PHYSICAL REVIEW A VOLUME 22, NUMBER 5 NOVEMBER 1980

Collisional redistribution of radiation. II. The effects of degeneracy on the equations of motion for the density matrix

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(Received 7 January 1980)

We apply the analysis of paper I to degenerate atomic systems and calculate the effect of correlations between an atom (the absorber) and perturbers in the binary-collision approximation. The result of our calculation is a generalized absorption profile that specifies the final state of the atom after an absorption event. This profile is then related to the total intensities of Rayleigh scattering and fluorescence (redistributed radiation) from the atom. The profile is expressed in terms of collision operators that depend on the index of the multipole of the atom that is created. Some of the operators represent correlations between radiative and collisional events and cannot, except in certain limits, be expressed in terms of the usual line-broadening operators. This, of course, implies that one needs extra dynamical information, on top of that obtainable from ordinary absorption experiments, to be able to describe redistribution. Conversely, redistribution offers a probe of collisional dynamics, not given by absorption experiments, via the polarization of fluorescent light. We give practical expressions for the calculation of these operators and discuss their implications.

I. INTRODUCTION

In the previous paper[1] we established a formal equation of motion for the density matrix of an atom in the presence of radiative and collisional relaxation. The example we gave of these general equations of motion was the two-level atom (each nondegenerate). (Degeneracy was discussed explicitly only for the radiative self-energies. See Appendix B of paper I.) We saw [in the binary-collision approximation (BCA)] that the correlation effects we included in our equation of motion were important in the region where the driving-field incident on the atom is detuned by an amount comparable with $kT/\hbar$. When degeneracy is present the correlations can play an important role as soon as we go outside the impact region for the collisional broadening, i.e., as soon as $|\Delta\omega_2| = |\omega_0 - \omega_2| \gtrsim 1/\tau_c$. (Here ω_0 is the natural frequency of the transition being driven by the field whose frequency is ω_L, τ_c is the duration of a strong collision.) The reason for this is that the *orientation* of atom and perturber are more strongly coupled than their translational states, and the "separation of time scales" assumption for the internal states breaks down before it does for the translational motion.

Our main result will be an absorption profile that is generalized to allow for the effects of correlations. These correlations amount physically to the m_j mixing that occurs, after an absorption event in the middle of a strong collision, and they should offer an excellent probe of collision dynamics via the polarization of the fluorescent light.

In our analysis we shall assume for simplicity that the perturber distribution for each radiator is spherically symmetric. This is not an exact symmetry as the motion of the radiator establishes a preferred axis for collision. For most practical cases (and especially in the line wings) we can ignore this complication. We shall, therefore, be able to use irreducible tensor techniques. This subject, in the context of density operators for atomic systems, has been discussed in detail elsewhere.[2] Our correlation collision operators are more complex than the usual collision operators that appear in line-profile theory. They are, however, still amenable to irreducible tensor analysis.

In Sec. II we shall derive the equation of motion for a two-level system (both levels degenerate) in irreducible form, including the correlation terms. We have already discussed the radiative self-energy operator $\tilde{S}$ for this case in Appendix B of paper I. We shall also consider the case where the lower level of this two-level system does not interact with perturbers as this is a case of some practical importance. In Sec. III we shall calculate the steady-state response of this system to a monochromatic driving field. We shall also discuss the implications of the correlation terms for the intensity and polarization of the integrated Rayleigh and fluorescence peaks in a scattering experiment.

II. THE EQUATION OF MOTION FOR THE DENSITY MATRIX IN IRREDUCIBLE COMPONENTS

The reason for employing an irreducible basis for the reduced density matrix of an atomic system is to exploit the spherical symmetry of the distribution of perturbers. In a $|j_1 m_1 j_2 m_2\rangle\rangle$ basis the ordinary collision operator (with no corrections from the effect of the driving field) mixes the states. If we transform to a basis that is irreducible with respect to the rotation group (in three dimensions), e.g.,

$$|j_1j_2KQ\rangle\rangle = \sum_{m_1m_2} |j_1m_1j_2m_2\rangle\rangle(-1)^{j_1-m_2-Q} \times \begin{pmatrix} j_1 & j_2 & K \\ m_1 & -m_2 & -Q \end{pmatrix} (2K+1)^{1/2} \tag{2.1}$$

(Ref. 2), then we find that the ordinary collision operator (averaged over atom-perturber orientation) becomes simple in this basis. The correlation terms cannot, of course, be reduced to diagonal form by such a transformation since they couple different manifolds of the density matrix. The angle-averaged correlation operators do, however, reduce to a particularly convenient form in an irreducible basis. In particular, in the one interacting level (OIL) approximation the first-order corrections (in the driving-field strength) to the collision operators are rather straightforward.

We shall now proceed to the equation of motion and discuss each term in turn. The BCA equation of motion for the density matrix may be written formally in the following manner (see Sec. III of paper I):

$$\begin{aligned}\partial_t\hat{\sigma}(t) = {}&[\tilde{L}_0^A + \tilde{S} + \tilde{L}^E(t)]\hat{\sigma}(t) + \int_{-\infty}^{t} N\,\mathrm{Tr}_1[\tilde{V}_1\tilde{U}_1(t-t')\tilde{V}_1\hat{\rho}_1(-\infty)]\hat{\sigma}(t')dt' \\ &+ \int_{-\infty}^{t} N\,\mathrm{Tr}_1\left(\tilde{V}_1\tilde{U}_1(t-t')\tilde{L}^E(t')\int_{-\infty}^{t'}\tilde{U}_1(t'-t'')\tilde{V}_1\hat{\rho}_1\right)\hat{\sigma}(t'')dt''dt' \\ &+ N\int_{-\infty}^{t} dt'\,\mathrm{Tr}_1\left(\tilde{V}_1\tilde{U}_1(t-t')\tilde{L}^E(t')\int_{-\infty}^{t'}dt''\,U(t'-t'')\tilde{L}^E(t'')\int_{-\infty}^{t''}\tilde{U}_1(t''-t''')\tilde{V}_1\hat{\rho}_1(-\infty)\right)\hat{\sigma}(t''')dt''' .\end{aligned} \tag{2.2}$$

Here, $\tilde{V}_1$ is the single perturber-atom (radiator, absorber) interaction,

$$\tilde{U}_1(\tau) = \exp[(\tilde{L}_0^A + \tilde{L}_0^P(1) + \tilde{S} + \tilde{V}_1)\tau] , \tag{2.3}$$

$\tilde{L}_0^A$ and $\tilde{L}_0^P(1)$ are, respectively, the free-atom and single-perturber Liouville operators, and $\hat{\rho}_1(-\infty)$ is the single-perturber density matrix of the atom-perturber pair (at time $t=-\infty$).

The first term we consider is the simplest, i.e., $\tilde{L}_0^A$. We find from Eq. (A5), Ref. 1,

$$\langle\langle j_1\vec{p}_1j_2\vec{p}_2KQ|\tilde{L}_0^A|j_3\vec{p}_3j_4\vec{p}_4K'Q'\rangle\rangle = \delta(K',K)\delta(Q,Q)\delta(j_1,j_2)\delta(j_2,j_4)\{[E(j_3)-E(j_4)]/i\hbar\}\delta(\vec{p}_1,\vec{p}_3)\delta(\vec{p}_2,\vec{p}_4) . \tag{2.4}$$

We have assumed, as we did in paper I, that we do not need to consider the translational states of the atom explicitly. The "p" labels, therefore, refer only to the perturbers. The components of the radiative-damping operator may be established using the results of Appendix B of paper I. One finds (see Ref. 2 also)

$$\begin{aligned}\langle\langle j_1\vec{p}_1,j_2\vec{p}_2;KQ|\tilde{S}|j_3\vec{p}_3,j_4\vec{p}_4;K'Q'\rangle\rangle = {}&\Bigg[-\frac{\Gamma_{eg}}{(2j_e+1)}[\delta(2,4)\delta(e,1)\delta(e,3)+\delta(1,3)\delta(e,4)\delta(e,2)] + 2\Gamma_{eg}(-1)^{j_g+j_e+K+1} \\ &\times \begin{Bmatrix} K & j_e & j_e \\ 1 & j_g & j_g \end{Bmatrix}\delta(1g)\delta(2g)\delta(3e)\delta(4e)\delta(\vec{p}_1-\vec{p}_3)\delta(\vec{p}_2-\vec{p}_4)\Bigg]\delta(K,K')\delta(Q,Q') .\end{aligned} \tag{2.5}$$

Here j_e and j_g are the angular momenta of the upper and lower states of the transition. The tetradic elements of the Liouville operator for the driving field have been given by Ducloy,[3] and we reproduce his results here. We assume the Hamiltonian $H^E(t)$, corresponding to $\tilde{L}^E(t)$, has the form

$$H^E(t) = -\vec{d}\cdot\vec{E}(t) . \tag{2.6}$$

Here, $\vec{E}(t)$, the laser electric field at the position of the atom is assumed to be polarized with polarization vector $\vec{\epsilon}$:

$$\vec{E} = \mathcal{E}\vec{\epsilon}_1 + \mathcal{E}^*\vec{\epsilon}_1^{\,*} , \tag{2.7}$$

where

$$\mathcal{E} = \mathcal{E}_0 e^{-i\omega_L t} . \tag{2.8}$$

In the rotating-wave approximation (RWA) we obtain the following tetradic elements:

$$\langle\langle j_e\vec{p}_1 j_e\vec{p}_2 KQ\,|\tilde{L}^{\mathrm{E}}(t)\,|j_g\vec{p}_3 j_e\vec{p}_4 K'Q'\rangle\rangle=\delta(\vec{p}_1-\vec{p}_3)\delta(\vec{p}_2-\vec{p}_4)\frac{i}{\hbar}\langle j_e\|\vec{d}\,\|j_g\rangle\sum_q \epsilon^{1}_{-q}\mathcal{E}\left[{}^{q}_{j_e j_g}G^{K'K}_{Q'Q}\right](-1)^{j_g-j_e}\,, \tag{2.9a}$$

$$\langle\langle j_e\vec{p}_1 j_e\vec{p}_2 KQ\,|\tilde{L}^{\mathrm{E}}(t)\,|j_e\vec{p}_3 j_g\vec{p}_4 K'Q'\rangle\rangle=\delta(\vec{p}_1-\vec{p}_3)\delta(\vec{p}_2-\vec{p}_4)\frac{i}{\hbar}\langle j_g\|\vec{d}\,\|j_e\rangle\sum_q (\epsilon^{1}_{+q})^*\mathcal{E}^*(-1)^{K+K'+Q}\left[{}^{q}_{j_e j_g}G^{K'K}_{Q'Q}\right](-1)^{j_e-j_g+Q'}\,, \tag{2.9b}$$

$$\langle\langle j_g\vec{p}_1 j_g\vec{p}_2 KQ\,|\tilde{L}^{\mathrm{E}}(t)\,|j_g\vec{p}_3 j_e\vec{p}_4 K'Q'\rangle\rangle=\delta(\vec{p}_1-\vec{p}_3)\delta(\vec{p}_2-\vec{p}_4)\frac{i}{\hbar}\langle j_e\|\vec{d}\,\|j_g\rangle\sum_q \epsilon^{1}_{-q}\mathcal{E}(-1)^{K+K'}\left[{}^{q}_{j_g j_e}G^{K'K}_{Q'Q}\right](-1)^{j_e-j_g}\,, \tag{2.9c}$$

$$\langle\langle j_g\vec{p}_1 j_g\vec{p}_2 KQ\,|\tilde{L}^{\mathrm{E}}(t)\,|j_e\vec{p}_3 j_g\vec{p}_4 K'Q'\rangle\rangle=\delta(\vec{p}_1-\vec{p}_3)\delta(\vec{p}_2-\vec{p}_4)\frac{i}{\hbar}\langle j_g\|\vec{d}\,\|j_e\rangle\sum_q (-1)^{j_e-j_g+Q-Q'}(\epsilon^{1}_{p})^*\mathcal{E}^*\left[{}^{q}_{j_g j_e}G^{K'K}_{Q'Q}\right], \tag{2.9d}$$

$$\langle\langle j_g\vec{p}^{1} j_e\vec{p}_2 KQ\,|\tilde{L}^{\mathrm{E}}(t)\,|j_e\vec{p}_3 j_e\vec{p}_4 K'Q'\rangle\rangle=\delta(\vec{p}_1-\vec{p}_3)\delta(\vec{p}_2-\vec{p}_4)\frac{i}{\hbar}\langle j_g\|\vec{d}\,\|j_e\rangle\sum_q (\epsilon^{1}_{-q})^*\mathcal{E}^*\left[{}^{q}_{j_e j_g}G^{KK'}_{QQ'}\right], \tag{2.9e}$$

$$\langle\langle j_g\vec{p}_1 j_e\vec{p}_2 KQ\,|\tilde{L}^{\mathrm{E}}(t)\,|j_g\vec{p}_3 j_g\vec{p}_4 K'Q'\rangle\rangle=\delta(\vec{p}_1-\vec{p}_3)\delta(\vec{p}_2-\vec{p}_4)\frac{i}{\hbar}\langle j_g\|\vec{d}\,\|j_e\rangle\sum_q (\epsilon^{1}_{-q})^*\mathcal{E}^*(-1)^{K+K'}\left[{}^{q}_{j_g j_e}G^{KK'}_{QQ'}\right]. \tag{2.9f}$$

Note also,

$$\sigma^{K}_{-Q}(j_g j_e)^*=\sigma^{K}_{Q}(j_e j_g)(-1)^{j_e-j_g-Q}\,. \tag{2.10}$$

Here, $\sigma^{K}_{Q}(j_e j_g)\equiv\langle\langle KQj_e j_g\,|\hat{\sigma}\rangle\rangle$ and in the notation of Ducloy,[3]

$$\left[{}^{q}_{j_1 j_2}G^{K'K}_{Q'Q}\right]=(-1)^{j_1+j_2+Q'}[(2K'+1)(2K+1)]^{1/2}$$
$$\times\begin{pmatrix}K' & 1 & K\\ Q' & q & -Q\end{pmatrix}\begin{Bmatrix}K' & 1 & K\\ \dot{J}_1 & j_1 & j_2\end{Bmatrix}. \tag{2.11}$$

$\langle j_g\|\vec{d}\,\|j_e\rangle$ is the reduced matrix element[4] which, unlike Ducloy, we do *not* assume to be real.

