

# Theory of Spin Relaxation via Quantum-Molecular Systems: Resonance Effects\*

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A relaxation equation is derived for the spin-density matrix on the assumptions that (1) the spins are weakly coupled to the molecular degrees of freedom which are described quantum mechanically and (2) the relaxation of the molecular systems is well represented by a general time-independent relaxation matrix which can include effects of weak as well as strong collisions. The irreversibility of the spin relaxation is achieved with no further assumptions, and is given in detail in terms of the normal modes of relaxation of the molecular systems. It is also pointed out that the present formulation inherently includes the assumption of resonant-type interactions between molecular systems and spins.

## I. INTRODUCTION

SPIN-RELAXATION techniques have been achieving considerable prominence in terms of the information they can provide on molecular-relaxation processes. Usually the molecular processes are analyzed from the viewpoint of classical-damped motions.<sup>1,2</sup> But the possible importance of quantum-mechanical analyses of the relevant molecular processes cannot be overlooked.<sup>3-5</sup> Any satisfactory understanding of the techniques must answer the questions pertaining to the spin-molecular interaction, or how the spins probe the molecular states, and how the molecular states interact with their surroundings. Since each question can in itself present significant complications, it is useful to separate them as much as possible. The purpose of the present note is to obtain such a separation appropriate to molecular states which are described quantum mechanically. The approach here may be regarded as a generalization of an earlier "strong-collision" theory<sup>3</sup> in which the relaxation of the molecular-rotational states was very simply treated. It was then possible to give, under certain assumptions, a relaxation equation for the spin-density matrix. In the present formulation, a generalized description of the relaxation of molecular states is introduced. As long as the spin-molecular coupling is weak compared to the relaxation of molecular states, an irreversible spin-relaxation equation ensues with no other assumptions needed.

It must also be noted that the present theory is essentially a resonant-type theory as are all related theories; (this includes semiclassical formulations where a continuous frequency distribution is available from the relaxation of the molecular systems). That is, spin relaxation occurs by a resonant—within the appropriate linewidth of molecular states—transfer of energy to the molecular systems which rapidly dis-

sipate it to the thermal bath. Nonresonant or higher-order processes (e.g., virtual excitations of molecular systems by the spins and then followed by loss of energy to the thermal modes) are not adequately treated by the present formalism, although a qualitative indication of their smallness compared to resonant terms is effectively included.

## II. THEORY

Let an ensemble of the combined spin-molecular systems be described by the density matrix  $\rho(t)$ . It is assumed that the equation of motion for  $\rho(t)$  may be written as

$$i(d\rho/dt) = [\mathcal{H}, \rho] - i\Gamma\rho, \quad (1)$$

where  $\mathcal{H}$  is the Hamiltonian for a combined system and is given by

$$\mathcal{H} = \mathcal{H}_M + \mathcal{H}_S + V = \mathcal{H}_0 + V. \quad (2)$$

Here  $\mathcal{H}_M$  and  $\mathcal{H}_S$  are the unperturbed Hamiltonians of the molecular and spin systems, respectively, while  $V$  is the coupling term operating on both molecular and spin variables, and  $\mathcal{H}$  is time independent. The term  $\Gamma\rho$  has been introduced phenomenologically<sup>6</sup> into Eq. (1) to describe in a general way the relaxation of the combined system as a result of its thermal contact. Equation (1) is formally equivalent to Bloch's Boltzmann equation of motion for weakly interacting spin systems.<sup>7</sup> The fact that only the molecular systems (and *not* the spins) are assumed to be directly coupled to the thermal modes means that the "relaxation" matrix  $\Gamma$  will only affect the molecular systems directly, and the spin relaxation is achieved indirectly via the spin-molecular coupling term. Equation (1) is clearly

\* N. Bloembergen and Y. R. Shen, Phys. Rev. **133**, A37 (1964) employ a similar starting point in their general treatment of the nonlinear susceptibilities in parametric media, etc. We are not explicitly including an interaction term with a coherent radiation field, although for the present purposes this could formally be regarded as contained in  $\mathcal{H}_S$ . It would then be helpful to transform to a rotating reference frame (Ref. 2, Chap. 12), and this will change the nature of the interaction representation in Eqs. (22). When the spin interaction with the radiation field is weak compared to  $\Gamma$ , the former should have no significant effects on the spin-relaxation terms derived in this paper (cf. Ref. 2, Chap. 12).  
<sup>7</sup> F. Bloch, Phys. Rev. **102**, 104 (1956).

\* Supported in part by the Advanced Research Projects Agency.

<sup>1</sup> N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. **73**, 679 (1948).

<sup>2</sup> A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, London, 1961).

<sup>3</sup> J. H. Freed, J. Chem. Phys. **41**, 7 (1964).

<sup>4</sup> J. H. Freed, J. Chem. Phys. **43**, 1710 (1965).

