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Fine structure of excitons in Cu_2O

G. M. Kavoulakis, Yia-Chung Chang, and Gordon Baym
Department of Physics, University of Illinois at Urbana-Champaign, 1110 West Green Street, Urbana, Illinois 61801

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Three experimental observations on $1s$ excitons in Cu_2O 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. [S0163-1829(97)05708-1]

I. INTRODUCTION

The absorption spectrum of light in Cu_2O (Ref. 1) 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.[2] 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 μ is the reduced electron-hole mass and ϵ_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] (2) The mass of the lowest (yellow series) ${}^3S_1$ (ortho) exciton is experimentally $M_o=(3.0\pm0.2)m$,[3,4] where m is the free-electron mass; on the other hand the sum of the electron effective mass $m_e=(0.99\pm0.03)m$ and hole mass $m_h=(0.69\pm0.04)m$ (Ref. 5) is only $m_e+m_h=(1.68\pm0.07)m$. (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 nonparabolicity of the bands.[3,7] Furthermore, the electron-hole interaction is more properly the bare Coulomb interaction modified by the *momentum* and *frequency* dependent dielectric function.[8,9] In addition, the spin-dependent exchange interaction between the electron and the hole lifts the degeneracy between the triplet- and the singlet-state excitons.[6] All these effects become important because the Bohr radius a_B is not large compared with the lattice constant a_{ℓ} of the material.[10] The lattice constant of the unit cell of Cu_2O is 4.26 Å.[11] The Bohr radius of the $1s$ state yellow excitons 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 nonparabolicity of the bands is expected to be significant, since the extent of the exciton wave function in momentum space is of order $1/a_B$, while the width of the Brillouin zone is of order $1/a_{\ell}$. 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 ϵ_∞ 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 ϵ_0 screens the electron-hole interaction. When the Bohr radius is comparable to the lattice constant a_{ℓ}, the momentum dependence of the dielectric function, on scales of $\hbar/a_{\ell}$, becomes important. The more localized $1s$ exciton states are screened by ϵ 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 (Γ_6^+) is at the same point in momentum space as the maximum of the highest valence band, (Γ_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[11] 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 $n\neq1$ lines correspond to excitons with relative angular momentum $l=1$ and for this reason the absorption process is dipole allowed. The electrons in the Γ_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

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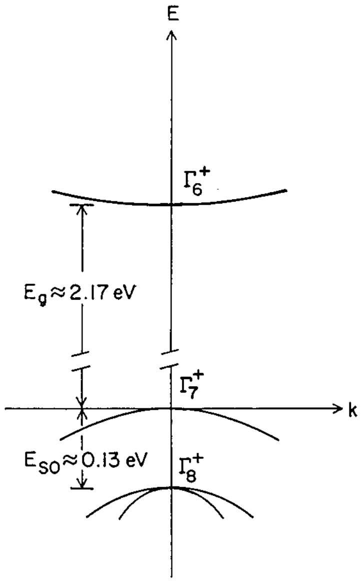

FIG. 1. Schematic band structure of Cu_2O showing the conduction Γ_6^+ band and the Γ_7^+, Γ_8^+ valence bands, split by the spin-orbit splitting, which form the yellow and green exciton series, respectively.

absent from the radiative recombination spectrum of Cu_2O. The lower Γ_8^+ valence band, which lies ≈ 130 meV below the Γ_7^+ band due to the spin-orbit interaction (Fig. 1), forms, with the Γ_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%,[12] and its only result is to modify slightly the exciton binding energies.

Recently high-density excitons in Cu_2O have been observed to obey Bose-Einstein statistics[13–15] and indeed Bose-Einstein condensation[16] has been observed.[17,18] These observations are directly related with the band structure of Cu_2O, as we have shown in Refs. 19 and 20.

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 that underlies the properties of excitons in Cu_2O.[21] We summarize our results in Sec. V.

