

# Interpretation of low-temperature Mössbauer spectra in the presence of Kondo deviations.

## I. General considerations

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(Received 27 December 1973)

In this paper, we first derive the general expression for the Mössbauer line shape of a powder source when cascade effects come into play. Then we consider the case of a paramagnetic impurity—in a metal—which exhibits an incipient Kondo effect, and we examine the problems which arise when the relaxation of this impurity by the conduction electrons is studied by Mössbauer spectroscopy, i.e., in the presence of hyperfine coupling. We extend conventional relaxation theory up to third order in  $\mathcal{X}_1 = -2J_{sf}\alpha\vec{S}\cdot\vec{s}$  and investigate under what conditions the third-order damping terms can be expressed as products of first- and second-order transition amplitudes. We find that this occurs when either “extreme narrowing” or “secular” approximations are valid; in these two cases, the Kondo correction to the relaxation matrix reduces to the standard computation of the second-order transition amplitude. In the following paper, these results are applied to the study of relaxation effects of the hyperfine populations at low temperatures, in the Mössbauer cascade of an  $Au^{170}\text{Yb}$  source.

### I. INTRODUCTION

The effects of electronic relaxation on the Mössbauer spectra of  $^{170}\text{Yb}$  in gold were considered in a previous publication.<sup>1a</sup> Let us recall that the 84-keV Mössbauer transition of  $^{170}\text{Yb}$  takes place between two nuclear levels:  $I=2$  (excited, inverse nuclear lifetime  $\Gamma=2\pi\times 69.4$  MHz) and  $I_g=0$  (fundamental). In cubic gold the lowest electronic level of the  $\text{Yb}^{3+}$  ion is the doublet  $\Gamma_7$  with effective spin  $S=\frac{1}{2}$ , which is separated from the next electronic levels by about 80 K. The electronic relaxation is due to the exchange coupling  $-2\alpha J_{sf}\vec{S}\cdot\vec{s}$  of the localized spin  $\vec{S}$  with the conduction electrons. In the experiments the  $Au^{170}\text{Yb}$  sample is used as a powder source.

Under the influence of the hyperfine coupling  $\mathcal{H}_{\text{hf}}=A\vec{I}\cdot\vec{S}$  inside  $\Gamma_7$ , the excited nuclear level splits into two hyperfine levels  $\vec{F}=\vec{I}+\vec{S}$  with  $F=\frac{5}{2}$  and  $F=\frac{3}{2}$ , separated by an interval  $\Delta=\frac{5}{2}A$  where  $A/h=910$  MHz. In Ref. 1, it was assumed that the temperature was much higher than  $\Delta/k_B\sim 0.11$  K. Then the Mössbauer line shape is given by the simple formula

$$I(\omega)\propto \text{Re} \int_0^\infty e^{-p\tau} d\tau \text{Tr}\{\vec{M}^\dagger(0)\vec{M}(-\tau)\}, \quad (1)$$

where  $p=\Gamma/2-i\omega$  ( $\omega$  is the distance to the center of the Mössbauer spectrum), and  $\vec{M}$  is the nuclear electromagnetic moment responsible for the Mössbauer transition.

In Ref. 1a, relaxation effects were calculated only up to second order in  $J_{sf}$ ; in that case, when  $T\gg\Delta/k_B$  it is possible to make the “extreme-narrowing” assumption. Then taking account of the “spherical” symmetry of the problem, the relaxation matrix  $R$  takes a very simple form and can be expressed as a function of a single parameter  $1/T_1$ , where  $T_1$  can be identified with the longitudinal

relaxation time  $T_{1s}$  which would characterize the electronic spin in the absence of hyperfine structure. As a function of temperature  $T_{1s}$  is given by the Korringa law:

$$1/T_{1s}=C_K T=(4\pi/\hbar)\alpha^2 J_{sf}^2 n^2(E_F)k_B T. \quad (2)$$

Interpretation of experimental data<sup>2</sup> according to the theory of Ref. 1a is indeed in agreement with such a law. But very careful measurements<sup>3</sup> indicate that below 5 K,  $1/T_1$  as deduced from Mössbauer spectra deviates slightly from linearity. This deviation has been attributed by Gonzalez and Imbert<sup>3</sup> to the onset of Kondo effect at low temperatures. However, the standard Kondo correction to  $1/T_{1s}$  is of third order in  $J_{sf}$ , while the theory of Ref. 1 is only valid up to second order in  $J_{sf}$ . Before interpreting the experimental data according to formula (15.2) of Kondo's review paper,<sup>4</sup> it is therefore necessary to be sure that this is legitimate when  $1/T_1$  is extracted from a Mössbauer spectrum in the presence of hyperfine structure.

Finally, as mentioned in Ref. 1a, it has been observed by Gonzalez and Imbert that at very low temperatures,  $T\sim\Delta/k_B$ , additional information on the electronic relaxation can be obtained using the fact that the ratio of the two residual Mössbauer lines tends to depart from its high-temperature value,  $\frac{2}{3}$ , owing to unequal populations of the hyperfine sublevels of the 84-keV state  $I$ . In a source, this state is populated by the radioactive decay of an upper state, with a population ratio which differs from the Boltzmann value. Then if electronic relaxation times at temperatures  $T\sim\Delta/k_B$  happen to be comparable to the nuclear lifetime of the 84-keV state, partial redistribution of the population will occur before the emission of the Mössbauer  $\gamma$  ray, which will alter the line in-

tensities. The study of these intensities will therefore give information on electronic relaxation in a temperature range where alteration of the line shape can no longer be used for such a purpose.<sup>5</sup> On the other hand, at such low temperature, it may be expected that the Kondo correction to relaxation rates will saturate and change from a form  $\ln|k_B T/D|$  to a form  $\ln|\Delta/D|$ .

For all these reasons, in the present paper, we will first give the general expression of the Mössbauer line shape of a powder source at arbitrary temperature. We shall also recall the form of the second-order relaxation equations at low temperatures.<sup>1b</sup> Then, we will formally extend relaxation equations to third order and investigate in what cases the third-order terms can be reduced to products of first- and second-order transition amplitudes  $A_1$  and  $A_2$ , since the standard Kondo correction to the electronic relaxation time<sup>4</sup> is derived from cross terms of type  $A_1 A_2$ . We will find that this reduction does occur in two cases: (a) "extreme narrowing" (which is realized at temperatures  $k_B T \gg \Delta$ ; it is then possible to justify *a posteriori* the interpretation of Ref. 3) and (b) "secular approximation" (which, in the case of  $Au^{170}Yb$ , is realized in the low-temperature range  $k_B T \sim \Delta$ , where population effects come into play).

As an application of these general considerations, in the following paper,<sup>6</sup> hereafter referred to as II, we will first derive the relaxation equations of the populations at low temperatures up to second order in  $J_{sf}$ . Then we shall compute the Kondo correction to the transition probabilities and examine how it behaves when  $k_B T \sim \Delta$ . Finally, we will indicate how electronic relaxation rates can be obtained from the Mössbauer line intensities. These results will be applied to the interpretation of the low-temperature Mössbauer spectra of  $Au Yb$ .

