\mathbf{q} + \alpha \mathbf{K}) \mathbf{p}_{nc}}{(E_c - E_v)(E_c - E_n)} + \frac{(\mathbf{q} - \gamma \mathbf{K}) \mathbf{p}_{nc} (\mathbf{q} - \gamma \mathbf{K}) \mathbf{p}_{vn}}{(E_v - E_c)(E_v - E_n)} \right] \right\}. \quad (18)$$

It can easily be seen that $m_{vcv}(\mathbf{0}, \mathbf{0}) = 0$ holds, for which reason the nonanalytic exchange interaction does not diverge at $K = 0$. The different terms describe the nonanalytic exchange energy of S excitons (K -independent and K -dependent) and of P excitons. In the literature usually only the leading terms of the exchange energy are treated, which are given by

$$E_{\text{exch}}^A = 2\delta_{S,0} \delta_{\mathbf{K},\mathbf{K}'} \sum_{\mathbf{G} \neq \mathbf{0}} \frac{e^2}{\varepsilon_0 \varepsilon V_{\text{uc}} G^2} \\ \times F_{vcv}^*(\mathbf{0}) F_{v'c'v'}(\mathbf{0}) I_{vc}^*(\mathbf{G}) I_{v'c'}(\mathbf{G}), \quad (19a)$$

$$E_{\text{exch}}^{\text{NA}} = 2\delta_{S,0} \delta_{\mathbf{K},\mathbf{K}'} \frac{e^2}{\varepsilon_0 \varepsilon V_{\text{uc}} K^2} F_{vcv}^*(\mathbf{0}) F_{v'c'v'}(\mathbf{0}) \\ \times \left(\frac{\hbar}{m_0} \right)^2 \frac{\mathbf{K} \mathbf{p}_{vc}^* \mathbf{K} \mathbf{p}_{v'c'}}{(E_v - E_c)(E_{v'} - E_{c'})}. \quad (19b)$$

Note that $E_{\text{exch}}^{\text{NA}}$ depends on $1/K^2$ and that this term cancels with the K^2 of the numerator. So $E_{\text{exch}}^{\text{NA}}$ depends only on the direction of \mathbf{K} but not on its amount $K = |\mathbf{K}|$. This explains the term ‘‘nonanalytic’’.

III. EXCITONS IN CUPROUS OXIDE

Before we investigate the exchange interaction for the special case of Cu_2O , we have to discuss some specific properties of this semiconductor. First, we have to consider the band structure of Cu_2O . Neglecting the spin-orbit coupling, the uppermost valence band has the symmetry Γ_5^+ and is threefold degenerate at the center of the Brillouin zone. In the literature, this degeneracy is often accounted for by the quasispin $I = 1$ [8,10,27–29]. This quasispin is a convenient abstraction to denote the three spatial functions $\phi_{v,xy}$, $\phi_{v,yz}$ and $\phi_{v,zx}$, which transform according to Γ_5^+ [10,15,27]. Especially, if we compare the states $|I, M_I\rangle$ with the functions $\phi_{v,xy}$, $\phi_{v,yz}$ and $\phi_{v,zx}$ given in Ref. [13], it is

$$|1, +1\rangle_I = -\frac{1}{\sqrt{2}}(\phi_{v,yz} + i\phi_{v,zx}), \quad (20a)$$

$$|1, 0\rangle_I = \phi_{v,xy}, \quad (20b)$$

$$|1, -1\rangle_I = \frac{1}{\sqrt{2}}(\phi_{v,yz} - i\phi_{v,zx}). \quad (20c)$$

Cuprous oxide has cubic symmetry, for which reason the symmetry of the bands is assigned by the irreducible representations Γ_i^\pm of the cubic group \mathcal{O}_h with the superscript \pm denoting the parity. The spin-orbit coupling between the spin S_h of a hole in the valence band and the quasispin I splits the sixfold-degenerate band (now including the hole spin) into a higher lying twofold-degenerate band (Γ_7^+) and a lower lying fourfold-degenerate band (Γ_8^+) (see Fig. 1), which

are characterized by the effective hole spins $J = I + S_h = 1/2$ and $J = 3/2$, respectively. Within the so-called simple band model the effective hole spin distinguishes between two independent exciton series, i.e., the yellow ($J = 1/2$) and the green exciton series ($J = 3/2$) [10,29]. Due to the nonspherical symmetry of the solid and interband interactions, the valence bands are not parabolic but deformed [10]. This leads to a coupling between the yellow and the green exciton series, which is described comprehensively in Ref. [10]. Here we will discuss only the most important points.

The coupling between the valence bands or the anisotropic dispersion of the orbital Γ_5^+ Bloch functions has to be considered in the Wannier equation by the so-called H_d term. The complete Hamiltonian of excitons in Cu_2O therefore reads [10]:

$$H = E_g - \frac{e^2}{4\pi \varepsilon_0 \varepsilon \beta} + H_s + H_d + H_{\text{so}} + H_{\text{exch}} + H_C. \quad (21)$$

The term

$$H_s = \frac{\gamma_1' p^2}{2m_0} \quad (22)$$

describes the average kinetic energy without the nonparabolicity and the coupling between the bands. The H_d term is given

