

## Quantum-Kinetic Theory of Hot Luminescence from Pulse-Excited Semiconductors

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A theory of time-resolved luminescence from photoexcited semiconductors is presented. It combines quantum kinetics of hot-carrier relaxation and quantum theory of spontaneous emission. Model calculations show the “transfer” of photoluminescence from the initial signal at the pump frequency via subsequent phonon replicas until the buildup of luminescence at the excitonic resonance. Time-resolved photoluminescence is predicted to be a sensitive measure of electron–LO-phonon quantum kinetics and bottleneck effects.

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In recent years, tremendous progress in femtosecond laser spectroscopy has enabled time-and-energy-resolved studies of the interaction between laser-induced electron-hole pairs and lattice vibrations in semiconductors [1–6]. These experiments have provided intriguing insight into the quantum-kinetic nature of the basic scattering mechanisms in photoexcited semiconductors. For time intervals shorter than the LO-phonon period, energy transfer between electrons and lattice cannot be described in terms of completed collisions because of the quantum-mechanical time-energy uncertainty principle. Quantum beats with nearly LO-phonon frequency—as observed in four-wave mixing (FWM) experiments on bulk GaAs [1]—were the first evidence for such non-Markovian effects. Later, the coherent control of the scattering events was achieved in GaAs [2] and ZnSe [3]. Recently, FWM experiments were also used to study ultrafast electron–LO-phonon scattering in CdTe [4] and CdSe [5]. Another milestone in detecting quantum-kinetic effects was achieved by Leitenstorfer *et al.* and Fürtst *et al.* [6] using pump-probe techniques. They time-resolved the violation of classical energy conservation during the step-by-step relaxation of conduction electrons via emission of LO phonons after pumping high above the fundamental gap.

Photoluminescence (PL) measurements provide another powerful tool to study relaxation dynamics in optically excited semiconductors. Continuous-wave PL spectroscopy on the hot-electron cascade in GaAs [7] has yielded a wealth of information on electron-phonon, electron-electron, and intervalley scattering rates. LO-phonon replicas of the photogenerated nonequilibrium carrier distribution have also been observed in time-integrated PL spectra after femtosecond excitation of GaAs [8]. *Time-resolved* PL measurements of hot-carrier relaxation remains a challenging task, however. Snoke *et al.* [9] have observed the thermalization process in GaAs using a sensitive streak camera, but the restricted time resolution of 10 ps did not allow the resolution of sharp phonon-emission peaks. On the other hand, PL up-conversion experiments [10] enable time resolutions of

100 fs. Such experiments—as performed in GaAs [11], InP [12], and InAs [13]—have so far been restricted to high electron-hole pair densities where carrier-carrier collisions dominate over carrier-phonon scattering. Principally, however, future improvements in the signal sensitivity should allow one to perform time-resolved PL experiments that directly monitor the hot-carrier relaxation via emission of LO phonons. Such studies will clarify the different stages of light emission after photoexcitation on a time scale shorter than the thermalization time. On longer time scales, they will also allow one to check the validity of introducing effective electron temperatures, a concept often used to analyze PL measurements. Time-resolved PL experiments may be more suitable for such investigations than standard pump-probe experiments, due to the background-free and incoherent nature of the PL signals.

In this Letter, we present the first theoretical studies of time-resolved PL spectra from coherently excited semiconductors. These studies show that hot luminescence can indeed serve as a very sensitive measure of the electron-lattice interaction on a sub-100-fs time scale. They indicate also how ultrafast PL spectroscopy can give insight into the conversion of secondary emission from hot luminescence after a few collisions into PL from thermalized carriers. The numerical calculations are performed in two steps. First, we determine the time evolution of the distribution functions for electrons and holes after pulse excitation. This is done by solving non-Markovian quantum-kinetic equations within the formalism of phonon-assisted density matrices. Recently, this method has been applied successfully to the calculation of FWM signals [1,14] and pump-probe signals [15,16]. Second, we convert the distribution functions into the PL signal by solving the Bethe-Salpeter equation for the polarization function. This is achieved by generalizing the recently developed theory of PL in semiconductors [17] which overcomes shortcomings and/or limitations of previous approaches [18–20]. Most importantly, it is guaranteed that the PL signal is non-negative, and the theory does

not rely on the explicit use of the Kubo-Martin-Schwinger relation, which allows us to treat arbitrary nonthermal situations, as exemplified in Ref. [17].