<sup>5</sup> See also references cited in Refs. 3 and 4.

valid in the limit  $V=0$ , since the molecular and spin systems are uncoupled, and it is proper to treat the relaxation of the molecular degrees of freedom as independent of the spins. As long as

$$|\Gamma| \gg V, \quad (3)$$

then even as  $V$  is introduced, the effects of  $V$  will be negligible upon the molecular states when compared to their lattice-induced widths and relaxation transitions contained in  $\Gamma$ . Thus it is perfectly sound from the point of view of the molecular systems to retain the same form of  $\Gamma$  in Eq. (1), which does include  $V$ , provided Eq. (3) holds. This argument is, however, not completely sound from the viewpoint of the spin states. Their relaxation will ultimately be found to be of order  $|V^2/\Gamma| \ll \Gamma$  by Eq. (3), so that small changes in  $\Gamma$  resulting from the introduction of  $V$  may not be negligible. The nonresonant spin-relaxation processes would arise from such effects. In the present formulation, nonresonant terms in  $V$  still appear but as a resonant interaction of spins with the extreme wings of the molecular line shape, which is described as a Lorentzian by Eq. (2), although this is clearly not true for the extreme wings.<sup>8</sup>

The relaxation transitions of the molecular-spin systems are described by

$$(\Gamma\rho)_{nn} = \sum_{n'} (W_{nn'}\rho_{n'n'} - W_{n'n}\rho_{nn}), \quad (4)$$

where  $W_{nn'}$  is the transition probability from state  $n'$  to  $n$  and  $\rho_{nn}$  is the diagonal density-matrix element for the  $n$ th molecular state but is still an operator on spin states. (We are not assuming anything at this point about the behavior of  $\rho$ , but are pointing out that the assumptions already discussed lead to a natural expansion of  $\Gamma\rho$  in terms of the molecular states uncoupled to the spins.) The assumption of detailed balance yields

$$W_{nn'} = W_{n'n} \exp(h\omega_{nn'}/kT), \quad (5)$$

where  $\hbar\omega_{nn'}$  is the energy separation between states  $n$  and  $n'$ , so that the relaxation is toward thermal equilibrium. However, *no restriction* is placed on the nature of the intermolecular interactions leading to the  $W_{nn'}$ . Thus, for example, either strong or weak collisions may be treated within the present formulation. However, the  $\mathfrak{H}$  diagonal elements  $\rho_{nn}$  will, in general, relax in a coupled fashion requiring a normal modes solution for the eigenvalues. The off-diagonal density-matrix elements, whose relaxation is associated with the transition linewidths, are assumed to obey

$$(\Gamma\rho)_{nn'} = - \sum_{m,m'} \Gamma_{nn',mm'} \rho_{mm'}, \quad (6)$$

where

$$(\omega_{nn'} - \omega_{mm'}) \Gamma^{-1} \ll 1. \quad (6')$$

Equation (6) implies that the off-diagonal elements may be coupled, but the "adiabatic assumption" which allows only off-diagonal elements between pairs of states with nearly the same energy differences to be coupled, is introduced by Eq. (6'). This is essentially an approximate conservation-of-energy requirement.<sup>7</sup> Any coupling via  $\Gamma$  between diagonal and off-diagonal elements of  $\rho_{nn'}$  is being neglected.<sup>9</sup> In the absence of any couplings of  $\rho_{nn'}$ , Eq. (6) becomes:

$$(\Gamma\rho_{nn'}) = -\Gamma_{nn',nn'}\rho_{nn'} \equiv -\Gamma_{nn'}\rho_{nn'}, \quad (7)$$

where  $\Gamma_{nn'}$  is the "linewidth" for the  $n \leftrightarrow n'$  transition. It is, in general, composed of secular effects—i.e., modulation of the eigenenergies of the  $n$  and  $n'$  levels and nonsecular—uncertainty broadening from transitions away from the  $n$  and  $n'$  levels.

It is useful to obtain a basis for  $\Gamma$  corresponding to the normal modes of relaxation of the molecular part of  $\rho(t)$ . First  $\rho(t)$  is partitioned into the distinct non-coupling components each distinguished by a different value for the subscript  $\lambda$ . The distinction between the normal modes for matrix elements of  $\rho(t)$  which are diagonal and off-diagonal in molecular states is represented by  $\lambda \rightarrow \delta$  and  $\lambda \rightarrow \nu$ , respectively. It is further useful to distinguish the normal modes in terms of the sets of molecular states whose diagonal density-matrix elements relax independently of one another (e.g., states of different spin symmetry). This leads to density-matrix components such as:

$\rho_{\delta,i}(t) \equiv \rho_i(t)$ —diagonal in the  $i$ th set of molecular states,  
 $\rho_{\nu,i}(t)$ —off-diagonal, involving only the  $i$ th set,  
 $\rho_{\nu,i,j}(t)$ —off-diagonal, involving both the  $i$ th and  $j$ th set.

Each such component is generally written as  $\rho_\lambda(t)$ .

Now  $\Gamma$  may be partitioned in the same manner to give the different component  $\Gamma_\lambda$ . Letting  $T_\lambda$  be the similarity transformation which diagonalizes  $\Gamma_\lambda$ , one has

$$(T_\lambda^{-1}\Gamma_\lambda T_\lambda)_{ab} = \Gamma'_{\lambda_a} \delta_{ab}, \quad (8)$$

and

$$\chi_\lambda(t) = T_\lambda^{-1}\rho_\lambda(t), \quad (9)$$

where  $\Gamma'_{\lambda_a}$  is the eigenvalue for the  $\lambda_a$ th normal mode represented by  $\chi_{\lambda_a}(t)$ . Thus the relaxation of the diagonal density-matrix elements of the  $i$ th set of molecular states, represented by  $\Gamma_i$ , is given by Eq. (4) replacing  $n$  and  $n'$  by  $n_i$  and  $n'_i$ . Note that  $\Gamma_i$  will not in general be symmetric unless the Boltzmann factors

<sup>9</sup> This requirement is not essential and it is conceivable that it is not valid in some cases where there are degenerate eigenlevels [cf. J. H. Freed, J. Chem. Phys. **43**, 2312 (1965)]. It does, however, greatly simplify the subsequent treatment and will often hold true.

