Theoretical derivation of the bi- and tri-molecular trion formation coefficients

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A theoretical investigation of the trion formation process from free carriers in a single GaAs/Al0.1−xGa0.9As quantum well is presented. The mechanism for the formation process is provided by the interaction of the electrons and holes with phonons. The contributions from both the acoustic and optical phonons are considered. The dependence of both bi-molecular and tri-molecular formation rates on temperature is calculated. We demonstrate that they are equivalent for negatively and positively charged excitons.

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I. INTRODUCTION

In semiconductor wells, the photoluminescence spectrum following the generation of electron hole plasma is dominated by an exciton line.12,3,4,5,6 The formation of excitons in quantum wells has been extensively investigated both experimentally12,3,4,5,6 and theoretically7,8,9,10. Recently, it was experimentally showed that the exciton formation is strongly density and temperature dependent; it is a bimolecular process in which an electron and a hole are bound by Coulomb interaction with the emission of the appropriate phonon.10 This experimental result unambiguously confirmed the theoretical prediction for luminescence spectrum is modified: a charged exciton resonance appears below that of the exciton.

In a previous publication13, we showed experimentally that the dynamics of exciton, trion and electron-hole plasma can be ruled by a simple rate equation model, in which we account for bimolecular formation of excitons from an electron-hole plasma, bimolecular formation of trions from excitons and free carriers and trimolecular formation from free carriers. Using only two fit parameters, we were able to extract experimentally the dependence of both bi-molecular and tri-molecular formation coefficients on temperature.

In this paper, we propose a theoretical derivation of these coefficients. We consider formation channels through which the formation channel and show that they correspond to experimental calculations.

II. BIMOLECULAR FORMATION OF EXCITONS

The dynamics of the exciton formation is considered in the framework of the Boltzmann equation for a system containing free electrons, free holes, and excitons. The residual Coulomb interaction between the free carriers is neglected, which is justified in the range of temperatures and densities considered.13 In this work we focus on the exciton formation mechanism and do not discuss the relaxation of the three species within their respective bands, the electron-hole scattering, and radiative recombination. We denote the occupation numbers for electrons, holes, and excitons by \( f_e(k_e) \), \( f_h(k_h) \), and \( f_X(k_X) \), respectively, where \( k_e \), \( k_h \), and \( k_X \) are the in-plane momenta for electrons, holes, and excitons. For the bimolecular formation, following Piermarocchi et al., the scattering terms in the Boltzmann equation process reads

\[
\frac{df_e(k_e)}{dt}_{form} = - \sum_{k_X, k_h} w_{k_e, k_h, -k_X} f_h(k_h) f_e(k_e),
\]

where \( w_{k_e, k_h, -k_X} \) represents the probability per unit time for a free electron and a free hole to bind together and form an exciton. Free carriers thermalize very quickly in comparison to the exciton formation time, notably through fast carrier-carrier scattering.14 It is thus assumed that during the evolution of the system, the free electrons and holes are thermalized at the same temperature \( T_e \). In the scattering term of Eq. (1), we use for \( f_e(k_e) \) and \( f_h(k_h) \) equilibrium Boltzmann distribution function at \( T_e \). Consequently, by summing Eq. (1) over \( k_e \), we obtain an adiabatic equation for the evolution of the electronic density \( n_e = \frac{1}{V} \sum_{k_e} f_e(k_e) \)

\[
\frac{dn_e}{dt} = - \sum_{k_X} F(k_X) n_e n_h \equiv -C n_e n_h.
\]

The coefficient \( C \) is the bimolecular formation coefficient, which depends on both \( T_e \) and the lattice temperature \( T_l \).
through the term
\[ F(k_X) = \left( \frac{2\pi\hbar^2}{m_e m_h S} \right) \frac{1}{k_B T_c} \times \sum_{k_x, k_h} \sum_{q, q_z} w_{k_x, k_h} e^{-\left( E_e(k_x) + E_h(k_h) \right)/k_B T_c} \]

where \( S \) denotes the QW surface area.

Free carriers are coupled to the exciton by a continuum of phonon states \((q, q_z)\) through a carrier-phonon interaction Hamiltonian \( \mathcal{H}_{c/\text{ph}} \). A phonon can be emitted (+) or absorbed (-) in the formation process of the exciton. We calculate both case separately using the Fermi’s golden rule

\[ \sum_{q, q_z} w_{k_x, k_h} = \frac{2\pi}{\hbar} \sum_{q, q_z} \left\{ \left| \langle k_X | \otimes (n_{q, q_z} \pm 1) \right| n_{q, q_z} \rangle \otimes | k_x \rangle \right\} \delta \left[ E_e(k_x) + E_h(k_h) - E_X(k_X) \mp \hbar \omega_{ph}(q, q_z) \right] \]

with \( E_e(k_x) \), \( E_h(k_h) \) and \( E_X(k_X) \) the energy dispersion of the electrons, holes and excitons respectively, and \( \hbar \omega_{ph}(q, q_z) \) the energy of the emitted (absorbed) phonon. We first build the bound and unbound electron-hole pair states \( |k_X\rangle \) and \( |k_x\rangle \otimes |k_h\rangle \).

