Collisional redistribution beyond the medium-coupling limit

Henk F Arnoldus and Thomas F George

Departments of Physics and Astronomy and Chemistry, 239 Fronczak Hall, State University of New York at Buffalo, Buffalo, New York 14260, USA

Received 12 August 1986

Abstract. The evaluation of the binary-collision operator $\Phi(\omega)$, pertaining to collisional redistribution of strong laser radiation, involves the computation of a time-ordered exponential, which only reduces to a scalar exponential in the medium-coupling limit. In this approximation one neglects the alteration of the collisional dynamics due to the presence of the laser field. A two-state atom is considered, for which we expand $\Phi(\omega)$ in the ratio of the Rabi frequency Ω to the detuning from resonance. This parameter vanishes in the medium-coupling case, and is small for common gas-phase experiments. It is shown that the correction to medium coupling can again be expressed in a scalar function, which represents the temporal correlation between the interaction potential and the full time evolution during a single collision. The decay constants for collisional transitions between dressed states, which are germane to the width of the spectral lines, appear to be sensitive to the deviation from medium coupling. Quite remarkably, a non-vanishing collisional contribution survives in the limit $\Omega \rightarrow 0$ of $\Phi(\omega)$.

1. Introduction

An optically active atom in a radiation field absorbs photons from the incident light beam, which are subsequently emitted as dipole radiation. Observation of this fluorescence in experiments (intensity, spectral distribution, temporal photon correlations) allows a detailed study of the dynamics of a driven atom, since the temporal properties of the emission are tantamount to the time evolution of the atomic density operator, according to the quantum-regression theorem (Lax 1968). Particularly the study of collisions between an active atom and neutrals can benefit from the fact that the time evolution of the atomic state in the course of a collision has its effect on the frequency distribution of the fluorescence. This feature implies the possibility of determining interaction potentials from atomic lineshapes, rather than from collisional cross sections. In common experiments the atoms (for instance sodium) are immersed in a gas of neutrals (usually a rare gas), and the vapour is irradiated by a CW laser. For not too high perturber densities and laser power, the spectral profile of the emitted fluorescence is given by the unified theory of collisional redistribution, which assumes the validity of the binary-collision approximation (Smith et al 1973). Contemporary CW laser fields, however, cannot be considered as weak fields regarding their modification of the collisional dynamics, which forces us to take into account the non-perturbative interaction with the radiation. This was accomplished by Nienhuis (1981) and Burnett et al (1982) with slightly different methods. The general expression

for the fluorescence spectrum of a two-state atom reads (Arnoldus and Nienhuis 1983)

$$I(\omega) = \frac{A}{\pi} \operatorname{Re} \operatorname{Tr} d^{\dagger} \frac{\mathrm{i}}{\omega - \omega_L - L_d + \mathrm{i}\Gamma + \mathrm{i}W + \mathrm{i}\Phi(\omega - \omega_L)} (\sigma d)$$
(1.1)

with $I(\omega) d\omega$ the number of emitted photons per unit of time in the frequency range $(\omega, \omega + d\omega)$. Here A denotes the Einstein coefficient for spontaneous decay of the excited state $|e\rangle$ to the ground state $|g\rangle$, $d = |e\rangle\langle g|$ is the atomic raising operator, ω_L is the laser frequency, L_d indicates the Liouvillian of the dressed atom (bare atom, laser field and interaction), Γ accounts for spontaneous decay and is proportional to A, W represents and is proportional to the laser linewidth (phase-diffusion model), $\Phi(\omega)$ is the binary-collision operator, and σ is the steady-state atomic density operator in the rotating frame. Evaluation of the operator inversion in equation (1.1) in terms of the matrix elements of the various Liouvillians and the density operator is straightforward. An expression similar to equation (1.1) can be derived for the probe-absorption profile of the driven atom (Arnoldus and George 1987).

In the impact limit of collisional line broadening, where the collision time is much smaller than any other time scale in the problem, apart from ω_L^{-1} , the operator $\Phi(\omega)$ assumes a constant value (Omont 1965). Hence information on the collisional dynamics is contained in the ω -dependence of $\Phi(\omega)$. There exist many equivalent forms of the collision operator, but the following integral representation will be the starting point of this paper. In terms of L_d and the time-evolution operator U(t) (which will be specified in § 3) for a single collision, and in the interaction picture, the binary-collision operator $\Phi(\omega)$ attains the form

$$\Phi(\omega) = (\omega - L_d) \int_0^\infty dt \, e^{i(\omega - L_d)t} \langle U(t) - 1 \rangle (\omega - L_d).$$
(1.2)

An average over the different perturber velocities, impact parameters and instants of closest approach is indicated by angle brackets. Expression (1.2) reveals clearly the significance of the ω -dependence of $\Phi(\omega)$. It arises as the Laplace parameter of the transform of $\exp(-iL_d t)\langle U(t)-1\rangle$, which is in addition sandwiched by the factors $\omega - L_d$.

Although the form of $\Phi(\omega)$ in equation (1.2) is very transparent, its explicit evaluation is obstructed by the appearance of the cumbersome operator U(t). Apart from the impact limit, the expression (1.2) can only be simplified in the mediumcoupling limit, which neglects the dipole coupling between the atom and laser field during a collision (Ben-Reuven 1975, Fiutak and Van Kranendonk 1980). Then $\Phi(\omega)$ can be expressed entirely in a scalar function $\phi(\omega)$ (no operator), which is related to the low-intensity collisional width and shift of the absorption line. If we denote the resonance of the two-level atom by ω_0 , and the detuning of the laser from resonance by $\Delta = \omega_L - \omega_0$, then $|\Delta|$ acquires a typical order of magnitude of 1 GHz. This is due to the inevitable Doppler shift of ω_L for atoms in the gas phase (Rautian and Sobel'man 1967). The coupling strength of the atomic dipole μ with the laser is expressed in the Rabi frequency $\Omega = \hbar^{-1} |\langle e | \boldsymbol{\mu} \cdot \boldsymbol{\epsilon} | g \rangle|$ where $\boldsymbol{\epsilon}$ is the polarisation of the electric field. In the medium-coupling limit one then asserts that $\Omega \ll |\Delta|$ in the evaluation of $\Phi(\omega)$. For strong CW laser irradiation (\sim 100 mW, not focused) of an alkali vapour, the value of Ω is of the order of 0.1-1 GHz, which implies that the medium-coupling assumption is not always satisfied. Besides that, for atoms in the velocity class $\Delta \cong 0$, the approximation $\Omega \ll |\Delta|$ breaks down for any field intensity.