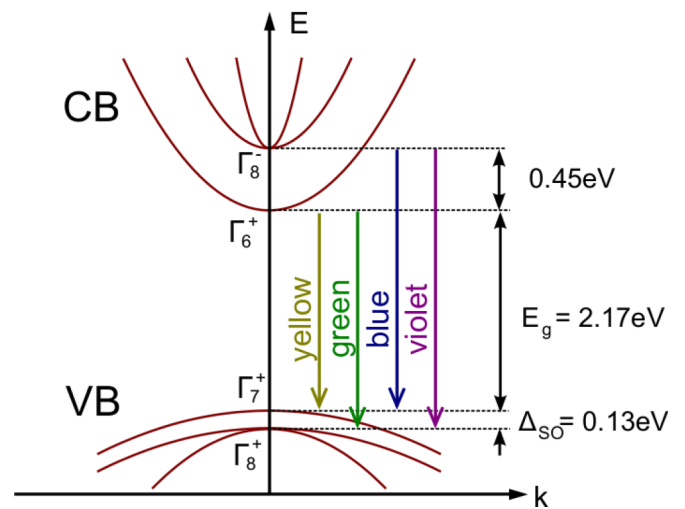


FIG. 1. Band structure of Cu_2O [2]. Due to the spin-orbit coupling the valence band splits into a higher lying twofold-degenerate band (Γ_7^+) and a lower lying fourfold-degenerate band (Γ_8^+). We treat the yellow and green exciton series, which are connected with these two valence bands and the lowest lying conduction band of symmetry Γ_6^+ .

by

$$H_d = \frac{\gamma'_1}{2\hbar^2 m_0} \left(-\frac{\mu'}{3} P^{(2)} \cdot I^{(2)} + \frac{\sqrt{70}\delta'}{15} [P^{(2)} \times I^{(2)}]_0^{(4)} + \frac{\delta'}{3} \sum_{k=\pm 4} [P^{(2)} \times I^{(2)}]_k^{(4)} \right) \quad (23)$$

with the irreducible tensors $P^{(2)}$ and $I^{(2)}$ defined in Ref. [10]. The parameters γ'_1 , μ' and δ' are connected to the Luttinger parameters of Cu_2O [8,10,29]. The H_d term couples the quasi spin I to the angular momentum L of the envelope function. The first summand in Eq. (23) has spherical symmetry while the other terms have cubic symmetry.

The anisotropic dispersion of the orbital Γ_5^+ Bloch functions is in direct competition with the spin-orbit coupling

$$H_{\text{so}} = \frac{2}{3} \Delta \left(1 + \frac{1}{\hbar^2} \mathbf{I} \cdot \mathbf{S}_h \right), \quad (24)$$

which is diagonalized by introducing the effective hole spin J . For an infinite spin-orbit coupling $\Delta \rightarrow \infty$ the Γ_7^+ valence band would be parabolic at the Γ point. However, as $\Delta = 0.131$ eV [9] is comparatively small in Cu_2O , the nonparabolicity of Γ_7^+ and Γ_8^+ valence band already occurs in the vicinity of the Γ point with a simultaneous mixing of both bands.

The H_d term was first introduced by Baldereschi *et al.* (see, e.g., Refs. [28,30–33] and further references therein) to describe the situation for an uppermost Γ_8^+ valence band in semiconductors such as germanium mathematically correct. The decisive breakthrough of their description is the use of modified Bloch functions, i.e., Bloch functions with a lattice periodic part u , which does not depend on the wave vector k . These functions form a complete basis and are thus just as suitable to describe excited states of the solid. The modification of Baldereschi *et al.* is always required if the lattice periodic part of the common Bloch function varies strongly with k . Only due to the constant lattice periodic part the Coulomb interaction between electron and hole will be proportional to $1/r$ if the Wannier equation is transformed from momentum space to position space via a Fourier transformation. The exciton envelope function in the formalism of Baldereschi *et al.* then contains only constant Γ_7^+ and Γ_8^+ components, i.e., the spin states with $J = 1/2$ and $J = 3/2$ given below.

A simple restriction to the Γ_7^+ band neglecting the Γ_8^+ band and considering the nonparabolicity via k^4 terms does not treat the problem correctly. Consequently, the exchange interaction has to be treated within the same formalism, for which reason we use $\mathbf{k} \cdot \mathbf{p}$ perturbation theory at the Γ point. This is in contrast to the treatment by Kavoulakis *et al.* [15] and to the best of our knowledge this has not been done before.

The term H_C in Eq. (21) accounts for the central cell corrections [15], which are needed to describe the $1S$ exciton correctly. Since the radius of this exciton is very small, it is an intermediate exciton between a Frenkel exciton and a Wannier exciton [1]. Therefore, the $1S$ exciton cannot be described

within the effective mass approach due to its large extension in momentum space. However, we neglect the central cell corrections in the following. The usage of the kinetic energy in the form of Eqs. (22) and (23) and the neglecting of higher-order terms in p is then justified if we use an average curvature of the bands instead of the curvature at the center of the Brillouin zone. Hence, the Bohr radius of the $1S$ exciton is smaller than the one of excitons with $n \geq 2$. Furthermore, we have to replace the dielectric constant $\varepsilon = 7.5$ by its high-frequency value $\varepsilon_\infty = 6.46$ [15].

Let us consider at first the Hamiltonian (21) without the H_d term and the exchange interaction. In this case we can treat spins and Wannier or Bloch functions separately from the envelope function. The yellow and green exciton series are described by the two states with $J = 1/2$ of symmetry Γ_7^+

$$\left| \frac{1}{2}, +\frac{1}{2} \right\rangle_J = \sqrt{\frac{2}{3}} | +1 \rangle_{I| \downarrow \rangle_h} - \frac{1}{\sqrt{3}} | 0 \rangle_{I| \uparrow \rangle_h}, \quad (25a)$$

$$\left| \frac{1}{2}, -\frac{1}{2} \right\rangle_J = \frac{1}{\sqrt{3}} | 0 \rangle_{I| \downarrow \rangle_h} - \sqrt{\frac{2}{3}} | -1 \rangle_{I| \uparrow \rangle_h}, \quad (25b)$$