Unless otherwise stated the notation will be the same as in Ref. 1.

## II. GENERAL EXPRESSION FOR THE MÖSSBAUER LINE SHAPE OF A MÖSSBAUER POWDER SOURCE

From Eqs. (A1) and (A2) of Ref. 7, the Mössbauer intensity  $I(\omega)$  emitted by a source is proportional to

$$I(\omega) \propto \text{Re} \int_{-\infty}^t dt' \int_{-\infty}^{t''} dt'' e^{(i\omega - \Gamma/2)(t-t')} e^{-\Gamma(t'-t'')} \times \text{Tr} \{ \bar{M} U^\dagger(t, t') \bar{M}^\dagger U(t, t') U(t', t'') \sigma_{in}^I(t'') \times U^\dagger(t', t'') \}, \quad (3)$$

where  $U(t', t'')$  is the evolution operator, between times  $t'$  and  $t''$ , of the radioactive atom under the effect of the Hamiltonian  $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1 + \mathcal{H}_B$  (as defined in Ref. 1:  $\mathcal{H}_1$  is the relaxation Hamiltonian,  $\mathcal{H}_B$  is the lattice Hamiltonian, and we assume no

electronic Zeeman effect so that  $\mathcal{H}_0 = \mathcal{H}_{nT}$ ) acting inside each nuclear state.  $\sigma_{in}^I(t'')$  is the density matrix of state  $I$  just after feeding by radioactive decay of an upper state  $I_i$  at time  $t''$ ; in practice it does not depend on  $t''$ ;

$$\sigma^I(t', t'') \equiv U(t', t'') \sigma_{in}^I U^\dagger(t', t'') \quad (4)$$

represents what this matrix has become at  $t'$ .  $\bar{M}$  is the nuclear electric or magnetic multipole moment which induces the Mössbauer transition. In the Heisenberg representation

$$\bar{M}^\dagger(t, t') = U^\dagger(t, t') \bar{M}^\dagger U(t, t'). \quad (5)$$

Then

$$I(\omega) \propto \text{Re} \int_{-\infty}^t dt' \int_{-\infty}^{t''} dt'' e^{(i\omega - \Gamma/2)(t-t')} \times e^{-\Gamma(t'-t'')} \text{Tr} \{ \bar{M}^\dagger(t, t') \sigma^I(t', t'') \bar{M} \}. \quad (6)$$

One notices that if the Hamiltonian  $\mathcal{H}$  is a stationary (no rf), the double time integral factorizes. Let us define

$$\sigma^I(1/\Gamma) = \Gamma \int_0^\infty e^{-\Gamma\tau'} U(\tau') \sigma_{in}^I U^\dagger(\tau') d\tau' \quad (7)$$

(average density matrix of level  $I$  in the presence of radiative feeding and deexcitation and of relaxation). We find that

$$I(\omega) \propto \text{Re} \int_0^\infty d\tau \text{Tr} \{ \bar{M}^\dagger(0) \sigma^I(1/\Gamma) \bar{M}(-\tau) \} \times e^{(i\omega - \Gamma/2)\tau}. \quad (8)$$

At high temperatures ( $k_B T \gg \Delta$ ),  $\sigma^I(1/\Gamma)$  as well as  $\sigma_{in}^I$  are proportional to the unit matrix and this formula reduces to Eq. (i) as it should.

Using the Liouville formalism, it is interesting to see how the explicit expression of the line shape derived from Eq. (8) compares with the high-temperature case, Eqs. (15) and (18) of Ref. 1a. After rearrangement of the matrix elements of the evolution operator  $U$ , and denoting by  $|f\rangle$  and  $|g\rangle$  some arbitrary basis sets for the excited and fundamental states of the radiative atom, it turns out that

$$I(\omega) \propto \text{Re} \sum_{f_1 f_2 f_3 f_4 f_5, g_1 g_2} \langle f_1 | \bar{M} | g_1 \rangle \langle g_2 | \bar{M}^\dagger | f_2 \rangle \times \left( \langle g_1 f_3 | \frac{-1}{i\omega - \Gamma/2 + (i/\hbar)\mathcal{H}_0^\times + R} | g_2 f_2 \rangle \right) \times \left( \langle f_3 f_1 | \frac{-\Gamma}{-\Gamma - (i/\hbar)\mathcal{H}_0^\times + S} | f_4 f_5 \rangle \langle f_4 | \sigma_{in}^I | f_5 \rangle \right), \quad (9)$$

in which the relaxation supermatrices  $R$  and  $S$  associated with  $\mathcal{H}_1$  are defined in Ref. 1b and the second parenthesis represents  $\langle f_3 | \sigma(1/\Gamma) | f_1 \rangle$ . Let us recall that  $R$  is the transposed matrix of  $S$ :  $R = S^T$ , and that at high temperatures:  $R = S^T = S$ .

It appears that the general expression for  $I(\omega)$  involves two Liouville matrices instead of one at

high  $T$  (where  $\langle f_1 | \sigma(1/\Gamma) | f_3 \rangle \propto \delta_{f_1 f_3}$ ). For  $Au^{170}Yb$ ,  $I=2$ ,  $I_g=0$ ,  $S=\frac{1}{2}$ , the first matrix is  $20 \times 20$  and the second one is  $100 \times 100$ . Since  $\sigma_{in}^I$  is due to radiative feeding, with respect to a basis  $|FF_z\rangle$  it is diagonal:  $F_4=F_5$ ,  $m_{F_4}=m_{F_5}$ . As we shall see below (Sec. V) in the presence of relaxation due to the conduction electrons, we must for symmetry reasons have  $m_{F_1}=m_{F_3}$ , but unless the secular approximation is valid  $F_1$  may differ from  $F_3$  (i. e., even if the initial density matrix is diagonal,  $\sigma$  may temporarily acquire off-diagonal elements before reaching Boltzmann equilibrium; see Sec. III). Therefore, with respect to a basis  $|FF_z\rangle$  the second Liouville matrix reduces to  $(18-1)^2$  without the secular approximation and to  $(10-1)^2$  with the secular approximation.

The first Liouville matrix was considered in Ref. 1a, where the high-temperature expression of  $R$  was calculated up to second order in  $J_{sf}$ . In that case, Gonzalez found that with respect to eigenvectors of  $(\vec{I}^2, I_z)$  and  $(\vec{S}^2, S_z)$  it could be reduced to matrices of dimension  $4 \times 4$  or less. A similar reduction occurs where the matrix is referred to a basis  $|FF_z\rangle$  in the excited state and a basis  $|SS_z\rangle$  in the ground state ( $I_g=0$ ): Indeed a matrix element  $\langle F, m_F | \vec{M} | S, \frac{1}{2} \rangle$  is only coupled by relaxation to elements of type  $\langle F'', m_{F''} | \vec{M} | S, \frac{1}{2} \rangle$  and  $\langle F'', m_{F''}-1 | \vec{M} | S, -\frac{1}{2} \rangle$ . The arguments of Sec. VB of the present paper show that these conclusions remain valid when  $R$  is computed up to third order in  $J_{sf}$  at arbitrary temperature.