<sup>8</sup> R. Kubo, in *Fluctuation, Relaxation and Resonance in Magnetic Systems*, D. ter Haar, Ed. (Oliver and Boyd, London, 1962).

in Eq. (5) may be ignored.<sup>10</sup> For the  $i$ th group of states there will be a zero root,  $\Gamma'_{i1}=0$ , corresponding to the conservation of probability in such states. The associated normal mode  $\chi_{i1}(t)$  must therefore be given by

$$\chi_{i1}(t) = \text{Tr}_{M_i} \rho_i(t) = \sum_{n \text{ in } i} [\rho_i(t)]_{nn}, \quad (10)$$

i.e., a sum over all the  $i$ th molecular states, but still a spin operator. We therefore define the partial trace in Eq. (10) as

$$\text{Tr}_{M_i} \rho_i(t) \equiv \sigma_i(t) \quad (10')$$

the reduced spin-density matrix associated with the  $i$ th set of molecular states. At thermal equilibrium we have (neglecting the perturbation  $V$ )

$$\rho^T = B(M)B(S), \quad (11)$$

where  $B(M)$  and  $B(S)$  are Boltzmann distributions in molecular and spin states, respectively. It is useful, however, to partition  $\rho^T$  according to the different groups of states. Thus,

$$\rho_i^T = f_i B_i(M) B_i(S), \quad (12)$$

where

$$B_i(M) = Z_i(M) [\exp(-\hbar\mathcal{H}_{\mathcal{C}_M}/kT)], \quad (13)$$

$$[Z_i(M)]^{-1} = \text{Tr}_{M_i} [\exp(-\hbar\mathcal{H}_{\mathcal{C}_M}/kT)], \quad (13')$$

while

$$B_i(S) = Z(S) [\exp(-\hbar\mathcal{H}_{\mathcal{C}_S}/kT)], \quad (14)$$

and

$$[Z(S)]^{-1} = \text{Tr}_S [\exp(-\hbar\mathcal{H}_{\mathcal{C}_S}/kT)]. \quad (14')$$

Also

$$f_i = \sum_j Z_j(M) / Z_i(M) \quad (15)$$

measures the fractional population of molecular systems of  $i$ th symmetry at thermal equilibrium. Here  $\mathcal{H}_{\mathcal{C}_M}$  and the trace operation  $\text{Tr}_{M_i}$  operate only on the  $i$ th set of molecular states (with similar definitions for the corresponding spin terms). Thus Eqs. (10') and (12) yield

$$\sigma_i^T = f_i B_i(S). \quad (16)$$

A comparison of Eqs. (9) and (10) gives

$$(T_i^{-1})_{1a} = 1, \text{ for all } a. \quad (17)$$

Or  $(T_i^{-1})_1$  may be considered as a row vector with elements of unity. Operation with this vector is then identical to taking a trace over the  $i$ th set of states:

$$(T_i^{-1})_1 = \text{Tr}_{M_i}. \quad (17')$$

<sup>10</sup> However, it is easy to verify that the matrix  $\Gamma_i$  is symmetrized by the similarity transformation

$$D_i^{-1} \Gamma_i D_i = \Gamma_i^*,$$

where  $D_i$  is a diagonal matrix with elements

$$D_{ni} = \exp(-E_{ni} / 2kT).$$

Thus  $\Gamma_i^*$  may be diagonalized by an orthogonal transformation  $U_i$ , where  $T_i = D_i U_i$ . This decomposition of  $T_i$  simplifies the normal mode problem.

Also  $(T_i)_1$  may be regarded as a column vector with components  $(T_i)_{a1}$  which are readily determined. This is done by first noting that  $(T_i)_{an}$  is the  $n$ th component of the  $a$ th eigenvector of  $\Gamma_i$  (i.e., the definition of the similarity transformation diagonalizing  $\Gamma_i$ ). Thus

$$\Gamma_i (T_i)_1 = \Gamma'_i (T_i)_1 = 0. \quad (18)$$

But Eq. (18) is identical to the equation for the thermal-equilibrium populations of the  $i$ th set of molecular states. Thus the components of  $(T_i)_1$  are just in the ratio of their respective Boltzmann factors. The arbitrary constant is fixed by noting

$$1 = \sum_n (T_i^{-1})_{1n} (T_i)_{n1} = \sum_n (T_i)_{n1} \quad (19)$$

so that

$$(T_i)_{n1} = B_i(M)_{nn}. \quad (19')$$

It is assumed that  $\Gamma_{nn'mm'}$  of Eq. (6) is real and symmetric (i.e., imaginary terms which give rise to frequency shifts are being neglected). Then the  $\nu$ th degenerate set of transitions is diagonalized by the orthogonal matrix  $T_\nu$ . It will usually be possible to write

$$V = \sum_q K^{(q)} F^{(q)}, \quad (20)$$

where  $K^{(q)}$  and  $F^{(q)}$  are spin and rotational operators, respectively. Also, it is assumed for the sake of simplicity, that

$$\text{Tr}_{M_i} [B_i(M) V] = \sum_q K^{(q)} \text{Tr}_{M_i} [B_i(M) F^{(q)}] = 0 \quad (21)$$

for each value of  $i$ .<sup>11</sup>

In the interaction representation Eq. (1) becomes

$$\dot{\rho}^*(t) = -\Gamma \rho^*(t) - i[V^*(t), \rho^*(t)], \quad (22)$$

where

$$\rho^*(t) = \exp(i\mathcal{H}_{\mathcal{C}_M} t) \rho(t) \exp(-i\mathcal{H}_{\mathcal{C}_M} t) \quad (22')$$

and

$$V^*(t) = \exp(i\mathcal{H}_{\mathcal{C}_M} t) V \exp(-i\mathcal{H}_{\mathcal{C}_M} t). \quad (22'')$$

