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Relaxation Effects in Spectra: Eigenvalue Treatment of Superoperators*

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Superoperators have been used in several recent papers to treat the effects of relaxation on the shape of spectrum lines. Although the emphasis in these papers has been on Mössbauer spectra, the generality of the treatments allows them to be applied in many fields of spectroscopy. To apply these theories it has been necessary in most cases of interest to plot out the spectrum, point by point, inverting a relatively large matrix at each point. In this paper it is shown that parameters of the spectrum, such as linewidths, may be obtained directly from the eigenvalues of the superoperators used in these theories. With the help of perturbation theory, some general results are then obtained in the limiting cases of slow and fast relaxation rates. This eigenvalue treatment greatly simplifies problems such as determining how a particular term in the Hamiltonian affects the shape of the spectrum.

I. INTRODUCTION

Recently, several papers[1–3] have appeared that use a superoperator formalism to obtain the Mössbauer line shape in the presence of spin relaxation. As has been pointed out,[3] the same formalism is applicable in other types of spectroscopy where random processes affect the line shape. All of these papers have the common feature that the spectrum shape is given by an expression in which the principal term is $(\omega-\mathcal{P})^{-1}$, where $\mathcal{P}$ is a superoperator. Except in a few simple cases, numerical methods have been the only feasible way of evaluating the spectra. This, however, obscures the relationship between the parameters characterizing the spectrum and the constituents of $\mathcal{P}$. For example, using numerical methods to obtain the linewidth produced by a given $\mathcal{P}$, one would first plot the spectrum by inverting $\omega-\mathcal{P}$ for different values of ω, and then "measure" the resulting linewidth. To obtain the dependence of the linewidth on the relaxation rate, it would be necessary to repeat this process for many values of the relaxation rate.

In this paper, we show that (i) the spectrum is given by a sum of resonance lines, the positions and widths of which are, respectively, the real and imaginary parts of the eigenvalues of $\mathcal{P}$. The amplitudes of the lines are obtained from matrix elements of the eigenvectors of $\mathcal{P}$. (ii) In cases where one part of $\mathcal{P}$ is small, a perturbation expansion can be used to obtain expressions for the line positions, widths, and amplitudes. With this perturbation technique it becomes fairly simple in many cases to examine how various terms of $\mathcal{P}$ affect the spectrum shape. The perturbation technique is particularly useful when the relaxation frequencies are either much larger or much smaller than the hyperfine frequencies. In these cases, the hyperfine terms in $\mathcal{P}$ or the relaxation terms, respectively, may be regarded as the perturbation.

In Sec. II we discuss the basic theory: the eigenvalue treatment and the perturbation expansion for the eigenvalues and eigenvectors. We then use the theory to discuss the case of slow relaxation in Sec. III, and the case of fast relaxation in Sec. IV. In order to avoid being too abstract and obscure, this paper discusses the relaxation effects in the context of Mössbauer spectroscopy. The changes necessary for application in other fields of spectroscopy will not generally alter the basic structure of the theory.

II. BASIC THEORY

One may use the fact that an operator and its inverse have the same eigenfunctions to show that the inverse of an Hermitian operator A may be written as[4]

$$A^{-1}=\textstyle\sum_i \lambda_i^{-1}|i\rangle\langle i| \qquad (1)$$

or, equivalently,

$$\langle a|A^{-1}|b\rangle=\textstyle\sum_i \langle a|i\rangle\langle i|b\rangle/\lambda_i\ , \qquad (2)$$

where λ_i and $|i\rangle$ are eigenvalues and eigenvectors of A.

Essentially the same idea may be used to invert the expression $\omega-\mathcal{P}$. Using the notation of Ref. 3, $\mathcal{P}$ is given by

$$\mathcal{P}=-\mathcal{H}_0^{\times}+i\mathcal{W}-\tfrac{1}{2}i\Gamma\ , \qquad (3)$$

where Γ is the natural linewidth. The Liouville superoperator $\mathcal{H}_0^{\times}$ is defined as the commutator of the static Hamiltonian $\mathcal{H}_0$:

$$\mathcal{H}_0^{\times}A=\mathcal{H}_0A-A\mathcal{H}_0\ , \qquad (4)$$

for any operator A. The Hamiltonian $\mathcal{H}_0$ contains all of the time-independent interactions of the nucleus and its surrounding electrons, principally the crystal field, Zeeman, and hyperfine interactions. The relaxation superoperator $\mathcal{W}$ contains all the information about the relaxation of the spin system; the exact form depends on the particular model used. Due to this last term, $\mathcal{P}$ is a non-Hermitian superoperator, so that finding the inverse of $\omega-\mathcal{P}$ is slightly more complicated than Eq. (1).

