Density-matrix approach to nonequilibrium free-carrier screening in semiconductors

U. Hohenester

Universität Graz, Institut für Theoretische Physik, A-8010 Graz, Austria

W. Pötz

Physics Department, University of Illinois at Chicago, Chicago, Illinois 60607

We address the problem of how to derive quantum kinetic transport equations for electrically or optically excited semiconductor systems, where the electron dynamics is dominated by Coulombic interparticle collisions. In particular for the density-matrix approach we show how, in contrast to the frequently used approximation of a (statically) prescreened Hamiltonian, to obtain consistently the screening of the Coulomb interactions. In this connection we present a critical comparison between the generalized Boltzmann equations as obtained within the frameworks of density matrices and nonequilibrium Green's functions. Particular emphasis is given to a general formulation of the problem that allows an extension of our approach to a wide range of different systems. [S0163-1829(97)08443-9]

I. INTRODUCTION

Experimental improvements within the last decade have made it possible to optically excite and probe semiconductor systems on a time scale of their shortest scattering times, opening the door to a variety of exciting effects. Particular interest has been devoted to the interplay of scatterings with the coherent excitation dynamics,[1–5] and to the quantum kinetic peculiarities of the carrier dynamics.[6–8]

The theoretical analysis of such experiments, on the other hand, has to provide transport equations which improve the semiclassical Boltzmann equation. In order to account properly for coherent phenomena, a fully quantum-mechanical treatment, based on a microscopic description, is required.[9] Various approaches have been used in the literature, like Green's functions,[10–14] density matrices,[15–23] the projection-operator technique,[24] or the functional-integral approach.[25] Among these different methods, the framework of nonequilibrium Green's functions has the appealing feature of being extensively used and critically reviewed over many years in various fields of physics (see, e.g., Refs. 26–29). However, when coming down to numerically feasible expressions, several severe approximations have to be introduced. Many authors have, thus, preferred the density-matrix approach, which describes a many-particle system in terms of correlation functions and has the advantage that its derivation only requires some basic knowledge of statistical physics; moreover, the approximations needed to obtain transport equations have an apparently simple form, and the underlying quantities are more directly related to physical observables.[30] We note in this connection that a similar controversy between different approaches to describe many-particle systems can also be found in other fields of physics, like the nuclear many-body problem.[31]

A loose end of the density-matrix approach has been, for many years, the puzzling question of how to incorporate free-carrier screening of interparticle interactions, which becomes extremely important for highly excited semiconductors where the carrier dynamics is dominated by these carrier-carrier collisions.[32] Many authors, confronted with this problem, have come to the conclusion that screening, indeed, is a problem in itself which requires further analysis. But most of these authors have decided to introduce free-carrier screening already within the basic Hamiltonian; such a procedure has, even when screening is treated as self-consistent, no *a priori* justification, but can be physically motivated, e.g., through the successful screened-exchange approach for equilibrium systems.[33] However, we think that a more rigorous analysis has to reveal how screening can be consistently described within the framework of density matrices.

It is somewhat surprising that similar problems had been tackled and solved by Prigogine,[34] Balescu,[35] and Résibois[36] in the early 1960s, but had very little impact on the community of semiconductor transport. Balescu derived transport equations for both classical and quantum-mechanical plasmas; unfortunately, the intermediate steps in his derivations are rather involved, and it is not very likely that his results can be applied to the problems of our present concern. Résibois, on the other hand, developed a more elementary derivation of the kinetic equation and showed, for a classical plasma, how to describe free-carrier screening within the random-phase approximation (RPA).[37]

The aim of this paper is twofold. First, we extend the method of Résibois in a general fashion to quantum-mechanical systems, and derive a quantum kinetic transport equation within the RPA. We are aware that a treatment of free-carrier screening beyond the RPA-approach could be of some importance,[38,39] and has to be clarified in more detail; however, it is hoped that our present analysis provides a first step into this difficult topic. Second, we present a critical comparison of the results as obtained within the frameworks of nonequilibrium Green's functions and density matrices, which should reveal the differences and similarities of the two approaches. This work has been basically inspired by two motivations. First, we think that, in view of the increasing interest in investigating carrier dynamics within the quantum kinetic regime, such a somewhat formal analysis is

of importance for future work related to this challenging field. Second, we feel a necessity to give a subsequent justification for the hitherto used prescreening of the Coulombic interparticle interactions.

We have organized the paper as follows: In Sec. II we introduce our basic Hamiltonian. In Sec. III a short survey over the method of density matrices is given, together with the discussion of how to treat free-carrier screening properly within this approach. To avoid cumbersome notations, we perform our analysis in real space; here, most of our notation has been adopted from Refs. 40 and 41. The comparison with the results of the nonequilibrium Green's function approach is presented in Sec. IV. In order to make our analysis more transparent, we have postponed major parts of the rather lengthy calculations to the appendixes.

II. HAMILTONIAN

Let us specify the Hamiltonian under consideration:

$$H = H_o + H_e + H_i$$

$$= \mathrm{Tr}_1 \psi^\dagger(1) \varepsilon(1) \psi(1) + \mathrm{Tr}_1 u(1;t) \psi^\dagger(1) \psi(1)$$

$$+ \tfrac{1}{2} \mathrm{Tr}_{12} v(12) \psi^\dagger(1) \psi^\dagger(2) \psi(2) \psi(1). \tag{2.1}$$

Here the ψ's are single-particle field operators, and the numbers $1, 2, \ldots$ label positions $\mathbf{r}_1, \mathbf{r}_2, \ldots$ in real space and the spin orientations of the particles. The symbol Tr_1 stands for the integration over the entire space and the sum over the spin degrees of freedom; we will extend this definition further below. The Hamiltonian of the free particles is given by

$$\varepsilon(1) = -\frac{\nabla_1^2}{2m_o} + \sum_{\mathbf{R}} V_{\mathrm{ei}}(\mathbf{r}_1 - \mathbf{R}),$$

where m_o is the free-electron mass, the $\mathbf{R}$'s are the positions of the ions of the crystal, and V_{ei} is the potential between electrons and ions; we set $\hbar = 1$. In order to simplify things we will not consider the effects of phonons, and hence we assume that all ions are at their equilibrium positions. In Eq. (2.1) we introduced a local coupling to an external time-dependent potential $u(1;t)$, which is treated classically; a generalization to different perturbations is straightforward. Finally $v(12)$ is the Coulomb potential (energy) $e^2/|\mathbf{r}_1 - \mathbf{r}_2|$ between particles 1 and 2, with the elementary charge e.

The field operators ψ and $\psi^\dagger$ obey the usual (anti)commutation rules

$$[\psi(1), \psi^\dagger(1')]_{-\eta} \equiv \psi(1) \psi^\dagger(1') - \eta \psi^\dagger(1') \psi(1) = \delta(11'), \tag{2.2}$$

and zero otherwise. Here $\eta = +1$ for bosons and -1 for fermions; although we will only consider electrons, we prefer to stick to the explicit use of η. Finally, $\delta(11')$ represents Dirac's delta function $\delta(\mathbf{r}_1 - \mathbf{r}_{1'})$, together with the Kronecker delta for the spin orientations.

III. DENSITY-MATRIX APPROACH

Density-matrix hierarchy

The concept of density matrices is based on the description of a system using its correlations at one instant of time. If the time evolution of a system is completely determined by the knowledge of its dynamic variables at one instant of time, as, e.g., in the density-matrix approach, we say that the time evolution is *Markovian*. In contrast to this, the method of Green's functions additionally uses dynamic correlations, and its equation of motions will, in general, be non-Markovian. For many problems it is sufficient to consider the one-particle density matrix

$$\rho(1'1;t) \equiv \langle \psi^\dagger(1') \psi(1) \rangle(t), \tag{3.1}$$

which contains information about one-particle properties in the perturbed system, and about effects of collisions on ρ. Here $\langle \rangle(t)$ denotes the statistical average at time t.

