

# Master equation theory applied to the redistribution of polarized radiation, in the weak radiation field limit

## I. Zero magnetic field case

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**Abstract.** This paper is devoted to describe the atom-radiation interaction in the formalism of non-relativistic quantum electrodynamics by means of a perturbative development extended to orders higher than 2. Atom and radiation are treated quantum mechanically, through the density matrix approach. Collision effects are also introduced, in the impact approximation. Polarization is taken into account. The following hypotheses are considered: (a) weak radiation field (stimulated emission is neglected with respect to spontaneous emission); (b) two-level atom; (c) unpolarized lower level; (d) atomic reference frame; (e) zero magnetic field. The perturbation series development has been summed. The result of the paper is twofold: (a) the profiles in the form of  $\delta$ -functions obtained in ordinary theories extended up to order 2 in the series development are now replaced by realistic profiles: line-broadening is derived from the present formalism; (b) a new term (Rayleigh scattering term) appears at order 4 in the emissivity. This term is responsible for frequency coherence in scattering processes.

**Key words:** atomic processes – line: formation – line: profiles – polarization – radiative transfer

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### 1. Introduction

The importance of coherent scattering in the problem of line formation in stellar atmospheres is well known since a long time: a brief historical review can be found in Mihalas (1978; see also Frisch 1996). More generally, the frequency redistribution function in the radiation scattering process plays a dominant role in the formation of the profile of scattered lines. A decisive step in the knowledge of this function has been made by Omont et al. (1972), who derive it for a three-level atom by using a quantum mechanical description of matter and radiation, and include the effect of collisions, which are responsible for the relative strengths of the coherent and completely redistributed contributions to the function. The same authors address in a

forthcoming paper (Omont et al. 1973) the same problem for a non-zero magnetic field.

On the other hand, the modelisation of line formation in optically thick and/or non-LTE atmospheres requires the solution of the coupled equations of statistical equilibrium and radiative transfer. In their general expression valid for multi-level atom, these equations depend on both level populations and specific intensities. The introduction of partial redistribution effects (namely coherent scattering) is not simple, because the frequency redistribution function (the result provided by Omont et al. 1972) is not explicitly contained neither in the first, nor in the second equation.

The growing interest for polarization studies led Bommier & Sahal-Bréchet (1978) and Bommier (1980) to write down the system of statistical equilibrium equations for the atomic density matrix (in the multi-level scheme), taking into account atomic polarization. By means of a quite similar formalism, Landi Degl'Innocenti (1983, 1984) succeeded in closing the set of equations by deriving, besides the statistical equilibrium equation for the atomic density matrix, the transfer equation for polarized radiation (the embryo of this derivation can be found in Landi Degl'Innocenti & Landi Degl'Innocenti, 1972). Collision effects (in the impact approximation) were introduced in the formalism by Landi Degl'Innocenti et al. (1990, 1991a, 1991b) and were derived, in a more consistent and detailed way, by Bommier & Sahal-Bréchet (1991). The resulting equations have been applied to polarized line formation and magnetic field diagnostic in Solar Prominences (Bommier et al. 1994 and refs. therein; see also Bommier 1996 and Landi Degl'Innocenti 1996 for a general discussion about the method).

The derivation of the statistical equilibrium equations is based on, or is quite similar to, the master equation theory applied to the evolution of the density matrix of an atom interacting with a reservoir, as described by Cohen-Tannoudji (1977). This theory makes use of a perturbative development in power series of the interaction, and involves multiple commutators of the interaction Hamiltonian with the atomic reduced density matrix.

Atom and radiation are treated quantum mechanically. The calculation is restricted to the lowest order non-zero term, namely the 2nd order term.

The resulting equations reduce, in the unpolarized case, to the usual equations (statistical equilibrium and radiative transfer eqs.) that are commonly used to solve non-LTE problems in stellar atmospheres, except from the fact that the line profiles appear as  $\delta$ -functions. Landi Degl'Innocenti (1983) proposes to substitute these  $\delta$ -functions with more realistic line profiles; however, this proposal remains to be theoretically confirmed.

Landi Degl'Innocenti et al. (1990, 1991a, 1991b) propose a method for the solution of the coupled equations of statistical equilibrium and radiative transfer, in the weak magnetic field regime (1990), and in the arbitrary (1991a) and intermediate (1991b) magnetic field regimes. However, as photon absorption and emission result in being two independent processes in the 2nd order formalism used by these authors, the frequency of the photon emitted is independent of the frequency of the absorbed photon, which results in an approximation generally known as complete frequency redistribution in astrophysics.

In this scheme, based on the 2nd order perturbative expansion of the interaction, an emitted photon cannot 'save memory' of the frequency of the absorbed photon. The aim of the present paper is to push the perturbative expansion to higher orders, so to include frequency coherence effects into the formalism. This is done in the frame of the following hypotheses:

- weak radiation field (stimulated emission is neglected with respect to spontaneous emission)
- two-level atom
- unpolarized lower level
- atomic reference frame
- zero magnetic field.

The case of non-zero magnetic field will be addressed in the following paper of this series.

Since the work of Omont et al. (1972, 1973), powerful formalisms have indeed been elaborated for treating the problem of redistribution of radiation in scattering events, like for instance the dressed atom approach (Reynaud & Cohen-Tannoudji 1982), which is well-adapted to treat the case of strong radiation fields (lasers); we consider here the opposite case of weak radiation field, the case that is generally encountered in stellar atmospheres.

Anticipating the conclusion, let us mention that the result of the present paper is twofold:

- the substitution of order-2  $\delta$ -functions by real profiles proposed by Landi Degl'Innocenti (1983) is confirmed; line-broadening is now included in the formalism
- a new term (Rayleigh scattering term) appears at order 4 in the emissivity, which is responsible for frequency coherence in the scattering process.

With respect to the work of Omont et al. (1972), we obtain the same result on the frequency redistribution function, and both derivations are not completely different. However, as a result, we obtain a new method for taking into account coherent scattering in the statistical equilibrium and radiative transfer equations.

This could lead to address the problem of non-LTE and partial redistribution in a renewed manner.

The outline of the present paper is the following. The physical conditions and main hypotheses are described in Sect. 2, and the basic equations are derived in Sect. 3. In this same section we also introduce and discuss some fundamental approximations. The results involve multiple integrals that are performed in Sect. 4. The perturbation series summation is achieved in Sect. 5, and the results are given in Sect. 6, where one can find the master equation for the atomic density matrix, the coefficients of the radiative transfer equation, and the redistribution matrix, after the summation over the perturbation series. The results are finally discussed in Sect. 7.

## 2. Physical conditions and main hypotheses

We are interested in the problem of radiation scattering by atoms, eventually embedded in a magnetic field  $\mathbf{B}$ , and suffering elastic or inelastic collisions with other particles having a maxwellian distribution of velocities characterized by the temperature  $T$ . In the present paper, though the direction of the vanishing magnetic field is used to define the atomic quantization axis, the magnetic field intensity will be assumed to be zero; the effect of a magnetic field will be studied in a forthcoming paper.

We consider in this paper a two-level atom, with a lower level  $a$  and an upper level  $b$ . The lower level  $a$  is not 'a-priori' assumed to be infinitely sharp. Levels  $a$  and  $b$  may eventually be degenerate (in order to take into account polarization effects). The density matrix formalism will be used (see, for instance, Bommier 1996, and refs. therein). The atomic density matrix will be denoted as  $\rho$  in the present section.

In the following, we consider two cases:

- the non-degenerate and unpolarized case

In this case, the levels  $a$  and  $b$  are assumed to be isolated and non-degenerate. The atomic density matrix has only 4 elements: 2 populations  $\rho_{aa}$  and  $\rho_{bb}$ , and 2 optical coherences  $\rho_{ab}$  and  $\rho_{ba}$ . The polarization of the radiation field cannot be taken into account in this case.

- the degenerate and polarized case

In this case, the levels  $a$  and  $b$  are also assumed to be isolated, but they may now be degenerate. The lower level  $a$  is assumed to have an angular momentum  $J$  (the other quantum numbers characterizing the level being summarized by the letter  $\alpha$ ) with Landé factor  $g_J$ ;  $\alpha'J'$  and  $g_{J'}$  denote the same quantities for the upper level  $b$ . The Zeeman sublevels of the lower level  $\alpha J$  are denoted as  $N, N' \dots$ , and those of the upper level  $\alpha'J'$  as  $M, M' \dots$ . We furthermore suppose that the lower level is unpolarized, so that the different Zeeman sublevels  $N, N' \dots$  have the same population and there are no coherences between them.

The atomic density matrix is normalized according to the equation

$$\text{Tr}[\rho] = 1. \quad (1)$$

For the present calculation, we consider as reference frame the atomic rest frame: the effect of atomic velocities will be postponed to a forthcoming paper (in particular, atomic recoil due to photon emission will be neglected). The quantization axis  $OZ$  is chosen along an arbitrary direction that can be thought of as the direction of an infinitely vanishing magnetic field. In this frame, the vectors can be developed over the basis of the unit vectors  $e_p$  ( $p = 0, \pm 1$ ), defined by

$$e_p \text{ vectors } (p = 0, \pm 1) \begin{cases} e_+ = -\frac{1}{\sqrt{2}}(e_X + ie_Y) \\ e_- = \frac{1}{\sqrt{2}}(e_X - ie_Y) \\ e_0 = e_Z = \frac{\mathbf{B}}{\|\mathbf{B}\|} \end{cases} . \quad (2)$$

As for the incident radiation field, we assume the weak radiation field limit, in such a way that stimulated emission can be neglected with respect to spontaneous emission. This hypothesis is valid for typical stellar atmospheres, considering visible and UV lines; for instance, under solar conditions that can be roughly represented by a radiation temperature

$$T_{\text{rad}} \approx 6000 \text{ K}$$

and a typical wavelength

$$\lambda \approx 600 \text{ nm} ,$$

the average photons number per mode (neglecting a possible dilution factor) is

$$\bar{n} = \frac{1}{\exp\left\{\frac{h\nu}{kT_{\text{rad}}}\right\} - 1} \approx 2 \times 10^{-2} , \quad (3)$$

which is also the ratio between stimulated and spontaneous emission probabilities. The weak radiation field limit corresponds to

$$\bar{n} \ll 1 . \quad (4)$$

As a consequence of the weak radiation field limit, the lower level population will be much larger than the upper level one.

We furthermore assume that the incident radiation contains no correlations (or coherences) between states of different energy; in other words, we assume (see Landi Degl'Innocenti 1983)

$$\begin{cases} \langle a(\mathbf{k}, q) \rangle = \langle a^\dagger(\mathbf{k}, q) \rangle = 0 \\ \langle a(\mathbf{k}, q) a(\mathbf{k}', q') \rangle = \langle a^\dagger(\mathbf{k}, q) a^\dagger(\mathbf{k}', q') \rangle = 0 \\ \langle a^\dagger(\mathbf{k}, q) a(\mathbf{k}', q') \rangle = 0 \text{ except if } \mathbf{k} = \mathbf{k}' \end{cases} , \quad (5)$$

where  $\langle \dots \rangle$  denotes the average value (in the quantum-mechanical sense), and where  $a(\mathbf{k}, q)$  and  $a^\dagger(\mathbf{k}, q)$  are respectively the annihilation and creation operators of a photon of wavevector

$\mathbf{k}$  and polarization parallel to one of the two unit vectors  $e_q$  ( $q = \pm 1$ ) perpendicular to  $\mathbf{k}$  and defined by

$$e_q \text{ vectors } (q = 0, \pm 1) \begin{cases} e_+ = -\frac{1}{\sqrt{2}}(e_x + ie_y) \\ e_- = \frac{1}{\sqrt{2}}(e_x - ie_y) \\ e_0 = e_z = \frac{\mathbf{k}}{\|\mathbf{k}\|} \end{cases} , \quad (6)$$

where the  $Oz$  axis of the radiation reference frame (denoted as  $Oxyz$ ) is chosen along the  $\mathbf{k}$  direction; this reference frame is different from the magnetic field reference frame previously defined for the atom and denoted as  $OXYZ$ . The unit vectors of both reference frames are distinguished by their index:  $p$  for the magnetic field reference frame, and  $q$  for the radiation reference frame.

The coherences between states of same  $\mathbf{k}$  and different  $q$  describe the polarization properties of the incident (or scattered) radiation beam. The hypothesis described by Eq. (5) is valid for the radiation field typical of stellar atmospheres, and would not be valid for the radiation of a laser source.

### 3. Basic equations and approximations

#### 3.1. Order-2 development

One considers two interacting systems  $A$  and  $B$ : system  $A$  is composed of atoms and system  $B$  is composed of photons (the effect of the atom-perturber collisions will be added in a following section).

$H_A$  is the Hamiltonian of the unperturbed atoms (including the interaction with a magnetic field, if present), and  $H_B$  is the one of the photons in vacuum. The density matrix of the total system  $A+B$ , now denoted as  $\rho$ , obeys the Schrödinger equation

$$i\hbar \frac{d}{dt} \rho(t) = [H, \rho(t)] , \quad (7)$$

where

$$H = H_0 + V , \quad (8)$$

$H_0$  being the Hamiltonian of the total unperturbed system

$$H_0 = H_A + H_B , \quad (9)$$

and  $V$  being the interaction Hamiltonian between systems  $A$  and  $B$ .

