

ESR RELAXATION AND LINESHAPES FROM THE GENERALIZED CUMULANT AND
RELAXATION MATRIX VIEWPOINT

Jack H. Freed

Department of Chemistry, Cornell University

Ithaca, New York 14850

VIII.1. GENERAL APPROACH¹

We start with the time rate of change of the spin density matrix for a single spin system:

$$\dot{\sigma}(t) = -i[\mathcal{K}, \sigma] \equiv -i\mathcal{K}^x \sigma \quad (1)$$

where $\mathcal{K} = \mathcal{K}_0 + \mathcal{K}_1(t)$, and we use the Kubo^{2,3} notation for super-operators: \mathcal{A}^x , such that $\mathcal{A}^x B = [A, B]$. We define an interaction representation by:

$$\sigma^\ddagger(t) = e^{i\mathcal{K}_0 t} \sigma = e^{i\mathcal{K}_0 t} \sigma e^{-i\mathcal{K}_0 t} \quad (3)$$

$$\text{and } \mathcal{K}_1^\ddagger(t) = e^{i\mathcal{K}_0 t} \mathcal{K}_1(t) = e^{i\mathcal{K}_0 t} \mathcal{K}_1(t) e^{-i\mathcal{K}_0 t} \quad (4)$$

Then, eq. (1) becomes in the interaction representation:

$$\dot{\sigma}^\ddagger(t) = -i[\mathcal{K}_1^\ddagger(t), \sigma^\ddagger] \quad (5)$$

We are, however, interested in an ensemble averaged $\sigma(t)$ which we denote by $\langle \sigma(t) \rangle$. One method of solution of eq. 5 is to iterate and then take ensemble averages.^{4,5} But it is better to first write the formal solution of eq. 5 in terms of an ordered exponent, designated by the subscript 0 (cf. Ch. I by Muus on time ordering):

$$\langle \sigma^\ddagger(t) \rangle = \langle \exp_0 \left[-i \int_0^t dt' \mathcal{K}_1^\ddagger(t') \right] \rangle \sigma(0) \quad (6)$$

where $\sigma(0)$ is an arbitrary initial value for the ensemble and the operator exponential is defined in terms of its infinite series expansion:

$$\langle \exp_0 [-i \int_0^t dt \mathcal{K}_1^\dagger(t)^\times] \rangle = \sum_{n=0}^{\infty} M_n(t) \quad (7)$$

$$\text{where } M_n(t) = \frac{(-1)^n}{n!} \langle 0 [\int_0^t dt \mathcal{K}_1^\dagger(t)]^n \rangle = (-1)^n \int_0^t dt_1 \int_0^{t_1} dt_2 \dots$$

$$\dots \int_0^{t_{n-1}} dt_n m_n(t_1, t_2, \dots, t_n) \text{ for } n \geq 1 \quad (8)$$

$$\text{and } M_0(t) = 1 \quad (8a)$$

Here

$$m_n(t_1, t_2, \dots, t_n) = \langle \mathcal{K}_1^\dagger(t_1)^\times \mathcal{K}_1^\dagger(t_2)^\times \dots \mathcal{K}_1^\dagger(t_n)^\times \rangle \quad (9)$$

is a generalized n^{th} order time correlation function of the random operator, $\mathcal{K}_1^\dagger(t)$. It may also be regarded as a generalized moment.

In the cumulant method,¹⁻³ we replace the expansion eq. by the ordered exponent

$$\langle \exp_0 [-i \int_0^t dt \mathcal{K}_1^\dagger(t)^\times] \rangle = \exp_0 K(t) \quad (10)$$

$$\text{where } K(t) = \sum_{n=1}^{\infty} K_n(t). \quad (11)$$

Each K_n is still an operator and is of n^{th} order in $\mathcal{K}_1^\dagger(t)^\times$. The precise definition of the n^{th} order cumulant is given by the infinite series expansion

$$\exp_0 \left[\sum_{n=1}^{\infty} K_n(t) \right] \equiv \sum_{p=0}^{\infty} (p!)^{-1} \exp_0 \left[\sum_{n=1}^{\infty} K_n(t) \right]^p \quad (12)$$

where we must preserve the time ordering in the cumulants. The K_n are then obtained by equating the terms in the two expansion eqs. 7 and 12 of the same order in $\mathcal{K}_1^\dagger(t)^\times$. Thus to fourth order one has:

$$K_1 = M_1 \quad (13a)$$

$$K_2 = M_2 - \frac{1}{2} O(M_1^2) \quad (13b)$$

$$K_3 = M_3 - \frac{1}{2} [O(M_1 M_2) + O(M_2 M_1)] + \frac{1}{3} O(M_1^3) \quad (13c)$$

$$K_4 = M_4 - \frac{1}{2} O(M_2^2) - \frac{1}{2} [O(M_1 M_3) + O(M_3 M_1)] + \frac{1}{3} [O(M_1^2 M_2) + O(M_1 M_2 M_1) + O(M_2 M_1^2)] - \frac{1}{4} O(M_1^4). \quad (13d)$$

The nature of the ordering prescription is obtained directly from eq. 8. Thus for example:

$$\begin{aligned} O(M_1^2) &= O[-1 \int_0^t dt_1 m_1(t_1)]^2 \\ &= -2 \int_0^t dt_1 \int_0^{t_1} dt_2 m_1(t_1) m_1(t_2). \end{aligned} \tag{14}$$

$$\begin{aligned} \text{Thus, } K_2 &= - \int_0^t dt_1 \int_0^{t_1} dt_2 [m_2(t_1, t_2) - m_1(t_1) m_1(t_2)] = \\ &= - \int_0^t dt_1 \int_0^{t_1} dt_2 K_2(t_1, t_2) \end{aligned} \tag{14a}$$

and is the dominant term which gives the Redfield theory.⁶ In general, Kubo² shows that

$$K_n(t) = (-1)^n \int_0^t dt_1 \int_0^{t_1} dt_2 \dots \int_0^{t_{n-1}} dt_n K_n(t_1, t_2 \dots t_n) \tag{15}$$

where the K_n are the appropriate collections of the m_n :

$$K_n(t, t_2 \dots t_n) \equiv \langle \mathcal{M}_1^\dagger(t_1) \times \mathcal{M}_1^\dagger(t_2) \times \dots \times \mathcal{M}_1^\dagger(t_n) \times \rangle_c \tag{15a}$$

The most important properties of the cumulants K_n are the following:

1) They are zero if any one of the (random) variables contained in them are uncorrelated with the others. For example, if $\mathcal{M}_1(t_1)$ is uncorrelated between two times t_1 and t_2 , then we have:

$$m_2(t_1, t_2) = m_1(t_1) m_1(t_2) \tag{16a}$$

$$\text{so } K_2(t) = 0. \tag{16b}$$

This property automatically removes potential divergences in calculating the $M_n(t)$ as $t \rightarrow \infty$ by replacing them with the $K_n(t)$.

2) As opposed to a moment expansion, the cumulant expansion maintains at each level of the approximation a "generalized exponential-decay" solution for the equations of motion, thus bearing a closer relation to what is expected physically. This removes the problems and ambiguities of the earlier formulations^{5, 6, 7}

which have to force a low order moment expansion into exponential form.

3) The approach is valid for all times t , whereas the earlier perturbation approaches require a coarse-graining in time solution, i.e. they are valid for $t \gg \tau_c$, where τ_c is a characteristic correlation time.

4) As long as the moment expansion is valid, the cumulant expansion represents a complete solution to the problem, which is valid for any stochastic process. It is usually assumed that: a) the stochastic process is stationary and b) it is ergodic. (a) means that the random process generating fluctuations in $\mathcal{K}_1(t)$ always remains at equilibrium, while (b) assumes that all the spin systems are able to experience the same range of effects from $\mathcal{K}_1(t)$. However these assumptions are not, in principle necessary. [In fact instead of a stochastic approximation, one can average over a canonical distribution of the ensemble, i.e. $\langle A \rangle_\beta = \text{Tr} A e^{-\beta H} / \text{Tr} e^{-\beta H}$, $\beta = \hbar/kT$.]