### A. Bound and unbound exciton states

Let \((r ||, z_e)\) and \((r \parallel, z_h)\) be the electron and hole position vectors respectively and \( \Phi^X[r ||, z_e, (r \parallel, z_h)] \) the exciton wavefunction, where we have separated the coordinates in the QW plane \((x,y)\) from the perpendicular coordinates \(z\). Denoting the electron (hole) in-plane momenta \( k_x \) (\( k_h \)), we write the in-plane Fourier transform of this function

\[ \Phi^X_{k_x, k_h}(z_e, z_h) = \frac{1}{S} \int d r || d r \parallel \Phi^X[r ||, z_e, (r \parallel, z_h)] \times e^{-i(k_x r || + k_h r \parallel)} \]

where \( S \) denotes the QW surface area. Transforming to center-of-mass (CM) and relative coordinates in the QW plane \(- R || = \alpha_X r || + \beta_X r \parallel, r \parallel = r || - r \parallel\), where \( \alpha_X = m_e/M_X, \beta_X = m_h/M_X \) and \( m_e, m_h, M_X \) are the electron, hole and exciton in-plane effective mass — we can apply Bloch’s theorem and decompose the exciton wavefunction into a free motion part \( e^{i k_X \cdot R ||} \) related to the exciton in-plane momenta \( k_X \) and an envelope function. To facilitate the calculation, we use an envelope function separable in \( z \) and \( r \parallel \), although it is strictly justifiable only for narrow well structures,

\[ \phi^X(r \parallel, z_e, z_h) = \chi_e(z_e) \chi_h(z_h) \varphi^X \]

The confinement functions \( \chi_e(z_e) \) (\( \chi_h(z_h) \)) is taken to be the wavefunction of an electron (hole) in the ground state of a finite square quantum well

\[ \chi_\alpha(z_\alpha) = \begin{cases} A_\alpha \cos \left( \frac{\sqrt{2} a}{2} \frac{z_\alpha}{a} \right) & \text{for } |z_\alpha| < \frac{L_z}{2} \\ B_\alpha \exp \left( - \frac{\sqrt{2} a}{2} \frac{|z_\alpha| - L_z/2}{a} \right) & \text{for } |z_\alpha| > \frac{L_z}{2} \end{cases} \]

with \( \alpha = e, h \) and we use the simplest electron orbital function

\[ \varphi^X = \sqrt{\frac{8 \pi \lambda_X^2}{S}} \frac{1}{1 + (\lambda_X k)^2} \]

The variational parameter \( \lambda_X \) is associated with the Bohr radius of the exciton in the QW. Eq. \( \ref{9} \) can be rewritten as

\[ \Phi^X_{k_x, k_h}(z_e, z_h) = \frac{1}{S} \int d R || d r \parallel \phi^X(r \parallel, z_e, z_h) \times e^{i k_X \cdot R ||} e^{-i \left( R || (k_x + k_h) + r \parallel (\beta_X k_x - \alpha_X k_h) \right)} \]

where \( \phi^X_k(z_e, z_h) = \chi_e(z_e) \chi_h(z_h) \varphi^X \) is the in-plane Fourier transform of the exciton envelope function. We can now construct the state of a single exciton with an in-plane momentum \( k_X \) in the Fermionic Hilbert space of electron-hole pairs. It is the superposition of wavefunctions \( \ref{10} \) with all electron momenta \( k_x \) and all electron \( z_e \) and hole \( z_h \) coordinates, given by

\[ |k_X\rangle = \sum_{k_x} \int dz_e dz_h \phi^X_{k_x, k_h}(z_e, z_h) \times e^{-i(k_x r || + k_h r \parallel)} \]

where \( c_{k_x, z_e, z_h}^\dagger (d_{k_x, z_e}^\dagger) \) is the electron (hole) creation operator with in-plane momentum \( k_X \) and \( z_e \) (\( z_h \)) coordinate.

Similarly, we choose plane waves for the free carriers. Thus the in-plane Fourier transform \( \psi^\alpha_k(z) \) of the carrier wavefunction takes the simple form

\[ \psi^\alpha_k(z) = \chi_\alpha(z), \quad \alpha = e, h \]

The unbound electron-hole pair then reads

\[ |k_x, k_h\rangle = \sum_{z_e, z_h} dz_e dz_h \psi^e_{k_x, z_e}(z_e) \psi^h_{k_h, z_h}(z_h) c_{k_x, z_e, z_h}^\dagger d_{k_h, z_h}^\dagger |0\rangle \]

