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# Collisional redistribution of radiation. III. The equation of motion for the correlation function and the scattered spectrum

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We present a calculation of the scattering of monochromatic radiation by a degenerate atom in the binary-collision approximation. We limit ourselves to field strengths such that $\Omega\tau_c \ll 1$, where $\Omega$ is the Rabi frequency for the atomic transition, and $\tau_c$ is the duration of a strong collision. Our calculation is not limited to the impact regime, $\Delta\omega \ll \tau_c^{-1}$, or to the region where thermal correlations may be neglected, i.e., $\Delta\omega \ll kT/\hbar$. (Here $\Delta\omega$ is the difference between either the incoming or outgoing photon's frequency and the atom's natural frequency.) To do this we derive an equation of motion for the correlation function, valid outside the quantum-regression regime, whose solution for practical cases is straightforward. We present solutions for the weak-field (linear-response) regime in terms of generalized absorption and emission profiles that depend on the indices of the atomic multipoles created.

## I. INTRODUCTION

We shall now turn to the calculation of the correlation function. This problem is similar to the ones we tackled in the first two papers[1,2]: We start with the formal and exact equation of motion for the correlation function and attempt to reduce it to a convenient subspace. The resulting equations of motion now differ slightly from those for the projected density matrix since the destruction terms must be kept (even when calculating a steady-state spectrum) and appear as separate inhomogeneous terms in the equation of motion for the correlation function. As far as weak-field scattering is concerned, the destruction terms play the same role with regard to emission as the correction to the collision operators did with regard to absorption. We obtain corrections to the scattered spectrum from the correlated events in absorption and emission. It is found that the type of event where absorption *and* emission takes place during a *single strong collision* is, in the context of the binary-collision approximation (BCA), of little importance except, perhaps, for the Stark broadening of hydrogenic lines. The same physical processes we include have been considered in a somewhat heuristic manner by Cooper.[3] Our treatment justifies his analysis, while at the same time giving more amenable expressions for the corrections to the scattered spectrum due to the breakdown of the factorization assumption.

The paper is divided as follows: In Sec. II, we discuss the formal implications, for the correlation function, of working outside the domain of the quantum-regression theorem. In Sec. III, the equation of motion for the dipole autocorrelation function of a degenerate system is derived and expressed in irreducible form. Using this equation, we derive the weak-incident-field scattered spectrum that includes all the effects of correlations. In Sec. IV the new terms due to correlation effects are discussed, their relative importance estimated, and their detailed evaluation for cases of importance outlined. Section V gives a summary and discussion of our principal results. It is shown how correlated events in the scattered spectrum are related to those in emission that may be observed by studying integrated intensities of fluorescence.

The analysis of this problem is novel in the following sense: We are able to calculate an exact two-time correlation function outside the domain of the quantum fluctuation-regression theorem. It shows clearly how extra dynamical information, from correlated events, appears in the scattered spectrum when either the microscopic process that causes relaxation cannot be assumed to be Markoffian, or one studies a system outside thermal equilibrium. We hope that as well as providing a means of describing collisional redistribution, and showing how the extra dynamical information—in this case for atom-perturber collisions—may be extracted, it provides a concrete model for some fundamental issues in statistical mechanics.

Alternative approaches[4,5] to the redistribution problem have been presented for nondegenerate systems that are, as yet, valid in a more restricted domain. They are, in the belief of the authors, quite capable of being generalized and we feel that they will reproduce the essential physics of our discussion.

## II. THE CORRELATION FUNCTION: FORMAL CONSIDERATIONS

We want to calculate the amount of scattering into a given mode of the radiation field and the way we do it is quite standard. First, we recognize that the rate of detection of photons may be related to the correlation function of the electric-field operator, i.e.,[6]

$$\langle \vec{E}^-(t_1)\cdot\vec{\epsilon}_2\vec{E}^+(t_2)\cdot\vec{\epsilon}_2^*\rangle \tag{2.1}$$

($\langle\ldots\rangle$ denotes an ensemble average). Here $E^-$ and $E^+$ are the negative and positive frequency components of the electric-field operator. This is, in turn, proportional to

$$C(t_1,t_2)=\langle \vec{d}^+(t_1)\cdot\vec{\epsilon}_2\vec{d}^-(t_2)\cdot\vec{\epsilon}_2^*\rangle\,, \tag{2.2}$$

where $\vec{d}$ is the dipole moment of the atom.[7]

We assume that both $t_1$ and $t_2$ are times when the atom has reached a stationary state in the presence of the driving field and, consequently, that $C(t_1,t_2)$ depends only on the difference between $t_1$ and $t_2$. In that case it can be shown[8] that the observed power spectrum is proportional to the quantity

$$2\,\mathrm{Re}\int_0^\infty e^{i\omega t}\langle \vec{d}^+(t)\cdot\vec{\epsilon}_2\vec{d}^-(t+\tau)\cdot\vec{\epsilon}_2^*\rangle\,. \tag{2.3}$$

In this expression $t$ must be a *typical* time in the steady state, so that we do not ignore the effect of initial correlations on the steady-state spectrum. We can write the ensemble average in the form

$$C(\tau)=\mathrm{Tr}[\hat\rho d^+(t)d^-(t+\tau)]\,, \tag{2.4}$$

where

$$d^+(t)=\vec{d}^+(t)\cdot\vec{\epsilon}_2\,,$$
$$d^-(t)=\vec{d}^-(t)\cdot\vec{\epsilon}_2^*\,,$$

and $\hat\rho$ is the complete density matrix for the atom in the presence of radiation and perturbers. For $t$ in (2.3) to be a typical time we must be consistent with our choice of initial conditions. We take the origin of the time evolution as $t=-\infty$, so that the Heisenberg picture operators (the $d^\pm$'s) coincide with the Schrödinger picture operators at this time. In papers I and II we argued that it was a very weak assumption to take $t=-\infty$ as a time when the density matrix for the complete system of atom + radiation + perturbers can be written in product form

$$\begin{aligned}\hat\rho(-\infty)&=\hat\rho_{\mathrm{atom}}\times\hat\rho_{\mathrm{pert}}\times\hat\rho_{\mathrm{RAD}}\\&=\hat\rho_{\mathrm{atom}}\times\hat\rho_{\mathrm{bath}}\,.\end{aligned} \tag{2.5}$$

It is then consistent to suppose that the $d$ operators commute with the perturber and radiation operators, i.e., are Schrödinger operators in the atomic subspace at $t=-\infty$.

Our aim is to reduce (2.4) to a single time average involving just the time difference $\tau$. To this end we write $C(\tau)$ in the form

$$C(\tau)=\mathrm{Tr}\{\tilde U(\tau)[\hat\rho(t)d^+]d^-\}\,, \tag{2.6}$$

where $\hat\rho(t)$ is the Schrödinger picture density operator at time $t$, and the Liouville-space evolution operator $\tilde U(\tau)^1$ acts only on $\hat\rho(t)d^+$. From papers I and II we know how to calculate the steady-state density operator $\hat\rho(t)$ in Eq. (2.6). We could directly reduce $C(\tau)$ if we could make the factorization assumption [Eq. (2.5)] at all times. Then Eq. (2.6), rewritten thus,

$$C(\tau)=\mathrm{Tr}_{\mathrm{atom}}(\mathrm{Tr}_{\mathrm{bath}}\{\tilde U(\tau)[\hat\rho(t)d^+]\}d^-)\,, \tag{2.7}$$

could be further simplified to the following form:

$$C(\tau)=\mathrm{Tr}_{\mathrm{atom}}\{\mathrm{Tr}_{\mathrm{bath}}[\tilde U(t)\hat\rho_{\mathrm{bath}}(0)][\hat\rho_{\mathrm{atom}}(t)d^+]d^-\}\,. \tag{2.8}$$

The equation of motion for $\hat\rho_{\mathrm{atom}}(t)d^+$ would then have precisely the same form as the equation of motion for the reduced density matrix $\hat\rho_a(t)$ (obtained using the factorization assumption). This is the quantum-regression theorem.[9] In a similar fashion we could reduce the correlation function in the case of thermal equilibrium. To see this we write

$$\begin{aligned}C(\tau)&=\mathrm{Tr}[e^{\tilde L\tau}(\hat\rho_{\mathrm{eq}}d^+)d^-]\\&=\mathrm{Tr}[\hat\rho_{\mathrm{eq}}(e^{\tilde L\tau}d^+)d^-]\\&=\mathrm{Tr}[\hat\rho_{\mathrm{eq}}d^+(\tau)d^-]\\&=\mathrm{Tr}_{\mathrm{atom}}\{\mathrm{Tr}_{\mathrm{bath}}[\hat\rho_{\mathrm{eq}}d^+(\tau)]d^-\}\,.\end{aligned} \tag{2.9}$$

The equation of motion for the correlation function would once again be obtained directly from the equation of motion for the reduced density matrix. Thus we would just need the equation of motion for a single time variable, $\mathrm{Tr}_{\mathrm{bath}}[\hat\rho_{\mathrm{eq}}d^+(\tau)]$, to obtain absorption and emission profiles. This is just Kirchoff's law for thermal equilibrium radiation processes in a different guise.

We are, of course, unable to use either of these simplifications. We cannot make the Markoff (or factorization at all times) approximation since it does not hold for the atom-perturber interaction[1] on the short time scales we want to study. Making the factorization assumption in calculating the emission spectrum amounts to the assumption that no emission evident is correlated with a particular perturber state or atom-perturber orientation. Since we know that emission in the far wings of a spectral line $\Delta\omega\gg 1/\tau_c$, *only* occurs during a strong collision—when atom and perturber are strongly coupled—the factorization assumption *must* fail at some point. Since, in addition, we are driving an atomic system with an external field the steady state cannot be thermal equilibrium and we must, therefore, stay with the general equation (2.6).

We shall proceed to derive an equation of motion for $C(\tau)$, using the same projection operators we did in paper I. The Markoff approximation for the matter-radiation interaction alone is, however, valid and it implies for our purposes that

$$\tilde{P}_{\mathrm{R}}\hat{\rho}(t) \equiv \hat{\rho}(t). \quad (2.10)$$

Physically, this means that the driving field has a negligible effect on the virtual processes that cause radiative relaxation, a direct result of their very short "memory" time. We can then write

$$C(\tau) = \mathrm{Tr}_{\mathrm{atom}}\{\mathrm{Tr}_{\mathrm{RAD}}[\tilde{U}(\tau)][\hat{\rho}_{\mathrm{atom}}(t)d^{+}]d^{-}\}, \quad (2.11)$$

where

$$\partial_t \mathrm{Tr}_{\mathrm{RAD}}[\tilde{U}(t)] = [\tilde{L}_0^{\mathrm{M}} + \tilde{V} + \tilde{S} + \tilde{L}^{\mathrm{E}}(t)]\,\mathrm{Tr}_{\mathrm{RAD}}[\tilde{U}(t)] \quad (2.12)$$

[see Eq. (2.32), paper I].

We concentrate now on the equation of motion for

$$\tilde{U}_{\mathrm{R}}(\tau)\hat{\rho}_{\mathrm{R}}(t)d^{+} = \hat{g}(\tau), \quad (2.13)$$

i.e.,

$$\partial_t \hat{g}(\tau) = \{\tilde{L}_0^{\mathrm{M}} + \tilde{V} + \tilde{S} + \tilde{L}^{\mathrm{E}}(t)\}\hat{g}(\tau). \quad (2.14)$$

The important quantity we need to calculate is $\tilde{P}_c\hat{g}(t)$. This is the projection of $\hat{g}(t)$ onto the factorized part of the atom-perturber system. Its equation of motion may be written in a similar form to that for the corresponding projection of the density operator $\tilde{P}_c\hat{\rho}(t)$, i.e.,

$$\partial_t \tilde{P}_c\hat{g}(t) = \tilde{P}_c[\tilde{L}_0^{\mathrm{A}} + \tilde{L}^{\mathrm{E}}(t) + \tilde{S}]\tilde{P}_c\hat{g}(t) + \int_0^t \tilde{P}_c\tilde{V}\tilde{Q}_c\tilde{\mathrm{g}}(t,t')\tilde{Q}_c\tilde{V}\tilde{P}_c\hat{g}(t')dt' + \tilde{P}_c\tilde{V}\tilde{Q}_c\tilde{\mathrm{g}}_c(t,0)[\tilde{Q}_c\hat{g}(0)]. \quad (2.15)$$

Note that the initial condition at some typical time, taken as $t=0$, now plays an important role since the last term in (2.15) is distinct from the others and cannot be simply combined to give an equation on the interval $(t,-\infty)$ of any use to us. Now $\tilde{Q}_c\hat{g}(0) = [\tilde{Q}_c\hat{\rho}_{\mathrm{R}}(t)]d^{+}$, since we assume that the dipole operator does not couple different translational states of the perturbers, and we have already calculated $\tilde{Q}_c\hat{\rho}_{\mathrm{R}}(t)$ [Eq. (3.6), paper I]:

$$\tilde{Q}_c\hat{\rho}_{\mathrm{R}}(t) = \int_{-\infty}^t \tilde{\mathrm{g}}_c(t,t')\tilde{Q}_c\tilde{V}\tilde{P}_c\hat{\rho}_{\mathrm{R}}(t')dt'. \quad (2.16)$$

