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Theory of Collision Effects on Line Shapes Using a Quantum-Mechanical Description of the Atomic Center-of-Mass Motion — Application to Lasers. I*

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We present a theory of pressure effects in which the atomic center-of-mass motion is treated quantum mechanically. The quantum-mechanical calculation treats the perturber-induced energy-level variations and the velocity changes of the emitter caused by collisions on an equal basis. Specifically, we shall treat the problem of a laser to first order in the laser field, allowing for the fact that the laser atoms are undergoing collisions, but our results will also be applicable to the cases of stimulated emission or absorption. It will be sufficient to carry out a perturbation solution of the problem assuming that the laser atoms undergo at most one collision in their lifetime, since such a restricted calculation reveals the salient features of the theory. We shall find that, in general, there is no classical limit for our results. Thus, previous treatments employing a classical Boltzmann-equation approach for the atomic center-of-mass motion are invalid, and a quantum-mechanical description is necessary to correctly treat cases where both the modified Doppler effect (modified by collisions) and perturber-induced energy-level variations are present.

I. INTRODUCTION

In a general study of atomic spectral line profiles, one must consider three factors which alter the line shapes from those associated with isolated stationary atoms. First, there is the normal Doppler effect, in which an isolated moving atom emits or absorbs radiation at a frequency shifted from its natural one. Second, there are collision effects in which the energy levels of the emitting or absorbing atom are perturbed by the presence of other atoms (perturbers), leading to both a shift and broadening of the spectral profiles [perturber-induced energy-level-variation effects (ELVE)]. The third factor is a combination of the first two. That is, collisions also change the atom's velocity, thus modifying the normal Doppler effect. We shall refer to this process as the generalized Doppler effect (GDE) with the understanding that it reduces to the normal Doppler effect for the case of no collisions. Of course, a proper theoretical treatment of line shapes must incorporate all the above factors. However, until the discovery of the laser, the experimental situation had not been conducive to such a study. We elaborate on this point.

At moderate or "high" perturber pressures[1] (≥ 0.5 atm), ELVE widths are larger than the Doppler broadening, and to a good approximation the Doppler effect (or GDE) can be neglected. On the other hand, at low pressures, ELVE effects have generally been regarded as an independent broadening mechanism to be superimposed on the normal Doppler effect. To this end, the solution of the ELVE problem for stationary emitters as developed by Lindholm, Foley, and Anderson[2] has been "folded into" the normal Doppler profile of the system under consideration to obtain the final line shape. Thus, any modifications of the line shape due to the GDE are lost by this method (which has also been applied in the intermediate-pressure range). It would certainly be desirable to have a consistent treatment for both the GDE and ELVE. Probably one reason that more attention has not been given to the GDE is that at low pressures the normal Doppler width is large and tends to mask any subtle collision effects.

The situation in gas lasers is quite different. The output of a gas laser is very nearly monochromatic and has no Doppler or collision width. However, both the gain and saturation parameters of a laser are sensitive to collisions of the laser atoms. Of interest in laser problems is the dependence of these parameters on cavity detuning (difference of cavity and laser transition frequencies). In the absence of collisions, the gain parameter α exhibits the normal Doppler width, but the saturation parameter β, arising from nonlinear terms, has only a slight dependence on the Doppler effect. Even though the saturation parameter ultimately has little Doppler dependence, it is indirectly sensitive to the center-of-mass motion of the laser atoms. As such, it should provide the most convenient place to study the GDE, once collisions are introduced. Hence, a study of the steady-state laser intensity (which is proportional to the ratio of gain and saturation parameters) as a function of cavity detuning will hopefully provide further insight into the GDE. It is necessary, therefore, that a theoretical study of pressure effects in lasers include both the ELVE (perturber-induced energy level variation effect) and the GDE (generalized Doppler effect).

Some recent calculations have appeared which attempt to treat the problem we have just outlined.[3,4] The ELVE is treated by standard pressure-broadening techniques for stationary atoms, while the GDE is treated by solving a Boltzmann equation for the atomic center-of-mass motion. The two results are then combined in either a statistically dependent (ELVE and GDE are assumed to be correlated) or statistically independent (ELVE and GDE are assumed to be uncorrelated) manner. Of course, the ELVE and GDE are correlated since a given collision simultaneously affects the energy levels and causes a change in velocity of the atom. The above method, which treats the atomic center-of-mass motion classically, seems reasonable. However, we shall now show that, in all but a limiting case, a classical description of the atomic center-of-mass motion proves to be invalid for the problem at hand.

In order to prove this assertion, we must consider the radiative process in some detail. For stationary atoms, the essential quantity in lasers and stimulated emission or absorption problems is the dipole moment which reflects the interaction of the radiative states a and b with some external field. A knowledge of the dipole moment at all times is sufficient to specify the line shape. The dipole moment is directly related to the off-diagonal density-matrix element $\rho_{ab}(t)$ of the atom, and, for the sake of brevity, we shall also refer to $\rho_{ab}(t)$ as the dipole moment of the atom. For moving atoms, one would also want to keep track of the center-of-mass motion, and it is most tempting to consider it as a classical variable $\vec{R}(t)$. In that case, the dipole moment is specified by $\rho_{ab}[\vec{R}(t), t]$ and the problem is solved for a classical center-of-mass motion. This procedure was followed by Lamb[5] for the case of no collisions and by several authors[3,4] for the case where collisions were included, corresponding to the Boltzmann-equation approach described above.

Let us now assume that an atom has acquired a dipole moment $\rho_{ab}[\vec{R}(t), t] \neq 0$ due to interaction with the field and then undergoes a collision. If the atom had been purely in state a or purely in state b, it would have been scattered in the respective directions shown in Fig. 1. However, if the atom enters the collision in a linear combination of states a and b, one can no longer retain a classical trajectory for $\rho_{ab}[\vec{R}(t), t]$ unless the a and b trajectories differ by a negligible amount. To be more specific, let $\Delta\vec{v}_a$ and $\Delta\vec{v}_b$ be the velocity changes undergone by the atom for pure-state-a and pure-state-b scattering, respectively. If the atom has a lifetime τ, then the Doppler effect will be modified by those collisions that produce additional Doppler phase shifts $\vec{k}\cdot\Delta\vec{v}_a\tau$ or $\vec{k}\cdot\Delta\vec{v}_b\tau$ which are comparable with unity ($\vec{k}$ is the radiation propagation vector). For

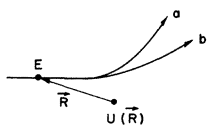

FIG. 1. Two possible trajectories for scattering of an atom E by a potential $U(\vec{R})$. Atom E would follow trajectory a if it entered the collision in a state a and trajectory b if it entered the collision in state b. If the atom entered the collision in a linear combination of states a and b, this classical picture is no longer well-defined.

a classical picture to hold, the difference in additional Doppler phase shifts for the two paths must be negligible. That is, one must require

$$|\vec{k}\cdot(\Delta\vec{v}_a - \Delta\vec{v}_b)\tau| \ll 1, \tag{1}$$

so that paths a and b are, in effect, equivalent for defining the atomic trajectory. Equation (1) will be true only in the limit of nearly equal scattering interaction for both radiative states (paths a and b coincide), a highly unlikely situation, but one for which a classical picture is valid. In general, however, one state dominates the broadening ($\Delta v_a \gg \Delta v_b$ or $\Delta v_b \gg \Delta v_a$), so that inequality (1) fails, as does this classical picture. An alternate "classical" approach would be to take $\rho_{ab}[\vec{R}(t), t] = 0$ after any collision since there is no overlap of the a and b trajectories. However, this model is not satisfactory since it fails to predict the observed pressure shifts in spectral profiles.

For the present, we conclude that a theory is needed which treats the atomic center-of-mass motion quantum mechanically and consequently considers both the ELVE and GDE on an equal footing. In order to reveal some general properties of the quantum-mechanical solution, it will suffice to consider the problem of a laser to first order in the laser field and in the limit that the laser atoms undergo at most one collision in their lifetimes. Although the latter assumption is not valid at normal operating laser pressures (typical laser atoms average about ten collisions per lifetime), it is likely that our results may be easily generalized to higher pressures. The saturation effects of third-order laser theory will be given in a future paper. We shall find that, in our quantum-mechanical solution, the dipole moment $\rho_{ab}[\vec{R}(t), t]$ is replaced by the dipole-moment density $\rho_{ab}(\vec{R}, t)$ (to be discussed in Sec. III), in which $\vec{R}$ is a quantum-mechanical variable. We should note that the results of this paper are also applicable to the cases of stimulated emission or absorption.

Although the major purpose of this work is to provide a quantum-mechanical description of the collision process, we shall find that our results allow an interpretation in terms of a pseudoclassical model. This model is first mentioned in Sec.

V and described briefly thereafter. The term "pseudoclassical" is used since the model is intimately connected with the quantum-mechanical calculation, yet permits the use of classical techniques in the actual evaluation of the line shapes. In the present paper we restrict our discussion to the *basis* for the model and do not present the calculational rules needed for applying it to the problem at hand. A more detailed description of the pseudoclassical model will be given in a subsequent paper where it will be used both in the calculation of third-order laser-field effects and in the extension of our one-collision result to the many-collision region.

The content of the paper is as follows. The general method of approach and further approximations will be given in Sec. II. In Sec. III, a slightly different form of the Lamb laser theory[5] is developed which is better suited to our quantum-mechanical calculations. The basic working equations of the model are derived in Sec. IV, and the first-order laser theory for collision interaction in the upper laser state only and the lower laser state only are given in Secs. V and VI, respectively. In Sec. VII we present a treatment of first-order laser theory when both radiating states are subject to the collision interaction. In the extreme limit of equal collision interactions for both laser states, we shall be able to achieve a correspondence with a classical model since, for this case, the state a and b trajectories of Fig. 1 coincide. The final results for the gain and frequency-pulling parameters of the laser are derived in Sec. VIII. In Sec. IX, we present a summary and discussion of our results with suggestions for generalizing the theory.

II. METHOD OF APPROACH AND APPROXIMATIONS

Our laser calculation will follow the general approach given by Lamb,[5] modified to treat the motion of the atoms from a quantum-mechanical viewpoint. The laser transition levels of the emitter atom are shown in Fig. 2, where the decay parameters γ_a and γ_b give the radiative decay rates of the states a and b, respectively, to some lower states not shown in the figure. The emitter atoms will undergo collisions with ground-state perturber atoms which we shall take as rigidly fixed in the laser medium. Of course, real perturber atoms do move, and the assumption of fixed perturbers is made solely for mathematical convenience; a method for generalizing the results to the case of moving perturbers is given in Sec. IX.

We shall assume that at $t=0$ a given emitter atom is excited in a plane-wave state[6] and begins to interact with both the laser field and the scattering centers (perturbers). The problem will be solved by time-dependent perturbation theory to first order

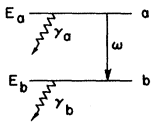

FIG. 2. Two states a and b involved in the laser transition have energies E_a and E_b, respectively, with $\omega = E_a - E_b$. Both levels are allowed to decay to lower states with the rates γ_a and γ_b, respectively.

in the laser field. This is a generalization of the treatment of a scattering problem given by Bethe.[7]

We shall calculate only the lowest-order contributions of the scattering interaction at each perturber site and then generalize the results to all orders in the scattering interaction by a method to be described in Sec. V. The final results will give a complete description of the one-collision process. The one-collision approximation will be valid if the average time between collisions is larger than the lifetimes γ_a^{-1} or γ_b^{-1}. In other words, a wave scattered from one perturber will not have time to interact with another perturber.

The following additional approximations will be made. (i) Excitation of laser atoms only to state a is to be discussed. Generalization to allow for excitation to state b is not particularly difficult, but does not afford any new physical insight. (ii) The laser field will be treated classically. (iii) The laser calculation is to be done for single-mode operation. (iv) The perturbing atoms are assumed to act as foreign-gas perturbers (i.e., resonant broadening effects are ignored), which is a good approximation. (v) Any degeneracy in states a or b is ignored.

One should further note that photon recoil effects (although negligible) are automatically included in this calculation even though the laser field is taken as a classical quantity.[8] Such effects follow from a quantum-mechanical description of the atomic center-of-mass motion.

III. LASER FORMALISM

The approach basically follows that of Lamb.[5] We consider a laser cavity of the Fabry-Perot type operating in a single cavity mode with eigenfunction $\sin(\vec{k}\cdot\vec{R})$. The laser-cavity axis is in the $\vec{k}$ direction, and we shall assume the laser field to be polarized in a direction $\hat{n}$ which is perpendicular to $\vec{k}$. Writing the laser electric field magnitude as

$$E(\vec{R},t) = \mathcal{E}(t)\sin(\vec{k}\cdot\vec{R}), \tag{2}$$

one obtains[5] the differential equation for $\mathcal{E}(t)$ in mks units:

$$\frac{d^2\mathcal{E}}{dt^2} + \frac{\Omega}{Q}\frac{d\mathcal{E}}{dt} + \Omega^2\mathcal{E} = \frac{\Omega^2}{\epsilon_0}P(t), \tag{3}$$

where $\Omega^2 = k^2c^2$, Q is the quality factor of the cavity, and $P(t)$ is the projection of the macroscopic polarization $P(\vec{R},t)$ on the cavity mode, i.e.,

$$P(t) = (2/V)\int dV P(\vec{R}, t)\sin(\vec{k}\cdot\vec{R}), \quad (4)$$

where V is the laser volume. In deriving Eq. (3) it is assumed that the variation of $E(\vec{R}, t)$ across the cavity diameter may be neglected, and that $P(t)$ is nearly monochromatic at frequency Ω.

We try solutions of the forms

$$\mathcal{E}(t) = E(t)\cos[\Omega t + \varphi(t)], \quad (5a)$$

$$P(t) = C(t)\cos[\Omega t + \varphi(t)] + S(t)\sin[\Omega t + \varphi(t)]. \quad (5b)$$

Substituting Eqs. (5a) and (5b) into Eq. (3) and assuming that E, S, C, and φ are slowly varying in time with respect to $e^{i\Omega t}$, we arrive at the amplitude and phase equations for self-consistency:

$$\dot{E} + (\Omega/2Q)E = -(\Omega/2\epsilon_0)S, \quad (6a)$$

$$\dot{\varphi}E = -(\Omega/2\epsilon_0)C. \quad (6b)$$

It remains to calculate the polarization $P(\vec{R}, t)$ in order to obtain C and S, which will be functions of the field $E(t)$.

