

SPIN RELAXATION VIA QUANTUM MOLECULAR SYSTEMS

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Very often one has to consider the quantum nature of the molecular systems whose modulation induces spin relaxation. We first consider a "gas-like" model wherein strong collisions randomize the molecular degrees of freedom, more specifically the rotational states. Then we generalize the results to cover more general descriptions of the way that the molecular degrees of freedom relax through thermal contact.

IX.1. STRONG COLLISIONAL RELAXATION¹

We start with the density matrix ρ which refers to the combined spin-molecular degrees of freedom:

$$\dot{\rho} = -i\mathcal{K}^x \rho \quad (1)$$

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

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

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 rotational and spin variables, and \mathcal{K} is time independent. We often only include the rotational part of \mathcal{K}_M designated by \mathcal{K}_R . Let us define V and \mathcal{K}_S such that

$$\langle V \rangle \equiv \text{Tr}_R \{ B(R)V \} = 0 \quad (3)$$

where $B(R)$ is the Boltzmann distribution in rotational states:

$$B(R) = Z(R)e^{-h\nu_R/kT} ; Z(R)^{-1} = \text{Tr}_R \left\{ e^{-h\nu_R/kT} \right\} \quad (3a)$$

In the interaction representation with

$$\rho^\ddagger(t) = e^{i(\nu_R + \nu_S)t} \rho(t) e^{-i(\nu_R + \nu_S)t} \quad (4a)$$

and

$$V^\ddagger(t) = e^{i(\nu_R + \nu_S)t} V e^{-i(\nu_R + \nu_S)t} \quad (4b)$$

one has

$$\frac{1}{i} \frac{d\rho^\ddagger(t)}{dt} = -[V^\ddagger(t), \rho^\ddagger(t)]. \quad (5)$$

Equation 5 may be solved by integrating to successive approximations obtaining a series expansion for the dependence of $\rho^\ddagger(t)$ on its value at some earlier time $\rho^\ddagger(t_0)$ (or better, by the cumulant expansion approach).

To proceed further, the following assumptions will be introduced.

1) $\rho(t)$ is approximately factorable into the product $\lambda(t)\sigma(t)$ where $\lambda(t)$ and $\sigma(t)$ are reduced density matrices depending only on the rotational and spin degrees of freedom respectively.

2) Collisions affect only the rotational degrees of freedom (i.e., they are perturbations with no matrix elements between spin states).

3) The collision takes place over an interval of time which is short enough that $\sigma(t)$ remains essentially constant.

4) The collision is strong in the sense that the distribution of rotational states just after collision is given by a Boltzmann distribution at the kinetic temperature of the molecules and is independent of their distribution just before collision, so that

$$\rho(t_0) = B(R)\sigma(t_0). \quad (6)$$

However, in order to be consistent with assumption (2), collisions must not change the spin symmetry. Thus, the symmetry of the

rotational states will be unchanged and $B(R)$ will be understood as normalized only over states R having the symmetry of interest.

5) The collisions are random with a mean time interval τ . The basic nature of this model is that collisions represent a very strong perturbation which rapidly restores the rotational states to equilibrium, while the spin-rotational interaction, V is a much weaker perturbation that slowly tends to bring the spins to equilibrium.

Assuming that a collision occurred at t_0 , expanding Eq. 5 to second order, and taking Tr_R (i.e. a trace over rotational states) gives:

$$\frac{\partial \sigma^\ddagger(t, t_0)}{\partial t} = -i \text{Tr}_R \left\{ [V^\ddagger(t), B(R)\sigma^\ddagger(t_0)] \right\} - \text{Tr}_R \left\{ \int_{t_0}^t dt' [V^\ddagger(t), [V^\ddagger(t'), B(R)\sigma^\ddagger(t_0)]] \right\} + \dots \quad (7)$$

If V does not connect states of different nuclear spin symmetry, and any change of nuclear spin symmetry resulting from collisions is neglected, then all molecules of a particular spin symmetry may be treated as a separate subensemble represented by a separate Eq. 7. It immediately follows from Eqs. 3 and 4 that the first term on the left of Eq. 7 vanishes.

To obtain $\sigma^\ddagger(t)$ from Eq. 7, $\sigma^\ddagger(t, t_0)$ must be integrated over all values of $t_0 = t - \theta$. Thus

$$\sigma^\ddagger(t) = \int_0^\infty \sigma^\ddagger(t, t-\theta) \tau^{-1} e^{-\theta/\tau} d\theta. \quad (8)$$

Differentiating partially with respect to time gives

$$\begin{aligned} \frac{\partial}{\partial t} \sigma^\ddagger(t) &= \int_0^\infty \left[\frac{\partial}{\partial t} \sigma^\ddagger(t, t_0) \right]_{t_0=t-\theta} \tau^{-1} e^{-\theta/\tau} d\theta \\ &\quad - \int_0^\infty \frac{\partial}{\partial \theta} \sigma^\ddagger(t, t-\theta) \tau^{-1} e^{-\theta/\tau} d\theta. \end{aligned} \quad (9)$$

The term $\left[\frac{\partial}{\partial \theta} \sigma^\ddagger(t, t_0) \right]_{t_0=t-\theta}$ in Eq. 9 is just that given by Eq. 7.

