Resonant scattering of Mössbauer gamma quanta under relaxation conditions

A. M. Afanas'ev and V. D. Gorobchenko

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A general expression for the resonant scattering cross section, which is valid for Mössbauer gamma quanta under conditions of relaxation of the electron spin producing the hyperfine field at the nucleus, is derived within the framework of the superoperator method. [12, 5–7] The expression for the scattering cross section is valid for an arbitrary ratio of the electron spin relaxation time to the hyperfine splitting. An advantage of the derived formula is that it contains the same relaxation parameters that determine the resonance absorption spectrum and the calculation of the resonant scattering cross section is mathematically not more difficult than the calculation of the absorption cross section in the general case. As a typical application of the general results, the case of gamma quantum scattering in the limit of fast relaxation and in the presence of quadrupole splitting is considered.

1. INTRODUCTION

At the present time, γ-resonance spectroscopy has become one of the effective methods of investigating relaxation phenomena in solids, primarily in paramagnetic substances, in which magnetic hyperfine splitting of the nuclear levels (and consequently the resonant absorption and scattering spectra) are determined essentially by the character of the relaxation of the electron spin of the Mössbauer atom.

As to the absorption problem, it was considered in detail theoretically (see[1-7] and the references contained therein), and extensive experimental research has been carried out in this field. The question of resonant scattering of Mössbauer quanta in the presence of relaxation processes has not yet been considered theoretically, but there is every reason for expecting experimental research to develop in this direction. Resonant scattering as an experimental method has been used for a long time in various investigations[8-10]. There is also a report of the use of resonant scattering for the study of relaxation phenomena near the Morin phase-transition point in hematite[11]. Consequently, the solution of the corresponding theoretical problem seems timely to us.

In this paper we obtain a solution of the general problem of resonant scattering of Mössbauer γ quanta, which is valid in the entire range of relations between the relaxation time of the electron spin and the value of the hyperfine interaction. In the analysis we use the super-operator method developed by Zwanzig[12] and by others[5-7]. The general formula (10) obtained in Sec. 2 for the cross section of resonant scattering has a relatively simple form and contains the same relaxation parameters which enter in the absorption problem.

In the third section we analyze the general formula (10) in the case of intermediate relaxation, when the frequencies $1/\tau_{\mathrm{rel}}$ of the relaxation transitions between the electron-spin state are comparable with nuclear-spin possession frequency ω_{hf} in the magnetic field produced at the nucleus by the electron shell, and rapid relaxation, when $1/\tau_{\mathrm{rel}} \gg \omega_{\mathrm{hf}}$. In the fourth section we analyze in detail the important case of slow relaxation. At intermediate relaxation times, in the region where the calculations of the absorption spectra are the most laborious, the cross section for resonant scattering acquires becomes particularly simple (see formula (23)) and is expressed in fact in terms of the product of the absorption cross section by the function describing the emission spectrum under conditions when the "memory" of the excitation process is completely lost during the lifetime of the excited state, and the populations of all the sublevels of the excited state of the nucleus can be regarded as equally probable.

In the fifth and final section we consider a concrete example of fast relaxation in the presence of quadrupole splitting. As is well known, in absorption spectra there is observed for these situations an asymmetry of the quadrupole doublets (the Blume effect)[2,13]. In the investigation of the absorption spectra we can obtain only rather rough information on the relaxation process. The use of resonant scattering, as shown in the fifth section, makes it possible to extract more detailed information on the relaxation process. We note also that this very simple and very frequently encountered situation with asymmetrical doublets possesses that peculiarity that all the sublevels, of both the ground and the excited states of the nucleus, subjected to the action of fluctuating hyperfine magnetic fields, are doubly degenerate, and consequently this case calls for the use of the theory developed in the present paper in its most general formulation.

2. DERIVATION OF GENERAL FORMULA FOR THE RESONANT SCATTERING CROSS SECTION

Let us examine a process in which, during the first stage, a γ quantum with wave vector **k**, energy ω, and polarization vector η is resonantly absorbed by a Mössbauer atom, whose nucleus is then raised to an excited state. During the second stage, the nucleus decays and emits a γ quantum ($\mathbf{k}'$, ω', η'). We are interested in a situation in which an important role is played in the course of such a resonant rescattering by the interaction of the spin of the electron shell of the Mössbauer atom with the surrounding medium (which we shall henceforth call arbitrarily the thermal bath or thermostat). The influence of the thermostat comes into play in the distributions of the emitted γ quanta with respect to the energy and over the emission directions, in their polarization, and also in the resonant characteristics of the scattering cross sections, such as the widths, positions, and intensities of the lines.

The cross section for the indicated resonant process was described by the formula

$$\sigma(\omega,\omega')=\frac{2\pi}{\hbar c}\sum_{\alpha,\beta}\rho_\alpha|M_{\beta\alpha}(\omega)|^2\delta(\omega+E_\alpha-\omega'-E_\beta), \tag{1}$$

where $|\alpha\rangle$ are quantum mechanical states, and E_α are the corresponding energies of the total system, which includes the resonant atoms and the thermostat. In formula (1) we average over the initial and sum over the final states of the complete system, the matrix element of which we designate by ρ.

Apart from an inessential constant factor, the matrix element of the transition $M_{\beta\alpha}(\omega)$ is given by

$$M_{\beta\alpha}(\omega)=\sum_{\gamma}\frac{(\boldsymbol{\eta}'^*\mathbf{j}(\mathbf{k}')e^{i\mathbf{k}'\mathbf{R}})_{\beta\gamma}(\boldsymbol{\eta}\mathbf{j}^+(\mathbf{k})e^{-i\mathbf{k}\mathbf{R}})_{\gamma\alpha}}{\omega+E_\alpha-E_\gamma+i\Gamma/2}. \tag{2}$$

Here $\mathbf{j}^+(\mathbf{k})$ is the Fourier component of the current density operator in the nucleus and is responsible for its transition from the ground state to the excited state, Γ is the width of the excited level of the nucleus, and $\mathbf{R}$ is a radius vector describing its position.

