

Breakdown of the "white-noise approximation" in the Mössbauer relaxation spectra: The case of $\text{Cs}_2\text{NaYbCl}_6$ †

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There are many restrictions on using the white-noise approximation to describe the line shape of radiation emitted by a Mössbauer atom experiencing paramagnetic relaxation. Using a resolvent operator method we have obtained an expression for the line shape without making such an approximation. As a result the relaxation matrix depends on the hyperfine frequencies as well as on correlation functions of the bath variables. The situation has been illustrated for the case of spin-spin relaxation of a "rigid lattice" using an exponential form for the correlation function. The calculations have been utilized to analyze the Mössbauer relaxation spectra of $\text{Cs}_2\text{NaYbCl}_6$ measured using the 84.6-keV transition in ^{170}Yb . The analysis permits us to deduce the dipolar field and the correlation time for the spin bath in this material.

I. INTRODUCTION

In the past several years, there have been a number of theoretical approaches to the study of Mössbauer line shapes in the presence of paramagnetic relaxation effects.¹⁻¹⁰ In the stochastic method, developed by Blume and co-workers,¹⁻³ one considers the hyperfine interaction between the nucleus and surrounding electrons, when this system is placed in a fluctuating environment. It is assumed that fluctuations driven by the bath, which are described by a δ function in time, cause transitions between different states of the electron-nuclear system. The form of the interaction between the electron-nuclear system and the bath is not specified in this approach, but the time distribution of the bath pulses is treated within a stochastic model. In most other approaches, an attempt is made to specify the total Hamiltonian which is made up of an electron-nuclear (or ion) part, a bath part corresponding to the external environment, and an ion-bath interaction. The line shape is then calculated within perturbation-theory approximations (with the details of the calculation varying somewhat among various authors) and is found to be dependent on certain spectral density functions for the bath variables.^{6,8} The stochastic model approaches have the distinct advantage of not relying on perturbation-theory arguments, whereas the *ab initio* calculations have the advantage of treating the interaction between the ion and its surroundings, and hence the details of the relaxations mechanism, on a microscopic basis.

Thus the two approaches are complementary to each other, and in fact yield line-shape expressions that are closely related.⁸

A more subtle problem, common to both approaches described above, arises from the assumption of the so-called "white-noise approximation" (WNA). In this approximation, one assumes that the fluctuations driving the relaxation occur at frequencies ν_c which are much greater than the unperturbed frequencies of the electron-nuclear system. That is, if $\tau_c = 1/\nu_c$ is a correlation time for the fluctuations, and A is a measure of the hyperfine energies of the electron-nuclear system (for example, the magnetic hyperfine coupling parameter), the WNA assumes $h\nu_c \gg A$. In the existing stochastic models, this approximation arises because the bath pulses are assumed to be δ functions and hence their width τ_c is zero.¹¹ In other theories, the WNA is not a part of the starting assumptions, but in practice has always been invoked by assuming that the spectral density functions $J(\omega)$ are frequency independent over the range of hyperfine frequencies and so can be replaced by $J(0)$.^{6,8} As a result of applying the WNA, the *ab initio* and stochastic approaches come on a much more equal footing, and practical calculations in both cases become greatly simplified.

Owing largely to the advantages gained from the great reduction in complexity, the WNA has been used in virtually every calculation performed to present, and applied in the evaluation of every experimentally measured Mössbauer line shape

modified due to spin-relaxation effects, although its limitations have been realized.^{7,8,11} Often it is easy to predict whether the WNA is applicable to the experimental situation investigated. For example, given the hyperfine energies in most situations encountered in Mössbauer experiments, the WNA should be valid in cases of a paramagnetic impurity coupled to a conduction-electron bath. Here τ_c is the lifetime of an electron at a paramagnetic spin [$\tau_c \sim h/(\text{Fermi energy}) \sim 10^{-15}$ sec], which is short compared to \hbar/A for virtually all systems. Two-phonon spin-lattice processes such as Raman, Orbach, etc. (τ_c of the order of the high-energy phonon lifetime), belong to the same class. However, in one-phonon processes, especially in Kramer's ions where the degenerate ground state is split only by the hyperfine interaction, the validity of the WNA is not clear, since τ_c is determined by the lifetime of phonons with energies comparable to hyperfine energies.⁹ In cases of spin-spin coupling where energy conservation is maintained by dissipation to the phonon bath, the WNA is probably valid. However, in *rigid-lattice* spin-spin systems, where energy conservation is maintained among the dipolar coupled spins alone, some problems may arise. Here one may crudely estimate the value of τ_c by calculating the rms dipolar field of the spin bath. For d transition systems, because of the smaller values of A compared to those for rare-earths and actinides, the WNA should be valid in most situations. In dipole coupled rare-earth and actinide systems, the WNA may frequently be invalid. Numerous bits of experimental data falling in this category have been published. There is, therefore, a need to consider the effects of the failure of the WNA in more detail than has previously been done.

In Sec. II, we present a theoretical formulation of the line shape of radiation emitted by a Mössbauer ion in the presence of spin relaxation *without* making any explicit assumptions regarding the WNA. Our approach here is similar in many respects to the approach of Gabriel *et al.*⁵ However, we have avoided the use of projection operators. It also differs from the calculations of Hirst⁶ or Hartmann-Boutron,⁸ in that it utilizes a resolvent-operator method such as used by Fano¹² in pressure-broadening problems of atomic spectroscopy. In Sec. III, the "relaxation matrix" containing the dynamics of the bath and its effect on the ion is calculated explicitly. In Sec. IV, the theory is applied specifically to relaxation via spin-dipolar coupling. A number of spectra are calculated for 0-2 nuclear transitions with an electron spin $S = \frac{1}{2}$ in a cubic dipolar field, using a simple assumption for the spin-correlation functions. In