The microscopic polarization is determined from the quantum-mechanical generalization of its classical definition, namely the average or expectation value of the dipole-moment operator of the atom. For our two-state system, the wave function will be of the form

$$\psi(\vec{R}, \vec{r}, t) = B_a(\vec{R}, t)\psi_a(\vec{r}) + B_b(\vec{R}, t)\psi_b(\vec{r}), \quad (7)$$

where the $\psi_\alpha(\vec{r})$ $(\alpha = a, b)$ are atomic-state eigenfunctions and the $B_\alpha(\vec{R}, t)$ are probability amplitudes in the sense that $|B_\alpha(\vec{R}, t)|^2 d^3R$ is the probability that an atom is in state α at time t and in a volume d^3R about $\vec{R}$. The macroscopic polarization is obtained by summing the contributions from all the active atoms. Thus, using the selection rules for the dipole-moment operator, the polarization in the $\hat{n}$ direction is given by

$$P(\vec{R}, t) = \wp\sum_i[\rho_{ab}(\vec{R}, t, \vec{v}_i, t_i) + \text{c.c.}], \quad (8)$$

where $\wp$ (assumed real) is the matrix element for the $\hat{n}$ component of the electric dipole moment of the atom between states a and b,

$$\rho_{ab}(\vec{R}, t, \vec{v}_i, t_i) = B_a(\vec{R}, t, \vec{v}_i, t_i)[B_b(\vec{R}, t, \vec{v}_i, t_i)]^*$$

is the off-diagonal density matrix element of the ith atom which was initially excited to state a at time t_i with velocity $\vec{v}_i$, and the sum is over all laser atoms. (The dependence of the polarization on all the $\vec{v}_i$ and t_i has not been explicitly indicated.) We shall refer to $\rho_{ab}(\vec{R}, t, \vec{v}_i, t_i)$ as the dipole-moment density since its integral over $\vec{R}$ gives $\rho_{ab}(t, \vec{v}_i, t_i)$, the "dipole moment" of atom i.[9] One can proceed to calculate the polarization according to Eq. (8), average it over the $\vec{v}_i$ and t_i, and then use Eqs. (5b) and (6) to determine the self-consistent amplitude and phase of the electric field. This method has been described by Lamb.

However, when one is dealing with collision phenomena, it is easier to regard the electric field as being formed from the individual contributions of each laser atom. The mathematical description of this viewpoint will become clearer if we integrate Eq. (6a) for an interval of time δt that is long compared with the lifetimes γ_a^{-1} and γ_b^{-1}, but short compared with the characteristic time variation of $E(t)$ and $\varphi(t)$. That is, we may consider $E(t)$ and $\varphi(t)$ essentially constant in the interval δt; but any atom that is excited at some time in the interval will certainly have decayed by the end of the interval.[10] Equation (6a) so integrated is

$$\delta E(t) = E(t + \delta t) - E(t)$$
$$\approx -(\Omega/2Q)\delta t E(t) - (\Omega/2\epsilon_0)\int_t^{t+\delta t} S(t')\,dt'. \quad (9)$$

To obtain a more meaningful expression for $S(t')$ for use in Eq. (9), we write the dipole-moment density in the form

$$\rho_{ab}(\vec{R}, t, \vec{v}_i, t_i) = A(\vec{R}, t, \vec{v}_i, t_i)\,e^{-i[\Omega t + \varphi(t)]}, \quad (10)$$

where the coefficient $A(\vec{R}, t, \vec{v}_i, t_i)$ contains pertinent information on the dipole-moment density of atom i and will be called the polarization-function density. Combining this with Eqs. (4), (5b), and (8) gives

$$S(t) = \sum_i S(t, \vec{v}_i, t_i), \quad (11)$$

where

$$S(t, \vec{v}_i, t_i) = 2\wp\,\mathrm{Im}A(t, \vec{v}_i, t_i), \quad (12)$$

$$A(t, \vec{v}_i, t_i) = (2/V)\int dV A(\vec{R}, t, \vec{v}_i, t_i)\sin(\vec{k}\cdot\vec{R}). \quad (13)$$

Note that for consistency of Eqs. (5b) and (11)–(13), the polarization-function density must be a slowly varying function of time compared with $e^{i\Omega t}$.

Substituting Eq. (11) into (9) and using (12), one finds that, in a time interval δt,

$$\delta E(t) = -(\Omega/2Q)\delta t E - (\Omega\wp/\epsilon_0)$$
$$\times \mathrm{Im}\Big[\sum_i \int_t^{t+\delta t} A(t', \vec{v}_i, t_i)\,dt'\Big].$$

We now wish to average this equation over all initial $\vec{v}_i$ and times t_i of excitation in the interval δt. By our previous assumption on δt we get a contribution to $\delta E(t)$ from all atoms excited in the interval δt. The time of excitation within the interval is unimportant since any time is as good as another [recall that we assume that $E(t)$ and $\varphi(t)$ are essentially constant in δt], so that we may drop the t_i label. Also, on the average, each atom excited in δt will contribute equally to the field. Thus, averaging Eq. (14) yields

$$\langle\delta E(t)\rangle = -(\Omega/2Q)\delta t\langle E\rangle - (\Omega\wp/\epsilon_0)$$
$$\times \mathrm{Im}\Big[\sum_m \int_t^{t+\delta t} P_m(\delta t) m\langle A(t', \vec{v}_0)\rangle_{\vec{v}_0}\,dt'\Big],$$

where $P_m(\delta t)$ is the probability that m atoms are excited in a time δt, and $\langle A(t,\vec{v}_0)\rangle_{\vec{v}_0}$ represents the contribution to the polarization function of a single atom averaged over its initial velocity distribution $W(\vec{v}_0)$ (for simplicity we assume the excitation rate to be independent of position and time).

Equation (15) may be further reduced if one notes that the average number of atoms excited in time δt is given by

$$\overline{m}(\delta t)=\sum_m P_m(\delta t)m\,; \tag{16}$$

and if the average excitation rate is specified by λ, then we have

$$\overline{m}(\delta t)=\lambda\,\delta t\,. \tag{17}$$

Combining Eqs. (15)–(17) gives

$$\langle\delta E\rangle=-(\Omega/2Q)\delta t\langle E\rangle-(\Omega\wp\lambda/\epsilon_0)\delta t \times\mathrm{Im}\Big[\int_t^{t+\delta t}\langle A(t',\vec{v}_0)\rangle_{\vec{v}_0}\,dt'\Big]\,. \tag{18}$$

If $\dot{E}\,\delta t\ll E$, as is assumed, Eq. (18) may be transformed into the corresponding differential equation

$$\frac{dE}{dt}+\frac{\Omega}{2Q}E=-\frac{\Omega\wp\lambda}{\epsilon_0}\,\mathrm{Im}\int_t^{t+\delta t}A(t')\,dt', \tag{19}$$

where the average signs have been dropped on the E's and

$$A(t')\equiv\langle A(t',\vec{v}_0)\rangle_{\vec{v}_0}\,. \tag{20}$$

A similar treatment for the phase equation yields

$$\frac{d\varphi}{dt}E=-\frac{\Omega\wp\lambda}{\epsilon_0}\,\mathrm{Re}\int_t^{t+\delta t}A(t')\,dt'. \tag{21}$$

The problem is reduced to a determination of the polarization function $A(t')$ which, as defined by Eqs. (10), (13), and (20), represents the average slowly varying amplitude of the dipole moment of a single atom excited in the time interval between t and $t+\delta t$.

IV. BASIC WORKING EQUATIONS

In order to determine the polarization function we must solve the time-dependent Schrödinger equation for the problem. The Hamiltonian for a single-laser atom in a medium of fixed perturbers is of the form

$$H(\vec{R},\vec{r},t)=H^{\mathrm{c.m.}}(\vec{R})+H_0(\vec{r})+V(\vec{R},\vec{r},t)+\sum_j U^j(\vec{R}-\vec{R}_j,\vec{r})-\tfrac{1}{2}i\Gamma\,,$$

where $\vec{r}$ stands for all the relative electronic coordinates of the atom, $\vec{R}$ is the center-of-mass coordinate, and $\vec{R}_j$ is the position of the jth perturber. The terms in $H(\vec{R},\vec{r},t)$ have the following meanings: (i) $H^{\mathrm{c.m.}}(\vec{R})$ is the free-laser-atom center-of-mass Hamiltonian for which we choose the eigenfunctions

$$\psi_{\vec{p}}(\vec{R})=(2\pi)^{-3/2}e^{i\vec{p}\cdot\vec{R}} \tag{22}$$

(we have set $\hbar=1$, i.e., energy and frequency will have the same units as will momentum and wave number); (ii) $H_0(\vec{r})$ is the free-laser-atom electronic Hamiltonian which we assume possesses eigenfunctions $\psi_\alpha(\vec{r})$; (iii) $V(\vec{R},\vec{r},t)$ is the laser-atom–laser-field interaction given by

$$V(\vec{R},\vec{r},t)=-eE(\vec{R},t)\textstyle\sum_i\vec{r}_i\cdot\hat{n}\,, \tag{23}$$

where $\vec{r}_i$ is the relative coordinate of the ith laser-atom electron and $\hat{n}$ is a unit vector in the direction of $E(\vec{R},t)$; (iv) $U^j(\vec{R}-\vec{R}_j,\vec{r})$ is the potential of the jth perturber; (v) Γ is a diagonal matrix which describes the spontaneous decay of the atomic states.

Since the set of products $\psi_{\vec{p}}(\vec{R})\psi_\alpha(\vec{r})$ forms a complete basis, we can expand an arbitrary wave function as

$$\psi(\vec{R},\vec{r},t)=(2\pi)^{-3/2}\int d^3p\textstyle\sum_\alpha b_\alpha(\vec{p},t)\,e^{i\vec{p}\cdot\vec{R}} \times e^{-i(E_{\vec{p}}+E_\alpha)t}\psi_\alpha(\vec{r})\,, \tag{24}$$

where E_α is the energy of state α,

$$E_{\vec{p}}=p^2/2m\,, \tag{25}$$

and we have used Eq. (22). Substituting Eq. (24) into the time-dependent Schrödinger equation

$$i\dot{\psi}(\vec{R},\vec{r},t)=H(\vec{R},\vec{r},t)\psi(\vec{R},\vec{r},t)$$

and taking the appropriate scalar products yields the differential equations for the probability amplitudes $b_\alpha(\vec{p},t)$:

$$i\dot{b}_\alpha(\vec{p},t)=\textstyle\sum_\beta\int d^3p'\big(V_{\alpha\beta;\vec{p},\vec{p}'}+\sum_j U^j_{\alpha\beta;\vec{p},\vec{p}'}\big)\,b_\beta(\vec{p}',t) \times e^{i(E_{\vec{p},\vec{p}'}+E_{\alpha\beta})t}-i(\tfrac{1}{2}\gamma_\alpha)b_\alpha(\vec{p},t)\,, \tag{26}$$

where

$$V_{\alpha\beta;\vec{p},\vec{p}'}+\textstyle\sum_j U^j_{\alpha\beta;\vec{p},\vec{p}'}=(2\pi)^{-3}\int d^3R\,e^{i(\vec{p}'-\vec{p})\cdot\vec{R}} \times\int d^3r[\psi_\alpha(\vec{r})]^*[V(\vec{R},\vec{r},t) +\textstyle\sum_j U^j(\vec{R}-\vec{R}_j,\vec{r})]\psi_\beta(\vec{r})\,, \tag{27}$$

$$E_{\alpha\beta}=E_\alpha-E_\beta,\quad E_{\vec{p},\vec{p}'}=E_{\vec{p}}-E_{\vec{p}'}\,, \tag{28}$$

and γ_α is the spontaneous decay rate for the state-α population.

We shall restrict this calculation to the two-state subspace shown in Fig. 2, i.e., α and β may take on the values a or b only. If the collision is adiabatic [duration of a collision $\gg(E_a-E_b)^{-1}$], the nonvanishing matrix elements of the effective collision potential $U^j(\vec{R}-\vec{R}_j,\vec{r})$ will be $U^j_{aa;\vec{p},\vec{p}'}$ and $U^j_{bb;\vec{p},\vec{p}'}$.[11] Using Eqs. (23) and (27), we find the nonvanishing matrix elements of $V(\vec{R},\vec{r},t)$ to be

$$V_{ab;\vec{p},\vec{p}'}=V_{ba;\vec{p},\vec{p}'}=-(2\pi)^{-3}\wp\int d^3R\,e^{i(\vec{p}'-\vec{p})\cdot\vec{R}}E(t)$$

$$\times \cos[\Omega t + \varphi(t)] \sin(\vec{k}\cdot\vec{R}), \tag{29}$$

where $\wp$, as defined in Sec. III, is given by

$$\wp = e\sum_i \int d^3r[\psi_a(\vec{r})]^* \vec{r}_i \cdot \hat{n}\psi_b(\vec{r}) = \wp^*.$$

Substituting these results in Eq. (26), defining probability amplitudes $a(\vec{p}, t) \equiv b_a(\vec{p}, t)$ and $b(\vec{p}, t) \equiv b_b(\vec{p}, t)$, and doing some of the integrals leads to the two coupled differential equations (in the rotating-wave approximation):

$$i\dot{a}(\vec{p}, t) = -i(\tfrac{1}{2}\gamma_a)a(\vec{p}, t) - [\wp E(t)/4i]e^{i[(\omega-\Omega)t-\varphi(t)]}e^{-i(k^2/2m)t}[e^{i(\vec{p}\cdot\vec{k}/m)t}b(\vec{p}-\vec{k}, t) - e^{-i(\vec{p}\cdot\vec{k}/m)t}b(\vec{p}+\vec{k}, t)] + \sum_j \int d^3p' U^j_{aa;\vec{p},\vec{p}'} e^{iE_{\vec{p},\vec{p}'}t} a(\vec{p}', t), \tag{30a}$$

$$i\dot{b}(\vec{p}, t) = -i(\tfrac{1}{2}\gamma_b)b(\vec{p}, t) - [\wp E(t)/4i]e^{-i[(\omega-\Omega)t-\varphi(t)]}e^{-i(k^2/2m)t}[e^{i(\vec{p}\cdot\vec{k}/m)t}a(\vec{p}-\vec{k}, t) - e^{-i(\vec{p}\cdot\vec{k}/m)t}a(\vec{p}+\vec{k}, t)] + \sum_j \int d^3p' U^j_{bb;\vec{p},\vec{p}'} e^{iE_{\vec{p},\vec{p}'}t} b(\vec{p}', t), \tag{30b}$$

where

$$\omega = E_a - E_b; \tag{31}$$

it should be remembered that $\vec{k}$ is the propagation vector given in Eq. (2) for the laser field. Equations (30a) and (30b) are the basic working equations of the theory.