Passing to the interaction representation (which 'follows' the evolution of the unperturbed system)

$$\begin{cases} \tilde{\rho}(t) = \exp\left\{\frac{i}{\hbar} H_0 t\right\} \rho(t) \exp\left\{-\frac{i}{\hbar} H_0 t\right\} \\ \tilde{V}(t) = \exp\left\{\frac{i}{\hbar} H_0 t\right\} V \exp\left\{-\frac{i}{\hbar} H_0 t\right\} \end{cases} , \quad (10)$$

the Schrödinger equations involves only the interaction Hamiltonian  $\tilde{V}(t)$

$$i\hbar \frac{d}{dt} \tilde{\rho}(t) = [\tilde{V}(t), \tilde{\rho}(t)] . \quad (11)$$

After a formal integration between times 0 and  $t$

$$\tilde{\rho}(t) = \tilde{\rho}(0) + \frac{1}{i\hbar} \int_0^t [\tilde{V}(t-\tau), \tilde{\rho}(t-\tau)] d\tau, \quad (12)$$

one obtains, by substituting Eq. (12) into the r.h.s. of Eq. (11), the evolution equation for the total system

$$\frac{d}{dt} \tilde{\rho}(t) = \frac{1}{i\hbar} [\tilde{V}(t), \tilde{\rho}(t)] - \frac{1}{\hbar^2} \int_0^t [\tilde{V}(t), [\tilde{V}(t-\tau), \tilde{\rho}(t-\tau)]] d\tau \quad (13)$$

which is an exact equation.

The aim of the present work is however to derive the evolution equation for the *reduced density matrices*,  $\sigma_A$  and  $\sigma_B$ , describing separately each of the systems  $A$  and  $B$ . The reduced matrices are obtained from the density matrix  $\rho$  by the partial trace operation

$$\begin{cases} \sigma_A(t) = \text{Tr}_B[\rho(t)] \\ \sigma_B(t) = \text{Tr}_A[\rho(t)] \end{cases} \Rightarrow \begin{cases} \tilde{\sigma}_A(t) = \text{Tr}_B[\tilde{\rho}(t)] \\ \tilde{\sigma}_B(t) = \text{Tr}_A[\tilde{\rho}(t)] \end{cases}. \quad (14)$$

As we will see in the following, the treatment of the time integral appearing in Eq. (13) requires an important approximation that is at the basis of the present work.

Before entering the description of this approximation, let us introduce one preliminary approximation and one hypothesis on the interaction potential:

(a) *Approximation 1: factorization of  $\rho$*

Following Fano (1957), Blum (1981), Cohen-Tannoudji (1977), we assume that the density matrix of the total system  $\rho$  can be factorized at any time in the form

$$\rho(t) = \sigma_A(t) \otimes \sigma_B(t) \Rightarrow \tilde{\rho}(t) = \tilde{\sigma}_A(t) \otimes \tilde{\sigma}_B(t), \quad (15)$$

which means that correlations induced by the interaction between systems  $A$  and  $B$  are neglected. This approximation is justified by the following arguments: we are interested in the evolution of one of the two systems, considered as the ‘small system’, interacting with the other system, considered as the ‘reservoir’. It is assumed that the reservoir has so many degrees of freedom that the effects of the interaction with the small system dissipate away quickly, do not react back onto the small system to any significant extent (‘no back-reaction’ approximation) and do not modify the average state of the reservoir, irrespectively of the amount of energy and polarization diffusing into it from the small system (Blum, 1981). The reaction of the small system on the reservoir is neglected. Consequently, the reservoir is assumed to be in equilibrium. It is not necessary to assume here, as usual, the *thermodynamical* equilibrium for the reservoir: the density matrix of the reservoir can contain some non-zero coherences, responsible for the radiation polarization. Therefore, it will only be assumed that the reservoir is in equilibrium, namely that its density matrix is time-independent. On the other hand, we aim to derive the evolution of the small system; no time-independence is assumed for the density matrix of the small system.

(b) *Hypothesis on the interaction potential*

If the average interaction potential is zero for each of the two separate systems  $A$  and  $B$

$$\text{Tr}_B[\sigma_B V] = 0 \Rightarrow \text{Tr}_B[\tilde{\sigma}_B(t) \tilde{V}(t')] = 0 \quad (16)$$

(and the same for  $A$ ), the first term in the r.h.s. of Eq. (13) vanishes in the partial trace operation. Considering now as interaction potential the dipolar electric interaction, we have:  
– for the photons (system  $B$ ), Eq. (16) is always satisfied because of the hypotheses summarized in Eq. (5), valid for stellar atmospheres.

– for the atoms (system  $A$ ), the analogous of Eq. (16) is satisfied when optical coherences are zero, a result that is valid in stationary situations, when the equilibrium equation  $d\sigma_A/dt = 0$  is solved (see Sect. 6.6).

$\text{Tr}_B[\sigma_B V]$  is an operator of the Hilbert space of  $A$ , which represents the energy of  $A$  in the average potential exerted by  $B$  upon  $A$  when  $B$  is in the equilibrium state  $\sigma_B$  (some sort of ‘Hartree potential’). So, we assume this average potential to be 0. If this were not the case, an additional commutator describing the effect of this ‘Hartree potential’ should be taken into account in the master equation (Cohen-Tannoudji, 1977).

Considering as ‘small system’ the average atom  $A$  interacting with the reservoir of photons, the master equation for the atomic density matrix  $\sigma_A$  can be directly derived from Eq. (13), taking into account Eqs. (14-16)

$$\begin{aligned} \frac{d}{dt} \tilde{\sigma}_A(t) = & -\frac{1}{\hbar^2} \int_0^t d\tau \\ & \times \text{Tr}_B \left[ \tilde{V}(t), \left[ \tilde{V}(t-\tau), \right. \right. \\ & \left. \left. \tilde{\sigma}_A(t-\tau) \otimes \tilde{\sigma}_B(t-\tau) \right] \right] \end{aligned} \quad (17)$$

Considering now as ‘small system’ a beam of radiation, interacting with the reservoir of atoms, one is interested in the transfer equation for the beam of radiation. Following Landi Degl’Innocenti & Landi Degl’Innocenti (1975), but with a slightly different definition of the polarization unit vectors (compare Eq. (6) of the present paper and their definition at p. 140 of their paper), let us introduce the operators

$$I_{qq'} = \frac{h\nu^3}{c^2} a^\dagger(\mathbf{k}, q') a(\mathbf{k}, q), \quad (18)$$

where the indices refer to the basis of the  $\mathbf{e}_q$  ( $q = \pm 1$ ) unit vectors defined in Eq. (6); the Stokes parameters  $I, Q, U, V$  (also denoted as  $S_i$  ( $i = 0, 1, 2, 3$ )) of the beam of radiation are given by

$$\begin{pmatrix} I \\ Q \\ U \\ V \end{pmatrix} = \begin{pmatrix} S_0 \\ S_1 \\ S_2 \\ S_3 \end{pmatrix} = \begin{pmatrix} \langle I_{++} \rangle + \langle I_{--} \rangle \\ -[\langle I_{+-} \rangle + \langle I_{-+} \rangle] \\ -i[\langle I_{+-} \rangle - \langle I_{-+} \rangle] \\ \langle I_{--} \rangle - \langle I_{++} \rangle \end{pmatrix} \quad (19)$$

(rectifying here an error in the definition of the  $V$  parameter in Bommier 1991), where  $\langle \dots \rangle$  denotes the average value of the operator (in the quantum-mechanical sense), defined by

$$\langle I_{qq'} \rangle = \text{Tr}_B [I_{qq'} \sigma_B(t)] . \quad (20)$$

It follows that the transfer equation is simply ( $s$  is the coordinate measured along the ray-path and  $c$  the speed of light)

$$\frac{d}{ds} \langle I_{qq'} \rangle = \frac{1}{c} \frac{d}{dt} \langle I_{qq'} \rangle = \frac{1}{c} \text{Tr}_B \left[ I_{qq'} \frac{d}{dt} \sigma_B(t) \right] . \quad (21)$$

Moreover, because the photons density matrix has no matrix element between states of different energy in physical situations typical of stellar atmospheres (see Eq. (5) and related topics), one has

$$[H_B, \sigma_B(t)] = 0 \implies \tilde{\sigma}_B(t) = \sigma_B(t) , \quad (22)$$

and, analogously to Eq. (17), the transfer equation is given by

$$\begin{aligned} \frac{d}{ds} \langle I_{qq'} \rangle = & -\frac{1}{c} \frac{1}{\hbar^2} \int_0^t d\tau \text{Tr}_B \left\{ I_{qq'} \right. \\ & \times \text{Tr}_A \left[ \tilde{V}(t), \left[ \tilde{V}(t-\tau), \right. \right. \\ & \left. \left. \tilde{\sigma}_A(t-\tau) \otimes \tilde{\sigma}_B(t-\tau) \right] \right] \left. \right\} \end{aligned} \quad (23)$$

### 3.2. Order-4 development

Equations (17) and (23) lead to the 2nd order term in the power-series development of the interaction potential. By performing suitable approximations on the time behavior of the quantities  $\tilde{\sigma}_A(t-\tau)$  and  $\tilde{\sigma}_B(t-\tau)$ , the time integrals appearing in Eqs. (17) and (23) can be performed so that one obtains the statistical equilibrium and radiative transfer equations to second order. Examples of this procedure can be found, for instance, in Cohen-Tannoudji (1977), Landi Degl'Innocenti (1983), Bommier & Sahal-Br  chot (1991) and Bommier (1991). However, as stated in the introduction, our aim is to push the development to higher orders.

Order-3 is obtained by substituting the integral equation (12) in the r.h.s. of the differential equation of order 2 (Eq. (13)). This procedure can be continued: the differential equation of order  $(n+1)$  is obtained by substituting the integral equation (12) in the r.h.s. of the differential equation of order  $n$ .

However, Eq. (16) can be generalized to higher orders; for instance, for the dipolar electric interaction, one has at order 3

$$\begin{aligned} \text{Tr}_B [\sigma_B V V V] &= 0 \implies \\ \text{Tr}_B [\tilde{\sigma}_B(t) \tilde{V}(t') \tilde{V}(t'') \tilde{V}(t''')] &= 0 \end{aligned} \quad (24)$$

(with a similar expression for the system  $A$ ). As a consequence, the first non-zero term in the development, after the term of order 2, is the term of order 4. Only even-order terms will be non-zero. The development up to order 4 gives:

– for the master equation of the atomic density matrix

$$\begin{aligned} \frac{d}{dt} \tilde{\sigma}_A(t) = & -\frac{1}{\hbar^2} \int_0^t d\tau \\ & \times \text{Tr}_B \left[ \tilde{V}(t), \left[ \tilde{V}(t-\tau), \tilde{\sigma}_A(0) \otimes \tilde{\sigma}_B(0) \right] \right] \\ & + \frac{1}{\hbar^4} \int_0^t d\tau_1 \int_0^{t-\tau_1} d\tau_2 \int_0^{t-\tau_1-\tau_2} d\tau_3 \\ & \times \text{Tr}_B \left[ \tilde{V}(t), \left[ \tilde{V}(t-\tau_1), \right. \right. \\ & \left. \left[ \tilde{V}(t-\tau_1-\tau_2), \left[ \tilde{V}(t-\tau_1-\tau_2-\tau_3), \right. \right. \right. \\ & \left. \left. \tilde{\sigma}_A(t-\tau_1-\tau_2-\tau_3) \otimes \right. \right. \right. \\ & \left. \left. \left. \tilde{\sigma}_B(t-\tau_1-\tau_2-\tau_3) \right] \right] \right] \left. \right] \left. \right] \end{aligned} ; \quad (25)$$

– for the radiative transfer equation

$$\begin{aligned} \frac{d}{ds} \langle I_{qq'} \rangle = & -\frac{1}{c} \frac{1}{\hbar^2} \int_0^t d\tau \text{Tr}_B \left\{ I_{qq'} \right. \\ & \times \text{Tr}_A \left[ \tilde{V}(t), \left[ \tilde{V}(t-\tau), \tilde{\sigma}_A(0) \otimes \tilde{\sigma}_B(0) \right] \right] \left. \right\} \\ & + \frac{1}{c} \frac{1}{\hbar^4} \int_0^t d\tau_1 \int_0^{t-\tau_1} d\tau_2 \int_0^{t-\tau_1-\tau_2} d\tau_3 \\ & \times \text{Tr}_B \left\{ I_{qq'} \text{Tr}_A \left[ \tilde{V}(t), \left[ \tilde{V}(t-\tau_1), \right. \right. \right. \\ & \left. \left[ \tilde{V}(t-\tau_1-\tau_2), \left[ \tilde{V}(t-\tau_1-\tau_2-\tau_3), \right. \right. \right. \\ & \left. \left. \tilde{\sigma}_A(t-\tau_1-\tau_2-\tau_3) \otimes \right. \right. \right. \\ & \left. \left. \left. \tilde{\sigma}_B(t-\tau_1-\tau_2-\tau_3) \right] \right] \right] \left. \right] \left. \right\} \end{aligned} . \quad (26)$$

### 3.3. The time-sequencing approximation

Solving the Schr  dinger equation requires the development at order 4, described in the previous subsection, to be pursued up to infinite order.

Since, on the one hand, the order-2 term in the r.h.s. of the order-4 equations (25-26) cannot be evaluated without introducing some further hypotheses on the initial conditions described by the term  $\tilde{\sigma}_A(0) \otimes \tilde{\sigma}_B(0)$  (a feature which holds at any order for the terms of order lower than the one considered), and since, on the other hand, lower order terms are in any case easier to evaluate than higher order terms, the idea is to evaluate all orders terms as if each of them were the last of the development of the Schr  dinger equation; by so doing, we avoid the complication introduced by the initial conditions. A term of order  $n$  represents a group of  $n/2$  interactions, and two cases have to be considered:

- either this group can be split into several independent groups of a lower number of interactions; in this case, the global interaction has already been taken into account at the preceding orders;
- or this group cannot be split in this way and represents a new process with respect to all the lower order terms.