First of all, we state some fundamental relations for an arbitrary quantum-statistical system. The expectation value of a (time-independent) operator $\mathcal{A}$ can be obtained by taking the average over the statistical operator $\hat{\rho}$ of the N-particle system at a given time t,

$$\langle \mathcal{A} \rangle(t) = \mathrm{Tr}_{1 \ldots N}[\hat{\rho}(t) \mathcal{A}], \tag{3.2}$$

whereas the time variation of $\langle \mathcal{A} \rangle$ can be found using Ehrenfest's theorem[42]

$$i \partial_t \langle \mathcal{A} \rangle = \langle [\mathcal{A}, H] \rangle. \tag{3.3}$$

From the basic relation (3.3) we then obtain the time evolution of the density matrices by simply evaluating the commutators with the Hamiltonian H defined in Eq. (2.1):

$$i \dot{\rho}(1'1) = [\varepsilon(1) - \varepsilon(1')] \rho(1'1) + [u(1;t) - u(1';t)] \rho(1'1) + \mathrm{Tr}_2[v(12) - v(1'2')] \rho_2(1'2',12),$$

$$i \dot{\rho}_2(1'2',12) = [\varepsilon(1) - \varepsilon(1') + \varepsilon(2) - \varepsilon(2')] \rho_2(1'2',12) + [u(1;t) - u(1';t) + u(2;t) - u(2';t)] \rho_2(1'2',12)$$

$$+ [v(12) - v(1'2')] \rho_2(1'2',12) + \mathrm{Tr}_3[v(13) - v(1'3') + v(23) - v(2'3')] \rho_3(1'2'3',123). \tag{3.4}$$

Here we have introduced the two- and three-particle density matrices

$$\rho_2(1'2',12) = \langle \psi^\dagger(1')\psi^\dagger(2')\psi(2)\psi(1)\rangle,$$ (3.5)

$$\rho_3(1'2'3',123) = \langle \psi^\dagger(1')\psi^\dagger(2')\psi^\dagger(3')\psi(3)\psi(2)\psi(1)\rangle.$$

Furthermore, we have extended the definition of Tr_2 in such a way that the expressions depend explicitly on $2'$ and 2, and we perform the limit $2'\to 2$ at the end of the algebraic manipulations; this is necessary as the free propagation (i.e., terms with ε) involves the infinitesimal off-diagonal ele-

ments of the density matrices. In the following we use the obvious shorthand notation $[h_o(1)+h_e(1),\rho]$ for the time evolution due to the free propagation and the coupling to the external field.

The set of equations (3.4) is not closed, as each ρ_n couples to the higher-density matrix ρ_{n+1}; this infinite set of equations has been known for a long time as the Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy.[37] Unfortunately, the formulation itself does not lead to a physically transparent truncation scheme. At this point it is convenient to change from density matrices to correlation functions c_m,

$$\rho_2(1'2',12) = (1+\eta\mathcal{P}_{12})\rho(1'1)\rho(2'2) + c_2(1'2',12)$$

$$\rho_3(1'2'3',123) = (1+\eta\mathcal{P}_{12}+\eta\mathcal{P}_{13}+\eta\mathcal{P}_{23}+\mathcal{P}_{13}\mathcal{P}_{12}+\mathcal{P}_{13}\mathcal{P}_{23})\rho(1'1)\rho(2'2)\rho(3'3)+(1+\eta\mathcal{P}_{12}+\eta\mathcal{P}_{13})\rho(1'1)c_2(2'3',23)$$

$$+(1+\eta\mathcal{P}_{23}+\eta\mathcal{P}_{21})\rho(2'2)c_2(1'3',13)+(1+\eta\mathcal{P}_{31}+\eta\mathcal{P}_{32})\rho(3'3)c_2(1'2',12)+c_3(1'2'3',123),$$ (3.6)

where the operator $\mathcal{P}_{12}$ exchanges 1 and 2 in the subsequent expression, e.g., through $\mathcal{P}_{12}\rho_1(1'1)\rho_1(2'2) = \rho_1(1'2)\rho_1(2'1)$. We should stress that there is no *a priori* motivation for the cumulant expansion of Eq. (3.6).

The crucial approximation inherent to most density-matrix approaches is the assumption that $c_m = 0$ for $m \geq n$ (to be more specific, we will neglect in the following all correlations beyond the two-particle level, i.e., $n = 3$). To find the time evolution of c_2, we have to insert Eq. (3.6) into Eq. (3.4). It has been shown that the factorization of Eq. (3.6), together with the neglect of three-particle interactions, is compatible with the conservation laws of density and energy.[41] The rather lengthy calculation can be considerably simplified by noting that only ''connected'' expressions, i.e., terms that cannot be factorized into two functions of different variables, contribute to $\dot{c}_2$.[41] For the sake of completeness, we state the final set of equations:

$$i\dot{\rho}(1'1) = [h_o(1)+h_e(1),\rho] + \mathrm{Tr}_2[v(12)-v(1'2')][(1+\eta\mathcal{P}_{12})\rho(1'1)\rho(2'2)+c_2(1'2',12)],$$ (3.7a)

$$i\dot{c}_2(1'2',12) = [h_o(1)+h_o(2)+h_e(1)+h_e(2),c_2] + [v(12)-v(1'2')][(1+\eta\mathcal{P}_{12})\underline{\rho(1'1)\rho(2'2)}+c_2(1'2',12)]$$

$$+\mathrm{Tr}_3\{(1+\eta\mathcal{P}_{12})[\underline{(v(13)-v(1'3'))}]\rho(1'1)[c_2(2'3',23)+\underline{\eta\rho(2'3)\rho(3'2)}]$$

$$+[v(23)-v(2'3')]\rho(2'2)[c_2(1'3',13)+\eta\rho(1'3)\rho(3'1)]+[v(13)-v(1'3')+v(23)-v(2'3')]$$

$$\times[(1+\eta\mathcal{P}_{13}+\eta\mathcal{P}_{23}+\eta\mathcal{P}_{1'3'}+\eta\mathcal{P}_{2'3'})\rho(3'3)c_2(1'2',12)+c_3(1'2'3',123)]\}.$$ (3.7b)

It is obvious that these equations are, even for $c_3 = 0$, too complicated to be solved without further approximations. Making contact with the Green's function approach, we show in Appendix E that the random-phase approximation corresponds to keeping in Eq. (3.7b) only the underlined contributions, i.e.,

$$i\dot{c}_2(1'2',12) = [h_o(1)+h_o(2)+h_e(1)+h_e(2),c_2] + [v(12)-v(1'2')]\rho(1'1)\rho(2'2) + \mathrm{Tr}_3\{[v(13)-v(1'3')]\rho(1'1)$$

$$\times[c_2(2'3',23)+\eta\rho(2'3)\rho(3'2)]+[v(23)-v(2'3')]\rho(2'2)[c_2(1'3',13)+\eta\rho(1'3)\rho(3'1)]\}.$$ (3.8)

One can easily check that in momentum space this approximation has the peculiarity that all interactions involve the *same* momentum exchange (i.e., summation of the ''most divergent contributions''[35]). Let us briefly comment on the meaning of the various contributions of Eq. (3.8). The first term on the right-hand side obviously accounts for the free propagation of c_2 and its coupling to the external field. Next, the terms containing solely one-particle density matrices act as source terms which describe the buildup of correlations through fluctuations in the system; here the second term on the right-hand side stands for a direct interaction between particles 1 and 2, whereas the two other terms can be traced to the Pauli principle correlations.[33] Finally, the correlation transfers on the right-hand side of Eq. (3.8) are, as will be

shown below, responsible for the proper description of dynamical screening within the RPA; these terms describe how the field produced by the charge distribution around one particle, in turn, effects a second particle.

What kinds of physical effects are missing in our RPA ansatz (3.8)? It is known that the RPA properly accounts for the correlation hole at large distances but fails at small distances.[33,38,43] Improvements over the present RPA framework thus (i) should provide a better description of the electron-electron interactions at small distances [e.g., through the inclusion of the second term on the right-hand side of Eq. (3.7b) (Ref. 44)] and (ii) should correct for the missing exchange contributions in the correlation dynamics.

