SPIN-INTERNAL-ROTATION INTERACTION
AND
RELAXATION OF NUCLEAR SPIN ON AN INTERNAL ROTOR

Thesis by

Jo Woong Lee

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To My Mother

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ABSTRACT

A magnetic nucleus located on an internal top can interact with the magnetic fields arising from the internal rotation as well as overall molecular rotation. The coupling Hamiltonian for this kind of magnetic nuclei has been derived following the method of Van Vleck for the spin-rotation interaction in rigid molecules. It is shown that the Hamiltonian for this problem may be written

$$\mathcal{H}_{S-R} = -\sum_{K} \vec{I}_K \cdot \underset{\sim}{C}^{(J)}(K) \cdot \vec{J} - \sum_{K} \vec{I}_K \cdot \underset{\sim}{D}^{(j)}(K) \cdot \vec{j} \quad ,$$

where the first term is the ordinary spin-rotation interaction and the second term arises from the spin-internal-rotation coupling. When the internal rotation is very fast compared with the overall rotation, it is shown that the effective spin-rotation Hamiltonian takes the approximate form

$$\mathcal{H}_{S-R} = -\vec{F} \cdot \underset{\sim}{C}^{(J)} \cdot \vec{J} - D_{\alpha}^{(j)} F \cdot \vec{j} \quad ,$$

where $\vec{F} = \sum_{K} \vec{I}_K$, $\underset{\sim}{C}^{(J)}$ is the effective spin-rotation coupling tensor, and $D_{\alpha}^{(j)}$ is a constant.

On the basis of this coupling model, an analytic expression of T_1, the spin-lattice relaxation time, for ^{19}F spins in ϕ-CF_3-type molecules has been derived and the effect of an internal barrier is discussed.

A physical model of molecular rotation in ϕ-CF_3-type molecules in their liquid state is proposed and temperature dependence of ^{19}F spin-lattice relaxation time is explained in terms of this model.

It seems that the rotation of the internal top ($-CF_3$) about its symmetry axis is inertial while rotations of the entire molecule can be described better by the diffusion model.

Thus, the temperature dependence of the internal rotation is likely to be different from that for the end-over-end rotation of entire molecule. Burke has successfully shown that the temperature dependence of fluorine spin-lattice relaxation time in benzotrifluoride can be interpreted in terms of the above model.

A more complete and quantitative theory of the nuclear spin relaxation via the spin-rotation interaction in the presence of internal rotation is developed and Hubbard's treatment is generalized for non-spherical molecules with internal rotors.

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CHAPTER I

INTRODUCTION

1.1 Spin-Rotation Interaction in Polyatomic Molecules

When a molecule rotates about its center of mass, the motion of its nuclear and electronic charges produce magnetic fields. The interaction between the nuclear magnetic moment and the thus produced magnetic fields was first indicated by Van Vleck,[1] and his suggestion was mathematically formulated by Foley[2] and Wick.[3] In his theory Wick has assumed that the interaction arises exclusively from the magnetic field which results from the circulation of electric charges of nuclei and electrons in the rotating molecules.

Although this assumption is approximately valid, it has been pointed out by Ramsey[4] that an appreciable correction is required when the effects of acceleration of the nucleus are considered. One of the corrections concerns the fact that the acceleration of the nucleus in the molecule is caused by an electric field and the moving nuclear magnetic moment interacts with this field. The other concerns the so-called Thomas precession.

The interaction between the thus produced magnetic fields and the nuclear magnetic moment is averaged over the electronic and vibrational states, since electronic and vibrational motions are much faster than rotational motions in a molecule.

The resulting spin-rotation coupling may be detected in the spectroscopy of either the nuclear spin (in a molecular beam resonance[5, 6]) or the molecular rotation (in a microwave spectrum[7, 8]). In a gaseous or liquid phase the rotational states of molecules constantly change because of incessant intermolecular collisions, and as a result the spin-rotation interaction energy also fluctuates. Thus the spin-rotation interaction can be an important mechanism for nuclear spin relaxation both in gaseous and liquid phases. Some experimental results have given indirect evidence for this mechanism,[9-13] but lack of knowledge about spin-rotation constants for many of the molecules studied so far has made firm conclusions difficult to obtain.

In spite of this defect, studies of spin-rotation interactions are very important since they can provide much information about molecular rotation and intermolecular collision processes. The rotation of molecules in liquids has been studied for a number of years by spectroscopic band shape, and by dielectric and magnetic resonance measurements. Nuclear magnetic resonance provides a convenient probe for the study of the molecular rotations in liquids since the nuclear spin relaxation times are dependent on the details of molecular motion. Measurement of NMR relaxation times has given useful information on molecular reorientation.[14-20]

1.2 Importance of the Spin-Rotation Interaction as a Spin Relaxation Mechanism

Since the spin-rotation interaction arises from the rotational motion of a molecule, its effectiveness as a spin relaxation mechanism will depend on how strong this interaction is and how rapidly the rotational states of a molecule fluctuate in gases or liquids. For example,[21] in H_2 the spin-rotation contribution to $(1/T_1)$ is only one third of the dipole-dipole contribution at room temperature, while for F_2 the dipole-dipole contribution is negligibly small compared with the spin-rotation contribution at the same temperature. Therefore it is expected that the spin-rotation interaction plays a more important role in the ^{19}F spin relaxation than in the case of proton spins.

Brown, Gutowsky, and Shimomura[22] found that the spin-rotation interaction is quite effective as a spin relaxation mechanism even in liquid phase. They measured the spin-lattice relaxation times both for the protons and ^{19}F nucleus in liquid CH_2FCl at several different temperatures. They discovered that both $(1/T_1)_F$ and $(1/T_1)_H$ are independent of the strength of applied static magnetic field but show different temperature dependences. At low temperatures both $(1/T_1)_F$ and $(1/T_1)_H$ decrease with increasing temperature; however, at high temperatures $(1/T_1)_F$ shows a positive slope while $(1/T_1)_H$ continues to fall as temperature rises.

In order to interpret their experimental results, Brown *et al.* carefully examined several relaxation mechanisms such as dipole-dipole interactions, quadrupolar effects, and the anisotropic chemical shift.[22] They concluded that none of three relaxation mechanisms mentioned above could provide satisfactory explanations for different temperature dependences of $(1/T_1)_F$ and $(1/T_1)_H$ at high temperatures. Thus, Brown *et al.* assumed that the spin-rotation interaction is a dominant relaxation mechanism for ^{19}F spin at high temperature and proposed a transient rotation model for molecular rotation in liquid phase. In terms of this model they could predict the correct, though qualitatively right, temperature dependence of $(1/T_1)_F$ at high temperatures. Similar effects have been observed by Powles and Green[24] in fluorobenzene and by Rugheimer and Hubbard[25] in CF_4.

Powles[13, 26] has studied the temperature dependence of the proton relaxation time of both the ring and side group protons in toluene, p-xylene, mesitylene, p-fluorotoluene, and ethylbenzene. From the melting point to the critical temperature the ring protons in all the compounds exhibit decreasing $(1/T_1)$ with increasing temperature characteristic of pure dipolar relaxation. However the sidegroup protons in all the compounds except ethylbenzene show decreasing $(1/T_1)$'s from the melting point to about 100° C where they have a minimum of about 0.10-0.13 sec^{-1} and then increase with increasing temperature. In ethylbenzene the $(1/T_1)$'s of both the $-CH_2$ and $-CH_3$ protons decrease continuously up to about 200° C where they are about 0.05 sec^{-1}.

These observations can be ascribed to the operation of the spin-rotation mechanism in the methyl group relaxation at high temperature. If this is the case, then we ask, 'Why does the spin-rotation interaction operate for the relaxation of protons of methyl group while it is relatively ineffective for the protons in the ring and ethyl group?' It is considered that the correct answer for this question lies in the fact that manners in which the methyl group and the ring and ethyl group undergo reorientation in liquids are different. In liquids the small and highly symmetric methyl group is supposed to rotate with relatively definite angular momentum between two successive intermolecular collisions while the larger and bulkier ring and ethyl group undergo diffusional rotations because of severe frictional forces due to neighboring molecules.

Although the detailed description of the phenomenon goes beyond the scope of this introductory chapter, we are going here to give a brief discussion of the matter to emphasize the importance of spin-rotation interaction as a spin relaxation mechanism.

For the convenience of discussion we assume that there are only two relaxation mechanisms, dipole-dipole interactions and spin-rotation interactions, which are the most important mechanisms in many cases. For simplicity imagine a system which is composed of two identical spins with distance between them fixed. For this system it is well-known that[27]

$$(1/T_1)_{\text{spin-rotation}} = A\,kT\,\tau_J \qquad (1.2\text{-}1)$$

and

$$(1/T_1)_{\text{dipole-dipole}} = B\,\tau_2 \qquad (1.2\text{-}2)$$

where τ_2 is the orientation correlation time and τ_J is the angular momentum correlation time. It should be kept in mind that the spin-rotation interaction depends only on the angular velocity (or momentum) of molecular rotation while other mechanisms such as dipole-dipole interactions, quadrupolar effects, and the anisotropic chemical shift are governed by the molecular orientation only. In a viscous liquid a molecule will rotate more and more freely as temperature rises, thus making τ_J longer. On the other hand, τ_2 will be shortened since the orientation of the molecule will change more and more frequently as temperature becomes higher. Therefore we are easily convinced that from Eqs. (1.2-1) and (1.2-2) $(1/T_1)_{S-R}$ will increase with increasing temperature while $(1/T_1)_{d-d}$ decreases. Of course these explanations are quite crude and qualitative. Exact answers should come from a detailed study of molecular dynamics which we will see in the next several chapters. The weight of importance of these two mechanisms are also dependent on the proportional constants A and B in Eqs. (1.2-1) and (1.2-2). It is well-known that in many liquids the angular momentum correlation times are much shorter than the orientation correlation times in wide range of temperature. In this case if the term AkT is of magnitude comparable to B, then the dipole-dipole interaction plays a dominant role in the spin relaxation as we see from Eqs. (1.2-1) and (1.2-2), which is the case for the protons of phenyl ring in many toluene derivatives. However, in some cases the term AkT is so large that the spin-rotation interaction completely dominates the relaxation process, which is the case for many liquids of fluorine compounds. In toluene small and highly symmetric methyl group is supposed to rotate relatively freely between intermolecular collisions. In this case the orientation correlation time is not much longer than the angular momentum correlation time. Moreover, as we shall see later, the spin rotation constant for internal rotation is larger than that for end-over-end molecular rotation, so that the spin-rotation mechanism is much more effective for the relaxation of sidegroup protons than of ring protons. Therefore, it is not surprising that the effect of spin-rotation mechanism shows up at high temperatures in the sidegroup protons.

In gases and in some nonviscous liquids such as liquid methane, all molecules apparently rotate with relatively definite angular momenta between intermolecular collisions. In this case τ_J should decrease with increasing temperature since the lifetime for a particular rotational state is shortened by increase of collision frequency. In this sense the analysis of spin-rotation contribution to $(1/T_1)$ can provide an important method for studying the rotational motion of molecules in liquids.

1.3 Spin-Rotation Interaction in the Presence of Internal Rotation

In the absence of internal rotation the spin-rotation interaction in the molecule-fixed frame can be written[28]

$$\mathcal{H}_{S-R} = -\vec{I}\cdot \underset{\frown}{C} \cdot \vec{J} \qquad (1.3\text{-}1)$$

where $\vec{I}$ is the spin angular momentum operator of the nucleus, $\underset{\frown}{C}$ is the spin-rotation tensor, and $\vec{J}$ is the rotational angular momentum of the molecule. Recently Dubin and Chan[29] indicated that a magnetic nucleus located on an internal rotor is not only coupled to the rotational magnetic field generated by end-over-end rotation of the molecule but is also coupled to the magnetic field produced by internal rotation of the top relative to the frame. This spin-internal-rotation coupling can be quite important, since the rotational magnetic field per unit angular momentum is always larger for internal rotation than for end-over-end molecular rotation. However, as the internal barrier becomes higher, the effect of this coupling on the spin-lattice relaxation will be less important, because as the height of barrier increases the internal motion of the top will be of more and more torsional character. In the case of benzotrifluoride it is supposed that the CF_3 group can rotate relatively freely[30, 31] with respect to the phenyl ring and therefore the nuclear spin-internal-rotation coupling must be included in the spin-rotation interaction Hamiltonian to correctly analyze the spin relaxation time data.

Thus, in the presence of internal rotation not only the modulation of total rotational angular momentum but also the modulation of internal rotational angular momentum should be taken into account. Green and Powles[13] and Faulk and Eisner[32] have measured the ^{19}F spin-lattice relaxation time in benzotrifluoride. Especially Faulk and Eisner attempted to interpret their experimental results in terms of the spin-overall-rotation interaction alone. However, the neglect of the importance of spin-internal-rotation interaction made their interpretations look unappropriate.

Burke[33] has shown that at room temperature the spin-internal-rotation is the dominant relaxation mechanism for ^{19}F spins in ϕ-CF_3 and thus cannot be ignored. Furthermore he has demonstrated that the contribution of the spin-overall-rotation interaction increases with increasing temperature more rapidly than that of the spin-internal-rotation interaction. As we shall see later, this difference in temperture dependences is due to the fact that the overall rotational motion of

ϕ-CF_3 molecule in liquid can be better described in terms of the diffusion-type model than the inertial-type model while the internal rotational motion of the CF_3 top is of more inertial character. If the internal rotation is of diffusional character, the spin-internal-rotation contribution to $(1/T_1)$ should increase with temperature as rapidly as the spin-overall-rotation contribution. The inertial character of internal rotation of the CF_3 top is probably due to its symmetry about the axis of internal rotation. A similar example was given by Moniz, Steele and Dixon[17] in monosubstituted methanes. On the other hand, rotations about other axes perpendicular to the molecular symmetry axis suffer severe frictional forces as shown by Shimizu.[34] Therefore it is supposed that the end-over-end rotational motion in ϕ-CF_3 can be described better by the diffusion-type model than by the inertial-type model. We will not go into further details of the problem here and postpone the discussion of dynamical processes which modulate the spin-rotation interaction in liquids until Chapter IV.