Note that Eq. (6') has led to the neglect of exponentially varying components in the first term on the rhs in Eq. (22) (but see below). We now look at the evolution of Eq. (22) for times of the order of  $t$  such that

$$|\Gamma| t \gg 1 \gg |V| t; \quad (23)$$

that is, for times long compared to the damping time of the molecular systems given formally by  $|\Gamma|^{-1}$  but short enough that the effect of  $V$  is small enough to be

<sup>11</sup> If Eq. (21) is not immediately fulfilled, then one need only add the nonvanishing part of  $\text{Tr}_{M_i} [B_i(M) V]$  onto  $\mathcal{H}_{\mathcal{C}_M}$ . The resultant  $\mathcal{H}_{\mathcal{C}_M}'$  will, in general, depend on  $i$ . Since  $V$  is being treated as a perturbation, it is readily seen that the nonvanishing effect of  $\text{Tr}_{M_i} [B_i(M) V]$  need only be retained to first order, yielding an extra term  $i \sum_q \text{Tr}_{M_i} [B_i(M) F^{(q)}] [K^{(q)}, \sigma_i^*(t)]$  in the equation of motion that will be derived for  $\sigma_i^*(t)$  (see below). In Ref. 4, the effects of such terms were explicitly retained. Note also that the subscripts  $i$  and  $j$  in this paper are equivalent to the superscripts  $i$  and  $j$  in Ref. 4.

expanded as a perturbation. Over this time domain an iterative expansion given by

$$\dot{\rho}_\lambda^{*(0)}(t) = -\Gamma_\lambda \rho_\lambda^{*(0)}(t), \tag{24a}$$

$$\dot{\rho}_\lambda^{*(1)}(t) = -\Gamma_\lambda \rho_\lambda^{*(1)} - i[V^*(t), \rho^{*(0)}(t)]_\lambda, \tag{24b}$$

$$\dot{\rho}_\lambda^{*(n)}(t) = -\Gamma_\lambda \rho_\lambda^{*(n)}(t) - i[V^*(t), \rho^{*(n-1)}(t)]_\lambda \tag{24c}$$

is employed. The commutator on the right corresponds to the  $\lambda$ th normal mode although  $\rho^{*(t)}$  within need not. Also, in this notation  $V^*_{\lambda ij} = \sum_q F_{\lambda i}^{(q)} K_{ij}^{(q)*}$  is restricted to only give matrix elements between pairs of states included in the  $\lambda_{ij}$ th set. The subscripts  $i$  and  $j$  are given explicitly to show the matrix elements will only be taken between allowed combinations of spin and molecular states. Thus the commutator in Eq. (24b) for the  $\lambda$ th mode will in general include terms such as  $V^*_{\lambda' i, \lambda \rho^*_{\lambda' i}}(t)$ , where  $\lambda'$  and  $\lambda''$  need not be the same as  $\lambda$ , although, the only nonvanishing contributions when actual matrix elements are taken are of course

$$(V^*_{\lambda' i, \lambda})_{nm, \alpha\beta} [\rho^*_{\lambda' i}(t)]_{mn' \beta \gamma},$$

where  $(n, m)$  is in the  $\lambda'$ th set, where  $(m, n')$  is in the  $\lambda''$ th set, but  $(n, n')$  is in the  $\lambda$ th set. Equation (24) is the zero-order approximation [i.e., neglect of  $V^*(t)$ ], Eq. (24b) is first order in  $V^*(t)$  while Eq. (24c) is the general  $n$ th-order expression for  $\rho^{*(n)}(t)$ . The solution to Eq. (24a) is given formally by

$$\rho_\lambda^{*(0)}(t) = \exp(-\Gamma_\lambda t) \rho_\lambda^{*(0)}(0) \tag{25a}$$

or, in terms of normal modes, by

$$\chi_{\lambda_a}^{*(0)}(t) = \exp(-\Gamma'_{\lambda_a} t) \chi_{\lambda_a}^{*(0)}(0). \tag{25b}$$

From Eq. (23) all relevant  $\Gamma'_{\lambda_a}$ , which are important in the spin-relaxation process, should yield

$$\Gamma'_{\lambda_a} t \gg 1 \text{ for } \lambda_a \neq i_1. \tag{26}$$

This leads to

$$\chi_{\lambda_a}^{*(0)}(t) = 0, \quad \lambda_a \neq i_1, \tag{27a}$$

and

$$\chi_{i_1}^{*(0)}(t) = \chi_{i_1}^{*(0)}(0). \tag{27b}$$

Then

$$\begin{aligned} \rho_i^{*(0)}(t) &= T_i \chi_i^*(t) = (T_i)_1 \chi_{i_1}^{*(0)}(0) \\ &= B_i(M) \sigma_i^*(0) \end{aligned} \tag{28a}$$

and

$$\rho_{i'}^{*(0)}(t) = 0. \tag{28b}$$

Equations (28) express the simple fact that to zero order in  $V$  the density matrix  $\rho^{*(0)}(t)$  remains constant in time with the molecular states at equilibrium. A substitution of Eqs. (28) into Eq. (24b) yields the first-order approximation. The time variation on the rhs of Eq. (24b) is then due to  $\rho^{*(1)}(t)$  and to  $V^*(t)$ . It is easy to show now that  $\sigma_i^{*(1)}(t)$  is constant. We first take a trace over molecular systems in Eq. (24b)

utilizing Eq. (28):

$$\begin{aligned} \text{Tr}_{M_i} \dot{\rho}_i^{*(1)}(t) &= \dot{\sigma}_i^{*(1)}(t) = -\sum_n [\Gamma_i(\rho_i^{*(1)})]_{n_i n_i} \\ &\quad - i \sum_{q, n} F_{n_i n_i}^{(q)}(t) B_i(M)_{n_i} [K^{(q)*}(t), \sigma_i^*(0)]. \end{aligned} \tag{29}$$

