Generalized Cumulant Expansions and Spin-Relaxation Theory*

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(Received 11 December 1967)

The generalized cumulant expansion method of Kubo is applied to an analysis of spin-relaxation theory appropriate for NMR and ESR studies of molecular systems. It leads to a general, formal solution of the equation of motion of a suitably averaged magnetization operator (and also the spin-density matrix). This solution permits a convenient perturbation expansion in the region of motional narrowing; i.e., when the random functional spin perturbation $\mathcal{H}_1(t)$ obeys $|\mathcal{H}_1(t)| \tau_c < 1$, where τ_c is a correlation time for the random process. It is shown how this expansion valid for times $t \gg \tau_c$ generates the time-independent R or relaxation matrix to all orders in $|\mathcal{H}_1(t)| \tau_c$, and detailed expressions are given through fourth order. While the R matrix supplies the linewidth and dynamic frequency shift of the main Lorentzian resonance line, it is found that by formulating the cumulant method without the restriction $t \gg \tau_c$, weak subsidiary Lorentzian lines are predicted. These subsidiary lines appear as second-order perturbation corrections in $|\mathcal{H}_1(t)| \tau_c$. They have widths given by τ_c^{-1} and, in general, large frequency shifts. The problem of (anisotropic)-rotational diffusion is discussed in detail, and it is shown that the spin-Hamiltonian approximation for liquids rests upon a Born–Oppenheimer-type approximation appropriate for random modulation of the nuclear coordinates, i.e., $\tau_c^{-1} \ll \omega_{n,o}$, where $\hbar\omega_{n,o}$ is the energy separation between the ground electronic state and the nth excited state coupled by the angular-momentum operator $\mathbf{L}$. The cumulant method is then used to obtain higher-order corrections to the g-tensor line-broadening mechanism.

I. INTRODUCTION

The earlier theories of spin relaxation of free radicals in liquids as developed by Freed and Fraenkel[1] and Kivelson[2] were based upon the general formulations of Kubo and Tomita,[3] Bloch,[4] Redfield,[5] and Abragam.[6] All these formulations are characterized by an approximate solution to the equation of motion of the magnetization operator (or equivalently the spin-density matrix) valid to second order in a spin-dependent perturbation $\mathcal{H}_1(t)$, which is a random function of time. The approximations, which are not easy to justify, are summarized by Abragam.[7] Furthermore, they may not be conveniently generalized to obtain further corrections, i.e., higher-order terms in an appropriate expansion series for the equations of motion. In fact, straightforward attempts at carrying out such an expansion series are found to lead to divergent terms. The problem lies in properly grouping the higher-order terms.

Kubo[8,9] has more recently shown how one may obtain a general and formally correct solution to the spin-relaxation problem by means of a generalized cumulant expansion method, and he develops several important theorems on the utility of this method. In the present work, we have developed the application of this method to the spin-relaxation problem, so that some useful results may be obtained from it.[10] Thus, it becomes possible to explicitly obtain the higher-order terms in the time-independent relaxation or R matrix which governs the relaxation of the spin-density matrix in the motionally narrowed region. This result is applicable to any well defined random process modulating $\mathcal{H}_1(t)$. It is also possible to remove the "coarse-graining" in time assumption (i.e., consideration of time intervals $t \gg \tau_c$, where τ_c is a correlation time for the random process) which is inherent in the R-matrix treatment even to higher orders. It is found that removal of this assumption usually leads to the appearance of weak Lorentzian subsidiary lines as well as the main Lorentzian resonance line (the widths and frequency shifts of the latter being given by the real and imaginary parts, respectively, of the R matrix). The inclusion of finite t, hence the appearance of the subsidiary lines, may also be regarded as a perturbation in $\mathcal{H}_1(t)$. While the cumulant method leads to a formally correct solution to all orders in roughly $\mathcal{H}_1(t)\tau_c$, it leads to reasonably convergent expansions only for $|\mathcal{H}_1(t)\tau_c| < 1$, and thus it is not expected to be very useful in the near-rigid solution or slow-motion region, except perhaps for special cases, such as a Gaussian random modulation.[8]

The general features of the cumulant method as applied to spin relaxation are developed in Sec. II. Explicit expressions for the R matrix to fourth order

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[2] D. Kivelson, J. Chem. Phys. **33**, 1094 (1960).
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[4] F. Bloch, Phys. Rev. **102**, 104 (1956).
[5] A. G. Redfield, IBM J. Res. Develop. **1**, 19 (1957).
[6] A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, London, 1961).
[7] Reference 6, p. 276. Note that assumption (b) of this reference was not utilized in the Kivelson–Kubo–Tomita approach, which is then not in a useful form to handle problems involving degenerate spin states, cf. Ref. 1.
[8] (a) R. Kubo in *Fluctuation, Relaxation, and Resonance in Magnetic Systems*, D. ter Haar, Ed. (Oliver and Boyd, London, 1962), p. 23. (b) R. Kubo, J. Math. Phys. **4**, 174 (1963).
[9] R. Kubo, J. Phys. Soc. Japan **17**, 1100 (1962).

[10] H. Sillescu and D. Kivelson [J. Chem. Phys. **48**, 3493 (1968)] have just developed a general method for calculating the resonance line shape which, however, requires at the outset that the molecular motion be determined by a classical rotational-diffusion equation. It appears to be more "tailor-made" for this particular case than the more general cumulant method. We wish to thank these authors for communication of their work prior to publication.

in essentially $\mathcal{K}_1(t)\tau_c$ are developed in Sec. III. In Sec. IV, the method is illustrated by applying it to a two-jump Markov modulation of the hyperfine-interaction term in ESR. Examples of rotational modulation of the spin–orbit operator and the g tensor are discussed in Secs. V and VI, respectively. The discussion in Sec. V leads to a Born–Oppenheimer-type approximation appropriate for *random* modulation of nuclear coordinates.

II. THE CUMULANT METHOD

We wish to develop the Cumulant Expansion Method so that it leads to a general and useful solution to the spin-relaxation problem. One starts with the line-shape function, or spectrum $I(\omega)$, which is given by[1,3,6]

$$I(\omega) = \frac{4}{\pi} \int_0^\infty G(t) \cos\omega t \, dt, \quad (2.1)$$

where $G(t)$ is the autocorrelation function of the spin angular momentum:

$$G(t) = \mathrm{Tr}[S_x(t) S_x]. \quad (2.2)$$

Here S_x is the x component of the angular momentum and $S_x(t)$ is given by

$$S_x(t) = \langle \tilde{S}_x(t) \rangle$$
$$= \langle \exp(i\mathcal{K}t) S_x \exp(-i\mathcal{K}t) \rangle, \quad (2.3)$$

where the angular brackets imply an ensemble averaging and the tilde indicates an operator for a single independent spin system (e.g., a single molecule or free radical). The trace in Eq. (2.2) is taken over the spin states of a single system. The Hamiltonian $\mathcal{K}$ for the system is separated into a time-independent component $\mathcal{K}_0$ and a perturbing $\mathcal{K}_1(t)$, which is a random function of time:

$$\hbar\mathcal{K} = \hbar\mathcal{K}_0 + \hbar\mathcal{K}_1(t). \quad (2.4)$$

The ensemble average of Eq. (2.3) (which is to be regarded as equivalent to a macroscopic sample containing many independent spins) is taken over the ensemble defined by the probability distribution characteristic of $\mathcal{K}_1(t)$. It is also assumed that the random process is stationary, and ergodic,[8] where the stationarity arises by assuming that the ensemble of $\mathcal{K}_1(t)$ remains at equilibrium, and the ergodicity assures that all the spin systems are able to experience the same range of effects from $\mathcal{K}_1(t)$.

It is convenient to define an interaction representation by

$$S_x{}^\ddagger(t) = \exp(-i\mathcal{K}_0 t) S_x(t) \exp(i\mathcal{K}_0 t) \quad (2.5a)$$

and

$$\mathcal{K}_1{}^\ddagger(t) = \exp(-i\mathcal{K}_0 t) \mathcal{K}_1(t) \exp(i\mathcal{K}_0 t). \quad (2.5b)$$

The equation of motion of $\tilde{S}_x{}^\ddagger(t)$ is then given as

$$(d/dt)\tilde{S}_x{}^\ddagger(t) = i[\mathcal{K}_1{}^\ddagger(t), \tilde{S}_x{}^\ddagger]$$
$$\equiv i\mathcal{K}_1{}^\ddagger(t)^\times \tilde{S}_x{}^\ddagger, \quad (2.6)$$

where we have employed a convention due to Kubo[8a] such that for any operators a and b

$$a^\times b \equiv [a, b]. \quad (2.6a)$$

This differential equation may be integrated formally to

$$\tilde{S}_x{}^\ddagger(t) = \exp_O \left[i \int_0^t dt' \mathcal{K}_1{}^\ddagger(t')^\times \right] S_x(0), \quad (2.7)$$

which becomes

$$S_x{}^\ddagger(t) = \left\langle \exp_O \left[i \int_0^t dt' \mathcal{K}_1{}^\ddagger(t')^\times \right] \right\rangle S_x \quad (2.8)$$

upon taking an ensemble average. The exponent in Eqs. (2.7) and (2.8) is an ordered operator (indicated by subscript O), which must be interpreted as[8,9]

$$\left\langle \exp_O \left[i \int_0^t dt' \mathcal{K}_1{}^\ddagger(t')^\times \right] \right\rangle = \sum_{n=0}^\infty M_n(t), \quad (2.9)$$

where

$$M_n(t) = \frac{i^n}{n!} O \left\langle \left[\int_0^t dt' \mathcal{K}_1{}^\ddagger(t)^\times \right]^n \right\rangle$$

$$= i^n \int_0^t dt_1 \int_0^{t_1} dt_2 \cdots \int_0^{t_{n-1}} dt_n$$

$$\times \langle \mathcal{K}_1{}^\ddagger(t_1)^\times \mathcal{K}_1{}^\ddagger(t_2)^\times \cdots \mathcal{K}_1{}^\ddagger(t_n)^\times \rangle, \quad \text{for} \quad n \geq 1. \quad (2.10)$$

$$M_O(t) = 1. \quad (2.10a)$$

The time ordering indicated in the first equality of Eq. (2.10) may be shown to imply the second equality.[11] Time ordering is necessary because, in general, the operator $\mathcal{K}_1(t_i)$ need not commute with $\mathcal{K}_1(t_j)$ for $t_i \neq t_j$. In the second equality the time ordering is automatically achieved such that

$$t \geq t_1 \geq t_2 \geq \cdots t_n. \quad (2.10b)$$

The expansion of Eq. (2.9) may be regarded as a generalized moment expansion, where the nth moment of the random function

$$m_n(t_1, t_2 \cdots t_n) = \langle \mathcal{K}_1{}^\ddagger(t_1)^\times \mathcal{K}_1{}^\ddagger(t_2)^\times \cdots \mathcal{K}_1{}^\ddagger(t_n)^\times \rangle \quad (2.11)$$

is itself an operator.

