Coherent and non-Markovian effects in ultrafast relaxation of photoexcited hot carriers: A model study

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We discuss two quantum effects that can influence the relaxation of carriers in a semiconductor excited by an ultrashort light pulse. Namely, the presence of nonzero interband optical polarization and the large energy uncertainty of carriers created by the short exciting pulse. The importance of both effects is investigated numerically for the case of electron–LO-phonon interaction assuming a model (exponential) pulse shape. Comparison of the results with the predictions based on the conventional Boltzmann equation indicates that both effects lead to a much more even distribution of carriers over **k** space, which may significantly shorten thermalization times.

I. INTRODUCTION

Photoexcited hot electrons have been studied for more than two decades now. In the past few years, the advent of femtosecond lasers has given a new dimension to this field by providing means to investigate the fastest and the "most nonequilibrium" stages of carrier relaxation processes.[1]

At present the theoretical description of such ultrafast phenomena is based on the semiclassic Boltzmann equation (BE), and the results of corresponding calculations[2–5] are in reasonably good accord with the experimental findings.[5,6] However, as the excitation pulses continue to get shorter, significant departures from the conventional semiclassic picture of relaxation phenomena can be expected to emerge.

Indeed, there are at least two reasons for the semiclassic description to break down in the limit of small exciting pulse durations. The first of them is that an optical pulse creates carriers in quantum states which are definitely not semiclassic—initially, carrier wave functions are superpositions of conduction- and valence-band states.[7] As long as this phase coherence (which manifests itself as the macroscopic interband polarization) (Refs. 8 and 9) is maintained, i.e., at times shorter than the dephasing time (experimental measurements[10,11] give values in the range 1 ps to 10 fs for this quantity), the carriers are not in definite-energy eigenstates and therefore cannot be described semiclassically. Hence, at early stages of the optical excitation, the presence of the interband polarization has to be explicitly taken into account in the kinetic equations for carrier dynamics.

Another important point is that for femtosecond pulses the time-energy uncertainty principle comes into play—*each* individual carrier created by such a pulse is distributed over a broad (some tens of meV) region of **k** space corresponding to the spectral width of the exciting pulse, so that once again we cannot regard it as a semiclassic particle with well-defined energy. In the currently used calculation schemes[3–5] this effect is summarily included by broadening the initial energy distribution of carriers by the excitation spectral width, but this alone can hardly be sufficient, since in this case the presence of energy-conserving δ functions in the BE is in clear violation of the time-energy uncertainty principle. Any consistent treatment of this problem must take into consideration the actual excitation history, which requires the use of non-Markovian generalizations of the BE.[12]

In our recent work[13] we have proposed a systematic way to incorporate both the interband polarization and the memory effects into the description of the carrier kinetics. However, the non-Markovian structure of the resulting "effective Bloch equations"[8] for the carrier kinetics and dephasing practically precludes any straightforward attempts to solve them numerically for more or less realistic situations. Therefore it seems reasonable to apply these equations to some simplified models first.

In the present paper we analyze a model situation when a two-band semiconductor is excited by an exponential light pulse. However unrealistic this model might seem, this particular shape of the excitation pulse allows one to get simple and *exact* expressions for the scattering rates which readily lend themselves to numerical evaluation. These scattering rates are used to assess the role that the above two quantum effects can play in the carrier relaxation phenomena.

The paper is organized as follows: Sec. II is devoted to a general formulation of the problem in terms of the effective Bloch equations specified for the case of the electron-phonon interaction. The origins,, as well as some general properties of the coherent and memory effects, are briefly discussed in this section. In Sec. III the exponential pulse model is introduced, and the corresponding simplified expressions for the scattering rates are derived. The numerical results for the scattering rates are presented and discussed in Sec. IV. Concluding remarks are confined to the final Sec. V.

II. GENERAL THEORY

The purpose of this section is to introduce basic equations for the carrier distribution functions and for the interband polarization (the effective Bloch equations),[8,13] which will be used as a starting point for the numerical studies in the subsequent sections.

We restrict ourselves to the case of a semiconductor with two (parabolic) bands, c and v (the intricate band-structure effects[5] are thereby left out). The Heisenberg creation operator $a^{\dagger}_{\alpha\mathbf{k}}$ creates an electron with the wave vector $\mathbf{k}$ in the band $\alpha=\{c.v\}$. Furthermore, we assume spatial homogeneity and therefore work in $\mathbf{k}$ space only.

We will be interested in the evolution of the one-particle density matrix (DM):

$$N^{\alpha\beta}_{\mathbf{k}}(t)\equiv \begin{bmatrix} \langle a^{\dagger}_{c\mathbf{k}}(t)a_{c\mathbf{k}}(t)\rangle & \langle a^{\dagger}_{v\mathbf{k}}(t)a_{c\mathbf{k}}(t)\rangle \\ \langle a^{\dagger}_{c\mathbf{k}}(t)a_{v\mathbf{k}}(t)\rangle & \langle a^{\dagger}_{v\mathbf{k}}(t)a_{v\mathbf{k}}(t)\rangle \end{bmatrix}_{\alpha\beta} \equiv \begin{bmatrix} n_{c\mathbf{k}}(t) & p_{\mathbf{k}}(t) \\ p^{*}_{\mathbf{k}}(t) & n_{v\mathbf{k}}(t) \end{bmatrix}_{\alpha\beta} . \tag{1}$$

(where $\langle\ \rangle$ denotes statistical average), whose diagonal components give the distribution functions of carriers within the bands, while the nondiagonal ones describe the quantum-mechanical coherence between the bands; $\sum_{\mathbf{k}}p_{\mathbf{k}}$ is known to be proportional to the optical polarization.[8,9]

In the Heisenberg representation $N^{\alpha\beta}_{\mathbf{k}}$ obeys the following equations of motion:

$$\left[\frac{\partial N^{\alpha\beta}_{\mathbf{k}}}{\partial t}\right]=i\langle[\hat{H}(t),a^{\dagger}_{\beta\mathbf{k}}(t)a_{\alpha\mathbf{k}}(t)]\rangle \tag{2}$$

($\hbar=1$ throughout the paper), where $\hat{H}$ is the full Hamiltonian of the problem. Besides the free-carrier Hamiltonian:

$$\hat{H}_0=\sum_{\alpha\mathbf{k}}\varepsilon_{\alpha\mathbf{k}}a^{\dagger}_{\alpha\mathbf{k}}a_{\alpha\mathbf{k}} \tag{3}$$

($\varepsilon_{\alpha\mathbf{k}}$ is the carrier dispersion in the band α), we will include in our treatment also the interaction with a classic optical field $E(t)$:

$$\hat{H}_{\mathrm{opt}}=-\sum_{\substack{\alpha\beta\\ \mathbf{k}}}\mu_{\alpha\beta}(\mathbf{k})a^{\dagger}_{\alpha\mathbf{k}}a_{\beta\mathbf{k}}E(t) \tag{4}$$

(where $\mu_{\alpha\beta}$ is the interband optical matrix element; we will neglect its diagonal elements,[8,9] as well as the $\mathbf{k}$ dependence of $\mu_{cv}=\mu^{*}_{vc}$), as well as the electron-phonon interaction:

$$\hat{H}_{\mathrm{ph}}=\sum_{\mathbf{q}}\omega_{\mathbf{q}}b^{\dagger}_{\mathbf{q}}b_{\mathbf{q}}+\sum_{\mathbf{k}\mathbf{q}\alpha}M_{\mathbf{q}}(b_{\mathbf{q}}+b^{\dagger}_{-\mathbf{q}})a^{\dagger}_{\alpha\mathbf{k}}a_{\alpha\mathbf{k}-\mathbf{q}} \tag{5}$$

(where the free phonons are included; $\omega_{\mathbf{q}}$ is the phonon dispersion. $M_{\mathbf{q}}$ is the electron-phonon coupling). Hence the full Hamiltonian reads

$$\hat{H}=\hat{H}_0+\hat{H}_{\mathrm{opt}}+\hat{H}_{\mathrm{ph}} . \tag{6}$$

Without phonons the commutator in (2) can be taken exactly, which results in the closed equations of motion for $N^{\alpha\beta}_{\mathbf{k}}$:

$$\frac{\partial n_{c\mathbf{k}}}{\partial t}=-2\,\mathrm{Im}(p^{*}_{\mathbf{k}}\mu_{cv}E) , \tag{7a}$$

$$\frac{\partial n_{v\mathbf{k}}}{\partial t}=-\left[\frac{\partial n_{c\mathbf{k}}}{\partial t}\right] , \tag{7b}$$

$$\frac{\partial p_{\mathbf{k}}}{\partial t}=-i(\varepsilon_{c\mathbf{k}}-\varepsilon_{v\mathbf{k}})p_{\mathbf{k}}+i\mu_{cv}E(n_{v\mathbf{k}}-n_{c\mathbf{k}}) . \tag{7c}$$

Equations (7) are nothing but the Bloch equations which are widely used to describe the optical response of two-level systems.[14] According to (7), in the absence of the electron-phonon (or the Coulomb) interaction $N^{\alpha\beta}_{\mathbf{k}}$ for each $\mathbf{k}$ state evolves independently. The general solution to the Bloch equations for an arbitrary $E(t)$ is not known; however, Eqs. (7) possess a useful integral of motion:[7,9,14]

$$4|p_{\mathbf{k}}|^2+(n_{v\mathbf{k}}-n_{c\mathbf{k}})^2=1 \tag{8}$$

(radius of the Bloch sphere),[14] which makes clear that as long as there is no relaxation, p and n [i.e., the diagonal and the nondiagonal components of the DM (1)] are generally of the same order. This is particularly obvious in the low-excitation limit ($n \ll 1$), where (8) reduces to

$$|p_{\mathbf{k}}|^2\approx n_{c\mathbf{k}}\approx(1-n_{v\mathbf{k}}) . \tag{9}$$

The electron-phonon interaction (5) gives rise to additional terms in the equations of motion (2), which are responsible for relaxation:

$$\frac{\partial N^{\alpha\beta}_{\mathbf{k}}}{\partial t}=\left[\frac{\partial N^{\alpha\beta}_{\mathbf{k}}}{\partial t}\right]_{\mathrm{coh}}+\left[\frac{\partial N^{\alpha\beta}_{\mathbf{k}}}{\partial t}\right]_{\mathrm{St}} , \tag{10}$$

where the "coherent" terms[8] are given by (7).