Examples of the diagrams corresponding to both types of interactions are shown in Fig. 2 (see the discussion of the figure in Sect. 4), in the case of order 4.

By so doing, a given process will obviously appear several times in the development, and the extension of the calculation from order  $n$  to order  $(n+2)$  requires, in a second step, the elimination of the non-new terms with respect to order  $n$ .

Consistently, the initial time of the interaction is assumed to be very far in the past, in such a way that one can make  $t \rightarrow \infty$  (pushing thus at  $t \rightarrow -\infty$  the moment of the initial contact between the small system and the reservoir) in the time integrals appearing in Eqs. (17, 23, 25, 26), transforming thus

$$\int_0^t d\tau \quad \text{and} \quad \int_0^t d\tau_1 \int_0^{t-\tau_1} d\tau_2 \int_0^{t-\tau_1-\tau_2} d\tau_3 \quad (27)$$

into

$$\int_0^\infty d\tau \quad \text{and} \quad \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \int_0^\infty d\tau_3 ; \quad (28)$$

this approximation has however to be discussed in more detail.

As an example, the integration domain of the double time integral

$$\int_0^t d\tau_1 \int_0^{t-\tau_1} d\tau_2 \quad (29)$$

that would appear at order 3 is given in Fig. 1. The integration domain is a triangle.

At this stage, it has to be taken into account that the interaction between the small system and the reservoir has a correlation time  $\tau_c$ , which may be large, but remains in any case finite. This correlation time is actually given by the result of the time integrations performed in Sect. 4.4 (see Eqs. (62-63) and (65-66)):  $\tau_c \leq 1/\gamma_{ba}$  or  $1/\gamma_b$  or  $1/\gamma_a$ . The  $\gamma$  parameters, that will be introduced later on, are finite (even if they can be very small) parameters and, as we have mentioned earlier,  $\tau_c$  is in any case finite, whatever the  $\gamma$  parameters are.

When  $t$  is large enough in comparison with the finite correlation time  $\tau_c$  of the interaction, the contribution to the integral of the remaining part of the quadrant is zero, in such a way that the upper limits of the integrals can be replaced by  $+\infty$  without adding a factor  $1/2$  in front of the integral

$$\int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \quad (30)$$

(nor a factor  $1/n!$  in front of the integral of order  $(n+1)$ ).

On the other hand,  $\tau_i$  being always positive, the time-ordering is ensured in the integrals of the type of Eq. (28), and no extra time-ordering operator has to be introduced in front of the integrals. In other words, the time-ordering is obviously already taken into account in  $\tilde{V}(t - \tau_1 - \tau_2 - \dots)$ .

One can then write (extending the calculation to any order):

– for the master equation of the atomic density matrix

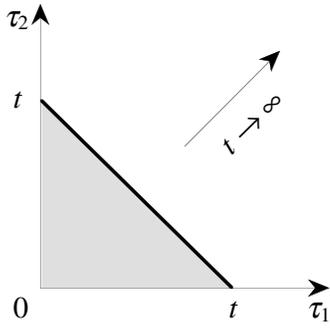
$$\begin{aligned} \frac{d}{dt} \tilde{\sigma}_A(t) = & -\frac{1}{\hbar^2} \int_0^\infty d\tau \\ & \times \text{Tr}_B \left[ \tilde{V}(t), \left[ \tilde{V}(t-\tau), \right. \right. \\ & \left. \left. \tilde{\sigma}_A(t-\tau) \otimes \tilde{\sigma}_B(t-\tau) \right] \right] \\ & + \mathcal{E} \frac{1}{\hbar^4} \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \int_0^\infty d\tau_3 \\ & \times \text{Tr}_B \left[ \tilde{V}(t), \left[ \tilde{V}(t-\tau_1), \right. \right. \\ & \left. \left. \left[ \tilde{V}(t-\tau_1-\tau_2), \left[ \tilde{V}(t-\tau_1-\tau_2-\tau_3), \right. \right. \right. \right. \\ & \left. \left. \left. \tilde{\sigma}_A(t-\tau_1-\tau_2-\tau_3) \otimes \right. \right. \right. \\ & \left. \left. \left. \tilde{\sigma}_B(t-\tau_1-\tau_2-\tau_3) \right] \right] \right] \right] \\ & - \mathcal{E} \frac{1}{\hbar^6} \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \int_0^\infty d\tau_3 \\ & \times \int_0^\infty d\tau_4 \int_0^\infty d\tau_5 \text{Tr}_B \left[ \dots \right] \end{aligned} \quad (31)$$

– for the radiative transfer equation

$$\begin{aligned} \frac{d}{ds} \langle I_{qq'} \rangle = & -\frac{1}{c} \frac{1}{\hbar^2} \int_0^\infty d\tau \text{Tr}_B \left\{ I_{qq'} \right. \\ & \times \text{Tr}_A \left[ \tilde{V}(t), \left[ \tilde{V}(t-\tau), \right. \right. \\ & \left. \left. \tilde{\sigma}_A(t-\tau) \otimes \tilde{\sigma}_B(t-\tau) \right] \right] \left. \right\} \\ & + \mathcal{E} \frac{1}{c} \frac{1}{\hbar^4} \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \int_0^\infty d\tau_3 \text{Tr}_B \left\{ I_{qq'} \right. \\ & \times \text{Tr}_A \left[ \tilde{V}(t), \left[ \tilde{V}(t-\tau_1), \right. \right. \\ & \left. \left. \left[ \tilde{V}(t-\tau_1-\tau_2), \left[ \tilde{V}(t-\tau_1-\tau_2-\tau_3), \right. \right. \right. \right. \\ & \left. \left. \left. \tilde{\sigma}_A(t-\tau_1-\tau_2-\tau_3) \otimes \right. \right. \right. \\ & \left. \left. \left. \tilde{\sigma}_B(t-\tau_1-\tau_2-\tau_3) \right] \right] \right] \right] \left. \right\} \\ & - \mathcal{E} \frac{1}{c} \frac{1}{\hbar^6} \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \int_0^\infty d\tau_3 \\ & \times \int_0^\infty d\tau_4 \int_0^\infty d\tau_5 \text{Tr}_B \left\{ I_{qq'} \dots \right. \end{aligned} \quad (32)$$

where the symbol  $\mathcal{E}$  (for ‘excluded’) means that the non-new terms, with respect to the preceding orders, have to be discarded.

At this stage, it is impossible to discriminate between new and non-new terms, even after the development of the nested commutators. The discrimination is possible only at the very end of the calculation, after having introduced an explicit interaction potential, and then projected the equations on the atomic and photon states, and performed all the integrations. At this final stage, it is possible to determine for each term if it is a



**Fig. 1.** Integration domain for the double integral over time obtained at order 3 and given in Eq. (29).

new one or if it is a combination of lower order terms. Non-new terms actually have characteristic expressions involving branching ratios, as it will be shown later. On the other hand, any order brings new terms.

Since, in this development, the interaction of the small system with the particles of the reservoir, considered along the entire time line, appears as in fact composed of a succession of independent groups of elementary interactions, each group involving a finite number of interactions, this image has suggested us the name of ‘time-sequencing approximation’ for describing this development.

### 3.4. Taking into account the relaxations

The small system interacting with the reservoir can actually be coupled to other reservoirs: this is the case when the small system is the atom  $A$  interacting with the reservoir of photons  $B$ : indeed, the atom also interacts with other reservoirs, composed of the perturbers (protons, electrons, ions, etc.). In the present work, we assume that the interactions of the small system with the various reservoirs are independent: by so doing, we neglect for instance photon interaction during a collision of the atom with a perturber. We moreover assume that the impact approximation is valid as far as collisions are concerned.

It will be seen in Sect. 4 that the duration of one interaction of the atom with a given mode of the electromagnetic field may not be short with respect to the various characteristic evolution times of the system. Then, the relaxation of the system due to the interaction with all the reservoirs has to be taken into account during the interaction itself. Following Baranger (1958a, 1958b, 1958c, 1962), this can be achieved by replacing the unperturbed evolution operator entering the definition of the interaction representation given in Eq. (10), by the evolution operator  $U(\tau)$  which takes into account the relaxation due to the presence of all the reservoirs (here,  $\tau$  has the meaning of a time interval)

$$\begin{cases} \exp\left\{-\frac{i}{\hbar}H_0\tau\right\} \rightarrow U(\tau) \\ \exp\left\{\frac{i}{\hbar}H_0\tau\right\} \rightarrow U^\dagger(\tau) \end{cases} \quad (33)$$

However, taking thus into account the relaxations during a process of a given order results actually in considering a higher number of interactions in this process, which are also taken into account at a higher order of the series development. Such a method, used together with the series development, leads then to ‘count’ each process several times. This problem is solved at the end of the calculation: the method of solution is described in Sect. 5.3.

Following also Omont et al. (1972), the matrix elements of  $U(\tau)$  are more easily evaluated in the Liouville space, where the evolution operator is denoted as  $\hat{U}(\tau)$  ( $i, j$  are atomic states)

$$\langle\langle ij | \hat{U}(\tau) | i'j' \rangle\rangle = \langle i | U(\tau) | i' \rangle \langle j' | U^\dagger(\tau) | j \rangle \quad (34)$$

Since the various evolution operators  $\hat{U}(\tau)$  appearing in a given term of our calculation do not overlap in time (as it will be seen later), they may be averaged separately (this is the impact approximation discussed by Baranger), and  $\hat{U}(\tau)$  may be replaced by its average over all the reservoirs

$$\hat{A}(\tau) = \left\{ \hat{U}(\tau) \right\}_{AV} \quad (35)$$

then, the matrix elements of  $\hat{A}(\tau)$  are given by

$$\langle\langle ij | \hat{A}(\tau) | i'j' \rangle\rangle = \delta_{ii'} \delta_{jj'} \exp\{-i\omega_{ij}\tau - \phi_{ij}\tau\} \quad (36)$$

where, following Baranger (1958b, 1962 – see also Omont et al. 1972),  $\phi_{ij}$  is the relaxation rate of the coherence between atomic states  $i$  and  $j$ . In other words, for the various cases considered in this work (assuming here non-degenerate levels  $a$  and  $b$  – for the degenerate case, see Omont et al. 1972, Eqs. (25-36)):

$$\begin{cases} \phi_{ab} = \gamma_{ab} + i\Delta_{ab} = \gamma_{ab}^{(c)} + \frac{1}{2}(\Gamma_a + \Gamma_b) + i\Delta_{ab} \\ \phi_{ba} = \phi_{ab}^* \\ \phi_{aa} = \gamma_a = \gamma_a^{(c)} + \Gamma_a \\ \phi_{bb} = \gamma_b = \gamma_b^{(c)} + \Gamma_b \end{cases} \quad (37)$$

where the index  $(c)$  refers to collisional relaxation rates and  $\Gamma$  refers to radiative relaxation rates.  $\gamma_{ab}$  is the relaxation rate of the optical coherence between states  $a$  and  $b$ , whereas  $\gamma_a$  and  $\gamma_b$  are the relaxation rates for the populations of the  $a$  and  $b$  states respectively. Following Baranger (1958b, 1962)

$$\begin{cases} \gamma_{ab}^{(c)} + i\Delta_{ab} = \left\{ 1 - \langle a | S | a \rangle \langle b | S | b \rangle^* \right\}_{AV} \\ \gamma_a^{(c)} = \left\{ 1 - |\langle a | S | a \rangle|^2 \right\}_{AV} \\ \gamma_b^{(c)} = \left\{ 1 - |\langle b | S | b \rangle|^2 \right\}_{AV} \end{cases} \quad (38)$$

where the first term (collisional relaxation of the optical coherence, with broadening and shift coefficients given respectively by the real and imaginary parts) accounts for elastic as well as inelastic collisions effects, whereas the second and third terms (relaxation of the populations) account for inelastic collisions effects only ( $S$  is the collision  $S$ -matrix).

Though the expressions of  $\gamma_{ab}$ ,  $\gamma_a$  and  $\gamma_b$  are provided above, one could consider them as unknowns at the present stage of our development: the full expressions of the relaxation rates, for the populations and optical coherences, will be obtained at the end of the calculation. We will then verify that they are those given in Eqs. (37-38), even after the perturbation series summation.

