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Collisional redistribution of radiation. I. The density matrix

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As a first step in deriving accurate, calculable expressions for collisional redistribution of radiation, valid outside the impact regime, we present a method for calculating an accurate binary-collision density operator for an atom in the presence of a driving field and perturbers. We use projection-operator techniques to establish first the precise validity of the Markoff approximation for radiative relaxation. Using the same techniques, we show how the collisional-relaxation problem may be analyzed in a practical manner outside the Markoff approximation. The effect of correlations between radiative and collisional events is included in a consistent way, and the physical implications of these correlation effects are demonstrated for a simple example, the two-level atom with nondegenerate levels.

I. INTRODUCTION

This is the first of a series of three papers that aim to discuss the subject of redistribution of radiation in a general setting; we shall not restrict our treatment to the familiar "impact" region of collisionally broadened line spectra, nor limit our treatment to detunings from line center less than $kT/\hbar$ [where k is the Boltzmann's constant and T the translational temperature of the bath of perturbers affecting the active atom (radiator, absorber)]. The only major approximation is the binary-collision approximation (BCA), a well-understood approximation that is valid under a wide range of practical circumstances. The effects of degeneracy on the problem are quite distinct and have been studied in detail; these will be presented in the papers that follow.

Our analysis uses the techniques of quantum-statistical mechanics and does not rely on any phenomenological arguments. We believe our treatment unifies some diverse theoretical treatments and supplies a rather complete framework for the discussion of the redistribution problem. The only other discussion of redistribution of radiation outside the impact approximation that also deals with the effects of degeneracy is that by Cooper.[1] He uses the formalism of Fiutak and Van Kranendonk[2] to produce "generalized emission and absorption profiles." We produce the essential physics of Cooper's arguments, but give a more explicit treatment that should prove better able to handle practical cases.

Our treatment involves the discussion of equations of motion for the density matrix projected onto relevant subspaces. This is a common procedure[3] and is usually linked with an assumption (often unwarranted) about the initial state of the density matrix lying within this subspace. For example, the subspace could be that in which the density matrix may be written in factorized form:

$$\hat{\rho} \equiv \hat{\rho}(\text{radiator}) \times \hat{\rho}(\text{perturbers}) .$$

Our discussion is a critique of when such assertions are valid and an extension of the theory to cases when it is not, where we are really dealing with the classic problem of the breakdown of the "separation of time scales" in kinetic theory.[4] In our case this means that we deal with events (absorption and emission) occurring *during*, and thus correlated with, the microscopic events (e.g., collisions) that cause the relaxation of the system. Formally, this implies that we cannot concern ourselves solely with an "important" factorized subspace, but need to consider the full density matrix. The projection operator onto a subspace may still be a very useful tool, but its use does not imply any physical assumption about the system.

This paper is split into the following sections: I. Introduction. II. Radiative damping and interatomic potentials; where we discuss the effect the radiation field has on the evolution of atomic states. III. Collisional damping; where we reduce the many-body problem of the interaction of radiation with an atom, in a bath of perturbers, to a two-body collisional problem (in the presence of radiation). IV. An example—the two level atom: Here we apply the general formalism to a concrete example and discuss the physical nature of "correlated events" more fully.

In paper II we shall address, in detail, the consequences of degeneracy for the correlated events; and hence for the steady-state multipoles of an atom in the presence of a driving field. We shall also discuss how the effect of these correlated events may be observed experimentally.

In paper III the full spectrum of the scattered light, with its dependence on frequency and polarization, of both the incoming and outgoing light, is derived. This provides an example of how one may derive a spectrum from an equation of motion for

the dipole autocorrelation function, when the quantum-regression theorem is invalid.[5]

The theoretical work presented here was motivated in great part by the pioneering experiments of Carlsten, Szöke, and Raymer.[6] We hope our work will stimulate further experiments and aid in their exploitation and interpretation.

II. RADIATIVE DAMPING AND INTERATOMIC POTENTIALS

In this section we shall consider the effect the free-radiation field has on the evolution of the density operator of the system we are studying. This is a dilute gas of "active" atoms (absorbers and/or radiators) mixed homogeneously with a gas of perturbers; the distinction between radiator and perturber breaks down in the case of resonance broadening and for this and sundry other reasons we shall not treat the case of resonance broadening explicitly. It is supposed that atom-perturber collisions are far more frequent than atom-atom collisions; this makes the problem a linear one as far as relaxation of the radiator is concerned. Both atom and perturber are, of course, imbedded in the free-radiation field. The free-radiation field has two effects on the atom-perturber system: (i) It shifts and damps the atomic levels and (ii) it modifies the interatomic potential from that provided by purely Coulombic interactions.[7]

In our treatment we will use the Coulomb gauge throughout. We single out one of the radiation modes and suppose that it carries real photons that are incident upon, and are scattered by, the gas. We shall show under what circumstances these incident photons do not change the effect of the virtual photons on the gas [i.e., (i) and (ii)]. Although this may seem somewhat straightforward, we shall establish the conditions with some care, since it will show the intimate relation of these effects to the collisional-relaxation problem.

The self-energies and the interatomic potentials are obtained in the following manner. The total Liouville space of the system may be written as a direct product of the radiation and matter (atom + perturbers) subspaces. We split the total Liouville operator (see Appendix A) for the gas in the presence of the radiation field into four parts

$$\tilde{L} = \tilde{L}_0^{\mathrm{M}} + \tilde{L}_0^{\mathrm{R}} + \tilde{L}^{\mathrm{MR}} + \tilde{V}^{\mathrm{M}} . \tag{2.1}$$

Here $\tilde{L}_0^{\mathrm{M}}$ and $\tilde{L}^{\mathrm{R}}$ are the Liouville operators for the free-matter and free-radiation fields, respectively, $\tilde{L}^{\mathrm{MR}}$ represents the interaction between radiation and matter, and $\tilde{V}^{\mathrm{M}}$ represents the interaction between atoms (and perturbers) from purely Coulombic potentials, defined thus

$$\tilde{L}^{\mathrm{MR}}\hat{0} \equiv \frac{1}{i\hbar}[\hat{V}_{\mathrm{MR}}, \hat{0}] , \tag{2.2a}$$

$$\hat{V}_{\mathrm{MR}} = \sum_j \left(\frac{1}{m_j}\right)\left(e_j \vec{p}_j \cdot \vec{A}(\vec{r}_j) + \frac{e_j^2}{2}\vec{A}(\vec{r}_j)^2\right) . \tag{2.2b}$$

Here $\hat{0}$ is an arbitrary operator, $\vec{A}(\vec{r})$ is the quantized transverse-radiation vector potential ($\mathrm{div}\,\vec{A} = 0$),[8] and $\vec{P}_j$ is the momentum operator for the jth charged particle. Equation (2.2b) is the result of a transformation, on the full relativistic interaction Hamiltonian, and the $\vec{A}(\vec{r})^2$ term comes from the elimination of negative energy states.[9] We shall not be concerned with the effects it gives rise to (diamagnetism, Thomson scattering) in this paper.

The external driving field will be treated as a prescribed time dependent classical field $\vec{E}^c(\vec{r},t)$, and its coupling to the active atoms, supposed to be predominantly through dipoles, may be written in the form

$$\tilde{L}(t)\hat{0} \equiv \frac{1}{i\hbar}[\hat{V}^{\mathrm{E}}(t), \hat{0}] , \tag{2.3a}$$

$$\hat{V}^{\mathrm{E}}(t) = -\sum_m \vec{E}^c(\vec{r}_m, t)\cdot\vec{d}_m . \tag{2.3b}$$

Here $\vec{d}_m$ is the dipole moment of the mth atom, whose center of mass has position vector $\vec{r}_m$. The transformation from the form of (2.2b) to (2.3b) is discussed in detail elsewhere.[10] Although we shall be primarily concerned with allowed electric-dipole transitions, we do not want to make the electric-dipole approximation on (2.2b); we shall see below that the full form of $\hat{V}_{\mathrm{MR}}$ has consequences for the time scale of spontaneous radiation couplings, but not for the coupling with the real driving field. Thus the equation of motion for the density operator $\hat{\rho}(t)$ of the full system is

$$\partial_t \hat{\rho}(t) = [\tilde{L} + \tilde{L}^E(t)]\hat{\rho}(t) . \tag{2.4}$$

In establishing the effects (i) and (ii) named above, we shall need the following projection operator in Liouville space (see Appendix A):

$$\tilde{P}_{\mathrm{R}}\hat{0} \equiv \hat{\rho}_{\mathrm{RAD}}(t=-\infty)\,\mathrm{Tr}_{\mathrm{RAD\ MODES}}[\hat{0}] , \tag{2.5}$$

where the trace excludes the driving-field mode. The operators we have to deal with, e.g., $\hat{0}$, in general, operate on the combined radiation and matter Hilbert space and cannot be written in a factorized (uncorrelated) form. $\tilde{P}_{\mathrm{R}}\hat{0}$, however, is by inspection a factorized operator. We emphasize that our choice of projection operator does not limit the physics we discuss, since we shall not be making any unwarranted assumptions about the correlated part of the density operator $\tilde{Q}_{\mathrm{R}}\hat{\rho}$, where $\tilde{Q}_{\mathrm{R}} \equiv 1 - \tilde{P}_{\mathrm{R}}$.

We can decompose the equation of motion for ρ

into two parts thus:

$$\partial_t \tilde{P}_R \hat{\rho}(t) = \tilde{P}_R[\tilde{L}_0^M + \tilde{L}^E(t) + \tilde{V}^M]\tilde{P}_R\hat{\rho}(t) + \tilde{P}_R\tilde{L}^{MR}\tilde{Q}_R\hat{\rho}(t)\,, \tag{2.6a}$$

$$\partial_t \tilde{Q}_R \hat{\rho}(t) = \tilde{Q}_R[\tilde{L}_0^M + \tilde{L}^E(t) + \tilde{L}_0^R + \tilde{V}^M + \tilde{L}^{MR}]\tilde{Q}_R\hat{\rho}(t) + \tilde{Q}_R\tilde{L}^{MR}\tilde{P}_R\hat{\rho}(t)\,. \tag{2.6b}$$

We have used the following results:

$$\tilde{P}_R\tilde{L}^{MR}\tilde{P}_R = 0\,, \tag{2.7a}$$

which holds since $\hat{\rho}_{RAD}(t=-\infty)$ is diagonal, and $\tilde{L}^{MR}$ linear, in the radiation annihilation and creation operators,

$$\tilde{P}_R\tilde{V}^M Q_R = \tilde{P}_R\tilde{L}^E(t)\tilde{Q}_R = \tilde{P}_R\tilde{L}_0^M\tilde{Q}_R = 0\,, \tag{2.7b}$$

since $\tilde{V}^M$, $\tilde{L}^E(t)$, and $\tilde{L}^M$ contain no free-radiation operators, and thus commute with $\tilde{P}_R$,

$$\tilde{P}_R\tilde{L}_0^R = 0\,. \tag{2.7c}$$

We can obtain the formal solution of (2.6b) in terms of the propagator $\tilde{\mathcal{G}}_R(t_2,t_1)$, defined by the equation of motion

$$\partial_{t_2}\tilde{\mathcal{G}}_R(t_2,t_1) = \tilde{Q}_R[\tilde{L} + \tilde{L}^E(t_2)]\tilde{\mathcal{G}}_R(t_2,t_1) \tag{2.8}$$

and the initial condition

$$\tilde{\mathcal{G}}_R(t_1,t_1) = \tilde{\mathcal{G}}\,. \tag{2.9}$$

Using the time-ordering operator T (Ref. 11), we can write the solution for $\tilde{\mathcal{G}}_R(t_2,t_1)$ in the following form:

$$\tilde{\mathcal{G}}_R(t_2,t_1) = T\exp\left[\tilde{Q}_R\int_{t_1}^{t_2}[\tilde{L} + \tilde{L}^E(t')]\,dt'\right]. \tag{2.10}$$

Equivalent to this definition is the following integral equation:

$$\tilde{\mathcal{G}}_R(t_2,t_1) = \tilde{G}_R(t_2,t_1) + \int_{t_1}^{t_2}\tilde{G}_R(t_2,t')\tilde{Q}_R\tilde{L}^E(t')\tilde{\mathcal{G}}_R(t',t_1)\,dt'\,, \tag{2.11}$$

where

$$\tilde{G}_R(t_2,t_1) \equiv \exp[\tilde{Q}_R\tilde{L}(t_2-t_1)]\,. \tag{2.12}$$

We can write the formal solution of (2.6b) in the form

$$\tilde{Q}_R\hat{\rho}(t) = \hat{\mathcal{G}}_R(t,t_0)\tilde{Q}_R\hat{\rho}(t_0) + \int_{t_0}^{t}\tilde{\mathcal{G}}_R(t,t')\tilde{Q}_R\tilde{L}^{MR}\tilde{P}_R\hat{\rho}(t')\,dt'\,. \tag{2.13}$$

Substituting (2.11) into (2.6a), we obtain

$$\partial_t\tilde{P}_R\hat{\rho}(t) = \tilde{P}_R[\tilde{L}_0^M + \tilde{V}^M + \tilde{L}^E(t)]\tilde{P}_R\hat{\rho}(t) + \tilde{P}_R\tilde{L}^{MR}\int_{t_0}^{t}\tilde{\mathcal{G}}_R(t,t')\tilde{Q}_R\tilde{L}^{MR}\tilde{P}_R\hat{\rho}(t')\,dt' + \tilde{P}_R\tilde{L}^{MR}\tilde{Q}_R\tilde{\mathcal{G}}_R(t,t_0)\tilde{Q}_R\tilde{\rho}(t_0)\,. \tag{2.14}$$

We should like to obtain a closed equation for $\tilde{P}_R\hat{\rho}(t)$, since we would then have a closed equation for the atomic evolution averaged over the free-radiation modes. Equation (2.14), however, still contains a $\tilde{Q}_R\hat{\rho}(t_0)$. This term is frequently referred to as the "destruction" term (Ref. 12), because it represents the destruction of correlations (between the radiation and matter), represented by $\tilde{Q}_R\hat{\rho}(t_0)$. *This term can be neglected when determining the steady-state density operator as we shall show below.*

We need to be able to calculate $\tilde{Q}_R\hat{\rho}(t_0)$ in order to discuss the destruction term, and to do this we suppose we have the following situation: At the time $t=t_0$ (when we start off the equation of motion), $\tilde{Q}_R\hat{\rho}(t_0)$ is the result of the evolution from the distant past. At some time in the distant past, we can safely assume that the portions of radiation and matter we are concerned with at time t_0 were uncorrelated. We can, therefore, put $\tilde{Q}_R\hat{\rho}(t=-\infty)=0$, and at time $t=t_0$,

$$\tilde{Q}_R\hat{\rho}(t_0) = \int_{-\infty}^{t_0}\tilde{\mathcal{G}}_R(t_0,t')\tilde{Q}_R\tilde{L}^{MR}\tilde{P}_R\hat{\rho}(t')\,dt'\,. \tag{2.15}$$

This is sometimes termed a "natural initial condition" (Ref. 13), and substituting it (2.15) into (2.14), we obtain a closed equation for $\tilde{P}_R\hat{\rho}(t)$. We see that the crucial quantity we need to study is the kernel

$$\tilde{\mathcal{M}}_R(t_2,t_1) = \tilde{P}_R\tilde{L}^{MR}\tilde{\mathcal{G}}_R(t_2,t_1)\tilde{Q}_R\tilde{L}^{MR}\tilde{P}_R\,, \tag{2.16}$$

i.e., the part of (2.16) that is zeroth order in the driving field and the interatomic potential $\tilde{V}^M$. As a first step in this study, we shall consider $\tilde{M}_R(t_2,t_1)$, given by (replacing $\mathcal{G}_R$ by G_R)

$$\tilde{M}_R(t_2,t_1) = \tilde{P}_R\tilde{L}^{MR}\tilde{G}_R(t_2,t_1)\tilde{Q}_R\tilde{L}^{MR}\tilde{P}_R\,. \tag{2.17}$$

Now it is well known that in the interaction between radiation and matter, theories that retain the coupling to second order can be used to describe spontaneous processes (e.g., virtual emission and reabsorption of photons). We shall, therefore, be content with the following approximation to $\tilde{M}_R(t_2,t_1)$:

$$\tilde{M}_R(t_2,t_1) = \simeq\tilde{P}_R\tilde{L}^{MR}\exp[\tilde{Q}_R(\tilde{L}_0^M + \tilde{L}_0^R)(t_2-t_1)]\tilde{Q}_R\tilde{L}^{MR}\tilde{P}_R\,. \tag{2.18}$$

There are two distinct classes of tetradic elements of $\tilde{M}_R$; the first, the single-atom elements, produce radiative self-energies which are in gen-

eral complex, the real part of which represents damping of the single-atom vectors (Liouville) by spontaneous emission; the second type of tetradic element represents the interaction *between* atoms from the exchange of virtual photons (and these give rise to modifications of the usual dipole–induced-dipole term in the van der Waals interaction at large internuclear separations). Fourth order and higher terms also only affect the long-range part of the potential. To emphasize that there are two parts of $\bar{M}_R(\tau)$, $[\bar{M}_R(\tau) \equiv \bar{M}_R(t_2,t_1)$, with $\tau = t_2 - t_1]$ we write

$$\bar{M}_R(\tau) = \bar{S}_R(\tau) + \bar{V}_R(\tau) . \tag{2.19}$$

Here $\bar{S}_R(\tau)$ is the single-atom self-action operator and $\bar{V}_R(\tau)$ is the two-atom interaction operator.