Here $\tilde{\mathrm{g}}_c(t,t')$ satisfies the usual equation of motion [Eq. (3.2a), paper I], which is equivalent to

$$\partial_t\tilde{\mathrm{g}}_c(t,t') = \tilde{Q}_c[\tilde{L}_0^{\mathrm{M}} + \tilde{V} + \tilde{S} + \tilde{L}^{\mathrm{E}}(t)]\tilde{\mathrm{g}}_c(t,t').$$

So the equation of motion for $\tilde{P}_c\hat{g}(t)$ may be written in the form

$$\partial_t \tilde{P}_c\hat{g}(t) = \tilde{P}_c[\tilde{L}_0^{\mathrm{A}} + \tilde{L}^{\mathrm{E}}(t) + \tilde{S}]\tilde{P}_c\hat{g}(t) + \int_0^t \tilde{P}_c\tilde{V}\tilde{Q}_c\tilde{\mathrm{g}}_c(t,t')\tilde{Q}_c\tilde{V}\tilde{P}_c\hat{g}(t')dt' + \tilde{P}_c\tilde{V}\tilde{Q}_c\tilde{\mathrm{g}}_c(\tau,0)\left[\left(\tilde{Q}_c\int_{-\infty}^0 \tilde{\mathrm{g}}_c(0,\tau')\tilde{Q}_c\tilde{V}\tilde{P}_c\hat{\rho}_{\mathrm{R}}(t')dt'\right)d^{+}\right]. \quad (2.17)$$

Note that the object in large parentheses must be calculated first, before it acts on the $d^{+}$ operator. Now that we have the equation of motion for $\tilde{P}_c\hat{g}(t)$, the initial condition through (2.13) and the steady state for $\hat{\rho}_{\mathrm{R}}(t)$, we can calculate the spectrum. We shall, as before, concentrate on the BCA to these equations of motion, i.e.,

$$\partial_t \tilde{P}_c^1\hat{g}(t) = \tilde{P}_c^1[\tilde{L}_0^{\mathrm{A}} + \tilde{S} + \tilde{L}^{\mathrm{E}}(t)]\tilde{P}_c^1\hat{g}(t) + N_p\int_0^t \tilde{P}_c^1\tilde{V}_1 Q_c^1\tilde{\mathrm{g}}_c^1(t,t')\tilde{V}_1\tilde{P}_c^1\hat{g}(t')dt' + N_p\tilde{P}_c^1\tilde{V}_1\tilde{Q}_c\tilde{\mathrm{g}}_c^1(t,0) \times\left[\left(\int_{-\infty}^0 \tilde{Q}_c^1\tilde{\mathrm{g}}_c^1(t,t')\tilde{Q}_c^1\tilde{V}_1\tilde{P}_c^1\hat{\rho}_{\mathrm{R}}(t')dt'\right)d^{+}\right]. \quad (2.18)$$

Here $N_p$ is the number of perturbers in the normalization volume we choose. These equations describe the formation of the emission spectrum via the time dependence of the correlation function. Emission can occur outside or during a collision, and Eq. (2.18) describes all possible sequences of radiative and collisional events. It is, therefore, not limited to either the impact $t \gg \tau_c$ or $t \gg \hbar/kT$ regimes where $T$ is the translational temperature of the perturbers. To use these equations we shall need to express them in irreducible form, as we did with the equations of motion for the density matrix. This is achieved in the next section.

## III. THE EQUATION OF MOTION FOR THE CORRELATION FUNCTION IN IRREDUCIBLE FORM

We shall now consider the correlation function for a driven two-level atom the upper and lower levels having angular momentum $j_e$ and $j_g$, respectively. There may be other states that the collision couples into these two states, but we assume that the direct coupling to these levels via the driving field may be neglected. We shall not be concerned with effects due to inelastic or repopulating collisions from these other levels, as this has been discussed elsewhere.[9,10] They are mentioned since they are necessary for the existence of an effective interaction within the upper-state manifold (see paper II). Equation (2.18) shows that we need the corrections to the collision operator that we calculated in paper II. We also need the destruction terms in Eq. (2.18). The destruction terms, and corrections to the collision operator, represent correlated emission and absorption events and have, therefore, a very similar structure when expressed in terms of collision matrix elements. To show this we use the same methods as we did above to expand the exact propagator $\tilde{\mathcal{G}}_c(t,t')$ in powers of the driving field. If we wish to calculate only the weak-field scattered spectrum, an examination of the destruction operator informs us that we need only the first-order correction to the destruction operator. This is so because the presence of the dipole operator in the definition of $\hat{g}(\tau)$ makes the zeroth-order term in the destruction operator equivalent to the first-order term in the correction to the collision operator. By the same token, we see that we only need to expand the destruction operator to first-order in the driving field to obtain a consistent set of equations in which the collision operator is expanded to second order. The validity of the expansion in the driving field is, of course, the same as discussed in paper I, i.e., $\Omega\tau_c \ll 1$ where $\Omega$ is the on-resonance Rabi frequency. We shall limit our detailed discussion to the weak-field case, but it should be borne in mind that $\Omega\tau_c \ll 1$ is the only fundamental limitation on our treatment.

We shall consider here the equations of motion in the one interacting level (OIL) approximation, as this case exemplifies the interesting physics without unrealistically simplifying the problem. In Appendix A, we give the form of the destruction operator for the more general case where upper and lower levels interact with the perturbers. We use the following, slowly varying, quantities rather than the matrix elements of $\hat{g}(\tau)$:

$$
\begin{aligned}
f^{KQ}_{j_e j_e}(t) &= \langle\langle KQ j_e j_e | \hat{g}(t)\rangle\rangle ,\\
f^{KQ}_{j_g j_g}(t) &= \langle\langle KQ j_g j_g | \hat{g}(t)\rangle\rangle ,\\
f^{KQ}_{j_e j_g}(t) &= \langle\langle KQ j_e j_g | \hat{g}(t)\rangle\rangle\, e^{i\omega_L t} ,\\
f^{KQ}_{j_g j_e}(t) &= \langle\langle KQ j_g j_e | \hat{g}(t)\rangle\rangle\, e^{-i\omega_L t} .
\end{aligned}
\tag{3.1}
$$

Here $\omega_L$ is the frequency of the driving field. Then the Laplace transform of Eq. (2.18), written in irreducible form, is

$$
\begin{aligned}
-i\omega f^{KQ}_{j_e j_e}(\omega) - f^{KQ}_{j_e j_e}(t=0) &= {}^{j_e j_e}_{j_e j_e}M^K(\omega) f^{KQ}_{j_e j_e}(\omega) - \frac{2\Gamma_{eg}}{(2j_e+1)} f^{KQ}_{j_e j_e}(\omega)\\
&\quad + \frac{i}{\hbar}\sum_{qQ'K'} \mathcal{E}_0^*(\vec{\epsilon}\,{}^1_q)^* \langle j_g \| \vec{\mathrm{d}} \| j_e\rangle\, {}^{q}_{j_e j_g}G^{K'K}_{Q'Q}(-1)^{K+K'+j_e-j_g+Q+Q'}\\
&\qquad \times [1+\mathfrak{C}^1(K;ee;eg;\omega,\omega_L)]\, f^{K'Q'}_{j_e j_g}(\omega)\\
&\quad - \frac{i}{\hbar}\sum_{qQ'K'} \mathcal{E}_0(\vec{\epsilon}_1)_{-q} \langle j_e \| \vec{\mathrm{d}} \| j_g\rangle\, {}^{q}_{j_e j_g}G^{K'K}_{Q'Q}(-1)^{j_e-j_g}[1+\mathfrak{C}^1(K;ee;ge,\omega,\omega_L)] f^{K'Q'}_{j_g j_e}(\omega) ,\\
\left(-i(\omega+\omega_L-\omega_{eg}) + \frac{\Gamma_{eg}}{2j_e+1}\right) f^{KQ}_{j_e j_g}(\omega) - f^{KQ}_{j_e j_g}(t=0)
&= {}^{j_e j_g}_{j_e j_g}M^K(\omega+\omega_L) f^{KQ}_{j_e j_g}(\omega) + \frac{1}{i\hbar}\sum_{q'Q'K'} \langle j_e \| \vec{\mathrm{d}} \| j_g\rangle (\vec{\epsilon}\,{}^1)_{-q'}\mathcal{E}_0\\
&\qquad \times \{ {}^{q'}_{j_g j_e}G^{KK'}_{-Q-Q'}(-1)^{K+K'+Q+Q'} f^{K'Q'}_{j_g j_g}(\omega)\\
&\qquad + {}^{q'}_{j_g j_e}G^{KK'}_{-Q-Q'}(-1)^{Q+Q'}[1+\mathfrak{C}^1(K',eg,ee,\omega,\omega_L)] f^{K'Q'}_{j_e j_e}(\omega)\}\\
&\quad + D_0(K,eg,ee,\omega) + D_1^{(iii)}(K,Q;eg,ee,eg) + D_1^{(ii)}(K,Q;eg,ee,ge) + D_1^{(i)}(K,Q;eg,gg,ge) .
\end{aligned}
\tag{3.2}
$$

Here

$$
D_0(K,eg,ee,\omega) = \sum_{K'Q'q'} (\vec{\epsilon}\,{}^2)_{q'} \langle j_e \| \vec{\mathrm{d}} \| j_g\rangle\, {}^{q'}_{j_e j_g}G^{KK'}_{QQ'}(-1)^{j_e+j_g+K'}\, \mathfrak{C}^1(K',eg,ee,\omega)\, \sigma^{K'Q'}_{j_e j_e} .
\tag{3.3}
$$

Then $f^{KQ'}_{j_g j_e}(\omega)$ can be obtained from the same equation for $f^{KQ}_{j_e j_g}$ by using the tensor relation $T^{KQ}(j_e j_g) = T^{K-Q}(j_g j_e)^*(-1)^{j_e+j_g+Q}$, and dropping the destruction terms

$$-i\omega f^{KQ}_{j_gj_g}(\omega)-f^{KQ}_{j_gj_g}(t=0)-\theta(j_e,j_g,K)f^{KQ}_{j_ej_e}(\omega)=\frac{i}{\hbar}\sum_{qQ'K'}\mathcal{E}_0\langle j_e\|\vec{d}\|j_g\rangle(\vec{\epsilon}^{\,1})_{-q}(-1)^{K+K'}[{}^{q}_{j_gj_e}G^{K'K}_{Q'Q}](-1)^{j_e-j_g}f^{K'Q'}_{j_gj_e}(\omega)$$
$$-\frac{i}{\hbar}\sum_{qQ'K'}\langle j_g\|\vec{d}\|j_e\rangle(-1)^{j_e-j_g+Q-Q'}[{}^{q}_{j_gj_e}G^{K'K}_{Q'Q}](\vec{\epsilon}^{\,\prime}_q)^*\mathcal{E}_0^*f^{K'Q'}_{j_ej_g}(\omega). \quad (3.4)$$

The driving field has the form $\vec{E}(t)=\mathcal{E}\vec{\epsilon}_1+\mathcal{E}^*\vec{\epsilon}_1^{\,*}$, $\mathcal{E}=\mathcal{E}_0e^{-i\omega_Lt}$, the outgoing scattered field has polarization vector $\vec{\epsilon}^{\,2}$, and $\theta$ is defined thus

$$\theta(j_e,j_g,K)=(-1)^{j_e+j_g+K+1}(2j_e+1)\begin{Bmatrix} j_e & j_e & K\\ j_g & j_g & 1\end{Bmatrix}2\Gamma_{eg}.$$

