Stochastic theory of spin relaxation in liquids

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A stochastic theory of line shape is considered for describing molecular reorientational processes in liquids. The theory takes into account both secular and nonsecular terms in the interaction Hamiltonian. A general solution for the line shape is given in a matrix form by assuming a Markovian modulation for the random process. The usefulness of the theory is demonstrated by doing perturbation theory calculations in the motionally narrowed limit. A resolvent-operator technique is employed for collecting higher-order terms in perturbation theory. Two models for molecular motion, (i) rotational diffusion and (ii) strong-collision approximation, are treated and their predictions compared. In the case of the rotational-diffusion model, the results are illustrated by considering a g-tensor interaction in liquids. Expressions for line width and shift are given up to fourth order in perturbation theory, and a detailed comparison is made with the existing theories.

I. INTRODUCTION

The random-frequency-modulation theory as developed by Kubo and Anderson, among others, has been widely applied to study relaxation effects in various line-shape problems.[1-4] In this theory, the frequency of the resonating system is assumed to undergo transitions, due to interaction with the surroundings, between a number of possible values. The effect of the rates of transition between these frequencies on the position and width of the resonance lines is then calculated by assuming a Markovian character for the stochastic process.

The generalization of the Kubo-Anderson model to include quantum-mechanical effects is seen to give rise to important contributions to the broadening and shift of the resonance lines.[5] These so-called nonsecular or nonadiabatic effects arise from the fact that the different forms between which the Hamiltonian of the system jumps do not commute with each other. The theory developed in Ref. 5 (hereafter referred to as I) is found to give simple and tractable results for interpreting various types of diffusion processes in solids.[6-8]

In this paper we present a theory, developed in parallel to I, which takes into account many cases of relaxation in liquids, e.g., quadrupolar relaxation through molecular reorientations, effects of molecular tumblings on the g tensor and chemical-shift tensor, etc., in electron and nuclear magnetic resonance experiments.[9] As an illustration of the theory, we consider a specific example throughout the paper. This involves a spin-resonance experiment on molecular ions in liquids where the g-tensor interaction between the ionic spin and the external magnetic field undergoes rotational relaxa-

tion due to molecular tumblings. We write the corresponding Hamiltonian in Sec. IIA in terms of rotation matrices. The Euler angles which appear in these rotation matrices and which describe the instantaneous orientation of the molecule with respect to a laboratory frame are assumed to be random functions of time. As in I, the stochastic process which governs the probability of change of the orientation of the molecular frame from one direction to another is assumed to be Markovian. In Sec. IIB, we give the solution to the line-shape problem for such a process.

The theoretical study of rotational relaxation in liquids is not new and has previously been undertaken by several authors.[10] In this paper we present a different approach to the problem and point out the relationship of our work to the existing treatments. Sillescu and Kivelson[11] start from a rotational diffusion equation which is assumed to describe the change in molecular orientation due to collisions. They write the final expression for the line shape in terms of a set of coupled differential equations. Our theory, on the other hand, does not require at the outset that the molecular motion be governed by a diffusion equation, and the final expression for the line shape is written in the form of a matrix which is the solution of an integral equation. This matrix form is quite suitable both for numerical and perturbation-theory calculations. We demonstrate the utility of the theory in Sec. III by doing perturbation theory in the region of fast relaxation or the so-called motionally narrowed limit and show how higher-order terms can be included in the theory. Our perturbation-theory calculation, albeit performed on a stochastic solution, is similar to the resolvent operator technique em-

ployed by Fano[12] in connection with the pressure broadening problem in atomic spectroscopy and later applied by others in the *ab initio* treatments of Mössbauer line shapes[13,14] and perturbed angular correlation of γ rays.[15]

A spin-relaxation calculation which also includes higher-order terms in perturbation theory has been developed by Freed,[16] who used the generalized cumulant expansion techniques introduced by Kubo.[17] This technique is quite powerful and leads in a straightforward manner to a number of results in the many-body theory of line shape, where the physical idea of motional narrowing is used, although not stated explicitly, in summing up the effects of higher-order diagrams in perturbation theory.[18,19] However, as Freed points out, the cumulant theorem is useful in the long-time limit $t \gg \tau_c$, where τ_c is a correlation time for the random process. This yields a time-independent relaxation or R matrix which in turn produces Lorentzian spectral lines. But as we well know, the intensity of a Lorentzian line does not fall off fast enough near the wings to yield convergent moments.[3,17] Freed demonstrates how the inclusion of finite-time effects leads to a weak, subsidiary line which has a negative intensity.[20] The very broad subsidiary line is most effective in subtracting out some intensity from the wings of the main line, and the resulting line does have finite moments. Our approach, on the other hand, has the advantage that the line-shape function is Fourier transformed at the very beginning of the calculation, before any perturbation expansion is performed. Therefore the frequency dependence of the R matrix and hence the appearance of the subsidiary line are natural outcomes of the theory. Also, the higher-order terms, both secular and nonsecular, turn out to be quite simple to handle.

Our method is also related to Kubo's stochastic Liouville equation approach.[21] However, while Kubo uses a density matrix, we prefer to work with a Hamiltonian, which we find conceptually simpler. The stochastic Liouville equation, like our method, also has the advantages of working in the frequency space and is free from some of the difficulties associated with the cumulant method, which is natural in the time domain.[22] Freed and his co-workers have extensively used the stochastic Liouville equation in the spin-relaxation problem.[10] The perturbation theory we develop is a different attack to the problem and provides a different intuitive understanding of the spin-relaxation phenomenon in liquids.

As we have mentioned before, our approach is closely related to the Fano-Zwanzig projection operator method.[12] The latter has recently been shown by Yoon *et al.*[22] to be equivalent to what has

been called the total time-ordered cumulant (TTOC) method, as opposed to the partial time-ordered cumulant (PTOC) method used earlier by Freed.[16] In fact, for secular perturbation in the rotational diffusion model (Sec. IV A), we shall derive results in Sec. V which are identical to the ones obtained by the TTOC method in Ref. 22.

To illustrate our perturbation-theory calculation, we consider the g-tensor interaction which we introduce in Sec. II A. Two different models for molecular motion in liquids are treated. In the first, the motion is assumed to be governed by a classical isotropic diffusion equation. The diffusion equation is introduced in Sec. IV A. In Sec. IV B, we write results up to fourth order in perturbation theory. The actual calculations are performed in the appendices. Analysis of the results, effects of secular and nonsecular terms on the position and width of the resonance line, and the appearance of the subsidiary line are subjects of Sec. V.

In the second model, which we refer to as the strong collision approximation, the effect of molecular collisions is assumed to make the directions of molecular axes change by any angle with equal probability after each collision.[6,23,24] This model therefore deals with a situation which is in some sense the opposite to the one described by the rotational diffusion equation. While in the rotational diffusion model the orientations of the molecular axes before and after a collision are correlated to each other through the diffusion equation, they are completely uncorrelated in the strong collision model. The actual physical picture of molecular tumbling in liquids may lie somewhere in between the two models. For this reason, it is instructive to compare the results of the two models. Although the strong collision model allows us to give the line shape for all values of the relaxation time, the comparison is most clearly seen in perturbation theory. This is done in Sec. VI. Finally, Sec. VII contains a brief summary of our work.

II. THEORY

A. Hamiltonian equations

The existence of rapid molecular motions of random character in liquids in the nature of rotational tumbling of individual molecules can be studied in a magnetic resonance experiment.[9] The effect of these motions is to reduce the coupling between different spins and that between spins and external fields and thereby give rise to narrow resonance lines. The spin-spin coupling in liquids of the dipole-dipole or quadrupole-quadrupole types, etc., and is so weak that it is appropriate to consider in-

dividual spins or groups of spins inside a molecule as separate systems coupled independently to a heat bath. The effect of the heat bath is then to produce fluctuating local magnetic fields or electrostatic field gradients at the positions of the spins. The aim of the theory is to study how these rapidly fluctuating fields or gradients induce transitions between the energy levels of the individual spins and broaden the resonance lines, which are very sharp in the first approximation. Many such problems involving molecular reorientations in liquids can be described by a Hamiltonian,

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1(t) , \tag{1}$$

where $\mathcal{H}_0$ is the time-independent part that gives rise to unperturbed resonance lines. The time-dependent part can be expressed as

$$\mathcal{H}_1(t) = \sum_{lmn} V_{mn}^{(l)} \mathfrak{D}_{mn}^{(l)*}(\Omega(t)) , \tag{2}$$

where the $V_{mn}^{(l)}$'s are spin operators and the Wigner rotation matrices $\mathfrak{D}_{mn}^{(l)}$ are functions of the Euler angles $\Omega(\phi, \theta, \psi)$ describing the instantaneous molecular orientation with respect to a laboratory frame. The Euler angles are random functions of time because of molecular motion in liquids. In general, $\mathcal{H}_0$ and $\mathcal{H}_1$ do not commute with each other, so that $\mathcal{H}_1$ can induce transitions between the different eigenstates of $\mathcal{H}_0$. This gives rise to the so-called nonsecular effects.

