Exchange interaction in the yellow exciton series of cuprous oxide

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We experimentally and numerically investigate the exchange interaction of the yellow excitons in cuprous oxide. By varying the material parameters in the numerical calculations, we can interpret experimental findings and understand their origin in the complex band structure and central-cell corrections. In particular, we experimentally observe the reversal of the ortho- and paraexciton for the 2S yellow exciton, and explain this phenomenon by an avoided crossing with the green 1S orthoexciton in a detailed numerical analysis. Furthermore, we discuss the exchange splitting as a function of the principal quantum number n and its deviation from the n⁻³ behavior expected from a hydrogenlike model. We also explain why the observed exchange splitting of the green 1S exciton is more than twice the splitting of the yellow 1S state.

I. INTRODUCTION

The yellow exciton series in cuprous oxide has been shown to closely match a hydrogenlike system in many respects [1]. Still, there are a number of characteristic effects of the complex band structure. For example, a fine structure splitting between P and F states can be observed [2]. In the case of small radii, additional central-cell corrections to the valence band Hamiltonian have to be added to achieve a satisfactory description [3]. Due to the cubic symmetry of the crystal, the angular momentum is not a good quantum number anymore, and thus the S states with small extension are also coupled to other angular momenta, such as the D states. This is especially important when considering the green 1S state, which lies in between the yellow spectrum. Because of this coupling, the central-cell corrections also affect the energetically higher lying states of the yellow series.

The exchange interaction, which is part of the central-cell corrections, causes a characteristic splitting between states depending on the relative alignment of the electron and hole spins, i.e., between the spin-singlet and spin-triplet states. The spin-triplet dark exciton states have been proposed for use in quantum computational studies [4−6]. The dark paraexciton series in cuprous oxide is not accessible by electric dipole and quadrupole absorption experiments, because the paraexcitons have no spin-singlet component and are therefore spin-flip forbidden to all orders in electric transitions. This selection rule can be circumvented using stress [7] or by application of an external magnetic field which leads to a mixing between spin-singlet and triplet states [8−9]. We use magnetic-field-induced Second Harmonic Generation (SHG) spectroscopy for the measurements of the paraexcitons, extrapolating their magnetic-field dependent energies to zero field strength.

A naive treatment of the exchange interaction leads to the expectation that the orthoexciton is shifted to higher energies than the paraexciton, a result in line with Hund’s rule. Numerical calculations have shown that this expectation is contradicted in the case of the yellow 2S exciton state in cuprous oxide [3]. This has now been confirmed in experiments by Farenbruch et al. [10]. They explain this by appealing to the influence of the green 1S state. In this paper, we discuss and confirm this explanation in greater detail, using the possibility of changing the material parameters in the numerical simulations to study the spectrum in experimentally inaccessible ways. Going beyond the discussion in Ref. [10], we present the precise mechanism responsible for the reversed energies of the 2S ortho- and paraexcitons. We then study the exchange splitting as a function of the principal quantum number n. Based on a hydrogenlike calculation, the splitting is expected to decrease with n⁻³. For the yellow excitons in cuprous oxide, there are deviations from this.

We numerically investigate the origin of these deviations. We also explain why the exchange splitting of the green 1S state is more than twice the exchange splitting of the yellow 1S state. To the best of our knowledge, this represents the first detailed discussion of these features of the dark exciton series in cuprous oxide.

The paper is organized as follows: We first introduce the Hamiltonian and focus on the central-cell corrections in Sec. IIA. We briefly explain our numerical methods in Sec. IIB and our experimental methods in Sec. IIC. In Sec. III, we discuss the reversal between the 2S ortho- and paraexcitons (Sec. IIIA), the exchange splitting as a function of the principal quantum number (Sec. IIIB) and the splitting of the yellow 1S state versus the green 1S state (Sec. IIIC). We finally conclude in Sec. IV.

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II. METHODS AND MATERIALS

In this section, we introduce the theoretical background for the description of the yellow exciton series and our method of numerical diagonalization. Furthermore, we explain our experimental methods.

A. Hamiltonian including central-cell corrections

Excitons are described as hydrogenlike excitations of the crystal, where an electron is lifted from one of the valence bands to the conduction band, leaving behind a hole. The complex valence band structure can be described via a quasispin $I$ in addition to the hole spin $S_h$. This description introduces additional degrees of freedom compared to the hydrogenlike model. For a detailed analysis, especially of the ortho and para 2S states, central-cell corrections are required. Details of derivations are already presented in the literature [3,11–15]. For the convenience of the reader in this paper we briefly recapsitulate the basic equations.

