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Quantum-Mechanical Transport Equation for Atomic Systems*

Paul R. Berman†
Physics Department, Yale University, New Haven, Connecticut 06520
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A quantum-mechanical transport equation (QMTE) is derived which should be applicable to a wide range of problems involving the interaction of radiation with atoms or molecules which are also subject to collisions with perturber atoms. The equation follows the time evolution of the macroscopic atomic density matrix elements of atoms located at classical position $\vec{R}$ and moving with classical velocity $\vec{v}$. It is quantum mechanical in the sense that all collision kernels or rates which appear have been obtained from a quantum-mechanical theory and, as such, properly take into account the energy-level variations and velocity changes of the active (emitting or absorbing) atom produced in collisions with perturber atoms. The QMTE represents a somewhat different formulation of the problem than that considered in earlier works. The present formulation is better suited to problems involving high-intensity external fields, such as those encountered in laser physics.

I. INTRODUCTION

In two previous papers[1,2] (hereafter referred to as QMI and QMII), a theory of pressure effects was developed which enables one to follow the time evolution of a moving atom which was interacting with some external radiation field and undergoing collisions with perturber atoms. Quantization of the atom's center-of-mass motions proved to be a key feature of this theory since it permitted a consistent treatment of both the energy-level variations and velocity changes of the active (emitting or absorbing) atom caused by collisions with perturber atoms. One drawback of the approach of QMII was that it was formulated in terms of a perturbation expansion in powers of the external field so that, in its present form, the approach was not well suited to problems involving high-intensity fields. In this paper, based on the results of QMI and QMII, we shall derive a quantum-mechanical transport equation (QMTE) which will not possess this drawback.

The equation to be derived is termed a transport equation because it will describe the evolution of the macroscopic density matrix (or distribution function) of the ensemble of active atoms specified by the classical variables $\vec{R}$, $\vec{v}$, t. On the other hand, the equation will be quantum mechanical in the sense that all collisions kernels and rates which appear will have been obtained by inference from the quantum-mechanical collision results of QMI and II. The fact that all our collision kernels are well-defined quantum-mechanical quantities distinguishes our theory from others[3] which make use of a similar equation with phenomenological (and sometimes incorrect) kernels based on a classical rather than quantum-mechanical description of the atomic center-of-mass motion.[4]

Of what use is the QMTE? Typically, transport equations enable one to determine the approach to equilibrium of an ensemble of atoms initially described by a nonequilibrium velocity distribution. However, although applicable to problems of this kind, the QMTE will be developed in a manner directed towards application to a different class of problems. Specifically, we have in mind a situation where the active and perturber atoms are permitted to reach some sort of thermal equilibrium. At that point, an excitation or external field interaction is "turned on" and tends to alter the equilibrium distribution of the active atoms. The QMTE will trace the evolution of the active atom density matrix from the original equilibrium to the new steady state.

In turn, the macroscopic density matrix elements obtained as solutions of the QMTE will, in general, enable one to calculate values for quantities of physical interest in a given problem. For example, in laser problems, the atomic polarization which serves as a driving function for the classical laser electric field is directly related to off-diagonal density matrix elements.[1,2] Similarly, spontaneous-emission spectral profiles are determined by the diagonal density matrix elements

which represent the probability of finding atoms in a given state with some specified photons present. In fact, just as the solution of a classical transport equation provides values for the system's distribution function from which the average values of system parameters may be calculated, the solution of the QMTE provides values for density matrix elements from which the expectation values of quantum-mechanical operators that act upon electronic state wave functions may be obtained. Hence, the QMTE may be used as a starting point for examining the role of collisions in atomic systems subject to external field interactions.

The approximations and regions of validity of the theory will be discussed in Sec. II, as well as our method of approach. In Sec. III, the QMTE is derived for the case of no collisions, and collisions are incorporated into this result in Sec. IV. Possible extensions of the theory and a discussion of the results are given in Secs. V and VI, respectively. Several calculations, which would hinder the flow of the derivation, are relegated to the Appendixes.

II. APPROXIMATIONS AND METHOD OF APPROACH

There are three interrelated implicit assumptions of the theory which should be noted. First, it is assumed that there is some way of distinguishing active atoms from perturber atoms. Usually this distinction may be made based on the fact that (a) the perturbers differ chemically from the active atoms or (b) the perturbers are in their ground state while the active atoms have a non-negligible excited-state population. Second, it is assumed that the perturber density is much greater than the active atom density so that active-atom–active-atom collisions (which would lead to a collisional contribution such as that encountered in the Boltzmann equation) may be neglected. Third, and somewhat justified by the fact that there are many more perturber-perturber than perturber–active-atom collisions, we assume that the perturber velocity distribution is effectively unaltered by pertruber–active-atom collisions and that it is both time and coordinate independent. If this assumption were not incorporated, one would be led to coupled transport equations for the perturber and active atom density matrix elements. The above assumptions are essential to our transport-theory approach.

Before listing some explicit approximations we shall employ, it will prove useful to introduce several parameters which characterize the collision process. These parameters and their typical values are as follows: The effective range $\mathcal{R}$ of the active atom-perturber interaction is $\approx 10^{-7}$ cm, the duration of a collision, τ_c, is $\approx 10^{-12}$ sec, and the average rate Γ_c at which collisions occur (or equivalently the inverse average time between collisions) is $\approx 10^{7}$ sec^{-1} at 1.0 Torr and increases linearly with pressure.

Approximations

(1) It is assumed that the duration of a collision is much less than the time between collisions, (i.e., $\Gamma_c \tau_c \ll 1$) so that we need consider binary collisions only. This binary-collisions approximation is generally valid to pressures of up to several hundred Torr.

(2) We shall work in the impact-theory limit on the assumption that the external-field values can be taken as constant throughout the duration of a collision. While the validity conditions for the impact approximation must be separately examined for each problem, one usually finds requirements like $\tau_c/\tau \ll 1$, and $\Delta\omega\tau_c \ll 1$, where τ is some effective lifetime of the atomic system and $\Delta\omega$ is some detuning from line center which may be of interest.

(3) An adiabatic approximation is made by assuming that the frequency separation of the energy levels of the atomic system is much greater than τ_c^{-1}. This implies that the collisions do not possess sufficient energy to induce transitions between the atomic states. While this approximation is valid for optically separated levels, it fails for any levels separated by $\lesssim 10^6$ MHz. For the present time, we defer comment on the additional modifications and complications which would be introduced if collision-induced transitions were included in the theory.

(4) We shall look upon the perturber atoms as moving sources of interaction potentials for the active atoms. That is, one can associate a potential $U(\vec{R}-\vec{R}_j)$ with a perturber located at position $\vec{R}_j$. In effect, this procedure neglects the possibility that the perturbers (which are assumed to be in their ground states before a collision) can become excited as a result of collision. Thus, we neglect all collision-induced excitation transfer processes such as those which may arise in collisions between atoms of the same kind and restrict the theory to foreign-gas-type collisions.[5]

(5) The atoms are assumed to be excited individually rather than coherently. In addition, excitation mechanisms such as radiation trapping and collision-induced excitation transfer which depend on the density matrix of the system are not included in the theory.

(6) We assume that the external fields do not significantly affect the active atom's center-of-mass motion. If the external fields are electromagnetic in nature, this assumption will be valid if the active atoms are neutral or if the electromagnetic field is oscillating rapidly and has zero time average, provided that the effects of atomic recoil when a photon is emitted or absorbed (called

"photon recoil," for short) are negligible. The neglect of photon recoil is generally a good approximation at optical frequencies; however, in high precision experiments on long-lived systems, photon recoil terms may have some significance.[6,7]

Although we have compiled a long list of approximations or assumptions, there are many situations of interest where most of them apply. Methods for relaxing some of the above restrictions will be given in Sec. V. However, the theory is directly applicable to a study of the effects of foreign-gas collisions on optical or near-optical atomic line shapes associated with low-density atomic systems.

Method of Approach

Rather than deal with the density matrix of a single atom as we did in QMI and II, we shall consider the macroscopic density matrix for the entire ensemble of active atoms. Considering this density matrix $\rho(\vec{R},\vec{v};t)$ as a function of independent classical variables $\vec{R}$, $\vec{v}$, and t, we shall first obtain a partial differential equation for $\rho(\vec{R},\vec{v},t)$ when collisions are absent. Collisions will then be incorporated into this partial differential equation by addition of a term $(\partial\rho(\vec{R},\vec{v},t)/\partial t)_{\text{coll}}$ which is calculated using an interpretation of the results of QMI and QMII. The resulting partial differeointegral equation for the classical macroscopic density matrix $\rho(\vec{R},\vec{v},t)$ will be referred to as quantum-mechanical transport equation (QMTE) since it will contain the quantum-mechanical line-shape parameters (i.e., collision rates, widths, shifts, kernels) of QMI and QMII. Alternatively, one might call it a pseudoclassical transport equation in line with the presentation of QMII.

III. DENSITY-MATRIX EQUATION WITH NO COLLISIONS

It is our aim to proceed from a quantum-mechanical to a classical description of the atom's center-of-mass motion. To accomplish this task, we shall first derive a time-evolution equation for an atom's density matrix in which the center-of-mass coordinate $\vec{R}$ is a quantum-mechanical variable. We shall then obtain an appropriate classical limit to this equation in which the quantum-mechanical variables $\vec{R}$ and $\vec{P}=(\hbar/i)\partial/\partial\vec{R}$ are replaced by the corresponding classical variables. It should be understood that when we speak of a "classical limit" or "classical density matrix" we are referring to the center-of-mass motion only; the atom's electronic-state spectrum is always taken to be quantized.

In the absence of collisions, the quantum-mechanical Hamiltonian for the jth atom is of the form

$$H(\vec{r}_j,\vec{R}_j,t)=H_0(\vec{r}_j)-(\hbar^2/2m)\vec{\nabla}^2+V(\vec{r}_j,\vec{R}_j,t)\,, \qquad (1)$$

where $\vec{r}_j$ stands for all the relative electronic coordinates of the jth atom, $H_0(\vec{r}_j)$ is the free atom's electronic Hamiltonian assumed to possess eigenfunctions $\psi_\alpha(\vec{r}_j)$, $\vec{R}_j$ is the atom's center-of-mass position, $\vec{\nabla}$ is the gradient with respect to $\vec{R}_j$, m is the atom's mass, and $V(\vec{r}_j,\vec{R}_j,t)$ represents the atom-field interaction (assumed not to be a function of momentum).