Here, we need the following quantities [for the definition of the $G$'s and $\mathcal{C}^1(K,eg,ee,\omega)$, see paper II]:

$$\mathcal{C}^1(K',eg,ee,\omega,\omega_L)=\sum(-1)^{Q+\mu_e^1+\mu_e^5}\begin{pmatrix} j_e & j_e & K'\\ \mu_e^4 & -\mu_e^5 & Q\end{pmatrix}\begin{pmatrix} j_e & j_e & K'\\ \mu_e^3 & -\mu_e^1 & -Q\end{pmatrix}$$
$$\times N_p\lim_{\epsilon\to 0}\left\langle\!\!\left\langle j_e\mu_e^1j_g\mu_g^1\right|\mathrm{Tr}'\left(\tilde{V}_1\frac{1}{\epsilon+i\omega+\omega_L+\tilde{L}_1+\tilde{S}}|j_e'\mu_e^2j_g\mu_g^1\rangle\rangle\right.\right.$$
$$\left.\left.\times\langle\langle j_e'\mu_e^2j_e\mu_e^3|\frac{1}{\epsilon+i\omega+\tilde{L}_1+\tilde{S}}\tilde{V}_1\hat{\rho}_1(-\infty)\right)\right|j_e\mu_e^4j_e\mu_e^5\rangle\!\!\rangle, \quad (3.5)$$

where the summation is over the $\mu$'s, $Q$, and $j_e'$. Here the Tr$'$ indicates the angular part of the average over perturbers, which has been performed. The number of perturbers in the quantization volume is $N_p$. Note that the intermediate states in the collision operator include other excited states coupled to $j_e$ by the collisional interaction:

$$D_1^{(i)}(K_1Q_1;eg,gg,ge,\omega)=\frac{1}{i\hbar}\sum(2K_1+1)^{1/2}(2K_2+1)^{1/2}\mathcal{E}_0(-1)^{j_e^3+j_g+K_1+K_3+q}$$
$$\times(\vec{\epsilon}_2)_{-q'}(\vec{\epsilon}_1)_{-q}d^{(i)}(K_3;eg,gg,ge,\omega)(2K_3+1)\begin{pmatrix} K_3 & 1 & K_1\\ Q_3 & -q^1 & Q_1\end{pmatrix}\begin{pmatrix} K_3 & 1 & K_2\\ -Q_3 & q & Q_2\end{pmatrix}$$
$$\times\begin{Bmatrix} j_e^3 & j_e^1 & K_3\\ K_1 & 1 & j_g\end{Bmatrix}\begin{Bmatrix} j_e^2 & j_e^4 & K_3\\ K_2 & 1 & j_g\end{Bmatrix}\langle j_e^2\|\vec{d}\|j_g\rangle\langle j_e^3\|\vec{d}\|j_g\rangle\sigma^{K_2Q_2}_{j_gj_e^4},$$

where the summation is over the $q$'s, $Q_3$, $K_2$, $K_3$, $j_e^2$, and $j_e^3$; and

$$d^{(i)}(K_3;eg,gg,ge,\omega)=\sum\begin{pmatrix} j_e^3 & j_e^1 & K_3\\ \mu_e^3 & -\mu_e^1 & Q_3^1\end{pmatrix}\begin{pmatrix} j_e^2 & j_e^4 & K_3\\ -\mu_e^2 & \mu_e^4 & -Q_3^1\end{pmatrix}(-1)^{\mu_e^2-\mu_e^1}$$
$$\times N_p\lim_{\epsilon\to 0}\left\langle\!\!\left\langle j_e^1\mu_e^1j_g\mu_g^1\right|\mathrm{Tr}_1'\left(\tilde{V}_1\frac{1}{i(\omega+\omega_L)+\tilde{L}_1+\tilde{S}+\epsilon}|j_e^2\mu_e^2j_g\mu_g^1\rangle\rangle\right.\right.$$
$$\times\langle\langle j_g\mu_g^1j_g\mu_g^1|\frac{1}{i\omega+\tilde{L}_1+\tilde{S}+\epsilon}|j_g\mu_g^2j_g\mu_g^1\rangle\rangle$$
$$\left.\left.\times\langle\langle j_g\mu_g^2j_e^3\mu_e^3|\frac{1}{-i\omega_L+\epsilon+\tilde{L}_1+\tilde{S}}\tilde{V}_1\hat{\rho}_1\right)\right|j_g\mu_g^2j_e^4\mu_e^4\rangle\!\!\rangle; \quad (3.6)$$

the summation being over the $\mu$'s and $Q_3^1$.

$$D_1^{(ii)}(K_1Q_1,eg,ee,ge,\omega)=\sum(2K_1+1)^{1/2}\frac{(2K_2+1)^{1/2}}{i\hbar}(2K_3+1)(-1)^{K_2-Q_2+j_e^6-j_g}$$
$$\times\mathcal{E}_0(\vec{\epsilon}_1)_{-q}(\vec{\epsilon}_2)_{-q^1}\begin{pmatrix} 1 & K_3 & K_1\\ q_1 & -Q_3 & Q_1\end{pmatrix}\begin{pmatrix} 1 & K_3 & K_2\\ -q & Q_3 & Q_2\end{pmatrix}\begin{Bmatrix} j_e^1 & j_g & j_e^3\\ 1 & K_3 & j_e\end{Bmatrix}$$
$$\times\langle j_g\|\vec{d}\|j_e^4\rangle\langle j_e^3\|\vec{d}\|j_e\rangle\begin{Bmatrix} 1 & j_g & j_e^4\\ j_e^4 & K_3 & K_2\end{Bmatrix}d^{(ii)}(K_3;eg,ee,ge,\omega)\sigma^{K_2Q_2}_{j_gj_e^6},$$

where the summation is over $K_2$, $K_3$, $j_e^2$, $j_e^3$, $j_e^4$, $j_e^5$, all the $Q$'s and $q$'s, and

$$d^{(ii)}(K_3; eg, ee, ge, \omega) = \sum \begin{pmatrix} j_e^1 & j_e^3 & K_3 \\ \mu_e^1 & -\mu_e^3 & Q_3^1 \end{pmatrix} \begin{pmatrix} j_e^6 & j_e^4 & K_3 \\ \mu_e^6 & -\mu_e^4 & -Q_3^1 \end{pmatrix} (-1)^{K_3+j_e^4+j_e^6+\mu_e^4+\mu_e^6}$$

$$\times \lim_{\epsilon\to 0} N_p \Big\langle\Big\langle j_e^1\mu_e^1 j_g\mu_g^1 \Big| \mathrm{Tr}_1'\Big(\tilde{V}_1 \frac{1}{\tilde{S}+\tilde{L}_1+i(\omega+\omega_L)+\epsilon} |j_e^2\mu_e^2 j_g\mu_g^1\rangle\rangle$$

$$\times \langle\langle j_e^2\mu_e^2 j_e^3\mu_e^3 | \frac{1}{\epsilon+\tilde{S}+\tilde{L}_1} | j_e^4\mu_e^4 j_e^5\mu_e^5\rangle\rangle$$

$$\times \langle\langle j_g\mu_g^2 j_e^5\mu_e^5 | \frac{1}{\tilde{S}+\tilde{L}_1-i\omega_L+\epsilon} \tilde{V}_1\rho\Big)\Big| j_g\mu_g^2 j_e^6\mu_e^6\Big\rangle\Big\rangle . \tag{3.7}$$

The summation in this case is over the $\mu$'s and $Q_3^1$.

$$D_1^{(iii)}(KQ; eg, ee, eg, \omega) = \sum (2K_1+1)^{1/2}(2K_2+1)^{1/2} \begin{pmatrix} 1 & K_3 & K_1 \\ q^1 & -Q_3 & -Q_1 \end{pmatrix} \begin{pmatrix} 1 & K_3 & K_2 \\ q & Q_3 & Q_2 \end{pmatrix}$$

$$\times \begin{Bmatrix} 1 & j_g & j_e^3 \\ j_e^1 & K_3 & K_1 \end{Bmatrix} \begin{Bmatrix} 1 & j_g & j_e^5 \\ j_e^5 & K_3 & K_2 \end{Bmatrix} (-1)^{K_2-Q_2+j_e^6-j_g}(2K_3+1)\langle j_g \|\vec{d}\| j_e^5\rangle\langle j_e^3\|\vec{d}\|j_g\rangle$$

$$\times (\vec{\epsilon}_1^{\,*})_{-q}(\vec{\epsilon}_2)_{-q^1} \frac{\mathcal{E}_0^*}{i\hbar} d^{(iii)}(K_3; eg, ee, eg)\sigma^{K_2Q_2}_{j_e^6 j_g},$$

where the summation is over $K_2$, $K_3$, all $q$'s and $Q$'s; and

$$d^{(iii)}(K_3; eg, ee, eg, \omega) = \sum \begin{pmatrix} j_e^1 & j_e^3 & K_3 \\ \mu_e^1 & -\mu_e^3 & Q_3^1 \end{pmatrix} \begin{pmatrix} j_e^5 & j_e^6 & K_3 \\ \mu_e^5 & -\mu_e^6 & -Q_3^1 \end{pmatrix} (-1)^{K_3+j_e^5+j_e^6+\mu_e^3+\mu_e^6+1}$$

$$\times \lim_{\epsilon\to 0} N_p \Big\langle\Big\langle j_e^1\mu_e^1 j_g\mu_g^1 \Big| \mathrm{Tr}_1'\Big(\tilde{V}_1 \frac{1}{\tilde{L}_1+\tilde{S}+i(\omega+\omega_L)+\epsilon} |j_e^2\mu_e^2 j_g\mu_g^1\rangle\rangle$$

$$\times \langle\langle j_e^2\mu_e^2 j_e\mu_e^3 | \frac{1}{\epsilon+\tilde{L}_1+\tilde{S}} | j_e^4\mu_e^4 j_e^5\mu_e^5\rangle\rangle$$

$$\times \langle\langle j_e^4\mu_e^4 j_g\mu_g^2 | \frac{1}{\tilde{L}_1+\tilde{S}+i\omega_L+\epsilon} \tilde{V}_1\hat{\rho}_1\Big)\Big| j_e^6\mu_e^6 j_g\mu_g^2\Big\rangle\Big\rangle ; \tag{3.8}$$

the summation being over the $\mu$'s and $Q_3^1$. Here the $\sigma$'s are the steady-state values of the reduced density matrix expressed in irreducible form (see paper II). The generalizations of these operators to the case where both levels interact with perturbers are given in Appendix A. We have labeled these destruction terms (*i*), (*ii*), and (*iii*) since they are, in essence, the correlation corrections to the $F^{(i)}$, $F^{(ii)}$, and $F^{(iii)}$ terms of Omont, Smith, and Cooper.[11] Cooper[3] has considered these corrections, but was not able to explicitly separate them from the "uncorrelated" terms. Our analysis achieves this separation and as we shall see clarifies his analysis. Now we note the following:

$$\begin{aligned} C(\omega) &= \mathrm{Tr}_{\mathrm{atom}}[\hat{g}(\omega)d^-] \\ &= \sum_{m_1m_2} \langle j_1m_1|\hat{g}(\omega)|j_2m_2\rangle\langle j_2m_2|\vec{d}|j_1m_1\rangle\cdot\vec{\epsilon}_2^{\,*} \\ &= \frac{1}{\sqrt{3}}\sum_q g^{1,-q}_{j_ej_g}(\omega)(-1)^{j_e-j_g}\langle j_g\|\vec{d}\|j_e\rangle(\vec{\epsilon}_2^{\,*})_{-q} . \end{aligned} \tag{3.9}$$

The weak-field solution for $g^{1,-q}_{j_ej_g}(\omega) = f^{1,-q}_{j_ej_g}(\omega-\omega_L)$ is then

$$f^{1,-q}_{j_ej_g}(\omega-\omega_L) = \frac{1}{-i(\omega-\omega_{eg}) + \dfrac{\Gamma_{eg}}{(2j_e+1)} - {}^{j_ej_g}_{j_ej_g}M^1(\omega)}$$

$$\times\Big(\frac{i/\hbar}{-i(\omega-\omega_L)} \sum_{K'Q'q'} \langle j_e\|\vec{d}\|j_g\rangle(\vec{\epsilon}_1)_{-q'}\mathcal{E}_0{}^{q'}_{j_gj_e}G^{1K'}_{q-Q'}(-1)^{K'+Q'+1-q'} f^{K'Q'}_{j_gj_g}(t=0)$$

$$+ f^{1,-q}_{j_ej_g}(t=0) + \sum_{K'Q'q'} (\vec{\epsilon}_2)_{q'}\langle j_e\|\vec{d}\|j_g\rangle{}^{q'}_{j_ej_g}G^{1K'}_{-qQ'}(-1)^{K'-Q'+q}\,\mathcal{C}^1(K', eg, ee, \omega)\sigma^{K'Q'}(j_ej_e)$$

$$+D^{(i)}(1,-q; eg, gg, ge, \omega-\omega_L) + D^{(ii)}(1,-q; eg, ee, ge, \omega-\omega_L) + D^{(iii)}(1,-q; eg, ee, eg, \omega-\omega_L)\Big). \tag{3.10}$$

We need the following:

$$f^{KQ}_{j_1 j_2}(t=0) = \langle\langle KQ j_1 j_2 |\, \hat{\sigma}(t=0)\vec{d}^{+}\cdot\vec{\epsilon}_2\rangle\rangle$$

$$= \sum_{K'Q'q'} \sigma^{K'Q'}_{j_1 j_e}(-1)^{q'+Q}(\vec{\epsilon}_2)_{-q'}(-1)^{j_1+j_g}\langle j_e \| \vec{d} \| j_g\rangle$$

$$\times (2K+1)^{1/2}(2K'+1)^{1/2}\begin{pmatrix} K' & 1 & K \\ -Q' & -q' & Q\end{pmatrix}\begin{Bmatrix} K' & 1 & K \\ j_g & j_1 & j_e\end{Bmatrix}\delta(j_2 j_g)\,. \tag{3.11}$$

So we have

$$f^{1,-q}_{j_e j_g}(t=0) = \sum_{K'Q'q'} \sigma^{K'Q'}_{j_e j_e}(-1)^{q'-q+j_e+j_g}(\vec{\epsilon}_2)_{+q'}$$

$$\times \sqrt{3}\,(2K'+1)^{1/2}\begin{pmatrix} K' & 1 & 1 \\ -Q' & q' & -q\end{pmatrix}\begin{Bmatrix} K' & 1 & 1 \\ j_g & j_e & j_e\end{Bmatrix}\langle j_e \| \vec{d} \| j_g\rangle\,. \tag{3.12}$$