The first term on the rhs becomes:

$$\sum_{n, n'} [W_{n_i n'_i}(\rho_i^{*(1)})_{n'_i n'_i} - W_{n'_i n_i}(\rho_i^{*(1)})_{n_i n_i}] = 0, \tag{29a}$$

which is seen to vanish upon permuting the dummy indices  $n$  and  $n'$  in one of the terms. The second term vanishes as a direct consequence of Eq. (21). Equation (24b) must be integrated to obtain the second-order approximation. For the sake of compactness, a convention utilized by Kubo is introduced.<sup>8</sup> Let

$$a^x b \equiv [a, b], \tag{30}$$

where  $a$  and  $b$  are operators. It then follows that

$$\exp(a^x) b = e^a b e^{-a}, \tag{30'}$$

which may be verified by direct expansion of the exponential operator. Then Eq. (24b) becomes, in terms of normal modes,

$$\begin{aligned} \dot{\chi}_{\lambda_a}^{*(1)}(t) &= -\Gamma'_{\lambda_a} \chi_{\lambda_a}^{*(1)}(t) - i(T_\lambda^{-1})_a \\ &\quad \times \{[\exp(i\mathcal{H}_0 t) V] \chi_{\lambda_a}^{*(0)}\}_\lambda, \end{aligned} \tag{31}$$

where  $(T_\lambda^{-1})_a$  is the  $a$ th-row vector of  $T_\lambda^{-1}$ . Now the formal solution to this operator differential equation (preserving the order of the operators) is given by

$$\begin{aligned} \chi_{\lambda_a}^{*(1)}(t) &= \exp(-\Gamma'_{\lambda_a} t) \\ &\quad \times [\chi_{\lambda_a}^{*(1)}(0) + i(T_\lambda^{-1})_a \{ [1/(\Gamma'_{\lambda_a} + i\mathcal{H}_0^x)] V \}_x \chi_{\lambda_a}^{*(0)}]_\lambda \\ &\quad - i(T_\lambda^{-1})_a \{ [\exp(i\mathcal{H}_0 t) / (\Gamma'_{\lambda_a} + i\mathcal{H}_0^x)] V \}_x \chi_{\lambda_a}^{*(0)} \}. \end{aligned} \tag{32}$$

Equation (23) may now be made more precise with the sufficiency condition that Eq. (26) should hold for each normal mode  $\lambda_a$  for which the last two terms in Eq. (32) are nonvanishing. The nonvanishing of such expressions depends upon the details of  $V$  and  $(T_\lambda^{-1})$ . A vanishing does occur for those diagonal modes where  $\Gamma'_{i_1} = 0$ , and these are the only normal modes with zero eigenvalues which need to be retained provided that the sufficiency condition is satisfied.

The formal properties of inverse operators like  $1/(\Gamma' + i\mathcal{H}_0^x)$  may be obtained from a power series expansion in  $\mathcal{H}_0^x$ , even though the expansion may not converge. Thus if  $\alpha$  and  $\beta$  are eigenstates of  $\mathcal{H}_0$ , it is found that

$$\{ [1/(\Gamma'_{\lambda_a} + i\mathcal{H}_0^x)] V \}_{\alpha\beta} = V_{\alpha\beta} / (\Gamma'_{\lambda_a} + i\omega_{\alpha\beta}). \tag{33}$$

It is clear that the operator expressions in Eqs. (31) and (32) are most easily evaluated in a basis composed of eigenstates of  $\mathcal{H}_0$ . Note also that  $1/(\Gamma'_{\lambda_a} + i\mathcal{H}_0^x)$  and  $\exp(i\mathcal{H}_0 t)$  commute. Applying Eq. (26) the asymp-

otic values,

$$\chi_{\lambda_a}^{*(1)}(t) = -i(T_\lambda^{-1})_a \times \{([\exp(i\mathcal{H}_0 t)] / (\Gamma'_{\lambda_a} + i\mathcal{H}_0) V) \rho^{*(0)}\}_\lambda, \quad \lambda_a \neq i_1, \tag{34a}$$

are obtained. Equations (10) and (29) immediately yield

$$\chi_{i_1}^{*(1)}(t) = \sigma_i^{*(1)}(0). \tag{34b}$$

When Eq. (34) and (35) are transformed back to the  $\rho_\lambda^{*(1)}(t)$  the expression

$$\rho_\lambda^{*(1)}(t) = B_i(M) \sigma_i^*(0) \delta_{\lambda, i} - i \sum_a' (T_\lambda)_a (T_\lambda^{-1})_a \times \{([\exp(i\mathcal{H}_0 t)] / (\Gamma'_{\lambda_a} + i\mathcal{H}_0) V) \rho^{*(0)}\}_\lambda \tag{35}$$

