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Collisional Redistribution of Weak Resonance Radiation

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(Received 24 May 1978)

We derive simple expressions for the collisional redistribution function which are not restricted by impact theory and hence encompass the cases of excitation and detection far from resonance. For an isolated resonance line, the redistribution function depends only on quantities already involved in the absorption profile. This implies simple relations between results obtained from light-scattering experiments and those obtained in emission or absorption spectroscopy.

In recent years increasing theoretical[1-3] and experimental[4-7] activity has centered on the study of the redistribution of resonance radiation by collisions. While this problem has for long been prominent in astrophysics,[8] it has received renewed interest in laboratory physics with the advent of tunable dye lasers. Frequency-selective laser scattering has indeed been revealed as a powerful tool for gas and plasma diagnostics as well as for the determination of atomic and molecular properties, interatomic potentials, etc.

The theoretical framework in which the redistribution problem has generally been treated is the impact theory.[1,2] As was stressed repeatedly,[6,7] this theory imposes serious restrictions on the frequency domain of both the incident and scattered light. Indeed, the validity is limited to frequency separations from the line center smaller than typical inverse collision durations. Hence this theory does not account for excitation nor detection far from resonance.

The breakdown of the impact theory on the line wings has recently been demonstrated experimentally[6,7] by displaying a strong asymmetry of the fluorescence signal with respect to the sign of the laser detuning around the resonance frequency. According to the predictions of the impact theory, the signal would not depend on the sign of the detuning.

A recent approach aimed at a more general theory[8] seems to be of limited validity in the frequency region beyond the impact domain because it leads to a fluoresence line profile which in some cases of far-wing excitation may become partly negative. This is to be traced to a factorization, in Ref. 3, of the time-evolution operator corresponding to separate time intervals in which collisions are treated independently.

Our purpose is to establish an expression for the redistribution function in the framework of quantum electrodynamics and quantum statistics. We define this function formally as the probability per unit time, $p(a,b)$, for an atom (undergoing collisions) to scatter one present photon from mode a into mode b. This notion makes sense for weak radiation intensities because the scattering probability in the presence of any number n_a of photons in mode a is then just proportional to n_a.

Let us consider one atom (A) embedded in a gas of N perturbers (P) and a radiation field (R). Using obvious notation, we write the Hamiltonian of the whole system APR as

$$H = H_A + H_P + H_R + V_{AP} + V_{AR} + V_{PR}. \quad (1)$$

To write transition probabilities we will em-

ploy the notation of Liouville–von Neumann space ($\mathfrak{L}$).[9-12] This is a Hilbert space spanned by the linear operators U, now denoted by $|U\rangle\rangle$, which act on the usual Hilbert space $\mathcal{H}$ of states. If $\{|x_n\rangle\}_n$ is a basis of $\mathcal{H}$, $\{|x_n\rangle\langle x_m|\rangle\rangle\}_{nm} \equiv \{|x_n x_m^\dagger\rangle\rangle\}_{nm}$ is a basis of $\mathfrak{L}$. As the scalar product we define $\langle\langle W|U\rangle\rangle = \mathrm{Tr}(W^\dagger U)$. Operators acting in $\mathfrak{L}$ will be denoted by a caret over them. Examples of such operators are the commutators

$$\hat{H} = [H, \cdots], \quad \hat{H}_A = [H_A, \cdots],$$

$$\hat{V}_{PR} = [V_{PR}, \cdots], \text{ etc.},$$

called Liouville operators.

In $\mathfrak{L}$-space formalism, the probability for a photon of mode b to be present at time t is given by

