Density Matrix Methods for Semiconductor Coulomb Dynamics

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ABSTRACT: Current experiments on semiconductor devices using femtosecond lasers provide new theoretical challenges for the description of charge carrier dynamics. Among the new features of such experiments are states driven very far from equilibrium and probes on time scales short compared to scattering and other characteristic material relaxation times. Standard many-body methods must be modified and extended to accommodate these features. We propose that the quantum hierarchy for reduced density operators is an ideal formulation of such initial value problems and describe how the dominant effects of exchange and charge correlations can be accounted for in a simple and physically transparent closure of the hierarchy of equations. The transformations, approximations, and interpretation can be accomplished independent of any particular matrix representation. Decomposition into kinetic equations for band occupation densities and polarization densities follows in a straightforward way after the many-body problem has been brought under control. © 1997 John Wiley & Sons, Inc. Int J Quant Chem **65**: 929–940, 1997

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Introduction

For the past decade, the fabrication of ultrasmall devices and associated developments in laser technology for exploration of their properties have raised important theoretical questions, both conceptual and practical. In particular, the short times sampled in femtosecond laser studies and the wealth of potential information from different initial preparations call for a description of Coulomb kinetics (e.g., electrons and holes) far from equilibrium, extending from initial times to times long compared to the characteristic collision times and dephasing times [1, 2]. Such theoretical considerations already have been explored in other contexts, such as transport in simple classical liquids and plasmas [3] and for nuclear matter [4], but their experimental relevance in these cases has been less compelling. The objective here is to formulate the problem of Coulomb kinetics in terms of the fundamental exact first two hierarchy equations for the one- and two-particle reduced density operators. Practical applications result from an approximate closure of the two-particle equation subject to important constraints on acceptable approximations associated with conservation laws, representability, stationary solutions, and quantum statistics. These structural properties are independent of considerations of classical or quantum effects and do not rely on the matrix representation appropriate to the specific problem. The theoretical analysis of a given approximation occurs at the compact abstract level for greatest simplicity and generality and in a formulation that allows exploitation of previous work on classical systems.

This approach is illustrated for a simple two-band model of a semiconductor, to show how corrections to the semiconductor Bloch equations can be constructed to include the effects of scattering and dynamic screening. In this discussion, only electron–electron and electron–laser interactions are considered; the lattice is presumed to be rigid. A simple closure approximation including exact three-particle exchange correlations and all residual pair correlations is indicated and its content discussed. Solution of the two-particle equation gives the two-particle reduced density operator as a functional of the one-particle density operator. Use of this result in the first hierarchy equation for the one-particle density operator gives a closed kinetic equation. The resulting non-Markovian kinetic equation describes the evolution of an arbitrary initial preparation from asymptotically short times to the long-time Boltzmann limit. The short time evolution includes the buildup of dynamical screening (polarization effects); at long times, the Boltzmann scattering rates are determined from the full T-matrix rather than from the weak coupling Born approximation.

In this brief presentation, only the theoretical structure and method are described as an overview of the general approach to carrier dynamics. More detailed calculations based on the approximation suggested here are in progress.

Reduced Density Operators and Hierarchy

We consider N electrons interacting with a rigid ionic lattice, with overall charge neutrality. The electrons interact with the lattice and with each other via bare Coulomb potentials. In addition, they interact with a classical (i.e., many photon) transverse electric field, $\mathbf{E}(t)$ via a dipole interaction. The Hamiltonian for the system is then

$$H(t) = H_0 + U + U_{ext}(t), \qquad H_0 = \sum_{i=1}^{N} h_0(i) \quad (1)$$

$$U = \frac{1}{2}\sum_{i \neq j}^{N} V(i, j), \qquad U_{ext} = -\mu \cdot \mathbf{E}(t), \quad (2)$$

where $h_0(i)$ is the single-particle Bloch Hamiltonian for interaction of electron i with the lattice, $V(i, j)$ is the Coulomb potential for interaction of electrons i, j, and $\mu = \sum_{i=1}^{N} \mu(i)$ is the total dipole moment due to all electrons. The external field $\mathbf{E}(t)$ characterizes the laser field, which may have a very short time scale in some pump experiments, but may also represent a longer time driving field with a duration comparable to various dephasing mechanisms. The details of this field are not important for the formal considerations here, but can play a role in the numerical method used to solve the equations. The eigenvalue problem for the Bloch Hamiltonian is described by

$$h_0 \psi_\alpha(\mathbf{k}) = \epsilon_\alpha(\mathbf{k}) \psi_\alpha(\mathbf{k}), \quad (3)$$

where α denotes the band index, and $\mathbf{k}$, the momentum quantum number (here and in the following we set $\hbar = 1$).

The initial state of the system is defined by an N-particle density operator, $\rho(1,\dots,N)$. This could be the Gibbs distribution if the electron–lattice system is initially in equilibrium, but it is not necessary to specify its form at this point. Implicit in the definition of the density matrix is an N-particle symmetrization operator so that a representation of its matrix elements in terms of unsymmetrized products of single particle states is possible [5]. This is an important feature that will be exploited in the next section to extract the exchange correlation of the reduced density operators associated with $\rho(1,\dots,N)$. The time evolution of the density operator is governed by the Liouville–von Neumann equation

$$\partial_t \rho(t) + i[H(t), \rho(t)] = 0. \tag{4}$$

The reduced density operators for m particles are defined by

$$f^{(m)}(1,\dots,m;t) = N^m Tr_{m+1\dots N}\,\rho(t). \tag{5}$$

The notation on the right side indicates a trace over the degrees of freedom associated with particles $m+1$ through N. More precisely, in matrix representation, it denotes summation over the diagonal quantum numbers for these particles. The reduced density operators $f^{(m)}$ inherit an M-particle symmetrization operator from the corresponding N-particle symmetrization operator in ρ. The BBGKY (Born, Bogoliubov, Green, Kirkwood, Yvon) hierarchy equations [5, 6] for the time dependence of the reduced distribution functions now follow directly from a partial trace of the Liouville–von Neumann equation,

$$\begin{aligned}\partial_t f^{(m)}(1,\dots,m;t) &+ \sum_{i=1}^{m} i\big[(h_0(i) - \mu(i)\cdot\mathbf{E}(t)),\\ &f^{(m)}(1,\dots,m;t)\big]\\ &+ \sum_{i\neq j}^{m} i[V(i,j), f^{(m)}(1,\dots,m;t)]\\ &= -\sum_{i=1}^{m} Tr_{m+1} i[V(i,m+1),\\ &f^{(m+1)}(1,\dots,m+1;t)].\end{aligned} \tag{6}$$

The left side of this equation is just the Liouville–von Neumann equation for m isolated particles. The right side expresses a coupling to the other degrees of freedom through the Coulomb interactions. In the following, it will be sufficient to consider only the cases with $m = 1$ and 2,

$$\partial_t f^{(1)}(1;t) + i[H(1;t), f^{(1)}(1;t)] + Tr_2 i[V(1,2), f^{(2)}(1,2;t)] = 0 \tag{7}$$

$$\partial_t f^{(2)}(1,2;t) + i[H(1,2;t), f^{(2)}(1,2;t)] + \sum_{i=1}^{2} Tr_3 i[V(i,3), f^{(3)}(1,2,3;t)] = 0, \tag{8}$$

where the single-particle and two-particle Hamiltonians are given by

$$H(1;t) = h_0(1) - \mu(1)\cdot\mathbf{E}(t) \qquad H(1,2;t) = \sum_{i=1}^{2}(h_0(i) - \mu(i)\cdot\mathbf{E}(t)) + V(1,2). \tag{9}$$