We now proceed to the discussion of the collision operators the simplest of which, the ordinary collision operator, has been discussed in detail elsewhere. See paper I and references cited therein.

Note first, that for $\mathrm{Im}z>0$,

$$\int_0^\infty e^{iz\tau}N_p\mathrm{Tr}_1[\tilde{V}_1\tilde{U}_1(\tau)\tilde{V}_1\hat{\rho}_1(-\infty)]d\tau$$
$$=N_p\mathrm{Tr}_1\left(\tilde{V}_1\frac{1}{-iz-\tilde{L}_1-\tilde{S}}\tilde{V}_1\hat{\rho}_1(-\infty)\right)\,. \tag{2.12}$$

Here N_p is the number of perturbers and $\tilde{L}_1=\tilde{L}^{\mathrm{A}}_0+\tilde{L}^{\mathrm{P}}_0(1)+\tilde{V}_1$ (see paper I). Its average over atom-perturber orientation is obtained using standard rotation operator techniques (see Appendix A and Ref. 5). We quote the result here for convenience,

$$N_p\left\langle\!\!\left\langle j_1 j_2 KQ\,\middle|\,\mathrm{Tr}_1\left(\tilde{V}_1\frac{1}{-iz-\tilde{L}_1-\tilde{S}}\tilde{V}_1\hat{\rho}_1\right)\middle|\,j_3 j_4 K'Q'\right\rangle\!\!\right\rangle$$
$$=\delta(K,K')\delta(Q,Q')M^{K}(z)\,. \tag{2.13}$$

Here

$${}^{j_1 j_2}_{j_3 j_4}M^{K}(z)=\sum_{\mu_1\mu_2\mu_3\mu_4}(-1)^{\mu_2-\mu_4}\begin{pmatrix}j_1 & j_2 & K\\ -\mu_1 & \mu_2 & Q\end{pmatrix}\begin{pmatrix}j_3 & j_4 & K\\ -\mu_3 & \mu_4 & Q\end{pmatrix}$$
$$\times\left\langle\!\!\left\langle j_1\mu_1,j_2\mu_2\middle|N_p\mathrm{Tr}_1'\left(\tilde{V}_1\frac{1}{-iz-\tilde{L}_1-\tilde{S}}\tilde{V}_1\rho_1(-\infty)\right)\middle|j_3\mu_3,j_4\mu_4\right\rangle\!\!\right\rangle\,. \tag{2.14}$$

The prime indicates that the angle average has been performed. Thus

$$\left\langle\!\!\left\langle j_1\mu_1 j_2\mu_2\middle|\mathrm{Tr}_1'\left(\tilde{V}_1\frac{1}{-iz-\tilde{L}_1+\tilde{S}}\tilde{V}_1\rho_1(-\infty)\right)\middle|j_3\mu_3,j_4\mu_4\right\rangle\!\!\right\rangle$$
$$\equiv\int d^3p_2\int_0^\infty p_1^2dp_1\left\langle\!\!\left\langle j_1\mu_1\vec{p}_2 j_2\mu_2\vec{p}_2\middle|\tilde{V}_1\frac{1}{-iz-\tilde{L}_1-\tilde{S}}\tilde{V}_1\middle|j_3\mu_3\vec{p}_1 j_4\mu_4\vec{p}_1\right\rangle\!\!\right\rangle\rho_{\vec{p}_1\vec{p}_1}(-\infty)\,. \tag{2.15}$$

It is often convenient to use the interaction picture to calculate the collision operators.[1,6] We define an interaction picture $\tilde{U}^{\mathrm{I}}_1(t_2,t_1)$ thus,

$$\tilde{U}^{\mathrm{I}}_1(t_2,t_1)=T\exp\left(\int_{t_1}^{t_2}\tilde{V}^{\mathrm{I}}_1(t')dt'\right)\,, \tag{2.16}$$

where $\tilde{V}^{\mathrm{I}}_1(t)=\tilde{U}^{0}_1(t)\tilde{V}_1\tilde{U}^{0}_1(-t)$, $\tilde{U}^{0}_1(t)=\exp[\tilde{L}^{0}t]$, $\tilde{L}^{0}=\tilde{L}^{\mathrm{A}}_0+\tilde{L}^{\mathrm{P}}_0(1)+\tilde{S}$, and T is the time-ordering operator.[7]

The collision operator may then be written in the form

$$
{}^{j_1 j_2}_{j_3 j_4}M^K(z)=\sum_{\mu_1\mu_2\mu_3\mu_4 Q}\int_0^\infty e^{i\Delta t}(-1)^{\mu_2-\mu_4}\begin{pmatrix} j_1 & j_2 & K\\ -\mu_1 & \mu_2 & Q\end{pmatrix}
\times\begin{pmatrix} j_3 & j_4 & K\\ -\mu_3 & \mu_4 & Q\end{pmatrix}\langle\langle j_1\mu_1 j_2\mu_2 | N_p \mathrm{Tr}_1[\tilde V_1^I(t)\tilde U_1^I(t,0)\tilde V_1^I(0)]\,| j_3\mu_3 j_4\mu_4\rangle\rangle . \qquad (2.17)
$$

Here, $\Delta = z - i\langle\langle 1,2|\tilde S|1,2\rangle\rangle - \omega_{12}$. We know that other states of the atom (and of the perturbers) will be mixed into the states we have labeled during a collision. If these other states are well separated in energy from those with which we are principally concerned, we can use an adiabatic approximation for their coupling into j_e and j_g. We can then construct a $\tilde V_{\mathrm{eff}}$ along the lines we discussed in paper I. We would then know that $|j_e\rangle$ and $|j_g\rangle$ form a complete set with respect to the interaction. If we cannot use an adiabatic approximation, then we have to label all the other states explicitly. This is the case if the states, to which our original state is coupled, are near degenerate with the initial states, e.g., in hydrogen. Since we do not want to limit our treatment to either case, we shall use the following procedure. We shall use the full interaction and include the labels of other excited states in the problem (j_e', etc.). At any point, however, we can replace $\tilde V_1$ and $\tilde U_1$ by $\tilde V_{\mathrm{eff}}$ and $\tilde U_{\mathrm{eff}}$, and add the first-order term $\mathrm{Tr}_1[\tilde V_{\mathrm{eff}}\hat\rho_1]$, which does not vanish. When we make these replacements, we can drop the extra labels for the states outside the j_e and j_g subspace.

Let us now consider the corrections to the collision operator that we derived in the first paper. We emphasize that *these corrections become important as soon as we go outside the impact approximation.* In the nondegenerate case we saw how the correlation terms took into account the effect of the interatomic potential on the distribution of perturbers. (Hence the proper Boltzmann factors in the absorption profile, paper I.) When degeneracy is present, however, we also have to take into account the fact that absorption of a photon by the atom occurs when the absorber-perturber pair have some definite orientation. This orientation is, moreover, linked to the energy difference the collision takes up. Thus if we are concerned with the final m_j state the atom is left in, after absorbing a photon, absorption events during a collision, linked to a definite orientation of the radiator-perturber pair, are important. Our corrections to the collision operator include precisely this physics in the equation of motion.

We start with the first-order correction to the collision operator, i.e., the third term in Eq. (2.2). Consider the coupling of $\langle\langle j_e j_g KQ|\sigma(t)\rangle\rangle$ to $\langle\langle j_e^1 j_e^2 KQ|\sigma(t)\rangle\rangle$. In the steady state, where $\langle\langle j_e j_g KQ|\sigma(t)\rangle\rangle$ oscillates like $e^{-i\omega_L t}$, this may be written in the following form:

$$
\lim_{t\to\infty}\sum_{m_e^3 m_e^4 j_e^3 j_e^4}\int_{-\infty}^t dt'\left\langle\!\!\left\langle j_e^1 j_e^2 K_1 Q_1\right|\mathrm{Tr}_1\Big(\tilde V_1\tilde U(t-t')\,|j_e^3 m_e^3 j_e^4 m_e^4\rangle\rangle\langle\langle j_e^3 m_e^3 j_e^4 m_e^4|\tilde L^E(t'-t'')\,|j_e^3 m_e^3 j_g m_g^1\rangle\rangle
\times\int_{-\infty}^{t'} dt''\langle\langle j_e^3 m_e^3 j_g m_g^1|\tilde U_1(t'-t'')\tilde V_1\hat\rho_1\Big)\left| j_e^5 j_g K_2 Q_2\right\rangle\!\!\right\rangle
$$

$$
=\lim_{\epsilon\to 0^+}\sum_{m_e^3 m_e^4 j_e^3 j_e^4}\left\langle\!\!\left\langle j_e^1 j_e^2 K_1 Q_1\right|\mathrm{Tr}_1\Big(\tilde V_1\frac{-1}{\epsilon+\tilde L_1+\tilde S}\,|j_e^3 m_e^3 j_e^4 m_e^4\rangle\rangle
\times\langle\langle j_e^3 m_e^3 j_e^4 m_e^4|\tilde L^E(0)|j_e^3 m_e^3 j_g m_g^1\rangle\rangle\langle\langle j_e^3 m_e^3 j_g m_g^1|\frac{-1}{\epsilon+i\omega_L+\tilde L_1+\tilde S}\tilde V_1\hat\rho_1\Big)\left| j_e^5 j_g K_2 Q_2\right\rangle\!\!\right\rangle . \qquad (2.18)
$$

The extra j_e''s label excited states that are coupled into $|j_e\rangle$ by $\tilde V_1$. In Appendix A we show how the angular average may be performed to yield the following result for (2.18):

$$
\sum_q \frac{\mathcal{E}_0^*}{i\hbar}(\epsilon^*)_q\langle j_g\|\vec d\|j_e^4\rangle(2K_1+1)^{1/2}(2K_2+1)^{1/2}\begin{pmatrix}K_1 & K_2 & 1\\ Q_1 & -Q_2 & -q\end{pmatrix}(-1)^{K_1-Q_2+j_g}\mathcal{C}^1(K_1K_2;e_1e_2,e_5g,\omega_L)\,, \qquad (2.19)
$$

where

$$
\begin{aligned}
\mathfrak{C}^1(K_1,K_2;e_1e_2,e_5g,\omega_L) = {} & N_p \sum (-1)^{j_e^1+j_e^5+\mu_e^1+\mu_g^1+\mu_g^2+Q_5^1} \\
& \times \begin{pmatrix} j_e^1 & j_e^2 & K_1 \\ -\mu_e^1 & \mu_e^2 & Q_3 \end{pmatrix} \begin{pmatrix} j_e^5 & j_g & K_2 \\ \mu_e^5 & -\mu_g^2 & Q_4 \end{pmatrix} \begin{pmatrix} j_e^4 & j_g & 1 \\ \mu_e^4 & -\mu_g^1 & -Q_3 \end{pmatrix} \begin{pmatrix} K_1 & K_2 & 1 \\ Q_3 & Q_4 & Q_5 \end{pmatrix} \\
& \times \lim_{\epsilon\to 0} \int d^3p_{1,2,3} \int dp_4 p_4^2 \left\langle\!\!\left\langle j_e^1\mu_e^1\vec{p}_1 j_e^2\mu_e^2\vec{p}_1 \left| \tilde{V}_1 \frac{1}{\epsilon+\tilde{L}_1+\tilde{S}} \right| j_e^3\mu_e^3\vec{p}_2 j_e^4\mu_e^4\vec{p}_3 \right\rangle\!\!\right\rangle \\
& \times \left\langle\!\!\left\langle j_e^3\mu_e^3\vec{p}_2 j_g\mu_g^1\vec{p}_3 \left| \frac{1}{\epsilon+\tilde{L}_1+\tilde{S}+i\omega_L}\tilde{V}_1 \right| j_e^5\mu_e^5\vec{p}_4 j_g\mu_g^2\vec{p}_4 \right\rangle\!\!\right\rangle \rho_{\vec{p}_4\vec{p}_4} \\
& (t=-\infty)\,.
\end{aligned} \tag{2.20}
$$

The summation extends over μ_e^1, μ_e^2, μ_e^4, μ_e^5, μ_g^1, μ_g^2, Q_3, Q_4, Q_5, j_e^3, and j_e^4. If we take the one interacting level (OIL) approximation,[3] where one level (we chose the lower) does not interact with perturbers, we obtain the following result for (2.18):

$$
\sum_q (\mathcal{E}_0)^*(\epsilon^*)_q (2K_1+1)^{1/2}(2K_2+1)^{1/2} \begin{pmatrix} K_1 & K_2 & 1 \\ Q_1 & -Q_2 & +q \end{pmatrix} \begin{Bmatrix} K_1 & 1 & K_2 \\ j_g & j_e^5 & j_e^4 \end{Bmatrix} (-1)^{1-Q_1+j_e^4+j_e^5} \mathfrak{C}^1(K_1;e_1e_2,e_5g,\omega_L) \frac{\langle j_g \| \vec{d} \| j_e^4 \rangle}{i\hbar}\,. \tag{2.21}
$$

Here

$$
\begin{aligned}
\mathfrak{C}^1(K;e_1e_2,e_5g,\omega_L) = {} & N_p \lim_{\epsilon\to 0} \int d^3p_{1,2} \int dp_3 p_3^2 \sum \begin{pmatrix} j_e^5 & j_e^4 & K \\ \mu_e^5 & -\mu_e^4 & Q \end{pmatrix} \begin{pmatrix} j_e^2 & j_e^1 & K \\ \mu_e^2 & -\mu_e^1 & Q \end{pmatrix} (-1)^{j_e^2+j_e^5+\mu_e^5-\mu_e^1} \\
& \times \left\langle\!\!\left\langle j_e^1\mu_e^1\vec{p}_1 j_e^2\mu_e^2\vec{p}_1 \left| \tilde{V}_1 \frac{-1}{\epsilon+\tilde{L}_1+\tilde{S}} \right| j_e^3\mu_e^3\vec{p}_2 j_e^4\mu_e^4\vec{p}_3 \right\rangle\!\!\right\rangle \\
& \times \left\langle\!\!\left\langle j_e^3\mu_e^3\vec{p}_2 j_g\mu_g^1\vec{p}_3 \left| \frac{-1}{\epsilon+i\omega_L+\tilde{L}_1+\tilde{S}}\tilde{V}_1 \right| j_e^5\mu_e^5\vec{p}_3 j_g\mu_g^1\vec{p}_3 \right\rangle\!\!\right\rangle \rho_{\vec{p}_3\vec{p}_3} \\
& (t=-\infty)
\end{aligned} \tag{2.22}
$$

where the summation is over the indices μ_e^1, μ_e^2, μ_e^3, μ_e^4, μ_e^5, μ_g^1, Q, j_e^3, and j_e^4.