$$w(a,b;t) = \langle\langle P_b|\mathrm{Tr}_{AP}\rho(t)\rangle\rangle, \tag{2}$$

where $\mathrm{Tr}_{AP}\rho(t)$ is the partial trace over the AP system of the total density operator $\rho(t)$ which has initially the form $\rho(0) = \rho_{AP}P_a$ with $P_c \equiv |c\rangle\langle c|$ for any mode c. The quantity $\mathrm{Tr}_{AP}\rho(t)$ can be obtained following exactly the line of a previous paper[13] treating pressure broadening in the framework of the Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) formalism. We may take over directly the result of Ref. 13 after extending the atom system there to our system AR and substitutin our ρ for the quantity F defined there. In addition, we have to note that the approximation on which the truncation of the BBGKY hierarchy is based, namely, the exclusion of simultaneous strong collisions, includes in our case that the interaction between the perturber gas and the radiation field only matters for a perturber which is very close to the atom. (This becomes significant on the far line wings beyond the Weisskopf frequency corresponding to the perturber ground state.) In this Letter we will neglect this interaction altogether and also take Eq. (4) of Ref. 13, just without the term representing initial correlations between the atom and perturbers. This is again an approximation exlcuding the very far wings ($\Delta\omega \gg kT/\hbar$). If we denote Laplace transforms of functions $f(t)$ by $\tilde{f}(s)$, Eq. (4) of Ref. 13 gives us

$$|\mathrm{Tr}_P\tilde{\rho}(s)\rangle\rangle = \hat{G}|\mathrm{Tr}_P\rho(0)\rangle\rangle = \hat{G}|\rho_A(0)P_a\rangle\rangle, \tag{3}$$

where $\rho_A(0)$ is the initial atomic density operator, and

$$\hat{G} \equiv [s + i(\hat{H}_A + \hat{H}_R + \hat{V}_{AR}) + \hat{K}]^{-1} \tag{4}$$

is the propagator of the AR system, in which the effect of perturbers is summarized in the collision operator

$$\hat{K} \equiv N\langle\langle I_1|\hat{V}_{A1}[s + i(\hat{H}_A + \hat{H}_R + \hat{V}_{AR} + \hat{H}_1 + \hat{V}_{A1})]^{-1}V_{A1}|\rho_1\rangle\rangle, \tag{5}$$

I_1 and ρ_1 being the unity operator and the free-particle density operator in the factor space of $\mathcal{H}$ corresponding to perturber 1.

Considering the special case that the atom is in its ground state $|\gamma\rangle$ before and after the transition, $\rho_A(0)$ becomes $|\gamma\rangle\langle\gamma|$, and $\mathrm{Tr}_{AP}\rho$ becomes $\langle\gamma|\mathrm{Tr}_P\rho|\gamma\rangle$. The Laplace transform of (2) then reads

$$\tilde{w}(a,b;s) = \langle\langle \gamma b, \gamma^\dagger b^\dagger|\hat{G}|\gamma a, \gamma^\dagger a^\dagger\rangle\rangle. \tag{6}$$

From this the redistribution function is obtained as

$$p(a,b) = \lim_{t\to\infty}[w(a,b;t)/t] = \lim_{s\to 0}[s^2\tilde{w}(a,b;s)]. \tag{7}$$

We evaluate this expression for two different model atoms, both assumed to be at rest: (1) a two-level atom, having a ground level ω_γ and one excited nondegenerate level ω_ϵ influenced by phase-changing collisions; (2) a three-level atom, having a ground level ω_γ and two excited levels ω_ϵ and $\omega_{\epsilon'}$, one of them ($\omega_{\epsilon'}$) being forbidden for radiative transitions to ω_γ. We choose $0 \leq |\omega_\epsilon - \omega_{\epsilon'}| \ll \omega_\epsilon - \omega_\gamma$ and assume that collisions affect the excited levels only through transitions between states $|\epsilon\rangle$ and $|\epsilon'\rangle$.

Since the treatments of the two cases are similar, we will give details of the calculations only for case (1) and just indicate the result for case (2).

We define projection operators acting on the factor space $\mathfrak{L}_{AR}$ of $\mathfrak{L}$ which corresponds to system AR:

$$\hat{P}_\epsilon \equiv |\epsilon 0\epsilon^\dagger 0^\dagger\rangle\rangle\langle\langle\epsilon 0\epsilon^\dagger 0^\dagger|, \quad \hat{P}_\gamma \equiv \textstyle\sum_{xy}|\gamma x\gamma^\dagger y^\dagger\rangle\rangle\langle\langle\gamma x\gamma^\dagger y^\dagger|, \quad \hat{P}' \equiv \textstyle\sum_x[|\gamma x\epsilon^\dagger 0^\dagger\rangle\rangle\langle\langle\gamma x\epsilon^\dagger 0^\dagger| + |\epsilon 0\gamma^\dagger x^\dagger\rangle\rangle\langle\langle\epsilon 0\gamma^\dagger x^\dagger|],$$

where the sums in these expressions are over single-photon modes x and y. The projector $\hat{P}_\epsilon + \hat{P}_\gamma + \hat{P}'$ selects a subspace $\mathfrak{L}_{AR}'$ of $\mathfrak{L}_{AR}$ in which the radiation vacuum $|0\rangle$ is associated with the excited state $|\epsilon\rangle$, single-photon states $|x\rangle$, $|y\rangle$ are associated with the ground state $|\gamma\rangle$, and multiple-photon states are neglected. In the following we will restrict ourselves to this subspace and use corresponding matrix representations of the operators $\hat{G}^{-1}$, $\hat{G}$, etc.