We may expand the wave function of the atom as

$$\psi^j(\vec{r}_j,\vec{R}_j,t)=\sum_\alpha A^j_\alpha(\vec{R}_j,t)\psi_\alpha(\vec{r}_j) \qquad (2)$$

and, from this expansion, form the density matrix elements in the interaction representation defined by

$$\tilde{\rho}^j_{\alpha\alpha'}(\vec{R}_j,t)=A^j_\alpha(\vec{R}_j,t)A^j_{\alpha'}(\vec{R}_j,t)^*\,e^{i\omega_{\alpha\alpha'}t}\,, \qquad (3)$$

with $\omega_{\alpha\alpha'}=\omega_\alpha-\omega_{\alpha'}$ and ω_α the eigenfrequency of state α. Using Schrödinger's equation, it is then an easy matter to derive the following equation of motion for the density matrix elements:

$$i\hbar\frac{\partial\tilde{\rho}^j_{\alpha\alpha'}(\vec{R}_j,t)}{\partial t}=-i\hbar\vec{\nabla}\cdot\tilde{\vec{J}}^j_{\alpha\alpha'}(\vec{R}_j,t) + [\tilde{V}(\vec{R}_j,t),\tilde{\rho}^j(\vec{R}_j,t)]_{\alpha\alpha'}\,, \qquad (4)$$

where

$$\tilde{\vec{J}}^j_{\alpha\alpha'}(\vec{R}_j,t)=\hbar(2mi)^{-1}[A^j_{\alpha'}(\vec{R}_j,t)^*\vec{\nabla}A^j_\alpha(\vec{R}_j,t) - A^j_\alpha(\vec{R}_j,t)\vec{\nabla}A^j_{\alpha'}(\vec{R}_j,t)^*]\,e^{i\omega_{\alpha\alpha'}t}\,, \qquad (5)$$

and the matrix elements of $\tilde{V}(\vec{R}_j,t)$ are given by

$$\tilde{V}_{\alpha\alpha'}(\vec{R}_j,t)=\int d^3r_j\,\psi_\alpha(\vec{r}_j)^*\,V(\vec{r}_j,\vec{R}_j,t)\psi_{\alpha'}(\vec{r}_j)e^{i\omega_{\alpha\alpha'}t}\,. \qquad (6)$$

Note that $\vec{R}_j$ is a quantum-mechanical variable.

In Appendix A, we show that, provided the field interaction $V(\vec{r}_j,\vec{R}_j,t)$ does not affect the atom's center-of-mass motion (as has been assumed in Sec. II), a classical limit for Eq. (4) is

$$\frac{\partial\tilde{\rho}^j_{\alpha\alpha'}(\vec{R}_j,\vec{P}_j,t)}{\partial t}=-m^{-1}\vec{P}_j\cdot\vec{\nabla}\tilde{\rho}^j_{\alpha\alpha'}(\vec{R}_j,\vec{P}_j,t) + (i\hbar)^{-1}[\tilde{V}(\vec{R}_j,t),\tilde{\rho}^j(\vec{R}_j,t)]_{\alpha\alpha'} \qquad (7)$$

in which $\vec{R}_j$ and $\vec{P}_j$ are classical variables for the position and momentum of the jth atom, respectively. The quantity $\tilde{\rho}^j_{\alpha\alpha'}(\vec{R}_j,\vec{P}_j,t)$, in effect, represents the amount of the atomic density matrix that one may associate with the volume $d^3R_j\,d^3P_j$ in phase space. In other words, $\tilde{\rho}^j_{\alpha\alpha'}(\vec{R}_j,\vec{P}_j,t)$ is the density in phase space such that $\int d^3R_j\,d^3P_j \times\tilde{\rho}^j_{\alpha\alpha'}(\vec{R}_j,\vec{P}_j,t)=\tilde{\rho}^j_{\alpha\alpha'}(t)$, the $\alpha\alpha'$ atomic density matrix element. Thus, Eq. (7) may be thought of as a transport equation that gives the time rate of change of atom j's density matrix elements when there are no collisions. The commutator in Eq. (7) represents the external field contribution while $-m^{-1}\vec{P}_j\cdot\vec{\nabla}\tilde{\rho}^j_{\alpha\alpha'}(\vec{R}_j,\vec{P}_j,t)$ represents the convective contribution to the time rate of change

$\tilde{\rho}^{j}_{\alpha\alpha'}(\vec{R}_j, \vec{P}_j, t)$.

Although Eq. (7) was derived for a single atom, it will serve equally well for the entire ensemble since each atom is assumed to interact independently with the field. That is, the macroscopic density matrix element defined by

$$\tilde{\rho}_{\alpha\alpha'}(\vec{R}, \vec{P}, t) = \sum_j \int d^3R_j\, d^3P_j\, \tilde{\rho}^{j}_{\alpha\alpha'}(\vec{R}_j, \vec{P}_j, t) \times \delta(\vec{R} - \vec{R}_j)\, \delta(\vec{P} - \vec{P}_j) = \sum_j \tilde{\rho}^{j}_{\alpha\alpha'}(\vec{R}, \vec{P}, t) \quad (8)$$

will also satisfy Eq. (7). The summation in Eq. (8) is over all the active atoms in the ensemble so that the normalization assumed is

$$\sum_\alpha \int d^3R\, d^3P\, \rho_{\alpha\alpha}(\vec{R}, \vec{P}, t) = N(t)\,, \quad (9)$$

where N is the total number of active atoms in the ensemble at time t.

It is sometimes convenient to include some additional terms in Eq. (7). If the system or subsystem under examination is not closed, one may introduce an injection or excitation-rate density $\Lambda_{\alpha\alpha'}(\vec{R}, \vec{P}, t)$ and some phenomenological decay or escape rate $\Gamma_{\alpha\alpha'}(\vec{R}, \vec{P}, t)$ for the $\alpha\alpha'$ density matrix element [it is assumed that neither $\Lambda_{\alpha\alpha'}(\vec{R}, \vec{P}, t)$ nor $\Gamma_{\alpha\alpha'}(\vec{R}, \vec{P}, t)$ depend on $\tilde{\rho}_{\alpha\alpha'}(\vec{R}, \vec{P}, t)$]. [The excitation would be termed "incoherent" if $\Lambda_{\alpha\alpha'}(\vec{R}, \vec{P}, t) \propto \delta_{\alpha\alpha'}$.] When the injection and loss terms are included in Eq. (7) and terms are suitably redefined so that the velocity $\vec{v} = \vec{P}/m$ is used as a variable instead of the momentum $\vec{P}$, Eq. (7) becomes

$$\left(\frac{\partial \tilde{\rho}_{\alpha\alpha'}(\vec{R}, \vec{v}, t)}{\partial t}\right)_{\text{no coll}} = \tilde{\Lambda}_{\alpha\alpha'}(\vec{R}, \vec{v}, t) - \Gamma_{\alpha\alpha'}(\vec{R}, \vec{v}, t)\, \tilde{\rho}_{\alpha\alpha'}(\vec{R}, \vec{v}, t) - \vec{v}\cdot\vec{\nabla}\tilde{\rho}_{\alpha\alpha'}(\vec{R}, \vec{v}, t) + (i\hbar)^{-1}[\tilde{V}(\vec{R}, t),\ \tilde{\rho}(\vec{R}, t)]_{\alpha\alpha'}\,, \quad (10a)$$

where

$$\tilde{\Lambda}_{\alpha\alpha'}(\vec{R}, \vec{v}, t) = \Lambda_{\alpha\alpha'}(\vec{R}, \vec{v}, t)\, e^{i\omega_{\alpha\alpha'}t}\,, \quad (10b)$$

$\vec{R}$ and $\vec{v}$ are classical variables, and coll is an abbreviation for "collision." The initial conditions for Eq. (10a) must be chosen for each problem. In a closed system, $\Lambda_{\alpha\alpha'}(\vec{R}, \vec{v}, t) = 0$ and $\Gamma_{\alpha\alpha'}(\vec{R}, \vec{v}, t) = 0$ so that excitation and decay can arise only through the field interaction $\tilde{V}(\vec{R}, t)$. For such a system, $\tilde{\rho}_{\alpha\alpha'}(\vec{R}, \vec{v}, -\infty)$ may be taken as an equilibrium or whatever other distribution is believed to characterize the active atoms before the external field interaction is "turned on." For open systems or excited-state subsystems (such as those considered in laser problems) one may take $\tilde{\rho}_{\alpha\alpha'}(\vec{R}, \vec{v}, -\infty) = 0$ and allow $\tilde{\Lambda}_{\alpha\alpha'}(\vec{R}, \vec{v}, t)$ to provide the excitation to and $\Gamma_{\alpha\alpha'}(\vec{R}, \vec{v}, t)$ the decay from this subsystem.

IV. INCORPORATION OF COLLISIONS—QUANTUM-MECHANICAL TRANSPORT EQUATION

It may be shown[8] that, in the impact- and binary-collision limits, the time rate of change of $\tilde{\rho}_{\alpha\alpha'}(\vec{R}, \vec{v}, t)$ is given simply by

$$\frac{\partial \tilde{\rho}_{\alpha\alpha'}(\vec{R}, \vec{v}, t)}{\partial t} = \left(\frac{\partial \tilde{\rho}_{\alpha\alpha'}(\vec{R}, \vec{v}, t)}{\partial t}\right)_{\text{no coll}} + \left(\frac{\partial \tilde{\rho}_{\alpha\alpha'}(\vec{R}, \vec{v}, t)}{\partial t}\right)_{\text{coll}}\,, \quad (11)$$

where the "no collision" contribution is specified by Eq. (10), and it remains to evaluate the collisional contribution $(\partial\tilde{\rho}_{\alpha\alpha'}(\vec{R}, \vec{v}, t)/\partial t)_{\text{coll}}$. In general, the collisional interaction will depend upon the atom's electronic wave function [i.e., an active atom may experience a much weaker interaction on collision with a perturber if it (the active atom) is in its ground state rather than an excited state.] Consequently, one must deal with a quantum-mechanical rather than classical treatment of the center-of-mass motion. However, the results of QMII may be used to show that, by studying the collisional changes in the quantum-mechanical density matrix $\tilde{\rho}(\vec{R}, t)$, one can reinterpret the results in terms of a classical density matrix and, in doing so, infer values for $(\partial\tilde{\rho}_{\alpha\alpha'}(\vec{R}, \vec{v}, t)/\partial t)_{\text{coll}}$. An alternative quantum-mechanical calculation which may also be interpreted as providing values for $(\partial\tilde{\rho}_{\alpha\alpha'}(\vec{R}, \vec{v}, t)/\partial t)_{\text{coll}}$ is given in Appendix B. From either calculation, one obtains

$$\left(\frac{\partial \tilde{\rho}_{\alpha\alpha'}(\vec{R}, \vec{v}, t)}{\partial t}\right)_{\text{coll}} = -\gamma^{\text{ph}}_{\alpha\alpha'}(\vec{v})\, \tilde{\rho}_{\alpha\alpha'}(\vec{R}, \vec{v}, t) - \Gamma^{vc}_{\alpha\alpha'}(\vec{v})\, \tilde{\rho}_{\alpha\alpha'}(\vec{R}, \vec{v}, t) + \int d^3v'\, W_{\alpha\alpha'}(\vec{v}' \to \vec{v})\, \tilde{\rho}_{\alpha\alpha'}(\vec{R}, \vec{v}', t)\,, \quad (12)$$

with each of the line-shape parameters $\gamma^{\text{ph}}_{\alpha\alpha'}(\vec{v})$, $\Gamma^{vc}_{\alpha\alpha'}(\vec{v})$, and $W_{\alpha\alpha'}(\vec{v}' \to \vec{v})$ to be discussed below.

