Fine structure of excitons in Cu$_2$O

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Three experimental observations on 1s-excitons in Cu$_2$O are not consistent with the picture of the exciton as a simple hydrogenic bound state: the energies of the 1s-excitons deviate from the Rydberg formula, the total exciton mass exceeds the sum of the electron and hole effective masses, and the triplet-state excitons lie above the singlet. Incorporating the band structure of the material, we calculate the corrections to this simple picture arising from the fact that the exciton Bohr radius is comparable to the lattice constant. By means of a self-consistent variational calculation of the total exciton mass as well as the ground-state energy of the singlet and the triplet-state excitons, we find excellent agreement with experiment.

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I. INTRODUCTION

The absorption spectrum of light in Cu$_2$O shows clear evidence for the existence of excitons. In the simplest picture the exciton is described as a hydrogenic atom formed from electrons and holes of given effective masses interacting through a Coulomb interaction modified by a dielectric constant. Three observations indicate that this simple picture needs to be refined: 1) The exciton Rydberg, $\mu e^4/2\hbar^2\epsilon_0^2$ (where $\mu$ is the reduced electron-hole mass and $\epsilon_0$ is the static dielectric constant of the material) is 98 meV; experimentally it is measured to be 97 meV for the $n=2, 3, \ldots$ states, however, for the 1s-state it has the anomalously high value of 153 meV. 2) The mass of the lowest (yellow series) $^3S_1$ (ortho) exciton is experimentally $M_o = (3.0 \pm 0.2)m$ [3], where $m$ is the free-electron mass; on the other hand the sum of the electron effective mass $m_e = (0.99 \pm 0.03)m$ and hole mass $m_h = (0.69 \pm 0.04)m$ [5] is only $m_e + m_h = (1.68 \pm 0.07)m$. 3) In a simple hydrogenic model the ortho and para ($^1S_0$) excitons would be degenerate. However the lowest ortho excitons lie 12 meV higher than the lowest para excitons [6].

Our purpose in this paper is to identify the salient physics responsible for these observations. These are several effects. First, one must take into account the non-parabolicity of the bands [3]. Furthermore, the electron-hole interaction is more properly the bare Coulomb interaction modified by the momentum and frequency dependent dielectric function [7,8]. In addition, the spin-dependent exchange interaction between the electron and the hole lifts the degeneracy between the triplet and the singlet-state excitons [3]. All these effects become important because the Bohr radius $a_B$ is not large compared with the lattice constant $a_L$ of the material [3]. For Cu$_2$O, $a_L = 4.26$ Å, while for the 1s-state yellow excitons the Bohr radius $a_B$ is expected to be on the order of $e^2/(2\epsilon_0 E_b) \approx 7$ Å, where $E_b$ is the observed binding energy, $\approx 153$ meV. Because the Bohr radius increases quadratically with the principal quantum number $n$, these effects are much more important for the $n = 1$ state.

The correction due to the non-parabolicity of the bands is expected to be significant, since the extent of the exciton wavefunction in momentum space is of order $1/a_B$, while the width of the Brillouin zone is of order $1/a_L$. This correction makes the exciton heavier, since away from the zone center and closer to the edge of the Brillouin zone, the dispersion relation of the bands flattens and the electron and hole bare-band masses effectively increase.

The coupling of the electron and the hole to the LO-phonons produces a frequency dependence of the dielectric function $\epsilon(k, \omega)$ on the scale of the phonon frequencies. In the limit that the frequency of the relative electron-hole motion is much larger than that of the LO-phonon, the electron-hole interaction is screened by the high-frequency dielectric constant, $\epsilon_\infty$, since the heavy ions cannot follow the motion of the electron and hole and therefore they do not contribute to the screening. In the opposite limit the low-frequency dielectric constant $\epsilon_0$ screens the electron-
hole interaction. When the Bohr radius is comparable to the lattice constant \( a_\ell \), the momentum dependence of the dielectric function, on scales of \( \hbar/a_\ell \), becomes important. The more localized 1s-exciton states are screened by \( \epsilon_0 \) at higher momenta, making the effective Coulomb interaction stronger than for the larger excited exciton states. Finally the exchange interaction is short-ranged and is negligible for excitons with \( a_B \gg a_\ell \). All these corrections, known as the “central-cell corrections,” act to produce the fine structure of excitons.

