

Impact of the valence band on Rydberg excitons in cuprous oxide quantum wells

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The complex valence band structure of bulk cuprous oxide necessitates going beyond the parabolic approximation to precisely estimate exciton binding energies. The same is true for excitons in cuprous oxide quantum wells, for which many effects have been obtained so far only qualitatively within a hydrogenlike two-band model. Here, we derive the complete Hamiltonian for excitons in cuprous oxide quantum wells based on the Luttinger-Kohn model, taking into account the full complex valence band structure. Symmetry properties of the system are discussed. Numerical results based on the diagonalization of the Hamiltonian using B-spline functions reveal the energy shifts and the lifting of degeneracies due to the nondiagonal coupling terms of the complex valence band. The relative oscillator strengths of the excitonic transitions induced by circularly polarized light are also calculated.

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I. INTRODUCTION

Electron-hole bound states in bulk cuprous oxide are characterized by large binding energies, allowing for high-resolution measurements of the excitonic transitions of yellow and green Rydberg series [1–3]. This paves the way for excitonic devices [4], sensors [5,6], and, potentially, room-temperature applications [4,7,8]. Due to strong spin-orbit coupling, an accurate theoretical description of exciton spectra in bulk Cu₂O requires taking into account the complex valence band structure that goes beyond the simple parabolic band approximation. Effects of the band structure on exciton energies have been investigated recently both theoretically and experimentally [9–15]. These works have significantly advanced our understanding of the exciton properties in bulk Cu₂O, in comparison to the pioneering studies of exciton energies and absorption [16–18].

Similar to other types of semiconductors such as GaAs [19,20] or CdSe [21,22], a greater tunability of electronic and optical properties of quasiparticles in Cu₂O can be achieved by fabrication of heterostructures [23,24]. The first films of cuprous oxide sandwiched between sapphire substrates and thus realizing the weak quantum confinement of lower exciton states have already been obtained [25,26]. When the size of a particular exciton state is comparable to the thickness of the film, the confinement effect dominates. Therefore, for very thin Cu₂O films or for Rydberg exciton states, the regime of strong confinement is reached, and the details of the complex

band structure play the role of a small perturbation. As a result, the parabolic approximation of the bands in the vicinity of the Γ point is a reasonable choice. However, for weak confinement the effects due to features of the band structure are comparable to the quantum-confinement effects. Thus, the full Cu₂O band structure has to be explicitly taken into account.

The quantum confinement appearing due to the band offsets at the heterojunction can, in its simplest form, be modeled by the quantum well (QW) potential [27]. Excitons in QWs exhibit a large variety of interesting phenomena and effects [28,29]. The theory of excitons and their radiative properties in GaAs-based QWs is well developed [19,30], though for cuprous oxide finite-sized crystals the energy spectrum as well as the relative oscillator strengths have been obtained only very recently [31,32]. These works significantly differ from a simplified consideration in Refs. [33,34] by studying the spectrum as a function of the QW width. A dependence of the exciton energy levels on the width of a QW allows one to study a crossover from weak confinement in the bulk to nearly two-dimensional excitons in case of strong confinement. Besides bound states, above the scattering threshold electron-hole resonances occur. Their spectral lines are usually additionally broadened due to coupling to the continuum. For GaAs-based QWs, the energies and linewidths of the electron-hole resonances have been estimated using Feshbach theory [35] in Refs. [36,37]. The resonant broadenings can also be computed by both the stabilization and the complex-coordinate-rotation method, as done for GaAs-based [38] and Cu₂O-based QWs [39]. When varying the confinement strength, so-called bound states in the continuum (BICs), i.e., long-lived Rydberg states of the confined electron-hole pairs, appear in the continuum background [40]. The BICs are uncoupled from the continuum of lower quantum-confinement subbands and thus have zero linewidths [41,42]. All these effects can be successfully studied numerically by expanding

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the electron-hole wave function over a basis of B splines [43,44]. The wave functions in coordinate space, computed using a B-spline representation, clearly illustrate, e.g., the quenching of states in the strong confinement regime, the localized nature of BICs and, furthermore, allow for the estimation of oscillator strengths.

In Refs. [31,32,39], the energy levels of excitons and electron-hole resonances in finite-sized cuprous oxide crystals have been calculated using the two-band model with simple parabolic dispersions of the bands. Although these works shed light on the crossover from the weak to the strong confinement regime as well as on the radiative properties of exciton states of different symmetries, the exciton states were studied within the hydrogenlike model, confined over one dimension. The complex structure of the Cu_2O valence subbands near the Γ point has not been considered so far. Taking into account the complex valence band dispersion leads to an increase in the number of coupled differential equations corresponding to different projections of the orbital momentum and spin. This makes the numerical treatment of the problem much more difficult.

The transition from bulk to a monolayer affects exciton states in many ways. Apart from restricting the motion of electron and hole along one dimension, it also leads to a suppression of the exciton kinetic energy, a change of the band structure, and a distortion of the Coulomb interaction. The reduction of the spatial dimension from three to two dimensions reduces the kinetic energy, thereby increasing the exciton binding energy from $E_b^{3D} = \text{Ry}/n^2$ to $E_b^{2D} = \text{Ry}/(n - 1/2)^2$, where Ry is the Rydberg energy and $n = 1, 2, \dots$ is the principal quantum number [28,45]. The band structure also depends on the geometry of the crystal structure: the effective mass parameters in the kinetic terms are modified during a crossover from bulk to a monolayer. Moreover, this crossover affects the potential energy of the electron-hole interaction. The dielectric contrast between the thin film and the environment (vacuum or a substrate) distorts the pure Coulomb interaction. For thin films, the resulting screening effect can be described by the Rytova-Keldysh potential [46,47]. Its impact on exciton states is well-known for transition metal dichalcogenide monolayers [48–50] and phosphorene monolayers [51], and has been studied for Dirac materials [52] and cuprous oxide thin films [31].

The aim of this article is to study the impact of the complex valence band on excitons in cuprous oxide QWs. Besides the quantization over the confinement direction, we consider the Luttinger Hamiltonian [53] or, equivalently, the Suzuki-Hensel Hamiltonian [54] for the hole dispersion in the QW together with a purely parabolic dispersion for the electron. Such a hole dispersion significantly complicates the Schrödinger equation for excitons in cuprous oxide QWs [31,32]. Moreover, it breaks some exact symmetries of the pure parabolic dispersion, in particular, the rotational invariance around the axis normal to the QW plane, causing the angular momentum quantum number m to be only an approximate quantum number. Nevertheless, using the B-spline representation of the wave function, we can calculate the matrix elements of all involved operators and solve the eigenvalue problem to obtain the energy levels as

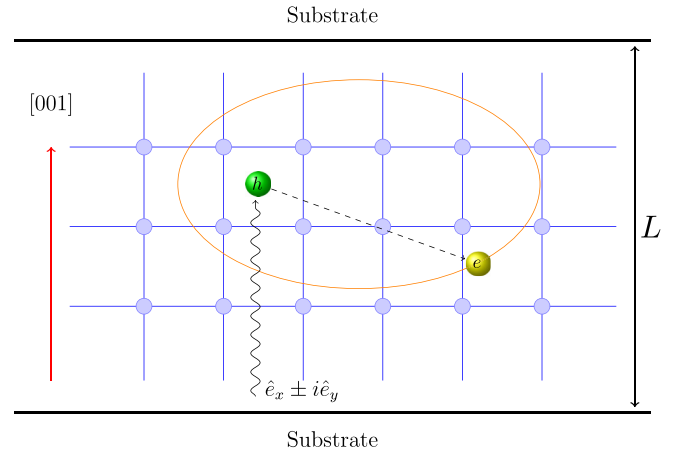


FIG. 1. Sketch of the general setup for the creation of excitons in a cuprous oxide QW. The [001] axis of the crystal is aligned perpendicular to the QW plane. Excitons are excited by circularly polarized light along this axis.

a function of the QW width. We study effects of the complex valence band, originating from coupling of states with different values of m . We also derive expressions for the relative oscillator strengths of the excitonic transitions induced by circularly polarized light. We show that the oscillator strengths are related to derivatives of certain projections of the exciton wave function at zero separation between electron and hole.

The article is organized as follows. In Sec. II, we derive the theory for excitons in cuprous oxide QWs taking into account the complex valence band structure. We obtain the Hamiltonian, expressions for relative oscillator strengths, and provide a numerical algorithm for the computation of exciton spectra and wavefunctions. Results are presented and discussed in Sec. III. Concluding remarks are given in Sec. IV.

II. THEORY AND METHODS

In this section, we describe excitons in cuprous oxide QWs by taking into account the complex structure of the valence band. The general setup of our system is illustrated in Fig. 1. Let L be the width of a thin layer of cuprous oxide sandwiched between another material with larger band gap. Due to band offsets at the heterojunction, this system can be regarded as a QW. Excitons in the QW are created by

TABLE I. Material parameters of Cu_2O used in the calculations.