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CHAPTER II

HAMILTONIAN OF SPIN-ROTATION INTERACTION IN THE PRESENCE OF INTERNAL ROTATION

As we have mentioned earlier, we have to include the spin-internal-rotation interaction in discussing the relaxation of a nuclear spin on an internal rotor. When a molecule rotates, the rotational motion perturbs the electron cloud around the molecule and this perturbing effect can be expressed as a coupling between the rotational angular momentum and the electronic orbital angular momentum. This coupling effect accounts for the greater part of the spin-rotation interaction in a molecule and can be mathematically formulated by the method of Van Vleck.[1] In order to apply the method of Van Vleck to our problem we first need to derive the Hamiltonian for the rotational motion of a polyatomic molecule with a symmetric internal rotor. A conventional way to obtain a quantum mechanical Hamiltonian is to replace dynamical variables in the classical Hamiltonian by corresponding quantum mechanical operators. Therefore we will first derive the classical kinetic energy expression for a molecule with a symmetric internal rotor. Then we will discuss the operator equivalent of classical angular momentum.

2.1 Classical Kinetic Energy Expression

The rotational Hamiltonian for a rotating frame with a symmetric top which can undergo its own internal rotational motion has been given by Wilson[2] and Lin,[3] but for a more general treatment we will review here their derivation of the rotational Hamiltonian.

Consider a rotating frame with a symmetric internal rotor which can rotate more or less freely about its own axis with respect to the frame.

As shown in Fig. 1, we pick the origin at the center of mass of the entire molecule and define $\vec{r}_i$, $\vec{r}_j$, m_i, m_j, $\vec{\sigma}_j$, and $\vec{\mu}$ as follows:

m_i = a mass point on the frame with mass m_i;
m_j = a mass point on the top whose mass is m_j;
$\vec{r}_i$ = position vector of m_i with respect to the origin;
$\vec{r}_j$ = position vector of m_j with respect to the same origin;
$\vec{\sigma}_j$ = position vector of m_j with respect to the center of mass of the internal top;

and

$\vec{\mu}$ = position vector of the center of mass of the internal top with respect to the origin 0.

From the above definitions we have

$$\vec{r}_j = \vec{\mu} + \vec{\sigma}_j \quad . \tag{2.1-1}$$

The rotational kinetic energy for the system can be written as

$$T = (1/2) \sum_i m_i \dot{\vec{r}}_i \dot{\vec{r}}_i + (1/2) \sum_j m_j \dot{\vec{r}}_j \dot{\vec{r}}_j \quad . \tag{2.1-2}$$

We will describe the internal rotation of the top about its symmetry axis by an angle variable, α. And let $\vec{\omega}$ be the angular velocity

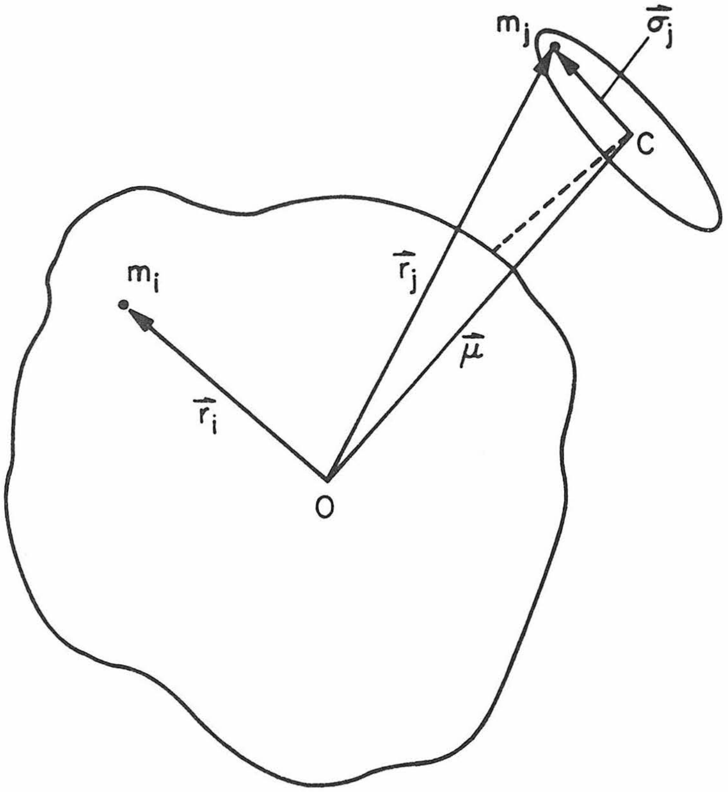


Fig. I A Rotating Body with a Symmetric Top of the overall rotation. Then

$$\dot{\vec{r}}_i = \vec{\omega} \times \vec{r}_i \tag{2.1-3}$$

and

$$\dot{\vec{r}}_j = \vec{\omega} \times \vec{r}_j + \dot{\vec{\alpha}} \times \vec{\sigma}_j \quad . \tag{2.1-4}$$

Substituting (2.1-3) and (2.1-4) in (2.1-2) and using the vector identity

$$(\vec{A} \times \vec{B}) \cdot (\vec{C} \times \vec{D}) = (\vec{A} \cdot \vec{C})(\vec{B} \cdot \vec{D}) - (\vec{A} \cdot \vec{D})(\vec{B} \cdot \vec{C}) \quad , \tag{2.1-5}$$

we obtain

$$\begin{aligned} T &= (1/2) \sum_i m_i (\vec{\omega} \times \vec{r}_i)^2 + (1/2) \sum_j m_j [(\vec{\omega} \times \vec{r}_j) + (\dot{\vec{\alpha}} \times \vec{\sigma}_j)]^2 \\ &= (1/2) \sum_i m_i [\omega^2 r_i^2 - (\vec{\omega} \cdot \vec{r}_i)^2] + (1/2) \sum_j m_j [\omega^2 r_j^2 - (\vec{\omega} \cdot \vec{r}_j)^2] \\ &+ (1/2) \sum_j m_j [\dot{\alpha}^2 \sigma_j^2 - (\vec{\sigma}_j \cdot \dot{\vec{\alpha}})^2] \\ &+ (1/2) \sum_j m_j [(\vec{\omega} \times \vec{r}_j) \cdot (\dot{\vec{\alpha}} \times \vec{\sigma}_j) + (\dot{\vec{\alpha}} \times \vec{\sigma}_j) \cdot (\vec{\omega} \times \vec{r}_j)] \quad . \end{aligned} \tag{2.1-6}$$

Let us consider the physical meanings of the terms on the right-hand side of Eq. (2.1-6). The first two terms represent the overall rotational energy of the system and may be rewritten as $(1/2)\, \vec{\omega}^{+} \cdot \underset{\wedge}{I} \cdot \vec{\omega}$, where $\underset{\wedge}{I}$ is the inertia tensor of the system. The third term describes the internal rotational energy of the top and may be condensed to $(1/2)\, \dot{\vec{\alpha}}^{+} \cdot \underset{\wedge}{I}_{\alpha} \cdot \dot{\vec{\alpha}}$, where $\underset{\wedge}{I}_{\alpha}$ is the inertia tensor of the internal top. We can also show that the last term may be abbreviated to

$(1/2)\,(\vec{\omega}^{+} \cdot \underset{\wedge}{I}_{\alpha} \cdot \dot{\vec{\alpha}} + \dot{\vec{\alpha}}^{+} \cdot \underset{\wedge}{I}_{\alpha} \cdot \vec{\omega})$, which represents the coupling between the overall and internal rotations.

Thus, the kinetic energy T takes the form

$$T = (1/2)\,\vec{\omega}^{+} \cdot \underset{\wedge}{I} \cdot \vec{\omega} + (1/2)\,\dot{\vec{\alpha}}^{+} \cdot \underset{\wedge}{I}_{\alpha} \cdot \dot{\vec{\alpha}} + (1/2)\,(\vec{\omega}^{+} \cdot \underset{\wedge}{I}_{\alpha} \cdot \dot{\vec{\alpha}} + \dot{\vec{\alpha}}^{+} \cdot \underset{\wedge}{I}_{\alpha} \cdot \vec{\omega}) \quad . \tag{2.1-7}$$

Let (a, b, c) be three principal axes and let (ξ, η, ζ) be the direction cosines of the symmetry axis of the internal top with respect to the frame (a, b, c). We denote the components of $\vec{\omega}$ along the a, b, and c axes and along the symmetry axis of the top by ω_a, ω_b, ω_c, and ω_α, respectively. Then

$$\omega_\alpha = \xi\,\omega_a + \eta\,\omega_b + \zeta\,\omega_c \quad . \tag{2.1-8}$$

Now, rewrite Eq. (2.1-7) as

$$T = (1/2)\,I_a\omega_a^2 + (1/2)\,I_b\omega_b^2 + (1/2)\,I_c\omega_c^2 + (1/2)\,I_\alpha\dot{\alpha}^2 + (1/2)\,I_\alpha(\omega_\alpha\,\dot{\alpha} + \dot{\alpha}\,\omega_\alpha) \quad , \tag{2.1-9}$$

where I_a, I_b, and I_c are three principal moments of inertia of the entire system, and I_α is the moment of inertia of the top about its symmetry axis. Substituting (2.1-8) in (2.1-9), we obtain

$$T = (1/2)\,I_a\omega_a^2 + (1/2)\,I_b\omega_b^2 + (1/2)\,I_c\omega_c^2 + (1/2)\,I_\alpha\dot{\alpha}^2 + I_\alpha\,\dot{\alpha}(\xi\,\omega_a + \eta\,\omega_b + \zeta\,\omega_c) \quad . \tag{2.1-10}$$

A conjugate momentum of a cannonical variable, say q, is defined by

$$p = \frac{\partial T}{\partial \dot{q}} \quad ,$$

and thus for T given by (2.1-10) we may define

$$P_a = \frac{\partial T}{\partial \omega_a} = I_a \omega_a + \xi I_\alpha \dot{\alpha} \quad , \tag{2.1-11a}$$

$$P_b = \frac{\partial T}{\partial \omega_b} = I_b \omega_b + \eta I_\alpha \dot{\alpha} \quad , \tag{2.1-11b}$$

$$P_c = \frac{\partial T}{\partial \omega_c} = I_c \omega_c + \zeta I_\alpha \dot{\alpha} \quad , \tag{2.1-11c}$$

and

$$p_\alpha = \frac{\partial T}{\partial \dot{\alpha}} = I_\alpha \dot{\alpha} + I_\alpha(\xi \omega_a + \eta \omega_b + \zeta \omega_c) \quad . \tag{2.1-11d}$$

As we will see later, P_a, P_b, and P_c are the components of the total rotational angular momentum of the entire system including the internal motion along a, b, and c axes, and p_α is the component of the total rotational angular momentum of the top along its symmetry axis.

Now, in order to formulate the quantum mechanical Hamiltonian we have to express the kinetic energy in terms of P_a, P_b, P_c, and p_α. For convenience define

$$p = I_\alpha \dot{\alpha} \quad , \tag{2.1-12}$$

where p is the internal rotational angular momentum of the top with respect to the frame (a, b, c).

From Eqs. (2.1-11a) through (2.1-11c) we may obtain

$$\omega_a = (P_a - \xi p)/I_a \quad , \tag{2.1-13a}$$

$$\omega_b = (P_b - \eta p)/I_b \quad , \tag{2.1-13b}$$

and

$$\omega_c = (P_c - \zeta p)/I_c \quad , \tag{2.1-13c}$$

where we should be careful not to confuse p with p_α.

Let us define

$$\vec{P} = \begin{pmatrix} P_a \\ P_b \\ P_c \\ p_\alpha \end{pmatrix} , \qquad \vec{W} = \begin{pmatrix} \omega_a \\ \omega_b \\ \omega_c \\ \dot{\alpha} \end{pmatrix} ,$$

and

$$\underset{\frown}{A} = \begin{pmatrix} I_a & 0 & 0 & \xi I_\alpha \\ 0 & I_b & 0 & \eta I_\alpha \\ 0 & 0 & I_c & \zeta I_\alpha \\ \xi I_\alpha & \eta I_\alpha & \zeta I_\alpha & I_\alpha \end{pmatrix} . \tag{2.1-14}$$

Then (2.1-10) and (2.1-11) may be rewritten as

$$\vec{P} = \underset{\frown}{A} \cdot \vec{W} \tag{2.1-15}$$

and

$$T = (1/2)\, \vec{W}^{+} \circ \underset{\frown}{A} \cdot \vec{W} \quad . \tag{2.1-16}$$

Assume the matrix $\underset{\frown}{A}$ is not singular, that is det A $\neq 0$, and also note that $\underset{\frown}{A}$ is a real symmetric matrix, i.e., $\underset{\frown}{A}^+ = \underset{\frown}{A}$.

Denote the inverse of the matrix $\underset{\frown}{A}$ by $\underset{\frown}{A}^{-1}$. Then we can write

$$\begin{aligned} T &= (1/2)(\underset{\frown}{A}^{-1} \cdot \vec{P})^+ \cdot \underset{\frown}{A} \cdot (\underset{\frown}{A}^{-1} \cdot \vec{P}) \\ &= (1/2)\, \vec{P}^+ \cdot (\underset{\frown}{A}^{-1})^+ \circ \vec{P} \quad . \end{aligned} \tag{2.1-17}$$

Since $\underset{\frown}{A}$ is a real symmetric matrix, so is $\underset{\frown}{A}^{-1}$. Therefore

$$T = (1/2)\, \vec{P}^+ \circ \underset{\frown}{A}^{-1} \cdot \vec{P} \quad . \tag{2.1-18}$$

Thus, the problem is reduced to finding the inverse of the matrix $\underset{\frown}{A}$. However, it is laborious to find $\underset{\frown}{A}^{-1}$ from (2.1-14). There is an alternate and easier way to do this, and we will consider it in what follows.

Introducing (2.1-13) into (2.1-10), we have

$$T = A\, P_a^{\,2} + B\, P_b^{\,2} + C\, P_c^{\,2} + D\, p^2 \quad , \tag{2.1-19}$$

where

$$A = \frac{1}{2I_a} \ , \quad B = \frac{1}{2I_b} \ , \quad C = \frac{1}{2I_c} \ ,$$

and

$$D = \frac{1}{2}\left[\frac{1}{I_\alpha} - \left(\frac{\xi^2}{I_a} + \frac{\eta^2}{I_b} + \frac{\zeta^2}{I_c}\right)\right] \quad . \tag{2.1-20}$$

Thus we can write our rotational Hamiltonian as

$$\mathcal{H}_{rot} = A\, P_a^{\,2} + B\, P_b^{\,2} + C\, P_c^{\,2} + D\, p^2 + V(\theta, \phi, \psi, \alpha) \quad , \tag{2.1-21}$$

where $V(\theta, \phi, \psi, \alpha)$ is the potential function governing the rotational motion of the molecule, expressed in terms of three Eulerian angles, θ, ϕ, ψ, of the rotating frame and an internal angle variable, α.