Sec. V, data are presented for the 84.6-keV Mössbauer spectra of ^{170}Yb in the cubic compound $\text{Cs}_2\text{NaYbCl}_6$. The WNA is shown to be invalid for this material and the data are explained using the approach developed here. In Sec. VI, we conclude with a summary of results obtained. The essentials of this work were previously presented in a letter form.¹³

II. CALCULATION OF THE LINE SHAPE

As described in the introduction, let the Hamiltonian of the entire system be given by

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_I + \mathcal{H}_S. \quad (1)$$

Here, \mathcal{H}_0 is the local ion Hamiltonian, \mathcal{H}_S describes the bath outside the central ion, and \mathcal{H}_I gives the interaction between the two. The Mössbauer line shape of radiation emitted by a system with the above Hamiltonian can be written^{5,6,8}

$$\phi(\nu) = \text{Re} \int_0^\infty dt \exp(i\nu t - \Gamma t) \times \text{Tr}(\rho M^\dagger e^{i\mathcal{H}^\times t} M), \quad (2)$$

where M is the electromagnetic multipole operator associated with the Mössbauer transition, Γ is the natural width of the resonance level, and \mathcal{H}^\times is a Liouville operator¹⁴ based on the total Hamiltonian of the system. The trace is performed over the equilibrium properties of the entire many-body system, governed by a density matrix

$$\rho = e^{-\beta\mathcal{H}} / \text{Tr}(e^{-\beta\mathcal{H}}), \quad (3)$$

where $\beta = 1/kT$, k being the Boltzmann constant and T the temperature of the bath. Equation (2) can be formally integrated to give

$$\phi(\nu) = \text{Re} \text{Tr}[\rho M^\dagger U(\nu)M], \quad (4)$$

where $U(\nu)$ is the resolvent operator

$$U(\nu) = (\Gamma - i\nu - i\mathcal{H}^\times)^{-1}. \quad (5)$$

We will now assume that $\mathcal{H}_I \ll \mathcal{H}_0 + \mathcal{H}_S$ and seek a solution in which \mathcal{H}_I is treated perturbatively. Expanding Eq. (5) and solving iteratively, one then obtains

$$U(\nu) = U^0(\nu) + U^0(\nu)G(\nu)U^0(\nu), \quad (6)$$

where $U^0(\nu)$ does not contain \mathcal{H}_I and is given by

$$U^0(\nu) = (\Gamma - i\nu - i\mathcal{H}_0^\times - i\mathcal{H}_S^\times)^{-1}. \quad (7)$$

The interaction terms are collected in the operator

$$G(\nu) = i\mathcal{H}_I^\times \sum_{n=0}^{\infty} [iU^0(\nu)\mathcal{H}_I^\times]^n. \quad (8)$$

Since the bath does not influence directly the radiating system (i.e., $[\mathcal{H}_S, \mathcal{H}_0] = 0$), and assuming \mathcal{H}_I

$\ll kT$, the density matrix can be expressed as a product of density matrices corresponding to the local ion and the bath. Thus,

$$\rho \approx \rho_0 \rho_s = [e^{-\beta \mathcal{H}_0} / \text{Tr}(e^{-\beta \mathcal{H}_0})] [e^{-\beta \mathcal{H}_s} / \text{Tr}(e^{-\beta \mathcal{H}_s})]. \quad (9)$$

Because of this, it is convenient to use a representation in which \mathcal{H}_0 and \mathcal{H}_s are simultaneously diagonal. We thus define the ion and bath eigenstates through

$$\begin{aligned} \mathcal{H}_0 |i\rangle &= (E_0^i / \hbar) |i\rangle, \\ \mathcal{H}_s |i_s\rangle &= (E_0^s / \hbar) |i_s\rangle. \end{aligned} \quad (10)$$

Using the fact that M operates only on nuclear states, Eq. (4) can now be explicitly written

$$\begin{aligned} \phi(\nu) &= \text{Re} \sum_{if'i'f'} \langle i | \rho_0 | i \rangle \langle i | M^\dagger | f \rangle \langle f' | M | i' \rangle \\ &\quad \times \sum_{i_s i'_s} (f i_s i_i | U(\nu) | f' i'_s i'_i) \langle i_s | \rho_s | i_s \rangle. \end{aligned} \quad (11)$$

Here, the elements of the Liouville operator for the entire system are labeled by eight indices governed by Eqs. (10). Following Fano,¹² we obtain

$$\begin{aligned} \sum_{i_s i'_s} \langle i_s | \rho_s | i_s \rangle (f i_s i_i | U(\nu) | f' i'_s i'_i) \\ = (f i | [\Gamma - i\nu - i\mathcal{H}_0^x + R(\nu)]^{-1} | f' i'), \end{aligned} \quad (12)$$

which has all the bath parameters contained in a "relaxation matrix" $R(\nu)$ given by

$$R(\nu) = \sum_{n=0}^{\infty} -\langle G(\nu) \rangle [-(\Gamma - i\nu - i\mathcal{H}_0^x)^{-1} \langle G(\nu) \rangle]^n, \quad (13)$$

with

$$\langle G(\nu) \rangle = \sum_{i_s i'_s} \langle i_s | \rho_s | i_s \rangle \langle i_s | G(\nu) | i'_s \rangle. \quad (14)$$