To more precisely demonstrate how the cumulant expansion theory generalizes the Redfield-type perturbation theory, we proceed by re-writing the solution eq. 6 for $\sigma^\ddagger(t)$. We now drop the explicit averaging notation, and utilize eq. 10 to obtain:

$$\dot{\sigma}^\ddagger(t) = \dot{K}(t)\sigma^\ddagger(t) . \quad (17)$$

When the substitution $\tau_1 = t_{i-1} - t_i$ is made, we have

$$\begin{aligned} \dot{K}_n(t) &= (-1)^n \int_0^t d\tau_1 \int_0^{t-\tau_1} d\tau_2 \dots \\ &\int_0^{t-\sum_{i=1}^{n-2} \tau_i} d\tau_{n-1} K_n(t, t-\tau_1, \dots, t-\sum_{j=1}^{n-1} \tau_j) . \end{aligned} \quad (18)$$

VIII.2. RELAXATION MATRIX AND SPECTRAL LINESHAPES

We recover the time-dependent perturbation theory by solving for $\dot{K}(t)$ for times $t \gg \tau_c$. Since the K_n vanish if any of the $\mathcal{K}_1^\ddagger(t)^x$ in eq. 15a are uncorrelated, the only non-vanishing contributions to

eq. 18 come from times $\tau_1 \lesssim \tau_c$. Thus, a negligible error is introduced into eq. 18 by letting all the upper limits tend to infinity. We also note that any correlations in K_n which decay with time (e.g. an exponential decay) will go to zero. Thus the $\dot{K}(t)$ approaches an asymptotic steady-state value $\dot{K}(\infty)$ independent of t except for sinusoidal-type oscillations. (For stationary random processes the correlations depend only on the time differences τ_1 , so we automatically obtain non-negligible steady-state values.) Thus we have

$$\dot{K}_n(t \gg \tau_c) \cong \dot{K}_n(t \rightarrow \infty) \equiv \exp(i\Omega_n t) R^{(n)}, \tag{19}$$

where $R^{(n)}$ and Ω_n are time-independent operators. [Note that it is also possible to obtain the limiting value from $\lim_{t \rightarrow \infty} \dot{K}_n(t) = \lim_{s \rightarrow 0} s \tilde{K}_n(s)$, where $\tilde{K}_n(s)$ is the Laplace-transform.] One can readily show that $\Omega_n = \mathcal{N}_0^X$, for all n .¹ Thus, the long-time approximation to eq. 17, is, in matrix elements of \mathcal{N}_0 :

$$\dot{\sigma}_{\alpha\alpha}^\ddagger(t) = \sum_{\beta\beta'} \exp [i(\omega_{\alpha\alpha} - \omega_{\beta\beta'})t] R_{\alpha\alpha'\beta\beta'} R_{\beta\beta'}^\ddagger(t) \tag{20a}$$

or

$$\dot{\sigma}_{\alpha\alpha}^\ddagger(t) = -i\omega_{\alpha\alpha} \sigma_{\alpha\alpha}^\ddagger + \sum_{\beta\beta'} R_{\alpha\alpha'\beta\beta'} \sigma_{\beta\beta'}^\ddagger, \tag{20b}$$

where $R_{\alpha\alpha'\beta\beta'}$ is the time-independent relaxation matrix given to all orders by:

$$R_{\alpha\alpha'\beta\beta'} = \sum_{n=1}^{\infty} R_{\alpha\alpha'\beta\beta'}^{(n)}. \tag{21}$$

The cumulants then provide a precise prescription for generating all the $R^{(n)}$.

We note from eqs. 18 and 15a that $R^{(n)}$ is of order $\langle |W_1^\ddagger(t)|^n \rangle_{\tau_c}^{n-1}$, so convergent expansions are expected only for $|W_1^\ddagger(t)|^2 \tau_c < 1$. When this condition is not fulfilled the relaxation-matrix approach involving times $t \gg \tau_c$ is no longer appropriate, and one must investigate $\dot{K}(t)$ more carefully for finite t .

Note that, in general, the matrix elements $R_{\alpha\alpha'\beta\beta'}$ are complex where $\text{Re}R_{\alpha\alpha'\beta\beta'}$ gives the relaxation effects and therefore must be

intrinsically negative; while $\text{Im}R_{\alpha\alpha',\beta\beta'}$ are the dynamic frequency shifts which must be added to the first term on the rhs of eq. 20b.

We note that the above method also applies to the solution of ensemble averaged operators, such as $S_x(t)$. Here we obtain:

$$\dot{S}_x^\dagger(t) = \sum_c e^{-it\omega_c} R^* S_x^\dagger(t) \quad (22)$$

where R^* is the complex conjugate of R , or

$$\dot{S}_{\alpha\alpha'}^\dagger(t) = i\omega_{\alpha\alpha'} S_{\alpha\alpha'}^\dagger + \sum_{\beta\beta'} R^*_{\alpha\alpha',\beta\beta'} S_{\beta\beta'}^\dagger \quad (23)$$

Eq. 23 expresses the fact that we can get coupled relaxation of different transitions corresponding to different matrix elements $S_{\alpha\alpha'}^\dagger$ and $S_{\beta\beta'}^\dagger$. One must therefore diagonalize the non-Hermitian matrix with elements

$$M_{\alpha\alpha',\beta\beta'} = [i\omega_{\alpha\alpha'} \delta_{\alpha\alpha',\beta\beta'} + R^*_{\alpha\alpha',\beta\beta'}] \quad (24)$$

Clearly, if

$$|R^*_{\alpha\alpha',\beta\beta'}| \ll |\omega_{\alpha\alpha'} - \omega_{\beta\beta'}| \quad (25)$$

the $\alpha\alpha'$ transition is "decoupled" from the $\beta\beta'$ transition and we can treat them independently. The most common case where we must consider coupled relaxation is when there are degenerate transitions, e.g.

$$\omega_{\alpha_1\alpha_1'} = \omega_{\alpha_j\alpha_j'} = \omega_0 \text{ for all } i, j = 1 \dots N \quad (26)$$

Then in this N -fold degenerate transition subspace, we must diagonalize the N -fold matrix $R_{i,j}^K$.

At this stage we discuss line-shapes from the point of view of linear response theory, so we can write a normalized line-shape function⁸ (see also Ch. X by Kivelson):

$$I(\omega) = \frac{4}{\pi} \int_0^\infty G(t) \cos \omega t dt \quad (27)$$

where $G(t) = \text{Tr}_B [S_x(t) S_x^\dagger]$, i.e. a trace over spin states. (28)

a) Simple line - Suppose $S_{\alpha\alpha'}$ is uncoupled to any other transition.

Then we have from eqs. 27, 28 and 23

$$G(t) = 2 \cos(\omega_0 t) \exp(-t/T_2) \quad (29a)$$

$$\text{and } I(\omega) = \frac{4}{\pi} \frac{T_2}{1+T_2^2(\omega-\omega_0)^2} \quad (29b)$$

$$\text{where } \omega_0 = \omega_{\alpha\alpha'} - \text{Im}R_{\alpha\alpha'\alpha\alpha'} \quad (30a)$$

$$\text{and } T_2^{-1} = -\text{Re}R_{\alpha\alpha'\alpha\alpha'} \quad (30b)$$

i.e. a Lorentzian with transverse relaxation time T_2^{-1} and resonant frequency ω_0 .

b) Multiple (Degenerate line)⁸ - We assume eq. 26 applies. We let the $S_{\alpha_1\alpha_1'}$ $\equiv S_{x,i}$ be the components $X_i^{(K)}$ of an N-dimensional vector $\vec{X}^{(K)}$. Let $U^{(K)}$ be the transformation that diagonalizes $R^{(K)}$; (we assume for now it is unitary, but see below):

$$\left(U^{(K)-1} R^{(K)} U^{(K)} \right)_{ij} = \lambda_i^{(K)} \delta_{ij} \quad (31)$$

$$\text{Then one has } I_K(\omega) = \frac{4}{\pi} \sum_{i=1}^N |Y_i^{(K)}|^2 \frac{T_{2,i}^{(K)}}{1+[T_{2,i}^{(K)}]^2(\omega-\omega_i^{(K)})^2} \quad (32)$$

where we have set

$$[-\text{Re}\lambda_i^{(K)}]^{-1} = T_{2,i}^{(K)} \quad (33a)$$

$$\omega_i^{(K)} = \omega_0^{(K)} - \text{Im}\lambda_i^{(K)} \quad (33b)$$

$$\text{and } Y_i^{(K)} = \sum_{j=1}^N [U^{(K)}]^{-1}_{ij} X_j^{(K)} \quad (33c)$$

Thus we have a superposition of Lorentzians. Of course, if the $T_{2,i}$ for different i do not differ greatly, one can adequately describe the line as a single Lorentzian with an average T_2 .⁸ We note, at this stage, that it is only the matrix elements of $\mathcal{K}_1(t)$ which are off-diagonal in eigenstates of \mathcal{K}_0 , that can lead to off-diagonal elements $R_{i,j}$. Physically, the non-zero $R_{i,j}$ for $i \neq j$ mean that the random perturbation is mixing up eigenlevels and/or transitions in a way that reflects its random time dependence. Thus, there is uncertainty on the individual molecular level, as to which are the correct zero-order transitions that are induced by the very weak perturbing rf field. When the correct zero-order eigenstates remain time-independent despite fluctuations of $\mathcal{K}_1(t)$, and when each eigen

level is involved in no more than one transition obeying eq. 25, then it will be possible to render the R matrix automatically diagonal by the proper choice of the zero-order eigenstates.