Cuprus oxide has in total ten valence and four conduction bands. It has a direct gap, since the minimum of the lowest conduction band (\( \Gamma^+_6 \)) is at the same point in momentum space as the maximum of the highest valence band, \( \Gamma^+_7 \); the gap energy is \( \approx 2.17 \) eV. See Fig. 1. The yellow-series excitons are formed between electrons and holes in these two bands. Since the conduction and valence bands have the same (positive) parity \([10]\) and the dipole moment between them vanishes, the radiative lifetimes of the excitons are relatively long. The \( n = 1 \) line in the one-photon absorption spectrum of light is weak due to the equal parity of the conduction and valence bands; the \( n \neq 1 \) lines correspond to excitons with relative angular momentum \( l = 1 \) and for this reason the absorption process is dipole-allowed. The electrons in the \( \Gamma^+_7 \) band are not in pure spin states, but rather in total angular-momentum states; the direct recombination process of the angular-momentum singlet-state para exciton is in fact highly forbidden, and the corresponding line is absent from the radiative recombination spectrum of \( \text{Cu}_2\text{O} \). The lower \( \Gamma^+_8 \) valence band, which lies \( \approx 130 \) meV below the \( \Gamma^+_7 \) band due to the spin-orbit interaction (Fig. 1), forms, with the \( \Gamma^+_6 \) band, the green-exciton series. Here we neglect for simplicity any possible mixing between the yellow and the green-exciton series. This mixing is expected to be on the order of 10% \([11]\), and its only result is to modify slightly the exciton binding energies.

Recently high-density excitons in \( \text{Cu}_2\text{O} \) have been observed to obey Bose-Einstein statistics \([12–14]\) and indeed Bose-Einstein condensation \([15]\) has been observed \([16,17]\). These observations are directly related with the band structure of \( \text{Cu}_2\text{O} \), as we have shown in Refs. \([18,19]\).

In this paper we start with the effective mass approximation, which we describe in Sec. II. In Sec. III we discuss the central-cell corrections. In Sec. IV we study the exchange interaction \([6]\), and review the band structure which underlies the properties of excitons in \( \text{Cu}_2\text{O} \) \([20]\). We summarize our results in Sec. V.

## II. EFFECTIVE MASS APPROXIMATION FOR EXCITONS

An exciton in the effective mass approximation is a hydrogen-like bound state of an electron and a hole, with center-of-mass in a plane-wave state. The exciton energies lie in discrete levels below the energy gap, determined by the binding energy plus the energy carried by the center-of-mass. In the effective mass approximation the Hamiltonian \( H \) of an electron and a hole which interact through their Coulomb attraction, modified by a dielectric constant \( \epsilon_0 \), is

\[
H = \frac{\vec{p}_e^2}{2m_e} + \frac{\vec{p}_h^2}{2m_h} - \frac{\epsilon^2}{\epsilon_0 |\vec{r}_e - \vec{r}_h|},
\]

where \( \vec{p}_i \) is the momentum operator of the electron and the hole and the \( m_i \) are the effective electron and hole masses. The Hamiltonian can be written in terms of the momentum and the coordinate operators of the relative motion of the electron and the hole, \( \vec{p} \) and \( \vec{r} \) respectively, and the momentum operator \( \vec{P} \) of the center-of-mass as

\[
H = \frac{\vec{P}^2}{2M} + \frac{\vec{p}^2}{2\mu} - \frac{\epsilon^2}{\epsilon_0 r},
\]

where \( M = m_e + m_h \) is the total exciton mass and \( \mu = m_e m_h / (m_e + m_h) \) is the reduced mass. The eigenfunctions of the above Hamiltonian are of the form

\[
\Psi_{K,nlm}(\vec{r}, \vec{R}) = \frac{1}{\sqrt{\Omega}} e^{i\vec{K} \cdot \vec{R}} \Phi_{nl}(r) Y_l^m(\theta, \phi),
\]

where \( \Omega \) is volume of the crystal, the \( Y_l^m \) are spherical harmonics and \( \Phi_{nl} \) are the radial hydrogenic eigenfunctions. In the state \( \mathbf{3} \) the center-of-mass of the exciton carries momentum \( \hbar \vec{K} \). The corresponding eigenenergies are
\[ E_{K,n} = E_g + \varepsilon_n^{(0)} + \frac{\hbar^2 K^2}{2M}, \]

where \( \varepsilon_n^{(0)} = -\mu e^4/2\hbar^2 \epsilon_0 n^2 \) and \( E_g \) is the band-gap energy.

If we assume for simplicity that the effective electron and hole masses are equal, the exciton wavefunction can be expressed as a linear superposition of electron and hole Bloch states as

\[ \Psi_{K,nlm}(r_e, r_h) = \sum_q \phi_q \Phi_{c.q + K/2}(r_e) \Phi_{v,-q + K/2}(r_h), \]

where the Bloch states are of the usual form

\[ \Phi_{j,k}(r) = u_{j,k}(r) e^{i k r}, \]

with \( u_{j,k}(r) \) periodic. To a good approximation we can identify \( \phi_q \) as the Fourier transform of the relative electron-hole wavefunction times \( \sqrt{\Omega} \).