The second term in Eq. 9 is shown to be zero by first integrating it by parts giving $\tau^{-1} [\sigma^\ddagger(t) - \sigma^\ddagger(t, t_0=t)]$ and then by utilizing assumptions (3) and (5), which permit Eq. 8 to be written where $\sigma^\ddagger(t)$ on the LHS is replaced by $\sigma^\ddagger(t, t_0=t)$, and $t-\theta$ on the RHS is the time of the collision previous to the one at $t=t_0$. This leaves the following expression:

$$\frac{\partial \sigma^\ddagger(t)}{\partial t} = -\text{Tr}_R \int_0^\infty \tau^{-1} e^{-\theta/\tau} d\theta \int_0^\theta dx [V^\ddagger(t), [V^\ddagger(t-x), B(R)\sigma^\ddagger(t-\theta)]] + \dots \quad (10)$$

Equation 10 may be solved using the approximations: a) Replace $\sigma^\ddagger(t-\theta)$ on the right by $\sigma^\ddagger(t)$, and b) neglect higher order terms in the expansion. These approximations require $V^2 \ll \tau^{-2}$, which will lead to $T_1, T_2 \gg \tau$, i.e., the relaxation effects of the perturbation V are much weaker than those of the collisions.

Equation 10 is evaluated in a basis diagonal in H_R and H_S . That is, if ψ_R and φ_S are respectively complete sets of eigenfunctions of H_R and H_S having the correct symmetry for the spin species of interest, then the appropriate basis would be the set of products $\psi_R \varphi_S$. The final results (neglecting the second order frequency shifts) may be expressed in the usual relaxation matrix form:

$$\frac{\partial \sigma^\ddagger(t)_{\alpha\alpha'}}{\partial t} = \sum_{\beta\beta'} R_{\alpha\alpha',\beta\beta'} \sigma^\ddagger(t)_{\beta\beta'} \quad (11)$$

where for $V = \sum_q K^{(q)} F^{(q)}$ with $K^{(q)}$ a spin operator and $F^{(q)}$ a rotation operator:

$$\begin{aligned} R_{\alpha\alpha',\beta\beta'} = & \sum_{q,q'} \left[K_{\alpha\beta}^{(q)} K_{\beta'\alpha'}^{(q')} 2j_{qq'}(\alpha-\beta) \right. \\ & - \sum_Y \delta_{\alpha\beta} K_{\beta'\gamma}^{(q')} K_{\gamma\alpha'}^{(q)} j_{qq'}(\gamma-\beta') \\ & \left. - \sum_Y \delta_{\alpha'\beta'} K_{\alpha\gamma}^{(q')} K_{\gamma\beta}^{(q)} j_{qq'}(\gamma-\beta) \right]. \quad (12) \end{aligned}$$

Here α, β , etc. label eigenstates of \mathcal{K}_S . Equation 12 is formally very similar to the Redfield Eq. (cf. eq. VIII-35) but the spectral densities $j(\alpha-\beta)$ are different:

$$j_{qq',(\alpha-\beta)} = Z(R) \sum_{r,r'} \left[e^{-E_{r'}/kT} F_{rr'}(q) F_{r'r}(q') \frac{\tau}{1+(\omega_{rr'} + \omega_{\alpha\beta})^2 \tau^2} \right] - \langle F(q) \rangle \langle F(q') \rangle \frac{\tau}{1+\omega_{\alpha\beta}^2 \tau^2}, \quad (13)$$

where r, r' , etc. label eigenstates of \mathcal{K}_R and $\hbar\omega_{rr'} = E_r - E_{r'}$, etc. Eq. 13 includes the correction for non-zero $\langle F(q) \rangle$ in case Eq. 3 is not fulfilled.

Equations 12 and 13 require the usual energy restriction that

$$E_\alpha - E_\beta = E_{\alpha'} - E_{\beta'}, \quad (14)$$

As is usually done, the ad hoc assumption that $\sigma^\ddagger(t)$ relaxes to

$$\sigma^T = Z(S) e^{-\hbar\mathcal{K}_S/kT}; \quad Z(S)^{-1} = \text{Tr}_S \left\{ e^{-\hbar\mathcal{K}_S/kT} \right\} \quad (15)$$

is introduced by replacing $\sigma^\ddagger(t)$ with $\sigma^\ddagger(t) - \sigma^T$ in Eq. 11.