The case of multiple lines⁸ represented by a superposition of Lorentzians becomes important when 1) there is hyperfine structure resulting from equivalent nuclei or 2) when $S > \frac{1}{2}$, so there are degenerate ESR transitions. In the case of equivalent nuclei, it is important to distinguish between cases where the fluctuating hyperfine and dipolar parameters of all equivalent nuclei are the same at all times, in which case the nuclei are said to be completely equivalent, or where only their time average hyperfine terms are equal, i.e. equivalent (but not completely equivalent) nuclei. Modulation of $a_i(t)$ for equivalent nuclei can lead to alternating line widths, wherein the components of a multiple hf line are affected very differently. Completely equivalent nuclei are best treated in the coupled representation, i.e. nuclear spin eigenfunctions of J and J_z where $J = \sum_i I_i$ the total spin of the completely equivalent group of nuclei. Then each component line belonging to a particular set of values of J and J_z will behave as a distinct and independent line in its relaxation properties.^{8,9}

The question now arises as to when the spectrum eq. 27 is determined by the asymptotic form eq. 23 valid for $t \gg \tau_c$. One knows from Fourier transform theory that $I(\omega - \omega_0)$, where ω_0 is the center frequency, is determined mainly by the behavior of $G(t)$ around the region $t \sim |\omega - \omega_0|^{-1}$. Now we have seen that $-\text{Re}(R)$ gives the line widths for the spectrum. Thus $I(\omega - \omega_0)$ is non-negligible only for $|\omega - \omega_0| \sim |\text{Re}(R)|$, so only times $t \gtrsim |\text{Re}(R)|^{-1}$ contribute to the main portion of the line. Thus if

$$|\tau_c \text{Re}(R)| \ll 1 \quad (34a)$$

it follows that only times $t \gg \tau_c$ contribute to the main portion of the line. Also, since $\text{Im}(R)$ gives the dynamic frequency shift, which shifts the resonant frequency from ω_0 to $[\omega_0 - \text{Im}(R)]$, these arguments also require:

$$|\tau_c \text{Im}(R)| \ll 1 \tag{34b}$$

Eqs. 34 are independent of the order to which R has been calculated.

A. Properties of the Relaxation Matrix

It is possible to generate all the $R^{(n)}$ utilizing the prescription given above. We wish to examine some of the properties of the $R^{(n)}$ now. We mainly examine $R^{(2)}$, although higher order terms are given elsewhere.¹ Thus,

$$R_{\alpha\beta, \beta'\alpha'}^{(2)} = L_{\alpha\beta, \beta'\alpha'}(\omega_{\alpha\beta}) + L_{\alpha\beta, \beta'\alpha'}(\omega_{\beta'\alpha'}) - \delta_{\alpha'\beta'} \sum_{\gamma} L_{\alpha\gamma, \gamma\beta}(\omega_{\gamma\beta}) - \delta_{\alpha\beta} \sum_{\gamma} L_{\beta'\gamma, \gamma\alpha'}(\omega_{\beta'\gamma}) \tag{35}$$

Here the spectral densities $L(\omega)$ are given as one-sided Fourier transforms of correlation functions, which may be written in terms of sine and cosine Fourier transforms:

$$L_{\alpha\beta, \beta'\alpha'} = J_{\alpha\beta, \beta'\alpha'}(\omega) - iK_{\alpha\beta, \beta'\alpha'}(\omega) = J_{\alpha\beta, \beta'\alpha'}(-\omega) + iK_{\alpha\beta, \beta'\alpha'}(-\omega) \tag{36}$$

where

$$J_{\alpha\beta, \beta'\alpha'} = \int_0^{\infty} [\langle X_1(t)_{\alpha\beta} X_1(t+\tau)_{\beta'\alpha'} \rangle - \langle X_1(t)_{\alpha\beta} \rangle \langle X_1(t)_{\beta'\alpha'} \rangle] \cos \omega \tau d\tau \tag{37a}$$

$$K_{\alpha\beta, \beta'\alpha'} = \int_0^{\infty} [\langle X_1(t)_{\alpha\beta} X_1(t+\tau)_{\beta'\alpha'} \rangle - \langle X_1(t)_{\alpha\beta} \rangle \langle X_1(t)_{\beta'\alpha'} \rangle] \sin \omega \tau d\tau \tag{37b}$$

It follows from the properties of stationary random functions, as well as from the Hermitian character of $X_1(t)$, that the spectral densities obey the relations:

$$J_{\alpha\beta, \beta'\alpha'}(\omega) = J_{\beta'\alpha', \alpha\beta}(\omega) = J_{\beta\alpha\alpha', \beta'}^*(\omega) \tag{38a}$$

$$K_{\alpha\beta, \beta'\alpha'}(\omega) = K_{\beta'\alpha', \alpha\beta}(\omega) = K_{\beta\alpha\alpha', \beta'}^*(\omega) \tag{38b}$$

It thus follows that

$$\text{Re}R_{\alpha\alpha, \beta\beta}^{(a)}, = \text{Re}R_{\beta, \beta\alpha, \alpha}^{(a)} = \text{Re}R_{\beta\beta, \alpha\alpha}^{(a)*} \tag{39a}$$

$$\text{Im}R_{\alpha\alpha, \beta\beta}^{(a)}, = \text{Im}R_{\beta, \beta\alpha, \alpha}^{(a)} = \text{Im}R_{\beta\beta, \alpha\alpha}^{(a)*} \tag{39b}$$

where by Re and Im we more precisely mean the $J(\omega)$ and $K(\omega)$ contributions respectively. Thus, both $\text{Re}R_{\alpha\alpha, \beta\beta}^{(a)}$, and $\text{Im}R_{\alpha\alpha, \beta\beta}^{(a)}$, are Hermitian matrices. We find in all examples of interest that they are also real, so they are real symmetric matrices. Thus the complete $R^{(a)}$ matrix is symmetric, but is neither Hermitian nor real. It may be diagonalized by a complex orthogonal matrix.

One often rewrites $\mathcal{N}_1(t)$ in the form:

$$\mathcal{N}_1(t) = \sum_q F_q(t) A_q \tag{40}$$

where $F_q(t)$ is a function of spatial variables and is thus a randomly varying classical function of the time, and A_q contains only the spin operators. Then

$$L_{\alpha\beta, \beta'\alpha'}(\omega_{\beta'\alpha'}) = \sum_{q,r} A_q \alpha\beta A_r \beta'\alpha' \ell(q,r; \omega_{\beta'\alpha'}) \tag{41a}$$

$$L_{\alpha\beta, \beta'\alpha'}(\omega_{\alpha'\beta'}) = \sum_{q,r} A_q \alpha\beta A_r \beta'\alpha' \ell(r,q; \omega_{\alpha'\beta'}) \tag{41b}$$

where the classical spectral densities $\ell(\omega)$ are Fourier transforms of correlation functions $g(\tau)$

$$\ell_2(q,r; \omega_{\alpha\beta}) = \int_0^\infty g_2(q,r;\tau) \exp(-i\omega_{\alpha\beta}\tau) d\tau \tag{42a}$$

$$\text{where } g_2(q,r;\tau) = \langle F_q(t) F_r(t-\tau) \rangle - \langle F_q(t) \rangle \langle F_r(t-\tau) \rangle. \tag{42b}$$

In an analogous manner to eq. 36, we can separate ℓ_2 into even and odd parts with respect to ω . Thus,

$$\ell_2(q,r;\omega) = j(q,r;\omega) - ik(q,r;\omega). \tag{43}$$

The higher order cumulants are found to involve one-sided Fourier transforms of higher-order time correlation functions, e.g. for $\langle F_q(t) \rangle = 0$ we get:

$$g_3(q, r, s; \tau_1, \tau_2) = \langle F_q(t) F_r(t-\tau_1) F_s(t-\tau_1-\tau_2) \rangle \quad (44)$$

and

$$g_4(q, r, s, u; \tau_1, \tau_2, \tau_3) = \langle F_q(t) F_r(t-\tau_1) F_s(t-\tau_1-\tau_2) F_u(t-\tau_1-\tau_2-\tau_3) \rangle - \langle F_q(t) F_r(t-\tau_1) \rangle \langle F_s(t-\tau_1-\tau_2) F_u(t-\tau_1-\tau_2-\tau_3) \rangle. \quad (45)$$

For a simple line uncoupled to other lines we have to consider only the diagonal line width term. Thus from $R^{(2)}$ we have:

$$\begin{aligned} T_2^{-1}{}_{a,b} &= -\text{Re}R_{ab,ab} = [J_{aa,aa}(0) + J_{bb,bb}(0) - 2J_{aa,bb}(0)] \\ &+ \sum_{\gamma \neq a} J_{a\gamma, \gamma a}(\omega_{\gamma a}) + \sum_{\gamma \neq b} J_{b\gamma, \gamma b}(\omega_{b\gamma}) \\ &= \int_0^\infty \langle \omega(t)\omega(t-\tau) \rangle d\tau + \frac{1}{2} \left(\sum_{\gamma \neq a} W_{a\gamma} + \sum_{\gamma \neq b} W_{b\gamma} \right) \end{aligned} \quad (46)$$

where we have let:

$$\omega(t) = [N_1(t)_{aa} - \langle N_1(t) \rangle_{aa}] - [N_1(t)_{bb} - \langle N_1(t) \rangle_{bb}] \quad (47)$$