To proceed further, we need to consider the explicit form of V^{MR} from which $\bar{L}^{MR}$ is obtained, i.e.,

$$V^{MR} = \sum_j -\frac{e_j}{m_j}\vec{A}(\vec{r}_j)\cdot\vec{p}_j = \sum_j -\frac{e_j}{m_j}\left[\sum_{\vec{k},\lambda}\left(\frac{\hbar}{2V\epsilon_0\omega_{\vec{k}}}\right)^{1/2}(\hat{a}_{\vec{k},\lambda}e^{i\vec{k}\cdot\vec{r}}\vec{\epsilon}_{\vec{k},\lambda} + \hat{a}^\dagger_{\vec{k},\lambda}e^{-i\vec{k}\cdot\vec{r}}\vec{\epsilon}^{\,*}_{\vec{k},\lambda})\right]\cdot\vec{p}_j . \tag{2.20}$$

Here $\hat{a}_{\vec{k},\lambda}$ and $\hat{a}^\dagger_{\vec{k},\lambda}$ are the annihilation and creation operators, respectively, and $\vec{\epsilon}_{\vec{k},\lambda}$ is the polarization vector of the mode $(\vec{k},\lambda)$. In order to calculate the matrix element of the operator $\vec{p}\,e^{i\vec{k}\cdot\vec{r}}$, it is convenient to factor explicitly the single-atom states into a product of the internal state and the center-of-mass translational state, i.e.,

$$|a\rangle = |\alpha,\vec{p}_\alpha\rangle = |\alpha\rangle|\vec{p}_\alpha\rangle . \tag{2.21}$$

For free-particles this is, of course, unnecessary. The latin letter a labels the complete state, while the Greek letter α labels the internal state, and $\vec{p}_\alpha$ labels the translational (momentum state) corresponding to $|a\rangle$. Thus,

$$\left\langle \alpha,\vec{p}_\alpha\left|-e\frac{\vec{p}_j}{m}e^{i\vec{k}\cdot\vec{r}}\right|\beta,\vec{p}_\beta\right\rangle = \delta(\vec{p}_\alpha - \vec{k} - \vec{p}_\beta)\left\langle\alpha\left|-e\sum_j\frac{\vec{p}_j}{m}e^{i\vec{k}\cdot\vec{r}_j}\right|\beta\right\rangle .$$

Here $\vec{r}_j$ is the position of the jth electron with respect to the center of mass. We have not yet distinguished between atoms and perturbers in the labeling of matter states. After we have eliminated the variables of the free-radiation field, however, we shall suppose the perturbers are structureless, and then the dipole moments in Eq. (2.3), will refer only to the active atoms. From Appendix A, we know that

$$\bar{L}^{MR}|n,m\rangle\rangle = \sum_{pq}|p,m\rangle\rangle\frac{1}{i\hbar}\langle p|\hat{V}^{MR}|n\rangle - |n,q\rangle\rangle\frac{1}{i\hbar}\langle m|\hat{V}^{MR}|q\rangle , \tag{2.22}$$

where, in this case

$$\langle p|\hat{V}^{MR}|n\rangle = \langle\pi,\vec{p}_\pi|\hat{V}^{MR}|\nu,\vec{p}_\nu\rangle = \sum_{\vec{k},\lambda}\left(\frac{\hbar}{2\epsilon_0 V\omega_{\vec{k}}}\right)^{1/2}[\vec{\epsilon}_{\vec{k},\lambda}\cdot\vec{f}_{\pi\nu}(\vec{k})\delta(\vec{p}_\pi - \vec{p}_\nu - \vec{k})\hat{a}_{k\lambda}] + [\vec{\epsilon}^{\,*}_{\vec{k},\lambda}\cdot\vec{f}_{\pi\nu}(-\vec{k})\delta(\vec{p}_\pi - \vec{p}_\nu + \vec{k})\hat{a}^\dagger_{\vec{k},\lambda}] , \quad \vec{f}_{\pi\nu}(\vec{k}) = \left\langle\pi\left|-\sum_j e\frac{\vec{p}_j}{m}e^{i\vec{k}\cdot\vec{r}_j}\right|\nu\right\rangle . \tag{2.23}$$

We have not made the conventional approximation ($e^{i\vec{k}\cdot\vec{r}_j} = 1$) in the evaluation of the atomic matrix element, since we wish to point out the importance of the $e^{i\vec{k}\cdot\vec{r}}$ factor in establishing the time scale of the matter-radiation interaction. To do this we shall consider an example—a diagonal tetradic element of $\bar{S}_R(\tau)$, i.e., $\langle\langle ab|\bar{S}_R(\tau)|ab\rangle\rangle$:

$$\langle\langle ab|\bar{S}_R(\tau)|ab\rangle\rangle = \mathrm{Tr}_{RAD}\{\hat{\rho}_{RAD}(t=-\infty)\langle\langle ab|\bar{L}^{MR}\exp[Q_R(\bar{L}^M_0 + \bar{L}^R_0)\tau]\bar{Q}_R\bar{L}^{MR}|ab\rangle\rangle\} = \sum_{\vec{k},\lambda,n}\left(\frac{\hbar\omega_k}{2\epsilon_0 V}\right)\left(\frac{1}{i\hbar}\right)^2\{|\vec{\epsilon}_{\vec{k},\lambda}\cdot\vec{f}_{\alpha\nu}(\vec{k})|^2\exp[i(\omega_{\vec{k}} + \omega_{nb})\tau]\delta(\vec{p}_\nu - \vec{p}_\alpha + \vec{k}) + |\vec{\epsilon}_{\vec{k},\lambda}\cdot\vec{f}_{\nu\beta}(\vec{k})|^2\exp[i(\omega_{an} - \omega_{\vec{k}})\tau]\delta(\vec{p}_\beta - \vec{p}_\nu - \vec{k})\} , \tag{2.24}$$

where we have assumed that, at time $t = -\infty$, none of the free-modes are occupied. This is an extremely complex object, and we shall not attempt to discuss it in detail. One crucial feature, however, will be appreciated if we consider the behavior of the "generalized" oscillator strengths $\vec{f}_{\pi\nu}(\vec{k})$ (Ref. 14). From the definition (2.23), which involves an integral over atomic wave functions, it can be seen that $\vec{f}_{\pi\nu}(\vec{k})$ will differ little from its value at $k = 0$ until $ka_0 \gtrsim 1$, i.e., $\omega a_0/c \gtrsim 1$ (where a_0 is the order of a Bohr radius). $\langle\langle ab|\bar{S}_R(\tau)|ab\rangle\rangle$ is, therefore, the Fourier-Laplace transform of a function (of frequency) cut off at $\omega \sim c/a_0$, and the usual transform argument implies that

$\langle\langle ab|\tilde{S}_R(\tau)|ab\rangle\rangle$ must decay on a time scale τ_R, where $\tau_R \sim a_0/c$, i.e., the time it takes light to cross the atom. This is the quantum-mechanical analog of the argument Lorentz used to obtain the classical self-energy of the electron (Ref. 15); it is the justification for the Markoff treatment of the atom-radiation problem and is closely linked to arguments that have been given elsewhere.[16] We thus conclude that the atom has a "memory" that is very short $\sim 10^{-18}$ sec.

Our argument is easily extended to the interatomic part of $\tilde{M}_R(\tau)$, i.e., $\tilde{V}_R(\tau)$. In discussing $\tilde{S}_R(\tau)$ we were considering the emission and reabsorption of photons by *a single atom*, whose characteristic distance a_0 determined the scale of variation of the $f(\vec{k})$'s, and hence of $\tilde{S}^R(\tau)$. $\tilde{V}^R(\tau)$ represents the exchange of a photon between two atoms. The relevant scale for $\tilde{V}_R(\tau)$ is, therefore, the internuclear separation and the time scale or "memory time" is thus ~size of quasimolecule/speed of light. The importance of this fact has been discussed for the resonance interaction by Milonni and Knight.[17] A characteristic internuclear separation for collision broadening is ~10–100 Å, so we can say the interatomic potential has a memory $\sim 10^{-16}$ sec.

We now have a qualitative idea of how $\tilde{M}_R(\tau)$ behaves as a function of τ. We argue, using Eq. (2.11), that $\mathfrak{M}_R(\tau)$ will only be modified from $\tilde{M}_R(\tau)$ by a term $\sim\Omega\tau_R$ (Ω is the on-resonance Rabi frequency for the external field driving a typical atomic transition $\Omega = \langle a|\vec{E}^c\cdot\vec{d}|b\rangle/\hbar$) for times much longer than τ_R, as it is only if the driving field causes appreciable changes in the state of the atom on a time scale $\sim\tau_R$ that the *average* damping can be altered. This modification of the damping operator may become important if we probe the time dependence on a scale comparable to or less than τ_R. This is the case if the driving field is detuned from an atomic resonance by an amount comparable to or greater than the inverse of τ_R. In a similar manner, the average damping of atomic states by spontaneous emission will affect the microscopic processes that cause that damping to order $\gamma_N\tau_R$, where γ_N is the natural damping rate. This quantity is, of course, quite negligible ($\gamma_N\tau_R \sim 10^{-10}$). Since the atoms are moving with respect to each other, we also need to consider how far they move compared to a typical interatomic separation d in a time τ_R. Thus, another condition we suppose is satisfied is

$$U\tau_R/d \ll 1 .$$

Here U is a mean relative velocity of an atom-perturber pair and d is a mean separation. In a typical case $U\tau_R/d \sim 10^{-6}$, so that the condition is well satisfied. With these considerations in mind we can rewrite Eq. (2.13) thus,

$$\begin{aligned}\partial_t P_R\hat{\rho}(t) = {}& \tilde{P}_R[\tilde{L}_0^M + \tilde{V}^M + \tilde{L}^E(t)]\tilde{P}_R\hat{\rho}(t) \\ & + \tilde{P}_R\tilde{L}^{MR}\int_{t_0}^{t}\tilde{G}_R(t,t')\tilde{Q}_R\tilde{L}^{MR}\tilde{P}_R\hat{\rho}(t')dt' \\ & + \tilde{P}_R\tilde{L}^{MR}\tilde{G}_R(t,t_0)\tilde{Q}_R \\ & \times\int_{-\infty}^{t_0}\tilde{G}_R(t_0,t')\tilde{Q}_R\tilde{L}^{MR}\tilde{P}_R\hat{\rho}(t')dt' . \end{aligned} \tag{2.25}$$

We note that we could put the last two terms together and obtain an equation valid on the interval $[t,-\infty]$. *We keep them separate, however, as we shall want to consider problems where we have an initial condition at* $t = t_0$. (See paper III for the most important example of such a problem—the equation of motion for the correlation function.) Since $\mathfrak{M}_R(t,t_0)$ decays as a function of $t-t_0$ on a time scale $\sim\tau_R$, we see that we can ignore the last term in Eq. (2.25) for times longer than τ_R. For the same reason, we can put $\tilde{P}_R\hat{\rho}(t') = \tilde{P}_R\exp[-\tilde{L}_0^M(t-t')]\hat{\rho}(t)$ and extend the upper limit on the integral to $t=\infty$ in the second term of Eq. (2.25). So if we only consider time scales much greater than τ_R, Eq. (2.25) becomes

$$\begin{aligned}\partial_t\tilde{P}_R\hat{\rho}(t) = {}& \tilde{P}_R[\tilde{L}_0^M + \tilde{L}^E(t) + \tilde{V}^M]\tilde{P}_R\hat{\rho}(t) \\ & + \int_0^\infty \tilde{P}_R\tilde{L}^{MR}\tilde{G}_R(\tau,0)\tilde{Q}_R\tilde{L}^{MR}e^{-\tilde{L}_0^M\tau}d\tau\,\tilde{P}_R\hat{\rho}(t) . \end{aligned} \tag{2.26}$$

The time-independent Liouville operator

$$\int_0^\infty \tilde{P}_R\tilde{L}^{MR}\tilde{G}_R(\tau',0)\tilde{Q}_R\tilde{L}^{MR}e^{-\tilde{L}_0^M\tau}\tilde{P}_R d\tau \tag{2.27}$$

is the sum of the self-action tetradic $\tilde{S}$ and the radiation contribution to the interatomic potential $\tilde{V}_R$. Using the notation $\mathrm{Tr}_{RAD}[\rho(t)] = \rho_R(t)$, the equation of motion becomes

$$\partial_t\hat{\rho}_R(t) = [\tilde{L}_0^M + \tilde{V} + \tilde{S} + \tilde{L}^E(t)]\hat{\rho}_R(t) . \tag{2.28}$$

Here

$$\tilde{V} = \mathrm{Tr}_{RAD}(\tilde{V}^R) + \tilde{V}^M \tag{2.29}$$

and

$$\tilde{S} = \mathrm{Tr}_{RAD}[\tilde{S}^R] . \tag{2.30}$$

This is the usual Markoff-master equation used in matter-radiation problems, and its explicit form for practical cases has been given elsewhere[18] (the tetradic elements of $\tilde{S}$ for some simple examples are given in Appendix B). We see that the effect of the radiation field is to give the familiar spontaneous emission widths and shifts (which should be renormalized) to the atomic states and, in addition, to change the interaction between the atoms and perturbers. Specifically, $\tilde{V}$ is now the interatomic potential Liouville oper-

ator that includes the effects of retardation. Neglecting the retardation, this is the usual Coulomb gauge interaction $\tilde{V}^M$ between two atoms. We must require, for self-consistency, that $|\tilde{V}|\tau_R$ (atom perturber) $\ll 1$. Thus (2.32) is valid if $\Omega\tau_R \ll 1$, $|\tilde{V}|\tau_R \ll 1$, and $|\tilde{S}|\tau_R \ll 1$ (by $|\tilde{V}|$, etc., we imply a typical value of a tetradic element of $\tilde{V}$).

We shall not pursue the analysis of these effects, as they are of no practical importance in the case of radiative damping. We shall, however, be concerned with precisely these effects for the collisional-relaxation problem and will be discussing them in detail. We also left out $\tilde{V}^M$ from the matter Hamiltonian in our approximation to $\tilde{G}_R(t_2,t_1)$ above. We now see that if the atoms change their translational states on a time scale τ_R that we need to consider its effect on the spontaneous processes. We thus need to require that $\tilde{V}^M\tau_R \ll 1$—this condition is easily satisfied for practical cases.

III. COLLISIONAL DAMPING

A. General formalism

We shall now discuss the effect of the interaction between radiator and perturber using precisely the same techniques as we did in the previous section. The crucial difference we find is, because the time scale of a typical collision τ_c may be greater than a macroscopic time of interest, we can no longer ignore the modification to the damping tetradic due to the driving field. This means that we need to retain additional terms in the equation of motion. We can ignore initial correlations (at a typical time t_0) for the purposes of finding steady-state single-time averages. However, we stress that when we calculate the spectrum of scattered light—directly related to the dipole autocorrelation function, a two-time average—we shall need to retain separate initial correlation terms in the equation of motion.