To illustrate the kind of physical problem that could be described by this picture, we consider an electron-spin-resonance experiment on a molecular ion of spin $\vec{S}$ in a liquid.[10] The interaction between this spin and an external magnetic field $\vec{H}$ is given by

$$\mathcal{H} = \mu_B \vec{S} \cdot \vec{g}^0 \cdot \vec{H} , \tag{3}$$

where μ_B is the Bohr magneton and the principal axes of the tensor $\vec{g}^0$ are fixed to the molecular frame. This Hamiltonian also describes the chemical-shift tensor interaction in a nuclear magnetic resonance experiment.[9]

Because of tumbling motions in liquids, the molecular frame changes its orientation randomly. The g tensor in the lab frame is related to that in the molecular frame by

$$g = \vec{R}(\Omega) g^0 R(\Omega) , \tag{4}$$

where $R(\Omega)$ is the rotation matrix corresponding to the Euler angles $\Omega(\phi, \theta, \psi)$ of the molecular frame relative to the lab frame. We assume, for simplicity, that the tensor g^0 is axially symmetric; thus

$$g_{kk}^0 = g_\perp + (g_\parallel - g_\perp) \delta_{kz} , \quad k = x, y, z , \tag{5}$$

where the molecule-fixed z direction is taken to be

the symmetry axis. We also assume that the external magnetic field is applied along the z direction in the lab frame. Then, writing the elements of the rotation matrix in terms of spherical harmonics[25] and using Eqs. (3)–(5), we have

$$\mathcal{H} = \mu_B S_z \bar{g} H + \mu_B (\tfrac{2}{15} \pi)^{1/2} (g_\parallel - g_\perp) H$$
$$\times [(\tfrac{8}{3})^{1/2} Y_{20}(\theta\phi) S_z + Y_{2-1}(\theta\phi) S_+ - Y_{21}(\theta\phi) S_-] , \tag{6}$$

where $\bar{g} = \tfrac{1}{3}(g_\parallel + 2g_\perp)$ and the $Y_{2m}(\phi, \theta)$'s are time dependent. Because of the axial symmetry of g^0 about the body-fixed z axis, angle ψ, which measures rotation about that axis, does not appear in Eq. (6). Comparing Eqs. (1), (2), and (6), we find, for $l = 2$, $n = 0$,

$$\mathcal{H}_0 = \mu_B S_z \bar{g} H ,$$
$$V_{20}^{(2)} = V_{-20}^{(2)} = 0 ,$$
$$V_{\pm 10}^{(2)} = \mp \mu_B (\tfrac{1}{6})^{1/2} (g_\parallel - g_\perp) H S_\mp , \tag{7}$$
$$V_{00}^{(2)} = \tfrac{2}{3} \mu_B (g_\parallel - g_\perp) H S_z .$$

In writing Eq. (7), we have used[25]

$$\mathfrak{D}_{m0}^{(2)*}(\phi, \theta, \psi) = (\tfrac{4}{5} \pi)^{1/2} Y_{2m}(\theta, \phi) . \tag{8}$$

B. Solution of the problem

In this section, we start with the Hamiltonian given by Eqs. (1) and (2) and derive an expression for the line shape by assuming that the probability distribution of the Euler angles Ω for the molecule-fixed frame undergoes a stationary Markovian modulation. Our derivation here is quite similar to that described in I, with, of course, different notations suitable for describing molecular reorientational processes in liquids. For the sake of completeness, we indicate here the essential steps in the derivation without getting into too much detail.

The magnetic resonance line shape is obtained from the Fourier or Laplace transform of a correlation function,[5,7]

$$\Phi(p) = \int_0^\infty dt\, e^{-pt} \mathrm{Tr}\{\rho([U(t)]_{\mathrm{av}} S_\perp) S_\perp\} , \tag{9}$$

where $p = i\omega$, ρ is a density matrix for the spin-system, the trace is calculated over the spin states, $S_\perp$ is the component of the spin in a direction perpendicular to the external magnetic field, $[\cdots]_{\mathrm{av}}$ denotes an average over the random properties of the system Hamiltonian and $U(t)$ is the so-called time-development superoperator for the system, given as a time-ordered exponentiated operator

$$U(t) = \exp\left(i \int_0^t \mathcal{H}^x(t')\, dt'\right) . \tag{10}$$

In Eq. (10), $\mathfrak{IC}^x(t)$ is the Liouville operator corresponding to the Hamiltonian $\mathfrak{IC}(t)$.[26] From Eqs. (1), (2), and (10), $U(t)$ is found to satisfy an integral equation,

$$U(t) = 1 + i \int_0^t dt' \, U(t') \left(\mathfrak{IC}_0 + \sum_{lmn} V_{mn}^{(l)x} \mathfrak{D}_{mn}^{(l)*} \left(\Omega(t) \right) \right),$$

(11)

where $V_{mn}^{(l)x}$ is the Liouville operator associated with $V_{mn}^{(l)}$. The average indicated in Eq. (9) is given

by

$$[U(t)]_{av} = \int d\Omega_0 \, d\Omega \, p(\Omega_0) \, (\Omega_0 | u(t) | \Omega),$$

(12)

where $p(\Omega_0)$ is the *a priori* probability of the occurrence of the initial orientation Ω_0. (For brevity of notation, we use a single integral instead of multiple integrals over solid angles throughout our paper.) As in I, we make use of the stationary Markov property and write, for Eq. (11),

$$(\Omega_0 | u(t) | \Omega) = (\Omega_0 | P(t) | \Omega) + i \int d\Omega_1 \, d\Omega_2 \int_0^t dt' \, (\Omega_0 | u(t') | \Omega_1)(\Omega_1 | \left(\mathfrak{IC}_0 + \sum_{lmn} V_{mn}^{(l)x} \tilde{\mathfrak{D}}_{mn}^{(l)*} \right) | \Omega_2) \, (\Omega_2 | P(t - t') | \Omega),$$

(13)

where $(\Omega_0 | P(t) | \Omega)$ is the probability that the orientation is Ω at time t, given that it was Ω_0 at $t = 0$, and $\tilde{\mathfrak{D}}_{mn}^{(l)}$ is a diagonal matrix[5] defined by

$$(\Omega_1 | \tilde{\mathfrak{D}}_{mn}^{(l)} | \Omega_2) = \mathfrak{D}_{mn}^{(l)}(\Omega_1) \, \delta(\Omega_1 - \Omega_2).$$

(14)

Equation (13) can be written in matrix form as

$$u(t) = P(t) + i \int_0^t dt' \, u(t')$$

$$\times \left(\mathfrak{IC}_0 + \sum_{lmn} V_{mn}^{(l)x} \tilde{\mathfrak{D}}_{mn}^{(l)*} \right) P(t - t').$$

(15)

The required Laplace transform in Eq. (9) in the line-shape expression is then given from Eq. (15) by

$$u(p) = P(p) + iu(p) \left(\mathfrak{IC}_0 + \sum_{l,m,n} V_{mn}^{(l)x} \tilde{\mathfrak{D}}_{mn}^{(l)*} \right) P(p),$$

(16)

where

$$P(p) = \int_0^\infty dt \, e^{-pt} P(t).$$

(17)

As in I, the matrix $P(t)$ is given by

$$P(t) = e^{Wt},$$

(18)

where W is a stochastic matrix whose off-diagonal elements $(\Omega_1 | W | \Omega_2)$ are equal to the probability per unit time that the orientation changes from Ω_1 to Ω_2 in time t. The conservation of total probability requires that

$$\int d\Omega_2 (\Omega_1 | W | \Omega_2) = 0.$$

(19)

Since the stochastic process is assumed to be stationary, detailed balance requires

$$p(\Omega_1) (\Omega_1 | W | \Omega_2) = p(\Omega_2) (\Omega_2 | W | \Omega_1),$$

(20)

where the $p(\Omega)$'s are the *a priori* probabilities introduced in Eq. (12). We also have

$$\int p(\Omega) \, d\Omega = 1.$$

(21)

On combining Eqs. (15), (16), and (18), we find

$$u(p) = \left[p\mathbf{1} - W - i \left(\mathfrak{IC}_0^x + \sum_{l,m,n} V_{mn}^{(l)x} \tilde{\mathfrak{D}}_{mn}^{(l)*} \right) \right]^{-1},$$

(22)

where $\mathbf{1}$ is the unit matrix. Equation (22) is equivalent in form to the solution of the stochastic Liouville equation.[21]

Equation (22) together with Eq. (9) consitute the solution to the line-shape problem. The matrix $u(p)$ is labeled by quantum-mechanical indices as well as the Euler angles Ω which are the stochastic variables of the problem. The form of the matrix W relevant to the physical problem under consideration has to be specified before the matrix inversion in Eq. (22) and subsequent calculations can be performed. However, useful progress can still be made in the two regimes of slow and fast motion.[11] We shall see this in Sec. III by treating the fast-motion regime.

III. PERTURBATION TREATMENT IN MOTIONALLY NARROWED LIMIT

The physical picture that we want to derive mathematically in perturbation theory is as follows: The role of the unperturbed Hamiltonian $\mathfrak{IC}_0$ in Eq. (1) is to generate resonance lines for the spin system. The effect of the time-dependent Hamiltonian $\mathfrak{IC}_1$ is to produce modulation of these lines. Although the instantaneous effect of $\mathfrak{IC}_1$ on $\mathfrak{IC}_0$ could be quite large if the relaxation processes are rapid enough, the resonating system "sees" only a time-averaged effect of the perturbation which is quite small. This makes a successful

perturbation theory possible. Thus the physical domain that we shall be concerned with in our calculation is where $W \gg \mathfrak{K}_1(t)$. This is a reasonable assumption for relaxation processes in low-viscosity liquids at not too low temperatures. The relative strength of $\mathfrak{K}_0$, however, is not crucial for our calculation.