Attempts to extend the evaluation of $\Phi(\omega)$ beyond the medium-coupling limit were recently made by Schuller and Nienhuis (1983, 1984). These authors adopted an expansion in the collision strength (the potential) up to second order, and retained the dependence on Ω up to all orders. This procedure obviously imposes constraints on the interaction, although they argued that an extrapolation of their results to higher order should be quite accurate. In this paper we expand $\Phi(\omega)$ in $\Omega/|\Delta|$, which is a small parameter, independent of the potential. It will appear that the deviations from the medium-coupling limit can again be expressed in scalar functions, which resemble the $\phi(\omega)$.

2. Dressed atom

The collision operator $\Phi(\omega)$ contains the Liouvillian L_d , which represents the free evolution of the dressed atom (Cohen-Tannoudji and Reynaud 1977). By definition, the operator L_d is diagonal with respect to the dressed states of Liouville space. If we indicate these states by the tetradic vectors $|+\rangle\langle+|, |-\rangle\langle-|, |+\rangle\langle-|$ and $|-\rangle\langle+|$, then the eigenvalue equations read

$$L_d |\pm\rangle\langle\pm| = 0 \qquad L_d |\pm\rangle\langle\mp| = \mp \Omega' |\pm\rangle\langle\mp| \qquad (2.1)$$

and the level separation Ω' is determined by Ω and Δ according to

$$\Omega' = \Delta (1 + \Omega^2 / \Delta^2)^{1/2}.$$
(2.2)

In Hilbert space the corresponding dressed states $|+\rangle$ and $|-\rangle$ are linear combinations of the bare states $|g\rangle$ and $|e\rangle$. Explicitly,

$$|\pm\rangle = a_{\pm}|g\rangle \pm a_{\pm}|e\rangle \tag{2.3}$$

with the coefficients given by

$$a_{\pm}^{2} = \frac{1}{2} (1 \pm \Delta/\Omega') \tag{2.4}$$

and the sign convention

$$a_{-} > 0 \qquad a_{+} / \Delta > 0.$$
 (2.5)

For later purposes we introduce the three parameters g_+ , g_- and g_0 as the matrix elements with respect to dressed states of the projector $P_g = |g\rangle\langle g|$ on the atomic ground state. From the definitions

$$g_{\pm} = \langle \pm | P_g | \pm \rangle$$
 $g_0 = \langle \pm | P_g | \mp \rangle$ (2.6)

and from the transformation (2.3), it follows that they are related to a_{\pm} according to

$$g_{\pm} = a_{\pm}^2 \qquad g_0 = a_+ a_-.$$
 (2.7)

Then g_{\pm} is expressed in the optical parameters Ω and Δ in equation (2.4), and for g_0 we obtain

$$g_0 = \Omega / 2\Omega'. \tag{2.8}$$

Notice that g_+ and g_- obey the relations $g_+ + g_- = 1$ and $g_+ g_- = g_0^2$.

3. Single-collision evolution

A semiclassical description of the perturber motion is in general accurate enough for the calculation of redistribution of radiation. Hence we can write the interaction potential for a collision with a single perturber as

$$V(t) = V_e(t)P_e + V_g(t)P_g$$
(3.1)

in terms of the projectors on the bare states and the adiabatic potential curves. Inelastic collisions are omitted, since they are also excluded in the derivation of the collision operator. The corresponding Liouvillian is now defined by

$$L(t) \cdot = \hbar^{-1} [V(t), \cdot].$$
(3.2)

Next we notice that V(t) can be written as $V = \frac{1}{2}(V_e + V_g)(P_e + P_g) + \frac{1}{2}(V_e - V_g)(P_e - P_g)$, and we recall that $P_e + P_g$ equals the unit operator for a two-state atom. Then the commutator (3.2) reduces to

$$L(t) \cdot = -\hbar^{-1} V_d(t) [P_g, \cdot]$$
(3.3)

with $V_d = V_e - V_g$ the difference potential.

The evolution operator U(t), as it appears in $\Phi(\omega)$ from equation (1.2), is defined in the interaction picture. We transform L(t) to $\hat{L}(t)$ according to

$$\hat{L}(t) = \exp(iL_d t)L(t)\exp(-iL_d t).$$
(3.4)

The U(t) is defined as the time-ordered exponential

$$U(t) = \theta \exp\left(-i \int_0^t ds \, \hat{L}(s)\right)$$
(3.5)

pertaining to a collision with a single perturber. Averaging over all possible trajectories then yields $\langle U(t) \rangle$, which is required for the evaluation of the $\Phi(\omega)$. From equation (3.3) it follows that L(t) is diagonal with respect to the bare states, whereas $\exp(\pm iL_d t)$ is diagonal in a dressed-state representation. Therefore the exponentials in equation (3.4) do not commute with L(t), which implies that the time-ordered exponential (3.5) cannot be reduced to an ordinary exponential.

The interaction L(t) is proportional to the commutator with P_g , for which the matrix elements with respect to dressed states are the optical parameters g_+ , g_- and g_0 . If we expand L(t) onto the dressed states of Liouville space, and substitute the result in equation (3.4), we obtain

$$\hat{L}(t) = v_{+}(t)L_{+} + v_{0}(t)L_{0} + v_{-}(t)L_{-}$$
(3.6)

with coefficient functions

$$v_{\pm}(t) = -\hbar^{-1} V_d(t) g_0 \exp(\pm i\Omega' t)$$
(3.7)

$$v_0(t) = -\hbar^{-1} V_d(t) (g_- - g_+)$$
(3.8)

and time-independent Liouvillians

$$L_{\pm} \cdot = [|\mp\rangle\langle\pm|,\cdot] \tag{3.9}$$

$$L_0 \cdot = [|-\rangle\langle -|, \cdot]. \tag{3.10}$$

These operators do not commute either, but they obey the relations

$$L_0 L_{\pm} L_0 = 0 \qquad \qquad L_0^3 = L_0 \tag{3.11}$$

which will facilitate the evaluation of U(t) considerably.