III. CENTRAL–CELL CORRECTIONS

As we mentioned earlier, the binding energy of excitons is modified by the non-parabolicity of the bands [3], the coupling of the electron and the hole with the longitudinal-optical (LO) phonons [7], the dependence of the dielectric function on the distance between the electron and the hole [3] and the exchange interaction [6]. In this section we study the first three mechanisms.

Let us start with the correction due to the non-parabolicity of the bands. In the tight-binding approximation, for example, the electron or hole dispersion relation is a cosine function of \( \ell a \). Expanding this function around zero, the zero-order term gives a constant. The first correction, \( \sim (\kappa a)^2 \), describes a free particle with an effective band mass \( m_{v,\ell} \). The next non-vanishing term is of the form

\[ \Delta V_i = \frac{p_i^2 a_i^2}{24\hbar^2 m_i}. \]

More generally, the perturbation \( \Delta V \) due to the non-parabolicity of the Hamiltonian is of the form,

\[ \Delta V = \frac{p_\alpha^2 a_\alpha^2 C_\alpha}{24\hbar^2 m_\alpha} + \frac{p_\beta^2 a_\beta^2 C_\beta}{24\hbar^2 m_\beta}, \]

where the constants \( C_i \) are on the order of unity. We proceed by writing Eq. (8) in terms of the center-of-mass coordinates, keeping terms up to order \( p^2 P^2 \),

\[ \Delta V = \Delta V_\alpha + \Delta V_\beta \equiv \frac{p^2 a^2}{24\hbar^2 \mu'} - \frac{p^2 P^2 a^2}{4\hbar^2 M'}, \]

where \( 1/\mu' \equiv (C_e/m_e) + (C_h/m_h) \) and \( M' \equiv (m_e/C_e) + (m_h/C_h) \). The \( \Delta V_\alpha \) in Eq. (9) refers to the relative electron-hole motion; the second couples the relative motion of the electron and hole with the motion of their center-of-mass and modifies the total exciton mass. We treat \( \Delta V_\alpha \) as a perturbation in calculating its contribution to the binding energy. For the central-cell corrections we use a trial hydrogen-like wavefunction of the form \( \Psi(r) = 1/(\pi a_B^3)^{1/2} e^{-r/a} \) but we truncate it outside the first Brillouin zone, assuming that \( \Psi_q \), the Fourier transform of \( \Psi(r) \), vanishes for \( |q| > \pi/a \). The reason for truncating \( \Psi_q \) is that for values of the Bohr radius smaller or comparable to \( a_B \), the exciton wavefunction is spread in momentum space and therefore without the truncation the central-cell corrections are overestimated. The expectation value of \( \Delta V_\alpha \) in \( \Psi_q \) is,

\[ \langle \Delta V_\alpha \rangle = \frac{\hbar^2 a^2}{24\mu'} \left( \sum_{|q|<\pi/a} |\Psi_q|^2 q^4 \right) \left( \sum_{|q|<\pi/a} |\Psi_q|^2 \right)^{-1} = -\frac{\hbar^2 a^2}{24\mu a_B^4} \frac{\hbar^2}{m_e + m_h} \frac{I_6(\pi a_B/a_\ell)}{I_2(\pi a_B/a_\ell)} \]

where the constants are expressed as a linear superposition of electron and hole Bloch states as

\[ \Psi_{K,nlm}(r_e, r_h) = \sum_q \phi_q \Phi_{c.q + K/2}(r_e) \Phi_{v,-q + K/2}(r_h), \]
where
\[ I_n(x) = \int_0^x \frac{y^n dy}{(1 + y^2)^4}. \] (11)

In the limit \( a_B \gg a_\ell \), Eq. (10) gives the result
\[ \langle \Delta V_\alpha \rangle = \frac{5 \hbar^2 a_\ell^2}{24 \mu a_B^2} m_i C_e + m_e C_h. \] (12)

The second term of Eq. (8), \( \Delta V_\beta \), is the first correction to the total exciton mass due to the non-parabolicity of the bands. This term modifies the free dispersion relation for the center-of-mass motion to
\[ E_\mathbf{K} = \frac{\hbar^2 K^2}{2M} + \frac{\langle p^2 \rangle a_\ell^2}{4M^2} K^2 = \frac{\hbar^2 K^2}{2M} \left( 1 - \frac{M a_\ell^2}{2M a_B^2} I_2(\frac{\pi a_B}{a_\ell}) \right), \] (13)
making the total exciton mass larger than \( M \). The above expression is in fact the total exciton mass, since the contribution of the exchange interaction to the mass is negligible, as shown in Sec. IV. Again, in the limit \( a_B \gg a_\ell \), Eq. (13) gives the result
\[ E_\mathbf{K} = \frac{\hbar^2 K^2}{2M} \left( 1 - \frac{M a_\ell^2}{2M a_B^2} \right). \] (14)