The perturbation expansion for $u(p)$ in Eq. (22) is written

$$u(p) = u^0(p) + u^0(p) M(p) u^0(p) , \qquad (23)$$

where

$$u^0(p) = [p\underline{1} - i\mathfrak{K}_0^x - W]^{-1} , \qquad (24)$$

$$M(p) = \mathfrak{A} + \mathfrak{A} u^0(p) \mathfrak{A} + \mathfrak{A} u^0(p) \mathfrak{A} u^0(p) \mathfrak{A} + \cdots , \qquad (25)$$

$$\mathfrak{A} = i \sum_{lmn} V_{mn}^{(l)x} \tilde{\mathfrak{D}}_{mn}^{(l)} . \qquad (26)$$

The desired average in Eq. (9) is then obtained from Eqs. (12) and (23) as

$$[u(p)]_{\text{av}} = [u^0(p)]_{\text{av}} + \int d\Omega_0 \, d\Omega \, p(\Omega_0)$$
$$\times (\Omega_0 | u^0(p) M(p) u^0(p) | \Omega), \qquad (27)$$

where

$$[u^0(p)]_{\text{av}} = \int d\Omega_0 \, d\Omega \, p(\Omega_0) (\Omega_0 | u^0(p) | \Omega) . \qquad (28)$$

If we make an expansion of $u^0(p)$ in the form

$$u^0(p) = (p\underline{1} - i\mathfrak{K}_0^x)^{-1} + (p\underline{1} - i\mathfrak{K}_0^x)^{-1} W (p\underline{1} - i\mathfrak{K}_0^x)^{-1}$$
$$+ (p\underline{1} - i\mathfrak{K}_0^x)^{-1} W (p\underline{1} - i\mathfrak{K}_0^x)^{-1} W (p\underline{1} - i\mathfrak{K}_0^x)^{-1}$$
$$+ \cdots \qquad (29)$$

under the integral in Eq. (28) and make use of the completeness and orthogonality relations

$$\int d\Omega | \Omega) (\Omega | = 1 , \qquad (30)$$

$$(\Omega_1 | \Omega_2) = \delta(\Omega_1 - \Omega_2) , \qquad (31)$$

and of Eqs. (19) and (21), we can show easily that

$$[u^0(p)]_{\text{av}} = (p\underline{1} - i\mathfrak{K}_0^x)^{-1} . \qquad (32)$$

($\mathfrak{K}_0^x$, although a quantum-mechanical Liouville operator, behaves like a number in the stochastic space spanned by the Euler angles Ω.) The result (32) is physically obvious. If the term $\mathfrak{A}$ which couples the spin system to the lattice is absent, $u(p)$ is given entirely by $u^0(p)$ [cf. Eq. (23)]. Upon taking the average over the stochastic variables, the effect of W must completely be gone, because the heat bath represented by the matrix W does not have any influence at all on the resonating system

in the absence of the coupling term.

Next, for the second term in Eq. (27) we have

$$\int d\Omega_0 \, d\Omega \, d\Omega_1 \, d\Omega_2 \, p(\Omega_0) (\Omega_0 | u^0(p) | \Omega_1)$$
$$\times (\Omega_1 | M(p) | \Omega_2) (\Omega_2 | u^0(p) | \Omega) ,$$

using Eq. (30), which is equal to

$$\int d\Omega_0 \, d\Omega_1 \, d\Omega_2 \, p(\Omega_0) (\Omega_0 | u^0(p) | \Omega_1)$$
$$\times (\Omega_1 | M(p) | \Omega_2) (p\underline{1} - i\mathfrak{K}_0^x)^{-1} ,$$

using Eqs. (19), (21), and (29)–(31) as before. In

$$\int d\Omega_0 \, p(\Omega_0) (\Omega_0 | u^0(p) | \Omega_1) ,$$

if we use the same procedure as above and also use the detailed balance condition (20), we can write

$$\int d\Omega_0 \, p(\Omega_0) (\Omega_0 | u^0(p) | \Omega_1) = p(\Omega_1) (p\underline{1} - i\mathfrak{K}_0^x)^{-1} .$$

We have, finally, for Eq. (27)

$$[u(p)]_{\text{av}} = (p\underline{1} - i\mathfrak{K}_0^x)^{-1} \{ \underline{1} + [M(p)]_{\text{av}} (p\underline{1} - i\mathfrak{K}_0^x)^{-1} \} , \qquad (33)$$

where

$$[M(p)]_{\text{av}} = \int d\Omega_1 \, d\Omega_2 \, p(\Omega_1) (\Omega_1 | M(p) | \Omega_2) , \qquad (34)$$

defined in accordance with Eq. (12).

After some algebraic manipulation,[12] we can rewrite (33) in a very useful form:

$$[u(p)]_{\text{av}} = [p\underline{1} - i\mathfrak{K}_0^x - M_c(p)]^{-1} , \qquad (35)$$

where

$$M_c(p) = \sum_{n=0}^{\infty} (-1)^n \{ [M(p)]_{\text{av}} (p\underline{1} - i\mathfrak{K}_0^x)^{-1} \}^n [M(p)]_{\text{av}} . \qquad (36)$$

The subscript c in Eq. (36), which stands for connected, is used in a manner similar to that of Fano,[12] who shows that the expansion for $M_c(p)$ is related to the "linked-diagram" expansion in many-body theory. The expansion (36) for $M_c(p)$, in conjunction with the expansion (25) for $M(p)$, gives us a series in the perturbation $\mathfrak{A}$. In principle, $M_c(p)$ can be calculated to any desired order in perturbation. In the generalized cumulant expansion technique, the higher-order terms are grouped in the exponent of the time-development superoperator $[u(t)]_{\text{av}}$ [cf. Eq. (10)].[16,17] In our method, on the other hand, they appear in a "resolvent superoperator." The frequency dependence of the relaxation matrix $[M_c(p)$, in our notation, where $p = i\omega]$ is already evident in Eq. (35).

The relaxation matrix $M_c(p)$ is defined in terms of the stochastic average of $M(p)$ given by Eq. (34). Thus $M_c(p)$ is a superoperator for the spin system only. Therefore the problem as expressed by (35) reduces to the determination of the inverse of a finite matrix which can often be handled on a computer. However, the average of $M(p)$ cannot be performed before the stochastic modulation process is specified. In Secs. IV–VI we shall consider two specific examples for such stochastic processes.

IV. MODELS

A. Diffusion equation

Molecules in liquids undergo rotational Brownian motion. We assume that this motion is correctly described by a diffusion equation.[9,11,16] Let $\Psi(\phi\theta\psi,t)$ $=\Psi(\Omega, t)$ be the probability of finding the orientation Ω of the molecule-fixed frame with respect to the lab frame at time t. We assume the Debye model, in which the motion of a liquid molecule is described by that of a rigid sphere of radius a in a medium of viscosity η:

$$\frac{\partial \Psi}{\partial t} = \frac{D_s}{a^2} \nabla_\Omega^2 \Psi = D \nabla_\Omega^2 \Psi , \qquad (37)$$

where ∇_Ω^2 is the Laplacian operator on the surface of a unit sphere and the rotational diffusion constants D_s is assumed to be given by the Stokes formula

$$D_s = KT/6\pi a\eta , \qquad (38)$$

where K is the Boltzmann constant and T is the absolute temperature of the liquid. The generalization of Eq. (37) to include the case of anisotropic diffusion is straightforward.[16]

To carry out our theory described in Secs. II and III, we need the function $(\Omega_0|P(t)|\Omega)$, which is the probability that the molecule-fixed frame has the orientation Ω at time t when we know that it has the orientation Ω_0 at time zero.

$(\Omega_0|P(t)|\Omega)$ is the solution of Eq. (37) which satisfies the initial condition

$$\Psi(\Omega, 0) = \delta(\Omega - \Omega_0) . \qquad (39)$$

The solution of (37) can be written in terms of rotational matrices as[27,28]

$$(\Omega_0|P(t)|\Omega) = \sum_{l,m,n} \frac{2l+1}{8\pi^2} \mathfrak{D}_{mn}^{(l)*}(\Omega_0)\, \mathfrak{D}_{mn}^{(l)}(\Omega)\, e^{-Dl(l+1)t} , \qquad (40)$$

the Laplace transform [cf. Eq. (17)] of which is

$$(\Omega_0|P(p)|\Omega) = \sum_{l,m,n} \frac{2l+1}{8\pi^2}\, \frac{\mathfrak{D}_{mn}^{(l)*}(\Omega_0)\, \mathfrak{D}_{mn}^{(l)}(\Omega)}{p + Dl(l+1)} . \qquad (41)$$

If we use the fact [cf. Eq. (18)] that

$$\left(\frac{dP}{dt}\right)_{t=0} = W , \qquad (42)$$

we can, from Eq. (40), write for the elements of the W matrix

$$(\Omega_0|W|\Omega) = - \sum_{l,m,n} \frac{2l+1}{8\pi^2}\, Dl(l+1)\, \mathfrak{D}_{mn}^{(l)*}(\Omega_0)\, \mathfrak{D}_{mn}^{(l)}(\Omega) . \qquad (43)$$

Equation (43) can be easily verified if we make an expansion of (18) into a power series in Wt and use (43) to make a term-by-term comparison with Eq. (40). In this procedure, we have to use Eq. (30) and the following properties of the $\mathfrak{D}$ matrices[25]:

$$\sum_{l,m,n} \frac{2l+1}{8\pi^2}\, \mathfrak{D}_{mn}^{(l)*}(\Omega_0)\, \mathfrak{D}_{mn}^{(l)}(\Omega) = \delta(\Omega - \Omega_0) , \qquad (44)$$

$$\frac{2l+1}{8\pi^2} \int d\Omega\, \mathfrak{D}_{mn}^{(l)*}(\Omega)\, \mathfrak{D}_{m'n'}^{(l')}(\Omega) = \delta_{ll'}\,\delta_{mm'}\,\delta_{nn'} . \qquad (45)$$

Also using[25]

$$\int d\Omega\, \mathfrak{D}_{mn}^{(l)}(\Omega) = 8\pi^2\, \delta_{l0}\,\delta_{m0}\,\delta_{n0} , \qquad (46)$$

the probability conservation equation (19) is checked for the form (43) of the W matrix. Furthermore, for isotropic diffusion, the *a priori* probabilities in (12) are all equal:

$$p(\Omega_0) = 1/8\pi^2 . \qquad (47)$$

Thus the detailed balance condition (20) is also satisfied if we remember that[25]

$$\mathfrak{D}_{mn}^{(l)*}(\Omega) = (-1)^{m-n}\, \mathfrak{D}_{-m-n}^{(l)}(\Omega) \qquad (48)$$

and that the summations over m and n in Eq. (43) run from $-l$ to $+l$, where l is an integer.