We choose the initial conditions for the laser atom as excitation to state a in a "plane-wave" state with a definite momentum $\vec{p}_0$.[6] The term "plane wave" is in quotations since we also require that the atom be confined to the laser volume V, making a pure plane-wave state impossible. However, for large laser volumes (compared with the de Broglie wavelength) and with neglect of cavity-wall collisions for the excited laser atom, a plane-wave state is a good approximation. Explicitly, we find

$$\psi(\vec{R}, \vec{r}, 0) = V^{-1/2} e^{i\vec{p}_0\cdot\vec{R}}\psi_a(\vec{r}), \tag{32}$$

and confinement to the laser volume is to be understood. Eventually, a weighted average over all possible $\vec{p}_0$ will be made. The initial condition (32) corresponds to

$$a(\vec{p}, 0) = (2\pi)^{3/2} V^{-1/2}\delta(\vec{p}-\vec{p}_0), \quad b(\vec{p}, 0) = 0. \tag{33}$$

The calculation may be outlined as follows: (i) solve, to various orders in perturbation theory, Eqs. (30) subject to the initial conditions (33), (ii) combine Eqs. (7) and (24) to find the dipole-moment density[12]:

$$\rho_{ab}(\vec{R}, t, v_0) = B_a(\vec{R}, t, v_0)[B_b(\vec{R}, t, v_0)]^* = (2\pi)^{-3}\int d^3p \int d^3p' e^{i(\vec{p}-\vec{p}')\cdot\vec{R}-iE_{\vec{p},\vec{p}'}t} \times e^{-i\omega t} a(\vec{p}, t)[b(\vec{p}'t)]^*, \tag{34}$$

(iii) obtain the polarization-function density $A(\vec{R}, t, \vec{v}_0)$ from $\rho_{ab}(\vec{R}, t)$ by the prescription (10), (iv) by use of Eqs. (13) and (20), calculate $A(t')$ from $A(\vec{R}, t', v_0)$ for use in the self-consistency equations (19) and (21).

Notation. Before proceeding, we should like to establish a notation which should be kept in mind when reading the next few sections. The contribution to an amplitude $a(\vec{p}, t)$ arising from an nth-order scattering interaction and an mth-order laser-field interaction will be written $a^{nm}(\vec{p}, t)$. In addition, a term like $A^{mn;rs}$ implies a contribution to the polarization function from the product of amplitudes a^{mn} and $(b^{rs})^*$. We shall also find it convenient to denote the range of the perturber potential by $\mathcal{R}$ and to introduce a vector $\vec{X}$ which will be a position coordinate of the active atom relative to a perturber site. Finally, we note the equality of unit vectors in the $\hat{v}_0$ and $\hat{p}_0$ directions ($\vec{v}_0 = \vec{p}_0/m$ is the initial laser-atom velocity). We shall sometimes interchange these quantities to bring added clarity to our equations.

V. FIRST-ORDER LASER THEORY - COLLISION INTERACTION IN UPPER LASER STATE ONLY

In this section we solve Eqs. (30) to first order in the laser field and ultimately to all orders in the scattering interaction for the one-collision process. The collision interaction will be assumed to act only on the upper laser state a, i.e.,

$$U^j_{aa;\vec{p},\vec{p}'} \equiv U^j_{a;\vec{p},\vec{p}'}; \quad U^j_{bb;\vec{p},\vec{p}'} = 0. \tag{35}$$

As already mentioned, the case where one state experiences a much stronger collision interaction than the other probably corresponds closely to the actual physical situation. Equations (30) should be simplified by use of Eqs. (35). We shall use diagrams to help visualize each contribution to the polarization-function density arising from the perturbation solution of Eqs. (30). The heading of each subsection will indicate the polarization function being calculated in that subsection. (Recall that the polarization function is the projection of the polarization-function density onto the laser-cavity mode.)

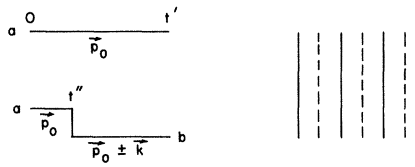

FIG. 3. Diagrams for the polarization-function density $A^{00;01}(\vec{R}, t', \vec{v}_0)$. Upper and lower lines on the left-hand side represent the $a^{00}(\vec{p}, t')$ and $b^{01}(\vec{p}', t')$ amplitudes, respectively. Solid and dashed figures on the right-hand side, respectively, represent the spatial extent of these amplitudes which are plane waves in coordinate space. Laser field acts at t''.

$$A^{00;01}(t', \vec{v}_0)$$

The polarization-function density $A^{00;01}(\vec{R}, t', \vec{v}_0)$ is the no-collision term and arises from the product of the amplitudes $a^{00}(b^{01})^*$. We picture this process in Fig. 3. The upper horizontal line corresponds to the a-state amplitude and the lower one to what finally yields the b-state amplitude. We observe the system at $t = t'$ after it has started at $t = 0$, while the interaction with the laser field occurs at $t = t''$ in a Feynman sense. The figure to the right of these amplitude lines is a diagram for the *spatial* extent of the amplitudes. Since there is no collision, both are plane-wave states. The vertical solid line corresponds to the plane wave with momentum $\vec{p}_0$ associated with state a while the dashed line corresponds to the plane wave with momentum $\vec{p}_0 \pm \vec{k}$ associated with state b. The polarization-function density is the product of these two waves which are in phase (except for the normal Dopler interference factor $e^{\pm i\vec{k}\cdot\vec{v}_0(t'-t'')}$). Thus, in projecting the polarization-function density onto the cavity mode to obtain the polarization function, there will be considerable contributions from all points in the laser volume, a result that is unique to the no-collision term.

The perturbation calculations for Eqs. (30) subject to the initial conditions (33) can be carried out in a straightforward manner. The results are

$$a^{00}(\vec{p}, t') = (2\pi)^{3/2} V^{-1/2} e^{-(1/2)\gamma_a t'} \delta(\vec{p} - \vec{p}_0), \tag{36}$$

$$b^{01}(\vec{p}', t') = \tfrac{1}{4}\wp E(t')\, e^{-i[(\omega-\Omega)t' - \varphi(t')]} \times \int_0^{t'} dt''\, e^{[(-1/2)\gamma_b + i\Delta\omega](t'-t'') - i(k^2/2m)t''} \times [e^{i(\vec{p}'\cdot\vec{k}/m)t''} a^{00}(\vec{p}' - \vec{k}, t'') - \text{term}(\vec{k} \to -\vec{k})]; \tag{37}$$

where

$$\Delta\omega = \omega - \Omega - \dot{\varphi}(t'), \tag{38}$$

and E and φ are evaluated at time t'. (Recall that E and φ are regarded as constant in the interval between t and $t+\delta t$, so that they may be evaluated at any t' in that interval.)

Using Eqs. (10), (34), (36), and (37) we find the polarization-function density:

$$A^{00;01}(\vec{R}, t', \vec{v}_0) = \tfrac{1}{4}[\wp E(t')/V] \int_0^{t'} dt''\, H(t', t'')\, e^{-i\vec{k}\cdot\vec{R}} \times e^{i\vec{k}\cdot\vec{v}_0(t'-t'')} - \text{term}(\vec{k} \to -\vec{k}), \tag{39}$$

where

$$H(t', t'') = e^{(-\gamma_{ab} - i\Delta\omega + iE_{\vec{k}})(t'-t'') - \gamma_a t''}, \tag{40}$$

$$\gamma_{ab} = \tfrac{1}{2}(\gamma_a + \gamma_b), \tag{41}$$

and $E_{\vec{k}} = k^2/2m$ is the photon recoil energy.

Using Eq. (13) to project Eq. (39) on the cavity mode and neglecting the rapidly varying terms involving $e^{(\pm 2 i\vec{k}\cdot\vec{R})}$ gives the "no-collision" contribution to the polarization function:

$$A^{00;01}(\vec{R}, t', \vec{v}_0) = -\tfrac{1}{4} i \wp E(t') V^{-1} \int_0^{t'} dt''\, H(t', t'') \times e^{i\vec{k}\cdot\vec{v}_0(t'-t'')} + \text{term}(\vec{k} \to -\vec{k}). \tag{42}$$

$$A^{10;01}(t', \vec{v}_0)$$

The polarization-function density $A^{10;01}(\vec{R}, t', \vec{v}_0)$ arises from the amplitude product $a^{10}(b^{01})^*$ and is the first term that involves the collision interaction. The diagrams for this term are shown in Fig. 4, where the cross represents the collision interaction. The scattering begins at $t = 0$ and continues until the time of observation $t = t'$ so that the spatial part for the state-a amplitude is a spherical scattered wave of radius $v_0 t'$ represented by a solid circle in the figure. Mathematically, this spherical wave will lead to a factor $X^{-1} e^{ip_0 X} f_a(\Omega)$, where X is a coordinate relative to the perturber site and $f_a(\Omega)$ is the scattering amplitude for state a. The b-state amplitude is still spatially a plane wave $e^{i(\vec{p}_0 \pm \vec{k})\cdot\vec{R}}$. Hence, we should expect that the polarization-function density will possess a rapidly varying phase in all but the forward direction (i.e., only in the forward direction are the two waves moving with the same velocity). In addition, the polarization-function density can be nonvanishing

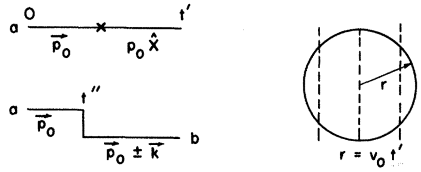

FIG. 4. Diagrams for the polarization-function density $A^{10;01}(\vec{R}, t', \vec{v}_0)$. Cross indicates the collision interaction which acts continuously from $t = 0$ to t'. The quantity $\hat{X}$ is an arbitrary unit vector from the perturber site so that $p_0\hat{X}$ indicates a spherical wave originating at the perturber site. This spherical wave, which is associated with $a^{10}(\vec{p}, t')$, is indicated by the circle in the figure.

only in the sphere of the scattered wave. This may be expressed mathematically by the step function $\theta(v_0t'-X)$, which equals 1 for positive argument and is 0 otherwise. With this insight we proceed to carry out the calculation.

From Eq. (30a) we deduce

$$a^{10}(\vec{p},t')=-i\int_0^{t'}dt''e^{-(1/2)\gamma_a(t'-t'')}\sum_j\int d^3p'\,U^j_{a;\vec{p},\vec{p}'}\exp(iE_{\vec{p},\vec{p}'}t'')a^{00}(\vec{p}',t'');$$

using Eq. (36) and doing the $\vec{p}'$ integral, this becomes

$$a^{10}(\vec{p},t')=-i(2\pi)^{3/2}V^{-1/2}e^{-(1/2)\gamma_at'}\sum_j\int_0^{t'}dt''U^j_{a;\vec{p},\vec{p}_0}\exp(iE_{\vec{p},\vec{p}_0}t''). \tag{43}$$

In the Feyman sense, Eq. (43) shows that the collision occurs at any time t'' between 0 and t'. Performing the t'' integral gives

$$a^{10}(\vec{p},t')=-(2\pi)^{3/2}V^{-1/2}e^{-(1/2)\gamma_at'}\sum_j U^j_{a;\vec{p},\vec{p}_0}[\exp(iE_{\vec{p},\vec{p}_0}t')-1]/E_{\vec{p},\vec{p}_0}. \tag{44}$$

The result for $b^{01}(\vec{p}',t')$ is given in Eq. (37), so that the polarization-function density determined from Eqs. (10), (34), (37), and (44) after a little algebra is

$$A^{10;01}(\vec{R},t',\vec{v}_0)=-\tfrac{1}{4}[\wp E(t')V^{-1}]\int d^3p\int d^3p'\,e^{i(\vec{p}-\vec{p}')\cdot\vec{R}-iE_{\vec{p},\vec{p}'}t'}[\exp(iE_{\vec{p},\vec{p}_0}t')-1](E_{\vec{p},\vec{p}_0})^{-1}\sum_j U^j_{a;\vec{p},\vec{p}_0}$$
$$\times\int_0^{t'}dt''\exp[-\gamma_at''-(\gamma_{ab}+i\Delta\omega)(t'-t'')+iE_kt''-i(\vec{p}'\cdot\vec{k}/m)t'']\delta(\vec{p}'-\vec{k}-\vec{p}_0)-\text{term}(\vec{k}\to-\vec{k}).$$

The $\vec{p}'$ integral may be done; noting that

$$E_{\vec{p},\vec{p}_0+\vec{k}}=(2m)^{-1}(p^2-|\vec{p}_0+\vec{k}|^2)=E_{\vec{p},\vec{p}_0}-\vec{k}\cdot\vec{v}_0-E_{\vec{k}},$$

one finds

$$A^{10;01}(\vec{R},t,\vec{v}_0)=\tfrac{1}{4}\wp E(t')V^{-1}e^{-i\vec{k}\cdot\vec{R}}\sum_j\int_0^{t'}dt''H(t',t'')g_j(\vec{R},t')e^{i\vec{k}\cdot\vec{v}_0(t'-t'')}-\text{term}(\vec{k}\to-\vec{k}), \tag{45}$$

where

$$g_j(\vec{R},t')=\int d^3p\,U^j_{a;\vec{p},\vec{p}_0}e^{i(\vec{p}-\vec{p}_0)\cdot\vec{R}}[1-\exp(-iE_{\vec{p},\vec{p}_0}t')](E_{\vec{p},\vec{p}_0})^{-1}, \tag{46}$$

and $H(t',t'')$ is given by Eq. (40). Inserting the explicit expression [Eq. (27)] for $U^j_{a;\vec{p},\vec{p}_0}$ into Eq. (46), we obtain

$$g_j(\vec{R},t')=(2\pi)^{-3}\int d^3R'\int d^3p\,U^j_a(\vec{R}'-\vec{R}_j)e^{i(\vec{p}-\vec{p}_0)\cdot(\vec{R}-\vec{R}')}[1-\exp(-iE_{\vec{p},\vec{p}_0}t')](E_{\vec{p},\vec{p}_0})^{-1}$$

where

$$U^j_a(\vec{R}'-\vec{R}_j)=\int d^3r\,\psi_a(\vec{r})^*U^j(\vec{R}'-\vec{R}_j,\vec{r})\psi_a(\vec{r}).$$

The angular integration over $\vec{p}$ yields

$$g_j(\vec{R},t')=(2\pi)^{-2}\int d^3R\int_0^\infty dp\,U^j_a(\vec{R}'-\vec{R}_j)\,p\,e^{-i\vec{v}_0\cdot(\vec{R}-\vec{R}')}\frac{e^{ip|\vec{R}-\vec{R}'|}-e^{-ip|\vec{R}-\vec{R}'|}}{i|\vec{R}-\vec{R}'|}\frac{1-e^{-iE_{\vec{p},\vec{p}_0}t'}}{E_{\vec{p},\vec{p}_0}}. \tag{47}$$

The integral has a major contribution in the vicinity of $E_{\vec{p}}=E_{\vec{p}_0}$ and we expand p about this value,[7] namely,

$$p\approx p_0+\frac{dp}{dE_{\vec{p}_0}}E_{\vec{p},\vec{p}_0}=p_0+(v_0)^{-1}E_{\vec{p},\vec{p}_0}. \tag{48}$$