and the four states with $J = 3/2$ of symmetry Γ_8^+

$$\left| \frac{3}{2}, +\frac{3}{2} \right\rangle_J = | +1 \rangle_{I| \uparrow \rangle_h}, \quad (26a)$$

$$\left| \frac{3}{2}, +\frac{1}{2} \right\rangle_J = \frac{1}{\sqrt{3}} | 1 \rangle_{I| \downarrow \rangle_h} + \sqrt{\frac{2}{3}} | 0 \rangle_{I| \uparrow \rangle_h}, \quad (26b)$$

$$\left| \frac{3}{2}, -\frac{1}{2} \right\rangle_J = \sqrt{\frac{2}{3}} | 0 \rangle_{I| \downarrow \rangle_h} + \frac{1}{\sqrt{3}} | -1 \rangle_{I| \uparrow \rangle_h}, \quad (26c)$$

$$\left| \frac{3}{2}, -\frac{3}{2} \right\rangle_J = | -1 \rangle_{I| \downarrow \rangle_h}. \quad (26d)$$

If we now add the electron spin and the Wannier function $\phi_{c,s}$ of the conduction band, which transform together according to $\Gamma_6^+ \otimes \Gamma_1^+ = \Gamma_6^+$, we obtain states with the total momentum $G = J + S_e = 0$ and $G = 1$. Subsequently, these states have to be multiplied by the hydrogenlike envelope function $F_v(\boldsymbol{\beta})$.

In the Cartesian basis the ground states of the yellow exciton are (cf. Ref. [13])

$$|P\rangle = F_{1,0,0}(\boldsymbol{\beta}) | 0, 0 \rangle_G, \quad (27a)$$

$$|O_{xy}\rangle = F_{1,0,0}(\boldsymbol{\beta}) | 1, 0 \rangle_G, \quad (27b)$$

$$|O_{yz}\rangle = \frac{1}{\sqrt{2}} F_{1,0,0}(\boldsymbol{\beta}) (| 1, -1 \rangle_G - | 1, +1 \rangle_G), \quad (27c)$$

$$|O_{zx}\rangle = \frac{i}{\sqrt{2}} F_{1,0,0}(\boldsymbol{\beta}) (| 1, -1 \rangle_G + | 1, +1 \rangle_G). \quad (27d)$$

The state $|P\rangle$ of symmetry Γ_2^+ is the paraexciton state and the states $|O_{ij}\rangle$ of symmetry Γ_5^+ are the orthoexciton states. It is possible to express these states using the eigenstates of the spin $S = S_e + S_h$ [13]:

$$|P\rangle = \frac{1}{\sqrt{6}} F_{1,0,0}(\boldsymbol{\beta}) \phi_{c,s} [\sqrt{2} \phi_{v,xy} | 1, 0 \rangle_S + (-\phi_{v,yz} + i \phi_{v,zx}) | 1, +1 \rangle_S + (\phi_{v,yz} + i \phi_{v,zx}) | 1, -1 \rangle_S], \quad (28a)$$

$$|O_{xy}\rangle = \frac{-1}{\sqrt{6}}F_{1,0,0}(\boldsymbol{\beta})\phi_{c,s}[-\sqrt{2}\phi_{v,xy}|0,0\rangle_S + (\phi_{v,yz} - i\phi_{v,zx})|1,+1\rangle_S + (\phi_{v,yz} + i\phi_{v,zx})|1,-1\rangle_S], \quad (28b)$$

$$|O_{yz}\rangle = \frac{1}{\sqrt{6}}F_{1,0,0}(\boldsymbol{\beta})\phi_{c,s}[\phi_{v,xy}|1,+1\rangle_S + \phi_{v,xy}|1,-1\rangle_S + i\sqrt{2}\phi_{v,yz}|0,0\rangle_S + \sqrt{2}\phi_{v,zx}|1,0\rangle_S], \quad (28c)$$

$$|O_{zx}\rangle = \frac{-i}{\sqrt{6}}F_{1,0,0}(\boldsymbol{\beta})\phi_{c,s}[\phi_{v,xy}|1,+1\rangle_S - \phi_{v,xy}|1,-1\rangle_S + \sqrt{2}\phi_{v,yz}|1,0\rangle_S + i\sqrt{2}\phi_{v,zx}|0,0\rangle_S]. \quad (28d)$$

One can see that the paraexciton state does not contain a singlet component, i.e., a component with $S = 0$. Therefore, this state is spin-flip forbidden in optical excitations, which explains the term “para” or “dark” exciton [2]. However, we may note at this point that the orthoexciton and paraexciton states are not eigenstates of the operators S^2 and S_z . Therefore, it may be misleading to speak of singlet and triplet states [2,12].

The exciton states are generally mixed by the H_d term (23) due to the coupling between L and I . Since parity is a good quantum number in Cu_2O , the H_d term mixes only exciton states with even values of L or with odd values of L [29]. Therefore, D excitons are admixed to S excitons and vice versa. The coupling due to the H_d term leads to an energy gain in the system, which was discussed in Ref. [10].

As the radius of the yellow $1S$ exciton is small in position space, it is extended in momentum space, for which reason we expect its coupling to the green series to be strong. Due to the admixture, the yellow orthoexciton becomes more and more a pure singlet state as the total spin $S = S_e + S_h$ is a good quantum number in the limit of $\Delta = 0$.