Similar results for the other corrections to the collision operator are given (up to second order in the driving-field strength) in Appendix A. These corrections may also be expressed directly in terms of interaction picture operators, e.g.,

$$
\begin{aligned}
\mathfrak{C}^1(K;e_1e_2;eg,\omega_L) = {} & N_p \int d^3p_{1,2} \int dp_3 p_3^2 \sum \begin{pmatrix} j_e^5 & j_e^4 & K \\ \mu_e^5 & -\mu_e^4 & Q \end{pmatrix} \begin{pmatrix} j_e^2 & j_e^1 & K \\ \mu_e^2 & -\mu_e^1 & Q \end{pmatrix} (-1)^{j_e^2+j_e^5+\mu_e^5-\mu_e^1} \\
& \times \int_0^\infty e^{i(i\gamma_N)\tau_2} d\tau_2 \\
& \times \langle\langle j_e^1\mu_e^1\vec{p}_1 j_e^2\mu_e^2\vec{p}_1 | \tilde{V}_1^{\mathrm{I}}(\tau_1+\tau_2)\tilde{U}_1^{\mathrm{I}}(\tau_1+\tau_2,\tau_1) | j_e^3\mu_e^3\vec{p}_2 j_e^4\mu_e^4\vec{p}_3 \rangle\rangle \\
& \times \int_0^\infty e^{i[\omega_L-\omega_{eg}+(i\gamma_N/2)\tau_1]} \\
& \times \langle\langle j_e^3\mu_e^3\vec{p}_2 j_g\mu_g^1\vec{p}_3 | \tilde{U}_1^{\mathrm{I}}(\tau_1,0)\tilde{V}_1^{\mathrm{I}}(0) | j_e^5\mu_e^5\vec{p}_3 j_g\mu_g^1\vec{p}_3 \rangle\rangle \rho_{\vec{p}_3\vec{p}_3} \quad (t=-\infty)\,,
\end{aligned} \tag{2.23}
$$

the summation being over Q, j_e^3, j_e^4, μ_e^1, μ_e^2, μ_e^3, μ_e^4, and μ_e^5. Here $\gamma_N = 2\Gamma_{eg}/(2j_e+1)$. If we further assume that we can use classical path methods to evaluate this operator, we can reduce it to the following:

$$\mathcal{C}^1(K,e_1e_2;eg,\omega_L)=N_p\sum\begin{pmatrix} j_e^5 & j_e^4 & K\\ \mu_e^5 & -\mu_e^4 & Q\end{pmatrix}\begin{pmatrix} j_e^2 & j_e^1 & K\\ \mu_e^2 & -\mu_e^1 & Q\end{pmatrix}(-1)^{\mu_e^5-\mu_e^1+j_e^2+j_e^5}$$

$$\times\int_0^\infty e^{-\gamma_N\tau_2}d\tau_2\int_0^\infty e^{i[\omega_L-\omega'_{eg}+(i\gamma_N/2)]\tau_1}[\langle\langle j_e^1\mu_e^1 j_e^2\mu_e^2|\tilde{V}_1^{\mathrm{I}}(\tau_1+\tau_2)\tilde{U}_1^{\mathrm{I}}(\tau_1+\tau_2,\tau_1)|j_e^3\mu_e^3 j_e^4\mu_e^4\rangle\rangle$$

$$\times\langle\langle j_e^3\mu_e^3 j_g\mu_g^1|\tilde{U}_1^{\mathrm{I}}(\tau_1,0)\tilde{V}_1^{\mathrm{I}}(0)|j_e^5\mu_e^5 j_g\mu_g^1\rangle\rangle]\,, \qquad (2.24a)$$

where the quantity in square brackets has been averaged over velocity and distance of approach (not over angles),

$$\mathcal{C}^1(K,e_1e_2;eg,\omega_L)=N_p\sum\begin{pmatrix} j_e^5 & j_e^4 & K\\ \mu_e^5 & -\mu_e^4 & Q\end{pmatrix}\begin{pmatrix} j_e^2 & j_e^1 & K\\ \mu_e^2 & -\mu_e^1 & Q\end{pmatrix}(-1)^{\mu_e^5-\mu_e^1+j_e^2+j_e^5}$$

$$\times\int_0^\infty e^{-\gamma_N\tau_2}d\tau_2\int_0^\infty e^{i[\omega_L-\omega_{eg}^3+(i\gamma_N/2)]\tau_1}\left\langle\!\!\left\langle j_e^1\mu_e^1 j_e^2\mu_e^2\left|\frac{d}{d\tau_2}\tilde{U}_1^{\mathrm{I}}(\tau_2,0)\right|j_e^3\mu_e^3 j_e^4\mu_e^4\right\rangle\!\!\right\rangle$$

$$\times\left\langle\!\!\left\langle j_e^3\mu_e^3 j_g\mu_g^1\left|\frac{d}{d\tau_1}\tilde{U}_1^{\mathrm{I}}(0,-\tau_1)\right|j_e^5\mu_e^5 j_g\mu_g^1\right\rangle\!\!\right\rangle . \qquad (2.24b)$$

In Eqs. (2.24a) and (2.24b) the summation is over Q, j_e^3, j_e^4, μ_e^1, μ_e^2, μ_e^3, μ_e^4, and μ_e^5. Using an adiabatic approximation for the coupling into other excited states implies that we can write

$$\mathcal{C}^1(K,ee;eg,\omega_L)=-\gamma_N i[\omega_L-\omega_{eg}+(i\gamma_N/2)]N\sum_{\mu'SQ}\begin{pmatrix} j_e & j_e & K\\ \mu_e^4 & -\mu_e^5 & Q\end{pmatrix}\begin{pmatrix} j_e & j_e & K\\ \mu_e^2 & -\mu_e^1 & Q\end{pmatrix}(-1)^{\mu_e^5-\mu_e^1}$$

$$\times\int_0^\infty e^{-\gamma_N\tau_2}d\tau_2\int_0^\infty e^{i[\omega_L-\omega_{eg}+(i\gamma_N/2)]\tau_1}$$

$$\times\{\langle j_e\mu_e^1|\hat{U}_1^{\mathrm{I}}(\tau_2,-\tau_1)_{\mathrm{eff}}-\hat{U}_1^{\mathrm{I}}(\tau_2)_{\mathrm{eff}}|j_e\mu_e^5\rangle$$

$$\times\langle j_e\mu_e^4|\hat{U}_1^{\mathrm{I}\dagger}(\tau_2,0)_{\mathrm{eff}}|j_e\mu_e^2\rangle$$

$$-\langle j_e^1\mu_e^1|[\hat{U}_1^{\mathrm{I}}(\tau_1,0)_{\mathrm{eff}}-1]|j_e\mu_e^5\rangle\langle j_e\mu_e^4|j_e\mu_e^2\rangle\}$$

$$=-\gamma_N i[\omega_L-\omega_{eg}+(i\gamma_N/2)]\left\{\left[N\sum_{\mu'S,Q}\begin{pmatrix} j_e & j_e & K\\ \mu_e^4 & -\mu_e^5 & Q\end{pmatrix}\begin{pmatrix} j_e & j_e & K\\ \mu_e^2 & -\mu_e^1 & Q\end{pmatrix}(-1)^{\mu_e^5-\mu_e^1}\right.\right.$$

$$\times\int_0^\infty e^{-\gamma_N\tau_2}d\tau_2\int_0^\infty e^{i[\omega_L-\omega'_{eg}+(i\gamma_N/2)]\tau_1}d\tau_1$$

$$\times\langle j_e\mu_e^1|\hat{U}_1^{\mathrm{I}}(\tau_2,-\tau_1)_{\mathrm{eff}}-\hat{U}_1^{\mathrm{I}}(\tau_2,0)_{\mathrm{eff}}|j_e\mu_e^5\rangle$$

$$\left.\left.\times\langle j_e\mu_e^4|\hat{U}_1^{\mathrm{I}\dagger}(\tau_2,0)_{\mathrm{eff}}|j_e\mu_e^2\rangle\right]\right\}$$

$$-[\omega_L-\omega_{eg}+i(\gamma_N/2)]^{-2}\,{}^{j_e j_g}_{j_e j_g}M^1(\omega_L)(\gamma_N^{-1})\,. \qquad (2.25)$$

[Note that making an adiabatic approximation involves ignoring the density matrix elements $\langle\langle j_e^1 j_e^2 KQ|\hat{\sigma}(t)\rangle\rangle$ where j_e^1 and j_e^2 are distinct from j_e.]

There are various other forms in which we may express $\mathcal{C}^1(K,ee,eg,\omega_L)$, but the essential physics is the following. Absorption in the far wings occurs when the energy of an incoming photon matches the energy separation between the quasimolecular states of the colliding atom-perturber system. If we use the Born-Oppenheimer approximation then we can associate a given interatomic separation and orientation with a specific energy separation between upper and lower states. The intensity of transitions is then determined by the Franck-Condon principle which embodies the fact that, during an electronic transition the translational motion of the nuclei of the quasimolecule is unchanged. Thus when an absorption event occurs in the far wings of a line, it is the interatomic potential that first takes up the energy defect (with respect to the free-atom's frequency). If the upper state of the transition is nondegenerate the subsequent evolution—the completion of the collision—is unimportant (Sec. IV, paper I). When the atom is degenerate the subsequent evolution mixes the molecular state back into atomic m_J states and affects the atomic multipole that is formed by the overall absorption process. This process is not taken into account in the normal absorption profiles. Now that we have expressions for the correlation operators we can discuss their effect for a specific example.

III. STEADY-STATE RESPONSE (IN OIL APPROXIMATION)

To demonstrate the effect the correlation terms have on the density matrix, we shall, in this section, calculate the response of a two-level atom to a weak driving field. We shall consider the OIL collision operators only since the generalization is quite straightforward. The equations for the steady-state components of the density matrix may be written in the following manner.

$$\lim_{t\to\infty}\langle\langle KQj_1j_2|\sigma(t)\rangle\rangle=\sigma^{KQ}_{j_1j_2}\,,$$

$$\sigma^{KQ}_{j_ej_e}=\frac{1}{-{}^{j_ej_e}_{j_ej_e}M^K(0)+\dfrac{2\Gamma_{eg}}{2j_e+1}}\left(\frac{i}{\hbar}\sum_{qQ'K'}\mathcal{E}_0^*(\epsilon^1_q)^*\langle j_g\|\vec{\mathrm{d}}\|j_e\rangle\right.$$
$$\left.\times\,{}^{\;q}_{j_ej_g}G^{K'K}_{Q'Q}(-1)^{K+K'+j_e-j_g+Q+Q'}[1+\mathfrak{C}^1(K;ee;eg,\omega_L)]\right)\sigma^{K'Q'}_{j_ej_g}$$
$$+\,\mathcal{E}_0\epsilon^1_{-q}\langle j_e\|\vec{\mathrm{d}}\|j_g\rangle\,{}^{\;q}_{j_ej_g}G^{K'K}_{Q'Q}[(1+\mathfrak{C}^1(K;ee;ge,\omega_L)](-1)^{j_e-j_g}\sigma^{K'Q'}_{j_gj_e}\,, \tag{3.1}$$

$$\sigma^{KQ}_{j_ej_g}=\frac{1/i\hbar}{i(\omega_{eg}-\omega_L)-{}^{j_ej_g}_{j_ej_g}M^K(\omega_L)+(\Gamma_{eg}/2j_e+1)}$$
$$\times\sum_{q'Q'K'}\langle j_e\|\vec{\mathrm{d}}\|j_g\rangle\epsilon^1_{-q'}\mathcal{E}_0\left\{{}^{\;q'}_{j_gj_e}G^{KK'}_{-Q-Q'}\sigma^{K'Q'}_{j_gj_g}(-1)^{K+K'+Q+Q'}+{}^{\;q'}_{j_gj_e}G^{KK'}_{-Q-Q'}(-1)^{Q+Q'}[1+\mathfrak{C}^1(K',eg,ee,\omega_L)]\right\}\sigma^{K'Q'}_{j_ej_e}\,. \tag{3.2}$$