The matrix of G^{-1} involves that of $\bar{K}$ which we evaluate to second order in V_{AR}. [Note that neglecting $\hat{V}_{AR}$ in Eq. (5) leads to the results of Ref. 3.] The zero-order term is the collision matrix of the absorption profile.[13] It is particular to case (1) that it has only the following nonvanishing matrix elements: $K_{xx} = K_{x\dagger x\dagger}{}^* \equiv K_x \equiv K_x{}^r + iK_x{}^i \equiv K(\omega_{x0})$, where we have used the short-hand notations

$$\langle\langle \gamma x \epsilon^\dagger 0^\dagger | \hat{M} | \gamma y \epsilon^\dagger 0^\dagger \rangle\rangle \equiv M_{xy}, \quad \langle\langle \gamma x \epsilon^\dagger 0^\dagger | \hat{M} | \epsilon 0 \gamma^\dagger y^\dagger \rangle\rangle \equiv M_{xy\dagger}, \text{ etc.},$$

and $\omega_{x0} \equiv \omega_x - \omega_0$ with $\omega_0 \equiv \omega_{\epsilon\gamma} = \omega_\epsilon - \omega_\gamma$ being the resonance frequency. The term of first order in $\hat{V}_{AR}$ vanishes, and the second-order term has the elements $K_{xy} = K_{x\dagger y\dagger}{}^*$ and $K_{xy\dagger} = K_{x\dagger y}{}^*$. As examples, we indicate

$$K_x = N \sum_{\lambda\lambda'} \frac{\langle \epsilon\lambda | V_{A1} | \overline{\epsilon\lambda'} \rangle \langle \overline{\epsilon\lambda'} | V_{A1} | \epsilon\lambda \rangle \rho_\lambda}{s + i(\omega_{\lambda\lambda'} + \omega_{x0})}, \tag{8a}$$

$$K_{xy} = N V_x{}^* V_y \sum_{\lambda\lambda'} \frac{\langle \epsilon\lambda | V_{A1} | \overline{\epsilon\lambda'} \rangle \langle \overline{\epsilon\lambda'} | V_{A1} | \epsilon\lambda \rangle \rho_\lambda}{[s + i(\omega_{\lambda\lambda'} + \omega_{x0})][s + i\omega_{\lambda\lambda'}][s + i(\omega_{\lambda\lambda'} + \omega_{y0})]}. \tag{8b}$$

Here λ and λ' label free one-perturber states and $|\overline{\epsilon\lambda}\rangle$ denotes the scattering state associated with the free state $|\epsilon\lambda\rangle$. In (8b) we have put $\langle \gamma\lambda x | V_{AR} | \overline{\epsilon\mu} 0 \rangle \approx \langle \gamma x | V_{AR} | \epsilon 0 \rangle \delta_{\lambda\mu} \equiv V_x{}^* \delta_{\lambda\mu}$ because of the neglect of the interaction between the perturbers and the radiation field. Expression (8b) may be further simplified by decomposing it into partial fractions. This yields [with $K(0) \equiv K_0$]

$$K_{xy} = (V_x{}^* V_y / \omega_{xy})[(K_x - K_0)/\omega_{x0} - (K_y - K_0)/\omega_{y0}].$$

Similarly we obtain [with $K(\omega_{xy}) \equiv K_{(xy)}$]

$$K_{x\dagger y} = (V_x V_y / \omega_{x0}\omega_{y0})(K_x{}^* + K_y - K_0 - K_{(xy)}),$$

provided that we replace $|\overline{\epsilon\lambda}\rangle$ by $|\epsilon\lambda\rangle$ in elements like $\langle \epsilon\lambda' | V_{A1} | \overline{\epsilon\lambda} \rangle$, which amounts to a second-order expansion in V_{A1} of some of the off-diagonal elements of $\hat{K}$. This approximation limits our treatment to frequency separations below the Weisskopf frequency, except when at least one of the two frequencies ω_a or ω_b is inside the impact domain, in which case elements like $K_{b\dagger a}$ vanish.