The formal expression for the line shape is thus given by

$$\begin{aligned} \phi(\nu) &= \text{Re} \sum_{if'i'f'} \langle i | \rho_0 | i \rangle \langle i | M^\dagger | f \rangle \\ &\quad \times (f i | [\Gamma - i\nu - i\mathcal{H}_0^x + R(\nu)]^{-1} | f' i') \\ &\quad \times \langle f' | M | i' \rangle, \end{aligned} \quad (15)$$

with $R(\nu)$ given by Eqs. (8), (13), and (14). Since \mathcal{H}_0 and \mathcal{H}_s are diagonal, the matrix elements of \mathcal{H}_0^x are given by

$$(f i | \mathcal{H}_0^x | f' i') = (E_0^f - E_0^i) \delta_{ff'} \delta_{ii'}, \quad (16)$$

and the matrix elements of $R(\nu)$ are discussed in Sec. III. We note that Eq. (15) is formally identical with several other results, except for the appearance in the present case of a frequency dependence in the relaxation matrix $R(\nu)$. In the resolvent operator approach, however, the result is obtained with a minimum of difficulty with regard to limits of integration, time ordering of operators, etc. As Fano¹² notes, the assumptions used here are very weak, primarily in the form of the Hamiltonian, Eq. (1), and in the factorization of the density matrix, Eq. (9). In addition, there is an implicit assumption that the series of Eqs. (8) and (13) converge. This relies on the physical assumption that the bath has a very large number of degrees of freedom. As a result, the eigenvalues of H_s will cover a large range of values. On the average, $U^0(\nu)$ [Eq. (7)] will be small compared to \mathcal{H}_I^x , and the product $U^0(\nu) \mathcal{H}_I^x$ will be effectively small.¹² Given that, however, $R(\nu)$ can be calculated to any degree of approximation desired. In Sec. III, we will calculate $R(\nu)$ to second order in \mathcal{H}_I^x .

III. CALCULATION OF THE RELAXATION MATRIX

Combining Eqs. (7), (8), (13), and (14) gives $R(\nu)$ to second order in \mathcal{H}_I^x as

$$\begin{aligned} R(\nu) &= -\langle G(\nu) \rangle \\ &= \sum_{i_s i'_s} \langle i_s | \rho_s | i_s \rangle \\ &\quad \times (i_s i_s | \mathcal{H}_I^x (\Gamma - i\nu - i\mathcal{H}_0^x - i\mathcal{H}_s^x)^{-1} \\ &\quad \times \mathcal{H}_I^x | i'_s i'_s \rangle, \end{aligned} \quad (17)$$

where we assume without any loss of generality that the first-order contribution vanishes, $\langle \mathcal{H}_I^x \rangle = 0$. Making use of the properties of Liouville operators,¹⁴ the matrix element of the relaxation matrix can be expressed in the integral form

$$\begin{aligned} (f i | R(\nu) | f' i') &= \sum_{i_s i'_s} \langle i_s | \rho_s | i_s \rangle \int_0^\infty dt e^{i\nu t - \Gamma t} \left(\delta_{ii'} \delta_{i_s i'_s} \sum_{f'' i''_s} e^{it(E_0^{f''} - E_0^{i''})/\hbar} \langle f i_s | \mathcal{H}_I | f'' i''_s \rangle \langle f'' i''_s | \mathcal{H}_I(t) | f' i'_s \rangle \right. \\ &\quad + \delta_{ff'} \delta_{i_s i'_s} \sum_{i'' i''_s} e^{it(E_0^{f''} - E_0^{i''})/\hbar} \langle i' i'_s | \mathcal{H}_I(t) | i'' i''_s \rangle \langle i'' i''_s | \mathcal{H}_I | i i_s \rangle \\ &\quad - e^{it(E_0^{f''} - E_0^{i''})/\hbar} \langle f i_s | \mathcal{H}_I | f' i'_s \rangle \langle i' i'_s | \mathcal{H}_I(t) | i i_s \rangle \\ &\quad \left. - e^{it(E_0^f - E_0^{i'})/\hbar} \langle f i_s | \mathcal{H}_I(t) | f' i'_s \rangle \langle i' i'_s | \mathcal{H}_I | i i_s \rangle \right), \end{aligned} \quad (18)$$

where

$$\mathcal{H}_I(t) = e^{i\mathcal{H}_s t} \mathcal{H}_I e^{-i\mathcal{H}_s t}. \quad (19)$$

We next assume that the coupling between the bath and the local ion can be written

$$\mathcal{H}_I(t) = \sum_q K^q F^q(t), \quad (20)$$

where K^q depends only on operators of the local ion and $F^q(t)$ describes the bath variables. Equation (18) then becomes

$$\begin{aligned} \langle f i | R(\nu) | f' i' \rangle = & \sum_{q, q'} \int_0^\infty dt \langle F^q(t) F^{q'}(0) \rangle e^{i\nu t - \Gamma t} \left(\sum_{f''} e^{i(E_0^{f''} - E_0^i)t/h} \langle f | K^q | f'' \rangle \langle f'' | K^{q'} | f' \rangle \delta_{ii'} \right. \\ & + \sum_{i''} e^{i(E_0^{i''} - E_0^i)t/h} \langle i' | K^q | i'' \rangle \langle i'' | K^{q'} | i \rangle \delta_{ff'} \\ & - e^{i(E_0^f - E_0^i)t/h} \langle f | K^q | f' \rangle \langle i' | K^{q'} | i \rangle \\ & \left. - e^{i(E_0^f - E_0^{i'})t/h} \langle f | K^{q'} | f' \rangle \langle i' | K^q | i \rangle \right). \quad (21) \end{aligned}$$

It should be pointed out that the bath enters in above the expression only through the correlation functions which are assumed to be symmetric in time and are defined by

$$\langle F^q(t) F^{q'}(0) \rangle = \text{Tr}_s [\rho_s F^q(t) F^{q'}(0)]. \quad (22)$$

For any assumed form of the correlation function, one may then use Eqs. (15), (16), and (21) to calculate the line shape. Compared to previous theories, the form of the relaxation matrix appears rather complicated, being dependent on the hyperfine frequencies, but its relation to previous work is clear. One may suppress the ν dependence of $R(\nu)$ in two possible ways. The first is to adopt the *secular approximation*, whereby one includes the intensity only in the vicinity of a transition, and thus little is lost if we take $h\nu \approx E_0^i - E_0^f$. Then Eq. (21) becomes equivalent to the results of Hirst⁶ or of Hartmann-Boutron and Spanjaard.¹⁵ More stringently, and what has always been done in practice, is to make the *white-noise approximation*. This is equivalent to saying that $\langle F^q(t) F^{q'}(0) \rangle$ fluctuates with frequencies much greater than the unperturbed hyperfine frequencies; i.e., there exists a correlation time τ_c such that $\nu_c = 1/\tau_c$