If, however, we now allow the possibility that V may connect states of different nuclear spin symmetry even though the collisions do not, we may utilize assumption (1) to write $\rho^i(t) = \lambda^i(t)\sigma^i(t)$ as that portion of the density matrix which only includes all states corresponding to the i^{th} nuclear spin symmetry.² Then we may write ρ as the partitioned matrix:

$$\rho = \begin{pmatrix} \lambda^i \sigma^i & \lambda^{ij} \sigma^{ij} & \dots & \dots \\ \lambda^{ji} \sigma^{ji} & \lambda^j \sigma^j & \dots & \dots \\ \vdots & \vdots & \ddots & \vdots \\ \vdots & \vdots & \vdots & \ddots \\ \vdots & \vdots & \vdots & \vdots \end{pmatrix} \quad i \neq j \quad (16)$$

where submatrices $\lambda^{ij} \sigma^{ij}$ include all off-diagonal elements between states belonging to the i^{th} and j^{th} symmetry classes. Terms such as $\lambda^{ji} \sigma^{ij}$ or $\lambda^{ij} \sigma^i$ for $i \neq j$ are not allowed, since they violate

the Exclusion Principle. Note that the mixed superscripts may not be simply permuted. However, the Hermitian property of the density matrix and the separability of the two reduced matrices leads to

$$(\sigma^{ji} \lambda^{ji})^\dagger = \sigma^{ij} \lambda^{ij} \quad (17)$$

where \dagger indicates the Hermitian conjugate. The normalization of the density matrices is taken to be

$$\text{Tr}_S(\sigma) = 1 \quad (18a)$$

and

$$\text{Tr}_{R_i}(\lambda^i) = \text{Tr}_{R_j}(\lambda^j) = 1 \quad (18b)$$

so that any differences in population of states of different nuclear spin symmetries are contained in σ . The subscripts S_i and R_i limit the trace operations to spin states and to rotational states of i^{th} symmetry, respectively.

The equation of motion for ρ may be written in terms of each submatrix. Thus for example

$$\frac{d}{dt} (\sigma^{jj} \lambda^{jj}) = -i [\mathcal{K}, \rho(t)]^{jj} \quad (19)$$

Note that, while the matrix elements of the commutator itself are restricted to states of symmetry j in eq. 19, both \mathcal{K} and $\rho(t)$ within the commutator could have matrix elements involving states of other symmetry.

After a strong collision we have:

$$\text{Tr}_R \{ \rho^\dagger(t_0) \} = \text{Tr}_R \{ B(R) \times \sigma(t_0) \} =$$

$$\begin{pmatrix} \sigma^{i\dagger}(t_0) & 0 & \dots & \dots \\ 0 & \sigma^{j\dagger}(t_0) & \dots & \dots \\ \vdots & \vdots & \ddots & \ddots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \quad (20)$$

where $B(R)$ may be partitioned so that

$$B^i(R) = Z^i(R) [\exp(-\hbar \mathcal{K}_R / kT)]^i \quad (21)$$

and

$$[Z^i(R)]^{-1} = \text{Tr}_{R_i} [\exp(-h\lambda_R/kT)]. \quad (22)$$

$[Z^i(R)]^{-1}$ is the rotational partition function normalized for the i^{th} symmetry states. Thus the strong collision is assumed to restore each set of rotational states belonging to a particular spin symmetry to its respective Boltzmann distribution, while also having no effect on $\sigma(t_0)$, which includes the relative populations of states of different spin symmetry. The disappearance of off-diagonal submatrices $\lambda^{ij}(t_0)$ in Eq. 20 after a strong collision does not necessarily require that important nuclear-spin dependent intermolecular forces exist. These submatrices contain only off-diagonal elements between rotational eigenstates, so they are relaxed by secular mechanisms which broaden each of the coupled rotational states differently and by all nonsecular processes involving these levels. A derivation similar to that given above yields:

$$\dot{\sigma}^\ddagger(t)_{\alpha_i \alpha'_i} = \sum_{\beta_j \beta'_j} R_{\alpha_i \alpha'_i \beta_j \beta'_j} [\sigma^\ddagger(t)_{\beta_j \beta'_j} - \sigma_{\beta_j \beta'_j}] \quad (23)$$

where $R_{\alpha_i \alpha'_i \beta_j \beta'_j}$ is again given by Eq. 12 after letting $\alpha \rightarrow \alpha_i$, $\beta \rightarrow \beta_j$, $\gamma \rightarrow \gamma_k$, etc. and

$$j_{qq'}(\alpha_i - \beta_j) = [Z^j(R) \sum_{r_i, r'_j} \exp(-E_{r'_j} / kT) F_{r_i r'_j}^{(q)} F_{r_i r'_j}^{(q')} \frac{\tau}{1 + (\omega_{r_i r'_j} + \omega_{\alpha_i \beta_j})^2 \tau^2} - \langle F^{(q)} \rangle_i \langle F^{(q')} \rangle_i \frac{\tau}{1 + \omega_{\alpha_i \beta_j}^2 \tau^2} \delta_{ij} \quad (24)$$