Now we take the following initial condition and in the weak-field approximation assume it is not changed appreciably:

$$\sigma^{KQ}_{j_gj_g}=\frac{N_a}{(2j_g+1)^{1/2}}\frac{1}{2}\delta(K=0)\delta(Q=0)\,. \tag{3.3}$$

Here N_a is the ground-state population of the atoms. This initial condition supposes that the ground state is unpolarized, which is certainly valid in the absence of external magnetic fields. It is well known that if we illuminate the atoms with polarized light, we will create orientation and alignment of the ground state. For the purposes of this paper we shall assume that this optical pumping does not affect the ground state appreciably. If we were considering a single-photon scattering event this would certainly be valid. If we consider the steady state in a constant driving field, then we have to require that some relaxation mechanism disorients the ground state after each absorption and reemission cycle. In either case, we would obtain the scattering amplitude for unpolarized atoms. There is, of course, no intrinsic difficulty in calculating the scattering from an arbitrary steady state, and we have chosen the unpolarized state since it is the most important in applications. So to order $|\mathcal{E}_0|^2$, we obtain the following upper-state multipoles:

$$\sigma^{KQ}_{j_ej_e}=\frac{|\mathcal{E}_0|^2}{\hbar^2}\langle j_g\|\vec{\mathrm{d}}\|j_e\rangle\langle j_g\|\vec{\mathrm{d}}\|j_e\rangle^*(2K+1)^{1/2}\sum_{qq'}(\epsilon_q)^*(\epsilon_{-q'})\begin{pmatrix}1&1&K\\q'&q&-Q\end{pmatrix}(-1)^{j_e-j_g+1+K-Q}\begin{Bmatrix}1&1&K\\j_e&j_e&j_g\end{Bmatrix}$$
$$\times\frac{1}{-{}^{j_ej_e}_{j_ej_e}M^K(0)+\dfrac{2\Gamma_{eg}}{2j_e+1}}\frac{N_a}{(2j_g+1)}$$
$$\times 2\,\mathrm{Re}\left[\frac{1}{-{}^{j_ej_g}_{j_ej_g}M'(\omega_L)+i(\omega_{eg}-\omega_L)+\dfrac{2\Gamma_{eg}}{(2j_e+1)}}\right.$$
$$\left.\times[1+\mathfrak{C}^1(K,ee,eg,\omega_L)]\right]\,, \tag{3.4}$$

$$\sigma_{j_e j_e}^{KQ}=\frac{|\mathcal{E}_0|^2}{\hbar^2}\frac{|\langle j_g\|\vec{d}\|j_e\rangle|^2}{(2j_g+1)}N_a\sum_K\frac{D_{-Q}^K(\vec{\epsilon}_1^*\vec{\epsilon}_1)}{\left(M^K(0)+\frac{2\Gamma_{eg}}{(2j_e+1)}\right)}\times 2\,\mathrm{Re}\left(\frac{1}{-{}^{j_e j_g}_{j_e j_g}M'(\omega_L)+i(\omega_{eg}-\omega_L)+\frac{\Gamma_{eg}}{(2j_e+1)}}[1+\mathcal{C}^1(K,ee,eg,\omega_L)]\right). \quad (3.5)$$

Here

$$D_Q^K(\vec{\epsilon}_1^*\vec{\epsilon}_1)=|\langle j_e\|\vec{d}\|j_g\rangle|^2(-1)^{j_e+j_g+1}\begin{Bmatrix}1 & 1 & K\\ j_e & j_e & j_g\end{Bmatrix}P_Q^K(\vec{\epsilon}_1^*\vec{\epsilon}) \quad (3.6)$$

and

$$P_Q^K(\vec{\epsilon}_1^*\vec{\epsilon}_1)=\sum_{qq'}(-1)^{1-q}\langle 1-q,q'|KQ\rangle(\vec{\epsilon}_{q'}^{\,1})(\vec{\epsilon}_q^{\,1})^*. \quad (3.7)$$

Using this result one can calculate total scattered intensities.

The *total* intensity of light scattered in the direction of the wave vector $\vec{k}_2$ with polarization $\vec{\epsilon}_2$ is

$$I(\vec{k}_2,\vec{\epsilon}_2)=I_0\sum_{K=0,Q}^{2j_e}D_{+Q}^K(\vec{\epsilon}_2^*\vec{\epsilon}_2)\sigma_{j_e j_e}^{KQ}. \quad (3.8)$$

Here I_0 is a constant.

This is not quite sufficient since we want to discuss the total intensity of the *redistributed* radiation. This can be done by simple subtraction if we know the total intensity of the light that is scattered *without* its frequency being changed. To know this we should, in principle, have to calculate the full correlation function. This will be done in the following paper. For the purposes of continuity of our present argument, however, we note that scattering with no frequency change occurs when there is no perturber present. This means that the energy-conserving component does not depend on the collisions. This implies that we can take the result of Ref. 9 for this component and subtract it from the total intensity to obtain the integrated intensity of the redistributed component. If we do this we obtain the following result:

$$I_{\text{redistrib}}=I_0\sum_{K=0}^{2j_e}D_{+Q}^K(\vec{\epsilon}_2^*\vec{\epsilon}_2)\frac{|\mathcal{E}_0|^2}{\hbar^2}\frac{N}{(2j_g+1)}D_{-Q}^K(\vec{\epsilon}_1^*\vec{\epsilon}_1)$$
$$\times\left[2\,\mathrm{Re}\frac{1}{-{}^{j_e j_e}_{j_e j_e}M^K(0)+\frac{2\Gamma_{eg}}{(2j_e+1)}}\left(\frac{1}{-{}^{j_e j_g}_{j_e j_g}M^1(\omega_L)+i(\omega_{eg}-\omega_L)+\frac{\Gamma_{eg}}{2j_e+1}}[1+\mathcal{C}^1(k,ee,eg,\omega_L)]\right)\right.$$
$$\left.-\left|\frac{1}{{}^{j_e j_g}_{j_e j_g}M^1(\omega_L)+i(\omega_{eg}-\omega_L)+\frac{\Gamma_{eg}}{2j_e+1}}\right|^2\right]. \quad (3.9)$$

Let us use the following notation:

$${}^{j_e j_e}_{j_e j_e}M^K(0)=-\gamma^K, \quad (3.10a)$$

$${}^{j_e j_g}_{j_e j_g}M^1(\omega_L)=-i\Delta_c^1(\omega_L)-\gamma_c^1(\omega_L), \quad (3.10b)$$

$$\frac{2\Gamma_{eg}}{(2j_e+1)}=\gamma_N. \quad (3.10c)$$

Then we can write the redistributed intensity in the form

$$I_{\text{redistrib}}=I_0\sum_{K=0}^{2j_e}(-1)^Q D_{+Q}^K(\vec{\epsilon}_2^*\vec{\epsilon}_2)\frac{|\mathcal{E}_0|^2}{\hbar^2}\frac{N}{(2j_g+1)}\frac{1}{(\omega_{eg}+\Delta_c^1(\omega_L)-\omega_L)^2+[(\gamma_N/2)+\gamma_c^1(\omega_L)]^2}D_{-Q}^K(\vec{\epsilon}_1^*\vec{\epsilon}_1)$$
$$\times\left(\frac{1}{\gamma^K+\gamma_N}\{[\gamma_N+2\gamma_c^1(\Delta\omega_L)]1+\mathrm{Re}[\mathcal{C}^1(K,ee,eg,\omega_L)]\right.$$
$$\left.+[\Delta\omega_L+\Delta_c^1(\omega_L)]2\,\mathrm{Im}[\mathcal{C}^1(K,ee,eg,\omega_L)]\}-1\right). \quad (3.11)$$

Thus we have

$$I_{\text{redistrib}} = I_0 \sum_{K=0}^{2j_e} (-1)^Q D_Q^K(\vec{\epsilon}_2^{\,*}\vec{\epsilon}_2)\pi \frac{|E_0^2|}{\hbar^2} D_{-Q}^K(\vec{\epsilon}_1^{\,*}\vec{\epsilon}_1)\frac{N}{(2j_g+1)} \times \left(\frac{2f_{\text{abs}}^K(\Delta\omega_L)}{\gamma^K+\gamma_N} - \frac{f(\Delta\omega_L)}{\gamma^1(\Delta\omega_L)}\right), \tag{3.12}$$

where we have introduced the *generalized absorption profile* $f_{\text{abs}}^K(\Delta\omega_L)$, defined by

$$f_{\text{abs}}^K(\Delta\omega_L) = f(\Delta\omega_L)[1+\operatorname{Re}\mathcal{C}^1(K,ee,eg,\omega_1)] + n(\Delta\omega_L)\operatorname{Im}[\mathcal{C}^1(K,ee,eg,\omega_L)]. \tag{3.13}$$

Here, $f(\Delta\omega_L)$ and $n(\Delta\omega_L)$ are the unified theory response functions that have no correlation terms in them:

$$f(\Delta\omega_L) = \frac{1}{\pi}\frac{\gamma^1(\Delta\omega_L)}{[\omega_{eg}+\Delta_c^1(\omega_L)-\omega_L]^2+\gamma^1(\Delta\omega_L)^2}, \tag{3.14}$$

$$n(\Delta\omega_L) = \frac{1}{\pi}\frac{\omega_L-\omega_{eg}-\Delta_c^1(\Delta\omega_L)}{[\omega_{eg}+\Delta_c^1(\omega_L)-\omega_L]^2+\gamma^1(\Delta\omega_L)^2}, \tag{3.15}$$

$$\gamma^1(\Delta\omega_L) = \tfrac{1}{2}\gamma_N + \gamma_c^1(\Delta\omega_L),$$

$$\Delta\omega_L = \omega_{eg} - \omega_L. \tag{3.16}$$

This is our principal result and the subsequent discussion will explain the significance of our generalized absorption profile.

To demonstrate the importance of the correlation terms we consider this expression in the antistatic wing of the line profile where $\Delta\omega_L < -1/\tau_c < 0$. In this limit $\gamma^1(\Delta\omega_L) \to 0$. If it were not for the correlation term this *would imply that the redistributed intensity from the $K \neq 0$ terms would go negative*. In the antistatic wing the correlation term may be evaluated quite straightforwardly. The main contribution to the collision integral comes in a semiclassical treatment from the points of stationary phase where the energy defect is made up to directly by the potential. It is precisely this stationary-phase contribution that goes to zero in the antistatic wing. There is still, however, the contribution from the mixing of m_J states at large internuclear separation (of atom and perturber) where the states are nearly degenerate. This contribution can be quite accurately determined by an expansion in $1/\Delta\omega_L$. In like fashion, we can similarly use an expansion in $1/\Delta\omega_L$ to evaluate the correlation operator when points of stationary phase are unimportant. We find that (see Appendix B)

$$\Delta\omega_L 2\operatorname{Im}[\mathcal{C}^1(K,ee,eg,\omega_L)] \to \gamma_K$$

(in the antistatic wing). This implies that the scattered intensity is always positive as we would hope and expect. The fact that we need to include correlation terms to satisfy this most of basic requirements indicates how important they are.