The use of superoperators was first introduced by Kubo[5] and then applied by Zwanzig.[6] Since then, the formalism has been used in several fields by a number of authors. The present work uses several properties of superoperators which have previously been discussed by Fano[7] and Ben-Reuven.[8] The properties of superoperators have been summarized in the appendices of papers by Primas,[9] Blume,[2] and Gabriel.[10] The notation in the present paper is a mixture of that of Blume and of Gabriel. One new convention has been introduced: script letters (except $\mathcal{H}$) denote superoperators.

The complications caused by the non-Hermiticity of $\mathcal{P}$ are due to the fact that the eigenvectors of a non-Hermitian matrix are not necessarily orthogonal. We will denote the eigenvectors of $\mathcal{P}$ by B_α and the eigenvalues by p_α:

$$\mathcal{P}B_\alpha = p_\alpha B_\alpha \ . \tag{5}$$

The Hermitian conjugate of $\mathcal{P}$ has eigenvectors which we denote C_β; the corresponding eigenvalues are the complex conjugates p_β^*. As $\mathcal{P}$ is a superoperator, B_α and C_β are ordinary operators. In matrix element form the eigenvalue equations are

$$\sum_{kl} (ij|\mathcal{P}|kl)\langle k|B_\alpha|l\rangle = p_\alpha \langle i|B_\alpha|j\rangle \ , \tag{6}$$

$$\sum_{ij} \langle i|C_\beta|j\rangle^* (ij|\mathcal{P}|kl) = p_\beta \langle k|C_\beta|l\rangle^* \ . \tag{7}$$

The notation of Eqs. (6) and (7) is somewhat clumsy for manipulative purposes. By using superoperator notation, we may write the eigenvalue equations more compactly:

$$\mathcal{P}|B_\alpha) = p_\alpha |B_\alpha) \ , \tag{8}$$

$$(C_\beta|\mathcal{P} = p_\beta (C_\beta| \ . \tag{9}$$

By multiplying both sides of Eq. (8) by $(C_\beta|$ on the left, and Eq. (9) by $|B_\alpha)$ on the right, we obtain the result[11] that $(C_\beta|B_\alpha)=0$ unless $\alpha=\beta$. Since the eigenvalue equations do not determine the normalization of A or B, we may choose it such that

$$(C_\beta|B_\alpha) = \delta_{\beta\alpha} \ . \tag{10}$$

This provides the necessary orthogonality relation, from which we may obtain

$$\sum\nolimits_\alpha |B_\alpha)(C_\alpha| = 1 \ . \tag{11}$$

Using Eq. (11) we may obtain an expression for $(\omega-\mathcal{P})^{-1}$ which is similar to Eq. (1). Making use of the fact that $\mathcal{P}$, $\omega-\mathcal{P}$, and $(\omega-\mathcal{P})^{-1}$ all have the same eigenvectors, we obtain

$$\begin{aligned}(\omega-\mathcal{P})^{-1} &= \sum_{\alpha\beta} |B_\alpha)(C_\alpha|(\omega-\mathcal{P})^{-1}|B_\beta)(C_\beta| \\ &= \sum\nolimits_\alpha (\omega-p_\alpha)^{-1}|B_\alpha)(C_\alpha| \ . \end{aligned} \tag{12}$$

The spectrum shape is obtained from the function $g(\omega)$ defined as

$$g(\omega) = i\,\mathrm{Tr}[\rho A^\dagger(\omega-\mathcal{P})^{-1}A] \ , \tag{13}$$

where ρ is the density matrix, and A is the operator for the emission (or absorption) of a photon. In superoperator notation, Eq. (13) may be written

$$g(\omega) = i(A\rho|(\omega-\mathcal{P})^{-1}|A) \ , \tag{14}$$

where we have assumed that ρ is Hermitian. Using Eq. (12) the inversion is readily obtained,

$$g(\omega) = \sum_\alpha \frac{i(A\rho|B_\alpha)(C_\alpha|A)}{\omega-p_\alpha} \ . \tag{15}$$

