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Quantum-Mechanical Transport Equation for Atomic Systems. II. Inelastic Collisions and General Line-Shape Considerations*

Paul R. Berman
Physics Department, New York University, Bronx, New York 10453
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Inelastic-collisional effects are incorporated into a quantum-mechanical transport equation (QMTE) that was developed in an earlier paper. The QMTE enables one to follow the quantum-state evolution of moving atoms which are interacting with some external fields while undergoing collisions with perturber atoms. The collisional processes are treated quantum mechanically and then reinterpreted in terms of classical variables so that the QMTE becomes an integrodifferential equation for atomic density-matrix elements containing both well-defined quantum-mechanical collision parameters (i.e., scattering amplitudes) and density-matrix elements which are functions of *classical* position and velocity variables. Solutions of the QMTE enable one to derive line-shape formulas, and a discussion will be given of the general features to be expected for spectral profiles, Hanle-effect line shapes, and laser output curves, as well as the manner in which these features differ from those predicted by theories that neglect some quantum-mechanical aspects of the collision events. The inclusion of inelastic-collisional effects does not cover cases in which the frequency spacing of the atomic levels under consideration is comparable to the inverse duration time of a collision; nevertheless, the QMTE to be derived will be applicable to the analysis of a large number of atomic systems.

I. INTRODUCTION

In a series of papers,[1-3] we have shown that it is possible to write a quantum-mechanical transport equation (QMTE) for the density-matrix elements associated with an atomic system. This equation, in effect, enables one to follow the time development of an ensemble of atoms which are interacting with some external fields while undergoing collisions with perturber atoms. Solutions of the QMTE may be used to obtain expressions for characteristic quantities of atomic systems such as their macroscopic polarization and absorption coefficients.

The QMTE is a transport equation in the sense that each density-matrix element is given as a function of *classical* position and velocity variables as well as the time. It is quantum mechanical in the sense that collisional processes are treated quantum mechanically and all collision kernels and rates which appear in the QMTE are well-defined quantum-mechanical functions. A quantum-mechanical treatment of collisions is necessary because the collisional interaction is state dependent, making it impossible to associate a classical trajectory with the atoms' off-diagonal density-matrix elements when a collisions occurs.[1] (This result is analogous to that of the Stern–Gerlach experiment where it is also impossible to designate a classical path for off-diagonal density-matrix elements.) However, one may *reinterpret* the quantum-mechanical collision results and associate a classical position and velocity with *individual* density-matrix elements rather than with the atom as a whole. The procedure for carrying out this program was given in a previous paper[3] (the method should also be applicable to an analysis of the Stern–Gerlach experiment).

The QMTE presented in our earlier work did not allow for collision-induced transitions; that is, only elastic scattering was considered. There are, however, many systems in which inelastic processes play an important role. Certainly, if there are degenerate or near-degenerate (energy-level spacing less than thermal energy) levels in an atom, collision-induced transitions may be possible. It is the purpose of this paper to extend our earlier results to cover such cases. A similar calculation, carried out using a somewhat different viewpoint, has recently appeared.[4]

The new QMTE to be derived should enable one to study the effects of collision-induced magnetic relaxation in Hanle-effect or level-crossing experiments as well as to examine the spectral profiles associated with transitions in which one or both of the levels are degenerate. While explicit line-shape calculations will be left for future papers, I shall indicate here some general features of the line shapes which one might expect.

The physical system to be considered and approximations of the theory will be given in Sec. II. In Sec. III the QMTE will be derived, and in Sec. IV I shall show that, for straight-line atomic paths during collisions, the QMTE reduces to "semiclassical" expressions[5,6] for the collisional processes. An alternative form for the QMTE will be described in Sec. V. Finally, a discussion of the QMTE and its general implications regarding

theoretical line-shape predictions will be given in Sec. VI.

We shall have some need to make use of the equations of an earlier paper[3] (hereafter referred to as QMTE-I). Equations from QMTE-I will be prefixed by a I. Some familiarity with QMTE-I is helpful, but not essential, for the reading of this paper.

II. PHYSICAL SYSTEM UNDER CONSIDERATION

The physical system consists of "active" atoms and ground-state perturber atoms. The active atoms are the ones of interest and usually interact with some external fields in addition to undergoing collisions with perturber atoms. We assume that the pressure is low enough so that only binary collisions need be considered (generally valid at pressures less than several hundred Torr) and that the external fields are essentially constant over the duration time of a collision (impact approximation). In addition, we assume that the active atom density is low enough so that resonant broadening and radiation trapping effects are negligible.[7] Changes in the perturber atoms' distribution function due to collisions with the active atoms are also ignored.[8]

We wish to treat inelastic collisions. Fortunately, it is possible to describe the great majority of collisions in one of two approximations. First, energy levels of the atoms whose frequency spacing is small compared to the inverse duration time ω_c of a collision (typically $\omega_c \approx 10^{12}$ sec^{-1} so that magnetic sublevel separations are almost always less than $\hbar\omega_c$) may be treated as degenerate with respect to the collisional processes. On the other hand, collisions cannot induce transitions between those energy levels separated in frequency by an amount somewhat greater than ω_c (e.g., optically separated levels) and, for such levels, the collision process is effectively elastic. We shall assume that all collisional processes for our system fall into one of the two categories above and visualize the level structure of our active atoms as shown in Fig. 1.

Our model is one in which collision-induced transitions between different groups of levels are not possible and where the energy levels *within* a group may be taken as degenerate in considering collisional processes. This model is applicable to most atomic systems. It does not cover cases where the frequency separation of the energy levels under consideration is on the order of ω_c; certain fine-structure separations and the rotational spacings of molecular levels may fall into this class. The theory can be extended to cover these cases, but the additional complexities involved will not be discussed here.

The above assumptions are meant to apply to both the active atom and perturber levels. However, for simplicity, we shall take the perturber atoms as structureless moving centers of potential. Generalization to account for the level structure of the perturbers is neither difficult nor illuminating, provided the other assumptions of our model are valid.

III. QUANTUM-MECHANICAL TRANSPORT EQUATION

The derivation of the QMTE proceeds as in QMTE-I. First, we separate the time rate of change of density-matrix elements into two parts, writing

$$\frac{\partial\tilde{\rho}_{\alpha\beta}(\vec{R},\,\vec{v},\,t)}{\partial t} = \left.\frac{\partial\tilde{\rho}_{\alpha\beta}(\vec{R},\,\vec{v},\,t)}{\partial t}\right|_{\text{no coll}} + \left.\frac{\partial\tilde{\rho}_{\alpha\beta}(\vec{R},\,\vec{v},\,t)}{\partial t}\right|_{\text{coll}}, \quad (1)$$

where $\tilde{\rho}_{\alpha\beta}(\vec{R},\,\vec{v},\,t)$ is the $\alpha\beta$ active-atom ensemble density-matrix element (the tilde above a variable will indicate the interaction representation; i.e., $\tilde{F}_{\alpha\beta} = F_{\alpha\beta}e^{i\omega_{\alpha\beta}t}$ for any variable $F_{\alpha\beta}$) and $\vec{R}$ and $\vec{v}$ are classical variables for the atomic center-of-mass position and velocity, respectively, associated with the element. The term $(\partial\tilde{\rho}_{\alpha\beta}/\partial t)_{\text{no coll}}$ gives the time rate of change of $\tilde{\rho}_{\alpha\beta}$ in the absence of collisions and $(\partial\tilde{\rho}_{\alpha\beta}/\partial t)_{\text{coll}}$ gives the collisional time rate of change of $\tilde{\rho}_{\alpha\beta}$ obtained from a quantum-mechanical calculation.