The theoretical description of hot-carrier generation and relaxation is based upon electron-LO-phonon quantum-kinetic equations which can be derived using phonon-assisted density matrices [21] or within the framework of nonequilibrium Green functions [14]. The density matrix of a photoexcited semiconductor is defined as  $(n_{\mathbf{k}})_{\alpha\beta} = \langle \hat{a}_{\beta\mathbf{k}}^\dagger \hat{a}_{\alpha\mathbf{k}} \rangle$  with band indices  $\alpha, \beta = c, v$  and Bloch wave vectors  $\mathbf{k}$ . In analogy, the phonon-assisted density matrix is given by  $(R_{\mathbf{k}\mathbf{k}'} )_{\alpha\beta} = g_{\mathbf{k}-\mathbf{k}'}^{-1} \langle \hat{a}_{\beta\mathbf{k}}^\dagger \hat{a}_{\alpha\mathbf{k}'} \hat{b}_{\mathbf{k}-\mathbf{k}'} \rangle$ , with the Fröhlich coupling parameter  $g_{\mathbf{q}}^2 = \hbar \omega_{\text{LO}} (2\Omega)^{-1} V_{\mathbf{q}} (1 - \epsilon_\infty / \epsilon_s)$ . Here  $V_{\mathbf{q}} = e^2 / [\epsilon_0 \epsilon_\infty (q^2 + \kappa^2)]$  is the Coulomb potential including quasistatic nonequilibrium Thomas-Fermi screening due to the excited electrons and holes. The numerical calculations are based on the second Born approximation. Using a matrix notation with respect to the band indices, the equations of motion can be written as

$$i\hbar \frac{\partial}{\partial t} n_{\mathbf{k}} = [H_{\mathbf{k}}^{\text{HF}}, n_{\mathbf{k}}] + i\hbar \frac{\partial}{\partial t} n_{\mathbf{k}} \Big|_{\text{relax}}, \quad (1)$$

$$i\hbar \frac{\partial}{\partial t} n_{\mathbf{k}} \Big|_{\text{relax}} = \sum_{\mathbf{k}'} g_{\mathbf{k}-\mathbf{k}'}^2 [R_{\mathbf{k}\mathbf{k}'} - R_{\mathbf{k}'\mathbf{k}} - \text{H.c.}], \quad (2)$$

$$i\hbar \frac{\partial}{\partial t} R_{\mathbf{k}\mathbf{k}'} = H_{\mathbf{k}'}^{\text{HF}} R_{\mathbf{k}\mathbf{k}'} - R_{\mathbf{k}\mathbf{k}'} H_{\mathbf{k}}^{\text{HF}} + \hbar \omega_{\text{LO}} R_{\mathbf{k}\mathbf{k}'} + (1 - n_{\mathbf{k}'}) n_{\mathbf{k}} (1 + N) - n_{\mathbf{k}'} (1 - n_{\mathbf{k}}) N. \quad (3)$$

Here  $N$  denotes the occupation number of the LO phonons, which are assumed to be in thermal equilibrium. The source term in Eq. (3) is related to (spontaneous and induced) downward scattering and (induced) upward scattering, while the homogeneous part of Eq. (3) describes the energy transfer related to these scattering events. The electronic Hamiltonian

$$(H_{\mathbf{k}}^{\text{HF}})_{\alpha\beta} = \begin{pmatrix} E_c(\mathbf{k}) & -\mu E_p(t) \\ -\mu^* E_p^*(t) & E_v(\mathbf{k}) \end{pmatrix} - \frac{1}{\Omega} \sum_{\mathbf{q}} \left[ V_{\mathbf{q}} (n_{\mathbf{k}-\mathbf{q}})_{\alpha\beta} - \frac{e^2}{\epsilon_0 \epsilon_\infty q^2} (n_{\mathbf{k}-\mathbf{q}})_{\alpha\beta}^{(0)} \right] \quad (4)$$

contains the band dispersions  $E_{c,v}(\mathbf{k}) = \pm E_g/2 \pm \hbar^2 k^2 / (2m_{e,h})$ , the coupling to the laser field  $E_p(t)$ , and the Hartree-Fock Coulomb interaction between electrons and holes, including band-gap renormalization.