Usually the exponential factors in (2) lead to the appearance of Mössbauer factors that determine the probabilities of recoilless absorption and emission of the γ rays. The role of these exponential factors remains the same as when account is taken of relaxation processes, if one excludes the fluctuations that lead to the time variation of the position of the Mössbauer nucleus in the lattice (i.e., diffusion processes). The latter problem was considered in a number of studies (see, e.g.,[14] and the references therein). In this case we are interested in the fluctuations connected with the hyperfine interaction, and to simplify the problem, the exponential factors in (2) will henceforth be omitted.

Substituting (2) in (1) and expressing the δ-function in the form

$$\delta(x)=-\frac{1}{\pi}\operatorname{Im}\frac{1}{x+i\delta},$$

we have for $\sigma(\omega,\omega')$

$$\begin{aligned}\sigma(\omega,\omega')=-\frac{2}{\hbar c}\operatorname{Im}\sum_{\alpha,\beta,\delta,\gamma}\rho_\alpha j_{\alpha\delta}\left(\omega+E_\alpha-E_\delta-\frac{i\Gamma}{2}\right)^{-1}j_{\delta\beta}'^{+}\\ \times(\omega-\omega'+E_\alpha-E_\beta+i\delta)^{-1}j_{\beta\gamma}'\left(\omega+E_\alpha-E_\gamma+\frac{i\Gamma}{2}\right)^{-1}j_{\gamma\alpha}^{+},\end{aligned} \tag{3}$$

where we have introduced the notation $j=\boldsymbol{\eta}^*\cdot\mathbf{j}(\mathbf{k})$ and $j'=\boldsymbol{\eta}'^*\cdot\mathbf{j}(\mathbf{k}')$. As will be shown later on, it is convenient to carry out the following identity transformation of the product of three resonant factors that enters in (3):

$$\begin{aligned}&(\omega+E_\alpha-E_\delta-i\Gamma/2)^{-1}(\omega-\omega'+E_\alpha-E_\beta+i\delta)^{-1}(\omega+E_\alpha-E_\gamma+i\Gamma/2)^{-1}\\ &=(\omega'-E_\delta+E_\beta-i\Gamma/2)^{-1}(\omega-\omega'-E_\beta+E_\alpha+i\delta)^{-1}(\omega-E_\gamma+E_\alpha+i\Gamma/2)^{-1}\\ &+(\omega-E_\delta+E_\alpha-i\Gamma/2)^{-1}(-E_\delta+E_\gamma-i\Gamma)^{-1}(\omega'-E_\delta+E_\beta-i\Gamma/2)^{-1}\\ &-(-E_\delta+E_\gamma-i\Gamma)^{-1}(\omega'-E_\delta+E_\beta-i\Gamma/2)^{-1}(\omega-E_\gamma+E_\alpha+i\Gamma/2)^{-1}.\end{aligned} \tag{4}$$

Taking (4) into account, expression (3) for $\sigma(\omega,\omega')$ breaks up into a sum of three terms of the following type:

$$\begin{aligned}\sigma(\omega;\omega')=-\frac{2}{\hbar c}\operatorname{Im}\sum_{\alpha,\beta,\gamma,\delta}\rho_\alpha j_{\alpha\delta}\{[(\omega'-E_\delta+E_\beta-i\Gamma/2)^{-1}j_{\delta\beta}'^{+}]\\ \times(\omega-\omega'-E_\beta+E_\alpha+i\delta)^{-1}j_{\beta\gamma}'(\omega-E_\gamma+E_\alpha+i\Gamma/2)^{-1}\\ +(\omega-E_\delta-E_\alpha-i\Gamma/2)^{-1}[(-E_\delta+E_\gamma-i\Gamma)^{-1}[(\omega'-E_\delta+E_\beta-i\Gamma/2)^{-1}j_{\delta\beta}'^{+}]j_{\beta\gamma}']\\ -[(-E_\delta+E_\gamma-i\Gamma)^{-1}[(\omega'-E_\delta+E_\beta-i\Gamma/2)^{-1}j_{\delta\beta}'^{+}]j_{\beta\gamma}']\cdot\\ \times(\omega-E_\gamma+E_\alpha+i\Gamma/2)^{-1}\}j_{\gamma\alpha}^{+}.\end{aligned} \tag{5}$$

The transformation (4) was carried out in such a way that each of the terms in the right-hand side of (5), regarded as a function of the complex variables E_α, E_β, etc., would have poles either only in the upper part of the complex plane of the corresponding variable, or only in the lower one. With such a subdivision, it is possible to obtain in very simple form a final answer for $\sigma(\omega,\omega')$ under relatively weak assumptions concerning the parameters of the system.

We write down the complete Hamiltonian of the system, breaking it up in natural fashion into a sum of three terms:

$$H_\kappa=H_A^\kappa+H_B+H_I.$$

Here κ = e or g (κ = e for a Mössbauer nucleus in the excited state and κ = g for the ground state), H_A^κ is the Hamiltonian of the Mössbauer atom and includes both the hyperfine interaction and the interaction of the electron shell with the crystal and external magnetic fields, H_B is the Hamiltonian of the heat bath, and H_I is the energy of the interaction of the electron-shell spin with the heat bath.

We now assume that the interaction H_I is small enough to be neglected in the expression for the density matrix. In other words, we assume that the relaxation times $\tau_{\rm rel}$ that characterize the behavior of the spin of the electron shell and are due to the interaction H_I satisfy the condition

$$\tau_{\rm rel}\gg\hbar/k_{\rm Boltz}T, \tag{6}$$

where $k_{\rm Boltz}$ is the Boltzmann constant and T is the temperature. The density matrix of the complete system is broken up in this case into the product

$$\rho\cong\rho_A\rho_B,$$

where ρ_A and ρ_B are the density matrices of the Mössbauer atom and of the heat bath, respectively. This factorization of the density matrix makes it possible to carry out in (5) independent averaging over the initial state of the Mössbauer atom and of the heat bath.