The complex line-shape parameter $\gamma^{\text{ph}}_{\alpha\alpha'}(\vec{v})$ is given by

$$\gamma^{\text{ph}}_{\alpha\alpha'}(\vec{v}) = \int d^3v_p\, W_p(\vec{v}_p)\left[\tfrac{1}{2}\Gamma^{\text{ph}}_{\alpha}(\vec{v}_r) + \tfrac{1}{2}\Gamma^{\text{ph}}_{\alpha'}(\vec{v}_r)^* - \mathfrak{N}v_r \int d\Omega_{v_r'} f_\alpha(\vec{v}_r \to \vec{v}_r') f_{\alpha'}(\vec{v}_r \to \vec{v}_r')^*\right]\,, \quad (13)$$

where

$$\Gamma^{\text{ph}}_{\alpha}(\vec{v}_r) = \mathfrak{N}(4\pi\hbar/i\mu) f_\alpha(\vec{v}_r \to \vec{v}_r)\,, \quad \vec{v}_r = \vec{v} - \vec{v}_p\,. \quad (14)$$

$W_p(\vec{v}_p)$ is the perturber velocity distribution, μ is the active atom-perturber reduced mass, $f_\alpha(\vec{v}_r \to \vec{v}_r')$ is the state-α scattering amplitude for a particle of mass μ, $\mathfrak{N}$ is the perturber density, and the superscript ph stands for "phase-shifting collisions." To be quite general, we have assumed $\gamma^{\text{ph}}_{\alpha\alpha'}$ and $\Gamma^{\text{ph}}_{\alpha}$ are functions of the velocity $\vec{v}$. However, if the scattering amplitude $f_\alpha(\vec{v}_r \to \vec{v}_r')$ is a function only of $\vec{v}_r$ and the angle between $\vec{v}_r$ and $\vec{v}_r'$ and, in addition, if W_p is a function of speed only, then $\gamma^{\text{ph}}_{\alpha\alpha'}$ and $\Gamma^{\text{ph}}_{\alpha}$ (as well as $\Gamma^{vc}_{\alpha\alpha'}$, to be discussed below) will be functions of speed rather than velocity. The quantity

$\Gamma^{ph}_{\alpha\alpha'}(\vec{v})$ contains the standard quantum-mechanical width and shift of impact-broadening theory[9] which arises when one considers collisions which induce a relative phase shift between the α- and α'-state amplitudes but result in no change in the velocity associated with $\tilde{\rho}_{\alpha\alpha'}(\vec{R},\vec{v},t)$. Such collisions are termed *phase-shifting collisions* and manifest themselves in the line-shape parameter $\gamma^{ph}_{\alpha\alpha'}(\vec{v})$. Note that $\gamma^{ph}_{\alpha\alpha'}$ affects only off-diagonal density matrix elements since for $\alpha=\alpha'$, $\gamma^{ph}_{\alpha\alpha'}=0$.

The quantity $W_{\alpha\alpha'}(\vec{v}'\to\vec{v})$ is given by

$$W_{\alpha\alpha'}(\vec{v}'\to\vec{v})=\Re(m/\mu)^3\int d^3v_p'\int d^3v_r\; W_p(\vec{v}_p')\,v_r^{-1}\times\delta(\vec{v}_r+(m/m_p)\vec{v}'-(m/\mu)\vec{v}+\vec{v}_p')\,\delta(v_r-v_r')\times f_\alpha(\vec{v}_r'\to\vec{v}_r)\,f_{\alpha'}(\vec{v}_r'\to\vec{v}_r)^*\,, \quad (15)$$

where

$$\vec{v}_r'=\vec{v}'-\vec{v}_p'\,,$$

and m and m_p are the active-atom and perturber-atom masses, respectively. If $\alpha=\alpha'$, $W_{\alpha\alpha}(\vec{v}'\to\vec{v})$ is real and represents the quantum-mechanical probability density or collision kernel for a collision to change the velocity associated with an atom in state α from $\vec{v}'$ to $\vec{v}$. However, if $\alpha\neq\alpha'$, $W_{\alpha\alpha'}(\vec{v}'\to\vec{v})$ is complex and possesses no simple physical interpretation of which we are aware. For this case, one might write

$$W_{\alpha\alpha'}(\vec{v}'\to\vec{v})=|W_{\alpha\alpha'}(\vec{v}'\to\vec{v})|\,e^{i\chi_{\alpha\alpha'}(\vec{v}'\to\vec{v})}$$

with $\chi_{\alpha\alpha'}(\vec{v}'\to\vec{v})$ a real phase shift. In this form, $W_{\alpha\alpha'}(\vec{v}'\to\vec{v})$ appears to be the product of a real collision kernel $|W_{\alpha\alpha'}(\vec{v}'\to\vec{v})|$ and a correlated effective average phase-shift factor $e^{i\chi_{\alpha\alpha'}(\vec{v}'\to\vec{v})}$ so that one could say that the complex "kernel" $W_{\alpha\alpha'}(\vec{v}'\to\vec{v})$ is related to collisions that simultaneously result in a phase shift for and change in the velocity associated with $\tilde{\rho}_{\alpha\alpha'}(\vec{R},\vec{v},t)$. Unfortunately we have found no simple classical analogs for either $|W_{\alpha\alpha'}(\vec{v}'\to\vec{v})|$ or $\chi_{\alpha\alpha'}(\vec{v}'\to\vec{v})$ so that the usefulness of this interpretation is questionable.

The line-shape parameter $\Gamma^{vc}_{\alpha\alpha'}(\vec{v})$ is

$$\Gamma^{vc}_{\alpha\alpha'}(\vec{v})=\int d^3v'\;W_{\alpha\alpha'}(\vec{v}\to\vec{v}')=\Re\int d^3v_p\;W_p(\vec{v}_p)\,v_r\;\sigma_{\alpha\alpha'}(\vec{v}_r)\,, \quad (16)$$

where

$$\sigma_{\alpha\alpha'}(\vec{v}_r)=\int d\Omega_{v_r'}\,f_\alpha(\vec{v}_r\to\vec{v}_r')\,f_{\alpha'}(\vec{v}_r\to\vec{v}_r')^* \quad (16a)$$

and

$$\vec{v}_r=\vec{v}-\vec{v}_p\,.$$

For $\alpha=\alpha'$, $\Gamma^{vc}_{\alpha\alpha}(\vec{v})$ is real and is just the rate at which velocity changing collisions occur for atoms in state α moving with velocity $\vec{v}$. For $\alpha\neq\alpha'$, $\Gamma^{vc}_{\alpha\alpha'}(\vec{v})$ is a complex "rate" and lacks a simple interpretation in the same sense as did $W_{\alpha\alpha'}(\vec{v}'\to\vec{v})$ for $\alpha\neq\alpha'$.

We should note that it is possible to separate those velocity changing collisions which significantly alter $\tilde{\rho}_{\alpha\alpha'}(\vec{R},\vec{v},t)$ from those which do not. The benefits of this cutoff procedure which was used in QMI and QMII, and the necessary alterations of the equations which it entails are discussed in Appendix C.

Although Eqs. (13)–(16) lend themselves to a first-principle calculation of the line-shape parameters, it would be very difficult to perform such a calculation since a knowledge of all the quantum-mechanical scattering amplitudes is needed. Methods for simplifying the evaluation of the line-shape parameters will be given later in this section.

When Eqs. (10) and (12) are inserted into Eq. (11), we arrive at the QMTE:

$$\frac{\partial\tilde{\rho}_{\alpha\alpha'}(\vec{R},\vec{v},t)}{\partial t}+\vec{v}\cdot\vec{\nabla}\tilde{\rho}_{\alpha\alpha'}(\vec{R},\vec{v},t)=\tilde{\Lambda}_{\alpha\alpha'}(\vec{R},\vec{v},t)-\Gamma_{\alpha\alpha'}(\vec{R},\vec{v},t)\,\tilde{\rho}_{\alpha\alpha'}(\vec{R},\vec{v},t)+(i\hbar)^{-1}[\tilde{V}(\vec{R},t),\,\tilde{\rho}(\vec{R},t)]_{\alpha\alpha'}$$
$$-\gamma^{ph}_{\alpha\alpha'}(\vec{v})\,\tilde{\rho}_{\alpha\alpha'}(\vec{R},\vec{v},t)-\Gamma^{vc}_{\alpha\alpha'}(\vec{v})\,\tilde{\rho}_{\alpha\alpha'}(\vec{R},\vec{v},t)+\int d^3v'\;W_{\alpha\alpha'}(\vec{v}'\to\vec{v})\,\tilde{\rho}_{\alpha\alpha'}(\vec{R},\vec{v}',t), \quad (17)$$

in which the contributions to $\partial\tilde{\rho}_{\alpha\alpha'}(\vec{R},\vec{v},t)/\partial t$ due to convective flow, injection, phenomenological loss, external-field interaction, and collisional interactions have already been discussed. As can be seen from the equation, a velocity is associated with each density matrix element rather than with the atom as a whole. This feature is a direct consequence of the quantum-mechanical treatment of state-dependent collisional interactions. Since collisional interaction is different for the different electronic states, the velocity changes associated with different density matrix elements will also differ, rendering it impossible to assign a single velocity to an entire atom which has undergone a collision. Equation (17) is the basic result of this paper and provides the starting point for calculations involving the interaction of radiation fields with atoms, allowing for collisions of the atoms. It has been derived and is valid under the approximations of Sec. II. We shall discuss some applications of the equation in Sec. VI. For most problems, it will be all but impossible to solve the QMTE unless additional approximations are incorporated.