Energy gap	$E_g = 2.17208 \text{ eV}$	[1]
Spin-orbit coupling	$\Delta = 0.131 \text{ eV}$	[10]
Effective electron mass	$m_e = 0.99m_0$	[55]
Dielectric constant	$\epsilon = 7.5$	[56]
Valence band parameters	$\gamma_1 = 1.76$	[10]
	$\gamma_2 = 0.7532$	[10]
	$\gamma_3 = -0.3668$	[10]
	$\eta_1 = -0.020$	[10]
	$\eta_2 = -0.0037$	[10]
	$\eta_3 = -0.0337$	[10]

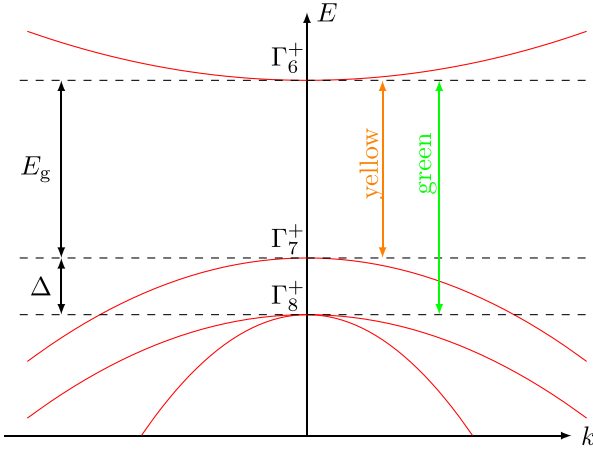


FIG. 2. Sketch of the band structure of the Γ_6^+ conduction bands, as well as the Γ_7^+ and Γ_8^+ valence bands near the Γ point.

circularly polarized laser light propagating perpendicularly to the QW plane. In general, the exciton spectra depend on the orientation of the crystal relative to the QW. In this article, we consider a geometry in which the principal axis [001] of the crystal is aligned along the z direction perpendicular to the QW plane. The Hamiltonian including the impact of the valence band is derived in Sec. II A and its symmetry properties are discussed in Sec. II B. The computation of the oscillator strengths and the numerical algorithm for the diagonalization of the Hamiltonian using an appropriate basis set are explained in Secs. II C and II D, respectively.

A. Hamiltonian

The Hamiltonian for electron and hole in the QW is given by

$$H = H_e(\mathbf{p}_e) + H_h(\mathbf{p}_h) - \frac{e^2}{4\pi\epsilon_0\epsilon} \frac{1}{|\mathbf{r}_e - \mathbf{r}_h|} + V_e(z_e) + V_h(z_h), \quad (1)$$

where

$$H_e(\mathbf{p}_e) = E_g + \frac{\mathbf{p}_e^2}{2m_e}, \quad (2)$$

$$\begin{aligned} H_h(\mathbf{p}_h) = & H_{SO} + \frac{1}{2\hbar^2 m_0} [\hbar^2(\gamma_1 + 4\gamma_2)\mathbf{p}_h^2 \\ & + 2(\eta_1 + 2\eta_2)\mathbf{p}_h^2(\mathbf{I} \cdot \mathbf{S}_h) - 6\gamma_2(p_{1h}^2 I_1^2 + \text{c.p.}) \\ & - 12\eta_2(p_{1h}^2 I_1 S_{h1} + \text{c.p.}) \\ & - 12\gamma_3[\{p_{1h}, p_{2h}\}\{I_1, I_2\} + \text{c.p.}] \\ & - 12\eta_3[\{p_{1h}, p_{2h}\}(I_1 S_{h2} + I_2 S_{h1}) + \text{c.p.}]], \end{aligned} \quad (3)$$

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

$$V_{e,h}(z_{e,h}) = \begin{cases} 0 & \text{if } |z_{e,h}| < L/2 \\ \infty & \text{if } |z_{e,h}| \geq L/2 \end{cases}. \quad (5)$$

Here, E_g is the gap energy, m_0 is the free electron mass, and γ_i, η_i are the Luttinger parameters. The material parameters of cuprous oxide are given in Table I. $\mathbf{I}$ and $\mathbf{S}_h$ are the quasispin with $I = 1$ and the hole spin with $S_h = 1/2$, whose components I_i and S_{hi} with $i = 1, 2, 3$ satisfy the commutation relations of an angular momentum or spin, Δ is the spin-orbit coupling parameter, $\{a, b\} = (ab + ba)/2$ is the symmetrized product, and c.p. denotes cyclic permutation.

The potentials $V_{e,h}(z_{e,h})$ confine the motion of electron and hole across the QW along the z direction. For a finite-sized crystal surrounded by vacuum or air, the confinement potential of the QW can be well approximated by an infinite potential well, given in Eq. (5). The energies of electron and hole states in such a QW,

$$E_{N_e, N_h}(L) = \frac{\hbar^2 \pi^2}{2L^2} \left(\frac{N_e^2}{m_e} + \frac{N_h^2}{m_h} \right), \quad (6)$$

can be described by two quantum numbers $N_e, N_h = 1, 2, 3, \dots$. Here, $m_e = 0.99m_0$ is the electron mass in the crystal and $m_h = m_0/\gamma_1$ is the hole mass. The quantum-confinement energies (6) play the role of scattering thresholds, where bound states or resonances can accumulate [39].

The inclusion of the full set of Luttinger parameters leads to the nontrivial band structure shown in Fig. 2. Using the notation for the symmetry group O_h [57], we can classify the bands as in the bulk crystal. The lowest conduction band has the symmetry Γ_6^+ , whereas the uppermost valence bands are split into the uppermost Γ_7^+ band associated with the yellow exciton Rydberg series, and the lower Γ_8^+ bands associated with the green series. Note that for excitons in the QW we use the same values of the Luttinger parameters as in the bulk.

We use the same dielectric constant $\epsilon = 7.5$ for the crystal and the substrate and thus do not consider the dielectric contrast described by the Rytova-Keldysh potential [46,47] for the interaction between electron and hole as discussed, e.g., in Ref. [31]. We also do not consider central-cell corrections, which can affect even-parity excitons [58].

In contrast to the bulk with its translational invariance in three dimensions, for excitons in QWs there is a translational invariance only in the two-dimensional (x, y) QW plane. We introduce relative and center-of-mass coordinates

$$x = x_e - x_h, \quad y = y_e - y_h, \quad (7a)$$

$$X = \frac{m_e x_e + m_h x_h}{m_e + m_h}, \quad Y = \frac{m_e y_e + m_h y_h}{m_e + m_h} \quad (7b)$$

in this plane. Using relative and center-of-mass momenta, $\mathbf{p}_{(2D)} = (p_1, p_2)$ and $\mathbf{P}_{(2D)} = (P_1, P_2)$, respectively, and additionally setting the conserved center-of-mass momenta to zero, $P_1 = P_2 = 0$, we obtain

$$\begin{aligned}
 H(x, y, z_e, z_h, \mathbf{I}, \mathbf{S}_h) = & E_g + H_{\text{SO}} - \frac{e^2}{4\pi\epsilon_0\epsilon} \frac{1}{\sqrt{x^2 + y^2 + (z_e - z_h)^2}} + V_e(z_e) + V_h(z_h) + \frac{p_{ez}^2}{2m_e} \\
 & + \left[\frac{\gamma'_1}{2m_0} + \frac{2\gamma_2}{m_0} + \frac{\eta_1 + 2\eta_2}{\hbar^2 m_0} (\mathbf{I} \cdot \mathbf{S}_h) \right] p_{(2D)}^2 \\
 & + \left[\frac{\gamma_1}{2m_0} + \frac{2\gamma_2}{m_0} + \frac{\eta_1 + 2\eta_2}{\hbar^2 m_0} (\mathbf{I} \cdot \mathbf{S}_h) - \frac{3\gamma_2}{\hbar^2 m_0} I_3^2 - \frac{6\eta_2}{\hbar^2 m_0} I_3 S_{h3} \right] p_{hz}^2 \\
 & - \frac{3\gamma_2}{\hbar^2 m_0} (p_1^2 I_1^2 + p_2^2 I_2^2) - \frac{6\gamma_3}{\hbar^2 m_0} [\{p_1, p_2\}\{I_1, I_2\}] + \frac{6\gamma_3}{\hbar^2 m_0} [\{p_2, p_{hz}\}\{I_2, I_3\} + \{p_{hz}, p_1\}\{I_3, I_1\}] \\
 & - \frac{6\eta_2}{\hbar^2 m_0} (p_1^2 I_1 S_{h1} + p_2^2 I_2 S_{h2}) - \frac{6\eta_3}{\hbar^2 m_0} [\{p_1, p_2\}(I_1 S_{h2} + I_2 S_{h1})] \\
 & + \frac{6\eta_3}{\hbar^2 m_0} [\{p_2, p_{hz}\}(I_2 S_{h3} + I_3 S_{h2}) + \{p_{hz}, p_1\}(I_3 S_{h1} + I_1 S_{h3})]
 \end{aligned} \tag{8}$$

with $\gamma'_1 = \gamma_1 + m_0/m_e$. When comparing the Hamiltonian (8) with the two-band model for excitons in a QW [31,32,39], it is important to note that not only the dimension of the Hamiltonian is increased by the additional spin degrees of freedom, i.e., the quasispin $\mathbf{I}$ and hole spin $\mathbf{S}_h$ describing the valence band, but also the coordinate space is increased from three degrees of freedom (ρ, z_e, z_h) in the two-band model to four degrees of freedom (x, y, z_e, z_h) when considering the complete structure of the valence band. This is a consequence of the reduced symmetry of the Hamiltonian (8) as discussed in Sec. II B.