From Eq. (I10) of QMTE-I we have, for a system in which the interaction between an active atom and the external fields is denoted by $V(\vec{r},\,\vec{R},\,t)$

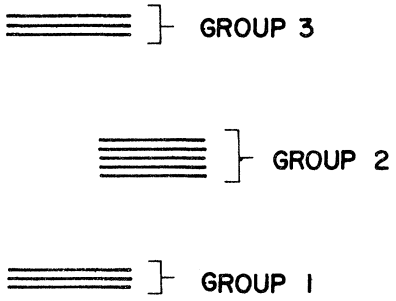

FIG. 1. Portion of the energy-level diagram of a typical active atom, showing three groups of levels (not drawn to scale). The energy separation between different groups of levels (which might represent energies corresponding to optical or infrared transitions) is assumed to be greater than the collisional energies available; thus, collision-induced transitions between different groups of levels may be neglected. On the other hand, it is assumed that the energy levels *within* a given group of levels (these levels might represent the different magnetic sublevels of a given angular momentum state) may be taken as degenerate with regard to collisional processes.

($\vec{r}$ represents active-atom relative electronic coordinates),

$$\left.\frac{\partial\tilde{\rho}_{\alpha\beta}(\vec{R},\vec{v},t)}{\partial t}\right|_{\text{no coll}} = \tilde{\Lambda}_{\alpha\beta}(\vec{R},\vec{v},t) - \Gamma_{\alpha\beta}(\vec{R},\vec{v},t)\tilde{\rho}_{\alpha\beta}(\vec{R},\vec{v},t) - \vec{v}\cdot\vec{\nabla}\tilde{\rho}_{\alpha\beta}(\vec{R},\vec{v},t) + (i\hbar)^{-1}[\tilde{V}(\vec{R},t),\tilde{\rho}(\vec{R},t)]_{\alpha\beta}, \quad (2)$$

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

$$\tilde{V}_{\alpha\beta}(\vec{R},t) = e^{i\omega_{\alpha\beta}t}\int\psi_\alpha(\vec{r})^* V(\vec{r},\vec{R},t)\psi_\beta(\vec{r})d^3r \quad (3)$$

and $\psi_\alpha(\vec{r})$ is the unperturbed electronic-state eigenfunction of state α. The quantities $\tilde{\Lambda}_{\alpha\beta}(\vec{R},\vec{v},t)$ and $\Gamma_{\alpha\beta}(\vec{R},\vec{v},t)$ which appear in (2) have been introduced to cover situations where the systems under consideration are not closed[9]; $\tilde{\Lambda}_{\alpha\beta}(\vec{R},\vec{v},t)$ provides an excitation rate density into and $\Gamma_{\alpha\beta}(\vec{R},\vec{v},t)$ a phenomenological decay rate out of such systems. The term $\vec{v}\cdot\vec{\nabla}\tilde{\rho}_{\alpha\beta}$ in Eq. (2) is simply the convective contribution to $\partial\tilde{\rho}_{\alpha\beta}/\partial t$.

As in QMTE-I, $(\partial\tilde{\rho}_{\alpha\beta}/\partial t)_{\text{coll}}$ is obtained by examining the quantum-mechanical scattering of a wave packet from a perturber site and then reinterpreting the results in terms of classical coordinate and velocity variables as was done in Appendix B of QMTE-I. An outline of a similar calculation taking into account the inelastic-collisional effects described above is presented in the Appendix of this paper, leading to the desired result

$$\left.\frac{\partial\tilde{\rho}_{\alpha\beta}(\vec{R},\vec{v},t)}{\partial t}\right|_{\text{coll}} = \sum_{\alpha'\beta'}\left(T^{\alpha'\beta'}_{\alpha\beta}(\vec{v})\tilde{\rho}_{\alpha'\beta'}(\vec{R},\vec{v},t) - \Gamma^{\alpha'\beta'}_{\alpha\beta}(\vec{v},\text{vc})\tilde{\rho}_{\alpha'\beta'}(\vec{R},\vec{v},t) + \int d^3v' W^{\alpha'\beta'}_{\alpha\beta}(\vec{v}'-\vec{v})\tilde{\rho}_{\alpha'\beta'}(\vec{R},\vec{v}',t)\right), \quad (4)$$

where

$$T^{\alpha'\beta'}_{\alpha\beta}(\vec{v}) = -N\int d^3v_p W_p(\vec{v}_p)v_r\left(\frac{2\pi\hbar}{i\mu v_r}[f_{\alpha\alpha'}(\vec{v}_r\to\vec{v}_r)\delta_{\beta\beta'} - f_{\beta\beta'}(\vec{v}_r\to\vec{v}_r)^*\delta_{\alpha\alpha'}] - \int d\Omega_{v_r'} f_{\alpha\alpha'}(\vec{v}_r\to\vec{v}_r')f_{\beta\beta'}(\vec{v}_r\to\vec{v}_r')^*\right), \quad (5)$$

$W_p(\vec{v}_p)$ is the perturber velocity distribution,

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

and μ are the active-atom–perturber relative velocity and reduced mass, respectively, N is the perturber density, and $f_{\alpha\alpha'}(\vec{v}_r\to\vec{v}_r')$ is the inelastic scattering amplitude for scattering from state α' with velocity $\vec{v}_r$ to state α with velocity $\vec{v}_r' = \hat{v}_r' v_r$ subject to the *additional restriction* that

$$f_{\alpha\alpha'}(\vec{v}_r\to\vec{v}_r') = 0 \quad \text{[if } \alpha \text{ and } \alpha' \text{ are in different groups of atomic levels (see Fig. 1)]}; \quad (6)$$

$$W^{\alpha'\beta'}_{\alpha\beta}(\vec{v}'-\vec{v}) = N\left(\frac{m}{\mu}\right)^3\int d^3v_p'\int d^3v_r W_p(\vec{v}_p')v_r^{-1} \times\delta\left(\vec{v}_r+\frac{m}{m_p}\vec{v}'-\frac{m}{\mu}\vec{v}+\vec{v}_p'\right)\delta(v_r-v_r') \times f_{\alpha\alpha'}(\vec{v}_r'\to\vec{v}_r)f_{\beta\beta'}(\vec{v}_r'\to\vec{v}_r)^*, \quad (7)$$