B. Results up to fourth order in perturbation theory

In this section we work with the Hamiltonian given in Eqs. (1) and (2) and assume the diffusion equation introduced in Sec. IV A for the molecular motion in liquids. Our perturbation theory in the motionally narrowed limit will be seen to be good when the diffusion constant D is large compared to the matrix element of $\mathcal{K}_1$ [cf. Eq. (2)]. The diffusion constant D, however, could be comparable in magnitude to the eigenvalues of $\mathcal{K}_0$. This condition can be reasonably realized in the laboratory for small-sized molecules in low-viscosity liquids at moderate temperatures [cf. Eq. (38)]. Perturbation-theory calculations are performed in Appendixes A–C. Here we simply write the results.

From Eq. (35), we can write, up to fourth order in perturbation theory,

$$[u(p)]_{av} \cong \left(p\underline{1} - i\mathcal{K}_0^x - \sum_{k=1}^{4} M_c^{(k)}(p)\right)^{-1} , \qquad (49)$$

where $M_c^{(k)}$ is the expression for M_c in the kth order of perturbation $(k = 1, 2, 3, 4, \ldots)$.

1. First-order contribution

From Eqs. (36), (25), and (26), we have

$$M_c^{(1)}(p) = [\mathcal{Q}]_{\mathrm{av}} = i \sum_{l,m,n} V_{mn}^{(l)x} (\bar{\mathfrak{D}}_{mn}^{(l)*})_{\mathrm{av}}$$

$$= i \sum_{l,m,n} V_{mn}^{(l)x} \frac{1}{8\pi^2}$$

$$\times \int d\Omega_0 \, d\Omega \, (\Omega_0 | \bar{\mathfrak{D}}_{mn}^{(l)} | \Omega) ,$$

using (34) and (47); this equals

$$i \sum_{l,m,n} V_{mn}^{(l)x} \frac{1}{8\pi^2} \int d\Omega \, \mathfrak{D}_{mn}^{(l)*}(\Omega) ,$$

from Eq. (14), and equals 0, from Eqs. (46) and (7).

2. Second-order contribution

Equations (36) and (25) yield

$$M_c^{(2)}(p) = [\mathcal{Q} u^0(p) \mathcal{Q}]_{\mathrm{av}} . \tag{50}$$

Since, from Eq. (18), we have

$$P(p) = (p\underline{1} - W)^{-1} , \tag{51}$$

and we can write

$$u^0(p) = (p\underline{1} - W - i\mathcal{H}_0^x)^{-1} = P(p\underline{1} - i\mathcal{H}_0^x) , \tag{52}$$

because $\mathcal{H}_0^x$ acts like a number in the stochastic space. The matrix elements of $u^0(p)$ in the stochastic space are therefore given from Eqs. (41) and (52) by

$$(\Omega_0 | u^0(p) | \Omega) = \sum_{l,m,n} \frac{2l+1}{8\pi^2} \frac{\mathfrak{D}_{mn}^{(l)*}(\Omega_0) \, \mathfrak{D}_{mn}^{(l)}(\Omega)}{p\underline{1} - i\mathcal{H}_0^x + Dl(L+1)} . \tag{53}$$

Using Eqs. (50) and (53), we show in Appendix A that

$$M_c^{(2)}(p) = - \sum_{l,m,n} \frac{(-1)^{m-n}}{2l+1} V_{mn}^{(l)x}$$

$$\times [p\underline{1} - i\mathcal{H}_0^x + Dl(l+1)]^{-1} V_{-m-n}^{(l)x} . \tag{54}$$

3. Third-order contribution

$$M_c^{(3)}(p) = [\mathcal{Q} u^0(p) \, \mathcal{Q} u^0(p) \, \mathcal{Q}]_{\mathrm{av}}$$

$$= -i \sum_{\substack{l,m,n \\ l_1,m_1,n_1 \\ l_2,m_2,n_2}} V_{mn}^{(l)x} [p\underline{1} - i\mathcal{H}_0^x + Dl(l+1)]^{-1} V_{m_1 n_1}^{(l_1)x} [p\underline{1} - i\mathcal{H}_0^x + Dl_2(l_2+1)]^{-1} V_{m_2 n_2}^{(l_2)x} \begin{pmatrix} l & l_1 & l_2 \\ m & m_1 & m_2 \end{pmatrix} \begin{pmatrix} l & l_1 & l_2 \\ n & n_1 & n_2 \end{pmatrix} , \tag{55}$$

where the

$$\begin{pmatrix} l & l_1 & l_2 \\ m & m_1 & m_2 \end{pmatrix}$$

are the Wigner 3-j symbols. This is worked out in Appendix B.

4. Fourth-order contribution

From Eqs. (36) and (25), we have

$$M_c^{(4)}(p) = [\mathcal{Q} u^0(p) \, \mathcal{Q} u^0(p) \, \mathcal{Q} u^0(p) \, \mathcal{Q}]_{\mathrm{av}} - [\mathcal{Q} u^0(p) \, \mathcal{Q}]_{\mathrm{av}} (p\underline{1} - i\mathcal{H}_0^x)^{-1} [\mathcal{Q} u^0(p) \, \mathcal{Q}]_{\mathrm{av}}$$

$$= [\mathcal{Q} u^0(p) \, \mathcal{Q} u^0(p) \, \mathcal{Q} u^0(p) \, \mathcal{Q}]_{\mathrm{av}} - M_c^{(2)}(p) (p\underline{1} - i\mathcal{H}_0^x)^{-1} M_c^{(2)}(p) , \tag{56}$$

from Eq. (50). From Appendix C, we find

$$[\mathcal{Q} u^0(p) \, \mathcal{Q} u^0(p) \, \mathcal{Q} u^0(p) \, \mathcal{Q}]_{\mathrm{av}} = \sum_{\substack{l,m,n \\ l',m',n'}} \sum_{\substack{l'',m'',n'' \\ l_3,m_3,n_3}} \sum_{l_2 \neq 0, m_2, n_2} V_{mn}^{(l)x} [p\underline{1} - i\mathcal{H}_0^x + Dl(l+1)]^{-1} V_{m'n'}^{(l')x}$$

$$\times (2l_2 + 1)(-1)^{m_2 - n_2} [p\underline{1} - i\mathcal{H}_0^x + Dl_2(l_2+1)]^{-1} V_{m''n''}^{(l'')x}$$

$$\times [p\underline{1} - i\mathcal{H}_0^x + Dl_3(l_3+1)]^{-1} V_{m_3 n_3}^{(l_3)x}$$

$$\times \begin{pmatrix} l & l' & l_2 \\ m & m' & m_2 \end{pmatrix} \begin{pmatrix} l & l' & l_2 \\ n & n' & n_2 \end{pmatrix} \begin{pmatrix} l_2 & l'' & l_3 \\ m_2 & m'' & m_3 \end{pmatrix} \begin{pmatrix} l_2 & l'' & l_3 \\ n_2 & n'' & n_3 \end{pmatrix}$$

$$+ \sum_{l,m,n} \frac{(-1)^{m-n}}{2l+1} V_{mn}^{(l)x} [p\underline{1} - i\mathcal{H}_0^x + Dl(l+1)]^{-1} V_{-m-n}^{(l)x} [p\underline{1} - i\mathcal{H}_0^x]^{-1}$$

$$\times \sum_{l''m''n''} \frac{(-1)^{m''-n''}}{2l''+1} V_{m''n''}^{(l'')x} [p\underline{1} - i\mathcal{H}_0^x + Dl''(l''+1)]^{-1} V_{-m''-n''}^{(l'')x} , \tag{57}$$

where we have used[24]

$$\begin{pmatrix} l & l' & 0 \\ m & m' & 0 \end{pmatrix} = \begin{pmatrix} 0 & l & l' \\ 0 & m & m' \end{pmatrix} = \frac{(-1)^{l-m}}{(2l+1)^{1/2}} \delta_{ll'} \delta_{m-m'} \ . \tag{58}$$

Comparing Eqs. (54), (56), and (57), we find

$$M_c^{(4)}(p) = \sum_{\substack{l,m,n \\ l',m',n'}} \sum_{\substack{l'',m'',n'' \\ l_3,m_3,n_3}} \sum_{l_2 \neq 0, m_2, n_2} V_{mn}^{(l)x}[p\underline{1} - i\mathcal{K}_0^x + Dl(l+1)]^{-1} V_{m'n'}^{(l')x}[p\underline{1} - i\mathcal{K}_0^x + Dl_2(l_2+1)]^{-1} V_{m''n''}^{(l'')x}$$

$$\times [p\underline{1} - i\mathcal{K}_0^x + Dl_3(l_3+1)]^{-1} V_{m_3 n_3}^{(l_3)x} (2l_2+1)(-1)^{m_2-n_2}$$

$$\times \begin{pmatrix} l & l' & l_2 \\ m & m' & m_2 \end{pmatrix} \begin{pmatrix} l & l' & l_2 \\ n & n' & n_2 \end{pmatrix} \begin{pmatrix} l_2 & l'' & l_3 \\ m_2 & m'' & m_3 \end{pmatrix} \begin{pmatrix} l_2 & l'' & l_3 \\ n_2 & n'' & n_3 \end{pmatrix} . \tag{59}$$

Since in a resonance experiment we expect a resonance to occur near $P = i\omega_0$ (ω_0 is the eigenvalue of the Liouville operator $\mathcal{K}_0^x$), the terms involving $(p\underline{1} - i\mathcal{K}_0^x)^{-1}$ are the most divergent terms in a perturbation theory. However, as we have seen above, these most divergent terms get canceled out exactly in the higher-order terms.