### B. Carrier-phonon interaction Hamiltonian.

We write the interaction Hamiltonian for a coupled electron-phonon system in the notation of the second quantization

\[ \mathcal{H}_{c-\text{ph}} = \sum_{q, q_z} \sum_{\alpha} v^\alpha_{q, q_z} \left( a_{q, q_z} + a_{q, q_z}^\dagger \right) \hat{a}^{\alpha}_{q, q_z} \]

\[ \mathcal{H}_{c-\text{ph}} = \sum_{q, q_z} \sum_{\alpha} v^\alpha_{q, q_z} \left( a_{q, q_z} + a_{q, q_z}^\dagger \right) \hat{a}^{\alpha}_{q, q_z} \]

\[ \mathcal{H}_{c-\text{ph}} = \sum_{q, q_z} \sum_{\alpha} v^\alpha_{q, q_z} \left( a_{q, q_z} + a_{q, q_z}^\dagger \right) \hat{a}^{\alpha}_{q, q_z} \]
where $\hat{a}_{q,+}^\dagger$ is the phonon creation operator. The electron density operator $\hat{a}_\alpha(r, z)$ and its counterpart in Fourier space $\hat{a}_\alpha(q, z)$ are expressed on the basis \(\{ \phi^\alpha_n(r, z, s) = e^{i k_0 r} \delta(z - \phi) \phi^\alpha(s) \}\)

\[
\hat{\rho}_e(r, z) = \sum_{k, k'} \delta^\sigma_{k, z, k', z} e^{-i (k - k') r},
\]

\[
\tilde{\rho}_e(q, z) = \sum_k \int dz e^{-i \tilde{q} z} \delta^\sigma_{k, z, \tilde{q}, z},
\]

\[
\tilde{\rho}_h(r, z) = \sum_{k, k'} \delta^\sigma_{k, z, k', z} e^{-i (k - k') r},
\]

\[
\tilde{\rho}_h(q, z) = - \sum_k \int dz e^{-i \tilde{q} z} \delta^\sigma_{k, z, q, z}.
\]

Spin states $\phi^\alpha(s) = |\alpha s\rangle$ have been introduced for their will be necessary when we treat the trion formation.

Only longitudinal acoustical (LA) and longitudinal optical phonons (LO) couple significantly to careers. We express the coupling vertex functions $V^\alpha_{q, q_0}$ for both coupling

\[
V^\alpha_{q, q_0} (LA) = i \alpha \sqrt{\frac{\hbar(|q|^2 + q_0^2)}{2 \rho_0 \omega_{q, q_0}}},
\]

\[
V^\alpha_{q, q_0} (LO) = \sqrt{\frac{2 \pi n \omega_{q, q_0} e^2}{(|q|^2 + q_0^2) V^2 (1/\epsilon_0 - 1/\epsilon_\infty)}},
\]

C. Matrix element calculation.

The matrix elements in Eq. (11) are calculated, making use of Eq. (11), (13) and (14).

Applying operators on the ground state

\[
\langle 0 | \hat{c}_{-k_e, z_e}^\dagger \hat{c}_{k_h, z_h} | 0 \rangle = \delta_{-k_e, k_h} \delta(z - z_e),
\]

\[
\langle 0 | \hat{d}_{k_h, z_h} | 0 \rangle = \delta_{k_h, k_h} \delta(z - z_h),
\]

\[
\langle n_{q, q_0} | \hat{a}_{q_0, q} + \hat{\alpha}_{q_0, -q} | n_{q, q_0} \rangle = \sqrt{n_{q, q_0} + \frac{1}{2} \delta_{q, q} \delta_{q, q_0}},
\]

we obtain

\[
\langle k_X, n_{q, q_0} | \hat{H}_e + \hat{H}_h | k_X, n_{q, q_0} \rangle
\]

\[
= \sum_{q, q_0, k, k_0} \int dz_e dz_h \delta^\sigma_{k, z_e, k_0, z_h} \langle n_{q, q_0} + 1 | \hat{a}_{q_0, q} + \hat{\alpha}_{q_0, -q} | n_{q, q_0} \rangle \chi_e^\star(z_e) \chi_h^\star(z_h) e^{-i \tilde{q} z}.
\]

where $\epsilon_0$ is the static dielectric constant and $\epsilon_\infty$ is the high frequency dielectric constant. We use the notation $\alpha$ for the deformation-potential constant (assumed to be associated with a non-degenerate conduction or valence band), $\rho_0$ for the density of the crystal, $e$ for the charge of the electron and $V$ for the volume of the sample. We follow Einstein interpolation scheme, so that the dispersion is merely $\omega_{q, q_0}^{LA} = v_s \sqrt{q^2 + q_0^2}$ for LA phonons and $\omega_{q, q_0}^{LO} = \omega_{LO}$ for LO phonons, $v_s$ standing for the Debye sound velocity and $\omega_{LO}$ for the reststrahl frequency.
Finally, if we choose the bound and unbound electron-hole pairs dispersion to be parabolic, the probability transition \( w_{k_z,k_h}^{\pm} \) reads

\[
w_{k_z,k_h}^{\pm} = \frac{2\pi}{\hbar} \sum_{q_z} (n_{q_z} + \mathbf{1} \pm \mathbf{1}) |V_{q_z} \varphi^X_{\beta|X} - V_{q_z} \varphi^X_{\alpha|X}|^2 \\
\times \delta \left[ \frac{h^2 k_z^2}{2m_e} + \frac{h^2 k_h^2}{2m_h} + E_b - \frac{h^2 k_X^2}{2M} \mp \hbar \omega_{ph}(q_z) \right] \delta_{q_z,k_z,k_h,k_X}.
\] (23)

\[D. \text{ LA phonons assisted formation}\]