4. Transformation of U(t)

Differentiation of equation (3.5) shows that U(t) obeys

$$i \frac{d}{dt} U(t) = \hat{L}(t)U(t)$$
 $U(0) = 1$ (4.1)

and this differential equation with initial condition is equivalent to the definition of U(t) as a time-ordered exponential. If we now read for $\hat{L}(t)$ the three-term expression (3.6), then the properties (3.11) suggest a transformation to an interaction-like picture, which considers $v_0(t)L_0$ as the free-evolution Liouvillian. Hence we introduce

$$P(t) = \exp\left(iL_0 \int_0^t ds \, v_0(s)\right) U(t) \tag{4.2}$$

which satisfies the equation

$$i\frac{d}{dt}P(t) = (v_{+}(t)L'_{+}(t) + v_{-}(t)L'_{-}(t))P(t) \qquad P(0) = 1.$$
(4.3)

Here the primed operators are given by

$$L'_{\pm}(t) = \exp\left(iL_0 \int_0^t ds \, v_0(s)\right) L_{\pm} \exp\left(-iL_0 \int_0^t ds \, v_0(s)\right).$$
(4.4)

Expansion of the exponentials on both sides and application of the relations (3.11) yields the simple result

$$L'_{+}(t) = \eta(t)^{*}L_{+} \qquad L'_{-}(t) = \eta(t)L_{-}$$
(4.5)

which involves the scalar exponential

$$\eta(t) = \exp\left(-i\int_0^t ds \, v_0(s)\right). \tag{4.6}$$

Inspection of equations (3.7) and (3.8) shows that we can express $v_{\pm}(t)$ in $v_0(t)$ according to

$$v_{\pm}(t) = \alpha v_0(t) \exp(\pm i\Omega' t) \tag{4.7}$$

which contains the optical parameter

$$\alpha = \frac{g_0}{g_- - g_+} = \frac{\Omega}{2\Delta}.$$
(4.8)

Combining everything finally amounts to the equation for P(t)

$$i\frac{d}{dt}P(t) = \alpha v_0(t)[L_+\eta(t)^* \exp(i\Omega' t) + L_-\eta(t)\exp(-i\Omega' t)]P(t).$$
(4.9)

It might seem that this is not a great simplification in comparison with equation (4.1), but it will turn out that equation (4.9) is especially suitable for the study of the deviation from the medium-coupling limit. This is due to the fact that the right-hand side is proportional to α , which vanishes for $\Omega/|\Delta| \rightarrow 0$.

With the transformation (4.2) the collision operator (1.2) attains the form

$$\Phi(\omega) = (\omega - L_d) \int_0^\infty \mathrm{d}t \; \mathrm{e}^{\mathrm{i}(\omega - L_d)t} \left\langle \exp\left(-\mathrm{i}L_0 \int_0^t \mathrm{d}s \, v_0(s)\right) P(t) - 1 \right\rangle (\omega - L_d). \tag{4.10}$$

If we again expand the exponential in brackets we find that the collisional factor which has to be evaluated can be written as

$$\left\langle \exp\left(-iL_{0}\int_{0}^{t} ds \, v_{0}(s)\right) P(t) \right\rangle$$

= $(1-L_{0}^{2})\langle P(t) \rangle -\frac{1}{2}(L_{0}-L_{0}^{2})\langle \eta(t)^{*}P(t) \rangle +\frac{1}{2}(L_{0}+L_{0}^{2})\langle \eta(t)P(t) \rangle.$ (4.11)

This exhibits clearly that it is not sufficient to solve equation (4.9) for the average $\langle P(t) \rangle$, but that also the operators $\langle \eta(t)^* P(t) \rangle$ and $\langle \eta(t) P(t) \rangle$ are required. Since a factorisation as $\langle \eta(t) P(t) \rangle = \langle \eta(t) \rangle \langle P(t) \rangle$ cannot be justified, we have to solve equation (4.9) for three averages, rather than only for $\langle P(t) \rangle$.

5. Basic equations

The three occurring quantities, which have to be averaged, will be denoted by

$$P_0(t) = P(t) \qquad P_+(t) = \eta(t)^* P(t) \qquad P_-(t) = \eta(t) P(t). \tag{5.1}$$

From the definition of $\eta(t)$, equation (4.6), we have

$$i \frac{d}{dt} \eta(t) = v_0(t) \eta(t)$$
 $\eta(0) = 1.$ (5.2)

Then the equations for P_0 , P_+ and P_- follow immediately from equation (4.9), and we obtain

$$i \frac{d}{dt} P_{0}(t) = \alpha [v_{0}(t) \eta(t) \exp(-i\Omega't)L_{-} + v_{0}(t) \eta(t)^{*} \exp(i\Omega't)L_{+}]P_{0}(t)$$

$$i \frac{d}{dt} P_{+}(t) = -v_{0}(t) \eta(t)^{*}P_{0}(t)$$

$$+ \alpha [v_{0}(t)\eta(t) \exp(-i\Omega't)L_{-} + v_{0}(t)\eta(t)^{*} \exp(i\Omega't)L_{+}]P_{+}(t)$$

$$i \frac{d}{dt} P_{-}(t) = v_{0}(t)\eta(t)P_{0}(t)$$
(5.3)

+
$$\alpha [v_0(t)\eta(t) \exp(-i\Omega' t)L_+ + v_0(t)\eta(t)^* \exp(i\Omega' t)L_+]P_-(t).$$
 (5.5)

If we write the equations in this way, we have a set of three coupled equations. Alternatively we could replace, for instance, $\eta(t)^* P_0(t)$ in the first term at the right-hand side of equation (5.4) by $P_+(t)$. In this fashion we can decouple the set, but it will turn out that the form (5.3)-(5.5) is most convenient, because the collisional factors now only appear as $v_0(t)\eta(t)$ and its complex conjugate. In view of equation (5.2), these factors are essentially the time-derivative of $\eta(t)$, which implies that only $\eta(t)$ enters the equations, rather than $\eta(t)$ and $v_0(t)$ separately. We will take advantage of that in the next section.