We should note that if we are only interested in calculating the angle-averaged scattering, it is only the $K=0$ multipole that contributes.[8] Let us consider the $\mathcal{C}^1$ operator for $K=0$:

$$\begin{aligned}
\mathcal{C}^1(K=0,ee,eg,\omega_L) &= N_P \lim_{\epsilon\to 0}\int d^3p_{1,2}\int dp_3 p_3^2 \\
&\times \sum_{\mu_e^1\mu_e^2\mu_e^3\mu_e^4\mu_e^5 j_e'} \begin{pmatrix} j_e & j_e & 0 \\ \mu_e^4 & -\mu_e^5 & 0\end{pmatrix}\begin{pmatrix} j_e & j_e & 0 \\ \mu_e^2 & -\mu_e^1 & 0\end{pmatrix}(-1)^{\mu_e^5-\mu_e^1} \\
&\times \left\langle\!\left\langle j_e\mu_e^1\vec{p}_1 j_e\mu_e^2\vec{p}_1 \right| \tilde{V}_1\frac{1}{\epsilon+\tilde{L}_1+\tilde{S}}\left| j_e'\mu_e^3\vec{p}_2 j_e\mu_e^4\vec{p}_3\right\rangle\!\right\rangle \\
&\times \left\langle\!\left\langle j_e'\mu_e^3\vec{p}_2 j_g\mu_g^1\vec{p}_3 \right| \frac{+1}{\epsilon+i\omega_L+\tilde{L}_1+\tilde{S}}\tilde{V}_1\left| j_e\mu_e^5\vec{p}_3 j_g\mu_g^1\vec{p}_3\right\rangle\!\right\rangle \rho_{\vec{p}_3\vec{p}_3} \quad (t=-\infty) \\
&= \lim_{\epsilon\to 0}\int d^3p_{1,2}\int dp_3 p_3^2 \sum_{\mu_e^1\mu_e^4 j_e'} \frac{1}{(2j_e+1)} \left\langle\!\left\langle j_e\mu_e^1\vec{p}_1 j_e\mu_e^1\vec{p}_1 \right| \tilde{V}_1\frac{1}{\epsilon+\tilde{L}_1+\tilde{S}}\left| j_e'\mu_e^3\vec{p}_2 j_e\mu_e^4\vec{p}_3\right\rangle\!\right\rangle \\
&\times \left\langle\!\left\langle j_e'\mu_e^3\vec{p}_2 j_g\mu_g^1\vec{p}_3 \right| \frac{1}{\epsilon+i\omega_L+\tilde{L}_1+\tilde{S}}\tilde{V}_1\left| j_e\mu_e^4\vec{p}_3 j_g\mu_g^1\vec{p}_3\right\rangle\!\right\rangle \rho_{\vec{p}_3\vec{p}_3} \quad (t=-\infty).
\end{aligned} \tag{3.17}$$

Now we know that if we can ignore inelastic coupling to other levels,

$$\lim_{\epsilon\to 0}\int d^3p_1 \sum_{\mu_e^1}\left\langle\!\left\langle j_e\mu_e^1\vec{p}_1 j_e\mu_e^1\vec{p}_1\right| \tilde{V}_1\frac{1}{i\epsilon+\tilde{L}_1+\tilde{S}}\left|0\right\rangle\!\right\rangle \equiv 0,$$

where $|0\rangle\rangle$ is an arbitrary Liouville vector (of the two-particle space); this is a consequence of unitarity, if one ignores bound states (see Ref. 1), thus $\mathcal{C}^1(K=0, ee, eg, \omega_L)$ vanishes. We can see why this should be so as follows. We stated above that the correlation terms allow us to account properly for the specific m_J state an atom is left in when absorption occurs during a strong collision. If we only want to calculate the angle-averaged fluorescence, the final m_J state the atom is left in, after such an event, is irrelevant (hence the summation over the final m_J states $\mu_e^1 - \mu_e^2$). If we want just the sum over final m_J states, the mixing of those states after the absorption event, correlated with a given atom-perturber orientation, is likewise irrelevant. We expect, therefore, that $\mathcal{C}^1(K=0, ee, eg, \omega_L)$ should vanish as it does.

If we want to study the angular distribution and polarization of the scattered light, we have to calculate the correlation operators. This is, in general, a rather complex task. From Eqs. (2.23) and (3.11) we know that the redistributed intensity in the quasi-static wing may be written thus

$$I_0 \sum_{K=0}^{2j_e} (-1)^Q D_Q^K(\vec{\epsilon}_2^{\,*}\vec{\epsilon}_2) \frac{|\mathcal{E}_0|^2}{\hbar^2} \frac{N_a}{(2j_g+1)} D_{-Q}^K(\vec{\epsilon}_1^{\,*}\vec{\epsilon}_1) \frac{[\Gamma^K(\Delta\omega_L) - \gamma^K]}{(\gamma^K+\gamma_N)(\Delta\omega_L)^2}. \tag{3.18}$$

Here

$$\Gamma^K(\Delta\omega_L) = -\gamma_N(\Delta\omega_L)^2 N_p \sum_{Q,\mu_e^1,\mu_e^2,\mu_e^3,\mu_e^4,\mu_e^5} \begin{pmatrix} j_e & j_e & K \\ \mu_e^4 & -\mu_e^5 & Q \end{pmatrix} \begin{pmatrix} j_e & j_e & K \\ \mu_e^2 & -\mu_2^1 & Q \end{pmatrix} (-1)^{\mu_e^5-\mu_e^1}$$
$$\times 2\,\mathrm{Re}\bigg[\int_0^\infty e^{-\gamma_N\tau_2} d\tau_2 \int_0^\infty e^{i[\omega_L-\omega_{eg}+(i\gamma_N/2)]\tau_1} d\tau_1$$
$$\times \langle j_e\mu_e^1 | \tilde{U}_1^{\mathrm{I}}(\tau_2,-\tau_1)_{\mathrm{eff}} - \tilde{U}_1^{\mathrm{I}}(\tau_2,0)_{\mathrm{eff}} | j_e\mu_e^5\rangle$$
$$\times \langle j_e\mu_e^4 | (U_1^{\mathrm{I}}(\tau_2,0))_{\mathrm{eff}}^\dagger | j_e\mu_e^2\rangle\bigg]. \tag{3.19}$$

Note that we have converted to a $\tilde{U}_{\mathrm{eff}}^{\mathrm{I}}$ for calculating $\Gamma^K(\Delta\omega_L)$ when an adiabatic approximation can be used. We see that in the quasistatic wing the term that depends on $\gamma_c^1(\Delta\omega_L)$ is cancelled out by part of the correlation terms, leaving only the correlated events that are represented by $\Gamma^K(\Delta\omega_L)$. This justifies our earlier statement that the correlated events dominate absorption in the far wings. A model calculation of $\Gamma^K(\Delta\omega_L)$ for a $J=1$ to 0 transition where only the upper ($J=1$) level interacts with perturbers, via a van der Waals potential, has been performed. It indicates that these correlation terms are rather important for far-wing scattering. Furthermore, it shows that light scattered in the far wings is not completely depolarized, contrary to the conclusions of Behmenberg and Schuller.[10] This might be expected on the basis of the calculations of Berman and Lamb,[11] who showed that an angle-averaged collision does not completely destroy the orientation of an atomic dipole. Thus we should expect some memory of the orientation of a dipole, after an absorption event, to affect the scattered intensity as long as collisional and radiative relaxation rates are comparable, otherwise subsequent strong collisions will destroy the orientation before the atom has a chance to radiate.[12]

IV. CONCLUSION

In this paper we have tried to show how degeneracy affects the discussion of correlations between radiative and collision events. To be specific, we have seen that the propagation in the excited state, after an absorption event in the middle of a strong collision, affects the polarization of the fluorescent light. This polarization can, therefore, be used to study this correlated event and should be sensitive to the anisotropy of the long-range part of the interatomic potential; this mixes the m_J states of the scatterer as the quasimolecule flies apart. There is, therefore, extra information contained in the *generalized absorption profile* we introduced above [see specifically Eq. (3.12)], and we would emphasize that it is not possible to obtain it from the absorption or emission profiles alone. In conclusion, we have shown that there is a great deal more to be studied and learned in redistribution experiments[12] than can be obtained from those on simple absorption or emission if one studies the angular distributions and polarization of the scattered light.

ACKNOWLEDGMENTS

Stimulating and informative discussions with R. J. Ballagh, B. S. Frost, A. Ben-Reuven, J. B. Yelnik (deceased), J. L. Carlsten, M. G. Raymer, A. Szöke, D. N. Stacey, A. Omont, and E. W. Smith are gratefully acknowledged. This work was supported in part by National Science Foundation Grant No. PHY76-04761 and in part by National Aeronautics and Space Administration Grant No.

NGL-06-003-057 (both through the University of Colorado) and also by the Atomic and Plasma Radiation Division of the National Bureau of Standards.

APPENDIX A: CORRECTIONS TO THE COLLISION OPERATOR

In this appendix we shall cast the corrections to the collision operator into irreducible form. So that our results may be more generally useful, we shall derive them assuming there may be more than one upper level. We start with the RHS of Eq. (2.18), a first-order correction to the collision operator, that couples the off-diagonal ground-excited matrix elements into those of the upper state alone:

$$\lim_{\epsilon\to 0}\sum_{m_e^3,\, m_e^4,\, j_e^3,\, j_e^4,\, m_g'} N_p \left\langle\!\!\left\langle j_e^1 j_e^2 K_1 Q_1 \middle| \mathrm{Tr}_1\!\left(\tilde{V}_1 \frac{-1}{\epsilon+\tilde{L}_1+\tilde{S}}|j_e^3 m_e^3 j_e^4 m_e^4\rangle\rangle \right.\right.\right.$$
$$\left.\left.\left.\times\langle\langle j_e^3 m_e^3 j_e^4 m_e^4|\tilde{L}^{\mathrm{E}}(0)|j_e^3 m_e^3 j_g m_g'\rangle\rangle\langle\langle j_e^3 m_e^3 j_g m_g'|\frac{-1}{\epsilon+i\omega_L+\tilde{L}_1+\tilde{S}}\tilde{V}_1\hat{\rho}_1\right)\middle| j_e^5 j_g K_4 Q_4\right\rangle\!\!\right\rangle .$$

Consider just the tetradic element,

$$T=\lim_{\epsilon\to 0}\int d^3p_{2,3}\langle\langle j_e^1\vec{p}_1 j_e^2\vec{p}_1 K_1 Q_1|j_e^1 m_e^1\vec{p}_1 j_e^2 m_e^2\vec{p}_1\rangle\rangle\left\langle\!\!\left\langle j_e^1 m_e^1\vec{p}_1 j_e^2 m_e^2\vec{p}_1\middle|\tilde{V}_1\frac{-1}{\epsilon+\tilde{L}_1+\tilde{S}}\middle|j_e^3 m_e^3\vec{p}_2 j_e^4 m_e^4\vec{p}_3\right\rangle\!\!\right\rangle$$
$$\times\langle\langle j_e^3 m_e^3\vec{p}_2 j_e^4 m_e^4\vec{p}_3|\tilde{L}^{\mathrm{E}}(0)|j_e^3 m_e^3\vec{p}_2 j_g m_g^1\vec{p}_3\rangle\rangle$$
$$\times\left\langle\!\!\left\langle j_e^3 m_e^3\vec{p}_2 j_g m_g^1\vec{p}_3\middle|\frac{-1}{\epsilon+i\omega_L+\tilde{L}_1+\tilde{S}}\tilde{V}_1\middle|j_e^5 m_e^5\vec{p}_4 j_g m_g^2\vec{p}_4\right\rangle\!\!\right\rangle\langle\langle j_e^5 m_e^5\vec{p}_4 j_g m_g^2\vec{p}_4|j_e^5\vec{p}_4 j_g\vec{p}_4 K_2 Q_2\rangle\rangle , \tag{A1}$$

which for convenience we write in the following form:

$$\int d^3p_{2,3}\langle\langle j_e^1\vec{p}_1 j_e^2\vec{p}_1 K_1 Q_1|j_e^1 m_e^1\vec{p}_1 j_e^2 m_e^2\vec{p}_1\rangle\rangle\langle\langle j_e^1 m_e^1\vec{p}_1 j_e^2 m_e^2\vec{p}_1|\tilde{C}_1|j_e^3 m_e^3\vec{p}_2 j_e^4 m_e^4\vec{p}_3\rangle\rangle$$
$$\times\langle\langle j_e^3 m_e^3\vec{p}_2 j_e^4 m_e^4\vec{p}_3|\tilde{L}^{\mathrm{E}}(0)|j_e^3 m_e^3\vec{p}_2 j_g m_g^1\vec{p}_3\rangle\rangle$$
$$\times\langle\langle j_e^3 m_e^3\vec{p}_2 j_g m_g^1\vec{p}_3|\tilde{C}_2|j_e^5 m_e^5\vec{p}_4 j_g m_g^2\vec{p}_4\rangle\rangle\langle\langle j_e^5 m_e^5\vec{p}_4 j_g m_g^2\vec{p}_4|j_e^5\vec{p}_4 j_g\vec{p}_4 K_2 Q_2\rangle\rangle . \tag{A2}$$

Here

$$\tilde{C}_1=\tilde{V}_1\frac{1}{\epsilon+\tilde{L}_1+\tilde{S}} \tag{A3}$$

and

$$\tilde{C}_2=\frac{1}{\epsilon+i\omega_L+\tilde{L}_1+\tilde{S}}\tilde{V}_1 . \tag{A4}$$

The angular average (denoted by $\langle\rangle$) is achieved, thus

$$\langle T\rangle=\frac{1}{8\pi^2}\int d\Omega\sum\langle\langle j_e^1\vec{p}_1 j_e^2\vec{p}_1 K_1 Q_1|j_e^1 m_e^1\vec{p}_1 j_e^2 m_e^2\vec{p}_1\rangle\rangle\langle\langle j_e^1\mu_e^1\vec{p}_1 j_e^2\mu_e^2\vec{p}_1|\tilde{C}_1|j_e^3\mu_e^3\vec{p}_2 j_e^4\mu_e^4\vec{p}_3\rangle\rangle$$
$$\times\langle\langle j_e^3 m_e^3\vec{p}_2 j_e^4 m_e^4\vec{p}_3|\tilde{L}^{\mathrm{E}}(0)|j_e^3 m_e^3\vec{p}_2 j_g m_g^1\vec{p}_3\rangle\rangle$$
$$\times\int d^3p_{2,3}\langle\langle j_e^3\mu_e^3\vec{p}_2 j_g\mu_g^1\vec{p}_3|\tilde{C}_2|j_e^5\mu_e^5\vec{p}_4 j_g\mu_g^2\vec{p}_4\rangle\rangle\langle\langle j_e^5 m_e^5\vec{p}_4 j_g m_g^2\vec{p}_4|j_e\vec{p}_4 j_g\vec{p}_4 K_2 Q_2\rangle\rangle$$
$$\times D^{j_e^1}_{\mu_e^1 m_e^1}(\Omega)^* D^{j_e^2}_{\mu_e^2 m_e^2}(\Omega) D^{j_e^3}_{\mu_e^3 m_e^3}(\Omega) D^{j_e^4}_{\mu_e^4 m_e^4}(\Omega)^* D^{j_e^3}_{\mu_e^3 m_e^3}(\Omega)^* D^{j_g}_{\mu_g^1 m_g^1}(\Omega) D^{j_e^5}_{\mu_e^5 m_e^5}(\Omega) D^{j_g}_{\mu_g^2 m_g^2}(\Omega)^* , \tag{A5}$$

where the summation is over all μ's, m's, j_e^3, j_e^4, and j_e^5. Here, $D^j_{m\mu}(\Omega)$ is a matrix element of the rotation operator that rotates a system through the Euler angles specified by Ω; (α,β,γ) (Ref. 13, p. 20).