Considering that the sample volume \( V = L_z S \) is macroscopic the sum over the orthogonal phonon wavevectors may be replaced by the integral

\[
\sum_{q_z} \longrightarrow \left( \frac{L_z}{2\pi} \right) \int dq_z
\] (24)

makes the integration \( 24 \) trivial for LA phonons:

\[
w_{k_z,k_h}^{\pm} = \frac{4\pi L_z}{\hbar} \left( \frac{\hbar}{2\pi} \rho V_{\text{ls}} \right) \left[ q_z^2 + q_z^{(0)} \right] \\
\times \left[ \alpha_e \varphi_{\beta|X} - \alpha_h \varphi_{\alpha|X} \right] \\
\times \left\{ \begin{array}{l}
n_{q_z} + \mathbf{1} \\
\mathbf{1} \\
\end{array} \right\} \\
\times \left\{ \begin{array}{l}
\theta \left( \frac{h^2 k_z^2}{2m_e} + \frac{h^2 k_h^2}{2m_h} + E_b - \frac{h^2 k_X^2}{2M} \right) \\
\right. \\
\left. + n_{q_z} \theta \left( -\frac{h^2 k_z^2}{2m_e} - \frac{h^2 k_h^2}{2m_h} - E_b + \frac{h^2 k_X^2}{2M} \right) \right\}.
\] (27)

\[E. \text{ LO phonons assisted formation}\]

In the case of interaction with LO phonons, Eq. \( 23 \) becomes

\[
w_{k_z,k_h}^{\pm} = \sum_{q_z} \frac{2\pi}{\hbar} \hbar \omega_{LO} e^2 (1/\epsilon_{\infty} - 1/\epsilon_0) \left| V_{q_z} \varphi^X_{\beta|X} - \varphi^X_{\alpha|X} \right|^2 \\
\times \delta \left[ \frac{h^2 k_z^2}{2m_e} + \frac{h^2 k_h^2}{2m_h} + E_b - \frac{h^2 k_X^2}{2M} \mp \hbar \omega_{LO} \right] \\
\times \left\{ \begin{array}{l}
n_{q_z} + \mathbf{1} \\
\mathbf{1} \\
\end{array} \right\} \\
\times \left\{ \begin{array}{l}
\theta \left( \frac{h^2 k_z^2}{2m_e} + \frac{h^2 k_h^2}{2m_h} + E_b - \frac{h^2 k_X^2}{2M} \right) \\
\right. \\
\left. + n_{q_z} \theta \left( -\frac{h^2 k_z^2}{2m_e} - \frac{h^2 k_h^2}{2m_h} - E_b + \frac{h^2 k_X^2}{2M} \right) \right\}.
\] (28)

This expression already includes the sum over absorbed and emitted phonon contributions. The phonon in-plane momentum needs to be substituted by \( q = k_z + k_h - k_X \).
FIG. 1: The exciton formation coefficient $C$ as a function of the carrier temperature $T_c$, at a fixed lattice temperature $T_l = 10$ K. Other parameters are given in the text.

with

$$k_X(0)(k_e, k_h) = \sqrt{\frac{2M_X}{\hbar^2} \left( \frac{\hbar^2 k_e^2}{2m_e} + \frac{\hbar^2 k_h^2}{2m_h} + E_b - \hbar \omega_{LO} \right)}.$$

(30)

F. Numerical Results.

If we change all the sum in Eq. 24, 25 and 28 into integrals, the bimolecular formation coefficient $C$ can be numerically calculated by Monte Carlo integration. In Fig. 1 we report $C$ as a function of $1/T_c$ for a fixed lattice temperature $T_l = 5$ K, for a GaAs QW of 80 Å. The two contributions from the acoustic and optical phonons are shown separately. The acoustical phonon dominates for temperatures smaller than 40 K and does not depend on $T_l$. We see that these results perfectly match those published by Piermarocchi et al. We show in Table I the numerical value of the different parameters entering in the calculation.

III. BIMOLECULAR FORMATION OF TRIONS

We now extend our formalism to the derivation of the bimolecular formation of trions. We restrict ourselves to negatively charged excitons and will give at the end of this work some indication on how to retrieve their positive counterpart.

We write the scattering term in the Boltzmann equation process for the bimolecular formation of trions:

$$\left( \frac{df_e(k_e)}{dt} \right)_{form} = - \sum_{k_T, k_e} F_{k_X, k_e \rightarrow k_T} f_X(k_X) f_e(k_e),$$

(31)

where $F_{k_X, k_e \rightarrow k_T}$ represents the probability per unit time for a bound electron-hole pair and a free electron to bind together and form an exciton. We assume that bound and unbound carriers are thermalized and use Boltzmann distribution function $f_X(k_X)$ and $f_e(k_e)$ for exciton and electron population, respectively. By summing Eq. (31) over $k_e$, we obtain an adiabatic equation for the evolution of the electron density

$$\frac{dn_e}{dt} = - \sum_{k_T} F(k_T)n_X n_e \equiv -A^{-}_2 n_X n_e.$$  

(32)

