Coulomb quantum kinetics and optical dephasing on the femtosecond time scale

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Quantum kinetic equations with memory are formulated and solved for the femtosecond Coulomb kinetics of an optically excited electron-hole plasma. In a time interval smaller than the inverse plasma frequency screening and energy conservation are still absent. The resulting decay of the optical interband polarization is shown to be nonexponential and is in qualitative agreement with the results of the quasiclassical theory of Gurevich *et al.*

I. INTRODUCTION

On very short time and length scales the semiclassical Boltzmann kinetics has to be replaced by a quantum kinetics. The quantum mechanical coherence of the electronic wave function introduces memory effects, which make the quantum kinetics non-Markovian.[1–4] Because the screened Coulomb potential $V_s(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2)$ is in this regime itself a retarded function that has to be determined by its own quantum kinetic equation, Coulomb quantum kinetics becomes in general rather difficult.[5,6] We will show in the present treatment that the Coulomb kinetics can be simplified considerably in the early stage during and shortly after a femtosecond optical pulse excitation.

Nonequilibrium screening is known to give rise to new effects. For example, in the presence of a homogeneous electric field it causes a higher electron-impurity scattering rate[7] and for carrier distribution function with empty low energy states new plasmon resonances can arise.[8] Nonequilibrium screening in the nonstationary regime after an ultrafast optical excitation was investigated in Refs. 9 and 10. In the later work it was shown that the buildup of screening occurs in a time of the order of a typical inverse plasma frequency. This is a rather natural result because the inverse plasma frequency can be understood as the characteristic time the plasma needs to respond to a disturbance. If a new charge is created in the plasma faster than this time, the plasma cannot screen it. In a plasma excited by an ultrashort optical pulse, all charge carriers are unscreened and thus the early, transient quantum kinetics is dominated by the bare Coulomb potential. For an estimate, one can take the plasma frequency $\omega_{\rm pl}$ of the maximum plasma density, which the pulse excites, and neglect screening up to $t \lesssim \omega_{\rm pl}^{-1}$ after the pulse. Energy cannot be conserved better than with an accuracy of the inverse time elapsed from the excitation. For very small time intervals the energy broadening is larger than the characteristic energy transfer in a two-particle collision and thus also the energy conservation in the individual collisions can be neglected (incomplete collisions). These two ideas lead to a rather unconventional non-Markovian quantum kinetics. We will show that the bare Coulomb potential in this new quantum kinetics without energy conservation yields no divergence in contrast to the situation in the semiclassical Boltzmann kinetics.

We calculate with this quantum kinetics the decay of the induced interband polarization, which has been measured in femtosecond four-wave-mixing experiments.[11,12] We show that the resulting optical dephasing, in a certain time window, is in qualitative agreement with a simplified analytic treatment of Gurevich *et al.*[13] In this theory the dephasing of an initially given polarization is calculated quasiclassically by considering the motion of an excited electron-hole pair in the Coulomb field of the plasma, which is assumed to be "frozen" and randomly distributed. Particularly, we see in the time window where the two theories can be compared a nonexponential decay of the form $\exp(-ant^3)$. The exponent is proportional to the plasma density and to the third power of time. a is a numerical constant. So far, this fast nonexponential decay has not been observed experimentally.

In Sec. II we discuss briefly the general Coulomb quantum kinetics and its reduction in the early, transient stage to a retarded kinetics with a bare Coulomb potential and without energy conservation in the two-particle collision. We formulate this theory for a laser-pulse-excited two-band semiconductor. In Sec. III the properties of the transient scattering integrals are investigated and discussed. In Sec. IV we give a short adopted version of the quasiclassical theory due to Gurevich *et al.*[13] In Sec. V we present the results of numerical simulations of the transient Coulomb kinetics and compare them with the quasiclassical theory.

II. EARLY STAGE OF COULOMB KINETICS

We derive the Coulomb quantum kinetic equations in the framework of the Keldysh nonequilibrium Green function technique (see, e.g., Refs. 4 and 14–16). The self-energy is taken in random phase approximation. For the description of the interaction with the driving (classical) light field we use the rotating wave approximation. This gives a closed set of Dyson equations for the two-time Keldysh matrices of the particle and the

screened potential propagators. In order to get a closed set of equations for the one-particle reduced density matrix, i.e., the equal-time limit of the Keldysh matrix element $G^{+-}(t,t)$, we use the generalized Kananoff-Baym ansatz.[1,3,17] In a two-band model the diagonal elements of the reduced density matrix are the distributions $f_{i\mathbf{k}}$ of the electron ($i=e$) and the holes ($i=h$), while the off-diagonal elements are given in terms of the polarization $P_{\mathbf{k}}$.

In the present investigation, we concentrate on the first 10–40 femtoseconds during and after an ultrashort optical excitation. In this regime the involved quantum kinetic equations can be drastically simplified. In Ref. 10 we have shown that the time required for the buildup of screening is approximately given by the inverse plasma frequency $\omega_{\rm pl}^{-1}$

$$\omega_{\rm pl}(t)=\sqrt{\frac{4\pi e^2}{\epsilon_0\mu}n(t)}, \tag{2.1}$$

where $1/\mu=1/m_e+1/m_h$ is the reduced electron-hole mass and $n(t)$ is the induced plasma density. This has a simple physical meaning. A charge is screened due to a displacement of the plasma. The surrounding charges of opposite sign are attracted, the others are repelled, giving rise to a charged cloud. This rearranging of carriers needs some time. If a new charge carrier is introduced faster than the plasma can adjust to it, this charge remains initially unscreened. The typical time needed for the adjustment is related to the only characteristic time constant of the plasma, namely, the inverse plasma frequency. In a time interval $\Delta t\lesssim\omega_{\rm pl}^{-1}$ after a femtosecond pulse excitation, the screened retarded and advanced potentials can be replaced by the bare Coulomb potential, i.e.,

$$V^{r,a}_{s,\mathbf{q}}(t_1,t_2)\approx V_q\delta(t_1-t_2)\quad\text{with}\quad V_q=\frac{4\pi e^2}{\mathcal{V}\epsilon_\infty q^2}. \tag{2.2}$$

V_q is the bare Coulomb potential and $\mathcal{V}$ is the normalization volume. Only the high-frequency components of the unexcited crystal polarization will contribute to the background dielectric function ϵ_∞ of the crystal. With this approximation one neglects oscillations of the potential $\exp(-i\omega_{\rm pl}t)$. Consistent with this approximation, we also neglect oscillations with the difference of single-particle energies, e.g., terms as $\exp[i\hbar^{-1}(\varepsilon_{jk}-\varepsilon_{j|\mathbf{k}-\mathbf{q}|})t]$ coming from combinations of the spectral functions $G^{r,a}$. A kinetics based on the bare Coulomb potential is dominated by small-angle scattering ($q\to 0$). Therefore, also the characteristic energy differences are small. Indeed, if t_1 is only a little later than t_2, the retarded Green function becomes simply

$$i\hbar G^r_{j_1j_2\mathbf{k}}(t_1,t_2)\approx\langle[a_{j_1\mathbf{k}}(t_1),a^\dagger_{j_2\mathbf{k}}(t_1)]_+\rangle=\delta_{j_1j_2}, \tag{2.3}$$

where $a_{j\mathbf{k}}$ are the electron field operators in the Heisenberg picture and $[\,,\,]_+$ is the anticommutator. With the two short-time approximations (2.2) and (2.3), the extremely difficult Coulomb quantum kinetics reduces to a tractable set of equations. If we use approximation (2.3) in the Dyson equation of the retarded Coulomb potential (see, e.g., Ref. 10), we recover Eq. (2.2), which shows again that the two approximations are indeed consistent.