The term in $\omega(t)$ in eq. 46 is thus seen to be a secular line width contribution, i.e. fluctuations in the energy difference between the two states a and b. The terms in eq. 46 of type $W_{a\gamma}, W_{b\gamma}$ give the mean of all the transitions away from states a and b. These are the non-secular terms yielding line-broadening due to the Heisenberg uncertainty in lifetime effect. Thus, as we shall see later, the transition probability between states a→b or $W_{a \rightarrow b}$ is given by

$$W_{a \rightarrow b} = 2J_{ba,ab}(\omega_{ab}) \quad (48)$$

so we have $W_{b \rightarrow a} = 2J_{ab,ba}(\omega_{ba}) = W_{a \rightarrow b}$ by eq. 37a. This is the usual microscopic reversibility, which is, however, not in general true in higher order, although $W_{Kb \rightarrow Ka} = W_{a \rightarrow b}$ where K is time reversal operator, if the Hamiltonian is invariant under time-reversal.¹⁰

The equivalent second-order time-dependent transition probability is, for non-resonant intermediate states, (i.e. $\omega_{a\gamma}, \omega_{b\gamma}, \omega_{a\gamma'}$, $\omega_{b\gamma'}$, very large) and for $N_1(t)_{ab} = 0$:

$$W_{a \rightarrow b}^{(2)} = - \sum_{\gamma, \gamma'} [J_{a\gamma, \gamma b, b\gamma', \gamma'a}(\omega_{\gamma a}, \omega_{b a}, \omega_{b\gamma'}) + J_{a\gamma, \gamma b, b\gamma', \gamma'a}(\omega_{a\gamma}, \omega_{ab}, \omega_{\gamma b})] \quad (49)$$

where $J_{a\gamma, \gamma b, b\gamma', \gamma'a}(\omega_1, \omega_j, \omega_k) =$

$$\text{Re} \sum_{q, r, s, u} A_q \alpha_{\gamma}^A \alpha_r^A \gamma_{\beta}^A \beta_{\gamma'}^A \alpha_{u\gamma'}^A \ell_4(q, r, u, s; \omega_1, \omega_j, \omega_k) \quad (50)$$

$$\text{with } \ell_4(\dots) = \int_0^{\infty} d\tau_1 e^{-i\omega_1 \tau_1} \int_0^{\infty} d\tau_2 e^{-i\omega_j \tau_2} \int_0^{\infty} d\tau_3 e^{-i\omega_k \tau_3} \times \\ \times g_4(q, r, s, u; \tau_1, \tau_2, \tau_3) \quad (51)$$

But now we must be careful in defining $W_{a \rightarrow b}$. Specifically we let

$$\dot{\sigma}_{aa} = + \sum_b R_{aa} \gamma_{bb} \sigma_{bb} = W_{b \rightarrow a} \sigma_{bb} - \sum_{b \neq a} W_{a \rightarrow b} \sigma_{aa} \quad (52)$$

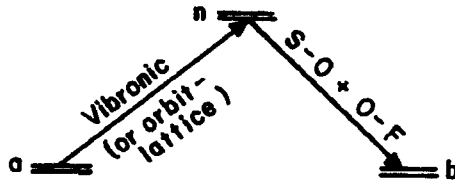
One then finds that:

$$W_{b \rightarrow a}^{(2)} = \sum_{\gamma, \gamma'} J_{a\gamma, \gamma b, b\gamma', \gamma'a}(\omega_{\gamma a}, \omega_{b a}, \omega_{\gamma'a}) + J_{a\gamma, \gamma b, b\gamma', \gamma'a}(\omega_{a\gamma}, \omega_{ab}, \omega_{a\gamma'}) \quad (53)$$

Given that $\omega_{a\gamma}, \omega_{b\gamma}, \omega_{a\gamma'}$ and $\omega_{b\gamma'}$ are very large, the terms in $W_{b \rightarrow a}$ are proportional to $(\omega_{\gamma a} \omega_{\gamma'a})^{-1}$, while the equivalent terms in $W_{b \rightarrow a}$ (i.e. having the same matrix elements), are proportional to $(\omega_{\gamma a} \omega_{\gamma'b})^{-1}$ or $(\omega_{\gamma'a} \omega_{\gamma b})^{-1}$. Thus $W_{b \rightarrow a}$ and $W_{a \rightarrow b}$ are not quite equal if $E_a \neq E_b$.

A particular example of such a second-order lattice-induced transition in liquids is the g-tensor mechanism. In general, it is the spin-orbit (SO) and orbit-field (O-F) interactions $\vec{\lambda} \cdot \vec{L} \cdot \vec{S}$ and $B_e \vec{L} \cdot \vec{B}_0$ which are random functions, since \vec{L} is quantized in the molecular frame, while S for a polyatomic molecule and large values of B_0 is coupled to the laboratory frame. From this point of view, g-tensor relaxation effects come from $R^{(4)}$, since they are quadratic in both S-O and O-F terms. (One must now consider matrix elements in combined spin and electronic space.) Furthermore, the g-shift is naturally found to be the dynamic frequency shift of $R^{(2)}$ arising from these terms. There is an associated rotational

spin-orbit (RSO) relaxation mechanism from $\text{Re}R^{(2)}$, which should be unimportant. Various Orbach-type processes (cf. Kivelson Ch. X) illustrated by:



can be calculated in this way even when the orbit-lattice or vibronic modulation is approximated by a stochastic process that is independent of the rotational motion modulating the S-O process.¹¹ The relaxation terms are quadratic in both vibronic (or O-L) and in S-O, while the associated dynamic g-shift-type terms are quadratic in vibronic (or O-L) terms but linear in both S-O and O-F terms.

Note that when $\omega_{na} \sim \omega_{nb} \gg \omega_{ba}$, the results outlined above for $W_{b \rightarrow a}^{(2)}$ are well treated by utilizing a "quasi-solid" approximation and then only $R^{(2)}$. The "quasi-solid" approximation in the case of the g-tensor is just the usual approach of first calculating the solid g-tensor from S-O and O-F terms and then introducing rotational modulation into the resulting spin Hamiltonian.

Note that one usually finds $T_1 = T_2$ for the spin-orbit induced relaxation mechanisms in liquids.¹¹ The other mechanisms such as spin orbit pulse (SOP) and spin-orbit tunneling (SOT) are discussed elsewhere.¹¹

VIII.3. NON-ASYMPTOTIC SOLUTIONS

The general solutions for $\dot{K}_n(t)$ instead of $R^{(n)}$, are obtained by replacing the infinite upper limits of the time integrals in the spectral densities by the appropriate finite values obtained from eq. 15. Let us examine the $\dot{K}_2(t)$ term (see also Nielsen, Ch. V). If we consider only a secular perturbation with

$$\langle \mathcal{K}_1(t) \rangle = 0 \tag{54}$$

$$\text{and } \Delta^2 \equiv \langle |\mathcal{K}_1(t)_{aa} - \mathcal{K}_1(t)_{bb}|^2 \rangle. \tag{55}$$

$$\text{Then } \dot{K}_2(t)_{ab, ab} = -\Delta^2 \int_0^t \bar{E}_2(\tau) d\tau \tag{56}$$

$$\text{with } \bar{g}_2(\tau) \equiv \frac{\langle \mathcal{N}_1(t)^x \mathcal{N}_1(t-\tau)^x \rangle_{ab, ab}}{\langle |\mathcal{N}_1(t)^x|^2 \rangle_{ab, ab}} = \frac{\langle \mathcal{N}_1(t)^x \mathcal{N}_1(t-\tau)^x \rangle_{ab, ab}}{\Delta^2}. \quad (57)$$