We agree to designate the statistical averaging over the states of the Mössbauer atom with the Hamiltonian H_A^g by means of angle brackets

$$\langle\ldots\rangle\equiv\operatorname{Sp}(\rho_A\ldots).$$

To designate the analogous procedure in the case of the heat bath, we introduce the operator P:

$$P\ldots\equiv\operatorname{Sp}(\rho_B\ldots).$$

In addition, we shall need the operator $Q = 1 - P$. Obviously, $P^2 = P$ and $Q^2 = Q$, i.e., both are projection operators. Finally, we introduce the Liouville operators $\hat{L}_{\kappa\kappa'}$:

$$\hat{L}_{\kappa\kappa'}a=H_\kappa a-aH_{\kappa'},$$

where a is an ordinary quantum-mechanical operator, and also the Green superoperators

$$\hat{G}_{\kappa\kappa'}(\omega)=(\omega-\hat{L}_{\kappa\kappa'})^{-1}.$$

See[12,5-7] concerning the superoperator method.) Then, as can be easily verified, we can represent expression (5) for $\sigma(\omega,\omega')$ in the following operator form:

$$\begin{aligned}&\sigma(\omega,\omega')\\ &=-(2/\hbar c)\operatorname{Im}\langle jP\{[\hat{G}_{eg}(\omega'-i\Gamma/2)j'^{+}]\hat{G}_{gg}(\omega-\omega'+i\delta)j'\hat{G}_{eg}(\omega+i\Gamma/2)\\ &+\hat{G}_{eg}(\omega-i\Gamma/2)[\hat{G}_{ee}(-i\Gamma)[\hat{G}_{eg}(\omega'-i\Gamma/2)j'^{+}]j']\\ &-[\hat{G}_{ee}(-i\Gamma)[\hat{G}_{eg}(\omega'-i\Gamma/2)j'^{+}]j']\hat{G}_{eg}(\omega+i\Gamma/2)\}j^{+}\rangle.\end{aligned} \tag{7}$$

It is convenient to break up each of the superoperators $\hat{G}$ in (7) into four terms of the type

$$\hat{G}\equiv(P+Q)\hat{G}(P+Q)=P\hat{G}P+P\hat{G}Q+Q\hat{G}P+Q\hat{G}Q. \tag{8}$$

Substituting (8) in (7) and separating the term that contains only the Green superoperators $\bar{G} \equiv P\hat{G}P$ averaged over the states of the heat bath, we obtain as a result

$$\sigma(\omega, \omega') = \bar{\sigma}(\omega, \omega') + \Delta\sigma(\omega, \omega'), \tag{9}$$

where

$$\begin{aligned} \bar{\sigma}(\omega, \omega') = -(2/\hbar c)\,\mathrm{Im}\,\langle j\{[\bar{G}_{eg}(\omega' - i\Gamma/2)j'^{+}]\bar{G}_{gg}(\omega - \omega' + i\delta)j'\bar{G}_{eg}(\omega + i\Gamma/2) \\ + \bar{G}_{eg}(\omega - i\Gamma/2)[\bar{G}_{ee}(-i\Gamma)[\bar{G}_{eg}(\omega' - i\Gamma/2)j'^{+}]j'] \\ - [\bar{G}_{ee}(-i\Gamma)[\bar{G}_{eg}(\omega' - i\Gamma/2)j'^{+}]j']\bar{G}_{eg}(\omega + i\Gamma/2)\}j^{+}\rangle, \end{aligned} \tag{10}$$

and $\Delta\sigma(\omega, \omega')$ includes all the remaining combinations made up of the terms of the sum (8).

If the system in question has the property that the characteristic energy $\hbar\omega_B$ of the spectrum of the heat-bath excitations that take part inthe relaxation process is much higher than $\hbar/\tau_{\mathrm{rel}}$, then the term $\Delta\sigma(\omega, \omega')$, as can be directly verified, is small in comparison with the principal term $\sigma(\omega, \omega')$ to the extent that the parameter $(\omega_B\tau_{\mathrm{rel}})^{-1}$ is small. We shall assume that the condition

$$\omega_B\tau_{\mathrm{rel}} \gg 1 \tag{11}$$

is satisfied. In this case the sought resonant-scattering cross section will be determined by formula (10), which solves our problem completely.

An advantage of formula (10) is that it contains only Green's functions $\bar{G}$ that ave averaged over the heat bath and determine in turn also the resonant absorption spectrum $\varphi_{\mathrm{Abs}}(\omega)$. Indeed, we have for $\varphi_{\mathrm{Abs}}(\omega)$ the formula (see, e.g.,[6,7])

$$\varphi_{Abs}(\omega) = -\mathrm{Im}\,\langle j\bar{G}_{eg}(\omega + i\Gamma/2)j^{+}\rangle. \tag{12}$$

For many concrete situations, the Green superoperators $\bar{G}_{eg}$ were calculated earlier (see[5-7] and the references therein). In the general case, we have for $\bar{G}_{\kappa\kappa'}(\omega)$ the formulas[6]

$$\bar{G}_{\varkappa\varkappa'}(\omega) = [\omega - \hat{L}_A^{\varkappa\varkappa'} - \hat{M}(\omega)]^{-1}, \tag{13}$$

where the "mass" superoperator is

$$\hat{M}(\omega) = P\hat{L}_I(\omega - \hat{L}_A^{\varkappa\varkappa'} - \hat{L}_B - Q\hat{L}_I Q)^{-1}\hat{L}_I P. \tag{14}$$

The Hamiltonian H_I for the interaction between the spin of the electron shell of the Mössbauer atom and the heat bath can always be represented in the form

$$H_I = \sum_q A_q B_q,$$

where A_q are operators pertaining to the electron spin and B_q are operators that act in the space of the states of the heat bath, with $PB_q = 0$. If we assume that the condition (11) is satisfied, then we can neglect the term $Q\hat{L}_I Q$ in the denominator of (14). The mass superoperator $\hat{M}(\omega)$ can then be broken up into two parts:

$$\hat{M}(\omega \pm i\delta) = \Delta\hat{L}_A^{(2)} \mp i\hat{\gamma}/2. \tag{15}$$

