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Rayleigh component of the redistribution function

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A formal investigation of the redistribution of weak near-resonance radiation is presented for the case that the radiative transitions of the scattering atom occur between two well-separated groups of states. The lower states are assumed stable while the upper states are allowed to undergo arbitrary interactions with an environment. If the lower states are also degenerate, a Rayleigh component which is infinitesimally narrow in the atom's rest frame is shown to exist under extremely wide conditions and independent of the approximations made in previous work on redistribution. Like the absorption profile, the intensity of this component as a function of the detuning (Rayleigh response function) can be expressed in terms of the mean atomic time evolution operator projected on the upper-state manifold. As compared to the absorption profile, however, the Rayleigh response function is different in shape and may provide complementary information on the scattering medium.

I. INTRODUCTION

The scattering of weak narrow-band radiation by interacting atoms is known to result usually in a double-peaked spectrum if the incident frequency is tuned close to an atomic resonance. The two peaks represent Rayleigh scattering (centered about the incident frequency) and collisionally aided fluorescence (centered about the atomic resonance). Mathematically, the spectrum is described by the so-called redistribution function. Although derivations of this function have been presented for various physical situations (for a recent review see Burnett[1]), most of these treatments share a common approximation, namely, the binary-collision assumption which is usually connected with a rather approximate treatment of the intercorrelation between collisional and radiative events. For the idealized case where the redistribution function is established in the rest frame of an atom having one stable lower level and scattering purely monochromatic light, these treatments lead to a Rayleigh component which is infinitesimally narrow (δ function of the scattered frequency). This means that the energy exchange between the atom and the perturbing particles does not entail a broadening of the Rayleigh component; the only manifestation of energy nonconservation in the atom-radiation subsystem is the occurrence of the broadened fluorescence component in addition to the sharp Rayleigh component.

Since it does not seem that simple arguments like energy conservation or nonconservation allow one to infer this behavior on intuitive grounds, the question arises whether the occurrence of a sharp Rayleigh component is a fundamental property of the redistribution function, or if it is just a consequence of the approximations made in the binary-collision treatments. A partial answer to this question has been given recently, namely, for the simple case of two-state atoms suffering adiabatic perturbations of their upper level.[2] For this case it has been shown that including slow perturbations on avoiding the binary-collision approximation, and taking full account of the perturbation-radiation correlations results in three components of the scattering spectrum: a sharp Rayleigh component, a broadened Rayleigh component (both centered about the incident frequency), and a broadened fluorescence component (centered about the atomic resonance). Thus, for the two-state model considered in Ref. 2, broadened Rayleigh scattering has been shown to exist in addition to, but not instead of, sharp Rayleigh scattering.

The generality of the arguments employed to derive those results in Ref. 2 which concern the sharp Rayleigh component, suggests that analogous results might hold in still more general situations. Indeed, it will be shown in the present note that the assumption of an adiabatic two-state model is not essential for proving the existence of a sharp component of the spectrum and for deriving its intensity. The formalism presented here will treat the general case of radiative transitions between state multiplets, where the upper multiplet is allowed to undergo almost arbitrary interactions with a surrounding bath. The treatment will provide a general prescription for separating the redistribution function into a broadened part (which may be multiple peaked) and a part consisting of one or more infinitesimally narrow peaks (representing Rayleigh and Raman components). The latter part will turn out to be expressible in terms of the mean atomic time evolution operator, a fact which in some situations may be exploited to use preferably this part for gaining information on the scattering medium.

II. DECOMPOSITION INTO SHARP AND BROADENED COMPONENTS

We assume that the radiative transitions occur between two energetically well-separated groups of atomic states, the lower ones being completely stable (i.e., unaffected by collisions and radiative decay). The upper group of states (degenerate or not) may decay by spontaneous emission and is assumed to undergo interactions with the environment, called the bath. Except that we exclude quenching (bath-induced transitions between the groups), the nature of these interactions is left unspecified. In particular, we neither assume binary collisions nor adiabaticity. For simplicity we will assume, however, that the interactions can be treated semiclassically, i.e., by means of a time-dependent potential in the atomic Hamiltonian. As for the statistical behavior of the interactions, we will make two rather weak assumptions: (1) The stochastic process governing the atom-bath interactions is stationary; (2) The autocorrelation time of the atom-bath interaction potential is short compared to the observation time. Both assumptions simply correspond to our aim of determining the scattering spectrum under stationary conditions; they do not introduce any restriction of practical importance.