If we assume a simple exponential decay:

$$\bar{g}_2(\tau) = \exp(-|\tau|/\tau_c) \quad (58)$$

$$\text{then } K_2(t) = -\Delta^2 \tau_c^2 [t/\tau_c - 1 + \exp(-|t|/\tau_c)] \quad (59)$$

$$\text{and } S_{x\alpha\alpha'}^{(a)}(t) = [\exp K_2(t)]_{\alpha\alpha'} S_{x\alpha\alpha'}^{(0)} \quad (60)$$

$$\begin{aligned} \text{Now } I^{(a)}(\omega) &= \frac{1}{\pi} \text{Re} \int_0^\infty e^{-i\omega t} S_x^{(a)}(t) dt \\ &= \frac{\tau_c}{\pi} e^{\Delta^2 \tau_c^2} \text{Re} [(\Delta \tau_c)^{-2z} \gamma(z, \Delta^2 \tau_c^2)] \end{aligned} \quad (61)$$

where $\gamma(z, a)$ is the incomplete gamma function and $z = i(\omega - \omega_0)\tau_c + \Delta^2 \tau_c^2$. A series expansion gives:

$$I^{(a)}(\omega) = \frac{e^{\Delta^2 \tau_c^2}}{\pi \Delta} \sum_{n=0}^{\infty} \frac{(-)^n}{n!} (\Delta \tau_c)^{2n} \frac{(n/\Delta \tau_c) + \Delta \tau_c}{[(n/\Delta \tau_c) + \Delta \tau_c]^2 + [(\omega - \omega_0)^2/\Delta^2]} \quad (62)$$

which is a superposition of Lorentzians of width $n/\tau_c + \Delta^2 \tau_c$ and resonance frequency ω_0 . But the intensity of each such component is proportional to $(\Delta^2 \tau_c^2)^n$, i.e. this is an expansion in powers of $(\Delta \tau_c)^2$. Thus, within the validity of utilizing only $K^{(a)}(t)$ we retain only the $n=0$ and 1 terms to get

$$I^{(a)}(\omega) \approx \frac{\Delta^2 \tau_c}{\pi} \left[\frac{1}{(\Delta^2 \tau_c)^2 + (\omega - \omega_0)^2} - \frac{1}{\tau_c^{-2} + (\omega - \omega_0)^2} \right] \quad (63)$$

for $\Delta^2 \tau_c^2 \ll 1$. There is thus a subsidiary line, opposite in intensity to the main line, which has at resonance an amplitude $\Delta^4 \tau_c^4$ times the subsidiary line. The negative sign may be understood on simple physical grounds. It is well known that the Lorentzian line shape is not a very good approximation to the true line in the far wings, because its intensity does not decrease fast enough to yield convergent moments. The very broad subsidiary line will, however, be most effective in subtracting out some intensity from the wings of the main Lorentzian component, so that the resulting composite

line does decay more rapidly. It is shown elsewhere¹ by considering $K_3(t)$, that the subsidiary line is shifted from ω_0 to $\omega_0 + \Delta$.

In general, one must be more precise about specifying the stochastic process than by just writing eq. 58. We now discuss stochastic averaging.

VIII.4. STOCHASTIC AVERAGING (cf. Ch. II by Pedersen)

A. Gaussian Processes

A Gaussian random process which modulates $F_q(t)$ is characterized by the vanishing of all correlation functions $g_n(\tau_1 \dots \tau_n)$ for $n > 2$.³ This leads to the result $K_n = 0$ for $n > 2$, so that the spectrum is entirely described by K_2 , (where it is assumed that K_0 has been defined so that $K_1 = 0$). Gaussian processes apply to physical situations, where each spin is weakly affected by many perturbers. Such an example is the exchange coupling in solids. Thus we have

$$K(t)_{\alpha\alpha', \beta\beta'} = \int_0^t K(t')_{\alpha\alpha', \beta\beta'} dt' \tag{64}$$

where $\dot{K}(t')^{(a)}$ is obtained from $R^{(a)}$ by utilizing the time-dependent spectral density:

$$h_2(t, q, r; \alpha\beta) = \int_0^t g_2(q, r, \tau) e^{-i\omega\tau} \alpha\beta^T d\tau \tag{65}$$

Once a proper choice is made for $g_2(q, r, \tau)$, it is, in principal, possible to determine the spectrum over the whole range from slow to fast modulation. To illustrate, we again assume a simple exponential decay, and a secular perturbation. Such a correlation function can only be an approximate choice, since it is discontinuous at $\tau=0$, but it is useful for illustrative purposes. In this case, the expansion eq. 62 yields all the higher order terms as an expansion in Lorentzians. For $\Delta\tau_c \ll 1$ only a simple Lorentzian of width $\Delta^2\tau_c$ is retained in the central portion. Gaussian random processes are known to lead to Gaussian widths in the limit of no modulation. This result is obtained in the present case by rewriting $K_2(t)$ with $\Delta\tau_c \equiv x \rightarrow \infty$ as:

$$K_2(t, x \rightarrow \infty) = \lim_{x \rightarrow 0} \{-x^2 [\exp(-t\Delta/x) - 1 + t\Delta/x]\} = -\frac{1}{2}(\Delta t)^2 \tag{66}$$

so that
$$e^{Kt} \xrightarrow{x \rightarrow \infty} \exp[-\frac{1}{2}(\Delta t)^2] \quad (67)$$

and the Fourier transform of this result leads to a Gaussian line-shape with a second moment of Δ^2 .* In general we note that a line is Lorentzian for $|\omega - \omega_0| \ll \tau_c^{-1}$ and Gaussian for $|\omega - \omega_0| \gg \tau_c^{-1}$.

Kubo and Tomita⁵ find that the half-half width T_2^{-1} obtained from numerical solutions of eq. 62 is given well by:

$$T_2^{-2} \cong \frac{4 \ln 2}{\pi} \Delta^2 \tan^{-1} \left\{ \frac{\pi \tau_c}{(4 \ln 2) T_2} \right\} \quad (68)$$

Also the Lorentzian approximation is valid for $|\omega - \omega_0| = K\Delta$ where K obeys the inequality

$$\Delta \tau_c \cong K \left[\tan \frac{\pi}{2} \left(1 - \frac{4}{9K^2} \right)^{-1} \right] \quad (69)$$

B. Markov Processes

A stationary Markov process $y(t)$ is completely determined by specifying the a priori probability $W(y_2)dy_2$ of finding y_2 in the range (y_2, y_2+dy_2) and the conditional probability $P(y_1 | y_2, \tau)dy_1$ that given y_1 at an initial time, one finds y in the range (y_2, y_2+dy_2) at a time τ later. For Brownian motion problems the two are related by $W(y_2) = \lim_{\tau \rightarrow \infty} P(y_1 | y_2, \tau)$. The joint probability

*A Gaussian correlation function of form $\bar{g}(\tau) = e^{-a^2 \tau^2}$, which is continuous at $\tau=0$, is often used in analyzing Gaussian random processes. For example in the simple theory of exchange narrowing, $a^2 = \frac{1}{4} \pi \omega_e^2$ where ω_e is the "exchange frequency". This choice of correlation function leads to:

$$\begin{aligned} K_2(t) &= -\Delta^2/a [\text{terf}(at) + (1/2a)(e^{-a^2 t^2} - 1)] \\ &= -\Delta^2/a [t - \text{terfc}(at) + \frac{1}{2a}(e^{-a^2 t^2} - 1)] \end{aligned}$$

where $\text{erf}(y) = 1 - \text{erfc}(y) = \int_0^y e^{-z^2} dz$. The first expression is useful for expanding about the zero modulation region, $\Delta/a \rightarrow \infty$ (where $K_2(t) \cong -\Delta^2 t^2$), while the latter is for $\Delta/a \rightarrow 0$ (where $K_2(t) \cong \Delta^2 t/a$). In neither case are simple Lorentzian expansions like that of eq. 62 obtained.

density of finding y in the range $(y_2, y_2 + dy_2)$ at any time t_2 and in the range $(y_1, y_1 + dy_1)$ at a later time $t_1 = t_2 + \tau$ is given by

$$W_2(y_2; y_1 \tau) = W(y_2)P(y_2 | y_1, \tau) \tag{70}$$

This may be generalized to an n^{th} order joint probability density:

$$\begin{aligned} W_n(y_n, t_n; y_{n-1} t_{n-1}; \dots; y_2 t_2, y_1 t_1) &= W_n(y_n; y_{n-1} \tau_{n-1}; \dots; y_2 \tau_2, y_1 \tau_1) = \\ &= W(y_n) \prod_{i=1}^{n-1} P(y_{n-i+1} | y_{n-i} \tau_{n-i}) \end{aligned} \tag{71}$$

where $t_1 > t_2 \dots > t_{n-1} > t_n$.

Alternatively from the symmetry between the past and future we have:

$$W_n = W(y_1) \prod_{i=1}^{n-1} P(y_1 | y_{i+1}, \tau_i) \tag{71a}$$

Then, for the n^{th} order time correlation of the random function

$$\begin{aligned} F_q(y): & \langle F_{q_1}(t) F_{q_2}(t-\tau_1) \dots F_{q_n}(t - \sum_{i=1}^{n-1} \tau_i) \rangle \\ &= \int dy_n W(y_n) F_{q_n}(y_n) \int \dots \int dy_{n-1} \dots dy_2 dy_1 \prod_{i=1}^{n-1} P(y_{n-i+1} | y_{n-i}, \tau_{n-i}) \\ & F_{q_{n-1}} \dots F_{q_2} F_{q_1}. \end{aligned} \tag{72}$$

The integrals in eq. 72 may be changed to summations when the variable y_i takes on a discrete set of values.

We shall consider internal rotations and (anisotropic) rotations below.

VIII.5. DIFFUSION MODELS

A. Internal Rotations

Very often the paramagnetic molecule will have an internal rotor, e.g. a methyl group or hydroxyl group. When one uses classical models for these motions, we have limiting cases of free rotation and torsional oscillations. We now consider the former.