A detailed description of the straightforward but lengthy algebra leading to the simplified equations can be found in Ref. 4. We will give here only the final result. In order to get compact expressions, we will assume isotropy in momentum space from now on, but this assumption is not necessary. The final quantum kinetic equations for the polarization P_k and the electron and hole distributions f_{ik} can be written as

$$\begin{aligned}\frac{\partial}{\partial t}P_k&=\frac{\partial}{\partial t}P_k\Big|_{\rm coh}+\frac{\partial}{\partial t}P_k\Big|_{\rm scatt},\\ \frac{\partial}{\partial t}f_{ik}&=\frac{\partial}{\partial t}f_{ik}\Big|_{\rm coh}+\frac{\partial}{\partial t}f_{ik}\Big|_{\rm scatt}.\end{aligned} \tag{2.4}$$

The coherent parts of Eq. (2.4) are the coherent semiconductor Bloch equations[15,18]

$$\begin{aligned}\frac{\partial}{\partial t}P_k\Big|_{\rm coh}&=-i\hbar^{-1}[e_{ek}(t)+e_{hk}(t)]P_k(t)\\&\quad+i\left[1-f_{ek}(t)-f_{hk}(t)\right]\Omega^R_k(t),\\ \frac{\partial}{\partial t}f_{ik}\Big|_{\rm coh}&=-2{\rm Im}\left[\Omega^R_k(t)P^*_k(t)\right].\end{aligned} \tag{2.5}$$

The instantaneous parts of the self-energy, i.e., the Hartree-Fock (HF) self-energy (see, e.g., Ref. 15), contribute to the Rabi frequency Ω^R ("local" or HF field) and to the single-particle energies e_i (band gap shrinkage)

$$\begin{aligned}\hbar\Omega^R_k(t)&=\frac{d_kE(t)}{2}+\sum_{\mathbf{q}}V_qP_{|\mathbf{k}-\mathbf{q}|}(t),\\ e_{ik}(t)&=\varepsilon_{ik}-\sum_{\mathbf{q}}V_qf_{i|\mathbf{k}-\mathbf{q}|}(t).\end{aligned} \tag{2.6}$$

Within the rotating wave approximation, $E(t)$ denotes only the pulse envelope. $d_{\mathbf{k}}$ is the interband optical matrix element. The single-particle energies are given by

$$\varepsilon_{ek}=\frac{(\hbar k)^2}{2m_e}-\Delta_0,\quad\varepsilon_{hk}=\frac{(\hbar k)^2}{2m_h}. \tag{2.7}$$

Here $\Delta_0=\hbar\omega_0-E_g$ is the detuning between the central frequency ω_0 of the pulse and the unrenormalized band gap E_g. The quantum kinetic scattering integrals, which will be called transient scattering integrals (TSI's) are given by

$$\begin{aligned}\frac{\partial}{\partial t}P_k\Big|_{\rm scatt}&=\frac{4}{\hbar^2}\sum_{\mathbf{q}}\int_{-\infty}^{t}dt'\,V_q^2\left[P_{|\mathbf{k}-\mathbf{q}|}(t')-P_k(t')\right]\\&\quad\times F_q(t'),\\ \frac{\partial}{\partial t}f_{ik}\Big|_{\rm scatt}&=\frac{4}{\hbar^2}\sum_{\mathbf{q}}\int_{-\infty}^{t}dt'\,V_q^2\left[f_{i|\mathbf{k}-\mathbf{q}|}(t')-f_{ik}(t')\right]\\&\quad\times F_q(t'),\end{aligned} \tag{2.8}$$

with

$$F_q(t') = \sum_{j=e,h} \sum_{\mathbf{p}} \{f_{jp}(t')[1 - f_{j|\mathbf{p}+\mathbf{q}|}(t')] - \mathrm{Re}[P_{|\mathbf{p}+\mathbf{q}|}(t') P_p^*(t')]\}.$$

III. PROPERTIES OF THE TRANSIENT SCATTERING INTEGRALS

In order to show the characteristic features of the proposed new femtosecond carrier kinetics, we compare it with the well-known Boltzmann scattering integral (BSI)

$$\left.\frac{\partial}{\partial t} f_{ik}\right|_{\mathrm{scatt}} = \frac{4\pi}{\hbar} \sum_{j=e,h} \sum_{\mathbf{q},\mathbf{p}} V_{s,q}^2 (\varepsilon_k - \varepsilon_{|\mathbf{k}-\mathbf{q}|})\, \delta(\Delta\varepsilon) \{ f_{i|\mathbf{k}-\mathbf{q}|}(t) f_{j|\mathbf{p}+\mathbf{q}|}(t)[1 - f_{ik}(t)][1 - f_{jp}(t)] - f_{ik}(t) f_{jp}(t)[1 - f_{i|\mathbf{k}-\mathbf{q}|}(t)][1 - f_{j|\mathbf{p}+\mathbf{q}|}(t)] \}, \tag{3.1}$$

with

$$\Delta\varepsilon \equiv \varepsilon_k - \varepsilon_{|\mathbf{k}-\mathbf{q}|} + \varepsilon_p - \varepsilon_{|\mathbf{p}+\mathbf{q}|}.$$

The BSI describes a stochastic process, which is local in time. The TSI, on the other hand, describes a partially coherent process and is consequently nonlocal in time. The memory to the history of the system is a trademark of quantum kinetics. Formally, the integration extends from $-\infty$ to the actual time t, but the integrand is nonzero only during and after pulse excitation. The effective range of integration is proportional to the time interval after the ultrashort pulse, i.e., the scattering integrals build up in time.