The general non-Markovian result for the collision term in lowest order in the electron-phonon coupling is[13]

$$\begin{aligned}\left[\frac{\partial N^{\alpha\beta}_{\mathbf{k}}}{\partial t}\right]_{\mathrm{St}}=\sum_{\gamma\mathbf{q}}M^2_{\mathbf{q}}\int_{-\infty}^{t}dt'\{&e^{i(t'-t)(\varepsilon_{\alpha\mathbf{k}}-\varepsilon_{\beta\mathbf{k}-\mathbf{q}}-\omega_{\mathbf{q}})}[(\delta_{\alpha\gamma}-N^{\alpha\gamma}_{\mathbf{k}})N^{\gamma\beta}_{\mathbf{k}-\mathbf{q}}\mathcal{N}_{\mathbf{q}}-N^{\alpha\gamma}_{\mathbf{k}}(\delta_{\gamma\beta}-N^{\gamma\beta}_{\mathbf{k}-\mathbf{q}})(1+\mathcal{N}_{\mathbf{q}})]\\ &+e^{i(t'-t)(\varepsilon_{\alpha\mathbf{k}}-\varepsilon_{\beta\mathbf{k}-\mathbf{q}}+\omega_{\mathbf{q}})}[(\delta_{\alpha\gamma}-N^{\alpha\gamma}_{\mathbf{k}})N^{\gamma\beta}_{\mathbf{k}-\mathbf{q}}(1+\mathcal{N}_{\mathbf{q}})-N^{\alpha\gamma}_{\mathbf{k}}(\delta_{\gamma\beta}-N^{\gamma\beta}_{\mathbf{k}-\mathbf{q}})\mathcal{N}_{\mathbf{q}}]\\ &+e^{i(t'-t)(\varepsilon_{\alpha\mathbf{k}-\mathbf{q}}-\varepsilon_{\beta\mathbf{k}}+\omega_{\mathbf{q}})}[N^{\alpha\gamma}_{\mathbf{k}-\mathbf{q}}(\delta_{\gamma\beta}-N^{\gamma\beta}_{\mathbf{k}})\mathcal{N}_{\mathbf{q}}-(\delta_{\alpha\gamma}-N^{\alpha\gamma}_{\mathbf{k}-\mathbf{q}})N^{\gamma\beta}_{\mathbf{k}}(1+\mathcal{N}_{\mathbf{q}})]\\ &+e^{i(t'-t)(\varepsilon_{\alpha\mathbf{k}-\mathbf{q}}-\varepsilon_{\beta\mathbf{k}}-\omega_{\mathbf{q}})}[N^{\alpha\gamma}_{\mathbf{k}-\mathbf{q}}(\delta_{\gamma\beta}-N^{\gamma\beta}_{\mathbf{k}})(1+\mathcal{N}_{\mathbf{q}})-(\delta_{\alpha\gamma}-N^{\alpha\gamma}_{\mathbf{k}-\mathbf{q}})N^{\gamma\beta}_{\mathbf{k}}\mathcal{N}_{\mathbf{q}}]\} ,\end{aligned} \tag{11}$$

where $N_{\mathbf{k}}^{\alpha\beta}$ and the phonon occupation numbers $\mathcal{N}_{\mathbf{q}}$ depend on the integration time variable t'.

To get an insight into the contents of Eq. (11), let us first pass to the Markovian limit by assuming that $n_{\alpha\mathbf{k}}$ and $|p_{\mathbf{k}}|$ vary slowly with time. Taking into account the free interband oscillations of the polarization, $p_{\mathbf{k}} \propto \exp[i(\varepsilon_{c\mathbf{k}}-\varepsilon_{v\mathbf{k}})t]$, we can perform the time integration in (11), which yields

$$\begin{aligned}\left[\frac{\partial N_{\mathbf{k}}^{\alpha\beta}}{\partial t}\right]_{\mathrm{St}} = \sum_{\mathbf{q}\gamma} M_{\mathbf{q}}^2 \{ & \delta_-(\varepsilon_{\gamma\mathbf{k}}-\varepsilon_{\gamma\mathbf{k}-\mathbf{q}}-\omega_{\mathbf{q}})[(\delta_{\alpha\gamma}-N_{\mathbf{k}}^{\alpha\gamma})N_{\mathbf{k}-\mathbf{q}}^{\gamma\beta}\mathcal{N}_{\mathbf{q}}-N_{\mathbf{k}}^{\alpha\gamma}(\delta_{\gamma\beta}-N_{\mathbf{k}-\mathbf{q}}^{\gamma\beta})(1+\mathcal{N}_{\mathbf{q}})] \\ & +\delta_-(\varepsilon_{\gamma\mathbf{k}}-\varepsilon_{\gamma\mathbf{k}-\mathbf{q}}+\omega_{\mathbf{q}})[(\delta_{\alpha\gamma}-N_{\mathbf{k}}^{\alpha\gamma})N_{\mathbf{k}-\mathbf{q}}^{\gamma\beta}(1+\mathcal{N}_{\mathbf{q}})-N_{\mathbf{k}}^{\alpha\gamma}(\delta_{\gamma\beta}-N_{\mathbf{k}-\mathbf{q}}^{\gamma\beta})\mathcal{N}_{\mathbf{q}}] \\ & +\delta_+(\varepsilon_{\gamma\mathbf{k}}-\varepsilon_{\gamma\mathbf{k}-\mathbf{q}}-\omega_{\mathbf{q}})[N_{\mathbf{k}-\mathbf{q}}^{\alpha\gamma}(\delta_{\gamma\beta}-N_{\mathbf{k}}^{\gamma\beta})\mathcal{N}_{\mathbf{q}}-(\delta_{\alpha\gamma}-N_{\mathbf{k}-\mathbf{q}}^{\alpha\gamma})N_{\mathbf{k}}^{\gamma\beta}(1+\mathcal{N}_{\mathbf{q}})] \\ & +\delta_+(\varepsilon_{\gamma\mathbf{k}}-\varepsilon_{\gamma\mathbf{k}-\mathbf{q}}+\omega_{\mathbf{q}})[N_{\mathbf{k}-\mathbf{q}}^{\alpha\gamma}(\delta_{\gamma\beta}-N_{\mathbf{k}}^{\gamma\beta})(1+\mathcal{N}_{\mathbf{q}})-(\delta_{\alpha\gamma}-N_{\mathbf{k}-\mathbf{q}}^{\alpha\gamma})N_{\mathbf{k}}^{\gamma\beta}\mathcal{N}_{\mathbf{q}}]\}\ , \end{aligned} \tag{12}$$

where all N and $\mathcal{N}$ are now taken at the current time t; and

$$\int_{-\infty}^{0} d\tau\, e^{i\tau\varepsilon} = \pi\delta(\varepsilon) - i\lim_{\delta\to 0}\frac{\varepsilon}{\varepsilon^2+\delta^2} \equiv \pi\delta_-(\varepsilon)\ , \tag{13a}$$

$$\delta_+(\varepsilon)=\delta_-^*(\varepsilon)=\delta_-(-\varepsilon)\ . \tag{13b}$$

Let us first consider the equation for the electron distribution function $n_{c\mathbf{k}}(t)$, which follows from (12) at $\alpha=\beta=c$. Taking the diagonal term ($\gamma=c$) in (12), we immediately recover the standard Boltzmann collision integral:

$$\begin{aligned}\left[\frac{\partial n_{c\mathbf{k}}}{\partial t}\right]_{\mathrm{Boltzmann}} = \sum_{\mathbf{q}} M_{\mathbf{q}}^2 \{ & 2\pi\delta(\varepsilon_{c\mathbf{k}}-\varepsilon_{c\mathbf{k}-\mathbf{q}}-\omega_{\mathbf{q}})[\mathcal{N}_{\mathbf{q}}n_{c\mathbf{k}-\mathbf{q}}(1-n_{c\mathbf{k}})-(1+\mathcal{N}_{\mathbf{q}})n_{c\mathbf{k}}(1-n_{c\mathbf{k}-\mathbf{q}})] \\ & +2\pi\delta(\varepsilon_{c\mathbf{k}}-\varepsilon_{c\mathbf{k}-\mathbf{q}}+\omega_{\mathbf{q}})[(1+\mathcal{N}_{\mathbf{q}})n_{c\mathbf{k}-\mathbf{q}}(1-n_{c\mathbf{k}})-\mathcal{N}_{\mathbf{q}}n_{c\mathbf{k}}(1-n_{c\mathbf{k}-\mathbf{q}})]\}\ . \end{aligned} \tag{14}$$