The coefficient $A^{-}_2$ is the bimolecular formation coefficient, which depends on both $T_c$ and the lattice temperature $T_l$ through the term

$$F(k_T) = \left( \frac{2\pi \hbar^2}{k_B T_c} \right)^2 \frac{1}{m_X m_e S} \sum_{k_X, k_e} w_{k_X, k_e \rightarrow k_T}$$

$$\times e^{-\left( E_X(k_X) + E_e(k_e) \right) / k_B T_c},$$

(33)

(34)

We calculate the formation rate using Fermi’s golden rule

$$w_{k_X, k_e \rightarrow k_T} = \frac{2\pi}{\hbar} \sum_{q, \nu}$$

$$\left| \langle k_T | \otimes \langle n_{q, \nu} \pm 1 | h_e \otimes | n_{q, \nu} \rangle \otimes | k_X \rangle \otimes | k_e \rangle \right|^2$$

$$\times \delta \left[ E_X(k_X) + E_e(k_e) - E_T(k_T) + \hbar \omega_{ph}(q, \nu) \right],$$

(35)

with $E_X(k_X)$, $E_e(k_e)$ and $E_T(k_T)$ the energy dispersion of the electrons, holes and excitons respectively, and $\hbar \omega_{ph}(q, \nu)$ the energy of the emitted (absorbed) phonon. We first build the bound and unbound electron-hole pair states $|k_T\rangle$ and $|k_X\rangle \otimes |k_e\rangle$. 

\[ \text{TABLE I: GaAs Material Parameters} \]

| Parameter                  | Symbol | Value Unit       |
|---------------------------|--------|-----------------|
| Band gap energy           | $E_g$  | 1519 meV        |
| Electron effective mass   | $m_e$  | 0.08 m$_0$      |
| Heavy hole effective mass | $m_{hh}$ | 0.17 m$_0$  |
| LO phonon energy         | $\hbar \omega_{LO}$ | 36 meV |
| Static dielectric constant| $\varepsilon_0$ | 12.85          |
| High frequency dielectric constant | $\varepsilon_\infty$ | 10.88 |
| Crystal density          | $\rho$ | 5.3162 g·cm$^{-3}$ |
| Sound velocity           | $v_s$  | 4726.5 m·s$^{-1}$ |
| Conduction band deformation potential | $a_c$ | -7.0 eV |
| Valence band deformation potential | $a_h$ | 3.5 eV |
| Exciton binding energy   | $E_T$  | 6.5 meV         |
| Trion binding energy     | $E_T$  | 1.77 meV        |
| Exciton Bohr radius      | $\lambda_X$ | 11.0 nm  |
| Trion variational parameter #1 ($X^-$) | $\lambda_T$ | 15 nm  |
| Trion variational parameter #2 ($X^-$) | $\lambda_T$ | 30.0 nm  |
| Trion variational parameter #1 ($X^+$) | $\lambda_T$ | 16 nm  |
| Trion variational parameter #2 ($X^+$) | $\lambda_T$ | 25.0 nm  |
A. Trion state.

The two electrons and the hole are positioned at \((r_{1\parallel}, z_1), (r_{2\parallel}, z_2)\) and \((r_{h\parallel}, z_h)\) respectively, while the center-of-mass (CM) and relative coordinates in the QW plane are now given by \(R_{\parallel} = \alpha_T r_{\parallel} + r_{2\parallel}\) and \(r_{ih\parallel} = r_{\parallel} - r_{h\parallel}\) \((i = 1, 2)\); \(\alpha_T = m_e/M_T\), \(\beta_T = m_h/M_T\) and \(M_T\) is the trion mass. We consider a simple two parameter Chandrasekhar-type trial envelope function that was successively used to calculate trion-electron scattering:\[ \phi^T(r_{1\parallel}, r_{2\parallel}, z_1, z_2, z_h) = N_T \chi_e(z_1) \chi_e(z_2) \chi_h(z_h) \]

where the \(+(-)\) sign applies to the singlet (triplet) spin configuration and the trion wavefunction normalization factor is given by

\[ N_T = \frac{1}{\sqrt{2(1 + \kappa^2)}}. \]

with

\[ \kappa = \frac{4AX}{(\lambda + \lambda^2)^2}. \]

Its in-plane Fourier transform reads

\[ \Phi^T_{k_1, k_2, k_3}(z_1, z_2, z_h) = \delta_{k_3 - k_1 - k_2 - k_h} \phi^T_{\alpha_T k_T + k_1, \alpha_T k_T + k_2}(z_1, z_2, z_h) \]

and the state of a single trion with an in-plane CM momentum \(k_T\) is constructed similarly to that of a single exciton

\[ \begin{align*} |k_T^S\rangle &= \sum_{k_1, k_2} \int dz_1 dz_2 dz_h \phi^T_{\alpha_T k_T + k_1, \alpha_T k_T + k_2}(z_1, z_2, z_h) \\ &\times \xi_S^{*}(s_1, s_2) \hat{c}_{-k_1, z_1}^{\dagger} \hat{c}_{-k_2, z_2}^{\dagger} \hat{a}_{k_T + k_1 + k_2, z_h} \langle 0 |, \quad (40) \end{align*} \]