The yellow and green exciton series in cuprous oxide (Cu$_2$O) belong to the $\Gamma^+_7$ and $\Gamma^+_8$ valence band, respectively. They can be described using the Hamiltonian [11]

$$H = E^e_H + H_e(p_e) + H_h(p_h) + V(r_e - r_h) + V_{\text{CCC}}^H(r).$$

Here $E^e_H$ is the band gap between the uppermost $\Gamma^+_7$ valence band and the lowermost $\Gamma^+_6$ conduction band. The kinetic energies of electron and hole are given by

$$H_e(p_e) = \frac{p_e^2}{2m_e},$$

$$H_h(p_h) = \frac{1}{2\hbar^2 m_h}(\hbar^2 \gamma_1 + 4\gamma_2)p_h^2$$

$$+ 2(\eta_1 + 2\eta_2)p_h^2(\mathbf{I} \cdot \mathbf{S}_h)$$

$$- 6\gamma_2(p_h^2 \mathbf{I}^2 + \text{c.p.}) - 12\eta_2(p_h^2 \mathbf{I} \mathbf{S}_h + \text{c.p.})$$

$$- 12\eta_3 \{\{p_{h1}, p_{h2}\} \{\mathbf{I}_1, \mathbf{I}_2 \} + \text{c.p.}\}$$

$$- 12\eta_3 \{\{p_{h1}, p_{h2}\} \{\mathbf{I}_1, \mathbf{S}_{h2} + \mathbf{I}_2, \mathbf{S}_{h1} \} + \text{c.p.}\}. \tag{3}$$

We use the electron mass in the crystal $m_e$ and in vacuum $m_0$, the Luttinger parameters $\gamma_i$, $\eta_i$, the spin $\mathbf{S}_h$ and quasispin $\mathbf{I}_i$ of the hole, the momenta $p_e$ and $p_h$ of the electron and hole, respectively. The indices $i = 1, 2, 3$ for the momenta, positions, quasispin and hole spin denote the Cartesian $x$, $y$, and $z$-components, “c.p.” denotes cyclic permutation. The spin-orbit coupling term reads

$$H_{\text{SO}} = \frac{2}{3} \Delta \left(1 + \frac{1}{\hbar^2} \mathbf{I} \cdot \mathbf{S}_h\right). \tag{4}$$

Electron and hole interact via the screened Coulomb potential

$$V(r_e - r_h) = -\frac{e^2}{4\pi \varepsilon_0 \varepsilon |r_e - r_h|}, \tag{5}$$

with the dielectric constant $\varepsilon = \varepsilon_{\text{el}}$ and the positions of the electron $r_e$ and hole $r_h$. We express the system in relative and center-of-mass coordinates [10].

$$r = r_e - r_h, \quad R = \frac{m_e r_e + m_h r_h}{m_e + m_h},$$

$$P = p_e + p_h, \quad p = \frac{m_e p_e - m_h p_h}{m_e + m_h}, \tag{6}$$

with vanishing center-of-mass momentum $P = 0$.

For small separations, the electron-hole pair probes features of the crystal structure not captured by the valence band terms given in Eq. (3). Furthermore, the dielectric constant $\varepsilon$ in Eq. (5) is no longer constant. The corresponding corrections to the Hamiltonian are the central-cell corrections [12–15], and they primarily concern the states with principal quantum number $n \leq 2$. As derived in Ref. [3], the central corrections in cuprous oxide are given by

$$V_{\text{CCC}}^H(r) = V^H + H_{\text{exch}} + V_d, \tag{7}$$

where

$$V^H = -\frac{e^2}{4\pi \varepsilon_0 r} \left[\frac{1}{2\varepsilon_1^2} \left(e^{-r/\rho_{h1}} + e^{-r/\rho_{e1}}\right) + \frac{1}{2\varepsilon_2^2} \left(e^{-r/\rho_{h2}} + e^{-r/\rho_{e2}}\right)\right], \tag{8}$$

is the Haken potential describing the modification of the dielectric constant for electron-hole separations on the order of the polaron radii, with further corrections modeled by a contact interaction