We now turn to the matrix inversion $\hat{G}^{-1} \to \hat{G}$. A straightforward application of Zwanzig's projection-operator method[9] yields

$$\hat{P}_\gamma \hat{G} \hat{P}_\gamma = \hat{G}_\gamma - \hat{G}_\gamma \hat{V}_{AR} \hat{G}' \hat{V}_{AR} \hat{G}_\gamma + \hat{G}_\gamma \hat{V}_{AR} \hat{G}' \hat{V}_{AR} \hat{G}_\epsilon \hat{V}_{AR} \hat{G}' \hat{V}_{AR} \hat{G}_\gamma, \tag{9}$$

where

$$\hat{G}_\gamma \equiv \hat{P}_\gamma [s + i\hat{P}_\gamma (\hat{H}_A + \hat{H}_R) \hat{P}_\gamma]^{-1}, \quad \hat{G}' \equiv \hat{P}' [s + i\hat{P}' (\hat{H}_A + \hat{H}_R - i\hat{W}) \hat{P}']^{-1},$$
$$\hat{G}_\epsilon \equiv \hat{P}_\epsilon [s + \hat{P}_\epsilon \hat{V}_{AR} \hat{G}' \hat{V}_{AR} \hat{P}_\epsilon]^{-1}, \quad \hat{W} \equiv \hat{K} + \hat{R}, \quad \hat{R} = \hat{P}' \hat{V}_{AR} \hat{G}_\gamma \hat{V}_{AR} \hat{P}'.$$

$\hat{R}$ has the meaning of a radiative width operator. Its nonvanishing matrix elements are easily derived to be

$$R_{xx} = R_{x\dagger x\dagger}{}^* = \textstyle\sum_z V_z{}^* V_z / (s + i\omega_{xz}) \equiv R_x \equiv R_x{}^r + iR_x{}^i \equiv R(\omega_{x0}), \quad R_{xy\dagger} = R_{x\dagger y} = -V_x{}^* V_y{}^* / (s + i\omega_{xy}).$$

Next we use the Dyson equation for $\hat{G}$ to write in the second term on the right-hand side of Eq. (9) $\hat{G}' = \hat{G}_d' - \hat{G}_d'(\hat{W}_n - \hat{W}_n \hat{G}' \hat{W}_n) \hat{G}_d'$, and in the third term $\hat{G}' \hat{V}_{AR} \hat{P}_\epsilon = \hat{G}_d' \hat{V}_{\rm eff} \hat{P}_\epsilon$, $\hat{P}_\epsilon \hat{V}_{AR} \hat{G}' = \hat{P}_\epsilon \hat{V}_{\rm eff} \hat{G}_d'$, with

$$\hat{V}_{\rm eff} = \hat{V}_{AR} - \hat{P}' \hat{W}_n \hat{G}' \hat{V}_{AR} \hat{P}_\epsilon - \hat{P}_\epsilon \hat{V}_{AR} \hat{G}' \hat{W}_n \hat{P}',$$

where subscripts d and n refer to the diagonal and off-diagonal parts of the corresponding matrices, respectively. Equation (9) then takes a form which is suitable for approximations based on the fact that the width functions $K(\Delta\omega)$ and $R(\Delta\omega)$ are much smaller than the characteristic frequency intervals

ω_K and ω_R over which they vary noticeably. We have found that approximating $\hat{W}_n\hat{G}'\hat{W}_n$, $\hat{V}_{\rm eff}$, and $\hat{G}_\epsilon$ by substituting $\hat{R}_n$ for $\hat{W}_n$ and $\hat{G}_d'$ for $\hat{G}'$ in these quantities leads to relative errors of the order of K/ω_K and R/ω_R in the final result. With this approximation the nonvanishing matrix elements of the three quantities become

$$(\hat{R}_n\hat{G}_d\hat{R}_n)_{xy}=(\hat{R}_n\hat{G}_d\hat{R}_n)_{x\dagger y\dagger}{}^*=-(V_x{}^*V_y/\omega_{xy})[(R_x-R_0)/\omega_{x0}-(R_y-R_0)/\omega_{y0}],$$