The Hamiltonian in the form of Eq. (8) with Cartesian coordinates is not well suited for the computation of matrix elements in the basis introduced in Sec. II D, which takes advantage of the polar coordinates (ρ, ϕ) in the QW plane

and contains angular momentum functions $\exp(im\phi)$ and spin states $|J, m_J\rangle$ for the coupled quasispin and hole spin $\mathbf{J} = \mathbf{I} + \mathbf{S}_h$. For this basis, it is more convenient to introduce creation and annihilation operators

$$I_{\pm} = I_1 \pm iI_2, \quad S_{h\pm} = S_{h1} \pm iS_{h2}, \quad p_{\pm} = p_1 \pm ip_2, \tag{9}$$

where the operators $I_{\pm}$ and $S_{h\pm}$ couple states with $\Delta m_J = \pm 1$ and the operators $p_{\pm}$ couple states with $\Delta m = \pm 1$. Representing the Hamiltonian (8) in terms of these operators and sorting terms with respect to their action on the angular momentum and spin part of the basis states, the complete Hamiltonian can finally be written as

$$H = H_{\text{diag}} + H_{\Delta m=0} + H_{\Delta m=1} + H_{\Delta m=2} + H_{\Delta m_F=4}, \tag{10}$$

where

$$H_{\text{diag}} = E_g + H_{\text{SO}} + V_C + \frac{1}{2m_e} p_{ez}^2 + \frac{\gamma'_1}{2m_0} p_{+} p_{-} + \frac{\gamma_1}{2m_0} p_{hz}^2 + \left[\frac{2\gamma_2}{m_0} + \frac{\eta_1 + 2\eta_2}{\hbar^2 m_0} (\mathbf{I} \cdot \mathbf{S}_h) \right] (p_{+} p_{-} + p_{hz}^2), \tag{11a}$$

$$H_{\Delta m=0} = \left[-\frac{3\gamma_2}{2\hbar^2 m_0} \{I_{+}, I_{-}\} - \frac{3\eta_2}{2\hbar^2 m_0} (I_{+} S_{h-} + I_{-} S_{h+}) \right] p_{+} p_{-} + \left[-\frac{3\gamma_2}{\hbar^2 m_0} I_3^2 - \frac{6\eta_2}{\hbar^2 m_0} I_3 S_{h3} \right] p_{hz}^2, \tag{11b}$$

$$H_{\Delta m=1} = \frac{3\gamma_3}{\hbar^2 m_0} (\{I_3, I_{+}\} p_{hz} p_{-} + \text{H.c.}) + \frac{3\eta_3}{\hbar^2 m_0} [(I_3 S_{h+} + I_{+} S_{h3}) p_{hz} p_{-} + \text{H.c.}], \tag{11c}$$

$$H_{\Delta m=2} = -\frac{3(\gamma_2 + \gamma_3)}{8\hbar^2 m_0} (I_{+}^2 p_{-}^2 + \text{H.c.}) - \frac{3(\eta_2 + \eta_3)}{4\hbar^2 m_0} (I_{+} S_{h+} p_{-}^2 + \text{H.c.}), \tag{11d}$$

$$H_{\Delta m_F=4} = -\frac{3(\gamma_2 - \gamma_3)}{8\hbar^2 m_0} (I_{-}^2 p_{-}^2 + \text{H.c.}) - \frac{3(\eta_2 - \eta_3)}{4\hbar^2 m_0} (I_{-} S_{h-} p_{-}^2 + \text{H.c.}). \tag{11e}$$

Here, V_C is the Coulomb potential and H.c. denotes the Hermitian conjugate. The operator H_{diag} is diagonal with respect to the angular momentum and spin quantum numbers m, J , and $m_J = m_I + m_{S_h}$. For an appropriately chosen effective hole mass, this part of the Hamiltonian describes the exciton within a hydrogenlike two-band model as discussed in Refs. [31,32,39]. The operator $H_{\Delta m=0}$ couples basis states with quantum numbers $J = 1/2$ and $J = 3/2$ but the same angular momentum quantum number m , i.e., this term causes

a coupling between the yellow and green exciton series without breaking the continuous rotational symmetry around the z axis. The operators $H_{\Delta m=1}$ and $H_{\Delta m=2}$ couple states with different angular momentum quantum numbers m , and thus m is not a good quantum number when considering the impact of the valence band. Finally, the operator $H_{\Delta m_F=4}$ couples states with $\Delta m_F = \pm 4$, where $m_F = m + m_J$ is the quantum number for the z component of the coupled spin and angular momenta $\mathbf{F} = \mathbf{L} + \mathbf{J} = \mathbf{L} + \mathbf{I} + \mathbf{S}_h$. Note that when

using basis states with given quantum numbers m_F the matrix representation of the Hamiltonian (10) has a block structure with four blocks, which can be diagonalized separately. This block structure is directly related to the symmetry properties of the Hamiltonian (10) as shown below in Sec. II B. Note also that $H_{\Delta m_F=4}$ would vanish in case of equal Luttinger parameters $\gamma_2 = \gamma_3$ and $\eta_2 = \eta_3$, i.e., m_F would be an exact quantum number in that case.

B. Symmetry properties

In comparison to the hydrogenlike model of excitons in a QW [32], the inclusion of the complex valence band leads to a further reduction of the symmetry. We consider the situation in which the [001] axis of the crystal is perpendicular to the QW plane. In this case, the symmetry of the system is reduced from $D_{\infty h}$, and the complete Hamiltonian (10) is now only invariant under the symmetry operations of the D_{4h} symmetry group [57], containing rotations C_4 and C_2 , inversion I , improper rotations S_4 , and reflections σ_h , σ_v , and σ_d , as illustrated in Fig. 3. With $m_J = m_l + m_{s_h}$ and $m_F = m + m_J$, the C_4 symmetry implies that the Hamiltonian only couples basis states with $\Delta m_F = 0, \pm 4$. Note that this symmetry-derived constraint on matrix elements only applies to the total angular momentum, i.e., individual angular momenta like m or m_J are not restricted in this way in their possible couplings, as can be seen by the terms in the Hamiltonian (10). Due to the reduced symmetry of the system, the eigenstates can no longer be classified according to their angular momentum quantum numbers but instead by the irreducible representations of the symmetry group D_{4h} or, rather, as there are also spin degrees of freedom, the corresponding double group to D_{4h} . Without consideration of the electron spin S_e , the total angular momentum F in the system is half-integer valued, and only the irreducible representations Γ_6^+ , Γ_6^- , Γ_7^+ , and Γ_7^- are possible for the eigenstates [57], where the superscript + or – indicates the total parity of the corresponding eigenstates under inversion I . The eigenstates are superpositions of states with m_F differing by multiples of 4, and thus can be assigned to one of the following groups:

$$m_F = \begin{cases} \dots, -\frac{13}{2}, -\frac{5}{2}, \frac{3}{2}, \frac{11}{2}, \dots \\ \dots, -\frac{11}{2}, -\frac{3}{2}, \frac{5}{2}, \frac{13}{2}, \dots \end{cases} \quad (12a)$$

$$m_F = \begin{cases} \dots, -\frac{15}{2}, -\frac{7}{2}, \frac{1}{2}, \frac{9}{2}, \dots \\ \dots, -\frac{9}{2}, -\frac{1}{2}, \frac{7}{2}, \frac{15}{2}, \dots \end{cases} \quad (12b)$$

Here, blocks related by a sign change of m_F are degenerate due to time-reversal symmetry. Equations (12a) and (12b) describe twofold degenerate states in subspaces $\Gamma_6^\pm$ and $\Gamma_7^\pm$, respectively, as can be seen as follows.

To understand how these blocks relate to the irreducible representations $\Gamma_{6,7}^\pm$, we can look at a state with total angular momentum $F = 1/2$. We need to take into account that the eigenstates of the quasispin I do not behave exactly like eigenstates of a standard angular momentum. In D_{4h} , the eigenstates of the quasispin transform like the sum of irreducible representations $\Gamma_4^+ + \Gamma_5^+ = (\Gamma_2^+ + \Gamma_5^+) \times \Gamma_3^+$, while the eigenstates of a standard spin of 1 behave like $\Gamma_2^+ + \Gamma_5^+$. Hence, one obtains the total symmetry by the usual addition of angular momenta, followed by a multiplication with Γ_3^+ .

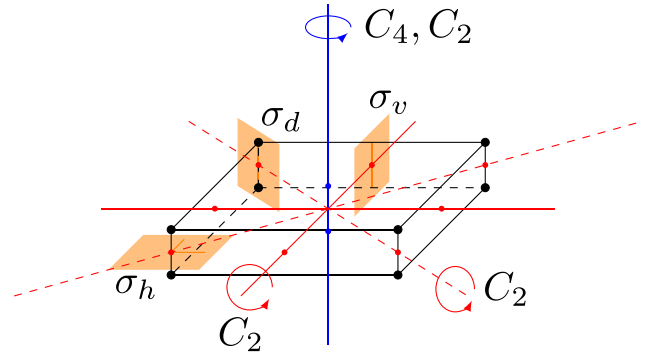


FIG. 3. Illustration of symmetry operations of the group D_{4h} . C_2 and C_4 denote two- and fourfold rotations, respectively, σ_h , σ_v , and σ_d reflections with respect to different kinds of symmetry planes. In addition to the depicted operations, there is also the inversion I and the improper rotation $S_4 = \sigma_h C_4$.

With this prescription in mind, we can use that an angular momentum of $1/2$ transforms according to $\Gamma_6^\pm$ in D_{4h} [57]. Multiplying by Γ_3^+ , we find that a state with total angular momentum $F = 1/2$, and thus states with $m_F = 1/2$ and $m_F = -1/2$ transform according to $\Gamma_7^\pm$.