As before, we define a projection operator $\tilde{P}_c$, such that

$$\tilde{P}_c\hat{0} \equiv \hat{\rho}_{\text{pert}}(t=-\infty)\text{Tr}_{\text{pert}}(\hat{0}) , \tag{3.1}$$

and it is useful to explicitly separate $\tilde{L}_0^M$ as

$$\tilde{L}_0^M \equiv \tilde{L}_0^A + \tilde{L}_0^P , \tag{3.2}$$

where $\tilde{L}_0^A$ is the Liouville operator for the free-atoms, and $\tilde{L}_0^P$ the Liouville operator for the free-perturbers. The derivation of the equation of motion proceeds in the same general manner as before, but since we shall now be concerned with evaluating the driving-field correction terms, it is convenient at the outset to transform to an interaction picture defined by

$$\hat{\rho}_R^I(t) = e^{-\tilde{L}_0^P t}\,\hat{\rho}_R(t) , \tag{3.3}$$

so that Eq. (2.31) becomes

$$\partial_t\hat{\rho}_R^I(t) = [\tilde{L}_0^A + \tilde{V}^I(t) + \tilde{S} + \tilde{L}^E(t)]\hat{\rho}_R^I(t) , \tag{3.4}$$

with

$$\tilde{V}^I(t) = e^{-\tilde{L}_0^P t}\,\tilde{V}\,e^{\tilde{L}_0^P t} . \tag{3.5}$$

The two orthogonal projections of Eq. (3.4) are

$$\begin{aligned}\partial_t\tilde{P}_c\hat{\rho}_R^I(t) &= \tilde{P}_c[L_0^A + \tilde{S} + \tilde{L}^E(t)]\tilde{P}_c\hat{\rho}_R^I(t) \\ &\quad + \tilde{P}_c\tilde{V}^I(t)\tilde{Q}_c\hat{\rho}_R^I(t),\end{aligned} \tag{3.6}$$

$$\begin{aligned}\partial_t\tilde{Q}\hat{\rho}_R^I(t) &= \tilde{Q}_c[L_0^A + \tilde{V}^I(t) + \tilde{S} + \tilde{L}^E(t)]\,\tilde{Q}_c\hat{\rho}_R^I(t) \\ &\quad + \tilde{Q}_c\tilde{V}^I(t)\tilde{P}_c\hat{\rho}_R^I(t) ,\end{aligned} \tag{3.7}$$

where we have used $\tilde{P}_c\tilde{V}^I(t)\tilde{P}_c = 0$ (i.e., the average collisional interaction is assumed to be zero) and

$$[\tilde{P}_c, \tilde{L}_0^A] = 0 = [\tilde{P}_c, \tilde{S}] = 0 = [\tilde{P}_c, \tilde{L}^E(t)] , \tag{3.8}$$

where Eq. (3.8) follows, because none of the three Liouville operators involved acts on the perturbers. Defining propagators

$$\tilde{G}_c^I(t_2,t_1) = T\exp\!Q_c\int_{t_1}^{t_2}[\tilde{L}_0^A + \tilde{S} + \tilde{V}^I(s)]ds \tag{3.9}$$

(here T is the time-ordering operator, see Ref. 11) and

$$\begin{aligned}\tilde{\mathcal{G}}_c^I(t_2,t_1) &= \tilde{G}_c^I(t_2,t_1) \\ &\quad + \int_{t_1}^{t_2} dt'\tilde{G}_c^I(t_2,t')\tilde{L}^E(t')\,\tilde{\mathcal{G}}_c^I(t',t_1) ,\end{aligned} \tag{3.10}$$

we can formally solve Eq. (3.7) to give

$$\begin{aligned}\tilde{Q}_c\hat{\rho}_R^I(t) &= \tilde{\mathcal{G}}_c^I(t,t_0)\tilde{Q}_c\hat{\rho}_R^I(t_0) \\ &\quad + \int_{t_0}^{t} dt'\,\tilde{\mathcal{G}}_c^I(t,t')\tilde{Q}_c\tilde{V}^I(t')\tilde{P}_c\hat{\rho}_R^I(t')\end{aligned} \tag{3.11a}$$

$$\begin{aligned}&= \tilde{\mathcal{G}}_c^I(t,-\infty)\tilde{Q}_c\hat{\rho}_R^I(-\infty) \\ &\quad + \int_{-\infty}^{t} dt'\,\tilde{\mathcal{G}}_c^I(t,t')\tilde{Q}_c\tilde{V}^I(t')\tilde{P}_c\hat{\rho}_R^I(t').\end{aligned} \tag{3.11b}$$

If $\hat{\rho}_R^I$ relates only to the perturbers which interact with the atoms after the initial time t_0, the correlation between the atoms and those perturbers which interact at $t=-\infty$ $[\tilde{Q}_c\hat{\rho}_R^I(-\infty)]$ can be taken as zero. This is because perturbers that interact at $t=-\infty$ *will have moved away* from the atom by time t_0. This is usually the case, but it will

be invalid if the perturbers are bound to the atoms (in which case the *average* interaction between atom and perturber is greater than the thermal energy and they remain together for all time) but then the concept of a collision time will also be invalid. This assumption then is really very weak for practical situations. Substituting Eq. (3.11) into (3.6) gives

$$\partial_t \tilde{P}_c \hat{\rho}_R^I(t) = \tilde{P}_c[L_0^A + \tilde{S} + \tilde{L}^E(t)]\tilde{P}_c\hat{\rho}_R^I(t) + \tilde{P}_c\tilde{V}^I(t)\int_{-\infty}^{t} dt' \tilde{\mathcal{G}}_c^I(t,t')\tilde{Q}_c\tilde{V}^I(t')\tilde{P}_c\hat{\rho}_R^I(t'). \tag{3.12}$$

The memory kernel has the form

$$\tilde{\mathfrak{M}}_c(t_2,t_1) = \tilde{P}_c\tilde{V}^I(t_2)\tilde{\mathcal{G}}_c^I(t_2,t_1)\tilde{Q}_c\tilde{V}^I(t_1)\tilde{P}_c\ , \tag{3.13}$$

or to zero order in the laser field

$$\tilde{\mathfrak{M}}_c(t_2,t_1) \simeq \tilde{M}_c(t_2,t_1) \equiv \tilde{P}_c\tilde{V}^I(t_2)\tilde{G}_c^I(t_2,t_1)\tilde{Q}_c\tilde{V}^I(t_1)\tilde{P}_c\ . \tag{3.14}$$

This is more difficult to discuss than the radiation memory kernel since we cannot, in general, treat the atomic collision problem by perturbation theory. However, under the binary-collision approximation (discussed in detail later), which implies that two or more simultaneous strong collisions rarely occur, the general behavior can be inferred. Physically, it is clear that $\tilde{V}^I(t_2)$ and $\tilde{V}^I(t_1)$ can only be correlated if they both refer to the same collision, so the memory kernel is nonzero only if $t_2 - t_1 \lesssim \tau_c$ where τ_c is the duration time of a collision. More rigorously (as we will show below) the Laplace transform of $\tilde{M}_c(t_2-t_1)$ can be expressed directly in terms of the off-shell T operator of formal scattering theory.[19,20] It is known that the tetradic elements of $T(E)$ vary appreciably from the on-shell elements only for a charge of E such that $\Delta E \sim \hbar/\tau_c$ (for an example, see the semiclassical calculations in Ref. 21). Thus the usual transform arguments allow us to conclude that $\tilde{M}_c(\tau)$ has a value comparable to $\tilde{M}_c(0)$ only for times $\tau \lesssim \tau_c$.

The typical duration of a collision τ_c is 10^{-12} sec (strong collision duration for a van der Waals broadening collision), and so by detuning the driving field more than $\sim 10^{12}/2\pi$ Hz from resonance (i.e., making the macroscopic time scale less than τ_c), we begin to examine the time dependence of the individual collision. This means that we cannot ignore the temporal behavior of $\tilde{P}_c\rho_R(t')$ in the integral in Eq. (3.12) (i.e., we cannot make the Markoff approximation). We, therefore, have to retain all the terms in the equation of motion.

One simplification, however, is that we can be content with the expansion of $\tilde{\mathcal{G}}_c(\tau)$ in the driving field $L^E(t)$. We have to consider to what order in $\tilde{L}^E$ we should take this expansion and to do this we must consider the physical significance of the different terms in the expansion. We shall show below that the zeroth-order term in the expansion will give just the usual "unified" theory of collisional broadening.[22] (This point will be made clearer below when we reduce this first term to a more familiar collision operator.) The first-order term in the expansion represents the process where an off-diagonal density matrix (that corresponds to, say, a dipole transition) is coupled to a population or a Zeeman coherence (or vice versa) "during a collision." By during a collision, we mean during the time that the perturber is in the region where the density matrix, for a given atom-perturber pair, is not well approximated by a factorized form. This term is of order $\Omega\tau_c$ or less. This is easily seen to be so, since the interaction [i.e., matrix elements of $L^E(t)$] is of order Ω and the maximum change it can produce in a time τ_c is of order $\Omega\tau_c$. So the parameter for the expansion of the collisional propagator, in terms of the driving field, i.e., $\Omega\tau_c$, is in most cases very small. This expansion is actually a function of frequency and becomes, as we shall see below $\sim\Omega/\Delta\omega$, when $\Delta\omega \gg \tau_c$. We must bear in mind that these terms in the collision operator that depend on the driving field are off-diagonal in the atomic subspace. Furthermore, $\Omega/\Delta\omega$ is also the expansion parameter for the coupling of the pure atomic states in the presence of the driving field. Now we know that this can become large (as $\Delta\omega \to \gamma_N$) in many situations of practical interest. This means that a perturbation expansion cannot necessarily be used for the free-evolution [part of Eq. (3.12)]. During a collision, however, the coupling is bounded by $\Omega\tau_c$ and can still remain small. In the wings $\Delta\omega \gg \tau_c$ the validity criteria for the two expansions are the same and we have to consider them on the same footing. For the case of pure radiative relaxation, we can never get to $\Delta\omega \sim 10^{18}$ Hz and thus never need to consider the corrections to the relaxation operator compared to the normal coupling of the atomic states.

Some of the second-order corrections to the collision operator also contribute new off-diagonal matrix elements in the atomic subspace, and they have to be retained. If we are considering, say, a two-level atom with nondegenerate levels then the second-order terms exhaust the qualitatively different types of corrections to the collision operators. For degenerate levels the higher-order terms can contribute to higher-order multipole moments of the system. If we are studying

scattering or absorption by an allowed transition we can still argue that these higher-order terms (higher than second order in $\tilde{L}^E$) are unimportant. This is easily shown once one observes that the probability of an *extra* photon being absorbed, during a collision, is $\sim|\Omega|^2\tau_c^2$ times the probability for any given number of photons (say one) being absorbed during a collision. A more careful estimate of the second-order correction to the collisional damping operator $\gamma^1(\Delta\omega)$ (Ref. 1) shows that it is of order $\gamma^1(\Delta\omega)|\Omega|^2\tau_c^2$ near line center $|\Delta\omega| \ll 1/\tau_c$, and $\sim[\gamma^1(\Delta\omega)/\Delta\omega]\ |\Omega|^2\tau_c$ in the wings $|\Delta\omega| \gg 1/\tau_c$.

We note that even though the expansion of $\mathcal{G}_c(t_2,t_1)$ is truncated, the effect of spontaneous emission on the evolution of an individual collision has been consistently included by the retention of the self-action operator $\tilde{S}$ in the definition of the propagator $\tilde{G}_c$. In taking matrix elements of Eq. (3.15), coupling between density matrix components is retained only to leading order in $\Omega\tau_c$. In Eq. (3.12), carrying out the expansion of $\mathcal{G}_c(t,t')$ to second order, gives the following equation:

$$\partial_t\tilde{P}_c\hat{\rho}_R(t)=\tilde{P}_c[\tilde{L}_0^A+\tilde{S}+\tilde{L}^E(t)]\tilde{P}_c\hat{\rho}_R(t)+\tilde{P}_c\tilde{V}^I(t)\int_{-\infty}^{t}dt'\tilde{G}_c^I(t,t')\tilde{Q}_c\tilde{V}^I(t')\tilde{P}_c\hat{\rho}_R(t')$$
$$+\tilde{P}_c\tilde{V}^I(t)\int_{-\infty}^{t}dt_1\int_{-\infty}^{t_1}dt'\tilde{G}_c^I(t,t_1)\tilde{L}^E(t_1)\tilde{G}_c^I(t_1,t')\tilde{Q}_c\tilde{V}^I(t')\tilde{P}_c\hat{\rho}_R(t')$$
$$+\tilde{P}_c\tilde{V}^I(t)\int_{-\infty}^{t}dt_1\int_{-\infty}^{t_1}dt_2\int_{-\infty}^{t_2}dt'\tilde{G}_c^I(t,t_1)\tilde{L}^E(t_1)\tilde{G}_c(t_1,t_2)\tilde{L}^E(t_2)\tilde{G}_c^I(t_2,t')Q_c\tilde{V}^I(t')\tilde{P}_c\hat{\rho}_R(t')\ , \tag{3.15}$$

where we have used $\tilde{P}_c\hat{\rho}_R^I(t)=\tilde{P}_c\hat{\rho}_R(t)$. This equation, (3.15), limits our treatment to situations where $\Omega\tau_c \ll 1$. The reader may then wonder why we are concerned with these terms of order $|\Omega\tau_c|^2$ at all. This is because it is these correlated terms, associated with transitions during the collision, that dominate the wings of the line (where the absorption spectrum is proportional to $\Omega^2/\Delta\omega^2$). This will be apparent when we treat a practical case. In the strong-field case (when $\Omega\tau_c \lesssim 1$) the above perturbation expansion for the collision propagator will be inappropriate in the same way that perturbation theory is inappropriate for the free-evolution. Then, instead of expanding in powers of $L^E(t)$, a more convenient (but in many ways more complicated) procedure would be to use states ("dressed" states) in Eq. (3.4) *et seq.* which are eigenstates of $\tilde{L}_0^A+\tilde{L}^E(t)$, and compute in an interaction representation in terms of these states. This procedure, however, does not allow for interpretation in terms of simple modifications of collision operators in the absence of collisions.

We shall now reduce the equation of motion to a more useful form using the binary-collision approximation. In the context of this approximation, we shall be able to use the equation of motion to calculate absorption spectra from an atom in the presence of a driving field. In succeeding papers we shall use the density operators we calculate here in the determination of scattered spectra. No extra restrictions are necessary, e.g., we do not have to limit ourselves to $|\Delta\omega| \ll kT/\hbar$ as the effects of the interatomic potential on the distribution of perturbers has been consistently included (such correlations are built up in the interval $[t,-\infty]$).

B. The binary-collision approximation

The binary-collision approximation (BCA), which implies that strong collisions between atom and perturber are well separated in time, is a central assumption of most line broadening theories and we shall use it here.

For simplicity, we will take the case of a single isolated atom immersed in a bath of N perturbers [so that $\mathrm{Tr}_{\mathrm{pert}}(\hat{\rho}_R)$ is the reduced density matrix of this one atom], although generalization to the case of n atoms is trivial. The operator $\tilde{V}(t)$, which appears, for example, in Eqs. (3.12) and (3.15), may be written as a sum of two parts. One is a sum $\sum_j\tilde{V}_j(t)$, where $\tilde{V}_j(t)$ is the interaction between the radiator and the jth perturber. The other is the sum $\sum_{i\neq j}\tilde{V}_{ij}(t)$ where $V_{ij}(t)$ is the interaction between perturber i and j. Suppose we were to write any one of the time-ordered expansions explicitly. We would obtain sets of products of the following form:

$$\tilde{P}_c\cdots\tilde{Q}_c\tilde{V}_j(t)\tilde{Q}_c\tilde{V}_k(t')\tilde{Q}_c\cdots\tilde{P}_c\ , \tag{3.16}$$

in the BCA. The approximation assumes that strong collisions are separated in time; weak collisions that may be dealt with by a second-order perturbation expansion may overlap since their effects are additive. The BCA implies that (because of the chronological ordering) a $\tilde{V}_j(t)$ cannot appear again in any product after a $\tilde{V}_i(t)$

appears. [This is the same reason that $\tilde{V}_{ij}(t)$'s do not appear in (3.16).] If we write $\tilde{Q}_c = 1 - \tilde{P}_c$ then we can write

$$\tilde{P}_c \cdots \tilde{Q}_c \tilde{V}_i(t) \tilde{Q}_c \tilde{V}_j(t) \cdots \tilde{P}_c = \tilde{P}_c \cdots \tilde{Q}_c \tilde{V}_i(t) \tilde{V}_j(t) \cdots \tilde{P}_c - P_c \cdots \tilde{Q}_c \tilde{V}_i(t) \tilde{P}_c \tilde{V}_j(t) \cdots \tilde{P}_c . \tag{3.17}$$

It would, of course, be inconsistent to suppose that the interaction between perturbers was strong *on the average* and try at the same time to make a binary collision (atom + perturber) approximation. We suppose, therefore, that $\hat{\rho}_{\text{pert}}(-\infty)$ may be written as a product of single perturber-density operators; this is the same as saying the perturbers are statistically independent. Then we can write

$$\tilde{P}_c = \prod_j \tilde{P}_c^j ,$$

where

$$\tilde{P}_c^j \hat{0} \equiv \hat{\rho}^j(-\infty) \operatorname{Tr}_{\substack{j\text{th pert's} \\ \text{states}}} [\hat{0}] . \tag{3.18}$$

Then

$$\tilde{P}_c \cdots \tilde{Q}_c \tilde{V}_i(t) \tilde{V}_j(t) \cdots \tilde{P}_c = \tilde{P}_c \cdots \tilde{Q}_c \tilde{V}_i(t) \prod_\alpha \tilde{P}_c^\alpha \tilde{V}_j(t) \cdots \tilde{P}_c = \tilde{P}_c \cdots \tilde{Q}_c \tilde{V}_i(t) \prod_\beta \tilde{P}_c^\beta \tilde{P}_c^\alpha \tilde{V}_j(t) \tilde{P}_c . \tag{3.19}$$

Here α labels all the perturbers that are included in the product to the right of $\prod_\beta \tilde{P}_c^\beta$, and β labels all the perturbers that are included in the product to the left of $\prod_\alpha \tilde{P}_c^\alpha$.