### 3.5. The Markov approximation

The following step of the calculation is to develop the multiple commutators appearing in Eqs. (31-32), taking into account that the operators in the interaction picture are obtained by performing the substitution of Eq. (33) in Eq. (10). Taking also into account that the density matrix of the reservoir is time-independent (the reservoir being assumed to be in equilibrium), the result can be written as:

– for the master equation of the atomic density matrix

$$\begin{aligned} \frac{d}{dt} \sigma_A(t) &= -\frac{i}{\hbar} [H_A, \sigma_A(t)] \\ &- \frac{1}{\hbar^2} \sum (-1)^{n(V)} \int_0^\infty d\tau \\ &\times \text{Tr}_B \left\{ \mathcal{Z}^{(1)} U(\tau) \mathcal{Z}^{(2)} \right. \\ &\quad \left. \times \sigma_A(t-\tau) \otimes \sigma_B \mathcal{Z}^{(2)} U^\dagger(\tau) \mathcal{Z}^{(1)} \right\} \\ &+ \mathcal{E} \frac{1}{\hbar^4} \sum (-1)^{n(V)} \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \int_0^\infty d\tau_3 \\ &\times \text{Tr}_B \left\{ \mathcal{Z}^{(1)} U(\tau_1) \mathcal{Z}^{(2)} U(\tau_2) \mathcal{Z}^{(3)} U(\tau_3) \mathcal{Z}^{(4)} \right. \\ &\quad \left. \times \sigma_A(t-\tau_1-\tau_2-\tau_3) \otimes \sigma_B \right. \\ &\quad \left. \times \mathcal{Z}^{(4)} U^\dagger(\tau_3) \mathcal{Z}^{(3)} U^\dagger(\tau_2) \mathcal{Z}^{(2)} U^\dagger(\tau_1) \mathcal{Z}^{(1)} \right\} \\ &+ \dots \end{aligned} \quad ; \quad (39)$$

– for the radiative transfer equation

$$\begin{aligned} \frac{d}{ds} \langle I_{qq'} \rangle &= -\frac{1}{c} \frac{1}{\hbar^2} \sum (-1)^{n(V)} \int_0^\infty d\tau \\ &\times \text{Tr}_{A,B} \left\{ [I_{qq'}, V] U(\tau) \mathcal{Z}^{(2)} \right. \\ &\quad \left. \times \sigma_A \otimes \sigma_B(t-\tau) \mathcal{Z}^{(2)} U^\dagger(\tau) \right\} \\ &+ \mathcal{E} \frac{1}{c} \frac{1}{\hbar^4} \sum (-1)^{n(V)} \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \int_0^\infty d\tau_3 \\ &\times \text{Tr}_{A,B} \left\{ [I_{qq'}, V] \right. \\ &\quad \left. \times U(\tau_1) \mathcal{Z}^{(2)} U(\tau_2) \mathcal{Z}^{(3)} U(\tau_3) \mathcal{Z}^{(4)} \right. \\ &\quad \left. \times \sigma_A \otimes \sigma_B(t-\tau_1-\tau_2-\tau_3) \right. \\ &\quad \left. \times \mathcal{Z}^{(4)} U^\dagger(\tau_3) \mathcal{Z}^{(3)} U^\dagger(\tau_2) \mathcal{Z}^{(2)} U^\dagger(\tau_1) \right\} \\ &+ \dots \end{aligned} \quad . \quad (40)$$

The symbol  $\mathcal{Z}^{(i)}$  appearing in this equation has the following meaning: each term contains the same symbol twice, one symbol being located at the left of  $\sigma_A \otimes \sigma_B$  and the other at the right of  $\sigma_A \otimes \sigma_B$ . There are two possibilities: either the first symbol is the operator  $V$  and the second is 1, or vice-versa. For a given choice, which involves a choice for  $\mathcal{Z}^{(1)}$ , a choice for  $\mathcal{Z}^{(2)}$ , etc..., the sign of the term is  $(-1)^{n(V)}$ , where  $n(V)$  is the number of times the  $V$  operator is present at the left (or at the right) of  $\sigma_A \otimes \sigma_B$ . One has then to sum over all the possible choices, which are in the number of  $2^2 = 4$  at order 2,  $2^4 = 16$  at order 4,  $2^6 = 64$  at order 6, etc...

In this development, unitarity of the evolution operator  $U(\tau)$  has been assumed

$$U(\tau) U^\dagger(\tau) = U^\dagger(\tau) U(\tau) = 1 ; \quad (41)$$

non-unitarity will be introduced later by the averaging process described in Sect. 3.4, when relaxation due to all the reservoirs (which brings to an irreversible evolution) is taken into account, and when the  $\hat{U}(\tau)$  operator is replaced by the  $\hat{A}(\tau)$  operator.

The Markov approximation usually consists in assuming that the evolution of the reduced density operators in the interaction representation (that ‘follows’ the evolution of the unperturbed system), is slow with respect to the correlation time of the interaction potential averaged over the reservoir. One then substitutes in Eqs. (31-32)  $\tilde{\sigma}_A(t-\tau)$  and  $\tilde{\sigma}_B(t-\tau)$  by  $\tilde{\sigma}_A(t)$  and  $\tilde{\sigma}_B(t)$ , respectively, and the integrals over  $\tau$  can be easily performed. By so doing, however, the evolution of the system becomes independent of its ‘past history’ – a characteristic feature of a Markov process.

In the present calculation, we furthermore take into account, during the time interval  $\tau$ , the relaxation due to the interaction with all the reservoirs; we then substitute in the master equation for the atomic density matrix

$$\sigma_A(t-\tau)$$

by

$$U^\dagger(\tau) \sigma_A(t) U(\tau) . \quad (42)$$

As for the radiative transfer equation, owing to the hypothesis that the photons density matrix has no matrix elements between states of different energy in physical conditions typical of stellar atmospheres (see Eq. (22)),  $\sigma_B(t-\tau)$  will be simply replaced by  $\sigma_B(t)$ .

As a result of these substitutions, in most of cases, the evolution operator  $\hat{U}(\tau_i)$  appears only once for each time interval  $\tau_i$ , and the averaging process described in Sect. 3.4 can then be performed. In other cases however,  $\hat{U}(\tau_i)$  may appear twice or even more times; the method described in Sect. 3.4 will be applied to one of the  $\hat{U}(\tau_i)$ , the other ones being still given by the unperturbed expression of Eq. (10); it can be shown that this procedure does not affect the final results of the present paper.

A close inspection to the diagrams representing the various terms issued from the development of the commutators at order 4, as discussed in Sect. 4.1, shows that the fact that a given term

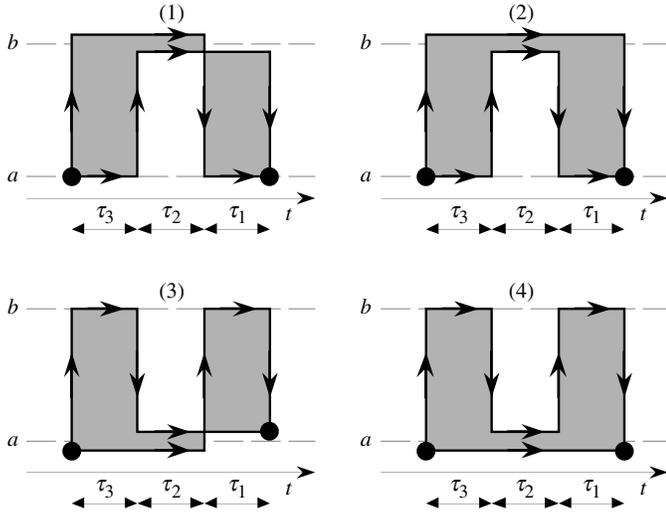


Fig. 2. Diagrams for the order-4 terms.

is ‘new’ or ‘non-new’ depends only on the order in which the various  $U(\tau_i)$  and  $V$  appear in the term, and has actually nothing to do with the order of magnitude of the correlation time of the interaction  $\tau_c$ . The time-sequencing approximation is in fact very general (when extended up to infinite order); when completed by the method described above for treating  $\sigma_{A,B}(t-\tau)$ , it seems to the author that the usually performed Markov approximation has been completely avoided. The only necessary hypothesis is that the correlation time  $\tau_c$  is finite and small in comparison with the total duration of the contact between the small system and the reservoir, in order to extend to  $+\infty$  the limits of the time integrals. But the order of magnitude of  $\tau_c$  is insignificant in the following of the derivation.

#### 4. Performing the integrations

The following step is to apply the formalism described above to the dipolar electric interaction (Eqs. (39-40), modified by using Eq. (42), have to be projected on atomic and photon states), and to perform all the integrations.

##### 4.1. Diagrams

One can represent the order-4 terms of Eq. (39) under the form of diagrams.

The construction of a diagram can be achieved as follows: considering the order-4 term of Eq. (39) and a given choice for the  $\mathcal{Z}^{(i)}$  terms, one starts from both sides of  $\sigma_A \otimes \sigma_B$  which represents the initial state of the atom (that is assumed to be in the lower state  $a$ ), beginning thus both lines of the diagram from the lower left corner. Each line represents a transition amplitude, as a function of time. When an interaction Hamiltonian  $V$  is encountered, a transition from  $a$  to  $b$  (or from  $b$  to  $a$ ) is drawn under the form of a vertical line; when an evolution operator  $U(\tau_i)$  or  $U^\dagger(\tau_i)$  is encountered, the evolution of the atom (which remains in the same atomic state during  $\tau_i$ , see Eq. (36)) is drawn under the form of a horizontal line of length  $\tau_i$ . The number

of absorptions and of emissions having to be an even number (in order that they correspond to real physical processes), both lines encounter at the lower right corner of the diagram, which represents the final atomic state which is also  $a$  (it may be necessary, for those terms having an odd  $n(V)$ , to perform a circular permutation inside the Trace operator for the last  $V$  term). For the 16 terms issued from the different possible choices for the  $\mathcal{Z}^{(i)}$ , 4 different diagrams are obtained, which are shown in Fig. 2.

It is assumed that, at the initial time, the atom is in the lower state  $a$ , and the atomic state (in the Liouville space) is  $|a\rangle\langle a|$ . A photon is absorbed, and the absorption is followed by an emission. The final state is also  $|a\rangle\langle a|$ , after 3 intermediate states. Always referring to the Liouville space, we have:

– in diagrams (1) and (2):

1. during  $\tau_3$  the atomic state is  $|a\rangle\langle b|$  and/or  $|b\rangle\langle a|$
2. during  $\tau_2$  the atomic state is  $|b\rangle\langle b|$
3. during  $\tau_1$  the atomic state is  $|b\rangle\langle a|$  and/or  $|a\rangle\langle b|$

– in diagrams (3) and (4):

1. during  $\tau_3$  the atomic state is  $|a\rangle\langle b|$  and/or  $|b\rangle\langle a|$
2. during  $\tau_2$  the atomic state is  $|a\rangle\langle a|$
3. during  $\tau_1$  the atomic state is  $|b\rangle\langle a|$  and/or  $|a\rangle\langle b|$ .

What about such atomic states as  $|a\rangle\langle b|$  and/or  $|b\rangle\langle a|$ ?

In such a state, the average atomic dipole value is non-zero. Such a state is peculiar, because the corresponding density matrix has zero diagonal elements and one or two non-zero off-diagonal element only. This does not satisfy the Schwartz inequality of the usual density matrix theory, namely

$$|\rho_{nm}|^2 \leq \rho_{nn}\rho_{mm}, \quad (43)$$

which implies that non-zero coherences can only connect states having non-zero population. In other words, such a density matrix having only an optical coherence does not correspond to any atomic state  $|\psi\rangle$  or to any mixture of atomic states. The optical coherence is a quantity oscillating at the angular frequency  $\omega_{ba}$ .

The  $|a\rangle\langle b|$  and/or  $|b\rangle\langle a|$  state suffers relaxation due to radiative, inelastic and elastic collisions. The relaxation rate of the optical coherences between levels  $a$  and  $b$  is  $\gamma_{ba}$ . The integration over time of the combined oscillation and relaxation directly provides the absorption (or emission) profile

$$\frac{1}{\gamma_{ba} \pm i(\omega - \omega_{ba})} \quad (44)$$

where  $\omega$  is the radiation angular frequency and  $\omega_{ba}$  the resonance angular frequency between levels  $a$  and  $b$ . It results that the average time-interval for absorption (for a given mode of the electromagnetic field) is given by this expression. At resonance ( $\omega = \omega_{ba}$ ), this time is equal to the relaxation time  $1/\gamma_{ba}$ . Far from resonance ( $|\omega - \omega_{ba}| \gg \gamma_{ba}$ ), this time is of the order of  $1/|\omega - \omega_{ba}|$ , which is very short with respect to the various relaxation times of the problem.

Considering now the various diagrams:

– in diagrams (1) and (2): the absorption duration is  $\tau_3$ , the emission duration is  $\tau_1$ , with the orders of magnitude given above.  $\tau_2$

is always of the order of the relaxation time of the excited state (because the atom state is  $|b\rangle\langle b|$  in this time interval: the excited state is populated during the process). The corresponding relaxation rate is  $\gamma_b$ , and is due to radiative decay and inelastic collisions only.

– in diagrams (3) and (4): the absorption takes place during  $\tau_3 + \tau_2$ , and the emission takes place during  $\tau_2 + \tau_1$ . Emission begins before the absorption is completed.  $\tau_3$  and  $\tau_1$  have the orders of magnitude given above. During  $\tau_2$ , the atom is in the lower state  $|a\rangle\langle a|$  (the excited state  $b$  is not populated during the process). If the relaxation rate of this state ( $\gamma_a$ ) is small (negligible), the time  $\tau_2$  is very long (infinite) and the integration over time leads to an energy conservation function  $\delta(\nu_1 - \nu_2)$  ( $\nu_1$  and  $\nu_2$  are the absorbed and emitted photon frequencies respectively). Both absorption and emission take place during this time and are coupled, leading to frequency coherence and the atom remaining in the lower state  $a$ . So, the total duration of absorption,  $\tau_3 + \tau_2$ , is very long, as well as the total duration of emission  $\tau_2 + \tau_1$  (in the absence of collisions, which interrupt the process).

The process can also be interrupted if the incoming radiation is not purely monochromatic. In this case, the radiation has a finite (i.e., non-infinite) correlation time, which leads to ending such a process. Indeed, all the preceding considerations have been developed assuming monochromatic incident radiation. If the radiation is not monochromatic, the integration over frequencies leads to shorten the times  $\tau_3$  and  $\tau_1$ . As a limiting case, if one considers an incident radiation having an infinitely flat spectrum,  $\tau_3$  and  $\tau_1$  tends towards zero after integration over frequencies, and the contribution of diagrams (3) and (4) goes to zero.

As for the energy:

– in diagrams (1) and (2): during  $\tau_3$ , energy is absorbed from the incident radiation by the vibrating atomic dipole. This energy is transferred to the atom, which is in the excited state during  $\tau_2$ . During  $\tau_1$ , the vibrating atomic dipole radiates.