$$V_d = -\frac{V_0}{2} V_{\text{ac}} \delta(r), \tag{9}$$

with the volume of a lattice unit cell $V_{\text{ac}} = a^3$ and the lattice constant $a$. We use

$$\frac{1}{\varepsilon_{\text{el}}} = \frac{1}{\varepsilon_{\text{bi}}} - \frac{1}{\varepsilon_{\text{st}}}, \tag{10}$$

and the polaron radii

$$\rho_{ei} = \sqrt{\frac{\hbar}{2m_e \omega_{\text{Loi}}}}, \quad \rho_{hi} = \sqrt{\frac{\hbar \gamma_1}{2m_h \omega_{\text{Loi}}}, \tag{11}$$

with the energies $\hbar \omega_{\text{Loi}}$ of the longitudinal $\Gamma^-_4$ phonons. The relevant phonon branches are marked with $i = 1, 2$. The exchange interaction is given in Ref. [3] and reads

$$H_{\text{exch}} = J_0 \left(1 - \frac{1}{3} \frac{\hbar^2}{\mathbf{S}_e \cdot \mathbf{S}_h} \right) V_{\text{ac}} \delta(r)$$

$$= J_0 \left(1 - \frac{1}{\mathbf{S}^2} \right) V_{\text{ac}} \delta(r), \tag{12}$$

where we use the total spin $\mathbf{S} = \mathbf{S}_e + \mathbf{S}_h$ in the second part of the equation. We want to take a closer look at the exchange interaction [12] in the following.

We first note, that only $L = 0$ states are affected due
FIG. 1. Level scheme of $S$ states as a function of the ratio between the exchange interaction strength $J_0$ and the spin-orbit coupling $\Delta$. For $L = 0$, the total angular momentum $F_t$ can be obtained by either coupling the quasispin of the hole $I$ with the total spin $S = S_h + S_e$ or by coupling the electron spin $S_e$ with the effective hole spin $J = I + S_h$. According to Eq. (12), the $S = 0$ singlet states are lifted above the $S = 1$ triplet states for vanishing spin-orbit coupling $\Delta$. For $\Delta / J_0 \to \infty$, the splitting between the green $J = 3/2$ and yellow $J = 1/2$ states predominates. For general values inbetween, the levels split according to the total angular momentum $F_t$. As discussed in Sec. III A with reference to the matrix element (16), for both the green and yellow $S$ states, the $F_t = 1$ states are lifted above the $F_t = 2$ and $F_t = 0$ states, respectively.

To the presence of the $\delta$ term. From the second line in Eq. (12) it is clear, that the effect is a lifting of the states with $S = 0$ over the states with $S = 1$. When taking into account the quasispin $I$ in the crystal, $S$ is not a good quantum number anymore, and we additionally need to consider the spin-orbit coupling given in Eq. (13). In Fig. 1 we show the level-scheme of the $S$ states caused by the competition between the exchange interaction and the spin-orbit coupling as a function of the ratio $\Delta / J_0$. Note that for the yellow $J = 1/2$ states only the threefold degenerate $F_t = 1$ orthoexcitons have an $S = 0$ component and are therefore dipole allowed.

Here, $F_t = J + S_e = I + S$ is the total angular momentum. While the singlet state $S = 0$ is lifted above the triplet state $S = 1$, it is the threefold degenerate $F_t = 1$ state which is lifted above the non-degenerate $F_t = 0$ state, when only considering the yellow $J = 1/2$ states.

We want to perform a quick calculation to understand the behavior of the exchange interaction in a simplified model. This will allow us to investigate the impact of the correction terms, i.e., the band structure and central-cell corrections, by comparing our findings here with the results of the exact numerical calculation further below. Evaluating the integral for the matrix elements for the exchange interaction (12) with wavefunctions $\psi_1$ and $\psi_2$ over the $\delta$ term leads to a proportionality to $\psi_i^*(0)\psi_2(0)$. In a hydrogenlike model we choose the $S$ states $\psi_1 = \psi_2 = \psi_{n,t=0,M=0}$. This yields

$$\langle n, L = 0, M = 0 | H_{\text{exch}} | n, L = 0, M = 0 \rangle = J_0 \left(1 - \frac{1}{2\hbar^2} S^2\right) V_{\text{uc}} \left(\frac{1}{\pi n a_B}\right)^3,$$

