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► **To cite this version:**

F. Hartmann-Boutron. Relaxation effects in mössbauer transmission and scattering. II Introduction of relaxation. *Journal de Physique*, 1976, 37 (5), pp.549-556. 10.1051/jphys:01976003705054900 . jpa-00208449

**HAL Id: jpa-00208449**

**<https://hal.science/jpa-00208449>**

Submitted on 4 Feb 2008

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Classification  
 Physics Abstracts  
 4.200 — 8.610 — 8.680

## RELAXATION EFFECTS IN MÖSSBAUER TRANSMISSION AND SCATTERING II INTRODUCTION OF RELAXATION

F. HARTMANN-BOUSTRON

Laboratoire de Physique des Solides  
 Université Paris-Sud, 91405 Orsay, France  
 and

Laboratoire de Spectrométrie Physique (\*)  
 U.S.M.G., B. P. 53, 38041 Grenoble-Cedex, France (\*\*)

(Reçu le 6 octobre 1975, accepté le 9 janvier 1976)

**Résumé.** — Dans la première partie de ce travail (réf. [1]) nous avons étudié la transmission et la diffusion Mössbauer en l'absence de relaxation. Nous introduisons maintenant la relaxation. Nous trouvons que l'indice de réfraction mesuré dans une expérience de transmission dépend seulement d'une matrice de Liouville ; au contraire le spectre diffusé fait intervenir la somme de trois produits de trois matrices de Liouville. Il s'ensuit que la diffusion n'est pas une très bonne méthode d'étude de la relaxation, à l'exception de la relaxation des populations à température finie. Au contraire la comparaison entre les spectres en émission et en transmission pourrait donner d'utiles informations sur les réarrangements électroniques dans les sources.

**Abstract.** — In part I of this paper (ref. [1]) we have studied Mössbauer transmission and scattering in the absence of relaxation. Here we introduce relaxation. We find that the refraction index observed in a transmission experiment only depends on one Liouville matrix, while the scattered spectrum involves a sum of three products of three Liouville matrices. It follows that scattering is not a very good method to study relaxation except for the case of population relaxation at finite temperature. On the contrary comparison between emission and transmission spectra might give useful information on electronic rearrangement effects in source experiments.

1. **Introduction.** — In appendix I of reference [2] we have derived a rule for introducing thermal relaxation in an atomic physics problem. Let

$$U_0(t) = \exp\left(-\frac{i}{\hbar} \mathcal{H}_0 t\right)$$

be the evolution operator of the atom in the absence of relaxation. For introducing relaxation, the atomic observable of interest is first written as a trace with all operators  $U_0$  on the left of the atomic density matrix  $\sigma$  and all operators  $U_0^+$  on its right, the corresponding time intervals being ordered. The trace is then expressed in terms of Liouville evolution superoperators

$$\mathcal{U}_0(t) \equiv \exp\left(-\frac{i}{\hbar} \mathcal{H}_0^\times t\right)$$

which satisfy the identity :

$$\langle ad | \mathcal{U}_0(t) | bc \rangle \equiv \langle a | U_0(t) | b \rangle \langle c | U_0^+(t) | d \rangle. \quad (1)$$

Finally  $\mathcal{U}_0(t)$  is replaced by the associated Liouville evolution superoperator in the presence of relaxation :

$$\mathcal{U}_0(t) \rightarrow \overline{\mathcal{U}}(t) = \exp\left[\left(-\frac{i}{\hbar} \mathcal{H}_0^\times + S\right)t\right] \quad (2)$$

where  $S$  is the relaxation matrix, defined in reference [2], which characterizes the relaxation of the atomic density matrix  $\sigma$ .

2. **Relaxation effects in a transmission experiment.** —

As shown in part I of this paper [1], the refraction index  $n$  of the absorber is such that

$$n - 1 \propto \langle V_{\text{diff}} \rangle \quad (3)$$

(\*) Associés au C.N.R.S.  
 (\*\*) New address.

where, for a powder and in the absence of relaxation :

$$\langle V_{\text{diff}} \rangle = -\frac{i}{\hbar} \frac{8\pi}{2L+1} \int_{-\infty}^t \exp \left[ \left\{ -i(\Omega - \omega_{i_0}) - \frac{\Gamma + \Gamma'}{2} \right\} (t - t') \right] dt' \times \\ \times \sum_{\substack{f_1 g_1 \\ f_2 g_2}} \sigma_{g_1 g_1} \langle f_1 | \mathbf{T}_L | g_1 \rangle \langle g_2 | \mathbf{T}_L^+ | f_2 \rangle \langle f_2 g_2 | \mathcal{U}_0(t - t') | f_1 g_1 \rangle \quad (4)$$

in which  $f$  and  $g$  are assumed to be eigenstates of the atomic hamiltonian  $\mathcal{H}_0$ ;  $\sigma$ , the Boltzmann density matrix of the Mössbauer ground state, is then diagonal.