Here $\Delta\hat{L}_A^{(2)}$ is a superoperator that describes the renormalization of the energy of the electron shell, and corresponds to a certain effective Hamiltonian $\Delta H_A^{(2)}$, which determines the corrections to the energy levels by means of the usual formulas of the second-order perturbation theory of quantum mechanics. As a rule, these renormalizations are small, and we shall not write out explicitly the expression for $\Delta H_A^{(2)}$, assuming that $\Delta H_A^{(2)}$ is automatically included in H_A. On the other hand, the term with $\hat{\gamma}$ in (15) is determined by relaxation processes, and for it we can write in the general case the formula

$$\hat{\gamma} = 2\pi \sum_{qq'} \hat{A}_q \Big[\sum_{\alpha\beta} \rho_\alpha (B_q)_{\alpha\beta}\,\delta(\omega - \hat{L}_A^{\varkappa\varkappa'} - E_\beta + E_\alpha)(B_{q'})_{\beta\alpha} \Big] \hat{A}_{q'}, \tag{16}$$

where $\hat{A}_q$ are superoperators defined by the relation

$$\hat{A}_q a = A_q a - a A_q.$$

It must be emphasized that inasmuch as in the case considered by us the relaxation is due to the interaction of the electron spin with the heat bath, the superoperator $\hat{\gamma}$, and consequently also the mass superoperator $\hat{M}$, acts only on the electron-spin variables.

Formula (16) was obtained neglecting the term $Q\hat{L}_I Q$ in the denominator of (14). We note that, even in the presence of the small parameter (11), this term can be neglected in (14) only when, owing to the selection rules of symmetry, Eq. (16) does not vanish identically, as is the case, for example, for direct transitions between time-conjugate states of Kramers doublets (see, e.g.,[15]). These situations will be excluded from consideration from now on.

In the next section we present a general analysis of formula (10) for the resonant-scattering cross section.

3. GENERAL ANALYSIS OF THE EXPRESSION FOR $\bar{\sigma}(\omega, \omega')$

When considering the problem of resonant absorption of Mössbauer γ quanta under relaxation conditions, a distinction is usually made between the following two limiting situations, when the analysis of the form of the absorption spectrum is greatly facilitated, namely the case of the so-called slow relaxation when

$$\tau_{\mathrm{rel}} \gg 1/\omega_{\mathrm{hf}}, \tag{17}$$

and the case of fast relaxation, when

$$\tau_{\mathrm{rel}} \ll 1/\omega_{\mathrm{hf}} \tag{18}$$

(see, e.g.,[7]). The greatest complications arise in the analysis of the intermediate states, when $\tau_{\mathrm{rel}} \sim 1/\omega_{\mathrm{hf}}$.

In the problem of resonant scattering, an important role is assumed by a new parameter, namely the ratio τ_{rel}/τ, where $\tau = \hbar/\Gamma$ is the lifetime of the excited state of the nucleus. It is clear from physical considerations that at

$$\tau_{\mathrm{rel}}/\tau \ll 1 \tag{19}$$

the formula for the resonant-scattering cross section should have a relatively simple form. Indeed, in this case, during the lifetime of the nucleus in the excited state, the Mössbauer ion, as a result of the interaction with the heat bath, leave its initial state in which he was during the course of the resonant excitation of the nucleus, and has time to stay in all its possible states with a probability close to the equilibrium value at a given sample temperature. It is in one of these states that the decay of the nucleus will take place. This means in fact that when the condition (19) is satisfied the nucleus of the Mössbauer ion completely "forgets" the excitation process, and the γ-quantum emission process is independent of the absorption process.

We note that the condition (19) is fully equivalent to the condition

$$\Gamma \ll \gamma, \tag{20a}$$

where γ is the characteristic value of the matrix elements of the superoperator $\hat{\gamma}$. If in addition to (20a) there also satisfied the condition

$$\Gamma \ll \hbar\omega_{\mathrm{hf}}, \tag{20b}$$

then the following simple formula holds for the matrix elements of the Green superoperator $\bar{G}_{ee}(-i\Gamma)$

$$[\overline{G}_{ee}(-i\Gamma)]_{m,\tilde{m};m',\tilde{m}'} \cong \frac{i}{\Gamma}(\rho_A)_{m'}\delta_{m\tilde{m}}\delta_{m'\tilde{m}'}. \qquad (21)$$

Here m are the quantum numbers that characterize the levels of the system comprising the electron shell and the nucleus in the excited state. Analogously, for $\overline{G}_{gg}(\omega - \omega' + i\delta)$ at $\omega - \omega' \ll \gamma$ we have

$$[\overline{G}_{gg}(\omega-\omega'+i\delta)]_{n,\tilde{n};n',\tilde{n}'} \cong \frac{(\rho_A)_{n'}}{\omega-\omega'+i\delta}\delta_{\tilde{n}n}\delta_{n'\tilde{n}'}, \qquad (22)$$

where n describes the states of the Mössbauer ion with the nucleus in the ground state.

Substituting (21) and (22) in the initial formula (10), we obtain

$$\sigma(\omega,\omega') \cong \frac{4}{\hbar c\Gamma}\varphi_{Abs}(\omega)\varphi_{Em}(\omega') + \frac{2\pi}{\hbar c}|f_{coh}(\omega)|^2\delta(\omega-\omega'), \qquad (23)$$

where

$$\varphi_{Em}(\omega') = \mathrm{Im}\langle\langle j'\overline{G}_{eg}(\omega'-i\Gamma/2)j'^+\rangle\rangle, \qquad (24)$$

$$f_{coh}(\omega) = -\langle j\overline{G}_{eg}(\omega-i\Gamma/2)j'^+\rangle, \qquad (25)$$

and the double angle brackets denote statistical averaging over the state of the Mössbauer ion with the excited nucleus. The first term in (23) corresponds precisely to the physical picture considered above, with complete "loss of memory" by the nucleus during its lifetime in the excited state, while the second term, which is a result of the last two terms of (10), describes a purely elastic process. The scattering amplitude $f_{Coh}(\omega)$ of this pure elastic process is analogous in its physical nature to the amplitude of the elastic phononless scattering of the Mössbauer γ quantum. This amplitude determines the probability of resonant scattering under the condition that that the heat bath does not change its state during the course of the scattering.