In this limiting case with $\Delta = 0$, the introduction of the effective hole spin J would not be necessary. The exciton wave function could be written as the product of a space function, which also depends on I , and a spin function. Without the H_d term the ground states of the exciton would then read

$$|P_{1,j}\rangle = F_{1,0,0}(\boldsymbol{\beta})\phi_{c,s}\phi_{v,j}|1,1\rangle_S, \quad (29a)$$

$$|P_{0,j}\rangle = F_{1,0,0}(\boldsymbol{\beta})\phi_{c,s}\phi_{v,j}|1,0\rangle_S, \quad (29b)$$

$$|P_{-1,j}\rangle = F_{1,0,0}(\boldsymbol{\beta})\phi_{c,s}\phi_{v,j}|1,-1\rangle_S, \quad (29c)$$

$$|O_j\rangle = F_{1,0,0}(\boldsymbol{\beta})\phi_{c,s}\phi_{v,j}|0,0\rangle_S, \quad (29d)$$

with $j = xy, yz, zx$. In this case there are also three orthoexciton states. The paraexciton and orthoexciton states are true triplet states ($S = 1$) and singlet states ($S = 0$), respectively.

The Hamiltonian (21) is given for $K = 0$. In the general case with $K \neq 0$ additional terms appear [10]:

$$\begin{aligned} T_1(\mathbf{K}) &= \Omega_1 K^2 \mathbf{1} \\ &- \Omega_3 (K_1^2 (3I_1^2 - 2\hbar^2 \mathbf{1}) + \text{c.p.}) / \hbar^2 \\ &- \Omega_5 (K_1 K_2 (I_1 I_2 + I_2 I_1) + \text{c.p.}) / \hbar^2. \end{aligned} \quad (30)$$

As can be seen, these K^2 -dependent terms are 3×3 matrices and can again be divided into an H_s term, an H_d term of spherical symmetry, and an H_d term of cubic symmetry, i.e.,

we can write

$$\begin{aligned} T_1(\mathbf{K}) &= (\Omega_1)K^2 - \left(\frac{\Omega_5 + 2\Omega_3}{15\hbar^2} \right) K^{(2)} \cdot I^{(2)} \\ &+ \left(\frac{\Omega_5 - 3\Omega_3}{18\hbar^2} \right) \left(\frac{\sqrt{70}}{5} [K^{(2)} \times I^{(2)}]_0^{(4)} \right. \\ &\left. + \sum_{k=\pm 4} [K^{(2)} \times I^{(2)}]_k^{(4)} \right). \end{aligned} \quad (31)$$

To describe the exciton series in Cu_2O correctly, the Schrödinger equation with the operators (21) and (30) has to be solved for fixed values of K . However, as the effect of the K^2 -dependent terms on the relative motion is small, the effect of $T_1(\mathbf{K})$ can be treated within perturbation theory.

It has been shown in Ref. [10] that the coefficients Ω in $T_1(\mathbf{K})$ are of the correct order of magnitude to describe the K -dependent splitting of the $1S$ exciton state, which was observed experimentally and originally assigned to the exchange interaction [12–14]. In Sec. IV we will show that the exchange interaction is far too small to explain this splitting.

IV. EXCHANGE INTERACTION FOR CUPROUS OXIDE

In this section we want to estimate the maximum size of the exchange interaction for the exciton ground state in Cu_2O following the explanations given in Refs. [13,15]. Note that it would be necessary to solve the full exciton Hamiltonian (21) including all K -dependent terms to determine the true size of the exchange interaction. As has been stated in Sec. III, parity is a good quantum number and the exciton ground state contains mainly S -like but also D -like envelope functions. Due to the results of Sec. II the (K -dependent and K -independent) exchange interaction is strongest if the envelope function is purely S -like and if $n = 1$ holds. Furthermore, for the exchange interaction only the singlet component of the states is of importance. From Eqs. (28) and (29) we see that we can set

$$\rho_{vcv\mathbf{K}}^{(P)}(\mathbf{r}) = 0, \quad (32a)$$

$$\begin{aligned} \rho_{vcv\mathbf{K}}^{(O)}(\mathbf{r}) &= c_\rho e \sum_{\boldsymbol{\beta}} U_{vcv\mathbf{K}}(\boldsymbol{\beta}) \\ &\times \phi_{c,s}(\mathbf{r} - \boldsymbol{\beta}) \phi_{v,j}^*(\mathbf{r}), \end{aligned} \quad (32b)$$

with $j = xy, yz, zx$. The prefactor c_ρ is of the order 1. Even though the exchange energy is not diagonal with respect to v , we consider only the dominant contribution $E_{\text{exch}}(vc\ 1S\ \mathbf{K}, v'c\ 1S\ \mathbf{K}')$ with $v = v' = 1S$ or more precisely $v = (n, L, M) = (1, 0, 0)$.

A. Analytic exchange interaction

The K dependence of the analytic exchange interaction has been neglected in Ref. [15] and will be treated here. We estimate its magnitude to show that the K -dependent splitting of the $1S$ exciton state treated in Refs. [12–14] cannot be explained in terms of the exchange interaction.

In the case of the analytic exchange interaction we consider only the zero- and first-order terms in the function $m_{vcv}(\mathbf{K}, \mathbf{G})$ of Eq. (14). As can be seen from Eq. (6), the analytic

exchange energy depends on $m_{vcv}^*(\mathbf{K}, \mathbf{G})m_{v'c'v'}(\mathbf{K}, \mathbf{G})$. When calculating the exchange energy the second-order terms in $m_{v'c'v'}(\mathbf{K}, \mathbf{G})$ have to be multiplied with the zero-order term of $m_{vcv}^*(\mathbf{K}, \mathbf{G})$ and vice versa. Since the zero-order term is a diagonal 3×3 matrix, the resulting K^2 -dependent terms cannot describe a K -dependent splitting of the exciton ground state. Furthermore, we will estimate the size of these terms in the following and show that they are negligibly small.