$\vec{v}_r' = \vec{v}' - \vec{v}_p'$, and m and m_p are the active-atom and perturber masses, respectively; and

$$\Gamma^{\alpha'\beta'}_{\alpha\beta}(\vec{v},\text{vc}) = \int d^3v' W^{\alpha'\beta'}_{\alpha\beta}(\vec{v}\to\vec{v}') = N\int d^3v_p W_p(\vec{v}_p)v_r\sigma^{\alpha'\beta'}_{\alpha\beta}(\vec{v}_r), \quad (8)$$

with

$$\sigma^{\alpha'\beta'}_{\alpha\beta}(\vec{v}_r) = \int d\Omega_{v_r'} f_{\alpha\alpha'}(\vec{v}_r\to\vec{v}_r')f_{\beta\beta'}(\vec{v}_r\to\vec{v}_r')^*. \quad (8a)$$

The vc label appearing in Eq. (8) stands for "velocity changing," in reference to a classical limit associated with $\Gamma^{\alpha'\beta'}_{\alpha\beta}(\vec{v},\text{vc})$ which will be mentioned below. Note that as a result of condition (6) the sums over α' and β' in Eq. (4) are restricted to those sublevels α' and β' which are in the same group of levels (see Fig. 1) as are α and β, respectively. This is a manifestation of our assumption that collisions can induce transitions *within* a given group of levels but cannot induce transitions between different groups of levels.

It would be very useful if a simple physical interpretation for the terms appearing in Eq. (4) could be offered, but this has not been possible. Collisions result in (a) shifts of the active atoms' energy levels, (b) transitions between various sublevels of a group of levels, and (c) changes in the velocity associated with given density-matrix elements. These effects are all interrelated and cannot be correlated with individual terms which appear in Eq. (4). We can show (see Sec. IV) that the last two terms in Eq. (4) vanish if collisions result in negligible active-atom velocity changes. Thus, $T^{\alpha'\beta'}_{\alpha\beta}(\vec{v})$ in Eq. (4) does provide all the effects of collision-induced transitions and level shifts when the active atoms move on approximately straight lines. Moreover, one might like to think of $W^{\alpha'\beta'}_{\alpha\beta}(\vec{v}'-\vec{v})$ and $\Gamma^{\alpha'\beta'}_{\alpha\beta}(\vec{v},\text{vc})$ as a collision kernel and rate for velocity-changing collisions, respectively, since they can be so interpreted in the case of equal collisional interaction for all the states.[2,3] However, for the general case in which velocity changes are important and the different levels experience different collisional interactions, the various terms of Eq. (4) are no longer identifiable with specific collisional processes.

Equation (4) describes different situations de-

pending on whether or not α and β belong to the same group of levels. If α and β do belong to the same group of levels as would be the case if they were magnetic sublevels of a given angular momentum state, Eq. (4) can be used to examine the collisional relaxation of some polarization which has been imposed on the sublevels of the group (as is the case in Hanle and level-crossing experiments). On the other hand, if α and β belong to different groups of levels, $\tilde{\rho}_{\alpha\beta}$ is related to the electric dipole moment of the atom (provided states α and β have different parity) so that $(\partial\tilde{\rho}_{\alpha\beta}/\partial t)_{\text{coll}}$ may be instrumental in determining the effects of collisions on the spectral profiles associated with transitions between states α and β.

Using Eqs. (1), (2), and (4), we obtain the quantum-mechanical transport equation (QMTE)

$$\begin{aligned}\frac{\partial\tilde{\rho}_{\alpha\beta}(\vec{R},\vec{v},t)}{\partial t}&+\vec{v}\cdot\vec{\nabla}\tilde{\rho}_{\alpha\beta}(\vec{R},\vec{v},t)\\&=\tilde{\Lambda}_{\alpha\beta}(\vec{R},\vec{v},t)-\Gamma_{\alpha\beta}(\vec{R},\vec{v},t)\tilde{\rho}_{\alpha\beta}(\vec{R},\vec{v},t)\\&\quad+(i\hbar)^{-1}[\tilde{V}(\vec{R},t),\tilde{\rho}(\vec{R},t)]_{\alpha\beta}\\&\quad+\sum_{\alpha'\beta'}\Big(T^{\alpha'\beta'}_{\alpha\beta}(\vec{v})\tilde{\rho}_{\alpha'\beta'}(\vec{R},\vec{v},t)\\&\qquad-\Gamma^{\alpha'\beta'}_{\alpha\beta}(\vec{v},\mathrm{vc})\tilde{\rho}_{\alpha'\beta'}(\vec{R},\vec{v},t)\\&\qquad+\int d^3v'W^{\alpha'\beta'}_{\alpha\beta}(\vec{v}'-\vec{v})\tilde{\rho}_{\alpha'\beta'}(\vec{R},\vec{v}',t)\Big),\end{aligned}\tag{9}$$

which is the starting point for calculations involving the interactions of atoms with both external fields and perturber atoms. The equation should be particularly useful for determining collisional effects on spectral profiles, magnetic relaxation (Hanle-effect) line shapes, and laser output curves. Some general features of these lines shapes will be discussed in Sec. VI.

IV. STRAIGHT-LINE PATH LIMIT

It is of some interest to examine the expression for $(\partial\tilde{\rho}_{\alpha\beta}/\partial t)_{\text{coll}}$ in the limit of straight-line relative active-atom–perturber collisional paths, since this is an approximation commonly used in many previous theories.[5,6] By "straight-line paths" we shall mean that the scattering angle in the active-atom–perturber center-of-mass frame is less than some critical angle $\theta_c=\lambda_B/\mathcal{R}$, where λ_B is the de Broglie wavelength in the center-of-mass frame and $\mathcal{R}$ is the range of the collisional interaction.[10] The validity criterion for the straight-line-path limit is that the majority of significant collisions (significant with respect to their effect on the line shapes associated with the system) are characterized by scattering angles less than θ_c. The most favorable system for the straight-line-path limit to be valid is one where the interaction range is much greater than the kinetic radii of the atoms.

To obtain the straight-line-path limit for $(\partial\tilde{\rho}_{\alpha\beta}/\partial t)_{\text{coll}}$, which will be denoted by $(\partial\tilde{\rho}_{\alpha\beta}/\partial t)^{\text{slpl}}_{\text{coll}}$, we begin by noting that the last two terms of Eq. (4) may be written in a form containing only collisions with $\theta>\theta_c$ (see Appendix C of QMTE-I). However, since all collisions have $\theta<\theta_c$ by assumption, the last two terms in Eq. (4) must vanish in the straight-line-path limit. Thus, the equation to be considered is

$$\left.\frac{\partial\tilde{\rho}_{\alpha\beta}(\vec{R},\vec{v},t)}{\partial t}\right|^{\text{slpl}}_{\text{coll}}=\sum_{\alpha'\beta'}T^{\alpha'\beta'}_{\alpha\beta}(\vec{v})\tilde{\rho}_{\alpha'\beta'}(\vec{R},\vec{v},t),\tag{10}$$

with $T^{\alpha'\beta'}_{\alpha\beta}(\vec{v})$ given by Eq. (5).