Let us introduce relaxation by use of eq. (2) :

$$\langle V_{\text{diff}} \rangle = -\frac{i}{\hbar} \frac{8\pi}{2L+1} \sum_{\substack{f_1 g_1 \\ f_2 g_2}} \sigma_{g_1 g_1} \langle g_2 | \mathbf{T}_L^+ | f_2 \rangle \langle f_1 | \mathbf{T}_L | g_1 \rangle \times \\ \times \left\langle f_2 g_2 \left| \frac{-1}{-i(\Omega - \omega_{i_0}) - \frac{\Gamma + \Gamma'}{2} - \frac{i}{\hbar} \mathcal{H}_0^x + S} \right| f_1 g_1 \right\rangle. \quad (5)$$

This expression is to be compared with the corresponding result for an emitter, eq. (2) of part I, which, by virtue of eq. (31) of [2] and taking account of the width  $\Gamma'$  of the analyser, can be put into the form ( $\omega = \omega_k - \Omega$ ) :

$$I(\omega_k) \propto \text{Re} \sum_{\substack{f_1 f_2 f_3 \\ g_1 g_2}} \langle g_2 | \mathbf{T}_L^+ | f_2 \rangle \sigma_{f_3 f_1}^I(1/\Gamma) \langle f_1 | \mathbf{T}_L | g_1 \rangle \times \\ \times \left\langle f_2 g_2 \left| \frac{-1}{i(\omega_k - \Omega) - \frac{\Gamma + \Gamma'}{2} - \frac{i}{\hbar} \mathcal{H}_0^x + S} \right| f_3 g_1 \right\rangle \quad (6)$$

where :

$$\sigma_{f_3 f_1}^I(1/\Gamma) = \sum_{f_4 f_5} \left\langle f_3 f_1 \left| \frac{-1}{-\Gamma - \frac{i}{\hbar} \mathcal{H}_0^x + S} \right| f_4 f_5 \right\rangle \langle f_4 | \sigma_{\text{in}}^I | f_5 \rangle \quad (7)$$

and  $\sigma_{\text{in}}^I$  is the initial value of the density matrix of the excited Mössbauer state just after feeding by upper nuclear states.

At high temperatures, the density matrices of both the excited and the ground Mössbauer states are proportional to the unit matrix, and it is clear from eq. (5), (6), (7) that the quantity which is measured in the two experiments is exactly the same.

On the contrary at low temperatures,  $\sigma^I(1/\Gamma)$  depends on the relaxation in the excited state, while the Boltzmann density matrix of the ground state does not. Consequently as concerns relaxation, the transmission experiment can only give information on the range  $S \sim \mathcal{H}_0^x/\hbar$ , while as already discussed in [3, 4], the emission experiment can explore both domains  $S \sim \mathcal{H}_0^x/\hbar$  and  $S \sim \Gamma$  (in this last case however, only on the additional condition that simultaneously  $\mathcal{H}_0^x > k_B T$ ). Another difference is that in a emission experiment one might happen to observe highly excited electronic states out of thermal equilibrium due to incomplete electronic rearrangement following a  $\beta$  transition [5]. By contrast in a transmission (or scattering) experiment the electronic state of the absorber in the ground and excited nuclear states is the same.

**3. Relaxation effects in a scattering experiment.** — 3.1 GENERAL FORMULA. — In this case we have to use the expressions of  $I_1, I_2, I_3$  given by eq. (45), (46), (47) of part I and the expressions of the traces given by eq. (48), (49), (50) of part I. After replacing  $\mathcal{U}_0$  by  $\mathcal{U}$ , performing the triple time integration and adding  $I_1, I_2$  and  $I_3$ , we finally find that the number  $dn_k/dt$  of photons ( $\mathbf{k}, \omega_k$ ) scattered per second is given by :

$$\frac{dn_k}{dt} \propto 2 \text{Re } I \propto 2 \text{Re } (I_1 + I_2 + I_3) \quad (8)$$

where, with respect to the eigenstates  $f$  and  $g$  of  $\mathcal{H}_0$  :

$$\begin{aligned}
 I = & -\sum \langle g_4 | H_a^+(\mathbf{k}) | f_4 \rangle \langle f_1 | H_a(\mathbf{k}_i) | g_3 \rangle \sigma_{g_1 g_1} \langle g_6 | H_a^+(\mathbf{k}_i) | f_5 \rangle \langle f_7 | H_a(\mathbf{k}) | g_7 \rangle \times \\
 & \times \left\{ \left[ \delta_{g_1 g_6} \left\langle f_4 g_4 \left| \frac{1}{i(\omega_k - \Omega) - \frac{\Gamma}{2} - \frac{i}{\hbar} \mathcal{H}_0^x + S} \right| f_1 g_2 \right\rangle \left\langle g_3 g_8 \left| \frac{1}{i(\omega_k - \omega_{i_0}) - \frac{i}{\hbar} \mathcal{H}_0^x - \frac{\Gamma'}{2} + S} \right| g_2 g_7 \right\rangle \right. \right. \\
 & \times \left. \left. \left\langle g_2 f_7 \left| \frac{1}{-i(\omega_{i_0} - \Omega) - \frac{i}{\hbar} \mathcal{H}_0^x - \frac{\Gamma + \Gamma'}{2} + S} \right| g_1 f_5 \right\rangle \right] + \left[ \delta_{g_1 g_6} \left\langle f_4 g_4 \left| \frac{1}{i(\omega_k - \Omega) - \frac{\Gamma}{2} - \frac{i}{\hbar} \mathcal{H}_0^x + S} \right| f_3 g_7 \right\rangle \right. \right. \\
 & \times \left. \left. \left\langle f_3 f_7 \left| \frac{1}{-\Gamma - \frac{i}{\hbar} \mathcal{H}_0^x + S} \right| f_1 f_6 \right\rangle \left\langle g_3 f_6 \left| \frac{1}{-i(\omega_{i_0} - \Omega) - \frac{i}{\hbar} \mathcal{H}_0^x - \frac{\Gamma + \Gamma'}{2} + S} \right| g_1 f_5 \right\rangle \right] \right. \\
 & + \left[ \delta_{g_3 g_1} \left\langle f_4 g_4 \left| \frac{1}{i(\omega_k - \Omega) - \frac{\Gamma}{2} - \frac{i}{\hbar} \mathcal{H}_0^x + S} \right| f_3 g_7 \right\rangle \left\langle f_3 f_7 \left| \frac{1}{-\Gamma - \frac{i}{\hbar} \mathcal{H}_0^x + S} \right| f_2 f_5 \right\rangle \right. \\
 & \left. \left. \times \left\langle f_2 g_6 \left| \frac{1}{i(\omega_{i_0} - \Omega) - \frac{i}{\hbar} \mathcal{H}_0^x - \frac{\Gamma + \Gamma'}{2} + S} \right| f_1 g_1 \right\rangle \right] \right\}. \tag{9}
 \end{aligned}$$