where we have added the spin index to the electron creation operator and introduced \(\xi_S(s_1, s_2) = \langle S|s_1, s_2\rangle\) the projection of a generic spin configuration of two electrons on the singlet spin configuration. The in-plane Fourier transform of the trion singlet wavefunction in Eq. \((39)\) is given by

\[ \phi^T_{k_1, k_2}(z_1, z_2, z_h) = N_T \chi_e(z_1) \chi_e(z_2) \chi_h(z_h) \]

\[ \times \left[ \varphi_{k_1}^{\alpha_T} \varphi_{k_2}^{\alpha_T} + \varphi_{k_1}^{\lambda_T} \varphi_{k_2}^{\lambda_T} \right]. \]

where \(\varphi_{k_i}^{\lambda_T}\) has already been defined in Eq. \(9\). The exciton-free electron state is given by

\[ |k_X, e^e\rangle = \sum_{k_e} \int dz_e dz_h \langle \hat{c}_{-k_e, z_e}^{\dagger} \hat{c}_{-k_X + k_e, z_h} \rangle \psi_{k_e}(z_e) \]

\[ \times \langle \hat{c}_{-k_X + k_e, z_h}^{\dagger} \hat{a}_{k_X + k_e, z_h} \rangle \langle 0 | \]

B. Matrix element calculation.

We calculate the matrix elements in \((39)\) using the following scheme

\[ \begin{align*} 1 &= (-k_1', z_1', s_1') \quad 2 = (-k_2', z_2', s_2') \quad 3 = (k + q, z, s) \\ 4 &= (k, z, s) \quad 5 = (-k_1, z_1, s_1) \quad 6 = (k_2, z_2, s_2) \\ 7 &= (k_T + k_1', k_2', z_1', z_h) \quad 8 = (k_X + k_1, z_h, s_h) \end{align*} \]

Using the electron, holes anti-commutation relations, the Fermi vacuum expectation value of the operators read

\[ \langle 0 | \hat{c}_{1} \hat{c}_{2} \hat{c}_{3} \hat{c}_{6} | 0 \rangle = \delta_{13}(\delta_{25}\delta_{46} - \delta_{26}\delta_{45}) - \delta_{23}(\delta_{15}\delta_{46} - \delta_{16}\delta_{45}) \]

\[ \langle 0 | \hat{d}_{7} \hat{d}_{8}^\dagger | 0 \rangle = \delta_{87} \]

\[ \langle 0 | \hat{c}_{1} \hat{c}_{2} \hat{c}_{3} \hat{c}_{6} | 0 \rangle = \delta_{25}\delta_{16} - \delta_{15}\delta_{26} \]

\[ \langle 0 | \hat{d}_{7} \hat{d}_{3} \hat{d}_{4} \hat{d}_{8}^\dagger | 0 \rangle = \delta_{37}\delta_{48} \]

\[ \langle 0 | \hat{d}_{3} \hat{d}_{4} \hat{d}_{8}^\dagger | 0 \rangle = \delta_{87} \]

\[ \langle 0 | \hat{d}_{7} \hat{d}_{3} \hat{d}_{4} \hat{d}_{8}^\dagger | 0 \rangle = \delta_{37}\delta_{48} \]
Using the later results in Eq. (43) gives

\[
(\mathbf{k}_T^2; s'_k| (n_{q,q_z} \pm 1) \mathcal{H}_{e/h-ph} |n_{q,q_z}) \otimes |\mathbf{k}_X; s_1; s_k) \otimes |\mathbf{k}_2; s_2)
\]

\[
=\left[\xi_2(s_2, s_1) - \xi_1(s_1, s_2)\right] \sqrt{n_{q,q_z} + 1/2} \pm 1/2 \sum_k \phi_{nX}^{kX+k_1}
\]

\[
x \left\{ V_e^{kX}(q, q_z) [\phi_{\alpha \gamma}^{T^* X}(k - k_2, \alpha \gamma k_T + k_1 + q) + \phi_{\alpha \gamma}^{T^* X}(k - k_2, \alpha \gamma k_T + k_1 + q)] - V_{ph}^{kX}(q, q_z) \phi_{\alpha \gamma}^{T^* X}(k - k_2, \alpha \gamma k_T + k_1 + q) \right\} \delta_{qX,kX} + \delta_{kX,k_2} - k_T, \tag{48}
\]

Finally, for parabolic electron, exciton and trion dispersion, the probability transition is

\[
w_{kX,k_2 - kT}^\pm = \frac{2\pi}{\hbar} \sum_{q, q_z} (n_{q,q_z} + \frac{1}{2} \pm \frac{1}{2})
\]

\[
\times \left| \sum_k V_e^{kX}(q, q_z) [\phi_{\alpha \gamma}^{T^* X}(k - k_2, \alpha \gamma k_T + k_1 + q) + \phi_{\alpha \gamma}^{T^* X}(k - k_2, \alpha \gamma k_T + k_1 + q)] - V_{ph}^{kX}(q, q_z) \phi_{\alpha \gamma}^{T^* X}(k - k_2, \alpha \gamma k_T + k_1 + q) \right|^2
\]

\[
\times \delta \left[ \frac{\hbar^2 k^2}{2m_X} + \frac{\hbar^2 k^2}{2m_e} + E_T - \frac{\hbar^2 k^2}{2M_T} \mp \hbar \omega_{ph}(q, q_z) \right] \delta_{\pm qXX + k_2 - kT}, \tag{49}
\]

where we averaged over the initial electron spin states and exciton angular momentum states.