To obtain the straight-line-path limit of Eq. (5), we can use the following expression[11,12] for the scattering amplitude $f_{\alpha\beta}(\vec{v}_r\to\vec{v}'_r)$ which is valid for small-angle scattering:

$$f_{\alpha\beta}(\vec{v}_r\to\vec{v}'_r)=-\frac{i\mu v_r}{2\pi\hbar}\int d^2b\,e^{-i\vec{q}\cdot\vec{b}}[S_{\alpha\beta}(\vec{v}_r,\vec{b})-\delta_{\alpha\beta}],\tag{11}$$

with

$$\vec{q}=(\mu/\hbar)(\vec{v}'_r-\vec{v}_r),\tag{12}$$

and $\vec{b}$ a vector in a plane perpendicular to $\vec{v}_r$ giving the impact parameter of the collision. The quantity $S_{\alpha\beta}$ appearing in (11) is given by[12]

$$S_{\alpha\beta}(\vec{v}_r,\vec{b})=\{\exp[(i/\hbar)\textstyle\int U_{\alpha\beta}(\vec{R})d(\vec{R}\cdot\hat{v}_r)]\}_+,\tag{13}$$

where $U_{\alpha\beta}(\vec{R})$ is the $\alpha\beta$ matrix element of the active-atom–perturber collisional interaction $U(\vec{r},\vec{R})$ [see Eq. (A2b)],

$$\begin{aligned}U_{\alpha\beta}(\vec{R})&=\int\psi_\alpha(\vec{r})^*U(\vec{r},\vec{R})\psi_\beta(\vec{r})d^3r\\&\qquad\text{for }\alpha\text{ and }\beta\text{ in same group of levels}\\&=0\quad\text{otherwise},\end{aligned}\tag{14}$$

and the integral is over the straight-line path of the specific collision. The $\{\ \}_+$ symbol in Eq. (13) indicates that a time-ordered exponential is required. Substituting Eq. (11) into Eq. (5), letting v'_{r1} and v'_{r2} be two independent components of $\vec{v}'_r$ in a plane perpendicular to $\vec{v}_r$ (i.e., in the plane of $\vec{b}$), using the fact that[11]

$$\int d\Omega_{v'_r}\approx v_r^{-2}\int_{-\infty}^{\infty}dv'_{r1}\int_{-\infty}^{\infty}dv'_{r2}$$

when only small-angle scattering is important, and performing some elementary integrations, we find

$$\begin{aligned}T^{\alpha'\beta'}_{\alpha\beta}(\vec{v},\text{slpl})&=-N\int d^3v_pW_p(\vec{v}_p)v_r\\&\quad\times\int d^2b[\delta_{\alpha\alpha'}\delta_{\beta\beta'}-S_{\alpha\alpha'}(\vec{v}_r,\vec{b})S_{\beta\beta'}(\vec{v}_r,\vec{b})^*],\end{aligned}\tag{15}$$

where $T^{\alpha'\beta'}_{\alpha\beta}(\vec{v},\text{slpl})$ is the straight-line-path limit value of $T^{\alpha'\beta'}_{\alpha\beta}(\vec{v})$ and $S_{\alpha\alpha'}$ is given by Eq. (13).

Equation (10), with $T^{\alpha'\beta'}_{\alpha\beta}$ given by Eq. (15), is the straight-line-path limit for the collisional time rate of change of $\tilde{\rho}_{\alpha\beta}$ and agrees with earlier works that effectively treat this limit only. However, an

additional approximation—the replacement of $\int d^3v_p W_p(\vec{v}_p)$ by $\int d^3v_r W_r(\vec{v}_r)$ in Eq. (15), with $W_r(\vec{v}_r)$ the relative velocity distribution—has been consistently employed either implicitly or explicitly in previous treatments of the subject. This approximation, which is clearly valid only if the perturber mass is much less than the active mass or, equivalently, if $\vec{v}_r \simeq \vec{v}_p$, leads to two simplifications of the theory. First, $T^{\alpha'\beta'}_{\alpha\beta}(\vec{v}, \text{slpl})$ becomes velocity independent. Second, the angular integration over $d\Omega_{v_p}$ in Eq. (15) can be done in a simple fashion.

Our straight-line-path limit equation (15) possesses neither of these simplifications; consequently our results will differ from those of the earlier theories. The effects of the velocity dependence of $T^{\alpha'\beta'}_{\alpha\beta}(\vec{v}, \text{slpl})$ have been discussed in another paper.[13] The velocity dependence will lead to asymmetries in spectral profiles and deviations of line shapes from generally accepted forms. The deviation is greatest in systems with high perturber to active-atom mass.

The reason that the angular integrations in Eq. (15) are not simple to perform is that, for a given velocity subset of active atoms, the distribution of colliding perturber atoms is *not* isotropic.[14] This implies that a decomposition of the density matrix into its irreducible tensor components will not yield elements that relax with decay parameters depending only on the rank of the tensor involved.[15] It may be possible that some final average over the active-atom velocity distribution may restore a simple form to the results, but this is yet to be determined.

We conclude that, even in the straight-line-path limit, we should expect a deviation of collisional relaxation formulas from those calculated in earlier theories. The deviation will be largest in systems where the perturber mass is larger than the active-atom mass. In the more general case with no restrictions on collisional path, one might expect significant variance with earlier theories, although a specific evaluation using Eqs. (5)–(8) has yet to be performed.

V. ALTERNATIVE FORM FOR QMTE

It is always possible to transform the QMTE into an equation where all collisional effects are contained in certain propagator functions. In this way, the calculation of collisional effects is separated out as a distinct problem and the QMTE is cast in a form that is especially useful if a perturbation solution in powers of the external field is possible.