This expression is very complicated and suggests that, in general, Mössbauer scattering is not a good method to study relaxation, because of both the nine Liouville matrices which appear in the problem and the high dimensionality of some of these matrices.

As an example, if we assume that  $I = 2$ ,  $I_g = 0$ ,  $S = \frac{1}{2}$  (as in  $\text{Yb}^{170}\text{Au}$ , which does not mean that the experiment is possible in this case) :

$$\begin{aligned}
 \langle gg | | gg \rangle & \text{ is } 4 \times 4 \\
 \langle fg | | fg \rangle & \text{ is } 20 \times 20 \\
 \langle ff | | ff \rangle & \text{ is } 100 \times 100.
 \end{aligned}$$

We will however see that there is one situation where Mössbauer scattering might give information on relaxation which cannot be obtained by other techniques. In order to find it let us look in more detail at the properties of eq. (9).

3.2 PHYSICAL INTERPRETATION OF EQ. (9). — It is possible to show that the sum of the second and third terms  $I_2$  and  $I_3$  of eq. (9) is equal to :

$$-\frac{1}{\Gamma} \sum \langle g_4 | H_a^+(\mathbf{k}) | f_4 \rangle \langle f_7 | H_a(\mathbf{k}) | g_7 \rangle \left\langle f_4 g_4 \left| \frac{1}{i(\omega_k - \Omega) - \frac{\Gamma}{2} - \frac{i}{\hbar} \mathcal{H}_0^x + S} \right| f_3 g_7 \right\rangle \langle f_3 | \sigma_{ev}^I(1/\Gamma) | f_7 \rangle \tag{10}$$

with

$$\langle f_3 | \sigma_{ev}^I(1/\Gamma) | f_7 \rangle = \sum \left\langle f_3 f_7 \left| \frac{-\Gamma}{-\Gamma - \frac{i}{\hbar} \mathcal{H}_0^x + S} \right| f_1 f_5 \right\rangle \langle f_1 | \sigma_{in}^I | f_5 \rangle \tag{11}$$

and

$$\begin{aligned}
 \langle f_1 | \sigma_{in}^I | f_5 \rangle = & \left[ \sum \langle f_1 | H_a(\mathbf{k}_i) | g_3 \rangle \sigma_{g_1 g_1} \left\langle g_3 f_5 \left| \frac{-1}{-i(\omega_{i_0} - \Omega) - \frac{i}{\hbar} \mathcal{H}_0^x - \frac{\Gamma + \Gamma'}{2} + S} \right| g_1 f_6 \right\rangle \times \right. \\
 & \times \left. \langle g_1 | H_a^+(\mathbf{k}_i) | f_6 \rangle \right] + \left[ \sum \langle f_2 | H_a(\mathbf{k}_i) | g_1 \rangle \sigma_{g_1 g_1} \right. \\
 & \left. \times \left\langle f_1 g_6 \left| \frac{-1}{i(\omega_{i_0} - \Omega) - \frac{i}{\hbar} \mathcal{H}_0^x - \frac{\Gamma + \Gamma'}{2} + S} \right| f_2 g_1 \right\rangle \langle g_6 | H_a^+(\mathbf{k}_i) | f_5 \rangle \right]. \tag{12}
 \end{aligned}$$

It is not difficult to check that  $\sigma_{in}^I$  is the initial density matrix of the excited state associated with the absorption of an incident photon. The interpretation of eq. (10) is then clear : we create an initial density matrix  $\sigma_{in}^I$  in state I. During the nuclear lifetime it evolves to  $\sigma_{ev}^I(1/\Gamma)$ , and in terms of  $\sigma_{ev}^I(1/\Gamma)$  the lineshape of the emitted radiation is given by the same formula as for an emitter (eq. (6)).

This result looks perfectly reasonable if we think of a scattering experiment using irradiation with a *white spectrum* ( $\Gamma' \gg \Gamma$ ). In that case the first line of eq. (9) is negligible and we recover the similarity between emission and scattering which was emphasized in 4.2 of part I.