The basic idea of the cumulant method is to find a solution to Eq. (2.9) of form

$$\left\langle \exp_O \left[i \int_0^t dt' \mathcal{K}_1{}^\ddagger(t')^\times \right] \right\rangle = \exp_O K(t), \quad (2.12)$$

where

$$K(t) = \sum_{n=1}^\infty K_n(t). \quad (2.12a)$$

Each K_n is still an operator and is of nth order in the operator $\mathcal{K}_1{}^\ddagger(t)^\times$. It may be regarded as a generalized cumulant, which is known to be closely related to the

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[11] P. Roman, *Advanced Quantum Theory* (Addison-Wesley Publishing Co., Inc., Reading, Mass., 1965), p. 311.

moments.[9] The ordering prescription on the cumulants as implied by Eq. (2.12) means that

$$\exp_O \sum_{n=1}^{\infty} K_n(t) \equiv \sum_{p=0}^{\infty} (p!)^{-1} O\left[\sum_{n=1}^{\infty} K_n(t) \right]^p, \quad (2.13)$$

where the cumulant expansion also follows the time-ordering called for in the moment expansion. Thus, by comparing terms of the same order in Eqs. (2.9) and (2.13), while preserving operator and time ordering, expressions may be found for the K_n in terms of the M_n. In general, the K_n will be composed of sums of products of M_i where $i \leq n$. Kubo[9] gives general theorems for the validity of solutions like Eq. (2.12) in the form of generalized cumulant functions, and points out they are just as valid as the moment expansion in Eqs. (2.9) and (2.10). When the two expansions are compared, one obtains to fourth order

$$K_1 = M_1, \quad (2.14a)$$

$$K_2 = M_2 - \tfrac{1}{2} O(M_1{}^2), \quad (2.14b)$$

$$K_3 = M_3 - \tfrac{1}{2}[O(M_1 M_2) + O(M_2 M_1)] + \tfrac{1}{3} O(M_1{}^3), \quad (2.14c)$$

$$K_4 = M_4 - \tfrac{1}{2} O(M_2{}^2) - \tfrac{1}{2}[O(M_1 M_3) + O(M_3 M_1)]$$
$$+ \tfrac{1}{3}[O(M_1{}^2 M_2) + O(M_1 M_2 M_1) + O(M_2 M_1{}^2)]$$
$$- \tfrac{1}{4} O(M_1{}^4). \quad (2.14d)$$

The nature of the ordering prescription is illustrated by [cf. Eq. (2.10)]

$$O(M_1{}^2) = O\left[i \int_0^t dt_1 m_1(t_1) \right]^2$$
$$= -2 \int_0^t dt_1 \int_0^{t_1} dt_2 m_1(t_1) m_1(t_2). \quad (2.15a)$$

Thus,

$$K_2 = - \int_0^t dt_1 \int_0^{t_1} dt_2 [m_2(t_1, t_2) - m_1(t_1) m_1(t_2)], \quad (2.15b)$$

and it will be shown to be equivalent to the second-order term of the earlier theories.[3–6] Also,

$$O(M_2{}^2) = 2 \int_0^t dt_1 \int_0^{t_1} dt_2 m_2(t_1, t_2) \cdot \int_0^{t_1} dt_3 \int_0^{t_3} dt_4 m_2(t_3, t_4). \quad (2.16a)$$

Often, it is possible to define $\mathcal{H}_1{}^{\ddagger}(t)^{\times}$ so that $m_1(t) = 0$, which simplifies the cumulants to

$$K_1 = M_1, \quad K_2 = M_2, \quad K_3 = M_3, \quad K_4 = M_4 - \tfrac{1}{2} O(M_2{}^2).$$

Then K_4 becomes [utilizing Eq. (2.16a)]

$$K_4 = \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \int_0^{t_3} dt_4 [m_4(t_1, t_2, t_3, t_4) - m_2(t_1, t_2) m_2(t_3, t_4)] + \int_0^t dt_1 \int_0^{t_1} dt_2 \int_{t_1}^{t_2} dt_3 \int_0^{t_3} dt_4 m_2(t_1, t_2) m_2(t_3, t_4). \quad (2.16b)$$

It follows from a general theorem of Kubo[9] that the $K_n(t)$ may be written in the form

$$K_n(t) = i^n \int_0^t dt_1 \int_0^{t_1} dt_2 \cdots \int_0^{t_{n-1}} dt_n \langle O \mathcal{H}_1{}^{\ddagger}(t_1)^{\times} \mathcal{H}_1{}^{\ddagger}(t_2)^{\times} \cdots \mathcal{H}_1{}^{\ddagger}(t_n)^{\times} \rangle_c, \quad (2.17)$$

where the subscript c implies a "cumulant average," i.e., the appropriate collections of moments. Thus, for example, Eq. (2.16b) may be rewritten in this form as

$$K_4 = \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \int_0^{t_3} dt_4 [m_4(t_1, t_2, t_3, t_4) - m_2(t_1, t_2) m_2(t_3, t_4) - m_2(t_1, t_3) m_2(t_2, t_4) - m_2(t_1, t_4) m_2(t_2, t_3)], \quad (2.16c)$$

where the last two terms in Eq. (2.16c) are shown to be equal to the last term in Eq. (2.16b) by permuting the numbering of the t_i in Eq. (2.16c) to bring the $m_2(t_i, t_j)$ into standard order (while preserving the proper time ordering) and then interchanging the order of integration. We shall have occasion to use the general form Eq. (2.17) for $K_n(t)$. Another important property of the $K_n(t)$ is that a cumulant is zero if any one of the random variables contained in it is uncorrelated with the others.[9] For example, if $\mathcal{H}_1(t_1)$ and $\mathcal{H}_1(t_2)$ are uncorrelated, then

$$m_2(t_1, t_2) = m_1(t_1) m_1(t_2) \quad (2.18a)$$

and

$$K_2(t) = 0. \quad (2.18b)$$

In Eq. (2.16b), the second term under the first integral

subtracts out that component of $m_4(t_1, t_2, t_3, t_4)$ in which $\mathcal{H}_1(t_i)$ for $i = 1$ and 2 are uncorrelated with the values for $i = 3$ and 4. It has the very important role of subtracting out the component of $M_4(t)$ which diverges for large t.

The utility of the cumulant method can perhaps be better seen by transforming Eqs. (2.8) and 2.12) to the differential equation [cf. the form of Eqs. (2.6) and (2.7)]

$$\dot{S}_x{}^{\ddagger}(t) = \dot{K}(t) S_x{}^{\ddagger}(t) \quad (2.19)$$

with

$$\dot{K}_n(t) = i^n \int_0^t dt_1 \int_0^{t_1} dt_2 \cdots \int_0^{t_{n-2}} dt_{n-1}$$
$$\times \langle O \mathcal{H}_1{}^{\ddagger}(t)^{\times} \mathcal{H}_1{}^{\ddagger}(t_1)^{\times} \cdots \mathcal{H}_1{}^{\ddagger}(t_{n-1})^{\times} \rangle_c. \quad (2.19a)$$

It is convenient to transform the time integrals in Eq. (2.19a) by letting

$$\tau_i = t_{i-1} - t_i,$$

so that

$$t_i = t - \sum_{j=1}^{i} \tau_j.$$

Then

$$\dot{K}_n(t) = i^n \int_0^t d\tau_1 \int_0^{t-\tau_1} d\tau_2 \cdots \int_0^{(t-\Sigma_{i=1}^{n-2}\tau_i)} d\tau_{n-1}$$

$$\times \left\langle O\mathfrak{IC}_1{}^\ddagger(t)^{\times}\mathfrak{IC}_1{}^\ddagger(t-\tau_1)^{\times}\cdots\mathfrak{IC}_1{}^\ddagger\left(t - \sum_{j=1}^{n-1}\tau_j\right)^{\times} \right\rangle_c.$$

$$(2.19b)$$

The connection with what may be regarded as a more conventional time-dependent perturbation theory is obtained as follows. Solve for $\dot{K}(t)$ for times $t \gg \tau_c$, where τ_c is a correlation time appropriate for the random process modulating $\mathfrak{IC}_1(t)$.[8b] Since the cumulant average vanishes if any of the $\mathfrak{IC}_1{}^\ddagger(t_1)^{\times}$ in Eq. (2.19b) are uncorrelated, the only nonvanishing contributions to Eq. (2.19b) come from times $\tau_i \lesssim \tau_c$. Thus, a negligible error is introduced into Eq. (2.19b) by letting all the upper limits tend to infinity. Also, only those terms of Eq. (2.19b) which are not exponentially decaying in t (e.g., correlations depending only on the differences in times such as are characteristic of the assumed stationary-random functions) will remain nonnegligible. Thus $\dot{K}_n(t \gg \tau_c)$ achieves a steady-state value[8] with, at most, a sinusoidal time variation. We can therefore define

$$\dot{K}_n(t \gg \tau_c) \cong \dot{K}_n(t \to \infty) \equiv \exp(-i\Omega_n t) R^{(n)*} \quad (2.20)$$

where $R^{(n)*}$ is a time-independent operator and Ω_n is also an operator. It is shown in Appendix A that $\Omega_n = \Omega$ independent of n provided Ω operates on the eigenstates of $\mathfrak{IC}_0$. Thus we set

$$\dot{K}(t \to \infty) = \exp(-i\Omega t) R^* \quad (2.20a)$$

where

$$R^* = \sum_{n=1}^{\infty} R^{(n)*}.$$

The matrix R^* is the complex conjugate of the familiar relaxation matrix, and we now have a prescription for obtaining it to higher orders.[12] It is readily seen from Eq. (2.19b) that $R^{(n)}$ is of order $\langle |\mathfrak{IC}_1{}^\ddagger(t)|^n\rangle\tau_c{}^{n-1}$ or that successive terms differ by a factor of order $|\mathfrak{IC}_1{}^\ddagger|t)|\tau_c$. This may be expected to yield a convergent expansion provided that $|\mathfrak{IC}_1{}^\ddagger(t)|\tau_c < 1$. The validity of using this asymptotic limit rests upon having

$$|\tau_c \operatorname{Re}(R)| \ll 1 \quad (2.21)$$

and

$$|\tau_c \operatorname{Im}(R)| \ll 1. \quad (2.21a)$$

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[12] The reason for introducing R^* rather than R, at this point, is discussed in Sec. III.

Equation (2.21) follows when one recognizes that $-\operatorname{Re}(R)$ gives the linewidth for the line-shape function in Eq. (2.1), so that $I(\omega)$ is nonnegligible only for $|\omega - \omega_0| \sim |\operatorname{Re}(R)|$, (where ω_0 is the center frequency), and finally that $I(\omega)$ is determined mainly by the behavior of $G(t)$ around the region

$$t \sim |\omega - \omega_0|^{-1}.[8]$$

Note that Eq. (2.21) is a generalization of the more common narrowing condition $\langle |H_1(t)| \rangle\tau_c \ll 1$. We note also that the resonant frequency is shifted from ω_0 to $[\omega_0 - \operatorname{Im}(R)]$, so these arguments also require Eq. (2.21a).

Utilizing the cumulant method, it is, however, not necessary to pass immediately to the asymptotic limit of a time-independent R matrix. The cumulants may be explicitly determined for finite values of t. This results in corrections which will be seen to often have the characteristic of introducing subsidiary weak Lorentzian components into the spectrum. The general procedure may be illustrated by the following simple example. Suppose we have

$$[\mathfrak{IC}_1(t), \mathfrak{IC}_0] = 0,$$

so that

$$\mathfrak{IC}_1{}^\ddagger(t)^{\times} = \mathfrak{IC}_1(t)^{\times}$$

(i.e., only a secular perturbation); also let $\langle \mathfrak{IC}_1(t) \rangle = 0$. Suppose, further, that

$$\langle \mathfrak{IC}_1(t_1)^{\times}\mathfrak{IC}_1(t_1-\tau)^{\times}\rangle = \langle |\mathfrak{IC}_1(t_1)^{\times}|^2\rangle \exp(-|t|/\tau_c).$$

$$(2.22)$$

Then consider the second-order cumulant $K_2(t)$

$$\dot{K}_2(t) = -\langle |\mathfrak{IC}_1(t_1)^{\times}|^2\rangle \int_0^t \exp(-|\tau|/\tau_c)\,d\tau$$

$$= -\langle |\mathfrak{IC}_1(t_1)^{\times}|^2\rangle\tau_c[1 - \exp(-|t|/\tau_c)]$$

$$\xrightarrow{t \gg \tau_c} -\langle |\mathfrak{IC}_1(t_1)^{\times}|^2\rangle\tau_c. \quad (2.22a)$$

Now for secular perturbations, one has

$$[\mathfrak{IC}_1(t_1)^{\times}]_{\alpha\alpha'\beta\beta'} = [\mathfrak{IC}_1(t_1)_{\alpha\alpha} - \mathfrak{IC}_1(t_1)_{\alpha'\alpha'}]\delta_{\alpha\beta}\delta_{\alpha'\beta'}, \quad (2.23)$$

so that

$$\dot{S}_x{}^\ddagger{}_{\alpha\alpha'} = \sum_{\beta\beta'} \dot{K}_2(t)_{\alpha\alpha'\beta\beta'} S_x{}^\ddagger{}_{\beta\beta'}, \quad (2.24a)$$

where

$$\dot{K}_2(t)_{\alpha\alpha'\beta\beta'} = -\Delta^2\tau_c[1 - \exp(-|t|/\tau_c)]\delta_{\alpha\beta}\delta_{\alpha'\beta'} \quad (2.24b)$$

with

$$\Delta^2 \equiv \langle |\mathfrak{IC}_1(t)_{\alpha\alpha} - \mathfrak{IC}_1(t)_{\alpha'\alpha'}|^2\rangle. \quad (2.24c)$$