In conclusion, we have two simple situations: high  $T$ , i. e.,  $k_B T \gg \Delta$ , where the second parentheses in Eq. (9) may be replaced by  $\delta_{f_1 f_3}$  and where the computation of  $R$  is greatly simplified by the extreme-narrowing assumption (see Sec. VB1); very low  $T$ , for which  $R \ll \mathcal{H}_0^x$ , where we may use the secular approximation for calculating the Liouville matrices. In that case where  $\sigma^I$  remains diagonal (in the basis  $|FF_z\rangle$ ) we may drop  $\mathcal{H}_0^x$  in the denominator of the reduced form of the second Liouville matrix. On the contrary,  $\mathcal{H}_0^x$  plays a predominant role in the first one, which determines the line profile of the spectrum. If we neglect  $R$  in this matrix, it gives rise to a spectrum composed of two lines with separation  $\Delta$  and width  $\Gamma$ . If we now assume that  $R$  is nonzero but small compared with  $\mathcal{H}_0^x$ , it is possible to demonstrate (Sec. VB3) that  $R$  may alter the profile of the two hyperfine lines, but not their integrated intensities. The respective weights of these lines are therefore determined by  $\sigma^I(1/\Gamma)$ ; i. e., we have one line at  $A$  with weight  $P(1/\Gamma)$  and one line at  $-\frac{3}{2}A$  with weight  $Q(1/\Gamma)$ , where  $P(1/\Gamma)$  and  $Q(1/\Gamma)$  are the average populations of states  $F=\frac{5}{2}$  and  $F=\frac{3}{2}$ . Notice, however, that from an experimental point of view this temperature range, where  $R \ll \mathcal{H}_0^x$ , is interesting only if simultaneously  $R \sim \Gamma$  and  $k_B T$

$\sim \Delta$ : Indeed these are necessary conditions in order to be able to extract useful information on the relaxation from the experimental values of  $P(1/\Gamma)$  and  $Q(1/\Gamma)$ . As will be seen in paper II, these conditions happen to be fulfilled for  $Au^{170}Yb$ .

The intermediate region, where  $k_B T/\Delta$  is not big enough so that one can use the extreme-narrowing approximation, and  $R$  is not small enough so that one can use the secular approximation, is complicated and we shall not consider it in detail in what follows.

### III. FORMAL SECOND-ORDER RELAXATION THEORY

In this section, we shall first examine a minor point concerning the diagonal or nondiagonal character of the density matrix  $\sigma^I$ , which was mentioned in Sec. II. Then, with a view toward subsequent comparison between second- and third-order terms, we shall give a general formulation of relaxation equations of a density matrix in terms of the evolution operator  $U$ , and study the form of the different terms which appear.

#### A. Nondiagonal evolution of a diagonal density matrix not in thermal equilibrium

In the presence of coupling  $\mathcal{H}_1 = \sum_q K^q F^q$  with the lattice described by a Hamiltonian  $\mathcal{H}_B$  and a Boltzmann density matrix  $\rho$ , the equation of motion of the density matrix  $\sigma$  of the radioactive atom is,<sup>1b</sup> in the interaction representation,

$$\frac{d\sigma^*}{dt} = -\frac{1}{\hbar^2} \int_0^\infty \text{Tr}_{\text{latt}} \{ [\mathcal{H}_1^*(t), [\mathcal{H}_1^*(t-\tau), \rho\sigma^*(t)]] \} d\tau. \quad (10)$$

After standard manipulation of the correlation functions of the lattice, and assuming that for symmetry reasons only averages  $F^{-q} F^q$  are different from zero, it also takes the form, with respect to eigenstates of  $\mathcal{H}_0$  (unperturbed radioactive atom),

$$\begin{aligned} \frac{d}{dt} \sigma_{ad}^*(t) = \sum_{a,b,c} \frac{1}{2} [ & -e^{i(\omega_{ad}-\omega_{cd})t} K_{ab}^{-q} K_{bc}^q \sigma_{cd}^*(t) J_q(\omega_{cb}, T) \\ & + e^{i(\omega_{ad}-\omega_{bc})t} K_{ab}^{-q} \sigma_{bc}^*(t) K_{cd}^q J_{-q}(\omega_{cd}, T) \\ & + e^{i(\omega_{ad}-\omega_{bc})t} K_{ab}^q \sigma_{bc}^*(t) K_{cd}^{-q} J_q(\omega_{bc}, T) \\ & - e^{i(\omega_{ad}-\omega_{ab})t} \sigma_{ab}^*(t) K_{bc}^q K_{cd}^{-q} J_{-q}(\omega_{bc}, T) ], \end{aligned} \quad (11)$$

where we have defined  $\sigma^*(t) = e^{(i/\hbar)\mathcal{H}_0 t} \sigma e^{-(i/\hbar)\mathcal{H}_0 t}$ ,  $F^q \sigma^*(t) = e^{i\mathcal{H}_B t/\hbar} F^q e^{-i\mathcal{H}_B t/\hbar} \sigma^*$ , and

$$\begin{aligned} J_q(\omega_{cb}, T) = \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} d\tau e^{i\omega_{cb}\tau} \\ \times \text{Tr}_{\text{latt}} \{ \rho F^{-q}(t) F^q(t-\tau) \}, \end{aligned} \quad (12)$$

with

$$J_{-q}(-\omega, T) = e^{-\hbar\omega/k_B T} J_q(\omega, T). \quad (12')$$

Let us recall that by definition (Ref. 1b) of the relaxation supermatrix  $S$ , Eq. (11) may also be written as

$$\frac{d}{dt} \sigma_{ad}^*(t) = \sum_{bc} \exp[i(\omega_{ad} - \omega_{bc})t] S_{ad,bc} \sigma_{bc}^*(t). \quad (13)$$

Equations (11) and (13) were first given in the present form in Ref. 1b. The only new point which we want to emphasize here is that when  $\sigma$  is the density matrix  $\sigma^I$  of the excited nuclear state and when  $\sigma^{I*}$  is diagonal at time zero, but not in thermal equilibrium, it may temporarily acquire nondiagonal matrix elements before reaching equilibrium. Indeed, assuming  $a \neq d$  we have that

$$\begin{aligned} \frac{d}{dt} \sigma_{ad}^*(t) = & - \sum_{qb} \frac{1}{2} e^{i\omega_{ad}t} \{ K_{ab}^{-q} K_{bd}^q [\sigma_{ad}^*(0) J_q(\omega_{db}, T) \\ & - \sigma_{bb}^*(0) J_{-q}(\omega_{bd}, T)] \\ & + K_{ab}^q K_{bd}^{-q} [\sigma_{aa}^*(0) J_{-q}(\omega_{ab}, T) \\ & - \sigma_{bb}^*(0) J_q(\omega_{ba}, T)] \}. \quad (14) \end{aligned}$$

Taking account of Eq. (12'), it appears that in the general case, the right-hand side of this equation only vanishes when thermal equilibrium is reached. However, one should not forget that when the energy levels of the atom are nondegenerate,  $d\sigma_{ad}^*/dt$  also vanishes, even in the absence of thermal equilibrium, as soon as the secular approximation can be made ( $\omega_{ad} = 0 \rightarrow a = d$  in that case). All these conclusions, which were derived for a simple example are clearly valid for arbitrary  $\mathcal{H}_1$ .