However in actual experiments  $\Gamma' \sim \Gamma$  (which means that the absorption of the incident photon is not instantaneous) and we must take account of the first term  $I_1$  of eq. (9), whose physical interpretation is not so clear. Its only obvious property is that as a function of  $\omega_k$  its integrated area is zero. First, in the absence of relaxation it has two poles in the lower complex half plane; when we close the contour in the upper complex plane we get zero. Second, since relaxation is a dissipative process the eigenvalues of the non-hermitian hamiltonian  $-\frac{i}{\hbar} \mathcal{H}_0^x + S$  must have a negative real part. Therefore in the presence of relaxation all the poles remain in the lowest half plane and the integral remains zero.

In view of these remarks it seems that there is only one situation where Mössbauer scattering might give some interesting information on relaxation. It is the case  $S \sim \Gamma$ , where relaxation broadening is small so that relaxation effects enter the problem mainly through  $\sigma_{ev}^I(1/\Gamma)$  (eq. (10)). In these conditions, by using selective excitation we may populate one particular excited substate and detect relaxation in state I by observation, in the scattered spectrum, of new lines originating from other excited substates. This technique should give us access to the range  $S \sim \Gamma$  without any restriction on temperature, contrary to the emitter case where the condition  $\mathcal{H}_0/k_B T \gtrsim 1$  had to be fulfilled. Let us examine this possibility in more detail.

**3.3 SCATTERING IN THE PRESENCE OF SLOW RELAXATION ( $S \sim \Gamma \ll \mathcal{H}_0/\hbar$ )** <sup>(1)</sup>. — Let us assume for simplicity that the hyperfine levels  $f, g$  are non-degenerate, with different hyperfine splittings in the two Mössbauer nuclear states, and that the ground state is a doublet  $gg'$ .

Let us irradiate at  $\omega_{i_0} = \Omega_{f_s g_1}$ . As it concerns the contribution of the last two lines  $I_2$  and  $I_3$  of eq. (9), this has the effect of selectively populating level  $f_5$  :  $\langle f_5 | \sigma_{in}^I | f_5 \rangle \neq 0$ , all other matrix elements of  $\sigma_{in}^I$  being zero. Since  $S \ll \mathcal{H}_0^x/\hbar$ , relaxation

in the excited state can be treated within the secular approximation; it follows that  $\langle f_5 | \sigma | f_5 \rangle$  will only be coupled to other populations :

$$\begin{aligned} \langle f_5 | \sigma_{in}^I | f_5 \rangle &\rightarrow \langle f_3 | \sigma_{ev}^I | f_3 \rangle = \\ &= \left\langle f_3 f_3 \left| \frac{-\Gamma}{-\Gamma + S} \right| f_5 f_5 \right\rangle. \end{aligned} \quad (13)$$

The scattered spectrum will thus involve, in addition to the emission lines originating from  $f_5$ , new lines originating from the other excited states  $f_3$  with intensities proportional to (see eq. (10)) :

$$\begin{aligned} &-\sum \langle g_4 | H_a^+(\mathbf{k}) | f_4 \rangle \langle f_3 | H_a(\mathbf{k}) | g_7 \rangle \times \\ &\times \left\langle f_4 g_4 \left| \frac{1}{i(\omega_k - \Omega) - \frac{\Gamma}{2} - \frac{i}{\hbar} \mathcal{H}_0^x + S} \right| f_3 g_7 \right\rangle \\ &\times \langle f_3 | \sigma_{ev}^I(1/\Gamma) | f_3 \rangle. \end{aligned} \quad (14)$$

As shown by eq. (13) the quantities  $\langle f_3 | \sigma_{ev}^I(1/\Gamma) | f_3 \rangle$  depend on the Liouville matrix  $(-\Gamma)/(-\Gamma + S)$ . If  $S \ll \Gamma$  redistribution of the populations in the excited state cannot occur because the relaxation is too slow. If  $S \gg \Gamma$  equipartition is completely achieved. It is in the range  $S \sim \Gamma$  that the intensities of the extra lines will be most sensitive to relaxation. On the other hand since  $\mathcal{H}_0^x/\hbar \gg S$ , the broadening of the lines by relaxation will be very small compared to their distance; however, when  $S \sim \Gamma$ ,  $\Gamma'$  the absorbed intensity and therefore the number of atoms excited to state  $f_5$  will depend on  $S$  : it follows that information on relaxation must be deduced from the *relative intensities* of the lines of the scattered spectrum.

Up to now in this discussion we have ignored the contribution of the first line  $I_1$  of eq. (9). In the presence of selective excitation at  $\omega_{f_s g_1}$  we must have in the last Liouville matrix of this term :  $g_2 = g_1$  and  $f_7 = f_5$ . On the other hand, by virtue of the secular approximation the off-diagonal elements  $(\sigma_{gg'})$ ,  $(\sigma_{g'g})$  relax independently, while there is a coupling between the populations  $(\sigma_{gg})$ ,  $(\sigma_{g'g'})$ . Then the intermediate Liouville matrix can only have the form :

$$\left\langle gg' \left| \frac{1}{i(\omega_k - \omega_{i_0}) - i(\omega_g - \omega_{g'}) - \frac{\Gamma'}{2} + S_{gg',gg'}} \right| gg' \right\rangle \quad (15)$$

(and similar expression with  $g \rightleftharpoons g'$ ) ; or

$$\left\langle g' g' \left| \frac{1}{i(\omega_k - \omega_{i_0}) - \frac{\Gamma'}{2} + S} \right| gg \right\rangle \quad (16)$$

(and  $g \rightleftharpoons g'$ ). Finally since relaxation effects are small, in the first Liouville matrix we must have  $f_4 = f_1$ ,  $g_4 = g_8$ .