Equation (12), however, also contains terms with the nondiagonal components of the DM ($\gamma=v$):

$$\begin{aligned}\left[\frac{\partial n_{c\mathbf{k}}}{\partial t}\right]_{\mathrm{pol}} &= \sum_{\mathbf{q}} M_{\mathbf{q}}^2 \Bigg[(p_{\mathbf{k}}^* p_{\mathbf{k}-\mathbf{q}} + p_{\mathbf{k}} p_{\mathbf{k}-\mathbf{q}}^*)[\pi\delta(\varepsilon_{v\mathbf{k}}-\varepsilon_{v\mathbf{k}-\mathbf{q}}-\omega_{\mathbf{q}})-\pi\delta(\varepsilon_{v\mathbf{k}}-\varepsilon_{v\mathbf{k}-\mathbf{q}}+\omega_{\mathbf{q}})] \\ &\qquad + i(p_{\mathbf{k}}^* p_{\mathbf{k}-\mathbf{q}} - p_{\mathbf{k}} p_{\mathbf{k}-\mathbf{q}}^*)\frac{2\omega_{\mathbf{q}}}{(\varepsilon_{v\mathbf{k}}-\varepsilon_{v\mathbf{k}-\mathbf{q}})^2-\omega_{\mathbf{q}}^2}\Bigg] \\ &= -2\,\mathrm{Im}\sum_{\mathbf{q}} p_{\mathbf{k}}^* V_{\mathrm{eff}}^R(\mathbf{q},\omega=\varepsilon_{v\mathbf{k}}-\varepsilon_{v\mathbf{k}-\mathbf{q}})p_{\mathbf{k}-\mathbf{q}}\ , \end{aligned} \tag{15}$$

where

$$V_{\mathrm{eff}}^R(q\omega)=M_{\mathbf{q}}^2\frac{2\omega_{\mathbf{q}}}{(\omega+i\delta)^2-\omega_{\mathbf{q}}^2} \tag{16}$$

is the retarded Fröhlich interaction potential.[13]

The additional scattering terms (15) describe the influence of the interband polarization on the carrier kinetics and, according to (8) and (9), at early stages of the excitation are of the same order as the conventional Boltzmann terms (naturally, after a lapse of a few dephasing times these terms vanish, and the usual Boltzmann scattering regime is restored). The physical origin of these terms consists in the presence of a *local field,* $\sum_{\mathbf{q}} V_{\mathrm{eff}}(\mathbf{q})p_{\mathbf{k}-\mathbf{q}}$, which enters Eq. (15) just in the same way as the external field E appears in Eq. (7).

This local field generates carriers in some portions of $\mathbf{k}$ space while destroying them elsewhere. The total number of particles is left unchanged by this process, so that it can be regarded as just another kind of scattering ("polarization scattering").[13] Unfortunately, the analogy with scattering stops at particle conservation, since this process does not conserve the energy—some of the terms in (15) do not have the δ-function structure, so that the particles are no longer bound to gain or lose exactly one phonon energy in a scattering event. Of course this does not violate any laws of nature, since when $p_{\mathbf{k}}\neq 0$, the carriers do not have any definite energy in the first place, but it does make the polarization scattering nontrivial and worth investigating.

Apart from the polarization scattering, there is another reason for the BE to fail under femtosecond excitation conditions: the Markovian approximation may break down if the excitation pulse gets short enough. Therefore let us now consider the general non-Markovian form of the collision terms.

Introducing the notation:

$$\varepsilon_\alpha^+ \equiv \varepsilon_{\alpha\mathbf{k}} - \varepsilon_{\alpha\mathbf{k}-\mathbf{q}} + \omega_\mathbf{q} ,$$
$$\varepsilon_\alpha^- \equiv \varepsilon_{\alpha\mathbf{k}} - \varepsilon_{\alpha\mathbf{k}-\mathbf{q}} - \omega_\mathbf{q} , \tag{17}$$
$$\tau = t - t' .$$

we can extract the equation for $n_{c\mathbf{k}}$ from (11):

$$\begin{aligned}\frac{\partial n_{c\mathbf{k}}}{\partial t} = \sum_\mathbf{q} M_\mathbf{q}^2 \int_{-\infty}^{t} dt' (& -n_{c\mathbf{k}}(1-n_{c\mathbf{k}-\mathbf{q}})\{\mathcal{N}_\mathbf{q}[2\cos(\tau\varepsilon_c^+)] + (1+\mathcal{N}_\mathbf{q})[2\cos(\tau\varepsilon_c^-)]\} \\ & + (1-n_{c\mathbf{k}})n_{c\mathbf{k}-\mathbf{q}}\{(1+\mathcal{N}_\mathbf{q})[2\cos(\tau\varepsilon_c^+)] + \mathcal{N}_\mathbf{q}[2\cos(\tau\varepsilon_c^-)]\} \\ & + i(p_\mathbf{k} p^*_{\mathbf{k}-\mathbf{q}} e^{i\tau(\varepsilon_{c\mathbf{k}}-\varepsilon_{c\mathbf{k}-\mathbf{q}})} - p^*_\mathbf{k} p_{\mathbf{k}-\mathbf{q}} e^{+i\tau(\varepsilon_{c\mathbf{k}}-\varepsilon_{c\mathbf{k}-\mathbf{q}})})[2\sin(\tau\omega_\mathbf{q})]) \end{aligned} \tag{18}$$

(where all n, p, and $\mathcal{N}$ are now functions of t').

In the Markovian case, when n and $\mathcal{N}$ in (18) do not depend on τ, the integration in (18) picks out of the **q** sum only those components for which the integrands do not oscillate at all, that assures energy conservation. When the occupation numbers do depend on time, in general all terms in the sum over **q** space begin to contribute to the scattering rate. For example, if the carriers are created by an optical pulse with the duration τ_p, the integration in (18) will conserve the energy only with the accuracy $\hbar/\tau_p$, so that the carriers can scatter to a more broad region of **k** space out of a given state, with correspondingly smaller amplitude.

It is obvious that the additional time integral in the relaxation term (18) makes its straightforward evaluation almost unaccomplishable. It would be advantageous, however, to assess the importance of the memory effects on some simplified model in order to find out whether they are worth the tremendous numerical efforts involved in a full-fledged evaluation of expressions like (18). This is what we are going to do in the following section.

III. EXPONENTIAL PULSE MODEL

In this section we introduce a model which allows one to compare the relative importance of different scattering channels and to assess the role of the above-discussed quantum effects, without actually solving the full non-Markovian Bloch equations (10).

Let us assume the electron-phonon interaction to be weak compared to the interaction with the optical field $E(t)$. Then, if we were able to solve the coherent part (7) of the Bloch equation, we could insert the resulting time-dependent DM $N_\mathbf{k}^{\alpha\beta}(t)$ into the relaxation part (11) and evaluate the corresponding relaxation rates (such a procedure is always justified for pulse durations smaller than the shortest relaxation time). Of course, this way we cannot follow up the actual thermalization process since the DM dynamics is governed only by the external field in this case, but the scattering rates can indicate what the relaxation terms would do to the carrier distributions if they were not assumed to be negligible.

Even in this oversimplified form the problem is still complicated, since one cannot solve (7) analytically for an arbitrary pulse shape.[14] However, there is one particular pulse shape for which (7) can be solved in the weak-excitation limit, namely, the exponential pulse:

$$E(t) = E_0 \exp\left[\frac{t}{\tau_p} - i\omega_0 t\right] . \tag{19}$$

Equation (19) can be thought of as an approximation for the leading edge of the excitation pulse with the duration τ_p and the central frequency ω_0. Note that since only past values of the field can influence the evolution of the system at any given moment, the divergence of (19) at $t \to \infty$ does not cause any inconvenience.

The equation for polarization (7c), which in the weak-excitation limit ($n_{c\mathbf{k}} \ll 1$) reads

$$\frac{\partial p_\mathbf{k}}{\partial t} = i(\varepsilon_{v\mathbf{k}} - \varepsilon_{c\mathbf{k}})p_\mathbf{k} + i\mu_{cv}E(t) , \tag{20}$$

can be straightforwardly solved with the model pulse shape (19):

$$p_\mathbf{k}(t) = \frac{(i\mu_{cv}E_0\tau_p)\exp(t/\tau_p)}{1 + i\left[\dfrac{\mathbf{k}^2 - \mathbf{k}_0^2}{2m_0}\right]\tau_p} e^{-i\omega_0 t} , \tag{21}$$

where m_0 is the reduced mass: $m_0 = m_c m_v/(m_c + m_v)$, and $\mathbf{k}_0^2 = 2m_0(\omega_0 - E_g)$.

By virtue of the property (9), we can immediately write down the solution for $n_{\alpha\mathbf{k}}(t)$:

$$n_{c\mathbf{k}}(t) = (1 - n_{v\mathbf{k}}) = |p_\mathbf{k}|^2$$
$$= (\mu_{cv}^2 E_0^2 \tau_p^2) \frac{\exp(2t/\tau_p)}{1 + \left[\dfrac{\mathbf{k}^2 - \mathbf{k}_0^2}{2m_0}\right]^2 \tau_p^2} . \tag{22}$$

As is clear from (22), within the exponential pulse model the density distribution in **k** space just grows exponentially with time without changing shape. This self-similarity implies that normalized scattering rates, $(\partial n_{\alpha\mathbf{k}}/\partial t)/n_{\alpha\mathbf{k}_0}$, do not depend on time at all. In order to obtain these time-independent quantities, which will later be plotted in the figures, we will simply set the factor $(\mu_{cv}^2 E_0^2 \tau_p^2)$ in (22) (the peak density reached by $t=0$) equal to unity further on.