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$$\dot{\sigma}_{\alpha_i \alpha'_i}^*(t) = \sum_{\beta_j, \beta'_j} R_{\alpha_i \alpha'_i \beta_j \beta'_j} \sigma_{\beta_j \beta'_j}^*(t), \tag{37}$$

where

$$R_{\alpha_i \alpha'_i \beta_j \beta'_j} = \sum_{q, q'} \{ K_{\alpha_i \beta_j}^{(q)} K_{\beta'_j \alpha'_i}^{(q')} [k_{qq'}(\beta'_j - \alpha'_i) + \hat{k}_{qq'}(\alpha_i - \beta_j)] - \sum_{\gamma_k} K_{\alpha_i \gamma_k}^{(q')} K_{\gamma_k \beta_j}^{(q)} \delta_{\beta'_i \alpha'_i} \hat{k}_{qq'}(\gamma_k - \beta_j) - \sum_{\gamma_k} K_{\beta'_i \gamma_k}^{(q')} K_{\gamma_k \alpha'_i}^{(q)} \delta_{\alpha_i \beta_i} k_{qq'}(\beta'_j - \gamma_k) \}, \tag{38}$$

with

$$k_{qq'}(\beta'_j - \alpha'_i) = \sum_{\lambda, n, n', m, m'} (F_\lambda)^{(q)}_{n_i n'_i} (F_\lambda)^{(q')}_{m'_i m_i} B_{m'_i}(M) \sum_a (T_\lambda)_{(n'_i n_i), a} (T_\lambda^{-1})_{a, (m'_i m_i)} / [\Gamma'_{\lambda_a} + i(\omega_{\beta'_i \alpha'_i} + \omega_{m'_i m_i})] \tag{39a}$$

and

$$\hat{k}_{qq'}(\alpha_i - \beta_j) = \sum_{\lambda, n, n', m, m'} (F_\lambda)^{(q)}_{m_i m'_i} (F_\lambda)^{(q')}_{n'_i n_i} B_{m'_i}(M) \sum_a (T_\lambda)_{(n_i n'_i), a} (T_\lambda^{-1})_{a, (m_i m'_i)} / [\Gamma'_{\lambda_a} + i(\omega_{\alpha_i \beta_i} + \omega_{m_i m'_i})]. \tag{39b}$$

All terms in Eqs. (37) to (39b) are subject to the adiabatic restrictions.

$$\omega_{\alpha_i \beta_i} + \omega_{\beta'_i \alpha'_i} + \omega_{n_i n'_i} + \omega_{m'_i m_i} \approx 0. \tag{40}$$

Note that  $m_i$  and  $m'_i$  must constitute one of the  $\lambda$ th set of transitions, while in the  $\lambda$ 'th set the pairs of states are transposed. Thus by definition (Eq. 6a):

$$\omega_{n_i n'_i} + \omega_{m'_i m_i} \ll \Gamma_\lambda^{-1}, \tag{40'}$$

and we can expect the sum in Eq. (40') to be negligible in Eq. (40).<sup>12</sup> Note also that  $\sigma^*(t)$  has been substituted for  $\sigma^*(0)$  on the rhs of Eq. (37). (This will only introduce errors higher than second order in  $V$ .)<sup>13</sup> A particularly simple case exists when

$$\Gamma'_{\lambda_a} = \tau_c^{-1}, \quad \lambda_a \neq i_1, \tag{41}$$

otherwise independent of  $\lambda_a$ . Then, utilizing the prop-

<sup>12</sup> It is expected that the exponentially varying coefficients in the first term on the rhs in Eq. (22) that have been neglected for simplicity would, if included, have the effect of cancelling the contribution to Eq. (40) of the sum in Eq. (40'). It is also expected that the terms  $\omega_{m'_i m_i}$  and  $\omega_{m_i m'_i}$  in Eqs. (39) would be altered somewhat, but Eq. (40') indicates that such corrections can be neglected.

<sup>13</sup> Reference 2, Chap. 8.

erty of  $T_\lambda$ : is obtained. The prime on the summation requires  $a \neq 1$  when  $\lambda \rightarrow i_1$ . We now rewrite Eq. (24c) for the diagonal normal modes to second order in  $V$  as:

$$\dot{\rho}_i^{*(2)}(t) = -\Gamma_i \rho_i^{*(2)}(t) - i[V^*(t), \rho^{*(1)}(t)]_i. \tag{36}$$

The  $\text{Tr}_{M_i}$  is then performed on Eq. (36). The first term on the rhs in Eq. (36) vanishes just as the equivalent term in Eq. (29) did. Furthermore, when Eq. (35) is substituted into Eq. (36) (the  $\text{Tr}_{M_i}$  having been taken) the expression arising from the first term on the rhs in Eq. (35) vanishes in the same manner as the second term on the rhs in Eq. (29). When the remaining term is expanded out (with due caution to the significance of the  $\lambda$  subscripts) one obtains the following relaxation matrix expression:

erty of  $T_\lambda$ :

$$\sum_a' (T_\lambda)_{i, a} (T_\lambda^{-1})_{a, i'} = \delta_{i, i'} - B_i(M) \delta_{\lambda, i} \tag{42}$$

and Eq. (21) we find

$$k_{qq'}(\beta'_j - \alpha'_i) = \sum_{n, n'} \frac{F_{n_i n'_i}^{(q)} F_{n'_i n_i}^{(q')} B_{n'_i}(M)}{\tau_c^{-1} + i(\omega_{\beta'_i \alpha'_i} + \omega_{n'_i n_i})}, \tag{43}$$

while  $\hat{k}_{qq'}(\alpha_i - \beta_j)$  is obtained from Eq. (43) by changing the angular frequency term to  $(\omega_{\alpha_i \beta_i} + \omega_{n_i n'_i})$ . Equation (43) [taken with (37) and (38)] is identical to the result obtained utilizing a "strong-collision" approximation.<sup>3</sup>

Instead of diagonalizing each  $\Gamma_\lambda$  matrix, one may invert it (plus essentially a unit matrix). Thus for the nondiagonal modes<sup>14</sup>:

$$\sum_a (T_\nu)_{(n'_i n_i), a} (T_\nu^{-1})_{a, (m'_i m_i)} / (\Gamma'_\nu + i\omega) = [(\Gamma_\nu + i\omega \mathbf{1})^{-1}]_{(n'_i n_i)(m_i m'_i)}. \tag{44}$$