In more conventional notation, the expressions in the numerator are given by

$$(A\rho|B_\alpha) = \mathrm{Tr}[\rho A^\dagger B_\alpha] \ , \tag{16}$$

$$(C_\alpha|A) = \mathrm{Tr}[C_\alpha^\dagger A] \ . \tag{17}$$

The spectrum line shape is obtained from the real part of $g(\omega)$:

$$\mathrm{Re}[g(\omega)] = \sum_\alpha \frac{\frac{1}{2}a_\alpha\gamma_\alpha - b_\alpha(\omega-\omega_\alpha)}{(\omega-\omega_\alpha)^2 + (\gamma_\alpha/2)^2} \ , \tag{18}$$

where we have introduced the real and imaginary parts:

$$(A\rho|B_\alpha)(C_\alpha|A) = a_\alpha + ib_\alpha \ , \tag{19}$$

$$p_\alpha = \omega_\alpha - i\gamma_\alpha/2 \ . \tag{20}$$

The first term in the numerator of Eq. (18) yields a Lorentzian with width γ_α, area proportional to a_α, and centered at $\omega=\omega_\alpha$. There is also a dispersion term proportional to b_α. Thus, we see that the eigenvalues and matrix elements of the eigenvectors of $\mathcal{P}$ give the important parameters of the spectrum.

As a simple illustration of the theory, we take the trivial case of no relaxation. Setting $\mathcal{W}=0$ in Eq. (3) we have $\mathcal{P} = -\mathcal{H}_0^\times - \frac{1}{2}i\Gamma$. Since Γ is diagonal, the eigenvectors of $\mathcal{P}$ are the same as those of the Liouville operator $\mathcal{H}_0^\times$, which is Hermitian. As has been pointed out,[2,8] the eigenvalues and eigenvectors of $\mathcal{H}_0^\times$ may be obtained directly from those of $\mathcal{H}_0$, the static Hamiltonian of the system; thus,

$$\mathcal{P}|ij) = (\omega_{ij} - \tfrac{1}{2}i\Gamma)|ij) \ , \tag{21}$$

where[12] $\omega_{ij} = -(E_i - E_j)$, and i and j denote eigenstates of $\mathcal{H}_0$:

$$\mathcal{H}_0|i\rangle = E_i|i\rangle \ . \tag{22}$$

Since $\mathcal{H}_0^\times$ is Hermitian, the eigenvectors B_α and C_α are identical, and are given by

$$B_\alpha \equiv B_{ij} = |i\rangle\langle j| \ . \tag{23}$$

The spectrum is then given by

$$\mathrm{Re}[g(\omega)] = \sum_{ij} a_{ij} \frac{\Gamma/2}{(\omega-\omega_{ij})^2+(\Gamma/2)^2} \ , \tag{24}$$

where

$$a_{ij} = \langle j|\rho A^\dagger|i\rangle\langle i|A|j\rangle \tag{25}$$

(assuming the right-hand side is real). When the density matrix is diagonal (the usual case), this simplifies to

$$a_{ij} = \rho_{jj}|\langle i|A|j\rangle|^2 \ . \tag{26}$$

Equations (24)–(26) are, of course, just the expected result.

In many cases, one is interested more in the parameters, such as ω_α and γ_α which characterize the spectrum, than in the spectrum shape itself $g(\omega)$. We have shown that the task of finding these parameters in the *presence* of relaxation effects is essentially similar to finding them in the *absence* of relaxation effects: It is only necessary to find the eigenvalues and eigenvectors of a matrix. In the latter case, a number of techniques have been developed to help find the eigenvalues and eigenvectors. Perturbation theory is one of the more useful of these techniques, and may readily be adapted to our problem. As we shall see, it is very useful for investigating the limiting cases of fast or slow relaxation rates.