We solve the coupled set of non-Markovian equations of motion (1)–(3) completely. Details of the numerical implementation including stability and convergency issues

are given in Ref. [16]. While it is well known how to calculate FWM signals and pump-probe signals from the solutions of these quantum-kinetic equations, the conversion of the distribution functions into spontaneous emission spectra under consistent inclusion of Coulomb effects is a nontrivial problem. This requires the application of the recently developed theory of PL in semiconductors [17]. This theory relates the PL signal to the two-time two-wave-vector polarization function which is then calculated from the Bethe-Salpeter equation in ladder approximation. As a result, the time-dependent PL spectra  $I(\omega, t)$  can be conveniently expressed as

$$I(\omega, t) \propto \frac{1}{\Omega} \sum_{\mathbf{k}_1 \mathbf{k}_2 \mathbf{k}} [H - \hbar(\omega + i\epsilon)]_{\mathbf{k}_1 \mathbf{k}}^{-1} 2\hbar \epsilon(n_{\mathbf{k}})_{cc} \times [1 - (n_{\mathbf{k}})_{vv}] [H - \hbar(\omega + i\epsilon)]_{\mathbf{k} \mathbf{k}_2}^{-1\dagger}, \quad (5)$$

with an effective two-particle Hamiltonian

$$H_{\mathbf{k}_1 \mathbf{k}_2} = [(H_{\mathbf{k}_1}^{\text{HF}})_{cc} - (H_{\mathbf{k}_1}^{\text{HF}})_{vv}] \delta_{\mathbf{k}_1 \mathbf{k}_2} - [(n_{\mathbf{k}_1})_{vv} - (n_{\mathbf{k}_1})_{cc}] \frac{1}{\Omega} V_{\mathbf{k}_1 - \mathbf{k}_2}. \quad (6)$$

The inclusion of Coulomb effects in Eq. (6) allows for PL at the excitonic resonances and generalizes the textbook result of free-particle PL [22].

For the explicit calculations we used bulk GaAs parameters,  $E_g(0 \text{ K}) = 1.52 \text{ eV}$ ,  $E_g(300 \text{ K}) = 1.43 \text{ eV}$ ,  $m_e = 0.067m_0$ ,  $m_h = 0.442m_0$ ,  $\hbar\epsilon = 0.94 \text{ meV}$ ,  $\hbar\omega_{\text{LO}} = 36 \text{ meV}$ ,  $\epsilon_\infty = 11.1$ , and  $\epsilon_s = 13.1$ . The exciton binding energy is  $1 \text{ Ry}^* = 4.7 \text{ meV}$ . The pump-pulse parameters are fixed at a detuning of  $\hbar\omega_p - E_g = 112.8 \text{ meV}$  ( $24 \text{ Ry}^*$ ) and a maximum laser intensity of  $I_p \approx 0.5 \text{ MW/cm}^2$  ( $\mu E_p = 0.1 \text{ Ry}^*$ ) at  $t = 0$ . In order to optimize the spectral resolution, we choose a pump pulse length of 320 fs which is larger than the LO-phonon period  $T_{\text{LO}} \approx 115 \text{ fs}$ .

In Figs. 1 and 2, we present the time evolution of the energetic distributions of electrons (a) and holes (b) and the corresponding PL spectra (c),(d) for times of  $t = -70$  to 2800 fs (from top to bottom). The lattice temperature is  $T = 300 \text{ K}$  (Fig. 1) and  $T = 0 \text{ K}$  (Fig. 2), respectively.

From Fig. 1(a), it follows that the electrons start to relax already during the pumping process which is seen through a cascadelike buildup of phonon replicas of the initial distribution. These replicas start from an initially broad signal and narrow with increasing time. Such memory effects reflect the quantum-mechanical time-energy uncertainty principle and are a pronounced signature of quantum kinetics. At later times, the electrons accumulate near the band minimum, and after 2.8 ps an almost thermal distribution is reached. The same is true for the holes in Fig. 1(b). However, for energetic reasons only distinct phonon-absorption peaks emerge.

In the linear PL spectra [Fig. 1(c)], the relaxation process is nicely resolved. After the strong initial PL at the