<sup>14</sup> Equations (44) and (45) follow from

$$(\Gamma + \omega \mathbf{1})^{-1} = [T(\Gamma + \omega \mathbf{1}) T^{-1}]^{-1} = T(\Gamma' + \omega \mathbf{1})^{-1} T^{-1}.$$

When  $\Gamma_\nu$  is just a  $1 \times 1$  matrix (uncoupled molecular width), Eq. (44) shows that the relaxation effects of off-diagonal matrix elements of  $(F_\nu^{(a)})$  involve the lattice-induced molecular linewidths for the  $\nu$ th transition. The generalization to coupled widths is obvious. For the diagonal case, one obtains<sup>14,15</sup>

$$\sum_a' (T_i)_{n,a} (T_i^{-1})_{a,m} / (\Gamma'_{ia} + i\omega) \\ = [(\Gamma_i + i\omega \mathbf{1})^{-1}]_{nm} - [B_i(M)_{nn} / i\omega]. \quad (45)$$

Equation (45) shows that the relaxation effects of the diagonal-matrix elements of  $(F_i^{(a)})$  involve just the

lattice-induced transition probabilities amongst the  $i$ th set of molecular states. Equation (39) can be simplified for many applications. Thus, if (i)  $B(S)$  fulfills a high-temperature approximation,<sup>13</sup> (ii) the near-resonance condition

$$|\omega_{\beta'j\alpha'i} + \omega_{m'jm_i}| \lesssim \Gamma'_{\lambda_a} \quad (46)$$

is invoked; (iii) all molecular states belonging to the  $\nu$ th set of transitions have nearly the same Boltzmann factor,  $B_\nu(M)$ , given by Eq. (13), and (iv) imaginary terms are to be neglected, then one obtains

$$\text{Re} k_{qq'}(\alpha_j - \beta_i) = \text{Re} \hat{k}_{qq'}(\alpha_j - \beta_i) \equiv j(\alpha_j - \beta_i) = j^D(\alpha_j - \beta_i) + j^N(\alpha_j - \beta_i), \quad (47)$$

$$j_{qq'}^D(\alpha_j - \beta_i) = \sum_{mn} (F_i^{(a)})_{nn} (F_i^{(a')})_{mm} \delta_{ij} \text{Re} \left[ \sum_a (T_i)_{n,a} (T_i)_{m,a} / (\Gamma'_{ia} + i\omega_{\alpha_i\beta_i}) \right], \quad (48a)$$

$$j_{qq'}^N(\alpha_j - \beta_i) = \sum_{\nu, mn, m'n'} (F_\nu^{(a)})_{n_i n'_i} (F_\nu^{(a')})_{m'_i m_i} B_\nu(M) \text{Re} \left\{ \sum_a (T_\nu)_{(n'_i n_i), a} (T_\nu)_{(m'_i m_i), a} / [\Gamma'_{\nu a} + i(\omega_{\alpha_i\beta_i} + \omega_{m'_i m_i})] \right\}, \quad (48b)$$

and an operator form<sup>16</sup> of Eqs. (37) and (38) may be employed.

### III. APPLICATIONS

#### A. Gas-Phase Relaxation

Equation (39) [or the simplified Eqs. (47) and (48)] may be regarded as a generalization of the spectral densities which were obtained earlier for strong collisions.<sup>3</sup> They are detailed enough to permit an analysis of the effects of collisional selection rules for rotational relaxation on magnetic-resonance relaxation. Thus, for example, selection rules on changes in the magnetic sublevels  $m_J$  in orthohydrogen as suggested by Johnson and Waugh<sup>17</sup> and discussed further by Deutch and Waugh,<sup>18</sup> may be treated utilizing the present formulation. It should be noted, however, that these authors did not distinguish between the relaxation of diagonal and off-diagonal elements of  $(F^a)$ , since they assumed spherical-tensor components of the same rank should relax in the same fashion. This is expected to follow as long as the different magnetic sublevels of a given  $J$  are degenerate (within their linewidths), as a consequence of the isotropy of space. Although Eqs. (47)

and (48) appear to distinguish between the diagonal and off-diagonal elements of  $F$ , it should be noted that "transition degeneracies" between pairs of  $m_J$  states yield coupled rotational widths requiring diagonalization, the effect of which may be expected to be the same as the diagonalization required for the diagonal elements of  $F$ . It may also be noted that the Fourier transforms of these spectral densities yield the correlation functions for the  $(F^{(a)})$  which are discussed by Waugh *et al.*<sup>17-19</sup> The diagonal and off-diagonal spectral densities do, however, differ in the frequency terms in the denominators in Eqs. (48) but they are usually negligible compared to the  $\Gamma'_{\lambda_a}$ .

The proper inclusion of higher  $J$  states also follows directly from Eqs. (48). When the collision-induced transition probabilities between different  $J$  states,  $W_{(J,m) \rightarrow (J',m')}$ , obey Eq. (3), then thermal averages over all such states regarded as the  $i$ th set of states must be performed. When  $W_{(J,m) \rightarrow (J',m')} \ll W_{(J,m) \rightarrow (J,m')}$  for  $J \neq J'$  then the  $W_{(J,m) \rightarrow (J',m')}$  have no other noticeable effects. When the inequality no longer holds, it becomes necessary to spell out the details of these transitions. Then the  $\Gamma'_\lambda$  must be modified to include the added line broadening and relaxation effects of these transitions.

We also note that when there are important terms in  $V$  coupling different  $J$  levels, but the separation of  $J$  levels is considerably greater than separations of spin levels, then the near-resonant condition Eq. (46) is not fulfilled and the theory utilizing Eqs. (39) may not predict the effects of such terms properly, although

<sup>15</sup> If  $\omega$  in (45) is vanishingly small, then it may be evaluated as

$$\lim_{\epsilon \rightarrow 0} \{ [(\Gamma_i + \mathbf{1}\epsilon)^{-1}]_{nm} - [B_i(M)_{nn} / \epsilon] \},$$

where the source of the singularity is subtracted out before the limit is taken.