As before, the principal complication is that we are dealing with a non-Hermitian superoperator. It is straightforward to rederive perturbation theory for this case; we will only list some of the low-order results here. As a rule of thumb, one replaces $|i\rangle$ in ordinary perturbation theory with $|B_\alpha)$, and $\langle i|$ with $(C_\alpha|$. We divide $\mathcal{P}$ into two parts, $\mathcal{P}_0$ and $\mathcal{P}_1$, with $\mathcal{P}_1$ assumed much smaller than $\mathcal{P}_0$. We denote the two sets of eigenvectors and the eigenvalues of $\mathcal{P}_0$ by $|B_\alpha^0)$, $(C_\alpha^0|$, and p_α^0, respectively. The low-order terms with which we shall be concerned are

$$p_\alpha^{(1)} = \mathcal{P}_{\alpha\alpha} \ , \tag{27}$$

$$p_\alpha^{(2)} = \sum_{\beta(\neq\alpha)} \frac{\mathcal{P}_{\alpha\beta}\,\mathcal{P}_{\beta\alpha}}{\Delta p_{\alpha\beta}} \ , \tag{28}$$

$$|B_\alpha^1) = \sum_{\beta(\neq\alpha)} |B_\beta^0)\frac{\mathcal{P}_{\beta\alpha}}{\Delta p_{\alpha\beta}} \ , \tag{29}$$

$$(C_\alpha^1| = \sum_{\beta(\neq\alpha)} \frac{\mathcal{P}_{\alpha\beta}}{\Delta p_{\alpha\beta}}(C_\beta^0| \ , \tag{30}$$

where

$$\mathcal{P}_{\alpha\beta} = (C_\alpha^0|\mathcal{P}_1|B_\beta^0) \ , \tag{31}$$

$$\Delta p_{\alpha\beta} = p_\alpha^{(0)} - p_\beta^{(0)} \ . \tag{32}$$

From Eqs. (29) and (30) the first-order change in the size of the line is obtained:

$$a_\alpha^{(1)} + ib_\alpha^{(1)} = \sum_{\beta(\neq\alpha)} \frac{I_{\alpha\beta}\mathcal{P}_{\beta\alpha} + \mathcal{P}_{\alpha\beta}I_{\beta\alpha}}{\Delta p_{\alpha\beta}} \ , \tag{33}$$

where

$$I_{\alpha\beta} = (C_\alpha^0|A)(A\rho|B_\beta^0) \ . \tag{34}$$

In this notation the zero-order line size is just $I_{\alpha\alpha}$. Whenever $\mathcal{P}_0$ has a subset of degenerate eigenvectors, these must be chosen, as in ordinary perturbation theory, so that $\mathcal{P}_1$ is diagonal within this subset.

III. SLOW RELAXATION

When the relaxation rate is slow, the relaxation term $\mathcal{W}$ may be treated as a perturbation. The main part of $\mathcal{P}$ is then

$$\mathcal{P}_0 = -\mathcal{H}_0^\times - \tfrac{1}{2}i\Gamma \ , \tag{35}$$

while the perturbation term is

$$\mathcal{P}_1 = i\mathcal{W} \ . \tag{36}$$

The zero-order eigenvalues and eigenvectors have already been given in Eqs. (21)–(23) in terms of the eigenfunctions and eigenvalues of $\mathcal{H}_0$, which we will assume to be known. However, we might comment that if ordinary perturbation theory is used to diagonalize $\mathcal{H}_0$, one could just as well take the perturbation term out of $\mathcal{H}_0^\times$ and include it in $\mathcal{P}_1$.

The first-order correction to the eigenvalues produces a broadening[13]:

$$\tfrac{1}{2}\gamma_{ij}^{(1)} = -(ij|\mathcal{W}|ij) \ . \tag{37}$$

The second-order correction produces a line shift[14]:

$$\omega_{ij}^{(2)} = -\sum_{kl(\neq ij)} \frac{(ij|\mathcal{W}|kl)(kl|\mathcal{W}|ij)}{\omega_{ij}^{(0)} - \omega_{kl}^{(0)}} \ . \tag{38}$$

From Eqs. (37) and (38) the general features of slow relaxation may be discerned. The diagonal matrix elements of $\mathcal{W}$ lead to a broadening of the spectrum lines directly proportional to the relaxation rate. The remaining matrix elements cause a shift in the spectrum line that is quadratic in the relaxation rate. Since the numerator in Eq. (38) is usually positive, the relaxation causes the spectrum lines to be "attracted" to each other inversely proportional to their separation.