– in diagrams (3) and (4): during  $\tau_3$ , energy is absorbed from the incident radiation by the vibrating atomic dipole. However, the energy is not transferred to the atom and the vibrating dipole simultaneously absorbs and radiates during  $\tau_2$ . This leads to frequency coherence between the absorbed and emitted radiation. During  $\tau_1$ , the vibrating atomic dipole finishes to radiate (energy conservation). During this process, interaction takes place between the atom and the radiation field: the excited level  $b$  plays a role in the process (through the atomic dipole, even during time  $\tau_2$  when the dipole absorbs and radiates at the same time). However, the interaction does not lead to the excitation of the atom. The transition from  $a$  to  $b$  is never achieved. In such a process, one often speaks of “virtual transitions” or “virtual levels” (see, for instance, Omont 1977).

Diagrams (1), (2) and (3) are the same as those introduced in Omont et al. (1972), and Nienhuis & Schuller (1977): they represent the product of two transition amplitudes, each of them containing twice the interaction potential. Diagram (4) is of a different nature and corresponds to another process; it appears in the present work as a result of the perturbation series devel-

opment, which implies that, contrarily to these authors, we do not select ‘a-priori’ the process under study.

Each of the diagrams (1) and (2) actually corresponds to the combination of two order-2 diagrams, namely photon absorption followed some time later by photon emission; they have then to be discarded from the final summation as ‘non-new’ terms, if order-2 processes have already been considered. Diagrams (3) and (4) cannot be split into lower order diagrams: they represent new processes, where the photon emission begins before the photon absorption is ended. Such new processes appear at each order of the perturbation series development.

However, the method of diagrams cannot be easily applied to the inverse process (photon emission followed by absorption) in order to discard the ‘non-new’ terms; this can only be done at the end of the calculation.

#### 4.2. Dipolar electric interaction

We consider, as interaction potential  $V$ , the dipolar electric interaction potential

$$V = -\mathbf{D} \cdot \mathbf{E}(0) , \quad (45)$$

where  $\mathbf{D}$  is the atomic dipole operator, and  $\mathbf{E}(0)$  is the electric field operator, at the nucleus position.

The  $\mathbf{D}$  operator can be developed on the basis of the  $\mathbf{e}_p$  ( $p = 0, \pm 1$ ) vectors, defined in Eq. (2)

$$D_p = \mathbf{D} \cdot \mathbf{e}_p \implies \mathbf{D} = \sum_p (-1)^p D_{-p} \mathbf{e}_p . \quad (46)$$

In the second quantization formalism, the  $\mathbf{E}(0)$  operator, developed in plane waves, is (in c.g.s. units)

$$\begin{aligned} \mathbf{E}(0) = & \int d^3\mathbf{k} \sum_{\lambda} i \sqrt{\frac{\hbar\omega}{(2\pi)^3}} \\ & \times [a(\mathbf{k}, \lambda) \mathbf{e}_{\lambda} - a^{\dagger}(\mathbf{k}, \lambda) \mathbf{e}_{\lambda}^*] , \end{aligned} \quad (47)$$

where the sum over  $\lambda$  runs over the two polarization vectors  $\mathbf{e}_{\lambda}$  perpendicular to the wave vector  $\mathbf{k}$ .

The interaction potential is then

$$\begin{aligned} V = & (-i) \sum_p D_p \int d^3\mathbf{k} \sum_{\lambda} \sqrt{\frac{\hbar\omega}{(2\pi)^3}} \\ & \times [a(\mathbf{k}, \lambda) (-1)^p (\mathbf{e}_{\lambda})_{-p}] \\ & - (-i) \sum_p (-1)^p D_{-p} \int d^3\mathbf{k} \sum_{\lambda} \sqrt{\frac{\hbar\omega}{(2\pi)^3}} \\ & \times [a^{\dagger}(\mathbf{k}, \lambda) (-1)^p (\mathbf{e}_{\lambda})_{-p}^*] , \end{aligned} \quad (48)$$

where the components of the  $\mathbf{e}_{\lambda}$  vector are defined like those of  $\mathbf{D}$ , and where, in particular,

$$\begin{aligned} (\mathbf{e}_{\lambda}^*)_p & = \mathbf{e}_{\lambda}^* \cdot \mathbf{e}_p = (-1)^p (\mathbf{e}_{\lambda} \cdot \mathbf{e}_{-p})^* \\ & = (-1)^p [(\mathbf{e}_{\lambda})_{-p}]^* = (-1)^p (\mathbf{e}_{\lambda})_{-p}^* . \end{aligned} \quad (49)$$

### 4.3. Projection on the atomic and photon states

The master equation for the atomic density matrix and the transfer equation have then to be projected on the atomic and photon states, according to the hypotheses introduced in Sect. 2. Because all the processes beginning with a photon absorption from the lower level  $a$  are introduced, all the inverse processes (processes beginning with a photon emission from the upper level  $b$ ) have also to be introduced.

The explicit expression of the photons reduced density matrix  $\sigma_B(t)$  is not relevant, because  $\sigma_B(t)$  is always combined with a partial trace operation on the photon states. This leads to the evaluation of average values of photons operators of the form

$$\langle O \rangle = \text{Tr}_B [O \sigma_B] , \quad (50)$$

where  $O$  is an operator acting only on the photon states.

In our calculation, the operator  $O$  of Eq. (50) is a product of photon creation and annihilation operators of the form (in simplified notations)

$$a^\dagger a a^\dagger a a^\dagger a \dots , \quad (51)$$

for those processes beginning with a photon absorption, or

$$a a^\dagger a a^\dagger a a^\dagger \dots , \quad (52)$$

for those processes beginning with a photon emission (because we consider two-level atom processes). These operators obey the commutation rule (for a given mode)

$$a a^\dagger = 1 + a^\dagger a , \quad (53)$$

where the first term in the r.h.s. represents spontaneous emission, whereas the second term of the r.h.s. represents stimulated emission, that we neglect following our hypotheses (see Sect. 2): the average value of the second term is the average number of photons in the mode, which has to be compared to the value of the first term, which is 1. One has

$$\langle a^\dagger a \rangle = \bar{n} \ll 1 \quad (54)$$

and, consequently,

$$\langle a^\dagger a^\dagger a a \rangle = \overline{\bar{n}(\bar{n}-1)} \ll \langle a^\dagger a \rangle = \bar{n} \ll 1 \quad (55)$$

and so on. For any product of creation and annihilation operators, in the form given by Eqs. (51-52), the commutation rule of Eq. (53) can be applied as many times as necessary to reduce the different forms of the products into a summation of products of the basic form

$$a^\dagger a^\dagger a^\dagger \dots a a a \dots . \quad (56)$$

According to Eqs. (53-55), the average of such products can be reduced to their minimal form, namely:

– for those processes beginning with an absorption

$$\langle a^\dagger(\mathbf{k}_1, \lambda_1) a(\mathbf{k}_2, \lambda_2) \rangle = \delta(\mathbf{k}_1 - \mathbf{k}_2) \frac{c^2}{h\nu_1^3} \langle I_{\lambda_2 \lambda_1}(\nu_1, \Omega_1) \rangle , \quad (57)$$

which, after integration over the directions  $\Omega_1$ , leads to the specific intensity

$$J_{pp'}(\nu_1) = \oint \frac{d\Omega_1}{4\pi} \sum_{j=0}^3 \mathcal{T}_{pp'}(j, \Omega_1) S_j(\nu_1, \Omega_1) , \quad (58)$$

where such a definition and the spherical tensor of the polarization unit vectors  $\mathcal{T}_{pp'}(i, \Omega)$ , have been introduced by Landi Degl'Innocenti (1983), and where  $S_i(\nu, \Omega)$  is the Stokes parameter  $i$  ( $i = 0, \dots, 3$ ) of the radiation incoming in the  $\Omega$  direction at the frequency  $\nu$ . In the unpolarized case, the specific intensity is simply

$$J(\nu_1) = \oint \frac{d\Omega_1}{4\pi} S_0(\nu_1, \Omega_1) ; \quad (59)$$

– for those processes beginning with an emission

$$\delta(\mathbf{k}_1 - \mathbf{k}_2) \delta_{\lambda_2 \lambda_1} . \quad (60)$$

The reduction of the creation and annihilation operators products to the lowest order ones is due to the factor 1 appearing in the r.h.s. of Eq. (53), which represents spontaneous emission and is of quantum origin; by considering the non-lowest order terms of the perturbation series development we do not include non-linear effects. The new effects that appear are, in any case, linear with respect to the incident radiation intensity.

The commutation rule of Eq. (53) can also be applied to reduce the commutators  $[I_{qq'}, V]$  that appear in the transfer equation (40). One has

$$\begin{cases} [a^\dagger(\mathbf{k}, q') a(\mathbf{k}, q), a(\mathbf{k}', \lambda')] = \\ \quad - a(\mathbf{k}, q) \delta(\mathbf{k} - \mathbf{k}') \delta_{\lambda' q'} \\ [a^\dagger(\mathbf{k}, q') a(\mathbf{k}, q), a^\dagger(\mathbf{k}', \lambda')] = \\ \quad a^\dagger(\mathbf{k}, q') \delta(\mathbf{k} - \mathbf{k}') \delta_{\lambda' q} \end{cases} . \quad (61)$$

### 4.4. Time integration

The quantities to be integrated with respect to time are of the form of Eq. (36). The time integration of such quantities is immediate. Denoting now as  $\omega_0$  and  $\nu_0$  the resonance angular frequency and resonance frequency ( $\omega_0 = 2\pi\nu_0$ ), respectively, of the two-level atom (zero magnetic field is assumed), two cases have to be distinguished:

– integration over times  $\tau_1, \tau_3, \tau_5, \dots$

Here  $ij = ab$  or  $ba$ . Only two types of integrals are encountered in the calculation

$$\left\{ \begin{array}{l} \int_0^{\infty} d\tau \exp \{-i(\omega_0 - \omega)\tau - \phi_{ba}\tau\} = \\ \frac{1}{2} \Phi_{ba}^*(\nu_0 - \nu) \\ \int_0^{\infty} d\tau \exp \{-i(\omega - \omega_0)\tau - \phi_{ab}\tau\} = \\ \frac{1}{2} \Phi_{ba}(\nu_0 - \nu) \end{array} \right. , \quad (62)$$

where  $\Phi_{ba}(\nu_0 - \nu)$  is the frequency normalized complex profile

$$\frac{1}{2} \Phi_{ba}(\nu_0 - \nu) = \frac{1}{\gamma_{ba} - i(\omega_0 - \omega + \Delta_{ba})} , \quad (63)$$

whose real and imaginary parts are denoted as

$$\Phi_{ba}(\nu_0 - \nu) = \phi_{ba}(\nu_0 - \nu) + i\psi_{ba}(\nu_0 - \nu) . \quad (64)$$

– integration over times  $\tau_2, \tau_4, \tau_6, \dots$

Here  $ij = aa$  or  $bb$ . In our calculation, the terms in  $\phi_{bb}$  (which are associated to upper state  $b$  population during the process) never contain any frequency. The terms in  $\phi_{aa}$  (which are associated to lower state  $a$  population during the process) always contain a difference between two photon frequencies. One has then the two following types of integrals in our calculation

$$\left\{ \begin{array}{l} \int_0^{\infty} d\tau \exp \{-i(\omega_1 - \omega_2)\tau - \phi_{aa}\tau\} = \\ \frac{1}{2} \Phi_a^*(\nu_1 - \nu_2) \\ \int_0^{\infty} d\tau \exp \{-\phi_{bb}\tau\} = \frac{1}{\gamma_b} \end{array} \right. , \quad (65)$$

where

$$\frac{1}{2} \Phi_a(\nu_1 - \nu_2) = \frac{1}{\gamma_a - i(\omega_1 - \omega_2)} , \quad (66)$$

with

$$\Phi_a^*(\nu_2 - \nu_1) = \Phi_a(\nu_1 - \nu_2) . \quad (67)$$

#### 4.5. Frequency integration

It can be easily proved, by using the residue theorem, that the convolution product of two (or more) complex profiles (of the type of either Eq. (63), or Eq. (66), or a mixture of both) is zero

$$\int d\nu \Phi_x(\nu_1 - \nu) \Phi_y(\nu_2 - \nu) = 0 , \quad (68)$$

because both poles

$$\left\{ \begin{array}{l} z_1 = \frac{1}{2\pi} [(\omega_1 + \Delta_x) + i\gamma_x] \\ z_2 = \frac{1}{2\pi} [(\omega_2 + \Delta_y) + i\gamma_y] \end{array} \right. \quad (69)$$

lie on the same side of the real axis. This would not be true for the other product

$$\int d\nu \Phi_x(\nu_1 - \nu) \Phi_y^*(\nu_2 - \nu) \neq 0 , \quad (70)$$

because in this case, the two poles lie on opposite sides of the real axis. However, in our calculation all the frequency integrals are of the type of Eq. (68), and the corresponding terms vanish due to the frequency integration, if they do not contain any other dependence on the same frequency. In particular, we neglect the variation of

$$\frac{8\pi h\nu^3}{c^3} \quad (71)$$

along a profile. In the visible range ( $\lambda \approx 500$  nm), and for a typical width of  $10^8$  s<sup>-1</sup> for the profile, one has along the profile

$$\frac{\Delta\nu}{\nu_0} \approx 3 \times 10^{-8} ,$$

and then

$$\Delta \left( \frac{\nu^3}{\nu_0^3} \right) \approx 10^{-7} . \quad (72)$$

On the contrary, we do not ignore a possible variation of the specific intensity of the incoming radiation along the profile, and we do not integrate over frequencies those terms who include a dependence on it.