We have used the following properties of $\tilde{P}_c$:

$$\tilde{P}_c = \prod_\beta \tilde{P}_c^\beta \prod_\alpha \tilde{P}_c^\alpha = \left(\prod_\beta \tilde{P}_c^\beta \right)^2 \prod_\alpha \tilde{P}_c^\alpha = \prod_\beta \tilde{P}_c^\beta \tilde{P}_c = \tilde{P}_c \prod_\alpha \tilde{P}_c^\alpha . \tag{3.20}$$

We can, therefore, conclude that if the perturbers are statistically independent,

$$\tilde{P}_c \cdots \tilde{Q}_c \tilde{V}_i(t) \tilde{V}_j(t) \cdots \tilde{P}_c = \tilde{P}_c \cdots \tilde{Q}_c \tilde{V}_i(t) \tilde{P}_c \tilde{V}_j(t) \cdots \tilde{P}_c \tag{3.21}$$

and the average (3.16) must vanish if $i \neq j$. This implies that only product averages where the particle label stays the same throughout the average are nonzero. So we have the result that we can write the averages in (3.15) $N\times$ (single-particle averages). At the same time we can drop the projection operator in the single-particle averager, since this only affects[23] terms higher order in N.

We remarked above that weak collisions may overlap without affecting this single-particle average result. To see this consider a term in the expansion of the collision operator to second order in $\tilde{V}$. It will contain terms of the form

$$\sum_{ij} \tilde{P}_c \tilde{V}_i(t) \tilde{V}_j(t) \tilde{P}_c . \tag{3.22}$$

Now if we assume that the average of any given potential is zero, then $\tilde{P}_c \tilde{V}_i(t) \equiv 0$. This is certainly true in most practical cases. Thus, since

$$\tilde{P}_c \tilde{V}_i(t) \tilde{V}_j(t) \equiv \tilde{P}_c \tilde{V}_i(t) \tilde{P}_c \tilde{V}_j(t) , \tag{3.23}$$

again assuming the particles are statistically independent, we have the result that, to second-order weak collisions are additive, i.e.,

$$\sum_{ij} \tilde{P}_c \tilde{V}_i(t) \tilde{V}_j(t) \equiv N \tilde{P}_c \sum_i \tilde{V}_i(t) \tilde{V}_i(t') . \tag{3.24}$$

Here N is the number of perturbers. Weak collisions may, however, produce complications in the following manner. The correlation terms introduced by the driving field are of order $(\Omega\tau_c)^2$ and for short-range potentials, where a well-defined Weisskopf radius (and hence collision time) exists, it is easy to show that $(\Omega\tau_c)^2$ can be small in a wide range of practical situations. If, however, weak collisions due to a long-range potential dominate the problem (as in the case of electron broadening of Lyman α), τ_c can become quite large, so that the magnitude of $\Omega\tau_c$ should be carefully examined.

If we introduce $\tilde{V}_1^I(t)$, $\tilde{G}_1^I(t_2,t_1)$, and $\tilde{P}_c^1$ as the representative single-perturber Liouville operators, then we obtain the binary-collision-approximation equation of motion, by making the following substitutions in (3.15):

$$\tilde{V}^I(t) \to \tilde{V}_1^I(t) ,$$

$$\tilde{G}_c^I(t_2,t_1) \to \tilde{U}_1^I(t_2,t_1) = T \exp\left(\int_{t_1}^{t_2} dt \; \tilde{V}_1^I(t) + (\tilde{S} + \tilde{L}_0^A)(t_2 - t_1) \right) , \tag{3.25}$$

$$\tilde{P}_c \to \tilde{P}_c^1 ,$$

and multiplying each collision term by N. Note that the binary-collision propagator becomes the

normal Liouville time-development operator when we drop the projection operator $\bar{Q}_c^1$ (as we know we may[23]).

It is now a straightforward matter to write this resultant equation as an equation of motion for the reduced density matrix $\hat{\sigma}(t)$, defined by

$$\hat{\sigma}(t) \equiv \mathrm{Tr}_{\mathrm{pert}}[\hat{\rho}_R(t)] \ . \tag{3.26}$$

The equation of motion has the form

$$\partial_t \hat{\sigma}(t) = [\tilde{L}_0^A + \tilde{S} + \tilde{L}^E(t)]\,\hat{\sigma}(t) + N\int_{-\infty}^{t} \mathrm{Tr}_1[\tilde{V}_1^I(t)\tilde{U}_1^I(t,t')\tilde{V}_1^I(t')\hat{\rho}_1(-\infty)]\hat{\sigma}(t')dt' + K, \tag{3.27}$$

where K represents corrections to the collision operator. Now the second term in this equation gives the usual unified theory[22] of collisional relaxation. Let us consider the collision operator that occurs in this term, i.e.,

$$\mathrm{Tr}_1[\tilde{V}_1^I(t)\tilde{U}_1^I(t,t')\tilde{V}_1^I(t')\hat{\rho}_1(-\infty)] = \mathrm{Tr}_1[\tilde{V}_1\tilde{U}_1(t,t')\tilde{V}_1\hat{\rho}_1(-\infty)] = \mathrm{Tr}_1\{\tilde{V}_1 \exp[(\tilde{L}_0^A + \tilde{L}_0^P + \tilde{V}_1 + \tilde{S})(t-t')]\,\tilde{V}_1\hat{\rho}_1(-\infty)\} \tag{3.28}$$

$$= \frac{1}{2\pi i}\int_c dz\, \tilde{M}_c(z)e^{-iz\tau}\,dz, \quad \tau = t - t' \ . \tag{3.29}$$

Here c denotes the usual Fourier-Laplace inversion contour

$$\tilde{M}_c(z) = \int_0^\infty e^{iz\tau}\,\mathrm{Tr}_1\{\tilde{V}_1 \exp[\tau(\tilde{L}_0^A + \tilde{L}_0^P + \tilde{V}_1 + \tilde{S})] \times \tilde{V}_1\hat{\rho}_1(-\infty)\}$$

$$= \mathrm{Tr}_1\left[\tilde{V}_1 \frac{1}{iz + \tilde{L}_0^A + \tilde{L}_0^P + \tilde{S} + \tilde{V}_1}\tilde{V}_1\hat{\rho}_1(-\infty)\right] \mathrm{Im}z > 0, \quad \mathrm{Im}z > 0 \ . \tag{3.30}$$

This may be approximated, in the case where the effects of spontaneous emission during a collision may be neglected, by the simpler operator

$$\mathrm{Tr}_1\left[\tilde{V}_1 \frac{1}{iz + \tilde{L}_0^A + \tilde{L}_0^P + \tilde{V}_1}\ \tilde{V}_1\hat{\rho}_1(-\infty)\right] \ . \tag{3.31}$$

Fano[19] has shown how this operator may be reduced to T-matrix element form. The other terms in the equation of motion may be reduced in a similar manner. In some cases (for weak collisions) the effects of spontaneous emission during collisions may become important, i.e., $\gamma_N \tau_c \gtrsim 1$, and $\tilde{S}$ must then be retained in the definition of the collision operator. Retention of $\tilde{S}$ in the definition also ensures convergence of the integrals in the time-dependent formalism since it is equivalent to making z complex. $\tilde{M}_c(z)$ can be evaluated for complex z by analytic continuation from its form on the real axis, determined via the T-matrix element form. We shall not continue with our purely formal reduction, but resort to an example so as to make clear the nature of the correlation terms.

IV. AN EXAMPLE—THE TWO-LEVEL ATOM

In this section, we shall derive an expression for the steady-state response of a two-level atom to a driving field, in the presence of collisions, and show that the correlation terms arise from the modification of the free-perturber-density matrix due to the presence of the active atom.

Up to now, we have glossed over the question of how the translational motion of the *radiator* affects its response to the external driving field. In the absence of collisions this effect, the Doppler effect, is uncorrelated with the natural response and the two responses may be convolved. In the presence of collisions the two effects cannot be rigorously separated, since velocity classes can be coupled (if the radiator interacts with the perturbers when in both states of the transition). Even if this is not the case, the collision operator for a given class may depend on the velocity of that class. We shall suppose that we do not need to consider such effects (for a full discussion see Refs. 24, 25, and 26). Our equation of motion should thus be regarded as one for a single velocity class (or a set of such classes). The novel features of our equations of motion are only important in the far wings, outside the impact region, and for most cases far outside the Doppler core. Since it is only within the Doppler core that velocity correlations may be important, we can ignore them without affecting the main thrust of our arguments. A typical Liouville vector for the radiator-plus-single-perturber subspace will be written thus

$$|i\vec{p}j\vec{p}'\rangle\rangle \ .$$

Here i and j can be either 1 or 0, where 0 labels the stable ground state, and 1 denotes the upper level to which it is connected by an allowed electric-dipole transition. The $\vec{p}$ and $\vec{p}'$'s label the momenta of the perturber (which is supposed to be structureless) in the center-of-mass frame for the radiator-perturber pair. Any projection of the density matrix may be written in the form

$$\langle\langle i\vec{p}ij\vec{p}'\,|\hat{\rho}_R\rangle\rangle = \mathrm{Tr}[|j\vec{p}'\rangle\langle j\vec{p}\,|\hat{\rho}_R] \ . \tag{4.1}$$

We wish to study the steady-state response of the atom to an external field and this cannot depend on the *initial* correlations (between the radiator and perturber) but only on those that exist in the steady state. When we study the scattered spectrum (paper III), produced by the system, we shall construct an equation of motion for the dipole autocorrelation function. In this equation we shall find inhomogeneous terms that are the analog of the destruction in the equation of motion for the density matrix; even for the steady-state spectrum these terms are essential and cannot be eliminated or combined with other terms.

We now turn to the explicit form of the equation of motion for the two-level case, and write it thus (we have used the rotating-wave approximation),[18]

$$\begin{aligned}\partial_t\sigma_{11}(t) = &-\gamma\sigma_{11}(t) - \frac{\Omega}{2i}e^{-i\omega_L t}\sigma_{01}(t) + \frac{\Omega^*}{2i}e^{i\omega_L t}\sigma_{10}(t) + \int_0^t \mathcal{C}^0(t,\tau)_{11,11}\sigma_{11}(\tau)d\tau \\ &- \left(\frac{\Omega^*}{2i}\right)\int_0^t \mathcal{C}^1(t,\tau)_{11,10}\sigma_{10}(\tau)d\tau + \left(\frac{\Omega}{2i}\right)\int_0^t \mathcal{C}^1(t,\tau)_{11,01}\sigma_{01}(\tau)d\tau + \left(\frac{|\Omega|^2}{4}\right)\int_0^t \mathcal{C}^2(t,\tau)_{11,00}\sigma_{00}(\tau)d\tau \ ,\end{aligned} \tag{4.2a}$$

$$\begin{aligned}\partial_t\sigma_{10}(t) = &\left(-\frac{\gamma}{2} - i\omega_0\right)\sigma_{10}(t) - \frac{\Omega}{2i}e^{-i\omega_L t}[\sigma_{00}(t) - \sigma_{11}(t)] + \int_0^t \mathcal{C}^0(t,\tau)_{10,10}\sigma_{10}(\tau)d\tau \\ &- \left(\frac{\Omega}{2i}\right)\int_0^t \mathcal{C}^1(t,\tau)_{10,11}\sigma_{11}(\tau)d\tau + \left(\frac{\Omega}{2i}\right)\int_0^t \mathcal{C}^1(t,\tau)_{10,00}\sigma_{00}(\tau)dt + \left(\frac{\Omega^2}{4}\right)\int_0^t \mathcal{C}^2(t,\tau)_{10,01}\sigma_{01}(\tau)d\tau \ ,\end{aligned} \tag{4.2b}$$

$$\begin{aligned}\partial_t\sigma_{01}(t) = &\left(-\frac{\gamma}{2} + i\omega_0\right)\sigma_{01}(t) + \left(\frac{\Omega}{2i}\right)^* e^{i\omega_L t}[\sigma_{00}(t) - \sigma_{11}(t)] + \int_0^t \mathcal{C}^0(t,\tau)_{01,01}\sigma_{01}(\tau)d\tau \\ &+ \left(\frac{\Omega^*}{2i}\right)\int_0^t \mathcal{C}^1(t,\tau)_{01,11}\sigma_{11}(\tau)d\tau - \left(\frac{\Omega^*}{2i}\right)\int_0^t \mathcal{C}^1(t,\tau)_{01,00}\sigma_{00}(\tau)d\tau + \left(\frac{(\Omega^*)^2}{4}\right)\int_0^t \mathcal{C}^2(t,\tau)_{01,10}\sigma_{10}(\tau)d\tau \ ,\end{aligned} \tag{4.2c}$$

$$\begin{aligned}\partial_t\sigma_{00}(t) = &+\gamma\sigma_{11}(t) + \left(\frac{\Omega}{2i}e^{-i\omega_L t}\sigma_{01}(t) - \frac{\Omega^*}{2i}e^{i\omega_L t}\sigma_{10}(t)\right) + \int_0^t \mathcal{C}^0_{00,00}\sigma_{00}(t,\tau)(\tau)d\tau \\ &+ \left(\frac{\Omega^*}{2i}\right)\int_0^t \mathcal{C}^1(t,\tau)_{00,10}\sigma_{10}(\tau)d\tau - \left(\frac{\Omega}{2i}\right)\int_0^t \mathcal{C}^1(t,\tau)_{00,01}\sigma_{01}(\tau)d\tau + \frac{|\Omega|^2}{4}\int_0^t \mathcal{C}^2(t,\tau)_{00,11}\sigma_{11}(\tau)d\tau \ .\end{aligned} \tag{4.2d}$$

Here, we assumed the driving field $\vec{E}^c(t) = \mathrm{Re}(E_0 e^{-i\omega_L t}\vec{\epsilon})$, where $\vec{\epsilon}$ is its polarization vector. The Rabi frequency is $\Omega = E_0/\hbar\,\langle 1|\vec{d}|0\rangle\cdot\vec{\epsilon}$ with $\vec{d}$ the atomic dipole operator and γ is the radiative-relaxation rate. The quantities $\mathcal{C}^0$, $\mathcal{C}^1$, and $\mathcal{C}^2$ arise from our expansion of the collision operator [see Eq. (3.15)] and are given explicitly by

$$\begin{aligned}\mathcal{C}^0_{ij,ij}(t,\tau) &\equiv N\,\mathrm{Tr}_{\mathrm{pert}}\{\hat{\rho}_{\mathrm{pert}}(-\infty)\langle\langle ij\,|\,\tilde{V}_1\exp[(\tilde{L}_1+\tilde{S})(t-\tau)]\tilde{V}_1\,|ij\rangle\rangle\} \\ &= N\int d^3p_{1,2}\langle\langle i\vec{p}_1, j\vec{p}_1|\,\tilde{V}_1\exp[(\tilde{L}_1+\tilde{S})(t-\tau)]\tilde{V}_1\,|i\vec{p}_2 j\vec{p}_2\rangle\rangle\rho_{\vec{p}_2\vec{p}_2}(t=-\infty) \ ,\end{aligned} \tag{4.3a}$$

$$\begin{aligned}\mathcal{C}^1_{ij,lm}(t,\tau) = \int d^3p_{1,2,3,4}N\int_\tau^t dt'\langle\langle i\vec{p}_1 j\vec{p}_1|\,\tilde{V}_1\exp[(\tilde{L}_1+\tilde{S})(t-t')]|\,i\vec{p}_2 j\vec{p}_3\rangle\rangle\,\frac{\langle\langle i\vec{p}_2 j\vec{p}_3|\,\tilde{L}^E(t')\,|l\vec{p}_2 m\vec{p}_3\rangle\rangle}{\langle\langle i\vec{p}_2 j\vec{p}_3|\,\tilde{L}^E(0)\,|l\vec{p}_2 m\vec{p}_3\rangle\rangle} \\ \times\langle\langle l\vec{p}_2 m\vec{p}_3|\exp[(\tilde{L}_1+\tilde{S})(t'-\tau)]\tilde{V}_1\,|l\vec{p}_4 m\vec{p}_4\rangle\rangle\,\rho_{\vec{p}_4\vec{p}_4}(t=-\infty) \ ,\end{aligned} \tag{4.3b}$$

$$\mathcal{C}^2_{ij\,lm}(t,\tau)=\int d^3p_{1,2,3,4,5,6}N\int_\tau^t dt'\int_\tau^{t'}dt''\langle\langle i\vec{p}_1 j\vec{p}_1|\tilde{V}_1\exp[(\tilde{L}_1+\tilde{S})(t-t')]|i\vec{p}_2 j\vec{p}_3\rangle\rangle$$
$$\times\frac{\langle\langle i\vec{p}_2 j\vec{p}_3|\tilde{L}^E(t')|l\vec{p}_2 j\vec{p}_3\rangle\rangle}{\langle\langle i\vec{p}_2 j\vec{p}_3|\tilde{L}^E(0)|l\vec{p}_2 j\vec{p}_3\rangle\rangle}\langle\langle l\vec{p}_2 j\vec{p}_3|\exp[(\tilde{L}_1+\tilde{S})(t'-t'')]|l\vec{p}_4 j\vec{p}_5\rangle\rangle$$
$$\times\frac{\langle\langle l\vec{p}_4 j\vec{p}_5|\tilde{L}^E(t'')|l\vec{p}_4 m\vec{p}_5\rangle\rangle}{\langle\langle l\vec{p}_4 j\vec{p}_5|\tilde{L}^E(0)|l\vec{p}_4 m\vec{p}_5\rangle\rangle}\langle\langle l\vec{p}_4 m\vec{p}_5|\exp[(\tilde{L}_1+\tilde{S})(t''-\tau)]\tilde{V}_1|l\vec{p}_6 m\vec{p}_6\rangle\rangle\rho_{\vec{p}_6\vec{p}_6}(t=-\infty) \tag{4.3c}$$

plus the term with transitions in order $ij\rightarrow im\rightarrow lm$. Here $\tilde{L}_1=\tilde{L}_0^A+\tilde{L}_0^p(1)+\tilde{V}_1$, where $\tilde{L}_0^p(1)$ is the Liouville operator for a single perturber.