To examine Eq. (37) in more detail, let us consider the case where the hyperfine interactions are diagonal with respect to the electronic states. Specifically, we write the Hamiltonian $\mathcal{H}_0$ in three parts:

$$\mathcal{H}_0 = \mathcal{H}_e + \mathcal{H}_{en} + \mathcal{H}_n \ , \tag{39}$$

where $\mathcal{H}_e$ and $\mathcal{H}_n$ are the Hamiltonians for the electrons and the nucleus, respectively, and $\mathcal{H}_{en}$ is the interaction between them—the hyperfine interactions. When those matrix elements of $\mathcal{H}_{en}$ which involve different electronic states (of $\mathcal{H}_e$) are completely negligible (or zero) compared to the energy separation of the electronic states, $\mathcal{H}_{en}$ is said to be diagonal with respect to the electronic states. In this case, an eigenfunction of $\mathcal{H}_0$ is a product of an electronic and a nuclear wave function:

$$\mathcal{H}_0 | \mu m \rangle = E_{\mu m} | \mu m \rangle \ , \tag{40}$$

where μ denotes a state of $\mathcal{H}_e$; m simply denotes a nuclear state and not necessarily the z component of nuclear angular momentum. The right-hand side of Eq. (37) then becomes $-(\mu m, \nu n | \mathcal{W} | \mu m, \nu n)$. For Mössbauer spectra we need only consider the case $\mu = \nu$, since the intensities of Eq. (25) vanish otherwise. For purely electronic relaxation, Eq. (37) becomes[15]

$$\tfrac{1}{2}\gamma^{(1)}_{\mu mn} = -W_{\mu\mu} = \sum_{\mu(\neq\nu)} W_{\mu\nu} \ , \tag{41}$$

where $W_{\mu\nu}$ is the relaxation rate for the transition $\mu \to \nu$. Since the inverse of the right-hand side of Eq. (41) is just the relaxation lifetime of $|\mu\rangle$, this term simply represents lifetime broadening.

When "off-diagonal" terms of $\mathcal{H}_{en}$ (i.e., matrix elements $\langle \mu m | \mathcal{H}_{en} | \nu n \rangle$ for which $\mu \neq \nu$) are no longer negligible, the eigenstates of $\mathcal{H}_0$ are no longer simple products as in Eq. (40). Consequently, the interpretation is not so simple. Nevertheless, the results are quantitatively similar.

IV. FAST RELAXATION

When the relaxation rate is fast, the hyperfine interactions may be treated as a perturbation. The main part of $\mathcal{P}$ is then

$$\mathcal{P}_0 = i\,\mathcal{W} - \mathcal{H}_e^{\times} - \tfrac{1}{2} i \Gamma \ , \tag{42}$$

while the perturbation is

$$\mathcal{P}_1 = -\mathcal{H}_{en}^{\times} \ . \tag{43}$$

The nuclear Hamiltonian $\mathcal{H}_n$ consists of two parts: small terms such as a nuclear Zeeman interaction, which may be included in $\mathcal{P}_1$; and, in the Mössbauer effect, a large term giving the energies (several keV) of the nuclear levels. This latter term only adds a constant to ω_m, and will consequently be omitted here.

To illustrate the features of fast relaxation we use the stochastic model proposed by Clauser and Blume[3] for the general case of electronic relaxation. Since $\mathcal{P}_0$ has only electronic operators in this case, we will initially omit the nuclear quantum numbers for simplicity. The matrix $(\mu\nu | \mathcal{P}_0 | \mu'\nu')$ breaks up into two parts. The "principal" part of $\mathcal{P}_0$ is the square submatix for which $\mu = \nu$ and $\mu' = \nu'$. The matrix elements of this part are given by

$$(\mu\mu | \mathcal{P}_0 | \nu\nu) = -i(\tfrac{1}{2}\Gamma\delta_{\mu\nu} - W_{\mu\nu}) \ , \tag{44}$$

where $W_{\mu\nu}$ is the relaxation rate for the transition $\mu \to \nu$, and

$$W_{\mu\mu} = -\sum_{\nu(\neq\mu)} W_{\mu\nu} \ . \tag{45}$$

The remaining "nonprincipal" part of $\mathcal{P}_0$ is zero except for the diagonal terms