Using standard techniques this may be reduced to the following form:

$$\langle T\rangle = \sum (2K_3+1)(2K_4+1)(2K_5+1)\mathcal{E}_0^*(\epsilon_q)^*\langle j_g\|\vec{\mathrm{d}}\|j_e\rangle$$
$$\times\int d^3p_{2,3}\langle\langle j_e^1\mu_e^1\vec{\mathrm{p}}_1 j_e^2\mu_e^2\vec{\mathrm{p}}_1|\tilde{C}_1|j_e^3\mu_e^3\vec{\mathrm{p}}_2 j_e^4\mu_e^4\vec{\mathrm{p}}_3\rangle\rangle\langle\langle j_e^3\mu_e^3\vec{\mathrm{p}}_2 j_g\mu_g^1\vec{\mathrm{p}}_3|\tilde{C}_2|j_e^5\mu_e^5\vec{\mathrm{p}}_4 j_g\mu_g^2\vec{\mathrm{p}}_4\rangle\rangle$$
$$\times\begin{pmatrix} j_e^2 & j_e^1 & K_1\\ m_e^2 & -m_e^1 & Q_1\end{pmatrix}(2K_1+1)^{1/2}\begin{pmatrix} j_e^5 & j_g & K_2\\ m_e^5 & -m_g^2 & -Q_2\end{pmatrix}(2K_2+1)^{1/2}$$
$$\times\begin{pmatrix} j_e^1 & j_e^2 & K_3\\ -m_e^1 & m_e^2 & Q_3\end{pmatrix}\begin{pmatrix} j_e^1 & j_e^2 & K_3\\ -\mu_e^1 & \mu_e^2 & Q_3^1\end{pmatrix}\begin{pmatrix} j_e^5 & j_g & K_4\\ m_e^5 & -m_g^2 & Q_4\end{pmatrix}\begin{pmatrix} j_e^5 & j_g & K_4\\ \mu_e^5 & -\mu_g^2 & Q_4^1\end{pmatrix}$$
$$\times\begin{pmatrix} K_3 & K_4 & K_5\\ Q_3 & Q_4 & Q_5\end{pmatrix}\begin{pmatrix} K_3 & K_4 & K_5\\ Q_3^1 & Q_4^1 & Q_5^1\end{pmatrix}\begin{pmatrix} j_e^4 & j_g & K_5\\ m_e^4 & -m_g^1 & -Q_5\end{pmatrix}\begin{pmatrix} j_e^4 & j_g & K_5\\ \mu_e^4 & -\mu_g^1 & -Q_5^1\end{pmatrix}\begin{pmatrix} j_g & j_e^4 & 1\\ m_g^1 & -m_e^4 & q\end{pmatrix}$$
$$\times(-1)^{j_g-\mu_e^1-\mu_g^1-\mu_g^2+Q_5-Q_5^1-Q_2+K_1+j_e^1+j_e^5}, \qquad \text{(A6)}$$

where the summation extends over the m's, μ's, K_3, K_4, K_5, Q's, q, j_e^3, and j_e^4.

$$\langle T\rangle = \sum \mathcal{E}_0^*(\epsilon_q)^*\langle j_g\|\vec{\mathrm{d}}\|j_e^4\rangle(2K_1+1)^{1/2}(2K_2+1)^{1/2}$$
$$\times\int d^3p_{2,3}\langle\langle j_e^1\mu_e^1\vec{\mathrm{p}}_1 j_e^2\mu_e^2\vec{\mathrm{p}}_1|\tilde{C}_1|j_e^3\mu_e^3\vec{\mathrm{p}}_2 j_e^4\mu_e^4\vec{\mathrm{p}}_3\rangle\rangle\langle\langle j_e^3\mu_e^3\vec{\mathrm{p}}_2 j_g\mu_g^1\vec{\mathrm{p}}_3|\tilde{C}_2|j_e\mu_e^5\vec{\mathrm{p}}_4 j_g\mu_g^2\vec{\mathrm{p}}_4\rangle\rangle$$
$$\times\begin{pmatrix} j_e^1 & j_e^2 & K_1\\ -\mu_e^1 & \mu_e^2 & Q_3^1\end{pmatrix}\begin{pmatrix} j_e & j_g & K_2\\ \mu_e^5 & -\mu_g^2 & Q_4^1\end{pmatrix}\begin{pmatrix} j_e & j_g & 1\\ \mu_e^4 & -\mu_g^1 & -Q_5^1\end{pmatrix}\begin{pmatrix} K_1 & K_2 & 1\\ Q_1 & -Q_2 & -q\end{pmatrix}\begin{pmatrix} K_1 & K_2 & 1\\ Q_3^1 & Q_4^1 & Q_5^1\end{pmatrix}$$
$$\times(-1)^{K_1-\mu_e^1-\mu_g^1-\mu_g^2-Q_5^1-Q_1+j_g+j_e^1+j_e^5}$$
$$=\sum_q \mathcal{E}_0^*(\epsilon^*)_q\langle j_g\|\vec{\mathrm{d}}\|j_e^4\rangle(2K_1+1)^{1/2}(2K_2+1)^{1/2}\begin{pmatrix} K_1 & K_2 & 1\\ Q_1 & -Q_2 & +q\end{pmatrix}(-1)^{K_1-Q_1+j_g}\mathfrak{C}^1(K_1K_2;e_1e_2,e_5g)^{\vec{\mathrm{p}}_1,\vec{\mathrm{p}}_4}, \qquad \text{(A7)}$$

the summation being over the μ's, q, j_e^3, and j_e^4. Here,

$$\mathfrak{C}^1(K_1K_2;e_1e_2,eg,\omega_L)^{\vec{\mathrm{p}}_1,\vec{\mathrm{p}}_4}=\sum(-1)^{j_e^1+j_e^5-\mu_e^1-\mu_g^1-\mu_g^2-Q_5^1}\begin{pmatrix} j_e^1 & j_e^2 & K_1\\ -\mu_e^1 & \mu_e^2 & Q_3^1\end{pmatrix}\begin{pmatrix} j_e^1 & j_g^2 & K_2\\ \mu_e^5 & -\mu_g^2 & Q_4^1\end{pmatrix}\begin{pmatrix} j_e^4 & j_g & 1\\ \mu_e^4 & -\mu_g^1 & -Q_5^1\end{pmatrix}\begin{pmatrix} K_1 & K_2 & 1\\ Q_3^1 & Q_4^1 & Q_5^1\end{pmatrix}$$
$$\times\int d^3p_{2,3}\langle\langle j_e^1\mu_e^1\vec{\mathrm{p}}_1 j_e^2\mu_e^2\vec{\mathrm{p}}_1|\tilde{C}_1|j_e^3\mu_e^3\vec{\mathrm{p}}_2 j_e^4\mu_e^4\vec{\mathrm{p}}_3\rangle\rangle\langle\langle j_e^3\mu_e^3\vec{\mathrm{p}}_2 j_g\mu_g^1\vec{\mathrm{p}}_3|\tilde{C}_2|j_e^5\mu_e^5\vec{\mathrm{p}}_4 j_g\mu_g^2\vec{\mathrm{p}}_4\rangle\rangle, \qquad \text{(A8)}$$

the summation being over the μ's, Q's, j_e^3, and j_e^4. So the correction to the collision operator that couples $\sigma_{Q_1}^{K_1}(j_e^5 j_g)$ to $\sigma_{Q_2}^{K_2}(j_e^1 j_e^2)$ is

$$\frac{1}{i\hbar}\int d^3p_1\int dp_4 p_4^2\rho_{\vec{\mathrm{p}}_4\vec{\mathrm{p}}_4}(-\infty)\sum_q \mathcal{E}_0^*(\epsilon^*)_q\left\langle j_g\left\|\frac{d}{i\hbar}\right\|j_e^4\right\rangle(2K_1+1)^{1/2}(2K_2+1)^{1/2}$$
$$\times\begin{pmatrix} K_1 & K_2 & 1\\ Q_1 & -Q_2 & -q\end{pmatrix}(-1)^{K_1-Q_1+j_g}\mathfrak{C}^1(K_1K_2;e_1e_2,e_5g,\omega_L)^{\vec{\mathrm{p}}_1,\vec{\mathrm{p}}_4}. \qquad \text{(A9)}$$

Before we discuss the other tetradic elements of the correction to the collision operator, we shall consider the form (A9) takes when the lower level of the atom does not interact with perturbers (OIL approximation). In that case, $\mu_g^1\equiv\mu_g^2$ and we can use the identity

$$\sum_{\mu_g^1 Q_4^1 Q_5^1}\begin{pmatrix} j_e^5 & j_g & K_2\\ \mu_e^5 & -\mu_g^1 & Q_4^1\end{pmatrix}\begin{pmatrix} j_e^4 & j_g & 1\\ \mu_e^4 & -\mu_g^1 & -Q_5^1\end{pmatrix}\begin{pmatrix} K_1 & K_2 & 1\\ Q_3^1 & Q_4^1 & Q_5^1\end{pmatrix}(-1)^{Q_5^1}=(-1)^{j_g+\mu_e^5+j_e^4+j_e^5}\begin{pmatrix} j_e & j_e & K_1\\ \mu_e^4 & -\mu_e^5 & Q_3^1\end{pmatrix}\begin{Bmatrix} K_1 & 1 & K_2\\ j_g & j_e^5 & j_e^4\end{Bmatrix}$$

(Ref. 13, p. 142). Then we find (A9) reduces to

$$\sum_q (\mathcal{E}_0)^*(\epsilon^*)_q (2K_1+1)^{1/2}(2K_2+1)^{1/2} \begin{bmatrix} K_1 & K_2 & 1 \\ Q_1 & -Q_2 & +q \end{bmatrix} \begin{Bmatrix} K_1 & 1 & K_2 \\ j_g & j_e^5 & j_e^4 \end{Bmatrix}$$

$$\times (-1)^{1-Q_1+j_e^4+j_e^5} \sum_{j_e^3 j_e^4} \mathfrak{C}^1(K_1; e_1e_2, e_5g, \omega_L) \frac{\langle j_g \| \vec{\mathrm{d}} \| j_e^4\rangle}{i\hbar} = \sum_{j_e^3 j_e^4} \mathfrak{C}^1(k; e_1e_2, e_5g, \omega_L) \langle\langle j_e^5 j_e^4 K_1 Q_1 | \tilde{L}^E(0) | j_e^5 j_g K_2 Q_2 \rangle\rangle ,$$

where

$$\mathfrak{C}^1(K; e_1e_2, e_5g, \omega_L) = N_p \int d^3p_{1,2} \int dp_3 p_3^2 \sum_{\substack{KQ \\ \mu_e^1\mu_e^2\mu_e^3\mu_e^4\mu_e^5 j_e^3 j_e^4}} \begin{bmatrix} j_e^5 & j_e^4 & K \\ \mu_e^5 & -\mu_e^4 & Q \end{bmatrix} \begin{bmatrix} j_e^2 & j_e^1 & K \\ \mu_e^2 & -\mu_e^1 & Q \end{bmatrix}$$

$$\times (-1)^{j_e^2+j_e^5+\mu_e^5-\mu_e^1} \langle\langle j_e^1 \mu_e^1 \vec{p}_1 j_e^2 \mu_e^2 \vec{p}_1 | \tilde{C}_1 | j_e^3 \mu_e^3 \vec{p}_2 j_e^4 \mu_e^4 \vec{p}_3 \rangle\rangle$$

$$\times \langle\langle j_e^3 \mu_e^3 \vec{p}_2 j_g \mu_g^1 \vec{p}_3 | \tilde{C}_2 | j_e^5 \mu_e^5 \vec{p}_3 j_g \mu_g^1 \vec{p}_3 \rangle\rangle \rho_{\vec{p}_3\vec{p}_3} \quad (t=-\infty) . \tag{A10}$$

So we see that, in the OIL approximation, or rather no interaction in the lower-level approximation, the correction to the collision operator may be written in a particularly simple form.