We estimate now the order of magnitude of the constants \( C_i \), using \( \mathbf{k} \cdot \mathbf{p} \) perturbation theory. Among the ten valence and four conduction bands of Cu2O only one \( \Gamma_6 \) conduction band, which lies \( \approx 449 \) meV above the \( \Gamma_6^\prime \) band, and one very deep \( \Gamma_8 \) valence band, which lies \( \approx 5.6 \) eV below the \( \Gamma_7^\prime \) valence band, have negative parity. The mixing of the \( \Gamma_6^\prime \) and \( \Gamma_7^\prime \) bands with these two negative-parity bands modifies the bare masses of the electrons and the holes (in addition to the coupling of the electrons and the holes to the optical modes) and also makes the bands non-parabolic. To find the constants \( C_i \) in lowest order requires diagonalizing a \( 4 \times 4 \) matrix; here we give just an order of magnitude estimate. The correction to the masses is of order \( |\mathbf{p}_{i,j}|^2/m \Delta_{i,j} \), where \( \mathbf{p}_{i,j} \) is the dipole matrix element between the opposite-parity bands \( i \) and \( j \) and \( \Delta_{i,j} \) is the energy separation between them. The matrix elements \( \mathbf{p}_{i,j} \) can be extracted from experiment; if we assume, for example, that they are all of equal magnitude, then from Ref. [20], \( |\mathbf{p}_{i,j}|/\hbar \approx 0.13 \) Å\(^{-1}\), which implies that \( |\mathbf{p}_{i,j}|^2/m \Delta_{i,j} \approx 0.3 \), for \( \Delta_{i,j} \approx 0.5 \) eV. Dimensionally we find
\[ \frac{\hbar^2 a_\ell^2 C \hbar^4}{24m} \approx \frac{\hbar^2 k^2}{2m} \frac{|\mathbf{p}_{i,j}|^4}{m^2 \Delta_{i,j}^2} \frac{\hbar^2 k^2}{m \Delta_{i,j}}, \] (15)
which gives \( C \approx 1 \).

The Hamiltonian (1) describes the effective interaction between an electron and a hole at momentum transfer \( k \) as
\[ V(k) = \frac{4\pi e^2}{k^2 \epsilon_0}. \] (16)

More generally, the interaction is given by
\[ V(k, \omega) = \frac{4\pi e^2}{k^2 \epsilon(k, \omega)}, \] (17)
where \( \epsilon(k, \omega) \) is the momentum- and frequency-dependent dielectric function, and \( \hbar k \) and \( \hbar \omega \) are the momentum and energy transferred in the interaction. The coupling of the electron and the hole to the LO-phonons introduces the important frequency dependence \( \omega \) in the dielectric function \( \epsilon \). In Cu2O only the \( \Gamma_{15} \) LO-phonon modes with zone-center energies of 18.7 and 87 meV contribute to the Fröhlich interaction. For \( \hbar \omega \ll 18.7 \) meV, the dielectric function has the low-frequency value, \( \epsilon_0 = 7.5 \pm 0.2 \). As the \( \hbar \omega \) crosses 18.7 meV, \( \epsilon \) decreases to \( \epsilon_m = 7.11 \), while as \( \hbar \omega \) increases past 87 meV, \( \epsilon \) drops to \( \epsilon_\infty = 6.46 \). Comparing the LO-phonon frequencies with the frequency of the relative electron-hole motion, we see that the dielectric constant of the 1s-state is \( \lesssim \epsilon_\infty \), while for the excited
n = 2, 3, 4, ... states the dielectric constant is closer to \( \epsilon_0 \). Using the values for the effective electron and hole masses given in the introduction and \( \epsilon_0 = 7.5 \) we find 98 meV for the Rydberg of the excited states, which is very close to the experimentally determined value of 97 meV. Assuming that \( \epsilon_\infty \) screens the electron-hole interaction, the expectation value \( \langle PE \rangle \), of the Coulomb interaction in the 1s-state is

\[
\langle PE \rangle = -\frac{e^2}{\epsilon_\infty a_B^2}.
\]

Since the actual dielectric constant is \( \sim \epsilon_\infty \), the choice of \( \epsilon_\infty \) overestimates the correction to the potential energy due to the coupling of the electrons and holes to the optical modes of the crystal. Although there are more sophisticated methods of treating this problem [7], they cannot be applied in our problem because more than one LO-phonon branches contributes to the Fröhlich interaction.