At later times the phase factors become important and the connection between the TSI and the BSI can be seen clearly from the relation

$$\lim_{t\to\infty} \lim_{\gamma\to 0} \hbar^{-1} \int_{-\infty}^{t} dt' \exp\left[i\hbar^{-1}(\Delta\varepsilon t' - \gamma|t'|)\right] = 2\pi\delta(\Delta\varepsilon). \tag{3.2}$$

The integrand in the scattering integrals for small momentum transfer determines whether an unscreened Coulomb potential can be used or not. The critical part of the integrand in Eq. (2.8) is

$$\sum_{\mathbf{q}} V_q^2 (f_{|\mathbf{k}-\mathbf{q}|} - f_k) = \frac{\mathcal{V}}{(2\pi)^3} \int_0^\infty dq q^2 V_q^2 \int d\Omega_{\mathbf{q}} (f_{|\mathbf{k}-\mathbf{q}|} - f_k), \tag{3.3}$$

where $\Omega_{\mathbf{q}}$ is the solid angle of the $\mathbf{q}$ integration. At small $\mathbf{q}$ values, the distributions may be expanded

$$(f_{|\mathbf{k}-\mathbf{q}|} - f_k) \simeq q\,(\mathbf{e}_{\mathbf{q}} \cdot \nabla_{\mathbf{k}}) f_k + \frac{q^2}{2} (\mathbf{e}_{\mathbf{q}} \cdot \nabla_{\mathbf{k}})^2 f_k + \cdots. \tag{3.4}$$

Here $\mathbf{e}_{\mathbf{q}}$ is the unit vector in the $\mathbf{q}$ direction. Using Eq. (3.4), one finds

$$\lim_{q\to 0} q^2 V_q^2 \int d\Omega_{\mathbf{q}} (f_{|\mathbf{k}-\mathbf{q}|} - f_k) = \lim_{q\to 0} \frac{q^4}{2} V_q^2 \int d\Omega_{\mathbf{q}}\, (\mathbf{e}_{\mathbf{q}} \cdot \nabla_{\mathbf{k}})^2 f_k. \tag{3.5}$$

The angular integral over $(\mathbf{e}_{\mathbf{q}} \cdot \nabla_{\mathbf{k}}) f_k$ vanishes and only the second term of the expansion survives. $\lim_{q\to 0} q^4 V_q^2$ is finite [see Eq. (2.2)] and therefore the TSI with a bare Coulomb potential is well defined. (Although we have already assumed isotropy in order to get concise scattering integrals, the given proof does not depend on this assumption.)

In the BSI an unscreened potential leads to divergences for small transferred momenta because the energy conserving δ function in Eq. (3.1) restricts the angular integration to two isolated points and the q linear term of the expansion Eq. (3.4) contributes. Various approximations for the screened potential $V_{s,q}(\omega)$ have been used, e.g., a static screened potential, a plasmon-pole approximation, or even a Lindhard potential (see, e.g., Refs. 19 and 20). The solution of the kinetic equations with the BSI depend strongly on this choice. In the quantum kinetic equations on the femtosecond time scale, this ambiguity does not exist.

The kinetic energies in the argument of the δ function in Eq. (3.1) make the BSI mass dependent, and the evolution for the electrons and the holes is different. The TSI, on the other hand, does not depend on the band masses. It can be scaled, e.g, with the exciton Bohr radius $a_0 = \hbar^2\epsilon_\infty/e^2\mu$ and the Rydberg energy $E_0 = \hbar^2/2\mu a_0^2$ alone. The integrals are exactly the same for the two carrier species. The coherent terms have this symmetry also. Thus, in the initial quantum kinetic regime, the distributions of electrons and holes are exactly the same

$$f_{ek} = f_{hk} = f_k. \tag{3.6}$$

The superfluous index $i = (e,h)$ will be dropped from now on. For the BSI, often the terminology of in- and out-scattering rates is used. They are defined as the first and the second term in Eq. (3.1). This definition cannot be used for the TSI, because only the compensation of these two contributions at small transferred momenta ensures a finite result. Only effective rates can be defined.

The integrands of the TSI are symmetrical in the variables $\mathbf{k}$ and $\mathbf{k}' = \mathbf{k} - \mathbf{q}$. Therefore,

$$\sum_{\mathbf{k}} \frac{\partial}{\partial t} f_k \Big|_{\text{scatt}} = 0, \quad \sum_{\mathbf{k}} \frac{\partial}{\partial t} P_k \Big|_{\text{scatt}} = 0, \tag{3.7}$$

i.e., the TSI's conserve the number of carriers and the total polarization. The second sum rule in Eq. (3.7) illustrates that in the present model, polarization can be scattered from one k state to another. The sum rules hold also in the Markovian limit,[21] but cannot be understood in a two-level model for each k state. In Ref. 22 it is shown that, even in the Markovian limit, this "in scattering" is essential for the correct description of the polarization decay. The other important conservation law of the BSI, the conservation of the kinetic energy in a collision, is not fulfilled by the TSI [see Eq. (3.2)]. The coherent Bloch equations (2.5) describe a rotation of the Bloch vector and conserve its length $B_k(t)$,[4,23,24]

$$\frac{d}{dt}\Big|_{\text{coh}} B_k(t) = 0, \tag{3.8}$$

with

$$B_k(t) = [1 - 2f_k(t)]^2 + 4|P_k(t)|^2. \tag{3.9}$$

Together with the initial conditions $P_k = f_k = 0$ at $t = -\infty$ we get

$$B_k(t) = 1. \tag{3.10}$$

The conservation of the length of the Bloch vector can be written in the form

$$\frac{1 - B_k}{4} = (1 - f_k) f_k - |P_k|^2 = 0. \tag{3.11}$$

For $q \to 0$, the integrand of the TSI [Eq. (2.8)] is proportional to the expression (3.11), i.e., the small-angle scattering is suppressed if the plasma is still nearly coherent.

Femtosecond laser pulses are spectrally very broad. Except for very intense laser pulses, the induced carrier distribution is initially nondegenerate and the phase-space filling term $(1 - f_k)$ plays only a minor role. Due to the buildup of the scattering integrals, scattering is not important during the presence of the femtosecond laser pulse. From Eq. (2.5) it follows that the distribution f_k is proportional to the field intensity $\mathcal{E}^2$ and the polarization P_k to the field strength $\mathcal{E}$. Therefore, the initial effective scattering rate, no matter how it is defined in detail, must be proportional to $\mathcal{E}^2$, i.e., the density. This is a rather natural result for carrier-carrier scattering without screening.

The validity of the TSI is restricted to times $t \lesssim \omega_{\text{pl}}^{-1}$. Certainly we cannot expect that the carrier distribution will evolve towards an equilibrium Fermi distribution. To gain further insight, let us ignore the time restriction for a moment and discuss the behavior of the TSI for large times. The TSI vanishes if the distribution and the polarization are momentum independent. Therefore, the only stationary solution is $P_k = 0$ and $f_k = f^{\infty} = N/M$, where $N = 2\sum_k f_k$ is the number of carriers and $M = 2\sum_k 1$ is the number of states. It is not obvious that this stationary solution will ever be reached. Due to the infinite memory depth in Eq. (2.8) the value of the TSI increases strongly with time. This leads eventually to overshoots and the distribution will leave the $[0, 1]$ interval; the evolution will become unstable. On the other hand, scattering leads also to a loss of memory. A consisted treatment of these two effects avoids such unphysical artifacts. In Ref. 3 stable solutions of the quantum kinetic equations with LO-phonon interaction were obtained already when the memory depth was determined from Fermi's golden rule.

The time scale under consideration is shorter than the memory depth, so that the loss of memory can be neglected. The occurrence of overshoots marks the point where the present theory definitely becomes invalid.