$\gg (E_0^f - E_0^i)/h$. In that case, the time integrals in Eq. (21) are strongly dominated by the rapid decay of the correlation functions and we may approximate, for example,

$$\begin{aligned} \int_0^\infty dt \exp[-\Gamma t + i\nu t + i(E_0^f - E_0^i)t/h] \langle F^q F^{q'}(t) \rangle \\ \simeq \int_0^\infty \langle F^q F^{q'}(t) \rangle dt \equiv J_{qq'}(0), \quad (23) \end{aligned}$$

where $J_{qq'}(0)$ is a spectral density function evaluated at zero frequency. Equation (21) then reduces to results previously obtained.^{6, 8, 15}

In general, Eq. (21) cannot be cast into a more useful form without an explicit assumption concerning the form of the correlation functions. Very few specific calculations of the correlations functions exist. For illustrative purposes, we will adopt the stochastic approach of Kubo and Toyabe.¹⁶ We presume that the random variation of the bath parameters is *stationary*, *Gaussian*, and *Markoffian*, and take

$$\langle F^q(0) F^{q'}(t) \rangle = \langle F^q F^{q'} \rangle e^{-\lambda_{qq'} t}. \quad (24)$$

Then Eq. (21) becomes

$$\begin{aligned} \langle f i | R(\nu) | f' i' \rangle = & \sum_{q, q'} \langle F_q F_{q'} \rangle \left(\delta_{ii'} \sum_{f''} D_{qq'}(f'', i') \langle f | K^q | f'' \rangle \langle f'' | K^{q'} | f' \rangle \right. \\ & + \delta_{ff'} \sum_{i''} D_{qq'}(f', i'') \langle i' | K^q | i'' \rangle \langle i'' | K^{q'} | i \rangle \\ & \left. - D_{qq'}(f', i) \langle f | K^q | f' \rangle \langle i' | K^{q'} | i \rangle - D_{qq'}(f, i') \langle f | K^{q'} | f' \rangle \langle i' | K^q | i \rangle \right), \quad (25) \end{aligned}$$

where

$$D_{qq'}(f, i) = [\Gamma + \lambda_{qq'} - i\nu - i(E_0^f - E_0^i)/h]^{-1}. \quad (26)$$

The WNA is recovered here by taking $D_{qq'}(f, i) = 1/\lambda_{qq'}$, or $J_{qq'}(0) = \langle F^q F^{q'} \rangle / \lambda_{qq'}$.

IV. SPIN-SPIN INTERACTIONS IN CUBIC SALTS

The above formalism is applicable to a wide variety of mechanisms. We will consider here the case in which the Mössbauer atom is in a concentrated paramagnetic salt at low temperatures, where the dominant relaxation mechanism arises through the dipole-dipole coupling. Further we assume a "rigid lattice" so that the phonons do not modulate the dipolar coupling. Thus, the energy conservation is achieved within the dipolar coupled spin system alone, rather than through energy transfer into a phonon bath, conduction electrons, etc. In such a system, \mathcal{H}_0 contains the local hyperfine and Zeeman energies, \mathcal{H}_s contains the spin dipolar and Zeeman energies for the rest of the ions (outside the local ions), and \mathcal{H}_I is the dipolar energy between the local ion and its neighbors. This last term can be written

$$\begin{aligned} \mathcal{H}_I(t) &= \vec{S} \cdot \vec{h}(t) \\ &= S_x h_x(t) + \frac{1}{2}[S_+ h_-(t) + S_- h_+(t)], \end{aligned} \quad (27)$$

where \vec{S} is the electronic angular momentum of the ion and $\vec{h}(t)$ is the time-dependent field set up by the neighbors, with components

$$\begin{aligned} h_x &= \sum_j \frac{g g_j \mu_B^2}{r_j^3} [(1 - 3 \cos^2 \theta_j) S_{jx} - \frac{3}{2} \sin \theta_j \cos \theta_j \\ &\quad \times (e^{-i\phi_j} S_{j+} + e^{i\phi_j} S_{j-})], \end{aligned} \quad (28a)$$

$$\begin{aligned} h_+ &= \sum_j \frac{g g_j \mu_B^2}{r_j^3} [-\frac{1}{2}(1 - 3 \cos^2 \theta_j) S_{j+} \\ &\quad - 3 \sin \theta_j \cos \theta_j e^{i\phi_j} S_{jx} \\ &\quad - \frac{3}{2} \sin^2 \theta_j e^{2i\phi_j} S_{j-}], \end{aligned} \quad (28b)$$

$$h_- = h_+^\dagger. \quad (28c)$$

Here g is the electronic gyromagnetic ratio of the central ion, g_j that of the j th neighbor, and $(r_j,$

$\theta_j, \phi_j)$ are the coordinates of the j th neighbor with respect to the central ion. We recognize that the form of Eqs. (27) and (20) are the same with the K^q being components of S and the F^q being components of \vec{h} . Thus the relaxation matrix involves matrix elements of \vec{S} and correlation functions of $\vec{h}(t)$.