We turn now to the effects of the momentum dependence of the dielectric function. Equation (17) gives the interaction between the electron and the hole, where as discussed above the high-frequency dielectric function must be used. In the limit \( a_B \gg a_t \), \( \Psi_k \) is localized around zero, so we can ignore the \( k \)-dependence of the dielectric function, \( \epsilon(k) \approx \epsilon(k = 0) \approx \epsilon_\infty \). On the other hand, if the Bohr radius is comparable to the lattice constant, we need to consider corrections to \( \epsilon(k) \). For small values of \( k \)

\[
\epsilon(k) \approx \epsilon_\infty - (ka_t)^2 d,
\]

where, as we calculate below, \( d \approx 0.18 \) for Cu2O. Expanding,

\[
\frac{4\pi e^2}{k^2 \epsilon(k)} \approx \frac{4\pi e^2}{k^2 \epsilon_\infty} + \frac{4\pi e^2}{\epsilon_\infty^2} a_t^2 d,
\]

we see that the first-momentum correction to \( \epsilon(k) \) produces an effective contact interaction

\[
\Delta V_d(r) = -\frac{4\pi e^2}{\epsilon_\infty^2} da_t^2 \delta(r),
\]

which lowers the exciton energy by

\[
\langle \Delta V_d \rangle = -\frac{4\pi e^2}{\epsilon_\infty^2} da_t^2 |\Psi_{\text{exact}}(0)|^2,
\]

where \( \Psi_{\text{exact}}(r) \) is the exact (unknown) wavefunction of the 1s-state. If we evaluate \( \Delta V_d \) with the trial wavefunction \( \Psi(r) \) truncated outside the first Brillouin zone we find

\[
\langle \Delta V_d \rangle = -\frac{4\pi e^2}{\Omega \epsilon_\infty^2} da_t^2 \left| \sum_{|q|<\pi/a_t} \Psi_q \right|^2 \left( \sum_{|q|<\pi/a_t} |\Psi_q|^2 \right)^{-1} = -\frac{2da_t^2}{\pi \epsilon_\infty^2 a_B^2} \frac{I_2(\pi a_B/a_t)}{I_0(\pi a_B/a_t)},
\]

where \( \Psi_q \) is again the Fourier transform of \( \Psi(r) \). Also

\[
I_n'(x) = \int_0^\infty \frac{y^n dy}{(1+y^2)^{x+1}}.
\]

In the limit \( a_B \gg a_t \), Eq. (23) gives the result

\[
\langle \Delta V_d \rangle = -\frac{4\pi e^2}{\epsilon_\infty^2} da_t^2 |\Phi_{1s}(0)|^2 = -\frac{4de^2 a_t^2}{\epsilon_\infty^2 a_B^3}.
\]

To estimate the constant \( d \) we follow Ref. [21]. The Lindhard result gives for the dielectric function

\[
\epsilon(k, \omega) = 1 + \frac{4\pi e^2}{\Omega \epsilon k^2} \sum_{q, q'} \frac{|\langle u^\prime, k + q | u_{q} \rangle|^2}{\varepsilon_{\ell, k + q} - \varepsilon_{\ell, q} - \hbar \omega}.
\]
where $\Omega_c$ is the volume of the unit cell and $\varepsilon_{l,\bm{q}}$ is the energy of band $l$ at point $\bm{q}$ in momentum space. Since we are interested in energies much smaller than the gap energy, we assume that $\omega = 0$. The dominant contribution to the above sum, given the band structure of Cu$_2$O, involves virtual transitions between the $\Gamma_8^-$ conduction band $c'$ (which lies $\approx 449$ meV above the lowest $\Gamma_7^+$ conduction band) and the highest $\Gamma_7^+$ valence band $v$. The overlap integral in Eq. (26) satisfies the sum rule, which as in Ref. 21 allows us to write the approximate result for $\epsilon(k)$, with $\bm{k}$ restricted in the first zone,

$$\epsilon(k) \approx 1 + \frac{4\pi e^2 \hbar^2}{m\Omega_c} \sum_{\bm{q}} (\epsilon_{c',\bm{k}+\bm{q}} - \varepsilon_{v,\bm{q}})^{-2}.$$  

(28)

If we define

$$\Sigma(k) \equiv \sum_{\bm{q}} (\epsilon_{c',\bm{k}+\bm{q}} - \varepsilon_{v,\bm{q}})^{-2},$$  

(29)

the dielectric function can be written as

$$\epsilon(k) = 1 + (\epsilon_\infty - 1)\Sigma(k)/\Sigma(0).$$  

(30)

We calculate the above quantity numerically, using the effective mass of the conduction $\Gamma_8^-$ band $m_c' = 0.35m$, the effective mass of the valence $\Gamma_7^+$ band $m_h = 0.69m$ and the energy gap between them, $\approx 2.62$ eV. The integration over $\bm{q}$ is restricted to $q \leq k_D$, where $k_D^2 = 6\pi^2/\Omega_c$. For $k \to 0$, Eq. (30) is of the form of Eq. (13) with $d \approx 0.18$.