II. EFFECTIVE-MASS APPROXIMATION FOR EXCITONS

An exciton in the effective-mass approximation is a hydrogenlike bound state of an electron and a hole, with center of mass in a plane-wave state. In this picture 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 that interact through their Coulomb attraction, modified by a dielectric constant ϵ_0, is

$$H=\frac{p_e^2}{2m_e}+\frac{p_h^2}{2m_h}-\frac{e^2}{\epsilon_0|\mathbf{r}_e-\mathbf{r}_h|}, \tag{1}$$

where $\mathbf{p}_i$ 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, $\mathbf{p}$ and $\mathbf{r}$, respectively, and the momentum operator $\mathbf{P}$ of the center of mass as

$$H=\frac{P^2}{2M}+\frac{p^2}{2\mu}-\frac{e^2}{\epsilon_0 r}, \tag{2}$$

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

$$\Psi_{\mathbf{K},nlm}(\mathbf{r},\mathbf{R})=\frac{1}{\sqrt{\Omega}}e^{i\mathbf{K}\cdot\mathbf{R}}\Phi_{nl}(r)Y_l^m(\theta,\phi), \tag{3}$$

where Ω is volume of the crystal, Y_l^m are spherical harmonics, and Φ_{nl} are the radial hydrogenic eigenfunctions. In the state (3) the center of mass of the exciton carries momentum $\hbar\mathbf{K}$. The corresponding eigenenergies are

$$E_{\mathbf{K},n}=E_g+\varepsilon_n^{(0)}+\frac{\hbar^2K^2}{2M}, \tag{4}$$

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

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

$$\Psi_{\mathbf{K},nlm}(\mathbf{r}_e,\mathbf{r}_h)=\sum_{\mathbf{q}}\phi_{\mathbf{q}}\,\Phi_{c,\mathbf{q}+\mathbf{K}/2}(\mathbf{r}_e)\Phi_{v,-\mathbf{q}+\mathbf{K}/2}(\mathbf{r}_h), \tag{5}$$

where the Bloch states are of the usual form

$$\Phi_{j,\mathbf{k}}(\mathbf{r})=u_{j,\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{6}$$

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

Our starting point in this problem is the effective-mass approximation, Eq. (1), which as we now argue is valid as long as the excitons are sufficiently large, as they in fact are in Cu_2O, to satisfy the following restrictions. First of all use of the quadratic kinetic energy in the Hamiltonian [the first and second terms in Eq. (1)] requires that $\phi_{\mathbf{q}}$ be strongly peaked in momentum space around zero, so that the structure of the periodic part of the Bloch functions [Eqs. (5) and (6)] in the range where $\phi_{\mathbf{q}}$ is appreciable can be ignored.[10] For an exciton with a hydrogenic wave function, $\Psi(r)=e^{-r/a_B}/(\pi a_B^3)^{1/2}$, one has $\phi_{\mathbf{q}}=8(\pi a_B^3)^{1/2}/[1+(qa_B)^2]^2$. Quantitatively if k_D is the Debye wave vector, the radius of a sphere with volume equal to that of the first Brillouin zone, then $\phi_{k_D}/\phi_0\approx 7\times 10^{-4}$, for $a_B=5.3$ Å. This value of the Bohr radius is one of the results of our calculation; see Sec. III. In addition the correction terms to the kinetic energy from the nonparabolicity of the bands are, as we show, at most of order 20% of the terms in Eq. (1) for the $1s$ excitons, and considerably smaller for excited-state excitons.

The second approximation in our starting point, Eq. (1), is the use of the long-wavelength dielectric constant in the electron-hole interaction. A more accurate expression for the interaction between the electron and the hole involves the spatially dependent dielectric function,[22] which for large electron and hole separation, approaches the static dielectric constant of the material. This approximation is in general reasonable since the average exciton encompasses a large number of Cu_2O molecules. To see this, note that the lattice constant 4.26 Å describes a cube that includes two Cu_2O molecules, with O at the body center and corners and Cu in a tetrahedron about the central O. The volume of a $1s$ exciton of radius 5.3 Å is approximately eight times the volume of the unit cell, or sixteen times the volume per Cu_2O molecule; therefore to a first approximation, the electron and the hole can be considered to be at an average distance large enough generally to allow use of the static dielectric constant. In conclusion, use of Eq. (1) is quantitatively justifiable for excitons in Cu_2O, with, however, important corrections for the $1s$ exciton—the central-cell corrections. For the excited $(n \geqslant 2)$ states, this model gives excellent agreement with the experimental values of the energy levels.