<sup>16</sup> Reference 2, p. 279.

<sup>17</sup> C. S. Johnson, Jr., and J. S. Waugh, *J. Chem. Phys.* **36**, 2266 (1962).

<sup>18</sup> J. M. Deutch and J. S. Waugh, *J. Chem. Phys.* **43**, 1914 (1965).

<sup>19</sup> See also, M. Bloom and I. Oppenheim, *Can. J. Phys.* **41**, 1580 (1963).

it will emphasize the sound point that they are not significant.

### B. Effects of Hindered Internal Rotations

The strong-collision model has recently been employed in discussing effects of hindered motions of methyl groups.<sup>4</sup> It was noted that a quantum effect ensues if the torsional splitting between near-degenerate *A* and *E* symmetry levels is significantly greater than any terms in *V* coupling them. This is again equivalent to the assertion that a resonant mechanism is no longer operative for such terms, so their contribution must be small compared to the resonant effects between degenerate pairs of *E* levels. It should now also be possible to analyze in detail for effects of any differences in widths

of the *A* and *E* symmetry torsional levels on magnetic resonance observables.

### C. Nuclear Spin Relaxation via Rapid Electron-Spin Flips

This case is discussed by Abragam<sup>20</sup> and the present theory may in fact be regarded as a generalization. However if  $T_2$  for the electron spin obeys the inequality  $T_2^{-1} \ll |\omega_I - \omega_S|$ , where  $\omega_I$  and  $\omega_S$  are, respectively, the nuclear spin and electron spin Larmor frequencies, then the resonant form of the theory is no longer appropriate. Abragam points out the mixing of electron and nuclear spin states which must then be considered.

<sup>20</sup> Reference 2, pp. 310-312.

## Vibrational Relaxation in CO-D<sub>2</sub> Mixtures

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The vibrational relaxation of 0.1 D<sub>2</sub>+0.9 CO has been observed in a shock tube by means of optical interferometry and infrared photometry. From 940° to 1600°K deuterium and helium are found to be equally effective collision partners for the vibrational excitation of carbon monoxide. From 1600° to 2800°K the data suggest that vibrational exchange from the more rapidly excited D<sub>2</sub> contributes to the excitation of CO.

**T**HE vibrational relaxation of a mixture containing 10% deuterium and 90% carbon monoxide has been studied in a shock tube from 940° to 2800°K. Two techniques were employed; the gas density was measured by optical interferometry and the intensity of infrared emission near 2100 cm<sup>-1</sup> from the CO was monitored by a liquid N<sub>2</sub>-cooled indium antimonide detector. The shock tube and the measurement techniques have been described previously.<sup>1-3</sup>

The probability of excitation of CO in a collision with a vibrationally unexcited D<sub>2</sub> molecule is expected<sup>4</sup> to be very nearly that for a CO-He collision. Indeed, Millikan has found<sup>5</sup> D<sub>2</sub> and He to exhibit very nearly the same efficiency in the de-excitation of CO at room temperature. However, pure D<sub>2</sub> is known to relax at a more rapid rate<sup>6</sup> than pure CO, and its vibrational quantum is larger than that of CO ( $\theta=4303^\circ\text{K}$  for D<sub>2</sub> vs 3082°K for CO), so there is a possibility that at high tempera-

tures, where the D<sub>2</sub> excitation becomes significant, a vibrational exchange (*V-V*) process will contribute to the excitation of CO in a CO-D<sub>2</sub> mixture.

Three calculations of the shocked gas density were made with alternative assumptions on the degree of vibrational excitation: that no energy had gone into vibrational degrees of freedom, that only D<sub>2</sub> was vibrationally excited, and that both D<sub>2</sub> and CO had attained thermal equilibrium. These results are compared in Fig. 1 with density measurements made not only as close to the shock front as possible (circles), but also sufficiently far behind the shock that a steady-state density had been attained (crosses). The density increase behind the shock front is clearly due primarily to the CO relaxation; and although the circles are suggestive of a D<sub>2</sub> relaxation within the resolvable shock front, these data are not conclusive.

Relaxation time data are shown in Fig. 2 and compared with previous results (solid lines) for pure carbon monoxide<sup>3,7</sup> and for CO dilute in helium<sup>7</sup> ( $\ln_e p_{\text{rCO-He}} = 87T^{-1} - 19.1$ ). In general, the infrared emission technique requires longer relaxation times than interferometry, and there were no experiments where both types of data could be taken. Initial pressures ranged

<sup>1</sup> R. A. Alpher and D. R. White, *Phys. Fluids* **2**, 153 (1959).

<sup>2</sup> D. R. White and R. C. Millikan, *J. Chem. Phys.* **39**, 1803 (1963).

<sup>3</sup> W. J. Hooker and R. C. Millikan, *J. Chem. Phys.* **38**, 214 (1963).

<sup>4</sup> R. C. Millikan and D. R. White, *J. Chem. Phys.* **39**, 3209 (1963).

<sup>5</sup> R. C. Millikan, *J. Chem. Phys.* **38**, 2855 (1963).

<sup>6</sup> J. H. Kiefer and R. W. Lutz, *J. Chem. Phys.* **44**, 658 (1966); D. R. White, *ibid.* **42**, 447 (1965); **44**, 430 (1966).

<sup>7</sup> R. C. Millikan, *J. Chem. Phys.* **40**, 2594 (1964).