From (2.1-11d) and (2.1-13) we can see that p_α is related to p via

$$p = \frac{1}{2DI_\alpha}\left\{p_\alpha - I_\alpha\left(\frac{\xi}{I_a}P_a + \frac{\eta}{I_b}P_b + \frac{\zeta}{I_c}P_c\right)\right\} \tag{2.1-22}$$

which can be considered as a generalized Nielsen transformation.[4]

Substituting (2.1-22) in (2.1-19), we can easily find $\underset{\frown}{A}^{-1}$. The resulting Hamiltonian takes the following form:

$$\begin{aligned}\mathcal{H}_{\text{rot}} = &\left(A + \frac{\xi^2}{4DI_a{}^2}\right) P_a{}^2 + \left(B + \frac{\eta^2}{4DI_b{}^2}\right) P_b{}^2 \\ &+ \left(C + \frac{\zeta^2}{4DI_c{}^2}\right) P_c{}^2 + \frac{\xi\eta}{4DI_aI_b}\left(P_aP_b + P_bP_a\right) \\ &+ \frac{\xi\zeta}{4DI_aI_c}\left(P_aP_c + P_cP_a\right) + \frac{\eta\zeta}{4DI_bI_c}\left(P_bP_c + P_cP_b\right) \\ &- \frac{\xi}{4DI_\alpha I_a}\left(P_ap_\alpha + p_\alpha P_a\right) - \frac{\eta}{4DI_\alpha I_c}\left(P_cp_\alpha + p_\alpha P_c\right) \\ &- \frac{\zeta}{4DI_\alpha I_c}\left(P_cp_\alpha + p_\alpha P_c\right) + \frac{1}{4DI_\alpha{}^2}\, p_\alpha{}^2 \\ &+ V(\theta, \phi, \psi, \alpha) \ .\end{aligned} \tag{2.1-23}$$

All the knowledge about forces exerted on the system is contained in the potential function $V(\theta, \phi, \psi, \alpha)$. Since $V(\theta, \phi, \psi, \alpha)$ includes both external and internal forces exerted on the system, we assume that $V(\theta, \phi, \psi, \alpha)$ takes the form

$$V(\theta, \phi, \psi, \alpha) = V_{ext}(\theta, \phi, \psi, \alpha) + V_{int}(\alpha) \quad , \tag{2.1-24}$$

where $V_{ext}(\theta, \phi, \psi, \alpha)$ is the potential function due to the external source of force and $V_{int}(\alpha)$ is that due to the internal source. We may arbitrarily set $V_{ext}(\theta, \phi, \psi, \alpha)$ equal to zero when there is no external force.

Now, in order to obtain the quantum mechanical Hamiltonian we have to find quantum mechanical operators corresponding to angular momentum components involved in (2.1-23). We will discuss these operators in the next section.

2.2 Quantum Mechanical Operators for P_a, P_b, P_c, p_α, p and Quantum Mechanical Hamiltonian for Rotational Motion.

In order to obtain explicit expressions for P_a, P_b, P_c, p_α, and p we define the Eulerian angles (ϕ, θ, ψ) of the rotating frame (a, b, c) following Goldstein.[5]

As shown by Margenau and Murphy,[6] we may write

$$\omega_a = \dot{\phi} \sin\theta \sin\psi + \dot{\theta} \cos\psi \quad , \tag{2.2-1a}$$

$$\omega_b = \dot{\phi} \sin\theta \cos\psi + \dot{\theta} \sin\psi \quad , \tag{2.2-1b}$$

$$\omega_c = \dot{\phi} \cos\theta + \dot{\psi} \quad , \tag{2.2-1c}$$

or alternatively

$$\dot{\theta} = \omega_a \cos\psi - \omega_b \sin\psi \quad , \tag{2.2-2a}$$

$$\dot{\phi} = (\omega_a \sin\psi + \omega_b \cos\psi) \operatorname{cosec}\theta \quad , \tag{2.2-2b}$$

$$\dot{\psi} = \omega_c - (\omega_a \sin\psi + \omega_b \cos\psi) \cot\theta \quad . \tag{2.2-2c}$$

Substituting (2.1-1) into (2.1-10) and considering that

$$\frac{\partial T}{\partial \omega_a} = \frac{\partial T}{\partial \dot{\theta}} \frac{\partial \dot{\theta}}{\partial \omega_a} + \frac{\partial T}{\partial \dot{\phi}} \frac{\partial \dot{\phi}}{\partial \omega_a} + \frac{\partial T}{\partial \dot{\psi}} \frac{\partial \dot{\psi}}{\partial \omega_a} + \frac{\partial T}{\partial \dot{\alpha}} \frac{\partial \dot{\alpha}}{\partial \omega_a} \quad ,$$

we have

$$P_a = P_\theta \cos\psi + P_\phi \operatorname{cosec}\theta \sin\psi - P_\psi \sin\psi \cot\theta \quad ,$$

or

$$iP_a = \cos\psi \left(\frac{\partial}{\partial\theta}\right)_{\phi,\psi,\alpha} + \operatorname{cosec}\theta \sin\psi \left(\frac{\partial}{\partial\phi}\right)_{\theta,\psi,\alpha} - \sin\psi \cot\theta \left(\frac{\partial}{\partial\psi}\right)_{\theta,\phi,\alpha} \quad , \tag{2.2-3a}$$

where we have used the Dirac operator equivalence

$$P_\phi \rightarrow -i \frac{\partial}{\partial\phi} \quad , \qquad P_\theta \rightarrow -i \frac{\partial}{\partial\theta} \quad ,$$

and

$$P_\psi \rightarrow -i \frac{\partial}{\partial\psi} \quad .$$

Similarly, we can obtain

$$iP_b = -\sin\psi \left(\frac{\partial}{\partial\theta}\right)_{\phi,\psi,\alpha} + \operatorname{cosec}\theta \cos\psi \left(\frac{\partial}{\partial\phi}\right)_{\theta,\psi,\alpha} - \cot\theta \cos\psi \left(\frac{\partial}{\partial\psi}\right)_{\theta,\phi,\alpha} \quad , \tag{2.2-3b}$$

$$iP_c = \left(\frac{\partial}{\partial\psi}\right)_{\phi,\theta,\alpha} \quad , \tag{2.2-3c}$$

and

$$iP_\alpha = \left(\frac{\partial}{\partial\alpha}\right)_{\phi,\theta,\psi} \quad . \tag{2.2-3d}$$

The corresponding operator expression for p can be easily obtained from (2.1-22) and (2.2-3). Since P_a, P_b, and P_c are independent of α as we see in (2.2-3), they commute with p_α. However, they do not commute with one another as pointed out by Klein,[7] Casimir,[8] and Van Vleck,[1] whence p does not commute with P_a, P_b, P_c. In fact, as first noted by Klein, P_a, P_b, and P_c satisfy anomalous commutation relations

$$[P_a, P_b] = -iP_c \quad ,$$

$$[P_b, P_c] = -iP_a \quad ,$$

$$[P_c, P_a] = -iP_b \quad . \tag{2.2-4}$$

Thus, if we can express P_a, P_b, P_c, and p in terms of corresponding operators, we may use (2.1-21) as the corresponding quantum mechanical Hamiltonian without any change.

In a molecule like benzotrifluoride we may put $\xi = \eta = 0$ and $\zeta = 1$. Therefore (2.1-21) and (2.1-23) may be rewritten as

$$\mathcal{H}_{rot} = A\,P_a^2 + B\,P_b^2 + C\,P_c^2 + D\,p^2 + V(\theta,\phi,\psi,\alpha) \tag{2.2-5}$$

and

$$\mathcal{H}_{rot} = A\,P_a^2 + B\,P_b^2 + C_z P_c^2 + F\,p_\alpha^2 - 2\,C_z P_c p_\alpha + V(\theta, \phi, \psi, \alpha) \quad , \qquad (2.2\text{-}6)$$

respectively, where A, B, and C are given by (2.1-20) and

$$D = (1/2)(1/I_\alpha - 1/I_c), \quad F = (1/2)(I_c/I_\alpha)(1/(I_c - I_\alpha)) \quad ,$$

and

$$C_z = (1/2)(1/(I_c - I_\alpha)) \quad . \qquad (2.2\text{-}7)$$

As we shall see later, we are going to use (2.2-5) to derive the spin-rotation interaction Hamiltonian, while (2.2-6) is a more convenient form for evaluation of rotational energy levels. Before attempting to derive the Hamiltonian of spin-rotation interaction we will first be concerned with the evaluation of rotational energy levels and the spin statistics in ϕ-CF_3 since they are useful for our future discussion of the problem.

2.3 Rotational Energy Levels and Spin Statistics in Benzotrifluoride

(A) Rotational energy levels.

The benzotrifluoride molecule, in the rigid rotor approximation, can be considered as an asymmetric rotor with a symmetric internal rotor, where one of three principal axes of the entire molecule coincides with the symmetry axis of the CF_3 group. Let this axis be denoted by z, and the other two principal axes will be designated by x and y.

Then we may write the rotational Hamiltonian for ϕ-CF_3 as

$$\mathcal{H}_{rot} = \mathcal{H}_0 + \mathcal{H}_1 + V(\alpha) \quad , \tag{2.3-1}$$

where

$$\mathcal{H}_0 = (1/2)(A+B)(P_x{}^2 + P_y{}^2) + C_z P_z{}^2 + F\, p_\alpha{}^2 - 2\, C_z p_\alpha P_z \tag{2.3-2}$$

and

$$\mathcal{H}_1 = (1/2)(A-B)(P_x{}^2 - P_y{}^2) \tag{2.3-3}$$

with

$$A = \frac{\hbar^2}{2I_x} \;, \qquad B = \frac{\hbar^2}{2I_y} \;, \qquad C = \frac{\hbar^2}{2I_z} \;,$$

$$C_z = \frac{\hbar^2}{2(I_z - I_\alpha)} \;, \qquad \text{and} \qquad F = \frac{I_z \hbar^2}{2I_\alpha(I_z - I_\alpha)} \quad . \tag{2.3-4}$$

In the expressions for $\mathcal{H}_0$ and $\mathcal{H}_1$ the angular momentum components, P_x, P_y, P_z and p_α, are expressed in units of $\hbar$.

A complete set of eigenfunctions for the operator $(\mathcal{H}_0 + \mathcal{H}_1)$ is not available in any analytic form. However, by forming the energy matrix for this operator using a complete set of orthonormal functions and diagonalizing this matrix we can obtain eigenfunctions and energy levels. In the case of free internal rotation, that is, when $V(\alpha) = 0$, eigenfunctions and energy levels can be obtained in analytic forms for $J \leqslant 3$, where J is the total angular momentum quantum number.

If the asymmetry of the molecule is not too large, eigenfunctions for $\mathcal{H}_0$ can serve as a convenient basis set to form the energy matrix. These eigenfunctions can be represented by

$$|JMKm\rangle = S_{JMK}(\theta,\phi)\, e^{iK\psi}\, e^{im\alpha} \quad , \qquad (2.3\text{-}5)$$

where

$S_{JMK}(\theta,\phi)$

$$= (-1)^{\beta}\, e^{i(M+K)\frac{\pi}{2}}\, N_{JMK}\, e^{iM\phi}\, P_{JMK}(\theta) \quad , \qquad (2.3\text{-}6)$$

$$N_{JMK} = \left[\frac{(2J+1)\,(J+\frac{d}{2}+\frac{s}{2})!\ (J-\frac{s}{2}+\frac{d}{2})^{\frac{1}{2}}}{8\pi^2(J-\frac{s}{2}+\frac{d}{2})!\ d!\ (J+\frac{s}{2}-\frac{d}{2})^{\frac{1}{2}}}\right]^{\frac{1}{2}} \quad , \qquad (2.3\text{-}7)$$

and

$$P_{JMK}(\theta) = t^{-\frac{d}{2}}\,(1-t)^{-\frac{s}{2}}\,\frac{d!}{(d+p)!}\,\frac{d^p}{dt^p}\left[t^{d+p} + (1-t)^{s+p}\right] \qquad (2.3\text{-}8)$$

with

$$d = |M-K| \quad , \qquad s = |M+K| \quad ,$$

$$t = (1-\cos\theta)/2 \quad , \qquad \text{and} \qquad 2p = 2J-(d+s) \quad . \qquad (2.3\text{-}9)$$

$(-1)^{\beta}$ in $S_{JKM}(\theta,\phi)$ is the so-called Van Vleck phase factor, where β corresponds to the larger of M or K.

From symmetry considerations we see that $V(\alpha)$ for benzotrifluoride may be written

$$V(\alpha) = \sum_{n} \frac{V_{6n}}{2}\,(1-\cos 6n\,\alpha) \quad , \qquad (2.3\text{-}10)$$

where $n = 1, 2, 3, \ldots$.

It has been empirically shown that the series (2.3-10) rapidly converges in many cases, and therefore in our case we will retain the leading term

$$\frac{V_6}{2}(1-\cos 6\alpha) \quad . \tag{2.3-11}$$

Expression (2.3-11) may be rewritten as

$$\frac{V_6}{4}(2-e^{6i\alpha}-e^{-6i\alpha}) \quad .$$

The first term $(V_6/2)$ merely represents a common additional constant and may be dropped safely. Thus using (2.3-5) as basis functions the energy matrix elements can be written

$$\langle JKMm|\mathcal{H}|JKMm\rangle$$
$$= \tfrac{1}{2}(A+B)\,J(J+1) + \{C_z - \tfrac{1}{2}(A+B)\}\,K^2 + Fm^2 - 2mC_zK \quad , \tag{2.3-12}$$

$$\langle JKMm|\mathcal{H}|JK{\pm}2Mm\rangle$$
$$= -\tfrac{1}{4}(A-B)\,[\{J(J+1)-K(K\pm1)\}\{J(J+1)-(K\pm1)(K\pm2)\}]^{\frac{1}{2}} \quad , \tag{2.3-13}$$

and

$$\langle JKMm|\mathcal{H}|JKMm\pm6\rangle = -\tfrac{1}{4}V_6 \quad . \tag{2.3-14}$$

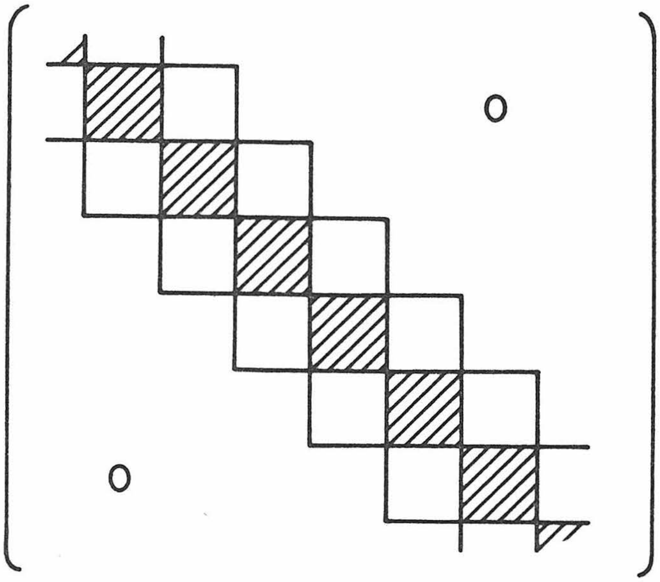
From now on we will drop M in describing the matrix elements since the quantum number M does not appear in the expression of energy matrix elements.