We have introduced the ad hoc assumption that $\sigma^{\ddagger j}(t)$ relaxes to a Boltzmann distribution given by:

$$\sigma_o^j = f_j Z(S) \exp(-h\lambda_S^j/kT) \quad (25)$$

where

$$[Z(S)]^{-1} = \text{Tr}_S \left\{ e^{-h\mathcal{K}_S/kT} \right\} \quad (25a)$$

and

$$f_j = \sum_i Z^i(R) / Z^j(R) \quad (26)$$

which measures the fractional population of rotational levels of j^{th} symmetry at thermal equilibrium, is introduced to account for the normalization of $B^i(R)$, $\sigma^i(t)$ and $\lambda^i(t)$ given respectively by Eqs. 22 and 18. Note that $\delta_{\alpha_i \beta_j}$ also implies δ_{ij} . The above result assumes $\langle v \rangle_j$ is the same for all j . When this is not so, the result is a little more complicated and is given in ref. 2.

IX. 2. GENERAL FORMULATION³

It is now assumed that the equation of motion for $\rho(t)$ may be written as

$$i(d\rho/dt) = [\mathcal{K}, \rho] - i\Gamma\rho, \quad (27)$$

The term $\Gamma\rho$ has been introduced phenomenologically into Eq. 27 to describe in a general way the relaxation of the combined system as a result of its thermal contact. 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 Γ will only affect the molecular systems directly, and the spin relaxation is achieved indirectly via the spin-molecular coupling term. Equation 27 is clearly valid in the limit $V=0$, since the molecular 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

$$|\Gamma| \gg V, \quad (28)$$

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 Γ .

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

$$(\Gamma\rho)_{nn} = \sum_n (W_{nn'}\rho_{n'n} - W_{n'n}\rho_{nn}), \quad (29)$$

where $W_{nn'}$ is the transition probability from state n' to n and ρ_{nn} is the diagonal density-matrix element for the n^{th} molecular state but is still an operator on spin states. The assumption of detailed balance yields

$$W_{nn'} = W_{n'n} \exp(\hbar\omega_{nn'}/kT). \quad (30)$$

However, no restriction is placed on the nature of the intermolecular interactions leading to the $W_{nn'}$. The n diagonal elements ρ_{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

$$(\Gamma\rho)_{nn'} = -\sum_{m,m'} \Gamma_{nn',mm'} \rho_{mm'}, \quad (31)$$

where

$$(\omega_{nn'} - \omega_{mm'})\Gamma^{-1} \ll 1. \quad (31a)$$

Equation 31 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. 31a. Any coupling via Γ between diagonal and off-diagonal elements of $\rho_{nn'}$ is being neglected. In the absence of any couplings of $\rho_{nn'}$, Eq. 31 becomes:

$$(\Gamma\rho_{nn'}) = -\Gamma_{nn',nn'}\rho_{nn'} \equiv -\Gamma_{nn'}\rho_{nn'}, \quad (32)$$

where $\Gamma_{nn'}$ is the "linewidth" for the $n \leftrightarrow n'$ transition. It is, in general, composed of secular and non-secular effects.

It is useful to obtain a basis for Γ 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 λ . 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, $\rho_{\nu_{ij}}(t)$ — off-diagonal, involving both the i^{th} and j^{th} set. Each such component is generally written as $\rho_\lambda(t)$.

Now Γ may be partitioned in the same manner to give the different component Γ_λ . Letting T_λ be the similarity transformation which diagonalizes Γ_λ , one has

$$(T_\lambda^{-1} \Gamma_\lambda T_\lambda)_{ab} = \Gamma'_\lambda \delta_{ab}, \quad (32a)$$

and

$$\chi_\lambda(t) = T_\lambda^{-1} \rho_\lambda(t), \quad (33)$$

where Γ'_λ is the eigenvalue for the λ_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 Γ_i , is given by Eq. 29 replacing n and n' by n_i and n_i' . 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.

In the interaction representation Eq. 27 becomes

$$\dot{\rho}^\ddagger(t) = -\Gamma \rho^\ddagger(t) - i[V^\ddagger(t), \rho^\ddagger(t)]. \quad (34)$$

We now look at the evolution of Eq. 34 for times of the order of t such that

$$|\Gamma|t \gg 1 \gg |V|t; \quad (35)$$

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

$$\dot{\rho}_\lambda^\ddagger(0)(t) = -\Gamma_\lambda \rho_\lambda^\ddagger(0)(t), \quad (36a)$$

$$\dot{\rho}_\lambda^{\dagger(1)}(t) = -\Gamma_\lambda \rho_\lambda^{\dagger(1)} - i[V^\dagger(t), \rho^{\dagger(0)}(t)]_\lambda, \quad (36b)$$

$$\dot{\rho}_\lambda^{\dagger(n)}(t) = -\Gamma_\lambda \rho_\lambda^{\dagger(n)}(t) - i[V^\dagger(t), \rho^{\dagger(n-1)}(t)]_\lambda \quad (36c)$$

is employed. The commutator on the right corresponds to the λ th normal mode although $\rho^\dagger(t)$ within need not. One obtains the relaxation matrix expression Eq. 23 where now