Changing variables from p to $E_{\vec{p}}$, Eq. (47) becomes

$$g_j(\vec{R},t')=(m/2\pi)(2\pi i)^{-1}\int d^3R'\,U^j_a(\vec{R}'-\vec{R}_j)|\vec{R}-\vec{R}'|^{-1}e^{-i\vec{p}_0\cdot(\vec{R}-\vec{R}')}$$
$$\times\int_0^\infty dE_{\vec{p}}\{\exp[i|\vec{R}-\vec{R}'|(p_0+E_{\vec{p},\vec{p}_0}/v_0)]-\exp[-i|\vec{R}-\vec{R}'|(p_0+E_{\vec{p},\vec{p}_0}/v_0)]\}[1-\exp(-iE_{\vec{p},\vec{p}_0}t')](E_{\vec{p},\vec{p}_0})^{-1}.$$

Assuming the major contribution occurs at $E_{\vec{p}}=E_{\vec{p}_0}$, we extend the integral over $E_{\vec{p}}$ to $-\infty$; then the contour integral may be easily evaluated (the result is independent of how we displace the pole at $E_{\vec{p}_0}$) as

$$g_j(\vec{R},t')=(m/2\pi)\int d^3R'\,U^j_a(\vec{R}'-\vec{R}_j)\,e^{ip_0|\vec{R}-\vec{R}'|-i\vec{p}_0\cdot(\vec{R}-\vec{R}')}$$
$$\times|\vec{R}-\vec{R}'|^{-1}\theta(v_0t'-|\vec{R}-\vec{R}'|). \tag{49}$$

It will be convenient to further reduce this equation for g before inserting it into Eq. (45) to get the polarization-function density. We define coordinates relative to the jth perturber:

$$\vec{X}_j=\vec{R}-\vec{R}_j,\quad \delta\vec{R}'_j=\vec{R}'-\vec{R}_j, \tag{50}$$

so that

$$\vec{R}-\vec{R}'=\vec{X}_j-\delta\vec{R}_j'.$$

We assume the interaction $U_a^j(\delta\vec{R}_j')$ has a range $\mathcal{R}$ $\approx 10^{-7}$ cm, which implies that for almost all regions of space $X_j \gg \delta R_j'$. Using this fact to expand

$$|\vec{R}-\vec{R}'| \approx X_j-\hat{X}_j\cdot\delta\vec{R}_j',$$

and changing integration variables to $\delta\vec{R}_j'$, Eq. (49) becomes

$$\mathcal{J}_j(R,t') \approx -[-(m/2\pi)\int d^3(\delta R_j')U_a(\delta\vec{R}_j')e^{ip_0\delta\vec{R}'_j\cdot(\hat{p}_0-\hat{X}_j)}]$$
$$\times e^{ip_0X_j-i\vec{v}_0\cdot\vec{X}_j}X_j^{-1}\theta(v_0t'-X_j). \quad (51)$$

The term in square brackets will be recognized as the leading term in the Born expansion of the scattering amplitude $f_a(\hat{X}_j,\vec{p}_0)$ for scattering of a plane wave with momentum $\vec{p}_0$ into the direction $\hat{X}_j$.

We generalize our result by postulating that higher-order scattering calculations at this particular perturber site will merely lead to higher-order terms in the Born expansion of $f_a(\hat{X}_j,\vec{p}_0)$ and that to all orders in the scattering interaction the term in square brackets in Eq. (51) may be replaced by the exact scattering amplitude $f_a(\hat{X}_j,\vec{p}_0)$.

To help justify this generalization, we recall the calculation of Bethe,[7] who treats scattering as a time-dependent problem and obtains solutions to first order in the scattering interaction. Since scattering problems may be solved with either time-independent or time-dependent methods, one must conclude that the time-dependent perturbation solution, if carried out to infinite order, would be equal to the exact time-independent solution. Thus, the sum of all orders of perturbation theory will lead to a result proportional to the exact scattering amplitude. With this assumption, Eq. (51) is substituted into (45) and we find the polarization-function density:

$$\sum_{n=1}^{\infty}A^{n0;01}(\vec{R},t,\vec{v}_0)=\tfrac{1}{4}i\wp E(t')V^{-1}\textstyle\sum_j f_a(\hat{X}_j,\vec{p}_0)X_j^{-1}$$
$$\times e^{ip_0\vec{X}_j\cdot(\hat{X}_j-\hat{p}_0)}\,e^{-i\vec{k}\cdot\vec{R}}\int_0^{t'}dt''H(t',t'')e^{i\vec{k}\cdot\vec{v}_0(t'-t'')}$$
$$\times\theta(v_0t'-X_j)-\text{term}(\vec{k}\to-\vec{k}). \quad (52)$$

As predicted, there is a phase factor $e^{ip_0\vec{X}_j\cdot(\hat{X}_j-\hat{p}_0)}$ which is rapidly varying in all but the forward direction, and the appropriate step function is present.

Using Eq. (13) we project (52) onto the laser-cavity mode to obtain the polarization function:

$$\sum_{n=1}^{\infty}A^{n0;01}(t',\vec{v}_0)=+\tfrac{1}{4}i\wp E(t')V^{-1}\frac{2}{V}\textstyle\sum_j\int_0^{t'}dt''H(t',t'')$$
$$\times e^{i\vec{k}\cdot\vec{v}_0(t'-t'')}\int d^3R\,f_a(\hat{X}_j,\vec{p}_0)X_j^{-1}e^{ip_0\vec{X}_j\cdot(\hat{X}_j-\hat{p}_0)}$$
$$\times e^{-i\vec{k}\cdot\vec{R}}\sin(\vec{k}\cdot\vec{R})\theta(v_0t'-X_j)-\text{term}(\vec{k}\to-\vec{k}), \quad (53)$$

where one should recall that $\vec{X}_j=\vec{R}-\vec{R}_j$. If we expand $\sin(\vec{k}\cdot\vec{R})$ in terms of exponentials, only the $(1/2i)e^{i\vec{k}\cdot\vec{R}}$ part contributes in the first term.[13] Changing the spatial integration variable to $\vec{X}_j$, we note that the integral is independent of the index j, so that in summing over j, we simply gain a factor N, where N is the total number of perturber sites in the laser volume. The fact that each perturber contributes equally to $A(t',\vec{v}_0)$ is a consequence of having taken plane-wave excitation for the laser atoms. That is, the laser atom is initially uniformly distributed over the perturber sites. Noting that the integrand in Eq. (53) contributes appreciably only in the forward direction, we may perform the integration over $\vec{X}_j$ to obtain the polarization function:

$$\sum_{n=1}^{\infty}A^{n0;01}(t',\vec{v}_0)=-\tfrac{1}{4}i\wp E(t)\mathfrak{N}V^{-1}\frac{2\pi i}{m}\int_0^{t'}dt''H(t',t'')$$
$$\times e^{i\vec{k}\cdot\vec{v}_0(t'-t'')}[f_a(0)]t'+\text{term}(\vec{k}\to-\vec{k}), \quad (54)$$

where $f_a(0)$ is the forward-scattering amplitude for state a and $\mathfrak{N}=N/V$ is the perturber density. Mathematically, this result could have been reached more easily if we had projected on the cavity mode before doing the integration in momentum space. However, we chose the above approach to obtain explicit formulas for the polarization-function density, which determines the spatial dependence of the macroscopic polarization.

$$A^{00:11}(t'\vec{v}_0)$$

The polarization-function density $A^{00;11}(\vec{R},t',\vec{v}_0)$ arises from the product of the amplitudes $a^{00}(b^{11})^*$ and the diagrams for this term are shown in Fig. 5. The a-state amplitude is unperturbed and spatially is a plane wave $e^{i\vec{p}_0\cdot\vec{R}}$. The b-state amplitude is formed from an amplitude $a^{10}(t'')$ which already contains the scattering interaction. Spatially, it corresponds to a spherically scattered wave begin-

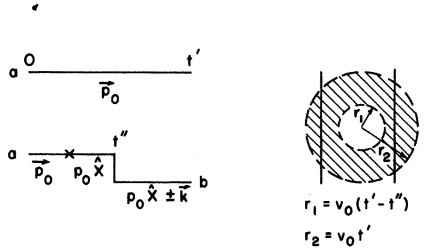

FIG. 5. Diagrams for the polarization-function density $A^{00;11}(\vec{R},t',\vec{v}_0)$. Collision interaction acts continuously from $t=0$ to t''. The spatial overlap of the two waves is indicated by the diagonal grid.

ning at time $t=0$ and terminating at time $t=t''$ since there is no collision interaction for the b-state amplitude after time t''. From time t'' to t' this scattered wave continues to propagate radially outward so that at time t' it occupies a spherical shell with inner radius $v_0(t'-t'')$ and outer radius v_0t' as shown in the figure. From the scattered wave, we should expect a contribution to $A^{00;11}(\vec{R},t',\vec{v}_0)$ proportional to $[X^{-1}e^{ip_0X}f_a(\Omega)]^*$ (conjugate since the polarization-function density is proportional to b^*). Again there will be a rapidly varying phase factor for the polarization-function density in all but the forward direction. Since the b-state amplitude is formed from an amplitude $a^{10}(t'')$ corresponding to motion in all directions $\hat{X}$, the Doppler factor will be changed from $e^{\pm i\vec{k}\cdot\vec{v}_0(t'-t'')}$ to $e^{\pm i\vec{k}\cdot\vec{v}(t'-t'')}$, where

$$\vec{v}=v_0\hat{X} \quad . \tag{55}$$

Furthermore, to restrict the contribution to the spherical shell, we must have the product of step functions $\theta(v_0t'-X)$ and $\theta[X-v_0(t'-t'')]$.

The details of the calculation are similar to that for the previous term, and the polarization-function density is

$$\sum_{n=1}^{\infty}A^{00;n1}(\vec{R},t',\vec{v}_0)=\tfrac{1}{4}\wp E(t')V^{-1}\sum_j[f_a(\hat{X}_j,\vec{p}_0)]^*X_j^{-1}e^{-ip_0\vec{X}_j\cdot(\hat{X}_j-\hat{p}_0)}$$
$$\times e^{-i\vec{k}\cdot\vec{R}}\int_0^{t'}dt''H(t',t'')\,e^{i\vec{k}\cdot\hat{X}_jv_0(t'-t'')}\theta(v_0t'-X_j)\theta[X_j-v_0(t'-t'')]-\text{term}(\vec{k}\to-\vec{k}) \quad , \tag{56}$$

which, when projected on the cavity mode, gives the polarization function

$$\sum_{n=1}^{\infty}A^{00;n1}(t',v_0)=-\tfrac{1}{4}i\wp E(t')\mathfrak{N}V^{-1}\frac{2\pi i}{m}\int_0^{t'}dt''H(t',t'')e^{i\vec{k}\cdot\vec{v}_0(t'-t'')}[f_a(0)]^*(-t'')+\text{term}(\vec{k}\to-\vec{k}) \quad . \tag{57}$$

Note that in Eq. (57) we have regained $\vec{v}_0$ in the exponential since the integrand in (56) contributes only in the forward direction $\hat{X}=\hat{v}_0$ on mode projection. The t'' factor arises from the integral of the step function over X_j.

$$A^{10;01}(t',\vec{v}_0)$$

The last first-order laser contribution for a-state scattering only comes from the product of amplitudes $a^{10}(b^{11})^*$, for which the diagrams are drawn in Fig. 6. Since we are dealing with only one collision, the interactions in the a and b states must *occur at the same perturber site*. The spatial diagrams for a^{10} and b^{11} have been previously discussed in reference to Figs. 4 and 5, respectively. The calculation must yield factors of

$$X^{-1}e^{ip_0X}f_a(\Omega)\theta(v_0t'-X) \quad ,$$

$$[X^{-1}e^{ip_0X}f_a(\Omega)]^*\theta(v_0t'-X)\theta[X-v_0(t'-t'')]$$

for the a- and b^*-states amplitudes, respectively, so that the total result for the polarization-function density, which is a product of these amplitudes, contains the differential scattering cross section $|f_a(\Omega)|^2$. Again the b-state amplitude is formed from an amplitude $a^{10}(t'')$ corresponding to motion in the $\hat{X}$ direction, so that the Doppler factor will be $e^{\pm i\vec{k}\cdot\vec{v}(t'-t'')}$ (recall that $\vec{v}=v_0\hat{X}$). It is most important to note that the polarization-function density is not a rapidly varying function of direction $\hat{X}$ since both the scattered waves originate at the same scattering center and propagate with speed v_0. Thus, there will be significant contributions to the polarization function in all directions. One may view the process as follows: An atom undergoes a collision while in state a and then interacts with the laser field while moving in a new direction $\hat{X}$. The probability for scattering into this new direction is simply $|f_a(\hat{X},\vec{v}_0)|^2d\Omega_X$ [note that $f_a(\hat{X},\vec{p}_0)$ and $f_a(\hat{X},\vec{v}_0)$ are meant to represent identical quantities provided $\vec{p}_0=m\vec{v}_0$].

Again the calculation for the polarization-function density and polarization function to all orders in the scattering interaction may be done explicitly to yield

$$\sum_{m,n=1}^{\infty}A^{m0;n1}(\vec{R},t',\vec{v}_0)=\tfrac{1}{4}\wp E(t')V^{-1}\sum_j|f_a(\hat{X}_j,\vec{v}_0)|^2X_j^{-2}$$
$$\times\ e^{-i\vec{k}\cdot\vec{R}}\int_0^{t'}dt''H(t',t'')e^{i\vec{k}\cdot\hat{X}_jv_0(t'-t'')}$$
$$\times\ \theta(v_0t'-X_j)\,\theta[X_j-v_0(t'-t'')]-\text{term}(\vec{k}\to-\vec{k}) \quad , \tag{58}$$

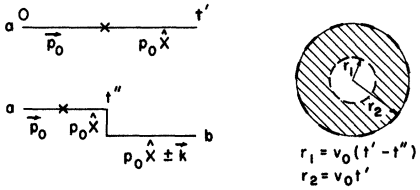

FIG. 6. Diagrams for the polarization-function density $A^{10;01}(\vec{R}, t', \vec{v}_0)$. Spatial overlap of the two waves is indicated by the diagonal grid.

$$\sum_{m,n=1}^{\infty} A^{m0;n1}(t', \vec{v}_0) = -\tfrac{1}{4} i \wp E(t') n V^{-1} \int_0^{t'} dt'' H(t', t'') \times v_0 t'' \int d\Omega_X \, |f_a(\hat{X}, \vec{v}_0)|^2 e^{i\vec{k}\cdot\hat{X} v_0 (t'-t'')} + \text{term}(\vec{k} \to -\vec{k}) \quad . \tag{59}$$

Since both $|f_a(\hat{X}, \vec{v}_0)|^2$ and $e^{i\vec{k}\cdot\hat{X}v_0(t'-t'')}$ possess $\hat{X}$ dependence, one cannot perform the angular integral over Ω_X without assuming an explicit form for $|f_a(\hat{X}, \vec{v}_0)|^2$, so that expression (59) is somewhat more complicated that the previous terms in the perturbation solution for $A(t', \vec{v}_0)$.[14]

Polarization Function $A^{(1)}(t')$

Summing Eqs. (42), (54), (57), and (59) and averaging the result over initial emitter velocities $\vec{v}_0$ with a distribution function $W(\vec{v}_0)$, we obtain the polarization function $A^{(1)}(t')$ to first order in the laser field for state-a scattering only:

$$A^{(1)}(t') = -\tfrac{1}{4} i \wp E(t') V^{-1} \int d^3 v_0 \, W(\vec{v}_0) \int_0^{t'} dt'' H(t', t'') \times e^{i\vec{k}\cdot\vec{v}_0(t'-t'')} \{1 + (2\pi i \mathfrak{N}/m)[f_a(0)t' - f_a(0)^* t''] + \mathfrak{N} v_0 t'' \int d\Omega_v \, |f_a(\hat{v}, \vec{v}_0)|^2 e^{i\vec{k}\cdot(\vec{v}-\vec{v}_0)(t'-t'')}\} + \text{term}(\vec{k} \to -\vec{k}), \tag{60}$$

where we have used Eq. (55) to change variables from $\hat{X}$ to $\hat{v}$ in the term involving $|f_a(\hat{v}, \vec{v}_0)|^2$.