In order to clarify the impact of the memory effects, let us consider the scattering-out term of (18) in the weak-excitation limit $[n \ll 1, \mathcal{N}_{\mathbf{q}}(t)=\text{const}]$:

$$\left[\frac{\partial n_{c\mathbf{k}}}{\partial t}\right]_{\text{out}} = -\int_{-\infty}^{t} dt'\, n_{c\mathbf{k}}(t') \sum_{\mathbf{q}} M_{\mathbf{q}}^2 [2\mathcal{N}_{\mathbf{q}} \cos(\tau \varepsilon_c^+) + 2(1+\mathcal{N}_{\mathbf{q}})\cos(\tau \varepsilon_c^-)] \ . \tag{23}$$

When $n_{c\mathbf{k}}$ depends on t' according to (22), the time integration turns the exponentials in (23) into Lorentzian peaks $1/\tau_p$ wide instead of the δ functions. Hence one could evaluate this and other terms of (18) by performing the integration over $\mathbf{k}$ space with the broadened δ functions instead of the true ones, just as it is done when the collisional broadening is taken into account.[5,12] We wish to stress that this treatment of the memory effects would break down beyond the nondegenerate limit, and that for more realistic (e.g., Gaussian) pulse shapes the broadened δ functions may be much more complex and even not positive definite.

Instead of performing the $\mathbf{k}$-space integration numerically, here we will take a different course of action. Let us note that the expression (23) can be written as

$$\left[\frac{\partial n_{c\mathbf{k}}}{\partial t}\right]_{\text{out}} = -\int_{-\infty}^{t} dt'\, n_{c\mathbf{k}}(t') \sigma_{c\mathbf{k}}^{\text{out}}(t-t') \ , \tag{24}$$

where the kernel

$$\sigma_{c\mathbf{k}}^{\text{out}}(\tau) = \sum_{\mathbf{q}} M_{\mathbf{q}}^2 [\mathcal{N}_{\mathbf{q}}(e^{i\tau\varepsilon_c^+} + e^{-i\tau\varepsilon_c^+}) + (1+\mathcal{N}_{\mathbf{q}})(e^{i\tau\varepsilon_c^-} + e^{-i\tau\varepsilon_c^-})] \tag{25}$$

describes the response of the semiconductor. At $\tau \to 0$ it diverges, because initially an electron can scatter to any $\mathbf{k}$ state regardless of its energy:

$$\sigma_{c\mathbf{k}}^{\text{out}}(\tau=0) = 2(1+2\mathcal{N}_{\mathbf{q}}) \sum_{\mathbf{q}} M_{\mathbf{q}}^2 \propto V_{\text{eff}}(r=0) = \infty \ , \tag{26}$$

and the oscillating energy exponentials make this sum finite at finite times. Since (24) has the form of a convolution, it is advantageous to make the Fourier transform:

$$\left[\frac{\partial n_{c\mathbf{k}}}{\partial t}\right]_{\text{out}} = \frac{1}{2\pi} \int_{-\infty}^{+\infty} d\omega\, n_{c\mathbf{k}}^r(\omega) \sigma_{c\mathbf{k}}^{\text{out}}(\omega) e^{i\omega t} \ , \tag{27}$$

where the retarded Fourier transform of the density is defined as

$$n^r(\omega) \equiv \int_{-\infty}^{t} n(t') e^{i\omega t'} dt' \ . \tag{28}$$

Assuming parabolic bands, the Fourier transform $\sigma(\omega)$ can be evaluated explicitly. For dispersionless polar optical phonons with[15]

$$M_{\mathbf{q}}^2 = \frac{2\pi e^2 \omega_{\text{LO}}}{\epsilon^* \mathbf{q}^2} \equiv \frac{C}{\mathbf{q}^2} \ , \tag{29}$$

we have, e.g., for the first term of (23),

$$\begin{aligned} \left[\sigma_{c\mathbf{k}}^{\text{out}}(\omega)\right]_I &= \int_{-\infty}^{+\infty} d\tau\, e^{i\omega\tau} \left[\sum_{\mathbf{q}} M_{\mathbf{q}}^2 \mathcal{N}_{\mathbf{q}} e^{i\tau(\varepsilon_{c\mathbf{k}} - \varepsilon_{c\mathbf{k}-\mathbf{q}} + \omega_{\mathbf{q}})}\right] \\ &= 2\pi \sum_{\mathbf{q}} M_{\mathbf{q}}^2 \mathcal{N}_{\mathbf{q}} \delta(\varepsilon_{c\mathbf{k}} - \varepsilon_{c\mathbf{k}-\mathbf{q}} + \omega_{\mathbf{q}} + \omega) = C_{c\mathbf{k}} \mathcal{N}_{\mathbf{q}} g\left[\frac{\omega_{\mathbf{q}}+\omega}{\varepsilon_{c\mathbf{k}}}\right] \end{aligned} \tag{30}$$

where

$$g(x) \equiv \ln\left[\frac{1+\sqrt{1-x}}{|1-\sqrt{1-x}|}\right] \ , \tag{31}$$

and

$$C_{c\mathbf{k}} = \frac{C m_c}{\pi |\mathbf{k}|} \ . \tag{32}$$

The $\mathbf{q}$ sum in (30) can be taken analytically because the integrand is a true δ function, not a broadened one. Equation (30) also shows that the frequency argument ω has a clear-cut physical sense: when absorbing a phonon, an electron now gains $\omega_{\mathbf{q}}+\omega$ instead of just $\omega_{\mathbf{q}}$, so that ω is a measure of energy nonconservation ("missing energy"). Thus the frequency integral (27) sums up the contributions of processes with all possible values of missing energy, whereas in the semiclassic description only processes with $\omega=0$ are taken into account.

Carrying out such summation over $\mathbf{q}$ in the remaining terms of (23), we arrive at

$$\sigma_{c\mathbf{k}}^{\text{out}}(\omega)=C_{c\mathbf{k}}\left\{(1+\mathcal{N}_{\mathbf{q}})\left[g\left[\frac{\omega_{\mathbf{q}}-\omega}{\varepsilon_{c\mathbf{k}}}\right]+g\left[\frac{\omega_{\mathbf{q}}+\omega}{\varepsilon_{c\mathbf{k}}}\right]\right]+\mathcal{N}_{\mathbf{q}}\left[g\left[\frac{-\omega_{\mathbf{q}}-\omega}{\varepsilon_{c\mathbf{k}}}\right]+g\left[\frac{\omega-\omega_{\mathbf{q}}}{\varepsilon_{c\mathbf{k}}}\right]\right]\right\}. \tag{33}$$

The response function $\sigma^{\text{out}}(\omega)$ (33) is shown in Fig. 1. The logarithmic singularity at $\omega=\pm\omega_{\mathbf{q}}$ is due to the $1/\mathbf{q}^2$ divergence of $M_{\mathbf{q}}^2$ (29) and accounts for the fact that the Fourier components of the density having such frequencies are resonant with respect to the phonons. In the exponential pulse model the retarded Fourier transform (28) of the density (22) reads

$$n^r(\omega)=n_{\mathbf{k}}(t)e^{i\omega t}\frac{\tau_p}{2+i\omega\tau_p} \tag{34}$$

(its real part is a Lorentzian and is also shown in Fig. 1), so that the general expression (27) for the scattering-out rate takes on the form

$$\left[\frac{\partial n_{c\mathbf{k}}}{\partial t}\right]_{\text{out}}=-\frac{n_{\mathbf{k}}(t)}{\pi}\int_0^{+\infty}d\omega\left[\frac{2\tau_p}{4+\omega^2\tau_p^2}\sigma_{c\mathbf{k}}^{\text{out}}(\omega)\right], \tag{35}$$

which can readily be evaluated numerically.

The fact that for the exponential pulse the population of all the $\mathbf{k}$ states has the same temporal dependence allows us to cast the remaining terms in the collisional integral (18) into essentially the same form. Indeed, let us consider the scattering-in term of (18):

$$\left[\frac{\partial n_{c\mathbf{k}}}{\partial t}\right]_{\text{in}}=\sum_{\mathbf{q}}\int_{-\infty}^{t}dt'\,n_{c\mathbf{k}-\mathbf{q}}(t')[(1+\mathcal{N}_{\mathbf{q}})e^{-i\tau\varepsilon_c^+}+\mathcal{N}_{\mathbf{q}}e^{-i\tau\varepsilon_c^-}+(1+\mathcal{N}_{\mathbf{q}})e^{i\tau\varepsilon_c^+}+\mathcal{N}_{\mathbf{q}}e^{i\tau\varepsilon_c^-}], \tag{36}$$

which, using the relation (22) to express $n_{c\mathbf{k}-\mathbf{q}}$ through $n_{c\mathbf{k}}$, can be transformed to the form

$$\left[\frac{\partial n_{c\mathbf{k}}}{\partial t}\right]_{\text{in}}=\frac{1}{\pi}\int_0^{+\infty}d\omega\,n_{c\mathbf{k}}^r(\omega)\sigma_{c\mathbf{k}}^{\text{in}}(\omega), \tag{37}$$

where the kernel $\sigma^{\text{in}}(\omega)$ can be calculated just like σ^{out} had been above:

$$\begin{aligned}\sigma_{c\mathbf{k}}^{\text{in}}(\omega)=C_{c\mathbf{k}}\Bigg[&\mathcal{N}_{\mathbf{q}}\frac{g\left[\frac{\omega_{\mathbf{q}}-\omega}{\varepsilon_{c\mathbf{k}}}\right]}{1+\tau_c^2(\varepsilon_{c\mathbf{k}}-\varepsilon_{c\mathbf{k}_0}+\omega-\omega_{\mathbf{q}})^2}+\mathcal{N}_{\mathbf{q}}\frac{q\left[\frac{\omega_{\mathbf{q}}+\omega}{\varepsilon_{c\mathbf{k}}}\right]}{1+\tau_c^2(\varepsilon_{c\mathbf{k}}-\varepsilon_{c\mathbf{k}_0}-\omega-\omega_{\mathbf{q}})^2}\\&+(1+\mathcal{N}_{\mathbf{q}})\frac{g\left[\frac{-\omega_{\mathbf{q}}-\omega}{\varepsilon_{c\mathbf{k}}}\right]}{1+\tau_c^2(\varepsilon_{c\mathbf{k}}-\varepsilon_{c\mathbf{k}_0}+\omega+\omega_{\mathbf{q}})^2}+(1+\mathcal{N}_{\mathbf{q}})\frac{g\left[\frac{\omega-\omega_{\mathbf{q}}}{\varepsilon_{c\mathbf{k}}}\right]}{1+\tau_c^2(\varepsilon_{c\mathbf{k}}-\varepsilon_{c\mathbf{k}_0}-\omega+\omega_{\mathbf{q}})^2}\Bigg][1+(\varepsilon_{c\mathbf{k}}-\varepsilon_{c\mathbf{k}_0})^2\tau_c^2], \end{aligned}\tag{38}$$

where $\tau_c\equiv\tau_p(m_0/m_c)$.

