Exploring excitonic signal in optical conductivity of ZnO through first-order electron-hole vertex correction

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Abstract. The emergence of excitonic signal in the optical response of a wide band-gap semiconductor has been a common knowledge in physics. There have been numerous experimental studies exploring the important role of excitons on influencing both the transport and optical properties of the materials. Despite the existence of much information on excitonic effects, there has not been much literature that explores detailed theoretical explanation on how the exitonic signal appears and how it evolves with temperature. Here, we propose a theoretical study on the optical conductivity of ZnO, a well-known wide band-gap semiconductor that we choose as a case study. ZnO has been known to exhibit excitonic states in its optical spectra in the energy range of ∼3.13-3.41 eV, with a high exciton binding energy of ∼60 meV. An experimental study on ZnO in 2014 revealed such a signal in its optical conductivity spectrum. We present a theoretical investigation on the appearance of excitonic signal in optical conductivity of ZnO. We model the wurtzite ZnO within an 8-band k.p approximation. We calculate the optical conductivity by incorporating the first-order vertex correction derived from the Feynman diagrams. Our calculation up to the first-order correction spectrum qualitatively confirms the existence of excitons in wurtzite ZnO.

1. Introduction

ZnO is a wide band gap semiconductor (∼3.37eV) [1] that has been interesting for decades for which a lot of research have been done considering its potential for optoelectronic application [2–5]. ZnO has been known to exhibit excitonic signals in its absorption and reflection spectra [6]. A pretty recent experimental study [7] shows further that ZnO posses a quite distinct excitonic level below the band gap. The combination of measurements of dielectric functions, photoluminescence, and optical conductivity unveil the excitonic signals at the energy range of ∼3.16-3.41 eV. Here we present a theoretical study on the appearance of such an excitonic signal in optical conductivity of wurtzite ZnO. We model the ZnO band structure within an 8-band k.p approximation, which has proved to be succesful for studying bulk and quantum-well semiconductors [4, 8, 9]. We calculate the optical conductivity using Feynman diagrams up to the first-order electron-hole vertex correction of the current-current correlation function defined in Matsubara frequency domain. Later we do analytic continuation to transform the optical conductivity into real frequency domain. The electron-hole interaction is incorporated in the calculation to reveal the excitonic signal in the optical conductivity spectrum.
2. Model
Our 8-band \( k.p \) model Hamiltonian is constructed as an extended version of the \( 6 \times 6 \) \( k \cdot p \) Hamiltonian for a strained wurtzite crystal derived by S. L. Chuang and C. S. Chang \([10]\). With the addition of the conduction \( s \)-like band and leaving out the strain elements, the Hamiltonian matrix we use to calculate the physical properties of our ZnO system is

\[
H_{\text{tot}} = \begin{pmatrix}
U_c & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & F & -K^* & -H^* & 0 & 0 & 0 & 0 \\
0 & -K & G & H & 0 & 0 & 0 & \Delta \\
0 & -H & H^* & \lambda & 0 & 0 & \Delta & 0 \\
0 & 0 & 0 & U_c & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & F & -K & H & 0 \\
0 & 0 & \Delta & 0 & -K^* & G & -H^* & 0 \\
0 & \Delta & 0 & 0 & H^* & -H & \lambda & 0
\end{pmatrix},
\]

(1)

with matrix elements

\[
U_c = E_c + A_2'(k_x^2 + k_y^2) + A_1'k_z^2,
\]

\[
F = \Delta_1 + \Delta_2 + \lambda + \theta,
\]

\[
G = \Delta_1 + \Delta_2 + \lambda + \theta,
\]

\[
\lambda = \frac{\hbar^2}{2m_o} \left[ A_1'k_x^2 + A_2'(k_x^2 + k_y^2) \right],
\]

\[
\theta = \frac{\hbar^2}{2m_o} \left[ A_1'k_z^2 + A_4'(k_x^2 + k_y^2) \right],
\]

\[
K = \frac{\hbar^2}{2m_o} A_0'(k_x^2 + ik_y)^2.
\]

\[
H = \frac{\hbar^2}{2m_o} A_0'(k_x^2 + ik_y)k_z,
\]

\[
\Delta = \sqrt{2}\Delta_3.
\]

\[
A_1' = \frac{\hbar^2}{2m_o||} - \frac{(P)_1^2}{E_g},
\]

\[
A_2' = \frac{\hbar^2}{2m_o^\parallel} - \frac{(P)_2^2}{E_g},
\]

\[
(P)_1^2 = \frac{\hbar^2}{2m_o} \left( \frac{m_o}{m_o^\parallel} - 1 \right) \frac{(E_g + \Delta_1 + \Delta_2)(E_g + 2\Delta_2) - 2\Delta_3^2}{(E_g + 2\Delta_2)},
\]

\[
(P)_2^2 = \frac{\hbar^2}{2m_o} \left( \frac{m_o}{m_o^\parallel} - 1 \right) \frac{E_g[(E_g + \Delta_1 + \Delta_2)(E_g + 2\Delta_2) - 2\Delta_3^2]}{(E_g + \Delta_1 + \Delta_2)(E_g + 2\Delta_2) - 2\Delta_3^2}.
\]

\( \Delta_1 \) is the crystal-field splitting parameter, \( \Delta_2 \) and \( \Delta_3 \) are parameters related to the spin-orbit splitting energy \( \Delta_s \), \( \Delta_2 = \Delta_3 = \frac{2\Delta_s}{3} \).