$$\langle\langle\gamma x\epsilon^\dagger 0^\dagger|\hat{V}_{\rm eff}|\epsilon 0\epsilon^\dagger 0^\dagger\rangle\rangle=\langle\langle\epsilon 0\gamma^\dagger x^\dagger|\hat{V}_{\rm eff}|\epsilon 0\epsilon^\dagger 0^\dagger\rangle\rangle{}^*=V_x[1+i(R_x-R_0)/\omega_{x0}],$$

$$\langle\langle\epsilon 0\epsilon^\dagger 0^\dagger|\hat{G}_\epsilon|\epsilon 0\epsilon^\dagger 0^\dagger\rangle\rangle=(s+2R_0{}^r)^{-1}.$$

The further evaluation of $\hat{P}_\gamma\hat{G}\hat{P}_\gamma$ is straightforward since all matrices to be inverted are now diagonal. Trivial algebra leads to a lengthy expression for $\tilde{w}(a,b;s)$ in which most of the terms are of higher order in K/ω_K and R/ω_R with respect to some leading terms which alone will be retained. Following Eq. (7), the redistribtuion function becomes (for $b\neq a$)

$$p(a,b)=\frac{2\pi^2V_b{}^*V_bV_a{}^*V_a}{R_0{}^r}L(\omega_{a0})\left[\frac{R_0{}^r}{K_a{}^r+R_a{}^r}\delta(\omega_{ba})+\frac{\gamma_{ab}}{K_a{}^r+R_a{}^r}L(\omega_{b0})\right], \tag{10}$$

where (with $c=a$ or b)

$$L(\omega_{c0})\equiv[(K_c{}^r+R_c{}^r)/\pi][(\omega_{c0}+K_c{}^i+R_c{}^i)^2+(K_c{}^r+R_c{}^r)^2]^{-1} \tag{11}$$

is the absorption profile, and

$$\gamma_{ab}=(K_a{}^rK_b{}^r+K_{(ab)}{}^rR_0{}^r)/(K_b{}^r+R_b{}^r). \tag{12}$$

This latter quantity provides an interpretation of the factor $\gamma_E(\Delta)$ found on experimental grounds in Refs. 6 and 7.

For case (2) the redistribution function takes again the form of Eq. (10); however, in this case we have

$$\gamma_{ab}=\bar{K}_a{}^r\bar{K}_b{}^r(\bar{K}_0{}^r+R_0{}^r)/\bar{K}_0{}^r(\bar{K}_b{}^r+R_b{}^r), \tag{13}$$

where $\bar{K}_c{}^r$ $(c=a,b)$ is the collisional width function of the absorption profile in case (2) [quite analogous to $K_c{}^r$ and also easily obtainable from (5)]. In both cases, Eq. (10) generalizes the results of the impact theory[1,2] for which one has $\gamma_{ab}=K_0{}^r$ (viz., $\bar{K}_0{}^r$). If at least one of the two frequency separations ω_{a0} or ω_{b0} is inside the impact domain, expressions (12) and (13) coincide in their functional dependence on $K_c{}^r$ (or $\bar{K}_c{}^r$). For far-wing excitation and near-resonance detection,[6,7] e.g., we have $\gamma_{ab}=K^r(\omega_{a0})$ [or $\bar{K}^r(\omega_{a0})$]. It is interesting to notice that for far-wing excitation and detection near the incident frequency, the presence of $K^r(\omega_{ab})$ in γ_{ab} for case (1) may entail a flat maximum superposed on the Rayleigh peak [term with $\delta(\omega_{ab})$ in Eq. (10)] in a similar manner as that occurring in the ac Stark effect in a strong radiation field. This maximum is due to collisional transitions of the atomic state between the virtual levels ω_a and ω_b.

In conclusion we emphasize that in both cases (1) and (2) the redistribution function involves only the frequency-dependent width functions $K^r(\Delta\omega)$ [or $\bar{K}^r(\Delta\omega)$] and $R^r(\Delta\omega)$ of the absorption profile (11). Results obtained from light scattering are therefore related in a simple manner to those obtained in emission or absorption spectroscopy. It might be of interest to check this relation experimentally.

We are grateful to Dr. J. Cooper, Dr. G. Nienhuis, and Dr. E. W. Smith for illuminating discussions.

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