$$(\mu\nu | \mathcal{P}_0 | \mu\nu) = \omega_{\mu\nu} - i(\lambda_{\mu\nu} + \tfrac{1}{2}\Gamma) \quad \text{for } \mu \neq \nu \ , \tag{46}$$

where $\omega_{\mu\nu} = -(E_\mu - E_\nu)$ and

$$\lambda_{\mu\nu} = -(W_{\mu\mu} + W_{\nu\nu}) \ , \tag{47}$$

which is the sum of the relaxation rates of the two electronic states. This part of $\mathcal{P}_0$ is already diagonal; however, the eigenvectors $|\mu m, \nu n)$ with $\mu \neq \nu$, are not immediately interesting since the zero- and first-order intensities vanish for Mössbauer spectra [see Eq. (34)].

We are not prepared to write down all the eigenvectors of the principal part of $\mathcal{P}_0$; however, there is one important eigenvector we can find. Equation (45) may be rewritten: $\sum_\nu W_{\mu\nu} = 0$, which says that the columns of the submatrix W are not linearly independent, and hence the determinant of W vanishes. Thus, one of the eigenvalues of W is zero; the corresponding eigenvalue of $\mathcal{P}$ is $-\tfrac{1}{2}i\Gamma$. The requirement of probability conservation,[16] which $\mathcal{W}$ satisfies, can be written

$$\sum_{\mu'} (\mu\nu | \mathcal{W} | \mu'\mu') = 0 \ , \tag{48}$$

from which it follows that an eigenvector of $\mathcal{P}_0$ is

$$|B_0^0) = \sum_\mu |\mu\mu) \ . \tag{49}$$

The requirement of thermal equilibrium,[17] which $\mathcal{W}$ should satisfy, can be written

$$\sum_\mu q_\mu (\mu\mu | \mathcal{W} | \mu'\nu') = 0 \ , \tag{50}$$

where q_μ is the probability of the electrons occupying the state $|\mu\rangle$. We have assumed that ρ is diagonal with $\rho_{\mu\mu} = q_\mu$. Even if this is not the case, a similar result may be obtained. From Eq. (50) it follows that C_0^0 is given by

$$(C_0^0| = \sum_\mu q_\mu (\mu\mu| \ . \tag{51}$$

The correct normalization for B_0^0 and C_0^0 is obtained with $\sum q_\mu = 1$.

Reintroducing the nuclear quantum numbers m and n, the zero-order intensity is

$$\begin{aligned} I_{00mn} &= (C_{0mn}^0 | A)(A\rho | B_{0mn}^0) \\ &= \left[\sum_\mu | q_\mu \langle \mu m | A | \mu n \rangle\right]\left[\sum_\mu q_\mu \langle \mu n | A^\dagger | \mu m \rangle\right] \\ &= |\langle m | A | n \rangle|^2 \ . \end{aligned} \tag{52}$$

Using the fact that the other eigenvectors are orthogonal to B_0^0 and C_0^0, it may be shown that all the other zero- and first-order intensities vanish: We will show that $(A\rho|B_{\alpha mn}^0)=0$, unless $\alpha=0$; a similar demonstration holds for $(C_{\alpha mn}^0|A)$. First we expand $B_{\alpha mn}^0$:

$$|B_{\alpha mn}^0)=\textstyle\sum_\mu b_\mu|\mu m,\ \mu n)\ . \tag{53}$$

Then

$$(A\rho|B_{\alpha mn}^0)=\langle n|A^\dagger|m\rangle\textstyle\sum_\mu q_\mu b_\mu\ . \tag{54}$$

However, from Eq. (10), B_α^0 and C_0^0 are orthogonal:

$$0=(C_0^0|B_\alpha^0)=\textstyle\sum_\mu q_\mu b_\mu\ . \tag{55}$$

Comparing Eqs. (54) and (55), we have the desired result. This shows why B_0^0 and C_0^0 are the important eigenvectors: Up to at least second order, all the others have zero intensity.