$$\begin{aligned} R_{\alpha_i \alpha'_i \beta_j \beta'_j} = & \sum_{q, q'} \left\{ K_{\alpha_i \beta_j}^{(q)} K_{\beta'_j \alpha'_i}^{(q')} [k_{qq', (\beta'_j - \alpha'_i) + \alpha_i - \beta_j} + \hat{k}_{qq', (\alpha_i - \beta_j)}] \right. \\ & - \sum_{\gamma, k} K_{\alpha_i \gamma_k}^{(q')} K_{\gamma_k \beta_i}^{(q)} \delta_{\beta'_j \alpha'_i} \hat{k}_{qq', (\gamma_k - \beta_j)} - \\ & \left. - \sum_{\gamma, k} K_{\beta'_j \gamma_k}^{(q')} K_{\gamma_k \alpha'_i}^{(q)} \delta_{\alpha_i \beta_j} \hat{k}_{qq', (\beta'_j - \gamma_k)} \right\} \quad (37) \end{aligned}$$

with

$$\begin{aligned} k_{qq', (\beta'_j - \alpha'_i)} = & \sum_{\lambda, n, n', m, m'} (F_{\lambda \dagger})_{n_j n'_j}^{(q)} (F_\lambda)^{m'_j m_i B_{m'_j}}(M) \\ & \times [\Delta_\lambda(\omega_{\beta'_j \alpha'_i} + \omega_{m'_j m_i})_{n'_j n_i m'_j m_i}] \quad (38a) \end{aligned}$$

and

$$\begin{aligned} \hat{k}_{qq', (\alpha_i - \beta_j)} = & \sum_{\lambda, n, n', m, m'} (F_\lambda)^{m_i m'_j} (F_{\lambda \dagger})_{n'_j n_i B_{m'_j}}(M) \\ & \times [\Delta_\lambda(\omega_{\alpha_j \beta_j} + \omega_{m_i m'_j})_{n_i n'_j m_i m'_j}] \quad (38b) \end{aligned}$$

$$\Delta_\nu(\omega)_{n'_j n_i m'_j m_i} = [(\Gamma_\nu + i\omega \mathbb{1})^{-1}]_{n'_j n_i m_i m'_j} \quad (39)$$

$$\Delta_i(\omega)_{m_n, m_n} = [(\Gamma_i + \omega \mathbb{1})^{-1}]_{n n m m} - [B_i(M)_{nn} / i\omega] \quad (40)$$

Note that m_i and m'_j must constitute one of the λ th set of transitions, while in the $\lambda \dagger$ th set the pairs of states are transposed. Also $\mathbb{1}$ is the unit matrix. A particularly simple case exists when

$$\Gamma'_{\lambda_a} = \tau_c^{-1}, \quad \lambda_a \neq i_1, \quad \Gamma_{i_1} = 0 \quad (41)$$

otherwise independent of λ_a . Then, one obtains the "strong-collision" approximation of Eq. 24.

When Γ_ν is just a 1×1 matrix (uncoupled molecular width), Eq. 39 shows that the relaxation effects of off-diagonal matrix elements of $(F_\nu^{(q)})$ involve the lattice-induced molecular linewidths for the ν th transition. Equation 40 shows that the relaxation effects of the diagonal-matrix elements of $(F_1^{(q)})$ involve just the lattice-induced transition probabilities amongst the i th set of molecular states.

IX.3. APPLICATIONS

A. Gas-Phase Relaxation

In applying the formalism to gas-phase relaxation, the rotational wavefunctions ψ_r must be reasonably well known so that the spectral density, Eq. 13 may be calculated. In cases where there are internal rotational degrees of freedom, ψ_r should include them as well. In this context it is important to recognize a difference that exists between the semiclassical theory of relaxation (cf. Ch. VIII) and the basically quantum mechanical formulation of the theory presented here. Internal and over-all rotations, as treated classically, will tend to average out anisotropic terms such as dipole-dipole interactions and will lead to spin relaxation effects which are dependent in part on the effective reorientation rates of the motions. However, in the quantum mechanical model, when collisions and related interactions are neglected, the molecule will be in a definite rotational quantum state and no significant spin relaxation is to be expected. Significant relaxation is introduced by the effect of collisions which themselves change the molecular rotational states and also broaden them so that V can be effective in energy transfers. Thus, in the present formulation the relaxation will depend directly upon the effective collision times causing reorientation and only indirectly on the quantum mechanical rotational frequencies.