These equations are exact but formal since they are not closed in terms of $f^{(1)}$ and $f^{(2)}$ alone. It is necessary to construct a suitable approximation that expresses $f^{(3)}$ as a functional of $f^{(1)}$ and $f^{(2)}$. Then Eqs. (7) and (8) provide the means to calculate $f^{(1)}$ and $f^{(2)}$. In particular, if the equation for $f^{(2)}$ is solved as a functional of $f^{(1)}$, i.e.,

$$f^{(2)}(1,2;t) = F^{(2)}(1,2;t \mid f^{(1)}), \tag{10}$$

then use of this solution in the first hierarchy Eq. (7) provides a closed *kinetic equation* for $f^{(1)}$:

$$\partial_t f^{(1)}(1;t) + i[H(1;t), f^{(1)}(1;t)] + Tr_2 i[V(1,2), F^{(2)}(1,2;t \mid f^{(1)})] = 0. \tag{11}$$

This is the approach proposed here for obtaining the appropriate kinetic equation for charge carriers. The procedure is representation-independent, and as a first-order equation in time, it is appropriately posed as an initial value problem. This is in contrast to the alternative nonequilibrium Keldysh Green's function method which requires a detailed reconstruction of the specified initial conditions from an artificial past history [7].

Exact Exchange Effects and Correlations

There are two important sources of correlations among the charge carriers. One is due to the long-range Coulomb interaction, while the other is due to the exchange symmetry among particles of the same species. It is useful to extract explicitly the dominant effects due to exchange symmetry by identifying the exchange operators implicit in the definitions of the reduced density operators. This will allow a more controlled identification of the residual correlations due to Coulomb interactions. The two- and three-particle reduced density operators are expressed as

$$\begin{aligned} f^{(2)}(1,2;t) &\equiv \bar{f}^{(2)}(1,2;t)\mathscr{S}(1,2) \\ &= \mathscr{S}(1,2)\bar{f}^{(2)}(1,2;t) \qquad (12) \\ f^{(3)}(1,2,3;t) &\equiv \bar{f}^{(3)}(1,2,3;t)\mathscr{S}(1,2,3) \\ &= \mathscr{S}(1,2,3)\bar{f}^{(3)}(1,2,3;t), \qquad (13) \end{aligned}$$

where $\mathscr{S}(1,2)$ and $\mathscr{S}(1,2,3)$ are the two- and three-particle antisymmetrization operators that convert product states for two and three electrons into antisymmetric states, respectively. Such symmetrization factors occur necessarily from the definition of the underlying N-particle density matrix. The last equality follows from the permutation symmetry of the reduced density operators and of the symmetrization operators. Next, the correlation operators associated with $\bar{f}^{(2)}(1,2;t)$ and $\bar{f}^{(3)}(1,2,3;t)$ are introduced:

$$\bar{f}^{(2)}(1,2;t) \equiv f^{(1)}(1;t)f^{(1)}(2;t) + \bar{g}(1,2;t) \qquad (14)$$

$$\begin{aligned} &\bar{f}^{(3)}(1,2,3;t) \\ &\quad \equiv f^{(1)}(1;t)f^{(1)}(2;t)f^{(1)}(3;t) \\ &\qquad + f^{(1)}(1;t)\bar{g}(2,3;t) + f^{(1)}(2;t)\bar{g}(1,3;t) \\ &\qquad + f^{(1)}(3;t)\bar{g}(1,2;t) + \bar{g}(1,2,3;t). \qquad (15) \end{aligned}$$

Since the symmetrization operators have been extracted explicitly in (12) and (13), the correlation functions $\bar{g}(1,2;t)$ and $\bar{g}(1,2,3;t)$ are primarily measures of correlations due to the Coulomb interactions. Conversely, even when there are no correlations in $\bar{f}^{(2)}(1,2;t)$ and $\bar{f}^{(3)}(1,2,3;t)$, the distribution functions $f^{(2)}(1,2;t)$ and $f^{(3)}(1,2,3;t)$ have two- and three-particle correlations induced by the antisymmetrization operators. Therefore, it is useful to rewrite the first two hierarchy equations in terms of $\bar{g}(1,2;t)$ and $\bar{g}(1,2,3;t)$. The first equation becomes

$$\begin{aligned} &\partial_t f^{(1)}(1;t) + i[H(1;t), f^{(1)}(1;t)] \\ &\quad + Tr_2 i\left[V_s(1,2), f^{(1)}(1;t)f^{(1)}(2;t)\right] \\ &\quad + Tr_2 i[V_s(1,2), \bar{g}(1,2;t)] = 0, \qquad (16) \end{aligned}$$

where $V_s(1,2) \equiv V(1,2)\mathscr{S}(1,2)$ is the pair potential with exchange effects. The left side of this equation is recognized as generating the time-dependent Hartree−Fock dynamics so the equation becomes

$$\begin{aligned} &\partial_t f^{(1)}(1;t) + i\left[H_{hf}(1;t), f^{(1)}(1;t)\right] \\ &\qquad = -Tr_2 i[V_s(1,2), \bar{g}(1,2;t)], \qquad (17) \end{aligned}$$

where the Hartree−Fock Hamiltonian is

$$\begin{aligned} H_{hf}(1;t) &= H(1;t) + V_{hf}(1;t), \\ V_{hf}(1;t) &\equiv Tr_2 f^{(1)}(2;t)V_s(1,2). \qquad (18) \end{aligned}$$

This is the expected result: The mean-field Hartree−Fock dynamics is modified by a coupling to other electrons due to the presence of Coulomb correlations.

The equation for the correlations, $\bar{g}(1,2;t)$, follows from the second hierarchy equation. The effects of the symmetrization operators are evaluated in detail in the Appendix leading to the exact equation for $\bar{g}(1,2;t)$:

$$\begin{aligned} &\partial_t \bar{g}(1,2;t) + i\left[\hat{H}(1,2;t)\bar{g}(1,2;t)\right. \\ &\quad \left. -\bar{g}(1,2;t)\hat{H}^{\dagger}(1,2;t)\right] \\ &\quad + Tr_3 i\left\{\left[V_s(1,3), f^{(1)}(1;t)\right]\right. \\ &\quad \times \bar{g}(2,3;t)\mathscr{S}(2,3) \\ &\quad + \left[V_s(2,3), f^{(1)}(2;t)\right] \\ &\quad \left. \times \bar{g}(1,3;t)\mathscr{S}(1,3)\right\} \\ &\quad = -i\left\{\hat{V}(1,2;t)f^{(1)}(1;t)f^{(1)}(2;t)\right. \\ &\quad \left. -f^{(1)}(1;t)f^{(1)}(2;t)\hat{V}^{\dagger}(1,2;t)\right\} \\ &\quad - \sum_{j=1}^{2} Tr_3 i[V(j,3), \bar{g}(1,2,3;t) \\ &\quad \times (1 - P_{13} - P_{23})], \qquad (19) \end{aligned}$$