We can obtain other tetradic elements in exactly the same manner as above; for the coupling of $\langle\langle K^1Q^1 j_g j_e | \sigma\rangle\rangle$ to $\langle\langle K^2 Q^2 j_e^1 j_e^2 | \sigma\rangle\rangle$ in the steady state we get

$$\frac{i}{\hbar} \sum_q \epsilon_q \mathcal{E}_0 \langle j_e \| \vec{\mathrm{d}} \| j_g\rangle (2K+1)^{1/2}(2K'+1)^{1/2}(-1)^{K_1-Q_2+j_g} \sum_{j_e^3 j_e^4} \begin{bmatrix} K^1 & K^2 & 1 \\ Q^1 & -Q^2 & q \end{bmatrix} \mathfrak{C}^1(K^1K^2; e_1e_2, ge, \omega_L) , \tag{A11}$$

where

$$\mathfrak{C}^1(K^1K^2; e_1e_2, ge, \omega_L) = N_p \lim_{\epsilon\to 0+} \int d^3p_{1\ldots 3} \int dp_4 (p_4)^2 \sum \left\langle\!\!\left\langle j_e^1 \mu_e^1 \vec{p}_1 j_e^2 \mu_e^2 \vec{p}_1 \middle| \tilde{V}_1 \frac{1}{\epsilon + \tilde{L}_1 + \tilde{S}} \middle| j_e^3 \mu_e^3 \vec{p}_2 j_e^4 \mu_e^4 \vec{p}_3 \right\rangle\!\!\right\rangle$$

$$\times \left\langle\!\!\left\langle j_g \mu_g^1 \vec{p}_2 j_e^4 \mu_e^4 \vec{p}_3 \middle| \frac{1}{\epsilon - i\omega_L + \tilde{L}_1 + \tilde{S}} \tilde{V}_1 \middle| j_g \mu_g^2 \vec{p}_4 j_e^5 \mu_e^5 \vec{p}_4 \right\rangle\!\!\right\rangle$$

$$\times \begin{bmatrix} j_e^1 & j_e^2 & K^1 \\ -\mu_e^1 & \mu_e^2 & Q_3 \end{bmatrix} \begin{bmatrix} j_g & j_e^5 & K^2 \\ \mu_g^2 & -\mu_e^5 & Q_4 \end{bmatrix} \begin{bmatrix} j_e^3 & j_g & 1 \\ \mu_e^3 & -\mu_g^1 & Q_5 \end{bmatrix} \begin{bmatrix} K^1 & K^2 & 1 \\ Q_1 & -Q_2 & q \end{bmatrix} \begin{bmatrix} K^1 & K^2 & 1 \\ Q_3 & Q_4 & Q_5 \end{bmatrix} , \tag{A12}$$

the summation being over the μ's, Q's, j_e^3, and j_e^4. In the OIL approximation, this further reduces to

$$\frac{i}{\hbar} \sum_{q, j_e^3 j_e^4} \mathfrak{C}^1(K, e_1e_2, g_5e, \omega_L) \epsilon_q \mathcal{E}_0 \langle j_e^3 \| \vec{\mathrm{d}} \| j_g\rangle (2K+1)^{1/2}(2K'+1)^{1/2}(-1)^{K^1+K-Q^1+1+j_e^3+j_e^5} \begin{bmatrix} K & K^1 & 1 \\ Q & -Q^1 & q \end{bmatrix} \begin{Bmatrix} K^1 & 1 & K \\ j_e^3 & j_e^5 & j_g \end{Bmatrix} , \tag{A13}$$

where

$$\mathfrak{C}^1(K, e_1e_2, ge, \omega_L) = N_p \sum \begin{bmatrix} j_e^2 & j_e^1 & K \\ \mu_e^2 & -\mu_e^1 & Q \end{bmatrix} \begin{bmatrix} j_e^3 & j_e^5 & K \\ \mu_e^3 & -\mu_e^5 & Q \end{bmatrix} (-1)^{\mu_e^1-\mu_e^3}$$

$$\times \int dp_2 p_2^2 \int d^3p_{1,3} \left\langle\!\!\left\langle j_e \mu_e^1 \vec{p}_1 j_e \mu_e^2 \vec{p}_1 \middle| \tilde{V}_1 \frac{1}{\epsilon + \tilde{L}_1 + \tilde{S}} \middle| j_e^3 \mu_e^3 \vec{p}_2 j_e^4 \mu_e^4 \vec{p}_3 \right\rangle\!\!\right\rangle .$$

$$\times \left\langle\!\!\left\langle j_g \mu_g^1 \vec{p}_2 j_e^4 \mu_e^4 \vec{p}_3 \middle| \frac{1}{\epsilon - i\omega_L + \tilde{L}_1 + \tilde{S}} \tilde{V}_1 \middle| j_g \mu_g^1 \vec{p}_2 j_e^5 \mu_e^5 \vec{p}_2 \right\rangle\!\!\right\rangle \rho_{\vec{p}_2\vec{p}_2} \quad (t=-\infty) , \tag{A14}$$

the summation being over the Q, μ's, j_e^3, and j_e^4. For the coupling of $\langle\langle K^1Q^1 j_e^4 j_e^5 | \sigma\rangle\rangle$ to $\langle\langle K^2Q^2 j_e^1 j_g | \sigma\rangle\rangle$ we get

$$\sum_q \frac{i}{\hbar} (2K+1)^{1/2}(2K'+1)^{1/2} \mathcal{E}_0 \epsilon_q \langle j_e^3 \| \vec{\mathrm{d}} \| j_g\rangle (-1)^{j_g-Q_2} \begin{bmatrix} K^1 & K^2 & 1 \\ Q^1 & -Q^2 & q \end{bmatrix} \mathfrak{C}^1(KK^2; eg, e_1e_2, \omega_L) . \tag{A15}$$

Here

$$\mathfrak{C}^1(K^1K^2;e_1g,e_4e_5,\omega_L)=N_p\sum\begin{pmatrix} j_e^1 & j_g & K^1\\ -\mu_e^1 & \mu_g^1 & Q_3\end{pmatrix}\begin{pmatrix} j_e^4 & j_e^5 & K^2\\ \mu_e^4 & -\mu_e^5 & Q_4\end{pmatrix}\begin{pmatrix} j_g & j_e^3 & 1\\ -\mu_g^2 & \mu_e^3 & Q_5\end{pmatrix}(-1)^{\mu_e^1+\mu_g^2+\mu_e^5}\begin{pmatrix} K^1 & K^2 & 1\\ Q_3 & Q_4 & Q_5\end{pmatrix}$$

$$\times\int d^3p_{1,3}\int dp_4 p_4^2\lim_{\epsilon\to 0}\left\langle\!\!\left\langle j_e^1\mu_e^1\vec{p}_1 j_g\mu_g^1\vec{p}_1\right|\tilde{V}_1\frac{1}{\epsilon+\tilde{L}_1+\tilde{S}+i\omega_L}\left|j_e^2\mu_e^2\vec{p}_2 j_g\mu_g^2\vec{p}_3\right\rangle\!\!\right\rangle$$

$$\times\left\langle\!\!\left\langle j_e^2\mu_e^2\vec{p}_2 j_e^3\mu_e^3\vec{p}_3\right|\frac{1}{\epsilon+\tilde{L}_1+\tilde{S}}\tilde{V}_1\left|j_e^4\mu_e^4\vec{p}_4 j_e^5\mu_e^5\vec{p}_4\right\rangle\!\!\right\rangle,\qquad\text{(A16)}$$

the summation being over the μ's, Q's, j_e^2, j_e^3, and j_e^4. In the OIL approximation the coupling coefficient reduces to the form

$$\sum_q\frac{i}{\hbar}(2K+1)^{1/2}(2K'+1)^{1/2}\mathcal{E}_0\epsilon_q\langle j_e^3\|\vec{d}\|j_g\rangle(-1)^{j_e^1-j_g-Q^2}\begin{Bmatrix} K^2 & 1 & K^1\\ j_g & j_e^1 & j_e^3\end{Bmatrix}\mathfrak{C}^1(K',e_5g,e_1e_2,\omega_L)\begin{pmatrix} K^1 & K^2 & 1\\ Q^1 & -Q^2 & q\end{pmatrix}.\qquad\text{(A17)}$$

Here

$$\mathfrak{C}^1(K,eg,e_1e_2,\omega_L)=N_p\sum(-1)^{Q+\mu_e^1+\mu_e^5+j_e^3+j_e^5}\begin{pmatrix} j_e^5 & j_e^4 & K\\ \mu_e^5 & -\mu_e^4 & Q\end{pmatrix}\begin{pmatrix} j_e^1 & j_e^3 & K\\ \mu_e^1 & -\mu_e^3 & -Q\end{pmatrix}$$

$$\times\lim_{\epsilon\to 0}\int d^3p_{1,2}\int dp_3p_3^2\left\langle\!\!\left\langle j_e^1\mu_e^1\vec{p}_1 j_g\mu_g^1\vec{p}_1\right|\tilde{V}_1\frac{1}{\epsilon+\tilde{L}_1+\tilde{S}+i\omega_L}\left|j_e^2\mu_e^2\vec{p}_2 j_g\mu_g^1\vec{p}_1\right\rangle\!\!\right\rangle$$

$$\times\left\langle\!\!\left\langle j_e^2\mu_e^2p_2 j_e^3\mu_e^3p_1\right|\frac{1}{\epsilon+\tilde{L}_1+\tilde{S}}\tilde{V}_1\left|j_e^4\mu_e^4\vec{p}_3 j_e^5\mu_e^5\vec{p}_3\right\rangle\!\!\right\rangle\rho_{\vec{p}_3\vec{p}_3}\ (t=-\infty),\qquad\text{(A18)}$$

where the summation is over the μ's, Q, j_e^2, and j_e^3. For the coupling of $\langle\langle K^2Q^2j_gj_g|\sigma\rangle\rangle$ into $\langle\langle K^1Q^1j_ej_g|\sigma\rangle\rangle$ we get

$$\sum_q\mathcal{E}_0\epsilon_q\langle\langle j_e\|\vec{d}\|j_g\rangle(-1)^{K^1-Q^2+j_g}\begin{pmatrix} K^1 & K^2 & 1\\ Q^1 & -Q^2 & q\end{pmatrix}\mathfrak{C}^1(K^1K^2;eg,gg,\omega_L),\qquad\text{(A19)}$$

where

$$\mathfrak{C}^1(K^1K^2;eg,gg)=N_p\sum(-1)^{\mu_e^1+\mu_g^3+\mu_g^5}\begin{pmatrix} j_e^1 & j_g & K^1\\ -\mu_e^1 & \mu_g^1 & Q_1\end{pmatrix}\begin{pmatrix} j_g & j_g & K^2\\ \mu_n^4 & \mu_g^5 & Q_2\end{pmatrix}\begin{pmatrix} j_e^2 & j_g & 1\\ \mu_e^2 & -\mu_g^3 & Q_3\end{pmatrix}\begin{pmatrix} K^1 & K^2 & 1\\ Q_1 & Q_2 & Q_3\end{pmatrix}$$

$$\times\int d^3p_{1\ldots 3}\int dp_4p_4^2\lim_{\epsilon\to 0}\left\langle\!\!\left\langle j_e^1\mu_e^1\vec{p}_1 j_g\mu_g^1\vec{p}_1\right|\tilde{V}_1\frac{1}{\epsilon-i\omega_L+\tilde{L}_1+\tilde{S}}\left|j_e^2\mu_e^2\vec{p}_2 j_g^3\mu_g^2\vec{p}_3\right\rangle\!\!\right\rangle$$

$$\times\left\langle\!\!\left\langle j_g\mu_g^3\vec{p}_2 j_g\mu_g^2\vec{p}_3\right|\frac{1}{\epsilon+\tilde{L}_1+\tilde{S}}\tilde{V}_1\left|j_g\mu_g^4\vec{p}_4 j_e^2\mu_g^5\vec{p}_4\right\rangle\!\!\right\rangle,\qquad\text{(A20)}$$

where the summation is over the μ's, Q's, and j_e^2. If the lower level does not interact with perturbers this term vanishes.

The only second-order correction of interest is the coupling of the ground to the excited-state manifold, i.e., $\langle\langle K^2Q^2j_gj_g|\sigma\rangle\rangle$ to $\langle\langle K^1Q^1j_e^1j_e^2|\sigma\rangle\rangle$. This may be reduced in the steady state to the following form:

$$\sum(2K+1)^{1/2}(2K'+1)^{1/2}(2K_2+1)(-1)^{K-Q'}(-1)^{\mu_e^1+\mu_e^4+\mu_g^3+\mu_g^5}|\mathcal{E}_0|^2(\vec{\epsilon})_q(\vec{\epsilon}^*)_q\langle j_g\|\vec{d}\|j_e\rangle\langle j_e\|\vec{d}\|j_g\rangle(-1)^{j_g+j_e+1}$$
$$\times\begin{bmatrix} j_e^1 & j_e^2 & K\\ -\mu_e^1 & \mu_e^2 & Q_3\end{bmatrix}\begin{bmatrix} j_e^4 & j_g & 1\\ -\mu_e^4 & \mu_g^1 & Q_4\end{bmatrix}\begin{bmatrix} j_e^5 & j_g & 1\\ \mu_e^5 & -\mu_g^3 & Q_5\end{bmatrix}\begin{bmatrix} j_g & j_g & K'\\ \mu_g^4 & -\mu_g^5 & Q_6\end{bmatrix}$$
$$\times\begin{bmatrix} K & 1 & K_1\\ Q_3 & Q_4 & Q_1\end{bmatrix}\begin{bmatrix} 1 & K' & K_1\\ Q_5 & Q_6 & -Q_1\end{bmatrix}\begin{bmatrix} K & 1 & K_1\\ Q & -q & Q_2\end{bmatrix}\begin{bmatrix} 1 & K' & K_1\\ -q & -Q' & -Q_2\end{bmatrix}$$
$$\times\int d^3p_{1\ldots5}\int dp p^2\lim_{\epsilon\to 0}\left\langle\!\!\left\langle j_e^1\mu_e^1\vec{p}_1 j_e^2\mu_e^2\vec{p}_1\left|\tilde{V}_1\frac{1}{\epsilon+\tilde{L}_1+\tilde{S}}\right|j_e^3\mu_e^3\vec{p}_2 j_e^4\mu_e^4\vec{p}_2\right\rangle\!\!\right\rangle$$
$$\times\left\langle\!\!\left\langle j_e^3\mu_e^3\vec{p}_2 j_g\mu_g^1\vec{p}_3\left|\frac{1}{\epsilon+i\omega_L+\tilde{L}_1+\tilde{S}}\right|j_e^5\mu_e^5\vec{p}_4 j_g\mu_g^2\vec{p}_5\right\rangle\!\!\right\rangle$$
$$\times\left\langle\!\!\left\langle j_g\mu_g^3\vec{p}_4 j_g\mu_g^2\vec{p}_5\left|\frac{1}{\epsilon+\tilde{L}_1+\tilde{S}}\tilde{V}_1\right|j_g\mu_g^4\vec{p}_6 j_g\mu_g^5\vec{p}_6\right\rangle\!\!\right\rangle, \quad (A21)$$

where the summation is over the Q's, q, μ's, j_e^3, j_e^4, and j_e^5. This term vanishes in the OIL approximation.