Finally, we note that we could have included in Eq. (3.8), the Hartree terms, i.e., the contributions on the right-hand side of Eq. (3.7b) containing $\rho(33)c_2(1'2',12)$; their neglect is somewhat arbitrary. These Hartree terms, however, can be reintroduced at any point of our analysis. A further discussion of such renormalization terms will be given in Sec. IV.

Transport equation within the random-phase approximation

Before we proceed, it seems appropriate to clarify the goal of our further analysis. If we had neglected c_2 in the time evolution of ρ, we would have recovered the time-dependent Hartree-Fock approximation. Hence we expect that c_2 describes the effects of collisions on the one-particle density matrix. Let us assume that, at a given time t_o, the system is in a completely uncorrelated state. At later times, however, correlations build up due to the two-particle interactions of H_i. We still can find an expression for the correlations which only depends on the one-particle density matrix, at the price of using a non-Markovian equation instead of the original Markovian BBGKY hierarchy.[42] In other words, we can describe the temporal evolution of a true many-particle system just knowing its one-particle correlations.

This formal aspect is inherent to any transport analysis. In many systems, however, it turns out that the one-particle density matrix changes on a much slower time scale than the two-particle correlations. Speaking loosely, the time between two subsequent scatterings is much longer than the time it takes for the scattering itself. One could solve the equation for c_2 under the assumption that during a two-particle interaction the density matrix ρ does not vary with time (with the exception of the trivial time dependence due to H_o, and, in case of an external optical excitation, to the fast time dependence of H_e), and insert the resulting expression into the equation for $\dot{\rho}$. Together with the adiabatic approximation, this procedure would then recover a Markovian time evolution of ρ. Our following analysis, of formally solving Eq. (3.8), is inspired by these ideas, although we shall not make use of the Markov approximation but stick to the most general case.

We finally want to point out that equations of motions similar to Eq. (3.8) have been derived by various authors;[17,18,32] however, these derivations have neglected contributions of correlation transfers in Eq. (3.8), i.e., terms involving v together with c_2. The correlation transfers give, as will be shown below, rise to the screening of the Coulomb potential.

In order to simplify things we introduce some additional shorthand notations. First, we notice that all terms of the RPA expressions involve $1'1$, $2'2$, and $3'3$ only pairwise; we hence use instead of these pairs just one boldfaced number, i.e., **1**, **2**, and **3**. Moreover, we introduce the ''Liouvillian operators''

$$\mathcal{L}_o(\mathbf{1}) \equiv \varepsilon(1) - \varepsilon(1'),$$

$$\mathcal{L}'(\mathbf{12}) \equiv v(12) - v(1'2'),$$

(3.9)

$$\hat{\mathcal{L}}(\mathbf{1})c(\mathbf{12}) \equiv \mathrm{Tr}_3 \mathcal{L}'(\mathbf{13})\rho(\mathbf{1})c(\mathbf{32}),$$

$$\hat{\mathcal{L}}(\mathbf{2})c(\mathbf{12}) \equiv \mathrm{Tr}_3 \mathcal{L}'(\mathbf{23})\rho(\mathbf{2})c(\mathbf{13}),$$

From now on we shall write c instead of c_2. Equation (3.8) then reads

$$i\dot{c}(\mathbf{12}) = [\mathcal{L}_o(\mathbf{1}) + \mathcal{L}_o(\mathbf{2})]c(\mathbf{12}) + [\hat{\mathcal{L}}(\mathbf{1}) + \hat{\mathcal{L}}(\mathbf{2})]$$
$$\times [c(\mathbf{12}) + S_o(\mathbf{12})]. \quad (3.10)$$

We have neglected the coupling of c to the external field, although it is possible to carry out the following analysis without this simplification. It should be noted that this neglect can become problematic in some systems, e.g., when describing the intracollisional field effect.[21] However, the interference between the scattering dynamics and effects of the external field would mainly introduce cumbersome notation without elucidating our discussion substantially.

Finally, we have introduced the static form factor[33]

$$S_o(\mathbf{12}) \equiv \rho(1'2)[\delta(2'1) + \eta\rho(2'1)]$$
$$= \langle [\psi^\dagger(1')\psi(1) - \rho(1'1)]$$
$$\times [\psi^\dagger(2')\psi(2) - \rho(2'2)]\rangle_o, \quad (3.11)$$

where $\langle\ \rangle_o$ means that the expectation value has to be taken for the *free* (i.e., uncorrelated) electron system.

Equation (3.10) can be solved formally,[42]

$$c(\mathbf{12};t) = \mathcal{U}(\mathbf{12};tt_o)c(\mathbf{12};t_o) - i\int_{t_o}^{t} dt' \mathcal{U}(\mathbf{12};tt')$$
$$\times [\hat{\mathcal{L}}(\mathbf{1};t') + \hat{\mathcal{L}}(\mathbf{2};t')]S_o(\mathbf{12};t'), \quad (3.12)$$

where the (super)operator $\mathcal{U}$ obeys the differential equation

$$i\partial_t \mathcal{U}(\mathbf{12};tt') = [\hat{\mathcal{L}}(\mathbf{1};t) + \hat{\mathcal{L}}(\mathbf{2};t)]\mathcal{U}(\mathbf{12};tt'), \quad (3.13)$$

with $\mathcal{U}(\mathbf{12};tt) = 1$. Equation (3.12) can be easily proven by differentiating with respect to t.

An apparently striking feature of our RPA ansatz is the fact that the correlation transfers of particles 1 and 2 occur independently of each other, i.e.,

$$[\hat{\mathcal{L}}(\mathbf{1}), \hat{\mathcal{L}}(\mathbf{2})] = 0. \quad (3.14)$$

In the following we will show that this peculiarity gives rise to an extremely useful factorization of $\mathcal{U}(\mathbf{12};tt')$.[36] Assume that we have

$$i\partial_t \mathcal{U}(tt') = \mathcal{L}(t)\mathcal{U}(tt'), \quad (3.15)$$

with $\mathcal{U}(tt) = 1$. If we can decompose $\mathcal{L}$ into two parts,

$$\mathcal{L}(t) = \mathcal{L}_1(t) + \mathcal{L}_2(t), \quad (3.16)$$

then the following operator identities hold between $\mathcal{U}$ and $\mathcal{U}_1$:

$$\mathcal{U}(tt') = \mathcal{U}_1(tt') - i\int_{t'}^{t} d\tau\, \mathcal{U}_1(t\tau)\mathcal{L}_2(\tau)\mathcal{U}(\tau t')$$
$$= \mathcal{U}_1(tt') - i\int_{t'}^{t} d\tau\, \mathcal{U}(t\tau)\mathcal{L}_2(\tau)\mathcal{U}_1(\tau t'),$$
(3.17)

where $\mathcal{U}_1$ obeys the differential equation

$$i\partial_t \mathcal{U}_1(tt') = \mathcal{L}_1(t)\mathcal{U}_1(tt'), \qquad (3.18)$$

with $\mathcal{U}_1(tt) = 1$. With the help of these identities we then obtain the important result

$$\mathcal{U}(\mathbf{12};tt') = \mathcal{U}(\mathbf{1};tt')\mathcal{U}(\mathbf{2};tt'), \qquad (3.19)$$

where $\mathcal{U}(\mathbf{1})$ obeys Eq. (3.17) [with $\mathcal{U}_1 = \mathcal{U}_o(\mathbf{1})$ and $\mathcal{U} = \mathcal{U}(\mathbf{1})$] and

$$\mathcal{U}_o(\mathbf{1};tt') = \exp\{-i[\varepsilon(1) - \varepsilon(1')](t - t')\}. \quad (3.20)$$

Here we have used that $\mathcal{U}(\mathbf{1})$ commutes at all times with $\mathcal{L}_o(\mathbf{2})$ and $\hat{\mathcal{L}}(\mathbf{2})$, and have exploited the properties

$$\mathcal{U}(\mathbf{1};t_o t_1)\mathcal{U}(\mathbf{1};t_1 t_2) = \mathcal{U}(\mathbf{1};t_o t_2),$$
$$\qquad (3.21)$$
$$\mathcal{U}_o(\mathbf{1};t_o t_1)\mathcal{U}_o(\mathbf{1};t_1 t_2) = \mathcal{U}_o(\mathbf{1};t_o t_2),$$

with $t_o \geq t_1 \geq t_2$. Corresponding expressions hold for $\mathcal{U}(\mathbf{2})$. Note that throughout this whole section we use retarded quantities, i.e., any function that depends on two time arguments tt' vanishes for $t' > t$ (with the only exception of advanced quantities introduced further below).