3. Calculation
The calculation of optical conductivity is performed in two steps according the Feynman diagrams of the current-current correlation function up to first-order in electron-hole vertex correction as depicted in Fig.1. First, we calculate the "bare" optical conductivity which does not incorporate the electron-hole interaction. The formula can be derived from the simple "bubble" diagram of the current-current correlation function (see Fig.1a) as

\[
\Pi_{\alpha\beta}(i\omega_n) = \frac{e^2}{\beta \hbar} \sum_{l=-\infty}^{\infty} \sum_{k} \text{Tr} \left[ v^{\alpha}(k)G_0(k, i\omega_l)v^{\beta}(k)G_0(k, i\omega_l + i\omega_n) \right],
\]

(3)
which is known as the Kubo formula. Second, we calculate the first-order electron-hole vertex correction to the "bubble" diagram (see Fig. 1b). The attractive Coulomb interaction between the excited electron in the conduction band and the hole created in the valence band is represented by the wiggly line. The second diagram can be translated into a mathematical form as

\[
\Pi_{\omega_n} = T \sum_{\omega_l} \sum_{\omega_q} \sum_{\omega_n} \sum_{k} \sum_{\lambda_7} \sum_{\lambda_3} \sum_{\lambda_0} \left( \sum_{\lambda_8} \Sigma_{\lambda_1} G_{\lambda_7,\lambda_8}(k, i\omega_l) \nu_{\lambda_8,\lambda_1}(k) G_{\lambda_3,\lambda_2}(k, i\omega_l + i\omega_n) \right) U(q) \\
\left( \sum_{\lambda_4} \Sigma_{\lambda_5} G_{\lambda_3,\lambda_4}(k + q, i\omega_l + i\omega_q + i\omega_n) \nu_{\lambda_4,\lambda_0}(k + q) G_{\lambda_5,\lambda_0}(k + q, i\omega_l + i\omega_q) \right).
\]

To transform the formula from Matsubara- to real-frequency domain we have to do analytic continuation. For the "bare" part of the optical conductivity, the analytic continuation from Matsubara- to real-frequency domain can be carried out analytically through Hilbert transformation, resulting the expression of optical conductivity as used in Ref. [11]. For the first-order diagram, however, Hilbert transformation is not practically implementable since we deal with the vertex function having two Matsubara frequency variables. To get around of this problem, we turn into an approximate method by using Padé approximant to transform our optical conductivity calculation data defined in imaginary (Matsubara) frequency domain into the physical optical conductivity defined in real-frequency domain. Note that the use of Padé approximant may affect the accuracy of our calculation results as we will discuss in Section 4.

4. Results and Discussion

For our overall calculation we use the following parameters: lattice constants \(a = 3.25 \text{Å}\) and \(c = 5.21 \text{Å}\) for the wurtzite ZnO; \(k.p\) parameters as used in Ref. [9] to calculate the band structure of strained wurtzite ZnO; and the empirical value of \(\sim 3.3 \text{ eV}\) for the energy gap taken at room temperature. Figure 2 displays the calculated density of states (DOS) of our \(k.p\) model for the wurtzite ZnO, where the red vertical line marks the position of the chemical potential.

The calculated "bare" optical conductivity \(\sigma_1(\omega)\) is shown in Fig. 3. The onset of the uprising spectrum reflects the energy gap of \(\sim 3.3 \text{ eV}\), which is the minimum energy to excite an electron from the valence band to the conduction band. The spectrum is getting higher as the given photon energy is increased, showing that more electrons contribute to the conductivity. The anisotropy along the three different axes are expected as the system possesses a hexagonal symmetry.
Figure 2: DOS

Figure 3: ZnO optical conductivity without vertex correction

Figure 4: ZnO optical conductivity with vertex correction in x direction

Figure 5: ZnO optical conductivity with vertex correction in y direction

Figure 6: ZnO optical conductivity with correction in z direction

The anisotropy behavior that appears in the "bare" $\sigma_1(\omega)$ also shows up in the first-order
correction results proportionally. $\sigma_{yy}(\omega)$ and $\sigma_{zz}(\omega)$ spectra are both showing a rising peak below the band gap energy, which we identify as the excitonic signal formed due to the electron-hole interaction. The peak in $\sigma_{yy}(\omega)$ arises at $\sim 3.2$ eV and the peak in $\sigma_{zz}(\omega)$ arises at $\sim 3.1$ eV, which are just around the value obtained from the experimental measurement. Being the smallest in value, $\sigma_{xx}(\omega)$ does not show any excitonic signal. We believe that this is not physically correct, and it appears so because of the uncontrollable error in the Padé approximant we use.

5. Conclusion

We have presented our 8-band $k.p$ model and calculation for the optical conductivity of wurtzite ZnO. The calculated DOS reveals the correct value of the band gap energy, which also manifests as the onset of the optical conductivity spectrum. Further, our calculation for the optical conductivity incorporating the electron-hole interaction through the first-order electron-hole vertex correction qualitatively confirms the existence of excitons in ZnO. We acknowledge some lack of accuracy in our calculation that may have resulted in the absence excitonic signal in $z$ direction. We suspect that one possible source of lack of accuracy is the sensitivity of the application of Padé approximation against any small error in the Matsubara frequency data of the quantity being analytically continued.

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