We assume a rotor characterized by its moment of inertia I and friction constant $\beta' = \beta I$. By analogy with translational Brownian motion¹² we have a Langevin equation in the angle of rotation θ :¹³

$$\frac{d^2\theta}{dt^2} + \beta \frac{d\theta}{dt} = A(t) \quad (73)$$

where $A(t)$ is the random rotational acceleration. Now the probability of finding the rotor at any angle θ_0 , $0 \leq \theta_0 \leq 2\pi$ is independent of θ_0 and is given by:

$$W(\theta_0)d\theta_0 = \frac{1}{2\pi}d\theta_0 \quad (74)$$

while the conditional probability that the rotor is at the angle θ at the time $t \geq 0$ if it was at θ_0 at the time $t=0$ is

$$P(\theta_0|\theta, t)d\theta = (4\pi Dt)^{-\frac{1}{2}} \exp[-(\theta-\theta_0)^2/4Dt]d\theta \quad (75)$$

This equation holds for long times, i.e. $t \gg \beta^{-1}$ and $D = kT/\beta I$. However, a real internal rotor may be better approximated by considering the possibility that free rotation occurs, in which the orientational changes are still partly determined by the angular velocity, which is not completely damped out for short enough times $t \lesssim \beta^{-1}$. We then use the more general solution:¹²

$$P(\theta_0, \dot{\theta}_0|\theta, t) = \left(\frac{Q}{\pi}\right)^{\frac{1}{2}} \exp[-Q|\theta - \theta_0 - \dot{\theta}_0(1 - e^{-\beta t})/\beta|^2] \quad (76)$$

where

$$Q = \frac{\beta}{2D} [2\beta t - 3 + 4e^{-\beta t} - e^{-2\beta t}]^{-1} \quad (77)$$

which has explicit dependence on the initial angular velocity $\dot{\theta}_0$, but becomes eq. 75 for $\beta t \gg 1$. I.e. for $\beta t \leq 1$ the process is a two dimensional Markoff process in $\theta, \dot{\theta}$. We now integrate eq. 76 over an initial Boltzmann distribution in velocity: $W(\dot{\theta}_0) =$

$$\left(\frac{I}{2\pi kT}\right)^{\frac{1}{2}} e^{-I\dot{\theta}_0^2/2kT} \quad \text{to obtain:}$$

$$P(\theta_0|\theta, t) = \left(\frac{S}{\pi}\right)^{\frac{1}{2}} \exp[-(\theta - \theta_0)^2 S] \quad (78)$$

$$S = \frac{\beta}{4D} [\beta t - 1 + e^{-\beta t}]^{-1} \quad (79)$$

the appropriate generalization of eq. 75, including short times. Note that since the rotating group can, in principle, make many complete revolutions during the time t , the angle θ in eqs. 75-77 can be anywhere in the range $-\infty \leq (\theta - \theta_0) \leq \infty$. An equivalent eigenfunction expansion for eq. 77 is obtained as a Fourier Series

expansion:

$$P(\theta_0 | \theta, t) = \frac{1}{2\pi} \sum_K e^{iK(\theta - \theta_0)} \exp[-K^2/4S] \quad (80)$$

where now the periodicity in θ has been accounted for so $0 \leq \theta \leq 2\pi$.¹⁴ The time dependence for each term in K is thus seen to be identical to that for the Gaussian random process, and we may analyze the spectral densities similarly. Thus, for example consider:

$$g(\tau) = \langle e^{in\theta(\tau)} e^{-in'\theta(0)} \rangle = e^{-n^2/4S} \delta_{n,-n'} \quad (81)$$

$$\begin{aligned} \text{Then } j(\omega) &= \text{Re} \int_0^\infty e^{-i\omega\tau} g(\tau) d\tau = \beta^{-1} e^{\text{Re } z} \text{Re} [p^{-z} \gamma(z, p)] \\ &= \frac{e^{\text{Re } z}}{\beta} \sum_{m=0}^\infty \frac{(-)^m}{m!} \frac{p^m}{p} \frac{m+p}{(m+p)^2 + (\omega/\beta)^2} \end{aligned} \quad (82)$$

where $p = n^2 D/\beta$ and $z = i\omega + p$. Thus $j(\omega)$ is essentially a Lorentzian if $p \ll 1$, while it is essentially a Gaussian if $p \gg 1$, i.e.

$$j(\omega) \xrightarrow{t \rightarrow \infty} \frac{p\beta}{p^2\beta^2 + \omega^2} \quad (83a)$$

$$j(\omega) \xrightarrow{t \rightarrow 0} \frac{1}{2} \sqrt{\frac{2\pi}{p\beta^2}} \exp\left[-\frac{1}{2} \frac{\omega^2}{\beta^2 p} t\right] \quad (83b)$$

Intermediate behavior consists of Lorentzian character near $\omega \sim 0$ and Gaussian character for asymptotically large ω .

Internal rotations are important mechanisms in the modulation of hyperfine interactions. That is, for an internal rotation with an n -fold symmetry axis, we may expand the instantaneous hyperfine interaction $a(t)$ in a Fourier series as:

$$a(t) = \sum_{n=0}^\infty B_n \cos n\theta(t) = B_0 + \frac{1}{2} \sum_{n=1}^\infty B_n (e^{in\theta} + e^{-in\theta}) \quad (84)$$

Usually only the leading terms $n = 0, \pm 1$ are kept. Note from eqs. 80 and 81 we have

$$\langle (a(t) - B_0)(a(0) - B_0) \rangle = \frac{1}{2} \sum_{n=1}^\infty B_n^2 e^{-n^2/4S}. \quad (85)$$

Other, more detailed classical models are discussed elsewhere including analogous discussions of torsional oscillator correlation functions and spectral densities.¹³

B. Anisotropic Rotational Diffusion^{14, 15}

Suppose we assume that the rotation of a molecule can be compared to that of a rigid sphere of radius a in a medium of viscosity η , and that it can be described by a diffusion equation in the probability $P(\Omega, t)$

$$\frac{\partial P(\Omega, t)}{\partial t} = R \nabla_S^2 P(\Omega, t) \quad (86)$$

Here ∇_S^2 is the Laplacian operator on the surface of a sphere and we may use R , the rotational diffusion coefficient in the Stokes-Einstein form:

$$R = \frac{kT}{8\pi a^3 \eta}. \quad (87)$$

The probability $P(\Omega, t)$ gives the probability that the Euler angles between molecule fixed axes and an appropriate laboratory co-ordinate system have the value Ω at time t . We note that there is an exact analogy between eq. 86 and the time-dependent Schrodinger equation for a spherical top

$$i\hbar \frac{\partial \Psi(\Omega, t)}{\partial t} = -H\Psi = -\frac{\hbar^2}{2I} \nabla_S^2 \Psi(\Omega, t). \quad (88)$$

Thus the eigenfunctions of both eqs. 86 and 88 are the spherical harmonics $Y_m^l(\theta, \varphi)$.

When we have a non-spherical particle in an otherwise isotropic medium, then it is not surprising that the diffusion equation obeyed by $P(\Omega, t)$ is just the analogue of the Schrodinger equation for an asymmetric top. Thus we have

$$\frac{\partial P(\Omega, t)}{\partial t} = \Lambda P(\Omega, t) \quad (89)$$

where Λ is the quantum mechanical Hamiltonian for an asymmetric top, but now we replace the rotational constants for the rigid rotor in units of Planck's constant by the principal values of a diffusion tensor: R_1 , R_2 , and R_3 along molecular axes x' , y' , and z' .

The eigenfunctions and eigenvalues of Λ become those of the rigid rotor, i.e.

$$\Lambda \varphi_n(\Omega) = E_n \varphi_n(\Omega) \quad (90)$$

where the $\varphi_n(\Omega)$ are a complete orthonormal set of rigid rotor wave

functions with eigenvalue E_n . Now we may write the general solution of eq. 89 as an eigenfunction expansion:

$$P(\Omega, t) = \sum_{n=0}^{\infty} C_n(t) \varphi_n(\Omega) . \tag{91}$$

Then from eqs. 89-91 and the orthonormality of the $\varphi_n(\Omega)$ we have:

$$\dot{C}_n(t) = -E_n C_n(t) \tag{91a}$$

with the solution:

$$C_n(t) = C_n(0) e^{-E_n t} \tag{91b}$$

If it is assumed that at $t=0$ the Euler angles are given by Ω_0 , then $P(\Omega, \tau=0)$ is just the delta function $\delta(\Omega - \Omega_0)$, which may be expanded as:

$$\delta(\Omega - \Omega_0) = \sum_{n=0}^{\infty} \varphi_n^*(\Omega_0) \varphi_n(\Omega) . \tag{92}$$

Thus $C_n(0) = \varphi_n^*(\Omega_0)$ (92a)

and we obtain an expression for the conditional probability

$P(\Omega_0 | \Omega, \tau)$:

$$P(\Omega_0 | \Omega, \tau) = \sum_{n=0}^{\infty} \varphi_n^*(\Omega_0) \varphi_n(\Omega) e^{-E_n \tau} \tag{93}$$