Equations (10), (18) and (23) give the total exciton energy as function of the Bohr radius,

$$E_{\text{tot}}(a_B) = \frac{\hbar^2}{2m a_B^2} - \frac{e^2}{\epsilon_\infty a_B} - \frac{C \hbar^2 a_B^2 I_6(\pi a_B/a_b)}{24 m a_B^2 I_2(\pi a_B/a)} - \frac{2 de^2 a_B^2}{\pi\epsilon_\infty^2 a_B^2} \frac{I_2(\pi a_B/a)}{I_2(\pi a_B/a_b)}.$$  

(31)

The first term is the kinetic energy of the electron-hole pair, $\langle KE \rangle$. The second term is the potential energy $\langle PE \rangle$, the third term is the correction due to the non-parabolicity of the bands, $\langle \Delta V_a \rangle$, and the last term is the correction due to the dependence of the dielectric function on the momentum, $\langle \Delta V_b \rangle$. In the third term we have made the simplifying assumption $C_c = C_h = C$. For given $C$ the binding energy has a minimum at $a_B = a_{B,0}$, which is the exciton Bohr radius for the specific choice of $C$. The corresponding binding energy is $E_{\text{tot}}(a_{B,0})$. The total exciton mass is then given by Eq. (13) with $a_B = a_{B,0}$. Equation (13) gave us an order of magnitude estimate $C \sim 1$. The value $C = 1.45$ gives the result $a_{B,0} = 5.3$ Å and the observed total ortho-exciton mass of $3m$. This choice for $C$ then yields $E_{\text{tot}}(a_{B,0}) = 166.9$ meV; see Fig. 2, in good agreement (10%) with the experimentally known binding energy of 153 meV. The expectation value of each of the terms separately in (31) is: $\langle PE \rangle = -420.4$ meV, $\langle KE \rangle = 335.8$ meV, $\langle \Delta V_a \rangle = -68.3$ meV and $\langle \Delta V_b \rangle = -14.0$ meV. We expect to find a larger binding energy here than the experimental value, since the choice of $\epsilon_\infty$ for the dielectric constant overestimates the potential energy. The Bohr radius used in the literature for excitons in Cu$_2$O is $7$ Å, the number resulting from the uncorrected formula $a_B = e^2/(2\epsilon_0 E_b)$ with $E_b = 153$ meV, the observed binding energy. The value of $E_b = 98$ meV, which is the Rydberg of the excited states, gives $a_B \approx 11.1$ Å in this way. But as we have seen the formula $a_B = e^2/(2\epsilon_0 E_b)$ neglects the central-cell corrections.

The total mass of the $n = 1$ para excitons must be the same as that of the ortho excitons, since the correction due to the non-parabolicity of the bands is the same for both the singlet and the triplet; the correction due to the exchange interaction which is nonzero only for the ortho excitons is negligible in our problem. Furthermore, the quadratic dependence of the Bohr radius on the quantum number $n$ implies that the total exciton mass is very close to $m_c + m_h \approx 1.68m$ for the excited states. Neither the $n = 1$ para-exciton mass nor the $n \geq 2$ exciton masses has yet been measured.
The virtual annihilation of an exciton, shown in Fig. 3, is responsible for raising the ortho exciton by an energy \( \Delta E_{\text{ex}} = 12 \text{ meV} \) above the para exciton at the zone center (\( K = 0 \)) of Cu$_2$O \[9\]. The energy splitting \( \Delta E_{\text{ex}}(K) \) is given by

\[
\Delta E_{\text{ex}}(K) = \frac{2}{3} \int \Psi_K(r, r') \frac{e^2}{\epsilon_\infty |r - r'|} \Psi_K(r', r') \, dr \, dr'.
\]

The factor 2/3 comes from the angular momentum states, as we show in the next section. If the electrons and the holes in the conduction and valence bands are in pure-spin states, the above interaction is non-zero for the singlet excitons only. Since it is positive, it shifts the energy of the singlet higher than the triplet. In the next section we explain how the band structure of Cu$_2$O makes the exchange interaction non-zero for the ortho excitons and zero for the para excitons, shifting the ortho excitons higher in energy than the para excitons. Using Eq. \[9\] for the exciton wavefunction we find that

\[
\Delta E_{\text{ex}}(K) = \frac{2}{3} \sum_{q,p,G \neq 0} \frac{4\pi e^2}{|G|^2 \epsilon_\infty} \phi_q(u_v,q|u_c,q)G \phi_p^*(u_v,p|u_c,p)G \\
+ \frac{2}{3} \sum_{q,p} \frac{4\pi e^2}{|\mathbf{K}|^2 \epsilon_\infty} \phi_q(u_v,q-K/2|u_c,q+K/2)G \phi_p^*(u_v,p-K/2|u_c,p+K/2)G,
\]

where

\[
\langle u_v,q|u_c,p \rangle_G = \int d\mathbf{x} u_v,p(\mathbf{x}) u_v,q^*(\mathbf{x}) e^{i\mathbf{G} \cdot \mathbf{x}}.
\]