It should be noted that the second term in (23) makes a relatively small contribution ($\sim\Gamma/\gamma$) to the integrated scattering cross section. However, by virtue of its narrowness, the peak described by this term can be easily registered, and we have therefore retained the second term of (23).

Actually, by virtue of the specifics of the relaxation process considered by us, formula (23) is not valid in the entire region where the conditions (20) are satisfied when the Mössbauer ion interaction with the heat bath is effected by the electron-shell spin and the changes of the projections of the nuclear spin are already as the result of the hyperfine interaction. The validity of (23) is limited also by the condition that the electron-spin relaxation times not be too short, i.e., more concretely, that

$$\tau_{\text{rel}} \cong \frac{\hbar}{\gamma} \gg \frac{\hbar}{\Gamma}\left(\frac{\Gamma}{\omega_{\text{hf}}}\right)^2. \qquad (26)$$

Indeed, the validity of (23) presupposes that a complete and equilibrium population of both the electronic (Stark) and nuclear (hyperfine) sublevels of the Mössbauer ion can occur during the lifetime of the excited state of the nucleus. As to the repopulation of the electronic sublevels in accordance with the sample temperature, times on the order of $\hbar/\gamma$ are sufficient for this purpose, so that equilibrium population is always reached when (20a) is satisfied. When it comes to relaxation with respect to the nuclear variables, the corresponding times depend on the ratio of γ and ω_{hf}. At $\gamma \sim \omega_{\text{hf}}$, the repopulation of the sublevels of the hyperfine structure occurs at the same rate as the repopulation of the Stark sublevels. On the other hand, if the frequency of the jumps to the electronic subsystems is too high, so that $\gamma \gg \omega_{\text{hf}}$, then the relaxation rate in the nuclear subsystem decreases abruptly and becomes of the order of $\omega_{\text{hf}}^2/\gamma$.[7] In fact, in the case of too fast a relaxation of the electron spin, the nucleus is incapable of "sensing" fully the hyperfine interaction, and if there is no special mechanism that causes additional relaxation of the nuclear spin, then the nuclear spin ceases to relax completely, for example in the limit as $\omega_{\text{hf}}/\gamma \to 0$.

Thus, the region of applicability of formula (23) is limited by the aggregate of the conditions (20) and (26), and it naturally includes the case of intermediate relaxation $\tau_{\text{rel}} \sim 1/\omega_{\text{hf}}$, which, as noted above, is the most difficult for concrete calculations even in the absorption problem. As seen from (23), in this case the scattering of absorption problems are very close to each other from the mathematical point of view.

It should be noted that in a number of specific cases, for example when the hyperfine interaction is given by

$$H_{hf} = AI_zS_z,$$

the nuclear variables remain integrals of the motion for any ratio of ω_{hf} and γ, and consequently formula (23) does not hold in these cases. Then, however, the initial formula (10) becomes much simpler and its analysis entails no great difficulty.

We note now that in the region of very fast relaxation, when

$$\tau_{\text{rel}} \ll \frac{\hbar}{\Gamma}\left(\frac{\Gamma}{\omega_{\text{hf}}}\right)^2, \qquad (27)$$

the scattering problem also becomes much simpler. Indeed, in this case we can consider as the scattering center only the nucleus of the Mössbauer ion, and the electron-shell spin can be included in the heat bath. It is then necessary to use the general formula (10), in which the Green superoperators $\overline{G}_{\kappa\kappa'}$, and consequently also $\hat{\gamma}_{\kappa\kappa'}$, act only in the space of the nuclear variables. These superoperators were calculated in[7], and we present below their explicit form:

$$\overline{G}_{\varkappa\varkappa'}(\omega) = [\omega - \hat{L}_{\varkappa\varkappa'} - \hat{M}_{\varkappa\varkappa'}]^{-1}. \qquad (28)$$

Here $\hat{L}_{\kappa\kappa'}$ is the Liouville operator corresponding to the hyperfine-interaction Hamiltonian averaged over the heat-bath variables

$$\overline{H}_{hf}^{\varkappa} = H_Q^{\varkappa} + A_\varkappa A_{ij}\langle S^i\rangle I_\varkappa^j, \qquad (29)$$

where H_Q^K is the Hamiltonian of the quadrupole interaction of the nucleus, while the second term describes the magnetic hyperfine interaction of the nuclear spin with the averaged electron spin. For the superoperator $\hat{M}_{\kappa\kappa'}$ we have the following formula

$$\hat{M}_{\varkappa\varkappa'} = -\beta^k\widehat{(A^2I^k)}_{\varkappa\varkappa'} \pm i\gamma_{ij}\widehat{(AI^i)}_{\varkappa\varkappa'}\widehat{(AI^j)}_{\varkappa\varkappa'}, \qquad (30)$$

where the superoperators $(A^nI^i)_{\kappa\kappa'}$ are defined in the following manner in accordance with their action on an ordinary quantum-mechanical operator a:

$$\widehat{(A^nI^i)}_{\varkappa\varkappa'}a = A_\varkappa^n I_\varkappa^i a - A_{\varkappa'}^n a I_{\varkappa'}^i; \qquad (31)$$

and the coefficients β^k and γ_{ij} are expressed in terms of the Fourier component of the correlation function of the electron-spin operator, and their explicit form is given in[7].