One is free to make various assumptions about the reorientational collision times, or more precisely the Γ matrix. The simplest is, as we have seen, a strong-collision assumption. The strong collision assumption can be modified somewhat by assigning a separate "effective collision time" τ for each sub-ensemble of molecules which can be approximately treated as isolated from the rotational states accessible to the rest of the ensemble. Such a separation into sub-ensembles is appropriate for molecules of different nuclear-spin symmetry provided V has no matrix elements between them (e.g. ortho-hydrogen¹). It is also possible, as has been discussed for ortho-hydrogen, to assume that for small molecules, because of the large energy differences between J levels, that collisions primarily redistribute molecules among the m_J magnetic substates of a given J and V is too weak to couple states of different J . Then Eq. 13 should be rewritten for each set of J states as:

$$j_{qq}^J(\alpha-\beta) = \frac{1}{2J+1} \sum_{m_J, m_{J'}} |F_{m_J m_{J'}}^{(q)}|^2 \frac{\tau_J}{1+(w_{m_J m_{J'}} + w_{\alpha\beta})^2 \tau_J^2} \quad (42)$$

and a separate relaxation equation (12 and 14) may be written for each sub-ensemble of molecules differing in their J value. One can then calculate the macroscopic magnetization $M_J(t)$ for each J state and appropriate $T_{1,J}$ and $T_{2,J}$ values are obtained. Now, provided collisional transition rates between J levels ($\tau_{J,J'}^{-1}$) are much smaller than $T_{1,J}^{-1}$ and $T_{2,J}^{-1}$ one can introduce such transitions into a form reminiscent of the modified Bloch equations for chemical exchange, except that the differences in Larmor frequencies of molecules in states having different values of J may be negligible,¹ the only differences being in their relaxation properties. One finds that if $\tau_{J,J'}^{-1}$ is much larger than differences in $T_{1,J}^{-1}$ and $T_{2,J}^{-1}$ between J levels, one still obtains a macroscopic magnetization characterized by a single $T_1^{-1} = \sum_J \frac{B_J}{T_{1,J}}$,¹ where B_J is the Boltzmann factor for the J th rotational state.

However, even a modified strong collision approach cannot deal with selection rules for changes in magnetic sublevels m_J . This would require specifying the detailed $W_{(J,m) \rightarrow (J',m')}$ in Γ .³ For heavier molecules, characterized by a closer spacing of the non-degenerate rotational energy levels, one would expect that collisions will be more effective in causing transitions between them, thus allowing for some significant changes in J . This may be treated in the strong collision approximation, or by introducing $W_{(J,m) \rightarrow (J',m')}$ terms into Γ .

A detailed discussion for the case of NMR of ortho-hydrogen is given elsewhere.¹ In general for NMR, the perturbation V should consist primarily of the dipole-dipole interactions of the nuclear spins, nuclear quadrupole interactions, and the nuclear spin-rotational magnetic coupling.

In the case of ESR, the electron spin-rotational magnetic coupling, the unquenched spin-orbit coupling, and electron-nuclear dipolar interactions should be the dominant terms to which the theory applies. One should, of course, also add to a relaxation equation (cf. Eq. 11) a Heisenberg spin-exchange term such as Eq. XVIII-105. Now, however, ω_{HE} of Eq. XVIII-106 should be calculated from the appropriate gas-phase collision theory rather than from liquid diffusion theory as is done in Ch. XVIII. The validity of uncorrelated R-matrix and ω_{HE} terms as employed in Ch. XVIII would probably require an experimental situation in which there is a dominant buffer gas present such that most collisions of radicals are with diamagnetic buffer molecules. Unless the pressure is high enough, it will not necessarily be true that the condition for the validity of the present theory (i.e. Eq. 28) is fulfilled; then an approach more like that of Ch. XIV would be required, i.e. Eq. 27 is solved explicitly without perturbation theory.

B. Quantum Effects of Methyl Group Tunneling²

This is an interesting case where V couples states of different nuclear-spin symmetry, so that a relaxation equation like Eqs. 23

and 24 is required. We illustrate with the ESR case where the dominant term in V usually (but not always) is the isotropic hyperfine interactions of the three methyl protons:

$$h\mathcal{K}_{\text{HF}} = \left(\frac{8}{3}\right) \pi \hbar^2 \gamma_e \gamma_p \sum_{i=1}^3 \delta(r-r_i) \vec{S} \cdot \vec{I}_i \quad (43)$$

One calculates the hyperfine interaction by assuming hyper-conjugative mixing of hydrogenic $1s$ orbitals and the methyl carbon orbitals with the unpaired electron in the carbon $2p_z$ orbital to which the methyl group is attached. Only the π -type symmetry linear combination of hydrogenic orbitals has the proper symmetry. One then obtains the hyperfine term as a function of the angle φ , which is the angle of rotation of the methyl group. The result is:

$$\mathcal{K}_{\text{HF}} \cong \left(a\vec{I} + \frac{a}{2} e^{i2\varphi} [\vec{I}_1 + \epsilon \vec{I}_2 + \epsilon^* \vec{I}_3] + \frac{a}{2} e^{-i2\varphi} [\vec{I}_1 + \epsilon \vec{I}_2 + \epsilon^* \vec{I}_3] \right) \cdot \vec{S} \quad (44)$$

where $\vec{I} = \sum_{i=1}^3 \vec{I}_i$, $\epsilon = \exp(2\pi i/3)$. In a classical average, only the first term of Eq. 44 remains. Quantum mechanically one must consider the permutation symmetry of the three protons, but the subgroup: E , (123) , and (321) is sufficient. It is isomorphous with point group C_3 with irreducible representations A , E_a , and E_b . The last two terms in Eq. 44 are of symmetry E_a and E_b in the rotational ($e^{\pm 2i\varphi}$) and nuclear spin parts, although they are of overall A symmetry. Thus they lead to transitions between internal rotational (or tunneling states) of different nuclear-spin symmetry.