We note also,

$$f^{KQ}_{j_g j_g}(t=0) = \sum_{K'Q'q'} \sigma^{K'Q'}_{j_g j_e}(-1)^{q'+Q}(\vec{\epsilon}_2)_{+q'}(2K+1)^{1/2}(2K'+1)^{1/2}\begin{pmatrix} K' & 1 & K \\ -Q' & q' & +Q\end{pmatrix}\begin{Bmatrix} K' & 1 & K \\ j_g & j_g & j_e\end{Bmatrix}\langle j_e \| \vec{d} \| j_g\rangle\,, \tag{3.13}$$

where

$$\sigma^{KQ}_{j_g j_e} = \sum_{q'}\left(\frac{1}{i\hbar}\right)\left(\frac{1}{-i(\omega_{eg}-\omega_L) - {}^{j_g j_e}_{j_g j_e}M^1(\omega_L) + \dfrac{\Gamma_{eg}}{2j_e+1}}\right)\langle j_g \| \vec{d} \| j_e\rangle(\vec{\epsilon}_1^{\,*})_{-q'}\mathcal{E}_0^{*}\frac{N_a}{(2j_g+1)}(-1)^{j_e+j_g+1-q'}\sqrt{3}$$

$$\times\,\delta(K=1)\delta(Q=q')\,. \tag{3.14}$$

Here, $N_a$ is the ground-state atomic population. Thus

$$f^{KQ}_{j_g j_g}(t=0) = \sum_{q_1 q_2}\frac{(\mathcal{E}_0)^*}{i\hbar}(-1)^{j_e+j_g+1}(\vec{\epsilon}_2)_{q_1}(\vec{\epsilon}_1^{\,*})_{-q_2}\begin{pmatrix} 1 & 1 & K \\ -q_2 & q_1 & +Q\end{pmatrix}$$

$$\times\langle j_e \| \vec{d} \| j_g\rangle\langle j_g \| \vec{d} \| j_e\rangle\frac{N}{(2j_g+1)}\begin{Bmatrix} 1 & 1 & K \\ j_g & j_g & j_e\end{Bmatrix}(2K+1)^{1/2}$$

$$\times\left(\frac{1}{-i(\omega_{eg}-\omega_L) - {}^{j_g j_e}_{j_g j_e}M^1(\omega_L) + \dfrac{\Gamma_{eg}}{2j_e+1}}\right). \tag{3.15}$$

From paper II we know also

$$\sigma^{KQ}(j_e j_e) = \frac{|\mathcal{E}_0|^2}{\hbar^2}\langle j_g \| \vec{d} \| j_e\rangle^2(2K+1)^{1/2}\sum_{q_1 q_2}(\vec{\epsilon}_1^{\,*})_{q_1}(\vec{\epsilon}_1)_{-q_2}\begin{pmatrix} 1 & 1 & K \\ q_2 & -q_1 & -Q\end{pmatrix}(-1)^{j_e+j_g+q_2+K+1}\begin{Bmatrix} 1 & 1 & K \\ j_e & j_e & j_g\end{Bmatrix}$$

$$\times\left(\frac{N_a}{\left(-{}^{j_e j_e}_{j_e j_e}M^K(0) + \dfrac{2\Gamma_{eg}}{(2j_e+1)}\right)(2j_g+1)}\right)$$

$$\times\,2\,\mathrm{Re}\left(\frac{1}{-{}^{j_e j_g}_{j_e j_g}M^1(\omega_L) + i(\omega_{eg}-\omega) + \dfrac{\Gamma_{eg}}{(2j_e+1)}}[1+\mathcal{C}^1(K, ee, eg, \omega_L)]\right). \tag{3.16}$$

Thus the weak-field scattered spectrum may be written in the following form:

$$C(\omega)=\sum_q \frac{f^{1,-q}_{j_e j_g}(\omega-\omega_L)}{\sqrt{3}}(-1)^{j_e-j_g}\langle j_g\|\vec{d}\|j_e\rangle(\vec{\epsilon}_2^{\,*})_{-q} \tag{3.17}$$

$$=\left(\frac{1}{-i(\omega-\omega_{eg})-\frac{\Gamma_{eg}}{2j_e+1}-{}^{j_e j_g}_{j_e j_g}M^1(\omega)}\right)$$

$$\times\sum_q(-1)^{j_e-j_g}\langle j_g\|\vec{d}\|j_e\rangle\frac{(\vec{\epsilon}_2^{\,*})_{-q}}{\sqrt{3}}$$

$$\times\Bigg[\sum_{K'Q'q'}(-1)^{j_e-j_g}(\vec{\epsilon}_2)_{q'}\sqrt{3}\,(2K'+1)^{1/2}\langle j_e^3\|\vec{d}\|j_g\rangle$$

$$\times[1+\mathcal{C}^1(K',eg,ee,\omega)]\begin{pmatrix}K & 1 & 1\\ -Q' & q' & -q\end{pmatrix}\begin{Bmatrix}K' & 1 & 1\\ j_g & j_e & j_e\end{Bmatrix}\sigma^{K'Q'}(j_e j_e)$$

$$+\frac{i/\hbar}{-i(\omega-\omega_L)}\sum_{K'Q'q'}\langle j_e\|\vec{d}\|j_g\rangle(\vec{\epsilon}_1)_{-q'}\mathcal{E}_0\,{}^{q'}_{j_g j_e}G^{1K'}_{q\,-Q'}(-1)^{K'+Q'-q}$$

$$\times\sum_{q_2q_1}\frac{(\mathcal{E}_0)^*}{i\hbar}(-1)^{j_e+j_g}(\vec{\epsilon}_2)_{q_1}(\vec{\epsilon}_1^{\,*})_{q_2}(2K'+1)^{1/2}$$

$$\times\begin{pmatrix}1 & 1 & K'\\ -q_2 & q_1 & Q'\end{pmatrix}\begin{Bmatrix}1 & 1 & K'\\ j_g & j_g & j_e^2\end{Bmatrix}\langle j_e\|\vec{d}\|j_g\rangle\langle j_g\|\vec{d}\|j_e^2\rangle\frac{N_a}{(2j_g+1)}$$

$$\times\left(\frac{1}{-i(\omega_{eg}-\omega_L)-{}^{j_g j_e}_{j_g j_e}M^1(\omega_L)+\Gamma_{eg}/(2j_e+1)}\right)$$

$$+D_1^{(i)}(1,-q;eg,gg,ge,\omega-\omega_L)+D_1^{(ii)}(1,-q;eg,ee,ge,\omega-\omega_L)+D_1^{(iii)}(1,-q;eg,ee,eg,\omega-\omega_L)\Bigg]. \tag{3.18}$$

## IV. CORRELATION TERMS IN THE SPECTRUM

Now that we have the formal result for the scattered spectrum we shall discuss the relative importance of the uncorrelated, the $D$, and the $C$ terms. First, let us consider the $D_1^{(i)}$ term which is a correction to the Rayleigh scattering, in the sense that the same sequence of density matrix elements occurs in it, as does in the normal $F^{(i)}$ term[3,7] that gives the Rayleigh scattering. This sequence includes a propagation in a superposition of the initial and final states—this is shown most clearly when one considers Raman rather than Rayleigh scattering (see Fig. 1).

We write the spherically averaged operator that occurs in $D^{(i)}$ and $d^{(i)}$ in the following form:

$$\sum(-1)^{K-Q_3+\mu_e^2-\mu_e^1}\begin{pmatrix}j_e & j_e & K\\ \mu_e^1 & -\mu_e^3 & Q\end{pmatrix}\begin{pmatrix}j_e & j_e & K\\ -\mu_e^2 & \mu_e^4 & Q\end{pmatrix}$$

$$\times\lim_{\epsilon\to 0}\int_0^\infty e^{-i\Delta\omega_2\tau_3}d\tau_3\int_0^\infty e^{i\Delta\omega_{12}\tau_2-\epsilon\tau_2}\int_0^\infty d\tau_1\,e^{i\Delta\omega_1\tau_1}$$

$$\times\mathrm{Tr}_1'[\langle\langle j_e\mu_e^1 j_g\mu_g^1|\tilde{V}_1^I(\tau_1+\tau_2+\tau_3)\tilde{U}_1^I(\tau_1+\tau_2+\tau_3,\tau_1+\tau_2)|j_e\mu_e^3 j_g\mu_g^1\rangle\rangle$$

$$\times\langle\langle j_g\mu_g^2 j_e\mu_e^2|\tilde{U}_1^I(\tau_1,0)\tilde{V}_1^I(0)\hat{\rho}_1(-\infty)|j_g\mu_g^2 j_e\mu_e^4\rangle\rangle], \tag{4.1}$$

the summation is over the $\mu$'s and $Q$. Here $\Delta\omega_2=\omega_{eg}-\omega+i\gamma_N/2$, $\Delta\omega_1=\omega_{eg}-\omega_L-i\gamma_N/2$, $\Delta\omega_{12}=\omega-\omega_L$, and we have introduced interaction picture operators $U_1^I$ (see II). This $D_1^{(i)}$ term vanishes in the weak-collision limit obtained by putting the $\tilde{U}^{I}$'s equal to the identity operator in Liouville space, since the expectation value of the interaction $\tilde{V}_1^I(\tau)$ in any given state vanishes. If we suppose that we can use an adiabatic approximation, for the coupling of other excited states of the atom into $j_e$, then we can replace

$\tilde{V}_1^{\rm I}$ by $\tilde{V}_1^{\rm I}$eff, and treat $|j_e\mu_e\rangle$ as a complete set of states. We can then reduce the $K=0$ component to the following form. We shall only estimate the $K=0$ components of $d^{(i)}$, $d^{(ii)}$, and $d^{(iii)}$, since we expect them to provide reasonable estimates for $K\neq 0$ also,

$$\lim_{\epsilon\to 0}\frac{1}{(2j_e+1)}\sum_{\mu_e^1}\int_0^\infty e^{-i\Delta\omega_2\tau_3}d\tau_3 \times\int_0^\infty e^{i\Delta\omega_{12}\tau_2-\epsilon\tau_2}\int_0^\infty e^{i\Delta\omega_1\tau_1} \times \mathrm{Tr}_1'[\langle j_e\mu_e^1|\hat{V}_1^{\rm I}(\tau_3+\tau_2)\hat{U}_1^{\rm I}(\tau_2+\tau_3,\tau_2)\hat{V}_1^{\rm I}(-\tau_1)\hat{U}_1^{\rm I}(0,-\tau_1)^\dagger|j_e\mu_e^1\rangle]. \qquad (4.2)$$

If $\omega-\omega_L=\Delta\omega_{12}$ is less than $\tau_c^{-1}$, we can use the following argument to give an upper estimate to the integral. We know that the integrand takes its maximum value (as a function of $\tau_2$) when $\tau_2=0$, and decays on a time scale comparable with the duration of a strong collision.[1] An upper estimate is, thus, given by

$$\lim_{\epsilon\to 0}\sum_{\mu_e^1}\frac{\tau_c}{(2j_e+1)}\int_0^\infty e^{-i\Delta\omega_2\tau_3}d\tau_3\int_0^\infty e^{i\Delta\omega_1\tau_1}d\tau_1\,\mathrm{Tr}_1'[\langle j_e\mu_e^1|\hat{V}(\tau_3)\hat{U}_1^{\rm I}(\tau_3,0)V(-\tau_1)\hat{U}_1^{\rm I}(0,-\tau_1)^\dagger|j_e\mu_e^1\rangle]$$
$$=\lim_{\epsilon\to 0}\sum_{\mu_e^1}\frac{\tau_c}{(2j_e+1)}(\Delta\omega_2\Delta\omega_1)\int_0^\infty e^{-i\Delta\omega_2\tau_3}d\tau_3\int_0^\infty e^{i\Delta\omega_1\tau_1}d\tau_1\,\mathrm{Tr}_1'\{\langle j_e\mu_e^1|[\hat{U}_1^{\rm I}(\tau_3,0)-1][\hat{U}_1^{\rm I}(0,-\tau_1)^\dagger-1]|j_e\mu_e^1\rangle\}. \qquad (4.3)$$

If, on the other hand, $\Delta\omega_{12}\gg\tau_c^{-1}$, we can replace $\tau_c$ by $1/i\Delta\omega_{12}$. Thus, we can summarize our estimates, for $d^{(i)}$ and $K=0$, in the following expression:

$$\frac{1}{(\Delta\omega_{12}+i\tau_c^{-1})}\left[\left(\frac{{}^{ge}_{ge}M^1(-\omega_L)}{\Delta\omega_1}-\frac{{}^{eg}_{eg}M^1(\omega)}{\Delta\omega_2}\right)+\frac{i\Delta\omega_1\Delta\omega_2}{(\omega-\omega_L+i\gamma_N)}\left(\frac{{}^{eg}_{eg}M^1(\omega)}{\Delta\omega_2^2}+\frac{{}^{ge}_{ge}M^1(-\omega_L)}{\Delta\omega_1^2}\right)\right] \qquad (4.4)$$

(see Appendix B).