It should be noted that the possibility of separating the nucleus as the principal scattering subsystem, and including the electron spin as part of the heat bath, is actually realized over a wider range of ratios $\omega_{\text{hf}}/\gamma$

than is given by the inequality (27). Actually formula (10), in which the Green superoperators $G_{\kappa\kappa'}$ are calculated in accordance with (28)–(31), can be used in the region where relation (18) holds. Thus, there exists a relaxation-time region

$$\frac{1}{\omega_{\text{hf}}}\left(\frac{\Gamma}{\omega_{\text{hf}}}\right) \ll \tau_{\text{rel}} \ll \frac{1}{\omega_{\text{hf}}}, \tag{32}$$

in which both formula (23) and (10) are valid in conjunction with (22)–(31).

It remains for us to analyze the case

$$\gamma \lesssim \Gamma, \tag{33}$$

which obviously completely overlaps the case of slow relaxation when the inequality (17) is satisfied. This analysis will be carried out in the next section.

4. CASE OF SLOW RELAXATION

When condition (17) is satisfied, one can assume that the superoperators $\bar{G}_{\kappa\kappa'}(\omega)$ have nonzero matrix elements $[\bar{G}_{\kappa\kappa'}(\omega)]_{ab;cd}$ only with indices $a = n_\kappa$, $b = \tilde{n}_{\kappa'}$, $c = n_{\kappa'}$, $d = \tilde{n}_{\kappa'}'$, for which

$$\begin{gathered} |\omega - E_a + E_b| \lesssim \Gamma,\ \gamma, \\ |\omega - E_c + E_d| \lesssim \Gamma,\ \gamma. \end{gathered} \tag{34}$$

Indeed, the matrix elements noted above will be of the order of either $1/\Gamma$ or $1/\gamma$. The remaining matrix elements, for which the conditions (34) are not satisfied, will be either of the order of $1/\omega_{\text{hf}}$ of $1/\Delta$, where Δ is the characteristic distance between the energy levels of the electron shell in the crystal field, by virtue of which they can be neglected. This circumstance greatly facilitates the problem of finding the concrete form of the superoperators $\bar{G}_{\kappa\kappa'}(\omega)$.

Let us consider first $\bar{G}_{eg}(\omega)$. If we assume that the lines of the absorption spectrum are not degenerate, i.e., that in the given interval of frequencies ω the relations (34) are satisfied only for one set of quantum numbers m, $m' = m^0$ and $\tilde{n}$, $\tilde{n}' = \tilde{n}^{(0)}$, then we can retain only the diagonal elements of the superoperator $\bar{G}_{eg}$

$$[\bar{G}_{eg}(\omega \pm i\Gamma/2)]_{m^{(0)}n^{(0)};\, m^{(0)}n^{(0)}} \approx (\omega - \varepsilon_{m^{(0)}n^{(0)}} \pm i\gamma_{m^{(0)}n^{(0)}}/2 \pm i\Gamma/2)^{-1}, \tag{35}$$

where $\epsilon_{mn} = E_m - E_n$, and for γ_{mn} we have in accordance with (16)

$$\gamma_{mn} = \gamma_{nn} + \gamma_{mm} + \pi_{mn}. \tag{36}$$

Here γ_{nn} and γ_{mm} are the total probabilities of transitions per unit time from the levels $|n\rangle$ and $|m\rangle$ of the Mössbauer ions:

$$\gamma_{nn} = \sum_{n' \neq n} \gamma_{nn'}, \qquad \gamma_{mm} = \sum_{m' \neq m} \gamma_{mm'}, \tag{37}$$

and γ_{ab} $(a \neq b)$ is the probability of the transition per unit time from the level $|a\rangle$ to the level $|b\rangle$:

$$\gamma_{ab} = \frac{2\pi}{\hbar} \sum_{\alpha\beta} (\rho_B)_\alpha |\langle b, \beta | H_I | a, \alpha \rangle|^2 \delta(E_a + E_\alpha - E_b - E_\beta). \tag{38}$$

For π_{mn} we have

$$\begin{gathered} \pi_{mn} = \frac{2\pi}{\hbar} \sum_{qq'} [(A_q)_{mm} - (A_q)_{nn}][(A_{q'})_{mm} - (A_{q'})_{nn}] \\ \times \sum_{\alpha\beta} (\rho_B)_\alpha (B_q)_{\alpha\beta} (B_{q'})_{\beta\alpha} \delta(E_\alpha - E_\beta). \end{gathered} \tag{39}$$

This term differs in its character from the coefficients γ_{nn} and γ_{mm}. It is connected with the fluctuations of the positions of the Mössbauer-ion levels under the influence of the heat bath, and its value is determined, in particular, by the difference between the interactions of the Mössbauer ion with the heat bath in cases when the nucleus is in the excited and the ground states. A detailed analysis of terms of this type was presented in[7] in an investigation of the absorption spectra in the limit of rapid relaxation. We note that if the energy levels of the electron shell are completely split by the internal crystal and external magnetic fields, and the distances between them is larger than the hyperfine interaction, then it is easy to verify that the coefficients (39) vanish identically, for in this case the matrix elements of the operators A_q do not depend on the quantum numbers that characterize the state of the nucleus.

Let us consider the structure of the matrix elements of the superoperator $\bar{G}_{gg}(\omega - \omega' + i\delta)$. We distinguish here between two regions of the values of the variables $\omega - \omega'$. In the first region the difference $\omega - \omega'$ lies near one of the frequencies of the hyperfine transition for the levels of the ground states of the nucleus. In this case, the situation for $\bar{G}_{gg}$ is perfectly analogous to that considered above for $\bar{G}_{eg}$. Here again, the only nonzero diagonal matrix elements are

$$[\bar{G}_{gg}(\omega - \omega' + i\delta)]_{nn';\, nn'} \approx (\omega - \omega' - \varepsilon_{nn'} + i\gamma_{nn'}/2)^{-1} \tag{40}$$

with indices for which

$$|\omega - \omega' - \varepsilon_{nn'}| \lesssim \gamma.$$

On the other hand, if the difference $\omega - \omega'$ satisfies the condition

$$|\omega - \omega'| \sim \gamma, \tag{41}$$

then the conditions (34) are certainly satisfied at $n = \tilde{n}$ and $n' = \tilde{n}'$. The nonzero matrix elements of the superoperator $\bar{G}_{gg}$ are then $(\bar{G}_{gg})_{nn;n'n'}$, and to find them it is necessary to invert the matrix $F_{nn'} \equiv (\bar{G}_{gg}^{-1})_{nn;n'n'}$, the elements of which are given by the formula

$$F_{nn'} = (\omega - \omega' + i\gamma_{nn}/2)\delta_{nn'} - {}^1\!/_2 i\gamma_{nn'}(1 - \delta_{nn'}). \tag{42}$$