Equation (60) may be written in a more suggestive form. We define a complex quantum-mechanical cross section $\bar{\sigma}_{QM}$ by

$$\bar{\sigma}_{QM} = (4\pi/ip_0) f(0) \, , \tag{61}$$

which implies

$$\mathrm{Re}\,\bar{\sigma}_{QM} = (4\pi/p_0)\,\mathrm{Im}[f(0)] = \sigma_{QM} \quad , \tag{62a}$$

$$\mathrm{Im}\,\bar{\sigma}_{QM} = -(4\pi/p_0)\,\mathrm{Re}[f(0)] \, , \tag{62b}$$

where the optical theorem[15] has been used in Eq. (62a) to relate $\mathrm{Im}[f(0)]$ to the normal quantum-mechanical cross section σ_{QM}. Furthermore, defining a complex-collision decay parameter

$$\bar{\Gamma}_{QM} = \mathfrak{N} v_0 \bar{\sigma}_{QM} \, ,$$

Eq. (60) becomes

$$A^{(1)}(t') = -\tfrac{1}{4} i \wp E(t') V^{-1} \int d^3 v_0 \, W(\vec{v}_0) \int_0^{t'} dt'' H(t', t'') \times e^{i\vec{k}\cdot\vec{v}_0(t'-t'')}[1 - \chi_a(\vec{v}_0, \vec{k}, t', t'')] + \text{term}(\vec{k} \to -\vec{k}) \quad (a \text{ scattering only}) \, , \tag{63a}$$

where the collision factor χ_a is given by

$$\chi_a(\vec{v}_0, \vec{k}, t', t'') = \tfrac{1}{2} \bar{\Gamma}^a_{QM}(v_0) t' + \tfrac{1}{2} \bar{\Gamma}^a_{QM}(v_0)^* t'' - \mathfrak{N} v_0 t'' \int d\Omega_v \, |f_a(\hat{v}, \vec{v}_0)|^2 e^{i\vec{k}\cdot(\vec{v}-\vec{v}_0)(t'-t'')} \tag{63b}$$

and we have explicitly indicated that the forward-scattering amplitude (and consequently the decay parameter) depends on the emitter speed v_0.

Interpretation of Result

Equation (63b) may be separated into terms representing binary-collision impact effects (the terms "impact effects" and ELVE refer to the same process and will be used interchangeably) and Doppler modifying collision effects (GDE). To see that this is possible, we first rewrite Eq. (63b) using the relationship $\bar{\Gamma}_{QM} + \bar{\Gamma}^*_{QM} = 2\mathfrak{N} v_0 \sigma_{QM}$ to obtain

$$\chi_a(\vec{v}_0, \vec{k}, t', t'') = \tfrac{1}{2} \bar{\Gamma}^a_{QM}(v_0)(t' - t'') + \mathfrak{N} v_0 \sigma^a_{QM}(v_0) t'' - \mathfrak{N} v_0 t'' \int d\Omega_v \, |f_a(\hat{v}, \vec{v}_0)|^2 \times e^{i\vec{k}\cdot(\vec{v}-\vec{v}_0)(t'-t'')} \, . \tag{64}$$

In order to separate out the GDE, we must note that Doppler-modifying collisions are those in which $k\Delta v/\gamma_{ab} \gtrsim 1$ or equivalently $\theta \gtrsim \gamma_{ab}/kv_0$ (θ is the angle between $\hat{v}$ and $\hat{v}_0$ and $\Delta v \approx v_0\theta$ for $\theta \ll 1$). This suggests that we break up the integral over Ω_v into the regions $\theta < \gamma_{ab}/kv_0$ and $\theta > \gamma_{ab}/kv_0$. In the first region the exponential factor in Eq. (64) can be set equal to unity and, after a little algebra, we find

$$\chi_a(\vec{v}_0, \vec{k}, t', t'') = \tfrac{1}{2} \bar{\Gamma}^a_{QM}(v_0)(t' - t'') + \mathfrak{N} v_0 t'' \times [\int' d\Omega_v |f_a(\hat{v}, \vec{v}_0)|^2 - \int' d\Omega_v$$

$$\times |f_a(\hat{v}, \vec{v}_0)|^2 e^{i\vec{k}\cdot(\vec{v}-\vec{v}_0)(t'-t'')}], \tag{65}$$

where we have used the fact that $\sigma^a_{QM} = \int d\Omega_v |f_a(\hat{v}, \vec{v}_0)|^2$, and the prime on the integrals indicate that the integration is to be performed only for the region $\theta > \gamma_{ab}/kv_0$ (Doppler-modifying-collision region). One now notes that

$$W_a(\hat{v}|\vec{v}_0)d\Omega_v \equiv \Im v_0 |f_a(\hat{v}, \vec{v}_0)|^2 d\Omega_v \tag{66}$$

is just the probability per unit time for an atom in state a to change its velocity from $\vec{v}_0$ to $\vec{v}$ [$W_a(\hat{v}|\vec{v}_0)$ is defined for Doppler-modifying collisions only], while

$$\Gamma^a_{DM}(v_0) \equiv \int' d\Omega_v W_a(\hat{v}|\vec{v}_0) \tag{67}$$

is the rate at which Doppler-modifying collisions occur for atoms in state a. With these assignments, Eq. (65) becomes

$$\chi_a(\vec{v}_0, \vec{k}, t', t'') = \tfrac{1}{2}\bar{\Gamma}^a_{QM}(v_0)(t'-t'') + \Gamma^a_{DM}(v_0)t'' - t''\int' d\Omega_v W_a(\hat{v}|\vec{v}_0) e^{i\vec{k}\cdot(\vec{v}-\vec{v}_0)(t'-t'')} . \tag{68}$$

This quantum-mechanical expression for χ_a clearly separates the ELVE [represented by the first term in Eq. (68), which is typical of impact-theory results] and the GDE [represented by the last two terms in Eq. (68)].

In fact, such a separation forms the basis for a pseudoclassical model, in which one allows classical Doppler-modifying collisions for times up to t'' and impact "collisions" for times between t'' and t' (see Fig. 3). That is, for times less than t'', the atom has not yet acquired a dipole moment [i.e., $\rho_{ab}(t) = 0$ for $t < t''$(see Fig. 3)] and we can still speak of a velocity-changing collision for the *atom* in state a.[16] In some classical limit, we can associate the quantities $W_a(\hat{v}|\vec{v}_0)$ and Γ^a_{DM} with the Boltzmann-collision kernel and classical rate for Doppler-modifying collisions, respectively, for atoms in state a. On the other hand, we can no longer speak of classical Doppler-modifying collisions for the time region t'' to t' since $\rho_{ab}(t)$ is nonzero in that time interval and inequality (1) is not satisfied, making it impossible to associate a classical trajectory with $\rho_{ab}(t)$. Using this observation, we complete our model by assuming that, in the time interval t'' to t', Doppler-modifying collisions are forbidden and only impact "collisions" are possible. One should recall that this time region was marked by scattering contributions to the polarization function that involved only the forward-scattering amplitude. The association of impact collisions with forward-scattering amplitudes is well founded.[17] Since ELVE cannot occur if $\rho_{ab}(t) = \int d^3R \rho_{ab}(\vec{R}, t) = 0$ [if $\rho_{ab}(t) = 0$ before a collision, the density matrix $\rho(t)$ will be unchanged as a result of the adiabatic collision], and Doppler-modifying collisions occur only if $\rho_{ab}(t) = 0$, the two types of collisions must occur at mutually exclusive times.

It is not our purpose to go into the analytic details of the pseudoclassical model in this paper. We have introduced it at this time (and shall refer to it briefly hereafter) since it arises naturally from the quantum-mechanical development. In third-order laser theory, the polarization function will again be expressable in terms of multiple integrals over the various time intervals between interactions with the laser field. The pseudoclassical model will provide the starting point for this calculation in which the Lindholm-Foley[2] or Baranger[17] theory is used to propagate the solution through time intervals where $\rho_{ab}(t) \neq 0$, and the Boltzmann-equation approach is used to propagate the solution through time intervals where $\rho_{ab}(t) = 0$. We should mention, in passing, that the pseudoclassical model will also enable one to readily generalize the one-collision result to the many-collision (binary) case.

In concluding this section, we note that if Doppler-modifying collisions are negligible [$\Gamma^a_{DM} \approx W_a(\hat{v}|\vec{v}_0) \approx 0$], Eq. (68) reads

$$\chi_a(\vec{v}_0, t', t'') = \tfrac{1}{2}\bar{\Gamma}^a_{QM}(v_0)(t'-t''), \tag{69}$$

which is typical of pure impact theories.

VI. COLLISION INTERACTION IN LOWER-LASER STATE ONLY

One might think that the form of our results would not change if the collision interaction occurred only in state b rather than only in state a; but the results for these cases are, in fact, distinct. This is due to the nature of the collision processes involved, as will be discussed below. For b scattering only, instead of Eq. (35), we take

$$U^j_{a;\vec{p},\vec{p}'} = 0 , \quad U^j_{b;\vec{p},\vec{p}'} \equiv U^j_{bb;\vec{p},\vec{p}'} \neq 0 ,$$

Only one term, in addition to the no-collision term $A^{00;01}$ [Eq. (42)] will contribute in the case of b scattering only. The calculation proceeds as in Sec. V.

$$A^{00;1'1} \quad (t', v_0)$$

The polarization-function density $A^{00;1'1}(\vec{R}, t', \vec{v}_0)$ arises from the product of the amplitudes $a^{00}(b^{1'1})^*$, and the corresponding diagrams are shown in Fig. 7. The prime in the superscript indicates that the collision interaction occurs in state b. The a-state amplitude is an unperturbed plane wave $e^{i\vec{p}_0\cdot\vec{R}}$. The b-state amplitude begins to experience the collision interaction as soon as the transition at time t'' occurs, and spatially is a spherical wave that begins propagating at time t'' and continues to propagate until the time of observation t'. The spherical wave propagates with speed $|\vec{p}_0 \pm \vec{k}|/m$. In this

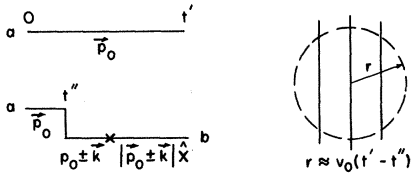

FIG. 7. Diagrams for the polarization-function density $A^{00;1'1}(\vec{R}, t', \vec{v}_0)$. Collision interaction acts continuously from $t = t''$ to t'.

case, it is important to keep the photon momentum in the expression since it will lead to a non-negligible phase shift. Therefore, the b-state amplitude should contribute a factor

$$\{X^{-1} f_b(\hat{X}, \vec{p}_0 \pm \vec{k})\, e^{i|\vec{p}_0 \pm \vec{k}|X}\, \theta[(|\vec{p}_0 \pm \vec{k}|/m)(t' - t'') - X]\}^*$$

to the polarization-function density. The step function confines the contribution to the sphere shown in Fig. 7. Since the b-state amplitude is formed an amplitude $a^{00}(t'')$ corresponding to an atom moving with velocity $\vec{v}_0$, the Doppler factor will be $e^{\pm i\vec{k}\cdot\vec{v}_0(t'-t'')}$. We expect the polarization-function density to have a rapidly varying phase factor in all but the forward direction.

Performing the calculation,[18] we find the polarization-function density,

$$\begin{aligned}\sum_{n'=1}^{\infty} A^{00;n'1}(\vec{R}, t', \vec{v}_0) = {} & \tfrac{1}{4}\wp\, E(t') V^{-1} \textstyle\sum_j [f_b(\hat{X}_j, \vec{p}_0 + \vec{k})]^* X_j^{-1} \\ & \times e^{-i|\vec{p}_0+\vec{k}|X_j}\, e^{i(\vec{p}_0+\vec{k})\cdot\vec{X}_j}\, e^{-i\vec{k}\cdot\vec{R}} \\ & \times \int_0^{t'} dt''\, H(t', t'')\, e^{i\vec{k}\cdot\vec{v}_0(t'-t'')} \\ & \times \theta[(|\vec{p}_0 + \vec{k}|/m)(t' - t'') - X_j] \\ & - \text{term } (\vec{k} \to -\vec{k}) \ . \end{aligned} \tag{70}$$

Using the fact that $k\mathcal{R} \ll 1$, one may easily show that

$$f(\hat{X}, \vec{p}_0 \pm \vec{k}) \approx f(\hat{X}, \vec{p}_0) \ , \tag{71}$$

so that when Eq. (70) is projected on the cavity mode we obtain (the integrand contributes significantly only in the forward direction)

$$\begin{aligned}\sum_{n'=1}^{\infty} A^{00;n'1}(t', \vec{v}_0) = {} & -\tfrac{1}{4} i\wp\, E(t') V^{-1} \int_0^{t'} dt''\, H(t', t'') \\ & \times e^{i\vec{k}\cdot\vec{v}_0(t'-t'')} \{-\tfrac{1}{2}[\overline{\Gamma}^b_{QM}(v_0)]^*(t' - t'')\} \\ & + \text{term } (\vec{k} \to -\vec{k}) \ , \end{aligned} \tag{72}$$

where

$$\overline{\Gamma}^b_{QM}(v_0) = \mathfrak{N} v_0 \overline{\sigma}^b_{QM}(v_0) \ , \tag{73}$$

$$\overline{\sigma}^b_{QM}(v_0) = (4\pi/ip_0) f_b(0) \ . \tag{74}$$

Combining Eq. (72) with Eq. (42), we arrive at the polarization function to first order in the laser field for b scattering only:

$$\begin{aligned} A^{(1)}(t') = {} & -\tfrac{1}{4} i\wp\, E(t') V^{-1} \int d^3 v_0\, W(\vec{v}_0) \int_0^{t'} dt''\, H(t', t'') \\ & \times e^{i\vec{k}\cdot\vec{v}_0(t'-t'')} [1 - \tfrac{1}{2}\overline{\Gamma}^b_{QM}(v_0)^*(t' - t'')] \\ & (b \text{ scattering only}). \end{aligned} \tag{75}$$

The simple impact nature of this result can be explained in terms of our pseudoclassical model, which is also applicable to the case of b scattering only. Reference to Fig. 7 will indicate that for b scattering only, all collision interactions occur when $\rho_{ab}(t) \neq 0$ and, as such, give rise to impact rather than to Doppler-modifying effects. We see that, in general, the result for pure a scattering [Eq. (63)] and pure b scattering [Eq. (75)] differ in form due to the presence of Doppler-modifying collisions in the former which are absent in the latter. (We should point out that if excitation of laser atoms to state b rather than to state a had been considered, the nature of the a-scattering-only and b-scattering-only results would be reversed.) A discussion of the significance of these findings will be given in Sec. VII.