We can write

$$\begin{aligned} m_{vcv}(\mathbf{K}, \mathbf{G}) &\approx \frac{ec_\rho}{\sqrt{N}} \sum_{\mathbf{q}} f_{vcv}(\mathbf{q}) \left[I_{vc}(\mathbf{G}) + \frac{\hbar}{m_0} \left\{ \sum_{n \neq v} \frac{(\mathbf{q} - \gamma \mathbf{K}) \mathbf{p}_{vn}}{(E_v - E_n)} I_{nc}(\mathbf{G}) + \sum_{n \neq c} \frac{(\mathbf{q} + \alpha \mathbf{K}) \mathbf{p}_{nc}}{(E_c - E_n)} I_{vn}(\mathbf{G}) \right\} \right] \\ &= ec_\rho F_{vcv}(\mathbf{0}) I_{vc}(\mathbf{G}) + ec_\rho \frac{\hbar}{m_0} [(-i \nabla_{\boldsymbol{\beta}}) F_{vcv}(\boldsymbol{\beta})]_{\boldsymbol{\beta}=\mathbf{0}} \left\{ \sum_{n \neq v} \frac{\mathbf{p}_{vn} I_{nc}(\mathbf{G})}{(E_v - E_n)} + \sum_{n \neq c} \frac{\mathbf{p}_{nc} I_{vn}(\mathbf{G})}{(E_c - E_n)} \right\} \\ &\quad + ec_\rho \frac{\hbar}{m_0} F_{vcv}(\mathbf{0}) \left\{ \sum_{n \neq v} \frac{-\gamma \mathbf{K} \mathbf{p}_{vn}}{(E_v - E_n)} I_{nc}(\mathbf{G}) + \sum_{n \neq c} \frac{\alpha \mathbf{K} \mathbf{p}_{nc}}{(E_c - E_n)} I_{vn}(\mathbf{G}) \right\}. \end{aligned} \quad (33)$$

If we now set $v = v' = 1S$, the gradient of $F_{vc1S}(\boldsymbol{\beta})$ at $\boldsymbol{\beta} = \mathbf{0}$ vanishes. Finally, we have

$$\begin{aligned} E_{\text{exch}}^A &= 2\delta_{S,0} \delta_{\mathbf{K},\mathbf{K}'} \frac{e^2 c_\rho^2}{\varepsilon_0 \varepsilon_\infty \pi a_{\text{exc}}^3} \sum_{\mathbf{G} \neq \mathbf{0}} \frac{1}{(\mathbf{K} + \mathbf{G})^2} \left[I_{v'c}(\mathbf{G}) + \frac{\hbar}{m_0} \left\{ \sum_{n \neq v'} \frac{-\gamma \mathbf{K} \mathbf{p}_{v'n}}{(E_{v'} - E_n)} I_{nc}(\mathbf{G}) + \sum_{n \neq c} \frac{\alpha \mathbf{K} \mathbf{p}_{nc}}{(E_c - E_n)} I_{v'n}(\mathbf{G}) \right\} \right] \\ &\quad \times \left[I_{vc}(\mathbf{G}) + \frac{\hbar}{m_0} \left\{ \sum_{n \neq v} \frac{-\gamma \mathbf{K} \mathbf{p}_{vn}}{(E_v - E_n)} I_{nc}(\mathbf{G}) + \sum_{n \neq c} \frac{\alpha \mathbf{K} \mathbf{p}_{nc}}{(E_c - E_n)} I_{vn}(\mathbf{G}) \right\} \right]^*. \end{aligned} \quad (34)$$

The component with $\mathbf{K} = \mathbf{0}$ describes the experimentally observed splitting between orthoexcitons and paraexcitons of 12 meV [34–36]. Therefore, we set

$$12 \text{ meV} = \frac{2e^2 c_\rho^2}{\varepsilon_0 \varepsilon_\infty \pi a_{\text{exc}}^3} \sum_{\mathbf{G} \neq \mathbf{0}} \frac{1}{G^2} |I_{vc}(\mathbf{G})|^2. \quad (35)$$

A restriction to the six summands with the smallest value G_0 of G as in Ref. [15] is in general not correct. Due to the symmetry of the Bloch functions other values of G will contribute even more strongly to the sum in Eq. (34). Indeed, it is worth mentioning that the symmetry group of the lattice in Cu_2O is only isomorphic to the cubic group O_h [18]. Since the Cu atoms in Cu_2O form an fcc sublattice, it can be seen from the unit cell of Cu_2O that the lattice is not invariant under reflections but under a glide reflection with a translation of $a/2$ (see also Supplemental Material of Ref. [2]), where a denotes the lattice constant $a = 4.26 \times 10^{-10}$ m of Cu_2O [37–39]. The Bloch functions must be invariant under this operation. If we write $u_{n\mathbf{K}}(\mathbf{r}) = \sum_{\mathbf{G}} C_{n\mathbf{K}}(\mathbf{G}) e^{i\mathbf{G}\mathbf{r}}$ [21], we see that the vector components of \mathbf{G} can only take whole-number multiples of $4\pi/a$ instead of $2\pi/a$.

The K dependence of the analytic exchange interaction arises from the $\mathbf{K} \mathbf{p}_{mn}$ terms and the factor $1/(\mathbf{K} + \mathbf{G})^2$ in Eq. (34). At first, we will estimate the effect of the $\mathbf{K} \mathbf{p}_{mn}$ terms. Due to reasons of symmetry, the terms linear in K must vanish when evaluating the product in Eq. (34). The

K^2 -dependent terms are of the same order of magnitude as the second-order terms in the function $m_{vcv}(\mathbf{K}, \mathbf{G})$, which we have neglected. We can now use Eq. (35) to give an upper limit for their magnitude and to prove that their neglecting is justified. Using the values $|\mathbf{p}_{nm}|/\hbar \approx 1.3 \times 10^9 \text{ m}^{-1}$ and $(E_m - E_n) \geq \Delta E = 449 \text{ meV}$ given in Ref. [15], we obtain

$$\left(\frac{\hbar}{m_0} |\mathbf{p}_{nm}| K_0 \frac{1}{\Delta E} \right)^2 \times 12 \text{ meV} \approx 0.4 \mu\text{eV}. \quad (36)$$

We see that this part of the analytic exchange interaction is very small.