<sup>(1)</sup> This situation has also been considered by Afanasev and Gorobchenko [8].

Neglecting  $S$  in the first and third Liouville matrices, the first term  $I_1$  of eq. (9) then takes one of the two forms :

$$\begin{aligned}
 & -\langle g_2 | H_a^+(\mathbf{k}) | f_1 \rangle \langle f_1 | H_a(\mathbf{k}_i) | g_2 \rangle \sigma_{g_1 g_1} \langle g_1 | H_a^+(\mathbf{k}_i) | f_5 \rangle \langle f_5 | H_a(\mathbf{k}) | g_1 \rangle \times \\
 & \quad \times \left\langle f_1 g_2 \left| \frac{1}{i(\omega_k - \Omega) - \frac{\Gamma}{2} - i(\omega_{f_1} - \omega_{g_2})} \right| f_1 g_2 \right\rangle \left\langle g_2 g_2 \left| \frac{1}{i(\omega_k - \omega_{i_0}) - \frac{\Gamma'}{2} + S} \right| g_1 g_1 \right\rangle \\
 & \quad \times \left\langle g_1 f_5 \left| \frac{1}{-i(\omega_{i_0} - \Omega) - (\omega_{g_1} - \omega_{f_5}) - \frac{\Gamma + \Gamma'}{2}} \right| g_1 f_5 \right\rangle \quad (17)
 \end{aligned}$$

or ( $g_2 \neq g_1$ ) :

$$\begin{aligned}
 & -\langle g_2 | H_a^+(\mathbf{k}) | f_1 \rangle \langle f_1 | H_a(\mathbf{k}_i) | g_1 \rangle \sigma_{g_1 g_1} \langle g_1 | H_a^+(\mathbf{k}_i) | f_5 \rangle \langle f_5 | H_a(\mathbf{k}) | g_2 \rangle \times \\
 & \quad \times \left\langle f_1 g_2 \left| \frac{1}{i(\omega_k - \Omega) - \frac{\Gamma}{2} - i(\omega_{f_1} - \omega_{g_2})} \right| f_1 g_2 \right\rangle \\
 & \quad \times \left\langle g_1 g_2 \left| \frac{1}{i(\omega_k - \omega_{i_0}) - i(\omega_{g_1} - \omega_{g_2}) - \frac{\Gamma'}{2} + S_{g_1 g_2, g_1 g_2}} \right| g_1 g_2 \right\rangle \\
 & \quad \times \left\langle g_1 f_5 \left| \frac{1}{-i(\omega_{i_0} - \Omega) - (\omega_{g_1} - \omega_{f_5}) - \frac{\Gamma + \Gamma'}{2}} \right| g_1 f_5 \right\rangle. \quad (18)
 \end{aligned}$$

Since  $\mathcal{H}_0^x \gg \Gamma$ ,  $S$  these contributions will be appreciable only if the imaginary parts of the denominators of the first and second Liouville matrices can be made to vanish simultaneously.

In the first case this implies :

$$\begin{cases} \omega_k = \omega_{i_0} = \Omega + \omega_{f_5} - \omega_{g_1} \\ \omega_k = \Omega + \omega_{f_1} - \omega_{g_2} \end{cases}$$

and therefore :

$$\omega_{f_1} - \omega_{g_2} = \omega_{f_5} - \omega_{g_1}$$

which in the absence of degeneracy can be achieved only if  $f_1 = f_5$  and  $g_2 = g_1$ . Anyhow this contribution corresponds to quasi-elastic scattering.

In the second case we must have :

$$\begin{cases} \omega_k = \omega_{i_0} + \omega_{g_1} - \omega_{g_2} = \Omega + \omega_{f_5} - \omega_{g_2} \\ \omega_k = \Omega + \omega_{f_1} - \omega_{g_2} \end{cases}$$

i.e.  $\omega_{f_5} = \omega_{f_1}$  and consequently  $f_1 = f_5$ . This contribution corresponds to inelastic scattering (Raman effect).

Let us now recapitulate the contributions to the scattered light, of the three terms of eq. (9).

— For the first term  $I_1$  (with zero integrated area) :

$$\omega_k = \omega_{i_0} \quad \text{or} \quad \omega_k = \omega_{i_0} + \omega_{g_1} - \omega_{g_2}$$

i.e. the frequency of the scattered light can differ from that of the incident light only by the hyperfine frequency of the ground state.

— For the second and third terms  $I_2$  and  $I_3$  :

$$\omega_k = \Omega + \omega_{f_3} - \omega_{g_7}.$$

If  $f_3 = f_5$  we have a contribution of the same type as that of the first term. This is what occurs when there is no relaxation in the excited state.