VII. COLLISION INTERACTION IN BOTH LEVELS

In some cases, the collision interaction in both levels a and b may be of comparable magnitude, in which case the treatment given in Secs. V and VI is incomplete. Although we feel this will not be the usual situation, for completeness we present the calculation with collision interaction in both levels. An added motivation for the calculation is provided by the fact that, in the limit of equal collision interaction in both levels, we expect to arrive at the results for a model which treats the atomic center-of-mass motion classically. Thus, we take $U^j_{a;\vec{p},\vec{p}'} \neq 0$ and $U^j_{b;\vec{p},\vec{p}'} \neq 0$, and there is one additional contribution to the polarization function which must be calculated.

$$A^{10;1'1}(t', \vec{v}_0)$$

The final term of first-order laser theory for the one-collision process arises from the product of amplitudes $a^{10}(b^{1'1})^*$; the corresponding diagrams are shown in Fig. 8. The contribution involves

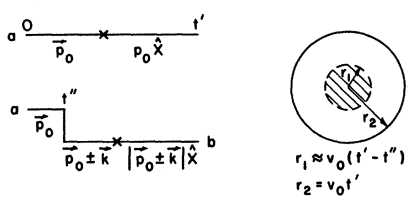

FIG. 8. Diagrams for the polarization-function density $A^{10;1'1}(\vec{R}, t', \vec{v}_0)$. This spatial overlap of the two waves is indicated by the diagonal grid.

scattering interactions in both states a and b. Since we are dealing with only one collision, both interactions must occur at the same perturber site. Following the discussion associated with Figs. 4 and 7, we expect the a-state amplitude to contribute a factor like

$$X^{-1} f_a(\hat{X}, \vec{p}_0)\, e^{i p_0 X}\, \theta(v_0 t' - X),$$

and the b-state amplitude one like

$$[X^{-1} f_b(\hat{X}, \vec{p}_0 \pm \vec{k})\, e^{i|\vec{p}_0 \pm \vec{k}|X}]^*\, \theta[(|\vec{p}_0 \pm \vec{k}|/m)(t' - t'') - X].$$

In this case, the polarization-function density will have a slowly varying phase factor since one spherical wave propagates with speed v_0, while the other propogates with speed $|\vec{v}_0 \pm \vec{k}/m|$. The resulting expression for the polarization-function density is found to be

$$\sum_{m,n'=1}^{\infty} A^{m0;n'1}(\vec{R}, t, \vec{v}_0) = \tfrac{1}{4}\wp E(t')\, V^{-1} \sum_j f_a(\hat{X}_j, \vec{p}_0)[f_b(\hat{X}_j, \vec{p}_0)]^*\, e^{-i\vec{k}\cdot\vec{R}}\, X_j^{-2}\, e^{i(p_0 X_j - \vec{p}_0\cdot\vec{X}_j)}\, e^{-i[|\vec{p}_0+\vec{k}|X_j - (\vec{p}_0+\vec{k})\cdot\vec{X}_j]}$$

$$\times \int_0^{t'} dt''\, H(t', t'')\, e^{i\vec{k}\cdot\vec{v}_0(t'-t'')}\, \theta(v_0 t' - X_j)\, \theta[v_0(t'-t'') - X_j] - \text{term}(\vec{k} \to -\vec{k}), \tag{76}$$

where Eq. (71) has been used.

It will be convenient to expand

$$|\vec{p}_0 + \vec{k}| \approx p_0 + \vec{k}\cdot\hat{p}_0, \tag{77}$$

which is valid since $k \ll p_0$.[19] Projecting Eq. (76) onto the cavity mode yields

$$\sum_{m,n'=1}^{\infty} A^{m0;n'1}(t', \vec{v}_0) = -\tfrac{1}{4} i \wp E(t') \mathfrak{N} V^{-1} \int_0^{t'} dt''\, H(t', t'')\, e^{i\vec{k}\cdot\vec{v}_0(t'-t'')}$$

$$\times \int d^3X f_a(\hat{X}, \vec{p}_0) f_b(\hat{X}, \vec{p}_0)^*\, X^{-2}\, e^{iX\vec{k}\cdot(\hat{X}-\hat{p}_0)}\, \theta[v_0(t'-t'') - X] + \text{term}(\vec{k} \to -\vec{k}). \tag{78}$$

Performing the integral over X, changing variables according to Eq. (55), and averaging over the initial velocity distribution leads to

$$\sum_{m,n'=1}^{\infty} A^{m0;n'1}(t') = -\tfrac{1}{4} i \wp E(t') \mathfrak{N} V^{-1} \int d^3v_0\, W(\vec{v}_0) \int_0^{t'} dt''\, H(t', t'')$$

$$\times v_0\, e^{i\vec{k}\cdot\vec{v}_0(t'-t'')} \int d\Omega_v\, G_{\vec{k}}(\hat{v}, \vec{v}_0, t'-t') f_a(\hat{v}, \vec{v}_0) f_b(\hat{v}, \vec{v}_0)^* + \text{term}(\vec{k} \to -\vec{k}), \tag{79}$$

where

$$G_{\vec{k}}(\hat{v}, \vec{v}_0, t'-t'') \equiv [e^{i\vec{k}\cdot(\vec{v}-\vec{v}_0)(t'-t'')} - 1][i\vec{k}\cdot(\vec{v}-\vec{v}_0)]^{-1}. \tag{80}$$

This is as far as we may go without explicit expressions for f_a and f_b. Combining Eqs. (63), (72), and (79), we arrive at the general one-collision result for the average polarization function to first order in the laser field:

$$A^{(1)}(t') = -\tfrac{1}{4} i \wp E(t') V^{-1} \int d^3v_0\, W(\vec{v}_0) \int_0^{t'} dt''\, H(t', t'')\, e^{i\vec{k}\cdot\vec{v}_0(t'-t'')} \{1 - \chi_a(\vec{v}_0, \vec{k}, t', t'') - \tfrac{1}{2}[\bar{\Gamma}^b_{QM}(v_0)]^*(t'-t'')$$

$$+ \mathfrak{N} v_0 \int d\Omega_v\, G_{\vec{k}}(\hat{v}, \vec{v}_0, t'-t'') f_a(\hat{v}, \vec{v}_0) f_b(\hat{v}, \vec{v}_0)^*\} + \text{term}(\vec{k} \to -\vec{k}), \tag{81}$$

where $G_{\vec{k}}$ is given by Eq. (80). It is of interest to look at several limiting cases of this general result.

Straight-line paths. The reader should recall that the normal Doppler effect is modified only by those collisions that produce changes in velocity $\Delta\vec{v}$ such that $k\Delta v \gtrsim \gamma_{ab}$. On the other hand, significant ELVE collisions will generally occur even if $k\Delta v \lesssim \gamma_{ab}$, so that in some cases, it may be a fair approximation to completely neglect the Doppler-modifying collisions (there will always be more collisions leading to $k\Delta v \lesssim \gamma_{ab}$ than $k\Delta v \gtrsim \gamma_{ab}$). Neglect of Doppler-modifying collisions is equivalent to taking straight-line paths for emitter trajectories, which is a common assumption of standard pressure-broadening theories. The assumption is valid if Doppler-modifying collisions are relatively unimportant compared with collisions producing ELVE, and may correspond to a classical description of relative emitter perturber motion.

Neglect of Doppler-modifying collision implies that we consider only the region $\theta \lesssim \gamma_{ab}/kv_0$ in the

angular integration over Ω_v in Eq. (81). In this region, we find that

$$G_{\vec{k}}(\vec{v}, \vec{v}_0, t'-t'') \approx t'-t'',$$

$$\chi_a(\vec{v}_0, \vec{k}, t', t'') \approx -\tfrac{1}{2}\bar{\Gamma}^a_{QM}(v_0)(t'-t''),$$

and Eq. (81) becomes

$$A^{(1)}(t') = -\tfrac{1}{4}i\wp E(t')V^{-1}\int d^3v_0\, W(\vec{v}_0) \times \int_0^{t'} dt''\, H(t', t'')\, e^{i\vec{k}\cdot\vec{v}_0(t'-t'')} \times\{1-(t'-t'')[\tfrac{1}{2}\bar{\Gamma}^a_{QM}(v_0)+\tfrac{1}{2}\bar{\Gamma}^b_{QM}(v_0)^* - \mathfrak{N}v_0\int d\Omega_v f_a(\hat{v}, \vec{v}_0) f_b(\hat{v}, \vec{v}_0)^*]\} + \text{term}(\vec{k}\to-\vec{k}) \quad \text{(straight-line-path limit)}, \tag{82}$$

which is in agreement with the quantum-mechanical result of Baranger,[20] who considered the problem of a fixed emitter and moving perturbers. For straight-line paths, it may be shown[21] that Eq. (82) reduces to the Lindholm-Foley result[2] for the problem which treats a fixed emitter and classically moving perturbers, folded into the unperturbed emitter velocity distribution.

Equal scattering interaction in both levels. The unlikely (but possible) case of $f_a = f_b \equiv f$ leads to the opposite limit. That is, ELVE are absent since the relative collision-induced phase shift is 0, and any modifications of line shapes must arise from the GDE. We should also expect a classical correspondence for this case since Eq. (1) is well satisfied (the a and b trajectories of Fig. 1 coincide). In this limit we find

$$\bar{\Gamma}^a_{QM} = \bar{\Gamma}^b_{QM}; \quad \bar{\Gamma}^a_{QM} + \bar{\Gamma}^b_{QM}{}^* = 2\mathfrak{N}v_0\sigma_{QM},$$

so that using Eq. (64), Eq. (81) becomes

$$A^{(1)}(t') = -\tfrac{1}{4}i\wp E(t')V^{-1}\int d^3v_0\, W(\vec{v}_0)\int_0^{t'} dt''\, H(t', t'')\, e^{i\vec{k}\cdot\vec{v}_0(t'-t'')} \quad [1-\mathfrak{N}v_0\sigma_{QM}t' + \mathfrak{N}v_0 t''\int d\Omega_v |f(\hat{v}, \vec{v}_0)|^2 \times e^{i\vec{k}\cdot(\vec{v}-\vec{v}_0)(t'-t'')} + \mathfrak{N}v_0\int d\Omega_v\, G_{\vec{k}}(\hat{v}, \vec{v}_0, t'-t'')|f(\hat{v}, \vec{v}_0)|^2] + \text{term}(\vec{k}\to-\vec{k}). \tag{83}$$

Employing a procedure indentical to the one used following Eq. (64), Eq. (83) may be transformed in

$$A^{(1)}(t') = -\tfrac{1}{4}i\wp E(t')V^{-1}\int d^3v_0\, W(\vec{v}_0)\int_0^{t'} dt''\, H(t', t'')\, e^{i\vec{k}\cdot\vec{v}_0(t'-t'')}\Big[1-\Gamma_{DM}(v_0)t' + \int' d\Omega_v W(\hat{v}|\vec{v}_0) \times\{t'' e^{i\vec{k}\cdot(\vec{v}-\vec{v}_0)(t'-t'')} + G_{\vec{k}}(\hat{v}, \vec{v}_0, t'-t'')\}\Big] + \text{term}\ (\vec{k}\to-\vec{k}) \qquad \text{(classical limit } f_a = f_b), \tag{84}$$

where, in the WKB limit,[22] $W(\hat{v}|v_0)$ and $\Gamma_{DM}(v_0)$ are equal to the probability density per unit time for a collision to change the emitter velocity from v_0 to $\vec{v}$ (Boltzmann-collision kernel defined for Doppler-modifying collisions only) and the rate of Doppler-modifying collisions, respectively. It may be shown that Eq. (84) is the leading term in a Boltzmann-equation approach to the problem and, as such, seems to indicate that a Boltzmann-equation approach is valid for the case $f_a = f_b$.[23] As predicted the result may be purely classical. If one wishes to study this case for the many-collision problem, it is probably easier to use the Boltzmann-equation approach than our method.

Collision interaction in one state only. If either $f_b \approx 0$ or $f_a \approx 0$, Eq. (81) reduces to (63) or (75), respectively. For the case of b scattering only, there is a great simplification since the collision terms in the result depend solely on the two parameters $\mathrm{Re}\bar{\Gamma}^b_{QM}$ and $\mathrm{Im}\bar{\Gamma}^b_{QM}$. We have also indicated that a pseudoclassical model is applicable when there is collision interaction in only one state. Our results are not equivalent to those which combine a Boltzmann-equation approach to treat velocity effects and an impact pressure-broadening theory to treat ELVE, except in the sense described in Sec. V.