Nevertheless, we have shown in Sec. II that a K -dependent exchange interaction of S excitons is connected to a K -independent analytic exchange interaction of P excitons. Using the result of Eq. (36), we can estimate the size of the analytic exchange energy of the $2P$ excitons via Eqs. (16) and (17). With the exciton Bohr radius $a_{\text{exc}} = 0.53 \text{ nm}$ of the $1S$ exciton, the corresponding value $a_{\text{exc}} = 1.1 \text{ nm}$ for P excitons [15] and $K_0 = 2.62 \times 10^7 \text{ m}^{-1}$ [13], the maximum size of the analytic exchange energy of the $2P$ excitons is

$$\frac{(0.53)^3}{3(1.1)^5 (0.0262)^2} \frac{2^2 - 1}{2^5} \times 0.4 \mu\text{eV} \approx 1.6 \mu\text{eV}. \quad (37)$$

We see that also this energy is negligibly small. Furthermore, the line widths of the P excitons in Cu_2O are too large to detect a splitting in the order of a few μeV .

Let us now treat the K dependence arising from the prefactor $1/(\mathbf{K} + \mathbf{G})^2$. This factor can be written as a Fourier series at $\mathbf{K} = \mathbf{0}$ for $\mathbf{K} \ll \mathbf{G}$,

$$\frac{1}{(\mathbf{K} + \mathbf{G})^2} \approx \frac{1}{G^2} - \frac{2(\mathbf{K}\mathbf{G})}{G^4} + \frac{1}{G^6} \mathbf{G}^T [-\mathbf{1}K^2 + 4\mathbf{K} \cdot \mathbf{K}^T] \mathbf{G}. \quad (38)$$

Inserting this expression in Eq. (34), the term proportional to K vanishes for reasons of symmetry. The magnitude of the K^2 -dependent term can be estimated assuming that K is oriented in [100] direction and using the reciprocal lattice vectors with the smallest modulus $4\pi/a$. This gives an upper limit of

$$12 \text{ meV} \times 3K_0^2 \left(\frac{a}{4\pi} \right)^2 \approx 28 \text{ neV} \quad (39)$$

for the prefactor of those K^2 -dependent terms in Eq. (34), which originate from the Fourier expansion of $1/(\mathbf{K} + \mathbf{G})^2$. We see that not only the result of Eq. (36) but also the result of Eq. (39) is at least one order of magnitude smaller than the experimentally observed values for the K -dependent splitting of the $1S$ exciton [13]. As the estimated values are upper limits for the prefactors, the actual magnitude of the analytic exchange interaction is generally much smaller.

However, using group theoretical considerations, it is obvious that in both cases the K^2 -dependent terms can be written as a sum of the invariant matrices $\mathbf{1}K^2$, $(3K_i^2 - K^2)(\hat{e}_i \otimes \hat{e}_i)$ and $K_i K_j (\hat{e}_i \otimes \hat{e}_j)$ with $i, j = 1, 2, 3$ and $i \neq j$, since every K -dependent energy as regards states of the symmetry Γ_5^+ must lead to matrices of this form [13,40]. This can be seen, e.g., from Eq. (30), where the dispersion of the exciton is described by the same matrices. Hence, the K -dependent splitting of the $1S$ exciton states must in any case be described by matrices of this form [13]. However, from the experimental point of view the physical origin of these matrices is *a priori* unknown. In Refs. [12–14] it has been assumed that the exchange interaction is responsible for the K -dependent splitting.

We have now shown that the K -dependent analytic exchange interaction is negligibly small in Cu_2O and that it cannot explain the K -dependent splitting of the $1S$ exciton. Furthermore, due to the specific form of the exchange interaction, it would not be experimentally distinguishable from the dispersion of the exciton described by Eq. (30).

Only the K -dependent nonanalytic exchange interaction may contribute to the splitting of the $1S$ ortho exciton. This will be investigated in Sec. IV B.

B. Nonanalytic exchange interaction

We will now treat the nonanalytic exchange interaction for Cu_2O . As the conduction band and the valence band in Cu_2O have the same (positive) parity and the momentum operator \mathbf{p} has negative parity, the matrix element $\mathbf{p}_{vc} = \langle u_{v0} | \mathbf{p} | u_{c0} \rangle$ vanishes. Therefore, the main contribution to the nonanalytic exchange interaction comes from the term in square brackets in Eq. (18).

We can see again the close connection between the nonanalytic exchange interaction and the oscillator strength:

Inserting the q K -dependent terms of Eq. (18) into Eq. (6), one obtains the K -independent nonanalytic exchange energy of P excitons. Since these excitons are dipole allowed, their oscillator strength is also K -independent. The exchange energy exactly equals the LT splitting when treating P exciton polaritons.

The K^2 -dependent terms of Eq. (18) will lead to a K^2 -dependent exchange energy for the S excitons. These excitons are quadrupole allowed and their oscillator strength is also K^2 dependent. For reasons of symmetry, the energy difference between longitudinal and transversal S excitons at $K = 0$ is exactly zero, as well. The fact that S excitons are quadrupole allowed for finite values of K can be understood from a symmetry reduction: The cubic group reduces for finite values of K to a group of lower symmetry, e.g., C_{4v} , which does not contain inversion as a group element [25,40]. This leads to a K -dependent admixture of P excitons to S excitons.