Direct evaluations of the correlation functions $\langle h_i h_j(t) \rangle$ are not presently available. Calculations have been published¹⁷ utilizing the "truncated" dipolar Hamiltonian, but these are not applicable here. We should point out that in EPR and NMR discussions of spin-spin interactions, it is common to retain only the first term in each component of Eqs. (28). This "truncated" Hamiltonian arises because only those terms are energy conserving in the presence of the external magnetic fields. However, for the case of zero-field relaxation or in situations where external magnetic fields are small compared to the dipolar field, it is important to retain the full spin-spin Hamiltonian of Eqs. (28). In the absence of calculated correlation functions in our case, we shall assume them to be of the form of Eq. (24). In addition, we shall make certain assumptions which are valid for the cubic system at high temperatures (see Appendix A), viz., that the spins along different directions are uncorrelated, that the rms values of the dipolar field in all directions are equal, and that a single correlation frequency $\nu_c \equiv \lambda_{qq'}$ applies in all directions. Thus we have

$$\langle h_q h_{q'}(t) \rangle = \delta_{qq'} \langle h_q h_q(t) \rangle = \frac{1}{3} \langle h^2 \rangle e^{-\nu_c t} \delta_{qq'}, \quad (29)$$

where $\langle h^2 \rangle = \langle h_x^2 \rangle + \langle h_y^2 \rangle + \langle h_z^2 \rangle = 3 \langle h_z^2 \rangle$. We furthermore require

$$\langle h_q h_q(t) \rangle = \langle h_q(t) h_q \rangle, \quad (30)$$

where $q = x, y, z$. Equation (30) assumes the correlation function to be symmetric in time. The relaxation matrix [Eq. (25)] then becomes

$$\begin{aligned} \langle f_i | R(\nu) | f' i' \rangle &= \frac{1}{3} \langle h^2 \rangle \sum_q \left(\delta_{ii'} \sum_{f''} D(f'', i') \langle f | K^q | f'' \rangle \langle f'' | K^q | f' \rangle + \delta_{ff'} \sum_{i''} D(f', i'') \langle i' | K^q | i'' \rangle \langle i'' | K^q | i \rangle \right. \\ &\quad \left. - D(f', i) \langle f | K^q | f' \rangle \langle i' | K^q | i \rangle - D(f, i') \langle f | K^q | f' \rangle \langle i' | K^q | i \rangle \right), \end{aligned} \quad (31)$$

where

$$D(f, i) = [\Gamma + \nu_c - i\nu - i(E_0^f - E_0^i)/\hbar]^{-1}, \quad (32)$$

and $K^q = S^q$ for $q = x, y, z$. We note that for this cubic case, the WNA merely replaces $D(f, i)$ by ν_c^{-1} , which can be factored out of the large parentheses in Eq. (31). Thus the bath variables enter only through a single "relaxation frequency"

$$W = \langle h_z^2 \rangle / \nu_c = \frac{1}{3} \langle h^2 \rangle / \nu_c. \quad (33)$$

Equation (31) then becomes identical with results obtained assuming the WNA.^{6,8} In the following, we will consider line-shape calculations using Eqs. (15) and (31) for specific values of $\langle h_z^2 \rangle$ and ν_c . In order to demonstrate the influence of a full theory without the WNA, we shall compare calculations with and without the WNA.

We now use the above formalism to calculate relaxation spectra, using parameters which are pertinent to the data to be discussed below. We consider the 84.4 keV, $0^+ - 2^+$ resonance in ^{170}Yb . We take the Yb^{3+} ion to be in a cubic crystal field with the ground state being a well-isolated Γ_6 Kramer's doublet.¹⁸ In the presence of a small external field, H_{ext} , the local ion Hamiltonian for the nuclear excited state is

$$\mathcal{H}_0^{\text{ex}} = A \vec{I} \cdot \vec{S} - g \mu_B S_z H_{\text{ext}}, \quad (34)$$

where A is the hyperfine coupling constant, g is the gyromagnetic ratio for the Γ_6 state, and $S = \frac{1}{2}$. A similar Hamiltonian without the hyperfine term exists for the nuclear ground state so that the Liouville operator $\mathcal{H}_0^{\text{ex}}$ can be formed. The static features of the Mössbauer hyperfine spectra for this case have been discussed by us previously.^{19,20}

Figure 1 shows spectra calculated using Eqs. (15) and (31) with $H_{\text{ext}} = 0$, $A = -699$ MHz ($= -10.28$ mm/sec), $\Gamma = 95$ MHz ($= 1.4$ mm/sec), and $\langle h_z^2 \rangle = 4.62 \times 10^5$ MHz². Three spectra shown by the solid lines correspond to different values of ν_c . For instance, in Fig. 1(a), ν_c is 2039 MHz. The spectrum is a typical two-line pattern for a ^{170}Yb , Γ_6 level case with slight distortions in line shape and relative line intensities (from those expected in the static situation) due to relaxation effects.

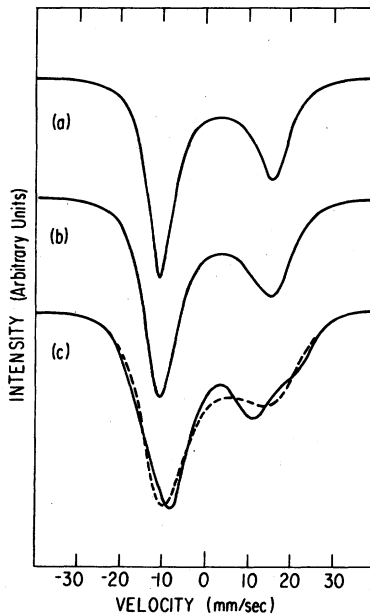


FIG. 1. Mössbauer relaxation spectra for the $0 \rightarrow 2$ transition in ^{170}Yb for $S = \frac{1}{2}$ in a cubic symmetry, calculated using the relaxation matrix of Eq. (31), with $A = -699$ MHz, $\Gamma = 95$ MHz, and $\langle h_z^2 \rangle = 4.6 \times 10^5$ MHz². (a) $\nu_c = 2039$ MHz; (b) $\nu_c = 1359$ MHz; and (c) $\nu_c = 680$ MHz. The dashed line in (c) represents the WNA line shape.