However, since M can take (2J+1) number of different values, that is, $M = -J, -J+1, \ldots, J-1, J$, all the energy levels in this problem are at least (2J+1)-fold degenerate. From (2.3-13) we see that $\mathcal{H}_1$ can only mix two states which differ in quantum number K by 2. Similarly $V(\alpha)$ gives nonvanishing matrix elements only between two states which differ in quantum number m by 6.

In this connection we are going to cite some results due to Wilson, Lin, and Lide.[2] Since our Hamiltonian is invariant under the 4s-operations when $V(\alpha)$ has s-fold symmetry, these 4s operations will form a group. For $s = 6$ this group will be isomorphous with the group D_{6h}, and its character table has been given by Wilson et al. According to them the energy matrix should be factored at least into six submatrices. Since there is no matrix element between states of even K and those of odd K, we have only to consider submatrices corresponding to either even or odd K. Next we also see that there is no matrix element between states with different values of m_0, where $m = m_0 + 6k$ with $m_0 = 1, 2, 3, 4, 5, 6$ and $k = 0, \pm 1, \pm 2, \ldots$. Let us call this submatrix the m_0-submatrix. Structure of each m-submatrix is diagramatically shown below.

Each submatrix represented by a square box in (2.3-15) spans over the K-space, where it can be factored into two smaller matrices, one for even K and the other for odd K, as we have already mentioned.

Because of symmetry of the type $E(K, m) = E(-K, -m)$, the $m_0 = 2$ matrix is identical with the $m_0 = 4$ matrix, and similarly the $m_0 = 1$ matrix can be shown identical with that for $m_0 = 5$.



(2.3-15)

The matrices for $m_0 = 3$ and $m_0 = 6$ can be further factored by performing a transformation on them which is equivalent to choosing wave functions of the type

$$\psi^{\pm}_{JKMm} = \frac{1}{\sqrt{2}} \left(|JKMm\rangle \pm |J\text{-}KM\text{-}m\rangle \right) \quad . \tag{2.3-16}$$

Using the structural data for φ-CF_3 due to Scott et al.,[9] we can evaluate I_x, I_y, I_z, and I_α as well as several rotational constants. The results are

$$I_x = 10.432 \times 10^{-38} \text{g.cm}^2 \;, \qquad I_y = 8.955 \times 10^{-38} \text{g.cm}^2 \;,$$

$$I_z = 2.946 \times 10^{-38} \text{g.cm}^2 \;, \qquad I_\alpha = 1.469 \times 10^{-38} \text{g.cm}^2 \;,$$

$$A = (\hbar^2/2I_x) = 5.33 \times 10^{-18} \text{ erg} \;,$$

$$B = (\hbar^2/2I_y) = 6.21 \times 10^{-18} \text{ erg} \;,$$

$$C_z = (\hbar^2/2(I_z - I_\alpha)) = 37.64 \times 10^{-18} \text{ erg} \;, \qquad \text{and}$$

$$F = (I_z\hbar^2/2I_\alpha(I_z - I_\alpha)) = 75.49 \times 10^{-18} \text{ erg} \quad .$$

In the zero barrier limit (i.e., $V_6 = 0$) some rotational energy levels have been evaluated on the IBM 7094 and results are tabulated in Table I. From (2.3-12) and (2.3-13) one sees that each nonvanishing value of $|m|$, there will be two identical secular equations, so all levels are doubly degenerate unless $m = 0$. In the case of $m = 0$, the ordinary rigid rotor levels are obtained, except that the moment of inertia about the z-axis is the moment of the framework group $(I_z - I_\alpha)$ as already shown. In Table I only the cases of $m > 0$ are tabulated.

If the anisotropy (A-B) is very small, the energy levels may be expanded in powers of (A-B). For large values of the quantum number, the diagonal elements of the secular equation will be large and the first terms in the expansion in powers of (A-B) may be adequate. Second-order perturbation theory then gives[2]

$$\begin{aligned} E = {} & K^2 - mdK + (b^2/8)\{[J^2 - (K-1)^2] \\ & \times [(J+1)^2 - (K-1)^2]/(2K - md - 2)\} \\ & - (b^2/8)\{[J^2 - (K+1)^2]\,[J+1)^2 - (K+1)^2/(2K - md + 2)\} \\ & + \ldots\ldots \quad , \end{aligned} \qquad (2.3\text{-}17)$$

where

$$b = \tfrac{1}{2}(A - B)/\{C_z - \tfrac{1}{2}(A+B)\}$$

and

$$d = 2C_z/\{C_z - \tfrac{1}{2}(A+B)\} \quad . \qquad (2.3\text{-}18)$$

TABLE I. First Few Rotational Levels in Benzotrifluoride in the Zero Barrier Limit

J	m	energy × 10^{16} ergs
1	0	0.1187
		0.4361
		0.4452
1	1	0.4319
		0.8726
		1.957
1	2	1.931
		3.134
		4.982
1	3	4.937
		6.903
		9.514
1	4	9.452
		12.18
		15.55
2	0	0.3560
		0.6645
		0.6919
		1.644
		1.644
2	1	0.6692
		1.111
		0.8721
		2.195
		3.923
2	2	1.609
		2.168
		3.372
		5.219
		7.710
2	3	3.853
		5.175
		7.141
		9.751
		13.01
2	4	7.604
		9.689
		12.42
		15.79
		19.81
3	0	0.7114
		1.007
		1.062
		2.000
		2.001
		3.610
		3.610
3	1	1.025
		1.226
		1.469
		2.076
		2.551
		4.279
		6.652
3	2	1.965
		2.049
		2.525
		3.728
		5.575
		8.067
		11.20
3	3	3.531
		4.209
		5.531
		7.497
		10.11
		13.36
		17.26
3	4	6.520
		7.961
		10.05
		12.77
		16.15
		20.16
		24.82

For large values of m, E approaches K^2 - mdK.

Since papers due to Wilson[2] and Lin[3] give an excellent review of this problem, we are not going into further detail. Instead we will give some discussion about the symmetry properties of rotational states and the spin statistics of φ-CF_3.

B. Symmetry of rotational levels and spin statistics.

As we have already noted in the previous section, the submatrix for $m_0 = 2$ is identical to that for $m_0 = 4$ because of symmetry of the type $E(K, m) = E(-K, -m)$ in the energy matrix. Similarly, the $m_0 = 1$ matrix can be shown to be identical to the $m_0 = 5$ matrix. For these submatrices the rotational states may be written

$$\Psi^{\pm}_{m_0} = \sum_{K^{\pm}} a^{(m_0)}_{K^{\pm}} \sum_{k} b^{(m_0)}_{k} |JKm_0 + 6k\rangle \qquad (2.3\text{-}19)$$

where $\sum_{K^+}$ means the sum over states of even K and $\sum_{K^-}$ stands for odd K, and superscript (±) on Ψ_{m_0} corresponds to the sum over states of $K^{\pm}$. If we arrange the matrix elements properly we can see that identity of the submatrix $m_0 = 2$ with that for $m_0 = 4$ requires that

$$a^{(2)}_{K^{\pm}} = a^{(4)}_{-K^{\pm}}$$

and

$$b^{(2)}_{k} = b^{(4)}_{-k} \quad .$$

Similarly, we can show that

$$a^{(1)}_{K^\pm} = a^{(5)}_{-K^\pm}$$

and

$$b^{(1)}_{k} = b^{(5)}_{-k} \quad .$$

The matrices for $m_0 = 3$ and $m_0 = 6$ can be factored by choosing wave functions of the type

$$\Psi^{\pm}_{m_0^{\pm}} = \sum_{K^\pm} a^{(m_0)}_{K^\pm} \sum_{k} b^{(m_0)}_{k} \{ |JKm_0 + 6k\rangle \pm |J - K - (m_0 + 6k)\rangle \} \quad . \qquad (2.3\text{-}20)$$

By checking these wave functions through every symmetry operation of the 4s group we can determine the symmetry classification given in Table II. To make this table we have used the following properties of the symmetric rotor wave functions:

(i) when we rotate the given molecule by an angle $2\pi j/n$ about the symmetry axis (identified as the z-axis in our case), where j and n are integers,

$$\psi_R = S_{JKM}(\theta, \phi)\, e^{iK\psi}\, e^{im\alpha} \xrightarrow{C_n^j}$$

$$\psi'_R = S_{JMK}(\theta, \phi)\, e^{iK(\psi + 2\pi j/n)}\, e^{im\alpha}$$

$$= e^{2\pi ijK/n}\, \psi_R \quad ; \qquad (2.3\text{-}21)$$

and

(ii) when we apply a twofold rotation about an axis perpendicular to the symmetry axis and making an angle δ with the axis x' which is the origin of the angle ψ measuring the rotation of the molecule about its symmetry axis, we can find that

$$S_{JKM}(\pi-\theta, \pi+\phi)\, e^{iK(\pi-\psi+2\delta)}\, e^{im\alpha}$$

$$= (-1)^{J+\zeta+M}\, e^{iK(\pi+2\delta)}\, e^{im\alpha}\, S_{J-KM}(\theta, \phi)\, e^{-iK\psi} \quad , \qquad (2.3\text{-}22)$$

where ζ is the larger of $|K|$ and $|M|$.

The character for the operation C_n^j is

$$\chi_c' = e^{2\pi ijK/n} + e^{-2\pi ijK/n} = 2\cos(2\pi jK/n) \quad \text{if } K \neq 0 \quad ,$$

and

$$\chi_c' = 1 \quad \text{if } K = 0 \quad . \qquad (2.3\text{-}23)$$

The character for the operation discussed in the case (ii) likewise is zero if $K \neq 0$, and $(-1)^J$ if $K = 0$.

Now, let us consider the problem of the spin statistical weight of rotational levels which is important in analyzing the spectral intensity. For the convenience of discussion we write the complete wave function as

$$\Psi = \psi_E \psi_V \psi_R \psi_T \psi_{NS} \quad , \qquad (2.3\text{-}24)$$

where the subscripts indicate that the corresponding factor is a function of the electronic (including electron spin), vibrational, rotational, translational, and nuclear spin coordinates, respectively. ψ_E

and ψ_V are symmetrical with respect to the permutation of nuclei in their ground states, and so is ψ_T since it does not contain any internal coordinates. Therefore we have only to consider the parity of $\psi_R\psi_{NS}$. More precisely for φ-CF_3 we write $\psi_R\psi_{NS}$ as $\psi_R\psi^H_{NS}\psi^F_{NS}$, where H and F mean proton and fluorine nuclei, respectively. All ψ^H_{NS}'s and ψ^F_{NS}'s are not compatible with a certain class of ψ_R since the Pauli principle requires that the total wave function should be antisymmetric with respect to the exchange of a pair of particles of half-integral spin. To exemplify this let us consider proton spins in φ-CF_3.

TABLE II. Symmetry Classification of Energy Eigenstates

Submatrix designation	K - m; even		K - m; odd	
	J : even	J : odd	J : even	J : odd
1, 5	E_{2o}	E_{2o}	E_{1o}	E_{1o}
2, 4	E_{1e}	E_{1e}	E_{2e}	E_{2e}
3^+	B_{yo}	B_{xo}	A_o	B_{zo}
3^-	B_{xo}	B_{yo}	B_{zo}	A_o
6^+	A_e	B_{ze}	B_{ye}	B_{xe}
6^-	B_{ze}	A_e	B_{xe}	B_{ye}

So far as proton spins are concerned, the only symmetry operation we have to consider is the C_2 rotation of the phenyl ring plane about the symmetry axis of φ-CF_3, which was described as $C_zC_6^3$ by Wilson et al.[2]. The operation $C_zC_6^3$ exchanges proton 1 with proton 5 and proton 2 with proton 4 [(15)(24)3]. Since the character χ' for a given permutation is equal to the number of spin functions unchanged by the given permutation,[10] the character for $C_Z C_6^3$ is 8.

TABLE III. Character Table for the C_2 Group

	E	C
A	1	1
B	1	-1

Thus we write

$$\psi_{NS}^{H} = 20A + 12B \quad . \tag{2.3-25}$$

A_e, B_{ze}, E_{1e}, B_{x0}, B_{y0}, and E_{20} have even parity while B_{xe}, A_0, B_{z0}, and E_{10} have odd parity with respect to the operation $C_Z C_6^3$. Therefore the rotational states corresponding to even values of (K - m) have the proton spin statistical weight 20, and those corresponding to odd values of (K - m) have the proton spin statistical weight 12. In a similar way for the fluorine spin statistical weight we may write

$$\psi_{NS}^{F} = 4A + 4E \quad , \tag{2.3-26}$$

that is, the fluorine spin statistical weights are the same, both for the nondegenerate and degenerate levels.

Therefore, the spin statistics of fluorine spins cannot produce any effect on the statistical average of a dynamical variable. The statistical average of a dynamical variable is given by

$$\langle \hat{O} \rangle = \frac{\mathrm{Tr}\{\hat{O}\, e^{-\beta \mathcal{H}}\}}{\mathrm{Tr}\{e^{-\beta \mathcal{H}}\}} \quad , \tag{2.3-27}$$

where $\hat{O}$ is a quantum mechanical operator corresponding to the given dynamical variable and $\mathcal{H}$ is the Hamiltonian for the system which we are concerned with. The importance of the spin statistical weight may be best exemplified by evaluating the statistical average of some angular momentum operators.