The first sum in Eq. \[33\] is over all the non-zero reciprocal lattice vectors \( \mathbf{G} \) of the crystal. In this equation we have used the high-frequency dielectric constant in the Coulomb interaction because the energy transfer in the virtual annihilation process of an exciton is on the order of the energy gap \( \epsilon_g \). As we show below, the overlap integrals \[23,24\] which appear in the second term of Eq. \[33\] are proportional to \( (K^2)^2 \) because the dipole moment between the conduction and the valence bands vanishes. The second term of \[33\] therefore goes as \( K^2 \), since it is proportional to \( 1/K^2 \) from the Coulomb interaction times \( (K^2)^2 \) from the overlap integrals; it vanishes at the zone center and renormalizes the ortho-exciton mass. To calculate \( \Delta E_{\text{ex}} \) at \( K = 0 \), we assume that the first sum of Eq. \[33\] is dominated by the terms with smallest \( \mathbf{G} \)’s (six in number because of the cubic symmetry of the crystal), which we denote by \( G_0 \); then

\[
\Delta E_{\text{ex}}(K = 0) \lesssim \frac{16\pi e^2}{\Omega_c \epsilon_\infty} \epsilon_g \Phi_{1s}(0) \left| \langle u_v,0|u_c,0 \rangle_{G_0} \right|^2 = \frac{e^2}{\alpha_B} \left( \frac{\epsilon_0}{\epsilon_\infty} \right) \left( \frac{\alpha}{\alpha_B} \right)^2 \left| \langle u_v,0|u_c,0 \rangle_{G_0} \right|^2.
\]

Since experimentally \( \Delta E_{\text{ex}}(K = 0) \approx 12 \text{ meV} \), we have \( \left| \langle u_v,0|u_c,0 \rangle_{G_0} \right| \approx 0.45 \).

In most semiconductors the dipole matrix element \( p_{c,v} \) between the conduction and the valence bands does not vanish. In this case the second term in Eq. \[33\] is proportional to \( 1/K^2 \) from the Coulomb interaction times \( K^2 \) from the overlap integrals and therefore from \( \mathbf{k} \cdot \mathbf{p} \) perturbation theory \[27\] is \( \propto (p_{c,v} \cdot \mathbf{K})^2 \), where \( \mathbf{K} \) is the unit vector in the direction of \( \mathbf{K} \). This term, therefore, is responsible for the non-analytic behavior of the energy of dipole-allowed excitons at the zone center, i.e., \( K \rightarrow 0 \), depending on the relative direction of \( \mathbf{K} \) with respect to \( p_{c,v} \) \[8\]. The exchange interaction in this case lifts the degeneracy between longitudinal (\( K \parallel p_{c,v} \)) and transverse (\( K \perp p_{c,v} \)) excitons, with the longitudinal lying higher than the transverse. The same phenomenon appears in optical phonons, i.e., the longitudinal modes have higher energy than the transverse at \( K = 0 \), because in the case of longitudinal oscillations there is charge accumulation (not present in the case of transverse oscillations), which creates an internal electric field \[23\].

By contrast, in Cu$_2$O, the second term of Eq. \[33\] \( \propto K^2 \) makes the total mass of the ortho excitons smaller than \( m_e + m_h \); for the para excitons it vanishes. To estimate this correction, we use \( \mathbf{k} \cdot \mathbf{p} \) perturbation theory to write
\[ |u_{l,q+K/2}\rangle \approx |u_{l,q}\rangle + \frac{\hbar}{m} \sum_{n \neq l} \frac{\langle u_{n,q} | (K/2) \cdot p | u_{l,q}\rangle}{\varepsilon_{l,q} - \varepsilon_{n,q}} |u_{n,q}\rangle, \]

where the sum is over all the bands of parity opposite to that of band \( l \). Thus, for the sums in the second term of Eq. [33],

\[ \sum_{q} \phi_q \langle u_{c,q+K/2} | u_{v,q-K/2}\rangle \approx \left( \frac{\hbar}{2m} \right)^2 \left( \sum_n \frac{\langle u_{c,0} | K \cdot p | u_{n,0}\rangle \langle u_{n,0} | K \cdot p | u_{v,0}\rangle}{(\varepsilon_{c,0} - \varepsilon_{n,0})(\varepsilon_{n,0} - \varepsilon_{v,0})} \right) \Omega_{c}^{1/2} \Phi_{1s}(0), \]

where the sum is over the two negative-parity bands of Cu\(_2\)O. This correction modifies the free dispersion relation of the ortho excitons to

\[ E_K = \frac{\hbar^2 K^2}{2M} \left[ 1 + \frac{1}{3} \frac{M}{\mu_e} \right] \left( \frac{\hbar}{m a_B} \right)^4 \sum_n \frac{(\mathbf{K} \cdot p_{c,n})^2(\mathbf{K} \cdot p_{v,n})^2}{(\varepsilon_{c,0} - \varepsilon_{n,0})^2(\varepsilon_{n,0} - \varepsilon_{v,0})^2}. \]

The above angular momentum functions explain why the exchange interaction is nonzero only for the ortho excitons, as well as why the direct recombination of the para excitons is highly forbidden. If we assume that there is no spin-flip (a higher-order effect), the above angular momentum functions imply that the exchange diagram shown in Fig. 1.