In the following, we will concentrate on the K^2 -dependent exchange energy of the $1S$ excitons to estimate its magnitude and investigate its angle dependency. Due to the close connection between exchange energy and oscillator strength, we expect the ratio of the K^2 -dependent exchange energy of S excitons and the K -independent exchange energy of P excitons to be of the same size as the ratio of the corresponding oscillator strengths.

We can write

$$m_{vc1S}(\mathbf{K}, \mathbf{0}) \approx \frac{ec_\rho \hbar^2}{m_0^2} F_{vc1S}(\mathbf{0}) \left(\langle u_{v0} | \langle \mathbf{K} \mathbf{p} \right| \left[\sum_{n \neq v,c} g_{vc}(E_n) \times |u_{n0}\rangle \langle u_{n0}| \right] (\mathbf{K} \mathbf{p}) | u_{c0} \rangle \right) \quad (40)$$

with

$$g_{vc}(E_n) = \frac{\gamma \alpha (E_v - E_c) - \alpha^2 (E_v - E_n) + \gamma^2 (E_c - E_n)}{(E_v - E_n)(E_c - E_n)(E_v - E_c)}. \quad (41)$$

Using group theory, we can determine the nonvanishing terms of the exchange energy. The operator in square brackets in Eq. (40) is a projection operator. For reasons of symmetry this operator has to transform according to the irreducible representation Γ_1^+ . On the other hand, the operator \mathbf{p} transforms according to Γ_4^- . The symmetry of the operator between the Bloch functions is therefore

$$\Gamma_4^- \otimes \Gamma_1^+ \otimes \Gamma_4^- = \Gamma_1^+ \oplus \Gamma_3^+ \oplus \Gamma_4^+ \oplus \Gamma_5^+. \quad (42)$$

The symmetry of the Bloch functions is

$$\Gamma_5^+ \otimes \Gamma_1^+ = \Gamma_5^+. \quad (43)$$

Consequently, the expression (40) does not vanish only if the operator has the symmetry Γ_5^+ [41]. We can then consider the coupling coefficients for the case $\Gamma_4^- \otimes \Gamma_4^- \rightarrow \Gamma_5^+$. With the basis functions $|X\rangle, |Y\rangle, |Z\rangle$ of Γ_4^- and the basis functions $|\tilde{X}\rangle = |YZ\rangle, |\tilde{Y}\rangle = |ZX\rangle$, and $|\tilde{Z}\rangle = |XY\rangle$ of Γ_5^+ , we see that, e.g., the Γ_5^+ -like part of the products $|X\rangle_1 |Y\rangle_2$ and $|Y\rangle_1 |X\rangle_2$ transforms as $|\tilde{Z}\rangle / \sqrt{2}$ [40]. So we write

$$\langle \tilde{Z} | (|X\rangle_1 |Y\rangle_2) = \frac{1}{\sqrt{2}}, \quad \langle \tilde{Z} | (|Y\rangle_1 |X\rangle_2) = \frac{1}{\sqrt{2}}, \quad (44)$$

and the expressions obtained via cyclic permutation. Writing the exchange energy as a 3×3 matrix with the valence band functions given in the order $\phi_{v,yz}$, $\phi_{v,zx}$, $\phi_{v,xy}$, we finally obtain the expression

$$E_{\text{exch}}^{\text{NA}} = \Delta_Q \frac{K^2}{K_0^2} \begin{pmatrix} \hat{K}_y^2 \hat{K}_z^2 & \hat{K}_z^2 \hat{K}_y \hat{K}_x & \hat{K}_x^2 \hat{K}_y \hat{K}_z \\ \hat{K}_z^2 \hat{K}_y \hat{K}_x & \hat{K}_x^2 \hat{K}_z^2 & \hat{K}_y^2 \hat{K}_x \hat{K}_z \\ \hat{K}_x^2 \hat{K}_y \hat{K}_z & \hat{K}_y^2 \hat{K}_x \hat{K}_z & \hat{K}_z^2 \hat{K}_y \hat{K}_x \end{pmatrix} \quad (45)$$

for the nonanalytic exchange energy with $\hat{K} = \mathbf{K}/K$. Contrary to dipole allowed excitons, the nonanalytic exchange energy depends on the fourth power of the angular coordinates of \mathbf{K} .

We can now explicitly give the coefficient Δ_Q of Refs. [12–14] from microscopic calculations and estimate its size using Eq. (16) and the values $|\mathbf{p}_{nm}|/\hbar \approx 1.3 \times 10^9 \text{ m}^{-1}$ and $(E_m - E_n) \geq \Delta E = 449 \text{ meV}$ given in Ref. [15]:

$$\Delta_Q = \frac{6c^2 e^2 K_0^2 \hbar^4}{\epsilon_0 \epsilon_\infty V_{\text{uc}} m_0^4} \left| F_{vc1S}(\mathbf{0}) \sum_{n \neq v,c} g_{vc}(E_n) p_{nc} p_{vn} \right|^2 \approx 9 \text{ neV}. \quad (46)$$

This value is significantly smaller than the result $\Delta_Q = 5 \mu\text{eV}$ from Ref. [12]. We see that also the K -dependent nonanalytic exchange interaction is negligibly small in Cu_2O .

As has been stated in Sec. II, it is nevertheless interesting to investigate the possible coupling between longitudinal and transverse exciton states. In the case of the orthoexciton these states are uncoupled only if the K vector is parallel to one of the main symmetry axes of the crystal. We will show that a general direction of the K vector an LT coupling appears, for which reason all three exciton states couple to light with a polarization not being orthogonal to the wave vector involved.