with the definitions

$$\hat{H}(1,2;t) = H_{hf}(1;t) + H_{hf}(2;t) + \hat{V}(1,2;t) \qquad (20)$$

$$\hat{V}(1,2;t) \equiv \{1 - f^{(1)}(1;t) - f^{(1)}(2;t)\}V(1,2). \qquad (21)$$

The first two terms on the left side describe pair dynamics generated by the Hamiltonian $\hat{H}(1,2;t)$. This Hamiltonian differs from $H(1,2)$ in two important ways: First, the single-particle energies are renormalized to the mean-field Hartree−Fock energies. Second, the pair potential is modified by the prefactor $\{1 - f^{(1)}(1;t) - f^{(1)}(2;t)\}$ describing "blocking" effects of the statistics. To see this, note that $\{1 - f^{(1)}(1;\, t) - f^{(1)}(2;\, t)\} = \{h^{(1)}(1;\, t)h^{(1)}(2;\, t) - f^{(1)}(1;\, t)f^{(1)}(2;\, t)\}$, where $h^{(1)}(1;t) = 1 - f^{(1)}(1;t)$ is the "hole" occupancy. Thus, the matrix elements of $\hat{V}(1,2;t)$ are restricted according to the occupation of carrier density in the nonequilibrium state. Both the blocking and mean-field effects in $\hat{H}(1,2;t)$ account for significant many-particle correlations in this effective pair dynamics. The third and fourth terms on the left side describe polarization or screening effects that are essential for a proper treatment of the long-ranged Coulomb interactions. In the classical limit, these are the linearized Vlasov operators leading to the Debye–Hückel dynamic screening and pair correlations. Here, these operators generate the random phase or chain approximation including exchange effects. The first term on the right side of (20) is a source of correlations due to the "commutator" of $\hat{V}(1,2;t)$ with the uncorrelated pair operator $f^{(1)}(1;t)f^{(1)}(2;t)$; equivalently, the time derivative of the uncorrelated state is correlated due to the Coulomb interactions. Here, this source of correlations is due to the pair interaction including blocking effects. Finally, all residual many-body effects are contained in the last term on the right side describing three-particle correlations not associated solely with three-particle exchange effects.

Equations (17) and (20) are still exact and fully equivalent to Eqs. (7) and (8). However, the analysis of the exchange effects and the transformation to the correlation functions provides a form in which the dominant mean field, polarization, and blocking effects are made explicit. This is a more convenient form for introduction of appropriate approximations or application to specific problems.

Bloch Representation

The above analysis has used only the abstract operator form of the reduced density operators and associated hierarchy equations. Specific applications require a particular matrix representation. For example, a fully ionized plasma might best be described in terms of single-particle momentum states. To show the relationship of the density matrix approach to the standard equations of semiconductor physics, we consider a representation using Bloch states $\psi_{\alpha\mathbf{k}}(\mathbf{r}) = \langle \mathbf{r} \mid \alpha\mathbf{k}\rangle$, $h(1) \mid \alpha\mathbf{k}\rangle = \epsilon_\alpha(\mathbf{k}) \mid \alpha\mathbf{k}\rangle$. Only the first hierarchy equation will be considered; the analysis for the second equation is similar:

$$\partial_t f^{(1)}(1;t) + i\left[H_{hf}(1;t), f^{(1)}(1;t)\right] + C(1;t) = 0, \tag{22}$$

where $C(1;t)$ is the "collision" operator due to pair correlations

$$C(1;t) = Tr_2 i[V_s(1,2), \bar{g}(1,2;t)]. \tag{23}$$

The band occupation densities, $n_\alpha(\mathbf{k};t)$, and the polarization densities, $p_{\alpha\alpha'}(\mathbf{k};t)$, are defined by

$$\begin{aligned} n_\alpha(\mathbf{k};t) &\equiv \langle \alpha\mathbf{k} \mid f^{(1)}(t) \mid \alpha\mathbf{k}\rangle \\ p_{\alpha\alpha'}(\mathbf{k};t) &\equiv \langle \alpha\mathbf{k} \mid f^{(1)}(t) \mid \alpha'\mathbf{k}\rangle, \end{aligned} \tag{24}$$

where the band indices $\alpha \neq \alpha'$ in the definition of the polarization density $p_{\alpha\alpha'}(\mathbf{k};t)$. To simplify the discussion, we consider the case of only two bands (conduction and valence). Also, we consider only homogeneous states, so that the one-particle density matrix is diagonal in the wave vector, $\mathbf{k}$. The equations are then found to be

$$\partial_t n_\alpha(\mathbf{k};t) - 2\mathrm{Im}\left\{\langle \alpha\mathbf{k} \mid H_{hf}(1;t) \mid \alpha'\mathbf{k}\rangle p_{\alpha'\alpha}(\mathbf{k};t)\right\} + C_{\alpha\alpha}(\mathbf{k};t) = 0 \tag{25}$$

$$\begin{aligned} \partial_t p_{\alpha\alpha'}(\mathbf{k};t) &+ i\left[\langle \alpha\mathbf{k} \mid H_{hf}(1;t) \mid \alpha\mathbf{k}\rangle \right. \\ &\left. - \langle \alpha'\mathbf{k} \mid H_{hf}(1;t) | \alpha'\mathbf{k}\rangle\right] p_{\alpha\alpha'}(\mathbf{k};t) \\ &+ i\langle \alpha\mathbf{k} \mid H_{hf}(1;t) \mid \alpha'\mathbf{k}\rangle \\ &\times [n_{\alpha'}(\mathbf{k};t) - n_\alpha(\mathbf{k};t)] \\ &+ C_{\alpha\alpha'}(\mathbf{k};t) = 0, \end{aligned} \tag{26}$$

where it is understood that $\alpha \neq \alpha'$. The matrix elements in these equations are easily evaluated:

$$\begin{aligned} &\langle \alpha\mathbf{k} \mid H_{hf}(1;t) \mid \nu\mathbf{k}\rangle \\ &= \epsilon_\alpha(\mathbf{k})\delta_{\alpha,\nu} + \langle \alpha\mathbf{k} \mid V_{hf} \mid \nu\mathbf{k}\rangle - \mathbf{E}(t)\cdot\mu_{\alpha\nu}, \end{aligned} \tag{27}$$

where $\mu_{\alpha\nu}(\mathbf{k}) \equiv \langle \alpha\mathbf{k} \mid \mu \mid \nu\mathbf{k}\rangle$. Equations (25) and (26) then become

$$\begin{aligned} \partial_t n_\alpha(\mathbf{k};t) &- 2\mathrm{Im}\left\{\left[\langle \alpha\mathbf{k} \mid V_{hf} \mid \alpha'\mathbf{k}\rangle - \mathbf{E}(t)\cdot\mu_{\alpha\alpha'}\right]\right. \\ &\left. \times p_{\alpha'\alpha}(\mathbf{k};t)\right\} + C_{\alpha\alpha}(\mathbf{k};t) = 0 \end{aligned} \tag{28}$$

$$\begin{aligned} \partial_t p_{\alpha\alpha'}(\mathbf{k};t) &+ i\left[\langle \alpha\mathbf{k} \mid H_{hf}(1;t) \mid \alpha\mathbf{k}\rangle \right. \\ &\left. - \langle \alpha'\mathbf{k} \mid H_{hf}(1;t) \mid \alpha'\mathbf{k}\rangle\right] p_{\alpha\alpha'}(\mathbf{k};t) \\ &+ i\left[\langle \alpha\mathbf{k} \mid V_{hf} \mid \alpha'\mathbf{k}\rangle - \mathbf{E}(t)\cdot\mu_{\alpha\alpha'}\right] \\ &\times (n_{\alpha'}(\mathbf{k};t) - n_\alpha(\mathbf{k};t)) + C_{\alpha\alpha'}(\mathbf{k};t) = 0. \end{aligned} \tag{29}$$