On the contrary when  $f_3 \neq f_5$  (and assuming a different h.f.s. in the excited and ground states) we have new lines in the scattered spectrum. The first term  $I_1$  of eq. (9) does not contribute to these new lines.

Consequently if we know the level scheme of the Mössbauer states, information on relaxation can be obtained by comparing the integrated area of the new lines with the sum of the integrated areas of the lines originating from the selectively populated state.

*Remark* : in this paragraph we have assumed that under the effect of selective excitation only the diagonal matrix element  $\langle f_5 | \sigma_{in}^I | f_5 \rangle$  of the excited density matrix was non-zero. In certain cases it could happen that off-diagonal matrix elements

$$\langle f_1 | \sigma_{in}^I | f_5 \rangle \quad \text{or} \quad \langle f_5 | \sigma_{in}^I | f_1 \rangle$$

be excited. But they are decoupled from the populations by the secular approximation and their contri-

bution to  $I_2$  and  $I_3$  would be negligible compared to that of  $\langle f_5 | \sigma_{in}^1 | f_5 \rangle$  because the intermediate Liouville matrix in  $I_2$  and  $I_3$  would be of order

$$|1/(\omega_{f_1} - \omega_{f_5})| \ll |1/(\Gamma - S)|.$$

We will now illustrate these considerations by a simple example where the ground state has no hyperfine structure so that the first term  $I_1$  of eq. (9) only gives rise to elastic scattering.

**3.4 SIMPLE NUMERICAL EXAMPLE.** — Let us consider a Mössbauer transition  $I = 2$  (excited)  $\rightarrow I_g = 0$  (ground state) in the presence of hyperfine coupling with an electronic spin  $S = \frac{1}{2}$  (as for  $\text{Yb}^{170}$  in gold). The excited state gives rise to two hyperfine levels  $F = \frac{5}{2}$  and  $F = \frac{3}{2}$ , while the ground state becomes a degenerate doublet  $G = S = \frac{1}{2}$ . In the absence of relaxation the absorption Mössbauer spectrum is composed of two lines, A with frequency

$$\omega_A = \omega_{F=5/2} - \omega_G$$

and B with frequency  $\omega_B = \omega_{F=3/2} - \omega_G$ .

We irradiate the atom with *natural* (unpolarized) gamma radiation and observe the frequency spectrum of the radiation scattered at right angle. The angular selection rules in this case ( $L = 2$ , electric quadrupole transition) are represented by eq. (69) of part I.

Since only  $P_{11}(\mathbf{k}_i)$  and  $P_{-1-1}(\mathbf{k}_i)$  are non-zero, the only elements of the density matrix of state I which can be excited have the form :

$$\sigma_{f_1 f_5} \propto \sum_{M=-1}^{+1} \langle f_1 | T_{LM} | g_1 \rangle \sigma_{g_1 g_1} \times \langle g_1 | T_{LM}^+ | f_5 \rangle \{ \dots \} \quad (19)$$

or in view of the selection rules for the  $T_{LM}$ , the form  $\sigma_{mm}^{FF'}$ . As mentioned in the preceding paragraph the off-diagonal terms  $F \neq F'$  can be neglected and we only have to consider the populations  $p_m$  of  $F = \frac{5}{2}$  and  $p'_m$  of  $F = \frac{3}{2}$ . On the other hand since  $I_g = 0$ , it is possible to show that the radiative transition amplitudes are simply given by :

$$\langle Fm_F | T_{LM} | Gm_g \rangle = \text{const} \langle LMGm_g | LGFm_F \rangle. \quad (20)$$

Let us for example irradiate at  $\omega_A \equiv \omega_{5/2} - \omega_G$ . We have for the populations the initial values  $p_{in}^1$  :

$$\begin{cases} p_{5/2} = p_{-5/2} = 0; \\ p_{3/2} = p_{-3/2} = \frac{4}{5}; \\ p_{1/2} = p_{-1/2} = \frac{2}{5}; \\ p'_m = 0 \text{ for all } m. \end{cases}$$

When we observe at  $\pi/2$  and take account of eq. (69) of I we have as a function of the final populations  $p_{ev}^1(1/\Gamma)$  :

— a line at  $\omega_A$  with integrated intensity proportional to :

$$p_{5/2} + p_{-5/2} + p_{3/2} + p_{-3/2} + \frac{2}{5}(p_{1/2} + p_{-1/2});$$

— a line at  $\omega_B$  with integrated intensity proportional to :

$$p'_{3/2} + p'_{-3/2} + \frac{3}{5}(p'_{1/2} + p'_{-1/2}).$$

If there is no relaxation in the excited state

$$p_{ev}^1(1/\Gamma) = p_{in}^1.$$

Then we have only one line at  $\omega_A$  with intensity 48/25 and nothing at  $\omega_B$ .

On the contrary if there is complete redistribution before reemission [3] we will have one line A' at  $\omega_A$  with intensity 288/250 and one line B' at  $\omega_B$  with intensity 192/250. Relaxation has given rise to an additional line in the spectrum.

More generally in the intermediate range  $S \sim \Gamma$  the ratio of the integrated areas of B' and A' will depend on  $S$  and, as already said, can be used to determine the relaxation time between the two hyperfine levels.