Interesting effects may be observed at low temperatures in solids when only the lowest torsional level is appreciably populated.

In the limit when $|\Gamma| \gg a$, the first term of Eq. 44 yields a four line hyperfine pattern of intensity ratio: 1:3:3:1. Each of the 3-fold degenerate lines are coupled to one another by the last two terms in Eq. 44, and if the torsional splitting Δ between ground-state A and E sub-levels obeys $|\Delta/\Gamma| \ll 1$ then the two central

lines are predicted to broaden. However, for $|\Delta/\Gamma| \gg 1$, the A and E sub-levels are well enough separated, so that the A component is not broadened, and one predicts four sharp lines in the ratio 1:1:1:1 with doubly degenerate components of the two center lines broadened out. In the static limit for $\Delta \gg a \gg \Gamma$ the E lines reappear between the A lines leading to a 7 line spectrum with intensity ratio: 1:1:1:2:1:1:1, which has been observed. If, however, $a \gg \Delta \Gamma$, the usual four line spectrum is observed. Detailed line-shape calculations have been made using a strong collision approximation,² but such features as differences of the widths and relaxation of the A and E symmetry torsional sub-levels would require the more general approach, Eq. 27.

C. Spin-Relaxation via Vibronic Relaxation

Another application of Eq. 27 is to the problem of spin-relaxation via excited electronic states. Various spin-orbit mechanisms in liquids were outlined in Ch. VIII which involved calculations from the appropriate terms in $R^{(4)}$. Orbach-type processes involving combined orbit-lattice (O-L) and spin-orbit (S-O) mechanisms can readily be calculated in the manner outlined for classical models of the dynamics of the O-L interaction. However, recent experimental work on degenerate ground-state free radicals⁴ has strongly suggested that, while the anomalously large relaxation is spin-orbit in nature, it is essentially an intramolecular process. This suggests a vibronic-spin-orbit mechanism which takes advantage of the molecular vibronic relaxation. Thus Γ in Eq. 27 must include the vibronic relaxation, and one may deduce the spin relaxation from steady-state solutions to Eq. 27 utilizing a generalized form of time-independent perturbation theory (cf. Ch. XIV, discussion leading to Eqs. XIV-49 and 50).⁵

D. Non-Resonant Effects

It has been pointed out that the theory given here is for resonance-type effects.³ That is, spin relaxation occurs by a resonant (within the appropriate linewidth of the molecular states)

transfer of energy to the molecular systems. These widths are represented as Lorentzians by Eqs. 27-32. When, however, energy differences are large in the spectral densities of Eqs. 38 and 39, e.g. for

$$|\omega_{\beta'j\alpha'j} + \omega_{m'jm_i}| \gg \Gamma_{m'jm_i}$$

where $\Gamma_{m'jm_i}$ is assumed to be a simple width, one may be looking too far into the "wings" of the line shape of the molecular transitions for the Lorentzian approximation to be valid. That is, the short time behavior of the intermolecular interactions, which determine the molecular line shapes in the wings may now be important. This is really no different than the short-time non-diffusive effects discussed in Ch. VIII with regard to classical Brownian-type diffusive reorientation. Quantum mechanically, we can speak of non-resonant or higher-order processes in this limit. And, as we shall note, the spectral densities of Eq. 38 and 39 given in this limit by terms of type

$$\frac{|F_{mm'}|^2 K_{\alpha\beta} K_{\beta\alpha}}{(\omega_{\beta\alpha} + \omega_{m'm})^2} \Gamma_{m'm} \equiv \alpha^2 \Gamma_{m'm} \quad (45)$$

are essentially of this non-resonant form. That is one reduces the molecular relaxation parameter $\Gamma_{m'm}$ by the mixing coefficient squared or α^2 which measures the degree to which the perturbation mixes molecular and spin states. However, one must exercise some caution in the proper interpretation of $\Gamma_{m'm}$ as we have just noted.