The matrix elements of the Hartree–Fock potential are easily evaluated and the resulting equations for $n_\alpha(\mathbf{k};t)$ and $p_{\alpha\alpha'}(\mathbf{k};t)$ are found to be

$$\begin{aligned}
&\partial_t n_c(\mathbf{k};t) + 2\mathrm{Im}(\mathbf{E}(t)\cdot\mu_{cv}\,p_{vc}(\mathbf{k};t))\\
&\quad + 2\mathrm{Im}\sum_{\mathbf{q}}\tilde{V}(q)[\,n_c(\mathbf{k}+\mathbf{q};t)\,I_{cc}(\mathbf{k},-\mathbf{q})\\
&\quad \times I_{vc}^{*}(\mathbf{k},-\mathbf{q}) + n_v(\mathbf{k}+\mathbf{q};t)\\
&\quad \times I_{cv}(\mathbf{k},-\mathbf{q})\,I_{vv}^{*}(\mathbf{k},-\mathbf{q})\\
&\quad + p_{cv}(\mathbf{k}+\mathbf{q};t)\,I_{cc}(\mathbf{k},-\mathbf{q})\,I_{vv}^{*}(\mathbf{k},-\mathbf{q})\\
&\quad + p_{vc}(\mathbf{k}+\mathbf{q};t)\,I_{cv}(\mathbf{k},-\mathbf{q})\,I_{vc}^{*}(\mathbf{k},-\mathbf{q})]\,p_{vc}(\mathbf{k};t)\\
&\quad + C_{cc}(\mathbf{k};t) = 0 \qquad (30)
\end{aligned}$$

$$\begin{aligned}
&\partial_t p_{cv}(\mathbf{k};t) + i(\epsilon_c(\mathbf{k}) - \epsilon_v(\mathbf{k}) - \mathbf{E}(t)\\
&\quad \cdot[\,\mu_{cc} - \mu_{vv}])\,p_{cv}(\mathbf{k};t)\\
&\quad - i\sum_{\mathbf{q}}\tilde{V}(q)\Big[\,n_c(\mathbf{k}+\mathbf{q};t)\\
&\quad \times\Big(|I_{cc}(\mathbf{k},-\mathbf{q})|^2 - |I_{vc}(\mathbf{k},-\mathbf{q})|^2\Big)\\
&\quad + n_v(\mathbf{k}+\mathbf{q};t)\Big(|I_{cv}(\mathbf{k},-\mathbf{q})|^2 - |I_{vv}(\mathbf{k},-\mathbf{q})|^2\Big)\\
&\quad + 2\,p_{cv}(\mathbf{k}+\mathbf{q};t)\mathrm{Re}(\,I_{cc}(\mathbf{k},-\mathbf{q})\,I_{cv}^{*}(\mathbf{k},-\mathbf{q})\\
&\quad - I_{vc}(\mathbf{k},-\mathbf{q})\,I_{vv}^{*}(\mathbf{k},-\mathbf{q}))]\,p_{cv}(\mathbf{k};t)\\
&\quad - i\Bigg\{\sum_{\mathbf{q}}\tilde{V}(q)[\,n_c(\mathbf{k}+\mathbf{q};t)\\
&\quad \times I_{cc}(\mathbf{k},-\mathbf{q})\,I_{vc}^{*}(\mathbf{k},-\mathbf{q}) + n_v(\mathbf{k}+\mathbf{q};t)\\
&\quad \times I_{cv}(\mathbf{k},-\mathbf{q})\,I_{vv}^{*}(\mathbf{k},-\mathbf{q})\\
&\quad + p_{cv}(\mathbf{k}+\mathbf{q};t)\\
&\quad \times I_{cc}(\mathbf{k},-\mathbf{q})\,I_{vv}^{*}(\mathbf{k},-\mathbf{q}) + p_{vc}(\mathbf{k}+\mathbf{q};t)\\
&\quad \times I_{cv}(\mathbf{k},-\mathbf{q})\,I_{vc}^{*}(\mathbf{k},-\mathbf{q})]\\
&\quad + \mathbf{E}(t)\cdot\mu_{cv}\Bigg\}\\
&\quad \times(n_v(\mathbf{k};t) - n_c(\mathbf{k};t)) + C_{cv}(\mathbf{k};t) = 0. \qquad (31)
\end{aligned}$$

Here, $I_{\alpha\alpha'}(\mathbf{k},\mathbf{q})$ arises from the Coulomb matrix elements

$$\begin{aligned}
&\langle\alpha_1\mathbf{k}_1;\alpha_2\mathbf{k}_2|V|\alpha_2'\mathbf{k}_2';\alpha_1'\mathbf{k}_1'\rangle\\
&\quad = \delta_{\mathbf{k}_1'+\mathbf{k}_2',\mathbf{k}_1+\mathbf{k}_2}\sum_{\mathbf{q}}\tilde{V}(q)\,\delta_{\mathbf{k}_1',\mathbf{k}_1+\mathbf{q}}\\
&\qquad \times I_{\alpha_1\alpha_1'}(\mathbf{k}_1,-\mathbf{q})\,I_{\alpha_2\alpha_2'}(\mathbf{k}_2,\mathbf{q}) \qquad (32)
\end{aligned}$$

$$\begin{aligned}
I_{\alpha\alpha'}(\mathbf{k},\mathbf{q}) &\equiv \int d\mathbf{r}\,e^{i\mathbf{q}\cdot\mathbf{r}}\psi_{\alpha\mathbf{k}}^{*}(\mathbf{r})\,\psi_{\alpha'\mathbf{k}-\mathbf{q}}(\mathbf{r})\\
&= I_{\alpha'\alpha}^{*}(\mathbf{k}-\mathbf{q},-\mathbf{q}) \qquad (33)
\end{aligned}$$

and $\tilde{V}(q)$ is the Fourier-transformed pair potential. The valence and conduction occupation numbers are related by $n_c(\mathbf{k};t) + n_q(\mathbf{k};t) = $ constant, and the polarization densities are related by $p_{cv} = p_{vc}\dagger$. These are the most general hierarchy equations.

The matrix elements $C_{\alpha\alpha'}(\mathbf{k};t)$ describe both inter- and intraband collisions and can be expressed in terms of the matrix elements of the correlation function $\bar{g}(1,2;t)$ using (23)

$$\begin{aligned}
&C_{\alpha\alpha'}(\mathbf{k};t)\\
&\quad = \langle\alpha\mathbf{k}|\{Tr_2 i[\,V_s(1,2),\bar{g}(1,2;t)]\}|\alpha'\mathbf{k}\rangle\\
&\quad = i\sum_{\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3}\ \sum_{\nu_1,\nu_2,\nu_3}\{\langle\alpha\mathbf{k};\nu_1\mathbf{k}_1|V_s|\nu_2\mathbf{k}_2;\nu_3\mathbf{k}_3\rangle\\
&\qquad \times\langle\nu_2\mathbf{k}_2;\nu_3\mathbf{k}_3|\bar{g}|\alpha'\mathbf{k};\nu_1\mathbf{k}_1\rangle\\
&\qquad - \langle\alpha\mathbf{k};\nu_1\mathbf{k}_1|\bar{g}|\nu_2\mathbf{k}_2;\nu_3\mathbf{k}_3\rangle\\
&\qquad \times\langle\nu_2\mathbf{k}_2;\nu_3\mathbf{k}_3|V_s|\alpha'\mathbf{k};\nu_1\mathbf{k}_1\rangle\}. \qquad (34)
\end{aligned}$$

Further reduction follows from substitution of the Coulomb matrix element (32).