We finally put all results together and obtain the quantum kinetic transport equation

$$\dot{\rho}(\mathbf{1};t) = -i[h_o(1) + h_e(1), \rho] - i\,\mathrm{Tr}_2\mathcal{L}'(\mathbf{12})S_o(\mathbf{12};t)$$

$$+ (-i)^2 \int_{t_o}^t dt'\,\mathrm{Tr}_2\mathcal{L}'(\mathbf{12})\mathcal{U}(\mathbf{1};tt')\mathcal{U}(\mathbf{2};tt')$$

$$\times [\hat{\mathcal{L}}(\mathbf{1};t') + \hat{\mathcal{L}}(\mathbf{2};t')]S_o(\mathbf{12};t')$$

$$- i\,\mathrm{Tr}_2\mathcal{L}'(\mathbf{12})\mathcal{U}(\mathbf{1};tt_o)\mathcal{U}(\mathbf{2};tt_o)c(\mathbf{12};t_o). \quad (3.22)$$

It is instructive to analyze the various contributions to Eq. (3.22) in more detail.[45] Obviously the first term on the right-hand side of Eq. (3.22) describes, once again, the free propagation of ρ together with the coupling to the external field, while the second term represents the mean-field contributions. Next, the third term describes the effects of the scattering dynamics on ρ. It has the familiar structure that (i) correlations are created at time t', (ii) they propagate from t' to t, and (iii) are finally destroyed at time t. The propagation of the correlation between particles 1 and 2 has, due to our RPA ansatz of Eq. (3.10), the peculiarity that the correlation transfers of particle 1 and 2, described by $\hat{\mathcal{L}}$, occur independently of each other;[36] this was the origin of the factorization of $\mathcal{U}(\mathbf{12})$. Finally, the fourth term on the right-hand side of Eq. (3.22) represents the effects of initial correlations on the time evolution of ρ; in the following we will neglect this contribution. Such an approximation is justified if we have a completely uncorrelated initial state before the external perturbation is turned on (e.g., an intrinsic semiconductor which is optically excited, with the onset of the laser pulse at t_o). However, the approximation becomes rather delicate in conjunction with the above mentioned Markov approximation, where the neglect of initial correlations would be in the spirit of Boltzmann's Stoßzahlansatz. We will return to this point below.

Details of the solution of Eq. (3.22) are sketched in Appendix C. We finally arrive at the result

$$\dot{\rho}(\mathbf{1};t) = -i[h_o^{\mathrm{HF}}(1) + h_e(1), \rho] + \mathcal{C}(\mathbf{1};tt_o), \quad (3.23)$$

with the abbreviations

$$[h_o^{\mathrm{HF}}(1), \rho] = [h_o(1), \rho] + \mathrm{Tr}_2[v(12)S_o'(\mathbf{12};t) - \mathrm{H.c.}],$$

$$\mathcal{C}(\mathbf{1};tt_o) = (-i)^2 \int_{t_o}^t dt'\,d\tau\,d\bar{\tau}\,\mathrm{Tr}_{2,3\bar{3}}[S_o'(\mathbf{12};tt')v_s^r(13;t\tau)S_o(3\bar{3};\tau\bar{\tau})v_s^a(\bar{3}2;\bar{\tau}t')$$

$$- S_o'(\mathbf{21};t't)v_s^r(13;t\tau)S_o(\bar{3}3;\bar{\tau}\tau)v_s^a(\bar{3}2;\bar{\tau}t') + \mathrm{H.c.}],$$

$$S_o(\mathbf{12};tt') = \theta(t - t')\mathcal{U}_o(\mathbf{1};tt')S_o(\mathbf{12};t') + \theta(t' - t)\mathcal{U}_o(\mathbf{2};t't)S_o(\mathbf{12};t).$$

Here H.c. means that one has to take the complex conjugate of the preceding expression together with an exchange of $1'$ and 1, and the prime on the dynamic form factor S_o' is a reminder that one does not have to perform the final limit $1' \to 1$. In addition we have introduced the retarded and advanced components of the screened Coulomb potential v_s which, as shown in Appendixes A and B, have to be obtained additionally from Dyson-like equations. We finally emphasize that the derivation of Eq. (3.23) contains only very few assumptions about the peculiarities of the system under consideration.

Generalized Boltzmann equation

The generalized collision integral $\mathcal{C}$ of Eq. (3.23) has an apparently simple form that we want to explore in more detail. We have chosen the dynamic form factor as our basic quantity, because it furnishes a direct measure of the excitation spectrum of the system; for an extensive discussion of this particularly important quantity the reader is referred to Ref. 33. To simplify our analysis, we restrict ourselves to a homogeneous bulk material. Moreover, we make use of the Markov approximation, i.e., we assume that the statistical operator $\hat{\rho}$ can be kept constant in time during a scattering process, and we turn on the carrier-carrier interaction adiabatically.[46] These approximations, together with the neglect of initial correlations, recover a purely kinetic description of the particles, where ''free'' carriers are redistributed due to their mutual Coulomb interactions, but collective excitations like plasmons can be neither absorbed, nor emitted, and only show up as virtual excitations in scattering events.

However, we think that our derivation of the transport equation (3.23) is well suited for an inclusion of these additional real plasmon processes by keeping initial correlations. Here, we will not inquire into these problematics in more detail. In some systems the restriction to describe the dynamics in terms of solely one-particle quantities can lead to spurious effects.[47]

In the following we consider a homogeneous bulklike material. It is assumed that before and after a scattering event the many-particle system is completely uncorrelated. If we can find a complete set of Hartree-Fock states $|\mu\rangle$, which are *simultaneously* eigenstates of H_o and of the statistical operator $\hat{\rho}$ of the uncorrelated system,[48] i.e., $H_o|\mu\rangle=E_\mu|\mu\rangle$ and $\hat{\rho}|\mu\rangle=\hat{\rho}_\mu|\mu\rangle$, we can rewrite the dynamic form factor within the Markov approximation as

$$S_o(12;tt')=\sum_{\mu\nu}\langle\mu|\hat{\rho}e^{iH_ot}\bar{n}(1)e^{-iH_o(t-t')}|\nu\rangle$$
$$\times\langle\nu|\bar{n}(2)e^{-iH_ot'}|\mu\rangle,$$

with the density fluctuation operator $\bar{n}(1)=\psi^\dagger(1)\psi(1)-\rho(11)$. We then immediately obtain the Fourier-transformed dynamic form factor

$$S_o(\mathbf{q},\omega)=\sum_{\mu\nu}\hat{\rho}_\mu|\langle\mu|\bar{n}(\mathbf{q})|\nu\rangle|^2 2\pi\delta(\omega-\omega_{\nu\mu}). \tag{3.24}$$

Here we have introduced $\bar{n}(\mathbf{q})=\mathrm{Tr}_1\exp(i\mathbf{q}\mathbf{r}_1)\bar{n}(1)$ and $\omega_{\nu\mu}=E_\nu-E_\mu$. By use of Eqs. (3.24) and (B3) we obtain for the retarded polarization the Fourier-transformed expression

$$P_o(\mathbf{q},\omega)=\int\frac{d\omega'}{2\pi}\frac{S_o(\mathbf{q},\omega')-S_o(-\mathbf{q},-\omega')}{\omega-\omega'+i0^+},$$

where the infinitesimally small quantity 0^+ ensures causality.