By the same token, using (21) to express $p_{\mathbf{k}-\mathbf{q}}p_{\mathbf{k}}^*$ through $n_{c\mathbf{k}}=|p_{\mathbf{k}}|^2$, we can rewrite the terms with polarization in (18) in a similar way:

$$\left[\frac{\partial n_{c\mathbf{k}}}{\partial t}\right]_{\text{pol}}=\frac{n_{\mathbf{k}}(t)}{\pi}\int_0^{+\infty}d\omega\left[\frac{2\tau_p}{4+\omega^2\tau_p^2}\text{Re}\sigma_{c\mathbf{k}}^{\text{pol}}(\omega)+\frac{\omega\tau_p^2}{4+\omega^2\tau_p^2}\text{Im}\sigma_{c\mathbf{k}}^{\text{pol}}(\omega)\right], \tag{39}$$

with the corresponding kernel being given by

$$\begin{aligned}\sigma_{c\mathbf{k}}^{\text{pol}}(\omega)=C_{c\mathbf{k}}\Bigg[&\frac{1+i(\varepsilon_{c\mathbf{k}}-\varepsilon_{c\mathbf{k}_0})\tau_c}{1+i(\varepsilon_{c\mathbf{k}}-\varepsilon_{c\mathbf{k}_0}+\omega-\omega_{\mathbf{q}})\tau_c}g\left[\frac{\omega_{\mathbf{q}}-\omega}{\varepsilon_{c\mathbf{k}}}\right]+\frac{1-i(\varepsilon_{c\mathbf{k}}-\varepsilon_{c\mathbf{k}_0})\tau_c}{1-i(\varepsilon_{c\mathbf{k}}-\varepsilon_{c\mathbf{k}_0}-\omega-\omega_{\mathbf{q}})\tau_c}g\left[\frac{\omega_{\mathbf{q}}+\omega}{\varepsilon_{c\mathbf{k}}}\right]\\&-\frac{1+i(\varepsilon_{c\mathbf{k}}-\varepsilon_{c\mathbf{k}_0})\tau_c}{1+i(\varepsilon_{c\mathbf{k}}-\varepsilon_{c\mathbf{k}_0}+\omega+\omega_{\mathbf{q}})\tau_c}g\left[\frac{-\omega_{\mathbf{q}}-\omega}{\varepsilon_{c\mathbf{k}}}\right]-\frac{1-i(\varepsilon_{c\mathbf{k}}-\varepsilon_{c\mathbf{k}_0})\tau_c}{1-i(\varepsilon_{c\mathbf{k}}-\varepsilon_{c\mathbf{k}_0}+\omega-\omega_{\mathbf{q}})\tau_c}g\left[\frac{\omega-\omega_{\mathbf{q}}}{\varepsilon_{c\mathbf{k}}}\right]\Bigg].\end{aligned}\tag{40}$$

Note that σ^{pol} does not depend on phonon occupancy $\mathcal{N}_{\mathbf{q}}$.

Now we are in a position to evaluate each of the components of the overall scattering rate:

$$\left[\frac{\partial n_{c\mathbf{k}}}{\partial t}\right]=\left[\frac{\partial n_{c\mathbf{k}}}{\partial t}\right]_{\mathrm{in}}-\left[\frac{\partial n_{c\mathbf{k}}}{\partial t}\right]_{\mathrm{out}}+\left[\frac{\partial n_{c\mathbf{k}}}{\partial t}\right]_{\mathrm{pol}}, \tag{41}$$

and to compare them with the predictions of the semiclassical BE:

$$\left[\frac{\partial n_{c\mathbf{k}}}{\partial t}\right]_{\mathrm{Boltzmann}}=\tfrac{1}{2}n_{c\mathbf{k}}(t)[\sigma_{c\mathbf{k}}^{\mathrm{in}}(0)-\sigma_{c\mathbf{k}}^{\mathrm{out}}(0)]\ . \tag{42}$$

Although the polarization scattering (39) is not included in the BE, we will call the Markovian limit of (39) "Boltzmann" polarization scattering rate:

$$\left[\frac{\partial n_{c\mathbf{k}}}{\partial t}\right]_{\mathrm{pol/Boltzmann}}=\tfrac{1}{2}n_{c\mathbf{k}}(t)\left[\mathrm{Re}\sigma_{c\mathbf{k}}^{\mathrm{pol}}(0)+\frac{2}{\pi}\int_0^{\infty}d\omega\frac{\mathrm{Im}\sigma_{c\mathbf{k}}^{\mathrm{pol}}(\omega)}{\omega}\right]. \tag{43}$$

Before we proceed to the evaluation of these expressions, let us also quote the results for the polarization dynamics. The general non-Markovian expression for $\partial p_{\mathbf{k}}/\partial t$ follows from (11) (see Ref. 13 for its explicit form). It has two terms, one of which describes the dephasing proper ("dephasing-out"), and the other is proportional to $p_{\mathbf{k}-\mathbf{q}}$ and accounts for the diffusion of polarization in **k** space ("dephasing-in").[8] We are going to consider here only the polarization decay, i.e., we will evaluate only $\partial|p_{\mathbf{k}}|/\partial t$ [note that all terms in (11) which produce energy renormalizations do not contribute to this quantity]; using the same method, we can express it as

$$\frac{\partial|p_{\mathbf{k}}|}{\partial t}=\frac{|p_{\mathbf{k}}(t)|}{2\pi}\int_{-\infty}^{+\infty}d\omega\left[\frac{\tau_p}{1+\omega^2\tau_p^2}\mathrm{Re}\xi_{\mathbf{k}}(\omega)+\frac{\omega\tau_p^2}{1+\omega^2\tau_p^2}\mathrm{Im}\xi_{\mathbf{k}}(\omega)\right], \tag{44}$$

where the kernel $\xi_{\mathbf{k}}$ has two parts:

$$\xi_{\mathbf{k}}\equiv\xi_{\mathbf{k}}^{\mathrm{out}}+\xi_{\mathbf{k}}^{\mathrm{in}}\ . \tag{45}$$

The functions ξ^{out} and ξ^{in} can be calculated as above:

$$\xi_{\mathbf{k}}^{\mathrm{out}}(\omega)=-C_{v\mathbf{k}}\left[(1+\mathcal{N}_{\mathbf{q}})g\left[\frac{\omega_{\mathbf{q}}-\omega_{\mathbf{k}}}{\varepsilon_{v\mathbf{k}}}\right]+\mathcal{N}_{\mathbf{q}}g\left[\frac{-\omega_{\mathbf{q}}-\omega_{\mathbf{k}}}{\varepsilon_{v\mathbf{k}}}\right]\right]-C_{c\mathbf{k}}\left[(1+\mathcal{N}_{\mathbf{q}})g\left[\frac{-\omega_{\mathbf{q}}-\omega_{\mathbf{k}}}{\varepsilon_{c\mathbf{k}}}\right]+\mathcal{N}_{\mathbf{q}}g\left[\frac{\omega_{\mathbf{q}}-\omega_{\mathbf{k}}}{\varepsilon_{c\mathbf{k}}}\right]\right], \tag{46}$$

$$\begin{aligned}\xi_{\mathbf{k}}^{\mathrm{in}}(\omega)=C_{v\mathbf{k}}&\left[\mathcal{N}_{\mathbf{q}}g\left[\frac{-\omega_{\mathbf{q}}-\omega_{\mathbf{k}}}{\varepsilon_{v\mathbf{k}}}\right]\frac{1+i\left[\frac{\mathbf{k}^2-\mathbf{k}_0^2}{m_0}\right]\tau_p}{1+i\tau_v(\varepsilon_{v\mathbf{k}}-\varepsilon_{v\mathbf{k}_0}+\omega_{\mathbf{k}}+\omega_{\mathbf{q}})}+(1+\mathcal{N}_{\mathbf{q}})g\left[\frac{\omega_{\mathbf{q}}-\omega_{\mathbf{k}}}{\varepsilon_{v\mathbf{k}}}\right]\frac{1+i\left[\frac{\mathbf{k}^2-\mathbf{k}_0^2}{m_0}\right]\tau_p}{1+i\tau_v(\varepsilon_{v\mathbf{k}}-\varepsilon_{v\mathbf{k}_0}+\omega_{\mathbf{k}}-\omega_{\mathbf{q}})}\right]\\+C_{c\mathbf{k}}&\left[\mathcal{N}_{\mathbf{q}}g\left[\frac{\omega_{\mathbf{q}}-\omega_{\mathbf{k}}}{\varepsilon_{c\mathbf{k}}}\right]\frac{1+i\left[\frac{\mathbf{k}^2-\mathbf{k}_0^2}{m_0}\right]\tau_p}{1+i\tau_c(\varepsilon_{c\mathbf{k}}-\varepsilon_{c\mathbf{k}_0}+\omega_{\mathbf{k}}-\omega_{\mathbf{q}})}+(1+\mathcal{N}_{\mathbf{q}})g\left[\frac{-\omega_{\mathbf{q}}-\omega_{\mathbf{k}}}{\varepsilon_{c\mathbf{k}}}\right]\frac{1+i\left[\frac{\mathbf{k}^2-\mathbf{k}_0^2}{m_0}\right]\tau_p}{1+i\tau_c(\varepsilon_{c\mathbf{k}}-\varepsilon_{c\mathbf{k}_0}+\omega_{\mathbf{k}}+\omega_{\mathbf{q}})}\right].\end{aligned} \tag{47}$$