For the computation of oscillator strengths in Sec. II C, the electron spin S_e must also be taken into account. The total symmetries of the system including the electron spin are discussed below in Sec. II C 1.

C. Oscillator strengths

For the computation of oscillator strengths, we generalize the theory developed in Ref. [32] within a two-band model. We consider excitons in the many-particle framework. The ground state $|\Phi_0\rangle$ of the crystal is the state where all electrons of the crystal are in the valence bands, while all conduction bands are empty. An exciton is created when one of these electrons is lifted from the valence bands into a conduction band. The resulting state can be written as

$$|\psi_{vc,v}^{\sigma\tau}\rangle = \sum_{\mathbf{q}_c, \mathbf{q}_v} f_{vc,v}^{\tau,\sigma}(\mathbf{q}_c, \mathbf{q}_v) c_{c,\mathbf{q}_c,\tau}^\dagger c_{v,\mathbf{q}_v,\sigma} |\Phi_0\rangle. \quad (13)$$

Here, $c_{c,\mathbf{q}_c}^\dagger$ denotes the creation operator for an electron with crystal momentum $\mathbf{q}_c$ and electron spin τ in the conduction band c , and $c_{v,\mathbf{q}_v}$ is the analogous annihilation operator in the valence band v , which creates a hole with crystal momentum $-\mathbf{q}_v$ and hole spin $-\sigma$. The coefficient $f_{vc,v}^{\tau,\sigma}(\mathbf{q}_c, \mathbf{q}_v)$ in the superposition is the envelope function, which is obtained as the solution of the exciton Schrödinger equation with Hamiltonian (10) transformed into crystal-momentum space. When considering the complex valence band structure, c and v are not good quantum numbers, and the correct states are obtained by forming superpositions. The subscript v denotes further quantum numbers or indices associated with the state.

Using relative and center-of-mass coordinates in the QW plane [see Eq. (7)], we can express the x and y components of $\mathbf{q}_c$ and $\mathbf{q}_v$ through the center-of-mass momentum $\mathbf{K}_{2D}$ and the relative in-plane momentum $\mathbf{q}$. As $\mathbf{K}_{2D}$ is conserved, we are discussing states $|\psi_{\mathbf{K}_{2D}}\rangle$, where the sum in Eq. (13) is restricted to a fixed value of $\mathbf{K}_{2D}$. Combining the symmetry

considerations and general selection rules in Refs. [32,57], the transition matrix elements fulfill

$$M_x \propto (\partial_y \langle u_{xy0} | + \partial_z \langle u_{zx0} |) \langle S=0 | \psi_{v\mathbf{K}_{2D}} \rangle \Big|_{r=0}, \quad (14a)$$

$$M_y \propto (\partial_z \langle u_{yz0} | + \partial_x \langle u_{xy0} |) \langle S=0 | \psi_{v\mathbf{K}_{2D}} \rangle \Big|_{r=0}, \quad (14b)$$

$$M_z \propto (\partial_x \langle u_{zx0} | + \partial_y \langle u_{yz0} |) \langle S=0 | \psi_{v\mathbf{K}_{2D}} \rangle \Big|_{r=0}. \quad (14c)$$

Here, the application of $\langle S=0 | = \langle S=0, M_S=0 |$ enforces the absence of spin flips of the total spin $\mathbf{S} = \mathbf{S}_e + \mathbf{S}_h$ with the electron spin $\mathbf{S}_e$ added to the description. The states $|u_{i0}\rangle$ with $i = yz, xz, xy$ denote the one-particle hole states in the valence band i at the Γ point. In the case of Cu_2O , these transform like the irreducible representation Γ_5^+ of the cubic group O_h . They are related to the eigenstates of the quasispin $\mathbf{I}$ introduced in Sec. II A via [59]

$$|I=1, m_I = +1\rangle = -(|u_{yz0}\rangle + i|u_{zx0}\rangle)/\sqrt{2}, \quad (15a)$$

$$|I=1, m_I = 0\rangle = |u_{xy0}\rangle, \quad (15b)$$

$$|I=1, m_I = -1\rangle = +(|u_{yz0}\rangle - i|u_{zx0}\rangle)/\sqrt{2}. \quad (15c)$$

We are specifically interested in the oscillator strengths for circularly polarized light. We thus need to take suitable linear combinations of the transition matrix elements in Eq. (14):

$$M_{\pm} \propto ((i\partial_y \mp \partial_x) \langle m_I = 0, S=0 | + \sqrt{2}\partial_z \langle m_I = \pm 1, S=0 |) |\psi_{v\mathbf{K}_{2D}}\rangle \Big|_{r=0}. \quad (16)$$

Other polarizations can be evaluated analogously.

Using these relations and the Clebsch-Gordan coefficients, the spin and quasispin bra vectors can be rewritten as

$$|S=0, m_I\rangle = \sum_{J, m_J, m_{S_e}} c_{J, m_J, m_{S_e}}^{m_I} |J, m_J, m_{S_e}\rangle, \quad (17)$$

with the coefficients

$$c_{J, m_J, m_{S_e}}^{m_I} = \langle J, m_J, m_{S_e} | S=0, M_S=0; I, m_I \rangle. \quad (18)$$

Generalizing the result from Ref. [32] when m is not a good quantum number, the spatial part of the wave function $|\psi_{vc, v\mathbf{K}_{2D}}^{\sigma\tau}\rangle$ can be written as

$$\begin{aligned} & \langle J, m_J, m_{S_e} | \langle \mathbf{K}, \rho, \phi, z | \psi_{v\mathbf{K}_{2D}} \rangle \\ &= \sum_m \int_{-\frac{L}{2}}^{\frac{L}{2}} \psi_{m, J, m_J, m_{S_e}}^{v\mathbf{K}_{2D}}(\rho, z, Z) \frac{e^{im\phi}}{\sqrt{2\pi L}} e^{-iK_z Z} dZ. \end{aligned} \quad (19)$$

The photon momenta for dipole transitions to yellow excitons ($\lambda \approx 580\text{nm}$) are negligibly small. We can thus set K_z and $\mathbf{K}_{2D}$ to zero and ignore it in the following. Common prefactors can also be dropped in the calculation of relative oscillator strengths. From the condition of continuity at the origin, we can deduce for the derivatives that [32]

$$\begin{aligned} & \frac{\partial}{\partial x} (\psi_{m, J, m_J, m_{S_e}}^v(\rho, z, Z) e^{im\phi}) \Big|_{\rho=z=0} \\ &= \delta_{|m|,1} \partial_\rho \psi_{m, J, m_J, m_{S_e}}^v(\rho, z, Z) \Big|_{\rho=z=0}, \end{aligned} \quad (20a)$$

$$\begin{aligned} & \frac{\partial}{\partial y} (\psi_{m, J, m_J, m_{S_e}}^v(\rho, z, Z) e^{im\phi}) \Big|_{\rho=z=0} \\ &= im\delta_{|m|,1} \partial_\rho \psi_{m, J, m_J, m_{S_e}}^v(\rho, z, Z) \Big|_{\rho=z=0}, \end{aligned} \quad (20b)$$

$$\begin{aligned} & \frac{\partial}{\partial z} (\psi_{m, J, m_J, m_{S_e}}^v(\rho, z, Z) e^{im\phi}) \Big|_{\rho=z=0} \\ &= \delta_{m,0} \partial_z \psi_{m, J, m_J, m_{S_e}}^v(\rho, z, Z) \Big|_{\rho=z=0}. \end{aligned} \quad (20c)$$

To obtain the oscillator strengths for the excitation of the twofold degenerate states in the irreducible subspaces with circularly polarized light, the contributions of both states must be added. Combining Eqs. (16), (19), and (20), and using the time-reversal symmetry between the two degenerate states discussed in Sec. II B, the desired oscillator strengths can be evaluated as

$$\begin{aligned} f_{\text{rel}} &= \left| \int_{-\frac{L}{2}}^{\frac{L}{2}} [\mathcal{M}_\rho^+(Z) + \mathcal{M}_z^+(Z)] dZ \right|^2 \\ &+ \left| \int_{-\frac{L}{2}}^{\frac{L}{2}} [\mathcal{M}_\rho^-(Z) + \mathcal{M}_z^-(Z)] dZ \right|^2 \end{aligned} \quad (21)$$

with the transition amplitude densities

$$\mathcal{M}_\rho^\pm(Z) = \sqrt{2} \sum_{J, m_J} c_{J, m_J, m_{S_e}}^{m_I=0,*} \partial_\rho \psi_{\pm 1, J, m_J, m_{S_e}}^v(\rho, z, Z) \Big|_{\rho=z=0}, \quad (22a)$$

$$\mathcal{M}_z^\pm(Z) = \sum_{J, m_J} c_{J, m_J, m_{S_e}}^{m_I=\pm 1,*} \partial_z \psi_{0, J, m_J, m_{S_e}}^v(\rho, z, Z) \Big|_{\rho=z=0}, \quad (22b)$$

and the complex conjugate of the coefficients given in Eq. (18). Note that the oscillator strengths f_{rel} in Eq. (21) do not depend on the handedness of the circularly polarized light. Details on the numerical evaluation of Eqs. (21) and (22) are presented in Sec. II D.

1. Selection rules for dipole transitions

As the dipole operator has odd parity, and parity is a good quantum number in the system, we can deduce that only states with odd total parity belonging to the irreducible representations Γ_6^- and Γ_7^- can be optically excited in the setup shown in Fig. 1. Correspondingly, the integrals in Eq. (21) must vanish for states with even total parity.