In principle, we can carry out our calculation, if necessary, to still higher orders in perturbation theory. This, however, is tedious and we do not present it here.

V. ANALYSIS OF RESULTS: COMPARISON WITH THE THEORIES OF SILLESCU AND KIVELSON AND OF FREED

In this section, we analyze the results obtained in Sec. IV B. For illustrative purposes, we consider the Hamiltonian for g-tensor interaction discussed in Sec. II. Also, for simplicity, we assume that the molecular spin is $\frac{1}{2}$ ($S = \frac{1}{2}$). We find, from Eq. (7) that in $V_{mn}^{(l)}$, $l = 2$, $m = 1, 0, -1$, and $n = 0$.

A. Second-order contribution

Using Eqs. (54) and (7),

$$M_c^{(2)}(p) = -\frac{1}{30}(\Delta\omega)^2 \left[\frac{8}{3} S_z^x(p\underline{1} - i\overline{\omega}S_z^x + 6D)^{-1}S_z^x \right.$$
$$+ S_+^x(p\underline{1} - i\overline{\omega}S_z^x + 6D)^{-1}S_-^x$$
$$\left. + S_-^x(p\underline{1} - i\overline{\omega}S_z^x + 6D)^{-1}S_+^x \right], \tag{60}$$

where

$$\Delta\omega = \mu_B(g_{\shortparallel} - g_{\perp})H , \tag{61}$$

$$\overline{\omega} = \mu_B \overline{g} H . \tag{62}$$

If we confine our attention to the $\frac{1}{2} \to -\frac{1}{2}$ transition, the ESR line shape at high temperatures ($\rho \approx$ const) from Eq. (9) is given by[7] $(\frac{1}{2} - \frac{1}{2} | [u(p)]_{av} | \frac{1}{2} - \frac{1}{2})$, where up to second order in perturbation theory

$$[u(p)]_{av} \approx [p\underline{1} - i\overline{\omega}S_z^x - M_c^{(2)}(p)]^{-1} \tag{63}$$

[cf. Eq. (49)]. The matrix elements for $S = \frac{1}{2}$ Liouville operators are written in Ref. 7. For the sake of completeness, we list them here again.

A Liouville operator of the form

$$\mathcal{L} = aS_+^x + bS_-^x + cS_z^x ,$$

for $S = \frac{1}{2}$, has matrix elements

$$\begin{pmatrix} 0 & 0 & -b & a \\ 0 & 0 & b & -a \\ -a & a & c & 0 \\ b & -b & 0 & -c \end{pmatrix} . \tag{64}$$

The rows and columns in (64) are labelled by $+\frac{1}{2}+\frac{1}{2}$, $-\frac{1}{2}-\frac{1}{2}$, $+\frac{1}{2}-\frac{1}{2}$, and $-\frac{1}{2}+\frac{1}{2}$, respectively.

If we use Eq. (64), we can, after some straightforward algebra, write for the line shape

$$\varphi(\omega) \sim \mathrm{Re}(\tfrac{1}{2} - \tfrac{1}{2} |[u(p)]_{av}| \tfrac{1}{2} - \tfrac{1}{2})$$

$$\approx \mathrm{Re}\left(i(\omega - \overline{\omega}) + \frac{4(\Delta\omega)^2}{45[i(\omega - \overline{\omega}) + 6D]} \right.$$

$$\left. + \frac{(\Delta\omega)^2}{15(i\omega + 6D)} \right)^{-1} , \tag{65}$$

where we have set $p = i\omega$.

1. Bloch-Wangsness-Redfield and Kubo-Tomita theories

Since in Eq. (65) there is a resonance near $\omega = \overline{\omega}$, we can write, by the method of successive approximations,

$$\varphi(\omega) \approx \mathrm{Re}\left(i(\omega - \overline{\omega}) + \frac{4(\Delta\omega)^2}{45(6D)} + \frac{(\Delta\omega)^2}{15(i\overline{\omega} + 6D)} \right)^{-1} . \tag{66}$$

This yields a Lorentzian line centered around $\omega = \overline{\omega}$. The result (66) can also be obtained from the Bloch-Wangsness-Redfield[29,30] or Kubo-Tomita[31] general theories as applied to this special problem.

The secular terms in $V_{m0}^{(2)}$ (terms which commute with the unperturbed Hamiltonian $\mathcal{H}_0$) produce a contribution to the linewidth given by

$$T_{2(\text{sec})}^{-1} = \tfrac{4}{45}(\Delta\omega)^2/6D. \tag{67}$$

The nonsecular terms (those which do not commute with $\mathcal{H}_0$), on the other hand, give a width

$$T_{2(\text{nsec})}^{-1} = \tfrac{1}{15}(\Delta\omega)^2\, 6D/[(6D)^2 + (\bar{\omega})^2] \tag{68}$$

and a shift

$$k = (\bar{\omega}/6D)T_{2(\text{nsec})}^{-1}. \tag{69}$$

T_2 is the so-called transverse spin-lattice relaxation time.[3]

Equations (67)–(69) are identical to Eqs. (A1), (A11), and (A12), respectively, obtained by Sillescu and Kivelson.[11] [See also Eq. (6.2a) of Freed.[16]]

The secular width of the second-order line decreases as the relaxation rate $(= 6D)$ increases. This is the usual phenomenon of motional narrowing.[3] The nonsecular width, on the other hand, increases with the relaxation rate as long as $6D < \bar{\omega}$, shows a maximum when $6D = \bar{\omega}$, and then starts to decrease when $6D > \bar{\omega}$. This broadening of the line with the increase of the relaxation rate, however, does not show up in the actual spectrum, because the nonsecular contribution in this case is dominated by the secular narrowing effect.[7] In the completely motionally narrowed region $(6D \gg \bar{\omega})$ the total width becomes $\tfrac{7}{4}$ times the purely secular width. This is analogous to the " $\tfrac{10}{3}$ effect" for the linewidth first suggested in connection with exchange narrowing in electron resonance.[32]

2. Subsidiary line

The approximation indicated above in obtaining Eq. (66) is seen to yield a frequency-independent relaxation matrix $[M_c(\omega)$, in our notation]. This assumption, in the generalized cumulant method, is equivalent to going to the asymptotic limit $t \gg \tau_c$ (the relaxation time τ_c is $1/6D$ in our notation).[16] This, however, yields a Lorentzian line which does not have finite moments.[3] Freed shows in the cumulant method how the inclusion of finite-time effects introduces a subsidiary line on top of the main line.[16,20] The net effect is to produce a line which is not Lorentzian. In our theory, we work in the frequency space, which is the natural space to work in for line-shape problems. (This is not so in a time-differential experiment such as angular correlation of γ rays.[4]) Hence the relaxation matrix in our theory turns out to be explicitly frequency dependent. This frequency dependence, while not being effective near the central line $\omega = \bar{\omega}$ [cf. Eq. (65)], has the effect of subtracting out

some intensity from the wings of the main Lorentzian line. We shall demonstrate this below by obtaining the subsidiary line of Freed.

If we retain only the secular part, the second-order line shape, from Eq. (65), is given by

$$\varphi(\omega) = \text{Re}\, \frac{i(\omega - \bar{\omega}) + \tau_c^{-1}}{[i(\omega - \bar{\omega})]^2 + i\tau_c^{-1}(\omega - \bar{\omega}) + \Delta^2},$$

where we use Freed's notation in setting

$$\tfrac{4}{45}(\Delta\omega)^2 = \Delta^2 \quad \text{and} \quad 6D = \tau_c^{-1}.$$

We rearrange the above expression in the following form:

$$\varphi(\omega) = \text{Re}\left(\frac{\tfrac{1}{2}[1 + \tau_c^{-1}(\tau_c^{-2} - 4\Delta^2)^{-1/2}]}{i(\omega - \bar{\omega}) + \tfrac{1}{2}\tau_c^{-1} - \tfrac{1}{2}(\tau_c^{-2} - 4\Delta^2)^{1/2}}\right.$$
$$\left. + \frac{\tfrac{1}{2}[1 - \tau_c^{-1}(\tau_c^{-2} - 4\Delta^2)^{-1/2}]}{i(\omega - \bar{\omega}) + \tfrac{1}{2}\tau_c^{-1} + \tfrac{1}{2}(\tau_c^{-2} - 4\Delta^2)^{1/2}}\right)$$
$$\approx \text{Re}\left(\frac{1}{i(\omega - \bar{\omega}) + \Delta^2\tau_c} - \frac{\Delta^2\tau_c^2}{i(\omega - \bar{\omega}) + \tau_c^{-1}}\right), \tag{70}$$

since $\Delta^2\tau_c^2 \ll 1$ in the motionally narrowed regime;

$$\varphi(\omega) \approx \Delta^2\tau_c\left(\frac{1}{(\omega - \bar{\omega})^2 + (\Delta^2\tau_c)^2} - \frac{1}{(\omega - \bar{\omega})^2 + \tau_c^{-2}}\right). \tag{71}$$

The result (71) is identical to Eq. (2.28) of Freed[16] and can be interpreted as follows: The first term in (71) yields the main Lorentzian line centered around $\omega = \bar{\omega}$ and of width $\Delta^2\tau_c = T_2^{-1}$ [cf. Eq. (67)]. The second term, on the other hand, produces a very broad Lorentzian line of width τ_c^{-2}. The intensity of this subsidiary line is negative and very weak; its amplitude at resonance is only $\Delta^4\tau_c^4$ times that of the main line (or very small) [cf. Eq. (70)]. The ratio of the integrated intensities is, however, $\Delta^2\tau_c^2$. Thus the subsidiary line is actually a second-order correction to the main line. The effect of the subsidiary line in subtracting out some intensity from the wings of the main line has been pictorially demonstrated by Sillescu and Kivelson[11] (cf. their Fig. 2).