IV. THE QUASICLASSICAL THEORY OF POLARIZATION DECAY

A rather different description of the polarization decay has been proposed by Gurevich *et al.*,[13] which, however, will turn out to be closely related to the early stage of the Coulomb quantum kinetics with a bare Coulomb potential and without energy conservation. The quasiclassical theory is used to calculate the femtosecond decay of an initially given interband polarization. We present here an adoption of this theory, in which we consider in more detail the nature of a pair excitation in a semiconductor.

In this theory one treats the motion of a newly created electron-hole pair in the electrostatic field of an already created plasma, which are assumed to be "frozen" and disordered. One computes at time t the average of the polarization component of wave vector $\mathbf{k}$

$$P_{\mathbf{k}}(t) = \langle \Psi | a_{e,\mathbf{k}}(t) a_{h,-\mathbf{k}}(t) | \Psi \rangle,$$

on an initial state $|\Psi\rangle$, which is a linear superposition of the vacuum state and all states with one electron-hole pair of total momentum zero. For a two-particle model it can be shown that $P_{\mathbf{k}}$ is identical to the wave function of the relative motion $\psi(\mathbf{x}_e - \mathbf{x}_h, t)$, with the initial condition

$$\psi(\mathbf{x}, t = 0) = \exp(i\mathbf{k} \cdot \mathbf{x})$$

taken at the origin $\mathbf{x} = 0$.

The wave function of the pair state will be treated in the quasiclassical approximation, followed by an averaging over the disordered plasma in order to get the phase decay. The wave function can be expressed through an action function S

$$\psi = \exp\left(\frac{iS}{\hbar}\right). \tag{4.1}$$

From the two-particle Schrödinger equation we find the following equation for the action:

$$-\frac{\delta}{\delta t}S=\sum_{i=e,h}\left[\frac{(\nabla_i S)^2}{2m_i}+\sum_{n=1}^{2N}V_{i,n}\right]$$
$$+V_{e,h}+E_g-i\hbar\sum_i\frac{\nabla_i^2 S}{2m_i}. \quad (4.2)$$

Here $V_{i,n}$ is the bare Coulomb interaction between the newly created carrier $i=e,h$ and the $2N$ randomly distributed charges

$$V_{i,n}=\frac{e_i e_n}{\epsilon_0|\mathbf{x}_i-\mathbf{x}_n|},$$

with $e_n=\pm 1$.

In the quasiclassical approximation one neglects the term linear in $\hbar$ and gets the time-dependent Hamilton-Jacobi equation

$$-\frac{\delta}{\delta t}S_{\rm cl}=\sum_i\left[\frac{(\nabla_i S_{\rm cl})^2}{2m_i}+\sum_{n=1}^{2N}V_{i,n}\right]+V_{e,h}+E_g. \quad (4.3)$$

For short times after the creation of the pair with $\mathbf{p}_e=\hbar\mathbf{k}$ and $\mathbf{p}_h=-\hbar\mathbf{k}$ at time $t=0$, the classical action $S_{\rm cl}$ is close to that of the free motion

$$S_{\rm cl}=S_{\rm cl}^0+\delta S, \quad (4.4)$$

where

$$S_{\rm cl}^0=\sum_i\left[\mathbf{p}_i\cdot\mathbf{x}_i-\frac{\mathbf{p}_i^2}{2m_i}t\right]-E_g t. \quad (4.5)$$

The linearized equation for δS is

$$\left(\frac{\delta}{\delta t}+\sum_i\frac{\mathbf{p}_i\cdot\nabla_i}{m_i}\right)\delta S=-\sum_{j,n}V_{i,n}-V_{e,h}\equiv -U, \quad (4.6)$$

with the solution

$$\delta S(t)=-\int_0^t dt' U[\mathbf{x}_e(t'),\mathbf{x}_h(t')], \quad (4.7)$$

where

$$\mathbf{x}_i(t)=\mathbf{x}_i+\frac{\mathbf{p}_i}{m_i}t. \quad (4.8)$$

In this approximation the wave function of the pair is

$$\psi(\mathbf{x}_e,\mathbf{x}_h,t)=\exp\left\{i\left[\sum_i\left(\mathbf{p}_i\cdot\mathbf{x}_i-\frac{\mathbf{p}_i^2}{2m_i}t\right)-E_g t\right.\right.$$
$$\left.\left.-\int_0^t dt' U[\mathbf{x}_e(t'),\mathbf{x}_h(t')]\right]\right\}. \quad (4.9)$$

A divergent Coulomb energy contribution at $\mathbf{x}_e=\mathbf{x}_h$ in the phase has to be compensated, but plays no physical role.

Now the pair wave function has to be averaged over all configurations of the disordered plasma. The absolute value of the averaged polarization is

$$|\langle P_k(t)\rangle|=\left|\left\langle\exp\left\{-i\int_0^t dt'\,U[\mathbf{x}_e(t'),\mathbf{x}_h(t')]\right\}\right\rangle\right|. \quad (4.10)$$

Averaging over the random positions $\mathbf{R}_n=\mathbf{x}_i-\mathbf{x}_n$ and random charges $e_n=\pm e$ of the background plasma means

$$\langle\cdots\rangle\equiv\sum_{e_1=\pm e}\cdots\sum_{e_N=\pm e}\int_{\mathcal{V}}\frac{d\mathbf{R}_1}{2\mathcal{V}}\cdots\int_{\mathcal{V}}\frac{d\mathbf{R}_N}{2\mathcal{V}}\cdots. \quad (4.11)$$

Taking into account that only the Coulomb interaction with the charges of the plasma is influenced by the averaging we have

$$|\langle P_k(t)\rangle|=\left\{1+\frac{1}{N}\sum_{e_n=\pm e}\int\frac{d\mathbf{x}_n N}{2\mathcal{V}}\right.$$
$$\left.\times\left[\exp\left(-\frac{i}{\hbar}\int_0^t dt'\sum_j V_{j,n}(t')\right)-1\right]\right\}^N. \quad (4.12)$$

Following Chandrasekar,[25] we use the relation

$$\lim_{N\to\infty}\left(1+\frac{x}{N}\right)^N=e^x$$

to find in the thermodynamic limit ($N\to\infty, V\to\infty$, and $N/V=n$ finite)

$$|\langle P_k(t)\rangle|=\exp\left(-n\int d\mathbf{R}\right.$$
$$\left.\times\left\{1-\cos\left[\frac{e^2}{\hbar}\int_0^t dt'\left(\frac{1}{|\,\hbar\mathbf{k}t'/m_e-\mathbf{R}\,|}\right.\right.\right.\right.$$
$$\left.\left.\left.\left.-\frac{1}{|\,\hbar\mathbf{k}t'/m_h+\mathbf{R}\,|}\right)\right]\right\}\right), \quad (4.13)$$

where the cosine has been generated by the sum over both kinds of charges in the plasma. Through a rescaling of the integration arguments to dimensionsless ones and introducing the natural units of length and time through the exciton Bohr a_0 radius and Rydberg energy E_0, we get

$$|\langle P_k(t)\rangle|=\exp\left\{-\left(\frac{t}{\tau_{\rm G}}\right)^3\right\}. \quad (4.14)$$