Let us elucidate the meaning of S_o in more detail by shortly discussing the simple case where an incoming ''external'' particle, with the position $\mathbf{R}_e$, is coupled to the system by a velocity-independent interaction potential $\mathcal{V}$ (for a complete discussion cf. Ref. 33)

$$H_{int}=\sum_\mathbf{q}\mathcal{V}(\mathbf{q})\bar{n}(-\mathbf{q})e^{i\mathbf{q}\cdot\mathbf{R}_e}.$$

According to the ''golden rule'' of second-order perturbation theory, the probability $\mathcal{P}(\mathbf{q},\omega)$ that the particle transfers momentum $\mathbf{q}$ and energy ω *to* the system is given by

$$\mathcal{P}(\mathbf{q},\omega)=|\mathcal{V}(\mathbf{q})|^2 S_o(\mathbf{q},\omega),$$

whereas the probability that the particle absorbs momentum $\mathbf{q}$ and energy ω *from* the system is given by $\mathcal{P}(-\mathbf{q},-\omega)$. Although similar discussions can be found in most textbooks on many-particle systems, we have included these remarks as we wanted to explicitly emphasize this strikingly simple interpretation of S_o.

Next, we want to derive an expression for the generalized collision integral of Eq. (3.23) within the adiabatic approximation, i.e., we turn on the interaction adiabatically and perform the limit $t_o\to-\infty$, assuming that the system is stable. We stress that this approximation has nothing to do with a physical damping process, but is rather a mathematical procedure to yield proper boundary conditions. After some simple steps, we arrive at

$$\lim_{t_o\to-\infty}\mathcal{C}(\mathbf{1};tt_o)=\int\frac{d\omega}{2\pi i}\sum_{\mu\nu,\mathbf{q}}\hat{\rho}_\mu|v_s(\mathbf{q},\omega)|^2\bigg(\langle\mu|\bar{n}(\mathbf{q})|\nu\rangle$$
$$\times\langle\nu|e^{i\mathbf{q}\cdot\mathbf{r}_1}\psi^\dagger(1')\psi(1)|\mu\rangle\frac{S_o(-\mathbf{q},-\omega)}{\omega-\omega_{\nu\mu}-i0^+}$$
$$-\langle\mu|e^{i\mathbf{q}\cdot\mathbf{r}_1}\psi^\dagger(1')\psi(1)|\nu\rangle$$
$$\times\langle\nu|\bar{n}(\mathbf{q})|\mu\rangle\frac{S_o(\mathbf{q},\omega)}{\omega+\omega_{\nu\mu}-i0^+}-\mathrm{H.c.}\bigg).$$

From our previous discussion of the dynamic form factor, it is apparent that the second term on the right-hand side describes how particle 1 transfers momentum and energy to the system, whereas the first term represents the transfer of momentum and energy from the system to the particle. In the spirit of the original Boltzmann equation these expressions can be considered as generalized in- and out-scattering terms (note also the change in sign).

We conclude this section with some short technical comments on the evaluation of the expressions presented above, for the particularly simple example of free carriers; a generalization to more complex systems is obvious. First we rewrite the field operators $\psi(1)$ in terms of the eigenfunctions of H_o (plane waves), i.e.,

$$\psi(1)=\sum_\mathbf{k}e^{i\mathbf{k}\cdot\mathbf{r}_1}a_\mathbf{k},$$

and a corresponding expression for $\psi^\dagger(1)$. We then find for the dynamic form factor and for $q\neq0$

$$S_o(\mathbf{q},\omega)=\sum_{\mu\nu,\mathbf{k}}\hat{\rho}_\mu|\langle\mu|a_\mathbf{k}^\dagger a_{\mathbf{k}+\mathbf{q}}|\nu\rangle|^2 2\pi\delta(\omega-\omega_{\nu\mu}).$$

It follows at once that the difference in energy between the two configurations μ and ν is

$$\omega_{\nu\mu}=\varepsilon(\mathbf{k}+\mathbf{q})-\varepsilon(\mathbf{k})\equiv\omega(\mathbf{k},\mathbf{q}),$$

where $\varepsilon(\mathbf{k})$ denotes the energy of a free carrier with wave vector $\mathbf{k}$. Hence we obtain

$$S_o(\mathbf{q},\omega)=\sum_{\mu,\mathbf{k}}\hat{\rho}_\mu\langle\mu|a_\mathbf{k}^\dagger a_{\mathbf{k}+\mathbf{q}}a_{\mathbf{k}+\mathbf{q}}^\dagger a_\mathbf{k}|\mu\rangle 2\pi\delta[\omega-\omega(\mathbf{k},\mathbf{q})]$$
$$=2\sum_\mathbf{k}\langle a_\mathbf{k}^\dagger a_{\mathbf{k}+\mathbf{q}}a_{\mathbf{k}+\mathbf{q}}^\dagger a_\mathbf{k}\rangle_o 2\pi\delta[\omega-\omega(\mathbf{k},\mathbf{q})]$$
$$=2\sum_\mathbf{k}f_\mathbf{k}(1+\eta f_{\mathbf{k}+\mathbf{q}})2\pi\delta[\omega-\omega(\mathbf{k},\mathbf{q})],$$

where we have introduced the distribution function $f_\mathbf{k}=\langle a_\mathbf{k}^\dagger a_\mathbf{k}\rangle_o$, and the factor 2 explicitly denotes the two possible spin orientations. The additional steps to rewrite Eq.

(3.23) in terms of distribution functions are completely analogous, and will not be presented here.

IV. COMPARISON WITH NONEQUILIBRIUM GREEN'S FUNCTIONS

In Sec. III we showed that it is, indeed, possible to describe free-carrier screening consistently within the density-matrix approach, by introducing the RPA ansatz of Eq. (3.8). However, we think that an additional justification for this ansatz would help to elucidate its limitations, as well as to indicate directions for further improvements.

A particularly important approach to describe many-particle systems has been, within the last decades, the framework of Green's functions. Extensions of this formalism to systems driven out of equilibrium were developed in the early 1960s, and have been applied successfully to many problems in solid-state physics; for details the reader is referred to the literature.[49,50] The Green's-function approach has, in contrast to the density-matrix approach, the advantage that it provides, at least for Coulombic systems, a consistent truncation scheme which has been critically reviewed for many years. However, in nonequilibrium systems, numerically feasible transport equations are, even for the simplest problems, difficult to obtain without further approximations, like the notorious Kadanoff-Baym ansatz.[49] Next we shall compare the previously derived results to those obtained within the framework of Green's functions. In doing so, we also hope to provide a more common basis for the different ''languages'' of Green functions and density matrices.

As there exist many reviews on nonequilibrium Green's functions,[49,26,10] we only present their most important ingredients in Appendix E. Within the framework of Green's functions the RPA ansatz neglects the dependence of Σ', which differs from the self-energy Σ in that it does not contain the Hartree term, on the screened potential u_s, i.e., $\delta\Sigma'/\delta u_s \approx 0$. We show in Appendix E that, within this approximation, we recover the RPA ansatz (3.8) if we replace the one-particle Green's functions g by the *free* propagators g_o.

Although we have given additional justification for our basic ansatz (3.8), this result is a severe drawback for our previously derived transport equation (3.22). In particular, we find that the non-Markovian equation (3.22) solely accounts for the change of the one-particle density matrix during a scattering process, but completely neglects *all* effects of dynamical renormalization on the propagation of the electron (described by $\mathcal{U}_o$). To make this point even stronger, at the end of Appendix E we rederive the non-Markovian transport equation, and show that only renormalized one-particle quantities show up in the corresponding Green's-function expressions. We note that this deficiency is in complete contrast to the Kadanoff-Baym ansatz,[49] where it is assumed that dynamical renormalization processes occur on a much shorter time scale than the change of the distribution function.[51] Our RPA ansatz (3.8), hence, is somewhat similar to a *free* Kadanoff-Baym ansatz within the nonequilibrium Green's function approach.[13]

Finally, we note that the discrepancy between the results as obtained within the frameworks of density matrices and Green's functions, respectively, can be attributed to our ne-glect of three-particle correlations.[52] The random-phase approximation is discussed in some detail in Ref. 53 for a homogeneous electron gas in thermal equilibrium, showing that nonvanishing correlations c_m exist up to infinite order. Improvements over the density-matrix approach presented in this paper, hence, certainly have to correct for this deficiency.