B. Third-order contribution

From Eqs. (55) and (7), we have

$$M_c^{(3)}(p) = -i\sum_{m, m_1, m_2} V_{m0}^{(2)x}(p\underline{1} - i\bar{\omega}S_z^x + 6D)^{-1}V_{m,0}^{(2)x}$$
$$\times (p\underline{1} - i\bar{\omega}S_z^x + 6D)^{-1}V_{m_20}^{(2)x}$$
$$\times \begin{pmatrix} 2 & 2 & 2 \\ m & m_1 & m_2 \end{pmatrix}\begin{pmatrix} 2 & 2 & 2 \\ 0 & 0 & 0 \end{pmatrix}.$$

Using[33]

$$\begin{pmatrix} 2 & 2 & 2 \\ 0 & 0 & 0 \end{pmatrix} = -(\tfrac{2}{35})^{1/2} \tag{72}$$

and the fact that

$$m + m_1 + m_2 = 0 , \tag{73}$$

we get

$$M_c^{(3)}(p) = i(\tfrac{2}{35})^{1/2} \sum_{m, m_1} V_{m0}^{(2)x} (p\underline{1} - i\overline{\omega}S_z^x + 6D)^{-1} V_{m_10}^{(2)x} \ (p\underline{1} - i\overline{\omega}S_z^x + 6D)^{-1} V_{-m-m_1,0}^{(2)x} \begin{pmatrix} 2 & 2 & 2 \\ m & m_1 & -(m+m_1) \end{pmatrix}.$$

From Eqs. (64) and (7), it follows that the matrix elements which make nonzero contributions to $(\tfrac{1}{2} - \tfrac{1}{2}|M_c^{(3)}(p)|\tfrac{1}{2} - \tfrac{1}{2})$ are given by

$$(\tfrac{1}{2} - \tfrac{1}{2}|M_c^{(3)}(p)|\tfrac{1}{2} - \tfrac{1}{2}) = i(\tfrac{2}{35})^{1/2}(\tfrac{1}{2} - \tfrac{1}{2}| \left[V_{00}^{(2)x} \frac{1}{p\underline{1} - i\overline{\omega}S_z^x + 6D} V_{00}^{(2)x} \frac{1}{p\underline{1} - i\overline{\omega}S_z^x + 6D} V_{00}^{(2)x} \begin{pmatrix} 2 & 2 & 2 \\ 0 & 0 & 0 \end{pmatrix} \right.$$

$$+ V_{-10}^{(2)x} \frac{1}{p\underline{1} - i\overline{\omega}S_z^x + 6D} \frac{1}{p\underline{1} - i\overline{\omega}S_z^x + 6D} V_{00}^{(2)x} \begin{pmatrix} 2 & 2 & 2 \\ -1 & 1 & 0 \end{pmatrix}$$

$$\left. + V_{00}^{(2)x} \frac{1}{p\underline{1} - i\overline{\omega}S_z^x + 6D} V_{-10}^{(2)x} \frac{1}{p\underline{1} - i\overline{\omega}S_z^x + 6D} V_{-10}^{(2)x} \begin{pmatrix} 2 & 2 & 2 \\ 0 & -1 & 1 \end{pmatrix} \right] |\tfrac{1}{2} - \tfrac{1}{2}).$$

Using (72) and[33]

$$\begin{pmatrix} 2 & 2 & 2 \\ -1 & 1 & 0 \end{pmatrix} = \begin{pmatrix} 2 & 2 & 2 \\ 0 & -1 & 1 \end{pmatrix} = (\tfrac{1}{70})^{1/2}$$

and Eqs. (7) and (64), we obtain

$$-(\tfrac{1}{2} - \tfrac{1}{2}|M_c^{(3)}(p)|\tfrac{1}{2} - \tfrac{1}{2}) = i\frac{2}{35 \times 27} (\Delta\omega)^3 \left(\frac{8}{(p - i\overline{\omega} + 6D)^2} + \frac{6}{p + 6D} \frac{1}{p - i\overline{\omega} + 6D} \right)$$

$$\cong i\frac{2(\Delta\omega)^3}{35 \times 27} \left(\frac{8}{(6D)^2} + \frac{6}{i\overline{\omega} + 6D} \frac{1}{6D} \right) , \tag{74}$$

since there is a resonance near $p = i\overline{\omega}$ (cf. Sec. VA);

$$-(\tfrac{1}{2} - \tfrac{1}{2}|M_c^{(3)}(p)|\tfrac{1}{2} - \tfrac{1}{2}) = \frac{i(2\sqrt{5})}{7} (6D)^{-1/2} T_{2(\text{sec})}^{-3/2} + \frac{2i}{7} \left(\frac{5}{6DT_{2(\text{sec})}} \right)^{1/2} (T_{2(\text{nsec})})^{-1} + \frac{2k}{7} \left(\frac{5}{6DT_{2(\text{sec})}} \right)^{1/2} , \tag{75}$$

using Eqs. (67)–(69). The first two terms in Eq. (75) yield the third-order line shift, and the third term gives the third-order contribution to the linewidth. A general feature of higher-order contributions is that a mixing between secular and nonsecular terms occurs, as is evident in Eq. (75). Equation (75) is identical to Eqs. (A6)–(A10) of Sillescu and Kivelson.[11] [Also, see Eq. (6.2b) of Freed.[16]]

C. Fourth-order contribution

The fourth-order contribution [cf. Eq. (59)] involves several terms, and the algebra, although straight-forward, becomes a bit messy. Thus instead of considering all the terms, we take into account the secular terms only in order to have a complete comparison with the theories of Sillescu and Kivelson and Freed.

From Eqs. (59) and (7) the fourth-order secular contribution is given by

$$M_{c(\text{sec})}^{(4)}(p) = \frac{(V_{00}^{(2)x})^4}{(p\underline{1} - i\mathcal{K}_0^\alpha + 6D)^2} \sum_{l_2 \neq 0} \left[(2l_2 + 1) \begin{pmatrix} 2 & 2 & l_2 \\ 0 & 0 & 0 \end{pmatrix}^4 \middle/ [p\underline{1} - i\mathcal{K}_0^\alpha + Dl_2(l_2 + 1)] \right] , \tag{76}$$

where we have used the symmetry properties of the 3-j symbols[33];

$$M_{c(\text{sec})}^{(4)}(p) = \frac{(V_{00}^{(2)x})^4}{(p\underline{1} - i\mathcal{K}_0^\alpha + 6D)^2} \left[5 \begin{pmatrix} 2 & 2 & 2 \\ 0 & 0 & 0 \end{pmatrix}^4 \middle/ (p\underline{1} - i\mathcal{K}_0^\alpha + 6D) + 9 \begin{pmatrix} 2 & 2 & 4 \\ 0 & 0 & 0 \end{pmatrix}^4 \middle/ (p\underline{1} - i\mathcal{K}_0^\alpha + 20D) \right] ,$$

where the triangle relations for the 3-j symbols have been used in concluding that only $l_2 = 2$ or 4 contributes to the summation in Eq. (76)[33];

$$M_{c(\text{sec})}^{(4)}(p) = \frac{16}{81} \frac{(\Delta\omega)^4 (S_z^x)^4}{(p\underline{1} - i\overline{\omega} S_z^x + 6D)^2} (\tfrac{2}{35})^2 \left(\frac{5}{p\underline{1} - i\overline{\omega} S_z^x + 6D} + \frac{9}{p\underline{1} - i\overline{\omega} S_z^x + 20D} \right),$$

using the tabulated values of the 3-j symbols.[33]   Therefore

$$- (\tfrac{1}{2} - \tfrac{1}{2} |M_{c(\text{sec})}^{(4)}(p)| \tfrac{1}{2} - \tfrac{1}{2}) = - \frac{4}{49} \frac{1}{(T_{2(\text{sec})})^2} \frac{(6D)^2}{(p - i\overline{\omega} + 6D)^2} \left(\frac{5}{p - i\overline{\omega} + 6D} + \frac{9}{p - i\overline{\omega} + 20D} \right), \tag{77}$$

using Eq. (67). The secular contributions up to fourth order [cf Eqs. (65), (74), and (77)] are found to be identical to Eqs. (5.18) of Yoon et al.[22]

If we consider secular interactions only, the line shape up to fourth order in perturbation theory is given from Eqs. (65), (67), (74), and (77) by

$$\varphi_{(\text{sec})}(\omega) \approx \left[i(\omega - \overline{\omega}) + \frac{1}{T_{2(\text{sec})}} \frac{6D}{i(\omega - \overline{\omega}) + 6D} \right.$$
$$\left. + \frac{i2\sqrt{5}}{7(T_{2(\text{sec})})^{3/2}} \frac{(6D)^{3/2}}{[i(\omega - \overline{\omega}) + 6D]^2} - \frac{4}{49} \frac{1}{(T_{2(\text{sec})})^2} \frac{6D}{[i(\omega - \overline{\omega}) + 6D]^2} \left(\frac{5}{i(\omega - \overline{\omega}) + 6D} + \frac{9}{i(\omega - \overline{\omega}) + 20D} \right) \right]^{-1}. \tag{78}$$

Now, $6D \gg (\omega - \overline{\omega})$ in the motionally narrowed limit. Thus we write

$$\frac{1}{i(\omega - \overline{\omega}) + 6D} \approx \frac{1}{6D} \left(1 - \frac{i(\omega - \overline{\omega})}{6D} - \frac{(\omega - \overline{\omega})^2}{(6D)^2} - \cdots \right). \tag{79}$$

When we substitute Eq. (79) into Eq. (78) we observe that there is a resonance near

$$i\omega \approx i\overline{\omega} - 1/T_{2(\text{sec})} + (\text{higher-order terms}).$$

Therefore we obtain by the method of successive approximations up to terms of order $(1/T_{2(\text{sec})})1/6DT_{2(\text{sec})}$

$$\varphi_{(\text{sec})}(\omega) \approx \left(i(\omega - \overline{\omega}) + \frac{1}{T_{2(\text{sec})}} + \frac{1}{T_{2(\text{sec})}} \frac{1}{6DT_{2(\text{sec})}} + \frac{i2\sqrt{5}}{7} \frac{1}{T_{2(\text{sec})}} \frac{1}{(6DT_{2(\text{sec})})^{1/2}} - \frac{22}{35} \frac{1}{T_{2(\text{sec})}} \frac{1}{6DT_{2(\text{sec})}} \right)^{-1}$$
$$= \left[i(\omega - \overline{\omega}) + \frac{1}{T_{2(\text{sec})}} \left(1 + \frac{i2\sqrt{5}}{7} \frac{1}{(6DT_{2(\text{sec})})^{1/2}} + \frac{13}{35} \frac{1}{6DT_{2(\text{sec})}} \right) \right]^{-1}. \tag{80}$$

Eq. (80) is identical to Eqs. (A5) and (A6) of Ref. 11 and Eq. (6.2c) of Ref. 16.