In practice, the relevant values of $\mathbf{q}$ may be sufficiently small to justify the approximation $I_{\alpha,\nu}(\mathbf{k},\mathbf{q}) \to I_{\alpha\nu}(\mathbf{k},0) = \delta_{\alpha,\nu}$. Then, these equations simplify to the usual forms

$$\begin{aligned}
&\partial_t n_c(\mathbf{k};t) + 2\mathrm{Im}(\mathbf{E}(t)\cdot\mu_{cv}\,p_{vc}(\mathbf{k};t))\\
&\quad + 2\mathrm{Im}\sum_{\mathbf{q}}\tilde{V}(q)\,p_{cv}(\mathbf{k}+\mathbf{q};t)\,p_{vc}(\mathbf{k};t)\\
&\quad + C_{cc}(\mathbf{k};t) = 0 \qquad (35)
\end{aligned}$$

$$\begin{aligned}
&\partial_t p_{cv}(\mathbf{k};t) + i(\epsilon_c(\mathbf{k}) - \epsilon_v(\mathbf{k}) - \mathbf{E}(t)\\
&\quad \cdot[\,\mu_{\alpha\alpha} - \mu_{\alpha'\alpha'}])\,p_{cv}(\mathbf{k};t)\\
&\quad - i\sum_{\mathbf{q}}\tilde{V}(q)[\,n_c(\mathbf{k}+\mathbf{q};t) - n_v(\mathbf{k}+\mathbf{q};t)]\\
&\quad \times p_{cv}(\mathbf{k};t)\\
&\quad - i\Bigg\{\sum_{\mathbf{q}}\tilde{V}(q)\,p_{cv}(\mathbf{k}+\mathbf{q};t) + \mathbf{E}(t)\cdot\mu_{cv}\Bigg\}\\
&\quad \times(n_v(\mathbf{k};t) - n_c(\mathbf{k};t))\\
&\quad + C_{cv}(\mathbf{k};t) = 0, \qquad (36)
\end{aligned}$$

with the collision matrix elements

$$\begin{aligned} C_{cc}(\mathbf{k};t) &= -2\mathrm{Im}\sum_{\mathbf{q}\neq 0,\mathbf{k}_1}\tilde{V}(q) \\ &\quad\times\{\langle c\mathbf{k}-\mathbf{q};c\mathbf{k}_1+\mathbf{q}|\bar{g}|c\mathbf{k};c\mathbf{k}_1\rangle \\ &\quad+\langle c\mathbf{k}-\mathbf{q};\nu\mathbf{k}_1+\mathbf{q}|\bar{g}|c\mathbf{k};\nu\mathbf{k}_1\rangle \\ &\quad-\langle c\mathbf{k}_1+\mathbf{q};c\mathbf{k}-\mathbf{q}|\bar{g}|c\mathbf{k};c\mathbf{k}_1\rangle \\ &\quad-\langle v\mathbf{k}_1+\mathbf{q};c\mathbf{k}-\mathbf{q}|\bar{g}|c\mathbf{k};v\mathbf{k}_1\rangle\} \end{aligned} \tag{37}$$

$$\begin{aligned} C_{c\nu}(\mathbf{k};t) &= -2\mathrm{Im}\sum_{\mathbf{q}\neq 0,\mathbf{k}_1}\tilde{V}(q) \\ &\quad\times\{\langle c\mathbf{k}-\mathbf{q};c\mathbf{k}_1+\mathbf{q}|\bar{g}|v\mathbf{k};c\mathbf{k}_1\rangle \\ &\quad+\langle c\mathbf{k}-\mathbf{q};v\mathbf{k}_1+\mathbf{q}|\bar{g}|v\mathbf{k};v\mathbf{k}_1\rangle\} \\ &\quad-\sum_{\mathbf{q}\neq 0,\mathbf{k}_1}\tilde{V}(q)\{\langle c\mathbf{k}_1+\mathbf{q};c\mathbf{k}-\mathbf{q}|\bar{g}|v\mathbf{k};c\mathbf{k}_1\rangle \\ &\quad+\langle v\mathbf{k}_1+\mathbf{q};c\mathbf{k}-\mathbf{q}|\bar{g}|v\mathbf{k};v\mathbf{k}_1\rangle \\ &\quad-\langle c\mathbf{k};c\mathbf{k}_1|\bar{g}|c\mathbf{k}_1+\mathbf{q};v\mathbf{k}-\mathbf{q}\rangle \\ &\quad-\langle c\mathbf{k};v\mathbf{k}_1|\bar{g}|v\mathbf{k}_1+\mathbf{q};v\mathbf{k}-\mathbf{q}\rangle\}. \end{aligned} \tag{38}$$

Aside from the small $\mathbf{q}$ limitation of the Coulomb matrix elements, the above equations are still exact. The detailed dependence of $C_{\alpha\alpha'}(\mathbf{k};t)$ on $n_\alpha(\mathbf{k};t)$ and $p_{\alpha\alpha'}(\mathbf{k};t)$ requires specification of $\bar{g}(1,2;t)$ as a functional of $f^{(1)}(1;t)$. This follows from an approximate solution to Eq. (19). To illustrate the procedure, consider the weak coupling limit in which $\bar{g}(1,2;t)$ is evaluated to first order in the Coulomb interactions. Since $\bar{g}(1,2,3;t)$ occurs in (19) multiplied by $V(1,2)$, it is sufficient to evaluate $\bar{g}(1,2,3;t)$ to zeroth order in the potential. However, since the correlations due to statistics have already been extracted, the three-particle correlation function vanishes to this order. Also, since the source term on the right side is of first order in the potential, then $\bar{g}(1,2;t)$ also is of first order. Thus, all explicit dependence on $V(1,2)$ can be neglected on the left side of the equation, leading to the weak coupling equation

$$\begin{aligned} \partial_t\bar{g}(1,2;t) &+ i[(H(1)+H(2)),\bar{g}(1,2;t)] \\ &= -i\big\{\hat{V}(1,2;t)f^{(1)}(1;t)f^{(1)}(2;t) \\ &\quad -f^{(1)}(1;t)f^{(1)}(2;t)\hat{V}^{\dagger}(1,2;t)\big\}, \end{aligned} \tag{39}$$

with the solution

$$\begin{aligned} \bar{g}(1,2;t) &= e^{-i(H(1)+H(2))t}\bar{g}(1,2;0)e^{i(H(1)+H(2))t} \\ &\quad -i\int_0^t d\tau e^{i(H(1)+H(2))(t-\tau)} \\ &\quad \times\big\{\hat{V}(1,2;\tau)f^{(1)}(1;\tau)f^{(1)}(2;\tau) \\ &\quad -f^{(1)}(1;\tau) \\ &\quad \times f^{(1)}(2;\tau)\hat{V}^{\dagger}(1,2;\tau)\big\}e^{i(H(1)+H(2))(t-\tau)}. \end{aligned} \tag{40}$$

Since the Hamiltonian $H(1)$ is diagonal in the Bloch representation, it is straightforward to calculate the matrix elements of $\bar{g}(1,2;t)$ given by (40) and obtain the collision operator as a quartic function of the occupation numbers [recall $\hat{V}(1,2;t)\equiv\{1-f^{(1)}(1;t)-f^{(1)}(2;t)\}V(1,2)$]. The result is a generalization of the Born–Boltzmann collision operator, extended to include the effects of initial correlations and non-Markovian effects at short times. In the long time limit, it becomes exactly the Uhlenbeck–Boltzmann collision operator with scattering calculated in the Born approximation. An improved approximation appropriate for most current experimental conditions is described in the next section, where strong scattering and polarization effects are accounted for as well.