6. Laplace transform

The set of equations (5.3)-(5.5) can be integrated directly, but the solution involves again time-ordered exponentials, so this does not give rise to any simplification in the

evaluation of $\Phi(\omega)$. In order to achieve a more transparent and manageable formulation, we make a Laplace transform. For an arbitrary function or operator we define

$$\tilde{f}(\omega) = \int_0^\infty \mathrm{d}t \; \mathrm{e}^{\mathrm{i}\omega t} f(t) \tag{6.1}$$

which has the inverse relation

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \ e^{-i\omega t} \tilde{f}(\omega) = \begin{cases} f(t) & t > 0\\ \frac{1}{2}f(0) & t = 0\\ 0 & t < 0. \end{cases}$$
(6.2)

It should be emphasised that ω is not necessarily real. We tacitly assume that ω includes a small positive imaginary part, which guarantees the convergence of the integral in equation (6.1). For the inverse (6.2) the integral then runs over the real ω -axis.

Now we substitute the inverse integrals for $P_0(t)$, $P_+(t)$ and $P_-(t)$ in equations (5.3)-(5.5), and we take the Laplace transform of the set. The result can be expressed consisely in terms of a function $\hat{b}(\omega)$, defined as the Laplace transform of $v_0(t)\eta(t)$, e.g.

$$\tilde{b}(\omega) = \int_0^\infty \mathrm{d}t \, \mathrm{e}^{\mathrm{i}\omega t} v_0(t) \,\eta(t). \tag{6.3}$$

With equation (5.2) this becomes

$$\tilde{b}(\omega) = \omega \tilde{\eta}(\omega) - i \tag{6.4}$$

and hence only the Laplace transform of $\eta(t)$ appears. Transformation of the set gives

$$\omega \tilde{P}_{0}(\omega) - i = \frac{\alpha}{2\pi} \int_{-\infty}^{\infty} d\omega' (\tilde{b}(\omega - \omega' - \Omega')L_{-} + \tilde{b}(\omega' - \omega - \Omega')^{*}L_{+}) \tilde{P}_{0}(\omega')$$
(6.5)

$$\omega \tilde{P}_{+}(\omega) - i = -\frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega' \tilde{b}(\omega' - \omega)^{*} \tilde{P}_{0}(\omega') + \frac{\alpha}{2\pi} \int_{-\infty}^{\infty} d\omega' (\tilde{b}(\omega - \omega' - \Omega')L_{-} + \tilde{b}(\omega' - \omega - \Omega')^{*}L_{+}) \tilde{P}_{+}(\omega')$$
(6.6)

$$\omega \tilde{P}_{-}(\omega) - i = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega' \, \tilde{b}(\omega - \omega') \tilde{P}_{0}(\omega') + \frac{\alpha}{2\pi} \int_{-\infty}^{\infty} d\omega' (\tilde{b}(\omega - \omega' - \Omega')L_{-} + \tilde{b}(\omega' - \omega - \Omega')^{*}L_{+}) \tilde{P}_{-}(\omega')$$
(6.7)

which constitutes a set of coupled integral equations.

The collision operator can be expressed immediately in the solution of this set. First we notice that the factor $\exp(-iL_d t)$ in the integrand of equation (4.10) can be moved into the brackets. Its effect on the average in equation (4.11) follows from

$$\exp(-iL_d t)(L_0 \pm L_0^2) = \exp(\mp i\Omega' t)(L_0 \pm L_0^2)$$
(6.8)

$$\exp(-iL_d t)(1-L_0^2) = 1 - L_0^2$$
(6.9)

and therefore the exponential will only shift the Laplace parameter ω over $\pm \Omega'$. Further, the -1 in equation (4.10) yields

$$\int_{0}^{\infty} \mathrm{d}t \, \mathrm{e}^{\mathrm{i}(\omega - L_{d})t} = (1 - L_{0}^{2}) \, \frac{\mathrm{i}}{\omega} - \frac{1}{2} (L_{0} - L_{0}^{2}) \, \frac{\mathrm{i}}{\omega + \Omega'} + \frac{1}{2} (L_{0} + L_{0}^{2}) \, \frac{\mathrm{i}}{\omega - \Omega'}. \tag{6.10}$$

With $\omega - L_d = \omega - \Omega' L_0$, and using $L_0^3 = L_0$, we move the factor $\omega - L_d$ on the left-hand side of the integral in equation (4.10) into the brackets. Finally, we then obtain $\Phi(\omega) = \langle (1 - L_0^2)(\omega \tilde{P}_0(\omega) - i) - \frac{1}{2}(L_0 - L_0^2)((\omega + \Omega')\tilde{P}_+(\omega + \Omega') - i) + \frac{1}{2}(L_0 + L_0^2)((\omega - \Omega')\tilde{P}_-(\omega - \Omega') - i)\rangle(\omega - \Omega' L_0).$ (6.11)

Although the evaluation of $\Phi(\omega)$ is now reduced to solving the set (6.5)-(6.7), the latter is not easy in general.

7. Expansion in α

For atoms in a perturber bath the parameter α is small, as was argued in § 1. This observation justifies an expansion of $\Phi(\omega)$ around $\alpha = 0$. In this section we solve the set of integral equations (6.5)-(6.7) up to order α , and in the next section we will apply the results for the elaboration of $\Phi(\omega)$.