In the last two expressions $\omega_{\mathbf{k}}$ means $\omega-(\mathbf{k}^2-\mathbf{k}_0^2)/(2m_0)$. Similarly, we can switch off the memory effects in (44) ("Boltzmann dephasing"):

$$\left[\frac{\partial|p_{\mathbf{k}}|}{\partial t}\right]_{\mathrm{Boltzmann}}=|p_{\mathbf{k}}|\mathrm{Re}\xi_{\mathbf{k}}(0)+\frac{|p_{\mathbf{k}}|}{2\pi}\int_{-\infty}^{\infty}d\omega\frac{\mathrm{Im}\xi_{\mathbf{k}}(\omega)}{\omega}\ . \tag{48}$$

The expressions (35), (37), (39), and (44) will be evaluated and compared to their Boltzmann counterparts in the next section.

IV. RESULTS AND DISCUSSION

In this section we present numerical results for the relaxation rates (41)–(44) for the case of a two-band semiconductor with the following set of material parameters: $m_c=0.067$; $m_v=0.62$; $\omega_{\mathrm{LO}}=36.8$ meV; $\epsilon^*=70$ [this quantity enters the coupling constant (29)], which loosely corresponds to the conduction and the heavy-hole bands of GaAs. The central frequency ω_0 of the exciting pulse is assumed to be 5 LO-phonon energies (183 meV) above the band gap; throughout this section we will use ω_{LO} as the unit of energy, and measure pulse durations in the units of the inverse phonon frequency $1/\omega_{\mathrm{LO}}=1/(2\pi T_{\mathrm{LO}})=17.9$ fs. In order to simplify interpreta-

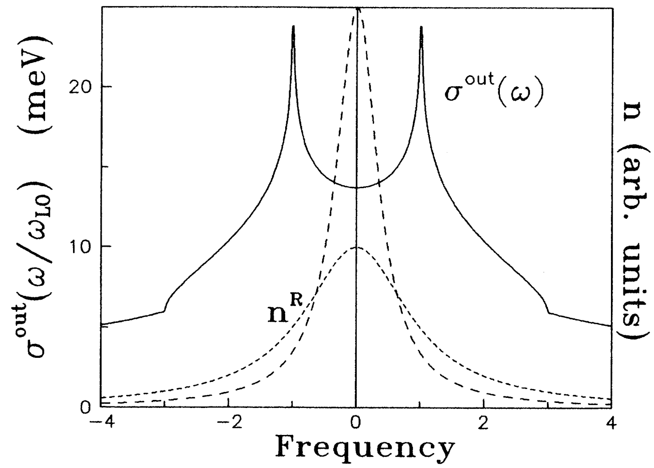

FIG. 1. Response function $\sigma^{out}_{c\mathbf{k}}(\omega/\omega_{LO})$ (33) for $\varepsilon_{c\mathbf{k}}=4\omega_{LO}$ (other parameters are those of Sec. IV A), and the retarded Fourier transform of the density (34) at two different pulse durations.

tion of the results, we will consider only the zero-temperature case ($\mathcal{N}_q=0$), i.e., only phonon emission processes.

A. Electrons

In our numerical example the electrons are excited $5\omega_{LO}m_0/m_c=4.51\omega_{LO}=166$ meV above the band edge, so that their relaxation is not affected by any "end effects." The scattering rates, calculated according to (41) and (42) with and without the coherent and memory effects, are plotted in Fig. 2 for three different pulse durations.

The quantity (42), labeled as "Boltzmann result" in Fig. 2, is quite in line with the conventional semiclassical picture of carrier relaxation: the exciting pulse produces a density distribution peaked around $\varepsilon_{c\mathbf{k}_0}$ with the width $1/\tau_p$ (it is not plotted in Fig. 2 since the Boltzmann scattering rate itself gives a fairly good idea of it). The electrons emit phonons, so that the initial peak at $\varepsilon_{c\mathbf{k}_0}$ subsides (negative part of the curve), while the second peak with *exactly the same width* grows one phonon energy below.

As is clear from Fig. 2, the electrons behave in a very different way when the coherent and memory effects are turned on (solid curves): while the initial density peak decays with roughly the same rate, the second peak is almost completely washed out (except for the longest pulse durations), and the gap between $\varepsilon_{c\mathbf{k}_0}$ and $\varepsilon_{c\mathbf{k}_0}-\omega_{LO}$ is now being filled rather rapidly. The overall impression is that both effects lead to much more even redistribution of the electrons over the $\mathbf{k}$ space.

Let us consider in more detail what each of these two effects does. In Fig. 3 we compare scattering-in and scattering-out rates, with the memory effects [(35) and (37)], to their semiclassical values (42). One sees that while the scattering-out rate does not change much [its

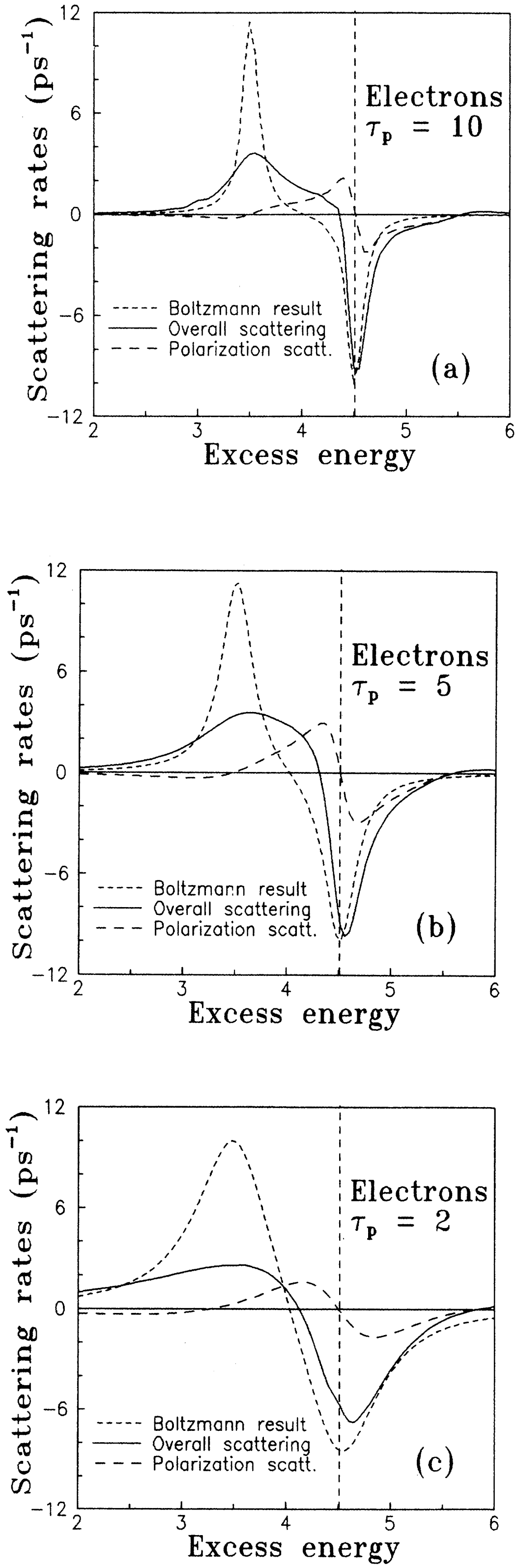

FIG. 2. Comparison of the overall scattering rates (41), which include the polarization scattering and memory effects, with Boltzmann values of the scattering rates (42) (τ_p and energy in dimensionless units, see Sec. IV).

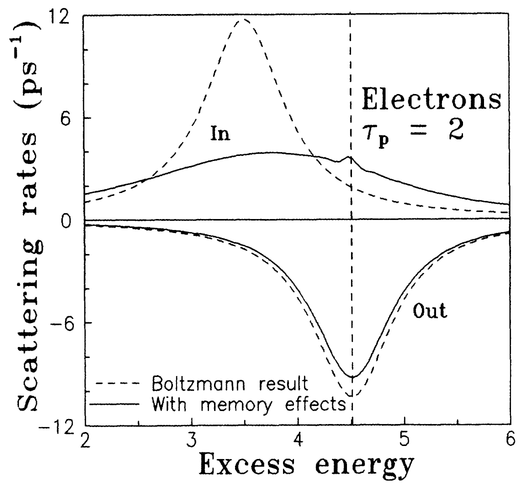

FIG. 3. Scattering-in rate (37) and scattering-out rate (35) compared with their Boltzmann counterparts (42).

slight diminution is explained by the decrease of $\sigma^{\text{out}}(\omega)$ at high frequencies (see Fig. 1)], the rate of scattering-in is profoundly modified by the memory effects. It still does have a peaked shape, but it is approximately three times as broad as its semiclassical counterpart, which can be readily understood in view of the above-mentioned loosening of energy-conservation requirements. It is also visibly shifted closer to the initial peak, because the strong **q** dependence of the interaction matrix element (29) now favors processes with smaller momentum (and hence energy) transfer.