It should be possible to introduce the idea of short time behavior of Γ by analogy to the generalized Langevin equation⁶ such that Eq. 27 is generalized to:

$$i\dot{\rho} = \mathcal{K}^x \rho - i \int_{t_0}^t \Gamma(t-t') \rho(t') dt' \quad (46)$$

where, as in Eq. 27 we have not included the random force (see Deutch Ch. VII). A proper analysis of Eq. 46, including the random force, may be written as a hierarchy of continued fractions, following Mori.⁷ That is, we write the ESR spectrum as being given by:

$$\chi(\omega) \propto \frac{1}{(\omega - \omega_{ab}) + i\Gamma_1(\omega) - \Delta_1(\omega)} \quad (47)$$

where $\Gamma_1(\omega)$ and $\Delta_1(\omega)$ are respectively the "frequency-dependent" width and shift of the ESR line. These widths and shifts come from the spectral densities of Eqs. 38 and 39. That is, next in the hierarchy of continued fractions we have

$$\Delta_1(\omega) + i\Gamma_1(\omega) \propto \frac{|F_{nm}|^2 |K|^2}{(\omega - \omega_{nm}) + i\Gamma_2(\omega) - \Delta_2(\omega)} \quad (48)$$

where the terms $\Gamma_2(\omega)$ and $\Delta_2(\omega)$ give the real and imaginary parts of the one-sided Fourier transform of $\Gamma(t)$ in eq. 46. The frequency shift $\Delta_2(0)$ due to intermolecular interactions has been implicitly included in the zero-order molecular energy states.

The next stage in the hierarchy would be to calculate $\Gamma_2(\omega)$ in terms of the intermolecular interactions, utilizing a form like Eq. 48. However, one can terminate the hierarchy to a good approximation, whenever $\Gamma_{n+1} \gg \Gamma_n$. This was the basis of our analysis utilizing Eq. 28 such that $\Gamma_1 \ll \Gamma_2(0)$, and frequency-independent ESR widths and shifts are obtained in the central portion of the spectrum.

The form Eq. 48 suggests that the non-resonant terms may be reasonably approximated by replacing the Γ_λ in Eqs. 39 and 40 by $\Gamma(\omega) [= \Gamma_2(\omega)]$. We illustrate this with a simple example.

Suppose we have a spin S (spin system) which relaxes by its coupling to another spin I (considered here as the molecular system) due to a simple perturbation of type

$$V = AI_z [S_+ + S_-] \quad (49)$$

$$\text{with I rapidly relaxing according to } (2T_1)^{-1} = W_I = \frac{|B|^2 \tau_c}{1 + \omega_I^2 \tau_c^2} \quad (49a)$$

where B is an appropriate perturbation matrix element. W_I in Eq. 49a belongs in Γ_2 and τ_c is, in principle, calculable from the intermolecular interactions (i.e. Γ_3). The usual, or resonant-type approach would yield:

$$W_S = \frac{A^2 W_I}{\omega_S^2 + 4W_I^2} \quad (50)$$

where W_S belongs in Γ_1 .

In the non-resonant-type calculation, one first uses Eq. 49 to correct the zero order wave-functions, so that to first order

$$|\pm, \pm\rangle' = |\pm, \pm\rangle + \alpha |\mp, \pm\rangle \tag{51a}$$

and

$$|\pm, \mp\rangle' = |\pm, \mp\rangle - \alpha |\mp, \mp\rangle \tag{51b}$$

$\alpha = \frac{A}{2\omega_S}$, and where the notation is $|M_S, M_I\rangle$, and primes indicate corrected wave functions. Now the unspecified calculation which lead to Eq. 49a, (i.e., a transition probability calculation from $R^{(2)}$ between states $|+, +\rangle \leftrightarrow |+, -\rangle$ and $|-, +\rangle \leftrightarrow |-, -\rangle$) is repeated for corrected states: $|+, +\rangle' \leftrightarrow |-, -\rangle'$ and $|+, -\rangle \leftrightarrow |-, +\rangle'$ [for matrix elements of type $B(t)(I_+ + I_-)$] and when averaged over a high temperature Boltzmann distribution in I_2 , yields:

$$W_S = \frac{\frac{1}{2}A^2}{\omega_S^2} [W_I(\omega_S) + W_I(-\omega_S)] \tag{52}$$

where $W_I(\pm\omega_S)$ is just W_I of Eq. 49a, but with $\omega_I \rightarrow \omega_I \pm \omega_S$.

If $W_I \gg \omega_S$, then only the resonant form, Eq. 50 is appropriate. If, however, $W_I \ll \omega_S$ then Eq. 50 becomes:

$$W_S = \frac{A^2}{\omega_S^2} W_I \tag{50a}$$

Eq. 53 predicts the same result as Eq. 50a only when $(\omega_I \pm \omega_S)^2 \tau_c^2 \sim \omega_I^2 \tau_c^2$. If $\omega_S \gg \omega_I$ then this requires $\omega_S^2 \tau_c^2 \ll 1$ or very short correlation times; or else if $\omega_S \ll \omega_I$, this is fulfilled.

When, however, $W_I \ll \omega_S$ and $|\omega_I \pm \omega_S|^2 \tau_c^2 \neq \omega_I^2 \tau_c^2$, then the non-resonant expression, Eq. 53, should be utilized. That is, the nature of Γ for Eqs. 38 and 39 has been changed.

IX.4. ACKNOWLEDGEMENT

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