In obtaining Eqs. (4.3), we have assumed that the collision operators

$$\tilde{V}_1\tilde{G}_c(\tau)\tilde{V}_1,\quad \tilde{V}_1\tilde{G}_c(\tau),\quad \tilde{G}_c(\tau)\tilde{V}_1$$

are diagonal in the atom tetradics. This means we assume that inelastic collision rates are negligible and, additionally, that radiation during a collision (i.e., which occurs via the operator $\tilde{S}$ and would mix atom tetradics) does not couple tetradics appreciably. The tetradic elements of the driving-field operator, namely, $\langle\langle i\vec{p}_2 j\vec{p}_3|\tilde{L}^E(t)|l\vec{p}_2 m\vec{p}_3\rangle\rangle$ are nonzero if ($i=l$ and $j\neq m$) or ($i\neq l$ and $j=m$), but are diagonal in perturber tetradics. Furthermore, they always appear normalized by an $\tilde{L}^E(0)$ element, since we have chosen to display explicitly the dependence of each term on the field strength by factoring out the Rabi frequencies.

In the steady state the off-diagonal elements of $\hat{\sigma}$, σ_{10}, and σ_{01} oscillate at the driving-field frequency, while σ_{11} and σ_{00} are constant. To anticipate this we cast the equations in terms of the new variables

$$\sigma^1_{10}(t)=e^{i\omega_L t}\sigma_{10}(t),\quad \sigma^1_{01}(t)=e^{-i\omega_L t}\sigma_{01}(t),\ \sigma^1_{11}(t)=\sigma_{11}(t),\quad \sigma^1_{00}(t)=\sigma_{00}(t).$$

The equations of motion take the following form in the limit $t\rightarrow\infty$ [$\sigma^1_{ij}(t\rightarrow\infty)\equiv\sigma_{ij}$]:

$$\gamma\sigma^1_{11}=-\frac{\Omega}{2i}\sigma^1_{01}+\frac{\Omega^*}{2i}\sigma^1_{10}+\int_0^\infty\mathcal{C}^0(\tau,0)_{11,11}d\tau\,\sigma^1_{11}\lim_{t\rightarrow\infty}\left(+\frac{\Omega}{2i}\int_0^t\mathcal{C}^1(t,\tau)_{11,01}e^{i\omega_L\tau}dt\,\sigma^1_{01}-\frac{\Omega^*}{2i}\int_0^t\mathcal{C}^1(t,\tau)_{11,10}e^{i\omega_L\tau}d\tau\,\sigma^1_{10}\right)$$
$$+\frac{|\Omega|^2}{4}\int_0^\infty\mathcal{C}^2(\tau,0)_{11,00}d\tau\,\sigma^1_{00}, \tag{4.4a}$$

$$\left(\frac{\gamma}{2}+i\omega_0-i\omega_L\right)\sigma^1_{10}=-\frac{\Omega}{2i}(\sigma^1_{00}-\sigma^1_{11})+\int_0^\infty\mathcal{C}^0(\tau,0)_{10,10}e^{+i\omega_L\tau}d\tau\,\sigma^1_{10}$$
$$-\lim_{t\rightarrow\infty}\left(\frac{\Omega}{2i}\int_0^t\mathcal{C}^1(t,\tau)_{10,11}e^{i\omega_L t}\sigma^1_{11}d\tau-\frac{\Omega}{2i}\int_0^t\mathcal{C}^1(t,\tau)_{10,00}e^{i\omega_L t}\sigma^1_{00}d\tau\right)$$
$$+\frac{\Omega^2}{4}\lim_{t\rightarrow\infty}\int_0^t\mathcal{C}^2(t,\tau)_{10,01}e^{i\omega_L(t+\tau)}\sigma^1_{01}d\tau, \tag{4.4b}$$

$$\left(\frac{\gamma}{2}-i\omega_0+i\omega_L\right)\sigma^1_{01}=+\frac{\Omega^*}{2i}(\sigma^1_{00}-\sigma^1_{11})+\int_0^\infty\mathcal{C}^0(\tau,0)_{01,01}e^{-i\omega_L\tau}d\tau\,\sigma^1_{01}$$
$$+\lim_{t\rightarrow\infty}\left(+\frac{\Omega^*}{2i}\int_0^t\mathcal{C}^1(t,\tau)_{01,11}e^{-i\omega_L t}\sigma^1_{11}d\tau-\frac{\Omega^*}{2i}\int_0^t\mathcal{C}^1(t,\tau)_{01,00}e^{-i\omega_L t}\sigma^1_{00}d\tau\right)$$
$$+\frac{(\Omega^*)^2}{4}\lim_{t\rightarrow\infty}\left(\int_0^t\mathcal{C}^2(t,\tau)_{01,10}e^{-i\omega_L(t+\tau)}d\tau\,\sigma^1_{10}\right), \tag{4.4c}$$

$$-\gamma\sigma^1_{11}=+\frac{\Omega}{2i}\sigma^1_{01}-\frac{\Omega^*}{2i}\sigma^1_{10}+\int_0^\infty\mathcal{C}^0_{00,00}(\tau,0)\,d\tau\,\sigma^1_{00}$$
$$+\lim_{t\rightarrow\infty}\left(\frac{\Omega^*}{2i}\int_0^t\mathcal{C}^1_1(t,\tau)_{00,10}e^{-i\omega_L\tau}\sigma^1_{10}d\tau-\frac{\Omega}{2i}\int_0^t\mathcal{C}^1(t,\tau)_{00,01}e^{i\omega_L\tau}d\tau\,\sigma^1_{01}\right)+\frac{|\Omega|^2}{4}\int_0^\infty\mathcal{C}^2(\tau,0)_{00,11}\sigma^1_{11}d\tau. \tag{4.4d}$$

A simplification arises for the model we are considering that is special to a case with nondegenerate levels: All the collision operators that have a final propagation in either $\langle\langle 1\vec{p}_1 1\vec{p}_1|$ or $\langle\langle 0\vec{p}_1 0\vec{p}_1|$ vanish. (This is discussed in detail in Appendix C.) Physically this means that once

an emission or absorption event is completed (during a collision) the subsequent propagation of the population during the collision is irrelevant unless, of course, the final state of the atom-perturber system is bound (see Appendix C). In the case of degenerate levels this propagation is important, since upper- (or lower-) level m_j states will be mixed as the collision is completed (see papers II and III). Let us now turn to those correlation terms that do not vanish and provide the qualitatively different effects in the equations of motion. The first we consider is

$$\mathcal{C}_{10,00}(\omega_L)=\lim_{t\to\infty}\int_0^t \mathcal{C}^1(t,\tau)_{10,00}\,e^{i\omega_L\tau}\,d\tau\,. \tag{4.5}$$

In Appendix C we show that we may express $\mathcal{C}_{10,00}(\omega_L)$ in the following form:

$$\mathcal{C}_{10,00}(\omega_L)=N\int d^3p_{1,2,3}\times\left\langle\!\!\left\langle\left|\vec{p}_1 0\vec{p}_1\right|\tilde{V}_1\frac{1}{i\omega_L+\tilde{L}_1-\frac{\gamma}{2}}\left\|\vec{p}_2 0\vec{p}_3\right\rangle\!\!\right\rangle\right. \times\{\langle\langle 0\vec{p}_2 0\vec{p}_3|\,[\hat{\rho}(kT)-\hat{\rho}_0(kT)]\rangle\rangle\}, \tag{4.6}$$

where $\hat{\rho}_0(kT)=\exp(-H_0/kT)$. Now this term is an extra contribution to the σ_{10} component of the density matrix which is proportional to the expectation value of the dipole moment, produced by the atom's response to the external field. This term describes the process where absorption occurs when the perturber is in the region of the interatomic potential where its motion is appreciably changed from that of a free-particle, i.e., when $\langle\langle 0\vec{p}_2 0\vec{p}_3|\,[\rho(kT)-\hat{\rho}_0(kT)]\rangle\rangle$ is appreciable, and the usual unified theories ignore this type of process. The kinetic theory of Hussey *et al.*,[27] however, does include this type of process by using an exact equilibrium density operator. If we wished to restrict ourselves to thermal equilibrium, we could include the correlated events (in the BCA) *without* resorting to corrections to the collision operator (due to the driving field). To do this, we would need to change our projection operator to one that projects onto a thermal equilibrium subspace,[3] rather than the separable subspace we have used so far. We show, in Appendix B, that the extra term that comes from a correction to the collision operator is only appreciable when $\Delta\omega_L=\omega_0-\omega_L$ is comparable with $kT/\hbar$. When $\Delta\omega_L\ll kT/\hbar$, we show that

$$\mathcal{C}_{10,00}(\omega_L)\simeq\gamma_c/(kT/\hbar)\,. \tag{4.7}$$

This shows us that for $\Delta\omega_L\ll kT/\hbar$ these extra terms contribute terms to the absorption spectrum smaller by $\sim[\Delta\omega_L/(kT/\hbar)]$ than the ordinary terms. This confirms the well-known fact that correlated terms in the density matrix may be ignored for detunings less than a thermal frequency.

In the far wings of the line these terms have a profound effect on the spectrum. We shall solve Eqs. (4.10) and show how, in the far wings, the new terms may be grouped with the normal unified theory terms to obtain the proper "one-perturber" absorption response[28] that includes the thermal distribution of perturbers. We shall write Eqs. (4.4a) through (4.4d) in the following form:

$$\gamma\sigma_{11}^1=-\frac{\Omega}{2i}\sigma_{01}^1+\frac{\Omega^*}{2i}\sigma_{10}^1\,,$$

$$\left(\frac{\gamma}{2}+i\Delta\omega_L-\mathcal{C}^0_{10,10}(\omega_L)\right)\sigma_{10}^1=-\frac{\Omega}{2i}\,\mathcal{C}^1(\omega_L)_{10,11}\sigma_{11}^1+\frac{\Omega}{2i}\,\mathcal{C}^1(\omega_L)_{10,00}\sigma_{00}^1+\frac{\Omega^2}{4}\,\mathcal{C}^2(\omega_L)_{10,01}\sigma_{01}^1-\frac{\Omega}{2i}(\sigma_{00}^1-\sigma_{11}^1)\,, \tag{4.8}$$

$$\left(\frac{\gamma}{2}-i\Delta\omega_L-\mathcal{C}^0_{01,01}(\omega_L)\right)\sigma_{01}^1=-\frac{\Omega^*}{2i}\,\mathcal{C}^1(\omega_L)_{01,11}\sigma_{11}^1+\frac{\Omega^*}{2i}\,\mathcal{C}^1(\omega_L)_{01,00}\sigma_{00}^1+\frac{(\Omega^*)^2}{4}\,\mathcal{C}^2(\omega_L)_{01,10}\sigma_{10}^1+\frac{\Omega^*}{2i}(\sigma_{00}^1-\sigma_{11}^1)\,.$$

Here $\Delta\omega_L=\omega_0-\omega_L$ and

$$\mathcal{C}^0(\omega_L)_{10,10}=\int_0^\infty \mathcal{C}^0(\tau,0)_{10,10}\,e^{i\omega_L\tau}\,d\tau\,, \tag{4.9a}$$

$$\mathcal{C}^0(\omega_L)_{01,01}=\int_0^\infty \mathcal{C}^0(\tau,0)_{01,01}\,e^{-i\omega_L\tau}\,d\tau\,, \tag{4.9b}$$

$$\mathcal{C}^1(\omega_L)_{10,11}=\lim_{t\to\infty}\int_0^\tau \mathcal{C}^1(t,\tau)_{10,11}\,e^{i\omega_L t}\,d\tau\,, \tag{4.9c}$$

$$\mathcal{C}^1(\omega_L)_{01,11}=\lim_{t\to\infty}\int_0^t \mathcal{C}^1(t,\tau)_{01,11}\,e^{i\omega_L t}\,d\tau\,, \tag{4.9d}$$

$$\mathcal{C}^1(\omega_L)_{10,00}=\lim_{t\to\infty}\int_0^t \mathcal{C}^1(t,\tau)_{10,00}\,e^{i\omega_L t}\,d\tau\,, \tag{4.9e}$$

$$\mathcal{C}^1(\omega_L)_{01,00}=\lim_{t\to\infty}\int_0^t \mathcal{C}^1(t,\tau)_{01,00}\,e^{-i\omega_L t}\,d\tau\,, \tag{4.9f}$$

$$\mathcal{C}^2(\omega_L)_{01,10}=\lim_{t\to\infty}\int_0^t \mathcal{C}^2(t,\tau)_{01,10}\,e^{-i\omega_L(t+\tau)}\,dt\,, \tag{4.9g}$$

$$\mathcal{C}^2(\omega_L)_{10,01}=\lim_{t\to\infty}\int_0^t \mathcal{C}^2(t,\tau)_{10,01}\,e^{i\omega_L(t+\tau)}\,d\tau\,. \tag{4.9h}$$

The general solution to this set of coupled linear equations may be obtained by standard techniques. Consider the solution for the upper-state population σ^1_{11}, to order $|\Omega|^2$. We find

$$\sigma^1_{10} \simeq \left(+\frac{\Omega}{2i}\,\mathcal{C}^1(\omega_L)_{10,00} - \frac{\Omega}{2i}\right)\frac{1}{\frac{1}{2}\gamma + i\Delta\omega_L - \mathcal{C}^0_{10,10}(\omega_L)}, \tag{4.10a}$$

$$\sigma^1_{01} \simeq -\frac{\Omega^*}{2i}[\mathcal{C}^1(\omega_L)_{01,00} - 1]\frac{1}{\frac{1}{2}\gamma - i\Delta\omega_L - \mathcal{C}^0_{01,01}(\omega_L)}, \tag{4.10b}$$

and thus

$$\sigma^1_{11} = \frac{|\Omega|^2}{4}\left[2\,\mathrm{Re}\left(\frac{1 - \mathcal{C}^1(\omega_L)_{10,00}}{\frac{1}{2}\gamma + i\Delta\omega_L - \mathcal{C}^0(\omega_L)_{10,10}}\right)\right]. \tag{4.11}$$

For $\Delta\omega_L \ll kT/\hbar$, this reduces to the unified theory expression, i.e.,

$$\sigma^1_{11} = \frac{|\Omega|^2}{4\gamma}\left(\frac{\gamma + 2\gamma_c(\Delta\omega_L)}{[\Delta\omega_L + \Delta_c(\Delta\omega_L)]^2 + [\gamma(\Delta\omega_L)]^2}\right). \tag{4.12}$$

Here we have split $\mathcal{C}^0(\omega_L)_{10,10}$ into its real and imaginary parts, i.e.,

$$\mathcal{C}^0(\omega_L)_{10,10} = -\gamma_c(\Delta\omega_L) - i\Delta_c(\Delta\omega_L). \tag{4.13}$$

Now, for $\Delta\omega_L$ comparable to or greater than $kT/\hbar$, the correlation terms have a profound effect on the spectrum. Far in the wings, we can write

$$\sigma^1_{11} = \frac{|\Omega|^2}{4\gamma}\left(\frac{\gamma + 2\gamma_c(\Delta\omega_L)}{(\omega_0 - \omega_L)^2} - \frac{2}{\Delta\omega_L}\,\mathrm{Im}[\mathcal{C}^1(\omega_L)_{10,00}]\right). \tag{4.14}$$

In Appendix B we show that this may be recast into the form

$$\frac{|\Omega|^2}{4\gamma}\left[\frac{\gamma}{(\Delta\omega_L)^2} + 2\pi N\int |\langle E^1(\vec{p}_2)|E^0(\vec{p}_3)\rangle|^2 \exp\left(-\frac{E(\vec{p}_3)}{kT}\right) \times d^3p_2 d^3p_3 \delta(E(\vec{p}_2) - E(\vec{p}_3) - \hbar\Delta\omega_L)\right]. \tag{4.15}$$

This is, of course, precisely the sort of response we should expect from the quasimolecular picture of line broadening,[28,29] showing that our theory can describe the complete BCA profile from line center to the kT wings. In detail the E/kT effects come in because the perturbers are allowed to follow the correct "trajectories." By writing $\hat{\rho}(-\infty)$ for the perturbers in product form, we assume they are uniformly distributed at large distances from the active atom. They then come in and interact with the atom under the influence of the interatomic potential. This modifies their distribution close to the atom and gives us the E/kT effects.