The slight bump at the excitation energy is not an artifact and is also due to the $1/q^2$ singularity in $M_{\mathbf{q}}^2$: it is caused by scattering events whereby an electron emits a phonon with a very small **q** and scatters to virtually the same state—such events are no longer forbidden by the energy conservation, and the mentioned singularity in $M_{\mathbf{q}}^2$ gives them an unproportionally large weight. Although this kind of scattering does not lead to any measurable effects in our example, it seems interesting from the fundamental point of view.

Figure 4 depicts the contribution of polarization scattering at different τ_p, again with [Fig. 4(b)] and without [Fig. 4(a)] the memory effects [some of the curves in Fig. 4(b) are also shown for comparison in Fig. 2]. The coherent effects seem to be of importance only in the vicinity of the excitation energy. The polarization scattering rate changes sign at $\varepsilon = \varepsilon_{c\mathbf{k}_0}$ and reaches its extreme values at $\varepsilon_{c\mathbf{k}_0} \pm 1/\tau_p$, i.e., at half-width of the initial density peak, so that its decay is slowed down at the low-energy half and speeded up at the high-energy one. Since the curves in Fig. 4(b) look very much like the derivatives of $n_{c\mathbf{k}}(\varepsilon)$, we can loosely say that the polarization scattering mainly shifts the initial density peak towards lower energies (or, which is the same, shifts the negative peak in the scattering rate to higher energies).

Although the peak value of the polarization scattering rate is considerably smaller than the maximum scattering-out rate, so that it seems that the scattering rate is shifted only slightly, in fact the coherent effects may push the density peak down the energy scale quite effectively: as one can read from Fig. 2(b), at $\tau_p = 5$ the density at $\varepsilon_{c\mathbf{k}_0} + 1/\tau_p$ (at half-height of the peak) decays *four times as fast* as at $\varepsilon_{c\mathbf{k}_0} - 1/\tau_p$, so that the effect can be quite observable.

In fact, a red shift of the spectral hole caused by the initial density peak is often observed experimentally[6] and is usually attributed to the band-gap renormalization due to carrier-carrier interaction.[15] Let us note, however, that experimental manifestations of the coherent effects would look very much like that, so that these effects might be partially responsible for the observed shifts.

It seems interesting that the polarization scattering is apparently most pronounced in some intermediate range

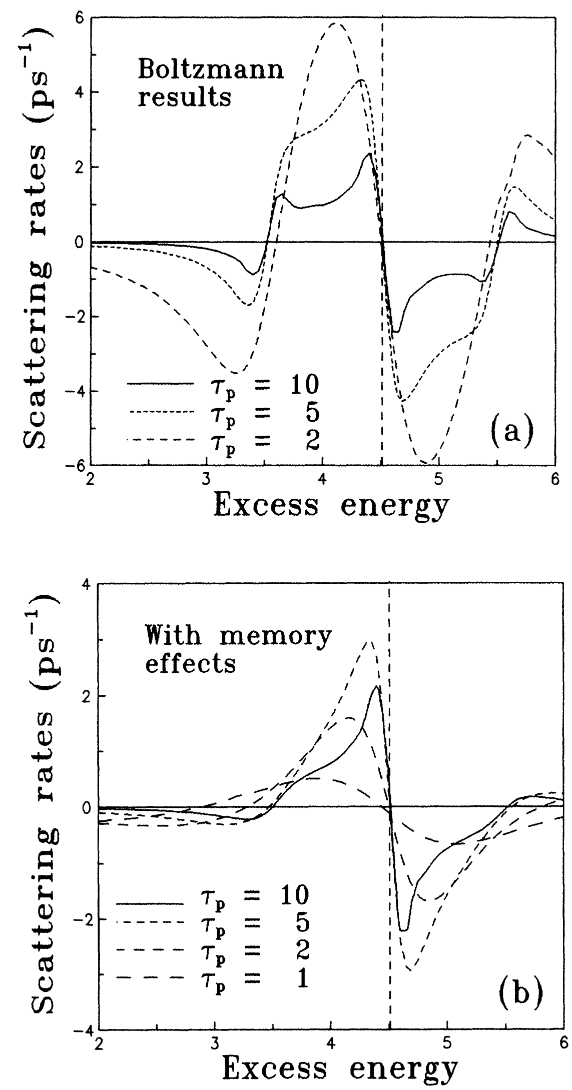

FIG. 4. Polarization scattering rate for the electrons: (a) without memory effects (44); (b) with memory effects (39).

of pulse durations [around $\tau_p=5$ in our example, as Fig. 4(b) suggests], since one would rather expect it to grow monotonously with diminishing τ_p because of the increasing spread of $p^*_{\mathbf{k}}p_{\mathbf{k}-\mathbf{q}}$. As is seen from Fig. 4(a), "Boltzmann" values (43) of the polarization scattering rate do just that, while the amplitude of the curves in Fig. 4(b) (with memory effects) at $\tau_p<5$ quickly diminishes with decreasing τ_p, so that at $\tau_p=2$ it is only $\frac{1}{4}$ of its Markovian value.

The fact that the memory effects suppress the polarization scattering can be explained by the peculiar temporal dependence of polarization terms in (18): they are proportional to $\sin(\omega_{\mathbf{q}}\tau)$ and, unlike the usual scattering terms, vanish at $\tau\to 0$. Therefore, for very short pulses, when the quantity $p^*_{\mathbf{k}}p_{\mathbf{k}-\mathbf{q}}(t)$ is nonzero only at small τ, its overlap with $\sin(\omega_{\mathbf{q}}\tau)$ also becomes small, while, e.g., for the scattering-out terms, the integral of $\sigma^{\mathrm{out}}(t-\tau)n(\tau)$ stays finite no matter how short the pulse is, because of the singularity (26).

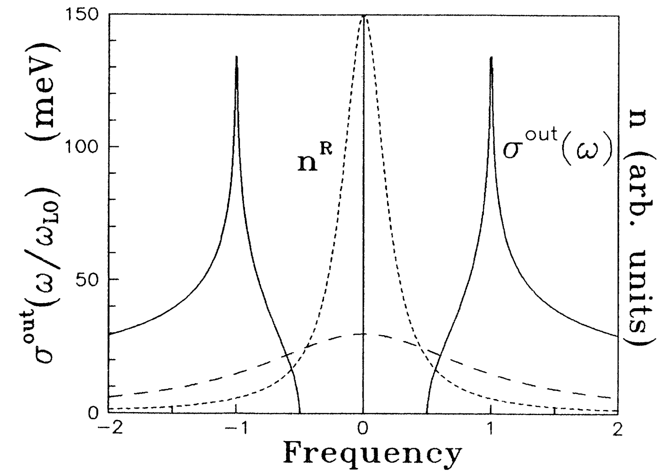

FIG. 6. Same as Fig. 1 for the case of holes excited below the emission threshold.

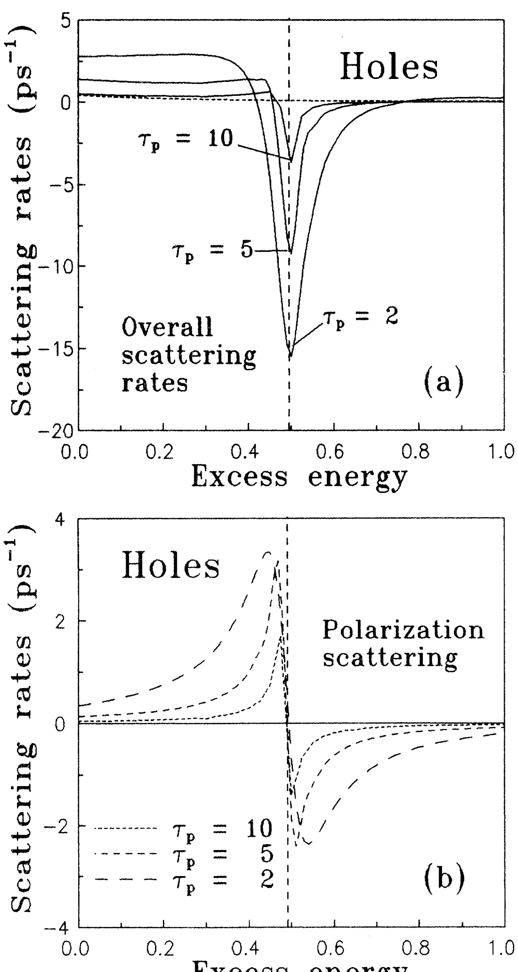

FIG. 5. Scattering rates for the holes excited below the phonon emission threshold, at different τ_p: (a) Overall scattering rate (41), dashed line, Boltzmann result for $\tau_p=2$; (b) polarization scattering rate.