**4. Diagonal case. Comparison with Balko and Hoy theory.** — Let us finally consider the case of a completely anisotropic h.f.s. in both the excited and ground nuclear states :

$$\begin{cases} \mathcal{H}_I = AI_z S_z \\ \mathcal{H}_{I_g} = AI_{gz} S_z \end{cases} \quad (21)$$

In this situation and if we take account of the fact that  $H_a(\mathbf{k})$  only acts on nuclear variables, and relaxation only acts on electronic variables, eq. (9) greatly simplifies. Let us set :

$$|f\rangle = |m, s\rangle \quad \text{and} \quad |g\rangle = |\mu, s\rangle$$

where  $m, \mu, s$  are eigenvalues respectively of  $I_z, I_{zg}$  and  $S_z$ .

If we assume that  $S = \frac{1}{2}$  and that the relaxation of S can be treated within the white spectrum approximation ( $k_B T \gg \mathcal{H}_0^x$ ), its relaxation properties are the same in the absence or in the presence of an hyperfine coupling. Therefore the relaxation matrix of S has the form

	++	--	++	--
++	$-\frac{1}{2T_1}$	$\frac{1}{2T_1}$	0	0
--	$\frac{1}{2T_1}$	$-\frac{1}{2T_1}$	0	0
+-	0	0	$-\frac{1}{T_2}$	0
-+	0	0	0	$-\frac{1}{T_2}$

There is no coupling between diagonal and off-diagonal elements. Consequently if the density matrix of  $S$  is initially diagonal it remains diagonal and we can reduce the above relaxation matrix to its upper left quarter (as already noted by Blume in another context). This means that a quantity

$$\left\langle f_4 g_4 \left| \frac{1}{i(\omega_k - \Omega) - \frac{\Gamma}{2} - \frac{i}{\hbar} \mathcal{H}_0^x + S} \right| f_1 g_8 \right\rangle$$

must have the form

$$\left\langle m_1 \mu_4, s_4 s_4 \left| \frac{1}{i(\omega_k - \Omega) - \frac{\Gamma}{2} - \frac{i}{\hbar} \mathcal{H}_0^x + S} \right| m_1 \mu_4, s_3 s_3 \right\rangle.$$

In what follows we shall therefore use the abbreviated notation

$$| m_1 \mu_4 s_3 s_3 \rangle \rightarrow | m_1 \mu_4 s_3 \rangle. \quad (22)$$

Let us now go back to eq. (9). There is nothing new with the interpretation of  $I_1$ . As concerns the second and third terms  $I_2$  and  $I_3$  the intermediate Liouville matrix will be appreciable only if the two nuclear states on each side are the same (no contribution of  $\mathcal{H}_0^x$ ).

Then they can be interpreted as

$$- \sum | \langle \mu_4 | H_a^+(\mathbf{k}) | m_1 \rangle |^2 \left\langle m_1 \mu_4 s_4 \left| \frac{1}{i(\omega_k - \Omega) - \frac{\Gamma}{2} - \frac{i}{\hbar} \mathcal{H}_0^x + S} \right| m_1 \mu_4 s_3 \right\rangle \langle m_1 m_1 s_3 | \sigma_{ev}(1/\Gamma) | m_1 m_1 s_3 \rangle \quad (23)$$

where

$$\langle m_1 m_1 s_3 | \sigma_{ev}(1/\Gamma) | m_1 m_1 s_3 \rangle = \sum_{s_2} \left\langle m_1 m_1 s_3 \left| \frac{-\Gamma}{-\Gamma + S} \right| m_1 m_1 s_2 \right\rangle \langle m_1 m_1 s_2 | \sigma_{in}^1 | m_1 m_1 s_2 \rangle. \quad (24)$$

If relaxation effects  $S \sim \Gamma$  we may as a first approximation neglect  $S$  in the first and third Liouville matrices of  $I_2$  and  $I_3$ . It follows that :

$$I_2 + I_3 \propto - \sum \left[ p_{m_{1\uparrow}}^{ev} \left( \frac{1}{\Gamma} \right) \frac{1}{i(\omega_k - \Omega) - \frac{\Gamma}{2} - i(\omega_{m_1} - \omega_{\mu_4})} + p_{m_{1\downarrow}}^{ev} \left( \frac{1}{\Gamma} \right) \frac{1}{i(\omega_k - \Omega) - \frac{\Gamma}{2} + i(\omega_{m_1} - \omega_{\mu_4})} \right]. \quad (25)$$

The second Liouville matrix in  $I_2$  and  $I_3$  is ( $W = \frac{1}{2} T_1$ ) :

$$\frac{1}{-\Gamma + S} = \left( \begin{array}{c|c} -W - \Gamma & W \\ \hline -W & -W - \Gamma \end{array} \right)^{-1} = \frac{1}{\Gamma(\Gamma + 2W)} \left( \begin{array}{c|c} -W - \Gamma & -W \\ \hline -W & -W - \Gamma \end{array} \right). \quad (26)$$

Assume that the incident radiation populates selectively state  $m_{1\uparrow} : p_{m_{1\uparrow}}^{in} = 1 ; p_{m_{1\downarrow}}^{in} = 0$ . The final populations  $p_{ev}(1/\Gamma)$  are given by  $(-\Gamma)$  the first column of the matrix (26)

$$p_{m_{1\uparrow}}^{ev} = \frac{W + \Gamma}{(\Gamma + 2W)} ; \quad p_{m_{1\downarrow}}^{ev} = \frac{W}{(\Gamma + 2W)}. \quad (27)$$