Precise selection rules can be deduced by application of group theory [57] when considering the symmetry of the dipole operator and the respective symmetries of the states. In the context of oscillator strengths, we add the electron spin symmetry Γ_6^+ , leading to the total symmetries that decompose into a sum of subspaces as

$$\Gamma_6^\pm \times \Gamma_6^+ = \Gamma_1^\pm + \Gamma_2^\pm + \Gamma_5^\pm, \quad (23a)$$

$$\Gamma_7^\pm \times \Gamma_6^+ = \Gamma_3^\pm + \Gamma_4^\pm + \Gamma_5^\pm. \quad (23b)$$

The dipole operator $D_{l=1}^-$, on the other hand, decomposes into the sum $\Gamma_2^- + \Gamma_5^-$ of irreducible representations. Here, Γ_2^- corresponds to linear polarization along the z direction, whereas the two-dimensional Γ_5^- corresponds to polarizations in the QW plane, including the circular polarizations we consider here. From this, it follows that light circularly polarized in the xy plane can create excitons in the twofold degenerate Γ_5^- spaces. As m_{S_e} is a good quantum number, the entire negative-parity subspaces in Eq. (23) are degenerate. As they both fully contain Γ_5^- spaces, it follows that they can both be excited by left- and right-circularly polarized light. In fact,

from time-reversal symmetry of the system, it follows that both polarizations lead to identical spectra.

Note that a more restricted selection rule is valid for z -polarized light. In that case, only Γ_6^- states can be excited. However, this would require light oriented in the QW plane, and thus a different experimental setup than shown in Fig. 1.

D. Numerical algorithm

To compute the exciton eigenenergies and eigenfunctions of the Hamiltonian (10), we extend the basis used in the hydrogenlike model [31,39] for the wave functions in the three-dimensional coordinate space (ρ, z_e, z_h) by the additional angular momentum and spin degrees of freedom. We use the ansatz

$$|\Psi\rangle = \sum_{J, m_J, m} \psi_{m, J, m_J}(\rho, z_e, z_h) |m, J, m_J\rangle \quad (24)$$

with the basis states

$$|m, J, m_J\rangle = e^{im\phi} |J, m_J\rangle \quad (25)$$

as the product of the eigenstates of the angular momentum operator L_z and the eigenstates of the coupled quasispin and hole spin $\mathbf{J} = \mathbf{I} + \mathbf{S}_h$. The wave functions $\psi_{m, J, m_J}(\rho, z_e, z_h)$ in Eq. (24) are expanded over a basis of B splines of order n as

$$\psi_{m, J, m_J}(\rho, z_e, z_h) = \frac{1}{\sqrt{\rho}} \sum_{i, j, k} c_{ijk}^{m, J, m_J} B_i^n(\rho) B_j^n(z_e) B_k^n(z_h), \quad (26)$$

similar to Refs. [31,39]. For convenience, the definition and some properties of B splines are collected in Appendix A. Note that we do not expand the ϕ dependence in Eq. (24) using B splines but rather use the angular momentum states $\exp(im\phi)$ as basis states.

The expansions (24) and (26) lead to a generalized eigenvalue problem

$$\sum_{\beta} H_{\alpha\beta} c_{\beta} = E \sum_{\beta} O_{\alpha\beta} c_{\beta} \quad (27)$$

for the energy eigenvalues of the Hamiltonian (10) and the expansion coefficients c_{ijk}^{m, J, m_J} of the corresponding eigenfunctions. Here, the indices α and β count both the elements of the total basis set composed of B splines, angular momentum, and spin states in Eq. (24) and the expansion coefficients c_{ijk}^{m, J, m_J} when arranged as one-dimensional vectors.

The elements of the matrices in Eq. (27) are computed as follows. The matrix elements of all terms of the Hamiltonian (10), except for the Coulomb potential V_C , can be factorized into products of one-dimensional integrals of B splines or their derivatives along coordinates ρ , z_e , and z_h , as well as analytically precalculated matrix elements of spin operators. Details of the computation of matrix elements of the momentum operators and the spin operators are given in Appendixes B and C, respectively. The matrix elements of the Coulomb potential V_C are diagonal with respect to the angular momentum and spin basis. The nontrivial three-dimensional integrals in the (ρ, z_e, z_h) coordinate space are computed, using the B-spline basis, as explained in Ref. [39]. The generalized eigenvalue problem (27) is solved using ARPACK routines optimized

TABLE II. Selected angular momentum and spin basis states $|m, J, m_J\rangle$ with quantum numbers $m_F = -7/2, 1/2$, and $9/2$ belonging to the irreducible subspaces $\Gamma_7^{\pm}$ and used for numerical calculations.

$m_F = -7/2$	$m_F = 1/2$	$m_F = 9/2$
$ -5, \frac{3}{2}, +\frac{3}{2}\rangle$	$ -1, \frac{3}{2}, +\frac{3}{2}\rangle$	$ 3, \frac{3}{2}, +\frac{3}{2}\rangle$
$ -4, \frac{3}{2}, +\frac{1}{2}\rangle$	$ +0, \frac{3}{2}, +\frac{1}{2}\rangle$	$ 4, \frac{3}{2}, +\frac{1}{2}\rangle$
$ -4, \frac{1}{2}, +\frac{1}{2}\rangle$	$ +0, \frac{1}{2}, +\frac{1}{2}\rangle$	$ 4, \frac{1}{2}, +\frac{1}{2}\rangle$
$ -3, \frac{1}{2}, -\frac{1}{2}\rangle$	$ +1, \frac{1}{2}, -\frac{1}{2}\rangle$	$ 5, \frac{1}{2}, -\frac{1}{2}\rangle$
$ -3, \frac{3}{2}, -\frac{1}{2}\rangle$	$ +1, \frac{3}{2}, -\frac{1}{2}\rangle$	$ 5, \frac{3}{2}, -\frac{1}{2}\rangle$
$ -2, \frac{3}{2}, -\frac{3}{2}\rangle$	$ +2, \frac{3}{2}, -\frac{3}{2}\rangle$	$ 6, \frac{3}{2}, -\frac{3}{2}\rangle$

for band matrices [60]. The band and sparse structure of the resulting Hamiltonian matrix $H_{\alpha\beta}$ and overlap matrix $O_{\alpha\beta}$ arises naturally from the compact support of the B-spline functions. We use 15 B-spline functions of order $n = 5$ for both the z_e and z_h directions, defined on equidistant grids, and 26 B-spline functions for the ρ direction. For the ρ coordinate, the grid nodes are distributed nonequidistantly with a decreasing density over the interval $[0, 200 \text{ nm}]$, providing a finer resolution near the origin where both the potential and the wave function vary most rapidly; see Appendix A for more details. Because only basis states with $\Delta m_F = 0, \pm 4$ are coupled, it is sufficient to use one of the sets in Eq. (12) for the numerical diagonalization of the Hamiltonian.

We are mainly interested in the optically active states with dominant $m = 0$ and $m = 1$ contributions. Convergence of these states is achieved when restricting the spin and angular momentum basis to the subset with $m_F = -7/2, 1/2$, and $9/2$ given in Table II in the irreducible subspace $\Gamma_7^{\pm}$ and to the subset with $m_F = -5/2, 3/2$, and $11/2$ in the subspace $\Gamma_6^{\pm}$. States in the remaining subsets in Eq. (12) do not need to be computed as they have the same eigenenergies and the twofold degenerate eigenstates just differ by time-reversal symmetry. The total number N of basis states and thus the dimension of the generalized eigenvalue problem (27) is given by the product of the number of B splines for the ρ , z_e , and z_h coordinates and the number of angular momentum and spin states $|m, J, m_J\rangle$ and was up to $N = 26 \times 15 \times 15 \times 18 = 105\,300$ in our calculations.

To compute oscillator strengths, we use the eigenstates obtained by solving the generalized eigenvalue problem. The solution yields the wave function for each state in the coordinates ρ , z_e , and z_h . For evaluating Eq. (22), the wave functions have to be expressed in relative coordinates in the z direction. As we only need the wave function at $z = 0$, i.e., at $z_e = z_h = Z$, the transformation is straightforward and given by

$$\psi(\rho, z=0, Z) = \psi(\rho, z_e=Z, z_h=Z). \quad (28)$$

The derivative with respect to z is calculated analytically by differentiating the B-spline basis functions according to Eq. (A1). It acts on a product of basis states as

$$\partial_z B_j^n(z_e) B_k^n(z_h) = \partial_{z_e} B_j^n(z_e) B_k^n(z_h) - B_j^n(z_e) \partial_{z_h} B_k^n(z_h). \quad (29)$$

By contrast, the derivative with respect to ρ at $\rho = 0$ is computed using the approximation $\partial_{\rho} \psi(\rho, z=0, Z)$