IV. TRIMOLECULAR FORMATION OF TRIONS

Again, we write the scattering term in the Boltzmann equation process

\[
\left( \frac{df_e(k_e)}{dt} \right)_{form} = - \sum_{k_2} F_{k_e, k_e', k_2 - k_T} f_e(k_e) f_e(k_e') f_h(k_2), \tag{50}
\]

where \( F_{k_e, k_e', k_2 - k_T} \) represents the probability per unit time for two free electrons and one free hole to bind together and form an exciton. We assume that bound and unbound carriers are thermalized and use Boltzmann distribution function \( f_x(k_x) \) and \( f_h(k_h) \) for exciton and electron population, respectively. By summing Eq. (50) over \( k_e \), we obtain an adiabatic equation for the evolution of the electron density

\[
\frac{dn_e}{dt} = - \sum_{k_T} F(k_T) n_h^2 n_e \equiv -A_3 n_h n_e. \tag{51}
\]

The coefficient \( A_3 \) is the trimolecular formation coefficient, which depends on both \( T_e \) and the lattice temperature \( T_l \) through the term

\[
F(k_T) = \left( \frac{2\pi \hbar^2}{k_B T_e} \right)^3 \frac{1}{m_e^2 m_h S_{e/h}^2} \sum_{k_e, k_e', k_h} w_{k_e, k_e', k_h - k_T}
\]

\[
\times e^{-\frac{(E_e(k_e) + E_e(k_e') + E_h(k_h) - E_T(k_T) \mp \hbar \omega_{ph}(q, q_z)\delta_{\pm qX + k_2 - kT}}{k_B T_e}}, \tag{52}
\]

We calculate the formation rate using Fermi’s golden rule

\[
w_{k_e, k_e', k_h - k_T}^\pm = \frac{2\pi}{\hbar} \sum_{q, q_z} \left| \langle k_T | (n_{q,q_z} \pm 1) \mathcal{H}_{e/h-ph} |n_{q,q_z}) \otimes |k_e \rangle \otimes |k_e' \rangle \otimes |k_h \rangle \right|^2
\]

\[
\times \delta \left[ E_e(k_e) + E_e(k_e') + E_h(k_h) - E_T(k_T) \mp \hbar \omega_{ph}(q, q_z)\right], \tag{53}
\]

with \( E_X(k_X) \), \( E_e(k_e) \) and \( E_T(k_T) \) the energy dispersions of the electrons, holes and excitons respectively, and \( \hbar \omega_{ph}(q, q_z) \) the energy of the emitted (absorbed) phonon. Finally, for parabolic electron, exciton and trion dispersion, the probability transition becomes

\[
w_{k_e, k_e', k_h - k_T}^\pm = \frac{2\pi}{\hbar} \sum_{q, q_z} (n_{q,q_z} + \frac{1}{2} \pm \frac{1}{2})
\]

\[
\times \left| V_e^{kX}(q, q_z) [\phi_{\alpha \gamma}^{T^* X}(k - k_2, \alpha \gamma k_T + k_1 + q) + \phi_{\alpha \gamma}^{T^* X}(k - k_2, \alpha \gamma k_T + k_1 + q)] - V_{ph}^{kX}(q, q_z) \phi_{\alpha \gamma}^{T^* X}(k - k_2, \alpha \gamma k_T + k_1 + q) \right|^2
\]

\[
\times \delta \left[ \frac{\hbar^2 k^2}{2m_e} + \frac{\hbar^2 k^2}{2m_e} + \frac{\hbar^2 k^2}{2m_h} + E_T - \frac{\hbar^2 k^2}{2M_T} \mp \hbar \omega_{ph}(q, q_z) \right] \delta_{\pm qX + k_2 - kT}, \tag{54}
\]
where we averaged over the initial electron spin states and exciton angular momentum states.

### A. Numerical results

**FIG. 2:** The bi- and tri-molecular trion formation coefficients $A_2^\alpha$ and $A_3^\alpha$ as a function of the inverse carrier temperature as calculated from our model for LA phonon assisted formation. The red curve indicates $X^+$ formation and the blue curve $X^-$ formation.

In Fig. 2 we represent the results of our numerical calculation for LA phonon assisted formation. We stress the fact that the results for LO phonons are orders of magnitude smaller and consequently negligible for bi- and tri-molecular processes. This shows that the exclusive formation mechanism for trions is governed by LA phonon interaction. We predict a decrease of the bi- or tri-molecular formation for raising temperatures. We also demonstrate that the bi and tri-molecular formation coefficients for negatively and positively charged excitons are approximatively equal ($A_2^+ = A_2^-$) and ($A_3^+ = A_3^-)$.