### A. Band structure of Cu\(_2\)O and optical properties

The \( \Gamma^+_6 \) conduction band in Cu\(_2\)O is formed by Cu 4s orbitals and the \( \Gamma^+_7 \) valence band by Cu 3d orbitals \([10]\). The fivefold degenerate (without spin) Cu 3d orbitals split under the crystal field into a higher threefold \( \Gamma^+_2 \) and a lower \( \Gamma^+_1 \) twofold degenerate band. Finally, \( \Gamma^+_2 \) splits further because of the spin-orbit interaction into two bands, a higher \( \Gamma^+_7 \) non-degenerate band and a lower twofold degenerate \( \Gamma^+_8 \) band (Fig. 1).

The total angular momentum functions for the yellow-exciton triplet states are

\[ |J = 1, J_z = 1\rangle = | \uparrow e, \uparrow h\rangle \]
\[ |J = 1, J_z = 0\rangle = \frac{1}{\sqrt{2}} \left( | \uparrow e, \downarrow h\rangle - | \downarrow e, \uparrow h\rangle \right) \]
\[ |J = 1, J_z = -1\rangle = | \downarrow e, \downarrow h\rangle, \]

and for the singlet states,

\[ |J = 0, J_z = 0\rangle = \frac{1}{\sqrt{2}} \left( | \uparrow e, \downarrow h\rangle + | \downarrow e, \uparrow h\rangle \right). \]

The indices \( e, H \) refer to the electron and the hole, respectively: while the electron states are pure spin states, the hole states are total angular momentum states,

\[ | \uparrow h\rangle = \frac{1}{\sqrt{3}} \left[ (X + iY) | \downarrow h\rangle + Z | \uparrow h\rangle \right] \]
\[ | \downarrow h\rangle = \frac{1}{\sqrt{3}} \left[ (X - iY) | \uparrow h\rangle - Z | \downarrow h\rangle \right], \]

where the states with lower case \( h \) are pure spin-states. The spatial functions \( X, Y, Z \) transform as yz, xz and xy, respectively.

The above angular momentum functions explain why the exchange interaction is nonzero only for the ortho excitons, as well as why the direct recombination of the para excitons is highly forbidden. If we assume that there is no spin-flip (a higher-order effect), the above angular momentum functions imply that the exchange diagram shown in Fig.
3 (virtual annihilation of the exciton) vanishes for the singlet. For the triplet state the exchange interaction does not vanish and raises the ortho-exciton with respect to the para-exciton energy. The factor of $2/3$ we used for the calculation of the exchange energy in Eq. (12) comes from the above angular momentum functions. The radiative recombination process of excitons is essentially described by the left (right) half of the virtual annihilation diagram, with the only difference that a real instead of a virtual photon is emitted. The matrix element for the recombination process, therefore, is proportional to $\sqrt{2/3}$ times the result from the spatial part of the calculation for the ortho excitons, but it vanishes for the para excitons. The same physics is responsible for the ortho excitons lying higher than the para excitons, and the direct recombination of the para excitons being highly forbidden.

V. SUMMARY

Based on the effective mass approximation, we have used perturbation theory and the variational method to calculate the binding energy, the Bohr radius as well as the total mass of the 1s-state of the yellow-exciton series. We have shown that the non-parabolicity of the bands gives consistent corrections for the total exciton mass and the exciton binding energy, as well. The coupling of the electrons and the holes to the LO-phonons and the momentum dependence of the dielectric function also contribute to the binding energy. The exchange interaction is responsible for the energy splitting between the triplet and the singlet-state excitons at the zone center, with the triplet lying higher because of the band structure of Cu$_2$O. Finally, the contribution of the exchange interaction to the exciton mass is negligible.

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FIG. 1. Schematic band structure of Cu$_2$O showing the conduction $\Gamma_{6}^{\uparrow}$ band and the $\Gamma_{7}^{\uparrow}$, $\Gamma_{8}^{\uparrow}$ valence bands, split by the spin-orbit splitting, which form the yellow and green-exciton series, respectively.

FIG. 2. The solid line shows the expectation value of the energy of the 1s-exciton in Cu$_2$O as function of the Bohr radius, Eq. (31); the dotted line shows the same function with the central-cell corrections not taken into account.

FIG. 3. The virtual annihilation of an exciton, possible only for pure spin-singlet states.