Pair Correlation Approximation

The exact transformed hierarchy Eq. (19) for $\bar{g}(1,2;t)$ is an appropriate form for the introduction of approximations since it makes explicit the physical mechanisms for renormalized single-particle states, blocking in the pair dynamics, and dynamic screening. The approximations entail some statement about the three-particle correlations in $\bar{g}(1,2,3;t)$. More specifically, the approximation should give $\bar{g}(1,2,3;t)$ in terms of the pair correlations and one-particle distribution function, so that the first two hierarchy equations become closed equations for $f^{(1)}(1;t)$ and $\bar{g}(1,2;t)$. The formal solution to the second equation provides the functional in (10) required for a kinetic equation

$$\begin{aligned} F^{(2)}&(1,2;t\,|\,f^{(1)}) \\ &= \{f^{(1)}(1;t)f^{(1)}(2;t)+\bar{g}(1,2;t\,|\,f^{(1)})\}\mathscr{S}(1,2). \end{aligned} \tag{41}$$

In general, there is no small parameter on which to base a systematic expansion. However, there are exact structural properties of the hierarchy equation that impose important constraints on the class of approximations considered acceptable. For example, the single-particle reduced density operator is representable as a trace over the two-particle reduced density operator, $Nf^{(1)}(1;t) = Tr_2 f^{(2)}(1,2;t)$ and, therefore, the exact first hierarchy equation for $f^{(1)}(1;t)$ should result from a partial trace over any acceptable approximate closure of the second hierarchy equation. Additional constraints follow from the invariance of the hierarchy equations under symmetry transformations derived from the Hamiltonian (e.g., rotations, translations, Galilean boosts). An important consequence of these invariances is the local conservation laws for mass, energy, and momentum. Constraints imposed by the requirement of exact conservation laws are discussed in [5, 8, 9]. Other constraints can be included as well. For example, if the reduced density operators for the equilibrium state are known, it can be required that they are also solutions to the approximate hierarchy equations. In this way, the class of approximations can be assured to have the most important properties of the exact hierarchy in a context that does not imply weak coupling or other small parameter limits.

For long-range Coulomb interactions, it is important to describe screening effects. This is included explicitly on the right side of (20), as are the mean field Hartree–Fock-renormalized single-particle energies and the Pauli blocking effects for the pair potential. Thus, all of the important mechanisms appear in this form even before considering three-particle correlations in $\bar{g}(1,2,3;t)$. Furthermore, it is shown in [5] that *any* choice for $\bar{g}(1,2,3;t)$ that is Hermitian and pairwise symmetric in the particle labels preserves both the representability of $f^{(1)}$ and the exact conservation laws. Consequently, we suggest that the residual three-particle correlations described by $\bar{g}(1,2,3;t)$ can be neglected entirely, except for the conditions of very strong coupling. The resulting approximation preserves the exact local conservation laws for mass, energy, and momentum and is time reversal invariant. It contains strong collision effects (ladder diagrams) through the dependence on the potential in $\hat{H}(1,2;t)$ and dynamical polarization effects in the random-phase approximation (ring diagrams). There are no a priori limitations on the time scale in this approximation so that a uniform treatment of the initial value problem is possible.

With this approximation, Eq. (19) becomes a closed equation for $\bar{g}(1,2;t)$ in terms of $f^{(1)}(1;t)$, with the form

$$\begin{aligned}(\partial_t - L(1,2;t))\bar{g}(1,2;t) &= -i\Big[\hat{V}(1,2;t)f^{(1)}(1;t)f^{(1)}(2;t) \\ &\quad - f^{(1)}(1;t)f^{(1)}(2;t)\hat{V}^{\dagger}(1,2;t)\Big]. \qquad (42)\end{aligned}$$

The formal solution provides the functional in (10) required for a kinetic equation

$$\begin{aligned}F^{(2)}(1,2;t \mid f^{(1)}) &= \{f^{(1)}(1;t)f^{(1)}(2;t) \\ &\quad + \bar{g}(1,2;t \mid f^{(1)})\}\mathscr{S}(1,2), \qquad (43)\\ \bar{g}(1,2;t \mid f^{(1)}) &= \mathrm{Tr}_{34}U(1,2,3,4;t,t_0)\bar{g}(3,4;t_0) \\ &\quad - i\mathrm{Tr}_{34}\int_{t_0}^{t} d\bar{t}\, U(1,2,3,4;t,\bar{t}) \\ &\quad \times\Big[\hat{V}(3,4;\bar{t})f^{(1)}(3;\bar{t})f^{(1)}(4;\bar{t}) \\ &\quad - f^{(1)}(3;\bar{t})f^{(1)}(4;\bar{t})\hat{V}^{\dagger}(3,4;\bar{t})\Big]. \qquad (44)\end{aligned}$$

Here, $U(1,2,3,4;t,t_0)$ is the two-particle propagator associated with the generator $L(2,2;t)$. Its form and reduction to familiar quantities such as scattering matrices and dielectric functions will be discussed elsewhere [10] and only the structural features noted here. The first term on the right side of (44) gives the pair dynamics due to initial correlations determined from the system preparation. The second term describes the correlation buildup even in the absence of such initial correlations. Both contributions can be of equal importance for initial value problems at short times.

The collision operator in the kinetic Eq. (22) reflects these two contributions:

$$\begin{aligned}C(1;t) &= -i\mathrm{Tr}_2[V_s(1,2), \bar{g}(1,2;t)] \\ &= I^c(1;t) + I(1;t) \qquad (45)\\ I^c(1;t) &= -i\mathrm{Tr}_{234}[V_s(1,2), \\ &\quad U(1,2,3,4;t,t_0)\bar{g}(3,4;t_0)] \qquad (46)\end{aligned}$$

$$\begin{aligned}I(1;t) &= -i\mathrm{Tr}_{234}\int_{t_0}^{t} d\bar{t}\Big[V_s(1,2), U(1,2,3,4;t,\bar{t}) \\ &\quad \times\big\{\hat{V}(3,4;\bar{t})f^{(1)}(3;\bar{t})f^{(1)}(4;t) \\ &\quad - f^{(1)}(3;\bar{t})f^{(1)}(4;\bar{t})\hat{V}^{\dagger}(3,4;\bar{t})\big\}\Big]. \qquad (47)\end{aligned}$$

The Hartree–Fock dynamics is modified at short times by the conditions of the initial preparation through $I_1^c(t)$. The other modification is independent of the initial preparation and represents the buildup of scattering effects. The term $I(1;t)$ grows from zero to an asymptotic value $I(1;\infty)$, while the initial correlations term $I_1^c(t)$ is expected to decrease to zero for most physical preparations. This initial transient period represents the transition from time scales short compared to the scattering time up to times long enough for completed collisions. On the long time scale, $C(1;t) \to I(1;\infty)$ and the kinetic equation takes the usual Markov form. In this limit, a Boltzmann–Uhlenbeck form is obtained with scattering determined by the full T-matrix [11]. During the transient period, the incomplete scattering is described by an effective potential with dynamical screening ranging from Coulomb at short times to fully screened at long times.