We now list some conditions under which it will be possible to simplify the expression for the line-shape parameters which appear in Eq. (17).

a. Collisional interaction in one state only. In some instances, only one of the states under consideration may experience a strong collisional interaction. (For example, in atomic absorption or emis-

sion experiments involving a transition between the ground and an excited state of an atom, the collisional interaction in the ground state may be neglected in first approximation.) Labeling the strongly interacting state "a", Eqs. (13)–(16) become, in this limit,

$$\gamma^{ph}_{\alpha\alpha'}(\vec{v}) = (\delta_{\alpha a} - \delta_{\alpha' a}) \int d^3v_p \, W(\vec{v}_p) \times [\tfrac{1}{2}\Gamma^{ph}_{\alpha}(\vec{v} - \vec{v}_p) - \tfrac{1}{2}\Gamma^{ph}_{\alpha'}(\vec{v} - \vec{v}_p)^*] , \quad (18a)$$

$$W_{\alpha\alpha'}(\vec{v}' \to \vec{v}) = W_{\alpha\alpha}(\vec{v}' \to \vec{v}) \delta_{\alpha a} \delta_{\alpha' a} , \quad (18b)$$

$$\Gamma^{vc}_{\alpha\alpha'}(\vec{v}) = \Gamma^{vc}_{\alpha\alpha}(\vec{v}) \delta_{\alpha a} \delta_{\alpha' a} , \quad (18c)$$

with both $W_{\alpha\alpha}(\vec{v}' \to \vec{v})$ and $\Gamma^{vc}_{\alpha\alpha}(\vec{v})$ real. Under these circumstances there are no collisional velocity changes associated with off-diagonal density matrix elements. The simplifications and consequences of this feature have been discussed in QMII. In general, one might try this approach as a first approximation when dealing with transitions between two electronic levels since it is likely that one of these levels experiences a significantly stronger collisional interaction than the other.[10]

b. Equal collisional interaction for all states. The other extreme, valid to a first approximation when all the states under consideration belong to the same electronic level (as do different vibrational states of a molecule) is to take the collisional interaction equal for all the states. In that case, $\gamma^{ph}_{\alpha\alpha'}(\vec{v}) = 0$ and both $W_{\alpha\alpha'}(\vec{v}' \to \vec{v})$ and $\Gamma^{vc}_{\alpha\alpha'}(\vec{v})$ are real and independent of α and α'. This is a true transport-equation limit since the collisional interaction is no longer state dependent and one can associate a velocity with the entire atom rather than with individual density matrix elements.

c. Classical limits. Since we are dealing with atoms, it is usually valid to evaluate Eqs. (13)–(16) in some classical limit. The prescribed method for taking the classical limit would be to evaluate the scattering amplitudes that appear in Eqs. (13)–(16) in either the WKB or eikonal approximation. Of course, to perform such a calculation, a knowledge of the emitter-perturber interaction is needed and this, by itself may constitute a very difficult auxiliary problem.

An alternative method of calculation is to use the standard classical expression[11] for $\gamma^{ph}_{\alpha\alpha'}(\vec{v})$ given by

$$\gamma^{ph}_{\alpha\alpha'}(\vec{v}) = \mathfrak{N} \int d^3v_p \, W_p(\vec{v}_p) |\vec{v} - \vec{v}_p| \int 2\pi b \, db \times \{\exp[i\chi_\alpha(b, \vec{v} - \vec{v}_p) - i\chi_{\alpha'}(b, \vec{v} - \vec{v}_p)] - 1\} , \quad (19)$$

where $\chi_\alpha(b, \vec{v}_r)$ and $\chi_{\alpha'}(b, \vec{v}_r)$ are the phase shifts produced in the α and α' levels, respectively, by a collision with impact parameter b and relative velocity $\vec{v}_r$. The line-shape parameters $W_{\alpha\alpha}(\vec{v}' \to \vec{v})$ and $\Gamma^{vc}_{\alpha\alpha}(\vec{v})$ may be obtained by determining a classical kernel for the collisional interaction experienced by an atom in state α. There is still the problem of evaluating $W_{\alpha\alpha'}(\vec{v}' \to \vec{v})$ and $\Gamma^{vc}_{\alpha\alpha'}(\vec{v})$ for $\alpha \neq \alpha'$ since these quantities have no simple classical analogs. Hence, unless approximations (a) or (b) above may be used, $W_{\alpha\alpha'}(\vec{v}' \to \vec{v})$ and $\Gamma^{vc}_{\alpha\alpha'}(\vec{v})$ must still be evaluated by either the WKB or eikonal methods for $\alpha \neq \alpha'$.

d. Other approximations. The classical limit described above still leaves formidable calculations in most cases. As a first attempt in understanding the role of collisions, some coarser approximations may be used. For example, phenomenological values for $W_{\alpha\alpha'}(\vec{v}' \to \vec{v})$ and $\Gamma^{vc}_{\alpha\alpha}(\vec{v})$ may be used in conjunction with either approximations (a) or (b) above. These values may be based on either "strong" or "weak" collisional models.[12] There is the danger that some collisional effects may be lost if such models are employed.

It may also be possible to do perturbation expansions with the line-shape parameters. That is, if one is dealing with transitions between different electronic states where approximation (a) is thought to be good, he could assume $W_{\alpha\alpha'}(\vec{v}' \to \vec{v})$ and $\Gamma^{vc}_{\alpha\alpha'}(\vec{v})$ are small for $\alpha \neq \alpha'$, make some estimate of their value, and keep only leading terms in these quantities when solving Eq. (17). On the other hand, if approximation (b) is thought to be applicable, then, for $\alpha \neq \alpha'$, $\gamma^{ph}_{\alpha\alpha'}(\vec{v})$, $W_{\alpha\alpha'}(\vec{v}' \to \vec{v}) - W_{\alpha\alpha}(\vec{v}' \to \vec{v})$, and $\Gamma^{vc}_{\alpha\alpha'}(\vec{v}) - \Gamma^{vc}_{\alpha\alpha}(\vec{v})$ should be taken as small quantities in attempts to solve Eq. (17). Each problem must be considered separately to determine the manner of getting maximal information with minimal effort.

V. EXTENSIONS OF THE THEORY

The theory may be extended by relaxing some of the approximations of Sec. II. The numbered paragraphs below correspond to similar paragraphs in Sec. II, where the approximations were listed.

(1) and (2) Because of the ultimate importance of the binary collision and impact approximations in this theory, we feel that another approach would be needed if either of these approximations fails.

(3) In this paper, we have not allowed for any collision-induced transitions. While collisions cannot, in general, produce transitions between optically separated levels, they may cause rearrangement of magnetic, fine structure, or rotational substate populations of a given electronic level of an atom or molecule. Thus, it is highly desirable to include rearrangement or inelastic collision effects in the QMTE and we hope to perform such a calculation in the near future. The major problem involved is keeping track of the center-of-mass velocity associated with each of the substate density matrix elements. It may turn out that, on average, the velocity associated with each substate density matrix element is the same after the collision. In that case, the inclusion of rearrangement effects could

be done in the same manner as for stationary active atoms.[8] However, it remains to be seen whether or not the actual calculation will yield such a simple result.

(4) If one wished to allow for resonant excitation transfer in collisions, he would have to study the quantum-mechanical problem of the collision of two atoms which may exchange excitation as a result of the collision. A study of the change in each atom's reduced density matrix resulting from the collision may then yield an interpretation in the change of the classical density matrix $\tilde{\rho}_{\alpha\alpha'}(\vec{R}, \vec{v}, t)$.

(5) In situations where atoms were excited coherently (in the sense that the density matrix of a given atom just after excitation was not independent of the density matrices of the other atoms of the ensemble), one would have to deal with the ensemble density matrix of the system and then perform the appropriate traces to get the reduced density matrices of individual atoms. Similarly, if one allowed for excitation by radiation trapping, the excitation mechanism would depend on previous values of the density matrix. A method for incorporating radiation trapping into the equation for $\tilde{\rho}_{\alpha\alpha'}(\vec{R}, \vec{v}, t)$ by means of an integral term has been given by Dyakonov and Perel,[13] and they have also noted that such effects may lead to modifications of laser line shapes.[14]

(6) We have assumed that the external field does not affect the center-of-mass motion. The effects of an external field that affects the center-of-mass motion in a state-independent manner (i.e., a constant electric field acting on an ion) may be easily incorporated into the QMTE by addition to the left-hand side of Eq. (17) a convective term

$$m^{-1}\vec{F}(\vec{R}, t)\cdot\vec{\nabla}_v\tilde{\rho}_{\alpha\alpha'}(\vec{R}, \vec{v}, t)$$

in which $\vec{F}(\vec{R}, t)$ is the force associated with the external field, and $\vec{\nabla}_v$ is the gradient with respect to velocity. However, if the external–field-atom interaction were state dependent, a quantum calculation of its effect would be necessary after which it might be possible to reinterpret the results in terms of a classical density matrix $\tilde{\rho}_{\alpha\alpha'}(\vec{R}, \vec{v}, t)$, as was done for the collision case. An alternative approach for treating such fields as well as photon recoil effects is through Wigner of quantum "distribution" functions.[6,15] Care must be taken in the use and interpretation of these functions since they are not positive definite and, consequently, cannot be regarded as true distribution functions.

Of course, inclusion of any of the above extensions will complicate the theory. The nature of the specific problem and effects under consideration will determine which, if any, of these extensions need be incorporated into the theory.

VI. DISCUSSION

In this paper we have derived a pseudoclassical or QMTE for the macroscopic density matrix of an atomic system subject to the restrictions of Sec. II. This treatment differs from that of QMI and QMII since the theory is no longer presented as a perturbation expansion in the external field. In addition, we have directly allowed for collisional interaction in more than one state in deriving the QMTE while the calculation of QMII stressed the limiting case of collisional interaction in one state only.

By working with the macroscopic density matrix, we have obtained a rather compact differentointegral equation for its time development, in contrast to the somewhat complex equations encountered in using the pseudoclassical collision model (PCM) of QMII to follow the microscopic density matrix's time development. It should be noted, however, that the PCM does provide a greater physical "feel" and understanding for the problem under consideration.

As noted in the Introduction, a knowledge of the macroscopic density matrix is usually sufficient to obtain theoretical values for many experimentally measurable quantities. If one is dealing with weak external fields, he would probably try to solve the QMTE by an iterative approach, and this procedure would, in effect, be equivalent to using the PCM. For strong external fields the PCM is less suitable and the QMTE should provide the starting point for the calculations. It is hoped that one will be able to use the QMTE to solve problems involving the interaction of high-intensity laser fields with atomic systems in which collisions play a significant role. Naturally, *any* solutions of the QMTE are difficult to obtain and, most likely, one will have to use very simple collision models in the first attempts at these calculations. Another use of the QMTE is the evaluation of atomic spectral profiles. Here it turns out that the calculations are quite feasible but that results are more easily achieved by use of the PCM of QMII. The details of the calculations will be presented in a subsequent work.

The applicability of the QMTE will be enhanced if it is extended to include collision-induced transitions, and some work along this line would definitely be appropriate. Even as it stands, the QMTE should provide a useful starting point for solving a certain class of problems in atomic physics.