#### B. Formulation of relaxation equations in terms of evolution operators

We go back to the general relaxation equations of the density matrix of the radioactive atom in the presence of an unspecified  $\mathcal{H}_1$ . Instead of handling double (and in third order triple) commutators, we may write

$$\frac{d\sigma^*}{dt} = \text{Tr}_{\text{latt}} \left\{ \frac{dU^*}{dt} \rho \sigma^*(t) U^{*\dagger} + U^* \rho \sigma^*(t) \frac{dU^{*\dagger}}{dt} \right\}, \quad (15)$$

where the evolution operator  $U^*$  in the interaction representation is given by

$$\begin{aligned} U^* = & 1 + U_1^*(t) + U_2^*(t) + U_3^*(t) \\ = & 1 - \frac{i}{\hbar} \int_{-\infty}^t \mathcal{H}_1^*(t_1) dt_1 - \frac{1}{\hbar^2} \int_{-\infty}^t dt_1 \int_{-\infty}^{t_1} dt_2 \mathcal{H}_1^*(t_1) \mathcal{H}_1^*(t_2) \\ & + \frac{i}{\hbar^3} \int_{-\infty}^t dt_1 \int_{-\infty}^{t_1} dt_2 \int_{-\infty}^{t_2} dt_3 \mathcal{H}_1^*(t_1) \mathcal{H}_1^*(t_2) \mathcal{H}_1^*(t_3) \\ & + \dots \quad (16) \end{aligned}$$

Then, denoting by greek letters the eigenstates of the lattice ( $\mathcal{H}_B$ ) and setting  $V = U^*$ , we have in second order

$$\begin{aligned} \left( \frac{d\sigma_{ab}^*}{dt} \right)_{\text{2nd order}} = & \sum_{cd, \gamma\alpha} \left\{ \langle a\alpha | \frac{dV_1}{dt} | c\gamma \rangle \rho_{\gamma\gamma} \sigma_{cd}^*(t) \right. \\ & \times \langle d\gamma | V_1^\dagger | b\alpha \rangle + \langle a\alpha | V_1 | c\gamma \rangle \rho_{\gamma\gamma} \\ & \times \sigma_{cd}^*(t) \langle d\gamma | \frac{dV_1^\dagger}{dt} | b\alpha \rangle \\ & + \langle a\alpha | 1 | c\gamma \rangle \rho_{\gamma\gamma} \sigma_{cd}^*(t) \langle d\gamma | \frac{dV_2^\dagger}{dt} | b\alpha \rangle \\ & + \langle a\alpha | \frac{dV_2}{dt} | c\gamma \rangle \rho_{\gamma\gamma} \sigma_{cd}^*(t) \\ & \left. \times \langle d\gamma | 1 | b\alpha \rangle \right\}. \quad (17) \end{aligned}$$

It appears that contrary to standard transition-probability calculations, which only involve the square of the first-order transition amplitude ( $W_{mn} \propto \langle m | dV_1^\dagger/dt | n \rangle \langle n | V_1 | m \rangle + \text{c. c.}$ ), some terms here involve the second-order transition amplitude  $V_2$ . These are terms for which the matrix elements of  $\sigma^*$  in the left-hand side and in the right-hand side have one common atomic index ( $c = a$  or  $d = b$ ).

Explicit evaluation of Eq. (17) under the assumption of adiabatic switching of the perturbation  $\mathcal{H}_1$  leads to

$$\begin{aligned} \frac{d\sigma_{ab}^*(t)}{dt} = & \frac{1}{\hbar} \sum_{cd, \alpha\gamma} e^{(i/\hbar)(E_a - E_b - E_c + E_d)t} \rho_{\gamma\gamma} \sigma_{cd}^*(t) \left\{ \langle a\alpha | \mathcal{H}_1 | c\gamma \rangle \langle d\gamma | \mathcal{H}_1 | b\alpha \rangle \frac{1}{i[(E_d + E_\gamma) - (E_b + E_\alpha)] + x} \right. \\ & + \langle a\alpha | \mathcal{H}_1 | c\gamma \rangle \langle d\gamma | \mathcal{H}_1 | b\alpha \rangle \frac{1}{-i[(E_c + E_\gamma) - (E_a + E_\alpha)] + x} - \delta_{ac} \delta_{\alpha\gamma} \sum_{e\epsilon} \langle d\gamma | \mathcal{H}_1 | e\epsilon \rangle \langle e\epsilon | \mathcal{H}_1 | b\alpha \rangle \\ & \left. \times \frac{1}{-i[(E_e + E_\epsilon) - (E_d + E_\gamma)] + x} - \delta_{db} \delta_{\gamma\alpha} \sum_{e\epsilon} \langle a\alpha | \mathcal{H}_1 | e\epsilon \rangle \langle e\epsilon | \mathcal{H}_1 | c\gamma \rangle \frac{1}{+i[(E_e + E_\epsilon) - (E_c + E_\gamma)] + x} \right\}. \quad (18) \end{aligned}$$

In these expressions  $x$  is infinitesimally small and positive so that

$$\frac{1}{iE + x} = -i\mathcal{P}\frac{1}{E} + \pi\delta(E). \quad (19)$$

In standard relaxation theory, one notices that the terms which contain  $\delta$  functions correspond to damping, while terms containing principal parts  $\mathcal{P}$  correspond to frequency shifts. Although they

have some importance as light shifts in optical-pumping experiments, frequency-shift terms are usually dropped because of their assumed smallness. Then, one gets again an equation of type (11).

It appears that there are two kinds of principal-part terms. Two of them involve a summation over an intermediate virtual state  $|e\rangle$  and can more or less be interpreted as classical second-order perturbation terms. On the contrary, the other two which we shall call "spurious" do not involve any intermediate state and have no very obvious simple physical interpretation. However, since we retain their real counterparts in Eq. (11), there is no reason why we should omit them. These two terms have the interesting property that they cancel out in two cases: First, in the "secular approximation," i. e., in Eq. (18), one only keeps the terms for which  $E_a - E_b - E_c + E_d = 0$  or  $+E_d$

$-E_b = E_c - E_a$ ; second, in the "extreme narrowing" approximation, i. e. in the denominators of Eq. (18), one can neglect all atomic energy terms [e. g.,  $(E_d - E_b)$ ,  $(E_c - E_a)$ , ...].