The upper-state population is, of course, related to the absorption profile, and the only slight complication, arising from bound states, is discussed in Appendix C. There, we discuss the fact that (4.15) is actually the expression one should use for simple absorption, rather than the one for the population of the excited atomic state. Again, this is a consequence of the existence of bound atom-perturber states that we may couple into after an absorption process if $\Delta\omega_L \gtrsim kT/\hbar$, *and* the potential in the excited state is attractive. (Notice, these excited bound states do not affect the factorization of $\hat{\rho}$ for the ground state at $t = -\infty$, which is the only matrix element of ρ that is important at low laser intensities.) The precise consideration of absorption and emission profiles will be left until later (see succeeding papers) when we discuss the correlation function in detail.

V. CONCLUSION

Starting from first principles, we have shown how an equation of motion for the density matrix of an atomic system, in the presence of radiation and collisions, may be derived. We avoided any serious assumptions about the form of the density matrix (i.e., whether it may be written in factorized form) and hence about the time scale of relevant interactions. We could then discuss the implications of the relevant time scales for the structure of the *exact equations* and show when the usual Markoff-master equations were valid and, more importantly, when they were not.

We found that the Markoff approximation was exact (for all practical purposes) in the radiative self-energy problem, but could break down (when interatomic distances are large) for the radiation part of the interatomic potential. For collisional damping our analysis was more fruitful; we were able to show how the "correlation" terms in the density matrix become important (for nondegenerate systems) when the driving field is detuned an amount comparable with a thermal frequency, i.e., $\Delta\omega_L \gtrsim kT/\hbar$. In the limit $\Delta\omega_L \gg 1/\tau_c$ we were able to show that the correlation terms produce the precise quasistatic profile with a Boltzmann distribution for the perturbers.

We had to use an expansion of the collision operator in powers of the driving field that limits our discussion to field strengths such that $|\Omega\tau_c|^2 \ll 1$. Our consistent treatment of spontaneous emission and collisions also enabled us to see precisely where the self-energy operator affects the collisions and, therefore, to conclude $\gamma\tau_c$ must be small for our operators to reduce to standard collision operators. In the succeeding papers we shall show how the correlation terms affect the response of a degenerate system. In this regard, we shall show that factorization of the

density matrix, at an initial time t_0 (ignoring "initial correlations"), although (as stated in Sec. III A) valid for calculating quantities related to one-time averages such as intensities (paper II), is not correct in the calculation of two-time averages; this implies the quantum-fluctuation-regression theorem is invalid (paper III). The effects discussed in these papers are rather more interesting and subtle than in the nondegenerate case and have consequences for the angular and polarization properties of light scattered by an atomic system. We hope that this work will lead to a better framework for the interpretation and exploitation of redistribution experiments.

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APPENDIX A: LIOUVILLE SPACE

Operators on a given Hilbert space (H space) may be regarded as vectors in an associated Liouville space (L space). Operators (sometimes called super operators) on the vectors of this Liouville-space transform Hilbert-space operators into other Hilbert-space operators. The most important example of such a super operator is the Liouville operator $\tilde{L}$ (all super operators will be denoted by a tilde "~"), defined via the Hamiltonian H:

$$\tilde{L}0 \equiv \frac{1}{i\hbar}[H, 0], \tag{A1}$$

where 0 is an arbitrary H-space operator. We note that 0 may be written in the form

$$0 = \sum_{a,b} |a\rangle\langle a|\hat{0}|b\rangle\langle b| \equiv \sum_{a,b} |a,b\rangle\rangle\langle a|\hat{0}|b\rangle . \tag{A2}$$

Thus the set $|a,b\rangle\rangle$ forms a basis for L space. We see then that an L-space operator is a four index or tetradic object, e.g.,

$$\tilde{L} \equiv \sum_{ab,cd} L_{cd;ab} |cd\rangle\rangle\langle\langle ab| . \tag{A3}$$

Here $\langle\langle ab|$ is the dual vector of $|ab\rangle\rangle$ defined via the inner product

$$\langle\langle ab|cd\rangle\rangle \equiv \mathrm{Tr}[|b\rangle\langle a||c\rangle\langle d|] = \langle d|b\rangle\langle a|c\rangle = \delta_{db}\delta_{ac} , \tag{A4}$$

so that the (tetradic) matrix element

$$L_{cd;ab} \equiv \langle\langle cd|\tilde{L}|ab\rangle\rangle = \frac{1}{i\hbar}(\langle c|\hat{H}|a\rangle\delta_{db} - \langle b|\hat{H}|d\rangle\delta_{ac}) = \frac{1}{i\hbar}(H_{ca}\delta_{db} - H_{bd}\delta_{ac}) . \tag{A5}$$

With the above definition of $\tilde{L}$ we can see that the equation of motion for the density matrix may be written thus,

$$\partial_t \hat{\rho}(t) = \tilde{L}\hat{\rho}(t) \tag{A6}$$

and the formal solution

$$\hat{\rho}(t) = \exp(\tilde{L}t)\hat{\rho}(0) \tag{A7}$$

may be shown by differentiation to be equivalent to

$$\hat{\rho}(t) = \exp(-i\hat{H}t/\hbar)\hat{\rho}(0)\exp(i\hat{H}t/\hbar) .$$

In our discussions above we make a good deal of use of projection operators in Liouville space. We note a few of their properties here and give an example. Suppose R and S are two systems with combined density matrix $\hat{\rho}_{RS}$. Suppose the density matrix of the system may be written in the following form at $t = -\infty$:

$$\hat{\rho}_{RS}(-\infty) = \hat{\rho}_R(-\infty)\otimes\hat{\rho}_S(-\infty) . \tag{A8}$$

Then we define a projection operator for $\tilde{P}_R$ such that

$$\tilde{P}_R\hat{0} \equiv \hat{\rho}_R(-\infty)\mathrm{Tr}_R(\hat{0}) . \tag{A9}$$

Then to show that $\tilde{P}_R$ is a projection operator we must show it satisfies the following relations[27]:

$$\tilde{P}_R^2 = \tilde{P}_R, \quad \tilde{Q}_R^2 = (1-\tilde{P}_R)^2 = \tilde{Q}_R , \quad \tilde{P}_R\tilde{Q}_R = \tilde{Q}_R\tilde{P}_R = 0 . \tag{A10}$$

These are easily shown to be true, e.g.,

$$\tilde{P}_R^2\hat{0} = \tilde{P}_R\tilde{P}_R\hat{0} = \hat{\rho}_R(-\infty)\mathrm{Tr}_R(\hat{\rho}_R(-\infty)\mathrm{Tr}_R(\hat{0})) = \hat{\rho}_R(-\infty)\mathrm{Tr}_R[\hat{\rho}_R(-\infty)]\mathrm{Tr}_R(\hat{0}) = \hat{\rho}_R(-\infty)\mathrm{Tr}_R(\hat{0}) \equiv \tilde{P}_R\hat{0} . \tag{A11}$$

Since $\hat{\rho}_R(-\infty)$ is assumed to be normalized to 1,

$$\mathrm{Tr}_R[\rho(-\infty)] = 1 .$$

Since these relations hold, $\tilde{P}_R$ and $\tilde{Q}_R$ separate the complete Liouville space of R⊗S into two orthogonal subspaces.[30]

APPENDIX B: EXPLICIT FORMS FOR THE RADIATION-DAMPING OPERATOR IN ROTATIONALLY DEGENERATE SYSTEMS

We use standard notation for the free-radiation field (see, e.g., Ref. 6). The radiation field can be expanded in terms of photon number states $|n_{\vec{k},\lambda}\rangle$ which is a state with n photons of wave vector $\vec{k}$ and polarization vector $\vec{\epsilon}_{\vec{k},\lambda}(\lambda=1,2)$. The photon creation and annihilation operators ($\hat{a}^{\dagger}_{\vec{k},\lambda}$ and $\hat{a}_{\vec{k},\lambda}$) are defined by their commutation relations, respectively,

$$[\hat{a}_{\vec{k},\lambda},\hat{a}^{\dagger}_{\vec{k}',\lambda}]=\delta_{\lambda\lambda'}\delta_{\vec{k}\vec{k}'_1}[\hat{a}_{\vec{k},\lambda}\hat{a}_{\vec{k}',\lambda}]=[\hat{a}^{\dagger}_{\vec{k},\lambda_1}\hat{a}^{\dagger}_{\vec{k}',\lambda'}]\equiv 0\,. \tag{B1}$$

Their names follow from their action on the photon number states

$$\hat{a}_{\vec{k}1\lambda}|n_{\vec{k},\lambda}\rangle=(n_{\vec{k},\lambda})^{1/2}|(n-1)_{\vec{k},\lambda}\rangle\,, \tag{B2a}$$

$$\hat{a}^{\dagger}_{\vec{k},\lambda}|n_{\vec{k},\lambda}\rangle=(n_{\vec{k},\lambda}+1)^{1/2}|[(n+1)_{\vec{k},\lambda}\rangle\,. \tag{B2b}$$

We quantize the free-radiation field in a box of volume V and take, say, periodic boundary conditions. The limit $V\to\infty$ is then taken at a later stage.

The vector potential operator is written thus,

$$\vec{A}(\vec{r})=\sum_{\vec{k},\lambda}\left(\frac{\hbar}{2\epsilon_0 V\omega_k}\right)^{1/2}\{\hat{a}_{\vec{k},\lambda}\vec{\epsilon}_{\vec{k},\lambda}e^{i\vec{k}\cdot\vec{r}}+\hat{a}^{\dagger}_{\vec{k},\lambda}\vec{\epsilon}^{*}_{\vec{k},\lambda}e^{-i\vec{k}\cdot\vec{r}}\}\,. \tag{B3}$$

Here $\hbar\omega_{\vec{k}}$ is the energy of a photon with wave vector $\vec{k}$, and ϵ_0 is the electric permittivity of free-space. From this expression for $\vec{E}(\vec{r})$ we deduce Eq. (2.20). We shall now derive explicit expressions for the self-energy tetradic $\tilde{S}$ for some simple systems.

A. Two-level atom

We consider first a two-level atom where the ground level (angular momentum j_g) and excited level (j_e) are connected by a dipole transition. We define a set of lowering operators for the atomic transition

$$R(m_e\vec{p}_1;m_g\vec{p}_2)=|j_g m_g p_1;j_e m_e p_2\rangle\,, \tag{B4a}$$

which also changes the center-of-mass momentum from $\vec{p}_1$ to $\vec{p}_2$ and, of course, there are $(2j_e+1)(2j_g+1)$ operators for fixed $\vec{p}_1$ and $\vec{p}_2$. The adjoint operators

$$R^{+}(m_e\vec{p}_1;m_g\vec{p}_2)=|j_e m_e\vec{p}_2;j_g m_g\vec{p}_1\rangle\rangle \tag{B4b}$$

form a set of raising operators. We make the electric-dipole approximation in evaluating the self-action operator for reasons given below. The dipole-form interaction can be written in the following form:

$$\tilde{V}_{MR}=\sum_{m_e,m_g\vec{k},\lambda,\vec{p}_1,\vec{p}_2}g_{\vec{k}\lambda}(m_e\vec{p}_1,m_g\vec{p}_2)R^{+}(m_e\vec{p}_1,m_g\vec{p}_2)\hat{a}_{\vec{k},\lambda}$$
$$+g^{*}_{\vec{k},\lambda}(m_g\vec{p}_2;m_e\vec{p}_1)R(m_e\vec{p}_1;m_g\vec{p}_2)\hat{a}^{\dagger}_{\vec{k},\lambda}+\text{H.c.} \tag{B5}$$

Here

$$g_{\vec{k},\lambda}(m_e\vec{p}_1,m_g\vec{p}_2)=+i(\hbar\omega_k/2\epsilon_0 V)^{1/2}\times\vec{f}_{j_e m_e;j_g m_g}\,\delta(\vec{p}_1-\vec{p}_2-\hbar\vec{k})\cdot\vec{\epsilon}_{\vec{k},\lambda} \tag{B6}$$

and $\vec{f}_{j_e m_e;j_g m_g}(\vec{k})=\langle\pi|-\sum_j e\vec{r}_j|\nu\rangle$. We now want to evaluate the operator, or to be precise, the single-atom part of

$$\int_0^{\infty}\mathrm{Tr}_{RAD}\{\tilde{L}^{MR}\tilde{Q}_R\exp[\tilde{Q}_R(\tilde{L}^{M}_0+\tilde{L}^{R}_0)\tau]\tilde{Q}_R\tilde{L}^{MR}\}\times e^{-\tilde{L}^{M}_0\tau}\tilde{P}_R\,d\tau\,. \tag{B7}$$

Now it is well known that calculations of radiative damping produce divergent energy shifts. Furthermore, it has been shown (Refs. 31 and 16) that the form of the divergence obtained is different depending on whether the rotating-wave approximation RWA is made on the interaction [corresponding to dropping terms in Eq. (B5) such as $R(m_e\vec{p}_1;m_g\vec{p}_2)\hat{a}_{\vec{k},\lambda}$ which do not conserve energy] or whether it is made later in the calculations, on the equations of motion. For most purposes it is sufficient to ignore explicit consideration of the shifts and to assume that their "renormalized" values are included in the original atomic energies. With this procedure, only the real part of $\tilde{S}$ is of interest and since this is not sensitive to the order in which the RWA is taken it is convenient to make the RWA directly on Eq. (B5), i.e., we use

$$V_{MR}=\sum_{\vec{k},\lambda,m_e,m_g,\vec{p}_1,\vec{p}_2}[g_{\vec{k},\lambda}(m_e\vec{p}_1,m_g\vec{p}_2)R^{+}(m_e\vec{p}_1,m_g\vec{p}_2)a_{\vec{k},\lambda}+\text{H.c.}]\,. \tag{B8}$$

Hence, in the RWA and Born approximations,

$$\tilde{S}\sigma=\int_0^{\infty}d\tau-\frac{1}{\hbar^2}\sum_{\vec{k},\lambda,m_e m'_e m_g m'_g,\vec{p}_1\vec{p}_2\vec{p}'_1\vec{p}'_2}\{g^{*}_{\vec{k},\lambda}(m_e\vec{p}_1,m_g\vec{p}_2)g_{\vec{k},\lambda}(m'_e\vec{p}'_1,m'_g\vec{p}'_2)$$
$$\times e^{i[\omega_{eg}+\omega(\vec{p}_1)-\omega(\vec{p}_2)-\omega_k]\tau}[R^{+}(m'_e\vec{p}'_1,m'_g\vec{p}'_2)R(m_e\vec{p}_1,m_g\vec{p}_2)\sigma]+\text{H.c.}\}\,, \tag{B9}$$

where $\hbar\omega_{eg}$ is the energy difference between the upper and lower states. In obtaining Eq. (B9) we have used the following results (see Ref. 16, p. 29):

$$\mathrm{Tr}_R[\rho_R(t=-\infty)\hat{a}_{\vec{k},\lambda}\hat{a}^{\dagger}_{\vec{k}',\lambda'}] = \delta_{\vec{k}\vec{k}'}\,\delta_{\lambda\lambda'}\,, \qquad \mathrm{Tr}_R[\rho_R(t=-\infty)\hat{a}_{\vec{k},\lambda}\hat{a}_{\vec{k}',\lambda'}] = 0, \text{ etc.} \tag{B10}$$

(see Ref. 16, p. 29). The time integral in Eq. (B9) can be recognized as Heitler's ζ function (multiplied by i), so the real part gives $\pi\delta(\omega_{eg}+\omega(\vec{p}_1)-\omega(\vec{p}_2)-\omega_k)$. The momentum-conserving δ function occurring in $g_{\vec{k}\lambda}(m_e\vec{p}_1, m_e\vec{p}_2)$ requires $\vec{p}_1-\vec{p}_2=\hbar\vec{k}$, so it is easy to deduce the usual result that the real photons emitted by a given velocity class are centered at the Doppler shifted frequency

$$\omega_k = \omega_{eg}[1+(\hat{k}\cdot\vec{p}_1/mc)]. \tag{B11}$$

Here $\hat{k}$ is a unit vector along $\vec{k}$ and naturally $\hat{k}\cdot\vec{p}_1/mc \ll 1$. The sum over radiation modes is now converted into an integral

$$\sum_{\vec{k},\lambda} \to \frac{V}{(2\pi)^3}\sum_{\lambda}\int k^2\,dk\int d\hat{\Omega}_k \tag{B12}$$

(note that the integration should strictly exclude the laser mode, but this small contribution is negligible).