with the Bohr radius $a_B$. The relative energetic placement of multiplet states affected by the exchange interaction does not depend on the principal quantum number $n$ in the hydrogenlike model, but only the strength of the splitting, since $n$ affects only an overall factor. As will be shown in Sec. III A this does not hold in the case of the yellow excitons in cuprous oxide, where ortho- and paraexcitons are reversed for $n = 2$. For the other principal quantum numbers, the order of states is as shown in Fig. 1. Additionally, the splitting decreases with $n^{-3}$ as a function of the principal quantum number in the simplified model. The situation is more complicated for the yellow exciton series in cuprous oxide, which will be more thoroughly discussed in Sec. III B.

B. Numerical diagonalization

To express the Schrödinger equation as a generalized eigenvalue problem, we use the complete basis introduced in Ref. 11. In our basis states, the quasispin $I$ and the hole spin $S_h$ are coupled to form the effective hole spin $J$. Near the $\Gamma$ point, $J$ is an approximate quantum number. Excitons with $J = 1/2$ and $J = 3/2$ belong to the yellow and green series, respectively. We further couple the effective hole spin $J$ and the angular momentum $L$ to $F_t$, which is then coupled with the electron spin $S_e$ to the total angular momentum $F_t$. The quantization axis is chosen along the [001] direction of the crystal and the corresponding $z$-component of $F_t$ is $M_{F_t}$. For the radial component we use the Coulomb-Sturmian functions [17], which are rescaled radial hydrogen atom solutions. The total basis states are thus given by

$$|\Pi\rangle = |N, L, (I,S_h)J, F, S_e, F_t, M_{F_t}\rangle.$$ (14)

The radial quantum number is defined as $N = n - L - 1$ with the principal quantum number $n$. The resulting generalized eigenvalue problem is solved using a suitable LAPACK routine [18]. The material parameters used in our calculations are listed in Table I.

C. Experimental methods

In this section, we present the experimental methods used in this paper for the observation of the dark excitons in cuprous oxide. In short, the method presented in Ref. 23 was adjusted to optically activate the paraexcitons and to sensitively detect the resulting weak signals.
The paraexcitons are made allowed by applying a magnetic field, by which they gain an admixture of orthoexcitons through the associated symmetry reduction. Because the symmetry for particular rotations around the magnetic field is still maintained, the mixing occurs between states of the same symmetry class, which would be the same magnetic quantum number in the hydrogenlike model. As a result of this coupling, the involved states, typically forming a two-level system, repel each other. Since the coupling by the field is weak, the increase of the splitting between the states in the doublet can be well described by a quadratic dependence on the magnetic field.

Despite of the hybridization of bright and dark states, the paraexciton oscillator strength remains small, so that efforts had to be made to distinguish the corresponding lines from orthoexciton states: In one-photon absorption the orthoexcitons with odd-symmetry envelopes, and among them mostly the $P$ excitons, clearly dominate the spectra, also in magnetic field. Therefore, we turned to two-photon excitation, detected subsequently by the coherent emission of photons at twice the frequency of the fundamental excitation laser, i.e., by second harmonic generation.

For the SHG experiments, we use 200 fs laser pulses with a spectral width of 10 meV. The 6 mm thick sample is cooled down to 1.4 K being in superfluid Helium. If allowed, the resulting spectra are typically dominated by orthoexcitons with even envelopes, but with much smaller oscillator strength compared to the $P$ lines in one-photon absorption. This setting turned out to be sufficient to detect the paraexcitons if they are in energy sufficiently separated from orthostates.

For the excited paraexciton states this separation may be too small, so that we in addition chose experimental configurations with respect to the crystal orientation relative to the light propagation as well as the polarization of the fundamental and second harmonic light, for which no SHG signal appears at zero magnetic field, but appears only due to the field application. Doing so facilitated carving out the weak paraexciton signals up to the principal quantum number $n = 6$. Further details of the experimental technique using optical second harmonic generation and its instrumental implementation are given in Ref. [23].