III. CENTRAL-CELL CORRECTIONS

As we mentioned earlier, the binding energy of excitons is modified by the nonparabolicity of the bands,[3,7] the coupling of the electron and the hole with the longitudinal-optical (LO) phonons,[8] the dependence of the dielectric function on the distance between the electron and the hole[9] and the exchange interaction.[6] In this section we study the first three mechanisms.

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

$$\Delta V_i = \frac{p_i^4 a_{\ell}^2}{24\hbar^2 m_i}. \tag{7}$$

More generally, the perturbation ΔV due to the nonparabolicity of the Hamiltonian is of the form

$$\Delta V = \frac{p_e^4 a_{\ell}^2 C_e}{24\hbar^2 m_e} + \frac{p_h^4 a_{\ell}^2 C_h}{24\hbar^2 m_h}, \tag{8}$$

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 $p^2 P^2$,

$$\Delta V = \Delta V_\alpha + \Delta V_\beta \equiv \frac{p^4 a_{\ell}^2}{24\hbar^2 \mu'} - \frac{p^2 P^2 a_{\ell}^2}{4\hbar^2 M'}, \tag{9}$$

where $1/\mu' \equiv (C_e/m_e) + (C_h/m_h)$ and $M' \equiv (m_e/C_e) + (m_h/C_h)$. The ΔV_α 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 ΔV_α as a perturbation in calculating its contribution to the binding energy. For the central-cell corrections we use a trial hydrogen-like wave function of the form $\Psi(r) = e^{-r/a_B}/(\pi a_B^3)^{1/2}$ but we truncate it outside the first Brillouin zone, assuming that $\Psi_{\mathbf{q}}$, the Fourier transform of $\Psi(r)$, vanishes for $|\mathbf{q}| > k_D$. The reason for truncating $\Psi_{\mathbf{q}}$ is that for values of the Bohr radius smaller or comparable to $1/k_D$, the exciton wave function is spread in momentum space and therefore without the truncation the central-cell corrections are overestimated. The expectation value of ΔV_α in $\Psi_{\mathbf{q}}$ is

$$\begin{aligned}\langle \Delta V_\alpha \rangle &= -\frac{\hbar^2 a_{\ell}^2}{24\mu'} \left(\sum_{|\mathbf{q}|<k_D} |\Psi_{\mathbf{q}}|^2 q^4 \right) \left(\sum_{|\mathbf{q}|<k_D} |\Psi_{\mathbf{q}}|^2 \right)^{-1} \\ &= -\frac{\hbar^2 a_{\ell}^2}{24\mu a_B^4} \frac{m_h C_e + m_e C_h}{m_e + m_h} \frac{I_6(k_D a_B)}{I_2(k_D a_B)},\end{aligned} \tag{10}$$

where

$$I_n(x) = \int_0^x \frac{y^n dy}{(1+y^2)^4}. \tag{11}$$

In the limit $a_B \gg k_D^{-1}$ Eq. (10) gives the result

$$\langle \Delta V_\alpha \rangle = -\frac{5\,\hbar^2 a_{\ell}^2}{24\mu a_B^4} \frac{m_h C_e + m_e C_h}{m_e + m_h}. \tag{12}$$

The second term of Eq. (9), ΔV_β, is the first correction to the total exciton mass due to the nonparabolicity of the bands. This term modifies the free dispersion relation for the center-of-mass motion to

$$E_{\mathbf{K}} = \frac{\hbar^2 K^2}{2M} + \frac{\langle p^2 \rangle a_{\ell}^2}{4M'} K^2 = \frac{\hbar^2 K^2}{2M} \left(1 - \frac{M a_{\ell}^2}{2M' a_B^2} \frac{I_4(k_D a_B)}{I_2(k_D a_B)} \right), \tag{13}$$