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APPENDIX A: CLASSICAL LIMIT OF EQ. (4)

Starting with Eqs. (4) and (5) of the text (dropping the j subscripts),

$$\frac{i\hbar\partial\tilde{\rho}_{\alpha\alpha'}(\vec{R}, t)}{\partial t} = -i\hbar\vec{\nabla}\cdot\tilde{\vec{J}}_{\alpha\alpha'}(\vec{R}, t) + [\tilde{V}(\vec{R}, t), \tilde{\rho}(\vec{R}, t)]_{\alpha\alpha'}, \quad \text{(A1)}$$

with

$$\vec{\tilde{J}}_{\alpha\alpha'}(\vec{R},t)=\hbar(2mi)^{-1}\left[A_{\alpha'}(\vec{R},t)^*\vec{\nabla}A_\alpha(\vec{R},t)-A_\alpha(\vec{R},t)\vec{\nabla}A_{\alpha'}(\vec{R},t)^*\right]e^{i\omega_{\alpha\alpha'}t}\ , \quad \text{(A2)}$$

we wish to determine a classical limit for this equation when such a limit does, in fact, exist. The quantity $\tilde{\rho}_{\alpha\alpha'}(\vec{R},t)$ is the density matrix element of an atom which is interacting with an external field (but not undergoing collisions). If we are to consider this atom as a classical particle, it must be localized in space. The only way this atom can remain localized in space is if the external field affects the center-of-mass motion in a state independent manner. Otherwise, the field would be constantly acting as a state selector, and the atom would disperse. Since an assumption of our theory is that $V(\vec{R},t)$ does not affect the center-of-mass motion at all, this problem does not enter our considerations, and we are able to look for a classical limit to Eq. (A1).

Let us first consider the current $\vec{\tilde{J}}_{\alpha\alpha'}(\vec{R},t)$. Recalling that the function $A_\alpha(\vec{R},t)$ as given in Eq. (2) is analogous to the wave function in (center-of-mass) coordinate space for an atom in state α, we write $A_\alpha(\vec{R},t)$ in terms of the corresponding momentum-state wave function. That is,

$$A_\alpha(\vec{R},t)=(2\pi\hbar)^{-3/2}\int d^3P\ \varphi_\alpha(\vec{P},t)e^{(i/\hbar)\vec{P}\cdot\vec{R}} \quad \text{(A3)}$$

which leads to the value

$$\vec{\nabla}A_\alpha(\vec{R},t)=(i/\hbar)(2\pi\hbar)^{-3/2}\int d^3P\ \vec{P}\varphi_\alpha(\vec{P},t)e^{(i/\hbar)\vec{P}\cdot\vec{R}}\ . \quad \text{(A4)}$$

The average momentum of the packet is given by

$$\langle\vec{P}\rangle_t=\int d^3P\ \vec{P}\,|\varphi_\alpha(\vec{P},t)|^2\ , \quad \text{(A5)}$$

where the t subscript is a reminder that $\langle\vec{P}\rangle_t$ is an explicit function of time. The fact that $\langle\vec{P}\rangle_t$ is independent of α is a consequence of the assumption that all states follow the same center-of-mass trajectories. Setting $\vec{P}=\langle\vec{P}\rangle_t+\vec{P}-\langle\vec{P}\rangle_t$ in Eq. (A4) and using Eq. (A3), we obtain

$$\vec{\nabla}A_\alpha(\vec{R},t)=(i/\hbar)\langle\vec{P}\rangle_t A_\alpha(\vec{R},t)+(i/\hbar)(2\pi\hbar)^{-3/2}\times\int d^3P(\vec{P}-\langle\vec{P}\rangle_t)\varphi_\alpha(\vec{P},t)e^{(i/\hbar)\vec{P}\cdot\vec{R}}\ . \quad \text{(A6)}$$

Since we are seeking a classical limit, we assume that $\varphi_\alpha(\vec{P},t)$ is a sharply peaked function centered about $\langle\vec{P}\rangle_t$ so that the integral term in Eq. (A6) may be neglected. In this limit, Eq. (A2) for the current becomes

$$\vec{\tilde{J}}_{\alpha\alpha'}(\vec{R},t)=m^{-1}\langle\vec{P}\rangle_t\tilde{\rho}_{\alpha\alpha'}(\vec{R},t)\ , \quad \text{(A7)}$$

where Eq. (3) has been used.

The next step is to eliminate the quantum variable $\vec{R}$ appearing in Eq. (A1) in favor of a classical variable $\langle\vec{R}\rangle$. Since the center-of-mass motion for all the states is assumed to be identical, one may write

$$\tilde{\rho}_{\alpha\alpha'}(\vec{R},t)=\tilde{\rho}_{\alpha\alpha'}(t)\,\Phi(\vec{R},t)\ , \quad \text{(A8)}$$

where $\Phi(\vec{R},t)$, which gives the α-independent spatial extent of the packet, is normalized in the sense that

$$\int d^3R\ \Phi(\vec{R},t)=1\ , \quad \text{(A9)}$$

where the integral is over a small region of space containing the packet. The packet is assumed to be localized in space about

$$\langle\vec{R}\rangle=\int d^3R\ \vec{R}\,\Phi(\vec{R},t)\ ,$$

and we expand both $\tilde{\rho}(\vec{R},t)$, $\tilde{V}(\vec{R},t)$, and $\vec{\tilde{J}}_{\alpha\alpha'}(\vec{R},t)$ about this value, i.e.,

$$\tilde{\rho}(\vec{R},t)=\tilde{\rho}(\langle\vec{R}\rangle,t)+(\vec{R}-\langle\vec{R}\rangle)\cdot\vec{\nabla}\tilde{\rho}(\langle\vec{R}\rangle,t)+\cdots\ , \quad \text{(A10a)}$$

$$\tilde{V}(\vec{R},t)=\tilde{V}(\langle\vec{R}\rangle,t)+(\vec{R}-\langle\vec{R}\rangle)\cdot\vec{\nabla}\tilde{V}(\langle\vec{R}\rangle,t)+\cdots\ , \quad \text{(A10b)}$$

$$\vec{\tilde{J}}_{\alpha\alpha'}(\vec{R},t)=\vec{\tilde{J}}_{\alpha\alpha'}(\langle\vec{R}\rangle,t)+[(\vec{R}-\langle\vec{R}\rangle)\cdot\vec{\nabla}]\times\vec{\tilde{J}}_{\alpha\alpha'}(\langle\vec{R}\rangle,t)+\cdots\ . \quad \text{(A10c)}$$

Substituting these expansions into Eq. (A1), using Eq. (A7) for $\vec{\tilde{J}}_{\alpha\alpha'}(\vec{R},t)$, multiplying the entire equation by $\Phi(\vec{R},t)$, integrating the resultant equation over a spatial region containing the packet, and keeping only the leading terms of the expansion, we obtain

$$\frac{\partial\tilde{\rho}_{\alpha\alpha'}(\langle\vec{R}\rangle,t)}{\partial t}=-\frac{\langle\vec{P}\rangle_t}{m}\cdot\vec{\nabla}\tilde{\rho}_{\alpha\alpha'}(\langle\vec{R}\rangle,t)+(i\hbar)^{-1}\left[\tilde{V}(\langle\vec{R}\rangle,t),\ \tilde{\rho}(\langle\vec{R}\rangle,t)\right]_{\alpha\alpha'}\ . \quad \text{(A11)}$$

It is important to note that, in deriving this equation, we have treated $\langle\vec{R}\rangle$ as an independent variable while $\langle\vec{P}\rangle_t$ is an explicit function of time. The density matrix in phase space is simply given by

$$\tilde{\rho}(\langle\vec{R}\rangle,\langle\vec{P}\rangle,t)=\tilde{\rho}(\langle\vec{R}\rangle,t)\,\delta(\langle\vec{P}\rangle-\langle\vec{P}\rangle_t), \quad \text{(A12)}$$

where $\langle\vec{P}\rangle$ is also an independent variable. Using Eq. (A11) and (A12), it is an easy matter to show that $\tilde{\rho}_{\alpha\alpha'}(\langle\vec{R}\rangle,\langle\vec{P}\rangle,t)$ satisfies the equation

$$\frac{\partial\tilde{\rho}_{\alpha\alpha'}(\langle\vec{R}\rangle,\langle\vec{P}\rangle,t)}{\partial t}=-\frac{\langle\vec{P}\rangle}{m}\cdot\vec{\nabla}\tilde{\rho}_{\alpha\alpha'}(\langle\vec{R}\rangle,\langle\vec{P}\rangle,t)+\frac{d\langle\vec{P}\rangle_t}{dt}\cdot\vec{\nabla}_{\langle\vec{P}\rangle}\tilde{\rho}_{\alpha\alpha'}(\langle\vec{R}\rangle,\langle\vec{P}\rangle,t)+(i\hbar)^{-1}\times\left[\tilde{V}(\langle\vec{R}\rangle,\langle\vec{P}\rangle,t),\ \tilde{\rho}(\langle\vec{R}\rangle,\langle\vec{P}\rangle,t)\right]_{\alpha\alpha'}\ . \quad \text{(A13)}$$

Taking $d\langle\vec{P}\rangle_t/dt=0$ as we have assumed and changing variables from $\langle\vec{R}\rangle$, $\langle\vec{P}\rangle$ to $\vec{R}$, $\vec{P}$, one arrives at Eq. (7) of the text.

One can show that the errors introduced by neglecting the integral term in Eq. (A6) as well as higher-order terms in the expansions (10) will be small provided the de Broglie wavelength of an atom is much smaller than the characteristic spatial variations of $\tilde{\rho}(\vec{R},t)$ and $\tilde{V}(\vec{R},t)$. Thus, Eq. (A13) will be valid if most of the ensemble atoms

possess this property.

We should point out that the entire approach of this section will fail if the external potential affects the center-of-mass motion in a state-dependent manner.[16] In Appendix B, it will be shown that collisions act in precisely this way. However, the purpose of this section was to derive an equation for $\tilde{\rho}_{\alpha\alpha'}(\vec{R}, \vec{P}, t)$ that was valid in the time interval *between* collisions, in which the classical limit, as discussed in this section, is, in fact, valid.

APPENDIX B: DERIVATION OF $(\partial\tilde{\rho}(\vec{R}, \vec{v}, t)/\partial t)_{coll}$

Although the value for $(\partial\tilde{\rho}(\vec{R}, \vec{v}, t)/\partial t)_{coll}$ given in Eq. (12) may be inferred from the results of QMII, we thought it might prove useful to indicate an alternative derivation which involves computing the change in the density matrix resulting from a single collision. Both developments depend strongly on the binary-collision and impact approximations for their validity.

As mentioned in the text, we must perform a quantum-mechanical calculation for the state-dependent collisional interaction. To examine the role of collisions, the effects of the external field are ignored in this calculation and the Hamiltonian for the jth atom is (again the label j is suppressed)

$$H(\vec{r}, \vec{R}) = H_0(\vec{r}) + \vec{P}^2/2m + U(\vec{r}, \vec{R}) , \tag{B1}$$

where $U(\vec{r}, \vec{R})$ is the potential due to a single perturber *fixed* at the origin of the coordinate system. (For simplicity, the case of a fixed perturber is treated. Generalization to the case of moving perturbers is discussed later on in this Appendix.)