Discussion

The objective of this presentation has been to give an overview of an approach to formulating practical kinetic theories for charged particle dynamics, with the potential for application to current and proposed experiments on semiconductors using femtosecond lasers to prepare and probe the charges. The new features of such experiments requiring reconsideration of standard kinetic theory are states far from equilibrium and the inclusion of short time scales. The approach here formulates the description in terms of the exact hierarchy for the one- and two-particle reduced density operators. These operators determine most directly the relevant observables of interest. There are two components to the analysis. First, an exact transformation of the first two hierarchy equations is performed to isolate the strong correlations due to quantum statistics from correlations due to the Coulomb forces. This description in terms of the excess correlations also makes explicit the mean-field effects associated with Hartree–Fock renormalization of the single-particle energies and the dominant polarization effects necessary to account for screening of the long-range Coulomb forces. As a single-time Markovian first-order set of differential equations, the description is formulated as an initial value problem, appropriate for the experimental conditions of interest. The second component of the analysis is an approximate closure of the second hierarchy equation, with the three-particle correlations expressed as explicit functionals of the two-particle correlations and the one-particle reduced density operator. The resulting approximation transforms the first two hierarchy equations into a closed set of coupled equations to determine the one-particle-reduced density operator and the two-particle correlations. Finally, a last step is possible where the approximate second hierarchy equation is solved formally to give the two-particle correlations in terms of the one-particle density operator. Use of this result in the exact first hierarchy equation gives a closed kinetic equation for the one-particle density operator. While the coupled pair of equations for the correlations and one-particle distribution is local in time (Markovian), the reduced kinetic theory description in terms of the one-particle distribution alone is necessarily nonlocal in time. This latter feature is essential for a proper treatment of relaxation and transport at short times.

The transformation of the hierarchy and resulting explicit representation of the most important physical mechanisms simplifies the choice of approximations considerably. Additional constraints are associated with the exact relationship on one- and two-particle reduced density operators, the exact conservation laws, and the existence of stationary states (equilibrium, in the absence of driving fields). It is proposed in the fifth section that these constraints are satisfied by an approximation obtained by neglecting $\bar{g}(1,2,3;t)$. The resulting approximate equations retain all of the desired physical mechanisms and time scales, excluding only conditions of strong Coulomb coupling. The detailed solution to the equation for the pair correlations is essentially an effective two-body problem and will be discussed elsewhere.

The analysis of the hierarchy and considerations leading to this approximation occurs at the abstract operator level and does not require explicit attention to the detailed structure of the physical system considered (e.g., the number of bands) and additional processes are easily accounted for at this abstract level. Having completed the many-body analysis, the physical properties of interest follow directly from an appropriate matrix representation of the operator equations, so that manipulation of complex notation is deferred to this late stage. Of course, the final measure of any approach is the ability to describe interesting new phenomena in quantitative applications. We hope to report on such results in the near future.

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Appendix: Transformation of the Hierarchy Equations

Define a superoperator, $\mathscr{P}_{12}$, that exchanges the labels of particles 1 and 2 in all operators to its right:

$$\mathscr{P}_{12} X(1,2) = X(2,1). \tag{48}$$

This operator should not be confused with the permutation operator defined over quantum states, P_{12}, that permutes the quantum labels of the states. The second equation of the BBGKY hierarchy then can be written in the compact form:

$$\begin{aligned}\partial_t f^{(2)}(1,2;t) &+ i[H(1,2;t), f^{(2)}(1,2;t)]\\ &+ (1+\mathscr{P}_{12}) Tr_3 i[V(1,3) f^{(3)}(1,2,3;t) - hc]\\ &= 0,\end{aligned} \tag{49}$$

where hc indicates the Hermitian conjugate of the preceding term in the brackets. The objective of this Appendix is to show how the exchange effects in the definitions of $f^{(2)}(1,2;t)$ and $f^{(3)}(1,2,3;t)$ can be evaluated exactly to give the Hartree–Fock energies, the blocking factors in the pair potential, and the linear operators responsible for polarization effects. Substitution of (14) into (49) and use of the first hierarchy equation gives

$$\begin{aligned}\mathscr{S}(1,2)\big\{\partial_t \bar{g}^{(2)}(1,2;t) &+ i[H(1,2;t), \bar{g}^{(2)}(1,2;t)]\\ &+ i[V(1,2;t), f^{(1)}(1;t) f^{(1)}(2;t)]\big\}\\ &- \mathscr{S}(1,2)(1+\mathscr{P}_{12}) Tr_3 i[V(1,3)\bar{f}^{(2)}(1,3;t)\\ &\times f^{(1)}(2;t)\mathscr{S}(1,3) - hc]\\ &+ (1+\mathscr{P}_{12}) Tr_3 i\\ &\times [V(1,3)\bar{f}^{(3)}(1,2,3;t)\\ &\times \mathscr{S}(1,2,3) - hc] = 0.\end{aligned} \tag{50}$$

First, note that the last term can be written with an overall prefactor of $\mathscr{S}(1,2)$ as well using the identity $\mathscr{S}(1,2,3) = (1 - P_{13} - P_{23})\mathscr{S}(1,2)$ and the fact that $\mathscr{S}(1,2)$ commutes with any symmetric two-particle operator. Consequently, the overall operator $\mathscr{S}(1,2)$ in (51) can be factored out, leaving the simpler result:

$$\begin{aligned}\partial_t \bar{g}^{(2)}(1,2;t) &+ i[H(1,2;t)\bar{g}^{(2)}(1,2;t)]\\ &+ i[V(1,2;t), f^{(1)}(1;t) f^{(1)}(2;t)]\\ &- (1+\mathscr{P}_{12}) Tr_3 i[V(1,3)\bar{f}^{(2)}(1,3;t)\\ &\times f^{(1)}(2;t)\mathscr{S}(1,3) - hc]\\ &+ (1+\mathscr{P}_{12}) Tr_3 i\\ &\times \big[V(1,3)\bar{f}^{(3)}(1,2,3;t)(1 - P_{13} - P_{23}) - hc\big]\\ &= 0.\end{aligned} \tag{51}$$

Next, represent $\bar{f}^{(3)}(1,2,3;t)$ in the last term using (15) in the equivalent form

$$\begin{aligned}\bar{f}^{(3)}&(1,2,3;t)\\ &= \bar{f}^{(2)}(1,3;t) f^{(1)}(2;t) + f^{(1)}(1;t)\bar{g}(2,3;t)\\ &\quad + f^{(1)}(3;t)\bar{g}(1,2;t) + \bar{g}(1,2,3;t)\end{aligned}$$

to obtain

$$\begin{aligned}V(1,3)&\bar{f}^{(3)}(1,2,3;t)(1 - P_{13} - P_{23})\\ &= V(1,3)\bar{f}^{(2)}(1,3;t) f^{(1)}(2;t)(\mathscr{S}(1,3) - P_{23})\\ &\quad + V(1,3)\{\bar{g}(2,3;t) f^{(1)}(1;t)\\ &\quad + \bar{g}(1,2;t) f^{(1)}(3)\\ &\quad + \bar{g}(1,2,3;t)\}(1 - P_{13} - P_{23}).\end{aligned} \tag{52}$$