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 $a_B \gg k_D^{-1}$ Eq. (13) gives the result

$$E_{\mathbf{K}} = \frac{\hbar^2 K^2}{2M} \left(1 - \frac{M a_{\ell}^2}{2M' a_B^2} \right). \tag{14}$$

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 Cu_2O only one Γ_8^- conduction band, which lies ≈ 449 meV above the Γ_6^+ band, and one very deep Γ_8^- valence band, which lies ≈ 5.6 eV below the Γ_7^+ valence band, have negative parity. The mixing of the Γ_6^+ and Γ_7^+ 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 nonparabolic. To find the constants C_i in lowest order requires diagonalizing a 4×4 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. 21, $|\mathbf{p}_{i,j}|/\hbar \approx 0.13$ 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

$$\frac{\hbar^2 a_\ell^2 C k^4}{24m} \sim \frac{\hbar^2 k^2}{2m} \frac{|\mathbf{p}_{i,j}|^4}{m^2 \Delta_{i,j}^2} \frac{\hbar^2 k^2}{m \Delta_{i,j}}, \tag{15}$$

which gives $C \sim 1$.

The Hamiltonian (1) describes the effective interaction between an electron and a hole at momentum transfer k as

$$V(k) = \frac{4\pi e^2}{k^2 \epsilon_0}. \tag{16}$$

More generally, the interaction is given by

$$V(k,\omega) = \frac{4\pi e^2}{k^2 \epsilon(k,\omega)}, \tag{17}$$

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 ω in the dielectric function.[8] In Cu$_2$O only the Γ_{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, ϵ decreases to $\epsilon_m = 7.11$, while as $\hbar\omega$ increases past 87 meV, ϵ 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 $n = 2,3,4,\ldots$ states the dielectric constant is closer to ϵ_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 ϵ_∞ screens the electron-hole interaction, the expectation value $\langle PE \rangle$, of the Coulomb interaction in the $1s$ state is

$$\langle PE \rangle = -\frac{e^2}{\epsilon_\infty \, a_B}. \tag{18}$$

Since the actual dielectric constant is $\lesssim \epsilon_\infty$, the choice of ϵ_∞ 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,[8] they cannot be applied in our problem because more than one LO-phonon branch 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 $a_B \gg a_\ell$, $\Psi_\mathbf{k}$ 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,

$$\epsilon(k) \approx \epsilon_\infty - (k a_\ell)^2 \, d, \tag{19}$$

where, as we calculate below, $d \approx 0.18$ for Cu$_2$O. Expanding,

$$\frac{4\pi e^2}{k^2 \epsilon(k)} \approx \frac{4\pi e^2}{k^2 \epsilon_\infty} + \frac{4\pi e^2}{\epsilon_\infty^2} a_\ell^2 d, \tag{20}$$

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

$$\Delta V_d(\mathbf{r}) = -\frac{4\pi e^2}{\epsilon_\infty^2} d a_\ell^2 \, \delta(\mathbf{r}), \tag{21}$$

which lowers the exciton energy by

$$\langle \Delta V_d \rangle = -\frac{4\pi e^2}{\epsilon_\infty^2} d a_\ell^2 |\Psi_{\text{exact}}(0)|^2, \tag{22}$$

where $\Psi_{\text{exact}}(r)$ is the exact (unknown) wave function of the $1s$ state. If we evaluate ΔV_d with the trial wave function $\Psi(r)$ truncated outside the first Brillouin zone we find

$$\begin{aligned} \langle \Delta V_d \rangle &= -\frac{4\pi e^2 d a_\ell^2}{\Omega \epsilon_\infty^2} \Big| \sum_{|\mathbf{q}|<k_D} \Psi_\mathbf{q} \Big|^2 \Bigg(\sum_{|\mathbf{q}|<k_D} |\Psi_\mathbf{q}|^2 \Bigg)^{-1} \\ &= -\frac{2 d e^2 a_\ell^2}{\pi \epsilon_\infty^2 a_B^3} \frac{[I_2'(k_D a_B)]^2}{I_2(k_D a_B)}, \end{aligned} \tag{23}$$