An obvious way to find a systematic expansion in α for the solution of the equations (6.5)-(6.7) is by iteration. For instance, in equation (6.5) we have $\tilde{P}_0(\omega) = i/\omega + \alpha \int d\omega'(\ldots)\tilde{P}_0(\omega')$. Then we can substitute the right-hand side with $\omega \to \omega'$, $\omega' \to \omega''$ for $\tilde{P}_0(\omega')$ in the integrand, which gives an additional term, proportional to α^2 , etc. Care should be exercised, however, because the operators L_+ and L_- also depend on α . They are defined with respect to the dressed states, and a transformation to the bare states will reveal an Ω and Δ dependence. This should be taken into account carefully, since otherwise inconsistencies will arise. Besides that, the Ω' in the argument of the \tilde{b} depends on α . For the time being we will omit these complications and make an iterative expansion of the set. We only keep track of the α dependence which is displayed as an overall factor in the various terms.

Iteration of equation (6.5) amounts to the expansion

$$\omega \tilde{P}_{0}(\omega) - i = \frac{\alpha}{2\pi} \int_{-\infty}^{\infty} d\omega' \frac{i}{\omega'} (\tilde{b}(\omega - \omega' - \Omega')L_{-} + \tilde{b}(\omega' - \omega - \Omega')^{*}L_{+}) + \dots$$
(7.1)

With the relations for an arbitrary Laplace transform $\tilde{f}(\omega)$

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} \mathrm{d}\omega' \frac{\mathrm{i}}{\omega'} \tilde{f}(\omega - \omega') = \tilde{f}(\omega)$$
(7.2)

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} \mathrm{d}\omega' \frac{\mathrm{i}}{\omega'} \tilde{f}(\omega' - \omega)^* = \tilde{f}(-\omega)^*$$
(7.3)

which can readily be deduced from equations (6.1) and (6.2), we find

$$\langle \omega \tilde{P}_0(\omega) - \mathbf{i} \rangle = \alpha L_- \langle \tilde{b}(\omega - \Omega') \rangle + \alpha L_+ \langle \tilde{b}(-\omega - \Omega')^* \rangle + \dots$$
(7.4)

Up to order α , the average of $\tilde{P}_0(\omega)$ over the different collisions only involves the average of $\tilde{b}(\omega)$.

Along the same lines, the iteration of equation (6.0) yields

$$\omega \tilde{P}_{+}(\omega) - i = -\tilde{b}(-\omega)^{*} + \alpha (\tilde{b}(\omega - \Omega')L_{-} + \tilde{b}(-\omega - \Omega')^{*}L_{+}) \\ - \frac{\alpha}{2\pi i} \int_{-\infty}^{\infty} d\omega' \frac{i}{\omega'} \tilde{b}(\omega' - \omega)^{*} (\tilde{b}(\omega' - \Omega')L_{-} + \tilde{b}(-\omega' - \Omega')^{*}L_{+}) \\ - \frac{\alpha}{2\pi i} \int_{-\infty}^{\infty} d\omega' \frac{i}{\omega'} \tilde{b}(-\omega')^{*} (\tilde{b}(\omega - \omega' - \Omega')L_{-} + \tilde{b}(\omega' - \omega - \Omega')^{*}L_{+}) + \dots$$
(7.5)

and a similar relation can be found for $\omega \tilde{P}_{-}(\omega) - i$. Here we used the result (7.4) for $\tilde{P}_0(\omega)$, and we performed a first integration with equations (7.2) and (7.3). The remaining integrals over ω' need some more manipulations, but with straightforward algebra and remembering that ω' in i/ω' includes a positive imaginary part, we can write equation (7.5) in the equivalent form

$$\omega \tilde{P}_{+}(\omega) - i = -\tilde{b}(-\omega)^{*} + \alpha L_{-}\tilde{b}(\omega - \Omega') + \alpha L_{+}\tilde{b}(-\omega - \Omega')^{*}$$
$$+ i\alpha L_{-} \int_{0}^{\infty} dt \, e^{i(\omega - \Omega')t} \int_{0}^{t} d\tau \, e^{i\Omega'\tau}b(t)^{*}b(t - \tau)$$
$$+ i\alpha L_{+} \int_{0}^{\infty} dt \, e^{i(\omega + \Omega')t} \int_{0}^{t} d\tau \, e^{-i\Omega'\tau}b(t)^{*}b(t - \tau)^{*} + \dots$$
(7.6)

After taking the average of this equation, we observe that the quantities $\langle b(t)b(t')\rangle$ can only depend on the time difference t - t'. Therefore, we introduce the correlation function of b(t) by

$$\zeta(t) = \langle b(0)b(t) \rangle \tag{7.7}$$

~

which equals $\langle b(0)^*b(t)\rangle$, since $b(0) = v_0(0)$ is real. Then the integrals in equation (7.6) can be expressed in the Laplace transform of $\zeta(t)$. We obtain

$$\langle \omega \tilde{P}_{+}(\omega) - \mathbf{i} \rangle = -\langle \tilde{b}(-\omega)^{*} \rangle + \alpha L_{-} \langle \tilde{b}(\omega - \Omega') \rangle + \alpha L_{+} \langle \tilde{b}(-\omega - \Omega')^{*} \rangle$$
$$-\frac{\alpha}{\omega - \Omega'} L_{-} (\tilde{\zeta}(-\omega)^{*} + \tilde{\zeta}(\omega - \Omega'))$$
$$-\frac{\alpha}{\omega + \Omega'} L_{+} (\tilde{\zeta}(-\omega)^{*} + \tilde{\zeta}(-\omega - \Omega')^{*}) + \dots$$
(7.8)

and in a similar way we find the solution of equation (6.7) to be

$$\langle \omega \tilde{P}_{-}(\omega) - i \rangle = \langle \tilde{b}(\omega) \rangle + \alpha L_{-} \langle \tilde{b}(\omega - \Omega') \rangle + \alpha L_{+} \langle \tilde{b}(-\omega - \Omega')^{*} \rangle$$
$$+ \frac{\alpha}{\omega - \Omega'} L_{-} (\tilde{\zeta}(\omega) + \tilde{\zeta}(\omega - \Omega')) + \frac{\alpha}{\omega + \Omega'} L_{+} (\tilde{\zeta}(\omega) + \tilde{\zeta}(-\omega - \Omega')^{*}) + \dots$$
(7.9)

Equations (7.4), (7.8) and (7.9) show that the solution of the set (6.5)-(6.7) up to order α can be expressed entirely in the two functions $\langle \tilde{b}(\omega) \rangle$ and $\tilde{\zeta}(\omega)$.