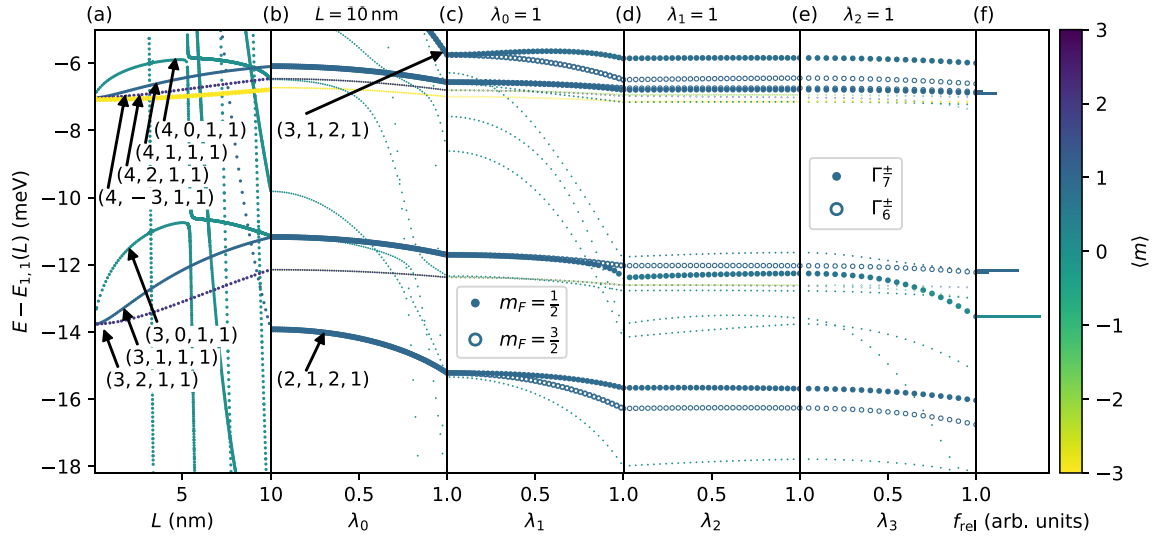


FIG. 4. Exciton spectra in a cuprous oxide QW. In (a), the QW width is increased from $L = 0$ to 10 nm for excitons described by the hydrogenlike part of the Hamiltonian given by the first two terms in Eq. (31). In (b)–(e), the nondiagonal coupling terms are successively switched on using the parameters $\lambda_{0,1,2,3} \in [0, 1]$ in the Hamiltonian (31) (see text). The photoabsorption spectrum for transitions with circularly polarized light and considering the complete structure of the valence band is given in (f). Some states are labeled by approximate quantum numbers (n, m, N_e, N_h) . The colors of symbols or lines indicate the expectation value $\langle m \rangle$ of the angular momentum of the exciton state.

$\approx \frac{1}{\rho} \psi(\rho, z=0, Z)$, which is extrapolated, analogously to Ref. [32], to $\rho = 0$. In Eq. (21) the contributions of both twofold degenerate states to the relative oscillator strength f_{rel} are considered. The integrands are evaluated at 100 positions on an equidistant grid, and the integrals are solved numerically using `numpy.trapz` [61]. Note that the most time-consuming part is the diagonalization of the generalized eigenvalue problem (27).

III. RESULTS AND DISCUSSION

The complex structure of the cuprous oxide valence bands has a significant effect on excitons in the QW. To observe the shifts of energy levels due to the impact of the different terms in the Hamiltonian (10), we apply the following strategy. We start by taking into account the diagonal part of the Hamiltonian,

$$H_{\text{hyd}} = H_{\text{diag}} + H_{\Delta m=0} \delta_{J'J}, \quad (30)$$

representing the hydrogenlike two-band model of excitons in a QW, and then switch on, term by term, the parts in the Hamiltonian, which are nondiagonal with respect to the angular momentum and spin quantum numbers of the basis. To this aim, we modify the Hamiltonian (10) to the form

$$H = H_{\text{diag}} + H_{\Delta m=0} \delta_{J'J} + \lambda_0 H_{\Delta m=0} (1 - \delta_{J'J}) + \lambda_1 H_{\Delta m=1} + \lambda_2 H_{\Delta m=2} + \lambda_3 H_{\Delta m_F=4} \quad (31)$$

by introducing the auxiliary parameters $\lambda_{0,1,2,3} \in [0, 1]$, which can be used to successively switch on the individual nondiagonal terms. Note that $H_{\Delta m=0}$ in Eq. (11b) has both nonzero diagonal and nondiagonal terms in the angular momentum and spin basis $|m, J, m_J\rangle$. In Eq. (31), the nonzero diagonal terms of $H_{\Delta m=0}$ are considered in the hydrogenlike model, described by the first and second terms, and the

nondiagonal terms, which couple $J = 1/2$ and $J = 3/2$ states of the yellow and green exciton series, respectively, are switched on by increasing λ_0 from 0 to 1.

For an energy range of the lowest, yellow exciton series, a sequence of spectra obtained by diagonalization of the Hamiltonian (31) is presented in Fig. 4. The figure allows for a detailed discussion of the impact of the valence band on excitons in a cuprous oxide QW of $L = 10$ nm width. We go through Fig. 4 from left to right. Figure 4(a) shows spectra of the hydrogenlike two-band model, Eq. (30), for excitons in a QW of width L in the range from $L = 0$ to $L = 10$ nm. The energies are given with respect to the first scattering threshold $E_{1,1}(L)$, given by the sum of the lowest quantum-confinement energies; see Eq. (6). Note that in the limit $L \rightarrow 0$, both the exciton energies E and the threshold energy $E_{1,1}(L)$ diverge, however, the energy differences $E - E_{1,1}(L)$ remain finite. This limit refers to the analytically solvable two-dimensional Coulomb problem [33,34], where states with the same principal quantum number n but different angular momentum quantum numbers m are degenerate, as can be clearly seen in Fig. 4. The degeneracy is lifted, when L is increased, in the transition region from strong to weak confinement [31]. Some of the states in Fig. 4(a) are marked by quantum numbers (n, m, N_e, N_h) , with m being an exact quantum number due to the rotational symmetry of the hydrogenlike problem. The colors of the states indicate the expectation values $\langle m \rangle$ of the angular momentum operator throughout Fig. 4.

In Figs. 4(b)–4(f), the QW width is fixed to $L = 10$ nm to study the impact of the complex valence band on the excitons at such a QW width. In Fig. 4(b), the nondiagonal terms of $H_{\Delta m=0}$, coupling the yellow ($J = 1/2$) and green ($J = 3/2$) excitons, are switched on by increasing λ_0 from 0 to 1. The coupling between yellow and green excitons has a strong impact on states with angular quantum number $m = 0$ and a smaller effect on states with $m \neq 0$; the energies of those are

moderately lowered. Note that for the states in this panel, the rotational symmetry around the z axis is still valid, and thus m and m_J are exact quantum numbers. As the eigenenergies do not depend on the sign of these quantum numbers, states with $m \neq 0$ are fourfold degenerate.

In Figs. 4(c) and 4(d), the nondiagonal terms $H_{\Delta m=1}$ and $H_{\Delta m=2}$ in the Hamiltonian (31) are successively switched on. These coupling terms break the rotational symmetry around the z axis in a way that m is not a good quantum number any longer, but the quantum number $m_F = m + m_J$ for the z component of the total angular momentum $\mathbf{F} = \mathbf{L} + \mathbf{J}$ still is. As an important consequence, the degeneracy of, e.g., some states with $m_F = 1/2$ and $m_F = 3/2$, marked by solid and open symbols, respectively, is reduced in Figs. 4(c) and 4(d) from fourfold to twofold degeneracy.

Finally, in Fig. 4(e) the nondiagonal terms $H_{\Delta m_F=4}$ in the Hamiltonian (31), which couple basis states with $\Delta m = \pm 2$ and $\Delta m_F = \pm 4$, are switched on. In this panel, m_F is not a good quantum number any longer, and states can only be classified as belonging to one of the four irreducible subspaces $\Gamma_6^\pm$ and $\Gamma_7^\pm$, as discussed in Sec. II B. The eigenenergies are shifted due to the coupling between different m_F states, however, there is no further lifting of degeneracies, i.e., all states remain twofold degenerate. The rightmost spectrum in Fig. 4(e) is the one with $\lambda_{0,1,2,3} = 1$, where the full impact of the valence band as described by the Hamiltonian (10) is taken into account. The relative oscillator strengths corresponding to this spectrum are shown in Fig. 4(f). Note that the spectrum significantly differs from that of the hydrogenlike model shown at QW width $L = 10$ nm in Fig. 4(a). This clearly illustrates that a precise description of exciton states in QWs requires taking into account the complex structure of the valence band to accurately determine all splittings of energy levels.

For a more detailed discussion, the photoabsorption spectrum of a cuprous oxide QW of width $L = 10$ nm is shown in Fig. 5. Excitons are excited by a laser beam oriented perpendicular to the QW plane with left- or right- ($\hat{e}_x \pm i\hat{e}_y$) circularly polarized light. Note that due to the selection rules discussed in Sec. II C 1, only states in the irreducible subspaces Γ_6^- and Γ_7^- can be excited. Their relative oscillator strengths f_{rel} are computed by evaluation of Eq. (21) and indicated in Fig. 5 by vertical light green and light blue bars, respectively. Parity-forbidden even states in the subspaces Γ_6^+ and Γ_7^+ are marked by dark blue and dark green arrows. The insets show the transition amplitude density $\mathcal{M}_\rho^\pm(Z)$ (orange lines) and $\mathcal{M}_z^\pm(Z)$ (red lines) given in Eqs. (22a) and (22b), respectively. As can be clearly seen, they are even functions in Z for the parity allowed and odd functions for the parity forbidden states. It should be noted that, contrary to the simple two-band model discussed in Ref. [32], both densities $\mathcal{M}_\rho^\pm(Z)$ and $\mathcal{M}_z^\pm(Z)$ are nonzero and constructively or destructively interfere to the sums shown as black lines in the insets of Fig. 5.