Then:

$$S_x{}^\ddagger{}_{\alpha\alpha'}{}^{(2)}(t) = [\exp K_2(t)]_{\alpha\alpha'\alpha\alpha'} S_{x\alpha\alpha'}, \quad (2.25)$$

where

$$[\exp K_2(t)]_{\alpha\alpha'\alpha\alpha'} = \exp[\Delta^2\tau_c{}^2] \sum_{n=0}^{\infty} \frac{(-)^n}{n!} \Delta^{2n}\tau_c{}^{2n}$$

$$\times \exp[-(n/\tau_c + \Delta^2\tau_c)|t|], \quad (2.26)$$

and the expansion

$$\exp[-\Delta^2\tau_c{}^2 \exp(-|t|/\tau_c)]$$
$$= \sum_n [(-)^n/n!]\Delta^{2n}\tau_c{}^{2n} \exp(-n|t|/\tau_c) \quad (2.27)$$

has been utilized in order to make Eq. (2.26) easy to invert according to Eq. (2.1). Equation (2.26) is seen to be essentially an expansion in powers of $\Delta^2\tau_c{}^2$. By making use of Eqs. (2.1) and (2.5), we obtain as the spectrum implied by Eqs. (2.25) and (2.26)

$$I^{(2)}(\omega) = \frac{\exp(\Delta^2\tau_c{}^2)}{\pi\Delta} \sum_{n=0}^{\infty} \frac{(-)^n}{n!} (\Delta\tau_c)^{2n}$$

$$\times \frac{(n/\Delta\tau_c)+\Delta\tau_c}{[(n/\Delta\tau_c)+\Delta\tau_c]^2+[(\omega-\omega_0{}^2)/\Delta^2]}$$

$$\cong (\Delta^2\tau_c/\pi)\{[(\Delta^2\tau_c)^2+(\omega-\omega_0)^2]^{-1}$$
$$-[\tau_c{}^{-2}+(\omega-\omega_0)^2]^{-1}\}, \quad (2.28)$$

where $\omega_0=\omega_{\alpha\alpha'}$ and the approximate result in Eq. (2.28) is valid if $\Delta^2\tau_c{}^2\ll1$. We note at resonance, the amplitude of the subsidiary line is $\Delta^4\tau_c{}^4$ times that of the main line (or very small in this approximation). The ratio of the integrated intensities is, however, $\Delta^2\tau_c{}^2$ emphasizing that the subsidiary line is, in fact, a second-order correction to the main line. It is a weakness of the cumulant expansion method that $K_2(t)$ evaluated for finite t includes corrections higher than second order in $\Delta\tau_c$ which have been dropped in the approximate equality of Eq. (2.28). In general, if one wishes to carry out a solution to mth order in $\Delta\tau_c$, it is necessary to evaluate all $K_i(t)$ for $i=1, 2\cdots m$ but then to retain only the terms up to mth order in each of the $K_i(t)$. For asymptotically large t, there is no such problem.

Equation (2.28) is not a useful result yet, because there are often large frequency shifts associated with the subsidiary lines, which may be obtained from the $K_3(t)$ term. In the present simple case, assuming

$$m_3 = \Delta^3 \exp[-(|\tau_1|+|\tau_2|)/\tau_c], \quad (2.29)$$

we have

$$K_3(t)_{\alpha\alpha'\alpha\alpha'} = -(i\Delta^3\tau_c{}^3)[(|t|/\tau_c)-2+2\exp(-|t|/\tau_c)$$
$$+(|t|/\tau_c)\exp(-|t|/\tau_c)]. \quad (2.29a)$$

Then

$$[\exp(K_2+K_3)]_{\alpha\alpha'\alpha\alpha'} = \exp-\{\Delta^2\tau_c(1+i\Delta\tau_c)|t|$$
$$+\Delta^2\tau_c{}^2(1+2i\Delta\tau_c+i\Delta|t|)\exp(-|t|/\tau_c)$$
$$-\Delta^2\tau_c{}^2(1+2i\Delta\tau_c)\}. \quad (2.30)$$

The second term in the exponent in Eq. (2.30) becomes negligible for $t\gg\tau_c$. Then, under the approximation $\Delta\tau_c\ll1$, we have $\Delta t\ll1$ for times of the order that make a nonnegligible contribution to this term. Thus, we can let

$$(1+2i\Delta\tau_c+i\Delta|t|)\cong\exp[2i\Delta\tau_c+i\Delta|t|],$$

so that

$$[\exp(K_2+K_3)]_{\alpha\alpha'\alpha\alpha'}\cong\exp-\{\Delta^2\tau_c(1+i\Delta\tau_c)|t|$$
$$+\Delta^2\tau_c{}^2\exp(2i\Delta\tau_c)\exp[-(\tau_c{}^{-1}-i\Delta)|t|]$$
$$-\Delta^2\tau_c{}^2(1+2i\Delta\tau_c)\}. \quad (2.30a)$$

When the second term in the braces of Eq. (2.30a) is expanded in the manner of Eq. (2.27) and only terms of lowest order are kept, then it is seen that $(\omega-\omega_0)^2$ in the denominator of the subsidiary line in Eq. (2.28) must be replaced by $(\omega-\omega_0-\Delta)^2$, which gives an appreciable frequency shift Δ, when compared to the width of the main line of $\Delta^2\tau_c$ for $\Delta\tau_c\ll1$. Similar techniques should be applicable to obtain still higher-order corrections to the subsidiary lines.

The above discussion is readily generalized for any secular perturbation [where Eq. (2.23) is valid], characterized by a single exponential decay of its correlation [e.g., Eqs. (2.22) and (2.29)]. Then the subsidiary line is approximated by

$$-(C_2/\pi)\{\tau_c{}^{-2}+[\omega-\omega_0-(C_3/C_2)\tau_c{}^{-1}]^2\}^{-1}, \quad (2.31)$$

where

$$C_2 = -R^{(2)*\text{sec}}{}_{\alpha\alpha'\alpha\alpha'} \quad (2.31a)$$

and

$$iC_3 = -R^{(3)*\text{sec}}{}_{\alpha\alpha'\alpha\alpha'}, \quad (2.31b)$$

and it has a maximum amplitude of $|C_2\tau_c|^2$ times that of the main line. The fact that the subsidiary line appears opposite in sign to the main line may be expected 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.[3,6,8] 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.[13]

In this simple example, we have avoided specifying the exact nature of the stochastic process. It is important to analyze the process carefully in a particular problem, because it is possible that divergences could be incorrectly introduced into the higher-order terms of R.[14] It is also necessary to specify the details of the

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[13] One may show that for $\Delta\tau_c<1$, the approximate expression of Eq. (2.28) does have a finite second moment unlike a pure Lorentzian.

[14] Thus, in our simple example, if we were to let

$$m_4 = \Delta^4 \exp[-(\tau_1+\tau_2+\tau_3)/\tau_c],$$

then

$$M_4(t_4\to\infty) = \Delta^4\tau_c{}^3t,$$

while

$$m_2(t_1, t_2)m_2(t_3, t_4) = \Delta^4 \exp[-(\tau_1+\tau_3)/\tau_c],$$

which diverges when integrated over τ_2 as the upper limit on τ_2 is allowed to approach infinity. In the examples of Markov processes of Secs. IV–VI, however, this latter term cancels an equivalent term in the proper expression for m_4.

stochastic process in order to obtain explicit formal expressions for the subsidiary lines following the method indicated above, since Eq. (2.31) has limited applicability.

III. THE RELAXATION MATRIX

Before explicitly developing equations for the R or relaxation matrix, we note that R is usually obtained as a solution to the equation of motion of the spin-density matrix $\tilde{\sigma}$ [1,4,5,6]:

$$d\tilde{\sigma}/dt = -i\mathcal{3C}_1(t)^\times \tilde{\sigma}(t). \quad (3.1)$$

To avoid confusion, we use Eq. (3.1) as the basis for generating the R matrix, utilizing the procedures of Sec. II. We define an ensemble averaged spin-density matrix $\sigma(t) = \langle \tilde{\sigma}(t) \rangle$ where the defining characteristics of the ensemble are the same as discussed after Eq. (2.4). Our solution is again valid for times $t \gg \tau_c$ as discussed with respect to Eq. (2.20). The final result may be expressed as

$$\dot{\sigma}_{\alpha\alpha'} = -i\omega_{\alpha\alpha'}\sigma_{\alpha\alpha'} + \sum_{n=1} R^{(n)}{}_{\alpha\alpha'\beta\beta'}\sigma_{\beta\beta'}, \quad (3.2)$$

where α, α', β, and β' are eigenstates of $\mathcal{3C}_0$. The equiva-

lent expression for $S_x(t)$ is then

$$\dot{S}_x(t)_{\alpha\alpha'} = i\omega_{\alpha\alpha'}S_{x\alpha\alpha'} + \sum_{n=1} R^{(n)*}{}_{\alpha\alpha'\beta\beta'}S_{x\beta\beta'}, \quad (3.3a)$$

where $R^{(n)*}{}_{\alpha\alpha'\beta\beta'}$ is the complex conjugate of $R^{(n)}{}_{\alpha\alpha'\beta\beta'}$. In the interaction representation [cf. Eqs. (2.5), (2.6)] Eq. (3.3a) becomes

$$\dot{S}_x{}^\dagger{}_{\alpha\alpha'} = \sum_{\beta\beta'} \exp[-i(\omega_{\alpha\alpha'}-\omega_{\beta\beta'})t] \sum_{n=1} R^{(n)*}{}_{\alpha\alpha'\beta\beta'} S_x{}^\dagger{}_{\beta\beta'}, \quad (3.3b)$$

where only terms for which

$$|\omega_{\alpha\alpha'} - \omega_{\beta\beta'}| \lesssim |R_{\alpha\alpha'\beta\beta'}|$$

need be retained.[1,3-6]

We now rewrite $\mathcal{3C}_1(t)$ in the form

$$\mathcal{3C}_1(t) = \sum_q F_q(t) A_q, \quad (3.4)$$

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. The subscript q labels the different components contributing to $\mathcal{3C}_1(t)$. We can then write down the R matrix to fourth (or higher) order using the results of Sec. II. Since it is usually possible to define $\mathcal{3C}_1(t)$ so that $\langle F_q(t) \rangle = 0$, we assume this to be true. Then

$$R^{(1)}{}_{\alpha\alpha'\beta\beta'} = 0,$$

$$R^{(2)}{}_{\alpha\alpha'\beta\beta'} = \mathrm{I}^{(2)} + \mathrm{II}^{(2)} + \mathrm{III}^{(2)}$$

$$= \sum_{q,r} \{ A_{q,\alpha\beta} A_{r,\beta'\alpha'} [\ell(q, r; \beta'\alpha') + \ell(r, q; \alpha\beta)] - \delta_{\alpha'\beta'} \sum_\gamma A_{q,\alpha\gamma} A_{r,\gamma\beta} \ell(q, r; \gamma\beta) - \delta_{\alpha\beta} \sum_\gamma A_{q,\beta'\gamma} A_{r,\gamma\alpha'} \ell(r, q; \beta'\gamma) \},$$

$$(3.5b)$$

$$R^{(3)}{}_{\alpha\alpha'\beta\beta'} = \mathrm{I}^{(3)} + \mathrm{II}^{(3)} + \mathrm{III}^{(3)} + \mathrm{IV}^{(3)}$$

$$= i \sum_{q,r,s} \{ \sum_\gamma A_{q,\alpha\gamma} A_{r,\gamma\beta} A_{s,\beta'\alpha'} [\ell(q, r, s; \gamma\beta, \beta'\alpha') + \ell(s, q, r; \alpha\gamma, \gamma\beta) + \ell(q, s, r; \beta'\alpha', \gamma\beta)]$$

$$- \sum_\gamma A_{q,\alpha\beta} A_{r,\beta'\gamma} A_{s,\gamma\alpha'} [\ell(s, q, r; \alpha\beta, \beta'\gamma) + \ell(q, s, r; \gamma\alpha', \beta'\gamma) + \ell(s, r, q; \beta'\gamma, \alpha\beta)]$$

$$+ \delta_{\alpha\beta} \sum_{\gamma\gamma'} A_{q,\beta'\gamma} A_{r,\gamma\gamma'} A_{s,\gamma'\alpha'} \ell(s, r, q; \gamma\gamma'; \beta'\gamma) - \delta_{\alpha'\beta'} \sum_{\gamma\gamma'} A_{q,\alpha\gamma} A_{r,\gamma\gamma'} A_{s,\gamma'\beta} \ell(q, r, s; \gamma\gamma', \gamma'\beta) \}, \quad (3.5c)$$

$$R^{(4)}{}_{\alpha\alpha'\beta\beta'} = \mathrm{I}^{(4)} + \mathrm{II}^{(4)} + \mathrm{III}^{(4)} + \mathrm{IV}^{(4)} + \mathrm{V}^{(4)} + \mathrm{VI}^{(4)}$$

$$= \sum_{q,r,s,u} \{ \sum_{\gamma\gamma'} A_{q,\alpha\gamma} A_{r,\gamma\beta} A_{s,\beta'\gamma'} A_{u\gamma'\alpha'} [\ell(q, r, u, s; \gamma\beta, \gamma'\alpha', \beta'\gamma') + \ell(q, u, r, s; \gamma'\alpha', \gamma\beta, \beta'\gamma')$$