The wave function is expanded as

$$\psi(\vec{r}, \vec{R}, \hat{t}) = \sum_\alpha \tilde{A}_\alpha(\vec{R}, \hat{t})\psi_\alpha(\vec{r})\, e^{-i\omega_\alpha t} , \tag{B2}$$

and, using Schrödinger's equation, it is easy to show that $\tilde{A}_\alpha(\vec{R}, t)$ obeys the equation

$$\frac{i\hbar\partial\tilde{A}_\alpha(R, \hat{t})}{\partial\hat{t}} = -\frac{\hbar^2}{2m}\nabla^2\tilde{A}_\alpha(\vec{R}, \hat{t}) + U_{\alpha\alpha}(\vec{R})\tilde{A}_\alpha(\vec{R}, \hat{t}) , \tag{B3}$$

where

$$U_{\alpha\alpha}(\vec{R}) = \int d^3r\, \psi_\alpha(\vec{r})\, U(\vec{r}, \vec{R})\psi_\alpha(\vec{r})^* , \tag{B4}$$

and we have used the fact that there are no collision-induced transitions to take U as diagonal in the atomic states. One can see that each $\tilde{A}_\alpha(\vec{R}, \hat{t})$ obeys its own Schrödinger equation with potential $U_{\alpha\alpha}(\vec{R})$. Hence, we can do a conventional scattering calculation for each $\tilde{A}_\alpha(\vec{R}, \hat{t})$ and then form the appropriate density matrix elements. Let us assume that the collision occurs at $\hat{t} = t$ and that at $\hat{t} = t - \delta t$ each $\tilde{A}_\alpha(\vec{R}, t - \delta t)$ describes a wave packet of cross-sectional area σ which is moving towards the scattering center with average velocity $\vec{v}'$ and has extent w in $\hat{v}'$ direction. The size of this wave packet is large compared to the scattering center (so it won't spread significantly) but still localized well enough in space for a classical limit to be applicable in the sense of Appendix A. At $\hat{t} = t - \delta t$, the packet is centered about $\vec{R}_0 = -\vec{v}'\delta t$ and is assumed to be well isolated from the scattering center as well as from other perturbers. For this situation to exist, the binary-collision approximation must be applicable.

By using conventional time-dependent scattering theory,[17] one may show that, at time $\hat{t} = t + \delta t$ (after the collision)

$$\tilde{A}_\alpha(\vec{R}, t + \delta t) = \exp[-(imv'^2/2\hbar)(2\delta t)]\left(\tilde{A}_\alpha(\vec{R} - 2\vec{v}'\delta t, t - \delta t) + \frac{f_\alpha(\vec{v}' \to v'\hat{R})}{R}\tilde{A}_\alpha(R\hat{v}' - 2\vec{v}'\delta t, t - \delta t)\right) , \tag{B5}$$

where $f_\alpha(\vec{v}' \to v'\hat{R})$ is the state-α scattering amplitude. The two terms in Eq. (B5) simply represent the unscattered and scattered packets, respectively. The scattered packet is confined to a spherical shell of width w centered about $R = v'\delta t$.

The density matrix elements are given as

$$\tilde{\rho}_{\alpha\alpha'}(\vec{R}, t) = \tilde{A}_\alpha(\vec{R}, t)\tilde{A}_{\alpha'}(\vec{R}, t)^* , \tag{B6}$$

and one may calculate the change in the density matrix elements resulting from the collision

$$\begin{aligned}\delta\tilde{\rho}_{\alpha\alpha'}(\vec{R}, t, \delta t) &= \tilde{\rho}_{\alpha\alpha'}(\vec{R}, t + \delta t) - \tilde{\rho}_{\alpha\alpha'}(\vec{R}, t - \delta t)\\ &= \tilde{\rho}_{\alpha\alpha'}(\vec{R} - 2\vec{v}'\delta t, t - \delta t) - \tilde{\rho}_{\alpha\alpha'}(\vec{R}, t - \delta t) + R^{-1}f_{\alpha'}(\vec{v}' \to v'\hat{R})^*\tilde{A}_\alpha(\vec{R} - 2\vec{v}'\delta t, t - \delta t)\tilde{A}_{\alpha'}(R\hat{v}' - 2\vec{v}'\delta t, t - \delta t)^*\\ &\quad + R^{-1}f_\alpha(\vec{v}' \to v'\hat{R})\tilde{A}_\alpha(R\hat{v}' - 2\vec{v}'\delta t, t - \delta t)\tilde{A}_{\alpha'}(\vec{R} - 2\vec{v}'\delta t, t - \delta t)^*\\ &\quad + R^{-2}f_\alpha(\vec{v}' \to v'\hat{R})f_{\alpha'}(\vec{v}' \to v'\hat{R})^*\tilde{\rho}_{\alpha\alpha'}(R\hat{v}' - 2\vec{v}'\delta t, t - \delta t) .\end{aligned} \tag{B7}$$

We must now interpret this result. The first step is to set $[\tilde{\rho}_{\alpha\alpha'}(\vec{R} - 2\vec{v}'\delta t, t - \delta t) - \tilde{\rho}_{\alpha\alpha'}(\vec{R}, t - \delta t)]$ equal to zero since, in the limit $\delta t \Rightarrow 0$, this term represents no change in the velocity, position, or density matrix element value associated with the packet. The other terms in Eq. (B7) contain scattering amplitudes

and may be thought to exhibit an "instantaneous" change in the velocity or value associated with each density matrix element due to the collision. To get the amount of density matrix element associated with a range of velocities centered about $\vec{v}=v'\hat{R}$ (note that $v=v'$ since the perturber is fixed and the collision elastic), one must multiply each of the terms on the right-hand side of Eq. (B7) by $R^2d\Omega/\sigma$, which is the area associated with this solid angle Ω_v normalized to the cross-sectional area of the initial packet. Ascribing the classical variable $\vec{v}$ to scattering in this direction, one may rewrite Eq. (B7) as

$$\delta\tilde{\rho}_{\alpha\alpha'}(\vec{R},\vec{v},t,\delta t)\,d\Omega_v = R\sigma^{-1}f_{\alpha'}(\vec{v}'\to\vec{v})^*\tilde{A}_\alpha(\vec{R}-2\vec{v}'\delta t,t-\delta t)\tilde{A}_{\alpha'}(R\hat{v}'-2\vec{v}'\delta t,t-\delta t)^*d\Omega_v$$
$$+R\sigma^{-1}f_\alpha(\vec{v}'\to\vec{v})\tilde{A}_\alpha(R\hat{v}'-2\vec{v}'\delta t,t-\delta t)\tilde{A}_{\alpha'}(\vec{R}-2\vec{v}'\delta t,t-\delta t)^*d\Omega_v$$
$$+\sigma^{-1}f_\alpha(\vec{v}'\to\vec{v})f_{\alpha'}(\vec{v}'\to\vec{v})^*\tilde{\rho}_{\alpha\alpha'}(R\hat{v}'-2\vec{v}'\delta t,t-\delta t)\,d\Omega_v\,. \quad \text{(B8)}$$

All the terms in the right-hand side of this equation relating to $\tilde{A}_\alpha(\vec{R},t-\delta t)$ correspond to the *initial* packet which had velocity $\vec{v}'$ associated with it. Explicitly, indicating $\vec{v}'$ as a variable and dropping the $d\Omega_v$, one obtains

$$\delta\tilde{\rho}_{\alpha\alpha'}(\vec{R},\vec{v},\vec{v}',t,\delta t)=R\sigma^{-1}f_{\alpha'}(\vec{v}'\to\vec{v})^*\tilde{A}_\alpha(\vec{R}-2\vec{v}'\delta t,\vec{v}',t-\delta t)\tilde{A}_{\alpha'}(R\hat{v}'-2\vec{v}'\delta t,\vec{v}',t-\delta t)^*$$
$$+R\sigma^{-1}f_\alpha(\vec{v}'\to\vec{v})\tilde{A}_\alpha(R\hat{v}'-2\vec{v}'\delta t,\vec{v}',t-\delta t)\tilde{A}_{\alpha'}(\vec{R}-2\vec{v}'\delta t,\vec{v}',t-\delta t)^*$$
$$+\sigma^{-1}f_\alpha(\vec{v}'\to\vec{v})f_{\alpha'}(\vec{v}'\to\vec{v})^*\tilde{\rho}_{\alpha\alpha'}(R\hat{v}'-2\vec{v}'\delta t,\vec{v}',t-\delta t)\,. \quad \text{(B9)}$$

To get an average $\delta\tilde{\rho}(\vec{R},\vec{v},t,\delta t)$, one must allow for all directions $\vec{v}'$ of incidence for the packet. Performing this average, we find that

$$\delta\tilde{\rho}_{\alpha\alpha'}(\vec{R},\vec{v},t,\delta t)=\langle\delta\tilde{\rho}_{\alpha\alpha'}(\vec{R},\vec{v},\vec{v}',t,\delta t)\rangle$$
$$=R\sigma^{-1}\int d\Omega_{v'}\,f_{\alpha'}(\vec{v}'\to\vec{v})^*\tilde{A}_\alpha(\vec{R}-2\vec{v}'\delta t,\vec{v}',t-\delta t)\tilde{A}_{\alpha'}(R\hat{v}'-2\vec{v}'\delta t,\vec{v}',t-\delta t)^*$$
$$+R\sigma^{-1}\int d\Omega_{v'}f_\alpha(\vec{v}'\to\vec{v})\tilde{A}_\alpha(R\hat{v}'-2\vec{v}'\delta t,\vec{v}',t-\delta t)\tilde{A}_{\alpha'}(\vec{R}-2\vec{v}'\delta t,\vec{v}',t-\delta t)^*$$
$$+\sigma^{-1}\int d\Omega_{v'}\,f_\alpha(\vec{v}'\to\vec{v})\,f_{\alpha'}(\vec{v}'\to\vec{v})^*\tilde{\rho}_{\alpha\alpha'}(R\hat{v}'-2\vec{v}'\delta t,\vec{v}',t-\delta t)\,. \quad \text{(B10)}$$

The integration in the first two terms is the same type that appears in derivations of the optical theorem.[17] One makes use of the fact that there is rapid interference in all but the $\hat{v}'=\hat{v}$ direction to evaluate these terms, and when the results of this calculation are inserted into Eq. (B10), it becomes

$$\delta\tilde{\rho}_{\alpha\alpha'}(\vec{R},\vec{v},t,\delta t)=-\sigma^{-1}[(2\pi\hbar/imv)f_{\alpha'}(\vec{v}\to\vec{v})]^*\tilde{\rho}_{\alpha\alpha'}(R\hat{v}-2\vec{v}\delta t,\vec{v},t-\delta t)-\sigma^{-1}[(2\pi\hbar/imv)f_\alpha(\vec{v}\to\vec{v})]\tilde{\rho}_{\alpha\alpha'}$$
$$\times(R\hat{v}-2\vec{v}\delta t,\vec{v},t-\delta t)+\sigma^{-1}\int d\Omega_{v'}\,f_\alpha(\vec{v}'\to\vec{v})f_{\alpha'}(\vec{v}'\to\vec{v})^*\tilde{\rho}_{\alpha\alpha'}(R\hat{v}'-2\vec{v}'\delta t,\vec{v}',t-\delta t)\,, \quad \text{(B11)}$$

where $f_\alpha(\vec{v}\to\vec{v})$ is the forward α-state scattering amplitude.