Suppose we evaluate $\langle P_z^2 \rangle$ in a molecule like φ-CF_3. In the $|JKMm\rangle$ representation we may write

$$\langle P_z^2 \rangle = \frac{\sum\limits_J \sum\limits_M \sum\limits_K \sum\limits_m \langle JKMm | P_z^2\, e^{-\beta \mathcal{H}} | JKMm \rangle}{\sum\limits_J \sum\limits_M \sum\limits_K \sum\limits_m \langle JKMm | e^{-\beta \mathcal{H}} | JKMm \rangle} \quad . \tag{2.3-28}$$

As we have already noted, rotational states with even values of (K - m) have the statistical weight 20 while states of odd values of (K - m) have the statistical weight 12. Therefore, we write (2.3-28) as

$$\langle P_z^2 \rangle = \frac{1}{Z} \sum_J \sum_M \Bigg\{ 20 \sum_{K^+} \sum_{m^+} K^2 Q_{JKm} + 20 \sum_{K^-} \sum_{m^-} K^2 Q_{JKm} + 12 \sum_{K^+} \sum_{m^-} K^2 Q_{JKm} + 12 \sum_{K^-} \sum_{m^+} K^2 Q_{JKm} \Bigg\} \quad , \tag{2.3-29}$$

where

$$Q_{JKm} = \langle JKMm | e^{-\beta \mathcal{H}} | JKMm \rangle \quad , \tag{2.3-30}$$

and

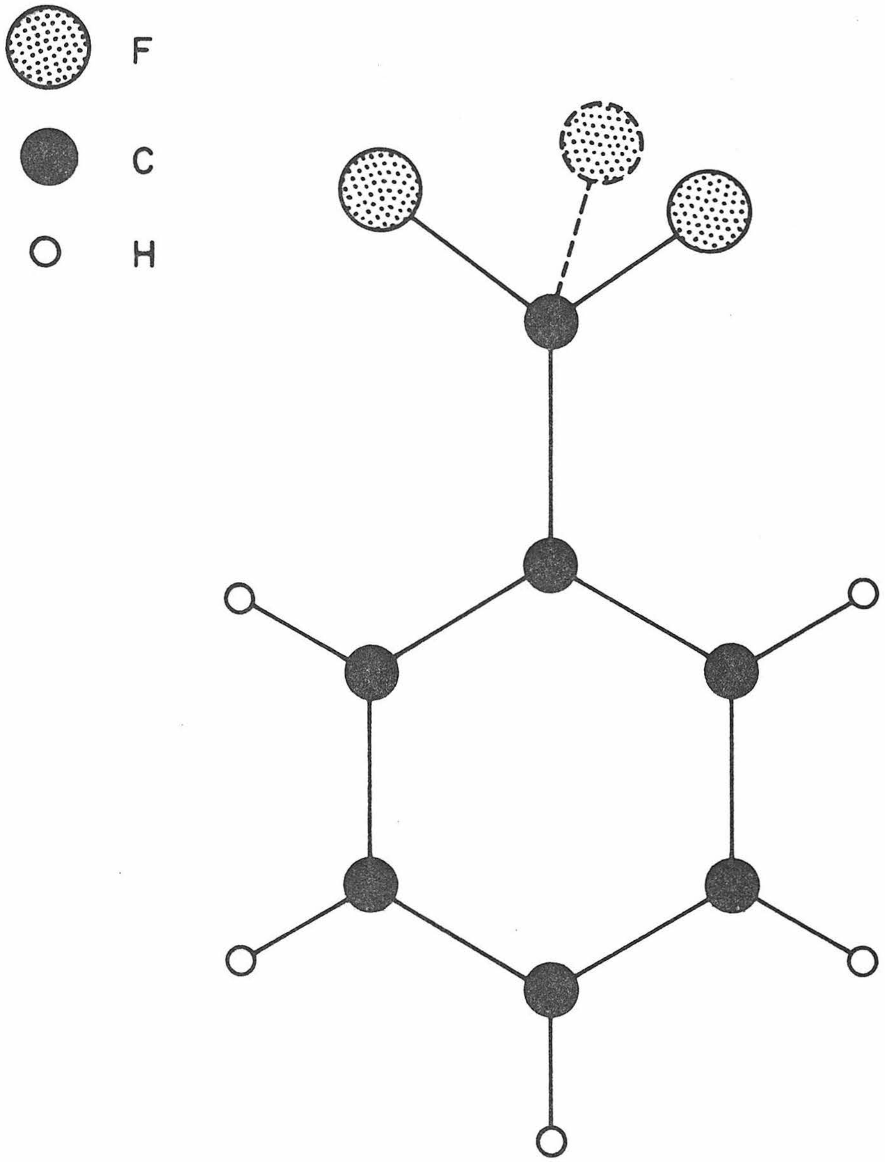


Fig.II Benzotrifluoride Molecule

Spin States	Degeneracy
↑ ↑ ↑ ↑ ↑	1
↑ ↑ ↑ ↑ ↓	5
↑ ↑ ↑ ↓ ↓	10
↑ ↑ ↓ ↓ ↓	10
↑ ↓ ↓ ↓ ↓	5
↓ ↓ ↓ ↓ ↓	1

Fig.III Proton Spin States in Benzotrifluoride

Spin States	Degeneracy
↑ ↑ ↑	1
↑ ↑ ↓	3
↑ ↓ ↓	3
↓ ↓ ↓	1

Fig.IV Fluorine Spin States in Benzotrifluoride

$$Z = \sum_J \sum_M \left\{ 20 \sum_{K^+} \sum_{m^+} Q_{JKm} + 20 \sum_{K^-} \sum_{m^-} Q_{JKm} + 12 \sum_{K^+} \sum_{m^-} Q_{JKm} + 12 \sum_{K^-} \sum_{m^+} Q_{JKm} \right\} . \qquad (2.3\text{-}31)$$

Positive (or negative) superscripts on K and m in the series $\sum_{K^+} \sum_{m^+}$, etc., signify that summations should be performed over rotational states of even (or odd) values of K and m.

TABLE IV. Character Table of C_3 Group

	E	$2C_3$
A	1	1
B	2	-1

Though eigenvalues of the operator $\mathcal{H}_0$ can be given in an analytic form, there is no way to obtain an analytic, compact expression for Z, nor is it recommendable to evaluate Z on a digital computer since rotational levels are appreciably occupied up to J = 100 in φ-CF_3 and thus evaluation of the partition function will consume an enormous amount of time even on a fast computing machine. To get out of this dilemma we use the corresponding classical expression.

In the next section we will derive a desired analytical expression of the spin-rotation interaction Hamiltonian for nuclear spins on a mobile internal rotor.

2.4 Hamiltonian of Spin-Rotation Interaction in the Presence of Internal Rotation

As we have mentioned briefly in the introductory chapter, the circulation of electrons and nuclei resulting from molecular rotation produces a molecular magnetic field at the site of a nuclear spin. This magnetic field is supposed to arise from the following two major effects. First when a molecule rotates, electron clouds do not necessarily follow the rotation of the nuclear framework. In fact they are supposed to lag slightly behind the nuclear framework, thus producing the net current required to produce a magnetic field. Second, even in the absence of this slippage of electron clouds magnetic fields produced by circulating nuclei and electrons do not exactly cancel each other since electronic charges are not centered on nuclei. Moreover, there will be some contributions from acceleration of the given nucleus due to the electric field produced by other nuclei and electrons and from Thomas precession.

In this chapter we will formulate the above ideas into a mathematical formula in a manner similar to Wick,[11] Van Vleck,[1] and Ramsey.[12]

The procedure of the formulation are as follows:

1. Assuming no electronic slippage, we evaluate magnetic fields arising from circulating nuclear and electronic charges. Effects of the acceleration of a given nucleus in the electric field produced by electrons and other nuclei and the Thomas precession will be included here. The resulting interaction between the nuclear magnetic moment

and thus produced magnetic fields will be averaged over electronic and vibrational states;

2. To include the perturbing effect of molecular rotation on electronic states we use the Van Vleck formalism,[1] where the perturbation is expressed as couplings between rotational and electronic orbital angular momentum. This effect will also be averaged over electronic and vibrational states using perturbation theory.

According to classical electrodynamics[13] magnetic fields produced by moving nuclear and electronic charges at the site of a given nucleus, say K, may be written

$$\vec{H}_1 = - \sum_{K'(\neq K)} \frac{Z_{K'}|e|}{C} \frac{\vec{r}_K - \vec{r}_{K'}}{r^3_{KK'}} \times \vec{v}_{K'}$$

$$+ \sum_k \frac{|e|}{C} \frac{\vec{r}_K - \vec{r}_k}{r^3_{Kk}} \times \vec{v}_k \quad , \tag{2.4-1}$$

where $\vec{v}_{K'}$ and $\vec{v}_k$ represent velocity vectors of nucleus K′ and electron k relative to the stationary frame. The summation $\sum_{K'(\neq K)}$ is carried out over all nuclei other than the nucleus K and $\sum_k$ will be summed over all electrons.

Since the acceleration of the nucleus K is caused by electric fields due to other nuclei and electrons, we write the equation of motion as

$$M_K \frac{d\vec{v}_K}{dt} = Z_K|e|\vec{E}_K \quad , \tag{2.4-2}$$

where M_K, $Z_K|e|$, $\vec{v}_K$, and $\vec{E}_K$ are the mass of the nucleus K, its charge, the velocity vector, and the electric field at the site of nucleus K. However, to the nucleus K moving with velocity $\vec{v}_K$ through the electric field $\vec{E}_K$, there will appear to be a magnetic field[13]

$$\vec{H}_2 = \vec{E}_K \times \vec{v}_K / C \quad . \tag{2.4-3}$$

In addition, there will be the purely kinematical Thomas precession[14, 15]

$$\begin{aligned} \vec{\omega}_K(T) &= (d\vec{v}_K/dt) \times \vec{v}_K/2C^2 \\ &= \frac{Z_K|e|}{2M_K C} \vec{E}_K \times \frac{\vec{v}_K}{C} \quad , \end{aligned} \tag{2.4-4}$$

where the last step comes from Eq. (2.4-2).

The associated magnetic field in the Thomas precession may be given by

$$\vec{H}_3 = -\frac{\vec{\omega}_K(T)}{\gamma_K} = \frac{-Z_K|e|}{2M_K\gamma_K C} \vec{E}_K \times \frac{\vec{v}_K}{C} \quad , \tag{2.4-5}$$

where γ_K is the magnetogyric ratio of the nucleus K. If we replace γ_K by $g_K\beta_N$, where g_K and β_N are the g-factor of nucleus K and the nuclear magneton, respectively, we may rewrite (2.4-5) as

$$\vec{H}_3 = -\frac{Z_K M_P}{g_K M_K} \vec{E}_K \times \frac{\vec{v}_K}{C} \quad . \tag{2.4-6}$$

Therefore, the internal magnetic field seen at the nucleus K due to the motion of the electrons and other nuclei is given by

$$\vec{H}^{(K)}_{int} = \vec{H}_1 + \vec{H}_2 + \vec{H}_3$$

$$= \sum_{K'(\neq K)} \frac{Z_{K'}|e|}{C} \frac{\vec{r}_K - \vec{r}_{K'}}{r^3_{KK'}} \times \left(\frac{\vec{v}_K}{\beta_K} - \vec{v}_{K'} \right)$$

$$+ \sum_k \frac{-|e|}{C} \frac{\vec{r}_K - \vec{r}_k}{r^3_{Kk}} \times \left(\frac{\vec{v}_K}{\beta_K} - \vec{v}_k \right) \quad , \qquad (2.4\text{-}7)$$

where we have used

$$\vec{E}_K = \sum_{K'(\neq K)} \frac{Z_{K'}|e|(\vec{r}_K - \vec{r}_{K'})}{r^3_{KK'}} - \sum_k \frac{|e|(\vec{r}_K - \vec{r}_k)}{r^3_{Kk}} \quad . \qquad (2.4\text{-}8)$$

The interaction between the nuclear magnetic moment of nucleus K, $\vec{\mu}_K$, and the magnetic field $\vec{H}^{(K)}_{int}$ takes the form

$$\mathcal{H}_1 = - \vec{\mu}_K \cdot \vec{H}^{(K)}_{int} \quad , \qquad (2.4\text{-}9)$$

where $\vec{\mu}_K$ may be expressed in terms of the spin angular momentum vector, $\vec{I}_K$, as

$$\vec{\mu}_K = g_K \beta_N \vec{I}_K \quad . \qquad (2.4\text{-}10)$$

When the electron clouds surrounding the nuclear framework are taken into consideration, the Hamiltonian (2.1-21) should be modified since only the rotation of bare nuclear framework is involved in the derivation of (2.1-21).

Remembering that only the total angular momentum is conserved when there is some coupling between the rotational angular momentum and the electronic angular momentum, we define $\vec{J}$ and $\vec{j}$ as

$$\vec{J} = \vec{P} + \vec{L} \tag{2.4-11}$$

and

$$\vec{j} = \vec{p} + \vec{\ell} \ , \tag{2.4-12}$$

where $\vec{P}$ is the total rotational angular momentum of bare nuclear framework of the entire molecule and $\vec{p}$ is the internal rotational angular momentum of bare framework of the internal top in the rotating frame. $\vec{L}$ is the total electronic orbital angular momentum and $\vec{\ell}$ can be considered to be the total orbital angular momentum of electrons localized to the internal top in the rotating frame.

Thus, replacing (2.4-11) and (2.4-12) in (2.1-21), we may write

$$\begin{aligned}\mathcal{H}'_{rot} = {} & AJ_a^2 + BJ_b^2 + CJ_c^2 + Dj^2 + V(\theta, \phi, \psi, \alpha) \\ & + AL_a^2 + BL_b^2 + CL_c^2 + D\ell^2 - 2AJ_aL_a \\ & - 2BJ_bL_b - 2CJ_cL_c - 2Dj\ell \ .\end{aligned}$$

Since terms involving L_a^2, etc, are negligibly small compared to those of J_a^2, etc., we see that the coupling between molecular rotation and electronic motions may be represented by a perturbation term

$$\begin{aligned}\mathcal{H}_2 = {} & - 2AJ_aL_a - 2BJ_bL_b - 2CJ_cL_c \\ & - 2Dj\ell \ .\end{aligned} \tag{2.4-13}$$

Now we see that it is these two terms, $\mathcal{H}_1$ and $\mathcal{H}_2$, that are responsible for the spin-rotation interaction.