We recall from Sec. II that the $\vec{k}$ dependence of the exact coupling cuts off the k integral at $k\sim 1/a_0$. This would be important in countering the apparent divergence of the imaginary part of $\tilde{S}$ (i.e., the level shifts), however, the real part of $\tilde{S}$ (i.e., the damping) picks out only those values $k\sim\omega_{eg}/c \ll 1/a_0$, and thus it is a good approximation to use $\vec{k}\simeq 0$ in the k integral. This is equivalent, of course, to taking the dipole approximation as we have already done. The scalar product $\vec{f}\cdot\hat{\epsilon}_{\vec{k},\lambda}$ can be written in terms of spherical components

$$\vec{f}\cdot\hat{\epsilon}_{\vec{k},\lambda} = \sum_{q=-1}^{1}(-)^q[f(0)]_q[\epsilon_{\vec{k},\lambda}]_{-q} \tag{B13}$$

and then using the Wigner-Eckart theorem[32] to write the matrix elements of $[\vec{f}(0)]_q$ in terms of the reduced matrix element $(j_e\|f(0)\|j_g)$ and 3-J symbols, we find

$$[\mathrm{Re}\,\tilde{S}]\sigma = -\frac{1}{8\pi^2\hbar c^3\epsilon_0}\sum_{\vec{p}_1}|\vec{p}_1\vec{p}_1\rangle\rangle \times\int d\hat{\Omega}_{\vec{k}}\int d\omega_k\,\omega_k^3\,\delta(\omega_{eg}+\omega(\vec{p}_1)-\omega(\vec{p}_1)-\hbar k)-\omega_k) \times\sum_{m_e m_g m_e' m_g'}|(j_e\|f(0)\|j_g)|^2\sum_{qq'}(-)^{2j_e-m_e-m_e'} \times\begin{pmatrix} j_e & 1 & j_g\\ -m_e & q & m_g\end{pmatrix}\begin{pmatrix} j_e & 1 & j_g\\ -m_e' & q' & m_g'\end{pmatrix}[\epsilon_{\vec{k}\lambda}]_{-q}[\epsilon_{\vec{k}\lambda}]^{*}_{-q'} \times\{[|j_e m_e';j_g m_g'\rangle\rangle, |j_g m_g;j_e m_e\rangle\rangle\delta] +[\sigma|j_e m_e;j_g m_g\rangle\rangle, |j_g m_g^1;j_e m_e^1\rangle\rangle]\}. \tag{B14}$$

Now since the Doppler shift $[\omega_{eg}(\hat{k}\cdot\vec{p}_1/mc)]$ is much smaller than the optical transition frequency ω_{eg}, the natural damping is essentially the same for different velocity classes of the atom. In other words, it is an excellent approximation to make the replacement

$$\delta(\omega_{eg}+\omega(\vec{p}_1)-\omega(\vec{p}_1)-\hbar k)-\omega_k)\to\delta(\omega_{eg}-\omega_k)\,. \tag{B15}$$

The sum over the atom translational states $\vec{p}_1$ then becomes just the unit operator in translational space, and we will henceforth not display it explicitly. The angular variables are now contained entirely in the polarization components, and the angular integration is easily evaluated using

$$d\hat{\Omega}_k[\epsilon_{\vec{k}\lambda}]_{-q}[\epsilon_{\vec{k}\lambda}]^{*}_{-q'} = \frac{4\pi}{3}\,\delta_{qq'}\,. \tag{B16}$$

A convenient way to take advantage of the rotational symmetry of the damping operator is to express it in terms of irreducible tensors (see Ref. 33) defined by

$$|j_g j_e;kq\rangle\rangle \equiv \sum_{m_e m_g}(-)^{j_e-m_e}\langle j_g m_g j_e - m_e|kq\rangle\,|j_g m_g;j_e m_e\rangle\rangle\,. \tag{B17}$$

Writing the decay rate of single upper state

$$\Gamma_{eg} = \frac{|(j_g\|f(0)\|j_g)|^2}{3\pi\hbar c^3\epsilon_0(2j_e+1)}\,\omega_{eg}^3 \tag{B18}$$

and denoting the two-level damping operator by

$\tilde{\gamma}_{eg}$, we have finally

$$[\mathrm{Re}\,\tilde{S}]\sigma = -\tilde{\gamma}_{eg}\sigma$$
$$= -\Gamma_{eg}\left(\frac{(2j_e+1)^{1/2}}{2}\left[\,|j_e j_e;00\rangle\rangle\sigma + \sigma|j_e j_e;00\rangle\rangle\right]\right.$$
$$\left. - \frac{(2j_e+1)}{3}\sum_q |j_g j_e;|q\rangle\rangle\sigma|j_g j_e;|q\rangle\rangle\right), \tag{B19}$$

which is in agreement with the result of Ducloy.[34]

B. The three-level atom

We consider here an atom possessing three distinct levels, a ground level (j_g), an excited level (j_e), and a "final" level (j_f). It is assumed that the j_e to j_g transition (energy separation $\hbar\omega_{eg}$) and the j_e to j_f transition (energy separation $\hbar\omega_{ef}$) are dipole allowed. Hence in addition to the raising and lowering operators defined above, we also need the set of $(2j_e+1)(2j_f+1)$ operators $|j_e m_e;j_f m_f\rangle\rangle$ [and their $(2j_e+1)(2j_f+1)$ adjoints]. We have dropped all reference to translational states of the radiator for the same reasons we discussed above; they do not affect the self-energy operator.

When the level j_f is lower in energy than j_e [case (a)] the $|j_e m_e;j_f m_f\rangle\rangle$ form a set of raising operators and, of course, if the energy of the j_f level is greater than j_e [case (b)] then they are lowering operators. The dipole interaction is now given by

$$\hat{V}_{MR} = \sum_{\vec{k},\lambda}\sum_{m_e,m_g,m_f}\left[g_{\vec{k}\lambda}(m_e m_g)\,|j_e m_e;j_g m_g\rangle\rangle\hat{a}_{\vec{k}\lambda}\right.$$
$$+ g_{\vec{k}\lambda}(m_f m_e)a_{\vec{k}\lambda}\,|j_f m_f;j_e m_e\rangle\rangle\hat{a}_{\vec{k},\lambda}$$
$$+ g_{\vec{k}\lambda}(m_g m_e)\,|j_g m_g;j_e m_e\rangle\rangle\hat{a}_{\vec{k}\lambda}$$
$$\left. + g_{\vec{k}\lambda}(m_e m_f)\,|j_e m_e;j_f m_f\rangle\rangle\hat{a}_{\vec{k}\lambda} + \mathrm{H.c.}\right], \tag{B20}$$

with

$$g_{\vec{k}\lambda}(m_e m_g) = +i(\hbar\omega_k/2\epsilon_0 V)^{1/2}\vec{f}_{j_e m_e;j_g m_g}(\vec{k}=\vec{0})\cdot\hat{\epsilon}_{\vec{k}\lambda}.$$

In the RWA, Eq. (B20) is modified by dropping terms 2 and 3 (and their conjugates) for case (a), and for case (b) by dropping terms 3 and 4 (and their conjugates).

Beginning with Eq. (B6), we now calculate $\tilde{S}$ for cases (a) and (b), and for the sake of simplicity we assume that the appropriate RWA is made on $\hat{V}_{MR}$ for each case. Of course it is possible to use the full expression (B19) for $\hat{V}_{MR}$, and to make the RWA after the commutators of Eq. (B6) have been evaluated, but again this will only affect the form of the shifts. The details of the calculation are as before so it is only necessary to present results.

Case (a): $(\omega_{ef}>0)$. For this case, we shall denote the damping operator by $\tilde{\gamma}^{(a)}_{egf}$ and the result is

$$\tilde{\gamma}^{(a)}_{egf}\sigma = \tilde{\gamma}_{eg}\sigma + \tilde{\gamma}_{ef}\sigma - \left(\Gamma_{ef}\frac{(j_e\|f(0)\|j_g)}{(j_e\|f(0)\|j_f)} + \Gamma_{eg}\frac{(j_e\|f(0)\|j_f)^*}{(j_e\|f(0)\|j_g)^*}\right)\frac{(2j_e+1)}{6}\sum_q(-)^{j_f-j_e+q}\,|j_f j_e;1-q\rangle\rangle\sigma|j_e j_g;1q\rangle\rangle$$
$$-\left(\Gamma_{eg}\frac{(j_e\|f(0)\|j_f)}{(j_e\|f(0)\|j_g)} + \Gamma_{ef}\frac{(j_e\|f(0)\|j_g)^*}{(j_e\|f(0)\|j_f)^*}\right)\frac{(2j_e+1)}{6}\sum_q(-)^{j_e-j_g-q}|j_g j_e;1-q\rangle\rangle\sigma|j_e j_g;1q\rangle\rangle, \tag{B21}$$

where $\tilde{\gamma}_{eg}(\tilde{\gamma}_{ef})$ is the damping operator for the two levels j_e and j_g (j_e and j_f), and is defined by Eq. (B18). Lines 2 and 3 of Eq. (B20) represent the transfer of $\sigma_{m_e m'_e}$ coherences to $\sigma_{m_f m_g}$ and $\sigma_{m_g m_f}$ coherences.

Case (b): $(\omega_{ef}<0)$. Denoting the damping operator for this case by $\gamma^{(b)}_{egf}$, we find

$$\gamma^{(b)}_{egf} = \tilde{\gamma}_{eg}\sigma + \tilde{\gamma}_{fe}\sigma - \left(\Gamma_{fe}\frac{(j_e\|f(0)\|j_g)}{(j_f\|f(0)\|j_e)} + \Gamma_{eg}\frac{(j_f\|f(0)\|j_e)^*}{(j_e\|f(0)\|j_g)^*}\right)\frac{(2j_e+1)}{6}\sum_q(-)^{j_e-j_f+q}\,|j_e j_f;1-q\rangle\rangle\sigma|j_e j_g;1q\rangle\rangle$$
$$-\left(\Gamma_{eg}\frac{(j_f\|f(0)\|j_e)}{(j_e\|f(0)\|j_g)} + \Gamma_{fe}\frac{(j_e\|f(0)\|j_g)^*}{(j_f\|f(0)\|j_g)^*}\right)\frac{(2j_e+1)}{6}\sum_q(-)^{j_g-j_e+q}|j_g j_e;1-q\rangle\rangle\sigma|j_f j_e;1q\rangle\rangle. \tag{B22}$$

The second line of (B21) represents transfer of σ_{fe} coherences to σ_{eg} coherences, while the final line represents transfer of σ_{ef} coherences to σ_{ge} coherences.

APPENDIX C: COLLISION OPERATORS

In this appendix we shall give some formal proofs needed in Sec. IV for the two-level model. Let us first consider the collision operators diagonal element for the upper-state population, i.e.,

$$\int_0^\infty \mathfrak{C}^0(\tau,0)_{11,11}d\tau = N\int d^3p_{1,2}\langle\langle 1\vec{p}_1 1\vec{p}_1\left|\tilde{V}_1\frac{-1}{iz+\tilde{L}_1+\tilde{S}}\tilde{V}_1\right|1\vec{p}_2 1\vec{p}_2\rangle\rangle\rho_{\vec{p}_2\vec{p}_2}(-\infty)$$
$$= N\int d^3p_{1,2}\int_0^\infty e^{iz\tau}d\tau\langle\langle 1\vec{p}_1 1\vec{p}_1|\,\tilde{V}_1^I(\tau)\tilde{U}_1^I(\tau,0)\tilde{V}_1^I(0)\,|1\vec{p}_2 1\vec{p}_2\rangle\rangle\rho_{\vec{p}_1\vec{p}_2}(-\infty)\quad(\mathrm{Im}z\to+0), \tag{C1}$$

Now we know that in a more realistic model $\tilde{V}_1$ would mix other levels into $\langle\langle 1\vec{p}_1 1\vec{p}_1|$ and it would be convenient to work with an "effective interaction" that eliminates these intermediate states from the problem.[21] This can be done if the other states mixed into 1 by $\tilde{V}$ are sufficiently separated in energy to make an adiabatic approximation. We write

$$\langle\langle 1\vec{p}_1 1\vec{p}_1 \left| \tilde{V}_1 \frac{1}{\tilde{S}+\tilde{L}_1} \tilde{V}_1 \right| 1\vec{p}_2 1\vec{p}_2\rangle\rangle$$

$$\simeq \langle\langle 1\vec{p}_1 1\vec{p}_1 \left| \tilde{V}_{eff} \frac{1}{\tilde{S}+\tilde{L}_0^A+\tilde{L}_0^p(1)+\tilde{V}_{eff}^1} \tilde{V}_{eff} \right| 1\vec{p}_2 1\vec{p}_2\rangle\rangle$$

$$+\langle\langle 1\vec{p}_1 1\vec{p}_1 | \tilde{V}_{eff} | 1\vec{p}_2 1\vec{p}_2\rangle\rangle , \qquad \text{(C2)}$$

where $\tilde{V}_{eff} = \tilde{V}_1[1/(s+\tilde{L}_0)]\tilde{V}_1$ is independent of frequency s when the adiabatic approximation is valid. Equation (C2) is true only if the expectation value of $\tilde{V}_1$ in any given state is zero, i.e., $\langle 1\vec{p}|\tilde{V}_1|1\vec{p}^1\rangle \equiv 0$. $\tilde{V}_{eff}$ and $\tilde{U}_{eff} = \exp[(\tilde{S}+\tilde{L}_0^A+\tilde{L}_0^P+\tilde{V}_{eff})\tau]$ then become operators in the two-level space alone. In a two-level atom the only state that can be mixed into the upper state is, of course, the lower one. This is not realistic: We could suppose that other closer lying levels are mixed into the upper state but that we can ignore their interaction with the external field. Now we know that the following is true:

$$\lim_{z\to i0} \sum_i \int d^3p \left\langle\left\langle i\vec{p}i\vec{p} \left| \tilde{V} \frac{1}{iz+\tilde{L}_1} \right| \tilde{O}\right\rangle\right\rangle = 0 , \qquad \text{(C3)}$$

where $\tilde{O}$ is an arbitrary operator since

$$\lim_{z\to i0} \frac{1}{(\tilde{L}_1+iz)} \tilde{V}_1 |j\vec{p}j\vec{p}\rangle\rangle = |j\vec{p}j\vec{p}\rangle\rangle - |E(\vec{p})j, E(\vec{p})j\rangle\rangle . \qquad \text{(C4)}$$