Up to now, all relaxation treatments were based on the secular approximation so that these spurious terms did not appear. We shall see below that the same kind of trouble arises in third order, even in the damping terms.

#### IV. FORMAL THIRD-ORDER RELAXATION THEORY

This section arose from a question by Imbert asking whether the results of the second-order transition-probability calculation of paper II could also be derived by third-order relaxation theory.

According to Eqs. (16) and (17), the third-order contribution to  $d\sigma_{ab}^*/dt$  is

$$\left(\frac{d\sigma_{ab}^*}{dt}\right)_{3\text{rd order}} = \sum_{cd, \alpha\gamma} \rho_{\gamma\gamma} \sigma_{cd}^*(t) \left\{ \langle a\alpha | \frac{dV_1}{dt} | c\gamma \rangle \langle d\gamma | V_2^\dagger | b\alpha \rangle + \langle a\alpha | V_1 | c\gamma \rangle \langle d\gamma | \frac{dV_2^\dagger}{dt} | b\alpha \rangle + \langle a\alpha | \frac{dV_2}{dt} | c\gamma \rangle \langle d\gamma | V_1^\dagger | b\alpha \rangle \right. \\ \left. + \langle a\alpha | V_2 | c\gamma \rangle \langle d\gamma | \frac{dV_1^\dagger}{dt} | b\alpha \rangle + \langle a\alpha | 1 | c\gamma \rangle \langle d\gamma | \frac{dV_3^\dagger}{dt} | b\alpha \rangle + \langle a\alpha | \frac{dV_3}{dt} | c\gamma \rangle \langle d\gamma | 1 | b\alpha \rangle \right\}. \quad (20)$$

Let us first consider the first three terms. Omitting the factor

$$(1/\hbar) \sum_{\alpha\gamma, cd} \sigma_{cd}^*(t) \rho_{\gamma\gamma} e^{(i/\hbar)(E_a - E_b - E_c + E_d)t},$$

they are equal to

$$\langle | \frac{dV_1}{dt} | \rangle \langle | V_2^\dagger | \rangle = i \sum_{e\epsilon} \langle a\alpha | \mathcal{H}_1 | c\gamma \rangle \langle d\gamma | \mathcal{H}_1 | e\epsilon \rangle \langle e\epsilon | \mathcal{H}_1 | b\alpha \rangle \frac{1}{-i[(E_b + E_\alpha) - (E_d + E_\gamma)] + x} \\ \times \frac{1}{-i[(E_e + E_\epsilon) - (E_d + E_\gamma)] + x}, \\ \langle | V_1 | \rangle \langle | \frac{dV_2^\dagger}{dt} | \rangle = i \sum_{e\epsilon} \langle a\alpha | \mathcal{H}_1 | c\gamma \rangle \langle d\gamma | \mathcal{H}_1 | e\epsilon \rangle \langle e\epsilon | \mathcal{H}_1 | b\alpha \rangle \frac{1}{i[(E_a + E_\alpha) - (E_c + E_\gamma)] + x} \\ \times \frac{1}{-i[(E_e + E_\epsilon) - (E_d + E_\gamma)] + x}, \\ \langle | \frac{dV_2}{dt} | \rangle \langle | V_1^\dagger | \rangle = -i \sum_{e\epsilon} \langle a\alpha | \mathcal{H}_1 | e\epsilon \rangle \langle e\epsilon | \mathcal{H}_1 | c\gamma \rangle \langle d\gamma | \mathcal{H}_1 | b\alpha \rangle \frac{1}{i[(E_e + E_\epsilon) - (E_c + E_\gamma)] + x} \\ \times \frac{1}{-i[(E_b + E_\alpha) - (E_d + E_\gamma)] + x}.$$

Damping terms in this case must clearly contain one  $\delta$  function and one principal part. Here too, we have "well behaved" principal parts containing a summation over an intermediate state  $|e\rangle$  and "spurious" principal parts which do not (and could perhaps be interpreted as indirect damping). How-

ever, here too we observe that in the two cases of secular approximation and extreme narrowing the spurious terms cancel out: This can be seen by comparing the first and second line above:  $(dV_1/dt)V_2^\dagger$  and  $V_1(dV_2^\dagger/dt)$ , and is also true for  $(dV_2/dt)V_1^\dagger$  and  $V_2(dV_1^\dagger/dt)$ . Terms in  $dV_3/dt$  are not

spurious in this respect.

Assuming that we have eliminated the spurious

terms, let us now combine  $(dV_1/dt)V_2^\dagger$  and  $(dV_2/dt)V_1^\dagger$ . We have that

$$\begin{aligned} \text{Re} \langle \left| \frac{dV_1}{dt} \right| \rangle \langle \left| V_2^\dagger \right| \rangle &= \pi \delta((E_d + E_\gamma) - (E_b + E_\alpha)) \langle a\alpha | \mathcal{H}_1 | c\gamma \rangle \left( \sum_{e\epsilon} \langle d\gamma | \mathcal{H}_1 | e\epsilon \rangle \mathcal{O} \frac{1}{(E_d + E_\gamma) - (E_e + E_\epsilon)} \langle e\epsilon | \mathcal{H}_1 | b\alpha \rangle \right), \\ \text{Re} \langle \left| \frac{dV_2}{dt} \right| \rangle \langle \left| V_1^\dagger \right| \rangle &= \pi \delta((E_d + E_\gamma) - (E_b + E_\alpha)) \left( \sum_{e\epsilon} \langle a\alpha | \mathcal{H}_1 | e\epsilon \rangle \mathcal{O} \frac{1}{(E_c + E_\gamma) - (E_e + E_\epsilon)} \langle e\epsilon | \mathcal{H}_1 | c\gamma \rangle \right) \langle d\gamma | \mathcal{H}_1 | b\alpha \rangle. \end{aligned} \quad (22)$$

In terms of first- and second-order transition amplitudes  $A_1$  and  $A_2$ , this can also be written as

$$\langle \left| \frac{dV_1}{dt} \right| \rangle \langle \left| V_2^\dagger \right| \rangle + \langle \left| \frac{dV_2}{dt} \right| \rangle \langle \left| V_1^\dagger \right| \rangle = \pi \delta((E_d + E_\gamma) - (E_b + E_\alpha)) [\langle a\alpha | A_1 | c\gamma \rangle \langle d\gamma | A_2^\dagger | b\alpha \rangle + \langle a\alpha | A_2 | c\gamma \rangle \langle d\gamma | A_1^\dagger | b\alpha \rangle], \quad (23)$$

so that this contribution can be associated with the first line of Eq. (18) which contains

$$\langle \left| \frac{dV_1}{dt} \right| \rangle \langle \left| V_1^\dagger \right| \rangle = \pi \delta((E_d + E_\gamma) - (E_b + E_\alpha)) \langle a\alpha | A_1 | c\gamma \rangle \langle d\gamma | A_1^\dagger | b\alpha \rangle. \quad (24)$$