Equation (B11) represents the change in $\tilde{\rho}_{\alpha\alpha'}(\vec{R},\vec{v},t)$ provided a collision occurs at time t. To get the average collisional change in $\tilde{\rho}_{\alpha\alpha'}$ in a time $\delta\tau>2\delta t$ we must multiply Eq. (B11) by the average number of collisions occurring in $\delta\tau$, which is given by $\mathfrak{N}v\sigma\delta\tau$, where $\mathfrak{N}$ is the perturber density. When this is done, the limit $\delta\tau\to 0$, $\delta t\to 0$ is taken, and the transformation from the quantum variable $\vec{R}$ to the classical variable $\vec{R}$ is performed as in Appendix A, one obtains

$$\left(\frac{\partial\tilde{\rho}_{\alpha\alpha'}(\vec{R},\vec{v},t)}{\partial t}\right)_{\text{coll}}=-\mathfrak{N}v\left(\frac{2\pi\hbar}{imv}\right)$$
$$\times[f_\alpha(\vec{v}\to\vec{v})-f_{\alpha'}(\vec{v}\to\vec{v})^*]\tilde{\rho}_{\alpha\alpha'}(\vec{R},\vec{v},t)$$
$$+\mathfrak{N}v\int d\Omega_{v'}\,f_\alpha(\vec{v}'\to\vec{v})f_{\alpha'}(\vec{v}'\to\vec{v})^*\tilde{\rho}_{\alpha\alpha'}(\vec{R},\vec{v}',t)\,. \quad \text{(B12)}$$

Admittedly, the derivation of Eq. (B12) has not been overly rigorous. However, it does provide a fairly simple way of arriving at the quantum-mechanical collisional rate of change of the density matrix. The general validity of this procedure for calculation of $(\partial\tilde{\rho}/\partial t)_{\text{coll}}$ and its subsequent use in the text is based on the binary-collision and impact approximations, as has been discussed in an earlier work.[8] Although Eq. (B12) was derived for a single atom, it is also true for the ensemble since the atoms act independently of each other.

For reasons related to separating phase-shifting and velocity-changing collisions, which will become clearer in Appendix C, we add and subtract a term $\Gamma^{vc}_{\alpha\alpha'}(\vec{v})\tilde{\rho}_{\alpha\alpha'}(\vec{R},\vec{v},t)$ ($\Gamma^{vc}_{\alpha\alpha'}$ will be defined below) to Eq. (B12) and rewrite it as

$$\left(\frac{\partial\tilde{\rho}_{\alpha\alpha'}(\vec{R},\vec{v},t)}{\partial t}\right)_{coll} = -\gamma^{ph}_{\alpha\alpha'}(\vec{v})\tilde{\rho}_{\alpha\alpha'}(\vec{R},\vec{v},t) - \Gamma^{vc}_{\alpha\alpha'}(\vec{v})\tilde{\rho}_{\alpha\alpha'}(\vec{R},\vec{v},t) + \int d\Omega_{v'}\, W_{\alpha\alpha'}(\vec{v}'\to\vec{v})\tilde{\rho}_{\alpha\alpha'}(\vec{R},\vec{v}',t)\,, \tag{B13}$$

where

$$\gamma^{ph}_{\alpha\alpha'}(\vec{v}) = \mathfrak{N}v(2\pi\hbar/imv)[f_\alpha(\vec{v}\to\vec{v}) - f_{\alpha'}(\vec{v}\to\vec{v})^*] - \mathfrak{N}v\int d\Omega_{v'} f_\alpha(\vec{v}\to\vec{v}')f_{\alpha'}(\vec{v}\to\vec{v}')^*\,, \tag{B14a}$$

$$W_{\alpha\alpha'}(\vec{v}'\to\vec{v}) = \mathfrak{N}vf_\alpha(\vec{v}'\to\vec{v})f_{\alpha'}(\vec{v}'\to\vec{v})^*\,, \tag{B14b}$$

and

$$\Gamma^{vc}_{\alpha\alpha'}(\vec{v}) = \int d\Omega_{v'}\, W_{\alpha\alpha'}(\vec{v}\to\vec{v}')\,. \tag{B14c}$$

These results may be generalized to the case of moving perturbers by performing the scattering calculation in the center-of-momentum frame and then transferring back to the lab frame. The resultant expressions are given in Eqs. (13)–(16) of the text.

The diagonal density matrix elements obey the usual transport equation, but the off-diagonal terms obey an equation without a classical analog. By an entirely different approach, Smith and co-workers[18] have effectively derived an equation for the off-diagonal density matrix elements which can be shown to be in agreement with our results.

APPENDIX C. CUTOFF PROCEDURE

In QMI and QMII, collisions were broken down into two categoreis—those which significantly affect $\tilde{\rho}_{\alpha\alpha'}(\vec{R},\vec{v},t)$ and those which do not (the precise definition of a "significant" collision will be given below). The usefulness of this approach is that it leads to a separation of phase-shifting collisions (with no velocity change) and velocity-changing collisions (which may or may not be accompanied by a phase shift). In addition, the cutoff procedure used to establish the results of this Appendix will assure that the rate for velocity-changing collisions will no longer include those collisions producing slight changes in velocity which have no real physical importance for the problem at hand.

The cutoff procedure may be seen to arise naturally if we begin with Eq. (12),

$$\left(\frac{\partial\tilde{\rho}_{\alpha\alpha'}(\vec{R},\vec{v},t)}{\partial t}\right)_{coll} = -\gamma^{ph}_{\alpha\alpha'}(\vec{v})\tilde{\rho}_{\alpha\alpha'}(\vec{R},\vec{v},t) + \left(\frac{\partial\tilde{\rho}_{\alpha\alpha'}(\vec{R},\vec{v},t)}{\partial t}\right)_{vc}, \tag{C1}$$

with

$$\left(\frac{\partial\tilde{\rho}_{\alpha\alpha'}(\vec{R},\vec{v},t)}{\partial t}\right)_{vc} = -\Gamma^{vc}_{\alpha\alpha'}(\vec{v})\tilde{\rho}_{\alpha\alpha'}(\vec{R},\vec{v},t) + \int d^3v'\, W_{\alpha\alpha'}(\vec{v}'\to\vec{v})\tilde{\rho}_{\alpha\alpha'}(\vec{R},\vec{v}',t)\,. \tag{C2}$$

Using Eqs. (15) and (16) and doing a little algebra, one can transform Eq. (C2) into

$$\left(\frac{\partial\tilde{\rho}_{\alpha\alpha'}(\vec{R},\vec{v},t)}{\partial t}\right)_{vc} = -\mathfrak{N}\int d^3v_r\int d^3v_r'\;\; W_p(\vec{v}-\vec{v}_r)\,v_r^{-1}\,\delta(v_r - v_r')f_\alpha(\vec{v}_r\to\vec{v}_r')f_{\alpha'}(\vec{v}_r\to\vec{v}_r')^*\tilde{\rho}_{\alpha\alpha'}(\vec{R},\vec{v},t)$$
$$+\mathfrak{N}\left(\frac{m}{\mu}\right)^3\int d^3v'\int d^3v_p'\int d^3v_r\; W_p(v_p')\,\delta\left(\vec{v}_r+\frac{m}{m_p}\vec{v}'+\vec{v}_p'-\frac{m}{\mu}\vec{v}\right)$$
$$\times v_r^{-1}\,\delta(v_r' - v_r)f_\alpha(\vec{v}_r'\to\vec{v}_r)f_{\alpha'}(\vec{v}_r'\to\vec{v}_r)^*\,\tilde{\rho}_{\alpha\alpha'}(\vec{R},\vec{v}',t)\,. \tag{C3}$$

Working on the second term in Eq. (C3) by (a) changing variables from $\vec{v}'$ to $\vec{v}_r' = \vec{v}' - \vec{v}_p'$, (b) doing the integral over $\vec{v}_p'$, (c) interchanging $\vec{v}_r$ and $\vec{v}_r'$ as integration variables, and (d) defining a vector

$$\vec{Y} = \vec{v} - \vec{v}' = (\mu/m)(\vec{v}_r - \vec{v}_r')\,, \tag{C4}$$

one can rewrite Eq. (C3) in the suggestive form

$$\left(\frac{\partial\tilde{\rho}_{\alpha\alpha'}(\vec{R},\vec{v},t)}{\partial t}\right)_{vc} = -\mathfrak{N}\int d^3v_r\int d^3v_r'\; f_\alpha(\vec{v}_r\to\vec{v}_r')\,f_{\alpha'}(\vec{v}_r\to\vec{v}_r')^*\,v_r^{-1}\,\delta(v_r - v_r')\,[W_p(\vec{v}-\vec{v}_r)\tilde{\rho}_{\alpha\alpha'}(\vec{R},\vec{v},t)$$
$$- W_p(\vec{v}-\vec{v}_r+\vec{Y})\tilde{\rho}_{\alpha\alpha'}(\vec{R},\vec{v}+\vec{Y},t)]\,. \tag{C5}$$

The vector $\vec{Y}$ represents the change in velocity of the active atom resulting from a collision. If this quantity is small enough such that

$$\tilde{\rho}_{\alpha\alpha'}(\vec{R},\vec{v}+\vec{Y},t) \approx \tilde{\rho}_{\alpha\alpha'}(\vec{R},\vec{v},t) \tag{C6a}$$

and

$$W_p(\vec{v}-\vec{v}_r)\approx W_p(\vec{v}-\vec{v}_r+\vec{Y}) \qquad \text{(C6b)}$$

for all $\vec{v}$, $\vec{v}_r$, $\vec{R}$, and t, the collision is not considered to be significant. Consequently, the integrations in Eq. (C5) are divided into regions where Eqs. (C6) are or are not satisfied. In the region where Eqs. (C6) hold, Eq. (C5) vanishes so that the integrals in Eq. (C5) may be limited to those values of $\vec{v}_r$ and $\vec{v}_r'$ where Eqs. (C6) are not valid. By substituting Eq. (C5) in Eq. (C1) and performing algebraic manipulations similar to the reverse of those leading to Eq. (C5), one may obtain

$$\frac{\partial\tilde{\rho}_{\alpha\alpha'}(\vec{R},\vec{v},t)}{\partial t} = -\gamma^{ph}_{\alpha\alpha'}(\vec{v})\tilde{\rho}_{\alpha\alpha'}(\vec{R},\vec{v},t) - [\Gamma^{vc}_{\alpha\alpha'}(\vec{v})]'\tilde{\rho}_{\alpha\alpha'}(\vec{R},\vec{v},t) + \int' d^3v'\, W_{\alpha\alpha'}(\vec{v}'-\vec{v})\tilde{\rho}_{\alpha\alpha'}(\vec{R},\vec{v}'t)\,, \qquad \text{(C7)}$$

where $\gamma^{ph}_{\alpha\alpha'}(\vec{v})$ and $W_{\alpha\alpha'}(\vec{v}'-\vec{v})$ are still given by Eqs. (13) and (15), respectively,

$$[\Gamma^{vc}_{\alpha\alpha'}(\vec{v})]' = \int' d^3v'\, W_{\alpha\alpha'}(\vec{v}-\vec{v}')\,, \qquad \text{(C8)}$$

and the prime restricts the integrations to only significant collisions—i.e., those in which Eqs. (C6) do not hold.