An identical spectrum can be obtained using the WNA with $W = 206$ MHz. This value is very close to $\langle h_z^2 \rangle / \nu_c = 226$ MHz. Thus in this case where $\nu_c \approx 3A$, the WNA is nearly valid. In Fig. 1(b), we have $\nu_c \approx 2A$, and the line shape cannot be well reproduced using the WNA unless the values of W and A are made parameters. The line shape, for example, can be reproduced in the WNA by setting $W = 287$ MHz (compared to $\langle h_z^2 \rangle / \nu_c = 340$ MHz), and $A = -795$ MHz (compared to -699 MHz). Thus the WNA analysis of data with $\nu_c \approx 2A$ will result in relaxation and hyperfine parameters which are not physically correct. Finally, in Fig. 1(c), we consider $\nu_c \approx A$. Here the dashed line represents the best approximation to the line shape using the WNA theory. One sees that the detailed structure of the true spectrum is considerably more complicated, and cannot be reproduced by a WNA calculation.

The solid lines in Fig. 2 show the spectra calculated using no WNA, with a fixed value of $\nu_c = 680$ MHz ($\nu_c \approx A$) for different values of $\langle h_z^2 \rangle$. The best approximation to these spectral shapes using the WNA is shown by the dashed lines, and discrepancies are clearly visible in all the cases.

Figure 3(a) shows the static hyperfine pattern calculated for the case of an external magnetic field of 450 G. The presence of the field removes the degeneracy of the hyperfine levels and causes substantial line splitting as described previously.²⁰

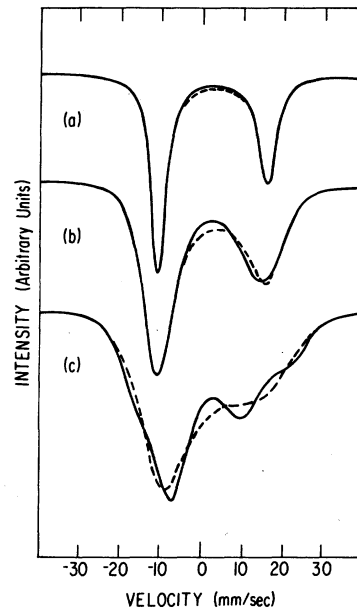


FIG. 2. As in Fig. 1, but with $\nu_c = 680$ MHz, and for $\langle h_z^2 \rangle$ values of (a) 9.2×10^4 MHz²; (b) 2.8×10^5 MHz²; and (c) 5.5×10^5 MHz². The dashed lines represent the WNA line shapes.

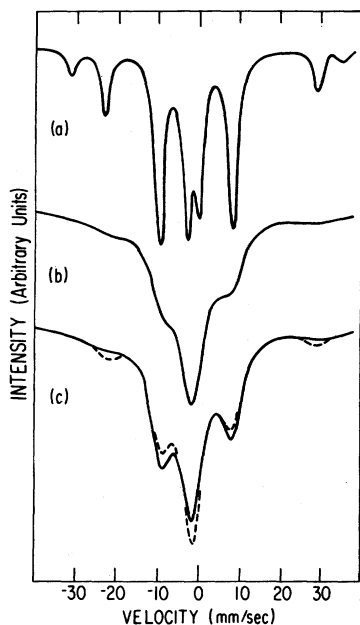


FIG. 3. As in Fig. 1, but with $H_{\text{ext}} = 450$ G and $g = 2.585$ (Ref. 23). (a) $\nu_c = 0$; $\langle h_z^2 \rangle = 0$; (b) $\nu_c = 2.0 \times 10^5$ MHz, $\langle h_z^2 \rangle = 6.1 \times 10^5$ MHz²; (c) $\nu_c = 2.0 \times 10^3$ MHz, $\langle h_z^2 \rangle = 6.8 \times 10^3$ MHz². The dashed line in (c) represents the WNA line shape.

Notice that some of the hyperfine frequencies occur at rather large energies of 2000 MHz (30 mm/sec). Figure 3(b) shows intermediate relaxation spectrum with $\nu_c \sim 300A$. In this case, the WNA is certainly valid, and the line shape shown was exactly reproduced with such a WNA calculation. Figure 3(c) shows the spectrum with roughly the same value of $\langle h_z^2 \rangle / \nu_c$, but with $\nu_c \approx 3A$. The dashed line is the closest line shape obtained with the WNA. We would like to point out that $\nu_c \approx 3A$ was sufficient to allow the WNA for the case with $H_{\text{ext}} = 0$ spectrum [Fig. 1(b)]. However, here, due to splitting of hyperfine levels by the external magnetic field, one has $h\nu_c$ approximately equal to the hyperfine transition energies, and hence a noticeable discrepancy.

V. ANALYSIS OF RESULTS FOR $\text{Cs}_2\text{NaYbCl}_6$

We now report the Mössbauer spectra of $\text{Cs}_2\text{NaYbCl}_6$ measured with and without an external magnetic field using the 84.3-keV $0^+ - 2^+$ transition in ^{170}Yb , and discuss the line-shape analysis using the theory developed in Secs. I-IV.

The compound $\text{Cs}_2\text{NaYbCl}_6$ has the ideal cryolite structure, in which the Yb^{3+} ion sits on a site of O_h symmetry.²¹ The cubic crystalline electric field experienced by the Yb^{3+} ion can be described by the Hamiltonian¹⁸

$$\mathcal{H}_{\text{CEF}} = W[x(O_4^0 + 5O_4^4) + (1-x)(O_6^0 - 21O_6^6)], \quad (35)$$

where the notations from Ref. 18 have been used. The Hund's ground state $F_{7/2}$ of the Yb^{3+} ion is split into three electronic levels corresponding to the irreducible representations Γ_6 , Γ_7 , and Γ_8 . Point-charge model calculations of the parameters W and x in Eq. (35) predict the ground state to be a Γ_6 doublet with an effective spin $S = \frac{1}{2}$. This has been confirmed from the analysis of the susceptibility²² and Mössbauer studies¹⁹ on this material. The first excited state (Γ_8) is about 400 K above the ground level,^{22,23} too high to make significant contributions at low temperatures. The hyperfine interaction Hamiltonian is hence given by Eq. (34). Previous work²³ has measured A by electron-nuclear double resonance (ENDOR) for ^{171}Yb in $\text{Cs}_2\text{NaYbCl}_6$. Converting their value to ^{170}Yb , we obtain $|A| = 699$ MHz. The negative g value for the Γ_6 state however makes A negative. Hence $A = -699$ MHz will be fixed in all our data analysis.