where $\Psi_\mathbf{q}$ is again the Fourier transform of $\Psi(r)$. Also

$$I_n'(x) = \int_0^x \frac{y^n dy}{(1+y^2)^2}. \tag{24}$$

In the limit $a_B \gg k_D^{-1}$ Eq. (23) gives the result

$$\langle \Delta V_d \rangle = -\frac{4\pi e^2}{\epsilon_\infty^2} d a_\ell^2 |\Phi_{1s}(0)|^2 = -\frac{4 d e^2 a_\ell^2}{\epsilon_\infty^2 a_B^3}. \tag{25}$$

To estimate the constant d we follow Ref. 23. The Lindhard result gives for the dielectric function

$$\epsilon(k,\omega) = 1 + \frac{4\pi e^2}{\Omega_c k^2} \sum_{\mathbf{q},l,l'} \frac{|\langle u_{l',\mathbf{k}+\mathbf{q}} | u_{l,\mathbf{q}} \rangle|^2}{\varepsilon_{l',\mathbf{k}+\mathbf{q}} - \varepsilon_{l,\mathbf{q}} - \hbar\omega}, \tag{26}$$

where Ω_c is the volume of the unit cell and $\varepsilon_{l,\mathbf{q}}$ is the energy of band l at point $\mathbf{q}$ 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 Γ_8^- conduction band c' (which lies $\approx$ 449 meV above the lowest Γ_6^+ conduction band) and the highest Γ_7^+ valence band v. The overlap integral in Eq. (26) satisfies the sum rule[24]

$$\sum_{l'} |\langle u_{l',\mathbf{k}+\mathbf{q}} | u_{l,\mathbf{q}} \rangle|^2 (\varepsilon_{l',\mathbf{k}+\mathbf{q}} - \varepsilon_{l,\mathbf{q}}) = \frac{\hbar^2 k^2}{2m}, \tag{27}$$

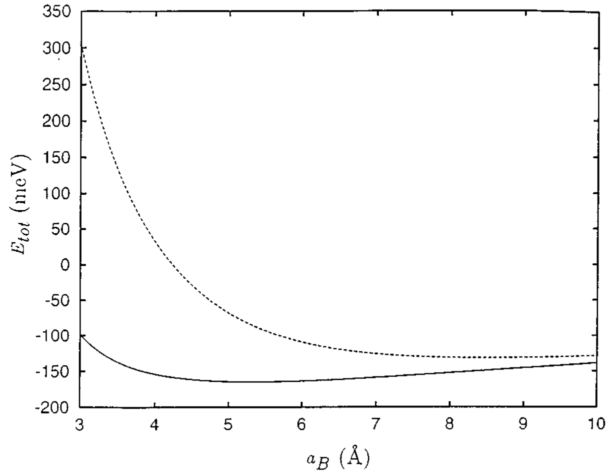

FIG. 2. The solid line shows the expectation value of the energy of the $1s$ exciton in Cu_2O as a function of the Bohr radius, Eq. (31); the dotted line shows the same function with the central-cell corrections not taken into account.

which as in Ref. 23 allows us to write the approximate result for $\epsilon(k)$, with $\mathbf{k}$ restricted in the first zone,

$$\epsilon(k) \approx 1 + \frac{4\pi e^2 \hbar^2}{m\Omega_c} \sum_{\mathbf{q}} (\varepsilon_{c',\mathbf{k}+\mathbf{q}} - \varepsilon_{v,\mathbf{q}})^{-2}. \tag{28}$$