We can estimate $d^{(ii)}$ in the same manner as we did $d^{(i)}$; the weak-collision limit vanishes, and the effect of the $\tau_2$ propagation, now in the excited rather than the ground state, can be estimated by putting $\tau_2=0$ and replacing $\int_0^\infty d\tau_2$ by $\tau_c$. Apart from angular factors $d^{(ii)}$ for $K=0$ may be written in the form

$$\sum_{\mu_e^1}\frac{\Delta\omega_1\Delta\omega_2\tau_c}{(2j_e+1)}\int_0^\infty d\tau_3\,e^{-i\Delta\omega_2\tau_3}\int_0^\infty d\tau_1\,e^{i\Delta\omega_1\tau_1}\,\mathrm{Tr}_1'\{\langle\mu_e^1|[\hat{U}_1^{\rm I}(\tau_3,0)-1][\hat{U}_1^{\rm I}(0,-\tau_1)^\dagger-1]|\mu_e^1\rangle\}$$
$$=-i\tau_c\left[\frac{{}^{ge}_{ge}M^1(-\omega_L)}{\Delta\omega_1}-\frac{{}^{eg}_{eg}M^1(\omega)}{\Delta\omega_2}+\frac{i\Delta\omega_1\Delta\omega_2}{(\omega-\omega_L+i\gamma_N)}\left(\frac{{}^{eg}_{eg}M^1(\omega)}{\Delta\omega_2^2}+\frac{{}^{ge}_{ge}M^1(-\omega_L)}{\Delta\omega_1^2}\right)\right. \qquad (4.5)$$

(where we have used the results of Appendix B). We have to take more care with the $D_1^{(iii)}$ term, as the weak-collision contribution does not vanish. We can, however, evaluate this contribution and express it in terms of width and shift operators. We now consider the $K=0$ component of $d^{(iii)}$, i.e.,

$$\sum_{j_e'j_e''\mu_e^1}\frac{1}{(2j_e+1)}\int_0^\infty d\tau_3\,e^{-i\Delta\omega_2\tau_3}\int_0^\infty e^{-\gamma_N\tau_2}d\tau_2\int_0^\infty d\tau_1\,e^{-i\Delta\omega_1\tau_1}$$
$$\times\mathrm{Tr}_1'[\langle\langle j_e\mu_e^1j_g\mu_g^1|\tilde{V}_1^{\rm I}(\tau_1+\tau_2+\tau_3)\tilde{U}_1^{\rm I}(\tau_1+\tau_2+\tau_3,\tau_1+\tau_2)|j_e''\mu_e^2j_g\mu_g^1\rangle\rangle]$$
$$\times\langle\langle j_e''\mu_{e''}^2j_e\mu_e^1|\tilde{U}_1^{\rm I}(\tau_1+\tau_2,\tau_1)|j_e'\mu_e^4j_e\mu_e^5\rangle\rangle$$
$$\times\langle\langle j_e'\mu_e^4j_g\mu_g^2|\tilde{U}_1^{\rm I}(\tau_1,0)\tilde{V}_1^{\rm I}(0)\hat{\rho}(-\infty)|j_e'\mu_e^5j_g\mu_g^2\rangle\rangle. \qquad (4.6)$$

The weak-collision contribution is

$$\sum_{\mu_e^1}\frac{1}{(2j_e+1)}\int_0^\infty d\tau_3\,e^{-i\Delta\omega_2'\tau_3}\int_0^\infty d\tau_2\,e^{-\gamma_N\tau_2}\int_0^\infty e^{-i\Delta\omega_1\tau_1}\left(\frac{1}{i\hbar}\right)^2\mathrm{Tr}_1'[\langle j_e\mu_e^1|\hat{V}_1^{\rm I}(\tau_1+\tau_2+\tau_3)\hat{V}_1^{\rm I}(0)\hat{\rho}_1(-\infty)|j_e\mu_e^1\rangle], \qquad (4.7)$$

where $\Delta\omega_2'=\omega_{eg}-\omega_L-i\gamma_N/2$. We note that we have taken the other states mixed into $e$ to be degenerate with it; this is true in the most important case, where this weak contribution may not be negligible, i.e., in the Stark broadening of hydrogen. Equation (4.7) may be written in the form

$$d_w^{(iii)}=\left(\frac{-{}^{j_ej_g}_{j_ej_g}M_w^1(\omega_L)}{(\omega_L-\omega)[\omega_L-\omega_{eg}+(i\gamma_N/2)]}-\frac{{}^{j_ej_g}_{j_ej_g}M_w(i\gamma_N/2)}{[\omega-\omega_{eg}+(i\gamma_N/2)][\omega_L-\omega_{eg}+(i\gamma_N/2)]}+\frac{{}^{j_ej_g}_{j_ej_g}M_w^1(\omega)}{(\omega_L-\omega)[\omega-\omega_{eg}+(i\gamma_N/2)]}\right). \qquad (4.8)$$

Here

$$ {}^{j_e j_g}_{j_e j_g} M^1_w(\omega) = \sum_{\mu_e^1} \frac{1}{(2j_e+1)} \int_0^\infty e^{i(\omega-\omega_{eg})\tau-(\gamma_N/2)\tau} \left(\frac{1}{i\hbar}\right)^2 \mathrm{Tr}_1'[\langle j_e\mu_e^1 | \hat{V}_1^I(\tau)\hat{V}_1^I(0)\hat{\rho}_1(-\infty) | j_e\mu_e^1\rangle]. \tag{4.9} $$

The weak-collision contribution to the spherically averaged operator in $D_1^{(iii)}$, $d^{(iii)}$, for $K \neq 0$, may be written in the same form with $M_w(\omega)$ replaced by $M_w^K(\omega)$, where

$$ M_w^K(\omega) = \sum \begin{pmatrix} j_e & j_e & K \\ \mu_e^1 & -\mu_e^3 & Q \end{pmatrix}^2 (2K_3+1)(-1)^{\mu_e^3+\mu_e^1} \int_0^\infty e^{i[\omega-\omega_{eg}+(i\gamma_N/2)]\tau} \times \langle j_e\mu_e^1 | \mathrm{Tr}_1'[\hat{V}_1(\tau_1)\hat{V}_1(0)\hat{\rho}_1(-\infty)] | j_e\mu_e^1\rangle, \tag{4.10} $$

the summation being over the $\mu$'s and $Q$. In estimating the relative sizes of the $D$'s and the other term in the spectrum below, we use the fact that for Stark broadening of hydrogen lines, it may be shown for $|\omega-\omega_{eg}| \ll \tau_w^{-1}$,

$$ {}^{j_e j_g}_{j_e j_g} M^1_w(\omega) \sim -\gamma_w - i\gamma_c\tau_w\Delta\omega . \tag{4.11} $$

Here $\gamma_w$ and $\gamma_c$ are, respectively, the weak- and strong-collision linewidths, and $\tau_w$ is the duration of a weak collision (inverse of the plasma frequency). We can estimate the strong-collision contribution using the same method as we did above for $d_1^{(i)}$ and $d_1^{(ii)}$. We find the following estimate for (4.5):

$$ d_s^{(iii)} = \frac{\tau_c}{i(\omega-\omega_L)} [{}^{j_e j_g}_{j_e j_g} M^1(\omega) - {}^{j_e j_g}_{j_e j_g} M^1(-\omega_L)]. \tag{4.12} $$

Now that we have estimates for these extra collision operators we can compare them with the other terms in the spectrum.[12]

We define the following quantities:

$$ f(\Delta\omega) = \frac{1}{\pi} \frac{\gamma^1(\Delta\omega)}{[\omega-\omega_{eg}-\Delta^1(\omega)]^2+\gamma^1(\Delta\omega)^2}, \tag{4.13a} $$

$$ n(\Delta\omega) = \frac{1}{\pi} \frac{\omega-\omega_{eg}-\Delta^1(\Delta\omega)}{[\omega-\omega_{eg}-\Delta^1(\Delta\omega)]^2+\gamma^1(\Delta\omega)^2}. \tag{4.13b} $$

Here, $\gamma^1(\Delta\omega) = \gamma^c(\Delta\omega) + \frac{1}{2}\gamma_N$, $\Delta^1(\Delta\omega) = \Delta^c(\Delta\omega)$, where

$$ \gamma^c(\Delta\omega) = -\mathrm{Re}[{}^{eg}_{eg}M^1(\omega)], \tag{4.14a} $$

$$ \Delta^c(\Delta\omega) = -\mathrm{Im}[{}^{eg}_{eg}M^1(\omega)] \tag{4.14b} $$

[see Eq. (3.10), paper II]. We can then write the frequency-dependent factors in the complete $F^{(i)}$ term (Rayleigh scattering plus the $D_1^{(i)}$ correction) in the following form:

$$ \mathrm{Re}\left\{\frac{1}{i\Delta\omega_{12}+\epsilon} + \frac{i}{i\Delta\omega_{12}+\tau_c^{-1}}\left[\frac{{}^{ge}_{ge}M^1(-\omega_L)}{\Delta\omega_1} - \frac{{}^{eg}_{eg}M^1(\omega)}{\Delta\omega_2} + \frac{\Delta\omega_1\Delta\omega_2}{(\omega-\omega_L+i\gamma_N)} \times \left(\frac{{}^{eg}_{eg}M^1(\omega)}{\Delta\omega_2^2} + \frac{{}^{ge}_{ge}M^1(-\omega_L)}{\Delta\omega_1^2}\right)\right]\right\} \{[f(\Delta\omega_1)+in(\Delta\omega_1)][f(\Delta\omega_2)-in(\Delta\omega_2)]\}. \tag{4.15} $$

This term is represented by the diagram given in Fig. 1. The first term of (4.14), the ordinary Rayleigh term, is obtained when we can average separately over the three time intervals[8] ($\tau_1$, $\tau_2$, and $\tau_3$). This is the same as ignoring the corrections to the collision operators destruction terms. The $D_1^{(i)}$ correction to Rayleigh scattering represents the physical process where a single strong collision overlaps the three time intervals.

Let us consider how the $D_1^{(i)}$ correction modifies the spectrum in the most important regions of the spectrum. Suppose we excite the atom in the far wing, $\Delta\omega_L \gg \tau_c^{-1}$, the $\delta$ function is modified by (i) a term of order $-\gamma_c(\Delta\omega_1)\tau_c$ times a function with width $\gamma_N$ and (ii) a term of order $\Delta_i(\Delta\omega_i)/\Delta\omega_1$ times a function with width $\tau_c^{-1}$, both these are negligible in practical circumstances. The modification to the $\delta$ function can be understood as follows. Rayleigh scattering occurs when the atom is unperturbed and $\gamma(\Delta\omega)\tau_c$ represents the fraction of atoms undergoing strong collisions. We should, therefore, expect the Rayleigh scattering to be affected to that order. The $D_1^{(i)}$ correction also affects the fluorescence, i.e., $\Delta\omega_2 \sim \gamma_c(0)$, by an

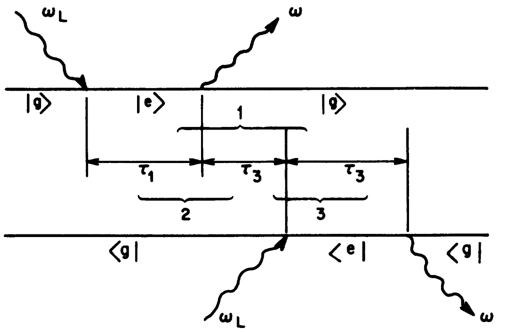


FIG. 1. The $F_{(i)}$ term: ⌐ represents overlap of the time intervals in (1): $D_1^{(i)}$, (2): $\mathfrak{C}^1(gg,eg)$, (3): $\mathfrak{C}^1(ge,gg)$.

amount of order $\gamma_N/\Delta\omega_1$ in the same limit ($\Delta\omega_1 \gg \tau_c^{-1}$). This, again, is negligible. In the impact limit $\Delta\omega_1$ and $\Delta\omega_2 \ll \tau_c^{-1}$ the $D_1^{(i)}$ term modifies the $\delta$ function by an amount $-\gamma_c(0)\tau_c$ times a function of width $\gamma_N$, and may be neglected. Our conclusion is that we may ignore the $D_1^{(i)}$ in all important regions of the spectrum.