The matrix elements of the superoperator $\bar{G}_{ee}(-i\Gamma)$ are determined in complete analogy with the last case. The problem is than to invert the matrix

$$F_{mm'} = -i(\Gamma + \gamma_{mm}/2)\delta_{mm'} + {}^1\!/_2 i\gamma_{mm'}(1 - \delta_{mm'}). \tag{43}$$

It should be noted that in the case of large spin S of the electron shell, the problem of inverting the matrices (42) and (43) is no longer so simple, since the rank of these matrices, which is equal to $(2S + 1)(2I_\kappa + 1)$, turns out to be relatively large.

Taking into account the arising simplifications, the general expression (10) for $\bar{\sigma}(\omega, \omega')$ in the case of slow relaxation takes the form

$$\begin{aligned} \bar{\sigma}(\omega, \omega') = -\frac{2}{\hbar c}\, \mathrm{Im}\Big\{ \sum_{mn} (\rho_A)_n \frac{|j_{nm}|^2}{\omega - \varepsilon_{mn} + {}^1\!/_2 i(\Gamma + \gamma_{mn})} \\ \times \frac{|j_{nm}'|^2}{\omega' - \varepsilon_{mn} - {}^1\!/_2 i(\Gamma + \gamma_{mn})} \Big[(\bar{G}_{gg}(\omega - \omega' + i\delta))_{nn;nn} + \frac{i(\Gamma + \gamma_{nm})}{\omega - \varepsilon_{mn} - {}^1\!/_2 i(\Gamma + \gamma_{mn})} \\ \times (\bar{G}_{ee}(-i\Gamma))_{mm;mm} \Big] + \sum_{\substack{m \\ n \neq n'}} (\rho_A)_n \frac{|j_{nm}|^2}{\omega - \varepsilon_{mn} + {}^1\!/_2 i(\Gamma + \gamma_{mn})} \\ \times \frac{|j_{n'm}'|^2}{\omega' - \varepsilon_{mn'} - {}^1\!/_2 i(\Gamma + \gamma_{mn'})} \Big[\frac{1}{\omega - \omega' - \varepsilon_{n'n} + {}^1\!/_2 i\gamma_{n'n}} \\ + \frac{i(\Gamma + \gamma_{mn})}{\omega - \varepsilon_{mn} - {}^1\!/_2 i(\Gamma + \gamma_{mn})} (\bar{G}_{ee}(-i\Gamma))_{mm;mm} \Big] \Big\} - \frac{i}{\hbar c} \sum_{\substack{m \neq m' \\ n \neq n'}} (\rho_A)_n \end{aligned}$$

$$\times(\overline{G}_{ee}(-i\Gamma))_{mm;m'm'}\frac{|j_{nm}|^2(\Gamma+\gamma_{mn})}{(\omega-\varepsilon_{mn})^2+{}^1/_4(\Gamma+\gamma_{mn})^2}\frac{|j'_{n'm'}|^2(\Gamma+\gamma_{m'n'})}{(\omega'-\varepsilon_{m'n'})^2+{}^1/_4(\Gamma+\gamma_{m'n'})^2} \tag{44}$$

In this formula, the first term describes a scattering process in which the energy ω' of the scattered quanta coincides with ω accurate to the common width of the absorption and emission lines. In the first term there is also a pure elastic Rayleigh contribution, described by the term with $(\overline{G}_{gg}(\omega - \omega' + i\delta))_{nn;nn}$. The two remaining terms describe inelastic scattering with change of energy by an amount on the order of the energy of the hyperfine interaction, the second term being responsible for those inelastic-scattering acts which are not connected with relaxation processes, while the third term represents that part of the inelastic-scattering cross section which arises only in the presence of relaxation processes.

We consider the case when all the relaxation widths $\gamma_{ab} \ll \Gamma$. In this limiting situation, greatest interest attaches to the fact that as γ_{ab} increases there appear in the scattering spectrum new lines described by the third term of (44). When the condition $\gamma_{mm'} \ll \Gamma$ is satisfied, the factor that determines the intensity of these lines will, as can be easily from Eq. (43), be given by the expression

$$-i(\overline{G}_{ee}(-i\Gamma))_{mm;m'm'} \cong \gamma_{mm'}/2\Gamma^2 \quad (m\neq m').$$

In other words, the intensity of these lines will be determined by the number of transitions from the state $|m_e\rangle$ to the state $|m'_e\rangle$ (see formula (38)), which occur during the lifetime $\tau = \hbar/\Gamma$ of the excited state of the nucleus.

In the other limiting case $\gamma_{ab} \gg \Gamma$, formula (44) goes over, into the previously obtained formula (23), accurate to terms of order γ/ω_{hf}, as can be easily verified.

Thus, formulas (44) and (23), as well as (26) and (28)–(30), cover the entire interval of variation of the parameter $\omega_{hf}\tau_{rel}$. It should be noted, however, that whereas formulas (23), (26), and (28)–(30) are applicable to all systems, provided that the frequency satisfies the corresponding conditions, formula (44) may not describe the resonant-scattering processes in most concrete situations, when degeneracy exists in the system, and this formula should be used with a certain caution. Indeed, for a number of electronic states, the sublevels of the hyperfine structure may turn out to be degenerate (as in the case, as a rule, if no external magnetic field is applied to the system); in this case the proposed formulas (35), (40), and (42) are naturally incorrect for the calculation of the matrix element $\overline{G}_{\kappa\kappa'}$, and the corresponding calculations must be carried out with allowance for the indicated degeneracy.