To transform the QMTE, we first define the Fourier transform $\tilde{P}_{\alpha\beta}(\vec{\kappa}, \vec{v}, t)$ of $\tilde{\rho}_{\alpha\beta}(\vec{R}, \vec{v}, t)$ by

$$\tilde{P}_{\alpha\beta}(\vec{\kappa}, \vec{v}, t) = (2\pi)^{-3/2} \int d^3R e^{-i\vec{\kappa}\cdot\vec{R}} \tilde{\rho}_{\alpha\beta}(\vec{R}, \vec{v}, t) \quad (16)$$

Then, multiplying Eq. (9) by $(2\pi)^{-3/2} e^{-i\vec{\kappa}\cdot\vec{R}}$ and integrating over $\vec{R}$, we obtain

$$\frac{\partial \tilde{P}_{\alpha\beta}(\vec{\kappa}, \vec{v}, t)}{\partial t} + i\vec{\kappa}\cdot\vec{v}\tilde{P}_{\alpha\beta}(\vec{\kappa}, \vec{v}, t) = \sum_{\alpha'\beta'} \Big(T^{\alpha'\beta'}_{\alpha\beta}(\vec{v}) \tilde{P}_{\alpha'\beta'}(\vec{\kappa}, \vec{v}, t) - \Gamma^{\alpha'\beta'}_{\alpha\beta}(\vec{v}, \text{vc}) \tilde{P}_{\alpha'\beta'}(\vec{\kappa}, \vec{v}, t) + \int d^3v' W^{\alpha'\beta'}_{\alpha\beta}(\vec{v}' \to \vec{v}) \tilde{P}_{\alpha'\beta'}(\vec{\kappa}, \vec{v}', t) \Big) + g_{\alpha\beta}(\vec{\kappa}, \vec{v}, t), \quad (17)$$

where

$$g_{\alpha\beta}(\vec{\kappa}, \vec{v}, t) = (2\pi)^{-3/2} \int d^3R e^{-i\vec{\kappa}\cdot\vec{R}} \{ \tilde{\Lambda}_{\alpha\beta}(\vec{R}, \vec{v}, t) - \Gamma_{\alpha\beta}(\vec{R}, \vec{v}, t) \tilde{\rho}_{\alpha\beta}(\vec{R}, \vec{v}, t) + (i\hbar)^{-1} [\tilde{V}(\vec{R}, t), \tilde{\rho}(\vec{R}, t)]_{\alpha\beta} \}. \quad (18)$$

A solution to Eq. (18) of the form

$$\tilde{P}_{\alpha\beta}(\vec{\kappa}, \vec{v}, t) = \int d^3v' \int_0^t dt' G_{\alpha\beta}(\vec{\kappa}, \vec{v}' \to \vec{v}, t - t') \times g_{\alpha\beta}(\vec{\kappa}, \vec{v}', t') \quad (19)$$

exists, provided that the functions $G_{\alpha\beta}(\vec{\kappa}, \vec{v}' \to \vec{v}, \tau)$ satisfy the integrodifferential equations

$$\frac{\partial G_{\alpha\beta}(\vec{\kappa}, \vec{v}' \to \vec{v}, \tau)}{\partial \tau} + i\vec{\kappa}\cdot\vec{v} G_{\alpha\beta}(\vec{\kappa}, \vec{v}' \to \vec{v}, \tau) = \sum_{\alpha'\beta'} \Big(T^{\alpha'\beta'}_{\alpha\beta}(\vec{v}) G_{\alpha'\beta'}(\vec{\kappa}, \vec{v}' \to \vec{v}, \tau) - \Gamma^{\alpha'\beta'}_{\alpha\beta}(\vec{v}, \text{vc}) G_{\alpha'\beta'}(\vec{\kappa}, \vec{v}' \to \vec{v}, \tau) + \int d^3v_1 W^{\alpha'\beta'}_{\alpha\beta}(\vec{v}_1 \to \vec{v}) G_{\alpha'\beta'}(\vec{\kappa}, \vec{v}' \to \vec{v}_1, \tau) \Big), \quad (20)$$

subject to the initial condition

$$G_{\alpha\beta}(\vec{\kappa}, \vec{v}' \to \vec{v}, 0) = \delta(\vec{v}' - \vec{v}). \quad (20a)$$

The quantity $G_{\alpha\beta}(\vec{\kappa}, \vec{v}' \to \vec{v}, \tau)$ is, in effect, a propagator which determines the probability density that there will be a collisional change in the velocity associated with $\tilde{P}_{\alpha\beta}(\vec{\kappa}, \vec{v}, t)$ from $\vec{v}'$ to $\vec{v}$ in a time τ.

If $\tilde{\rho}_{\alpha\beta}(\vec{R}, \vec{v}, t)$, appearing in Eq. (18) for $g_{\alpha\beta}(\vec{\kappa}, \vec{v}, t)$, is written in terms of its Fourier transform $\tilde{P}_{\alpha\beta}(\vec{\kappa}, \vec{v}, t)$, and if the resultant equation for $g_{\alpha\beta}(\vec{\kappa}, \vec{v}, t)$ is substituted into Eq. (19), one obtains

$$\tilde{P}_{\alpha\beta}(\vec{\kappa}, \vec{v}, t) = \int d^3v' \int_0^\infty dt' G_{\alpha\beta}(\vec{\kappa}, \vec{v}' \to \vec{v}, t - t') \times \{ \tilde{\Lambda}_{\alpha\beta}(\vec{\kappa}, \vec{v}', t') - (2\pi)^{-3/2} \times \int d^3\kappa' \Gamma_{\alpha\beta}(\vec{\kappa} - \vec{\kappa}', \vec{v}', t') \tilde{P}_{\alpha\beta}(\vec{\kappa}', \vec{v}', t') + (2\pi)^{-3/2} \int d^3\kappa' (i\hbar)^{-1} \times [\tilde{V}(\kappa - \kappa', t'), \tilde{P}(\vec{\kappa}', \vec{v}', t')]_{\alpha\beta} \}, \quad (21)$$

where $G_{\alpha\beta}(\vec{\kappa}, \vec{v}' - \vec{v}, \tau)$ is determined by Eq. (20) and $\tilde{\Lambda}_{\alpha\beta}(\vec{\kappa}, \vec{v}, t)$, $\tilde{\Gamma}_{\alpha\beta}(\vec{\kappa}, \vec{v}, t)$, and $\tilde{V}(\vec{\kappa}, t)$ are Fourier transforms of $\Lambda_{\alpha\beta}(\vec{R}, \vec{v}, t)$, $\Gamma_{\alpha\beta}(\vec{R}, \vec{v}, t)$, and $V(\vec{R}, t)$, respectively. As noted above, the QMTE, in the form given by Eqs. (21) and (20), is well suited to an iterative solution in powers of the external field.[16]

VI. DISCUSSION

The quantum-mechanical transport equation (QMTE) given by Eq. (9) is the basic result of this paper. A solution of the QMTE provides values for density-matrix elements from which theoretical expressions for quantities of physical interest may be obtained. The QMTE is applicable to atomic systems in which "active" atoms interact with some external fields while undergoing collisions with perturber atoms. It does not account for excitation transfer between active atoms and perturbers (resonant collisions), radiation trapping, or atomic recoil due to emission or absorption of radiation; we do not believe it is overly difficult to formally introduce these effects into the QMTE.[17] However, attempts to extend the QMTE to apply to systems with frequency spacings of atomic levels on the order of the inverse collision time (see Sec. II) will be accompanied by more severe complications.