$$+ \ell(q, u, s, r; \gamma'\alpha', \beta'\gamma', \gamma\beta) + \ell(u, q, r, s; \alpha\gamma, \gamma\beta, \beta'\gamma') + \ell(u, q, s, r; \alpha\gamma, \beta'\gamma', \gamma\beta) + \ell(u, s, q, r; \beta'\gamma', \alpha\gamma, \gamma\beta)]$$

$$- \sum_{\gamma\gamma} A_{q,\alpha\gamma} A_{r,\gamma\gamma'} A_{s,\gamma'\beta} A_{u,\beta'\alpha'} [\ell(q, r, s, u; \gamma\gamma', \gamma'\beta, \beta'\alpha') + \ell(q, r, u, s; \gamma\gamma'; \beta'\alpha', \gamma'\beta) + \ell(q, u, r, s; \beta'\alpha', \gamma\gamma', \gamma'\beta)$$

$$+ \ell(u, q, r, s; \alpha\gamma, \gamma\gamma', \gamma'\beta)] - \sum_{\gamma\gamma'} A_{q,\alpha\beta} A_{r,\beta'\gamma} A_{s,\gamma\gamma'} A_{u,\gamma'\alpha'} [\ell(q, u, s, r; \gamma'\alpha', \gamma\gamma', \beta'\gamma) + \ell(u, q, s, r; \alpha\beta, \gamma\gamma', \beta'\gamma)$$

$$+ \ell(u, s, q, r; \gamma\gamma', \alpha\beta, \beta'\gamma) + \ell(u, s, r, q; \gamma\gamma', \beta'\gamma, \alpha\beta)] + \delta_{\alpha'\beta'} \sum_{\gamma\gamma'\delta} A_{q,\alpha\gamma} A_{r,\gamma\gamma'} A_{s,\gamma'\delta} A_{u,\delta\beta} \ell(q, r, s, u; \gamma\gamma', \gamma'\delta, \delta\beta)$$

$$+ \delta_{\alpha\beta} \sum_{\gamma\gamma'\delta} A_{q,\beta'\gamma} A_{r,\gamma\gamma'} A_{s,\gamma'\delta} A_{u,\delta\alpha'} \ell(u, s, r, q; \gamma'\delta, \gamma\gamma', \beta'\gamma) \} + \sum_{\gamma\gamma'} \tilde{R}^{(2)}{}_{\alpha\alpha'\gamma\gamma'} R^{(2)}{}_{\gamma\gamma'\beta\beta'}. \quad (3.5d)$$

The spectral densities $\ell(\omega)$ in Eqs. (3.5) are given as one-sided Fourier transforms of correlation functions $g(\tau)$

$$\ell_2(q, r; \alpha\beta) = \int_0^\infty g_2(q, r; \tau) \exp(-i\omega_{\alpha\beta}\tau) d\tau, \tag{3.6a}$$

$$\ell_3(q, r, s; \omega_a, \omega_b) = \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \exp[-i(\omega_a + \omega_b)\tau_1] \exp(-i\omega_b\tau_2) g_3(q, r, s; \tau_1, \tau_2), \tag{3.6b}$$

$$\ell_4(q, r, s, u; \omega_a, \omega_b, \omega_c) = \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \int_0^\infty d\tau_3 \exp[-i(\omega_a + \omega_b + \omega_c)\tau_1]$$
$$\times \exp[-i(\omega_b + \omega_c)\tau_2] \exp(-i\omega_c\tau_3) g_4(q, r, s, u; \tau_1, \tau_2, \tau_3), \tag{3.6c}$$

where[15]

$$g_2(q, r; \tau) = \langle F_q(t) F_r(t-\tau) \rangle, \tag{3.7a}$$

$$g_3(q, r, s; \tau_1, \tau_2) = \langle F_q(t) F_r(t-\tau_1) F_s(t-\tau_1-\tau_2) \rangle \tag{3.7b}$$

$$g_4(q, r, s, u; \tau_1, \tau_2, \tau_3) = \langle F_q(t) F_r(t-\tau_1) F_s(t-\tau_1-\tau_2) F_u(t-\tau_1-\tau_2-\tau_3) \rangle$$
$$- \langle F_q(t) F_r(t-\tau_1) \rangle \langle F_s(t-\tau_1-\tau_2) F_u(t-\tau_1-\tau_2-\tau_3) \rangle. \tag{3.7c}$$

The $\tilde{R}^{(2)}{}_{\alpha\alpha'\gamma\gamma'}$ which appears in Eq. (3.5d) is obtained from $R^{(2)}{}_{\alpha\alpha'\gamma\gamma'}$ by replacing the $\ell(q, r; \omega_a)$, etc., by

$$\tilde{\ell}_2(q, r; \omega_a) = \int_0^\infty g_2(q, r; \tau) \left(\frac{1 - \exp[i(\omega_{\beta\beta'} - \omega_{\gamma\gamma'})\tau]}{i(\omega_{\beta\beta'} - \omega_{\gamma\gamma'})} \right) \exp(-i\omega_a\tau) d\tau. \tag{3.6d}$$

The equations (3.7) define multiple-time correlation functions, which depend only upon time *differences* due to the assumption of stationarity. The spectral densities of Eq. (3.6) are complex. Thus, for real values of the products of matrix elements in Eqs. (3.5), it is seen that the real and imaginary parts of both the second- and fourth-order spectral densities lead to the linewidth and frequency-shift contributions, respectively,[16] while the reverse is true for the third-order spectral densities. The expressions in Eqs. (3.5) involving Roman numerals are used to number conveniently the R-matrix terms corresponding to the different combinations of A_q matrix elements which appear in the same order on the right. We note that if $\tilde{K}_n(t)$ is desired instead of R_n, the infinite upper limits of the time integrals in the spectral densities given by (3.6) are replaced by the appropriate finite values as obtained from Eqs. (2.16) and (2.19). The resulting spectral densities are still explicit functions of t.

The terms in Eqs. (3.5c) and (3.5d) may be regarded as higher-order time-dependent perturbations. They include secular and nonsecular effects (as well as admixtures of the two). Thus, for example, term $IV^{(4)}$ with $\alpha = \beta$ (and neglecting a secular component) may be regarded as the linewidth contribution due to a second-order transition probability from state α to state γ' via the whole set of intermediate states γ and δ. (Such transition probabilities are, of course, fourth order in the perturbation.) These intermediate states may be nonresonant or (near)-resonant, where in the latter case, any small deviations from resonance are taken up by the spectral densities generated by the random process. Terms like $II^{(4)}$ are somewhat unusual in that they may be regarded as crossterms between third-order and first-order contributions. They are normally neglected in second-order time-dependent perturbation theory which is usually utilized when first-order terms are unimportant. Term $VI^{(4)}$ resembles $[R^{(2)}]^2$ and shows that powers of the lower-order R-matrix terms also appear in modified form in higher order. It indicates, in part, that if the transition defined by the pair of states $\beta\beta'$ is uncoupled by $R^{(2)}$ to $\alpha\alpha'$ in second order but both are coupled to a common transition $\gamma\gamma'$, then the $\beta\beta'$ and $\alpha\alpha'$ transitions become coupled in fourth order.

The significance of all these R-matrix terms will be seen to depend on the nature of the particular problem being investigated.

IV. APPLICATION TO A TWO-JUMP PROCESS

The two-jump problem, which has been treated by second-order R-matrix theory,[1] serves as a simple example of the application of the cumulant method to Markov processes involving discrete values of the random variable. Also, it is a case which can be solved exactly,[6,8,17,18] so the results of the cumulant method

[15] Our notation differs from the usual notation (cf. Refs. 1, 6), where $g_{qr}(\tau) \equiv \langle F_q(t) F_r^*(t+\tau) \rangle$. Our notation generalizes more easily to the formation of the higher-order time correlation functions, given by Eqs. (3.7). It follows from the properties of stationary random functions that $g_2(q, r; \tau) = g_2(r, q; \tau) = g_2(q, r; -\tau)$ and is not necessarily real.

[16] G. K. Fraenkel [J. Chem. Phys. **42**, 4275 (1965)] discusses dynamic frequency shift effects in ESR spectra arising form the second-order spectral-density contribution as given by Eq. (3.6a).

[17] P. W. Anderson, J. Phys. Soc. Japan **9**, 316 (1954).
[18] H. M. McConnell, J. Chem. Phys. **28**, 430 (1958).

may be compared with the exact solution (cf. Appendix B).

Consider two states, A and B, with *a priori* probabilities:

$$W_A + W_B = 1, \qquad (4.1)$$

and with mean lifetimes τ_A and τ_B. We may write the four relevant conditional probabilities[1] in the general form

$$P(i \mid j, \tau)$$

$$= W_j[1 - \exp(- \mid \tau \mid /\tau_c)] + \exp(- \mid \tau \mid /\tau_c)\delta_{ij}, \qquad (4.2)$$

where

$$i, j = A \quad \text{or} \quad B,$$

and

$$\tau_c = \tau_A \tau_B / (\tau_A + \tau_B). \qquad (4.3)$$

We assume that a radical jumping between these states experiences a modulation of its isotropic hyperfine interaction between the values a_A and a_B. Then

$$\hbar \mathcal{K}_0 = g\beta_e B_0 S_z + \hbar \mid \gamma_e \mid \bar{a} S_z I_z - \hbar \gamma_n B_0 I_z, \qquad (4.4a)$$

and

$$\hbar \mathcal{K}_1(t) = \hbar \mid \gamma_e \mid [a(t) - \bar{a}] I_z S_z = F(t) A, \qquad (4.4b)$$

with

$$\bar{a} = W_A a_A + W_B a_B. \qquad (4.5)$$

Equations (4.4) include only the secular contribution.[1] If we let $\mid \gamma_e \mid (a_A - a_B) = \Delta$, then it is easy to show utilizing Eq. (C2) and Eqs. (3.7) that

$$g_1 = 0, \qquad (4.6a)$$

$$g_2(\tau_1) \exp(+\tau_1/\tau_c)$$

$$= \gamma_e{}^2 \sum_i W_i [a_i(t) - \bar{a}]^2$$

$$= W_A W_B (2\Delta)^2, \qquad (4.6b)$$

$$g_3(\tau_1, \tau_2) \exp[(\tau_1 + \tau_2)/\tau_c]$$

$$= \mid \gamma_e \mid^3 \sum_i W_i [a_i(t) - \bar{a}]^3$$

$$= -W_A W_B (W_A - W_B)(2\Delta)^3, \qquad (4.6c)$$

$$g_4(\tau_1, \tau_2, \tau_3) \exp[(\tau_1 + \tau_2 + \tau_3)/\tau_c]$$

$$= \gamma_e{}^4 \sum_i W_i [a_i(t) - \bar{a}]^4 - \{\gamma_e{}^2 \sum_i W_i [a_i(t) - \bar{a}]^2\}^2$$

$$= W_A W_B (1 - 4W_A W_B)(2\Delta)^4. \qquad (4.6d)$$

Equations (3.5) and (3.6) may be simplified in the present case, because we have

$$\ell_4(q, r, s, u; \gamma\gamma', \gamma\beta, \beta\gamma) = \ell_4(a; o, o, o), \qquad (4.7)$$

since there is only one perturbing term in $\mathcal{K}_1(t)$ which is also secular. Also, $R_{\alpha\alpha'\beta\beta'} = R_{\alpha\alpha'\alpha\alpha'}\delta_{\alpha\beta}\delta_{\alpha'\beta'}$ for the $\alpha \to \alpha'$ electron-spin transition, (where α and α' represent the spin states characterized by $m_s = \frac{1}{2}$, m_I and $m_s = -\frac{1}{2}$,

m_I, respectively). Then Eqs. (3.5) become

$$R^{(2)*}{}_{\alpha\alpha'\alpha\alpha'} = -(A_{\alpha\alpha} - A_{\alpha'\alpha'})^2 \ell_2(a; o)$$

$$= -(\tfrac{1}{2}m_I)^2 \ell_2(a; o), \qquad (4.8a)$$

$$R^{(3)*}{}_{\alpha\alpha'\alpha\alpha'} = -i(A_{\alpha\alpha} - A_{\alpha'\alpha'})^3 \ell_3(a; o, o)$$

$$= -i(\tfrac{1}{2}m_I)^3 \ell_3(a; o, o), \qquad (4.8b)$$

$$R^{(4)*}{}_{\alpha\alpha'\alpha\alpha'} = (A_{\alpha\alpha} - A_{\alpha'\alpha'})^4 \ell_4(a; o, o, o) - \tau_c [R^{(2)*}{}_{\alpha\alpha',\alpha\alpha'}]^2$$

$$= (\tfrac{1}{2}m_I)^4 \{\ell_4(a; o, o, o) - \tau_c [\ell_2(a; o)]^2\}. \qquad (4.8c)$$