#### 4.6. Einstein coefficients

As a result, the Einstein coefficients for spontaneous emission and absorption between levels  $a$  and  $b$  are obtained as

– in the non-degenerate case

$$\left\{ \begin{array}{l} A_{ba} = \frac{2\pi}{3} \frac{1}{\hbar^2} \frac{8\pi h\nu_0^3}{c^3} |\langle a|D|b\rangle|^2 \\ B_{ab} = \frac{2\pi}{3} \frac{1}{\hbar^2} \frac{4\pi}{c} |\langle a|D|b\rangle|^2 \end{array} \right. . \quad (73)$$

– in the degenerate case (using the Racah convention cited by Messiah 1969 for defining the reduced matrix element)

$$\left\{ \begin{array}{l} A_{ba} = \frac{2\pi}{3} \frac{1}{\hbar^2} \frac{8\pi h\nu_0^3}{c^3} \frac{1}{2J'+1} |\langle \alpha' J' || D || \alpha J \rangle|^2 \\ B_{ab} = \frac{2\pi}{3} \frac{1}{\hbar^2} \frac{4\pi}{c} \frac{1}{2J'+1} |\langle \alpha' J' || D || \alpha J \rangle|^2 \end{array} \right. . \quad (74)$$

### 5. Perturbation series summation

#### 5.1. Elimination of the ‘non-new’ terms

Those terms of the development that are ‘non-new’ (as defined in Sect. 3.2) are those where, as a result of integrals of the type of the second one of Eq. (65), appears the coefficient  $\gamma_b$ , as

defined in Eq. (37). More precisely, those terms are found to be proportional to

$$\frac{A_{ba}}{\gamma_b}. \quad (75)$$

The ‘new’ terms involve only integrals such as the first one of Eq. (65), leading to profiles of the type  $\Phi_a(\nu - \nu')$ .

Though the value of the ratio  $A_{ba}/\gamma_b$  is nothing but 1 in the present case of a two-level atom, the generalization to a multilevel atom would imply that we have to keep for  $A_{ba}$  the value of the Einstein coefficient for the transition under interest, whereas  $\gamma_b$  could involve several transition probabilities. This ratio is nothing but a branching ratio, i.e., a ratio that appears in the statistical equilibrium equations when the populations of some levels are eliminated. Thus, those terms that contain this ratio can naturally be suspected to be the ‘non-new’ ones.

This can be verified by writing the equations with only those terms that are suspected to be ‘non-new’. In this case, the solution of the statistical equilibrium equation

$$\frac{d}{dt}\sigma_A(t) = 0 \quad (76)$$

is not modified with respect to its solution at the lower order, and, for the transfer equation, the emission coefficient is not modified with respect to the lower order, when the solution of the statistical equilibrium equation is substituted into it.

### 5.2. Perturbation series summation

The effect of the terms of order higher than 2 is twofold:

- a new term appears in the emission coefficient of the transfer equation at the 4th and higher orders. This is the Rayleigh scattering term (see next section)
- the absorption profile, as well as the emission profile, are modified. We have derived analytically the development up to order 4 (in the polarized and unpolarized cases) and up to order 6 (in the unpolarized case only), thus obtaining for the profile the first terms of a series development, that we generalize at all orders as

$$\frac{1}{2}\Phi_{ba}(\nu_0 - \nu) \left\{ \sum_{n=0}^{\infty} \left[ -\frac{A_{ba}}{2} \frac{1}{2} \Phi_{ba}(\nu_0 - \nu) \right]^n \right\}, \quad (77)$$

which is easily summed as

$$\frac{1}{2}\Phi_{ba}(\nu_0 - \nu) = \frac{\frac{1}{2}\Phi_{ba}(\nu_0 - \nu)}{1 + \frac{A_{ba}}{2} \frac{1}{2}\Phi_{ba}(\nu_0 - \nu)}. \quad (78)$$

The new profile results in being

$$\frac{1}{2}\Phi_{ba}(\nu_0 - \nu) = \frac{1}{\gamma_{ba} - i(\omega_0 - \omega + \Delta_{ba})}, \quad (79)$$

where

$$\bar{\gamma}_{ba} = \gamma_{ba} + \frac{A_{ba}}{2}, \quad (80)$$

which means that the full width of the new profile,  $2\bar{\gamma}_{ba}$ , is obtained by adding  $A_{ba}$  to the full width of the old profile,  $2\gamma_{ba}$ . This apparent contradiction with the usual results of the theory of line profiles will be solved in the next subsection.

The series development is illustrated in Fig. 3, where the summation of the series is restricted to  $N$  terms. The quantity plotted is the non-dimensional function

$$f(x) = -\text{Re} \left\{ \sum_{j=1}^N \left( -\frac{1}{\frac{2\gamma_{ba}}{A_{ba}} - ix} \right)^j \right\}. \quad (81)$$

The figure represents the real part of the profile  $\bar{\phi}_{ba}(\nu_0 - \nu)$  for the case  $2\gamma_{ba}/A_{ba} = 1$ . In this case, the convergence towards the double width profile appears clearly. It can also be seen from the figure that the doubling of the very far wing value of the profile is attained as early as the second term of the series is included.

It results from Eq. (68) that any term of the series of Eq. (77) vanishes when integrated over frequency, except for the first one, which is also the lowest order one. The higher order terms contribute with an effect of ‘frequency redistribution’ inside the profile.

### 5.3. Line-broadening and perturbation series summation

Further investigations of the perturbation series development for multi-level atoms have shown that  $A_{ba}$  has actually to be replaced in Eq. (77) by the quantity  $\Gamma_a + \Gamma_b$  introduced in Eq. (37). However, because of the weak radiation field approximation described in Sect. 2, which has led us to neglect stimulated emission with respect to spontaneous emission, the quantity  $\Gamma_a + \Gamma_b$  involves spontaneous emission transition probabilities only. The same investigations have also shown that the profile  $\Phi_a$ , as defined in Eq. (66), obeys also a series summation as the one of Eq. (77), involving, in place of  $A_{ba}/2$ , the sum of the spontaneous emission transition probabilities towards lower levels, when such levels are present.

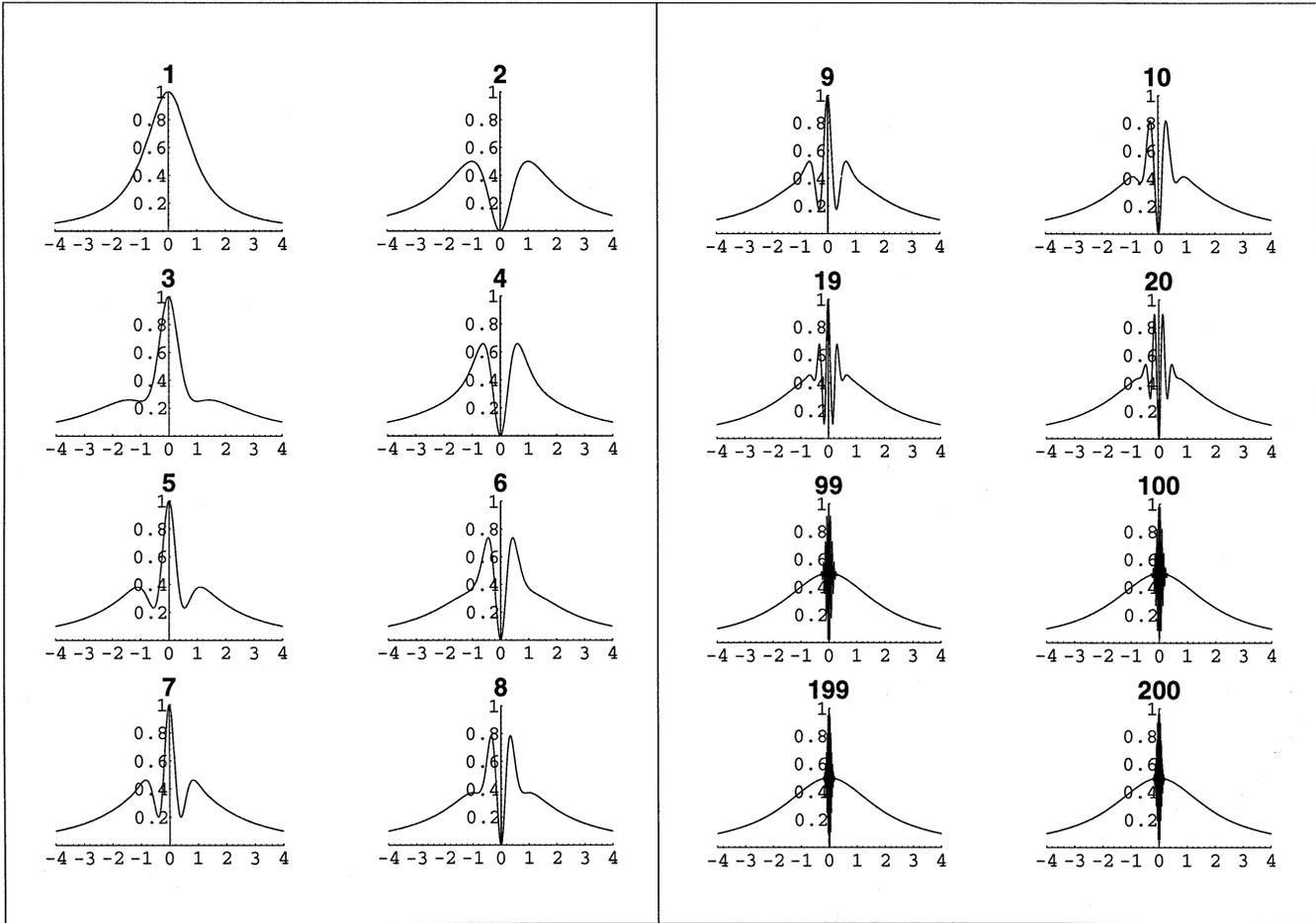
Atom-perturber collisions can also be considered; in this case, the Hamiltonian of the total system is

$$H = H_0 + V + V_c, \quad (82)$$

where the atom-perturber interaction Hamiltonian  $V_c$  is now added, and the perturbers Hamiltonian included in  $H_0$ . Considering processes involving both atom-radiation interaction  $V$  and atom-perturber interaction  $V_c$ , but assuming nevertheless that no photon absorption or emission occurs during a collision, and assuming also that the impact approximation is valid for collisions, we have obtained that  $\gamma_{ba}^{(c)}$  and  $\gamma_a^{(c)}$  have to be added to  $A_{ba}/2$  in Eq. (77), for  $\Phi_{ba}$  and  $\Phi_a$  respectively.

Thus, the result of the perturbation series summation is actually:

$$\begin{cases} \bar{\gamma}_{ba} = 2\gamma_{ba} \\ \bar{\gamma}_a = 2\gamma_a \end{cases}, \quad (83)$$



**Fig. 3.** Convergence of the Lorentzian absorption (and emission) line profile towards the double width profile, in the case where  $2\gamma_{ba}/A_{ba} = 1$  in Eq. (81), which defines the profile series summation, in reduced coordinates. The number in boldface is the number  $N$  of terms taken into account in the series development of the profile, as defined in Eq. (81).

instead of the result of Eq. (80) (and of the analogous obtained for  $\Phi_a$ ).

The factor 2 in the line-width which results from our derivation has a natural explanation in the following arguments: by using the method described in Sect. 3.4, the relaxation of the atom due to the interaction with the multiple reservoirs has been taken into account during each atom-photon interaction process. However, relaxation is a cumulative phenomenon resulting from all the interaction processes. Introducing the relaxation in each atom-photon process is equivalent to consider higher order terms in the perturbation development. In our derivation, where the perturbation development to higher orders is indeed achieved, relaxation is thus taken into account twice. This inconsistency can be solved by using one of the two following methods:

(a) the first method consists in applying the method described in Sect. 3.4 to the lowest order non-zero terms of the perturbation development. These terms are obviously the order-2 terms described by diagrams (1) and (2) of Fig. 2 with the addition of another independent lowest order term appearing at order 4, that corresponds to the diagram (3) of Fig. 2. Thus, only dia-