In order to solve the QMTE, one must first have expressions for the scattering amplitudes [see Eqs. (5)–(8)] which, in itself, poses a difficult auxiliary problem.[2,3] When one obtains exact, approximate, or phenomenological expressions for the scattering amplitudes, he will still be faced with solving the QMTE, a complex partial integrodifferential equation.

Although this may seem a formidable task for even the most simple atomic system, there may be some specific problems where solutions or partial solutions are tractable. In particular, we hope to derive expressions for the spectral line shapes, Hanle-effect line shapes, and laser output curves associated with atomic systems from solutions of the QMTE. While details of the calculations have not yet been performed, we shall indicate below some general features of the results which are expected.

i. Spectral profiles. In many circumstances, one measures the optical or infrared absorption or emission spectrum associated with a transition between states in different groups of levels (see Fig. 1). Traditional theoretical developments of line-shape formulas involve the assignation of a Doppler-shifted Lorentzian profile

$$\frac{\gamma_0 + \Gamma(\vec{v})}{[\gamma_0 + \Gamma(\vec{v})]^2 + [\omega - \omega_0 - \Delta(\vec{v}) - \vec{k}\cdot\vec{v}]^2} \tag{22}$$

to each velocity subset of the active atoms. The quantities $\Gamma(v)$ and $\Delta(v)$ in (22) are collisional width and shift parameters, and γ_0 is related to the natural width of the transition. The profiles (22) are then weighted according to the velocity distribution $W(\vec{v})$ of the active-atom subsets. If $W(\vec{v})$ is Gaussian, the resultant line shape is termed a speed or velocity-dependent Voigt profile.[13]

The physical situation predicted by the QMTE differs from this traditional result in several respects. First, each velocity subset of active atoms is no longer characterized by a Lorentzian profile, even in the straight-line-path limit. Second, the total line shape may reflect either obvious or subtle effects of collision-induced velocity changes of the active atoms.

In the extreme limit of equal collisional interaction for all the levels involved in the transition, collisions may cause a narrowing of the line shape. This phenomenon, predicted by Dicke,[18] is due to a collisional averaging of the Doppler phase factor. However, when the collisional interactions for the transition levels differ considerably (as they do for electronic transitions), the narrowing mechanism is all but lost and collision-induced velocity changes enter the theory in a more subtle manner.[2,3] Perhaps the most interesting cases are vibrational or rotational spectra, where the collisional interactions for the transition levels may be comparable but not equal. Under these circumstances both narrowing and broadening effects may be encountered (as well as asymmetries due to the interplay of both mechanisms). Experimental studies do, in fact, show both narrowing and broadening in rotational[19] and vibrational[20] transitions; these data are not in agreement with what are essentially semiclassical transport equations—a test of the QMTE will be its ability to explain the results of these experiments.

ii. Hanle-effect line shapes. In Hanle or level-crossing experiments, one may measure the collisional magnetic relaxation of a state with total angular momentum J. The prediction of traditional theories that treat this problem is that there are $2J+1$ independent real collisional decay parameters which characterize the relaxation. However, this result is based upon an assumed spatial isotropy of perturber collisions for each velocity subset of active atoms and, in Sec. IV, we have seen that this approximation is not valid, even in the straight-line-path limit. One might expect, therefore, that a solution of the QMTE will reveal that more than $2J+1$ independent parameters are needed to describe the relaxation and that the parameters may be complex (indicating possible collisional shifts as well as broadening in the line shapes).

iii. Laser output curves. It is possible to use curves of output laser intensity versus detuning of

the laser cavity from the atomic transition frequency to study collisional effects within the laser system. These curves tend to be a sensitive probe of collisional effects, since the line shape can be determined basically by the Lorentzian rather than Doppler contribution to the profile. Thus, asymmetries due to either the speed dependence of the collisional line-shape parameters or to the more complicated collisional processes predicted by the QMTE should be more pronounced than those observed in spectral profiles.

In addition, one might expect that laser experiments would be highly appropriate for measuring the velocity-changing aspects of collisions, since the laser uses only those atoms that have the correct Doppler shifts to interact with the laser field. A collision that changes the velocity of an atom interacting with the field will stop that atom's participation in the lasing process and the effects of such collisions should be reflected in the laser output. However, the output of single-mode lasers which operate on electronic transitions is not particularly sensitive to velocity-changing collisions, as has been noted previously.[2] Owing to the significant difference in the collisional interaction experienced by the different electronic levels involved in the laser transition, velocity-changing collisions affect the over-all intensity of the output more than the details of the line shape.

Velocity-changing collisions may lead to more interesting effects in multimode lasers. These collisions can change the velocity of an atom interacting with one field more into a new velocity which permits the atom to interact with a different field mode. In this manner, the collisions can serve to couple the field modes. The coupling will be especially important in lasers which exhibit neutral or near-neutral coupling in the absence of collisions, such as some ring and Zeeman lasers. There is a complicating factor, however. Usually, the active-atom density of lasers is high enough so that radiation trapping or resonant broadening effects are present. Since these processes can compete with or even dominate the velocity-changing aspects of collisions, care must be taken to include their effects when appropriate.

The QMTE may also lead to interesting predictions in the case of molecular lasers which operate on vibrational transitions. Here, the collisional interaction for the two laser levels might be comparable and the resulting line shape a better measure of the velocity-changing aspects of collisions. It is interesting to note that an asymmetry in CO laser output curves has been observed[21] and this may be due, in part, to the interplay of the velocity-changing and energy-level shifting aspects of collisions expected in systems with comparable collisional interactions for the transition levels.

For the three situations discussed above, we do not expect a dramatic variation from the predictions of earlier theories, since it is most likely that experimental studies would have revealed any large discrepancies. The deviation from traditional theories will be minimal when dealing with electronic transitions in systems with large active-atom to perturber mass ratio. In that case, there are few velocity-changing collisions and the relative active-atom–perturber velocity is almost equal to the perturber velocity so that the traditional theories form a good approximation to the QMTE. On the other hand, systems with comparable collisional interactions for the transition levels may require the completeness of the QMTE for a reasonably accurate description; the experimental data available that are applicable to such cases are quite limited. Regardless of the problem, it is best to start with an equation resulting from a theory that consistently and correctly takes into account the effects of collisions on the moving active atoms. The quantum-mechanical transport equation is offered as one equation that meets these requirements.