We assume that the incident radiation is weak so that we may deal with single-photon scattering events. The redistribution function $p(a,b)$ may then be defined as the probability per unit time that a photon is scattered from initial mode $|a\rangle$ into final mode $|b\rangle$. It can be written as

$$p(a,b)=\lim_{t\to\infty}\frac{1}{t}\sum_{l,l'}\langle|\langle l'b|(la)_t\rangle|^2\rangle\rho_l \ . \tag{1}$$

Here, $|lc\rangle=|l\rangle\otimes|c\rangle$ $(c=a,b)$ corresponds to the atom being in a lower state $|l\rangle$ and one photon being present in mode $|c\rangle$. Further, $|(la)_t\rangle$ designates the state to which the atom-radiation subsystem evolves after time t if it was initially in state $|la\rangle$. The ρ_l represent the initial lower-state populations, and the outer brackets designate an average over the atom-bath interactions.

The evolution of $|(la)_t\rangle$ is governed by the Schrödinger equation with the Hamiltonian $H_0(t)+V\equiv H_A(t)+H_R+V$, where the three parts in the last expression correspond to the atom (interacting with the bath), to the radiation field, and to the atom-radiation interaction, respectively. Perturbation theory to second order in V leads to

$$\langle l'b|(la)_t\rangle=-\int_0^t dt_b\int_0^{t_b}dt_a\langle l'b|T_0(t,t_b)VT_0(t_b,t_a)VT_0(t_a,0)|la\rangle \ , \tag{2}$$

where we have put $\hbar=1$. The "unperturbed" time evolution operator T_0 satisfies the Schrödinger equation with Hamiltonian $H_0(t)\equiv H_A(t)+H_R$. Since second-order perturbation theory cannot account for the natural linewidth, we hitherto assume $H_A(t)$ to include a non-Hermitian radiative damping part leading to complex energy levels in the upper-state manifold. Due to the absence of lower-state broadening we have

$$T_0(t_2,t_1)|lc\rangle=|lc\rangle\exp[-i(\omega_l+\omega_c)(t_2-t_1)] \ , \tag{3}$$

where ω_c is the frequency of photon mode $|c\rangle$ and ω_l the energy (in frequency units) of lower state $|l\rangle$. Using this in Eq. (2) and introducing the integration variable $\tau=t_b-t_a$ in place of t_a leads to

$$\langle l'b|(la)_t\rangle=-e^{-i(\omega_b+\omega_{l'})t}\int_0^t e^{i(\omega_{ba}+\omega_{l'l})t_b}dt_b\int_0^{t_b}e^{i(\omega_a+\omega_l)\tau}\langle l'b|VT_0(t_b,t_b-\tau)V|la\rangle d\tau \tag{4}$$

where $\omega_{ba}\equiv\omega_b-\omega_a$ and $\omega_{l'l}\equiv\omega_{l'}-\omega_l$. In Eqs. (2) and (4), the integration variables $t_a=t_b-\tau$ and t_b represent, respectively, the times at which photon a is absorbed and photon b is emitted. The τ integration accounts for all possible absorption times from $\tau=0$, where absorption takes place immediately before emission, back into the past, $\tau=t_b$, where absorption takes place long before emission. Since Eq. (1) involves the limit $t\to\infty$, only unlimitedly large values of t and hence of t_b will be significant in the evaluation of Eq. (4). Therefore, the τ integration can be extended to infinity, thus allowing for absorption at any time in the past. By this procedure the transient terms arising from "switching on" the incident radiation at $t=0$ are dropped and the scattering process becomes truly stationary.

After evaluating the matrix element in Eq. (4) more explicitly, this equation now reads

$$\langle l'b|(la)_t\rangle=-e^{-i(\omega_b+\omega_{l'})t}\int_0^t e^{i(\omega_{ba}+\omega_{l'l})t_b}P_{ll'}(t_b)dt_b \ , \tag{5}$$

with

$$P_{ll'}(t_b)\equiv\sum_{u,u'}\langle u'0|V|l'b\rangle^*\langle u0|V|la\rangle\int_0^\infty e^{i(\omega_a+\omega_l)\tau}\langle u'|T_A(t_b,t_b-\tau)|u\rangle d\tau \ , \tag{6}$$

where $|u0\rangle=|u\rangle\otimes|0\rangle$, $|u\rangle$ and $|0\rangle$ denoting an upper atomic state and the radiation vacuum, respectively. T_A designates the atomic time evolution operator without the radiation field. It obeys the Schrödinger equation with Hamiltonian $H_A(t)$. In writing Eq. (6), we have made the rotating-wave approximation, assuming that V connects lower states with one photon present only to upper states with no photon present. The right-hand side of Eq. (5) may now be inserted into Eq. (1) to yield

$$\begin{aligned}p(a,b)&=\lim_{t\to\infty}\frac{1}{t}\sum_{l,l'}\rho_l\int_0^t\int e^{i(\omega_{ba}+\omega_{l'l})(t_b-t_b')}\langle P_{ll'}(t_b)P^*_{ll'}(t_b')\rangle dt_b dt_b'\\&=\lim_{t\to\infty}\frac{1}{t}\sum_{l,l'}\rho_l\int_{-t}^t(t-|s|)e^{-i(\omega_{ba}+\omega_{l'l})s}\langle P_{ll'}(0)P^*_{ll'}(s)\rangle ds \ ,\end{aligned} \tag{7}$$

where the last equation holds because in a stationary situation the autocorrelation function in the integrand depends only on the time difference t_b-t_b'.