The velocity vector of the nucleus K may be rewritten

$$\vec{v}_K = (\vec{\omega} + \dot{\vec{\alpha}}\delta_K) \times \vec{r}_K \quad , \tag{2.4-14}$$

where

$$\delta_K \begin{cases} = 1, & \text{if the nucleus K is on the internal top} \\ = 0, & \text{otherwise.} \end{cases} \tag{2.4-15}$$

Substitution of (2.4-14) in (2.4-7) gives us

$$\vec{H}^{(K)}_{int} = \sum_{K'(\neq K)} \frac{Z_{K'}|e|}{C} \frac{\vec{r}_K - \vec{r}_{K'}}{r^3_{KK'}} \times \left\{ \frac{(\vec{\omega} + \dot{\vec{\alpha}}\delta_K) \times \vec{r}_K}{\beta_K} - (\vec{\omega} + \dot{\vec{\alpha}}\delta_{K'}) \times \vec{r}_{K'} \right\}$$

$$- \sum_k \frac{|e|}{C} \frac{\vec{r}_K - \vec{r}_k}{r^3_{Kk}} \times \left\{ \frac{(\vec{\omega} + \dot{\vec{\alpha}}\delta_K) \times \vec{r}_K}{\beta_K} - \vec{v}_k \right\} \quad . \tag{2.4-16}$$

Since electronic and vibrational motions are much faster than rotational motion in a molecule, we have to average $\mathcal{H}_1$ and $\mathcal{H}_2$ over electronic and vibrational states to get an effective form of the spin-rotation interaction.

Since $\mathcal{H}_1$ and $\mathcal{H}_2$ are considered to be very small compared with the Hamiltonian involving electronic and vibrational motions, we may use perturbation theory to evaluate the energy correction due to $\mathcal{H}_1$ and $\mathcal{H}_2$.

The first-order energy correction is[16]

$$W^{(1)} = \langle 0 | \mathcal{H}_1 + \mathcal{H}_2 | 0 \rangle \tag{2.4-17}$$

and the second-order contribution is

$$W^{(2)} = \sum_{n\neq 0} \frac{\langle 0|\mathcal{H}_1 + \mathcal{H}_2|n\rangle\langle n|\mathcal{H}_1 + \mathcal{H}_2|0\rangle}{W_0^{(0)} - W_n^{(0)}} \quad , \qquad (2.4\text{-}18)$$

where $|0\rangle$ and $|n\rangle$ stand for ground and excited states of electronic and vibrational motions, and $W_0^{(0)}$ and $W_n^{(0)}$ are the corresponding energy eigenvalues, respectively.

For a molecule in the electronic ground state $^1\Sigma$

$$\langle 0|\vec{v}_k|0\rangle = \langle 0|\vec{r}_k \times \vec{v}_k|0\rangle = 0 \quad . \qquad (2.4\text{-}19)$$

Therefore, from Eq. (2.4-9) and (2.4-16) we may write

$$\begin{aligned}\langle 0|\mathcal{H}_1|0\rangle \\ = -g_K\beta_N \sum_{K'(\neq K)} \frac{Z_{K'}|e|}{C} \langle 0|\vec{I}_K \cdot \frac{\vec{r}_K - \vec{r}_{K'}}{r^3_{KK'}} \times \Bigg\{ \frac{(\vec{\omega} + \dot{\vec{\alpha}}\delta_K)\times\vec{r}_K}{\beta_K} \\ - (\vec{\omega} + \dot{\vec{\alpha}}\delta_{K'})\times\vec{r}_{K'}\Bigg\}|0\rangle \\ + g_K\beta_N \sum_k \frac{|e|}{C} \langle 0|\vec{I}_K \cdot \frac{\vec{r}_K - \vec{r}_k}{r^3_{Kk}} \times \frac{(\vec{\omega} + \dot{\vec{\alpha}}\delta_K)\times\vec{r}_K}{\beta_K}|0\rangle \quad . \qquad (2.4\text{-}20)\end{aligned}$$

For most molecules in their electronic ground state ($^1\Sigma$) $\mathcal{H}_2$ does not contribute to the first-order energy correction since L_a, etc., have vanishing diagonal elements in the $^1\Sigma$ state; however, they have nonvanishing off-diagonal elements, thus giving the second-order contribution. The same thing is true for the term involving $\vec{v}_k$ in $\mathcal{H}_1$.

In the spin-rotation interaction we concern ourselves only with terms like

$$\Phi_{\nu\lambda}\,(\vec{I}_K)_\nu\, J_\lambda \quad . \tag{2.4-21}$$

Thus, the second-order energy correction may be written in the form

$$W^{(2)} = \sum_{n\neq 0} \frac{1}{W_0^{(0)} - W_n^{(0)}} \{\langle 0|\mathcal{H}_1|n\rangle\langle n|\mathcal{H}_2|0\rangle + \langle 0|\mathcal{H}_2|n\rangle\langle n|\mathcal{H}_1|0\rangle\} \quad . \tag{2.4-22}$$

The angular momentum of the electron k about the nucleus K can be defined as

$$\vec{\ell}_{Kk} = (\vec{r}_k - \vec{r}_K) \times m\vec{v}_k \quad , \tag{2.4-23}$$

whence we obtain

$$\begin{aligned}
&\langle 0|\mathcal{H}_1|n\rangle\langle n|\mathcal{H}_2|0\rangle \\
&= -\,2g_K\beta_N \langle 0|\,\vec{I}_K \cdot \sum_k \frac{|e|}{mC}\frac{\vec{\ell}_{Kk}}{r^3_{Kk}}\,|n\rangle \\
&\quad \times \langle n|AJ_aL_a + BJ_bL_b + CJ_cL_c + Dj\ell\,|0\rangle \quad .
\end{aligned}$$

Now, let us turn our attention to the Hellmann-Feynman theorem[17,18]

$$\langle 0|\sum_k \frac{\vec{r}_K - \vec{r}_k}{r^3{}_{Kk}}|0\rangle = -\frac{\vec{F}_K}{Z_K e^2} + \sum_{K'(\neq K)} \frac{Z_{K'}(\vec{r}_K - \vec{r}_{K'})}{r^3_{KK'}} \quad , \tag{2.4-24}$$

where $\vec{F}_K$ is the so-called Hellmann-Feynman force exerted on the nucleus K.

Application of (2.4-24) to (2.4-20) leads to

$$\langle 0|\mathcal{H}_1|0\rangle$$

$$= g_K\beta_N \sum_{K'(\neq K)} \frac{Z_{K'}|e|}{C} \vec{I}_K \cdot \frac{\vec{r}_K - \vec{r}_{K'}}{r^3_{KK'}} \times \{(\vec{\omega} + \dot{\vec{\alpha}}\,\delta_{K'}) \times \vec{r}_{K'}\}$$

$$- \frac{g_K\beta_N}{CZ_K|e|} \vec{I}_K \cdot \vec{F}_K \times \frac{(\vec{\omega} + \dot{\vec{\alpha}}\,\delta_K) \times \vec{r}_K}{\beta_K} \quad . \tag{2.4-25}$$

For convenience let

$$\vec{\pi}_K = \sum_k \frac{|e|}{mC} \frac{\vec{\ell}_{Kk}}{r^3_{Kk}} \quad . \tag{2.4-26}$$

Then, the second-order correction may be rewritten as

$$W^{(2)} = \sum_{n\neq 0} \frac{-4g_K\beta_N}{W^{(0)}_0 - W^{(0)}_n} \mathrm{Re}\{\langle 0|\vec{I}_K \cdot \vec{\pi}_K|n\rangle$$

$$\times \langle n|AJ_aL_a + BJ_bL_b + CJ_cL_c + Dj\ell|0\rangle\} \quad . \tag{2.4-27}$$

Now, by making use of the vector identity

$$\vec{A} \times (\vec{B} \times \vec{C}) = \vec{B}(\vec{A} \cdot \vec{C}) - \vec{C}(\vec{A} \cdot \vec{B}) \tag{2.4-28}$$

we have

$$(\vec{r}_K - \vec{r}_{K'}) \times \{(\vec{\omega} + \dot{\vec{\alpha}}\,\delta_{K'}) \times \vec{r}_{K'}\}$$

$$= (\vec{\omega} + \dot{\vec{\alpha}}\,\delta_{K'})(\vec{r}_K - \vec{r}_{K'}) \cdot \vec{r}_{K'} - \vec{r}_{K'}(\vec{r}_K - \vec{r}_{K'}) \cdot (\vec{\omega} + \dot{\vec{\alpha}}\,\delta_{K'}) \tag{2.4-29}$$

$$\vec{F}_K \times \{(\vec{\omega} + \dot{\vec{\alpha}}\delta_K) \times \vec{r}_K\}$$

$$= (\vec{\omega} + \dot{\vec{\alpha}}\delta_K)\, \vec{F}_K \cdot \vec{r}_K - \vec{r}_K \vec{F}_K \cdot (\vec{\omega} + \dot{\vec{\alpha}}\delta_K) \quad .$$

If the nucleus K under consideration is on the internal top and the only allowed motion of this internal top is the rotation about its symmetry axis, $\vec{F}_K$ should be perpendicular to this symmetry axis. Therefore,

$$\vec{F}_K \times \{(\vec{\omega} + \dot{\vec{\alpha}}) \times \vec{r}_K\}$$

$$= (\vec{\omega} + \dot{\vec{\alpha}}) \sum_g (\vec{F}_K)_g (\vec{R})_g - \vec{r}_K \sum_g (\vec{F}_K)_g\, \omega_g \quad , \tag{2.4-30}$$

where $\vec{R}$ is the distance vector from the origin O to the symmetry axis of the internal top.

Replacing (2.4-29) and (2.4-30) in (2.4-25), we obtain

$$W^{(1)} = g_K \beta_N \sum_{\substack{K'(\neq K) \\ \text{(for all } K')}} \frac{Z_{K'}|e|}{C r^3_{KK'}} \sum_{g,\,g'} (\vec{I}_K)_g (\vec{r}_K - \vec{r}_{K'})_{g'}$$

$$\times [\omega_g (\vec{r}_{K'})_{g'} - (\vec{r}_{K'})_g \;\; \omega_{g'}]$$

$$+ g_K \beta_N \sum_{\substack{K'(\neq K) \\ \text{(for } K' \text{ only} \\ \text{on top)}}} \frac{Z_{K'}|e|}{C r^3_{KK'}} \sum_{g,\,g'} (\vec{I}_K)_g (\vec{r}_K - \vec{r}_{K'})_{g'}$$

$$\times [\dot{\alpha}_g (\vec{r}_{K'})_{g'} - (\vec{r}_{K'})_g\, \dot{\alpha}_{g'}]$$

$$-\frac{g_K\beta_N}{C\beta_K Z_K|e|}\sum'_{g,g'}(\vec{I}_K)_g(\vec{F}_K)_{g'}[(\vec{\omega}+\dot{\vec{\alpha}})_g(\vec{r}_K)_{g'} - (\vec{r}_K)_g(\vec{\omega}+\dot{\vec{\alpha}})_{g'}] \quad . \qquad (2.4\text{-}31)$$

Now, recall the relations

$$\omega_g = (J_g - \xi_g j)/I_g \qquad (2.4\text{-}32)$$

and

$$\dot{\alpha}_g = \xi_g \alpha = (\xi_g/I_\alpha) j \quad , \qquad (2.4\text{-}33)$$

where

$$\xi_a = \xi \, , \qquad \xi_b = \eta \, , \qquad \xi_c = \zeta \quad ,$$

and

$$j = I_\alpha \dot{\alpha} \quad . \qquad (2.4\text{-}34)$$

From (2.4-27), (2.4-31), and (2.4-32) we may write the energy correction due to the spin-rotation interaction as

$$\mathcal{H}_{S-R} = -\vec{I}_K \cdot \underset{\wedge}{C}^{(J)}(K) \cdot \vec{J} - \vec{I}_K \cdot \underset{\wedge}{D}^{(j)}(K) \cdot \vec{j} \quad , \qquad (2.4\text{-}35)$$

or alternatively

$$\mathcal{H}_{S-R} = -\vec{I}_K \cdot \underset{\wedge}{C}^{(\omega)}(K) \cdot \vec{\omega} - \vec{I}_K \cdot \underset{\wedge}{D}^{(\dot{\alpha})}(K) \cdot \dot{\vec{\alpha}} \quad , \qquad (2.4\text{-}36)$$

where

$$\vec{j} = (\xi j, \ \eta j, \ \zeta j) \qquad (2.4\text{-}37)$$

and

$$\alpha = (\xi\dot{\alpha}, \ \eta\dot{\alpha}, \ \zeta\dot{\alpha}) \quad . \qquad (2.4\text{-}38)$$

Matrix elements of $\underset{\wedge}{C}^{(\omega)}(K)$, $\underset{\wedge}{D}^{(\dot{\alpha})}(K)$, $\underset{\wedge}{C}^{(J)}(K)$, and $\underset{\wedge}{D}^{(j)}(K)$ take the following form:

$$
\begin{aligned}
C^{(J)}(K)_{gg'} = {} & - g_K \beta_N \sum_{\substack{K'(\neq K)\\ \text{(for all}\\ \text{nuclei)}}} \frac{Z_{K'}|e|}{C r^3_{KK'}} \Bigg[\frac{1}{I_g} (\vec{r}_K - \vec{r}_{K'}) \cdot \vec{r}_{K'} \, \delta_{gg'} \\
& \qquad - \frac{1}{I_{g'}} (\vec{r}_K - \vec{r}_{K'})_{g'} (\vec{r}_{K'})_g \Bigg] \\
& + g_K \beta_N \frac{2}{I_{g'}} \, \mathrm{Re} \sum_{n \neq 0} \frac{\langle 0 | (\pi_K)_g | n \rangle \langle n | L_{g'} | 0 \rangle}{W_0^{(0)} - W_n^{(0)}} \\
& + \frac{g_K \beta_N}{C \beta_K Z_K |e|} \left[\frac{1}{I_g} \vec{F}_K \cdot \vec{r}_K \, \delta_{gg'} - \frac{1}{I_{g'}} (\vec{F}_K)_{g'} (\vec{r}_K)_g \right] , \qquad (2.4\text{-}39)
\end{aligned}
$$

$$
\begin{aligned}
D^{(j)}(K)_{gg'} = {} & - g_K \beta_N \sum_{\substack{K'(\neq K)\\ \text{(for nuclei}\\ \text{only on top)}}} \frac{Z_{K'}|e|}{C r^3_{KK'}} \frac{1}{I_\alpha} \Big[(\vec{r}_K - \vec{r}_{K'}) \cdot \vec{r}_K{}' \, \delta_{gg'} \\
& \qquad - (\vec{r}_K - \vec{r}_{K'})_{g'} (\vec{r}_{K'})_g \Big] \\
& + g_K \beta_N \sum_{\substack{K'(\neq K)\\ \text{(for all}\\ \text{nuclei)}}} \frac{Z_{K'}|e|}{C r^3_{KK'}} \Bigg[\frac{1}{I_g} (\vec{r}_K - \vec{r}_{K'}) \cdot \vec{r}_{K'} \, \delta_{gg'} \\
& \qquad - \frac{1}{I_{g'}} (\vec{r}_K - \vec{r}_{K'})_{g'} (\vec{r}_{K'})_g \Bigg] \\
& + g_K \beta_N \sum_{n \neq 0} \frac{4D}{W_0^{(0)} - W_n^{(0)}} \, \mathrm{Re} [\, \xi_{g'} \langle 0 | (\vec{\pi}_K)_g | n \rangle \langle n | \ell | 0 \rangle \,]
\end{aligned}
$$