Inserting this into eq. (25) we find that the scattered spectrum contains

$$\text{Re}(I_2 + I_3) \propto \text{Re} - \sum_{\mu_4} \left\{ \frac{W + \Gamma}{(\Gamma + 2W)} \frac{1}{i(\omega_k - \Omega) - \frac{\Gamma}{2} - i(\omega_{m_1} - \omega_{\mu_4})} + \frac{W}{(\Gamma + 2W)} \frac{1}{i(\omega_k - \Omega) - \frac{\Gamma}{2} + i(\omega_{m_1} - \omega_{\mu_4})} \right\}. \quad (28)$$

In the absence of relaxation ( $W = 0$ ) we only have the emission lines from the initially excited level  $m_{1\uparrow}$ . If there is relaxation we have in addition emission lines from  $m_{1\downarrow}$ . Notice that in practice the incident radiation populates simultaneously the degenerate levels  $m_{1\uparrow}$  and  $-m_{1\downarrow}$  but the spectrum remains the same. Notice also that eq. (28) would also be valid for a spin  $S \neq \frac{1}{2}$  in the case where the lowest electronic state associated with this spin would be a doublet  $| S_z = \pm S \rangle$ , the upper states  $S_z \neq S$  being empty.

We must now compare our results with those of

Balko and Hoy [6]. Our expressions (27) for  $p^{ev}$  are in agreement with eq. (19) of [6] and our eq. (28) for the lineshape is in agreement with eq. (14) of [6], if in  $A^{-1}$  (eq. (16) of [6]), we neglect broadening terms, as we have done in the denominators of our own eq. (28). Indeed, as already mentioned, because of the contribution of the first term  $I_1$  of eq. (9), only relative integrated areas have real significance and when the lines are well resolved, their integrated areas are usually not affected by relaxation broadening [3].

We may however wonder whether this simple



model is relevant to the Morin transition in  $\alpha\text{Fe}_2\text{O}_3$ . First, many authors admit that the gradual character of the Morin transition is due not to relaxation effects, but to a distribution of the transition temperatures of different crystallites. Second, if relaxation effects happened to exist, it would seem surprising that we would have slow critical relaxation over more than 10 K. Third the existence of additional lines in figure (18) of [6] is not absolutely evident : the experimental curves could be fitted differently. Finally at the Morin transition the ferromagnetic spins rotate by  $\pi/2$  and this situation would be better represented by a stochastic process in which the nuclear spin would see its hamiltonian jump between the values

$$\mathcal{H}_0^1 = -\hbar\gamma_n H_n I_z \quad \text{and} \quad \mathcal{H}_0^2 = -\hbar\gamma_n H_n I_x.$$

Since these two values do not commute one would have to resort to Blume's theory [7].

### 5. Summary. Comparison of the different Mössbauer techniques.

$\mathcal{H}_0$  = hyperfine hamiltonian ;

$\Gamma$  = natural linewidth of the excited Mössbauer level ( $\hbar\Gamma \ll \mathcal{H}_0$  for well resolved Mössbauer spectra) ;

$S$  = relaxation supermatrix.

Information on relaxation available from the different techniques is the following :

#### 5.1 EMISSION (two Liouville matrices)

$$\text{Ranges } \begin{cases} S \sim \mathcal{H}_0/\hbar \\ S \sim \Gamma \text{ if simultaneously } \mathcal{H}_0 > k_B T. \end{cases}$$

Possibility of observing excited electronic levels out of thermal equilibrium if incomplete rearrangement after a  $\beta$  transition.

#### 5.2 TRANSMISSION (one Liouville matrix)

$$\text{Range } S \sim \mathcal{H}_0/\hbar.$$

Electronic level(s) in the excited Mössbauer state is (are) the same as in the ground state

#### 5.3 SCATTERING (nine Liouville matrices)

Ranges  $S \sim \mathcal{H}_0/\hbar$  but extremely complicated  
 $S \sim \Gamma$  whatever  $\mathcal{H}_0/k_B T$  (by using selective excitation).

Electronic level(s) in the excited Mössbauer state is (are) the same as in the ground state.

It appears that Mössbauer scattering is the only technique available for studying the range  $S \sim \Gamma$  when  $\mathcal{H}_0/k_B T \ll 1$ . However situations where relaxation is slow enough so that  $S \sim \Gamma$  at temperatures  $k_B T \gg \mathcal{H}_0$  will probably not be very numerous.

On the other hand, and where possible, comparison between emission and transmission experiments would be a good way to check the existence of incomplete electronic rearrangement following  $\beta$  transitions : indeed in that case emission and transmission spectra should be quite different.

**Acknowledgments.** — I am very grateful to Dr. D. Spanjaard who kindly checked the algebra of these two papers. I also thank Drs A. M. Afanasev and V. D. Gorobchenko for a preprint of their work [8]. I am indebted to the referee for pointing out a small error in par  $\Gamma$ .

*Note added in proof* : The english translation of ref. [8] has been published recently : *Sov. Phys. JETP* **40** (1974) 1114.

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