Axially Symmetric Rotational Diffusion. When $R_1 = R_2 = R_{\perp}$ and $R_3 = R_{\parallel}$, eq. 89 reduces to the Hamiltonian of the symmetric rotor, whose symmetry axis corresponds to the z' axis. The φ_n are then the well-known symmetric rotor wave functions which may be classified in terms of the quantum numbers L, K , and M , i.e. $\varphi_n \rightarrow \varphi_{KM}^L(\Omega)$. It is useful to identify the wave functions with the Wigner rotation matrices. Thus

$$\varphi_{KM}^L(\Omega) = \left(\frac{2L+1}{8\pi^2} \right)^{\frac{1}{2}} D_{KM}^L(\Omega) \tag{94}$$

Eq. 93 becomes

$$P(\Omega_0 | \Omega, t) = \sum_{L, K, M} \left(\frac{2L+1}{8\pi^2} \right) D_{KM}^{L*}(\Omega_0) D_{KM}^L(\Omega) \exp(-E_{L, K} t) \tag{95}$$

where $E_{L, K} = R_{\perp} L(L+1) + (R_{\parallel} - R_{\perp}) K^2$ (96)

Asymmetric Rotational Diffusion. When $R_1 \neq R_2 \neq R_3$, then the eigenfunctions of eq. 93 become rather complex, but they may be

expressed as linear combinations of the symmetric rotor eigenfunctions. The nature of the problem is seen by writing the operator Λ as:

$$\Lambda = R_+ \vec{m}^2 + (R_3 - R_+) m_x^2 + \frac{1}{2} R_- (m_+^2 + m_-^2) \tag{97}$$

where \vec{m} is an "angular momentum" operator such that $m_x^L \varphi_{KM}^L(\Omega) = L(L+1) \varphi_{KM}^L(\Omega)$ and $m_y^L \varphi_{KM}^L(\Omega) = [(L+K)(L+K+1)]^{1/2} \varphi_{K+1, M}^L(\Omega)$. Also $R_{\pm} = \frac{1}{2}(R_1 \pm R_2)$ and $m_{\pm} = m_x \mp i m_y$. The last term in eq. 97 couples only symmetric rotor functions for which $L=L'$, $K=K' \pm 2$, and $M=M'$. The eigenfunctions corresponding to $L=2$ are given in ref. 15. When $R_- = 0$, the asymmetric rotor functions reduce to symmetric rotor functions (or simple linear combinations of the degenerate functions).

Eq. 93 may now be written for $L=2$ as:

$$P^{(2)}(\Omega_0 | \Omega, t) = \sum_{K', M} \Phi_{K'M}^{(2)}(\Omega_0) \Phi_{K'M}^{(2)}(\Omega) e^{-E_{2,K'} t} \tag{98}$$

A simplification for the asymmetric diffusion case occurs when $R_3 \gg R_{\pm}$. This corresponds to rotational relaxation about the molecular z' -axis being much more rapid than about the other two axes. The solutions for asymmetric diffusion are then approximated by the axially symmetric diffusion solutions with $E_{2, \pm 2} \cong 4R_3$ and $E_{2,0} \cong R_+$.

We may note that eq. 87 becomes for ellipsoids $R_i = kT/\beta_i$, where β_i are the principal values of the friction tensor. For an axially symmetric ellipsoid in the Stokes-Einstein approximation, letting $a_2 = a_3$, then the β_i become:

$$\beta_2 = \beta_3 = 3\pi\eta(a_1^4 - a_2^4)/3[(2a_1^2 - a_2^2)S - 2a_1] \tag{99a}$$

$$\beta_1 = 32\pi\eta a_2^2(a_1^2 - a_2^2)/3[2a_1 - a_2^2 S] \tag{99b}$$

where a_1 , a_2 , and a_3 are the lengths of the x' , y' and z' semi-axes. When $a_1 > a_2$

$$S = 2(a_1^2 - a_2^2)^{-1/2} \ln\{[a_1 + (a_1^2 - a_2^2)^{1/2}]/a_2\} \tag{100a}$$

When $a_1 < a_2$

$$S = 2(a_2^2 - a_1^2)^{-1/2} \tan^{-1} [(a_2^2 - a_1^2)^{1/2}/a_1] \tag{100b}$$

But on a more microscopic scale one would want to relate the β_i to

the anisotropic intermolecular potential of a molecule with the surrounding molecules.

One can also attempt to generalize these results to include short time free rotational effects. The general problem is complex,¹⁶⁻¹⁷ but for spherical symmetry a rough approximation is eq. 95 with now $E_L t = RL(L+1)/4S$ with S given by eq. 79 and R instead of D .

Another important diffusional model is jump diffusion where the molecule reorients through large angles as a result of strong collisions.¹⁸

Anisotropic rotational diffusion can, in principle, manifest itself through line width effects from the intramolecular anisotropic interactions: g -tensor, electron-nuclear dipolar, and quadrupolar.¹⁵ These terms, which are 2nd rank tensors may be written as irreducible tensor components in the form of eq. 40 as:

$$\chi_1(t) = \sum_{q, m, m'} F'_q(2, m) \delta_{-m, m'}^2(\Omega) A_q(2, m') \quad (101)$$

where the prime on $F'_q(2, m)$ indicates it is written in molecule-fixed axes, while unprimed $A_q(2, m')$ is in laboratory axes. The $\delta_{-m, m'}^2(\Omega)$ are the rotation matrix elements (with Ω the Euler angles) for the transformation between the two axis systems. One then needs correlation functions of form:

$$g(\tau) = \langle \delta_{-m, q}^L(t) \delta_{-m', q'}^{L'} \ast(t+\tau) \rangle_{\Omega} \quad (102)$$

which for axially-symmetric rotational diffusion is, from Eqs. 72, 95 and 96 and the orthonormality of the $\varphi_{KM}^L(\Omega)$ of Eq. 94:

$$g(\tau) = \frac{1}{2L+1} \exp[-E_{L, m} \tau] \delta_{L, L'} \delta_{m, m'} \delta_{qq'} \quad (103)$$

Then the spectral density terms, $J(\omega)$ of Eq. 37a become for $L = 2$

$$J(\omega) = \sum_{q, q', m} A_q(2, m) A_{q'} \ast(2, m) j^{(qq', 2)}(\omega) \quad (104)$$

with $j^{(qq', 2)}(\omega) = \frac{1}{2L+1} \sum_M F'_q(2, M) F_{q'} \ast(2, M) [E_{2, M}^{-1} / (1 + E_{2, M}^{-2} \omega^2)]$. (105)

This means that each irreducible tensor component $F'_q(2, M)$ is

"relaxed" with its own characteristic time $E_L |M|^{-1}$, and it illustrates the great advantages in using irreducible tensor formalism.

VIII.6. SUMMATION OF THE GENERALIZED MOMENTS FOR A MARKOFF PROCESS: STOCHASTIC LIOUVILLE EQUATION

We have for a Markoff process:

$$\frac{\partial}{\partial t} P(\Omega, t) = -\Gamma_{\Omega} P(\Omega, t) \tag{106}$$

where $P(\Omega, t)$ is the probability of finding Ω at the particular state at time t . The process is assumed to be stationary, so that Γ is a time-independent Markoff operator, (e.g. it is $-\lambda$ in eq. 89) and also that the process has a unique equilibrium distribution, $P_0(\Omega)$, characterized by:

$$\Gamma P_0(\Omega) = 0 \tag{107}$$

A formal solution to eq. 107 given that Ω initially had value Ω_0 is given by the conditional probability $P(\Omega_0 | \Omega, t)$ which obeys:

$$P(\Omega_0 | \Omega, t) = e^{-\Gamma_{\Omega} t} \delta(\Omega - \Omega_0) \tag{108}$$

An alternate form of eq. 108, in terms of orthogonal eigenfunctions G_m of the operator Γ_{Ω} is

$$\begin{aligned} P(\Omega_0 | \Omega; \tau) &= \sum_m G_m^*(\Omega_0) e^{-\Gamma_{\Omega} \tau} G_m(\Omega) = \sum_m G_m^*(\Omega_0) e^{-E_m \tau} G_m(\Omega) \\ &= \sum_m e^{-\Gamma_{\Omega} \tau} |G_m(\Omega)\rangle \langle G_m(\Omega_0)| \end{aligned} \tag{109}$$

where $|G_m(\Omega)\rangle$ and $\langle G_m(\Omega_0)|$ are ket and bra vectors in the Hilbert space defined by the variable Ω , with Γ Hermitian for convenience.