The spectral densities are easily calculated from Eqs. (4.6) (even for finite times, cf. end of Sec. III). We obtain a solution valid to fourth order for the main line associated with the $\alpha \to \alpha'$ transition and third order for the subsidiary line, from

$$K(t) \cong \int_0^t [\dot{K}_2(t') + \dot{K}_3(t')]dt' + R^{*(4)}t$$

$$= -m_I{}^2 W_A W_B \Delta^2 \tau_c \{t + \tau_c[\exp(-t/\tau_c) - 1]\}$$

$$+ im_I{}^3 (W_A - W_B) W_A W_B \Delta^3 \tau_c{}^2$$

$$\times [(t - 2\tau_c) + (t + 2\tau_c) \exp(-t/\tau_c)]$$

$$+ m_I{}^4 W_A W_B (1 - 5W_A W_B) \Delta^4 \tau_c{}^3 t. \qquad (4.9)$$

Then $\exp[K(t)]$ may be expanded according to the method illustrated by Eqs. (2.26)–(2.31) to yield

$$\exp[K(t)] \cong [\exp(Z) \exp(-Xt) - Z \exp(-Yt)], \qquad (4.10)$$

where

$$X \cong m_I{}^2 W_A W_B \Delta^2 \tau_c - im_I{}^3 \Delta^3 \tau_c{}^2 (W_A - W_B) W_A W_B$$

$$- m_I{}^4 W_A W_B (1 - 5W_A W_B) \Delta^4 \tau_c{}^3, \qquad (4.11a)$$

$$Y \cong \tau_c{}^{-1} + i(W_A - W_B)\Delta m_I, \qquad (4.11b)$$

$$Z \cong W_A W_B \Delta^2 \tau_c{}^2 m_I{}^2. \qquad (4.11c)$$

These results are in agreement (within the order of this calculation) with those obtained directly from the modified Bloch equations[17,18] as applied to this problem. (See Appendix B.) The interpretation of this result is similar to that of the simple example of Sec. II, where now the stochastic process has been defined properly. The first term in Eq. (4.10) gives rise to the main line for the particular value of m_I. Its width contributions are given by the real part of X in Eq. (4.11a) and the corrected frequency is given by $[\omega_{\alpha\alpha'} - \text{Im}X]$. The associated subsidiary line arises from the second term in Eq. (4.11) so that the width is $\tau_c{}^{-1}$ and the resonant frequency is

$$\omega_{\alpha\alpha'} - i(W_A - W_B)\Delta m_I.$$

We note that according to Eq. (4.8c), a line-broad-

ening mechanism involving modulation of the isotropic hyperfine interaction introduces higher-order corrections which depend upon powers of m_I. Thus, for free radicals with many equivalent nuclear spins [e.g., duroquinone and related radicals[19a] with twelve equivalent protons giving a total $m_I - (\text{max}) = 6$] there may well be a nonnegligible fourth-order correction to the widths of the outer lines when the correction is negligible for the central lines [e.g., for $\Delta\tau_c = 0.2$ and $W_A = W_B = \frac{1}{2}$, we have

$$R^{(4)}(m_I)/R^{(2)}(m_I) = (0.1m_I)^2$$

or a 1% correction for $m_I = 1$ but a 16% correction for $m_I = 4$]. Since the relative intensity of the subsidiary line associated with each of the main lines also depends on $m_I{}^2$, their effect becomes more pronounced for large values of m_I. (Considerations such as this, could have important consequences for the relative line shapes of different hyperfine lines.[19b]) These comments are expected to apply, in a modified form, to other dynamical processes which can modulate the isotropic hyperfine interaction[1,20] as well as other relaxation processes involving nuclear-spin quantum numbers.[1,2,19]

V. APPLICATION TO ROTATIONAL MODULATION OF THE SPIN–ORBIT OPERATOR

It is well known in ESR that the g tensor arises from a second-order time-independent-perturbation cross-term between the spin–orbit interaction $\hbar^{-1}\lambda \mathbf{L} \cdot \mathbf{S}$ and the orbit–field interaction $\hbar^{-1}\beta_e \mathbf{L} \cdot \mathbf{B}_0$. Thus

$$g_{ij} = g_e\delta_{i,j} - 2\lambda\sum_{n\neq0}[L_{i,o,n}L_{j,n,o}/(E_n - E_o)], \quad (5.1)$$

where $g_e = 2.00232$ is the free-electron value, g_{ij} is the ijth Cartesian component of the g tensor, and the sum over n is over *all* excited states with energy E_n. This result is appropriate for free radicals in solids, but it has also been implicitly carried over into the theory of spin relaxation in liquids.[1,2] That this may be done is not immediately obvious, because both perturbation terms must be expected to be random functions of time in the liquid state. That is, $\mathbf{L}$ is strongly coupled to the molecular frame, while $\mathbf{S}$ for large values of $\mathbf{B}_0$ is coupled to the laboratory frame defined by the direction of $\mathbf{B}_0$. The rotational tumbling randomly changes the relative orientations of the two coordinate systems. We may then ask what are the limits of validity in using Eq. (5.1) when "motional narrowing" of the g tensor is observed.

While this question may be dealt with by utilizing the formalism discussed below, we note that there are a number of experimental and theoretical studies which

bear upon it. Thus, a variety of ESR linewidth studies summarized by Fraenkel[19a] tend to support the conventional approach of calculating g tensors, as at least a good first approximation. The same may be said of the comparison between Stone's theory of g tensors in aromatic free radicals[21] and the measurements of liquid g shifts by Segal, Kaplan, and Fraenkel.[22] There is still the question as to whether there are other spin–orbit relaxation processes[23,24] which yield experimental linewidth effects in ESR spectra and are distinguishable from a g-tensor mechanism. More interesting, perhaps, are the as yet unresolved questions[25–28] relating to the anomalously large widths characteristic of radicals with degenerate ground vibronic states (in the gas phase) such as the benzene anion,[29] as well as the lack of correlation of the liquid g shifts of such radicals with those of other hydrocarbon radical anions.[22] With these considerations in mind, we examine the structure of the spin–orbit formalism in free radicals as applied to liquids (Our treatment in the present section is simplified by neglecting the breakdown of the spin–orbit interaction into a sum of localized atomic terms appropriate for a delocalized electron,[21] but this should not significantly affect the over-all nature of our results.)

A. Structure of the Theory

A generalized interpretation of the methods of the earlier sections must be utilized. Thus, for example, we write $\mathbf{L} \cdot \mathbf{S}$ in the notation of Eq. (C6)

$$\hbar^{-1}\lambda \mathbf{L} \cdot \mathbf{S} = \hbar^{-1}\lambda \sum_{m,m'} \mathfrak{D}^{(1)}{}_{-m,m'}(\Omega) L'^{(1,m)} S^{(1,m')}, \quad (5.2)$$

where both L and S are first rank irreducible tensors and are operators on the combined electronic and spin degrees of freedom. $\mathfrak{D}^{(1)}{}_{-m,m'}(\Omega)$ remains the only random time varying function. The molecular coordinate system defining $L'^{(1,m)}$ is so chosen that $g_{ij} = g_i\delta_{ij}$ in Eq. (5.1), and for simplicity it is taken as the principal axes of the diffusion tensor. Then the equations in Secs. II and III and Appendix C may be applied, provided the following approach is adopted. Instead of the matrix elements $(A_q{}^{(1,m')})_{\alpha\alpha'}$ which appear in Eqs. (3.5), we must evaluate $(F_q{}^{(1,m)})_{\alpha_n\alpha_{n'}} \times (A_q{}^{(1,m')})_{\alpha\alpha'}$, where α and α' are spin states and α_n and α'_n are the associated electronic states. Then each

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$F'_q{}^{(1,m)}$ in Eqs. (C10) is replaced by the appropriate $(F'_q{}^{(1,m)})_{\alpha_n\alpha'_n}$, where the F'_q matrix element is chosen to correspond to the associated A_q matrix element which appears in Eqs. (3.5). This may be regarded as a further generalization of the index q. The sums over $\beta, \beta', \gamma, \gamma'$, etc. in Eqs. (3.3) and (3.5) are interpreted as combined sums over $\beta, \beta_n, \gamma, \gamma_n$, etc., and the frequencies $\omega_{\alpha\beta}$,

etc., become $\omega_{\alpha\beta}+\omega_{\alpha_n,\beta_n}$. We illustrate with

$$R^{(2)}{}_{\alpha\alpha'\alpha\alpha'}\rightarrow R^{(2)}{}_{(\alpha,\alpha_n),(\alpha',\alpha'_n)}.$$

Since the diagonal matrix elements $(L'^{(1,m)})_{nn}$ vanish for a polyatomic molecule with a nondegenerate ground state,[30] then $I^{(2)}$ in Eq. (3.5b) is zero. The next two terms yield

$$R^{(2)}{}_{(\alpha,\alpha_n),(\alpha',\alpha'_n)} = -\tfrac{1}{3}\sum_{q,r,\gamma,m'} A_{q,\alpha\gamma}{}^{(1,+m')}A_{r,\gamma\alpha}{}^{(1,-m')}\sum_{m,\gamma_n\neq\alpha_n}(-)^{m+m'}F'_{q,\alpha_n,\gamma_n}{}^{(1,m)}F'_{r,\gamma_n\alpha_n}{}^{(1,-m)}[\tau_{1,m}{}^{-1}+i(\omega_{\gamma\alpha}+\omega_{\gamma_n\alpha_n})]^{-1}$$

$$-\tfrac{1}{3}\sum_{q,r,\gamma,m'} A_{q,\alpha'\gamma}{}^{(1,m')}A_{r,\gamma\alpha'}{}^{(1,-m')}\sum_{m,\gamma_n\neq\alpha'_n}(-)^{m+m'}F'_{q,\alpha'_n,\gamma_n}{}^{(1,-m)}F'_{r,\gamma_n,\alpha'_n}{}^{(1,m)}[\tau_{1,m}{}^{-1}+i(\omega_{\alpha'\gamma}+\omega_{\alpha'_n\gamma_n})]^{-1}, \quad (5.3)$$

where q and r sum over the S–O and O–F type perturbations, as given in Table. I

As long as there are no low-lying electronic states coupled by the operator $\mathbf{L}$ to the ground state, and if α_n and α'_n are taken as the ground electronic state $n=0$ for a spin doublet, then

$$\omega_{0,\gamma_n}\gg\omega_{\alpha'\gamma}; \tau_{1,m}{}^{-1}, \quad (5.4)$$

and Eq. (5.3) becomes

$$R^{(2)}{}_{(\alpha,0),(\alpha',0)}\cong+\tfrac{1}{3}i\sum_{q,r,\gamma}(-)^{m'}(A_{q,\alpha\gamma}{}^{(1,m')}A_{r,\gamma\alpha}{}^{(1,-m')}-A_{q,\alpha'\gamma}{}^{(1,m')}A_{r,\gamma\alpha'}{}^{(1,-m')})$$

$$\times\sum_{m,\gamma_n\neq 0}(-)^{m}(F'_{q,0,\gamma_n}{}^{(1,m)}F'_{r,\gamma_n,0}{}^{(1,-m)}/\omega_{\gamma_n,0}). \quad (5.4a)$$

If we let α correspond to spin-state $m_s=+\tfrac{1}{2}$ and α' to $m_s=-\tfrac{1}{2}$, then it is found that the only contribution to this expression comes for $q\neq r$, and one obtains utilizing Table I

$$R^{(2)}{}_{+1/2,-1/2}$$

$$={}^{(2)*}{}_{-1/2,+1/2}$$

$$=\tfrac{2}{3}i(\lambda\beta_e B_o/\hbar^2)\sum_{m,n\neq 0}(-)^{m}(L'_{o,n}{}^{(m)}L'_{n,o}{}^{(-m)}/\omega_{n,o}),$$

$$\quad (5.5)$$

which is just the dynamic frequency shift from the

TABLE I. Terms in the perturbation $\mathfrak{K}_1(t)$.