Spectra obtained at 4.2 K in external fields of 0, 350, and 450 G are shown in Fig. 4. The data with $H_{\text{ext}} = 0$ [Fig. 4(a)] has been analyzed using the WNA, and $A = -699$ MHz. The result is shown by the dashed line in the figure. Two problems arise here:

(i) The fitted curve does not agree in detail with the data. The discrepancy cannot be re-

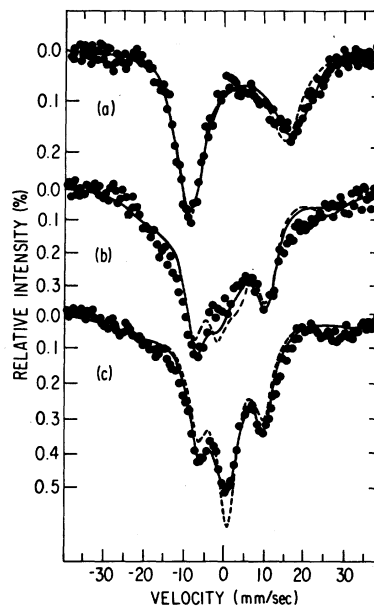


FIG. 4. Experimental spectra of $\text{Cs}_2\text{NaYbCl}_6$ measured at 4.2 K in external magnetic fields of (a) 0 G; (b) 350 G; and (c) 450 G. The solid lines are least-squares fits to the data using the relaxation matrix of Eq. (31) and the dashed lines represent the fit with the WNA in the relaxation matrix.

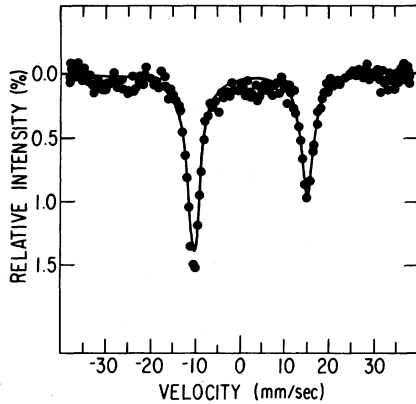


FIG. 5. Mössbauer paramagnetic hyperfine structure measured with a source of ^{170}Tm in $\text{Cs}_2\text{NaYCl}_6$ against a single-line absorber of YbAl_3 . The spectrum has been plotted with the absorber velocity convention.

moved by including absorber thickness effects,²⁴ or the dispersion term previously observed for the ^{170}Yb resonance.^{25,26} As we have previously discussed,¹⁹ if we allow A to be a variable, then an improved fit to the data is obtained with A being 7% greater than the ENDOR value, and even 4% greater than the free-ion value. This increase in A is nonphysical, since we know of no mechanism in an insulator to increase A above the free-ion value for the rare-earth ions.

Another test of whether the A anomaly is related to relaxation effects is to measure in a situation identical to the ENDOR experiment, viz., performing the Mössbauer experiment on the dilute impurity of Yb in $\text{Cs}_2\text{NaYCl}_6$. This was done as a source study in which we doped $\text{Cs}_2\text{NaYCl}_6$ with 0.1% radioactive ^{170}Tm . The spectrum measured against a single-line YbAl_3 absorber is shown in Fig. 5. The analysis gives the value of $A = -(685 \pm 40)$ MHz in excellent agreement with the ENDOR work. In addition, we see no relaxation effects at all as to be expected for a Kramers doublet in a nonmagnetic host at low temperatures.

(ii) As shown in Sec. IV, the WNA leads to description of the spectrum in terms of a single parameter $W = \langle h_z^2 \rangle / \nu_c$. The dashed line in Fig. 4(a) arises from a value of $W = 212$ MHz. In the Appendix A, we calculate $\langle h_z^2 \rangle = 2.99 \times 10^5 \text{ MHz}^2$ using a dipolar sum. This permits us to estimate $\nu_c = \langle h_z^2 \rangle / W \approx 1400$ MHz. Indeed, $\nu_c \approx 2A$, and as discussed in Sec. IV, the WNA is not valid for such a case. The solid line in Fig. 4(a) shows a fit with the formalism of Sec. IV using the relaxation matrix of Eq. (31). Here we have fixed A to the ENDOR value and made $\langle h_z^2 \rangle$ and ν_c parameters in a least-squares-fitting procedure. One sees that the line-shape discrepancy is now resolved. The fit yields

$\langle h_z^2 \rangle = (2.8 \pm 1.0) \times 10^5 \text{ MHz}^2$, in agreement with the calculated value, and a spin-correlation frequency $\nu_c = 830 \pm 200$ MHz.

Data taken in small external fields comparable to the dipolar fields in this salt (253 G, see Appendix A) are shown in Figs. 4(b) and 4(c). Again, the dashed lines show the WNA fits, and the solid lines the fits using the frequency-dependent relaxation matrix, in both cases keeping A equal to the ENDOR value. The results for the relaxation frequency W obtained from the WNA fit, and the dipolar bath parameters $\langle h_z^2 \rangle$ and ν_c from the fits using the frequency-dependent relaxation matrix of Eq. (31) are summarized in Table I. The general features visible from the table and the figure are the following: (a) As the external field increases, the hyperfine transition frequencies also increase²⁰ and become more comparable with ν_c . As a result, the line-shape distortions from the WNA calculations become increasingly more pronounced. (b) The values of W obtained by utilizing the WNA differ by a factor of 3 from the values estimated using $\langle h_z^2 \rangle / \nu_c$ found when a more correct line shape is employed using Eq. (31). (c) The value of $\langle h_z^2 \rangle$ is found to be nearly field independent for the values of H_{ext} used, since $g\mu_B H_{\text{ext}} \ll kT$, and in agreement with the calculated value. (d) The value of ν_c appears to be weakly field dependent.