If we define

$$\Sigma(k) \equiv \sum_{\mathbf{q}} (\varepsilon_{c',\mathbf{k}+\mathbf{q}} - \varepsilon_{v,\mathbf{q}})^{-2}, \tag{29}$$

the dielectric function can be written as

$$\epsilon(k) = 1 + (\epsilon_\infty - 1)\Sigma(k)/\Sigma(0). \tag{30}$$

We calculate the above quantity numerically, using the effective mass of the conduction Γ_8^- band $m_e' = 0.35m$, the effective mass of the valence Γ_7^+ band $m_h = 0.69m$ and the energy gap between them, $\approx$ 2.62 eV. The integration over $\mathbf{q}$ is restricted to $q \leq k_D$. For $k \to 0$, Eq. (30) is of the form of Eq. (19) with $d \approx 0.18$.

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

$$E_{\text{tot}}(a_B) = \frac{\hbar^2}{2\mu a_B^2} - \frac{e^2}{\epsilon_\infty a_B} - \frac{C}{24\mu a_B^4} \hbar^2 a_{\ell}^2 \frac{I_6(k_D a_B)}{I_2(k_D a_B)} - \frac{2}{\pi \epsilon_\infty^2 a_B^3} d e^2 a_{\ell}^2 \frac{[I_2'(k_D a_B)]^2}{I_2(k_D a_B)}. \tag{31}$$

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 nonparabolicity 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, $\langle \Delta V_d \rangle$. In the third term we have made the simplifying assumption $C_e = C_h = C$. 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 (15) gave us an order of magnitude estimate $C \sim 1$. The value $C = 1.35$ gives the result $a_{B,0} = 5.3$ Å and the observed total ortho-exciton mass of $3m$. This choice for C then yields $E_{\text{tot}}(a_{B,0}) = 164.9$ 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, $\langle \Delta V_a \rangle = -65.3$ meV, and $\langle \Delta V_d \rangle = -15.0$ meV. We expect to find a larger binding energy here than the experimental value, since the choice of ϵ_∞ for the dielectric constant overestimates the potential energy. The Bohr radius used in the literature for excitons in Cu_2O 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.

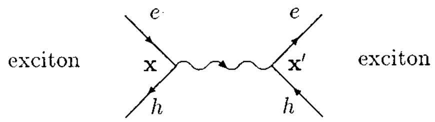

FIG. 3. The virtual annihilation of an exciton, possible only for pure spin-singlet states.

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 nonparabolicity of the bands is the same for both the singlet and the triplet; the correction due to the exchange interaction that 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 $m_e + m_h \approx 1.68m$ for the excited states. Neither the $n = 1$ para-exciton mass nor the $n \geq 2$ exciton masses has yet been measured.

IV. BAND STRUCTURE OF Cu_2O – EXCHANGE INTERACTION AND OPTICAL PROPERTIES OF EXCITONS IN Cu_2O

The virtual annihilation of an exciton, shown in Fig. 3, is responsible for raising the ortho exciton by an energy $\Delta E_{\text{ex}} = 12$ meV above the para exciton at the zone center ($K = 0$) of Cu_2O.[6] The energy splitting $\Delta E_{\text{ex}}(K)$ is given by

$$\Delta E_{\text{ex}}(K) = \frac{2}{3} \int \Psi_{\mathbf{K}}(\mathbf{x},\mathbf{x}) \frac{e^2}{\epsilon_\infty |\mathbf{x} - \mathbf{x}'|} \Psi_{\mathbf{K}}^*(\mathbf{x}',\mathbf{x}')\, d\mathbf{x}\, d\mathbf{x}'. \tag{32}$$