The remaining problem is the degeneracy of the nuclear states. To apply perturbation theory, the nuclear states m, m' must be chosen so that the off-diagonal matrix elements of $\mathcal{P}_1$ vanish,

$$(C_{0mn}^0|\mathcal{P}_1|B_{0m'n'}^0)=0\ , \tag{56}$$

unless both $m=m'$ and $n=n'$. As we shall show, the correct nuclear states are the eigenstates of the "effective hyperfine Hamiltonian" $\mathcal{H}_{\text{eff}}$ defined as

$$\mathcal{H}_{\text{eff}}=\textstyle\sum_\mu q_\mu\langle\mu|\mathcal{H}_{\text{en}}|\mu\rangle\ . \tag{57}$$

If, for example, the hyperfine Hamiltonian is

$$\mathcal{H}_{\text{en}}=a\vec{\mathrm{I}}\cdot\vec{\mathrm{S}}\ , \tag{58}$$

then the effective Hamiltonian is

$$\mathcal{H}_{\text{eff}}=\vec{\mathrm{h}}\cdot\vec{\mathrm{I}}\ , \tag{59}$$

where $\vec{\mathrm{h}}$ is an ordinary vector, not an operator:

$$\vec{\mathrm{h}}=a\textstyle\sum_\mu q_\mu\langle\mu|\vec{\mathrm{S}}|\mu\rangle\ , \tag{60}$$

a component of which is

$$h_z=a\textstyle\sum_\mu q_\mu\langle\mu|S_z|\mu\rangle\ . \tag{61}$$

To show that the eigenstates of $\mathcal{H}_{\text{eff}}$ are the correct nuclear states, we first write out the matrix elements of $\mathcal{P}_1$:

$$\begin{aligned}(C_{0mn}^0|\mathcal{P}_1|B_{0m'n'}^0)&=-\sum_{\mu\mu'}q_\mu(\mu m,\ \mu n|\mathcal{H}_{\text{en}}^\times|\mu'm',\ \mu'n')\\&=-\sum_\mu q_\mu[\delta_{nn'}\langle\mu m|\mathcal{H}_{\text{en}}|\mu m'\rangle-\delta_{mm'}\langle\mu n'|\mathcal{H}_{\text{en}}|\mu n\rangle]\ .\end{aligned} \tag{62}$$

If $|m\rangle$ is an eigenstate of $\mathcal{H}_{\text{eff}}$, the matrix elements become

$$\textstyle\sum_\mu q_\mu\langle\mu m|\mathcal{H}_{\text{en}}|\mu m'\rangle=\langle m|\mathcal{H}_{\text{eff}}|m'\rangle=E_m\delta_{mm'}\ , \tag{63}$$

and we obtain the desired result

$$(C_{0mn}^0|\mathcal{P}_1|B_{0m'n'}^0)=\delta_{mm'}\delta_{nn'}\omega_{mn}\ , \tag{64}$$

where $\omega_{mn}=-(E_m-E_n)$. Equation (64) also gives the first-order corrections to the line positions. Thus, through first order, the spectrum lines are determined by the effective Hamiltonian $\mathcal{H}_{\text{eff}}$.

The second-order contributions are of two types. The first comes from matrix elements involving the "principal" eigenvectors (i.e., the eigenvectors of the principal part of $\mathcal{P}_0$). Since we do not have a general formula for these eigenvectors or their eigenvalues, we cannot give the exact terms here. In spite of this, it is not difficult to see that they will produce terms of the form $i\langle\mu m|\mathcal{H}_{\text{en}}|\mu n\rangle\times\langle\mu'm'|\mathcal{H}_{\text{en}}|\mu'n'\rangle/w_\alpha$, where w_α is an eigenvalue of the matrix W [Eq. (44)] and is thus related to the relaxation rate. This is the "motional narrowing" term usually encountered in fast relaxation.

So far we have encountered terms involving only hyperfine matrix elements which are diagonal with respect to the electronic states. The "off-diagonal" matrix elements enter the second type of second-order contribution. This second type comes from matrix elements of the eigenvectors $|\mu m,\nu n)$, the eigenvalues of which are given by Eq. (46). This part of the second-order contribution, which we denote $p^{(2b)}$, is given by

$$p_{0mn}^{(2b)}=\sum_{\mu\nu}{}'\sum_{m'n'}\frac{(C_{0mn}^0|\mathcal{H}_{\text{en}}^\times|\mu m',\nu n')(\mu m',\nu n'|\mathcal{H}_{\text{en}}^\times|B_{0mn}^0)}{-\omega_{\mu\nu}+i\lambda_{\mu\nu}}\ , \tag{65}$$