APPENDIX

The calculation of $[\partial\tilde{\rho}_{\alpha\beta}(\vec{R}, \vec{v}, t)/\partial t]_{\text{coll}}$ is similar to that given in Appendix B of QMTE-I, and only a sketch of the calculation will be presented here. First, one considers a single active atom with center-of-mass coordinate $\vec{R}$ and relative electronic coordinates $\vec{r}$ interacting with a perturber atom fixed at the origin. The Hamiltonian for this system, neglecting all but the collisional interactions, is given by

$$H(\vec{r}, \vec{R}) = H_0(\vec{r}) - (\hbar^2/2m)\nabla_R^2 + U(\vec{r}, \vec{R}),$$

where $H_0(\vec{r})$ is the free-atom electronic Hamiltonian possessing eigenfunctions $\psi_\alpha(\vec{r})$, m is the active-atom mass, and $U(\vec{r}, \vec{R})$ is the potential due to the perturber atom. Expanding the active atom's wave function as

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

and using Schrödinger's equation for $\psi(\vec{r}, \vec{R}, t)$, it is an easy matter to see that the $\tilde{A}_\alpha(\vec{R}, t)$ obey the equation

$$\frac{i\hbar\partial\tilde{A}_\alpha(\vec{R}, t)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\tilde{A}_\alpha(\vec{R}, t) + \sum_\beta U_{\alpha\beta}(\vec{R})\tilde{A}_\beta(\vec{R}, t)e^{i\omega_{\alpha\beta}t}, \quad \text{(A1)}$$

where

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

and $\omega_{\alpha\beta} = \omega_\alpha - \omega_\beta$.

We are now ready to employ the collisional approximations outlined in Sec. II. First, if α and

β in Eq. (A1) belong to different groups of levels (see Fig. 1), the exponential term in Eq. (A1) is rapidly varying compared with $\tilde{A}_\beta(\vec{R}, t)$ and tends to destroy any contribution from the second term in the right-hand side of Eq. (A1). Equivalently, we could define $U_{\alpha\beta}=0$ if α and β belong to different groups of levels, implying that collision-induced transitions between different groups of levels are negligible. Second, if α and β belong to the same group of levels, we may set $e^{i\omega_{\alpha\beta}t}=1$ in Eq. (A1), since it has been assumed that, with regards to collisional processes, the energy levels *within* any group of levels may be taken as degenerate. Under these approximations, Eq. (A1) becomes

$$\frac{i\hbar\partial\tilde{A}_\alpha(\vec{R}, t)}{\partial t}=-\frac{\hbar^2}{2m}\nabla^2\tilde{A}_\alpha(\vec{R}, t)+\sum_\beta U_{\alpha\beta}(\vec{R})\tilde{A}_\beta(\vec{R}, t), \tag{A2a}$$

where

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

for α and β in same group of levels

$$=0 \quad \text{otherwise}. \tag{A2b}$$

Equation (A2a) is now in a form that is easily treated by formal scattering theory.[22] In keeping with the development of QMTE-I, we consider $\tilde{A}_\alpha(\vec{R}, t-\delta t)$ to represent a wave packet with average velocity $\vec{v}'$ moving towards the scattering center (perturber). After a time $2\delta t$, the wave packet has been scattered and the new amplitude is given by [compare with Eq. (IB5)]

$$\begin{aligned}\tilde{A}_\alpha(\vec{R}, t+\delta t)=&\exp[-(imv'^2/2\hbar)\,2\delta t]\\&\times[\tilde{A}_\alpha(\vec{R}-2\vec{v}'\delta t, t-\delta t)\\&+R^{-1}\textstyle\sum_\beta f_{\alpha\beta}(\vec{v}'\to v'\hat{R})\\&\times\tilde{A}_\beta(R\hat{v}'-2\vec{v}'\delta t, t-\delta t)],\end{aligned} \tag{A3}$$

where $f_{\alpha\beta}(\vec{v}'\to v'\hat{R})$ is the inelastic scattering amplitude for scattering from channel β with velocity $\vec{v}'$ to channel α with velocity $v'\hat{R}$. Note that from our definition of $U_{\alpha\beta}$ in Eq. (A2b), $f_{\alpha\beta}=0$ if α and β belong to different groups of levels.

From this point on, the calculation is the same as that of Appendix B of QMTE-I. One forms density-matrix elements, associates classical position and velocity variables with the wave packet, and averages over all types of collisions to obtain an equation valid for the ensemble of active atoms,

$$\begin{aligned}\frac{\partial\tilde{\rho}_{\alpha\beta}(\vec{R}, \vec{v}, t)}{\partial t}\bigg|_{\text{coll}}=&\sum_{\alpha'\beta'}\Big(-Nv\frac{2\pi\hbar}{imv}[f_{\alpha\alpha'}(\vec{v}\to\vec{v})\delta_{\beta\beta'}\\&-f_{\beta\beta'}(\vec{v}-\vec{v})^*\delta_{\alpha\alpha'}]\tilde{\rho}_{\alpha'\beta'}(\vec{R}, \vec{v}, t)\\&+Nv\int d\Omega_{v'}f_{\alpha\alpha'}(\vec{v}'\to\vec{v})f_{\beta\beta'}(\vec{v}'\to\vec{v})^*\tilde{\rho}_{\alpha'\beta'}(\vec{R}, \vec{v}', t)\Big),\end{aligned} \tag{A4}$$

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

In order to separate out collisions involving significant velocity changes from straight-line-path collisions (see Sec. IV), we add and substract a term

$$\sum_{\alpha'\beta'}\Gamma_{\alpha\beta}^{\alpha'\beta'}(\vec{v}, \text{vc})\tilde{\rho}_{\alpha'\beta'}(\vec{R}, \vec{v}, t)$$

($\Gamma_{\alpha\beta}^{\alpha'\beta'}$ will be defined below; the vc is a label meaning "velocity changing") to Eq. (A4) and rewrite it as

$$\begin{aligned}\frac{\partial\tilde{\rho}_{\alpha\beta}(\vec{R}, \vec{v}, t)}{\partial t}\bigg|_{\text{coll}}=&\sum_{\alpha'\beta'}\Big(T_{\alpha\beta}^{\alpha'\beta'}(\vec{v})\tilde{\rho}_{\alpha'\beta'}(\vec{R}, \vec{v}, t)\\&-\Gamma_{\alpha\beta}^{\alpha'\beta'}(\vec{v}, \text{vc})\tilde{\rho}_{\alpha'\beta'}(\vec{R}, \vec{v}, t)\\&+\int d\Omega_{v'}W_{\alpha\beta}^{\alpha'\beta'}(\vec{v}'\to\vec{v})\tilde{\rho}_{\alpha'\beta'}(\vec{R}, \vec{v}', t)\Big),\end{aligned} \tag{A5}$$

where

$$\begin{aligned}T_{\alpha\beta}^{\alpha'\beta'}(\vec{v})=&-Nv(2\pi\hbar/imv)[f_{\alpha\alpha'}(\vec{v}\to\vec{v})\delta_{\beta\beta'}\\&-f_{\beta\beta'}(\vec{v}\to\vec{v})^*\delta_{\alpha\alpha'}]\\&+Nv\int d\Omega_{v'}f_{\alpha\alpha'}(\vec{v}\to\vec{v}')f_{\beta\beta'}(\vec{v}\to\vec{v}')^*,\end{aligned} \tag{A6a}$$

$$W_{\alpha\beta}^{\alpha'\beta'}(\vec{v}'\to\vec{v})=Nvf_{\alpha\alpha'}(\vec{v}'\to\vec{v})f_{\beta\beta'}(\vec{v}'\to\vec{v})^*, \tag{A6b}$$

and

$$\Gamma_{\alpha\beta}^{\alpha'\beta'}(\vec{v}, \text{vc})=\int d\Omega_{v'}W_{\alpha\beta}^{\alpha'\beta'}(\vec{v}\to\vec{v}'). \tag{A6c}$$

When Eqs. (A6) are generalized to allow for moving perturbers, one arrives at Eqs. (5)–(8) of the text.