The nonexponential decay time τ_G is given by

$$\frac{1}{\tau_G^3}=\left(\frac{E_0}{\hbar}\right)^3 16\pi n a_0^3 k a_0 F(k a_0). \quad (4.15)$$

The function

$$F(x) \equiv x^2 \int_0^\infty dr r^2 \int_{-1}^1 dz \times \left[1 - \cos\left\{\frac{1}{x}\int_0^{1/r} du \left(\frac{1}{\sqrt{1+2zu\alpha_e+u^2\alpha_e^2}} - \frac{1}{\sqrt{1+2zu\alpha_h+u^2\alpha_h^2}}\right)\right\}\right], \quad (4.16)$$

is slowly varying and on the order of 1. Here $\alpha_i = \mu/m_i$ is the effective mass ratio. This unusual polarization decay law differs essential from the standard exponential one. Most important is the cubic time dependence in the exponent. It originates from the rescaling of the three-dimensional volume integral. In a two-dimensional quantum well structure one gets, consequently, a Gaussian polarization decay. The exponent is proportional to the plasma density. For small k the decay becomes increasingly slow, because in the quasiclassical model a slow pair stays a long time at the same point and therefore does not experience the disorder.

Finally, we discuss the expected validity of this result. Most important, the velocity $\mathbf{v}_i = \hbar\mathbf{k}_i/m_i$ of the electron and hole should be large so that (i) the motion of the background plasma can be neglected, (ii) the action is approximately given by the free one, and (iii) the binding of electron-hole pair is negligible. A bound electron state cannot be properly described in this quasiclassical approximation. The range of validity in time, on the other hand, increases with the inverse velocity.

V. SIMULATION OF THE QUANTUM KINETIC EQUATIONS AND COMPARISON WITH THE QUASICLASSICAL THEORY

In the simulation of the quantum kinetic equations we used GaAs parameters with an exciton Bohr radius $a_0 = 14$ nm and an exciton Rydberg energy $E_0 = 4.2$ meV.

Some extra care is necessary in the modeling of femtosecond experiments. Due to the spectrally broad pulses with high peak intensities very high-momentum states are excited for which the parabolic two-band model of the GaAs is no longer valid. Far from the resonance the induced polarization is given by

$$\lim_{k\to\infty} P_k(t) = \frac{d_k E(t)/2}{(\hbar k)^2/2\mu - \Delta_0} \quad (5.1)$$

[see Eq. (2.5)]. This behavior is a kind of adiabatic following. For ultrashort pulses the laser field peak value $E(t=0)$ is very large. If the optical matrix element d_k is assumed to be constant, the polarization in the adiabatically following tail is not negligible. The tail polarization contributes to the HF field $\sum_{\mathbf{q}} V_q P_{\mathbf{k}-\mathbf{q}}$ [see Eq. (2.6)] and influences in this way also the behavior near the resonance. We suppress the unphysical contribution of these states by an optical matrix element

$$d_k = d_0 \left[\exp\left(\frac{\varepsilon_k - \varepsilon_c}{\Delta_c}\right) + 1\right]^{-1}, \quad (5.2)$$

which decreases strongly above a cutoff energy ε_c, for which we took $\varepsilon_c = 64\ E_0$ (269 meV). This cutoff is somewhat smaller but of the order of the energetic difference between the Γ point and the the next higher band minimum, the L point, which is about 310 meV. For Δ_c we took $0.25E_0$, a value that ensures a smooth but sufficiently sharp decoupling. The proper matrix element would have to be evaluated using a real band structure calculation, which is beyond the aim of our paper. The total induced carrier density and polarization depend on the chosen parameters of the matrix element, but the results for the polarization decay and the relaxation times are not sensitive to this choice, as will be shown below. The necessity of a cutoff in the optical matrix element is only due to the ultrashort pulses. It is not related to the special form of the Coulomb scattering integrals which are treated here.

We solved the quantum kinetic equations for a Gaussian laser pulse envelope

$$E(t) = \mathcal{E} e^{-t^2/\tau^2}. \quad (5.3)$$

In Figs. 1 and 2 the evolution of the polarization amplitude $|P_k(t)|$ and of the carrier distribution $f_k(t)$ are shown for an excitation with an $\pi/8$ pulse, i.e.,

$$\frac{1}{\hbar}\int_{-\infty}^{\infty} dt\, d_{k=0} E(t) = \frac{\pi}{8}, \quad (5.4)$$

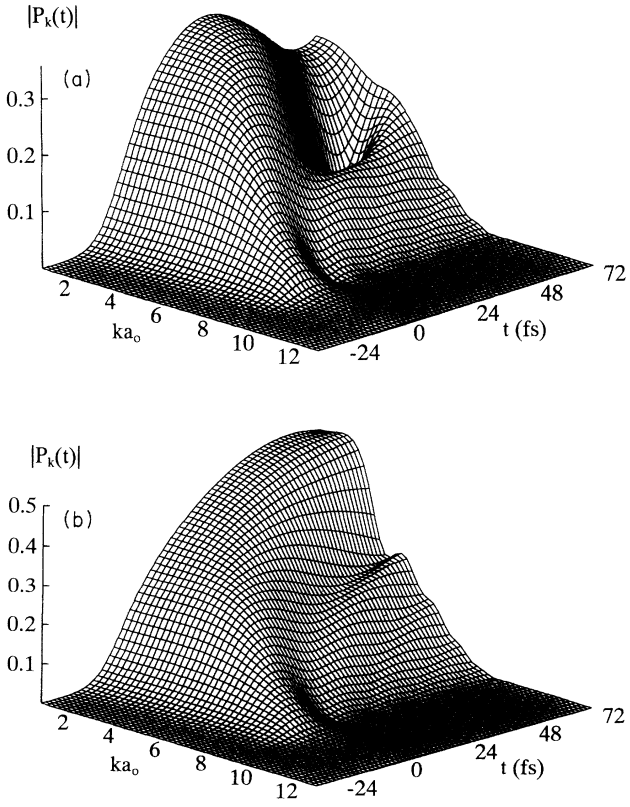

FIG. 1. Polarization amplitude $|P_k(t)|$ versus momentum and time calculated (a) with the full quantum kinetic equations and (b) with the coherent part only.