The contribution proportional to $\mathscr{S}(1,3)$ cancels the terms on the second line of (51) and the equation for $\bar{g}^{(2)}(1,2;t)$ becomes

$$\begin{aligned}\partial_t \bar{g}^{(2)}(1,2;t) &+ i[H(1,2;t), \bar{g}^{(2)}(1,2;t)]\\ &+ i[V(1,2;t), f^{(1)}(1;t) f^{(1)}(2;t)]\\ &- (1+\mathscr{P}_{12}) Tr_3 i\big[V(1,3)\bar{f}^{(2)}(1,3;t)\\ &\times f^{(1)}(2;t) P_{23} - hc\big]\\ &+ (1+\mathscr{P}_{12}) Tr_3 i\big[V(1,3)\\ &\times \{\bar{g}(2,3;t) f^{(1)}(1;t) + \bar{g}(1,2;t) f^{(1)}(3)\}\\ &\times (1 - P_{13} - P_{23}) - hc\big]\\ &+ (1+\mathscr{P}_{12}) Tr_3 i\big[V(1,3)\bar{g}^{(3)}(1,2,3;t)\\ &\times (1 - P_{13} - P_{23}) - hc\big] = 0.\end{aligned} \tag{53}$$

The fourth term on the left side can be simplified using the identities

$$\begin{aligned} P_{23}P_{23} &= 1, \qquad Tr_3 P_{23} = 1, \\ P_{23}X(1,2,3)P_{23} &= X(1,3,2) \end{aligned} \tag{54}$$

to write

$$\begin{aligned} &Tr_3 V(1,3)\bar{f}^{(2)}(1,3;t)f^{(1)}(2;t)P_{23} \\ &\quad = Tr_3 P_{23}P_{23}V(1,3)\bar{f}^{(2)}(1,3;t)f^{(1)}(2;t)P_{23} \\ &\quad = Tr_2 P_{23}V(1,2)\bar{f}^{(2)}(1,2;t)f^{(1)}(3;t) \\ &\quad = Tr_3 f^{(1)}(3;t)P_{23}V(1,2)\bar{f}^{(2)}(1,2;t) \\ &\quad = Tr_3 P_{23}P_{23}f^{(1)}(3;t)P_{23}V(1,2)\bar{f}^{(2)}(1,2;t) \\ &\quad = Tr_3 P_{23}f^{(1)}(2;t)V(1,2)\bar{f}^{(2)}(1,2;t) \\ &\quad = f^{(1)}(2;t)V(1,2)\bar{f}^{(2)}(1,2;t). \end{aligned} \tag{55}$$

The second equation of the BBGKY hierarchy now becomes

$$\begin{aligned} &\partial_t \bar{g}(1,2;t) + i[(H(1;t)+H(2;t)), \bar{g}^{(2)}(1,2;t)] \\ &\quad + i\big[\hat{V}(1,2;t)\bar{g}(1,2;t) - hc\big] \\ &\quad + (1+\mathscr{P}_{12})Tr_3 i\big[V(1,3)\{\bar{g}(2,3;t)f^{(1)}(1;t) \\ &\quad + \bar{g}(1,2;t)f^{(1)}(3)\}(1-P_{13}-P_{23}) - hc\big] \\ &\quad + i\big[\hat{V}(1,2;t)f^{(1)}(1;t)f^{(1)}(2;t) \\ &\quad - f^{(1)}(1;t)f^{(1)}(2;t)\hat{V}^{\dagger}(1,2;t)\big] \\ &\quad + (1+\mathscr{P}_{12})Tr_3 i\big[V(1,3)\bar{g}^{(3)}(1,2,3;t) \\ &\quad \times(1-P_{13}-P_{23}) - hc\big] = 0, \end{aligned} \tag{56}$$

with the definition

$$\hat{V}(1,2;t) \equiv [1 - f^{(1)}(1;t) - f^{(1)}(2;t)]V(1,2). \tag{57}$$

This shows clearly the origin of the Pauli blocking factor in the pair potential.

The remaining exchange terms in the second line of (56) can be analyzed in a similar way:

$$\begin{aligned} &Tr_3 V(1,3)[\bar{g}(2,3;t)f^{(1)}(1;t) \\ &\quad + \bar{g}(1,2;t)f^{(1)}(3)](1-P_{13}-P_{23}) \\ &= Tr_3 V(1,3)\big[\bar{g}(1,2;t)f^{(1)}(3) \\ &\quad - \bar{g}(2,3;t)f^{(1)}(1;t)P_{13}\big] \\ &\quad + Tr_3 V(1,3)\big[\bar{g}(2,3;t)f^{(1)}(1;t)(1-P_{23}) \\ &\quad - \bar{g}(1,2;t)f^{(1)}(3)(P_{13}+P_{23})\big] \\ &= Tr_3 V(1,3)\big[\bar{g}(1,2;t)f^{(1)}(3) \\ &\quad - P_{13}P_{13}\bar{g}(2,3;t)f^{(1)}(1;t)P_{13}\big] \\ &\quad + Tr_3 V(1,3)\big[\bar{g}(2,3;t)f^{(1)}(1;t)(1-P_{23}) \\ &\quad - P_{13}P_{13}\bar{g}(1,2;t)f^{(1)}(3)P_{13}(1+P_{13}P_{23})\big] \\ &= Tr_3 V_s(1,3)f^{(1)}(3)\bar{g}(1,2;t) \\ &\quad + Tr_3 V(1,3)\bar{g}(2,3;t)f^{(1)}(1;t)(1-P_{23}) \\ &\quad - P_{13}\bar{g}(2,3;t)f^{(1)}(1)(1+P_{13}P_{23}). \end{aligned} \tag{58}$$

The first term on the right side gives the Hartree–Fock single-particle energy shift:

$$\begin{aligned} V_{hf}(1;t) &= Tr_3 V_s(1,3)f^{(1)}(3), \\ V_s(1,3) &\equiv V(1,3)\mathscr{S}(1,3). \end{aligned}$$

The second term can be transformed by writing the factor $(1+P_{13}P_{23}) = (1-P_{23}) + (1+P_{13})P_{23} = (1-P_{23}) + P_{23}(1+P_{12})$. Recall that an overall factor of $\mathscr{S}(1,2)$ has been canceled out in writing (56). Since $(1+P_{12})\mathscr{S}(1,2) = 0$, the term $P_{23}(1+P_{12})$ vanishes in this context and Eq. (58) simplifies to

$$\begin{aligned} &Tr_3 V(1,3)[\bar{g}(2,3;t)f^{(1)}(1;t) \\ &\quad + \bar{g}(1,2;t)f^{(1)}(3)](1-P_{13}-P_{23}) \\ &= V_{hf}(1,2;t)\bar{g}(1,2;t) \\ &\quad + Tr_3 V_s(1,3)\bar{g}(2,3;t)f^{(1)}(1;t)(1-P_{23}). \end{aligned} \tag{59}$$

The second term gives the polarization effects with exchange. The exact equation for $\bar{g}(1,2;t)$ now takes the final form of (19).

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