Although the present theory gives marked improvement to the line shape over a WNA approach, some discrepancies are still visible in the measurements with the external magnetic field. This is partly due to the specific form of the correlation function that we have assumed [Eq. (29)]; in particular, to the assumption that the correlation function is isotropic even in the presence of the external fields. The present development, however, allows one to now begin a detailed consideration of such assumptions and to test the theoretical results against experimental spectra.

TABLE I. Values obtained for the dipolar bath parameters in $\text{Cs}_2\text{NaYbCl}_6$ at 4.2 K and various external fields.

H_{ext} (kOe)	$\langle h_z^2 \rangle$ (10^5 MHz^2) ^a	ν_c (10^3 MHz) ^a	$\langle h_z^2 \rangle / \nu_c$ (MHz)	W (MHz) ^b
0	2.8 ± 0.0	0.8 ± 0.2	336 ± 150	187 ± 15
350	3.3 ± 0.7	1.1 ± 0.2	308 ± 100	100 ± 15
450	4.1 ± 0.7	1.3 ± 0.2	305 ± 70	114 ± 15

^a Obtained from data using frequency-dependent relaxation.

^b Obtained from data assuming a white-noise approximation.

VI. CONCLUSIONS

We have considered the question of the white-noise approximation in the context of the calculation of paramagnetic relaxation line shapes in Mössbauer spectroscopy. An expression for the line shape was developed using a resolvent operator method. This avoids some of the complications of the other approaches to the problem and explicitly displays the manner in which the relaxation matrix is to be calculated from the ion-bath interaction \mathcal{H}_I . This matrix was calculated explicitly to second-order in \mathcal{H}_I , and then applied to a discussion of spin-spin relaxation in a "rigid lattice." In the absence of more concrete information, an exponential form was assumed for the spin-spin correlation functions and the resulting expressions were applied to illustrate the influence of the frequency-dependent relaxation matrix on the line shape. Finally, the theory was used to explain the spectra for ^{170}Yb in the cubic compound $\text{Cs}_2\text{NaYbCl}_6$. Discrepancies which were present if the white-noise approximation was assumed were resolved. The detailed analysis yielded values for the mean-square dipolar field in this material which was in agreement with calculation. The spin-correlation time τ_c was found to be $(1.2 \pm 0.3) \times 10^{-9}$ sec. The present work constitutes the first direct application of Mössbauer spectroscopy to a precise measurement of spin-correlation times.

APPENDIX A: CALCULATION OF MEAN-SQUARE DIPOLAR FIELD COMPONENTS

In evaluating the correlation function of Eq. (22), we must consider the bath averaged quantities $\langle h_q h_{q'} \rangle$ where the components are given by Eqs. (28). If $H_s \ll kT$, and $g\mu_B H_{\text{ext}} \ll kT$, $\langle h_q h_{q'} \rangle$ is pro-

portional to some *static* spin correlations at *infinite* temperatures. Using latin indices to denote lattice sites and greek indices to denote Cartesian components of the spin vector, we have for $j \neq k$,

$$\langle S_{j\mu} S_{k\nu} \rangle = \langle S_{j\mu} \rangle \langle S_{k\nu} \rangle = 0$$

and

$$\langle S_{j\mu} S_{j\nu} \rangle = \langle S_\mu S_\nu \rangle = \langle S_\mu^2 \rangle \delta_{\mu\nu} = \frac{1}{3} \langle \vec{S}^2 \rangle \delta_{\mu\nu}. \quad (\text{A1})$$

In the second line of Eq. (A1), we have used the translational invariance and the infinite-temperature properties of the spin correlations.

Using these relations, it follows from Eq. (28a),

$$\begin{aligned} \langle h_z^2 \rangle &= g^2 \mu_B^4 \sum_j \frac{g_j^2}{r_j^6} [(1 - 3 \cos^2 \theta_j) \langle S_z^2 \rangle \\ &\quad + \frac{3}{2} \sin^2 \theta_j \cos^2 \theta_j (\langle S_x^2 \rangle + \langle S_y^2 \rangle)] \\ &= \frac{1}{3} g^2 \mu_B^4 S(S+1) \sum_j \frac{g_j^2}{r_j^6} (1 + 3 \cos^2 \theta_j). \end{aligned} \quad (\text{A2})$$

A similar procedure for the other components yields

$$\langle h_x^2 \rangle = \langle h_y^2 \rangle = \frac{1}{6} g^2 \mu_B^4 S(S+1) \sum_j \frac{g_j^2}{r_j^6} (5 - 3 \cos^2 \theta_j) \quad (\text{A3})$$

and

$$\langle h_x h_y \rangle = \langle h_x h_z \rangle = \langle h_y h_z \rangle = 0. \quad (\text{A4})$$

For the case of Γ_6 state in $\text{Cs}_2\text{NaYbCl}_6$, we have $g = -\frac{8}{3}$, $S = \frac{1}{2}$, and the distance between the near-neighbor ions is 7.54 Å. Carrying out the lattice sum to the third-nearest neighbors in the cryolite structure yields $\langle h_x^2 \rangle = \langle h_y^2 \rangle = \langle h_z^2 \rangle = 2.99 \times 10^5 \text{ MHz}^2$. We may define an rms dipolar field H_d by

$$H_d = S \langle (h^2) \rangle^{1/2} = g \mu_B S H_d, \quad (\text{A5})$$

where $\langle h^2 \rangle = 3 \langle h_z^2 \rangle$. This gives $H_d = 253 \text{ G}$.

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¹¹It has recently been shown that the existing stochastic models (e.g., Ref. 3) can be generalized to also cover cases where the condition $\hbar\nu_c \gg A$ is not valid. Some of the results derived are then equivalent to expressions [e.g., Eq. (31)] used here. For details, see S. Dattagupta, *Phys. Rev. B* (to be published).

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