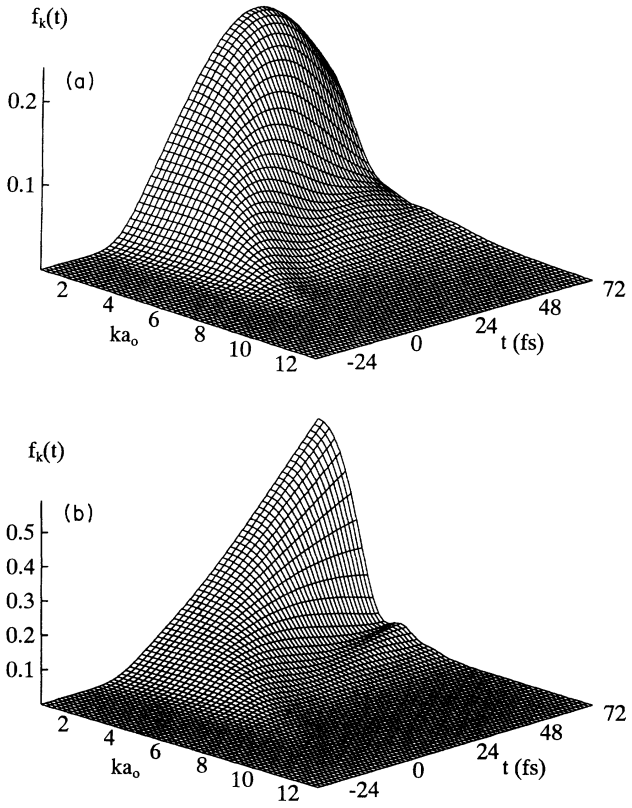

FIG. 2. Carrier distribution $f_k(t)$ versus momentum and time calculated (a) with the full quantum kinetic equations and (b) with the coherent part only.

and a duration $\tau = 12$ fs. The detuning is $\Delta_0 = 5E_0$. The resulting final carrier density is $na_0^3 = 0.364$ or $n = 1.32 \times 10^{17}\text{cm}^{-3}$, corresponding to an inverse plasma frequency of $\omega_{\text{pl}}^{-1} = 38$ fs. The solutions of the quantum kinetic equations with Coulomb scattering (2.4) are shown in Figs. 1(a) and 2(a), and should be compared to the solutions of the coherent equations (2.5) alone, which are shown in Figs. 1(b) and 2(b). A comparison of the two figures reveals a strong influence of excitonic correlations on the ultrashort time scale. The excitonic pair correlation is mediated by the HF field, i.e., by the polarization, which is still large at early times.

For low excitation, where $f_k \ll 1$, the equation of the polarization decouples from the equation of the carrier distribution [see Eq. (2.5)]. The resulting equation is known as the Wannier equation[15] and describes the response of a system of bound and free excitons. In Fig. 1 the shallow oscillations with time can be understood as beats between the $1s$ exciton and the ionization continuum. During a cycle of the exciton-band beating, the amplitude of the polarization rises and falls again. In the k-t plane the position of the oscillation maxima is approximately given by

$$\left(E_0 + \frac{(\hbar k)^2}{2\mu}\right) t = \hbar\left(\frac{\pi}{2} + 2\pi n\right), \quad n = 0, 1, 2, \ldots .$$

(The small deviations from this relation are due to the band gap shrinkage.) Please note in the coherent evolution [Fig. 1(b)] the rise of the polarization at $k = 0$ even after the laser pulse. This effect is even more pronounced for the carrier distribution [Fig. 2(b)]. It is due to the superposition of the response of the bound s excitons, which have oscillator strengths alternating in sign. Immediately after a short pulse, the polarizations of the excitons add, at least partially, destructively, but after about

$$\frac{\pi}{2}\frac{\hbar}{E_0} = 240 \text{ fs}$$

they add constructively. In Fig. 1(b) this oscillation is disturbed by saturation at $t \simeq 48$ fs, because f_k is no longer small. Afterwards, the evolution is governed by the fully coupled equations (2.5). Only for very low excitation the undisturbed oscillation can be seen clearly. A tail of the polarization follows the pulse envelope adiabatically as can be seen around $t = 0$ and $ka_0 \geq 8$. As discussed in Sec. III, the growth of the polarization after $t \geq 48$ fs $> \omega_{\text{pl}}^{-1}$ in Fig. 1(a) falls in the region where our theory is no longer valid.

The redistribution of the carriers and of the polarization caused by the coherent dynamics of the excitons obscures the influence of scattering. The two effects can be separated by plotting $B_k(t)$ of Eq. (3.9). $B_k(t) = 1$ holds for an unexcited or still coherently excited k state. Due to the buildup of the TSI in time, scattering gets important only well after the pulse for $t > 24$ fs, as can be seen in Fig. 3. The transitions at $ka_0 > 4$ are barely excited so that $B_k(t)$ tends to one. A comparison of Fig. 1(a) and 1(b) shows that the region of dominant scattering is 24 fs $< t <$ 48 fs and $0 < ka_0 < 4$, in agreement with Fig. 3. In this region the logarithmic derivative of $|P_k|$ can be regarded as time- and momentum-dependent inverse effective dephasing time

$$\frac{1}{T_2^{\text{eff}}} = -\frac{d}{dt}\ln(|P_k|). \tag{5.5}$$

A mean dephasing time can be extracted from the so-called incoherently summed polarization

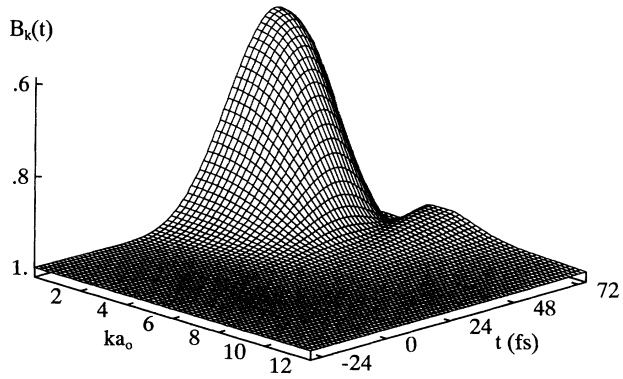

FIG. 3. Evolution of the length of the Bloch vector $B_k(t)$ versus momentum and time corresponding to Figs. 1(a) and 2(a).

$$P^{\rm in}(t) = \sum_{\mathbf{k}} d_k |P_k(t)|. \tag{5.6}$$

Because the polarization decay is measured optically, e.g., in a photon-echo experiment,[11,12] we included the optical matrix element in the definition. In Fig. 4 the incoherently summed polarization corresponding to Fig. 1 is shown on a logarithmic scale. The solid line gives the result for the full equations, the short-dashed line for the coherent equations. The long-dashed line shows the result of a simulation in which the term $\mathrm{Re}P_{|\mathbf{p}+\mathbf{q}|}P_p$ ("P^2 scattering") has been neglected. The TSI gives rise to a significant polarization decay in its range of validity. This makes us confident that the described kinetics may be observed experimentally. Even in the simulation of the coherent equations $P^{\rm in}$ is not strictly constant after the pulse. The shallow oscillations and the small slope are caused by the HF field. As already discussed in Sec. III, the P^2 scattering reduces the loss of coherence in the nearly coherent regime. During and directly after the excitation, the solution of the full equations follow closely the coherent solution, whereas the solution without P^2 scattering shows a stronger loss of coherence, which can be approximately modeled by an exponential decay. The crosses in Fig. 4 show an exponential fit with a decay time of 44 fs. The solution of the full equations follows much more a t^3 law, as predicted by Gurevich *et al.*[13] For comparison, we compute from our numerical results

$$\tau_{\rm G}^{\rm eff} \equiv \left(\frac{-d/dt \ln[P^{\rm in}(t)]}{3(t-t_0)^2} \right)^{-3}. \tag{5.7}$$