where $\sum'$ indicates that the terms with $\mu=\nu$ are to be omitted from the sum. By a straightforward derivation, the real and imaginary parts of Eq. (65) may be found in terms of ordinary matrix elements:

$$\omega_{0mn}^{(2b)}=\sum_{\mu\nu}{}'\,q_\nu\frac{F_{\mu\nu n}-F_{\mu\nu m}}{1+(\lambda_{\mu\nu}/\omega_{\mu\nu})^2}\ , \tag{66}$$

$$\frac{\gamma_{0mn}^{(2b)}}{2}=\sum_{\mu\nu}{}'\,q_\nu\frac{F_{\mu\nu n}+F_{\mu\nu m}-2G_{\mu\nu mn}}{(\lambda_{\mu\nu}/\omega_{\mu\nu})+(\omega_{\mu\nu}/\lambda_{\mu\nu})}\ , \tag{67}$$

where

$$F_{\mu\nu m}=\sum_{m'}\frac{|\langle\nu m|\mathcal{H}_{\text{en}}|\mu m'\rangle|^2}{E_\nu-E_\mu}\ , \tag{68}$$

$$G_{\mu\nu mn}=\frac{\langle\nu m|\mathcal{H}_{\text{en}}|\mu m\rangle\langle\mu n|\mathcal{H}_{\text{en}}|\nu n\rangle}{E_\nu-E_\mu}\ . \tag{69}$$

When the relaxation rates $(\lambda_{\mu\nu})$ are small compared with the electronic-level separations $(\omega_{\mu\nu})$, yet large compared with the hyperfine energies, Eq. (66) has a simple interpretation: When $F_{\mu\nu m}$ is summed over μ, the second-order correction to the energy of the state $|\nu m\rangle$ results. Neglecting the denominator, Eq. (66) then averages these second-order energies to give the second-order corrections to the energy differences of the effective Hamiltonian $\mathcal{H}_{\mathrm{eff}}$.

As the relaxation rate exceeds the electronic-level separation, the denominator of Eq. (66) causes the second-order terms to vanish. This behavior is caused by the presence of $\lambda_{\mu\nu}$ in the diagonal of the "nonprincipal" part of $\mathcal{W}$. It is also responsible for the existence of the broadening given by Eq. (67). As a function of $\lambda_{\mu\nu}$, this broadening has a maximum at $\lambda_{\mu\nu}=\omega_{\mu\nu}$ and has the appearance of a broad resonance.[18] Further discussion of this effect, including hypothetical examples, will be given in a forthcoming paper.

V. CONCLUSION

In this paper we have shown that the parameters characterizing line shapes may be obtained directly from the eigenvalues and eigenvectors of a superoperator $\mathcal{P}$. This superoperator appears in the results of several theories concerning the effects of relaxation of line shapes. By using a perturbation expansion, we have obtained some general results in the limiting cases of fast and slow relaxation. Some of these results have been obtained previously, though in somewhat more restrictive circumstances. When the relaxation rate is slow, there is a broadening of the spectrum lines proportional to the relaxation rate and a shift proportional to the square of the relaxation rate. When the relaxation rate is fast, the hyperfine spectrum line positions are determined primarily by a thermally averaged "effective" Hamiltonian. The lines are broadened (or narrowed) inversely proportional to the relaxation rate. If the hyperfine Hamiltonian contains terms which are not diagonal with respect to the electronic states, a new effect appears: a line broadening which has a maximum when the relaxation rate is of the order of the electronic-level spacing.

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[11] Degeneracies here may be handled the same way as for ordinary Hermitian operators.

[12] Note the unconventional minus sign in the definition of ω_{ij}.

[13] The diagonal elements of $\mathcal{W}$ are negative (see Ref. 3) so that $\gamma_{ij}^{(1)}$ is positive.

[14] The notation $kl(\neq ij)$ indicates that *the* term with $k=i$ and $l=j$ is to be omitted from the sum. The terms with $k=i$, $l\neq j$ or $k\neq i$, $l=j$ are *not* excluded. See Eq. (28).

[15] See Eqs. (49) and (53) of Ref. 3.

[16] See Eq. (58) of Ref. 3.

[17] See Eq. (61) of Ref. 3.

[18] The existence of this "resonance" was first suggested by M. Blume (private communication).