Radiative coupling between multi-component excitons in ZnO thin films

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Abstract. We study the linear optical responses of ZnO, in which the degeneracy of the p-like states at the Γ point is lifted by the crystal field and spin-orbit interaction, and the $n=1$ $(A$- and B-) excitons are optically allowed under the condition of $E \perp c$. The coupled system of the light and multi-component excitons forms the three branches, i.e., lower, middle, and upper branches through the radiative coupling between A- and B-excitons. We theoretically reveal the ratio of the components of A- and B-excitons in the respective branches which is determined from diagonalization of self-consistent equation of the nonlocal induced-polarization and Maxwell electric field.

1. Introduction
Wurtzite ZnO is one of the promising materials for opto-electronic devices because of its high excitonic stability due to the large exciton binding energy. In wZnO, the crystal field and spin-orbit interaction lifts the degeneracy of the p-like states at the Γ point of valence bands. We present a theoretical study to reveal that the main quantum number $n=1$ (namely A- and B-) excitons are coupled via radiation in bulk system and thin films. In particular for thin films, radiative properties, such as the radiative shift, and the radiative width of diagonalized eigenstates, which appear in the optical spectra, vary with the film thickness according to the thickness-dependent ratio of the components of A- and B-excitons. This situation is in striking contrast with the picture in conventional analysis to identify a single component solely contributing to each spectral peak. In this study, we consider the film thickness of weak confinement regime where the centre-of-mass (c. m.) motions of excitons are confined. Especially, we focus on the regime beyond the long wavelength approximation (LWA) where the microscopic nonlocal response plays an important role. In such regime, A- and B-exciton are coupled in a drastic way through the wave-wave coupling between radiation and excitons [1], forming upper branches (UBs), middle branches (MBs), and lower branches (LBs) as observed in cavity polaritons [2]. Further, the phase-matched modes exhibit ultrafast radiative decay time. This study will change the conventional view of ZnO excitons in film samples, which will be definitely helpful for future development of optical devices of this material.

2. Theoretical framework
As a model system, we considered c. m. motions of excitons are along the z-axis (the optical axis). In the case that relative motions of electron and hole are regarded as the same with...
that in bulk system, the transition matrix element of the polarization operator \( \rho_{\sigma \lambda}(z) \) is written as
\[
\rho_{\sigma \lambda}(z) = \sqrt{\frac{E_{\sigma} f_{\sigma}}{8\pi}} g_{\sigma \lambda}(z),
\]
where \( \sigma \) is a band index, \( E_{\sigma} \) is the bulk transverse energy of \( \sigma \) exciton, \( f_{\sigma} \) is the oscillator strength, and \( g_{\sigma \lambda}(z) \) is the wave function of excitons’ c. m. motion.

According to the Kubo formula in the site representation, the induced polarization \( P(z, \omega) \) is described as
\[
P(z, \omega) = \int dz' \chi(z, z'; \omega) E(z', \omega),
\]
where the nonlocal susceptibility \( \chi(z, z'; \omega) \) is given as
\[
\chi(z, z'; \omega) = \sum_{\sigma} \sum_{\lambda} \frac{\rho_{\sigma \lambda}(z) \rho_{\sigma \lambda}^*(z')}{E_{\sigma \lambda} - \hbar \omega - i\Gamma_{\sigma}}.
\]
In this expression, \( \Gamma_{\sigma} \) is a dephasing constant, and \( E_{\sigma \lambda} \) is the energy of excitons in the framework of standard effective-mass approximation written as
\[
E_{\sigma \lambda} = E_{\sigma} + \frac{k_{\sigma \lambda}^2}{2M_{\sigma}}, \quad \text{where} \quad k_{\sigma \lambda} \text{ is the} \ \lambda \text{th quantized wave vector, and } M_{\sigma} \text{ is the total mass of the exciton parallel to z-axis.}
\]

We can self-consistently solve this constitutive equation and the Maxwell equation, given by
\[
\frac{\partial}{\partial \omega} E(z, \omega) - q^2 \epsilon_b E(z, \omega) = 4\pi q^2 P(z, \omega), \quad \text{where} \quad q = \omega/c \quad \text{is the wavenumber of light and} \quad \epsilon_b \quad \text{is the background dielectric constant.}
\]