$$- \frac{g_K \beta_N}{C \beta_K Z_K |e|} \left\{ \left(\frac{1}{I_g} - \frac{1}{I_\alpha} \right) \vec{F}_K \cdot \vec{r}_K \, \delta_{gg'} - \left(\frac{1}{I_{g'}} - \frac{1}{I_\alpha} \right) (\vec{F}_K)_{g'} (\vec{r}_K)_g \right\} , \qquad (2.4\text{-}40$$

$$C^{(\omega)}(K)_{gg'} = - g_K \beta_N \sum_{\substack{K'(\neq K) \\ \text{(for all} \\ \text{nuclei)}}} \frac{Z_{K'} |e|}{C r^3_{KK'}} \{ (\vec{r}_K - \vec{r}_{K'}) \cdot \vec{r}_{K'} \delta_{gg'} - (\vec{r}_K - \vec{r}_{K'})_{g'} (\vec{r}_{K'})_g \}$$

$$+ \sum_{n \neq 0} \frac{2 g_K \beta_N}{W^{(0)}_0 - W^{(0)}_n} \mathrm{Re} \{ \langle 0 | (\vec{\pi}_K)_g | n \rangle \langle n | L_{g'} | 0 \rangle \}$$

$$+ \frac{g_K \beta_N}{C \beta_K Z_K |e|} \{ \vec{F}_K \cdot \vec{r}_K \delta_{gg'} - (\vec{F}_K)_{g'} (\vec{r}_K)_g \} , \qquad (2.4\text{-}41)$$

and

$$D^{(\dot{\alpha})}(K)_{gg'} = - g_K \beta_N \sum_{\substack{K'(\neq K) \\ \text{(for nuclei} \\ \text{only on top)}}} \frac{Z_{K'} |e|}{C r^3_{KK'}} [(\vec{r}_K - \vec{r}_{K'}) \cdot \vec{r}_{K'} \delta_{gg'} - (\vec{r}_K - \vec{r}_{K'})_{g'} (\vec{r}_{K'})_g]$$

$$+ \sum_{n \neq 0} \frac{4 g_K \beta_N}{W^{(0)}_0 - W^{(0)}_n} \mathrm{Re} \left\{ \frac{I_\alpha}{2 I_{g'}} \langle 0 | (\vec{\pi}_K)_g | n \rangle \langle n | L_{g'} | 0 \rangle + D I_\alpha \xi_{g'} \langle 0 | (\vec{\pi}_K)_g | n \rangle \langle n | \ell | 0 \rangle \right\}$$

$$+ \frac{g_K \beta_N}{C \beta_K Z_K |e|} \{ \vec{F}_K \cdot \vec{r}_K \delta_{gg'} - (\vec{F}_K)_{g'} (\vec{r}_K)_g \} , \qquad (2.4\text{-}42)$$

where I_g's represent the principal moments of inertia of the entire molecule.

When there are several equivalent nuclei on the internal top, we have to sum $\mathcal{H}_{S-R}$ given by (2.4-35) or (2.4-36) over these equivalent nuclei, thus giving

$$\mathcal{H}_{S-R} = -\sum_K \vec{I}_K \cdot \underset{\wedge}{C}^{(J)}(K) \cdot \vec{J} - \sum_K \vec{I}_K \cdot \underset{\wedge}{D}^{(j)}(K) \cdot \vec{j} \quad , \qquad (2.4\text{-}43)$$

or

$$\mathcal{H}_{S-R} = -\sum_K \vec{I}_K \cdot \underset{\wedge}{C}^{(\omega)}(K) \cdot \vec{\omega} - \sum_K \vec{I}_K \cdot \underset{\wedge}{D}^{(\dot{\alpha})} \cdot \vec{\dot{\alpha}} \quad . \qquad (2.4\text{-}46)$$

$\underset{\wedge}{C}^{(J)}(K)$ and $\underset{\wedge}{D}^{(j)}(K)$ (or $\underset{\wedge}{C}^{(\omega)}(K)$ and $\underset{\wedge}{D}^{(\dot{\alpha})}(K)$) are not the same even for equivalent nuclei, since they depend on the position vector of the nucleus under consideration. However, when the internal rotation is much faster than the overall rotation of a molecule, all the spins on the internal rotor will see the magnetic field averaged over the internal angle.

In the next section we will discuss the effective spin-rotation interaction averaged over the internal angle.

2.5 Spin-Rotation Interaction in the Presence of Fast Internal Rotation

As we have already mentioned in the section (1.3), a molecule like φ-CF_3 is supposed to undergo overall rotation of diffusion type while the CF_3 top apparently rotates with relatively definite angular momentum between intermolecular collisions. Therefore, the CF_3 group can continue its rotation even after the overall rotation of the molecule is quenched.[19] In this situation it is supposed that $\mathcal{H}_{S-R}$ given by (2.4-43) or (2.4-44) had better be averaged over the internal angle α to provide a more effective form of the spin-rotation interaction.

Now, we are going to show that when the averaging process is carried out $\mathcal{H}_{S-R}$ may take the form

$$\mathcal{H}_{S-R} = - \vec{F} \cdot \underset{\frown}{C}^{(J)} \cdot \vec{J} - D_{\alpha}^{(j)} \vec{F} \cdot \vec{j} \quad , \tag{2.5-1}$$

where

$$\vec{F} = \sum_{K} \vec{I}_{K} \quad , \tag{2.5-2}$$

$$\underset{\frown}{C}^{(J)} = \tfrac{1}{3} \langle \sum_{K} \underset{\frown}{C}^{(J)}(K) \rangle_{int} \tag{2.5-3}$$

and

$$D_{\alpha}^{(j)} = D_{zz}^{(j)} \quad . \tag{2.5-4}$$

The validity of Eq. (2.5-1) is best manifested by considering the case of φ-CF_3.

We denote three fluorine spin sites by (a), (b), (c) as shown in Fig. 5 and three fluorine spins will be designated 1, 2, and 3. Let us consider the following three different configurations:

$$\text{Configuration 1} = \begin{pmatrix} 1 & 2 & 3 \\ a & b & c \end{pmatrix} \quad ,$$

$$\text{Configuration 2} = \begin{pmatrix} 2 & 3 & 1 \\ a & b & c \end{pmatrix} \quad ,$$

and

$$\text{Configuration 3} = \begin{pmatrix} 3 & 1 & 2 \\ a & b & c \end{pmatrix} \quad ,$$

where the symbol $\begin{pmatrix} 1 & 2 & 3 \\ a & b & c \end{pmatrix}$ means that spin 1 occupies the site a; spin 2 site b; and spin 3 site c.

For configuration 1, (2.4-43) may be written

$$\begin{aligned} \mathcal{H}^{(1)}_{S-R} = & - \vec{I}_1 \cdot \underset{\wedge}{C}^{(J)}_{a} \cdot \vec{J} - \vec{I}_2 \cdot \underset{\wedge}{C}^{(J)}_{b} \cdot \vec{J} - \vec{I}_3 \cdot \underset{\wedge}{C}^{(J)}_{c} \cdot \vec{J} \\ & - \vec{I}_1 \circ \underset{\wedge}{D}^{(j)}_{a} \cdot \vec{j} - \vec{I}_2 \cdot \underset{\wedge}{D}^{(j)}_{b} \cdot \vec{j} - \vec{I}_3 \cdot \underset{\wedge}{D}^{(j)}_{c} \cdot \vec{j} \quad . \end{aligned} \qquad (2.5\text{-}5)$$

Similarly, for configuration 2 and 3 we may write

$$\begin{aligned} \mathcal{H}^{(2)}_{S-R} = & - \vec{I}_1 \cdot \underset{\wedge}{C}^{(J)}_{c} \cdot \vec{J} - \vec{I}_2 \cdot \underset{\wedge}{C}^{(J)}_{a} \cdot \vec{J} - \vec{I}_3 \cdot \underset{\wedge}{C}^{(J)}_{b} \cdot \vec{J} \\ & - \vec{I}_1 \cdot \underset{\wedge}{D}^{(j)}_{c} \cdot \vec{j} - \vec{I}_2 \cdot \underset{\wedge}{D}^{(j)}_{a} \cdot \vec{j} - \vec{I}_3 \cdot \underset{\wedge}{D}^{(j)}_{b} \cdot \vec{j} \quad , \end{aligned} \qquad (2.5\text{-}6)$$

and

$$\begin{aligned} \mathcal{H}^{(3)}_{S-R} = & - \vec{I}_1 \cdot \underset{\wedge}{C}^{(J)}_{b} \cdot \vec{J} - \vec{I}_2 \cdot \underset{\wedge}{C}^{(J)}_{c} \cdot \vec{J} - \vec{I}_3 \cdot C^{(J)}_{a} \cdot \vec{J} \\ & - \vec{I}_1 \circ \underset{\wedge}{D}^{(j)}_{b} \cdot \vec{j} - \vec{I}_2 \cdot \underset{\wedge}{D}^{(j)}_{c} \cdot \vec{j} - \vec{I}_3 \cdot \underset{\wedge}{D}^{(j)}_{a} \cdot \vec{j} \quad , \end{aligned} \qquad (2.5\text{-}7)$$

respectively.

When there is internal rotation, we just cannot tell which spin occupies a certain site. Moreover, the above three configurations are equally probable if we ignore small difference in magnetic interaction energies among them.

Therefore we may write

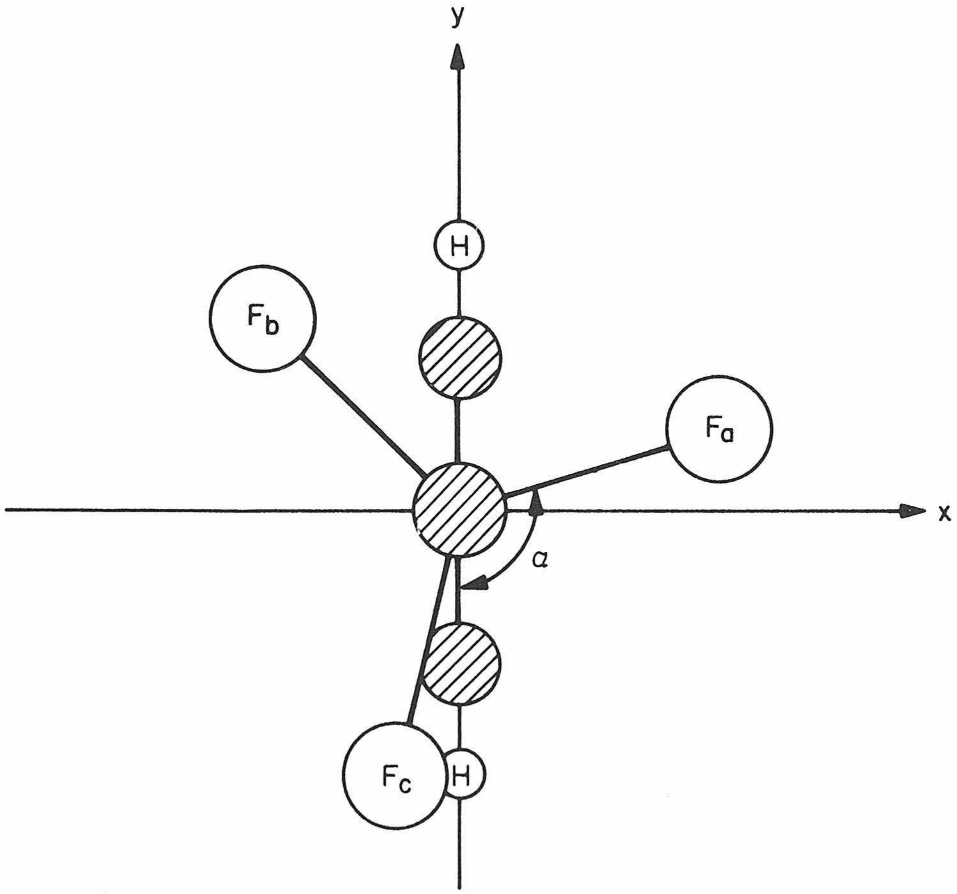


Fig. V Fluorine Spin Sites in Benzotrifluoride

$$\begin{aligned}\mathcal{H}_{S-R} &= (1/3)\left(\mathcal{H}^{(1)}_{S-R} + \mathcal{H}^{(2)}_{S-R} + \mathcal{H}^{(3)}_{S-R}\right) \\ &= -(1/3)\ (\vec{I}_1 + \vec{I}_2 + \vec{I}_3)\left(\underset{\sim}{C}_a^{(J)} + \underset{\sim}{C}_b^{(J)} + \underset{\sim}{C}_c^{(J)}\right)\cdot\vec{J} \\ &\quad -(1/3)\ (\vec{I}_1 + \vec{I}_2 + \vec{I}_3)\left(\underset{\sim}{D}_a^{(j)} + \underset{\sim}{D}_b^{)j)} + \underset{\sim}{D}_c^{(j)}\right)\cdot\vec{j}\ ,\end{aligned} \qquad (2.5\text{-}8)$$

where $\underset{\sim}{C}_a^{(J)}$, $\underset{\sim}{D}_a^{(j)}$, etc. depend on the angle α.