A more accurate calculation should rely on a better trion wavefunction. The Chandrashekar variational function is most likely to simple to yield quantitative results. We note however that electron-trion scattering will contribute to ionize trions. This effect will dramatically increase at high temperatures. We consequently propose that the electron-trion scattering reduce the experimental values for the trion formation coefficients.

### V. FORMATION RATES CLOSE TO EQUILIBRIUM

In this Section, we propose to derive formation rate for electrons, holes, excitons and trions assuming thermodynamical equilibrium. In this set of equations, we neglect both bie exciton channels and Auger channels because experiments on undoped samples demonstrate that, at the densities considered in the present work, these channels are not significant.

The dynamics of a plasma of electrons containing electrons ($e$), holes ($h$), excitons ($X$) and trions ($X^+$ and $X^-$) is governed by the following five channels:

$e + h \leftrightarrow X$

$X + e \leftrightarrow X^-$

$X + h \leftrightarrow X^+$

$2e + h \leftrightarrow X^-$

$2h + e \leftrightarrow X^+$

The different formation rates for these populations read

\[ F_X^X = C n_p - \gamma C K_X X, \]

\[ F_{2X}^X = A_2^X X n - A_2^X K_2^X X^{-}, \]

\[ F_{3X}^X = A_3^X n p - A_3^X K_3^X X^{-}, \]

\[ F_{2X}^X = A_2^X X p - A_2^X K_2^X X^+, \]

\[ F_{3X}^X = A_3^X n p - A_3^X K_3^X X^+, \]

where $C$, $A_2^\alpha$ and $A_3^\alpha$ are respectively the exciton, trion bimolecular and trion trimolecular formation rate calculated in this article; $E_{bX}$ is the exciton binding energy; $K_X$, $K_2^X$, $K_3^X$ the equilibrium coefficients. For a 2D system, they can be derived from the Boltzmann distribution

\[ n_\alpha = 2 g_\alpha \int \frac{d^2k}{2\pi} e^{-\hbar \omega k^2/2m_\alpha \hbar k} = g_\alpha m_\alpha \hbar k T \frac{k_B T}{2\pi \hbar^2} e^{-\mu_\alpha/k_B T}, \]

where $\alpha = e, h, X, T$, the factor $g_\alpha = 2$ is the spin degeneracy of the electron, hole, exciton and trion in the non degenerate regime, where Boltzmann statistics applies.

Using that fact that the chemical potential of the exciton $\mu_X$ is related to the chemical potential of electrons $\mu_e$ and holes $\mu_h$ as $\mu_X = \mu_e + \mu_h + E_X$ ($E_X$ is here defined as minus the exciton binding energy), one immediately obtains the Saha relation for the exciton density

\[ \frac{n_p}{X} = K_X(T) = g_e g_h m_e m_h \frac{k_B T}{m_X 2\pi \hbar^2} e^{-(E_X - E_h)/k_B T}. \]

Similarly, the chemical potential of the trions is $\mu_T = 2\mu_e + \mu_h + E_T$ ($E_T$ is here defined as minus the trion binding energy), so that Saha equations for trion bi-molecular formation are

\[ \frac{X n}{X^{-}} = K_2^X(T) = \frac{g_e^2 g_h m_e m_h}{g_T m_X} \frac{k_B T}{2\pi \hbar^2} e^{-(E_T - E_h)/k_B T}, \]

\[ \frac{X p}{X^+} = K_3^X(T) = \frac{g_e^2 g_h m_e m_h}{g_T m_X} \frac{k_B T}{2\pi \hbar^2} e^{-(E_T - E_h)/k_B T}. \]

Finally, the following set of equation is inferred for tri-molecular formation:

\[ \frac{n^2 h}{X^{-}} = K_3^X(T) = \frac{g_e^2 g_h m_e^2 m_h}{g_T m_X} \frac{k_B T}{2\pi \hbar^2} e^{-(E_T - E_h)/k_B T}, \]

\[ \frac{n h^2}{X^+} = K_3^X(T) = \frac{g_e g_h^2 m_e m_h^2}{g_T m_X} \frac{k_B T}{2\pi \hbar^2} e^{-(E_T - E_h)/k_B T}. \]
Such a set of equations, together with the equilibrium densities, allow to compute the dynamics of the different populations after non-resonant optical excitation. This may apply both to undoped as well as to doped quantum wells. The results in the case of a sample doped with electrons will be detailed in another publication. The experiments show that indeed, when the density of electrons is sufficient and at excitation densities of the order of $10^{10} \text{cm}^{-2}$ and above, the trimolecular formation process of trions has to be taken into account to properly reproduce the observed dynamics.

VI. CONCLUSION

In this paper, we have derived the appropriate model for computing the rates for exciton and trion formation. For the case of trions, we have derived the equations for both the bi- and tri-molecular phonon-assisted formation of trions. We have shown that bi- and tri-molecular formation rate of negatively and positively charged excitons have similar orders of magnitude for densities that are used in the experiments. We have then developed the set of relations and the equilibrium conditions allowing to calculate the dynamics of free carriers, excitons and trions. Our results are in very reasonable agreement with recent experiments and allow to confirm that, indeed, trimolecular trion formation may not be neglected in real samples.

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