This solution is based on the nonlocal response theory [3], and in particular, we extended the method in Ref. [4] to the multi-component excitons. Using Green’s function \( G(z, z'; \omega) \) [5], the electric field \( E(z, \omega) \) is written as follows:
\[
E(z, \omega) = E^{0}(z, \omega) + 4\pi q^2 \int dz G(z, z'; \omega) P(z', \omega), \quad \text{where} \quad E^{0}(z, \omega) \text{ is the electric field of the incident light.}
\]

We derived a simultaneous system of linear equations [4]:
\[
(E_{\sigma' \lambda'} - \hbar \omega - i\Gamma_{\sigma'}) H_{\sigma' \lambda'} + \sum_{\sigma} \sum_{\lambda} A_{\sigma' \sigma \lambda \lambda} H_{\sigma \lambda} = F_{\sigma' \lambda'}^{(0)},
\]
where \( H_{\sigma \lambda} \equiv (E_{\sigma \lambda} - \hbar \omega - i\Gamma_{\sigma})^{-1} \int dz \rho_{\sigma \lambda}^*(z) E(z, \omega) \) and \( F_{\sigma \lambda}^{(0)} \equiv \int dz \rho_{\sigma \lambda}^*(z) E^{0}(z, \omega) \). In Eq. (2), \( A_{\sigma' \sigma \lambda \lambda} \) indicates the interaction between the induced polarizations originating from the \( \lambda \)th states of the \( \sigma' \) exciton and the \( \lambda \)th states of the \( \sigma \) exciton.

Equation (2) can be rewritten in a matrix form as \( S H = F^{(0)} \). \( \det[S] \) provides the complex eigenvalues \( \Omega \) of the exciton-radiation coupled system. The real part of the eigenmodes \( \text{Re}[\hbar \Omega] \) provides the eigenenergies of the excitons including the radiative shift. The imaginary part of the eigenmodes \( \text{Im}[\hbar \Omega] \) indicates the radiative width. We defined the diagonalized density \( D_{\sigma \lambda} \)
\[
D_{\sigma \lambda} = \frac{|H_{\sigma \lambda}|^2}{\sum_{\sigma \lambda} |H_{\sigma \lambda}|^2}.
\]

This quantity indicates the ratio of the \( \lambda \)th \( \sigma' \) exciton component.

3. Exciton-polaritons in bulk system

In bulk system, the wavefunction of c. m. motion of free excitons is written as
\[
g_{\sigma \lambda}(z) = \sqrt{\frac{\Gamma}{L}} e^{ik_{\lambda z}},
\]
where \( L \) is normalization factor, and \( k_{\lambda} \) satisfies the periodic boundary condition. We use Green’s function of one-dimension free space in the wavenumber representation as
\[
\tilde{G}(k, k'; \omega) = \frac{\delta(k-k')}{\epsilon_b q^2 - k^2}.
\]

Radiative correction \( A_{\sigma' \sigma \lambda \lambda} \) is written as
\[
A_{\sigma' \sigma \lambda \lambda} = \frac{q^2}{2} \sqrt{\frac{\int \sigma' \sigma' E_{\sigma' \sigma} E_{\sigma'} \omega}{\epsilon_b q^2 - k^2}} \delta' \delta' \lambda \lambda.
\]

\( A_{\sigma' \sigma \lambda \lambda} \) has the finite value under the condition that both \( \sigma' \) and \( \sigma \) exciton have the same wavenumber (\( \lambda' = \lambda \)), even though \( \sigma' \) is different from \( \sigma \). Therefore, A- and B-excitons
couple with each other via radiation even in bulk system. Det[$\mathbf{S}$] provides the exciton-polariton dispersion relation in bulk system as follows

$$\frac{c^2 k^2}{\omega^2} = \epsilon_b + \frac{1}{2} f_A E_A \left( \frac{k^2}{2 M_A} - \hbar \omega - i \Gamma_A \right) + \frac{1}{2} f_B E_B \left( \frac{k^2}{2 M_B} - \hbar \omega - i \Gamma_B \right).$$  \hspace{1cm} (5)

Assuming a ZnO sample, we use the following parameters, $E_A = 3.3758$ eV, $E_B = 3.3810$ eV [6], $\epsilon_b = 3.75$, $f_A = 0.0125$, $f_B = 0.0125$, $\Gamma_A = \Gamma_B = 0$ meV, $M_A = 1.0 m_0$, $M_B = 0.8 m_0$, where $m_0$ is the electron rest mass.