More precisely terms 1 and 3 of Eq. (20) correspond to term 1 of Eq. (18); terms 2 and 4 of Eq. (20) correspond to term 2 of Eq. (18). Consequently, we have reduced these third-order terms to products of the form  $A_1 A_2$  and established a correspondence with second-order terms. We must now investigate whether this remains true for terms of type  $V_3$  (in which  $V_3$  is a *third-order* transition amplitude). With the same multiplicative factor as in Eq. (21) we have that

$$\begin{aligned} \langle \left| \left\langle \frac{dV_3^\dagger}{dt} \right| \right| \rangle &= -i \delta_{\alpha\gamma} \sum_{e\epsilon, f\phi} \langle d\alpha | \mathcal{H}_1 | f\phi \rangle \langle f\phi | \mathcal{H}_1 | e\epsilon \rangle \langle e\epsilon | \mathcal{H}_1 | b\alpha \rangle \\ &\quad \times \frac{1}{-i[(E_f + E_\phi) - (E_d + E_\alpha)] + x} \times \frac{1}{-i[(E_e + E_\epsilon) - (E_d + E_\alpha)] + x}, \end{aligned} \quad (25)$$

and we must extract contributions of the type  $\mathcal{O}\delta$  and  $\delta\mathcal{O}$ . Although these contributions have nothing spurious it appears that they cannot be reduced to products of the form  $A_1 A_2$  except if, in the second principal part,  $E$  can be replaced by  $E_b$ . One more, we meet the condition of the secular approximation or extreme narrowing. If one of these is fulfilled, it is easy to show that  $\langle \left| \left\langle \frac{dV_3^\dagger}{dt} \right| \right| \rangle$  may be cast into the form

$$\langle \left| \left\langle \frac{dV_3^\dagger}{dt} \right| \right| \rangle = \sum_{e\epsilon} [\langle d\alpha | A_1 | e\epsilon \rangle \langle e\epsilon | A_2^\dagger | b\alpha \rangle + \langle d\alpha | A_2 | e\epsilon \rangle \langle e\epsilon | A_1^\dagger | b\alpha \rangle] \pi \delta((E_e + E_\epsilon) - (E_b + E_\alpha)). \quad (26)$$

This contribution clearly corresponds to the third term of Eq. (18).

In conclusion, we have shown that under the conditions of the secular approximation or extreme narrowing, the third-order terms of the relaxation equation of  $\sigma^*$  can be reproduced to products of first- and second-order transition amplitudes  $A_1, A_2$ . Moreover, with each second-order term of the type  $\langle m | A_1 | n \rangle \langle l | A_1^\dagger | p \rangle$  we may associate two third-order terms  $\langle m | A_1 | n \rangle \langle l | A_2^\dagger | p \rangle$  and  $\langle m | A_2 | n \rangle \langle l | A_1^\dagger | p \rangle$ . In other words, in the second-order equation, we can replace  $A_1$  by  $A_1 + A_2$  and then extract second- and third-order terms.

We must now look at the implications of these results in the study of Kondo corrections to the electronic relaxation rate as deduced from Mössbauer spectra.

#### V. STUDY OF THE ONSET OF KONDO EFFECT BY MÖSSBAUER SPECTROSCOPY IN THE CASE $\Delta \gg k_B T_K$

Before looking at the study by the Mössbauer technique of a spin  $\vec{S}$  with hyperfine structure, we

shall first recall some simple results relative to a "bare" electronic spin.

##### A. Properties of a "bare" electronic spin

In Kondo's review paper, the relaxation rate  $1/T_{1S}$  of an electronic spin  $S$  in the presence of the onset of a Kondo effect ( $T \gg T_K$ ) is calculated by a transition-probability method. It contains a term  $|A_1|^2$  responsible for the usual Korringa law,  $1/T_1 = C_K T$ , and terms  $A_1^\dagger A_2$  and  $A_2^\dagger A_1$  which give rise to the Kondo deviation. The second-order transition amplitude  $A_2$  associated with the Kondo coupling  $2J_{sf} \alpha \vec{S} \cdot \vec{s}$  involves an intermediate state. If the energy of the localized spin in the corresponding energy denominator is zero or can be neglected, it turns out that all the matrix elements of  $A_2$  are proportional to those of  $A_1$  with a unique proportionality factor, i. e., with respect to the eigenstates  $m_S, m'_S$  of  $S_z$ :

$$\langle m'_S, \vec{k}' \sigma' | A_2 | m_S, \vec{k} \sigma \rangle = \langle m'_S, \vec{k}' \sigma' | A_1 | m_S, \vec{k} \sigma \rangle$$

$$\times [1 + 2\alpha J_{sf} g(\epsilon_k)], \quad (27)$$

where  $|\vec{k}'| = |\vec{k}|$  (elastic scattering, imposed by the energy-conservation condition) and  $g(\epsilon_k)$  is given by Eq. (14.6) of Ref. 4. Using these results a standard transition-probability calculation leads to [Eq. (15.2) of Ref. 4]

$$\left(\frac{1}{T_{1S}}\right)_K = C_K T \left[ 1 + 4J_{sf} \alpha n(E_F) \ln \left| \frac{k_B T}{D} \right| \right]. \quad (28)$$

One might wonder whether the same results could be derived using the third-order relaxation theory of the preceding paragraph. The answer is yes, because the neglect of the localized spin energy in the energy denominators amounts to the extreme-narrowing approximation. In addition, the symmetry of the relaxation leads to a decoupling of  $\langle S^+ \rangle$ ,  $\langle S^- \rangle$ ,  $\langle S^z \rangle$ , which is the same as would result from the secular approximation in the presence of a magnetic field. These conclusions remain valid when  $\vec{S}$  is actually submitted to dc magnetic fields  $H_0$  such that  $g\mu_B H_0 \ll k_B T$ . In this case  $\langle S^+ \rangle$ ,  $\langle S^- \rangle$ ,  $\langle S^z \rangle$  each exhibits simple exponential relaxation characterized by the classical relaxation rates  $1/T_{1S}$ ,  $1/T_{2S}$ , which by virtue of Eq. (28) are given by

$$\left(\frac{1}{T_{1S}}\right)_K = \left(\frac{1}{T_{2S}}\right)_K = C_K T \left[ 1 + 4J_{sf} \alpha n(E_F) \ln \left| \frac{k_B T}{D} \right| \right]. \quad (29)$$

In an EPR experiment  $\vec{S}$  is also submitted to an rf field with frequency  $\hbar\omega \sim g\mu_B H_0$ . Then, assuming that there is no trouble with bottleneck effects ( $g \neq 2$ , for example),  $\langle S^+ \rangle$ ,  $\langle S^- \rangle$ ,  $\langle S^z \rangle$  obey Bloch equations and the peak-to-peak linewidth of the derivative of the absorption curve is given by

$$\Delta\omega = \frac{1}{\sqrt{3}} \left( \frac{2}{T_{1S}} \right)_K. \quad (30)$$