In conclusion, we have presented a prescription of how to obtain free-carrier screening in quantum kinetic transport equations consistently within the density-matrix approach, and hereby have improved over the hitherto used approximation of starting already with a prescreened Hamiltonian. A critical comparison to results obtained within the framework of nonequilibrium Green's functions has revealed that the results of both approaches coincide, if one replaces in the non-Markovian collision terms the dressed Green's functions by the bare ones.

APPENDIX A: SCREENED COULOMB POTENTIAL

In this appendix we provide some useful results for the screened Coulomb potential; although most of them can be found in standard textbooks, we present this survey mainly in order to establish our notation. The following analysis can be either applied to quantities defined on Keldysh's time contour, or to quantities as obtained within the density-matrix approach. In the latter case we extend the definition of $1,2,\ldots$ in such a way that they contain additional time arguments $t_1,t_2,\ldots$, and we keep in mind that any retarded quantity with two time arguments tt' vanishes for $t'>t$.

Assume that we have a system which is perturbed by an external time-dependent potential $u(1)$ [cf. Eq. (2.1)]. An electron, however, will not ''feel'' the bare potential but rather the screened one

$$u_s(1) \equiv u(1) + \mathrm{Tr}_2 v(12)[\rho(2'2) - \rho(2'2;u=0)],$$
$$(A1)$$

where we have subtracted the density of the unperturbed system in the second term on the right-hand side to keep the expression finite when performing the thermodynamic limit.[49]

At this point it is convenient to introduce some additional quantities; this can be done using the method of functional derivatives,[54,55]

$$K(11') \equiv \frac{\delta u_s(1)}{\delta u(1')},$$

$$L(11') \equiv \frac{\delta \rho(11)}{\delta u(1')},$$
$$(A2)$$

$$P(11') \equiv \frac{\delta \rho(11)}{\delta u_s(1')},$$

$$v_s(11') \equiv \mathrm{Tr}_2 v(12) K(1'2).$$

Here K is the inverse dielectric function, L is the density-density correlation function, P is the polarization, and v_s the screened Coulomb potential.

With the help of the relation

$$\frac{\delta}{\delta u(2)} = \int d3 \, \frac{\delta u_s(3)}{\delta u(2)} \frac{\delta}{\delta u_s(3)},$$

we immediately obtain some useful relations between these quantities, which we write in a very shorthand notation:

$$K = \delta + vL,$$

$$L = P + PvL = P + LvP,$$

$$v_s = v + vLv,$$ (A3)

$$v_s = v + vPv_s = v + v_s Pv.$$

Here two subsequent quantities are connected by a convolution in space and time, together with an appropriate sum over the spin orientations.

APPENDIX B: POLARIZATION WITHIN THE DENSITY-MATRIX APPROACH

In this appendix we derive the expressions for the polarization P and the density-density correlation function L, as obtained within the density-matrix approach. We follow in this connection the work of Ref. 56, where the RPA was recovered by considering, within the linearized time-dependent Hartree approximation, fluctuations around the ground state.

Within this approximation we find

$$i\dot{\rho}(1'1) = [\varepsilon(1) - \varepsilon(1') + u_s(1) - u_s(1')]\rho(1'1),$$ (B1)

where we introduced the screened potential u_s from Eq. (A1). Using the definitions of Appendix A, for the polarization we obtain

$$P(\mathbf{12};tt') = -i\theta(t-t')\mathcal{U}_o(\mathbf{1};tt')$$
$$\times [\delta(12) - \delta(1'2)]\rho(\mathbf{1};t')|_{1' \to 1}.$$ (B2)

A more familiar expression can be obtained using the density fluctuation operator $\bar{n}(1) \equiv \psi^\dagger(1)\psi(1) - \rho(11)$,

$$P(12;tt') = -i\theta(t-t')\langle[\bar{n}(1;t), \bar{n}(2;t')]\rangle_o,$$ (B3)

with $\bar{n}(1;t) \equiv \exp(iH_o t)\bar{n}(1)\exp(-iH_o t)$. We finally recover, within the approximation of linearized screening, the relation

between polarization and density-density correlation by taking the functional derivative of Eq. (B1) with respect to the bare potential u:

$$L(\mathbf{12};tt') = P(\mathbf{12};tt')$$
$$+ \int_{t'}^{t} d\tau \, \mathrm{Tr}_{3\bar{3}} P(\mathbf{13};t\tau)v(3\bar{3})L(\overline{\mathbf{32}};\tau t').$$ (B4)

APPENDIX C: DERIVATION OF THE QUANTUM-KINETIC TRANSPORT EQUATION

In this appendix we present the necessary steps in order to go over from Eq. (3.22) to Eq. (3.23). We start with

$$\mathcal{U}(\mathbf{1};tt')\hat{\mathcal{L}}(\mathbf{1};t')S_o(\mathbf{12};t') = \mathrm{Tr}_{3\bar{3}}\mathcal{U}(\mathbf{1};tt')[\delta(13) - \delta(1'3)]$$
$$\times \rho(\mathbf{1};t')v(3\bar{3})S_o(\overline{\mathbf{32}};t').$$ (C1)

By use of Eq. (3.17), we find

$$\mathcal{U}(\mathbf{1};tt')[\delta(13) - \delta(1'3)]\rho(\mathbf{1};t')$$
$$= iP'(\mathbf{13};tt') - i\int_{t'}^{t} d\tau \, \mathrm{Tr}_{4\bar{4}} P'(\mathbf{14};t\tau)v(4\bar{4})\mathcal{U}(\overline{\mathbf{4}};\tau t')$$
$$\times [\delta(\bar{4}3) - \delta(\bar{4}'3)]\rho(\overline{\mathbf{4}};t').$$ (C2)

We have introduced the shorthand notation

$$P'(\mathbf{13};tt') \equiv -i\mathcal{U}_o(\mathbf{1};tt')[\delta(13) - \delta(1'3)]\rho(\mathbf{1};t'),$$

where the prime indicates that, in contrast to the polarization $P(\mathbf{13})$ (cf. Appendix B), we do not have to perform the final limit $1' \to 1$. Next, we observe that $\mathcal{U}(\overline{\mathbf{4}})$ acts on an expression where we have to perform the limit $\bar{4}' \to \bar{4}$ at the end of our algebraic manipulations, and we immediately arrive at

$$\mathcal{U}(\overline{\mathbf{4}};\tau t')[\delta(\bar{4}3) - \delta(\bar{4}'3)]\rho(\overline{\mathbf{4}};t') = iL(\overline{\mathbf{43}};\tau t'),$$ (C3)

with the density-density correlation function L defined in Appendix A. We note that, from a technical point of view, the iterative solution of the integral equation (C3) plays a crucial role in our analysis because here we have introduced the *screening of the Coulombic interactions*, described by the density-density correlation function L. This shows that the correlation transfers of Eq. (3.8) are indeed those describing free-carrier screening within the RPA. Putting all results together, we then obtain

$$\mathcal{U}(\mathbf{1};tt')\hat{\mathcal{L}}(\mathbf{1};t')S_o(\mathbf{12};t') = i\int_{t'}^{t} d\tau \, \mathrm{Tr}_3 P'(\mathbf{13};t\tau)v_s(32;\tau t')\rho(\mathbf{2};t').$$ (C4)

The effect of $\mathcal{U}(\mathbf{2};tt')$ on Eq. (C4) can be calculated in a completely analogous fashion:

$$\text{Tr}_2 v(12) \mathcal{U}(\mathbf{12};tt') \hat{\mathcal{L}}(\mathbf{1};t') S_o(\mathbf{12};t') = i \int_{t'}^{t} d\tau \, d\bar{\tau} \, \text{Tr}_{2,3\bar{3}} P'(\mathbf{13};t\tau) v_s(12;t\bar{\tau})[\mathcal{U}_o(\mathbf{2};\bar{\tau}t') S_o(\overline{\mathbf{3}}\mathbf{2};t')] v_s(3\overline{3};\tau t'). \quad \text{(C5)}$$