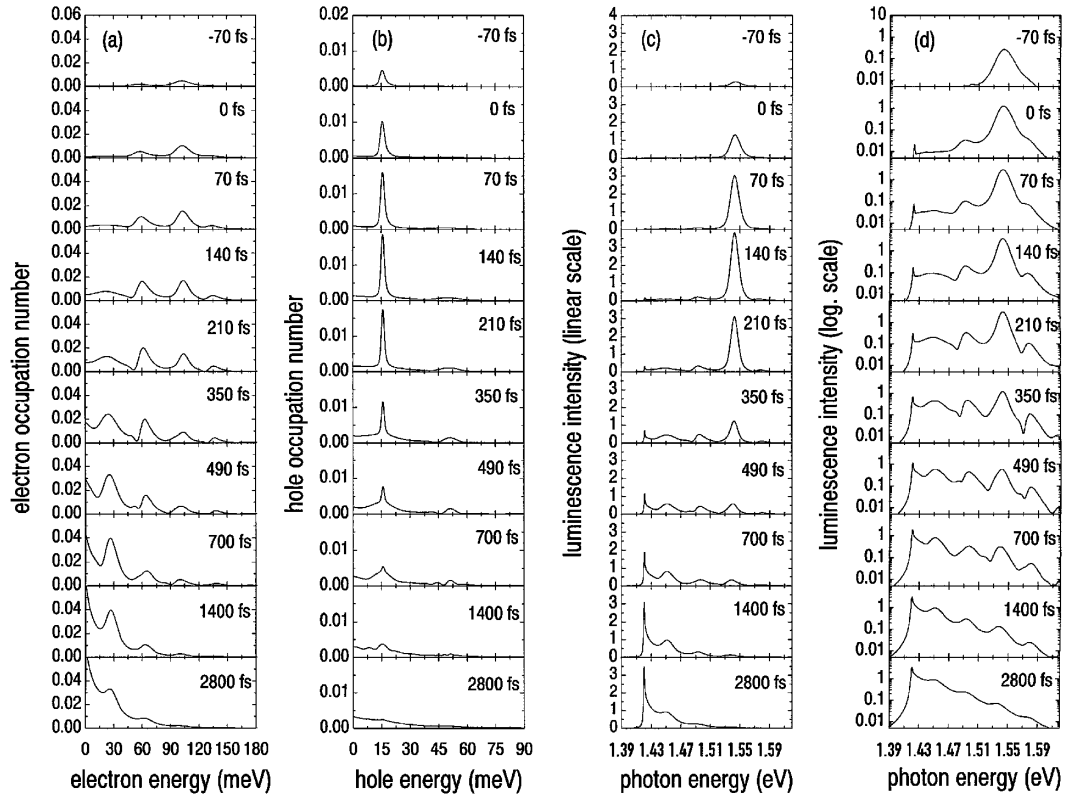


FIG. 1. From left to right: (a) electron distribution  $n_{ec}$ , (b) hole distribution  $1 - n_{vv}$ , (c) linear luminescence spectra  $I(\omega, t)$ , and (d) logarithmic luminescence spectra  $I(\omega, t)$  for times  $t = -70, \dots, 2800$  fs (from top to bottom). The pump parameters are  $\hbar\omega_p - E_g = 112.8$  meV and  $I_p \approx 0.5$  MW/cm<sup>2</sup>, and the pulse length is 320 fs. The temperature is  $T = 300$  K.