	Spin–Orbit (S–O)	
$A_\mu{}^{(1,m')}$	$m'=0$	S_z
	$m'=\pm 1$	$\mp 2^{-1/2}S_\pm$
$F_\mu'{}^{(1,m)}$	$m=0$	$\hbar^{-1}\lambda L_z$
	$m=\pm 1$	$\pm 2^{-1/2}\hbar^{-1}\lambda L_\pm$
	Orbit–Field (O–F)	
$A_\mu{}^{(1,m')}$	$m'=0$	B_0
	$m'=\pm 1$	0
$F_\mu'{}^{(1,m)}$	$m=0$	$\hbar^{-1}\beta_e L_z$
	$m=\pm 1$	$\pm 2^{-1/2}\hbar^{-1}\beta_e L_\pm$
	G Tensor	
$A_\mu{}^{(1,m')}$	$m'=0$	$+\tfrac{2}{3}2^{1/2}B_o S_z$
	$m'=\pm 1$	$\mp\tfrac{1}{2}B_o S_\pm$
$F_\mu'{}^{(l,m)}$	$m'=\pm 2$	0
	$=(-1)^{m}\hbar^{-1}\beta_e g^{(m)}$	
	$g^{(0)}=6^{-1/2}[2g_3-(g_1+g_2)]$	
	$g^{(\pm 1)}=0$	
	$g^{(\pm 2)}=\tfrac{1}{2}(g_1-g_2)$	

free-electron value given from Eq. (5.1) by

$$\left|\frac{(g_s-g_e)}{\hbar}\right| = \left|\frac{2\lambda}{3\hbar}\sum_{n\neq 0;\,i=x,y,z}\frac{|L_{i,o,n}|^2}{E_n-E_o}\right|, \quad (5.6)$$

where the irreducible tensor components $L'^{(m)}$ in Eq. (5.5) have been reexpressed in Cartesian components. The sign in Eq. (5.5) depends on whether $R_{+1/2,-1/2}$ or $R_{-1/2,+1/2}$ is taken, and leads to the observation of a resonance determined by $g_s=\tfrac{1}{3}(g_x+g_y+g_z)$, the average g value. Thus the g shift appears naturally as a second-order dynamic frequency shift and is much larger than any linewidth contribution, provided that the inequality (5.4) holds. For

$$|\tau_{1,m}{}^{-1}|\gtrsim|\omega_{o,n}|\gg\omega_{\alpha\gamma},$$

then $(\omega_{n,o})^{-1}$ in Eq. (5.5) for the frequency shift, must be replaced by $\omega_{n,o}/(\tau_{1,m}{}^{-2}+\omega_{n,o}{}^2)$, and the shift depends upon the rotational correlation time. There would now be an important linewidth contribution as well. It may be seen by utilizing Eq. (5.3) that for $R^{(2)}{}_{+1/2,-1/2}$ there are nonvanishing contributions only from terms where $q=r$. The O–F terms could in principle cause broadening because they induce transitions to excited electronic states (without a spin flip). But this effect will be unimportant if (1) the ESR resonant frequency (including g shift) differs only slightly in the excited state from that in the ground state, or (2) the equilibrium population of the excited state is small. For the present

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[30] This statement may not be entirely true in the case of the benzene anion. McConnell[26] has suggested a mechanism whereby a nonvanishing value could exist for short intervals of time,

we neglect the $S_z = S^{(1,0)}$ components of the S–O terms and consider only the effects of $S^{(1,\pm 1)}$ terms which do induce spin flips. They yield a contribution to $R_{+1/2,-1/2}$ for the ground state of

$$- \frac{2\lambda^2}{3\hbar^2} \sum_{m,n \neq 0} (-)^m \frac{\tau_{1,m}^{-1}}{\tau_{1,m}^{-1} + \omega_{o,n}^2} L'_{o,n}{}^{(m)} L'_{n,o}{}^{(-m)}. \quad (5.7)$$

This is very similar to a result obtained by Kivelson and Collins,[23] which they call a rotational spin–orbit mechanism. For $\omega_{o,n} \gg \tau_{1,m}^{-1}$, spectral densities of the form used here begin to lose their significance because short-time, nondiffusive motions become important, as do Boltzmann factor corrections to the spectral densities associated with transitions of large energy. Nevertheless, the result Eq. (5.5) for the frequency shift, which does not contain any explicit dependence on the tumbling motion, is expected to hold.

The normal line-broadening terms from the g tensor[1,2]

may now be recovered by examining the appropriately generalized form of the $R^{(4)}$ given by Eqs. (3.5d) and (C10d). Of the six main groups of terms in Eqs. (3.5d), only $I^{(4)}$, $IV^{(4)}$, and $V^{(4)}$ are found to have the necessary characteristics that lead to terms of the form of the g tensor squared, [e.g., for $I^{(4)}$,

$$\sum_{\gamma\gamma'} A_{q,\alpha\gamma} A_{r,\gamma\beta} A_{s,\beta'\gamma'} A_{u,\gamma'\alpha'} = (A_q A_r)_{\alpha\beta} (A_s A_u)_{\beta'\alpha'}].$$

Furthermore, only the first and last spectral densities in $I^{(4)}$ preserve the needed coupling of products of the F''s. We illustrate with the term of type

$$\sum_{q,r,s,u} \sum_{\gamma\gamma'} A_{q,\alpha\gamma} A_{r,\gamma\beta} A_{s,\beta'\gamma'} A_{u,\gamma'\alpha'} \ell(q,r,u,s;\gamma\beta,\gamma'\alpha',\beta'\gamma'). \quad (5.8)$$

Utilizing Eqs. (3.7c) and (C10d), properly generalized, we have

$$\ell(q,m_1';r,m_2';s,m_3';u,m_4';\gamma\beta,\gamma'\alpha',\beta'\gamma') = \sum_{j \neq 0; m,m'} \begin{pmatrix} 1 & 1 & j \\ m_1' & m_2' & m' \end{pmatrix} \begin{pmatrix} 1 & 1 & j \\ m_3' & m_4' & -m' \end{pmatrix} (2_j+1)(-)^{m-m'}$$

$$\times \sum_{\substack{\Sigma m_i, \text{ and} \\ \text{electronic states}}} \begin{pmatrix} 1 & 1 & j \\ -m_1 & -m_2 & m \end{pmatrix} \begin{pmatrix} 1 & 1 & j \\ -m_3 & -m_4 & -m \end{pmatrix} F'_{q,\alpha_n,\gamma_n}{}^{(1,m_1)} F'_{r,\gamma_n,\beta_n}{}^{(1,m_1)} F'_{s,\beta'_n,\gamma'_n}{}^{(1,m_3)} F'_{u,\gamma'_n,\alpha'_n}{}^{(1,m_4)}$$

$$\times [\tau_{j,m}^{-1} + i(\omega_{\beta'\alpha'} + \omega_{\gamma\beta} + \omega_{\beta'_n\alpha'_n} + \omega_{\gamma_n\beta_n})]^{-1} [\tau_{j,m}^{-1} + i(\omega_{\beta'\alpha'} + \omega_{\beta'_n\alpha'_n})]^{-1} [\tau_{1,-m_3}^{-1} + i(\omega_{\beta'\gamma'} + \omega_{\beta'_n\gamma'_n})]^{-1}$$

$$= \sum \begin{pmatrix} 1 & 1 & 2 \\ m_1' & m_2' & m' \end{pmatrix} \begin{pmatrix} 1 & 1 & 2 \\ m_3' & m_4' & -m' \end{pmatrix} (-)^{m-m'} \tilde{F}_{qr,\alpha_n,\gamma_n,\beta_n}{}^{(2,m)} \tilde{F}_{su,\beta'_n,\gamma'_n,\alpha'_n}{}^{(2,-m)} [\tau_{j,m}^{-1} + i(\omega_{\beta'\alpha'} + \omega_{\beta'_n\alpha'_n})]^{-1},$$

$$\quad (5.9)$$

where Eqs. (C11) and (C12) and the symmetry relation

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_1+j_2+j_3} \begin{pmatrix} j_1 & j_2 & j_3 \\ -m_1 & -m_2 & -m_3 \end{pmatrix}$$

have been employed, and we have introduced

$$\tilde{F}_{su,\beta'_n,\gamma'_n,\alpha'_n}{}^{(2,-m)} = \sum_{m_3,m_4} 5^{1/2} \begin{pmatrix} 1 & 1 & 2 \\ m_3 & m_4 & m \end{pmatrix} \frac{F'_{s,\beta'_n\gamma'_n}{}^{(1,m_3)} F'_{u,\gamma'_n,\alpha'_n}{}^{(1,m_4)}}{(\tau_{1,-m_3})^{-1} + i(\omega_{\beta'\gamma'} + \omega_{\beta'_n\gamma'_n})}$$

$$\cong +i \sum_{m_3,m_4} 5^{1/2} \begin{pmatrix} 1 & 1 & 2 \\ m_3 & m_4 & m \end{pmatrix} \frac{F'_{s,\beta_n,\gamma_n}{}^{(1,m_3)} F'_{u,\gamma'_n,\alpha'_n}{}^{(1,m_4)}}{\omega_{\gamma'_n\beta'_n}}. \quad (5.10)$$

The approximate equality of Eq. (5.10) holds when the inequality (5.4) applies. Then, if excited electronic states γ_n and γ'_n are independent of the particular γ and γ' spin states, etc., and $\alpha_n, \alpha'_n, \beta_n, \beta'_n$ are taken as the ground electron state for which $n = 0$, we have

$$\tilde{F}_{su}{}^{(2,+m)} = i 5^{1/2} \sum_{n \neq 0; m_3,m_4} \begin{pmatrix} 1 & 1 & 2 \\ m_2 & m_4 & m \end{pmatrix} \cdot \frac{F'_{s,0,n}{}^{(1,m_3)} F'_{u,n,0}{}^{(1,m_4)}}{\omega_{n,0}}. \quad (5.11)$$

Then letting s and u equal S–O and O–F terms and utilizing Table I, we have

$$2\tilde{F}_{\text{S-O,O-F}}{}^{(2,-m)} = i(-1)^m \beta_e \hbar^{-1} g^{(2,-m)} \equiv i F'_g{}^{(2,-m)}. \quad (5.12)$$

The $3j$ symbols may be evaluated using standard references.[31] Then

$$\ell(q, m_1'; r, m_2'; s, m_3'; u, m_4'; \gamma\beta; \gamma'\alpha', \beta'\gamma') \cong \sum_{m,m'} \begin{pmatrix} 1 & 1 & 2 \\ m_1' & m_2' & m' \end{pmatrix} \begin{pmatrix} 1 & 1 & 2 \\ m_3' & m_4' & -m' \end{pmatrix}$$

$$\times (-)^{m-m'} \tfrac{1}{4} F'_g{}^{(2,-m)} F'_g{}^{(2,m)} (\tau_{2,m}{}^{-1} + i\omega_{\beta'\alpha'})^{-1}. \quad (5.13)$$

When this result is substituted into Eq. (5.8), Eq. (5.9) is again used, and the appropriate summations are performed, we have

$$\tfrac{1}{5} \sum_{m,m'} A_{g,\alpha\beta}{}^{(2,-m')} A_{g,\beta'\alpha'}{}^{(2,m')} (-)^{(m-m')} F'_g{}^{(2,-m)} F'_g{}^{(2,m)} (\tau_{2,m}{}^{-1} + i\omega_{\beta'\alpha'})^{-1}. \quad (5.14)$$

Equation (5.14) is seen to correspond to the first spectral density term of $I^{(2)}$ in Eq. (3.5b), with Eq. (C8b) for a simple g-tensor line-broadening mechanism. The second spectral density in $I^{(2)}$ for the g tensor arises from the last spectral density term in $I^{(4)}$ of Eq. (3.5d), in the present treatment, etc. The other four spectral density terms in the first term of Eq. (3.5d) do not contribute to linewidth effects, when Eq. (5.4) applies, since one may show that the second and third spectral density terms in $I^{(4)}$ approximately cancel as do the fourth and fifth terms. Terms $II^{(4)}$ and $III^{(4)}$ lead to crossterms between third-order and first-order perturbation theory, and may be neglected in the approximation that first-order effects [e.g., the result Eq. (5.7)] are unimportant.[32]

The method outlined above, wherein the effect of excited electronic states is explicitly included (as opposed to assuming the validity of a "solid-state" spin Hamiltonian for liquids) could be applied to spin-rotational mechanisms[24a] as well as various higher-order processes[24b] including those which involve stochastic processes other than rotational diffusion.