It is then possible to show that

$$\begin{aligned} e^{-i\mathcal{H}_0^x t} m_n(t_1 \dots t_n) &= \langle P_0(\Omega) | e^{-(t-t_1)(i\mathcal{H}_0^x + \Gamma)} \mathcal{X}_1^x(\Omega) e^{-(t_1-t_2)(i\mathcal{H}_0^x + \Gamma)} \times \\ &\mathcal{X}_1^x(\Omega) e^{-(t_2-t_3)(i\mathcal{H}_0^x + \Gamma)} \dots \mathcal{X}_1^x e^{-(t_{n-1}-t_n)(i\mathcal{H}_0^x + \Gamma)} \times \\ &\mathcal{X}_1^x e^{-t_n(i\mathcal{H}_0^x + \Gamma)} |G_0\rangle \end{aligned} \tag{110}$$

$$\text{where } \langle P_0(\Omega) | Q(\Omega) |G_0\rangle \equiv \int d\Omega P_0^*(\Omega) Q(\Omega) G_0(\Omega) \tag{110a}$$

is a "matrix-element" of operator Q , and $|G_0(\Omega)\rangle \propto |P_0(\Omega)\rangle$.

In order to do this we first note that

$$[\mathcal{N}_0, \Gamma_\Omega] = 0 \tag{111a}$$

since \mathcal{N}_0 is taken to be independent of Ω , but in general,

$$[\mathcal{N}_0, \mathcal{N}_1] \neq 0 \tag{111b}$$

$$[\mathcal{N}_1, \Gamma] \neq 0 . \tag{111c}$$

Also, it is easy to see that the commutators of type $[\mathcal{N}_1^\dagger, B]$ obey:

$$[\mathcal{N}_1^\dagger, B] \equiv \mathcal{N}_1^{\dagger \times} B = (e^{it\mathcal{N}_0^\times} \mathcal{N}_1^\dagger e^{-it\mathcal{N}_0^\times}) B . \tag{112}$$

Thus $e^{-(i\mathcal{N}_0^\times + \Gamma)t} |G_0\rangle = e^{-i\mathcal{N}_0^\times t} e^{-\Gamma t} |G_0\rangle = e^{-i\mathcal{N}_0^\times t} |G_0\rangle$; similarly

$$\langle P_0(\Omega) | e^{-(i\mathcal{N}_0^\times + \Gamma)(t-t_1)} = e^{-i\mathcal{N}_0^\times t} \langle P_0(\Omega) | e^{+i\mathcal{N}_0^\times t_1} . \tag{113}$$

Thus from eq. 110 (and eqs. 111-113)

$$\begin{aligned} m_n(t_1 \dots t_n) &= \langle P_0(\Omega) | e^{it_1 \mathcal{N}_0^\times} \mathcal{N}_1^\dagger e^{-(t_1-t_2)(i\mathcal{N}_0^\times + \Gamma)} \mathcal{N}_1^\dagger e^{-(t_2-t_3)(i\mathcal{N}_0^\times + \Gamma)} \\ &\dots \mathcal{N}_1^\dagger e^{-(t_{n-1}-t_n)(i\mathcal{N}_0^\times + \Gamma)} \mathcal{N}_1^\dagger e^{-it_n \mathcal{N}_0^\times} |G_0\rangle \\ &= \langle P_0(\Omega) | \mathcal{N}_1^\dagger(t_1)^\times e^{-\Gamma(t_1-t_2)} \mathcal{N}_1^\dagger(t_2)^\times e^{-\Gamma(t_2-t_3)} \dots \\ &\dots \mathcal{N}_1^\dagger(t_{n-1})^\times e^{-\Gamma(t_{n-1}-t_n)} \mathcal{N}_1^\dagger(t_n)^\times |G_0\rangle \end{aligned} \tag{114}$$

We now note from eq. 108 that

$$\int P(\Omega | \Omega_1, t) Q(\Omega_1) d\Omega_1 = e^{-\Gamma t} Q(\Omega) \tag{115}$$

Eq. 115 is then used systematically from the right on the last form of eq. 114 to replace the operators $e^{\Gamma(t_{i-1}-t_i)}$, finally yielding the usual Markovian correlation expression,¹ (cf. eq. 72, but with eq. 71a utilized and with $\mathcal{N}_1^\dagger(\Omega_i, t_i)^\times$ instead of just $F(y_i)$). This completes the proof of eq. 110.

Now eq. 110 along with eqs. 6, 7 and 8 provides a solution for $\sigma(t)$

$$\sigma(t) = e^{-i\mathcal{N}_0^\times t} \sum_{n=0}^{\infty} M_n(t) \tag{116}$$

The Laplace transform of $e^{-i\mathcal{N}_0^\times t} M_n(t)$ or $\mathbb{M}_n(s)$ is shown to be

$$\mathfrak{m}_n(s) = \langle P_0 | \left(\frac{-i}{s + i\mathcal{N}_0^x + \Gamma_\Omega} \mathcal{N}_1(\Omega)^x \right)^n \frac{1}{s + i\mathcal{N}_0^x + \Gamma_\Omega} | G_0 \rangle \quad (117)$$

since the Laplace transform of the (multiple) convolution in eq. 8 is just the product of Laplace transforms. Then the Laplace transform of $\sigma(t)$ or $\tilde{\sigma}(s)$ is just:

$$\begin{aligned} \frac{\tilde{\sigma}(s)}{\sigma(0)} &= \sum_{n=0}^{\infty} \mathfrak{m}_n(s) = \langle P_0 | \frac{1}{1 + i\mathcal{N}_1^x (s + i\mathcal{N}_0^x + \Gamma_\Omega)^{-1}} \frac{1}{s + i\mathcal{N}_0^x + \Gamma_\Omega} | G_0 \rangle \\ &= \langle P_0 | [s + i\mathcal{N}^x + \Gamma_\Omega]^{-1} | G_0 \rangle \end{aligned} \quad (118)$$

This is equivalent to the stochastic Liouville result of Kubo,¹⁹ (cf. Jensen Ch. III). [An equivalent result but with $i \rightarrow -i$ is obtained for $\tilde{S}(s)$.] Then we have

$$\sigma(t) = \langle P_0 | \exp [(-t)(i\mathcal{N}^x + \Gamma)] | G_0 \rangle \sigma(0) \quad (119)$$

It follows from the definition, eq. 10 of $K(t)$ that:

$$K(t) = \ln \langle P_0 | e^{it\mathcal{N}_0^x} e^{(-i\mathcal{N}^x - \Gamma)t} | G_0 \rangle \quad (120)$$

and, if $[\mathcal{N}_0, \mathcal{N}_1] = 0$ then $K(t) = \ln \langle P_0 | e^{-i\mathcal{N}_1^x - \Gamma)t} | G_0 \rangle$. Also,

$$\dot{K}(t) = -e^{it\mathcal{N}_0^x} \langle P_0 | (i\mathcal{N}_1 - \Gamma_\Omega) e^{-(i\mathcal{N}^x + \Gamma)t} | G_0 \rangle \left[\langle P_0 | e^{-(i\mathcal{N}^x + \Gamma)t} | G_0 \rangle \right]^{-1} \times e^{-it\mathcal{N}_0^x}, \quad (121)$$

which does not appear to be very useful for calculation purposes, although we shall see eq. 118 is very useful for nonperturbative solutions (cf. Ch. XIV).

VIII.7. ACKNOWLEDGEMENT

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References

1. J. H. Freed, J. Chem. Phys. 49, 376 (1968).
2. R. Kubo, J. Phys. Soc. Japan 17, 1100 (1962).
3. R. Kubo, in "Fluctuation, Relaxation, and Resonance in Magnetic Systems", D. ter Haar, Ed. (Oliver and Boyd, London, 1962), p. 23; J. Math. Phys. 4, 174 (1963).
4. A. Abragam, "The Principles of Nuclear Magnetism" (Oxford University Press, London, 1961).
5. R. Kubo and K. Tomita, J. Phys. Soc. Japan 9, 888 (1954).
6. A. G. Redfield, IBM J. Res. Develop. 1, 19 (1957).
7. F. Bloch, Phys. Rev. 102, 104 (1956).
8. J. H. Freed and G. K. Fraenkel, J. Chem. Phys. 39, 326 (1963); G. K. Fraenkel, J. Phys. Chem 71, 139 (1967).
9. J. H. Freed, J. Chem. Phys. 43, 2312 (1965).
10. A. Messiah, "Quantum Mechanics" (John Wiley and Sons, New York, 1962), p. 727.
11. J. H. Freed and R. G. Kooser, J. Chem. Phys. 49, 4715 (1968); J. H. Freed (to be published).
12. S. Chandrasekhar, Rev. Mod. Phys. 15, 1 (1943).
13. J. H. Freed and G. K. Fraenkel, J. Chem. Phys. 41, 3623 (1964).
14. L. D. Favro, in "Fluctuation Phenomena in Solids", R. E. Burgess, Ed. (Academic Press, New York, 1965), p. 79.
15. J. H. Freed, J. Chem. Phys. 41, 2077 (1964) and references cited therein.
16. R. A. Sack, Proc. Phys. Soc. (London) 70, 402, 414 (1957).
17. W. A. Steele, J. Chem. Phys. 38, 2404, 2411 (1963).
18. E. N. Ivanov, Sov. Phys. JETP 18, 1041 (1964).
19. R. Kubo, J. Phys. Soc. Japan 26, Supplement, 1 (1969).