It can be seen from Eq. (6) that the quantity $P_{ll'}(t_b)$ involves the history of the atom-bath interaction only for times smaller than t_b. Actually, since the τ integration in Eq. (6) converges after some characteristic time τ_c [which is at most of the order of the inverse natural damping contained in the effective Hamiltonian $H_A(t)$], $P_{ll'}(t_b)$ is essentially determined by the interaction during $t_b-\tau_c<t<t_b$. As a consequence, $P^*_{ll'}(s)$ will statistically decorrelate from $P_{ll'}(0)$ after times so large that the time intervals $-\tau_c<t<0$ and $s-\tau_c<t<s$ no longer overlap and are separated from each other by more than the autocorrelation time of the atom-bath interaction. Since in a stationary experiment the observation time (ideally infinite) is long compared to both the radiative lifetime and the autocorrelation time of the atom-bath interaction, $P^*_{ll'}(s)$ decorrelates from $P_{ll'}(0)$ during observation and the autocorrelation function of this quantity is conveniently written as the sum of

$$C_{1ll'}\equiv\langle P_{ll'}(0)\rangle\langle P^*_{ll'}(s)\rangle=|\langle P_{ll'}(0)\rangle|^2\ , \tag{8}$$

which is independent of s, and

$$C_{2ll'}(s)\equiv\langle P_{ll'}(0)P^*_{ll'}(s)\rangle-\langle P_{ll'}(0)\rangle\langle P^*_{ll'}(s)\rangle\ , \tag{9}$$

which decays to zero when $s\to\infty$. Correspondingly, the redistribution function splits up into the part

$$p_1(a,b)=2\pi\sum_{l,l'}C_{1ll'}\rho_l\delta(\omega_{ba}-\omega_{ll'})\ , \tag{10}$$

which consists of infinitesimally narrow components, and the part

$$p_2(a,b)=\sum_{l,l'}\int_{-\infty}^{\infty}e^{-i(\omega_{ba}-\omega_{ll'})s}\rho_lC_{2ll'}(s)ds\ , \tag{11}$$

which contains only broadened components.

The evaluation of $p_2(a,b)$ can hardly be pushed further without making specifying assumptions on either the structure of the atom or the nature of its interaction with the environment. The most familiar assumption made is that of binary collisions. Examples where $p_2(a,b)$ can be evaluated without this assumption have been presented in Ref. 2.

In this note we concentrate on the part $p_1(a,b)$ which represents a collection of sharp Rayleigh and Raman components. These components, which occur despite the nonconservation of energy in the atom-radiation subsystem, have been shown here to exist under appreciably wide conditions. In particular, the nature of the atom-bath interaction has been left unspecified, except for some weak assumptions excluding quenching and lower-state interactions, and ensuring the stationarity of the scattering process. It has thus been demonstrated that sharp Rayleigh and Raman scattering occurs independently of some essential approximations (such as the binary-collision assumption) made in previous work on redistribution.

III. RAYLEIGH RESPONSE FUNCTION VERSUS ABSORPTION PROFILE

It is seen from Eq. (10) that when the lower group of states is degenerate, there is just one sharp Rayleigh component with intensity proportional to

$$\int_{-\infty}^{\infty}p_1(a,b)d\omega_b=2\pi\sum_{l,l'}C_{1ll'}\rho_l=2\pi\sum_{l,l'}|\langle P_{ll'}(0)\rangle|^2\rho_l\ . \tag{12}$$

For simplicity, we will restrict the following discussions to this case, although most of the statements made below have an obvious generalization to the nondegenerate case. We will call the right-hand side of Eq. (12) the "Rayleigh response function," with regard to its dependence on the incident detuning. A remarkable feature of this function [see Eq. (12) in conjunction with (6)] is that it just involves the averages of the quantities $P_{ll'}(0)$, i.e., it is entirely expressible in terms of the Fourier transform of the mean atomic time evolution operator $\langle T_A(t_b,t_b-\tau)\rangle=\langle T_A(\tau,0)\rangle\equiv\overline{T}_A(\tau)$ (where the latter notation will hitherto be used for brevity). This is a key quantity which is also required for the evaluation of the absorption profile. Therefore, the expense employed in usual line-broadening calculations is sufficient for also evaluating the Rayleigh response function. This is in contrast to the determination of the broadened part $p_2(a,b)$ of the redistribution function. Except for the binary-collision case where also $p_2(a,b)$ is determined by usual line-shape quantities,[3] the evaluation of the broadened part necessitates more elaborate techniques.[2] When the binary-collision assumption cannot be made, one may be faced with situations where no theory is available for the broadened part, while there is still some treatment possible to evaluate the mean time evolution operator and thus the Rayleigh response function and the absorption profile. Such situations may occur for light scattering in dense or cold plasmas, where one has to deal with the problem of "ion dynamics"[4,5] in high-pressure gases and in condensed matter. It may then happen that the fluorescence component, for lack of theoretical interpretability, cannot play its usual role for probing the medium, and that a better means for reaching this goal is to rely on the Rayleigh response function and the absorption profile. It is thus of interest to know how these two functions compare in their suitability for gaining the wanted information.