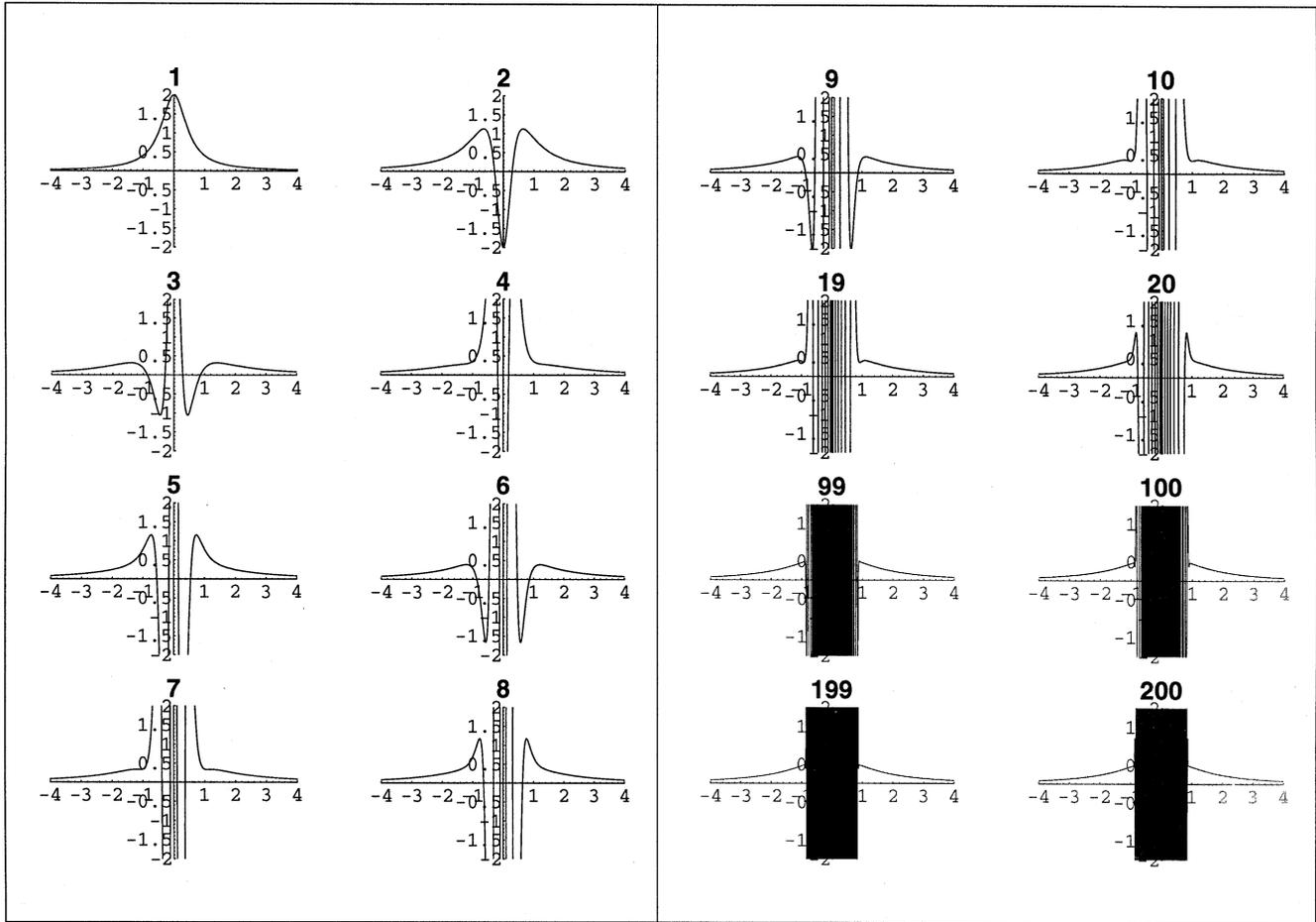
grams (1), (2) and (3) of Fig. 2 have to be considered, to which the method described in Sect. 3.4 has to be applied. The calculation is then identical to the one of Omont et al. (1972). The summation described in Eq. (77) has not to be performed in this case, and the line half-width is simply given by  $\gamma_{ba}$ .

(b) the second method consists in considering the coefficients  $\gamma_{ba}$ ,  $\gamma_a$  and  $\gamma_b$  introduced in Sect. 3.4 as small real quantities, necessary for the convergence of the time-integrals, that have now to be considered as quantities which tend towards zero (Eqs. (37-38) have then to be ignored). Performing the series summation, including multi-level and collisional effects that result in adding all the usual terms to the  $A_{ba}$  factor in Eq. (77), and taking the limit

$$\begin{cases} \gamma_{ba} \rightarrow 0 \\ \gamma_a \rightarrow 0 \end{cases} \quad (84)$$

in Eqs. (77-80), the resulting profile half-width is now

$$\begin{cases} \bar{\gamma}_{ba} = \gamma_{ba} \\ \bar{\gamma}_a = \gamma_a \end{cases}, \quad (85)$$



**Fig. 4.** Same as Fig. 3, but assuming now  $2\gamma_{ba}/A_{ba} = 0.5$  in Eq. (81). The figure shows the oscillations due to the non-convergence of the series towards its limit in line center, in the case where  $2\gamma_{ba}/A_{ba} < 1$ . The limit for  $N \rightarrow \infty$  however exists and is a lorentzian profile with half-width  $1 + (2\gamma_{ba}/A_{ba})$ .

where the values given in Eqs. (37-38) are now again assumed for  $\gamma_{ba}$  and  $\gamma_a$ .

Diagram (4) of Fig. 2, which is taken in consideration in the second method only, represents those processes that are responsible for the line broadening.

Both methods lead to the same result on the line profile. Method (a) is the one currently used in line-broadening theory; method (b) can also be considered as a suitable method for line-broadening calculations because both methods bring to the same result. Concerning method (b), it has however to be noticed that, *though the limit of the profile series exists*, the series described by Eq. (81) is not convergent at line-center when  $2\gamma_{ba}/A_{ba} < 1$  (a situation that is encountered in method (b) when  $\gamma_{ba} \rightarrow 0$ ). The series given by Eq. (81) is uniformly convergent only when

$$\left(\frac{2\gamma_{ba}}{A_{ba}}\right)^2 + x^2 > 1, \quad (86)$$

which implies that, though the series is uniformly convergent in the line wings (in any case when  $|x| > 1$ ), it is divergent at line center. Figure 4, which has been plotted for  $2\gamma_{ba}/A_{ba} = 0.5$ , shows the oscillations due to this divergence at line center

when the summation is restricted to the first terms of the series. However, the sum of the series exists, in such a way that a profile can be defined when passing to the limit  $N \rightarrow \infty$ . This shows that limiting the series development to a finite number of terms would lead to unphysical results: it is necessary to push the series development to infinite order. The validity of the perturbation series development for describing the atom-radiation interaction thus appears questionable when line profiles are concerned.

Both methods (a) and (b) are separately encountered in the literature for line-broadening calculations:

- concerning method (a), let us cite those works that, following Baranger (1958a, 1958b, 1958c, 1962), have been devoted to the problem of redistribution of radiation: Omont et al. (1972, 1973), Nienhuis & Schuller (1977). Voslamber & Yelnik (1978), Yelnik & Voslamber (1979) take into account non-impact broadening. In these works, the radiation field is described with a quantum theory. A parent method is applied to semi-classical calculations by Omont (1977) and Cooper et al. (1982).

– method (b) is encountered in calculations using the resolvent method, as it can be found in Cohen-Tannoudji et al. (1988, p. 185) and in Messiah (1969, XXI-13).

Let us cite also the method of Weisskopf & Wigner (1930), which is neither of the type of method (a), nor of the type of method (b).

Due to a misunderstanding of the point discussed in this subsection, some preliminary results relative to the present derivation published in Bommier (1996) are wrong. This remark applies to Eqs. (33-34) of the paper just quoted. The correct formulae are given in Eqs. (27) and (29) of the same paper.

## 6. Final equations

The results presented above allow to write the master equation for the atomic density matrix, and the radiative transfer equations for polarized radiation in a new form. The two equations can be combined to derive the redistribution matrix. It is however necessary to introduce some notations about collision effects.

### 6.1. Collisions

Under the hypotheses discussed in Sect. 3.4, the effect of collisions can be readily introduced in the master equation for the atomic density matrix. A more detailed derivation can be found in Bommier & Sahal-Br  chet (1991).

Besides to the collisional effects discussed in Sect. 3.4, we take into account inelastic collisions between levels  $a$  and  $b$ . The collisional excitation rate will be denoted as  $C_{ab}$  and the collisional deexcitation rate as  $C_{ba}$ .

For the perturbers, we assume a maxwellian distribution of velocities at temperature  $T$ . The collisional excitation probability can be related to the deexcitation probability

– in the non-degenerate case

$$C_{ab} = C_{ba} \exp \left\{ -\frac{h\nu_0}{kT} \right\}; \quad (87)$$

– in the degenerate case

$$C_{ab} = C_{ba} \frac{2J' + 1}{2J + 1} \exp \left\{ -\frac{h\nu_0}{kT} \right\}. \quad (88)$$

One of the effects of elastic collisions is to destroy the  $K$ -multipole component of the atomic density matrix, in the upper level. The corresponding probability is usually denoted as  $D_b^{(K)}$  ( $D_b^{(0)} = 0$ ).

### 6.2. The transfer equation coefficients

Neglecting stimulated emission, the transfer equation for the Stokes parameters is usually written in the form

$$\frac{d}{ds} \begin{pmatrix} I \\ Q \\ U \\ V \end{pmatrix} = - \begin{pmatrix} \eta_I & \eta_Q & \eta_U & \eta_V \\ \eta_Q & \eta_I & \rho_V & -\rho_U \\ \eta_U & -\rho_V & \eta_I & \rho_Q \\ \eta_V & \rho_U & -\rho_Q & \eta_I \end{pmatrix} \begin{pmatrix} I \\ Q \\ U \\ V \end{pmatrix}$$

$$+ \begin{pmatrix} \varepsilon_I \\ \varepsilon_Q \\ \varepsilon_U \\ \varepsilon_V \end{pmatrix}. \quad (89)$$

The Stokes parameters ( $I, Q, U, V$ ) may also be denoted as  $S_i$  ( $i = 0, 1, 2, 3$ ).

The transfer equation given in Eq. (40) has to be multiplied by the number of atoms in the elementary volume

$$(2\pi)^3 \mathcal{N}, \quad (90)$$

where  $\mathcal{N}$  is the number of atoms per unit volume – owing to the normalization condition of the atomic density matrix given in Eq. (1).

### 6.3. Final equations

In these equations, the atomic density matrix will be now denoted as  $\rho$ . In the degenerate case, this density matrix is developed in irreducible components  ${}^{bb}\rho_Q^K$  (see, for instance, Bommier 1996) for the upper level, and only one component  ${}^{aa}\rho_0^0$  for the lower level, which has been assumed to be unpolarized. These final equations are:

(a) in the non-degenerate and unpolarized case – master equation for the atomic density matrix

$$\begin{aligned} \frac{d}{dt} \rho_{bb} = & \rho_{aa} B_{ab} \int d\nu_1 J(\nu_1) \phi_{ba}(\nu_0 - \nu_1) \\ & - \rho_{bb} (A_{ba} + C_{ba}) \\ & + \rho_{aa} C_{ab}; \end{aligned} \quad (91)$$

– coefficients of the radiative transfer equation

$$\begin{aligned} \eta(\nu, \mathbf{\Omega}) = & \frac{h\nu}{4\pi} \mathcal{N} \rho_{aa} B_{ab} \phi_{ba}(\nu_0 - \nu) \\ \varepsilon(\nu, \mathbf{\Omega}) = & \frac{h\nu}{4\pi} \frac{\nu^3}{\nu_0^3} \mathcal{N} \rho_{bb} A_{ba} \phi_{ba}(\nu_0 - \nu) \\ & + \frac{h\nu}{4\pi} \frac{\nu^3}{\nu_0^3} \mathcal{N} \rho_{aa} B_{ab} \int d\nu_1 J(\nu_1) \\ & \times \left[ \frac{1}{2} \Phi_{ba}^*(\nu_0 - \nu) \frac{A_{ba}}{2} \Phi_a(\nu - \nu_1) \frac{1}{2} \Phi_{ba}(\nu_0 - \nu_1) \right. \\ & \left. + \text{c.c.} \right]; \end{aligned} \quad (92)$$

where the symbol ‘c.c.’ means ‘complex conjugate’.

(b) in the degenerate and polarized case

– master equation for the atomic density matrix

$$\begin{aligned} \frac{d}{dt} \left( \sqrt{2J' + 1} {}^{bb}\rho_Q^K \right) = & B_{ab} w_{J',J}^{(K)} \sqrt{2J + 1} {}^{aa}\rho_0^0 \\ & \times \int d\nu_1 (-1)^Q J_{-Q}^K(\nu_1) \phi_{ba}(\nu_0 - \nu_1); \\ & - \sqrt{2J' + 1} {}^{bb}\rho_Q^K \left( A_{ba} + C_{ba} + D_b^{(K)} \right) \\ & + \sqrt{2J + 1} {}^{aa}\rho_0^0 C_{ab} \delta_{K,0} \delta_{Q,0} \end{aligned} \quad (93)$$

– coefficients of the radiative transfer equation

$$\begin{aligned}
\eta_i(\nu, \Omega) &= \delta_{i,0} \frac{h\nu}{4\pi} \mathcal{N} \sqrt{2J+1} {}^{aa} \rho_0^0 B_{ab} \phi_{ba}(\nu_0 - \nu) \\
\rho_i(\nu, \Omega) &= 0 \\
\varepsilon_i(\nu, \Omega) &= \frac{h\nu \nu^3}{4\pi \nu_0^3} \mathcal{N} A_{ba} \phi_{ba}(\nu_0 - \nu) \\
&\times \sum_{K,Q} w_{J'J}^{(K)} \mathcal{T}_Q^K(i, \Omega) \sqrt{2J'+1} {}^{bb} \rho_Q^K \\
&+ \frac{h\nu \nu^3}{4\pi \nu_0^3} \mathcal{N} \sqrt{2J+1} {}^{aa} \rho_0^0 B_{ab} \\
&\times \sum_{K,Q} \left[ w_{J'J}^{(K)} \right]^2 \mathcal{T}_Q^K(i, \Omega) \int d\nu_1 (-1)^Q J_{-Q}^K(\nu_1) \\
&\times \left[ \frac{1}{2} \Phi_{ba}^*(\nu_0 - \nu) \frac{A_{ba}}{2} \Phi_a(\nu - \nu_1) \frac{1}{2} \Phi_{ba}(\nu_0 - \nu_1) \right. \\
&\left. + \text{c.c.} \right]
\end{aligned} \quad (94)$$

The symbol ‘c.c.’ stands for ‘complex conjugate’. In these equations, we have used the symbols  $\mathcal{T}_Q^K(i, \Omega)$ ,  $J_Q^K(\nu_1)$ , and  $w_{J'J}^{(K)}$  introduced by Landi Degl’Innocenti (1984). In particular,  $\mathcal{T}_Q^K(i, \Omega)$  is the irreducible spherical tensor of the polarization unit vectors, and the other symbols are defined by

$$J_Q^K(\nu_1) = \oint \frac{d\Omega_1}{4\pi} \sum_{j=0}^3 \mathcal{T}_Q^K(j, \Omega_1) S_j(\nu_1, \Omega_1), \quad (95)$$

$$w_{J'J}^{(K)} = \frac{\begin{Bmatrix} 1 & 1 & K \\ J' & J' & J \end{Bmatrix}}{\begin{Bmatrix} 1 & 1 & 0 \\ J' & J' & J \end{Bmatrix}}. \quad (96)$$

A table of the symbols  $w_{J'J}^{(K)}$  can be found in the paper just quoted.