For convenience, selected energy eigenvalues E of the Hamiltonian (10) at QW width $L = 10$ nm corresponding to the rightmost spectrum in Fig. 4(e) and the spectrum in Fig. 5 are given in Table III. They are compared to the energies E_{hyd} of the hydrogenlike model, i.e., the rightmost spectrum shown

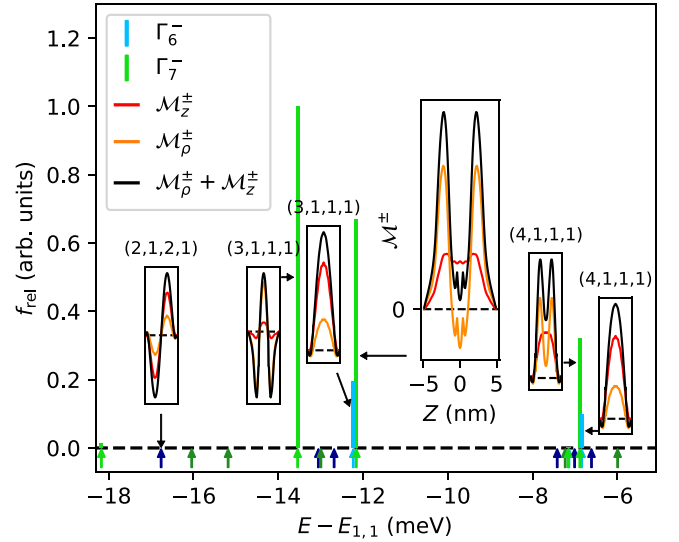


FIG. 5. Photoabsorption spectrum of a cuprous oxide quantum well of width $L = 10$ nm for transitions with circularly polarized light ($\hat{e}_x \pm i\hat{e}_y$). The relative oscillator strengths f_{rel} of parity-allowed transitions to states in the subspaces Γ_6^- and Γ_7^- are represented by vertical light blue and green bars, respectively. Parity-forbidden even states in the subspaces Γ_6^+ and Γ_7^+ are marked by dark blue and dark green arrows. The insets show the transition amplitude density $\mathcal{M}_\rho^\pm(Z)$ (orange lines) and $\mathcal{M}_z^\pm(Z)$ (red lines) given in Eqs. (22a) and (22b), respectively, together with their sums (black lines). Some states are marked by approximate quantum numbers (n, m, N_e, N_h) .

in Fig. 4(a). Where possible, approximate quantum numbers (n, m, N_e, N_h) are assigned to the states. The irreducible representations for the states calculated using the complete valence band and the relative oscillator strengths f_{rel} shown in Figs. 4(f) and 5 are also indicated in Table III.

So far, we have discussed the impact of the valence band on exciton spectra in a QW with fixed width $L = 10$ nm. In Fig. 6, we finally compare the dependence of the energy eigenvalues of the full Hamiltonian (10) (open symbols) and of the hydrogenlike model in Eq. (30) (closed symbols) on the QW width L . The change of energy levels during the crossover

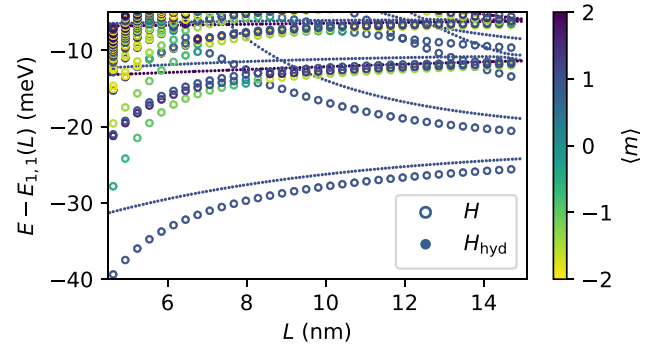


FIG. 6. Comparison of the exciton spectra of the $\Gamma_6^\pm$ states in a cuprous oxide quantum well as a function of the well width L . Results obtained from the full Hamiltonian H in Eq. (10) and the hydrogenlike model based on the Hamiltonian H_{hyd} given in Eq. (30) are presented by open and closed symbols, respectively. The threshold energy $E_{1,1}(L)$ has been subtracted from all energy eigenvalues.

TABLE III. Numerical values for selected states of the exciton spectrum at QW width $L = 10$ nm considering the complex band structure described by the Hamiltonian (10). The energy eigenvalues E are compared to those of the hydrogenlike model H_{hyd} given in Eq. (30). Approximate quantum numbers (n, m, N_e, N_h) are assigned where it was uniquely possible. All states are characterized by their irreducible representations. Oscillator strengths f_{rel} are given relative to the strongest line.

E (meV)	E_{hyd} (meV)	n	m	N_e	N_h	sym	f_{rel}
-112.95986	-97.28582	1	0	1	1	Γ_7^+	0
-65.16197	-24.64831	2	0	1	1	Γ_7^+	0
-27.80125	-26.25192	2	1	1	1	Γ_6^-	0.39413
-27.37152	-26.25192	2	1	1	1	Γ_7^-	0.00251
-18.16818	-9.81564					Γ_7^-	0.01186
-16.76044	-13.92396	2	1	2	1	Γ_6^+	0
-16.04019	-13.92396	2	1	2	1	Γ_7^+	0
-15.18094	-4.53941					Γ_7^+	0
-13.54263	-11.17306	3	1	1	1	Γ_7^-	1.00000
-13.05286	-11.14293	3	2	1	1	Γ_6^+	0
-12.99400	-6.48151	4	0	1	1	Γ_7^+	0
-12.68154	-11.14293	3	-2	1	1	Γ_6^+	0
-12.22872	-11.17306	3	1	1	1	Γ_6^-	0.19371
-12.15775						Γ_7^-	0.66918
-7.42073	-6.46143	4	2	1	1	Γ_6^+	0
-7.23267	-3.34728					Γ_7^+	0
-7.16253	-6.72711	4	-3	1	1	Γ_7^-	0.00012
-7.14464	-6.72711	4	-3	1	1	Γ_6^-	0.00002
-7.01147	-6.46143	4	-2	1	1	Γ_6^+	0
-6.88742	-6.08855	4	1	1	1	Γ_7^-	0.32152
-6.84615	-6.08855	4	1	1	1	Γ_6^-	0.09737
-6.61281	-2.08170	3	1	2	1	Γ_6^+	0
-5.99680	-2.08170	3	1	2	1	Γ_7^+	0

from the 2D limit (strong confinement regime) to the bulk semiconductor (weak confinement) in the range $5 \text{ nm} \leq L \leq 15 \text{ nm}$ can be observed. Since the Bohr radius of the lowest calculated exciton state is about 4 nm, the QW width of 15 nm can be considered for this state as a weak confinement regime. States obtained within the simplified hydrogenlike model exhibit only moderate variations in their separation from the threshold level $E_{1,1}(L)$. By contrast, due to strong state-mixing effects, the levels calculated using the more complex model show a pronounced sensitivity to changes in the QW width, particularly in the regime of small L . Energy levels for $L < 5$ nm are not shown because, for such widths, the Luttinger-Kohn model with the same material parameters as for the bulk is very approximate (see Sec. IV).

IV. CONCLUSION AND OUTLOOK

We have studied the impact of the valence band structure on the energies and level splittings of yellow excitons in cuprous oxide QWs. Based on the Luttinger-Kohn model, we derived the complete Hamiltonian, taking into account the full complex valence band structure. We calculated the exciton energies by expanding the wave function over a multidimensional basis of angular and spin eigenstates and the B splines for the coordinate part of the wave function. This allowed us to observe the breaking of the rotational symmetry, leading

to the quantum number m no longer being a good quantum number. The step-by-step inclusion of the nondiagonal coupling terms of the complex valence band Hamiltonian clearly demonstrated shifts and splittings of the energy levels. We also computed the relative oscillator strengths for the excitonic transitions in QWs with circularly polarized light.

In this article, we have considered the complete valence band structure but have still used some approximations and simplifications, which shall be addressed in future work. In the Hamiltonian (8), we have used the same Luttinger parameters as in the bulk material [10]. This may be a good approximation for sufficiently broad QWs ($L \gtrsim 5$ nm), however, the Luttinger parameters probably need to be adjusted for narrow QWs based on density functional theory calculations [62] of the electronic band structure of the thin films [63]. In our calculations, we have also assumed the same dielectric constant ϵ for both the crystal and the substrate. The dielectric contrast of a more realistic setup can be taken into account via the Rytova-Keldysh potential [46,47], similar to what has been done for the hydrogenlike model of excitons in QWs [31]. Furthermore, we have restricted our computations to a configuration in which the QW is aligned perpendicular to the [001] axis of the crystal, and excitons are invariant under symmetry transformations of the D_{4h} symmetry group. A more general orientation between the QW and the crystal can be considered, however, this will further reduce the symmetries of the problem. For the computation of spectra and oscillator strengths, we have focused on bound states of the yellow exciton series. In future work, this can be generalized to yellow and green resonance states above threshold by application of the complex-coordinate-rotation method as in Ref. [39]. This will also enable the search for BICs [40]. The obtained wave functions will make it possible to estimate the interband dipole transition matrix elements to investigate the usage of the confined Rydberg excitons for quantum sensing. The consideration of all these effects and radiative properties will certainly allow for detailed comparisons with future experimental spectra.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

APPENDIX A: B SPLINES

B splines of higher orders are an effective tool for discretizing and solving partial differential equations. The unknown function is expanded over a basis of B splines $B_i^k(x)$, $i = 1, \dots, \mathcal{N}$, which are piecewise polynomials of degree $k - 1$. Given the predefined series of the service nodes t_i , each B spline $B_i^k(x)$ of order k is defined on the interval $x \in [t_i, t_{i+k}]$. Values of the B splines $B_i^k(x)$ and their derivatives at a given

point x can be calculated by recursion formulas [44]

$$B_i^k(x) = \frac{x - t_i}{t_{i+k-1} - t_i} B_i^{k-1}(x) + \frac{t_{i+k} - x}{t_{i+k} - t_{i+1}} B_{i+1}^{k-1}(x),$$

$$\frac{dB_i^k(x)}{dx} = \frac{k-1}{t_{i+k-1} - t_i} B_i^{k-1}(x) - \frac{k-1}{t_{i+k} - t_{i+1}} B_{i+1}^{k-1}(x). \quad (\text{A1})$$

The expression for the second derivative can be derived from the above two equations.