The second part of the calculation is very similar; it turns out to be convenient to add (for the moment) the mean-field contributions, and we obtain

$$\text{Tr}_2 v(12)[\mathcal{U}(\mathbf{12};tt') \hat{\mathcal{L}}(\mathbf{2};t') S_o(\mathbf{12};t') + i S_o(\mathbf{12};t) \delta(tt')]$$

$$= i \, \text{Tr}_2 v_s(12;tt') \mathcal{U}_o(\mathbf{1};tt') S_o(\mathbf{12};t') + i \int_{t'}^{t} d\tau \, d\bar{\tau} \, \text{Tr}_{2,3\bar{3}} P'(\mathbf{13};t\bar{\tau}) v_s(12;tt')[\mathcal{U}_o(\overline{\mathbf{3}};\tau t') S_o(\overline{\mathbf{3}}\mathbf{2};t')] v_s(3\overline{3};\tau\bar{\tau}).$$

$$\text{(C6)}$$

Here we have explicitly exploited the fact that all quantities are retarded.

We then arrive, with the dynamic form factor

$$S_o(\mathbf{12};tt') \equiv \theta(t-t') \mathcal{U}_o(\mathbf{1};tt') S_o(\mathbf{12};t') + \theta(t'-t) \mathcal{U}_o(\mathbf{2};t't) S_o(\mathbf{12};t),$$

after some minor changes, at

$$\dot{\rho}(\mathbf{1};t) = [h_o(1) + h_e(1),\rho] - i \int_{t_o}^{t} dt' \text{Tr}_2[v_s^r(12;tt') S_o'(\mathbf{12};tt') - \text{H.c.}]$$

$$- i \int dt' d\tau \, d\bar{\tau} \, \text{Tr}_{2,3\bar{3}}[P'(\mathbf{12};tt') v_s^r(13;t\tau) S_o(\overline{\mathbf{3}}\overline{\mathbf{3}};\overline{\tau}\tau) v_s^a(\overline{\mathbf{3}}2;\overline{\tau}t') - \text{H.c.}], \quad \text{(C7)}$$

where H.c. means that one has to take the complex conjugate of the preceding expression, and one has to exchange $1'$ and 1. Moreover we have introduced, in addition to the retarded component of the screened Coulomb potential, the advanced one

$$v_s^a(12;tt') = v_s^r(21;t't),$$

and the prime on S_o is a reminder that we do *not* have to set $1' \rightarrow 1$. It is well known that the dynamic form factor determines the correlations between density fluctuations at different times, whereas P describes the linear response of the system to an external density probe. Thus Eq. (C7) shows explicitly how polarizations are coupled via the screened Coulomb potential to the density fluctuations of the system.

However, in order to obtain Eq. (3.23) in its final form, we split off once again the instantaneous part of the screened Coulomb potential $v_s^r(12;tt')$ on the second term on the right-hand side, and for $t \geq t'$, in shorthand notation, we obtain

$$v_s^r - v = v_s^r - v_s^a = v_s^r(P^r - P^a) v_s^a,$$

with

$$i[P^r(12;tt') - P^a(12;tt')] = S_o(12;tt') - S_o(21;t't).$$

Here $P^a(12;tt') = P^r(21;t't)$. The further steps to complete the calculation are straightforward, and will be omitted.

APPENDIX D: KELDYSH MATRICES

Consider two quantities $a(\underline{11'})$ and $b(\underline{11'})$, where a can be split up into

$$a(\underline{11'}) = \theta(t_1 - t_{1'}) a^>(\underline{11'}) + \theta(t_{1'} - t_1) a^<(\underline{11'}), \quad \text{(D1)}$$

and a corresponding decomposition holds for b; here underlined numbers label times on Keldysh's time contour,[50] whereas nonunderlined numbers label times on the real-time axis. Moreover we introduce the retarded and advanced components

$$a^r(11') \equiv \theta(t_1 - t_{1'})[a^>(11') - a^<(11')],$$

$$a^a(11') \equiv -\theta(t_{1'} - t_1)[a^>(11') - a]^<(11').$$

We then find, for the convolution

$$c(\underline{11'}) = \int d\underline{2} \, a(\underline{12}) b(\underline{21'}),$$

the results

$$c^{r,a}(11') = \int d2 \, a^{r,a}(12) b^{r,a}(21') \quad \text{(D2)}$$

$$c^{\gtrless}(11') = \int d2[a^r(12) b^{\gtrless}(21') + a^{\gtrless}(12) b(21')],$$

whereas for $c(\underline{11'}) = a(\underline{11'}) b(\underline{1'1})$ we obtain

$$c^r(11') = a^r(11') b^{\gtrless}(1'1) + a^{\gtrless}(11') b^a(1'1)$$

$$c^{\gtrless}(11') = a^{\gtrless}(11') b^{\gtrless}(1'1). \quad \text{(D3)}$$

APPENDIX E: DETAILS OF THE GREEN'S FUNCTION APPROACH

We define the Green's function[57]

$$g(11') \equiv \theta(t_1 - t_{1'})g^>(11') + \theta(t_{1'} - t_1)g^<(11') \quad \text{(E1)}$$

with the abbreviations

$$g^>(11') \equiv -i\langle \psi(1)\psi^\dagger(1') \rangle,$$

$$g^<(11') \equiv -i\eta\langle \psi^\dagger(1')\psi(1) \rangle. \quad \text{(E2)}$$

Throughout this whole section we assume that the numbers 1,2, ... contain additional time arguments $t_1, t_2, \ldots$; moreover, we extend times to the Keldysh time contour,[50] which runs from t_o to $+\infty$ on the upper branch, and back to t_o on the lower branch (further, below we will introduce Keldysh matrices and hereby recover times on just one branch[58]). It is then possible to carry over most results from the ordinary zero-temperature Green's function approach without further modifications, with the main difference that time arguments are defined on the Keldysh contour, rather than on the real axis.

With our basic Hamiltonian of Eq. (2.1), we obtain

$$[i\partial_{t_1} - \varepsilon(1) - u(1)]g(11') = \delta(11') + i\eta\, \text{Tr}_2 v(12)g_2(12,1'2^+)|_{t_2 = t_1^+},$$

$$[-i\partial_{t_{1'}} - \varepsilon(1') - u(1')]g(11') = \delta(11') + i\eta\, \text{Tr}_2 v(12)g_2(12,1'2^+)|_{t_2 = t_{1'}^-}, \quad \text{(E3)}$$

with the two-particle Green function g_2, which, using the elegant functional derivative method of Schwinger,[54,55] can be written

$$g_2(12,1'2^+) = \left(\eta\frac{\delta}{\delta u(2)} + g(22^+) \right)g(11'). \quad \text{(E4)}$$

Here we have introduced the shorthand notation t^+ (t^-) for a time infinitesimally later (earlier) than t. We notice that, taking the appropriate limit of equal times in Eq. (E3), we recover the BBGKY hierarchy of density matrices of Sec. III.

It is well known that in Coulombic systems any expansion in terms of the bare external field u fails; however, we can expect that physical quantities should vary rather slowly in their dependence on the screened field u_s (cf. Appendix A). In addition, it is convenient to perform an expansion of the self-energy

$$\Sigma'(11') \equiv g_o^{-1}(11';u_s) - g^{-1}(11'),$$

rather than of g; here the inverse free Green function is given as

$$g_o^{-1}(11';u_s) = [i\partial_{t_1} - \varepsilon(1) - u_s(1)]\delta(11'),$$

and Σ' differs from the proper self-energy Σ in that it contains no Hartree self-energy. The RPA ansatz within the Green's-function approach is then to neglect $\delta\Sigma'/\delta u_s$. A physically more transparent interpretation of the RPA can be given in terms of the two-particle Green's function, where two particles interact with each other through the screened Coulomb potential within the Born approximation.