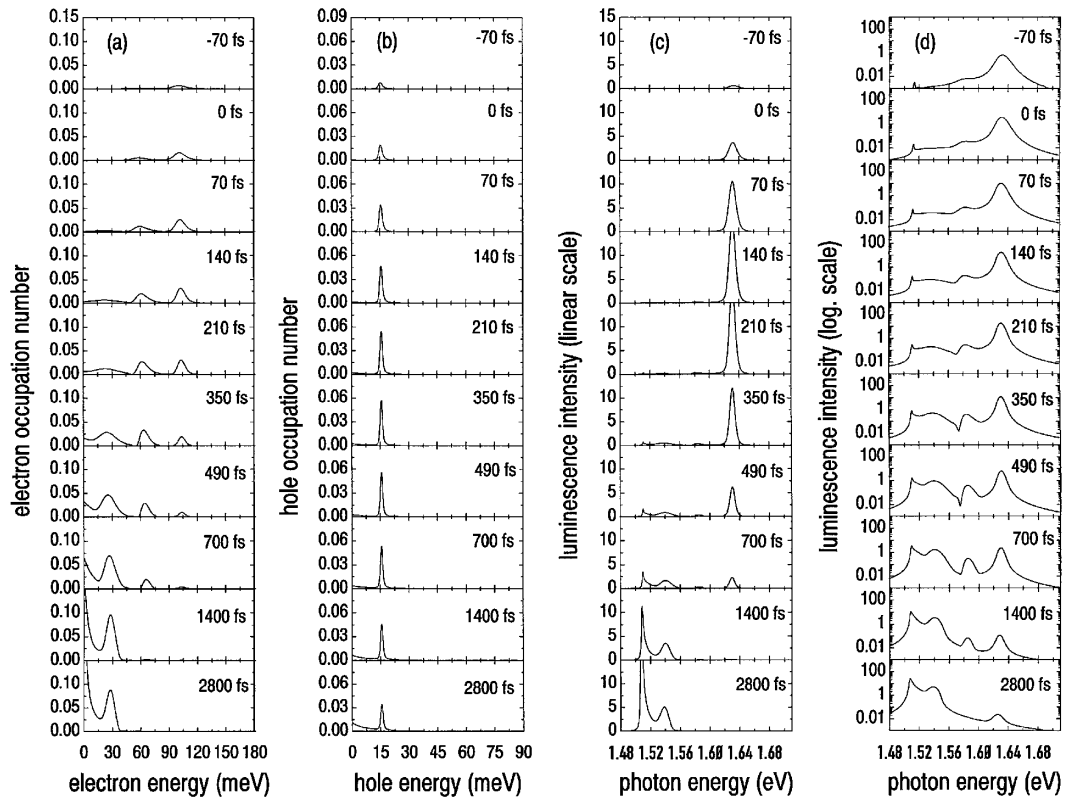


FIG. 2. Same as Fig. 1, but for temperature  $T = 0$  K.

pump frequency, subsequent phonon replicas emerge, on both the low- and high-energy sides. Here, the non-Markovian broadening is especially pronounced at the second phonon replica ( $\hbar\omega \approx 1.45$  eV). Furthermore, the relaxation process is accompanied by a gradual buildup of PL at the  $1s$  exciton resonance, which becomes the dominant contribution after about 1 ps. For smaller pump intensities (not shown) where screening is not so efficient because of smaller electron-hole pair densities, the PL peak from the  $2s$  exciton is also resolved.

The logarithmic-scale plot in Fig. 1(d) also shows that for large times the PL intensity above the band gap evolves into an exponentially decreasing tail. Assuming that electrons and holes are in quasiequilibrium, an exponential fit of this tail may be used to define a temperature of the electron gas, as it is done to extract information from PL experiments since many decades [23]. Nevertheless, the concept of an effective temperature cannot be fully justified from our microscopic analysis since exact quasiequilibrium is not reached.

Because of bottleneck effects, the situation is even more complicated for zero temperature. Since upward scattering is not possible in this case, the conduction electrons do not completely thermalize within the first few ps. This is evident from Fig. 2(a), where the distribution after 2.8 ps is still highly nonthermal. The signature of this bottleneck effect is clearly visible in the PL spectra [Fig. 2(c)] as a pronounced peak around  $\hbar\omega = 1.54$  eV. Analogously, the holes do not significantly relax on this time scale [Fig. 2(b)]. As a result, the PL signal at the pump frequency is still noticeable after 2.8 ps, as becomes clear from Fig. 2(d). Similar results were obtained in recent pump-probe experiments in GaAs [6], where the first phonon replica also vanished faster than the signal at  $\hbar\omega_p$ . This is no longer true for the more polar material CdTe, where stronger quantum-kinetic effects also lead to efficient hole relaxation.

Both series of PL spectra in Figs. 1 and 2, in particular using the linear scale, show a strong transition from PL at the pump frequency to excitonic PL within a few picoseconds. The hot-luminescence signals in between give insight into the relaxation process and related quantum-kinetic effects. We feel that principally the scenario described should be observable in sensitive time-resolved PL experiments. Effects beyond the present theory may be necessary for an improved description of the details of the relaxation process, but we believe they will not significantly alter the general picture presented in this Letter. Future refinements may include especially a density-dependent line broadening, e.g., by calculating the self-energy in  $T$ -matrix approximation, as recently done by Piermarocchi *et al.* within a simplified 1D model [19]. A generalization of the present approach towards a

fully dynamic theory, i.e., including a dynamic solution of the Bethe-Salpeter equation, is also highly desirable, but presently not at hand. Such investigations may also help to clarify the relation between our theory and the approach of Kira *et al.* [20].

In summary, we have presented the first quantum-kinetic studies of time-and-energy resolved photoluminescence from pulse-excited semiconductors. Our approach combines quantum kinetics of hot-electron relaxation and quantum theory of spontaneous emission under consistent inclusion of Coulomb interaction between the excited hot carriers. We predict time-resolved photoluminescence to be a sensitive measure of electron-LO-phonon quantum-kinetics and bottleneck effects. This is exemplified by model calculations that show how the luminescence intensity shifts from the initial signal at the pump frequency towards the excitonic resonance via emission of LO phonons.

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