B splines have some important characteristics. First, a B spline of order k on an equidistant grid approximates an analytical function with accuracy of h^k , where h is the step size of the grid. Thus, higher-order B splines give an accurate solution even for a relatively small number of nodes, which is particularly important for multidimensional problems. Second, one can choose nodes nonequidistantly and add service nodes at the boundaries in such a way as to have some B splines equal to 1 at the boundaries, while all other B splines are exactly zero there. Then, for example, zero boundary conditions can be easily implemented by removing the B splines which are nonzero at the boundaries. Third, the B splines are nonorthogonal functions, and thus the problem turns into a generalized eigenvalue problem. However, the B-spline functions have minimal support, i.e., each B spline vanishes, $B_i^k(x) = 0$, for $x \notin [t_i, t_{i+k}]$, which significantly reduces the number of integrations to calculate matrix elements. This leads to a sparse structure of the matrices of the generalized eigenvalue problem (27).

APPENDIX B: MATRIX ELEMENTS OF MOMENTUM OPERATORS

In polar coordinates (ρ, ϕ) , the creation and annihilation operators $p_{\pm}$ are given as

$$p_{\pm} = \frac{\hbar}{i} \exp(\pm i\phi) \left[\partial_{\rho} \mp \frac{1}{\rho} \left(\frac{L_z}{\hbar} \pm \frac{1}{2} \right) \right], \quad (\text{B1})$$

with $p_+ = p_-^\dagger$. Using Eq. (B1) and the commutator $[L_z/\hbar, \exp(\pm i\phi)] = \pm 1$, the squared operators $p_{\pm}^2$ are obtained as

$$p_{\pm}^2 = -\hbar^2 \exp(\pm 2i\phi) \left[\partial_{\rho}^2 \mp \frac{2}{\rho} \partial_{\rho} \left(\frac{L_z}{\hbar} \pm 1 \right) + \frac{1}{\rho^2} \left(\frac{L_z}{\hbar} \pm \frac{5}{2} \right) \left(\frac{L_z}{\hbar} \pm \frac{1}{2} \right) \right]. \quad (\text{B2})$$

The operator $p_+ p_-$ reads

$$p_+ p_- = -\hbar^2 \partial_{\rho}^2 + \frac{1}{\rho^2} \left(L_z^2 - \frac{\hbar^2}{4} \right), \quad (\text{B3})$$

and thus is diagonal with respect to the angular momentum functions $\exp(im\phi)$. For functions given as a product of a B spline over the ρ coordinate and an angular function $\exp(im\phi)$, it is now straightforward to evaluate matrix elements of the operators given above. The ϕ integrals are trivially solved analytically, yielding selection rules for nonzero matrix elements between states with quantum numbers m and m' . The B-spline functions as well as their derivatives are piecewise polynomials and can be easily integrated. Note that due to the boundary condition that the B splines vanish at

$\rho = 0$, the product of two B splines can be divided by ρ or ρ^2 without the occurrence of any singularity at the origin.

Using B splines over the coordinates z_e and z_h , matrix elements of the operators $p_{ez}^2 = -\hbar^2 \partial_{ez}^2$, $p_{hz} = (\hbar/i) \partial_{hz}$, and $p_{hz}^2 = -\hbar^2 \partial_{hz}^2$ are straightforwardly computed by integration of products of B splines and their derivatives.

APPENDIX C: MATRIX ELEMENTS OF SPIN OPERATORS

The matrix elements of the quasispin and hole spin operators $\mathbf{I}$ and $\mathbf{S}_h$ are computed in the six-dimensional basis $|J, m_J\rangle$ of the spin operator $\mathbf{J} = \mathbf{I} + \mathbf{S}_h$, which can also be expressed using Clebsch-Gordan coefficients in the basis $|I, m_I; S_h, m_{S_h}\rangle$, i.e.,

$$\begin{aligned} \left| \frac{3}{2}, \frac{3}{2} \right\rangle &= \left| 1, 1; \frac{1}{2}, \frac{1}{2} \right\rangle, \\ \left| \frac{3}{2}, \frac{1}{2} \right\rangle &= \sqrt{\frac{2}{3}} \left| 1, 1; \frac{1}{2}, -\frac{1}{2} \right\rangle - \sqrt{\frac{1}{3}} \left| 1, 0; \frac{1}{2}, \frac{1}{2} \right\rangle, \\ \left| \frac{1}{2}, \frac{1}{2} \right\rangle &= \sqrt{\frac{1}{3}} \left| 1, 1; \frac{1}{2}, -\frac{1}{2} \right\rangle + \sqrt{\frac{2}{3}} \left| 1, 0; \frac{1}{2}, \frac{1}{2} \right\rangle, \\ \left| \frac{1}{2}, -\frac{1}{2} \right\rangle &= -\sqrt{\frac{2}{3}} \left| 1, -1; \frac{1}{2}, \frac{1}{2} \right\rangle + \sqrt{\frac{1}{3}} \left| 1, 0; \frac{1}{2}, -\frac{1}{2} \right\rangle, \\ \left| \frac{3}{2}, -\frac{1}{2} \right\rangle &= \sqrt{\frac{1}{3}} \left| 1, -1; \frac{1}{2}, \frac{1}{2} \right\rangle + \sqrt{\frac{2}{3}} \left| 1, 0; \frac{1}{2}, -\frac{1}{2} \right\rangle, \\ \left| \frac{3}{2}, -\frac{3}{2} \right\rangle &= \left| 1, -1; \frac{1}{2}, -\frac{1}{2} \right\rangle. \end{aligned}$$

With these basis states, the matrix representations of the spin operators are obtained as

$$I_+ = \hbar \begin{pmatrix} 0 & -\frac{\sqrt{6}}{3} & \frac{2\sqrt{3}}{3} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{4}{3} & \frac{\sqrt{2}}{3} & 0 \\ 0 & 0 & 0 & -\frac{\sqrt{2}}{3} & \frac{4}{3} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{6}}{3} \\ 0 & 0 & 0 & 0 & 0 & \frac{2\sqrt{3}}{3} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}, \quad (\text{C1})$$

$$I_3 = \hbar \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{2}{3} & \frac{\sqrt{2}}{3} & 0 & 0 & 0 \\ 0 & \frac{\sqrt{2}}{3} & \frac{1}{3} & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{2}{3} & \frac{\sqrt{2}}{3} & 0 \\ 0 & 0 & 0 & \frac{\sqrt{2}}{3} & -\frac{1}{3} & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 \end{pmatrix}, \quad (\text{C2})$$

$$S_{h+} = \hbar \begin{pmatrix} 0 & \frac{\sqrt{6}}{3} & \frac{\sqrt{3}}{3} & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{1}{3} & -\frac{\sqrt{2}}{3} & 0 \\ 0 & 0 & 0 & \frac{\sqrt{2}}{3} & \frac{2}{3} & 0 \\ 0 & 0 & 0 & 0 & 0 & -\frac{\sqrt{6}}{3} \\ 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{3}}{3} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}, \quad (\text{C3})$$

$$S_{h3} = \hbar \begin{pmatrix} \frac{1}{2} & 0 & 0 & 0 & 0 & 0 \\ 0 & -\frac{1}{6} & -\frac{\sqrt{2}}{3} & 0 & 0 & 0 \\ 0 & -\frac{\sqrt{2}}{3} & \frac{1}{6} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{6} & -\frac{\sqrt{2}}{3} & 0 \\ 0 & 0 & 0 & -\frac{\sqrt{2}}{3} & -\frac{1}{6} & 0 \\ 0 & 0 & 0 & 0 & 0 & -\frac{1}{2} \end{pmatrix}. \quad (\text{C4})$$

The matrix elements of the annihilation operators are given by the conjugate transpose of the creation operator matrices, i.e., $L_- = L_+^\dagger$ and $S_{h-} = S_{h+}^\dagger$. The matrix elements of products of spin operators can be derived by multiplication of the corresponding spin matrices. Using $\mathbf{I} \cdot \mathbf{S}_h = \frac{1}{2}(\mathbf{J}^2 - \mathbf{I}^2 - \mathbf{S}_h^2)$, its matrix elements are

$$\langle J'm'_J | \mathbf{I} \cdot \mathbf{S}_h | Jm_J \rangle = \frac{1}{2} \left(J(J+1) - \frac{11}{4} \right) \delta_{J'J} \delta_{m'_J m_J}. \quad (\text{C5})$$

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