B. Subsidiary Lines

As will be seen shortly, the subsidiary line associated with the perturbation result given by Eqs. (5.7) and (5.5) can be neglected. However, we analyze it as a simple example of a subsidiary line arising from a non-secular term. We need only consider $K_2(t)$, which for nonsecular-only terms is given (in general notation) by

$$[K_2(t)_{\alpha\alpha'\alpha\alpha'}]^{\text{nonsec}} = -\tfrac{1}{2} \sum_{\gamma} [w^*_{\gamma\alpha}(t) + w^*_{\alpha'\gamma}(t)], \quad (5.15)$$

where from Eq. (3.5b)

$$w_{\gamma\alpha}(t) = 2 \sum_{q,r} A_{q,\alpha\gamma} A_{r,\gamma\alpha} g_2(q, r; o) (\tau_c{}^{-1} + i\omega_{\gamma\alpha})^{-1}$$

$$\times \{1 - \exp[-(\tau_c{}^{-1} + i\omega_{\gamma\alpha})t]\}. \quad (5.16)$$

Equation (5.16) just requires that $g_2(q, r; \tau)$ be expressible as

$$g_2(q, r; \tau) = g_2(q, r; o) \exp(-\tau/\tau_c). \quad (5.16a)$$

For $t \gg \tau_c$, we have

$$\mathrm{Re}\, w_{\gamma\alpha}(t \to \infty) \equiv \mathrm{Re}\, \bar{w}_{\gamma\alpha} = W_{\gamma\alpha},$$

where $W_{\gamma\alpha}$ is the lattice-induced transition probability between states α and γ.[6,33] By analogy to the method of Eqs. (2.22)–(2.28) and Eq. (2.1), we obtain subsidiary lines whose intensities, widths, and frequencies are determined by the Fourier transform of

$$-\tfrac{1}{2} \mathrm{Re} \sum \{\bar{w}^*_{\gamma\alpha} [\tau_c{}^{-1} - i\omega_{\gamma\alpha}]^{-1}$$

$$\times \exp[-(\tau_c{}^{-1} - i\omega_{\gamma\alpha} - i\omega_{\alpha\alpha'})t] + \bar{w}^*_{\alpha'\gamma} [\tau_c{}^{-1} - i\omega_{\alpha'\gamma}]^{-1}$$

$$\times \exp[-(\tau_c{}^{-1} - i\omega_{\alpha'\gamma} - i\omega_{\alpha\alpha'})t]\}.$$

That is, the widths are again given by $\tau_c{}^{-1}$, but the frequency shifts are $\omega_{\gamma\alpha}$ and $\omega_{\alpha'\gamma}$. In the present section, when $\tfrac{1}{2}\bar{w}_{\gamma\alpha}$ and $\tfrac{1}{2}\bar{w}_{\alpha'\gamma}$ are identified with the two sets of terms in Eq. (5.3), then the frequency shifts are of the order of $\omega_{o,n}$ or of electronic transitions, and they are not relevant for ESR.

C. Discussion

It is seen from the above analysis that for free radicals with nondegenerate ground states, the use of a solid-like g tensor in the liquid state is justified on theoretical grounds, and furthermore, there exists no other rotationally-modulated spin–orbit relaxation mechanism of importance (at least to fourth order). The g-tensor relaxation terms may be regarded as a second-order time-dependent process (from $R^{(4)}$), via virtual excited electronic states. This is then an example where a "higher-order" process makes a dominant linewidth contribution, and the generalized condition for motional narrowing Eq. (2.21) must be employed.

[31] M. Rotenberg et al., The 3j and 6j Symbols (Technology Press, Cambridge, Mass., 1959).
[32] It is readily shown, using an analysis similar to that above, that when Eq. (5.4) applies, the only contribution for a polyatomic molecule from the S–O and O–F terms in third order (i.e., from $R^{(3)}$) is a small dynamic frequency shift that is one order higher in essentially $\lambda/\hbar\omega_{0,n}$ than the g shift from $R^{(2)}$ and can therefore be neglected. Such dynamic frequency shifts that are of order $\lambda^4/\hbar^4\omega_{0,n}{}^3$ have been neglected in the above discussion. They arise from terms $IV^{(4)}$, $V^{(4)}$, and $VI^{(4)}$ in Eq. (3.5d). (They are the principal terms from $VI^{(4)}$.)
[33] J. H. Freed, J. Chem. Phys. 43, 2312 (1965).

On the other hand, there could be relevant implications for the benzene anion problem. In the liquid state, it is unreasonable to expect that the benzene anion will retain its vibronic degeneracy, except perhaps for a small fraction of the time,[26] although the actual magnitude of the (random)-solvent-induced splitting has only been guessed at.[25] It could be possible, then, that for at least short intervals in time (which are still longer than rotational correlation times), the inequality Eq. (7.4′) does not hold, where $\omega_{o,n}$ is taken as the splitting of the degenerate states. This suggestion is still insufficient to yield even a partial breakdown of the conventional formulation, because, to the extent that the degenerate benzene orbitals are pure $p\pi$ orbitals, the operator $\mathbf{L}$ will have no appreciable matrix elements between them.[26] However, McConnell has suggested a mechanism involving distortion of these orbitals with a small amount of atomic d character that leads to orbital angular momentum about the ring.[26] Another, perhaps more obvious, way of obtaining a nonvanishing $(\mathbf{L})_{o,n}$ would be to include the effects of $\sigma-\pi$ interaction (which is, in fact, the accepted mechanism generating the benzene-anion proton splitting[34]) mixing some σ^* character into the π orbitals. It should be noted that from Eq. (5.5) and the discussion following, the g shift could have a component that depends on the rotational correlation time, hence on temperature.[35] Also, the rotational spin–orbit mechanism of Eq. (5.7) could become effective. It is clear that further work is necessary to analyze the importance of such possibilities as compared to the suggested mechanisms of McConnell[26] and Kivelson.[28] In any event, all these spin–orbit mechanisms involve rotational modulation in an important way, and the formalism of this section should prove useful in analyzing them in a more rigorous fashion.

VI. HIGHER-ORDER g-TENSOR EFFECTS

The general applicability and limiting conditions of the g-tensor formalism in the case of liquids was discussed in the preceding section. Rather than continue with the spin-orbit operator to fifth and higher order, we now use the g-tensor formalism directly in the R-matrix expansion.

Since the higher order effects will begin to be important for slower tumbling rates, we consider the case of $\omega_e \gg \tau_{l,m}^{-1}$, so that nonsecular effects are negligible compared to secular effects. Thus, the only relevant spin operator is $A_g^{l,0}$ (see Table I). We shall further simplify the treatment by letting $E_{l,m} = \tau_l^{-1}$ independent of m, (i.e., isotropic rotational diffusion), although this is not a necessary assumption. These assumptions plus the inclusion of only g-tensor terms lead to the following

simplified spectral densities [from Eqs. (3.6) and (C10)]:

$$\ell_2(g, l=2; 0) = \tfrac{1}{5}\tau_2[(g^{(0)})^2 + 2(g^{(2)})^2]\beta_e^2\hbar^{-2} \quad (6.1a)$$

$$\ell_3(g; l=2; 0, 0) = (2/35)\tau_2^2 g^{(0)}[(g^{(0)})^2 - 6(g^{(2)})^2]\beta_e^3\hbar^{-3} \quad (6.1b)$$

$$\ell_4(g, l=2; 0, 0, 0) = (2/35)\tau_2^2[(g^{(0)})^2 + 2(g^{(2)})^2]^2\beta_e^4\hbar^{-4}$$
$$\times [(2/7)\tau_2 + (18/35)\tau_4] \quad (6.1c)$$

and

$$\tilde{\ell}_2(g, l=2; 0) = -\tau_2\ell_2(g, l=2; 0), \quad (6.1d)$$

where the $g^{(m)}$ are given in Table I and the $3j$ symbols have been evaluated from standard tables.[31] Note that Eqs. (C11) and (C12) have simplified the analysis of Eq. (6.1c). The first set of Eqs. (4.8) again apply, and we obtain

$$R^{(2)*}_{\alpha\alpha',\alpha\alpha'} = -(2/15)B_o^2\beta_e^2\hbar^{-2}\tau_2\sum_i(g_i^2 - g_s^2), \quad (6.2a)$$

$$R^{(3)*}_{\alpha\alpha',\alpha\alpha'} = -i(\tfrac{2}{3})^{3/2}B_o^3\ell_3(g, l=2; 0), \quad (6.2b)$$

and

$$R^{(4)*}_{\alpha\alpha',\alpha\alpha'} = -(13/35)\tau_2[R^{(2)*}_{\alpha\alpha',\alpha\alpha'}]^2. \quad (6.2c)$$

Thus, the fourth-order term leads to a small increase in the calculated width of the main line, while the third-order term gives its frequency shift.[36] The subsidiary line arising from the secular g-tensor perturbation has a width of τ_2^{-1} and a resonant frequency of

$$\omega_{\alpha\alpha'} + (\tfrac{2}{7})\cdot(\tfrac{2}{3})^{1/2}\beta_e B_o\hbar^{-1}g^{(0)}$$
$$\times\{[(g^{(0)})^2 - 6(g^{(2)})^2]/[(g^{(0)})^2 + 2(g^{(2)})^2]\}$$

and is obtained using Eq. (2.31).

The secular perturbation terms arising from the intramolecular electron-nuclear dipolar interaction could be treated in a manner analogous to the g tensor. However, the pseudosecular contributions from this interaction would not be negligible compared to the secular terms, because they involve low-frequency nuclear-spin transitions. One may note [cf. Eq. (5.17)] that the ESR subsidiary lines from these terms will be shifted by $(\mp\gamma_n B_o - \gamma_e \bar{a})$, i.e., the NMR frequencies of the radical. However, for large dipolar interaction terms, the frequency shift from the $K_3(t)$ term would have to be included as well.

APPENDIX A

We wish to outline a proof showing that the operator Ω_n in Eq. (2.20) is independent of index n. In Sec. III,

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[34] H. M. McConnell and D. B. Chestnut, J. Chem. Phys. **28**, 107 (1958).
[35] In Ref. 22 there is no specific mention of any temperature variation of the g value for the benzene anion.

[36] If the nonsecular g-tensor terms were retained, then there would be a width contribution from the real part of $R^{(3)*}_{\alpha\alpha'\alpha\alpha'}$, cf. Sec. III.

the detailed results for $n \leq 4$ are given, and it is found that in all cases

$$[\exp(-i\Omega t)]_{\alpha\alpha'\beta\beta'} = \exp[-i(\omega_{\alpha\alpha'} - \omega_{\beta\beta'})t], \quad (A1)$$

where α, α', β, and β' represent eigenstates of $\mathcal{K}_0$. We wish to show that Eq. (A1) applies for all n. This is readily done provided the operators in $K(t)$ are given matrix representations utilizing as a basis the eigenstates of $\mathcal{K}_0$. Then we may write $\mathcal{K}_1{}^{\ddagger}(t_j)^{\times}{}_{\alpha\alpha'\beta\beta'}$

$$= \mathcal{K}_1(t_j)^{\times}{}_{\alpha\alpha'\beta\beta'} \exp[-i(\omega_{\alpha\alpha'} - \omega_{\beta\beta'})t_j]$$

$$= [\mathcal{K}_1(t_j)_{\alpha\beta}\delta_{\alpha'\beta'} - \mathcal{K}_1(t_j)_{\beta'\alpha'}\delta_{\alpha\beta}]$$

$$\times \exp[-i(\omega_{\alpha\alpha'} - \omega_{\beta\beta'})t_j] \quad (A2)$$

where the definitions (2.5b) and (2.6a) have been used. Note that in Eq. (A2) only the $\mathcal{K}_1(t)$ matrix elements, and *not* the exponents, are affected by the stationary-random process. Note also that from the discussion of Sec. II and the implied form of $K_n(t)$ given by Eq. (2.17), $K_n(t)$ consists of a sum of terms each involving products of exactly n operators $\mathcal{K}_1{}^{\ddagger}(t_j)^{\times}$. Each of these

terms differ only in the ordering of the t_j and in the exact groupings of the operators over which the average operation is performed [cf. Eq. (2.16c)]. We then rewrite Eqs. (2.19) for $\dot{K}_n(t \to \infty)$ as

$$\dot{K}_n(\infty) = i^n I_n A_n P_n \mathcal{K}_1{}^{\ddagger}(t)^{\times} \mathcal{K}_1{}^{\ddagger}(t_1)^{\times} \cdots \mathcal{K}_1{}^{\ddagger}(t_{n-1})^{\times}, \quad (A3)$$

where the operator

$$I_n \equiv \int_0^{\infty} dt_1 \int_0^{t_1} dt_2 \cdots \int_0^{t_{n-2}} dt_{n-1}$$

$$\to \int_0^{\infty} d\tau_1 \int_0^{\infty} d\tau_2 \cdots \int_0^{\infty} d\tau_{n-1}. \quad (A3a)$$

P_n is a permutation operator which generates the required sums of products of $\mathcal{K}_1{}^{\ddagger}(t_j)^{\times}$, while the operator A_n performs the needed averaging operations. Now by letting $t_j = t - \zeta_j$ in Eq. (A3), the operations I_n, A_n, and P_n relate only to the ζ_j and the functions of ζ_j. The ζ_j decompose into proper sums of the τ_j of Eq. (2.19b) after P_n is applied, so that the second form of Eq. (A3a) becomes appropriate. Thus we may rewrite Eq. (A3) in terms of matrix elements as

$$K_n(\infty)_{\alpha\alpha'\beta\beta'} = i^n I_n A_n P_n \sum_{\text{all } \gamma_i, \gamma_i'} \mathcal{K}_1(t)^{\times}{}_{\alpha\alpha'\gamma_1\gamma_1'} \exp[-i(\omega_{\alpha\alpha'} - \omega_{\gamma_1\gamma_1'})t]\mathcal{K}_1(t-\zeta_1)^{\times}{}_{\gamma_1\gamma_1'\gamma_2\gamma_2'}$$

$$\times \exp[-i(\omega_{\gamma_1\gamma_1'} - \omega_{\gamma_2\gamma_2'})(t-\zeta_1)] \cdots \mathcal{K}_1(t-\zeta_{n-1})^{\times}{}_{\gamma_{n-1}\gamma_{n-1}'\beta\beta'} \exp[-i(\omega_{\gamma_{n-1}\gamma_{n-1}'} - \omega_{\beta\beta'})(t-\zeta_{n-1})]$$

$$= \exp[-i(\omega_{\alpha\alpha'} - \omega_{\beta\beta'})t]i^n I_n A_n P_n \sum_{\text{all } \gamma_1, \gamma_1'} \mathcal{K}_1(t)^{\times}{}_{\alpha\alpha'\gamma_1\gamma_1'}\mathcal{K}_1(t-\zeta_1)^{\times}{}_{\gamma_1\gamma_1'\gamma_2\gamma_2'} \exp[i(\omega_{\gamma_1\gamma_1'} - \omega_{\gamma_2\gamma_2'})\zeta_1] \cdots$$

$$\times \mathcal{K}_1(t-\zeta_{n-1})^{\times}{}_{\gamma_{n-1}\gamma_{n-1}'\beta\beta'} \exp[i(\omega_{\gamma_{n-1}\gamma_{n-1}'} - \omega_{\beta\beta'})\zeta_{n-1}]$$

$$= [\exp(-i\Omega t)]_{\alpha\alpha'\beta\beta'} R^{(n)*}{}_{\alpha\alpha'\beta\beta'}, \quad (A4)$$

which is the desired result.