According to the quasiclassical theory, $\tau_G^{\rm eff}$ should be time independent, i.e., the nonexponential decay time τ_G [see Eq. (4.14)]. In Eq. (5.7) we introduced explicitly the initial time t_0. The resulting decay time is given in Fig. 5

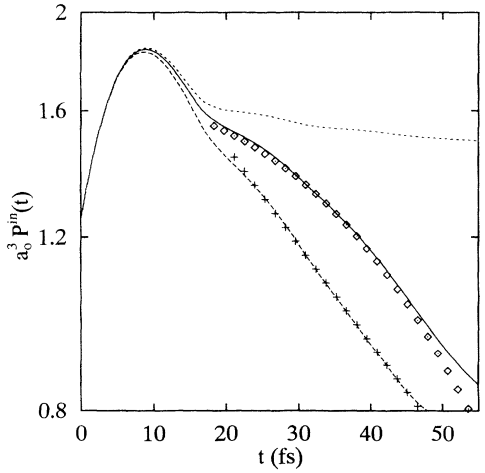

FIG. 4. Incoherently summed polarization $P^{\rm in}(t)$ versus time on a logarithmic scale. Full quantum kinetics (solid line), coherent equations (short-dashed line), quantum kinetics without P^2 scattering (long-dashed line), and quasiclassical theory (diamonds) with $\tau_{\rm G} = 73$ fs and $t_0 = -12$ fs. The exponential fit (crosses) has been obtained with a decay time $T_2 = 44$ fs.

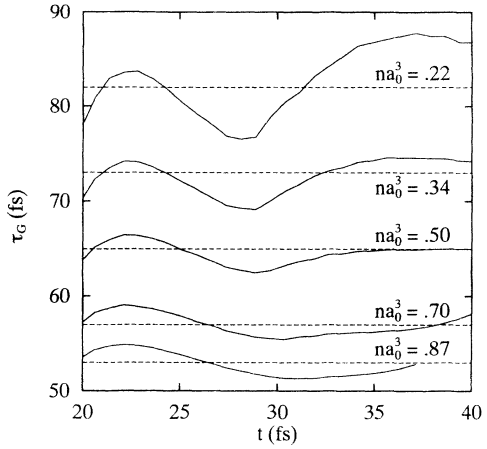

FIG. 5. Effective nonexponential decay time $\tau_{\rm G}$ versus time for various pulse intensities, corresponding to $2\pi/10$ to $\pi/10$ pulses with duration $\tau = 12$ fs and a detuning $\Delta_0 = 5E_0$.

for various pulse intensities corresponding to $2\pi/10$ to $\pi/10$ pulses with a duration $\tau = 12$ fs and a detuning $\Delta_0 = 5E_0$. We obtained the best, i.e., flattest, results for $t_0 = -12$ fs. That means the effective creation time is about one half width at half maximum time before the pulse maximum. The diamonds in Fig. 4 show the polarization decay predicted by the quasiclassical theory. The parameters have been taken from Fig. 5, i.e., $\tau_G = 73$ fs and $t_0 = -12$ fs. This nonexponential decay time corresponds to the expression Eq. (4.15) where the momentum is replaced by an effective momentum of $\langle ka_0 \rangle = 1.4$. Only if the P^2 scattering is included, one finds agreement with the quasiclassical theory.

The quasiclassical theory[13] makes distinct predictions concerning the time, momentum, and density dependences. In order to compare these predictions with our numerical results, we have to select carefully the region in the k-t plane, where a comparison is possible. The theory of Gurevich *et al.* assumes an instant creation of the polarized state. In our model the pulse has a finite duration. In the quasiclassical theory the polarization decays monotonically; in our model the polarization amplitude also oscillates due to excitonic effects. Furthermore, a transfer of polarization by scattering from one state to another is possible. Thus the comparison can be made only for times well after the pulse, during which scattering dominates over coherent dynamics. The predictions of the quasiclassical theory for the inverse dephasing time takes the form [see Eqs. (4.14) and (5.5)]

$$\frac{1}{T_2^{\rm eff\ G}} = \frac{3(t-t_0)^2}{(\tau_G)^3}. \tag{5.8}$$

We compare the inverse effective dephasing times computed from the quantum kinetic equations to those computed from the quasiclassical theory [see Eqs. (5.7) and (5.8)] and find astonishingly good agreement. The absolute values agree if we allow an uncertainty in the initial time t_0 on the order of the pulse width. The time and momentum dependences show the same tendencies.

Next we compare the predicted density dependences. In Fig. 6 the nonexponential polarization decay time τ_G is shown as a function of the induced plasma density. The dashed line corresponds to the quasiclassical theory. The diamonds show the data from Fig. 5 with $\tau = 12$ fs and $\Delta_0 = 5E_0$. The results for simulations with the pulse parameters $\tau = 6$ fs and $\Delta_0 = -E_0$ are shown as squares and those with $\tau = 24$ fs and $\Delta_0 = 0$ as triangles. Finally, the stars show results for the same pulse parameter, but different cutoff energies in the optical matrix element ($\varepsilon_c = 49$, 64, and 144 E_0). Due to the slow convergence of the HF field the change in the optical matrix element affects the induced plasma densities. Nevertheless, as a function of density n all results agree well with the $n^{-1/3}$ law from the quasiclassical theory shown by the dashed line [see Eq. (4.14)]. The only free parameter in the fit is the effective momentum for which we took as $\langle ka_0 \rangle = 1.4$. The nonexponential decay time is rather insensitive to details of the carrier distribution, caused by different excitation conditions or by different optical matrix elements. It depends mainly on the total induced plasma density. In summary, the agreement of the early-stage Coulomb quantum kinetics and the quasi-classical theory for the phase decay has been shown to be surprisingly good, wherever a comparison is possible.

Unfortunately, it is not possible to investigate a broader density range. On the high-density side we are limited, because the inverse plasma frequency has to be larger than the pulse duration, and on the low-density side the "coherent Bloch dynamics" dominates over the scattering.

Becker *et al.*[11] reported a photon-echo experiment performed with laser pulses as short as 6 fs. From their data they concluded that the polarization decay follows an exponential decay and a density dependence of $n^{-1/3}$ for the *exponential* decay time, in contrast to our prediction of a nonexponential decay in the form proportional $\exp(-ant^3)$. They explained their results with the influence of screening. We suggest that a mixture of LO-phonon and carrier-carrier scattering may have caused the reported density dependence. Due to the spectral width of the pulse also states deep in the band have been excited. These states are strongly coupled to LO phonons. From ultrafast luminescence experiments it has been deduced that LO scattering becomes important only after 100 fs,[19] where a modulation of the carrier distribution function with LO-phonon energy spacing has been found. In an earlier Raman-spectroscopy experiment[26] 12 LO-phonon emissions have been found to occur in 2 ps. These values agree with Markovian Monte Carlo simulations.[27] On the other hand, we have shown that in the early stage the energy conservation in the collision does not hold and a non-Markovian theory has to be used. Therefore, the LO-phonon coupling may also be faster in the early stage of the kinetics. Due to the broadening the early LO scattering will not cause a pronounced modulation of the distribution function. Becker *et al.*[28] and Bigot *et al.*[29] reported a Γ-X transfer after a 6 fs laser excitation deep in the band of less than 50 fs.