In order to see more clearly the significance of $\langle \tilde{b}(\omega) \rangle$ and $\tilde{\zeta}(\omega)$, we rewrite them in a slightly different form. With $b(t) = v_0(t)\eta(t)$, the definition of $\tilde{\zeta}(\omega)$ reads

$$\tilde{\zeta}(\omega) = \int_0^\infty \mathrm{d}t \; \mathrm{e}^{\mathrm{i}\omega t} \langle v_0(0)v_0(t)\eta(t)\rangle. \tag{7.10}$$

Then we substitute equation (5.2) for $v_0(t)\eta(t)$ and perform a partial integration, which gives

$$\tilde{\zeta}(\omega) = \omega \int_0^\infty \mathrm{d}t \; \mathrm{e}^{\mathrm{i}\omega t} \left\langle v_0(0) \left[\exp\left(-\mathrm{i} \int_0^t \mathrm{d}s \; v_0(s) \right) - 1 \right] \right\rangle. \tag{7.11}$$

A similar procedure for $\langle \tilde{b}(\omega) \rangle$ from equation (6.3) results in

$$\langle \tilde{b}(\omega) \rangle = \omega \int_0^\infty \mathrm{d}t \, \mathrm{e}^{\mathrm{i}\omega t} \left\langle \exp\left(-\mathrm{i} \int_0^t \mathrm{d}s \, v_0(s)\right) - 1 \right\rangle. \tag{7.12}$$

The optical factor $g_{-} - g_{+}$ in the definition (3.8) of $v_0(t)$ equals $1 - 2\alpha^2 + ...$ and can be set equal to unity in this limit of small α . Then $v_0(t)$ equals $-\hbar^{-1}V_d(t)$, and hence $\langle \tilde{b}(\omega) \rangle$ is essentially (the Laplace transform of the complex conjugate of) the average evolution operator for a single collision, whereas $\tilde{\zeta}(\omega)$ is the correlation of this operator with $V_d(0)$. The $\tilde{\zeta}(\omega)$ contributes only for $\alpha \neq 0$, which reveals that a strong laser field (Ω large, or $\alpha \neq 0$) does not only probe the time regression during a collision (accounted for by $\langle \tilde{b}(\omega) \rangle$), but also the time correlation during the impact.

8. Collision operator

With the results of the previous section, we are able to compose expression (6.11) for $\Phi(\omega)$. We already mentioned that the definitions (3.9) and (3.10) of L_{\pm} and L_0 imply an Ω and Δ , and thereby an α dependence, which arises after substitution of the representation (2.3) for the dressed states into (3.9) and (3.10). We notice, however, that the L_{\pm} operators, which appear in equations (7.4), (7.8) and (7.9), are always multiplied by α . Hence it suffices to take L_{\pm} at $\alpha = 0$, for which we obtain

$$L_{+} \cdot = [d^{\dagger}, \cdot] \qquad \qquad L_{-} \cdot = [d, \cdot]$$

$$\tag{8.1}$$

in terms of the raising operator $d = |e\rangle\langle g|$. The operators which embrace the $\langle \omega \tilde{P}(\omega) - i \rangle$ factors in equation (6.10) only contain L_0 , which has the expansion

$$L_0 \cdot = [P_g, \cdot] - \alpha [d + d^{\dagger}, \cdot] + \dots$$

$$(8.2)$$

Furthermore, we notice that operators $\pm \frac{1}{2}(L_0 \pm L_0^2)$ act on an $L_+(\alpha = 0)$ and $L_-(\alpha = 0)$ term from equations (7.8) and (7.9). It is easy to verify that

$$\pm \frac{1}{2} (L_0 \pm L_0^2) L_{\pm} (\alpha = 0) = 0 \tag{8.3}$$

which implies that half the number of α -terms in $\langle \omega \tilde{P}_{\pm}(\omega) - i \rangle$ vanishes. Next we note that

$$\Omega' = \Delta(1 + 2\alpha^2 + \ldots) \tag{8.4}$$

so we can replace Ω' by Δ in the arguments of $\langle \tilde{b}(\omega \pm \Omega') \rangle$ and $\tilde{\zeta}(\omega \pm \Omega')$. After combining everything and performing all the operator algebra, we then obtain for the collision operator

$$\Phi(\omega)\sigma = (\omega - \Delta)\langle \tilde{b}(\omega - \Delta)\rangle d^{\dagger} \operatorname{Tr} d\sigma - (\omega + \Delta)\langle \tilde{b}(-\omega - \Delta)^{*}\rangle d \operatorname{Tr} d^{\dagger}\sigma + \alpha(\omega\langle \tilde{b}(-\omega)^{*}\rangle - (\omega - \Delta)\langle \tilde{b}(\omega - \Delta)\rangle + \tilde{\zeta}(-\omega)^{*} + \tilde{\zeta}(\omega - \Delta)) d^{\dagger} \operatorname{Tr}(P_{e} - P_{g})\sigma - \alpha(-\omega\langle \tilde{b}(\omega)\rangle + (\omega + \Delta)\langle \tilde{b}(-\omega - \Delta)\rangle + \tilde{\zeta}(\omega) + \tilde{\zeta}(-\omega - \Delta)^{*}) d \operatorname{Tr}(P_{e} - P_{e})\sigma$$

$$(8.5)$$

which defines the action of $\Phi(\omega)$ on an arbitrary Liouville vector σ .