On the contrary, when  $\mu_B H_0 \gg k_B T$ , these simple results are no longer true. First, even in the absence of Kondo effect a complication arises when  $S \neq \frac{1}{2}$ ; in that case, if we define tensor operators  $T_k^q(S)$ , relaxations of operators with different  $q$ 's are still decoupled by virtue of the symmetry of the relaxation (this being equivalent to the secular approximation) but there is a coupling between  $T_k^q$ ,  $T_{k\pm 1}^q$ . Although the relaxation constants in this case can still be expressed in terms of quantities  $1/T_{1S}$ ,  $1/T_{2S}$  similar to their high-temperatures counterparts, the computation of the rf signal becomes complicated.<sup>8</sup> Second, in the evaluation of the Kondo corrections to relaxation, the appearance of electronic energies  $g\mu_B H_0$  in the energy denominator of  $A_2$  or in the energy-conservation condition will quench the Kondo correction,  $\ln|k_B T/D|$  being replaced by  $\ln|g\mu_B H_0/D|$ .<sup>4</sup> Also the simple proportionality relationship, Eq. (27), between  $A_1$  and

$A_2$  irrespective of  $m_S$  and  $m'_S$  will probably not hold any longer. However, these problems are not of current interest, since most EPR experiments are performed at temperature  $k_B T \gg g\mu_B H_0$ , and we will not consider them in more detail here.

#### B. Mossbauer study of an electronic spin with hyperfine structure

In this section, we will be particularly interested in the case of  $Au^{170}Yb$  for which  $\Delta \gg k_B T_K$  and  $\Delta \sim 0.11$  K. Taking account of the experimental data,<sup>2,3</sup> we can distinguish three temperature regions: (i)  $T > 1$  K, important relaxation broadening but no population effects; (ii)  $1 \text{ K} > T > 0.6$  K, relaxation broadening and incipient population effects; (iii)  $0.6 \text{ K} > T$ , small relaxation broadening but appreciable population effects.

First, in region (i) we can make the extreme-narrowing approximation. Also we only have to consider the first Liouville matrix in Eq. (9). The matrix elements  $\langle g_1 f_1 | R | g_2 f_2 \rangle$  of  $R$  up to second order in  $J_{sf}$  have been computed in Ref. 1a, Eq. (34), and it has been shown that with respect to a basis of eigenvectors of  $I_z$ ,  $I_{zz}$ , and  $S_z$ ,

$$\begin{aligned} & \langle I m S \nu, I_z m_z S \mu | R | I m' S \nu', I_z m'_z S \mu \rangle \\ &= \delta_{mm'} \delta_{m_z m'_z} \frac{1}{2T_1} \left\{ -2S(S+1) \delta_{\mu\mu'} \delta_{\nu\nu'} \right. \\ & \quad \left. + 2 \sum_{j=x,y,z} \langle \nu | S_j | \nu' \rangle \langle \mu' | S_j | \mu \rangle \right\}, \quad (31) \end{aligned}$$

where  $1/T_1$  is the relaxation rate which would characterize the "bare" electronic spin without hyperfine coupling. This second-order relaxation matrix is derived from products of transition amplitudes  $A_1, A_1'$  which are linear functions of  $S_x, S_y, S_z$ . Since, in this temperature region, the ratio of the matrix elements of  $A_2$  and  $A_1$  does not depend on the localized-spin quantum numbers [Eq. (27)], it follows that the relaxation matrix  $R$  up to third order is given by Eq. (31), in which  $(1/T_1)$ , Eq. (2), is replaced by  $(1/T_{1S})_K$ , Eq. (28). Thus justifies the interpretation of the spectra in Ref. 3. One could also say that in the presence of Kondo effect, it is sufficient in second-order terms to replace  $J_{sf}^2$  by  $J_{sf}^2 [1 + 4J_{sf} \alpha n(E_F) \ln|k_B T/D|]$ .

Second, region (ii) is the intermediate region discussed in Sec. II where no simplifying assumption can be made, and we shall not consider it here.

Third, in region (iii) we can make the secular approximation. We have already mentioned that with these conditions residual relaxation effects in the *first Liouville matrix* in Eq. (9) do not affect the integrated intensities of the two hyperfine lines. The demonstration is as follows: Let us use as basis states,  $|FF_z\rangle$  for the hyperfine state  $F = \frac{3}{2}$ ,  $|F'F'_z\rangle$  for the hyperfine state  $F' = \frac{5}{2}$ , and

$|SS_z\rangle$  for the ground state. With respect to this basis, the matrix  $R$  entering the first Liouville matrix in Eq. (9), which describes the relaxation of the transition operator  $\tilde{M}$  [Eq. (8)], has the form

$$\begin{array}{c} FS \quad F'S \\ \begin{array}{c} FS \\ F'S \end{array} \begin{bmatrix} R_F & R'' \\ R'' & R'_F \end{bmatrix} \end{array}.$$

Two matrix elements  $\tilde{M}_{Fm_F, sm_S}$  and  $\tilde{M}_{F'm'_F, sm'_S}$  which correspond to different values of  $F$  oscillate at circular frequencies differing by  $\Delta/\hbar$ . If  $R \ll \Delta/\hbar$ , the relaxation of two such elements are decoupled by virtue of the secular approximation; therefore, in the Liouville matrix of  $R$ , we may replace  $R''$  and  $R'''$  by zero. In other words, this matrix factorizes into two matrices  $R_F$  and  $R'_F$  corresponding to subspaces  $FS$  and  $F'S$ .

Having noticed that the matrix of  $\mathcal{K}_0^x$  factorizes in the same way, let us now go back to Eq. (9) and consider the operator associated with the first Liouville matrix:

$$\frac{-1}{i\omega - \Gamma/2 + i\mathcal{K}_0^x/\hbar + R} = \int_0^\infty dt \exp\left[\left(i\omega - \frac{\Gamma}{2} + \frac{i\mathcal{K}_0^x}{\hbar} + R\right)t\right].$$

Since  $R$  and  $\mathcal{K}_0^x$  factorize, it may also be written as

$$\begin{aligned} P_{FS} \int_0^\infty dt \exp\left[\left(i\omega - \frac{\Gamma}{2} + \frac{i\mathcal{K}_0^x}{\hbar} + R_F\right)t\right] P_{FS} \\ + P_{F'S} \int_0^\infty dt \exp\left[\left(i\omega - \frac{\Gamma}{2} + \frac{i\mathcal{K}_0^x}{\hbar} + R'_F\right)t\right] P_{F'S}, \end{aligned}$$

where  $P_{FS}$  and  $P_{F'S}$  are projection operators corresponding to subspaces  $FS$  and  $F'S$ . It is clear that if we insert this expression back into Eq. (9), terms in  $P_{FS}$  will correspond to the first hyperfine line and terms in  $P_{F'S}$  to the second hyperfine line:

$$I(\omega) = I_F(\omega) + I_{F'}(\omega).$$

Now the integrated intensity corresponding, say, to  $I_F(\omega)$  will involve

$$\begin{aligned} \int_{-\infty}^{+\infty} d\omega I_F(\omega) &\propto P_{FS} \int_{-\infty}^{+\infty} d\omega \int_0^\infty dt e^{i\omega t} \\ &\times \exp\left[\left(-\frac{\Gamma}{2} + \frac{i}{\hbar}\mathcal{K}_0^x + R_F\right)t\right] P_{FS} \\ &= P_{FS} \int_0^\infty 2\pi\delta(t) dt \exp\left[\left(-\frac{\Gamma}{2} + \frac{i}{\hbar}\mathcal{K}_0^x + R_F\right)t\right] P_{FS} \\ &= \pi P_{FS}, \end{aligned}$$

which does not depend any longer on the relaxation term  $R_F$  (Q.E.D.).