We start with \mathbf{K} being oriented in the [100] direction. In this case the cubic symmetry is reduced to the group C_{4v} , which leaves \mathbf{K} invariant. Since $K_y = K_z = 0$ holds, the nonanalytic exchange interaction (45) is zero. Therefore, we are allowed to choose appropriate linear combinations of the states $\phi_{v,yz}$, $\phi_{v,zx}$, $\phi_{v,xy}$ such that $\boldsymbol{\mu}_{vcv\mathbf{K}} \parallel \mathbf{K}$ and $\boldsymbol{\mu}_{vcv\mathbf{K}} \perp \mathbf{K}$ holds. To this aim, we insert the charge density

$$\begin{aligned} \rho_{vc,v\mathbf{K}}(\mathbf{r}) &= c_\rho e \sum_{\beta} U_{vcv\mathbf{K}}(\boldsymbol{\beta}) \\ &\times \phi_{c,s}(\mathbf{r} - \boldsymbol{\beta}) [c_{yz} \phi_{v,yz}^*(\mathbf{r}) \\ &+ c_{zx} \phi_{v,zx}^*(\mathbf{r}) + c_{xy} \phi_{v,xy}^*(\mathbf{r})] \end{aligned} \quad (47)$$

into

$$\boldsymbol{\mu}_{vcv\mathbf{K}} = \int d\mathbf{r} \mathbf{r} \rho_{vcv\mathbf{K}}(\mathbf{r}). \quad (48)$$

Using Eq. (11) and considering again the coupling coefficients for the case $\Gamma_4^- \otimes \Gamma_4^- \rightarrow \Gamma_5^+$ [cf. Eq. (44)], we obtain

$$\boldsymbol{\mu}_{vcv\mathbf{K}} \sim \begin{pmatrix} K_y c_{xy} + K_z c_{zx} \\ K_z c_{yz} + K_x c_{xy} \\ K_x c_{zx} + K_y c_{yz} \end{pmatrix}. \quad (49)$$

Hence, the two transverse states for $\mathbf{K} \parallel [100]$ are given by $c_{xy} = 1, c_{yz} = c_{zx} = 0$ and $c_{zx} = 1, c_{yz} = c_{xy} = 0$. This is not unexpected since the K vector causes a symmetry breaking in

the x direction, which affects the functions $\phi_{v,xy}$ and $\phi_{v,zx}$ in a different way than $\phi_{v,yz}$.

The fact that longitudinal and transverse exciton states are decoupled for $\mathbf{K} \parallel [100]$ can also be understood from group theoretical considerations: The exciton states transform according to Γ_5^+ in O_h while the dipole operator transforms according to the irreducible representation D^1 of the full rotation group or according to Γ_4^- in O_h . As the cubic symmetry reduces to C_{4v} , we have to consider the reduction of the irreducible representations of the cubic group O_h by the group C_{4v} :

$$\Gamma_5^+ \rightarrow \Gamma_4 \oplus \Gamma_5, \quad (50a)$$

$$\Gamma_4^- \rightarrow \Gamma_1 \oplus \Gamma_5. \quad (50b)$$

Comparing both equations, we immediately see that the two Γ_5 states are transverse states and that the Γ_4 state is a longitudinal state. Since there are now exciton states transforming according to Γ_5 and a dipole operator, which transforms according to Γ_5 , these exciton states can be excited by light. This describes the fact that the $1S$ exciton becomes quadrupole allowed due to the K -dependent admixture of P excitons. On the other hand, as the transverse states and the longitudinal state transform according to different irreducible representations, no coupling between these states occurs.

Let us now consider the exchange interaction (45) for an arbitrary \mathbf{K} with all vector components $K_i \neq 0$. The eigenvalues λ_i and eigenvectors v_i of the 3×3 matrix in Eq. (45) read

$$\lambda_1 = 0, \quad v_1 = \frac{(-b, a, 0)^T}{\sqrt{a^2 + b^2}}, \quad (51)$$

$$\lambda_2 = 0, \quad v_2 = \frac{(-c, 0, a)^T}{\sqrt{a^2 + c^2}}, \quad (52)$$

$$\lambda_3 = a^2 + b^2 + c^2, \quad v_3 = \frac{(a, b, c)^T}{\sqrt{a^2 + b^2 + c^2}}, \quad (53)$$

with the abbreviations $a = \hat{K}_y \hat{K}_z$, $b = \hat{K}_z \hat{K}_x$, and $c = \hat{K}_x \hat{K}_y$. Even though there is only one state with an eigenvalue $\lambda \neq 0$, we have to prove that this state is connected with a longitudinal polarization. Inserting v_3 into Eq. (49) yields

$$\boldsymbol{\mu}_{vcv\mathbf{K}} \sim \mathbf{K} - K (\hat{K}_x^3, \hat{K}_x^3, \hat{K}_x^3)^T. \quad (54)$$

Due to the second term, the dipole moment is not parallel to \mathbf{K} . Therefore, we have shown that longitudinal and transverse exciton states are coupled by the nonanalytic exchange interaction (45) if \mathbf{K} is not oriented in a direction of high symmetry. Furthermore, we see that two eigenstates of the matrix in Eq. (45) are degenerate. If the nonanalytic exchange interaction were the only reason for the K -dependent splitting of the $1S$ exciton, only two states would be observable in experiments for any direction of \mathbf{K} .

V. SUMMARY AND OUTLOOK

Using $\mathbf{k} \cdot \mathbf{p}$ perturbation theory, we could derive K -dependent higher-order terms of the analytic and nonanalytic exchange interaction of Wannier excitons. We have discussed

the specific properties of Cu_2O and in particular the effects of the valence band structure. Investigating the K -dependent exchange interaction of the 1S excitons in this semiconductor, we could show that the K -dependent terms of the analytic and the nonanalytic exchange interaction are negligibly small

compared to the effects of the nonisotropic dispersion. A closer examination of the K -dependent nonanalytic exchange interaction exhibited a coupling between longitudinal and transverse exciton states if \mathbf{K} is not oriented in a direction of high symmetry.

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