APPENDIX B: ANTISTATIC BEHAVIOR OF $\mathfrak{C}^1(K,ee,eg,\omega_L)$

We should like to investigate the form of $\mathfrak{C}^1(K,ee,eg,\omega_L)$ in the antistatic limit, that is, supposing we have an attractive interatomic potential for

$$\mathfrak{C}^1(K,ee,eg,\omega_L)=N_p\lim_{\epsilon\to 0^+}\int d^3p_{1,2}\int dp_3p_3^2\sum(-1)^{\mu_e^5-\mu_e^1+K}\begin{bmatrix} j_e & j_e & K\\ -\mu_e^1 & \mu_e^2 & Q\end{bmatrix}\begin{bmatrix} j_e & j_e & K\\ \mu_e^4 & -\mu_e^5 & Q\end{bmatrix}$$
$$\times\left\langle\!\!\left\langle j_e\mu_e^1\vec{p}_1 j_e\mu_e^2\vec{p}_1\left|\tilde{V}_1\frac{1}{\epsilon+\tilde{S}+\tilde{L}}\right|j_e'\mu_e^3\vec{p}_2 j_e\mu_e^4\vec{p}_3\right\rangle\!\!\right\rangle$$
$$\times\left\langle\!\!\left\langle j_e'\mu_e^3\vec{p}_2 j_g\mu_g^1\vec{p}_3\left|\frac{1}{\omega_L+\tilde{S}+\tilde{L}_1+\epsilon}\tilde{V}_1\right|j_e\mu_e^5\vec{p}_3 j_g\mu_g^1\vec{p}_3\right\rangle\!\!\right\rangle\rho_{\vec{p}_3\vec{p}_3}\ (t=-\infty), \quad (B1)$$

where the summation is over the μ's, Q, and j_e'. In the antistatic wing we suppose we can use an expansion $1/\Delta\omega_L$ for the first part of this collision operator, since there is no stationary phase contribution. Thus,

$$\mathfrak{C}^1(K,ee,eg,\omega_L)=N_p\int d^3p_{1,2}\int dp_3p_3^2\sum(-1)^{\mu_e^5-\mu_e^1+K}\begin{bmatrix} j_e & j_e & K\\ -\mu_e^1 & \mu_e^2 & Q\end{bmatrix}\begin{bmatrix} j_e & j_e & K\\ \mu_e^4 & -\mu_e^5 & Q\end{bmatrix}$$
$$\times\lim_{\epsilon\to 0}\left\langle\!\!\left\langle j_e\mu_e^1\vec{p}_1 j_e\mu_e^2\vec{p}_1\left|\tilde{V}_1\frac{1}{\epsilon+\tilde{S}+\tilde{L}}\right|j_e'\mu_e^3\vec{p}_2 j_e\mu_e^4\vec{p}_3\right\rangle\!\!\right\rangle$$
$$\times\left\langle\!\!\left\langle j_e'\mu_e^3\vec{p}_2 j_g\mu_g^1\vec{p}_3\left|\frac{1}{\omega_L+i\omega_{\vec{p}_3}-i\omega_{\vec{p}_2}-(\gamma_N/2)-i\omega_{eg}}\tilde{V}_1\right|j_e\mu_e^5\vec{p}_3 j_g\mu_g^1\vec{p}_3\right\rangle\!\!\right\rangle\rho_{\vec{p}_3\vec{p}_3}\ (t=-\infty), \quad (B2)$$

where the summation is over the μ's, Q, and j_e'. Here, $\omega_p=(1/\hbar)(p^2/2m)$, and $|\Delta\omega_L|>1/\tau_c$ implies that $|\Delta\omega_L|>|\omega_{\vec{p}_2}-\omega_{\vec{p}_3}-i(\gamma_N/2)|$, so that we can write

$$\mathfrak{C}^1(K,ee,eg,\omega_L)=N_p\int d^3p_{1,2}\int dp_3p_3^2\sum_{\mu_e^1\mu_e^2,\mu_e^3\mu_e^4,\mu_e^5,Q,j_e'}(-1)^{\mu_e^5-\mu_e^1+K}\begin{bmatrix} j_e & j_e & K\\ -\mu_e^1 & \mu_e^2 & Q\end{bmatrix}\begin{bmatrix} j_e & j_e & K\\ \mu_e^4 & -\mu_e^5 & Q\end{bmatrix}$$
$$\times\lim_{\epsilon\to 0^+}\left\langle\!\!\left\langle j_e\mu_e^1\vec{p}_1 j_e\mu_e^2\vec{p}_1\left|\tilde{V}_1\frac{1}{\epsilon+\tilde{S}+\tilde{L}}\right|j_e'\mu_e^3\vec{p}_2 j_e\mu_e^4\vec{p}_3\right\rangle\!\!\right\rangle$$
$$\times\frac{1}{i\Delta\omega_L}\left\langle j_e'\mu_e^3\vec{p}_2\left|\frac{V_1}{i\hbar}\right|j_e\mu_e^5\vec{p}_3\right\rangle. \quad (B3)$$

Evidently then,

$$2\,\mathrm{Im}\,\mathcal{C}^1(K,ee,eg,\omega_L)\Delta\omega_L = N_p\int d^3p_{1,2}\int dp_3 p_3^2 \sum_{\mu_e^1\mu_e^2\mu_e^3\mu_e^4\mu_e^5 Q j_e'} (-1)^{\mu_e^5-\mu_e^1+K}\lim_{\epsilon\to 0}\begin{bmatrix} j_e & j_e & K\\ -\mu_e^1 & \mu_e^2 & Q\end{bmatrix}\begin{bmatrix} j_e & j_e & K\\ \mu_e^4 & -\mu_e^5 & Q\end{bmatrix}$$

$$\times\Bigg[\left\langle\!\!\left\langle j_e\mu_e^1\vec{p}_1 j_e\mu_e^2\vec{p}_1\left|\tilde{V}_1\frac{1}{\epsilon+\tilde{S}+\tilde{L}}\right|j_e'\mu_e^3\vec{p}_2 j_e\mu_e^4\vec{p}_3\right\rangle\!\!\right\rangle$$

$$\times\left\langle j_e'\mu_e^3\vec{p}_2\left|\frac{V_1}{i\hbar}\right|j_e\mu_e^5\vec{p}_3\right\rangle$$

$$-\left\langle\!\!\left\langle j_e\mu_e^2\vec{p}_1 j_e\mu_e^1\vec{p}_1\left|\tilde{V}_1\frac{1}{\epsilon+\tilde{S}+\tilde{L}}\right|j_e\mu_e^4\vec{p}_3 j_e'\mu_e^3\vec{p}_2\right\rangle\!\!\right\rangle\Bigg]\rho_{\vec{p}_3\vec{p}_3}$$

$$(t=-\infty)$$

$$\times\left\langle j_e\mu_e^5\vec{p}_3\left|\frac{V_1}{i\hbar}\right|j_e'\mu_e^3\vec{p}_2\right\rangle$$

$$=\lim_{\epsilon\to 0}\int d^3p_1\int dp_3 p_3^2\sum_{\mu_e^1\mu_e^2\mu_e^3\mu_e^4\mu_e^5 Q}\begin{bmatrix} j_e & j_e & K\\ -\mu_e^1 & \mu_e^2 & Q\end{bmatrix}\begin{bmatrix} j_e & j_e & K\\ \mu_e^4 & -\mu_e^5 & Q\end{bmatrix}(-1)^{\mu_e^5-\mu_e^1+K}$$

$$\times N_p\left\langle\!\!\left\langle j_e\mu_e^1\vec{p}_1 j_e\mu_e^2\vec{p}_1\left|\tilde{V}_1\frac{1}{\epsilon+\tilde{S}+\tilde{L}_1}\tilde{V}_1\right|j_e\mu_e^4\vec{p}_3 j_e\mu_e^5\vec{p}_3\right\rangle\!\!\right\rangle\rho_{\vec{p}_3\vec{p}_3}$$

$$(t=-\infty)\,. \tag{B4}$$

Thus $\Delta\omega_L 2\,\mathrm{Im}\,\mathcal{C}^1(K,ee,eg,\omega_L)\to\gamma^K$ in the antistatic limit, since

$$\gamma^K\equiv\lim_{\epsilon\to 0}\int d^3p_1\int dp_3p_3^2\sum_{\mu_e^1\mu_e^2\mu_e^3\mu_e^4\mu_e^5 Q}\begin{bmatrix} j_e & j_e & K\\ -\mu_e^1 & \mu_e^2 & Q\end{bmatrix}\begin{bmatrix} j_e & j_e & K\\ \mu_e^4 & -\mu_e^5 & Q\end{bmatrix}(-1)^{\mu_e^5-\mu_e^1+K}$$

$$\times N_p\left\langle\!\!\left\langle j_e\mu_e^1\vec{p}_1 j_e\mu_e^2\vec{p}_1\left|\tilde{V}_1\frac{1}{\epsilon+\tilde{S}+\tilde{L}_1}\tilde{V}_1\right|j_e\mu_e^4\vec{p}_3 j_e\mu_e^5\vec{p}_3\right\rangle\!\!\right\rangle\rho_{\vec{p}_3\vec{p}_3}\quad(t=-\infty)\,. \tag{B5}$$

In the above, we have assumed that e' and e are degenerate. We can arrange this by following the procedure we discussed in the text. If, as in the case of Stark broadening of hydrogen, the states mixed by $\tilde{V}_1$ are degenerate, we have no trouble. If they are not, we replace $\tilde{V}_1$ by $\tilde{V}_{\mathrm{eff}}$ throughout our analysis.[14] $\tilde{V}_{\mathrm{eff}}$ is defined explicitly by

$$\tilde{V}_{\mathrm{eff}}\,\hat{0}\equiv\frac{1}{i\hbar}[\hat{V}_{\mathrm{eff}},\hat{0}] \tag{B6}$$

and

$$\hat{V}_{\mathrm{eff}}=\sum_{\mu_e^1,\mu_e^2}\frac{|j_e\mu_e^1\rangle\langle j_e\mu_e^1|\hat{V}_1|j_e'\mu_e^1\rangle\langle j_e'\mu_e^1|\hat{V}_1|j_e\mu_e^2\rangle\langle j_e\mu_e^2|}{\hbar\omega_{ee'}}\,, \tag{B7}$$

where $\omega_{ee'}=[E(j_e)-E(j_{e'})]/\hbar$. Here $j_{e'}$ labels the states that are coupled (adiabatically) into the j_e manifold. We note there is no problem with the first-order contribution in $\tilde{V}_{\mathrm{eff}}$ to ${}^{j_ej_e}_{j_ej_e}M^K(z)$, since it vanishes. Explicitly, this first-order contribution may be written in the form

$${}^{j_ej_e}_{j_ej_e}M^K(z)=\sum_{\mu_e^1,\mu_e^2,\mu_e^3,\mu_e^4 Q}(-1)^{\mu_e^2-\mu_e^4}\begin{bmatrix} j_e & j_e & K\\ -\mu_e^1 & \mu_e^2 & Q\end{bmatrix}\begin{bmatrix} j_e & j_e & K\\ -\mu_e^3 & \mu_e^4 & Q\end{bmatrix}N_p\langle\langle j_e\mu_e^1 j_e\mu_e^2|\mathrm{Tr}_1'[\tilde{V}_{\mathrm{eff}}\hat{\rho}_1(-\infty)]|j_e\mu_e^3 j_e\mu_e^4\rangle\rangle$$

$$=\sum_{\mu_e^1,\mu_e^2,\mu_e^3,\mu_e^4 Q}(-1)^{\mu_e^2-\mu_e^4}\begin{bmatrix} j_e & j_e & K\\ -\mu_e^1 & \mu_e^2 & Q\end{bmatrix}\begin{bmatrix} j_e & j_e & K\\ -\mu_e^3 & \mu_e^4 & Q\end{bmatrix}\frac{N_p}{i\hbar}$$

$$\times(\langle j_e\mu_e^1|\mathrm{Tr}_1'[\hat{V}_{\mathrm{eff}}\hat{\rho}_1(-\infty)]|j_e\mu_e^3\rangle\delta(\mu_e^2,\mu_e^4)-\langle j_e\mu_e^4|\mathrm{Tr}_1'[\hat{V}_{\mathrm{eff}}\hat{\rho}_1(-\infty)]|j_e\mu_e^2\rangle\delta(\mu_e^1,\mu_e^3))$$

$$=\sum_{\mu_e}\frac{N_p}{i\hbar(2j_e+1)}(\langle j_e\mu_e|\mathrm{Tr}_1'[\hat{V}_{\mathrm{eff}}\hat{\rho}_1(-\infty)]|j_e\mu_e\rangle-\langle j_e\mu_e|\mathrm{Tr}_1'[\hat{V}_{\mathrm{eff}}\hat{\rho}_1(-\infty)]|j_e\mu_e\rangle)$$

$$\equiv 0\,. \tag{B8}$$

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