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 nonzero 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_2O makes the exchange interaction nonzero for the ortho excitons and zero for the para excitons, shifting the ortho excitons higher in energy than the para excitons. Using Eq. (5) for the exciton wave function we find that

$$\begin{aligned}\Delta E_{\mathrm{ex}}(K)=&\frac{2}{3}\frac{1}{\Omega_c}\sum_{\mathbf{q},\mathbf{p},\mathbf{G}\neq 0}\frac{4\pi e^2}{|\mathbf{G}|^2\epsilon_\infty}\phi_{\mathbf{q}}\langle u_{v,\mathbf{q}}|u_{c,\mathbf{q}}\rangle_{\mathbf{G}}\\ &\times\phi^*_{\mathbf{p}}\langle u_{v,\mathbf{p}}|u_{c,\mathbf{p}}\rangle^*_{\mathbf{G}}+\frac{2}{3}\frac{1}{\Omega_c}\\ &\times\sum_{\mathbf{q},\mathbf{p}}\frac{4\pi e^2}{|\mathbf{K}|^2\epsilon_\infty}\phi_{\mathbf{q}}\langle u_{v,\mathbf{q}-\mathbf{K}/2}|u_{c,\mathbf{q}+\mathbf{K}/2}\rangle\\ &\times\phi^*_{\mathbf{p}}\langle u_{v,\mathbf{p}-\mathbf{K}/2}|u_{c,\mathbf{p}+\mathbf{K}/2}\rangle^*,\end{aligned}\tag{33}$$

where

$$\langle u_{v,\mathbf{q}}|u_{c,\mathbf{p}}\rangle_{\mathbf{G}}=\int d\mathbf{x}\; u_{c,\mathbf{p}}(\mathbf{x})u^*_{v,\mathbf{q}}(\mathbf{x})e^{i\mathbf{G}\cdot\mathbf{x}}.\tag{34}$$

The first sum in Eq. (33) is over all the nonzero 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 E_g. As we show below, the overlap integrals[25,26] that 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 Eq. (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 ΔE_{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

$$\begin{aligned}\Delta E_{\mathrm{ex}}(K=0)\lesssim&\frac{16\pi e^2}{\Omega_c\epsilon_\infty}\Omega_c|\Phi_{1s}(0)|^2\frac{a_\ell^2}{4\pi^2}|\langle u_{v,\mathbf{0}}|u_{c,\mathbf{0}}\rangle_{\mathbf{G}_0}|^2\\ =&\frac{e^2}{a_B\epsilon_0}\frac{4}{\pi^2}\left(\frac{\epsilon_0}{\epsilon_\infty}\right)\left(\frac{a_\ell}{a_B}\right)^2|\langle u_{v,\mathbf{0}}|u_{c,\mathbf{0}}\rangle_{\mathbf{G}_0}|^2.\end{aligned}\tag{35}$$

Since experimentally $\Delta E_{\mathrm{ex}}(K=0)\approx 12$ meV, we have $|\langle u_{v,\mathbf{0}}|u_{c,\mathbf{0}}\rangle_{\mathbf{G}_0}|\approx 0.45$.

In most semiconductors the dipole matrix element $\mathbf{p}_{c,v}$ 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 $\sim(\mathbf{p}_{c,v}\cdot\hat{\mathbf{K}})^2$, where $\hat{\mathbf{K}}$ is the unit vector in the direction of $\mathbf{K}$. This term, therefore, is responsible for the nonanalytic behavior of the energy of dipole-allowed excitons at the zone center, i.e., $K\to 0$, depending on the relative direction of $\mathbf{K}$ with respect to $\mathbf{p}_{c,v}$.[10] The exchange interaction in this case lifts the degeneracy between longitudinal ($\mathbf{K}\|\mathbf{p}_{c,v}$) and transverse ($\mathbf{K}\perp\mathbf{p}_{c,v}$) 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.[28]

By contrast, in $\mathrm{Cu_2O}$, the second term of Eq. (33) ($\sim K^2$) 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

$$|u_{l,\mathbf{q}+\mathbf{K}/2}\rangle\approx|u_{l,\mathbf{q}}\rangle+\frac{\hbar}{m}\sum_{n\neq l}\frac{\langle u_{n,\mathbf{q}}|(\mathbf{K}/2)\cdot\mathbf{p}\;|u_{l,\mathbf{q}}\rangle}{\varepsilon_{l,\mathbf{q}}-\varepsilon_{n,\mathbf{q}}}|u_{n,\mathbf{q}}\rangle,\tag{36}$$