We now turn to the $F^{(ii)}$ term which is represented by the diagram in Fig. 2. Again, dropping the destruction terms and, of course, the correction to the collision operator, is the same as averaging separately over the three time intervals. The $D_1^{(ii)}$ correction represents the process where a single collision overlaps the three intervals. For $\Delta\omega_{12} \ll \tau_c^{-1}$ the analysis of this correction is identical to that for $D_1^{(i)}$. When we excite in the wings, i.e., $\Delta\omega_1 \gg \tau_c^{-1}$ then (3.23) shows that $D_1^{(ii)}$ produces a correction $\sim\gamma_N\tau_c$ to the fluorescence. Once again, this should be expected, for the following reason. Once a photon has been absorbed during a strong collision, the probability that it will be reemitted during the same strong collision must be ~Einstein $A$ coefficient × duration of collision, i.e., $\sim\gamma_N\tau_c$. Note that $\tau_c$ is the duration of a *strong* collision, since the correction vanishes for weak collisions. If $\tau_c$ was the duration of a weak collision $\tau_w$, then there are practical cases, e.g., in the Stark broadening of hydrogen where $\gamma_N\tau_w$ can be comparable with 1. So we are just left with $D_1^{(iii)}$ to analyze (see Fig. 3). It appears in the scattered spectrum in the form

$$\mathrm{Re}\{d^{(iii)}[f(\Delta\omega_1)+in(\Delta\omega_1)][f(\Delta\omega_2)+in(\Delta\omega_2)]\}. \quad (4.16)$$

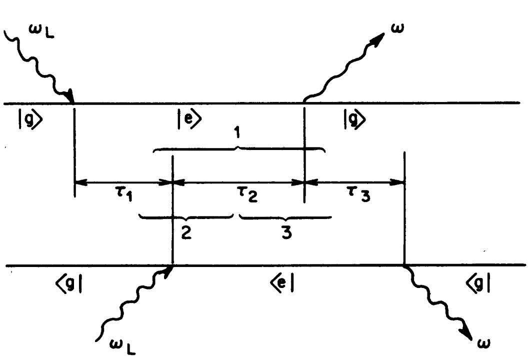


FIG. 2. The $F_{(ii)}$ term: ⌐ represents overlap of the time intervals in (1): $D_1^{(ii)}$, (2): $\mathfrak{C}^1(ee,eg)$, (3): $\mathfrak{C}^1(ge,ee)$.

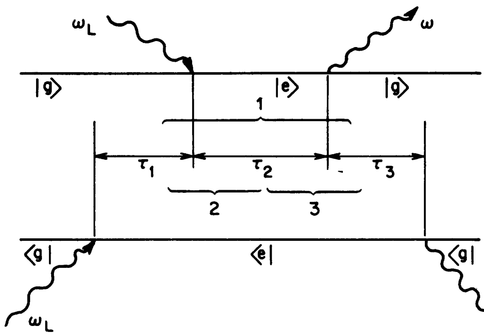


FIG. 3. The $F_{(iii)}$ term: ⌐ represents overlap of the time intervals in (1): $D_1^{(iii)}$, (2): $\mathfrak{C}^1(ee,ge)$, (3): $\mathfrak{C}^1(ge,ee)$.

Let us first consider the strong-collision contribution Eq. (4.12). When $\Delta\omega_1 \gg \tau_c^{-1}$ then we obtain a correction $\sim\gamma_N\tau_c$ to the fluorescence. This is the same order as the $D_1^{(ii)}$ correction, and is expected on the same basis as the argument we gave for $D_1^{(ii)}$. For $\Delta\omega_1 \gg \tau_c^{-1}$, the Rayleigh peak ($\delta$ function) is changed in magnitude by the order $\gamma_c(\Delta\omega_1)\tau_c$. In the impact limit $\Delta\omega_1$ and $\Delta\omega_1$ and $\Delta\omega_2 \ll \tau_c^{-1}$, the corrections to the Rayleigh and fluorescence peaks are, respectively, $\sim\gamma_N\tau_c[d\gamma(\Delta\omega_1)/d\omega_1]$ and $\gamma_c\tau_c[d\gamma(\Delta\omega_1)/d\omega_1]$ $[\gamma_c=\gamma^c(\Delta\omega=0)]$. Though we can always neglect the strong-collision contribution from $D_1^{(iii)}$, the weak-collision contribution [Eq. (4.8)] needs a little more care. When $|\Delta\omega_1| \gg \tau_c$ this weak-collision contribution gives terms $(\gamma_N\tau_w)[\gamma_c/\gamma^1(\Delta\omega_1)]$ compared to the fluorescence peak and a term $\sim\gamma_c(\Delta\omega_1)/\Delta\omega_1$ compared to the Rayleigh peak. In the impact limit the correction is of order $(\gamma_c+\gamma_N)\tau_w$ compared to the fluorescence. For neutral perturbers we can ignore this correction in most circumstances of interest. For Stark broadening of hydrogen lines, however, it may (under extreme circumstances, e.g., in the sun) be important if $\gamma_N\tau_w[\gamma^c/\gamma^1(\Delta\omega)]$ is of order one. Note that in this situation the correction to the normal collision operator, from the effects of spontaneous emission [via the presence of $\tilde{S}$ in the definition of the $M(z)$'s, Eq. (2.17), paper II], also becomes important. In fact, the weak-collision limit is quite calculable, as we saw above [Eq. (4.8)]. In the above discussion we have been careful to show how the correction terms $D^{(i)}$, etc., may be estimated for both weak and strong collisions. We note here that there are also weak-collision contributions to the $\mathfrak{C}^1$ operators that may be of comparable importance in the Stark broadening of hydrogen. In fact, for Lyman $\alpha$ (in work performed in collaboration with the late Yelnik), it is possible to show for scattering from the far line wings, that a weak-collision contribution from a $\mathfrak{C}^1$ term *exactly* cancels the $D^{(iii)}$ weak-collision contribution. Once again, we stress these weak-collision contributions are straightforward to calculate and present no problem [similar to Eq. (4.8)].

We conclude that for most purposes we can ignore the first-order [in $L^E(t)$] terms in the destruction operator and need retain only the zeroth-order terms. The important quantities we have left in the spectrum that have to be calculated are, therefore, the $\mathfrak{C}^1$'s that arise in the first-order corrections to the collision operator and the zeroth-order destruction operator. We can see from Figs. 1–3 that the destruction terms, for emission, are the inverses of the corrections to the collision operator for absorption. That is why we use the same symbol $\mathfrak{C}^1$ for the angular-averaged operators we need to calculate, in order to emphasize their close relationship. The $\mathfrak{C}^1$'s allow us to account for the physical processes where a strong collision overlaps the processes of absorption (or emission) and propagation of the atom in the upper-state manifold.

## V. RESULTS AND DISCUSSION

Now that we have a formal result for the scattered spectrum, along with estimates of the relative importance of the correction terms, we should like to cast our result for the scattered spectrum in terms of generalized absorption and emission profiles,[3] and link up our discussion with that of papers I and II. To do this we use the following definitions (valid in the OIL approximation):

$$f_{ab}^K(\Delta\omega) = f(\Delta\omega)[1+\mathrm{Re}\,\mathfrak{C}^1(K, ee, eg, \omega)] + n(\Delta\omega)\,\mathrm{Im}[\mathfrak{C}^1(K, ee, eg, \omega)], \qquad (5.1)$$

$$f_{em}^K(\Delta\omega) = f(\Delta\omega)[1+\mathrm{Re}\,\mathfrak{C}^1(K, eg, ee, \omega)] + n(\Delta\omega)\,\mathrm{Im}[\mathfrak{C}^1(K, eg, ee, \omega)]. \qquad (5.2)$$

The scattered spectrum may then be written in the form

$$\sum_K M^K\left(\frac{f(\Delta\omega_1)}{\gamma(\Delta\omega_1)}\delta(\Delta\omega_{12}) + \frac{2}{\gamma^K+\gamma^N} f_{ab}^K(\Delta\omega_1) f_{em}^K(\Delta\omega_2) - \frac{1}{\Delta\omega_{12}}[f(\Delta\omega_1)n(\Delta\omega_2) - n(\Delta\omega_1)f(\Delta\omega_2)]\right). \qquad (5.3)$$

The $M^K$ in this equation is defined in Ref. 11 and contains all the angular information relevant to the ingoing and outgoing fields. *It is not related to our collision operators* (the authors apologize for the double use of this symbol). Note that we have left out the weak-collision contribution from $D_1^{(iii)}$. We should point out that there may be regions of the spectrum where the other destruction corrections, ignored in our discussion, become comparable with the terms in Eq. (5.3). These regions are, however, ones where the scattering is, in any case, negligible. Equation (5.3) thus describes the spectrum accurately in most regions of importance. This profile is valid in the BCA and OIL approximation from line center to the far $kT$ wings. The way in which the $\mathfrak{C}^1(K, ee, eg, \omega_L)$ describes absorption accurately in the far $kT$ wings was discussed in paper I. The $\mathfrak{C}^1(K, eg, ee, \omega)$, that appears in the destruction operator plays exactly the same role in the emission spectrum. For $K=0$ we show in Appendix C that this $\mathfrak{C}^1$ is of order $\gamma_c/(kT/\hbar)$, when $\Delta\omega \ll kT/\hbar$ and may be neglected in this region. This correlation term allows for the effect the upper-state potential has on the trajectories of the perturbers as they come in and begin a collision with the atom, during which a photon is emitted. For the $K \neq 0$ terms we would, of course, also be concerned with how the $m_j$ levels were mixed by the collision as well as the effect on the trajectories. $m_j$ state mixing becomes important long before we get to the thermal correlation $\Delta\omega \gtrsim kT/\hbar$ regime, and the $K \neq 0$ terms have to be retained *as soon as we go outside the impact approximation.* Since the $K \neq 0$ terms contain extra information about the mixing of $m_J$ states in the excited level of the atom before the emission of a photon we believe that they can be used to extract more detailed information about the interatomic potential than is possible from the usual pure emission or absorption profiles. When $\Delta\omega$ and $\Delta\omega_L \ll kT/\hbar$, i.e., we can ignore the effects of the curvature of perturber trajectories, it is straightforward to show that $f_{em}^K(\omega) = f_{ab}^K(\omega)$ (as is required by detailed balance).

The scattered spectrum [Eq. (5.3)] was obtained using an equation of motion for the dipole autocorrelation function for the atomic system derived outside the validity of the quantum-regression theorem. The quantum-regression theorem fails, since we are studying systems outside thermal equilibrium, and outside the Markoff (impact) approximation. The scattered spectrum is expressible in terms of generalized absorption and emission profiles, in the OIL case [see Eq. (5.3)], the former of which may be studied via the relative intensities of the integrated Rayleigh and fluorescence peaks if the polarization of the light is studied (see paper II). Most importantly, the scattered spectrum has been shown to contain information that is not contained in the emission or absorption profiles alone. It is, therefore, as we stated above possible to extract a great deal more information about the collisional interaction from scattering experiments than is accessible from pure absorption or emission profiles. In particular, the polarization of the scattered light is sensitive to the mixing of $m_J$ states, and thus to the anisotropy of the interatomic potentials, at large internuclear separation.

## ACKNOWLEDGMENTS

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## APPENDIX A: DESTRUCTION TERMS IN IRREDUCIBLE FORM

In this appendix, we shall present the forms of the destruction operator, including corrections to it from the driving field, that are valid when both levels of a transition interact with perturbers. We shall not give a detailed derivation, as it would follow the lines of Appendix B of paper II very closely.

The zeroth order in $L^E$ has two terms, the first of which couples $|K_2Q_2ee\rangle\rangle$ into $|K_1Q_1eg\rangle\rangle$, and is

$$D_0(K_1K_2, eg, ee, \omega) = \sum_q (2K_1+1)^{1/2}(2K_2+1)^{1/2}(\vec{\epsilon}^{\,2})_q \langle j_e \| \vec{\mathrm{d}} \| j_g\rangle (-1)^{j_g - Q_2} \times \begin{pmatrix} K_1 & K_2 & 1 \\ Q_1 & -Q_2 & q \end{pmatrix} \mathfrak{C}^1(K_1, K_2; eg, ee, \omega)\sigma^{K_2Q_2}_{j_ej_e}, \qquad \text{(A1)}$$

see Appendix B, Eq. (B15), for the definition of $\mathfrak{C}^1(K_1,K_2; eg, ee, \omega)$. If the lower level does interact with perturbers, this reduces to

$$\sum_q (2K_1+1)^{1/2}(2K_2+1)^{1/2}(\vec{\epsilon}_2)_q \langle j_e \| \vec{\mathrm{d}} \| j_g\rangle (-1)^{j_e+j_g-Q_2} \begin{Bmatrix} K_2 & 1 & K_1 \\ j_g & j_e & j_e \end{Bmatrix} \mathfrak{C}^1(K^2, eg, ee, \omega) \begin{pmatrix} K_1 & K_2 & 1 \\ Q_1 & -Q_2 & q \end{pmatrix}. \qquad \text{(A2)}$$