General case. If none of the above limits are achieved, one must consider the general expression (81) for the polarization function. Evaluation will be extremely difficult since a complete knowledge of $f_a(\Omega)$ and $f_b(\Omega)$ is required. If one attempts to find a pseudoclassical model for the general case, he immediately runs into difficulty. In the region $t'' < t < t'$ (see Fig. 8), one can no longer absolutely exclude Doppler-modifying collisions since the a and b trajectories (Fig. 1) may differ only slightly for some collisions [inequality (1) approximately safisfied] allowing for the possiblity of classical velocity-changing collisions. On the other hand, impact effects are certainly allowed in this time region, so that ELVE and GDE are simultaneously occurring; and the basis for our pseudoclassical model is destroyed. In any event, the one-collision results indicate that combining ELVE and Boltzmann-equation results, as has been done in the past,[3,4] does not lead to the correct result for the polarization function, and one concludes that the quantum-mechanical formulation is needed.[24]

VIII. AMPLITUDE AND PHASE EQUATIONS

In this section, we obtain the self-consistent amplitude and phase equations in the one-collision approximation which will enable us to derive expressions for the gain and frequency-pulling parameters of the laser. We shall work in the limit of collision interaction in one state only, and, to facilitate the calculation, we introduce a quantity

$$\chi(\vec{v}_0, \vec{k}, t', t'') = \begin{cases} \chi_a(\vec{v}_0, \vec{k}, t', t'') & a \text{ scattering only} \\ \frac{1}{2}\bar{\Gamma}^b_{QM}(v_0)^*(t'-t'') & b \text{ scattering only} \end{cases} . \tag{85}$$

Equations (63) and (75) give the polarization function which must be integrated between times t and $t+\delta t$ to be used in the amplitude and phase equations (19) and (21). By our assumption on δt, the integral may be taken from 0 to ∞ with both $E(t')$ and $\varphi(t')$ evaluated at $t' = t$. Thus, performing this integration and using Eq. (85), we find

$$\mathcal{A}^{(1)}(t) \equiv \int_t^{t+\delta t} A^{(1)}(t')dt' = -\tfrac{1}{4}i\wp E(t)V^{-1}\int d^3v_0\, W(\vec{v}_0) \times \int_0^\infty dt' \int_0^{t'} dt''\, H(t', t'')e^{i\vec{k}\cdot\vec{v}_0(t'-t'')} \times [1-\chi(\vec{v}_0, \vec{k}, t', t'')] + \text{term}(\vec{k}\to -\vec{k}) .$$

By changing variables to

$$\tau = t' - t'' \text{ and } t'' = t'' ,$$

and using Eq. (40), the above integral becomes

$$\mathcal{A}^{(1)}(t) = -\tfrac{1}{4}i\wp E(t)V^{-1}\int d^3v_0\, W(\vec{v}_0)\int_0^\infty d\tau e^{(-\gamma_{ab}-i\Delta\omega+i\vec{k}\cdot\vec{v}_0+iE_{\vec{k}})\tau} \times \begin{cases} \int_0^\infty dt''\, e^{-\gamma_a t''}[1-\chi_a(\vec{v}_0, \vec{k}, t', t'')] & a \text{ scattering} \\ \gamma_a^{-1}e^{-(1/2)\bar{\Gamma}^b_{QM}(v_0)^*\tau} & b \text{ scattering} \end{cases} + \text{term}(\vec{k}\to -\vec{k}) , \tag{86}$$

where we have approximated

$$1-\tfrac{1}{2}\bar{\Gamma}^b_{QM}{}^* \approx e^{-(1/2)\bar{\Gamma}^b_{QM}{}^*\tau} \tag{87}$$

in the b scattering result based on the one-collision approximation $|\bar{\Gamma}^b_{QM}| \ll \gamma_{ab}$. Substituting Eq. (86) into the amplitude equation (19) and using (68), we find

$$\dot{E} + \alpha E = 0 , \tag{88}$$

where the gain parameter α is given by

$$\alpha = -\tfrac{1}{2}\Omega/Q + \tfrac{1}{8}(\Omega\wp^2\Lambda/\epsilon_0)\int d^3v_0\, W(v_0)\left(\int_0^\infty d\tau\int_0^\infty dt'' \exp\{[-\gamma_{ab} - i(\omega-\Omega-\dot{\varphi}) + i\vec{k}\cdot\vec{v}_0 + iE_k]\tau - \gamma_a t''\} \times [1 - \tfrac{1}{2}\bar{\Gamma}^a_{QM}(v_0)\tau - \Gamma^a_{DM}(v_0)t'' + \mathfrak{N}v_0 t''\int' d\Omega_v |f_a(\hat{v}, v_0)|^2 e^{i\vec{k}\cdot(\vec{v}-\vec{v}_0)\tau}] + \text{c.c.} + \text{term}(\vec{k}\to -\vec{k})\right)$$

(a scattering only) (89a)

$$\alpha = -\tfrac{1}{2}\Omega/Q + \tfrac{1}{4}(\Omega\wp^2\Lambda/\epsilon_0)\int d^3v_0\, W(v_0) \times \left(\frac{\gamma_a^{-1}[\gamma_{ab} + \frac{1}{2}\mathrm{Re}\bar{\Gamma}^b_{QM}(v_0)]}{[\gamma_{ab} + \frac{1}{2}\mathrm{Re}\bar{\Gamma}^b_{QM}(v_0)]^2 + [\omega - \Omega - \dot{\varphi} + \frac{1}{2}\mathrm{Im}\bar{\Gamma}^b_{QM}(v_0)^* - \vec{k}\cdot\vec{v}_0 - E_{\vec{k}}]^2} + \text{term}(\vec{k}\to -\vec{k})\right)$$

(b scattering only) (89b)

and $\Lambda = \lambda/v$ is the excitation rate per unit volume. The phase equation (21) is approximately

$$\dot{\varphi} = +\tfrac{1}{8}i(\Omega\wp^2\Lambda/\epsilon_0)\int d^3v_0\, W(v_0)\int_0^\infty d\tau\int_0^\infty dt'' \exp\{[-\gamma_{ab} - i(\omega-\Omega) + i\vec{k}\cdot\vec{v}_0 + iE_{\vec{k}}]\tau - \gamma_a t''\}[1 - \tfrac{1}{2}\bar{\Gamma}^a_{QM}(v_0)\tau - \Gamma^a_{DM}(v_0)t'' + \mathfrak{N}v_0 t''\int' d\Omega_v |f_a(\hat{v}, v_0)|^2 e^{i\vec{k}\cdot(\vec{v}-\vec{v}_0)\tau}] + \text{c.c.} + \text{term}(\vec{k}\to -\vec{k})$$

(a scattering only) (90a)

$$\dot{\varphi} = +\tfrac{1}{4}(\Omega\wp^2\Lambda/\epsilon_0)\int d^3v_0\, W(v_0) \times \frac{\gamma_a^{-1}[\omega - \Omega + \frac{1}{2}\mathrm{Im}\bar{\Gamma}^b_{QM}(v_0)^* - \vec{k}\cdot\vec{v}_0 - E_{\vec{k}}]}{[\gamma_{ab} + \frac{1}{2}\mathrm{Re}\bar{\Gamma}^b_{QM}(v_0)]^2 + [\omega - \Omega + \frac{1}{2}\mathrm{Im}\bar{\Gamma}^b_{QM}(v_0)^* - \vec{k}\cdot\vec{v}_0 - E_{\vec{k}}]^2} + \text{term}(\vec{k}\to -\vec{k}),$$

(b scattering only) (90b)

and gives the frequency pulling $\dot{\varphi}$.

b scattering only. As discussed in Sec. VI and depicted in Eqs. (89b) and (90b), the results are of a purely impact nature, with the net modification of the no-collision result being $\gamma_{ab} \to \gamma_{ab} + \frac{1}{2}\bar{\Gamma}^b_{QM}(v_0)^*$. Since our pseudoclassical model predicts that no

Doppler-modifying collisions can occur, it will turn out that Eq. (87) provides the correct path for going from the one-collision to the many-collision (binary) problem, and Eqs. (89b) and (90b) will be valid at all pressures where binary-collision (impact) theory may be used. If one assumes that the decay parameter $\overline{\Gamma}^b_{QM}(v_0)$ is a slowly varying function of v_0 compared with $W(\vec{v}_0)$, then it may be evaluated at the average speed $\langle v_0 \rangle$. For an even distribution function $W(v_0)$, the resultant gain profile will be a symmetric function of cavity detuning about the frequency $\frac{1}{2}\,\mathrm{Im}\,\overline{\Gamma}^b_{QM}(\langle v_0 \rangle)^* - E_{\vec{k}}$. If this approximation is not made, the integrals in Eqs. (89b) and (90b) must be evaluated numerically. We should point out that the pure impact nature of the result will be lost in third-order laser theory.

a scattering only. The results [Eqs. (89a) and (90a)] reflect the presence of Doppler-modifying collisions and are not of a particularly simple nature. Only in the straight-line-path limit [see Eq. (69)] will the a-scattering result assume the same impact theory form as the b-scattering result. It is possible to generalize the one-collision result using our pseudoclassical model and, not going into details, the net effect will be that the integrands in Eqs. (89a) and (90a) are replaced by

$$H(\tau + t'', t'') \int d\Omega_v\, e^{i\vec{k}\cdot\vec{v}\tau} g(\hat{v}, \vec{v}_0, t'')\, e^{-(1/2)\overline{\Gamma}^a_{QM}(v)\tau}], \tag{91}$$

where Eq. (40) has been used and $g(\hat{v}, \vec{v}_0, t'')$ is effectively the probability density that the laser atom has a velocity $\vec{v}$ at time t'' if it had velocity v_0 at time $t=0$. Thus, we see that the Doppler-modifying collisions affect the results by altering the velocity $\vec{v}$ with which the laser atom moves in the time τ of interest. We defer an actual calculation using Eq. (91) until we have completed third-order laser theory.

Finally, we comment on the implication of having different forms for the a-scattering-only and b-scattering-only results. Let us forget the laser for the time being and consider a two level atom with a ground state b and excited state a. Realistically, we could neglect the scattering interaction in the ground state and consider that a scattering only is present. Let a monochromatic field of frequency Ω be applied to the system which has $E_a - E_b = \omega$. If an absorption experiment is performed (atom in state b at $t=0$), the absorption coefficient will be of the form of Eq. (89b) (replace $\overline{\Gamma}^{b}_{QM}{}^*$ with $\overline{\Gamma}^a_{QM}$), but if a stimulated-emission experiment is performed (atom in state a at $t=0$), the gain parameter will be of the form of Eq. (89a). Thus, the stimulated-emission and absorption profiles appear to differ.

However, based on the following argument, we now believe that it is possible to rule out the above-mentioned difference between emission and absorption profiles. Recall that the difference between absorption and emission profiles was due to the absence of velocity-changing collisions in the former which were present in the latter (assuming a scattering only). Although these collisions do alter the velocity of individual excited atoms, it is their effect on the excited atom velocity *distribution* which is important in determining spectral profiles. Furthermore, if the ground-state atoms had an equilibrium velocity distribution (as may be assumed) and if the process of excitation of an atom to state a does not affect its velocity (which may not be true but is assumed in this work), then, at their time of excitation, the active atoms will also be characterized by an equilibrium velocity distribution that subsequent collisions will not alter. Hence, the velocity distributions and consequently the spectral profiles of emitting and absorbing atoms will be identical. If this argument is accepted, one concludes that any actual difference in the emission and absorption profiles calculated from the equations of this work must be attributed to the fact that we are working in the one-collision limit, and that such differences would disappear when the calculations are extended to include the effect of many binary collisions in an atomic lifetime.[25] (We should point out that, in third-order laser theory and radiation theory with collision interaction in both radiative states, it is important to keep track of *each* atom's velocity, since changes in an individual atom's velocity will tend to produce phase variations which may affect the emitted or absorbed radiation. For these cases, velocity changing collisions can be significant.)

IX. SUMMARY AND DISCUSSION

A. Summary

We have attempted to solve the Schrödinger equation for an active atom immersed in a medium of perturbing atoms and subject to an external classical electric field. Since exact solutions of the Schrödinger equation are difficult to obtain, we proceeded to construct a series of simplifying assumptions or approximations that enabled us to obtain the leading terms of a perturbation solution to the problem. Taking the perturber atoms rigidly fixed in the medium, we followed the time development of the active atom to first order in the external field and lowest order in the collision interaction. We then generalized our result to all orders in the scattering interaction *at each individual perturber site*, so that our resultant expressions reflected the case of a single collision for our active atom. With these assumptions we derived the general expression (81) for the average polarization function of a laser medium. Several limiting cases for this general expression were discussed in Sec. VII. In partic-

ular, we looked at the situation for straight-line collision paths (impact-pressure-broadening–theory limit) and equal collision interaction in both radiative states (Boltzmann-equation-approach limit). Equation (81) also simplified in the case where one of the two radiative states underwent a much stronger collision interaction than the other with the result given by Eq. (63) or (75). Using these results, we obtained expressions for the gain [Eq. (89)] and frequency pulling [Eq. (90)] of the laser. Although our calculation was specifically directed towards lasers, it could equally well describe stimulated emission or absorption within the confines of our model.

In Secs. V and VI, we introduced a pseudoclassical model for the case of scattering interaction in only one state based upon the fact that Doppler-modifying and impact collisions occur at mutually exclusive times. This model will allow one to easily generalize the one-collision results to the many- (binary) collision case. A detailed discussion of the pseudoclassical model will be given in the paper on third-order laser theory.

B. Discussion

The discussion given below, unless otherwise noted, *will pertain only to the case of collision interaction in one state only* since we believe that, in general, this is a good approximation to the physical situation.

We have been concerned with a one-collision model, but can indicate what is to be expected if one goes to the many-collision problem. For this purpose we assume a lifetime of $\tau = 10^{-8}$ sec for the active atom and an optical-collision cross section $\pi\Re^2 \approx \pi 10^{-14}$ cm^2 for a relative emitter-perturber speed of $v \approx 10^5$ cm/sec and consider three pressure regions: (a) $\mathfrak{N} \ll 3\times10^{16}$ atoms/cm^3. This is the region of validity for our one-collision model ($\mathrm{Re}\bar{\Gamma}_{\mathrm{QM}} \ll \gamma_{ab}$). (b) 3×10^{16} atoms/cm^3 $< \mathfrak{N} \ll 3\times10^{20}$ atoms/cm^3. This is the region where the binary collision or impact theory of ordinary pressure-broadening theory is valid ($v/\Re \gg \mathrm{Re}\bar{\Gamma}_{\mathrm{QM}}$). In our quantum-mechanical model, it would correspond to zero overlap of the perturber potentials. In performing the calculation, the active atom would now be able to undergo subsequent collisions at various perturber sites; i.e., the wave scattered at one site will reach another one before the atom has decayed. Actually, in future work, it will prove convenient to develop the pseudoclassical model to treat this region. (c) $\mathfrak{N} \gg 3\times10^{20}$ atoms/cm^3. This is the region where the statistical theory of pressure broadening is supposed to be valid. In our model, it corresponds to overlap of the potentials of various perturbers and will lead to very difficult integrals.

In this paper, we have worked to first order only in the laser field, but shall give the results for the third-order calculation in a future publication. As one goes to higher order in the field or in the collision interaction, the calculation becomes increasingly complex, but it is hoped that the diagrammatic techniques given here or the pseudoclassical model which will be derived from them will enable one to treat collision terms more easily.