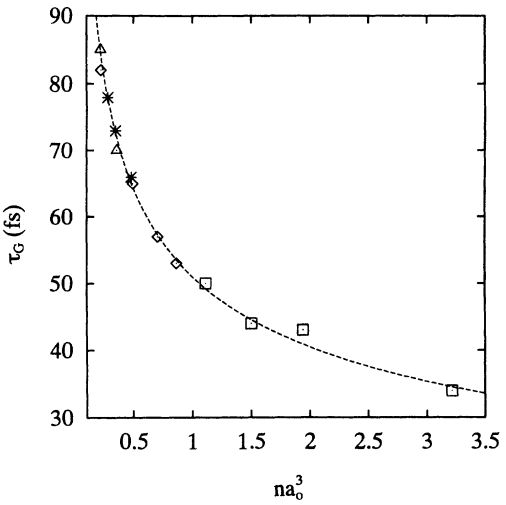

FIG. 6. Nonexponential decay time τ_G versus density for pulses with a duration $\tau = 6$ fs and a detuning $\Delta_0 = -E_0$ (squares), with $\tau = 12$ fs and $\Delta_0 = 5E_0$ (diamonds) and with $\tau = 24$ fs and $\Delta_0 = 0$ (triangles). The stars correspond to $\tau = 12$ fs and $\Delta_0 = 5E_0$, but for different cutoff energies of the optical matrix element ($\varepsilon_c = 49$, 64, and 144 E_0). The dashed line corresponds to the quasiclassical theory with $\langle ka_0 \rangle = 1.4$.

In conclusion, we have presented a Coulomb quantum kinetics for the early stage of the carrier kinetics during and shortly after a femtosecond pulse excitation. It is a retarded kinetics, without energy conservation in the two-particle scattering and without screening, differing strongly from the usual Boltzmann kinetics. In our opinion it is worthwhile to reexamine recent femtosecond experiments in the light of the above described theory.

ACKNOWLEDGMENTS

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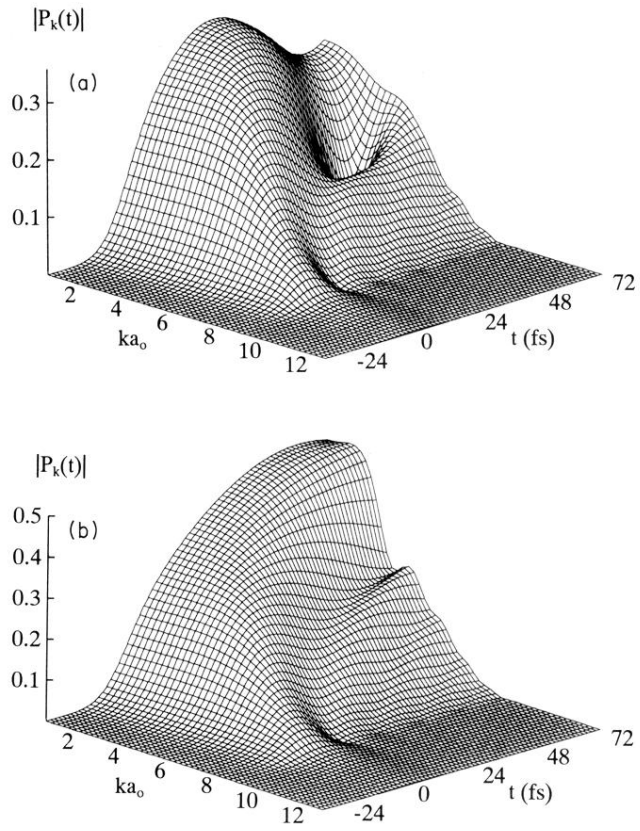

FIG. 1. Polarization amplitude $|P_k(t)|$ versus momentum and time calculated (a) with the full quantum kinetic equations and (b) with the coherent part only.

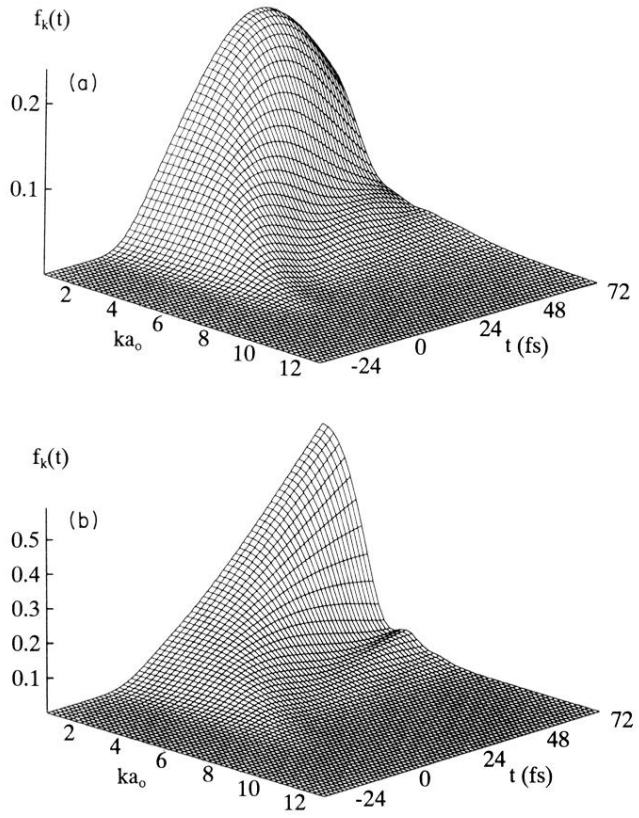

FIG. 2. Carrier distribution $f_k(t)$ versus momentum and time calculated (a) with the full quantum kinetic equations and (b) with the coherent part only.

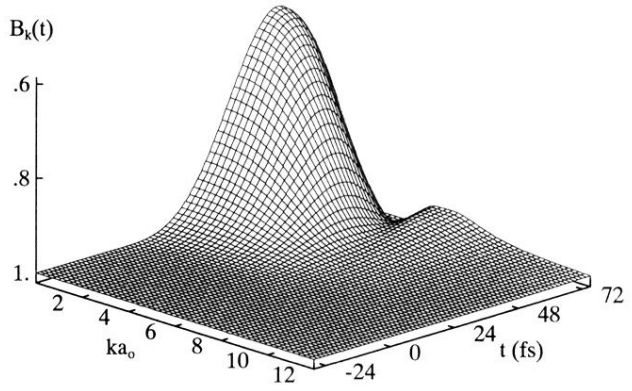

FIG. 3. Evolution of the length of the Bloch vector $B_k(t)$ versus momentum and time corresponding to Figs. 1(a) and 2(a).