The other term couples $|K_2Q_2; ee\rangle\rangle$ to $|K_1Q_1; eg\rangle\rangle$:

$$D_0(K_1, K_2; gg, eg, \omega) = \sum_q (2K_1+1)^{1/2}(2K_2+1)^{1/2}(\vec{\epsilon}_2)_{-q} \langle j_e \| \vec{\mathrm{d}} \| j_g\rangle (-1)^{j_e - Q_2} \times \mathfrak{C}^1(K_1, K_2; gg, eg, \omega) \begin{pmatrix} K_1 & K_2 & 1 \\ Q_1 & -Q_2 & q \end{pmatrix} \sigma^{K_2Q_2}_{j_ej_e}, \qquad \text{(A3)}$$

$$\mathfrak{C}^1(K_1, K_2; gg, eg, \omega) = N_p \sum (-1)^{\mu_g^1+\mu_e^2\mu_e^1} \begin{pmatrix} j_e & j_g & K_1 \\ -\mu_g^1 & \mu_g^2 & Q_3 \end{pmatrix} \begin{pmatrix} j_g & j_e & K_2 \\ \mu_g^5 & -\mu_e^2 & Q_4 \end{pmatrix} \begin{pmatrix} j_g & j_e & 1 \\ \mu_g^4 & -\mu_e^1 & Q_5 \end{pmatrix} \begin{pmatrix} K_1 & K_2 & 1 \\ Q_3 & Q_4 & Q_5 \end{pmatrix}$$
$$\times \lim_{\epsilon\to 0} \left\langle\!\!\left\langle j_g\mu_g^1 j_g\mu_g^2 \right| \mathrm{Tr}_1' \left[ \tilde{V}_1 \frac{1}{\epsilon + i\omega + \tilde{L}_1 + \tilde{S}} |j_g\mu_g^3 j_g\mu_g^4\rangle\rangle \times \langle\langle j_g\mu_g^3 j_e\mu_e^1 | \frac{1}{-i\omega_L + \epsilon + \tilde{L}_1 + \tilde{S}} \tilde{V}_1 \hat{\rho}_1 \right] \left| j_g\mu_g^5 j_e\mu_e^2 \right\rangle\!\!\right\rangle. \qquad \text{(A4)}$$

Here the summation is over all $\mu$'s and $Q$'s. This term, of course, vanishes if the lower level does not interact with perturbers. We now give the first order (in $\tilde{L}^E$) correction to the destruction operator. The first we consider is a correction to the normal $F_{(i)}$ term; it couples $|K_2Q_2j_gj_e\rangle\rangle$ to $|K_1Q_1j_ej_g\rangle\rangle$. We have

$$D_1^{(i)}(K_1Q_1, eg, gg, ge, \omega-\omega_L)$$

$$=N_p\sum_{qq'}(2K_1+1)^{1/2}(2K_2+1)^{1/2}\left(\frac{i}{\hbar}\right)\mathcal{E}_0(\vec{\epsilon}_1)_{-q}(\vec{\epsilon}_2)_{-q}(\langle j_e\|\vec{d}\|j_g\rangle)^2$$

$$\times\sum_{K_7 Q_2 Q_3 Q_4 Q_5 Q_6 Q_7}\begin{pmatrix}K_1 & 1 & K_7\\ Q_1 & q & Q_7\end{pmatrix}\begin{pmatrix}1 & K_2 & K_7\\ q^1 & Q_2 & -Q_7\end{pmatrix}\begin{pmatrix}K_1 & 1 & K_7\\ Q_3 & Q_4 & Q_7\end{pmatrix}\begin{pmatrix}1 & K_2 & K_7\\ Q_5 & Q_6 & -Q_7^1\end{pmatrix}\begin{pmatrix}j_e & j_g & K_1\\ \mu_e^1 & -\mu_g^1 & Q_3\end{pmatrix}$$

$$\times\begin{pmatrix}j_e & j_g & 1\\ -\mu_e^2 & \mu_g^3 & Q_4\end{pmatrix}\begin{pmatrix}j_g & j_e & 1\\ \mu_g^5 & -\mu_e^5 & Q_5\end{pmatrix}\begin{pmatrix}j_g & j_e & K_2\\ -\mu_g^6 & \mu_e^7 & Q_6\end{pmatrix}$$

$$\times\lim_{\epsilon\to 0}\left\langle\!\!\left\langle j_e\mu_e^1 j_g\mu_g^1\right|\mathrm{Tr}_1'\left[\tilde{V}_1\frac{1}{i\omega+\epsilon+\tilde{L}_1+\tilde{S}}|j_e\mu_e^2 j_g\mu_g^2\rangle\rangle\right.\right.$$

$$\times\langle\langle j_g\mu_g^3 j_g\mu_g^2|\frac{1}{i(\omega-\omega_L)+\epsilon+\tilde{L}_1}|j_g\mu_g^4 j_g\mu_g^5\rangle\rangle$$

$$\left.\left.\times\langle\langle j_g\mu_g^4 j_e\mu_e^5|\frac{1}{-i\omega_L+\epsilon+\tilde{L}_1+\tilde{S}}\tilde{V}_1\hat{\rho}(-\infty)\right]\right|j_g\mu_g^6 j_e\mu_e^7\right\rangle\!\!\right\rangle$$

$$\times\sigma_{j_g j_e}^{K_2Q_2}(-1)^{-\mu_g^1-\mu_e^2-\mu_e^5-\mu_g^6+Q_7-Q_7^1}. \qquad \text{(A5)}$$

The OIL form of this operator has been given in the text.

The correction to the $F^{(ii)}$ part of the scattering can be written in the form

$$D_1^{(ii)}(K_1, Q_1; eg, ee, ge, \omega-\omega_L)$$

$$=N_p(2K_1+1)^{1/2}(2K_2+1)^{1/2}\frac{i}{\hbar}\sum_{qq'}(\vec{\epsilon}_2)_{-q'}(\vec{\epsilon}_1)_{-q}(\langle j_e\|\vec{d}\|j_g\rangle)^2$$

$$\times\sum_{\mu's K_2K_3K_4K_5K_6K_7Q_2Q_3Q_4Q_5Q_6Q_7Q_1^1}\begin{pmatrix}K_1 & 1 & K_7\\ Q_1 & q' & Q_7\end{pmatrix}\begin{pmatrix}1 & K_2 & K_7\\ q & Q_2 & -Q_7\end{pmatrix}\begin{pmatrix}K_1 & 1 & K_7\\ Q_3 & Q_4 & -Q_7^1\end{pmatrix}\begin{pmatrix}1 & K_2 & K_7\\ Q_5 & Q_6 & -Q_7^1\end{pmatrix}\begin{pmatrix}j_e & j_g & K_1\\ \mu_e^1 & -\mu_g^1 & Q_3\end{pmatrix}$$

$$\times\begin{pmatrix}j_g & j_e & 1\\ \mu_g^2 & -\mu_e^3 & Q_4\end{pmatrix}\begin{pmatrix}j_e & j_g & 1\\ \mu_e^4 & -\mu_g^3 & Q_5\end{pmatrix}\begin{pmatrix}j_g & j_e & K_7\\ -\mu_g^6 & \mu_e^3 & Q_6\end{pmatrix}$$

$$\times\lim_{\epsilon\to 0}N_p\left\langle\!\!\left\langle j_e\mu_e^1 j_g\mu_g^1\right|\mathrm{Tr}_1'\left[\tilde{V}_1\frac{1}{i\omega+\epsilon+\tilde{L}_1+\tilde{S}}|j_e\mu_e^2 j_g\mu_g^2\rangle\rangle\right.\right.$$

$$\times\langle\langle j_e\mu_e^2 j_e\mu_e^3|\frac{1}{\epsilon+\tilde{L}_1+\tilde{S}}|j_e\mu_e^4 j_e\mu_e^5\rangle\rangle$$

$$\left.\left.\times\langle\langle j_g\mu_g^3 j_e\mu_e^5\frac{1}{-i\omega_L+\epsilon+\tilde{L}_1+\tilde{S}}\tilde{V}_1\hat{\rho}(-\infty)\right]\right|j_g\mu_g^6 j_e\mu_e^7\right\rangle\!\!\right\rangle$$

$$\times(-1)^{j_e+j_g-\mu_g^1-\mu_g^6+Q_7-Q_7^1-\mu_g^2-\mu_g^3}\sigma_{j_g j_e}^{K_2Q_2}. \qquad \text{(A6)}$$

Finally we have the $D^{(iii)}$ correction

$D^{(iii)}(K, eg, ee, eg, \omega-\omega_L)$

$$=\frac{\epsilon_0}{i\hbar}\sum_{qq'}\begin{pmatrix}K_1 & 1 & K_7\\ -Q_1 & q^1 & Q_7\end{pmatrix}\begin{pmatrix}1 & K_2 & K_7\\ q & Q_2 & -Q_7\end{pmatrix}(\vec{\epsilon}_1)_q(\vec{\epsilon}_2)_{q'}|\langle j_g\|\vec{d}\|j_e\rangle|^2(-1)^{K_2+q+q^1}(2K_1+1)^{1/2}(2K_2+1)^{1/2}(2K_7+1)$$

$$\times\sum\begin{pmatrix}j_e & j_g & K_1\\ \mu_e^1 & -\mu_g^1 & Q_3\end{pmatrix}\begin{pmatrix}j_g & j_e & 1\\ \mu_g^2 & -\mu_e^3 & Q_4\end{pmatrix}\begin{pmatrix}j_e & j_g & 1\\ \mu_e^5 & -\mu_g^3 & Q_5\end{pmatrix}$$

$$\times\begin{pmatrix}j_e & j_g & K_2\\ -\mu_e^6 & \mu_g^4 & Q_6\end{pmatrix}\begin{pmatrix}K_1 & 1 & K_7\\ Q_3 & q^1 & Q_7^1\end{pmatrix}\begin{pmatrix}1 & K_2 & K_7\\ q & Q_6 & -Q_7^1\end{pmatrix}(-1)^{j_e+j_g-\mu_e^1-\mu_e^3-\mu_g^3-\mu_e^6}$$

$$\times N_p\Big\langle\Big\langle j_e\mu_e^1 j_g\mu_g^1\Big|\mathrm{Tr}_1'\Big[\tilde{V}_1\frac{1}{i\omega+\mathcal{L}_1+\epsilon+S}|j_e\mu_e^2 j_g\mu_g^2\rangle\rangle\langle\langle j_e\mu_e^2 j_e\mu_e^3|\frac{1}{\epsilon+\mathcal{L}_1+S}|j_e\mu_e^4 j_e\mu_e^5\rangle\rangle$$

$$\times\langle\langle j_e\mu_e^4 j_g\mu_g^3|\frac{1}{i\omega_L+\mathcal{L}_1+S}\tilde{V}_1\hat{\rho}_1(-\infty)\Big]\Big|j_e\mu_e^6 j_g\mu_g^4\Big\rangle\Big\rangle\,\sigma^{K_2Q_2}_{j_e^6 j_g}\,, \tag{A7}$$

where the second summation is over $K_2, K_7$, the $\mu$'s and the $Q$'s, except $Q_1$.

## APPENDIX B: ESTIMATES FOR THE $D^{(i)}$ AND $D^{(ii)}$ OPERATORS

We start with the RHS of Eq. (4.3), i.e.,

$$\tau_c\sum_{\mu_e^1}\frac{1}{(2j_e+1)}\Delta\omega_2\Delta\omega_1\int_0^\infty e^{-i\Delta\omega_2\tau_3}d\tau_3\int_0^\infty e^{+i\Delta\omega_1\tau_1}d\tau_1\,\mathrm{Tr}_1'\{\langle j_e\mu_e^1|[\hat{U}_1^I(\tau_3,0)-1][\hat{U}_1^I(0,-\tau_1)^\dagger-1]|j_e\mu_e^1\rangle\}$$

$$=-\tau_c\sum_{\mu_e^1}\frac{1}{(2j_e+1)}\Delta\omega_1\Delta\omega_2\int_0^\infty e^{-i\Delta\omega_2\tau_3}d\tau_3$$

$$\times\int_0^\infty e^{i\Delta\omega_1\tau_1}d\tau_1\,\mathrm{Tr}_1'\{\langle j_e\mu_e^1|[\hat{U}_1^I(\tau_3,0)-1]|j_e\mu_e^1\rangle+\langle j_e\mu_e^1|[\hat{U}_1^I(0,-\tau_1)^\dagger-1]\;|j_e\mu_e^1\rangle$$

$$-\langle j_e\mu_e^1|[\hat{U}_1^I(\tau_3,0)\hat{U}_1^I(0,-\tau_1)^\dagger-1]|j_e\mu_e^1\rangle\}\,. \tag{B1}$$

Consider the following integral:

$$\int_0^\infty e^{-i\Delta\omega_2\tau_3}d\tau_3\int_0^\infty e^{i\Delta\omega_1\tau_1}d\tau_1\,\mathrm{Tr}_1'[\langle j_e\mu_e^1|\,\hat{U}_1^I(\tau_3,0)\hat{U}_1^I(0,-\tau_1)^\dagger|j_e\mu_e^1\rangle]$$

$$=\int_0^\infty e^{-i\Delta\omega_2\tau_3}d\tau_3\int_0^\infty e^{i\Delta\omega_1\tau_1}d\tau_1\int_0^\infty p^2dp\langle j_e\mu_e^1\vec{p}|\,e^{iH_0\tau_3/\hbar}\,e^{-iH\tau_3/\hbar}\int d^3p^1|\vec{p}_1\rangle\langle\vec{p}_1|$$

$$\times\sum_{\mu_2^2}|\,\mu_e^2\rangle\langle\mu_e^2|\,e^{-iH_0\tau_1/\hbar}\,e^{+iH\tau_1/\hbar}|j_e\mu_e^1\vec{p}\rangle$$

$$=\sum_{\mu_e^2}\int_0^\infty p^2dp\int d^3p_1\langle j_e\mu_e^1\vec{p}|\frac{1}{(i/\hbar)(E_e+E(\vec{p})-\hat{H})-i\Delta\omega_2}|j_e\mu_e^2\vec{p}_1\rangle$$

$$\times\langle j_e\mu_e^2\vec{p}_1|\frac{1}{-(i/\hbar)(E_e+E(\vec{p}\,')-\hat{H})+i\Delta\omega_1}|j_e\mu_e^1\vec{p}\rangle\,. \tag{B2}$$