Let us now consider the *second Liouville matrix* in Eq. (9) which describes the evolution of the

density matrix  $\sigma^I$  of state  $I$ . We have already mentioned that the initial value of this matrix just after radiative feeding is diagonal with respect to  $|FF_z\rangle$ .

We will now show that, owing both to the symmetry of the relaxation process and to the secular approximation, it remains diagonal, which is an important simplification. In what follows, the eigenvalues of  $F_z$  will be denoted by  $m$ . Also, using tensor-operator formalism, we will write the relaxation Hamiltonian as:

$$\mathcal{H}_1 = -2J_{sf} \alpha \vec{S} \cdot \vec{s} \propto \sum_q (-1)^q S^q s^{-q}$$

with  $S^1 = -S^+/\sqrt{2}$ ,  $S^0 = S_z$ ,  $S^{-1} = S^-/\sqrt{2}$ , and with corresponding identification for  $s^q$ .

Second-order contributions to the relaxation matrix involve terms of the form  $\mathcal{H}_1 \mathcal{H}_1 \sigma$  (or  $\sigma \mathcal{H}_1 \mathcal{H}_1$ ) and  $\mathcal{H}_1 \sigma \mathcal{H}_1$ , and there is a summation over the conduction-electron variables which appear in  $\mathcal{H}_1$ . Products of two  $\mathcal{H}_1$  are of the form

$$\sum_q (-1)^q S^{-q} s^q \sum_{q'} (-1)^{q'} S^{-q'} s^{q'}, \quad (32)$$

and it is clear that averaging over the conduction-electron variables will give a nonzero result only if  $q+q'=0$  (conduction-electron spin conservation). This results in conservation of the localized spin. Accordingly, with respect to the atomic variables,  $d\sigma_{mm}^{FF'}/dt$  will contain only terms of the form

$$\langle Fm | S^q S^{-q} \sigma | F'm' \rangle, \quad \langle Fm | \sigma S^q S^{-q} | F'm' \rangle$$

or

$$\langle Fm | S^q \sigma S^{-q} | F'm' \rangle.$$

At this stage, we may use either the Wigner-Eckart theorem or the matrix elements of Lamb and Feld,<sup>9</sup> which show that

$$\langle Fm | S^q | F''m'' \rangle = \delta_{m, m''+q} \langle F, m''+q | S^q | F'm'' \rangle. \quad (33)$$

Consequently contributions  $\mathcal{H}_1 \mathcal{H}_1 \sigma$  couple  $\sigma_{mm}^{FF'}$  with  $\sigma_{mm}^{F''F'''}$  and contributions  $\mathcal{H}_1 \sigma \mathcal{H}_1$  couple  $\sigma_{mm}^{FF'}$  with  $\sigma_{m''q, m''+q}^{F''F'''}$ , where  $q=0, \pm 1$ . In particular,  $\sigma_{mm}^{FF'}$  is only coupled with  $\sigma_{nn}^{F''F'''}$  ( $n=m, m\pm 1$ ).

It is easy to check that all these conclusions are also valid in third order.

We shall now restrict ourselves to terms of type  $\sigma_{mm}^{FF'}$  and investigate the consequences of the secular approximation. For  $Au^{170}Yb$ ,  $F = \frac{3}{2}$  or  $F = \frac{5}{2}$ . The ten diagonal matrix elements  $\sigma_{mm}^{3/2, 3/2}$  and  $\sigma_{mm}^{5/2, 5/2}$  oscillate at zero frequency. On the other hand, the sets  $\sigma_{mm}^{5/2, 3/2}$  and  $\sigma_{mm}^{3/2, 5/2}$  oscillate at  $-\Delta/\hbar$  and  $+\Delta/\hbar$ . When the electronic relaxation rates between  $F = \frac{3}{2}$  and  $F = \frac{5}{2}$  are small compared to  $\Delta/\hbar$ , the secular approximation is valid, and the three above sets are decoupled from one another. Then, if  $\sigma$  is initially diagonal, it remains diagonal, populations are only coupled with



populations and relaxation can be studied by means of transition-probability methods, as will be done in the following paper, II. These conclusions would remain valid for higher electronic spin  $S \neq \frac{1}{2}$ .

On the other hand, we have already mentioned that in this temperature range, the integrated intensities of the hyperfine Mössbauer lines only depend on the total populations of the hyperfine levels  $P_F = \sum_m p_m^F$ . Within the secular approximation, these populations obey general rate equations of the type

$$\frac{d}{dt} P_F = - \sum_{mm', F'} W_{m-m'}^{F-F'} p_m^F + \sum_{mm', F'} W_{m'-m}^{F'-F} p_{m'}^{F'} , \quad (34)$$

where the  $W$  are transition probabilities. In the presence of such equation it is always interesting to investigate whether the  $W$  obey simple sum rules. We shall see in paper II that when relaxation is due to the conduction electrons, this is indeed the case:

$$\sum_{m'} W_{m-m'}^{F-F'} = W^{F-F'} \quad \text{independent of } m \quad (35)$$

$$\sum_m W_{m'-m}^{F'-F} = W^{F'-F} \quad \text{independent of } m' .$$

In that case, relaxation equations take the very simple form

$$\frac{d}{dt} P_F = - \sum_{F'} W^{FF'} P_{F'} + \sum_{F'} W^{F'F} P_{F'} , \quad (36)$$

in which the transition probabilities  $W$  must satisfy the Boltzmann equilibrium condition

$$\frac{W^{FF'}}{W^{F'F}} = \left( \frac{P_{F'}}{P_F} \right)_{\text{eq}} = \frac{2F'+1}{2F+1} e^{(E_{F'} - E_F) / k_B T} . \quad (37)$$

In the presence of the Kondo effect, we shall have to check that in our calculations, relations (35) and (37), are satisfied both in second and in third order.

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<sup>4</sup>J. Kondo, Solid State Phys. **23**, 183 (1969).

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<sup>9</sup>B. T. Feld and W. E. Lamb, Phys. Rev. **67**, 15 (1945), Eq. III(11).