VI. STRONG COLLISION MODEL

In this model it is assumed that the molecule-fixed axes jump instantaneously from one orientation to another due to collisions, with a probability which does not depend on the initial or the final orientations before and after a jump.[6,23,24] This means that the jumps are completely uncorrelated and occur in angular steps of arbitrary size. This is in contrast to the rotational diffusion model, where the molecule reorients in small angular steps. While in the rotational diffusion model progress can only be made in perturbation theory in the regions of slow and fast relaxations,[10,11] the strong collision model, on the other hand, is exactly soluble for all values of the relaxation rate.

Oversimplified as it may seem, the strong collision model may actually, in some circumstances,

give a better description of molecular reorientational processes in liquids than the rotational diffusion model.[23,34] Also, in cases where the strong collision model is not strictly applicable, it can still serve a very useful role of providing an interpolation scheme for the line shape from slow to fast relaxation rates. The model has been treated in detail in Ref. 6 and here we simply apply the results of that paper to Eq. (22). The matrix W, in the strong collision model, can be expressed as

$$W = \lambda(\mathcal{J} - \underline{1}), \tag{81}$$

where λ is the relaxation rate (λ^{-1} measures the mean time between two successive jumps) and the matrix $\mathcal{J}$ is given by

$$(\Omega_0 |\mathcal{J}| \Omega) = 1/8\pi^2. \tag{82}$$

The special form of the transition matrix in Eq.

(82) enables us to perform the stochastic average in $[u(p)]_{av}$ exactly. It is given by

$$[u(p)]_{av} = G^0/(1 - \lambda G^0) , \tag{83}$$

where

$$G^0 = \frac{1}{8\pi^2} \int d\Omega \left[(p+\lambda)\underline{1} - i \left(\mathfrak{K}_0^x + \sum_{l,m,n} V_{mn}^{(l)x} \, \mathfrak{D}_{mn}^{(l)*}(\Omega) \right) \right]^{-1} , \tag{84}$$

is a quantum-mechanical superoperator for the resonating system alone and does not depend on the heat-bath variables.

The matrix G^0 in Eq. (82) can be obtained by inverting a finite matrix (4×4 in the case of g-tensor interaction for a spin-$\frac{1}{2}$ ion[7]) and by a numerical integration over the solid angle $d\Omega$. Equation (81) then yields the line shape for all values of λ.

Let us now examine the results predicted by Eqs. (81) and (82) in the regime of rapid relaxation (i.e., λ large compared to the eigenvalue of $V_{mn}^{(l)x}$ and compare them with the results of the rotational diffusion model. Such a perturbation expansion up to fourth order may be written[6]

$$[u(p)]_{av}^{-1} = (G^0)^{-1} - \lambda \approx p - i\mathfrak{K}_0^x + \sum_{\substack{l,m,n \\ l_1,m_1,n_1}} V_{mn}^{(l)x}[(p+\lambda)\underline{1} - i\mathfrak{K}_0^x]^{-1} V_{m_1 n_1}^{(l_1)x} \frac{1}{8\pi^2} \int d\Omega \, \mathfrak{D}_{mn}^{(l)*}(\Omega) \, \mathfrak{D}_{m_1 n_1}^{(l_1)*}(\Omega)$$

$$+ i \sum_{\substack{l,m,n \\ l_1,m_1,n_1 \\ l_2,m_2,n_2}} V_{mn}^{(l)x}[(p+\lambda)\underline{1} - i\mathfrak{K}_0^x]^{-1} V_{m_1 n_1}^{(l_1)x}[(p+\lambda)\underline{1} - i\mathfrak{K}_0^x]^{-1} V_{m_2 n_2}^{(l_2)x}$$

$$\times \int \frac{d\Omega}{8\pi^2} \mathfrak{D}_{mn}^{(l)*}(\Omega) \, \mathfrak{D}_{m_1 n_1}^{(l_1)*}(\Omega) \mathfrak{D}_{m_2 n_2}^{(l_2)*}(\Omega)$$

$$- \left(\sum_{\substack{l,m,n \\ l_1,m_1,n_1}} \sum_{\substack{l_2,m_2,n_2 \\ l_3,m_3,n_3}} V_{mn}^{(l)x}[(p+\lambda)\underline{1} - i\mathfrak{K}_0^x]^{-1} V_{m_1 n_1}^{(l_1)x}[(p+\lambda)\underline{1} - i\mathfrak{K}_0^x]^{-1} V_{m_2 n_2}^{(l_2)x}[(p+\lambda)\underline{1} - i\mathfrak{K}_0^x]^{-1} \right.$$

$$\left. \times V_{m_3 n_3}^{(l_3)x} \frac{1}{8\pi^2} \int d\Omega \, \mathfrak{D}_{mn}^{(l)*}(\Omega) \, \mathfrak{D}_{m_1 n_1}^{(l_1)*}(\Omega) \mathfrak{D}_{m_2 n_2}^{(l_2)*}(\Omega) \mathfrak{D}_{m_3 n_3}^{(l_3)*}(\Omega) \right.$$

$$- \sum_{\substack{l,m,n \\ l_1,m_1,n_1}} V_{mn}^{(l)x}[(p+\lambda)\underline{1} - i\mathfrak{K}_0^x]^{-1} V_{m_1 n_1}^{(l_1)x} \frac{1}{8\pi^2} \int d\Omega \, \mathfrak{D}_{mn}^{(l)*}(\Omega) \mathfrak{D}_{m_1 n_1}^{(l_1)*}(\Omega)$$

$$\times \sum_{\substack{l_2,m_2,n_2 \\ l_3,m_3,n_3}} V_{m_2 n_2}^{(l_2)x}[(p+\lambda)\underline{1} - i\mathfrak{K}_0^x]^{-1} V_{m_3 n_3}^{(l_3)x} \frac{1}{8\pi^2}$$

$$\times \int d\Omega' \, \mathfrak{D}_{m_2 n_2}^{(l_2)*}(\Omega') \, \mathfrak{D}_{m_3 n_3}^{(l_3)*}(\Omega') \right) . \tag{85}$$

Comparing this result with that of Sec. IV B, we find that up to the third order in perturbation theory the two models yield identical expressions if we set $\lambda = Dl(l+1)$, l being a fixed integer determined by the nature of interaction ($l = 2$, for example, in the g-tensor interaction problem). Since the rotational diffusion constant D is a parameter in the theory (to be determined by fitting the results to experimental data), this identification is not unreasonable.[23] The fourth- and higher-order terms are, however, different in the two models, as pointed out also by Lynden-Bell.[24]

The above analysis shows that although the strong collision model gives a much simplified picture of spin relaxation in liquids, its predictions are in accord with those of the rotational diffusion model in the motionally narrowed region.[23,24] They are also, on physical grounds, expected to be similar, at least qualitatively, in the slow-motion regime (when λ or D is very small). The actual physical mechanism of molecular reorientation in liquids may be expected to lie somewhere in between the two pictures painted by the rotational diffusion and the strong collision models. Since in the intermediate regime of relaxation perturbation theory fails and therefore the rotational diffusion model becomes untractable, the strong collision model

gives us some useful notions of what goes on in that region.

VII. SUMMARY

A stochastic theory model for magnetic resonance line shape is developed in this paper for describing molecular reorientational processes in liquids. The solution for the line shape, albeit obtained from a Hamiltonian picture, is found to be equivalent to the stochastic Liouville equation for a density matrix. The line shape is obtained in the frequency space. The advantages of working in the frequency space for magnetic resonance problems over other methods which are natural in the time domain are pointed out. The solution for the line shape, which is given in a matrix form, is found to be quite suitable for numerical as well as perturbation-theory calculations. We demonstrate this by developing a perturbation theory in the motionally narrowed regime. It is shown that the theory can be worked out to any desired order in perturbation.

Two different models for molecular motions in liquids are considered. In the first the molecules are assumed to undergo rotational Brownian motion, while in the second they are assumed to reorient through arbitrary angles after each collision. Although the physics of the two models are different, they are seen to yield identical results for the line shape in the fast-motion regime. The fact that the strong collision model is at least not qualitatively incorrect gives us a rather manageable handle on the theory in the intermediate regime of relaxation. For illustrative purposes, we consider the g-tensor interaction for molecular ions and compare our results with those obtained by other methods.