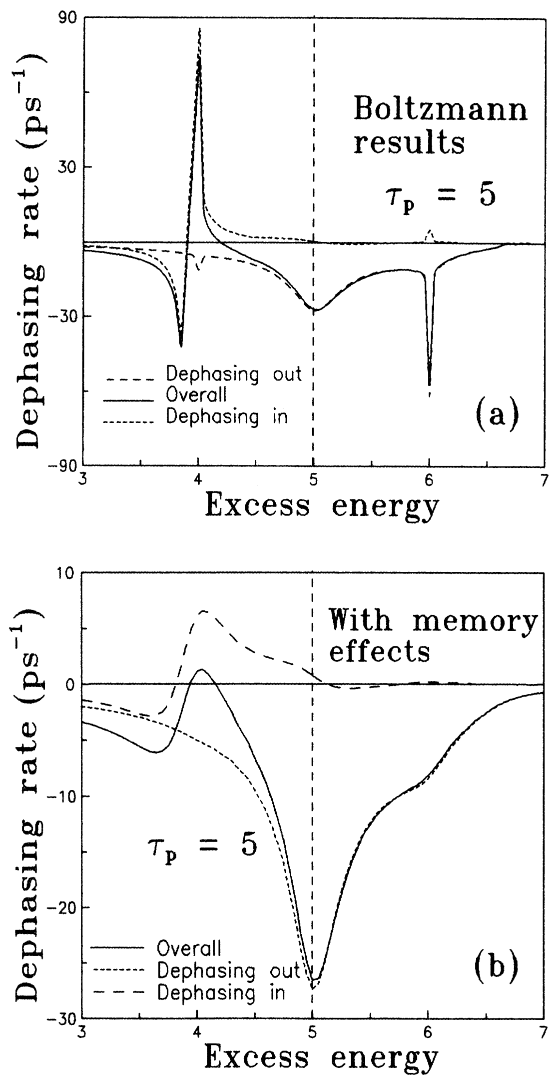

FIG. 7. Polarization decay rates at $\tau_p=5$: (a) Without the memory effects (48); (b) with memory effects.

B. Holes

The scattering rates for the holes are presented in Fig. 5. In our example the holes, because of their greater mass, are excited only $0.5\omega_{\mathrm{LO}}$ above the gap, i.e., well below the phonon emission threshold. In the semiclassical description such holes are not able to emit phonons and at zero temperature the electron-phonon interaction should not affect the holes at all (such an arrangement is sometimes used in experiments in order to single out the effects of carrier-carrier scattering).[6]

As is clear from Fig. 5, nothing like that happens when the quantum effects are taken into account: the phonon emission is no longer forbidden, since a hole created by a short pulse can now emit a phonon and scatter to the bottom of the band while losing less than phonon energy. This leads to the development of a pronounced scattering-out peak at excitation energy with diminishing pulse durations [Fig. 5(a)], which again is slightly shifted by the polarization scattering [Fig. 5(b)].

Figure 6 may help to understand the situation: the scattering-out kernel $\sigma^{\mathrm{out}}(\omega)$ is strictly zero at $\omega=0$— in the Markovian approximation the holes cannot scatter out. However, it is nonzero at $|\omega|>0.5\omega_{\mathrm{LO}}=\varepsilon_{v\mathbf{k}_0}$, and the overlap integral (35) always has a finite value, which grows as the spectral width of $n_r(\omega)$ increases, i.e., with decreasing pulse durations.

This example perfectly demonstrates that at least in some cases the quantum effects can completely dominate carrier dynamics.

C. Polarization dynamics

We are not going to analyze the polarization dynamics in any detail and will only present here one set of results for illustrative purposes. Figure 7 depicts the polarization decay rates at one particular value of the pulse duration, $\tau_p=5$.

The Markovian dephasing rates [Fig. 7(a)] display sharp spikes at $\omega_0\pm\omega_{\mathrm{LO}}$, which are nothing but phonon sidebands;[15] these structures are integrated out when memory effects are included [Fig. 7(b)]. Somewhat unexpectedly, the diffusion term (47), which is normally omitted, actually causes the polarization to grow, not to decay, in some portions of $\mathbf{k}$ space, which can lead to a buildup of polarization in the sidebands.

Let us note that the mean value of the dephasing time [about 40 fs in Fig. 7(b)] is in surprisingly good accord with the experimental values of Ref. 10 (10–40 fs). This value of 40 fs represents the shortest relaxation time in our example, so that, strictly speaking, our results are valid only for pulse durations shorter than this value, i.e., for $\tau_p \ll 2$. In reality, for longer pulses the carrier dynamics are not determined by the external field alone and are also affected by the relaxation processes. This means that our results must be taken for what they are—the results of a model which assumes weak interaction in a situation when the coupling is not weak. However, they still give a good idea of the role of the effects in question, which is what one should expect of a model calculation.

V. CONCLUSIONS

Our aim in the present work has been to assess the role of quantum effects in the relaxation of photoexcited carriers. It turned out that both the coherent and the memory effects are rather important and can even dominate the relaxation processes, at least when the exciting pulse is shorter than approximately 100 fs$\approx 2\pi/\omega_{\mathrm{LO}}$ (one phonon period) in GaAs.

Of course our calculations are model ones, and we do not even try to compare the results with the experiment, since we have left out numerous effects which are known to influence the relaxation of carriers in GaAs: valence-band anisotropy, carrier-carrier and intervalley scattering, collisional broadening, and so on (see Ref. 5 for an excellent account of the real situation in GaAs). However, our results indicate that the coherent and memory effects should be added to this relevance list if one aims at a comprehensive description of the relaxation phenomena.

The main feature of both quantum effects that we have considered above seems to be their ability to destroy any sharp structures (e.g., phonon replicas of the initial density peak) in distribution functions. They may help to explain the extremely rapid thermalization of carriers in femtosecond experiments.[10] Indeed, it seems that valence-band anisotropy, carrier-carrier scattering, and collisional broadening are included in the Monte Carlo simulations[5] mainly to get a more uniform distribution of carriers over $\mathbf{k}$ space, which is in better accord with the experiment. The memory effects offer another (and rather powerful) source of broadening, which, in our opinion, could explain the rapid thermalization of ultrafast-excited carriers even in the absence of the above-mentioned factors. Besides, the coherent effects may also play a role in the experimentally observed red shift of the pump-induced spectral hole, although it can prove difficult to distinguish this effect from the Coulomb renormalization of transition energy.

Since not only the electron-phonon scattering, but also other types of scattering must be modified by these quantum effects, it seems very desirable to perform a full numerical solution of the Bloch equations (10) for some experiment-oriented situation in order to reassess the role of the many factors affecting the relaxation of carriers. Unfortunately, the extreme complexity of numerically simulating non-Markovian systems like Eq. (11) puts such a project far beyond our computer capabilities.

Let us conclude by noting that the important physics that comes in under femtosecond excitation conditions apparently deserves further exploration, although the tremendous numerical problems involved are likely to confine such studies to the level of simplified models for some time to come.

[1]For reviews of experimental and theoretical work in this direction see J. Shah, Solid State Electron. **32**, 1051 (1989); Superlatt. Microstruct. **6**, 293 (1989); the theory is reviewed in S. E. Esipov and Y. B. Levinson, Adv. Phys. **36**, 331 (1986).

[2]J. Collet and T. Amand, J. Phys. Chem. Solids **47**, 153 (1986); J. Collet, J. L. Oudar, and T. Amand, Phys. Rev. B **34**, 5443 (1986).

[3]S. M. Goodnick and P. Lugli, Phys. Rev. B **37**, 2578 (1988); **38**, 10 135 (1988); P. Lugli, Helv. Phys. Acta **62**, 691 (1989).

[4]C. W. W. Bradley, R. A. Taylor, and J. F. Ryan, Solid State Electron. **32**, 1173 (1989).

[5]C. J. Stanton, D. W. Bailey, and K. Hess, Phys. Rev. Lett. **65**, 231 (1990); D. W. Bailey, C. J. Stanton, and K. Hess, Phys. Rev. B **42**, 3423 (1990).

[6]W. H. Knox, D. S. Chemla, G. Livescu, J. E. Cunningham, and J. E. Henry, Phys. Rev. Lett. **61**, 1290 (1988); W. H. Knox, Solid State Electron. **32**, 1057 (1989).

[7]V. M. Galitzky and V. F. Yelesin, *Resonant Interaction of Electromagnetic Fields with Semiconductors* (Energoatomizdat, Moscow, 1986).

[8]M. Lindberg and S. W. Koch, Phys. Rev. B **38**, 3342 (1988).

[9]S. Schmitt-Rink, D. S. Chemla, and H. Haug, Phys. Rev. B **37**, 941 (1988).

[10]P. C. Becker *et al.*, Phys. Rev. Lett. **61**, 1647 (1988).

[11]L. Schultheis, J. Kuhl, A. Honold, and C. W. Tu, Phys. Rev. Lett. **57**, 1635 (1986); A. Honold, L. Schultheis, J. Kuhl, and C. W. Tu, Phys. Rev. B **40**, 6442 (1989).

[12]For a review, see A.-P. Jauho, Solid State Electron. **32**, 1265 (1989); memory effects in polarization and their impact on optical properties were also considered by R. Zimmermann, Phys. Status Solidi B **159**, 317 (1990); W. Schäfer and K. Henneberger, *ibid.* **159**, 59 (1990); G. Böhne, T. Sure, R. G. Ulbrich, and W. Schäfer, Phys. Rev. B **41**, 7549 (1990).

[13]A. V. Kuznetsov, Phys. Rev. B **44**, 8721 (1991).

[14]L. Allen and J. H. Eberly, *Optical Resonance and Two-Level Atoms* (Wiley, New York, 1975).

[15]H. Haug and S. Schmitt-Rink, Prog. Quantum Electron. **9**, 3 (1984).