### III. RESULTS AND DISCUSSION

#### A. Reversal of yellow $2S$ ortho- and paraexcitons

In this section, we first briefly recapitulate the experimental observation of the positions of the yellow $2S$ ortho- and paraexcitons, presenting additional data not shown in Ref. [10]. Note that we assign the labels green and yellow, as well as the principal and angular quantum numbers in accordance with the assignments given in Ref. [3]. We then present the underlying mechanisms. Since the paraexciton is spin-flip forbidden in electrical dipole and quadrupole transition experiments, we use a magnetic field to make them experimentally accessible. It is possible to include this magnetic field in the Hamiltonian introduced in Sec. II A, see for example Refs. [24–26]. In this work, we extrapolate the experimental values to vanishing magnetic field and analyze those in the numerical calculations. We therefore do not consider the magnetic field in the theory.

In the central panel of Fig 2, we show a contour plot of the second derivatives of the SHG spectra of the $2S$ excitons. The corresponding SHG spectra measured at a magnetic field of 10 T and 0 T are presented in the top and bottom panel respectively. Spectra are measured with a spectral resolution of 80 μeV from 0 T to 10 T in steps of 0.25 T in order to demonstrate the spectral shift of the $2S$ para- and orthoexciton in a magnetic field. The wave vector is directed along the SHG-allowed [11] axis and the magnetic field is applied orthogonally to this in the [112] direction. The polarization of the incoming and outgoing light is parallel to the magnetic field, i.e. $E^\text{in} \parallel E^\text{out} \parallel [112]$. This leads to a nonvanishing SHG signal of the paraexciton [27]. It is much weaker than the intensity of the orthoexciton and only faintly becomes visible at about 5 T. We therefore extrapolate the position of the paraexciton to zero magnetic field, using a quadratic fit. We obtain $E_B^\text{para} = 2.13897 \text{ eV}$ for the paraexciton and $E_B^\text{ortho} = 2.13771 \text{ eV}$ for the orthoexciton. We can therefore experimentally confirm one of the curious features of the yellow paraexciton series in cuprous oxide predicted by Schweiner et al. in Ref. [29], viz. the observation that the 2S paraexciton is located at a higher energy than the 2S orthoexciton. This shows that the experimentally observed behavior of the yellow excitons, clearly dominate the spectra, also in magnetic field. Therefore, we turned to two-photon excitation, detected subsequently by the coherent emission of photons at twice the frequency of the fundamental excitation laser, i.e., by second harmonic generation.

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### TABLE I. Material parameters of Cu$_2$O used in the calculations.

| Parameter                        | Value          |
|----------------------------------|----------------|
| Energy gap $E_g$                 | 2.17208 eV     |
| Spin-orbit coupling $\Delta$     | 0.131 eV       |
| Effective electron mass $m_e$    | 0.99m$_0$      |
| Effective hole mass $m_h$        | 0.58m$_0$      |
| Valence band parameters          |                |
| Exchange interaction $J_0$       | 0.792 eV       |
| Short distance correction $V_0$  | 0.539 eV       |
| Lattice constant $a$             | 0.42696 nm     |
| Dielectric constants             |                |
| $\varepsilon_{11}$              | 7.5            |
| $\varepsilon_{12}$              | 7.11           |
| $\varepsilon_{22}$              | 6.46           |
| Energy of $\Gamma_4$-LO phonons |                |
| $\hbar \omega_{LO1}$            | 18.7 meV       |
| $\hbar \omega_{LO2}$            | 87 meV         |
FIG. 2. Experimental SHG spectrum of the yellow 2S ortho- and paraexcitons. The wave vector $\mathbf{K}$ is parallel to the [111] axis and the magnetic field is applied in Voigt geometry along the [11\bar{2}] direction. The polarizations of the incoming and outgoing light are parallel to the magnetic field. We show a contour plot of the second derivative of the SHG intensity in gray scale. The positions of the ortho- and paraexcitons extracted by a Gaussian fit to the SHG intensity are marked with orange dots. Using a quadratic fit (red dashed line), we can extrapolate the energy of the paraexciton to $E_{\text{para}}^{B=0} = 2.13897$ eV at vanishing magnetic field. An analogous fit to the orthoexciton energies yields an energy $E_{\text{ortho}}^{B=0} = 2.13771$ eV at vanishing magnetic field. The top and bottom panels show the SHG intensity and its second derivative at a magnetic field $B = 10$ T and $B = 0$ T, respectively.

excitons here is qualitatively different from the hydrogenic model in this respect. Farenbruch et al. identify the origin of this reversal in the influence of the green 1S exciton [10]. In the following, we want to corroborate this with a detailed numerical analysis.