APPENDIX A

From Eqs. (36), (34), (25), (26), (30), and (14) we have

$$M_c^{(2)}(p) = [\mathcal{G}u^0(p)\mathcal{G}]_{av} = -\frac{1}{8\pi^2} \int d\Omega_0\, d\Omega \sum_{l,m,n} V_{mn}^{(l)x}\, \mathfrak{D}_{mn}^{(l)*}(\Omega_0)(\Omega_0|u^0(p)|\Omega) \sum_{l',m',n'} V_{m'n'}^{(l')x}\, \mathfrak{D}_{m'n'}^{(l')*}(\Omega)$$

$$= -\frac{1}{8\pi^2} \int d\Omega_0 \sum_{l,m,n} V_{mn}^{(l)x}\, \mathfrak{D}_{mn}^{(l)*}(\Omega_0) \sum_{l_1,m_1,n_1} \frac{2l_1+1}{8\pi^2} [p\underline{1} - i\mathfrak{K}_0^x + Dl_1(l_1+1)]^{-1} \mathfrak{D}_{m_1 n_1}^{(l_1)*}(\Omega_0)\, \mathfrak{D}_{m_1 n_1}^{(l_1)}(\Omega)$$

$$\times \sum_{l',m',n'} V_{m'n'}^{(l')x}\, \mathfrak{D}_{m'n'}^{(l')*}(\Omega),$$

from Eq. (53). Using Eqs. (48) and (45), we obtain

$$M_c^{(2)}(p) = -\sum_{l,m,n} \frac{(-1)^{m-n}}{2l+1} V_{mn}^{(l)x} [p\underline{1} - i\mathfrak{K}_0^x + Dl(l+1)]^{-1} V_{-m-n}^{(l)x}. \tag{A1}$$

APPENDIX B

From Eqs. (36), (34), (25), (26), (30), and (14), we obtain

$$M_c^{(3)}(p) = [\mathcal{G}u^0(p)\mathcal{G}u^0(p)\mathcal{G}]_{av}$$

$$= -\frac{i}{8\pi^2} \int d\Omega_0\, d\Omega\, d\Omega_1 \sum_{l,m,n} V_{mn}^{(l)x}\mathfrak{D}_{mn}^{(l)*}(\Omega_0)(\Omega_0|u^0(p)|\Omega_1) \sum_{l',m',n'} V_{m'n'}^{(l')x}\mathfrak{D}_{m'n'}^{(l')*}(\Omega_1)(\Omega_1|u^0(p)|\Omega)$$

$$\times \sum_{l'',m'',n''} V_{m''n''}^{(l'')x}\mathfrak{D}_{m''n''}^{(l'')*}(\Omega)$$

$$= -\frac{i}{8\pi^2} \int d\Omega_0\, d\Omega\, d\Omega_1 \sum_{l,m,n} V_{mn}^{(l)x} \mathfrak{D}_{mn}^{(l)*}(\Omega_0) \sum_{l_1,m_1,n_1} \frac{2l_1+1}{8\pi^2} [p\underline{1} - i\mathfrak{K}_0^x + Dl_1(l_1+1)]^{-1} \mathfrak{D}_{m_1 n_1}^{(l_1)*}(\Omega_0)\mathfrak{D}_{m_1 n_1}^{(l_1)}(\Omega_1)$$

$$\times \sum_{l',m',n'} V_{m'n'}^{(l')x}\mathfrak{D}_{m'n'}^{(l')*}(\Omega_1)$$

$$\times \sum_{l_2,m_2,n_2} \frac{2l_2+1}{8\pi^2} [p\underline{1} - i\mathfrak{K}_0^x + Dl_2(l_2+1)]^{-1}$$

$$\times \mathfrak{D}_{m_2 n_2}^{(l_2)*}(\Omega_1)\mathfrak{D}_{m_2 n_2}^{(l_2)}(\Omega)$$

$$\times \sum_{l'',m'',n''} V_{m''n''}^{(l'')x}\mathfrak{D}_{m''n''}^{(l'')*}(\Omega),$$

from Eq. (53);

$$M_c^{(3)}(p) = -\frac{i}{8\pi^2} \int d\Omega_1 \sum_{l,m,n} (-1)^{m-n} V_{mn}^{(l)x} \mathfrak{D}_{-m-n}^{(l)}(\Omega_1) [p\underline{1} - i\mathfrak{K}_0^x + Dl(l+1)]^{-1}$$

$$\times \sum_{l',m',n'} V_{m'n'}^{(l')x} \mathfrak{D}_{m'n'}^{(l')*}(\Omega_1) \sum_{l_2,m_2,n_2} \mathfrak{D}_{m_2n_2}^{(l_2)*}(\Omega_1) [p\underline{1} - i\mathfrak{K}_0^x + Dl_2(l_2+1)]^{-1} V_{m_2n_2}^{(l_2)x} ,$$

from Eqs. (48) and (45).

Using Eq. (48) and the relation[33]

$$\frac{i}{8\pi^2} \int d\Omega\, \mathfrak{D}_{m_1n_1}^{(l_1)}(\Omega) \mathfrak{D}_{m_2n_2}^{(l_2)}(\Omega) \mathfrak{D}_{m_3n_3}^{(l_3)}(\Omega) = \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l_3 \\ n_1 & n_2 & n_3 \end{pmatrix} , \tag{B1}$$

we finally obtain for $M_c^{(3)}(p)$ the expression given by Eq. (55).

APPENDIX C

In the expression for $M_c^{(4)}(p)$ in Eq. (56), we obtain the term

$$[\mathfrak{G}u^0(p)\mathfrak{G}u^0(p)\mathfrak{G}u^0(p)\mathfrak{G}]_{av}$$

$$= \frac{1}{8\pi^2} \int d\Omega_0\, d\Omega\, d\Omega_1\, d\Omega_2 \sum_{l,m,n} V_{mn}^{(l)x} \mathfrak{D}_{mn}^{(l)*}(\Omega_0)(\Omega_0 | u^0(p) | \Omega_1) \sum_{l',m',n'} V_{m'n'}^{(l')x} \mathfrak{D}_{m'n'}^{(l')*}(\Omega_1)(\Omega_1 | u^0(p) | \Omega_2)$$

$$\times \sum_{l'',m'',n''} V_{m''n''}^{(l'')x} \mathfrak{D}_{m''n''}^{(l'')*}(\Omega_2)(\Omega_2 | u^0(p) | \Omega) \sum_{l''',m''',n'''} V_{m'''n'''}^{(l''')x} \mathfrak{D}_{m'''n'''}^{(l''')*}(\Omega)$$

$$= \frac{1}{8\pi^2} \int d\Omega_0\, d\Omega\, d\Omega_1\, d\Omega_2$$

$$\times \sum_{l,m,n} V_{mn}^{(l)x} \mathfrak{D}_{mn}^{(l)*}(\Omega_0)$$

$$\times \sum_{l_1,m_1,n_1} \frac{2l_1+1}{8\pi^2} [p\underline{1} - i\mathfrak{K}_0^x + Dl_1(l_1+1)]^{-1} \mathfrak{D}_{m_1n_1}^{(l_1)*}(\Omega_0) \mathfrak{D}_{m_1n_1}^{(l_1)}(\Omega_1)$$

$$\times \sum_{l',m',n'} V_{m'n'}^{(l')x} \mathfrak{D}_{m'n'}^{(l')*}(\Omega_1) \sum_{l_2,m_2,n_2} \frac{2l_2+1}{8\pi^2} \mathfrak{D}_{m_2n_2}^{(l_2)*}(\Omega_1) \mathfrak{D}_{m_2n_2}^{(l_2)}(\Omega_2) [p\underline{1} - i\mathfrak{K}_0^x + Dl_2(l_2+1)]^{-1}$$

$$\times \sum_{l'',m'',n''} V_{m''n''}^{(l'')x} \mathfrak{D}_{m''n''}^{(l'')*}(\Omega_2)$$

$$\times \sum_{l_3,m_3,n_3} \frac{2l_3+1}{8\pi^2} \mathfrak{D}_{m_3n_3}^{(l_3)*}(\Omega_2) \mathfrak{D}_{m_3n_3}^{(l_3)}(\Omega)$$

$$\times [p\underline{1} - i\mathfrak{K}_0^x + Dl_3(l_3+1)]^{-1}$$

$$\times \sum_{l''',m''',n'''} V_{m'''n'''}^{(l''')x} \mathfrak{D}_{m'''n'''}^{(l''')*}(\Omega) ,$$

from Eq. (53).

If we use Eqs. (48) and (45) in the above expression, we obtain

$$[\mathfrak{G}u^0(p)\mathfrak{G}u^0(p)\mathfrak{G}u^0(p)\mathfrak{G}]_{av}$$

$$= \frac{1}{8\pi^2} \int d\Omega_1 d\Omega_2 \sum_{l,m,n} (-1)^{m-n} V_{mn}^{(l)x} \mathfrak{D}_{-m-n}^{(l)}(\Omega_1) [p\underline{1} - i\mathfrak{K}_0^x + Dl(l+1)]^{-1}$$

$$\times \sum_{l',m',n'} V_{m'n'}^{(l')x} \mathfrak{D}_{m'n'}^{(l')*}(\Omega_1) \sum_{l_2,m_2,n_2} \frac{2l_2+1}{8\pi^2} \mathfrak{D}_{m_2n_2}^{(l_2)*}(\Omega_1) \mathfrak{D}_{m_2n_2}^{(l_2)}(\Omega_2) [p\underline{1} - i\mathfrak{K}_0^x + Dl_2(l_2+1)]^{-1}$$

$$\times \sum_{l'',m'',n''} V_{m''n''}^{(l'')x} \mathfrak{D}_{m''n''}^{(l'')*}(\Omega_2)$$

$$\times \sum_{l_3,m_3,n_3} \mathfrak{D}_{m_3n_3}^{(l_3)*}(\Omega_2) [p\underline{1} - i\mathfrak{K}_0^x + Dl_3(l_3+1)]^{-1} V_{m_3n_3}^{(l_3)x} .$$

This, together with Eq. (B1), yields Eq. (57).

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