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),

$$\begin{aligned}&\sum_{\mathbf{q}}\phi_{\mathbf{q}}\langle u_{c,\mathbf{q}+\mathbf{K}/2}|u_{v,\mathbf{q}-\mathbf{K}/2}\rangle\\ &\approx\left(\frac{\hbar}{2m}\right)^2\left(\sum_n\frac{\langle u_{c,0}|\mathbf{K}\cdot\mathbf{p}\;|u_{n,0}\rangle\langle u_{n,0}|\mathbf{K}\cdot\mathbf{p}\;|u_{v,0}\rangle}{(\varepsilon_{c,0}-\varepsilon_{n,0})(\varepsilon_{n,0}-\varepsilon_{v,0})}\right)\\ &\quad\times\Omega_c^{1/2}\Phi_{1s}(0),\end{aligned}\tag{37}$$

where the sum is over the two negative-parity bands of $\mathrm{Cu_2O}$. This correction modifies the free dispersion relation of the ortho excitons to

$$\begin{aligned}E_{\mathbf{K}}=&\frac{\hbar^2K^2}{2M}\left[1+\frac{1}{3}\frac{M}{\mu}\frac{\epsilon_0}{\epsilon_\infty}\left(\frac{\hbar}{ma_B}\right)^4\right.\\ &\left.\times\sum_n\frac{(\hat{\mathbf{K}}\cdot\mathbf{p}_{c,n})^2(\hat{\mathbf{K}}\cdot\mathbf{p}_{n,v})^2}{(\varepsilon_{c,0}-\varepsilon_{n,0})^2(\varepsilon_{n,0}-\varepsilon_{v,0})^2}\right].\end{aligned}\tag{38}$$

The above equation predicts that the ortho-exciton mass due to the correction caused by the exchange interaction is not isotropic. Using the estimate $|\mathbf{p}_{i,j}|/\hbar\approx 0.13$ Å^{-1} and the energy levels of $\mathrm{Cu_2O}$, we find that the correction [i.e., the second term in the parentheses in Eq. (38)] of the exchange interaction to the (ortho) exciton mass is negligibly small, ≈ 0.001.

A. Band structure of Cu$_2$O and optical properties

The Γ_6^+ conduction band in $\mathrm{Cu_2O}$ is formed by Cu $4s$ orbitals and the Γ_7^+ valence band by Cu $3d$ orbitals.[11] The fivefold degenerate (without spin) Cu $3d$ orbitals split under the crystal field into a higher threefold Γ_{25}^+ and a lower Γ_{12}^+ twofold degenerate band. Finally, Γ_{25}^+ splits further because of the spin-orbit interaction into two bands, a higher Γ_7^+ nondegenerate band and a lower twofold degenerate Γ_8^+ band (Fig. 1).

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

$$|J=1,J_z=1\rangle=|\uparrow_e,\uparrow_H\rangle,\tag{39}$$

$$|J=1,J_z=0\rangle=\frac{1}{\sqrt{2}}(|\uparrow_e,\downarrow_H\rangle-|\downarrow_e,\uparrow_H\rangle),\tag{40}$$

$$|J=1,J_z=-1\rangle=|\downarrow_e,\downarrow_H\rangle,\tag{41}$$

and for the singlet states,

$$|J=0,J_z=0\rangle=\frac{1}{\sqrt{2}}(|\uparrow_e,\downarrow_H\rangle+|\downarrow_e,\uparrow_H\rangle).\tag{42}$$

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,

$$|\uparrow_H\rangle = -\frac{1}{\sqrt{3}}[(X+iY)\ |\downarrow_h\rangle + Z\ |\uparrow_h\rangle] \tag{43}$$

and

$$|\downarrow_H\rangle = -\frac{1}{\sqrt{3}}[(X-iY)\ |\uparrow_h\rangle - Z\ |\downarrow_h\rangle], \tag{44}$$

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. (32) 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 nonparabolicity 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_2O. Finally, the contribution of the exchange interaction to the exciton mass is negligible.

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