The fact that the Rayleigh response function and the absorption profile stem from the same operator $\overline{T}_A$ does not mean that they bear the same information on the scattering medium. Indeed, the two functions are rather different in structure and also involve different linear combinations of matrix elements of $\overline{T}_A$. As to their suitability for probing the scattering medium, both functions show advantages and disadvantages. An obvious disadvantage of the absorption profile is that it cannot be measured locally but only as an integral over the line of sight. A disadvantage of the Rayleigh response function is that it depends only on the absolute values (not on the phases) of the quantities $\langle P_{ll'}\rangle$. The loss of information connected with this dependence leads to the well-known fact that far-wing Rayleigh scattering becomes independent of the bath variables (which may be considered as an advantage if one is not interested in the effects of the bath). To obtain information on the atom-bath interaction one is thus confined to the close line wing, the line center being possibly excluded too because the Rayleigh component may there be obscured by the fluorescence component. These limitations do not exist for the absorption profile, which has a useful frequency range extending from the line center to the far wings. An advantage of the Rayleigh response function over the absorption profile is, however, that it not only depends on the incident mode $|a\rangle$ but also on the scattered mode $|b\rangle$ [see Eq. (6)]. Since both modes can be varied independently by changing the direction and polarization of the incident and observed light beams, there is more flexibility in extracting information from the Rayleigh response function than there is from the absorption profile. For example, the modes $|a\rangle$ and $|b\rangle$ may be chosen in such a way that particular matrix elements of $\overline{T}_A$ may be favored with respect to others, thus possibly allowing one to investigate the atom-bath interaction with regard to particular atomic states or to check special features of line broadening theories. This may be of interest especially in anisotropic media, e.g., in the presence of external fields where $\overline{T}_A$ may have off-diagonal matrix elements in the representation of atomic eigenstates including these fields. But even in the absense of external fields there are simple cases where the usefulness of the Rayleigh response function can be easily illustrated. Consider, for instance, a $J_l=1$ to $J_u=2$ transition of an atom embedded in an isotropic medium such that $\overline{T}_A$ is diagonal in the angular momentum eigenstates $|JM\rangle$. Suppose that lower-state broadening is negligible so that the formalism of the present note can be applied. The best one could do using the absorption profile would be to probe the medium with a polarized light beam. This, however, would imply that a combination of at least three of the diagonal matrix elements of $\overline{T}_A$ would enter the measured signal, as can be seen by writing the absorption profile as

$$L(\omega_a)\sim\mathrm{Re}\sum_{l,u}\rho_l|\langle u0|V|la\rangle|^2 \times\int_0^\infty e^{i(\omega_a+\omega_l)\tau}\langle u|\overline{T}_A(\tau)|u\rangle d\tau\ ,$$

and considering dipole radiation (where $\langle u0|V|la\rangle$ is proportional to $\langle u|\mathbf{D}|l\rangle\cdot\mathbf{e}_a$ with $\mathbf{D}$ being the dipole operator and $\mathbf{e}_a$ the polarization vector of the incident radiation). With a quantization axis parallel to the light beam, the matrix elements of $\overline{T}_A$ occurring in the absorption signal would correspond to the states $|2M\rangle$ with $M=0,\pm 1,\pm 2$ in case of linear polarization, with $M=0,1,2$ in case of left circular polarization and with $M=-2,-1,0$ in case of right circular polarization. If, on the other hand, one uses the Rayleigh response function instead of the absorption profile, one has the advantage that only one or two matrix elements may be probed selectively. For example, if the incident light beam has left circular polarization, and the scattered radiation is observed forward in right circular polarization or backward in left circular polarization, the only matrix element of $\overline{T}_A$ occurring in Eq. (12) [in conjunction with Eq. (6)] corresponds to the state $|20\rangle$.

In summary, we conclude that the Rayleigh response function and the absorption profile may play a complementary role in providing information on the scattering medium. In the above discussion we have deliberately omitted those problems which are related to optical thickness, saturation and background emission. The advantages which in this context the use of Rayleigh scattering presents over resonance (fluorescence) scattering have been discussed previously in the literature (see, e.g., Ref. 6).

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