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

[3]P. R. Berman, Phys. Rev. A 5, 927 (1972). This paper is referred to as QMTE-I and contains references to other attempts at quantum-mechanical transport equations.

[4]V. A. Alekseev, T. L. Andreeva, and I. I. Sobelman, Zh. Eksperim. i Teor. Fiz. 62, 614 (1972) [Sov. Phys. JETP (to be published)].

[5]E. Lindholm, Arkiv Mat. Astron. Fysik 32A, 17 (1945); H. M. Foley, Phys. Rev. 69, 616 (1946); P. W. Anderson, *ibid.* 76, 647 (1949).

[6]P. R. Berman and W. E. Lamb, Jr., Phys. Rev. 187, 221 (1969). This paper contains many references to other works that essentially neglect all collision-induced velocity changes. Such works are referred to as "earlier" or "traditional" in this paper.

[7]Radiation trapping becomes important at densities on

the order of (radiative wavelength)$^{-3}$, which is typically about 10^{13} cm^{-3}. Resonant broadening effects typically become significant at active-atom densities of 10^{15} atoms/cm^3. If the density of "foreign-gas" perturbers is much greater than that of "resonant" perturbers, the resonant broadening effects may still be negligible by comparison.

[8]We are, in effect, assuming that the atomic system is in equilibrium before the external fields are "turned on" and that the presence of the fields cannot alter the velocity distribution of the active atoms to an extent where they, in turn, can modify the perturber velocity distribution. To allow for changes in the perturber velocity distribution, one would have to consider the density matrix for the total system of active atoms plus perturbers and obtain a Boltzmann equation for its time development. Reduced density matrices for either the active atoms or perturbers are then obtained by appropriate traces of the solutions to this equation.

[9]For example, in many laser problems, one considers a two-level problem with both levels representing excited states. This system is not closed and allowance is made for excitation to and decay from this subsystem.

[10]Note that this is a much stronger condition than that given in Appendix C of QMTE-I for the neglect of velocity-changing collisions. There are really two considerations here. Equation (10) is valid provided velocity-changing collisions have no significant effect on the output of the atomic system. However, the value of $T^{\alpha'\beta'}_{\alpha\beta}(\vec{v})$ to be derived will agree with semiclassical calculations only if the stronger condition $\theta < \theta_c$ is satisfied; in all other cases $T^{\alpha'\beta'}_{\alpha\beta}(\vec{v})$ should be computed from Eq. (5).

[11]R. J. Glauber, in *Lectures in Theoretical Physics*, edited by W. E. Brittin *et al.* (Interscience, New York, 1959), Vol. I.

[12]R. J. Cross, Jr., J. Chem. Phys. 47, 3724 (1967). Cross does not explicitly recognize the scattering amplitude as a time-ordered exponential and subsequently neglects the time ordering in his calculation. The neglect of time ordering can lead to substantial errors in some cases (see Ref. 6).

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[14]J. Ward, Ph.D. thesis (University of Colorado, 1971) (unpublished). In his thesis, Ward discusses the effects of nonisotropic perturber collisions as well as other features of the quantum-mechanical solution as they apply to the problem of theoretical spectral-line-shape predictions. (I should like to thank Professor J. Cooper for providing a copy of this thesis.)

[15]A. Ben Reuven, Phys. Rev. 141, 34 (1966).

[16]The QMTE, in the form given by Eqs. (21) and (22), actually provides the connection between the QMTE and the pseudoclassical collision model (PCM) developed in Refs. 1 and 2, in which a laser problem was solved by an iterative method in powers of the laser field. The propagators $G_{\alpha\beta}(\vec{\kappa}, \vec{v}' \to \vec{v}, \tau)$ appearing in Eq. (21) are, in essence, the same propagators that appear in Ref. 2.

[17]Attempts to include radiation trapping {M. I. D'Yakonov and V. I. Perel, Zh. Eksperim. i Teor. Fiz. 47, 1483 (1964) [Sov. Phys. JETP 20, 997 (1965)]}, photon recoil {A. P. Kol'chenko, S. G. Rautian, and R. I. Sokolovskii, *ibid.* 55, 1864 (1968) [*ibid.* 28, 986 (1961)]}, and resonant broadening {E. G. Pestov and S. G. Rautian, *ibid.* 56, 902 (1969) [*ibid.* 29, 458 (1969)]} effects in transport equations have already been made in various approximations.

[18]R. H. Dicke, Phys. Rev. 89, 472 (1953).

[19]V. G. Cooper, A. D. May, E. H. Hara, and H. F. P. Knapp, Can. J. Phys. 46, 2019 (1968).

[20]F. De Martini, E. Santamato, and F. Capasso, in Proceedings of the Seventh International Quantum Electronics Conference, Montreal, 1972, p. 24 (unpublished). There actually may have been no narrowing observed in this experiment, which would indicate that the collisional interaction for the two vibrational states is different enough so that the Dicke narrowing mechanism is suppressed.

[21]C. Freed and H. A. Haus, in Ref. 20, p. 99.

[22]See, for example, R. G. Newton, *Scattering Theory of Waves and Particles* (McGraw-Hill, New York, 1966), Eq. (16.58). Equation (A3) above is actually a transformation of Newton's equation (16.58), obtained from time-independent collision theory, to the time-dependent-wave-packet picture.

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Inelastic *S*-Wave Positron-Hydrogen Scattering

Josef Stein and Raphael Sternlicht
Racah Institute of Physics, The Hebrew University, Jerusalem, Israel
(Received 23 March 1972)

The variational methods of Kohn and Hulthén are used to calculate the scattering parameters of the positron-hydrogen rearrangement collision. The R-matrix elements are computed for positron energies 0–0.33 a.u. with accuracy of (1–10)%. It is also shown that a good approximation to the diagonal elements of the R matrix can be obtained by ignoring the coupling between the channels.

I. INTRODUCTION

The problem of low-energy scattering of positrons by hydrogen atoms has attracted many researchers by its simple structure and because of the hope that its solution might lead to the development of approximate methods for solving more complex scattering problems. The main difficulty