A glance at Eq. (C7) immediately reveals that if no significant velocity-changing collisions occur, the only nonzero line-shape parameter is $\gamma^{ph}_{\alpha\alpha'}(\vec{v})$. This is as it should be since $\gamma^{ph}_{\alpha\alpha'}(\vec{v})$ corresponds to the line-shape parameter which arises in theories which assume the active-atom velocity to be unaltered by collisions.[9] In addition, the "rate" for velocity-changing collisions given by (C8) no longer contains collisions involving small momentum transfer; as such, one can be sure that $[\Gamma^{vc}_{\alpha\alpha'}(\vec{v})]'$ will be finite [whereas $\Gamma^{vc}_{\alpha\alpha'}(\vec{v})$ would be infinite if it were calculated for a classical interaction with infinite range.]

As an example of application of conditions (C6), consider an atomic radiation problem with active atoms of average speed u, lifetime τ, and transition wavelength λ subject to collisions with perturbers of average speed u_p. In such a problem,[1,2] $\tilde{\rho}_{\alpha\alpha'}(\vec{R},\vec{v},t)$ will have velocity dependence given by $e^{i\vec{k}\cdot\vec{v}t}$ (normal Doppler factor) so that conditions (C6) will be valid for all $\vec{Y}$'s which satisfy $\vec{k}\cdot\vec{Y}\ll 1$ and $Y/u_p\ll 1$. All $\vec{Y}$'s which do not satisfy both of these requirements are considered to represent "significant" velocity-changing collisions.

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†Present addrsss: Physics Department, New York University, University Heights, Bronx, N. Y. 10453.

[1]P. R. Berman and W. E. Lamb, Jr., Phys. Rev. A 2, 2435 (1970).

[2]P. R. Berman and W. E. Lamb, Jr., Phys. Rev. A 4, 319 (1971).

[3]S. G. Rautian, Zh. Eksperim. i Teor. Fiz. 51, 1176 (1966) [Sov. Phys. JETP 24, 788 (1967)]; A. B. Kol'chenko and S. G. Rautian, Zh. Eksperim. i Teor. Fiz. 54, 959 (1968) [Sov. Phys. JETP 27, 511 (1968)].

[4]The author has recently been made aware of additional works which lead to quantum-mechanical transport equations. Equations similar to ours have been derived by Andreeva {T. L. Andreeva, Zh. Eksperim i. Teor. Fiz. 54, 641 (1968) [Sov. Phys. JETP 27, 342 (1968)]} for the case of stationary perturbers; by Pestov and Rautian {E. G. Pestov and S. G. Rautian, Zh. Eksperim. i Teor. Fiz. 56, 902 (1969) [Sov. Phys. JETP 29, 458 (1969)]} in Born approximation to the scattering amplitudes; and by W. R. Chappell, J. Cooper, E. W. Smith, and T. Dillon (unpublished) for off-diagonal density matrix elements. Our approach is less formal than that of the above references (who use the BBGKY approximation scheme) and enables one to gain physical insight into the QMTE by derivation in terms of the effects of collisions on individual atoms (see Appendices). I am grateful to W. R. Chappell for having provided a report of his work (unpublished).

[5]Collisions between atoms of the same kind may still be of a "foreign-gas" nature if the resonant excitation exchange cross section is small compared with competing nonresonant processes. This situation is favored when one is dealing with those highly excited states whose oscillator strength with the ground state is negligible. For more details, see Ref. 8.

[6]A. P. Kol'chenko, S. G. Rautian, and R. I. Sokolovskii, Zh. Eksperim. i Teor. Fiz. 55, 1864 (1968) [Sov. Phys. JETP 28, 986 (1969)].

[7]S. G. Rautian and A. M. Shalagin, Zh. Eksperim. i Teor. Fiz. 58, 962 (1970) [Sov. Phys. JETP 31, 518 (1970)]. The photon-recoil terms will be important in the saturation terms of laser theory if the photon-recoil phase shift accumulated in the effective lifetime τ of the atom is on the order of unity. It is easy to show that this phase shift is given by $(\lambda_{dB}/\lambda)kv\tau$, where λ_{dB} is the de Broglie wavelength and v the speed of the atom or molecule, while $\lambda = 2\pi/k$ is the transition wavelength. For $\tau \gtrsim 10^{-3}$ sec (which is typical of certain molecular transitions) the photon-recoil phase shift may be significant. One should note that photon-recoil effects related to actual velocity changes or to Doppler broadened profiles are $\approx \lambda_{dB}/\lambda$ and are negligible.

[8]P. R. Berman and W. E. Lamb, Jr., Phys. Rev. 187, 221 (1969). The procedure for obtaining $\partial\rho/\partial t = \partial\rho/\partial t|_{\text{no coll}} + \partial\rho/\partial t|_{\text{coll}}$ and the necessity of imposing both the impact and binary-collision approximations for its validity is similar to the methods employed in Secs. VII and VIII of this reference.

[9]Equations (13) and (14) are equivalent to Eqs. (77) of the paper of Baranger [M. Baranger, Phys. Rev. 112, 855 (1958)] provided his result, which is for fixed active atoms, is generalized to moving active atoms whose velocity is *unchanged* in collisions. Also, see Refs. 1 and 2.

[10]The difference in collisional interaction for electronic levels is due mainly to the different orbital radii and

polarizabilities of the levels.

[11]E. Lindholm, Arkiv Mat. Astron. Fysik 32A, 17 (1945); H. M. Foley, Phys. Rev. 69, 616 (1946).

[12]S. G. Rautian and I. I. Sobelman, Usp. Fiz. Nauk 90, 209 (1966) [Sov. Phys. Usp. 9, 701 (1967)]. The velocity after a "strong" or "weak" collision is uncorrelated or highly correlated, respectively, to the velocity before the collision.

[13]M. I. D'Yakonov and V. I. Perel, Zh. Eksperim. i Teor. Fiz. 47, 1483 (1964) [Sov. Phys. JETP 20, 997 (1965)]. It should be noted that this radiation-trapping contribution was derived under the assumptions that (a) average separation of atoms $\gg$ resonant transition wavelength and (b) Doppler width $\gg$ collision or natural width. In Ref. 8, Sec. VIII, it was conjectured that condition (b) alone was sufficient for the validity of the radiation-trapping term. Even so, under typical conditions at a few Torr, the ratio of collision to Doppler width ≈ 0.1 so that errors of 10% may already be introduced at these pressures.

[14]M. I. D'Yakonov and V. I. Perel', Zh. Eksperim. i Teor. Fiz. 58, 1090 (1970) [Sov. Phys. JETP 31, 585 (1970)]. The same cautionary comments given in Ref. 13 still apply.

[15]For a discussion of quantum distribution functions and a related bibliography, see Leon Cohen, Ph. D. thesis (Yale University, 1966) (unpublished); J. Math. Phys. 7, 781 (1966). Wigner's paper on the subject is given in Phys. Rev. 40, 749 (1932).

[16]For example, in a Stern-Gerlach experiment where the external magnetic field does act in a state-dependent manner, there is no correct classical trajectory that one can associate with an off-diagonal density matrix element.

[17]K. Gottfried, *Quantum Mechanics* (Benjamin, New York, 1966), Vol. 1, Sec. 12.

[18]E. W. Smith, J. Cooper, W. R. Chappell, and T. Dillon, J. Quant. Spectry. Radiative Transfer 11, 1547 (1971); 11, 1567 (1971). The author would like to thank Dr. Smith for providing preprints of their articles, which contain results in agreement with those of Ref. 4.

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Equilibrium Theory of Simple Liquids

Loup Verlet and Jean-Jacques Weis
Laboratoire de Physique Théorique et Hautes Energies, 91-*Orsay*, *France* *
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The perturbation theory of liquids developed recently by Weeks, Chandler, and Andersen (WCA) is examined in detail: Each assumption introduced by these authors is tested by comparison with "exact" computer results. It is shown that the basic assumptions of WCA are justified. An improved expression for the radial distribution function of the hard-sphere gas enables us to correct for some further inconsistent assumptions of the WCA theory. We then succeed in giving simple analytical expressions for the thermodynamic functions of the Lennard-Jones fluid shown to be quite good at high density. We show that the remainder of the perturbation series, which converges slowly at lower density, can be evaluated with the help of the Percus-Yevick equation. We therefore possess a unified theory of liquids which is especially simple at high density. Finally we reexpress the original WCA theory in an analytical form.

I. INTRODUCTION

A perturbation theory of liquids has been introduced by Zwanzig, [1] and been revived and generalized recently by several authors[2-4]: The excess free energy is expanded as a series in a parameter λ multiplying some part of the interaction considered as a perturbation (e.g., the attractive part); the statistical averages of the terms of the series are calculated for a system interacting with the remaining part of the interaction, the so-called "reference system." The first-order term of the expansion involves the evaluation of the perturbing interaction averaged over the reference system. The next-order terms involve the averages of the fluctuations with respect to the average perturbed energy and they are very complicated to evaluate.

The method is feasible and useful because advantage can be taken of the similarity between the reference system interacting with repulsive interactions and that composed of hard spheres. Such a similarity is, as a matter of fact, already present for the full system at high density: It is well known that the structure factors of dense liquids can be interpreted with a hard-sphere model. [5]

A prerequirement of that kind of theory is therefore a correct knowledge of the hard-sphere system. The equation of state of a hard-sphere system is quite well known at present[6] owing to the extensive computer work of Alder and Wainwright. [7] The situation regarding the radial distribution function (rdf) is not so satisfactory. It is well known that the Wertheim[8]-Thiele[9] (WT) analytical solution of the Percus-Yevick (PY) equation is good when the density is not too high: It becomes quite unsatisfactory for very dense states. We use hard-sphere rdf obtained through computer experiments[10,11] in order to improve the WT solution.