![Figure 1](image.png)

**Figure 1.** (a) Exciton-polariton dispersion relation obtained from Eq. (5), and wavenumber dependence of the diagonalized density $D_\sigma$ for (b) lower polariton branch (LPB), (c) middle polariton branch (MPB), (d) upper polariton branch (UPB).

Three exciton-polariton branches, namely LPB, MPB, and UPB, appear in the dispersion relation in Figs. 1(a). The diagonalized density $D_{\sigma\lambda}$ that indicates the ratio of A- and B-component for each branch is shown in Figs. 1(b), (c), and (d). We found that $D_A : D_B \approx 0.7 : 0.3$ for MPB and $D_A : D_B \approx 0.3 : 0.7$ for UPB at $k = 0$. This means that the radiative coupling effect between A- and B-exciton is significant even in bulk system. We should remark that LT-splitting energy of $\sigma$ exciton is not proportional to oscillator strength $f_\sigma$ due to this effect.

### 4. A and B excitons including radiative correction in thin films

We considered a thin film whose film thickness is $d$. In order to address the distortion of wavefunctions near the surface of the film, we employed the Transition Layer Model (TLM) [7]. In this model, $k_{\sigma\lambda}$ satisfies the following quantization condition: $k_{\sigma\lambda} d - 2 \tan^{-1}(k_{\sigma\lambda}/P_\sigma) = \lambda \pi$ ($\lambda = 1, 2, \cdots$), where $P_\sigma$ ($P_A = 1/1.6 \text{ cm}^{-1}$, $P_B = 1/1.8 \text{ cm}^{-1}$) is a decay constant of evanescent wave of c. m. motion (see Ref [7]). Radiative correction $A_{\sigma'\sigma\lambda\lambda}$ is written as

$$A_{\sigma'\sigma\lambda\lambda} = -4\pi q^2 \int \int \rho_{\sigma'\lambda'}(z) G(z, z'; \omega) \rho_{\sigma\lambda}(z') dz dz', \hspace{1cm} (6)$$

where $G(z, z'; \omega)$ is Green’s function for planar structure in the site representation [5].
Figure 2. (a) Diagonalized density $D_{\sigma \lambda}$ for the film thickness $d = 150$ nm, which indicates the ratio of $\lambda$th $\sigma$ exciton component. Red (blue) dots means A- (B-) exciton components. (b) Eigen energies of excitons including radiative correction obtained from $\text{Det}[S]$. Horizontal dashed line means the film thickness 150 nm. (c) Radiative widths.

Figures 2 show (a) diagonalized density $D_{\sigma \lambda}$ for the film thickness $d = 150$ nm, which indicates the ratio of $\lambda$th $\sigma$ exciton component, (b) eigen energies of excitons including radiative correction obtained from $\text{Det}[S]$, and (c) radiative widths. Each exciton mode shows a large and strongly size-dependent radiative shift, depending on the radiation phase matching [1]. Additionally, the radiative width of each mode attains a maximum value at the best radiation phase matching (Figs. 2(c)), which leads to ultrafast radiative decays. In regard to the ratio of the component (Figs. 2 (a)), $\lambda = 1, 2$th A and B exciton have significant values in MBs and UBs, though A-exciton components are dominant in LBs.

5. Conclusion

Eigenmodes and its ratio of each (A- and B-) exciton component in bulk system and thin film structures for ZnO are theoretically revealed by the nonlocal response theory. In bulk system, both A- and B-exciton components have significant density $D_{\sigma}$ in three branches, namely LPB, MPB, and UPB, even for $k = 0$. In thin film structures, the radiative coupling between A and B components strongly affects the formation of mode structures. Due to this effect, a very large radiative shift and width are realized. From the aspect of ratio of the components, both A- and B-exciton components have significantly high rate in MBs and UBs.

These results are also expected to be important in the discussion of the valence-band-ordering of ZnO [8] because the density of each A- and B-exciton components through the radiative coupling determine the ratio of the components in the optical spectra.

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