When $\Delta\omega_1\gg\tau_c^{-1}$, we can use a quasimolecular picture for the absorption process and the Franck-Condon principle then tells us that the internuclear (atom-perturber) translational motion is not changed in the absorption process. We can then put $E(\vec{p}\,')=E(\vec{p})$ in the second resolvent [i.e., in $(z-H)^{-1}$] and remove the complete set of intermediate states to obtain

$$\int_0^\infty p^2 dp \langle j_e \mu_e^1 \vec{p}| \frac{1}{(i/\hbar)[E_e + E(\vec{p}) - \hat{H}] - i\Delta\omega_2} \frac{1}{-(i/\hbar)[E_e + E(\vec{p}') - \hat{H}] + i\Delta\omega_1} |j_e \mu_e^1 \vec{p}\rangle$$

$$= \int_0^\infty p^2 dp \frac{1}{+i\Delta\omega_1 - i\Delta\omega_2} \left\langle j_e \mu_e^1 \vec{p} \right| \left( \frac{1}{(i/\hbar)[E_e + E(\vec{p}) - \hat{H}] - i\Delta\omega_2} + \frac{1}{-(i/\hbar)[E_e + E(\vec{p}) - \hat{H}] + i\Delta\omega_1} \right) \left| j_e \mu_e^1 \vec{p} \right\rangle$$

$$= \frac{i}{(\omega_L - \omega + i\gamma_N)} \int_0^\infty p^2 dp \left\langle j_e \mu_e^1 \vec{p} \right| \left( \frac{1}{(i/\hbar)[E_e + E(\vec{p}) - \hat{H}] - i\Delta\omega_2} + \frac{1}{-(i/\hbar)[E_e + E(\vec{p}) - \hat{H}] + i\Delta\omega_1} \right) \left| j_e \mu_e^1 \vec{p} \right\rangle . \quad \text{(B3)}$$

So this term gives a function of width $\gamma_N$, peaked around $\omega = \omega_L$, which will appear, therefore, as a modification Rayleigh scattering.

Using (B3) we can write the complete expression (B1) in the form

$$-\tau_c \sum_{\mu_e^1} \frac{(-i\Delta\omega_2)(+i\Delta\omega_1)}{(2j_e+1)} \int_0^\infty e^{-i\Delta\omega_2 \tau_3} d\tau_3 \int_0^\infty e^{+i\Delta\omega_1 \tau_1} d\tau_1 \langle j_e \mu_e^1 | \operatorname{Tr}_1' \Big( [\hat{U}_1^I(\tau_3, 0) - 1] + [\hat{U}_1^I(0, -\tau_1)^\dagger - 1]$$
$$+ \frac{\Delta\omega_2}{(\omega_L - \omega + i\gamma_N)} [\hat{U}_1^I(0, -\tau_1)^\dagger - 1]$$
$$+ \frac{-\Delta\omega_1}{(\omega_L - \omega + i\gamma_N)} [\hat{U}_1^I(\tau_3, 0) - 1] \Big) | j_e \mu_e^1 \rangle$$

$$= -\tau_c \left( \frac{{}^{eg}_{eg}M^1[\omega + (i\gamma_N/2)]}{(-i\Delta\omega_2)} + \frac{{}^{ge}_{ge}M[-\omega_L + (i\gamma_N/2)]}{(i\Delta\omega_1)} \right) + \frac{i}{(\omega_L - \omega + i\gamma_N)} \left[ \left( \frac{\Delta\omega_1}{\Delta\omega_2} \right) {}^{eg}_{eg}M^1 [\omega + (i\gamma_N/2)] + \left( \frac{\Delta\omega_2}{\Delta\omega_1} \right) {}^{ge}_{ge}M[-\omega_L + (i\gamma_N/2)] \right] . \quad \text{(B4)}$$

This argument ignores one important feature of the problem. The average in (B1) may be expressed if we use semiclassical wave functions as integrals over velocity and distance of closest approach $b$. The largest contributions to the integral over $b$ comes from points of stationary phase of the semiclassical overlap integrals. These points of stationary phase occur at positions where the potential can make up the energy defect $\hbar\Delta\omega$ directly (since the translational motion only takes up the energy as the collision is completed). For each trajectory there are two such positions, one on the way in and one on the way out. That is why one obtains a factor of two outside the integral when one writes $\gamma^c(\Delta\omega)$ in the quasistatic limit, i.e., *twice* the quantity

$$\int_0^\infty 4\pi R^2 dR\, \delta[V(R) - \hbar\Delta\omega] . \quad \text{(B5)}$$

Remembering for small $\tau_3$ that $\hat{U}(\tau_1 + \tau_2 + \tau_3, \tau_1 + \tau_2) \sim e^{-i\bar{V}[(\tau_1+\tau_2)/\hbar]\tau_3}$, we can for $\Delta\omega_1 \sim \Delta\omega_2$ express (B1) in the same form as (B5). We obtain

$$\text{const} \times \int_0^\infty 4\pi R^2 dR\, \delta(V(R) - \hbar\Delta\omega_2)\delta(V(R) - \hbar\Delta\omega_1) . \quad \text{(B6)}$$

If $\tau_2 > 0$, i.e., there is *any* propagation the first $\delta$ function must correspond to absorption on the way in, and the second to emission on the way out. This excludes the other three points of stationary phase that we would pick up by putting $\tau_2 \equiv 0$. We should expect, therefore, that we would obtain a better estimate of $D_1^{(ii)}$ and $D_1^{(i)}$ if we divided (B1) by a factor of four.

## APPENDIX C: QUASISTATIC LIMIT FOR $\mathfrak{C}^1$ EMISSION OPERATORS

In this appendix we shall discuss the physics of, and give estimates for, the collision operator that gives the effects of correlation events in emission. We shall concentrate on $\mathfrak{C}^1(0, eg, ee, \omega)$, which is given by

$$\mathfrak{C}^1(0, eg, ee, \omega) = \sum_{\mu_e^1 \mu_e^2 \mu_e^3 \mu_e^4} \frac{1}{(2j_e+1)} \left\langle\!\!\left\langle j_e \mu_e^1 j_g \mu_g^1 \right| \operatorname{Tr}_1' \left( \tilde{V}_1 \frac{1}{\epsilon + i\omega + \underline{L}_1 + \underline{S}} | j_e' \mu_e^2 j_g \mu_g^1 \rangle\rangle \right.\right.$$
$$\times \langle\langle j_e' \mu_e^2 j_e \mu_e^1 | \frac{1}{\epsilon + \underline{L}_1 + \underline{S}} \tilde{V}_1 \hat{\rho}_1(-\infty) \Big) \; j_e \mu_e^4 j_e \mu_e^4 \Big\rangle\!\!\Big\rangle . \quad \text{(C1)}$$

If we ignore bound states, the effect of the spontaneous emission damping operator, and use an adiabatic approximation for the coupling to other excited states, we know the following identity holds:

$$\sum_{\mu_e^4} \lim_{\epsilon\to 0} \frac{1}{\epsilon+\tilde{L}_1} \tilde{V}_1 \hat{\rho}_1(-\infty)|j_e\mu_e^4 j_e\mu_e^4\rangle\rangle = \exp[-(\hat{H}^e+\hat{H}_0^p)/kT] - \sum_{\mu_e^4} |j_e\mu_e^4 j_e\mu_e^4\rangle\rangle \hat{\rho}_1(-\infty)$$
$$\equiv \hat{\rho}_e(kT) - \hat{\rho}_0(kT). \tag{C2}$$

Here, $\hat{H}^e = \hat{H}_0^e + \hat{H}_0^p + \hat{V}_1^e$, where $\hat{H}_0^e$ is the atomic Hamiltonian for the upper-level manifold, $\hat{H}_0^p$ is the free-perturber Hamiltonian, and $\hat{V}_1^e$ is the effective interaction with the perturbers when the atom is in the upper level. (The effective interaction is obtained by making the adiabatic approximation.) This identity implies

$$\mathcal{C}^1(0, eg, ee, \omega) = \int_0^\infty p^2 dp \sum_{\mu_e^1} \frac{1}{(2j_e+1)} \int d^3p_1 \langle \vec{p} j_e \mu_e^1 | \hat{V}_1^e \frac{1}{\hbar[i\epsilon+\omega-\omega_{eg}-\omega_{\vec{p}}-(H_e/\hbar)]} | j_e\mu_e^2 \vec{p}_1\rangle$$
$$\times \langle j_e\mu_e^2\vec{p}_1 | [\hat{\rho}_e(kT) - \hat{\rho}_0(kT)] | j_e\mu_e^1\vec{p}\rangle, \tag{C3}$$

where $E(p) = \hbar\omega_{\vec{p}} = \vec{p}_2/2m$, $m$ being the mass of a perturber. We can use the same method as we did in paper I to estimate $\langle j_e\mu_e^2\vec{p}_1|\hat{\rho}_e(kT)-\hat{\rho}_0(kT)|j_e\mu_e^1\vec{p}\rangle$ [see paper I, Eq. (4.15)]. We find

$$\langle j_e\mu_e^2\vec{p}_1|\hat{\rho}_e(kT)-\hat{\rho}_0(kT)|j_e\mu_e^1\vec{p}\rangle \simeq e^{-E(\vec{p})/kT}\left(\frac{1-e^{-[E(\vec{p}_1)-E(\vec{p})]/kT}}{E(\vec{p}_1)-E(\vec{p})}\right)\langle j_e\mu_e^2\vec{p}_1|\hat{V}_1^e|j_e\mu_e^1\vec{p}\rangle. \tag{C4}$$

Inserting this in (3.37) we find, for $\Delta\omega = \omega - \omega_{eg} \ll kT/\hbar$, that

$$\mathcal{C}^1(0, eg, ee, \omega) \simeq \int_0^\infty \frac{p^2dp}{kT} \sum_{\mu_e^1} \frac{1}{(2j_e+1)} \langle \vec{p} j_e\mu_e^1 | \hat{V}_1^e \frac{1}{\hbar(i\epsilon+\omega-\omega_{eg}-\omega_{\vec{p}}-\hat{H}^e/\hbar)} \hat{V}_1^e | \vec{p} j_e \mu_e^1\rangle, \tag{C5}$$

i.e., $\mathcal{C}^1(0, eg, ee, \omega) \simeq (-\gamma_c - i\Delta_c)/(kT/\hbar)$. Thus the $K=0$ term for a correlated emission event is negligible unless $\Delta\omega \gtrsim kT/\hbar$. The physics is the same as we discussed for the corresponding term in absorption [see Eq. (4.18), paper I].

Now in the wings of the line one can show (as we did in paper II) that it is only the part of (3.37) with the full density matrix $\hat{\rho}_e$ that contributes. Thus, we need just

$$\lim_{\epsilon\to 0}\int_0^\infty p^2dp \sum_{\mu_e^1\mu_e^2} \frac{1}{(2j_e+1)} \int d^3p_1 \langle \vec{p} j_e\mu_e^1|\hat{V}_1 \frac{1}{\hbar[i\epsilon+\omega-\omega_{eg}+\omega_{\vec{p}}-(H_e/\hbar)]} |j_e\mu_e^2\vec{p}_1\rangle\langle j_e\mu_e^2\vec{p}_1|\hat{\rho}_e(kT)|j_e\mu_e^1\vec{p}\rangle$$
$$= \lim_{\epsilon\to 0}\int_0^\infty p^2dp \sum_{\mu_e^1\mu_e^2} \frac{1}{(2j_e+1)} \int d^3p_1 \frac{\langle \vec{p} j_e\mu_e^1|\hat{V}_1|j_e\mu_e^2 E(\vec{p}')+\rangle\langle j_e\mu_e^2 E(\vec{p}')+|j_e\mu_e^1\vec{p}\rangle}{\hbar(\epsilon+\omega-\omega_{eg}+\omega_{\vec{p}}-\omega_{\vec{p}'})} e^{-E(p')/kT}$$
$$= \lim_{\epsilon\to 0}\int_0^\infty p^2dp \sum_{\mu_e^1\mu_e^2} \int d^3p_1 \frac{|\langle \vec{p} j_e\mu_e^1|j_e\mu_e^2 E(\vec{p}')+\rangle|^2}{\hbar(i\epsilon+\omega-\omega_{eg}+\omega_{\vec{p}}-\omega_{\vec{p}'})} e^{-E(\vec{p}')/kT}\hbar(\omega_{\vec{p}}-\omega_{\vec{p}'}). \tag{C6}$$

Here[12]

$$|j_e\mu_e^2 E(\vec{p})+\rangle \equiv \lim_{\epsilon\to 0}\left(1+\frac{1}{E(\vec{p})+E_e-\hat{H}^e+i\epsilon}\hat{V}_1^e\right)|j_e\mu_e^2\vec{p}\rangle.$$

Then the real part of the RHS of Eq. (C6) is just the type of overlap integral we should expect to obtain if we approached the emission problem in the thermal equilibrium case using a quasimolecular picture.


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