For $\alpha \rightarrow 0$, only the first two terms on the right-hand side survive, and we recover the medium-coupling expression for the binary-collision operator. These terms are proportional to the coherences Tr $d\sigma = \langle g | \sigma | e \rangle$ and Tr $d^{\dagger}\sigma = \langle e | \sigma | g \rangle$ of the matrix σ . The correction terms, which account for the strong-field effect on $\Phi(\omega)$, appear to be proportional to the population inversion $\langle e | \sigma | e \rangle - \langle g | \sigma | g \rangle$ of σ . It is noteworthy that $\Phi(\omega)\sigma$ has two terms proportional to d^{\dagger} and two proportional to d, but no terms with P_e or P_g . This reflects the fact that we only considered elastic collisions, which cannot directly alter the populations of σ with respect to the bare states, but only through affecting its coherences. We mention the two properties of $\Phi(\omega)$,

$$\operatorname{Tr}(\Phi(\omega)\sigma) = 0 \qquad (\Phi(\omega)\sigma)^{\dagger} = \Phi(-\omega)\sigma^{\dagger} \qquad (8.6)$$

which follow immediately from equation (8.5).

At this stage it is convenient to make a change in notation. We replace the functions $\langle \tilde{b}(\omega) \rangle$ and $\tilde{\zeta}(\omega)$ by

$$\phi(\omega) = (\omega_0 - \omega) \langle \tilde{b}(\omega_0 - \omega)^* \rangle \tag{8.7}$$

$$\psi(\omega) = \phi(\omega) - \tilde{\zeta}(\omega_0 - \omega)^*$$
(8.8)

which have the integral representations

$$\phi(\omega) = (\omega - \omega_0)^2 \int_0^\infty \mathrm{d}t \; \mathrm{e}^{\mathrm{i}(\omega - \omega_0)t} \left\langle \exp\left(\mathrm{i} \int_0^t \mathrm{d}s \, v_0(s)\right) - 1 \right\rangle \tag{8.9}$$

$$\psi(\omega) = -\mathrm{i}\langle v_0(0)\rangle - (\omega - \omega_0) \int_0^\infty \mathrm{d}t \, \mathrm{e}^{\mathrm{i}(\omega - \omega_0)t} \left\langle (v_0(t) - v_0(0)) \exp\left(\mathrm{i} \int_0^t \mathrm{d}s \, v_0(s)\right) \right\rangle. \tag{8.10}$$

The shift over the atomic resonance frequency ω_0 is made, in order to relate the behaviour of the averages $\langle \ldots \rangle$ for $t \to \infty$ to the behaviour of $\phi(\omega)$ and $\psi(\omega)$ around $\omega = \omega_0$, rather than around $\omega = 0$. In terms of $\phi(\omega)$ and $\psi(\omega)$, the collision operator (8.5) attains the simple form

$$\Phi(\omega)\sigma = \phi(\omega_L + \omega)P_e\sigma P_g + \phi(\omega_L - \omega)^* P_g\sigma P_e$$

+ $\alpha(\psi(\omega_L + \omega) + \psi(\omega_0 - \omega)^*)(d\sigma P_g - P_e\sigma d)$
+ $\alpha(\psi(\omega_L - \omega)^* + \psi(\omega_0 + \omega))(P_g\sigma d^* - d^*\sigma P_e).$ (8.11)

Apparently the function ϕ represents the medium-coupling limit, whereas ψ accounts for the deviation from this limit for $\alpha \neq 0$. We notice that around $\omega = 0$ the function ϕ is centred with ω_L , whereas ψ occurs both as centred around ω_L and around ω_0 .

9. Rate of optical collisions

Radiationless transitions between the states $|e\rangle$ and $|g\rangle$ are prohibited, since we neglect inelastic collisions, but photon and collision assisted transitions can occur. During the impact of a collision the energy levels of $|e\rangle$ and $|g\rangle$ are temporarily shifted with the adiabatic potentials $V_e(t)$ and $V_g(t)$, which can provide a resonance for a laser photon with energy $\hbar\omega_L$. Thus for large detunings the presence of collisions enhances the photon absorption rate. These collision-mediated photon absorptions or emissions have been called optical collisions by Lisitsa and Yakovlenko (1974). For strong laser fields, the bare atomic states lose their significance since the diagonal Liouvillian is L_d , corresponding to a dressed atom. Hence the optical collision rate is more appropriately defined with respect to the dressed states. The rate constants for the transitions are determined by the collision operator $\Phi(\omega)$ for $\omega = 0$, accordinging to Nienhuis (1982)

$$k(\pm \to \mp) = -\langle \mp |(\Phi(0)|\pm)\langle \pm |)|\mp\rangle \tag{9.1}$$

and with expression (8.11) we derive

$$k(+ \to -) = k(- \to +)$$

= $\frac{\Omega^2}{2\Omega'^2} \operatorname{Re}(\phi(\omega_L) - \psi(\omega_L) - \psi(\omega_0)).$ (9.2)

First we notice that the rate constant for transitions from $|+\rangle$ to $|-\rangle$ equals the rate constant for $|-\rangle \rightarrow |+\rangle$, which was not the case for the expansion of $\Phi(\omega)$ to second order in the interaction potential (Schuller and Nienhuis 1983, 1984). This implies that a possible asymmetry in the rate of optical collisions is only induced by very strong fields, which can presumably not be generated by a CW laser, at least not for gas-phase experiments, with the inherent large detunings. Second, in the medium-coupling limit, equation (9.2) should be replaced by

$$k(\pm \to \mp) = \frac{\Omega^2}{2{\Omega'}^2} \operatorname{Re} \phi(\omega_L)$$
(9.3)

and we remark that this is not the limit of equation (9.2) for $\alpha \rightarrow 0$. The dependence on the laser intensity in equations (9.2) and (9.3) is the same, since ϕ and ψ are independent of Ω . We obtain equation (9.3) from the definition (9.1), with α set equal to zero in equation (8.11), which is the correct procedure, as mentioned before. For very strong irradiances the Ω dependence of $k(\pm \rightarrow \mp)$ changes considerably, as was shown by Yeh and Berman (1979) with numerical model calculations.