Application of an external magnetic field usually lifts completely the degeneracy of the hyperfine structure of both the ground and the excited states of the nucleus, so that formulas (40)–(43) for the matrix elements of the superoperators $\overline{G}_{ee}$ and $\overline{G}_{gg}$ remain in force in this case. At a large spin S of the electron shell, however, and consequently at a large number of Stark levels, there is as a rule degeneracy of the transitions between the sublevels of the hyperfine structure; in other words, the conditions (34) are satisfied simultaneously for several sets of n and m, and the calculation of the matrix elements of the superoperators $\overline{G}_{eg}$ must be carried out with allowance for this degeneracy.

We proceed to consider a number of concrete cases.

5. CONCRETE EXAMPLES. CASE OF RAPID RELAXATION IN THE PRESENCE OF QUADRUPOLE SPLITTING

We consider resonant scattering by paramagnetic ions containing Mössbauer nuclei with ground- and excited-state spins $I_g = 1/2$ and $I_g = 3/2$ (we have in mind here primarily the Mössbauer isotope Fe^{57}), under conditions when the rapid relaxation of the electron-shell spin causes the hyperfine-structure spectrum to collapse to a quadrupole doublet. Here, however, the relaxation frequencies are assumed to still not extemely large, so that the magnetic hyperfine interaction becomes manifest in the absorption spectra in the form of asymmetry of the quadrupole doublet (the Blume effect; see, e.g.,[2,13,7]).

We note immediately that in this situation, even when account is taken of the quadrupole splitting, all the sublevels of the nucleus, both in the ground and in the excited states, turn out to be doubly degenerate, and to describe the resonant-scattering spectrum it is necessary to use the general formula (10), the only simplification being that the presence of the fast relaxation processes makes it possible to regard as the scattering center only the nucleus of the Mössbauer ion, and the spin of its electron shell can be relegated to the heat bath (see Sec. 3). The latter circumstance decreases the rank of the matrices representing the superoperators $\overline{G}_{\kappa\kappa'}$, and by the same token simplifies greatly the concrete calculations.

We consider systems without an external magnetic field. In this case the second term of (29) vanishes identically, as does the first term of (30) (see[7]). We assume for simplicity that the electrostatic-field gradient at the location of the Mössbauer nucleus has axial symmetry. In this case

$$H_Q = Q[I_z^2 - {}^1/_3 I(I+1)]. \tag{45}$$

This interaction splits the levels of the excited state of the nucleus into two doublets with $m_e = \pm 3/2$ and

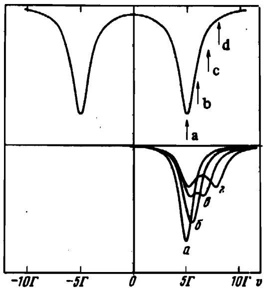

FIG. 1. Absorption spectra (top) in scattering spectra (bottom) at $\gamma_\| = \gamma_\perp = 0$, $Q = 5\Gamma$.

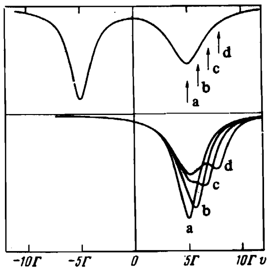

FIG. 2

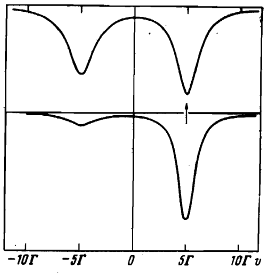

FIG. 3

FIG. 2. Absorption spectra (top) in scattering spectra (bottom) at $\gamma_\| A_g^2 = 1/2\,\Gamma$, $\gamma_\perp = 0$, $Q = 5\Gamma$.

FIG. 3. Absorption spectra (top) and scattering spectra (bottom at $\gamma_\perp A_g^2 = 1/4\Gamma$, $\gamma_\| = 0$, $Q = 5\Gamma$.

$m_e = \pm 1/2$. The ground state remains doubly degenerate in this case.

Under conditions of axial symmetry, the superoperator $\hat{M}_{\kappa\kappa'}$ (see formula (30)) is given by

$$\hat{M}_{\kappa\kappa'} = \pm i\gamma_{\parallel}(\widehat{AI^z})^2_{\kappa\kappa'} \pm i\gamma_{\perp}[(\widehat{AI^x})^2_{\kappa\kappa'} + (\widehat{AI^y})^2_{\kappa\kappa'}]. \tag{46}$$

The problem of determining the matrix elements of the superoperator $\bar{G}_{gg}$, $\bar{G}_{eg}$, and $\bar{G}_{ee}$, with allowance for the symmetry of $\hat{L}_{\kappa\kappa'}$ and $\hat{M}_{\kappa\kappa'}$ relative to replacement of m_κ and $m_{\kappa'}$ by $-m_\kappa$ and $-m_{\kappa'}$, reduces to the inversion of matrices of seventh, fourth, and eighth rank, respectively. The results of the calculations in accordance with the scheme indicated above are shown in Figs. 1–3, which show the spectra of the resonant absorption at different values of the parameters $\gamma_{\parallel}$ and $\gamma_{\perp}$. The arrows on the absorption spectra mark the values of the energies of the incident γ quanta.

In the case of longitudinal relaxation ($\gamma_{\perp} = 0$) there are observed in the scattered spectrum, naturally, only γ quanta whose energies are grouped around the energy of the excited state. Unlike the scattered state ($\gamma_{\parallel} = \gamma_{\perp} = 0$), the scattering-spectrum lines show a noticeable asymmetry when the energy of the incident quanta is varied. This circumstance is an independent confirmation of the presence of relaxation.

In the case of transverse relaxation ($\gamma_{\parallel} = 0$), the scattering spectrum contains in addition to the excited line also a second quadrupole-doublet line. Its intensity turns out to be low, but enough to be observed in experiment.

A detailed discussion of other numerous possible variants of relations between $\gamma_{\parallel}$ and $\gamma_{\perp}$ is beyond the scope of the present article.

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