We saw in Sec. III that a particularly important quantity in Coulombic many-particle systems is the dynamic form factor S. Hence, we want to investigate its temporal evolution within the framework of Green's functions. However, instead of the dynamic form factor we take the (nondiagonal) density-density correlation function L as our basic quantity,

where, as can be inferred from Appendix A, both quantities differ only by a trivial factor of $-i$. We immediately arrive at

$$L'(11',2) = i[g_2(12,1'2^+) - g(11')g(22^+)]_{t_{1'} = t_1^+}$$

$$= -i\langle T[\psi^\dagger(1')\psi(1) - \rho(1'1)]_{t_{1'} = t_1^+}$$

$$\times [\psi^\dagger(2)\psi(2) - \rho(22)]\rangle, \quad \text{(E5)}$$

with the contour-ordering operator T that orders the subsequent operators according to the position of their time arguments on the contour. The prime, once again, is a reminder that 1 does not have to equal 1' (although we set $t_{1'} = t_1^+$). In lowest order we then obtain the expression

$$L_o'(11',2) \equiv i\eta g(12)g(21'), \quad \text{(E6)}$$

whereas the difference

$$i\bar{L}'(11',2) \equiv i[L'(11',2) - L_o'(11',2)]$$

gives the two-particle correlation function $c_2(1'2,12)$ if we perform the limit of equal times in such a way that t_1 (t_2) lies on the upper (lower) branch of Keldysh's time contour. Hence we find

$$\dot{\rho}(1'1) = -i[h_o^{HF}(1) + h_e(1), \rho]$$

$$-i\text{Tr}_2[v(12)i\bar{L}'^>(11',2) - \text{H.c.}]_{t_1 = t_2}, \quad \text{(E7)}$$

where $L'^>$ indicates the proper choice of the two time arguments.

Equation of motion for the two-particle correlation function

Next we want to recover the equation of motion for the two-particle correlation function (3.8). By use of Eq. (E4), we find

$$L'(11',2)=i\eta\int d\bar{2}\frac{\delta g(11')}{\delta u_s(\bar{2})}\frac{\delta u_s(\bar{2})}{\delta u(2)},$$

where the two expressions on the right-hand side can be rewritten as[59]

$$i\eta\frac{\delta g(11')}{\delta u_s(\bar{2})}=L_o(11',\bar{2})+\mathcal{O}\left(\frac{\delta\Sigma'}{u_s}\right),$$

$$\frac{\delta u_s(\bar{2})}{\delta u(2)}=\delta(\bar{2}2)+\int d3\,v(\bar{2}3)L(33,2).$$

Within our RPA ansatz we then obtain the equation of motion for the nondiagonal density-density correlation function

$$L'(11'2)=L'_o(11',2)+\int d3\,d\bar{3}L'_o(11',3)v(3\bar{3})L(44,2)$$

$$=L'_o(11',2)+\int d3\,d\bar{3}L'(11',3)v(3\bar{3})L_o(44,2).$$

$$(E8)$$

Moreover, we find

$$\int d\bar{1}[g_o^{-1}(1\bar{1})L'_o(\bar{1}1',2)-L'_o(1\bar{1},2)g_o^{-1}(\bar{1}1')]$$

$$\times[\delta(12)-\delta(1'2)]\rho(1'1)+\mathcal{O}(\Sigma').$$

Neglecting in lowest-order expressions that contain the self-energy Σ', we find, from Eq. (E8), the equations of motion

$$\{i\partial_{t_1}-[\varepsilon(1)-\varepsilon(1')]\}\bar{L}(11',2)$$

$$\approx\mathrm{Tr}_{3\bar{3}}[\delta(13)-\delta(1'3)]\rho(1'1)v(3\bar{3})$$

$$\times[\bar{L}(\bar{3}3,2)+L_o(\bar{3}3,2)],$$

$$\{i\partial_{t_2}-[\varepsilon(2)-\varepsilon(2')]\}\bar{L}(11',22')_{2'\to2^+}$$

$$\approx\mathrm{Tr}_{3\bar{3}}[\bar{L}(11',3)+L_o(11',3)]v(3\bar{3})$$

$$\times[\delta(2\bar{3})-\delta(2'\bar{3})]\rho(2'2).\qquad(E9)$$

In the second equation, $\bar{L}(11',22')_{2'\to2^+}$ obviously means that the drift operator $[\varepsilon(2)-\varepsilon(2')]$ has to act upon $\bar{L}$ *before* performing the limit $2'\to2^+$. The sum of both expressions in Eqs. (E9) gives, in the proper limit of equal times, the RPA ansatz of Eq. (3.8).

Quantum kinetic transport equation

Finally, we sketch how to derive a generalized Boltzmann equation on the basis of Eq. (E8). This can be done by mapping the contour-ordered quantities (e.g., g, Σ', L'), specified by the Keldysh contour, onto the Keldysh space[50,28] (we use $\gtrless$ instead of $_{+-}^{-+}$); some useful relations for these mapped quantities are provided in Appendix D. Note that, from now on, all time arguments are defined on the real-time axis running from t_o to ∞. We then find, in a shorthand notation,

$$L'^a=L'^a_o+L'^a_ovL^a=L'^a_o+L'^avL^a_o,$$

$$\bar{L}'^{\gtrless}=\bar{L}'^rvL^{\gtrless}_o+\bar{L}'^{\gtrless}vL^a_o+L'^r_ovL^{\gtrless}_o,\qquad(E10)$$

which, together with the obvious relation

$$(1-vL^a_o)L^{a-1}_oL^a=1,\qquad(E11)$$

gives

$$\bar{L}'^{\gtrless}=L'^{\gtrless}_o+L'^r_ov^r_sL^{\gtrless}_o(1+vL^a).\qquad(E12)$$

Inserting this expression into Eq. (E7), we then obtain, after some straightforward steps, the collision integral

$$\mathcal{C}(1'1;tt_o)=\int d2\{L'^{>}_o(11',2)[v^r_s(12)-v(12)]-\mathrm{H.c.}\}+\int d2\,d3\,d\bar{3}[L'^r_o(11'2)v^r_s(13)L_o(3\bar{3})v^a_s(\bar{3}2)-\mathrm{H.c.}];\qquad(E13)$$

note the similarity to Eq. (C7). We finally follow the guidelines of Appendix C, and arrive at

$$\mathcal{C}(11';tt_o)=-i\int d2\,d3\,d\bar{3}[L'^{>}_o(11',2)v^r_s(13)$$

$$\times L'^{>}_o(3\bar{3})v^a_s(\bar{3}2)-L'^{<}_o(11',2)v^r_s(13)$$

$$\times L'^{<}_o(3\bar{3})v^a_s(\bar{3}2)-\mathrm{H.c.}],\qquad(E14)$$

with

$$L'^r_o(11',2)=i\eta[g^r(12)g^{\gtrless}(21')+g^{\gtrless}(12)g^a(21')]$$

$$\times L'^{\gtrless}_o(11',2)=i\eta g^{\gtrless}(12)g^{\lessgtr}(21').$$

Equation (E14) should be compared to the quantum kinetic transport equation (3.23) of the density-matrix approach. One observes that both expressions are very similar, with the main difference that dynamical renormalizations, described by the dressed propagators g, are completely missing within the framework of density matrices.

We finally emphasize that Eq. (E14) together with Eq. (3.23) does not form a closed set of equations, as L_o still contains the Green functions g for different time arguments, and g has to be obtained additionally from Dyson's equation.

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[46] At this point we should add a word of precaution. If we were to derive the optical Bloch equations the one-particle states would be the quasistationary solutions to $H_o + H_e$, where H_e describes the coupling to the external laser-field within the rotating-wave approximation, and we certainly had to take the corresponding time dependence of $\hat{\rho}$ into account. However, it is our feeling that such a modification would not affect the conclusions of our rather general discussion of the generalized Boltzmann equation, but would introduce mainly cumbersome notation. Hence we prefer to stick to the simplest case, and assume that a generalization of our results to different systems is straightforward.

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