APPENDIX B

The well-known solution to the modified Bloch equations for a two-jump system[17,18] may be applied directly to the formulation in Sec. IV to give a line-shape function

$$I(\omega) \propto \frac{\tau_c{}^{-1} + i(W_A - W_B)\Delta m_I + i\omega}{-\omega^2 + i\omega[\tau_c{}^{-1} + i(W_A - W_B)\Delta m_I] + W_A W_B \Delta^2 m_I{}^2}. \quad (B1)$$

The frequency $\omega = 0$ is taken at the center of the particular hyperfine line of resonant frequency:

$$\hbar\omega_{\alpha\alpha'} = g_s\beta_e B_o + \hbar |\gamma_e| \bar{a}m_I.$$

The inverse transform of Eq. (B1), which gives $G(t)$ of Eq. (2.1), may be obtained by straightforward application of Laplace transforms and yields

$$G(t) \propto [r_2 \exp(-r_1 t) - r_1 \exp(-r_2 t)]/(r_2 - r_1), \quad (B2)$$

where $-r_1$ and $-r_2$ are the two values of $\frac{1}{2}[-c \pm (c^2 - 4d)^{1/2}]$ while

$$c = \tau_c{}^{-1} + i(W_A - W_B)\Delta m_I$$

and

$$d = W_A W_B (m_I \Delta)^2.$$

For $|m_I \Delta \tau_c| < 1$, then $(c^2 - 4d)^{1/2}$ may be expanded in powers of $m_I \Delta \tau_c$. Then the approximate form of Eq. (B2) has

$$r_1 = m_I{}^2 \Delta^2 \tau_c W_A W_B - i m_I{}^3 \Delta^3 \tau_c{}^2 (W_A - W_B) W_A W_B - W_A W_B m_I{}^4 \Delta^4 \tau_c{}^3 (1 - 5W_A W_B) \cdots \quad (B3a)$$

$$r_2 = \tau_c{}^{-1} + i(W_A - W_B)m_I\Delta - m_I{}^2\Delta^2\tau_c W_A W_B \cdots. \quad (B3b)$$

When Eqs. (B3) are substituted in Eq. (B2) and terms of proper order are retained, one obtains Eqs. (4.10) and (4.11).

APPENDIX C: CORRELATION FUNCTIONS FOR MARKOV PROCESSES AND ROTATIONAL DIFFUSION

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 $P(y_1 \mid y_2, \tau)\, dy_2$ 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. One may then write an nth order joint probability density[37]:

$$W_n(y_n, t_n; y_{n-1}t_{n-1}; \cdots y_2t_2; y_1t_1) = W_n(y_n; y_{n-1}\tau_{n-1}; \cdots y_2\tau_2; y_1\tau_1)$$

$$= W(y_n)\prod_{i=1}^{n-1}P(y_{n-i+1} \mid y_{n-i}, \tau_{n-i}), \qquad (C1)$$

where

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

Then, for the nth-order time correlation of the random function $F_q(y)$:

$$\langle F_{q_1}(t)F_{q_2}(t-\tau_1)\cdots F_{q_n}(t-\sum_{i=1}^{n-1}\tau_n) \rangle$$

$$= \int dy_n W(y_n) F_{q_n}(y_n) \iint \cdots \int dy_{n-1}\cdots dy_2 dy_1 \prod_{i=1}^{n-1}P(y_{n-i+1} \mid y_{n-i}, \tau_{n-i}) F_{q_{n-1}}\cdots F_{q_2}F_{q_1}. \quad (C2)$$

The integrals in Eq. (C2) may be changed to summations when the variable y_i takes on a discrete set of values.

The conditional probability function for rotational diffusion, $P(\Omega_0 \mid \Omega; \tau)$, (where Ω_0 and Ω represent values of Euler angles for a tumbling molecular axis with respect to a fixed laboratory axis system) is well known even for anisotropic diffusion. For simplicity we assume axially symmetric diffusion, where[38]

$$P(\Omega_0 \mid \Omega; \tau) = \sum_{L,K,M} [(2L+1)/8\pi^2]\mathfrak{D}_{KM}^{(L)*}(\Omega_0)\mathfrak{D}_{KM}^{(L)}(\Omega) \exp(-E_{L,K}\tau) \qquad (C3)$$

and

$$W(\Omega_0) = 1/8\pi^2. \qquad (C4)$$

The $\mathfrak{D}_{KM}{}^L$ are the Wigner rotation matrices and

$$\tau_{L,K}^{-1} = E_{L,K} = \mathfrak{R}_1 L(L+1) + (\mathfrak{R}_3 - \mathfrak{R}_1)K^2, \qquad (C5)$$

where $\mathfrak{R}_1$ and $\mathfrak{R}_2 = \mathfrak{R}_3$ the principal values of the rotational diffusion tensor. When $\mathfrak{R}_3 - \mathfrak{R}_1 = 0$ the isotropic tumbling result is obtained.

The perturbation $\mathfrak{K}_1(t)$ may be written as[39]

$$\mathfrak{K}_1(t) = \sum_{L,m,m',q} \mathfrak{D}_{-m,m'}{}^{(L)}(\Omega) F'_q{}^{(L,m)} A_q{}^{(L,m')}, \qquad (C6)$$

where both the $F'_q{}^{(L,m)}$ and the $A_q{}^{(L,-m)}$ are irreducible tensor components of rank L and component m. The F' in Eq. (C6) are expressed in molecule-fixed coordinates, while A is a spin operator quantized in space-fixed axes. The $D_{-m,m'}{}^{(L)}(\Omega)$ terms include the transformation from space-fixed to molecule-fixed axes and are the random functions of time. The needed correlation functions [Eqs. (3.7) and (C2)] may be obtained by utilizing the relations[40]

$$\int d\Omega \mathfrak{D}_{m_1,m'_1}{}^{(l_1)*}(\Omega)\mathfrak{D}_{m_2,m'_2}{}^{(l_2)}(\Omega) = [8\pi^2/(2l_1+1)]\delta_{l_1 l_2}\delta_{m_1 m_2}\delta_{m'_1 m'_2} \qquad (C7)$$

[37] M. C. Wang and G. E. Uhlenbeck, Rev. Mod. Phys. **17**, 323 (1945).
[38] J. H. Freed, J. Chem. Phys. **41**, 2077 (1964).
[39] Equation (C6) follows the notation utilized in Refs. 1 and 38. It differs from that of Edmonds[40] and others where

$$\mathfrak{K}_1(t) = \sum_{L,m,m'} \mathfrak{D}_{-m,m'}{}^{(L)}(-1)^m F'^{(L,m)} A^{(L,m')}$$

by incorporating $(-1)^m$ into the definition of $F'^{(L,m)}$.
[40] A. R. Edmonds, *Angular Momentum In Quantum Mechanics* (Princeton University Press, Princeton, N.J., 1957).

and

$$\int d\Omega \mathfrak{D}_{m_1m'_1}{}^{l_1}(\Omega) \mathfrak{D}_{m_2m'_2}{}^{l_2}(\Omega) \mathfrak{D}_{m_3,m'_3}{}^{l_3}(\Omega) = 8\pi^2 \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l_3 \\ m'_1 & m'_2 & m'_3 \end{pmatrix}, \tag{C8}$$

where the terms in parenthesis in Eq. (C8) are the $3j$ symbols.[31,40] Also

$$\mathfrak{D}^l_{m,m'}{}^* = (-)^{m-m'}\mathfrak{D}^l_{-m,m'}. \tag{C9}$$

We then obtain

$$g_1(\tau) = 0 \tag{C10a}$$

$$g_2(l_1m'_1q, l_2m'_2r; \tau) = (2l_1+1)^{-1}\delta_{l_1,l_2}\delta_{m'_2,-m'_1}\sum_m (-)^{m+m_1'}F'_q{}^{(l_1,m)}F'_r{}^{(l_1,-m)} \exp[-(E_{l_1,m})\tau] \tag{C10b}$$

$$g_3(l_1m'_1q, l_2m'_2r, l_3m'_3s; \tau_1, \tau_2)$$

$$= \begin{pmatrix} l_1 & l_2 & l_3 \\ m'_1 & m'_2 & m'_3 \end{pmatrix} \sum_{m_1,m_2,m_3} F'_q{}^{(l_1m_1)}F'_r{}^{(l_2m_2)}F'_s{}^{(l_3m_3)} \begin{pmatrix} l_1 & l_2 & l_3 \\ -m_1 & -m_2 & -m_3 \end{pmatrix}$$

$$\times \exp[-(E_{l_3,-m_3})\tau_2]\exp[-(E_{l_1,m_1})\tau_1] \tag{C10c}$$

$$g_4(l_1m'_1 q, l_2m'_2r, l_3m'_3s; l_4m'_4u; \tau_1, \tau_2, \tau_3)$$

$$= \sum_{j,m,m';j\neq 0} \begin{pmatrix} l_1 & l_2 & j \\ m'_1 & m'_2 & m' \end{pmatrix} \begin{pmatrix} l_3 & l_4 & j \\ m'_3 & m'_4 & -m' \end{pmatrix} (2j+1)(-)^{m-m'}$$

$$\times \sum_{m_1,m_2,m_3,m_4} \begin{pmatrix} l_1 & l_2 & j \\ -m_1 & -m_2 & m \end{pmatrix} \begin{pmatrix} l_3 & l_4 & j \\ -m_3 & -m_4 & -m \end{pmatrix} F'_q{}^{(l_1,m_1)}F'_r{}^{(l_2,m_2)}F'_s{}^{(l_3m_3)}F'_u{}^{(l_4,m_4)}$$

$$\times \exp[-(E_{l_4,-m_4})\tau_3]\exp[-(E_{j,m})\tau_2]\exp[-(E_{l_1,m_1})\tau_1]. \tag{C10d}$$

Note that in Eqs. (C10), each subscript q has been expanded to include explicitly the particular irreducible tensor component by the indices l and m. The restriction of the summation in Eq. (C10d) to $j\neq 0$ comes about because the second term in Eq. (3.7c) leads to the cancellation of the $j=0$ component from the first term.

In applying these results, it is useful to employ the spherical tensor coupling expression[40]

$$T_{a,b}{}^{(l,m)} = \sum_{m_1,m_2} (2l+1)^{1/2}(-1)^{-l_1+l_2-m} \begin{pmatrix} l_1 & l_2 & l \\ m_1 & m_2 & -m \end{pmatrix} T_a{}^{(l_1,m_1)}T_b{}^{(l_2,m_2)}. \tag{C11}$$

It may be shown from this expression and the symmetry relation[40]

$$\begin{pmatrix} l_1 & l_1 & l \\ m_1 & -m_1 & 0 \end{pmatrix} = (-)^l \begin{pmatrix} l_1 & l_1 & l \\ -m_1 & m_1 & 0 \end{pmatrix}, \tag{C12}$$

that if $T_a{}^{l_1}$ and $T_b{}^{l_1}$ have only real components, or if $a=b$, then for l-odd $T_{a,b}{}^{(l,m)}=0$.