In Fig. 3(a) we show the exchange splitting for the yellow 2S state as a function of the parameter $J_0$, with the green states removed from the spectrum. For this calculation, we only used states with $J = 1/2$ in the basis. We see that in this case, the exchange interaction lifts the orthoexciton above the paraexciton as predicted. This confirms that the mixing with the 1S green orthoexciton is responsible for the surprising reversal, because without the green state, the reversal is absent.

For a better understanding, we calculate the positions of the yellow 2S and green 1S states as a function of the spin-orbit coupling, revealing an avoided crossing. In (b), we show this avoided crossing in the spectrum near the yellow 2S orthoexciton state as a function of the spin-orbit coupling $\Delta$. We added lines to help guide the eyes. The green admixture $F_{J=3/2}$ to the states is indicated by the color bar. The horizontal line at $\Delta = 0.131$ eV marks the actual value of $\Delta$ in cuprous oxide. We can clearly see the avoided crossing between the yellow 2S orthoexciton and the $\Gamma_4^+$ green 1S state, marked in red. It is this avoided crossing that places the 2S orthoexciton below the 2S paraexciton. For larger values of $\Delta$, the influence of the green 1S state diminishes and the 2S orthoexciton crosses the 2S paraexciton again and the usual order between those states is re-established. The experimental positions of the exciton states are marked as blue diamonds. We point out that the green $\Gamma_4^+$ and $\Gamma_3^+$ states are degenerate in our model calculations, but show a small splitting in the experiment. This splitting is compatible with the cubic symmetry of the crystal, but the effect is not captured by our Hamiltonian.

Fig. 3(b) we show this avoided crossing between the yellow 2S and the green 1S orthoexciton. The green admixture of the states given by the expectation value

$$F_{J=3/2} = \langle \psi | P_{J=3/2} | \psi \rangle ,$$

of the projection operator onto the $J = 3/2$ Hilbert space for the exciton state $\psi$ is indicated by the color bar.
ing this green \(J = 3/2\) fraction we can identify the green states coming from the left-hand side and follow them through the crossing. This avoided crossing was already noted in Ref. \[3\], but the implications for the relative placement of the 2S para- and orthoexcitons was not discussed. We can see that the avoided crossing leads to the yellow 2S orthoexciton being placed below the 2S paraexciton for the actual value of the spin-orbit coupling \(\Delta = 0.131\) eV. For higher values at \(\Delta \approx 0.15\) eV, the ortho and paraexcitons cross each other again, when the influence of the green \(\Gamma_5^+\) 1S state is small enough. This further confirms and elucidates the influence of the mixing between the yellow and green series and its importance for a detailed understanding of the yellow excitons.

**B. Dependence of the exchange splitting on the principal quantum number**

Since the removal of the mixing with the green 1S state restores the expected placement of ortho- and paraexcitons also in the case of the yellow 2S state, it is a natural question whether the exchange splitting decreases with the third power of the principal quantum number \(n\) as in the hydrogenlike model, Eq. (13). In this section we want to investigate the exchange splitting of the yellow \(S\) excitons as a function of \(n\). To remove the influence of the green 1S states, we only use the basis states with \(J = 1/2\) belonging to the yellow series for the calculations here. In Fig. 4(a) we compare the numerical data for the full basis extracted from Table III in Ref. \[3\] with the exchange splitting if the influence of the green states is removed. We additionally show the actual experimental values for reference. A fit of the form \(\Delta E_{\text{exch}}(n) = An^B\) reveals an exponent \(B = -3.34\) still differing from the expected \(B = -3\) in the hydrogenlike model.

We identify two factors that explain this discrepancy. On the one hand, the Haken potential modifies the dielectric constant for small radii. This leads to a change in the effective Bohr radius and thus to a change in the value of the wavefunction at the origin. This disproportionally affects small quantum numbers, and thus changes the dependency of the splitting on \(n\). On the other hand, the exchange interaction is not diagonal in the principal quantum number, i.e., the 2S state also influences the 1S state and so on. Going back to Eq. (12), we see that the matrix elements do not necessarily vanish if the principal quantum numbers of the coupled states differ. This also leads to a small but significant deviation from the \(n^{-3}\) behavior.