The final basic approximation in the model is that of stationary perturber atoms. It is possible to extend the quantum-mechanical calculation to cover the case of moving perturbers. Since the emitter's speed need no longer remain constant in elastic collisions with moving perturbers, one must replace $\int' d\Omega_v\, W(\hat{v}\,|\,\vec{v}_0)\, y(\hat{v}, \vec{v}_0)$ by $\int' d^3v\, W(\vec{v}\,|\,\vec{v}_0) y(\vec{v}, \vec{v}_0)$, where $W(\vec{v}\,|\,\vec{v}_0)\, d^3v$ is the probability per unit time that Doppler-modifying collisions change the emitter's velocity from $\vec{v}_0$ to $\vec{v}$ (y is some arbitrary function). Implicitly contained in $W(\vec{v}\,|\,\vec{v}_0)$ is an average over all types of emitter-perturber collisions giving rise to the change in emitter velocity $\vec{v}_0 \rightarrow \vec{v}$. Similarly, $\bar{\Gamma}_{\mathrm{QM}}(v_0)$ will be replaced by $\gamma_{\mathrm{QM}}(v_0)$, which is an average of $\bar{\Gamma}_{\mathrm{QM}}(v_r)$ over all perturber velocities (v_r is the relative emitter-perturber speed). The above results may be incorporated into Eqs. (67), (68), (75), (84), (89), and (90). Since $\bar{\gamma}^b_{\mathrm{QM}}$ is a function of v_0, the gain profile for b scattering only [Eq. (89b)] is not a true Voigt profile (convolution of Gaussian and Lorentzian profiles) for a Gaussian $W(v_0)$. However, if $\bar{\gamma}^b_{\mathrm{QM}}(v_0)$ is a slowly varying function of v_0 with respect to $W(v_0)$, the gain profile will very nearly be Voigt in nature.[26] In addition, the a-scattering-only result [Eq. (89a)], although different in form, will probably be similar to the b-scattering-only result, for reasons given in Sec. VII. This may explain why Voigt profiles have been successful in describing line shapes, although slight deviations would be difficult to detect experimentally.[27] Perhaps the best test of the theory will be afforded by laser experiments, but we defer a discussion of these experiments until we present the third-order theory.

In spite of all our approximations, we feel that we have conclusively demonstrated the need for a quantum-mechanical description of atomic center-of-mass motion in many atomic radiation problems. Only in limited cases can one expect a classical description to suffice.

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[1]All pressures will refer to those of ground-state perturbing atoms. The excited atom pressure is assumed

to be negligible.

[2]E. Lindholm, Arkiv Mat. Astron. Fysik 32A, 17 (1945); H. M. Foley, Phys. Rev. 69, 616 (1946); P. W. Anderson, *ibid.* 76, 647 (1949). For more complete bibliography see P. Berman and W. E. Lamb, Jr., *ibid.* 187, 221 (1969).

[3]S. G. Rautian, Zh. Eksperim. i Teor. Fiz. 51, 1176 (1966) [Soviet Phys. JETP 24, 788 (1967)].

[4]B. L. Gyorffy, M. Borenstein, and W. E. Lamb, Jr., Phys. Rev. 169, 340 (1968).

[5]W. E. Lamb, Jr., Phys. Rev. 134, A1429 (1964).

[6]One must choose initial conditions for the laser atoms consistent with the macroscopic picture of the gas. That is, we assume the active atoms to be isotropically distributed in the laser volume and to have some velocity distribution $W_0(\vec{v})$. There are three obvious possible choices for initial conditions that will satisfy the macroscopic properties. First, one could assign a classical distribution function to the atoms, but, as we have argued, a classical description is not adequate for this problem. Second, one could choose quantum-mechanical wave packets [with a velocity spread much less than the velocity spread of $W_0(\vec{v})$] and, at some point, average over the initial average position and momenta of the packets according to the desired distribution. Mathematically, it is not convenient to work with wave-packet states. Finally, one may choose plane-wave states as the initial condition, and ultimately perform an average over initial velocities according to $W_0(\vec{v})$. The latter choice is the one we make, and it will be discussed more fully in Sec. IV.

[7]H. Bethe, Ann. Physik 4, 443 (1930).

[8]Other authors have treated photon recoil in related problems. See A. P. Kol'chenko, S. G. Rautian, and R. I. Sokolovskii, Zh. Eksperim. i Teor. Fiz. 55, 1864 (1968) [Soviet Phys. JETP 28, 986 (1969)]; D. M. Kim, M. O. Scully, and W. E. Lamb, Jr. (unpublished).

[9]For brevity, we refer to $\rho_{ab}(t, \vec{v}_i, t_i)$ as a "dipole moment" even though the actual dipole moment is given by $\wp\rho_{ab}(t, \vec{v}_i, t_i) + \text{c.c.}$

[10]This approach is similar to that of M. O. Scully and W. E. Lamb, Jr., Phys. Rev. 159, 208 (1967). For a typical laser, $\gamma_{ab} \approx 10^8$ sec^{-1} and the gain parameter $\alpha \approx 10^4$ sec^{-1}, so that it is easy to find the required δt such that $\gamma_{ab}^{-1} \ll \delta t \ll \alpha^{-1}$.

[11]The effective collision Hamiltonian involves a sum over intermediate states of the perturber and emitter. See P. Berman and W. E. Lamb, Jr., Phys. Rev. 187, 221 (1969).

[12]Although $B_\alpha(\vec{R}, t)$ and $b_\alpha(\vec{p}, t)$ are Fourier transforms of each other, note that density-matrix elements in the coordinate and momentum representations given by $B_\alpha(\vec{R}, t)[B_\beta(\vec{R}, t)]^*$ and $b_\alpha(\vec{p}, t)[b_\beta(\vec{p}, t)]^*$, respectively, are *not* Fourier transforms of each other.

[13]$(1/2i)\, e^{-i\vec{k}\cdot\vec{R}}$ part does not contribute since it leads to a factor $e^{2i\vec{k}\cdot\vec{X}_j}\, e^{-2i\vec{k}\cdot\vec{R}_j}$, which when averaged over perturber positions $\vec{R}_j$, vanishes.

[14]There is no rapidly varying phase factor to confine the integrand's contribution to the forward direction. Both $|f(\hat{X}, \vec{v}_0)|^2$ and $e^{i\vec{k}\cdot\hat{X}v_0(t'-t'')}$ vary with $\hat{X}$ at approximately the same rate, so that the integral in Eq. (59) can not be simplified. If we were to average Eq. (59) over initial emitter velocities using an isotropic velocity distribution (a reasonable choice), the angular integral over Ω_{v_0} may be done first. This would greatly simplify the expression for $A^{10;11}$ and remove the need for assuming an explicit form for $|f_a(\hat{X}, \vec{v}_0)|^2$ (i.e., $\int d\Omega_{v_0} |f_a(\hat{X}, \vec{v}_0)|^2$ = quantum-mechanical cross section). However, such a simplification arises from our model of elastic scattering by stationary perturbers, and we prefer to use Eq. (59) which is more easily generalized to the case of moving perturbers.

[15]E. Merzbacher, *Quantum Mechanics* (Wiley, New York, 1961), p. 499.

[16]The reader should note that the description we are giving in terms of the diagrams represents a calculational method for achieving the results. Whether or not it can be viewed as providing a physical explanation of the situation is not the point at issue.

[17]See M. Baranger, Phys. Rev. 111, 481 (1958). In the impact theory limit, Baranger shows that the complex-collision decay parameter for a scattering only is directly related to the forward-scattering amplitude.

[18]In Secs. VI and VII, the actual calculations leading to the polarization-function density differ slightly from those in Sec. V. The main difference is that the energy denominator appearing in the calculation [see Eq. (47)] will be $E_{\vec{p}', \vec{p}_0+\vec{k}}$. In performing the expansion analogous to Eq. (48) one must expand p' about $E_{\vec{p}_0+\vec{k}}$ rather than $E_{\vec{p}_0}$. We should also like to point out that our discussion of the diagrams is intended to make our results seem reasonable, but is not offered as an alternative to doing the actual calculations.

[19]By neglect of terms of order k^2/p_0 in the expansion (77) we are, in effect, omitting quantities leading to energies comparable with the photon recoil energy. Hence, the expression for $A^{10;1'1}$ may be in error as far as the photon recoil energy is concerned, but this is a small effect.

[20]See. Ref. 17. We believe that Baranger's results are strictly valid only for the case of collisions resulting in small momentum transfer to the emitting atom. This will be true for electron perturbers but will not, in general, be true for atom perturbers.

[21]Baranger (Ref. 17) shows that, in a classical limit, Eq. (82) is in agreement with the results of Ref. 2, at least for the case of a spherically symmetric scattering potential. To see this explicitly, one makes a partial-wave expansion of f_a and f_b and is then able to do the Ω_v integral. Part of the result will exactly cancel the other collision terms with the remainder yielding a term $-\frac{1}{2}\Gamma_{\text{QM}}^{ab}(v_0)(t'-t'')$, where $\Gamma_{\text{QM}}^{ab}(v_0) = (Nv_0\pi/p_0^2)\sum_l(2l+1) \times(1-e^{2i\delta_l(a)-\delta_l(b)})$ and $\delta_l(a)$ and $\delta_l(b)$ are the lth quantum-mechanical phase shifts for a and b scattering, respectively. If the phase shifts are evaluated in the WKB limit for straight-line paths, the quantity $2[\delta_l(a) - \delta_l(b)]$ approximates the differential-collision-induced phase shift induced by classically moving perturbers, and the agreement with Ref. 2. is schieved. For a discussion of non-straight-line paths, see G. P. Reck, J. Quant. Spectry. Radiation Transfer 9, 1419 (1969).

[22]N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions*, 2nd ed. (Clarendon, Oxford, 1949), Chap. VII.

[23]This Boltzmann-equation approach is being used by M. Borenstein and W. E. Lamb, Jr. (unpublished) to study pressure effects in high-intensity lasers for the binary-collision pressure region. This approach will prove useful if the physical situation corresponds to $f_a \approx f_b$.

[24]It seems possible to describe a calculational quantum-

mechanical model that is easily generalized to the many-collision case. If it becomes necessary to consider the case $f_a \neq 0$, $f_b \neq 0$ in greater detail, we shall discuss the features of such a model at some later time.

[25]Mathematically, this result can be seen if Eq. (91) is substituted into Eq. (89a) and the integration over v_0 performed. Then, using the definition of $g(\hat{v}, \vec{v}_0, t'')$ and the fact that $W(\vec{v}_0)$ is assumed to represent an equilibrium distribution (stationary process), one may obtain from simple probability theory that $\int d\Omega_v \int d^3v_0\, W(\vec{v}_0) g(\hat{v}, \vec{v}_0, t'') \times h(\vec{v}) = \int d^3v\, W(\vec{v}) h(\vec{v})$ (h is some arbitrary function of $\vec{v}$). Using this result, one may easily show that the forms of the equations for the emission and absorption profiles [Eqs. (89a) with (91) and (89b), respectively] are the same.

[26]The question as to whether or not $\bar{\gamma}_{QM}(v_0)$ is a slowly varying function of v_0 is one that requires further study. The major problem is to obtain an accurate expression for $\bar{\Gamma}_{QM}(v_r)$. If one can achieve this, the average over perturber velocities can be done by numerical integration to give the explicit form of $\bar{\gamma}_{QM}(v_0)$. In the past (Ref. 2), it was assumed that the average of $\bar{\Gamma}_{QM}(v_r)$ over perturber velocities could be replaced by an average over relative emitter-perturber speeds leading to a $\bar{\gamma}_{QM}$ that is independent of v_0. It would be useful to determine the error introduced by such an assumption.

[27]To make a comparison with experiment, it will be necessary to choose or calculate values for the collision parameters $\bar{\Gamma}^2_{QM}$, $\bar{\Gamma}^b_{QM}$, $\bar{\gamma}^a_{QM}$, $\bar{\gamma}^b_{QM}$, and $W_a(\vec{v} \mid \vec{v}_0)$. This, in itself, constitutes a separate problem since all these quantities depend on knowing values for the scattering amplitudes which are not readily available. In some cases, it may be possible to use a classical impact-collision parameter for $\frac{1}{2}\bar{\gamma}_{QM}$ (see Ref. 2 – associate $\frac{1}{2}\bar{\gamma}_{QM}$ with the classical impact-collision parameter averaged over relative emitter-perturber speeds) and a classical Boltzmann-collision kernel for $W_a(\vec{v} \mid \vec{v}_0)$, but the accuracy of such an approach is yet to be determined.

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Correlations among Ions, Electrons, and Screened Potentials in a Hot Dilute Gas

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The asymptotic pair correlations between charged particles, ions and electrons, in a hot dilute gas are found through the use of a perturbation theory for a system of molecules, where a molecule is specified by the totality of its bound and scattering states. The derived screened electrostatic potential (as well as the charge distribution) around an ion is given by $\varphi_i(r) = (C_S e^{-\kappa_S r} + C_O \cos\kappa_O r)/r$, where $\kappa_S > \kappa_O$, $|C_S/C_O| \gg 1$, thus leading to a main contribution from the Debye-Hückel–type term at moderately large distances, and from the oscillating Coulomb term mainly at very large distances. Since κ_S, $\kappa_O \propto \kappa = (4\pi\beta e^2 n)^{1/2}$, where n is the molecular density, the oscillatory term is more pronounced at increasing densities.

I. INTRODUCTION

There appears a basic difficulty in applying statistical mechanics of ideal gases to a high-temperature dilute gas of molecules. Once kT is large compared to the electronic excitation energy of the molecule, the complete electronic partition function diverges since it consists of an infinite sum of terms of the form $e^{-\beta\epsilon_j}$ approaching a constant, i.e., the electronic excitation energy levels ϵ_j form an infinite sequence converging to the ionization energy level. This difficulty stems from the long-range character of the Coulomb potential, which is essentially the potential that the electron sees when in highly excited states.[1] Since on the one hand the radii of the Bohr orbits of these states grow beyond all bounds, and on the other hand the contribution of these states to the partition function is overwhelming, the neglect of the interaction of a molecule with its neighbors cannot be justified at any finite density, however large the average distance between neighboring molecules.

This interaction is taken into account by introducing various physical *ad hoc* assumptions. Among others, according to a notion borrowed from the theory of fully ionized gases, it is assumed that the collective effect of free electrons and ions produced by the partial ionization of the molecules is to modify the potential of the ionic charge inside a molecule into a screened Coulomb potential acting on the electron.[2] This potential, $e\exp(-\kappa r)/r$, where the reciprocal Debye length is defined by $\kappa^2 = 4\pi e^2 \beta n$, with n the effective number density of the free electrons, then leads to a finite number of bound states for the electron and thus eliminates the difficulty of the divergence of the partition function.

In the following, the asymptotic form of the screened Coulomb potential is derived by a more direct approach which avoids the necessity of defining and estimating an effective degree of