In the impact limit, where the collision time is effectively zero, the ω dependence of $\phi(\omega)$ vanishes, and we have Re $\phi(\omega) \rightarrow \gamma$, with γ the collisional width of the low-intensity absorption profile (Omont 1965). For the medium-coupling case the ω dependence of $\phi(\omega)$ follows from equation (8.9), which can equivalently be written as

$$\operatorname{Re} \phi(\omega_L) = (\omega_0 - \omega_L) \operatorname{Re} \int_0^\infty \mathrm{d}t \, \mathrm{e}^{-\mathrm{i}(\omega_0 - \omega_L)t} \left\langle v_0(t) \exp\left(\mathrm{i} \int_0^t \mathrm{d}s \, v_0(s)\right) \right\rangle. \tag{9.4}$$

Beyond the medium-coupling limit we find for the collisional factor in $k(\pm \rightarrow \mp)$ the representation

$$\operatorname{Re}(\phi(\omega_{L}) - \psi(\omega_{L}) - \psi(\omega_{0})) = (\omega_{0} - \omega_{L}) \operatorname{Re} \int_{0}^{\infty} dt \, e^{-i(\omega_{0} - \omega_{L})t} \left\langle v_{0}(0) \left[\exp\left(i \int_{0}^{t} ds \, v_{0}(s)\right) - 1 \right] \right\rangle \\ - \lim_{t \to \infty} \operatorname{Im} \left\langle (v_{0}(t) - v_{0}(0)) \exp\left(i \int_{0}^{t} ds \, v_{0}(s)\right) \right\rangle.$$

$$(9.5)$$

Here use has been made of the identity $-i\omega f(\omega) = f(\infty)$ in the limit $\omega \to 0$ for any Laplace transform. The relevance of the consideration of the rate of optical collisions is that this quantity is directly amenable to experiment. The collisional width of atomic spectral lines, as they follow from equation (1.1) in the limit of well-separated lines, is proportional to the rate of optical collisions (Nienhuis 1982). Hence it should be feasible to determine whether the correlations during a collision, represented by $\psi(\omega_L)$ and $\psi(\omega_0)$ in equation (9.2), are significant or not.

10. Conclusions

In the medium-coupling limit the stimulated radiative transitions between the states $|e\rangle$ and $|g\rangle$ and the AC Stark shift of the resonances are neglected. This simplification

amounts to the substitution

$$L_d \to \Delta[P_g, \cdot] \tag{10.1}$$

in expression (1.2) for $\Phi(\omega)$, and in equation (3.4) for $\hat{L}(t)$. Then every appearing operator is diagonal with respect to the tetradic bare states, and $\Phi(\omega)$ reduces immediately to the first two terms on the right-hand side of equation (8.11). This mediumcoupling limit of collisional redistribution is reminiscent of the treatment of relaxation, due to the coupling with a thermal bath, and in the presence of a harmonic interaction (Louisell 1973) (which gives, for instance, an expression for the spontaneous-decay operator Γ in equation (1.1)). Generally, the medium-coupling approximation is tacitly assumed. Modifications which take into account the strong-field effect on the decay constants lead to a relaxation theory with respect to dressed states. This was accomplished in a full quantum mechanical way by Cohen-Tannoudji and Reynaud (1977), and for a classical driving field by Arnoldus *et al* (1986), yielding the same results.

The analogue of the Einstein coefficients for spontaneous decay of dressed states is the rate of optical collisions in the theory of redistribution. Due to the non-Markovian nature of a collision process (except in the impact limit), the extension of $\Phi(\omega)$ beyond medium coupling is much more involved than its thermal-bath analogue. The finitememory effect results from the finite collision time and is reflected in the ω dependence of $\Phi(\omega)$. Already in the medium-coupling case the function ϕ has a frequency dependence, which displays the probing of the time evolution of a collision. We have shown that for stronger fields also the correlation between $v_0(t)$ and $\exp(i \int_0^t ds v_0(s))$ enters, which could be incorporated with a single function $\psi(\omega)$. We emphasise that the numerical evaluations of the scalar functions ϕ and ψ for model systems have the same complexity, which should be obvious from equations (8.9) and (8.10). In replacing $\Phi(\omega)$ by a combination of $\phi(\omega)$ and $\psi(\omega)$, we avoid the cumbersome computation of time-ordered exponentials. Result (8.11) can be applied immediately for the evaluation of spectral lineshapes. We merely substitute the expression in equation (1.1), and invert the matrix.

Acknowledgments

This research was supported by the National Science Foundation under Grant CHE-8519053 and the Air Force Office of Scientific Research (AFSC), United States Air Force, under Contract F49620-86-C-0009.

References

Arnoldus H F and George T F 1987 Phys. Rev. A submitted

- Arnoldus H F and Nienhuis G 1983 J. Phys. B: At. Mol. Phys. 16 2325
- Arnoldus H F, van Smaalen S and George T F 1986 Phys. Rev. B 34 6902
- Ben-Reuven A 1975 Adv. Chem. Phys. 33 235
- Burnett K, Cooper J, Kleiber P D and Ben-Reuven A 1982 Phys. Rev. A 25 1345
- Cohen-Tannoudji C and Reynaud S 1977 J. Phys. B: At. Mol. Phys. 10 345
- Fiutak J and Van Kranendonk J 1980 J. Phys. B: At. Mol. Phys. 13 2869
- Lax M 1968 Phys. Rev. 172 350
- Lisitsa V S and Yakovlenko S I 1974 Sov. Phys.-JETP 39 759
- Louisell W H 1973 Quantum Statistical Properties of Radiation (New York: Wiley)

Nienhuis G 1981 J. Phys. B: At. Mol. Phys. 14 3117

- Omont A 1965 J. Physique 26 26
- Rautian S G and Sobel'man I I 1967 Sov. Phys.- Usp. 9 701
- Schuller F and Nienhuis G 1983 Physica 121C 281
- Smith E W, Cooper J and Rossman L J 1973 J. Quant. Spectrosc. Radiat. Transfer 13 1523
- Yeh S and Berman P R 1979 Phys. Rev. A 19 1106