We illustrate the effects of the different factors in Fig. 4(b). We find that only if both of the factors discussed above are corrected for does the \(n^{-3}\) behavior from the hydrogenlike model emerge again.

Interestingly, the removal of the green 1S state also has a significant effect on the absolute size of the splitting between ortho and paraexcitons in the range of principal quantum numbers shown, as can be seen in Fig. 4.

The most important effect accounting for this is the level repulsion caused by the exchange interaction and \(V_J\) matrix elements between the green orthoexciton and the yellow \(\Gamma_5^+\) states. The green \(\Gamma_5^+\) exciton repels the yellow \(\Gamma_5^+\) states, but the green \(\Gamma_5^+\) and \(\Gamma_3^+\) states leave the yellow paraexcitons of symmetry \(\Gamma_3^+\) unaffected. For yellow states energetically higher than the green 1S state,
this increases the splitting, whereas for those lower, it decreases it. The blue squares in Fig. 1(a) show the splittings of the yellow excitons when this repulsion is removed. The resulting splittings in the yellow exciton series are far smaller than the experimental values for \( n \geq 4 \) and more in line with the values when the green 1S state is removed completely, as can be seen by comparison with the red circles. For the yellow 1S state, the effect is reversed and the removal of the level repulsion increases the splitting instead.

### C. Splitting of yellow 1S state vs green 1S state

In this section we investigate the difference in the strength between the exchange splitting of the green 1S state as compared to the yellow 1S state. We want to explain why the splitting of the green states is more than double that of the yellow states.

Diagonalizing the yellow series alone without the green \( J = 3/2 \) basis states, we find that the splitting of the yellow 1S excitons is approximately 7.02 meV, which is even smaller than with the full basis. Diagonalizing the green states alone, the splitting of the green 1S excitons is approximately 27.07 meV. The discrepancy can therefore not be explained by the mutual level shifts between the green 1S state and the yellow spectrum.

We again find that there are two factors which actually explain this difference. The first factor is the fact that the eigenvalues of the operator \( \mathbf{S}_c \cdot \mathbf{S}_b \) differ between the \( J = 1/2 \) and \( J = 3/2 \) Hilbert space. According to the appendix of Ref. 3, the matrix elements in the basis \( 14 \) are given by

\[
M = \langle \Pi \mid \mathbf{S}_c \cdot \mathbf{S}_b \delta (r) \mid \Pi \rangle \\
= \delta_{L',0} \delta_{L,0} \delta_{F_c,F_b} \delta_{M_c,M_b} \frac{3}{2\pi} \left( -1 \right)^{F'_c + F'_b + F + J + J'} \\
\times \left\{ (2F + 1)(2F' + 1)(2J + 1)(2J' + 1) \right\}^{1/2} \\
\times \left\{ F' \ 1 \ \frac{1}{2} \ \frac{1}{2} \ \\
F \ 1 \ J' \ J \right\} \\
\left\{ F' \ 1 \ \frac{1}{2} \ \frac{1}{2} \ \\
F \ 1 \ J' \ J \right\} \\
\left\{ J' \ J \ 1 \ \frac{1}{2} \ \frac{1}{2} \ \\
J \ J \ 1 \ \frac{1}{2} \ \frac{1}{2} \right\}. \quad (16)
\]

Fixing either \( J = J' = 1/2 \) or \( J = J' = 3/2 \), the operator is already diagonal in the given basis. We can evaluate the matrix elements for the yellow and green series and \( L = L' = 0 \). For \( J = J' = 1/2 \), we calculate \( M = 1/4\pi \) with \( F'_c = 0 \) and \( M = -1/12\pi \) with \( F'_c = 1 \). For \( J = J' = 3/2 \) it is \( M = 1/4\pi \) when \( F'_c = 2 \) and \( M = -5/12\pi \) when \( F'_c = 1 \). Note that the exchange interaction \( 12 \) contains this operator with reversed sign. The exchange interaction therefore lifts the \( F'_c = 1 \) states above the others in both the yellow and green series as depicted in Fig. 1. We thus find that the splitting in the eigenvalues for \( J = 3/2 \) is \( \Delta M_{\text{green}} = 2/3\pi \) and consequently exactly double the splitting for \( J = 1/2 \), which is \( \Delta M_{\text{yellow}} = 1/3\pi \).