Here we have assumed the scattering states form a complete set (i.e., we have ignored bound states). This may be proved as

$$\int_0^\infty e^{\tilde{L}_1 t}\tilde{V}_1 dt\, |j\vec{p}j\vec{p}\rangle\rangle = \lim_{T\to\infty} \int_0^T e^{\tilde{L}_1 t}\tilde{L}_1 dt\, |j\vec{p}j\vec{p}\rangle\rangle = \lim_{T\to\infty} (e^{\tilde{L}_1 T}-1)|j\vec{p}j\vec{p}\rangle\rangle = \lim_{T\to-\infty} [e^{i\hat{H}_1 T}\,|j\vec{p}\rangle\langle j\vec{p}\,|e^{-i\hat{H}_1 T} - |j\vec{p}\rangle\langle j\vec{p}\,|]$$

$$= \lim_{T\to-\infty} [e^{i\hat{H}_1 T}e^{-i\hat{H}_0 T}|j\vec{p}\rangle\langle j\vec{p}\,|e^{i\hat{H}_0 T}e^{-i\hat{H}T} - |j\vec{p}\rangle\langle j\vec{p}\,|] = \Omega_+^j |j\vec{p}\rangle\langle j\vec{p}\,|\Omega_+^j - |j\vec{p}\rangle\langle j\vec{p}\,|$$

$$= |E^j(\vec{p})j\rangle\langle E^j(\vec{p})j| - |j\vec{p}\rangle\langle j\vec{p}\,| . \qquad \text{(C5)}$$

Here Ω_+^j is the Moller wave operator (see Ref. 35) where $|E^j(\vec{p})j\rangle$ is the scattering state associated with $|j\vec{p}\rangle$, i.e.,

$$|E^j(\vec{p})j\rangle = \Omega_+^j|\vec{p}j\rangle = |\vec{p}j\rangle + \lim_{\epsilon\to 0} \frac{1}{E(\vec{p}_j)-H_1^j+i\epsilon} V_1^j|\vec{p}j\rangle . \qquad \text{(C6)}$$

So we see that if we can ignore the effect of spontaneous emission during the collision ($\gamma_N\tau_c \ll 1$), (C4) implies

$$\int_0^\infty \mathfrak{C}_{11,11}^0(\tau,0)d\tau = \lim_{z\to i0} \sum_j N\left\langle\left\langle j\vec{p}_1 j\vec{p}_1 \left| \tilde{V}_1 \frac{1}{-iZ+\tilde{L}_1} \tilde{V}_1 \right| 1\vec{p}_2 1\vec{p}_2\right\rangle\right\rangle \rho_{\vec{p}_2\vec{p}_2} d^3p_{1,2} . \qquad \text{(C7)}$$

This is just the total inelastic rate to the levels coupled to $|11\rangle\rangle$ by $\tilde{V}_1$. We are supposing, in keeping to our "two-level" model, that this inelastic rate is negligible and hence that we can put

$$\int_0^\infty d\tau\, \mathfrak{C}_{11,11}^0(\tau,0)d\tau = 0 . \qquad \text{(C8)}$$

By the same token we can put all collision operators that have a final propagation in $|1\vec{p}_1 1\vec{p}\rangle\rangle$ or $|0\vec{p}_1;0\vec{p}_2\rangle\rangle$ will vanish. As stated in Sec. IV, this shows that once an absorption or emission has been completed during a collision, the subsequent propagation of the excited-state population is irrelevant. The subsequent propagation is important for these correlation terms when the final state of the atom-perturber system is bound, as far as calculation of the $\tilde{P}_c\hat{\rho}$ part of the density matrix is concerned; e.g., then the part of $\tilde{P}_c\hat{\rho}$ we want to calculate is σ_{11} (which corresponds to free-final states). This means that one would have to wait a natural lifetime for the bound pair to reradiate and then move apart again before the collision could be completed. The absorption depends, of course, on the total excited-state population, which includes bound states; this means that we need the sum of $\tilde{P}_c\rho$ *and* $\tilde{Q}_c\rho$. Examination of the terms $\mathfrak{C}_{11,10}^1$ and $\mathfrak{C}_{11,01}^1$, which are nonzero when one includes bound states, shows the following. The complete expression for σ_{11} (including all correlation terms) does not have any contribution from bound states since it comes from $\tilde{P}_c\rho$ alone, whereas the total absorption is given by an expres-

sion the same as (4.15), which does include the bound states.

We now turn to the evaluation of the correlation term $\mathfrak{C}^1_{10,00}(\omega_L)$:

$$\mathfrak{C}^1_{10,00}(\omega_L) = \lim_{t\to\infty}\int_0^t \mathfrak{C}^1(t,\tau)_{10,00}e^{i\omega_L\tau}d\tau \qquad \text{(C9)}$$

$$= \lim_{t\to\infty}\int_0^t d\tau\int d^3p_1 N\int_\tau^t dt'\langle\langle 1\vec{p}_1 0\vec{p}_1|\tilde{V}_1\exp[(\tilde{L}_1+\tilde{S})(t-t')]|1\vec{p}_2 0\vec{p}_3\rangle\rangle e^{i\omega_L t}$$

$$\times\frac{\langle\langle|\vec{p}_2 0\vec{p}_3|\tilde{L}^E(t')|0\vec{p}_2 0\vec{p}_3\rangle\rangle}{\langle\langle|\vec{p}_2 0\vec{p}_3|\tilde{L}^E(0)|0\vec{p}_2 0\vec{p}_3\rangle\rangle}\langle\langle 0\vec{p}_2 0\vec{p}_3|\exp[(\tilde{L}_1+\tilde{S})(t'-\tau)]\tilde{V}_1|0\vec{p}_4 0\vec{p}_4\rangle\rangle\rho_{\vec{p}_4\vec{p}_4} \quad (t=-\infty)$$

$$= N\int d^3p_{1\ldots4}\left\langle\left\langle 1\vec{p}_1 0\vec{p}_1\right|\tilde{V}_1\frac{1}{i\omega_L+\tilde{L}_1+\tilde{S}}\left|1\vec{p}_2 0\vec{p}_3\right\rangle\right\rangle\lim_{\epsilon\to0}\left\langle\left\langle 0\vec{p}_2 0\vec{p}_3\right|\frac{1}{\epsilon+\tilde{L}_1+\tilde{S}}\tilde{V}_1\left|0\vec{p}_4 0\vec{p}_4\right\rangle\right\rangle\rho_{\vec{p}_4\vec{p}_4} \quad (t=-\infty)$$

$$= N\int d^3p_{1\ldots4}\left\langle\left\langle 1\vec{p}_1 0\vec{p}_1\right|\tilde{V}_1\frac{1}{i\omega_L+\tilde{L}_1-\frac{1}{2}\gamma}\left|1\vec{p}_2 0\vec{p}_3\right\rangle\right\rangle\lim_{\epsilon\to0}\left\langle\left\langle 0\vec{p}_2 0\vec{p}_3\right|\frac{1}{\epsilon+\tilde{L}_1}\tilde{V}_1\left|0\vec{p}_4 0\vec{p}_4\right\rangle\right\rangle\rho_{\vec{p}_4\vec{p}_4} \quad (t=-\infty)\,. \qquad \text{(C10)}$$

We have already noted the result

$$\lim_{\epsilon\to0}\frac{1}{\epsilon+\tilde{L}_1}\tilde{V}_1|0\vec{p}_4 0\vec{p}_4\rangle\rangle = |0\vec{p}_4 0\vec{p}_4\rangle\rangle - |E^0(\vec{p}_4),E^0(\vec{p}_4)\rangle\rangle \qquad \text{(C11)}$$

and we combine this identity with

$$|\hat{\rho}(kT)\rangle\rangle \equiv e^{-\hat{H}_1/kT} = \int d^3p_4|E^0(\vec{p}_4),E^0(\vec{p}_4)\rangle\rangle\rho_{\vec{p}_4\vec{p}_4} \quad (-\infty)\,, \qquad \text{(C12)}$$

where $\hat{H}_1$ is the full Hamiltonian for the perturber's motion in the presence of the active atom, to obtain

$$\mathfrak{C}_{10,00}(\omega_L) = N\int d^3p_{1,2,3}\left\langle\left\langle 1\vec{p}_1,0\vec{p}_1\right|\tilde{V}_1\frac{1}{i\omega_L+\tilde{L}_1-\frac{1}{2}\gamma}\left|1\vec{p}_2 0\vec{p}_3\right\rangle\right\rangle[\langle\langle 0\vec{p}_2 0\vec{p}_3|(\hat{\rho}(kT)-\hat{\rho}_0(kT))\rangle\rangle]\,. \qquad \text{(C13)}$$

Here

$$\hat{\rho}_0(kT) = \exp(-\hat{H}_0/kT)\,.$$

We can obtain an estimate for $\mathfrak{C}_{10,00}(\omega_L)$ in the following fashion. First we estimate $\hat{\rho}(\beta)-\hat{\rho}_0(\beta)$, where $\beta = kT$, as follows:

$$\hat{\rho}(\beta)-\hat{\rho}_0(\beta) \simeq -\int_0^\beta d\beta' e^{-\beta H_0}e^{\beta' H_0}V_1 e^{-\beta' H_0} \qquad \text{(C15)}$$

(Ref. 36). So we have

$$\langle\langle 0\vec{p}_2 0\vec{p}_3|[\rho_0(\beta)-\rho(\beta)]\rangle\rangle = \langle 0\vec{p}_2|[\hat{\rho}_0(\beta)-\hat{\rho}(\beta)]|0\vec{p}_3\rangle \simeq \exp[-\beta E(\vec{p}_2)]\frac{\langle 0\vec{p}_2|\tilde{V}_1|0\vec{p}_3\rangle}{E(\vec{p}_2)-E(\vec{p}_3)}\,(e^{+\beta[E(\vec{p}_2)-E(\vec{p}_3)]}-1)\,. \qquad \text{(C16)}$$

Thus we have the following estimate for $\mathfrak{C}_{10,00}(\omega_L)$

$$\mathfrak{C}_{10,00}(\omega_L) \simeq N\int d^3p_{1,2,3}\left\langle\left\langle 1\vec{p}_1 0\vec{p}_1\right|\tilde{V}_1\frac{1}{i\omega_L+\tilde{L}_1-\frac{1}{2}\gamma}\left|1\vec{p}_2 0\vec{p}_2\right\rangle\right\rangle\exp[-\beta E(\vec{p}_2)]\frac{\langle 0\vec{p}_2|\hat{V}|0\vec{p}_3\rangle}{E(\vec{p}_2)-E(\vec{p}_3)}$$

$$\times\{\exp[-\beta E(\vec{p}_2)-\beta E(\vec{p}_3)]-1\}\,. \qquad \text{(C17)}$$

Now if $\omega-\omega_L$ is much less than $kT/\hbar$ then $E(\vec{p}_2)-E(\vec{p}_3)$ will also be much less than kT in the important region for the integrand. We can then say

$$\mathfrak{C}_{10,00}(\omega_L) \simeq \frac{N}{kT}\int d^3p_{1,2,3}\left\langle\left\langle 1\vec{p}_1 0\vec{p}_2\right|\tilde{V}_1\frac{1}{i\omega_L+\tilde{L}_1-\frac{1}{2}\gamma}\left|1\vec{p}_2 0\vec{p}_3\right\rangle\right\rangle\langle 0\vec{p}_2|\hat{V}_1|0\vec{p}_3\rangle\rho_{\vec{p}_2\vec{p}_2}(t=-\infty)\,. \qquad \text{(C18)}$$

Now if, e.g., there were no interaction with the perturbers when the atom is in the upper level than we could

immediately write

$$\mathcal{C}^1_{10,00}(\omega_L) \simeq \gamma_c/(kT/\hbar)\,. \tag{C19}$$

In the far wings $\Delta\omega_L \gg 1/\tau_c$ it is useful to relate $\mathcal{C}_{10,00}(\omega_L)$ to the quasistatic expression for the absorption profile. In the text we have the solution, to order $|\Omega|^2$, for the upper-state population

$$\begin{aligned}
\sigma_{11} &= \frac{|\Omega|^2}{4\gamma}\left(\frac{\gamma+2\gamma_c(\Delta\omega_L)}{(\omega_0-\omega_L)^2} - \frac{2}{\Delta\omega_L}\,\mathrm{Im}[\mathcal{C}^1(\omega_L)_{10,00}]\right)\\
&= \frac{|\Omega|^2}{4\gamma}\left[\frac{\gamma}{(\Delta\omega_L)^2} + \frac{2\,\mathrm{Re}}{(\Delta\omega_L)^2}\left(\int d^3p_{1,2}\left\langle\left\langle 1\vec{p}_1 0\vec{p}_1\right|\tilde{V}_1\frac{-1}{i\omega_L+\tilde{L}_1+\tilde{S}}V_1\left|1\vec{p}_2 0\vec{p}_2\right\rangle\right\rangle\rho_{\vec{p}_2\vec{p}_2}(-\infty)\right)\right.\\
&\qquad\left. - \frac{2\,\mathrm{Im}}{\Delta\omega_L}\left(N\int d^3p_{1,3}\left\langle\left\langle 1\vec{p}_1 0\vec{p}_1\right|\tilde{V}_1\frac{1}{i\omega_L+\tilde{L}_1+\tilde{S}}\left|1\vec{p}_2 0\vec{p}_2\right\rangle\right\rangle\langle\langle 0\vec{p}_2 0\vec{p}_3|\,[\rho(kT)-\rho_0(kT)]\rangle\rangle\right)\right]\\
&= \frac{|\Omega|^2}{4\gamma}\left[\frac{\gamma}{(\Delta\omega_L)^2} + \frac{2\,\mathrm{Re}}{(\Delta\omega_L)^2}\left(\int d^3p_{1,2}N\langle\langle 1\vec{p}_1 0\vec{p}_1|E^1(\vec{p}_2)E^0(\vec{p}_3)\rangle\rangle\right.\right.\\
&\qquad\left.\left.\times\frac{\langle\langle E^1(\vec{p}_2)E^0(\vec{p}_3)|1\vec{p}_4 0\vec{p}_5\rangle\rangle\langle\langle 0\vec{p}_4 0\vec{p}_5|\hat{\rho}_0(kT)\rangle\rangle}{i(\omega_L-\omega_0)-\frac{1}{2}\gamma-i[E(\vec{p}_2)-E(\vec{p}_3)]/\hbar}\;\frac{[E(\vec{p}_2)-E(\vec{p}_3)]^2}{-\hbar^2}\right)\right.\\
&\qquad - \frac{2}{\Delta\omega}\,\mathrm{Im}\left(N\int d^3p_{1\ldots5}\langle\langle 1\vec{p}_1 0\vec{p}_1|E^1(\vec{p}_2)E^0(\vec{p}_3)\rangle\rangle\langle\langle E^1(\vec{p}_2)E^0(\vec{p}_3)\rangle\rangle|1\vec{p}_4 0\vec{p}_5\rangle\rangle\right.\\
&\qquad\left.\left.\times\frac{\langle\langle 0\vec{p}_4 0\vec{p}_5|(\hat{\rho}(kT)-\hat{\rho}_0(kT))\rangle\rangle}{i(\omega_L-\omega_0)-\frac{1}{2}\gamma-i[E^1(\vec{p}_2)-E^0(\vec{p}_3)]/\hbar}\;\frac{E^1(\vec{p}_2)-E^0(\vec{p}_3)}{i\hbar}\right)\right].
\end{aligned} \tag{C20}$$

If we now suppose that natural damping has a negligible effect on the collision we can let $\frac{1}{2}\gamma = +0$ and then combine the second two terms to obtain

$$\begin{aligned}
\sigma^1_{11} &= \frac{|\Omega|^2}{4\gamma}\left(\frac{\gamma}{(\Delta\omega_L)^2} + 2\pi N\int d^3p_{1,2,3}\langle\langle 1\vec{p}_1 0\vec{p}_1|E^1(\vec{p}_2)E^0(\vec{p}_3)\rangle\rangle\langle\langle E^1(\vec{p}_2)E^0(\vec{p}_3)|1\vec{p}_4 0\vec{p}_5\rangle\rangle\langle\langle 0\vec{p}_4 0\vec{p}_5|\rho(kT)\rangle\rangle\right)\\
&\quad\times\delta(E(\vec{p}_2)-E(\vec{p}_3)-\hbar(\omega_0-\omega_L))\,.
\end{aligned} \tag{C21}$$

Thus,

$$\sigma^1_{11} = \frac{|\Omega|^2}{4\gamma}\left[\frac{\gamma}{(\Delta\omega_L)^2} + 2\pi N\int |\langle E^1(\vec{p}_2)|E^0(\vec{p}_3)\rangle|^2\exp\left(-\frac{E(\vec{p}_3)}{kT}\right)\delta(E(\vec{p}_2)-E(\vec{p}_3)-\hbar\Delta\omega_L)\right], \tag{C22}$$

with, of course, the proviso with regard to bound states discussed above.

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