The master equation for the lower level component of the density matrix can be derived from the normalization condition given in Eq. (1), which reduces to

– in the non-degenerate case

$$\rho_{aa} + \rho_{bb} = 1; \quad (97)$$

– in the degenerate case

$$\sqrt{2J+1} {}^{aa} \rho_0^0 + \sqrt{2J'+1} {}^{bb} \rho_0^0 = 1. \quad (98)$$

These equations have the usual form found with the perturbative development at order 2, except from two features:

– the  $\delta$ -functions, that describe the profiles in rigorous derivations of the equations at order 2, are replaced by the profile  $\phi_{ba}(\nu_0 - \nu)$ , thus confirming the proposal of Landi Degl’Innocenti (1983);

– In the emission coefficient of the transfer equation there is a second term which arises at order 4 (and higher). This term,

which originates from the diagram (3) of Fig. 2, represents the scattering of a photon without population of the excited state. When the lower level is infinitely sharp, this term contains a frequency function  $\delta(\nu - \nu_1)$  which represents conservation of energy in the scattering process; we thus call this term the ‘Rayleigh scattering term’. Usually, the emissivity is given by only the first term, in which the emission profile is eventually assumed to be different from the absorption profile, in order to take into account redistribution effects. Presently, the emission profile in the first term is the same as the absorption profile; partial redistribution effects are taken into account through the second term.

#### 6.4. The Rayleigh scattering term

This is the second term in the emission coefficient of the transfer equation Eqs. (92,94). Due to Eq. (68), the product of the 3 complex profiles vanishes when it is integrated over any of the frequencies appearing as arguments in its expression. Using the identity

$$[(\omega_0 - \omega_1 + \Delta_{ba}) - (\omega_0 - \omega + \Delta_{ba})]^2 = (\omega - \omega_1)^2, \quad (99)$$

this product can be transformed in the following way

$$\begin{aligned}
&\left[ \frac{1}{2} \Phi_{ba}^*(\nu_0 - \nu) \frac{A_{ba}}{2} \Phi_a(\nu - \nu_1) \frac{1}{2} \Phi_{ba}(\nu_0 - \nu_1) \right. \\
&\left. + \text{c.c.} \right] = \\
&\frac{A_{ba}}{2\gamma_{ba}} \left\{ \left[ \frac{\gamma_a}{\gamma_a^2 + (\omega - \omega_1)^2} \right] \right. \\
&\times [\phi_{ba}(\nu_0 - \nu_1) + \phi_{ba}(\nu_0 - \nu)] \\
&- \left[ 1 + \frac{\gamma_a}{2\gamma_{ba}} \right] \left[ 1 - \frac{\gamma_a^2}{\gamma_a^2 + (\omega - \omega_1)^2} \right] \\
&\left. \times \phi_{ba}(\nu_0 - \nu_1) \phi_{ba}(\nu_0 - \nu) \right\}
\end{aligned} \quad (100)$$

In the case where the lower level is infinitely sharp

$$\gamma_a \rightarrow 0 \Rightarrow$$

$$\frac{\gamma_a}{\gamma_a^2 + (\omega - \omega_1)^2} \rightarrow \frac{1}{2} \delta(\nu - \nu_1), \quad (101)$$

one has

$$\begin{aligned}
&\left[ \frac{1}{2} \Phi_{ba}^*(\nu_0 - \nu) \frac{A_{ba}}{2} \Phi_a(\nu - \nu_1) \frac{1}{2} \Phi_{ba}(\nu_0 - \nu_1) \right. \\
&\left. + \text{c.c.} \right] = \\
&\frac{A_{ba}}{2\gamma_{ba}} \left\{ \delta(\nu - \nu_1) \phi_{ba}(\nu_0 - \nu_1) \right. \\
&\left. - \phi_{ba}(\nu_0 - \nu_1) \phi_{ba}(\nu_0 - \nu) \right\}
\end{aligned} \quad (102)$$

### 6.5. Redistribution matrix

The redistribution matrix is the joint probability that, given an incident radiation beam described by the Stokes vector  $S_j(\nu_1, \Omega_1)$ , the scattered radiation beam is described by the Stokes vector  $S_i(\nu, \Omega)$ .

The redistribution matrix can be derived from the preceding equations by solving the master equation for the atomic density matrix in stationary situations

$$\frac{d}{dt}\rho = 0. \quad (103)$$

The upper level density matrix elements are obtained as a function of the lower level ones and they are then substituted into the emission coefficient of the transfer equation.

For simplicity purposes, we now consider the case of a resonance line, and we now denote by  $\Gamma_R$  the radiative deexcitation rate, by  $\Gamma_I$  the inelastic collisions deexcitation rate, and by  $\Gamma_E$  the elastic collisions rate, associated to the  $K$ -multipole destruction rate  $D^{(K)}$ . Thus

$$\begin{cases} A_{ba} = \Gamma_b = \Gamma_R \\ C_{ba} = \gamma_b^{(c)} = \Gamma_I \\ \gamma_a = \gamma_a^{(c)} = \Gamma_a = 0 \\ \gamma_{ba}^{(c)} = \frac{1}{2}(\Gamma_I + \Gamma_E) \\ D_b^{(K)} = D^{(K)} \end{cases}, \quad (104)$$

from which one has

$$\gamma_{ba} = \frac{1}{2}(\Gamma_R + \Gamma_I + \Gamma_E). \quad (105)$$

The result of the substitution is the following:

– in the non-degenerate and unpolarized case

$$\begin{aligned} \varepsilon(\nu, \Omega) &= \eta^{(0)} \frac{\nu^4}{\nu_0^4} \int d\nu_1 \oint \frac{d\Omega_1}{4\pi} S_0(\nu_1, \Omega_1) \\ &\times \left\{ \frac{\Gamma_R}{\Gamma_R + \Gamma_I + \Gamma_E} \delta(\nu - \nu_1) \phi_{ba}(\nu_0 - \nu_1) \right. \\ &+ \frac{\Gamma_R}{\Gamma_R + \Gamma_I} \frac{\Gamma_E}{\Gamma_R + \Gamma_I + \Gamma_E} \\ &\left. \times \phi_{ba}(\nu_0 - \nu_1) \phi_{ba}(\nu_0 - \nu) \right\} \\ &+ \eta^{(0)} \frac{\nu^4}{\nu_0^4} \frac{\Gamma_I}{\Gamma_R + \Gamma_I} B_{\nu_0} \phi_{ba}(\nu_0 - \nu) \end{aligned}, \quad (106)$$

where  $\eta^{(0)}$  is the line absorption coefficient

$$\eta^{(0)} = \frac{h\nu_0}{4\pi} \mathcal{N} \rho_{aa} B_{ab}, \quad (107)$$

and where  $B_{\nu_0}$  is the Planck function in the Wien limit (coherently with the fact that we have neglected stimulated emission)

$$B_{\nu_0} = \frac{2h\nu_0^3}{c^2} \exp\left\{-\frac{h\nu_0}{kT}\right\}. \quad (108)$$

We thus recover the result of Omont et al. (1972). In this case, the redistribution matrix is a scalar function which only describes frequency redistribution effects, because the radiation polarization is ignored.

– in the degenerate and polarized case

$$\begin{aligned} \varepsilon_i(\nu, \Omega) &= \eta^{(0)} \frac{\nu^4}{\nu_0^4} \int d\nu_1 \oint \frac{d\Omega_1}{4\pi} \\ &\times \sum_K \left[ w_{J'J}^{(K)} \right]^2 \sum_{j=0}^3 \left[ \mathcal{F}_R^{(K)}(\Omega, \Omega_1) \right]_{ij} S_j(\nu_1, \Omega_1) \\ &\times \left\{ \frac{\Gamma_R}{\Gamma_R + \Gamma_I + \Gamma_E} \delta(\nu - \nu_1) \phi_{ba}(\nu_0 - \nu_1) \right. \\ &+ \frac{\Gamma_R}{\Gamma_R + \Gamma_I + D^{(K)}} \frac{\Gamma_E - D^{(K)}}{\Gamma_R + \Gamma_I + \Gamma_E} \\ &\left. \times \phi_{ba}(\nu_0 - \nu_1) \phi_{ba}(\nu_0 - \nu) \right\} \\ &+ \eta^{(0)} \frac{\nu^4}{\nu_0^4} \frac{\Gamma_I}{\Gamma_R + \Gamma_I} B_{\nu_0} \phi_{ba}(\nu_0 - \nu) \delta_{i,0} \end{aligned} \quad (109)$$

where the Rayleigh phase matrix  $K$ -component is given by (see Landi Degl'Innocenti, 1984)

$$\begin{aligned} \left[ \mathcal{F}_R^{(K)}(\Omega, \Omega_1) \right]_{ij} &= \\ \sum_Q (-1)^Q \mathcal{F}_Q^K(i, \Omega) \mathcal{F}_{-Q}^K(j, \Omega_1) \end{aligned} \quad (110)$$

The line absorption coefficient is now

$$\eta^{(0)} = \frac{h\nu_0}{4\pi} \mathcal{N} \sqrt{2J+1} \rho_{00}^{aa} B_{ab}. \quad (111)$$

We thus recover the result of Domke & Hubeny (1988). It can be seen that, in this case, the redistribution matrix factorizes into the product of a phase matrix times a frequency redistribution function. In the absence of collisions, ( $\Gamma_E = \Gamma_I = D^{(K)} = 0$ ), the frequency redistribution function reduces to

$$\delta(\nu - \nu_1) \phi_{ba}(\nu_0 - \nu_1). \quad (112)$$

This result translates the physical fact that only collisions can modify the frequency of the scattered photon, in accordance with the energy conservation principle.

### 6.6. Optical coherences

For the evolution equation of the optical coherence, we obtain (in the non-degenerate case)

$$\frac{d}{dt} \rho_{ba} = -i\omega_{ba} \rho_{ba} - \frac{1}{2} (A_{ba} + i\Delta_{ba}) \rho_{ba}, \quad (113)$$

where  $A_{ba}$  is the Einstein coefficient for spontaneous emission given by Eq. (73), and where  $\Delta_{ba}$  is given by

$$\Delta_{ba} = \int d\nu_1 \frac{2\pi}{3} \frac{1}{\hbar^2} \frac{8\pi h\nu_1^3}{c^3} |\langle a|D|b\rangle|^2 \psi_{ba}(\nu_0 - \nu_1), \quad (114)$$

a quantity which requires renormalization techniques to be evaluated (Lamb-shift).

Owing to the dipolar character of the interaction, the evolution equations for the optical coherences form a system of equations independent of the populations. This is a homogeneous system of linear equations, whose solution is zero in stationary situations: the optical coherences vanish at equilibrium.

We have however obtained the relaxation rate of the optical coherences. Together with the relaxation rate of the populations (second line of Eqs. (91,93)), these relaxation rates

- are already obtained as early as at the lowest order perturbation development
- are not modified when the higher orders are taken into account.

Moreover, in the generalization to multi-level atoms, these relaxation rates acquire the form given in Eqs. (37-38). It can then be verified that the relaxation rates there assumed were convenient, and that they are not modified by the perturbation series summation.

As discussed in Sect. 4.1, the relaxation rate of the optical coherence is responsible for line broadening.

## 7. Discussion

In the weak radiation field limit, the high order perturbation series development of the atom-radiation field interaction leads to the introduction of new processes, besides photon absorption and emission. These new processes involve coherent photon re-emission and reabsorption: before the end of a photon absorption (or emission), a photon re-emission (or reabsorption) can begin. Such processes are responsible for frequency coherence in the scattering process, and natural line-broadening. This coherent process can however be interrupted by collisions.

In the system of coupled equations of statistical equilibrium and transfer equations, a new term, that we have called ‘Rayleigh scattering term’, appears at order 4 of the perturbation series development. It is responsible for frequency redistribution leading to frequency coherence in the scattering process.

The Rayleigh scattering term vanishes when integrated over the incident or emitted frequency. Consequently, it is responsible for frequency redistribution effects in the emitted profile. As a consequence, the usual order-2 equations (with  $\delta$ -functions substituted by realistic profiles, as we have shown) can be considered valid when the Rayleigh scattering term is very small or zero; this happens:

- (a) when the incoming radiation is approximately constant over a frequency interval comparable to or larger than the line-width (in the atomic reference frame). This is well verified at the center of a Doppler broadened incident line. It is a well-known result that complete frequency redistribution, as derived by order-2 equations, is a convenient scheme for describing the line core;
- (b) when the (optically thin) emitted line is integrated over frequencies;
- (c) when the collisional broadening is much larger than the natural broadening (see the factor  $A_{ba}/2\gamma_{ba}$  in front of Eq. (100));

however, in this case, the depolarizing role of collisions may be important also.

The frequency redistribution function that we have obtained is the same as the one derived by Omont et al. (1972), and the discussion of the role of collisions in frequency redistribution needs not to be repeated here.

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