These calculations account for part of the difference between the yellow and green splitting. A factor of approximately 1.93 between the green and yellow splitting remains to be explained. Because of the \( \delta \) term, the exchange splitting is proportional to \( |\psi(0)|^2 \), which in turn is proportional to the inverse third power of the Bohr radius \( \delta B \). Since the Bohr radius is proportional to the reduced mass \( \mu \), it follows that \( |\psi(0)|^2 \sim \mu^3 \). This seems to be the explanation for the factor 1.93, as explained in the following. The reduced mass is proportional to the Rydberg energy in a hydrogenlike system. To approximate the latter, we calculated the binding energy of the yellow and green 1S states while varying the exact form of the potential. The results are listed in Table I. Based on these data, we can estimate the ratio of the reduced masses of the green and yellow 1S states with the ratio of the binding energies. Since the latter are not only affected by the Coulomb interaction, but also by the additional terms \( V^H \) and \( V_d \) in Eq. 7, we need to correct for those. Using the values where the central-cell corrections are removed completely, we get

\[
\left( \frac{\mu_{\text{green}}}{\mu_{\text{yellow}}} \right)^3 \approx \left( \frac{E_{\text{green}}^{\text{Ryd}}}{E_{\text{yellow}}^{\text{Ryd}}} \right)^3 \approx \left( \frac{105.3 \text{ meV}}{86.1 \text{ meV}} \right)^3 \approx 1.223 \approx 1.82. \quad (17)
\]

This is in good agreement with the factor of 1.93. The explanation for the different strengths of the exchange splitting in the yellow and green 1S exciton states therefore is on the one hand the factor two due to the operator \( \mathbf{S}_c \cdot \mathbf{S}_b \) for \( J = 1/2 \) and \( J = 3/2 \) and on the other hand the difference in the reduced mass \( \mu \) for the yellow and green 1S exciton.

### IV. SUMMARY AND CONCLUSION

Experimental investigations into the paraexciton series of yellow excitons in \( Cu_2O \) and corresponding exchange splittings reveal a number of ways in which a simple hydrogenlike model is insufficient. In this manuscript, we numerically investigated spectra with modified material parameters and thus gained experimentally inaccessibly insights. We used this to interpret the experimental find-
We first investigated the reversal of the yellow 2S para- and orthoexcitons. Farenbruch et al. [10] identified the mixture with the 1S green orthoexciton as the origin of the reversal. We were able to corroborate this explanation with detailed calculations. We show that the orthoexciton is lifted above the paraexciton if the influence of the green excitons is removed in the simulation. Varying the spin-orbit coupling reveals an avoided crossing between the yellow 2S orthoexciton and the green 1S exciton which explains the placement of the orthoexciton below the paraexciton. We were thus able to show how the coupling of the yellow and green series leads to a behavior that qualitatively differs from the hydrogen-like approximation, underscoring its importance for the understanding of the yellow exciton series.

Removing the influence of the green states, the expected order of states is restored. In this case, does the exchange splitting decrease with the third power of the principal quantum number \(n\)? Our calculations show that this is not exactly the case. We identify two reasons for this. First of all, the Haken potential changes the Haken potential below the paraexciton. We were thus able to show how the coupling of the yellow and green series leads to a behavior that qualitatively differs from the hydrogen-like approximation, underscoring its importance for the understanding of the yellow exciton series.

We conclude by studying the origin of the large difference between the exchange splittings of the yellow and green 1S states. Farenbruch et al. [10] confirmed the prediction by Schweiner et al. [3] that the splitting of the green 1S exciton is over 30 meV and therefore about two and a half times the splitting of about 12 meV for the yellow 1S state. We also identified two reasons to account for this. The first is the difference in the matrix elements of \(S_i \cdot S_i \delta(r)\) for \(J = 1/2\) and \(J = 3/2\). Since the exchange splitting depends upon the relative orientation of the electron and hole spins, different values of the effective hole spin \(J = I + S_i\) lead to different strengths of the exchange splitting. The second is the difference in the reduced masses between the yellow and green 1S states. The reduced mass of the green 1S state is significantly higher than the reduced mass of the yellow 1S state as revealed by a detailed analysis of the Rydberg energy when correcting for the influence of short distance terms in the Hamiltonian. This leads to a higher value of the wavefunction at the origin and a corresponding increase of the exchange splitting.

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