In order to obtain the averaged spin-rotation interaction we have to eliminate the angle dependence of $\underset{\sim}{C}_a^{(J)}$, $\underset{\sim}{D}_a^{(j)}$, etc. If we ignore contributions to $\underset{\sim}{C}_a^{(J)}$, $\underset{\sim}{D}_a^{(j)}$, etc. from nuclei which are located on the phenyl ring (but not on the z-axis) and from electrons localized in the phenyl ring, we can write

$$\underset{\sim}{C}_b^{(J)} = \underset{\sim}{R}^{-1}(120^\circ)\cdot\underset{\sim}{C}_a^{(J)}\cdot\underset{\sim}{R}(120^\circ) \qquad (2.5\text{-}9)$$

and

$$\underset{\sim}{C}_c^{(J)} = \underset{\sim}{R}^{-1}(-120^\circ)\cdot\underset{\sim}{C}_a^{(J)}\cdot\underset{\sim}{R}(-120^\circ)\ , \qquad (2.5\text{-}10)$$

where $\underset{\sim}{R}(\alpha)$ is the rotation matrix given by

$$\underset{\sim}{R}(\alpha) = \begin{pmatrix}\cos\alpha & -\sin\alpha & 0\\ \sin\alpha & \cos\alpha & 0\\ 0 & 0 & 1\end{pmatrix}\ . \qquad (2.5\text{-}11)$$

Similar relations hold for $\underset{\sim}{D}_a^{(j)}$, $\underset{\sim}{D}_b^{(j)}$, and $\underset{\sim}{D}_c^{(j)}$. If the angle α shown in Fig. 5 is zero, then it can be shown by symmetry considerations[20] that

$$\underset{\wedge}{D}_a^{(j)} = \begin{pmatrix} D_{xx}^{(j)} & 0 & 0 \\ 0 & D_{yy}^{(j)} & D_{yz}^{(j)} \\ 0 & D_{zy}^{(j)} & D_{zz}^{(j)} \end{pmatrix} \tag{2.5-12}$$

By making use of (2. 5-9) and (2. 5-10) we obtain from (2. 5-12)

$$\underset{\wedge}{D}_b^{(j)} = \tfrac{1}{4} \begin{pmatrix} D_{xx}^{(j)} + 3D_{yy}^{(j)} & \sqrt{3}\left(D_{xx}^{(j)} - D_{yy}^{(j)}\right) & 2\sqrt{3}\, D_{yz}^{(j)} \\ \sqrt{3}\left(D_{xx}^{(j)} - D_{yy}^{(j)}\right) & 3D_{xx}^{(j)} + D_{yy}^{(j)} & -2D_{yz}^{(j)} \\ 2\sqrt{3}\, D_{zy}^{(j)} & -2D_{zy}^{(j)} & 4D_{zz}^{(j)} \end{pmatrix} \tag{2.5-13}$$

and

$$\underset{\wedge}{D}_c^{(j)} = \tfrac{1}{4} \begin{pmatrix} D_{xx}^{(j)} + 3D_{yy}^{(j)} & -\sqrt{3}\left(D_{xx}^{(j)} - D_{yy}^{(j)}\right) & -2\sqrt{3}\, D_{yz}^{(j)} \\ -\sqrt{3}\left(D_{xx}^{(j)} - D_{yy}^{(j)}\right) & 3D_{xx}^{(j)} + D_{yy}^{(j)} & -2D_{yz}^{(j)} \\ -2\sqrt{3}\, D_{zy}^{(j)} & -2D_{zy}^{(j)} & 4D_{zz}^{(j)} \end{pmatrix} \tag{2.5-14}$$

If we replace $D_{xx}^{(j)}$, etc., by $C_{xx}^{(J)}$, etc., in (2. 5-12), (2. 5-13), and (2. 5-14), we obtain the corresponding expressions for $\underset{\wedge}{C}_a^{(J)}$, $\underset{\wedge}{C}_b^{(J)}$, and $\underset{\wedge}{C}_c^{(J)}$, respectively.

When α is not zero, $\underset{\wedge}{D}_a^{(j)}$, $\underset{\wedge}{D}_b^{(j)}$, and $\underset{\wedge}{D}_c^{(j)}$ may be written in the following forms:

$$\underset{\sim}{D}_a^{(j)}(\alpha) = \begin{pmatrix} \begin{array}{l} D_{xx}^{(j)} \cos^2\alpha \\ + D_{yy}^{(j)} \sin^2\alpha \end{array} & \begin{array}{l} -(D_{xx}^{(j)} - D_{yy}^{(j)}) \\ \times \sin\alpha \cos\alpha \end{array} & D_{yz}^{(j)} \sin\alpha \\ \begin{array}{l} -(D_{xx}^{(j)} - D_{yy}^{(j)}) \\ \times \sin\alpha \cos\alpha \end{array} & \begin{array}{l} D_{xx}^{(j)} \sin^2\alpha \\ + D_{yy}^{(j)} \cos^2\alpha \end{array} & D_{yz}^{(j)} \cos\alpha \\ D_{zy}^{(j)} \sin\alpha & D_{zy}^{(j)} \cos\alpha & D_{zz}^{(j)} \end{pmatrix} \tag{2.5-15}$$

$$\underset{\sim}{D}_b^{(j)}(\alpha) = \frac{1}{4} \begin{pmatrix} \begin{array}{l} 2\sqrt{3} \cos\alpha \sin\alpha \, (D_{xx}^{(j)} - D_{yy}^{(j)}) \\ + \cos^2\alpha \, (D_{xx}^{(j)} + 3D_{yy}^{(j)}) \\ + \sin^2\alpha \, (3D_{xx}^{(j)} + D_{yy}^{(j)}) \end{array} & \begin{array}{l} (D_{xx}^{(j)} - D_{yy}^{(j)}) \\ \times (2\cos\alpha \sin\alpha + \\ \sqrt{3} (\cos^2\alpha - \sin^2\alpha)) \end{array} & \begin{array}{l} 2D_{yz}^{(j)} (-\sin\alpha \\ + \sqrt{3} \cos\alpha \end{array} \\ \begin{array}{l} (D_{xx}^{(j)} - D_{yy}^{(j)}) \\ \times (2\cos\alpha \sin\alpha + \\ \sqrt{3} (\cos^2\alpha - \sin^2\alpha)) \end{array} & \begin{array}{l} 2\sqrt{3} \cos\alpha \sin\alpha \\ \times (D_{xx}^{(j)} - D_{yy}^{(j)}) \\ + \cos^2\alpha \, (3D_{xx}^{(j)} + D_{yy}^{(j)}) \\ + \sin^2\alpha \, (D_{xx}^{(j)} + 3D_{yy}^{(j)}) \end{array} & \begin{array}{l} -\, 2D_{yz}^{(j)} (\cos\alpha + \\ \sqrt{3} \sin\alpha) \end{array} \\ \begin{array}{l} 2D_{zy}^{(j)} (-\sin\alpha \\ + \sqrt{3} \cos\alpha) \end{array} & \begin{array}{l} -\, 2D_{zy}^{(j)} (\cos\alpha \\ + \sqrt{3} \sin\alpha) \end{array} & 4D_{zz}^{(j)} \end{pmatrix} \tag{2.5-16}$$

$$\underset{\sim}{D}_c^{(j)}(\alpha) = \frac{1}{4} \begin{pmatrix} \begin{array}{l} -\, 2\sqrt{3} \cos\alpha \sin\alpha \\ (D_{xx}^{(j)} - D_{yy}^{(j)}) \\ + \cos^2\alpha \, (D_{xx}^{(j)} + 3D_{yy}^{(j)}) \\ + \sin^2\alpha \, (3D_{xx}^{(j)} + D_{yy}^{(j)}) \end{array} & \begin{array}{l} -(D_{xx}^{(j)} - D_{yy}^{(j)}) \\ \times (2\cos\alpha \sin\alpha \\ + \sqrt{3} (\cos^2\alpha - \sin^2\alpha)) \end{array} & \begin{array}{l} 2D_{yz}^{(j)} (\sin\alpha \\ -\sqrt{3} \cos\alpha) \end{array} \\ \begin{array}{l} -(D_{xx}^{(j)} - D_{yy}^{(j)}) \\ \times (2\cos\alpha \sin\alpha \\ + \sqrt{3} (\cos^2\alpha - \sin^2\alpha)) \end{array} & \begin{array}{l} 2\sqrt{3} \cos\alpha \sin\alpha \\ \times (D_{xx}^{(j)} - D_{yy}^{(j)}) \\ + \cos^2\alpha \, (3D_{xx}^{(j)} + D_{yy}^{(j)}) \\ + \sin^2\alpha \, (D_{xx}^{(j)} + 3D_{yy}^{(j)}) \end{array} & \begin{array}{l} -2D_{yz}^{(j)} (\cos\alpha \\ + \sqrt{3} \sin\alpha \end{array} \\ 2D_{zy}^{(j)} (\sin\alpha - \sqrt{3} \cos\alpha) & -\, 2D_{zy}^{(j)} (\cos\alpha + \sqrt{3} \sin\alpha) & 4D_{zz}^{(j)} \end{pmatrix} \tag{2.5-17}$$

It goes without saying that similar expressions can be obtained for $\underset{\sim}{C}_a^{(J)}$, $\underset{\sim}{C}_b^{(J)}$, and $\underset{\sim}{C}_c^{(J)}$.

According to classical statistical mechanics under thermal equilibrium any function of the angle α can be averaged like

$$\overline{f(\alpha)} = \frac{\int_{-\pi}^{\pi} f(\alpha)\, e^{-V(\alpha)/kT}\, d\alpha}{\int_{-\pi}^{\pi} e^{-V(\alpha)/kT}\, d\alpha} \qquad (2.5\text{-}18)$$

where $V(\alpha)$ is the potential barrier for internal rotation and is an even function of α.

Since $V(\alpha)$ has the six-fold symmetry in benzotrifluoride, we can readily show that

$$\overline{\sin \alpha} = \overline{\cos \alpha} = 0 \quad .$$

Moreover $V(\alpha)$ is symmetric and $\sin 2\alpha$ is antisymmetric about $\alpha = 0$.

Therefore, we have

$$\overline{\cos \alpha \, \sin \alpha} = \overline{\sin 2\alpha} = 0 \quad .$$

(Note, however, that $\overline{\cos 2\alpha}$ does not vanish unless the barrier height, V_6, is zero.)

Therefore, $\underset{\sim}{D}^{(j)}$ matrices take the following forms when averaged over the internal angle:

$$\underset{\sim}{D}_a^{(j)} = \begin{bmatrix} D_{xx}^{(j)} - (D_{xx}^{(j)}-D_{yy}^{(j)})\,\overline{\sin^2\alpha} & 0 & 0 \\ 0 & D_{xx}^{(j)} - (D_{xx}^{(j)}-D_{yy}^{(j)})\,\overline{\cos^2\alpha} & 0 \\ 0 & 0 & D_{zz}^{(j)} \end{bmatrix} \tag{2.5-19}$$

$$\underset{\sim}{D}_b^{(j)} = \begin{bmatrix} (\tfrac{1}{4})(D_{xx}^{(j)}+3D_{yy}^{(j)}) + (\tfrac{1}{2})(D_{xx}^{(j)}-D_{yy}^{(j)}) \times \overline{\sin^2\alpha} & (\sqrt{3}/4)(D_{xx}^{(j)}-D_{yy}^{(j)}) \times \overline{\cos 2\alpha} & 0 \\ (\sqrt{3}/4)(D_{xx}^{(j)}-D_{yy}^{(j)}) \times \overline{\cos 2\alpha} & (\tfrac{1}{4})(3D_{xx}^{(j)}-D_{yy}^{(j)}) - (\tfrac{1}{2})(D_{xx}^{(j)}-D_{yy}^{(j)}) \times \overline{\sin^2\alpha} & 0 \\ 0 & 0 & D_{zz}^{(j)} \end{bmatrix} \tag{2.5-20}$$

and

$$\underset{\sim}{D}_c^{(j)} = \begin{bmatrix} (\tfrac{1}{4})(D_{xx}^{(j)}+3D_{yy}^{(j)}) + (\tfrac{1}{2})(D_{xx}^{(j)}-D_{yy}^{(j)}) \times \overline{\sin^2\alpha} & -(\sqrt{3}/4)(D_{xx}^{(j)}-D_{yy}^{(j)}) \times \overline{\cos 2\alpha} & 0 \\ -(\sqrt{3}/4)(D_{xx}^{(j)}-D_{yy}^{(j)}) \times \overline{\cos 2\alpha} & (\tfrac{1}{4})(3D_{xx}^{(j)}-D_{yy}^{(j)}) - (\tfrac{1}{2})(D_{xx}^{(j)}-D_{yy}^{(j)}) \times \overline{\sin^2\alpha} & 0 \\ 0 & 0 & D_{zz}^{(j)} \end{bmatrix} \tag{2.5-21}$$

Thus, unless the height of the barrier is zero, the three matrices $\underset{\sim}{D}_a^{(j)}$, $\underset{\sim}{D}_b^{(j)}$, and $\underset{\sim}{D}_c^{(j)}$ do not all have the same form, nor are they diagonal.

However, for all three matrices there is one thing in common which can be seen in Eqs. (2.5-19) through (2.5-21). This is that all three matrices have the same zz element, that is, $D_{zz}^{(j)}$, and also they have vanishing zx, zy, xz, and yz elements.

Therefore, we can rewrite (2.5-8) as

$$\mathcal{H}_{S-R} = -\vec{F} \cdot \underset{\sim}{C}^{(J)} \cdot \vec{J} - D_{\alpha}^{(j)} \vec{F} \cdot \vec{j} \quad , \tag{2.5-22}$$

since $\vec{j}$ has only the z component in the body-fixed frame. Thus we have proved the validity of (2.5-1) in the presence of fast internal rotation.

The spin-internal rotation interaction represented by $-D_{\alpha}^{(j)} \vec{F} \cdot \vec{j}$ plays an important role in the spin relaxation especially when the height of barrier is much less than the average thermal energy of the internal top, kT, and therefore we will restrict our attention to this case.

Thus, in case $(V_6/kT) \ll 1$, we can approximate $\exp(-V(\alpha)/kT)$ in Eq. (2.5-18) by $(1 - V(\alpha)/kT)$, giving

$$\overline{\cos 2\alpha} \approx 0$$

and

$$\overline{\sin^2 \alpha} \approx 1/2 \quad .$$

Therefore, for the case of low barrier matrices $\underset{\sim}{D}_a^{(j)}$, $\underset{\sim}{D}_b^{(j)}$, and

$\underset{\sim}{D}_c^{(j)}$ are all the same and approximately diagonal. Discussions given so far can also be applied to $\underset{\sim}{C}_a^{(J)}$, $\underset{\sim}{C}_b^{(J)}$, and $\underset{\sim}{C}_c^{(J)}$.

From (2.5-19), (2.5-20), and (2.5-21) we expect that

$$C_{xx}^{(J)} \approx C_{yy}^{(J)}$$

which is confirmed by Burke.[21]

However, in later discussions of spin relaxation we will assume that $\underset{\sim}{C}^{(J)}$ is diagonal but $C_{xx}^{(J)} \neq C_{yy}^{(J)}$.

Thus, we have confirmed that $\mathcal{H}_{S-R}$ given by (2.5-1) is the effective spin-rotation interaction energy in the presence of fast internal rotation.

Discussions about the magnetic shielding effect for a nuclear spin on an internal rotor will be given in the next section, since the magnetic shielding tensor is closely related to the spin-rotation tensor.

2.6 Theory of Magnetic Shielding for a Nuclear Spin on Internal Top

In a molecule exposed in the static magnetic field $\vec{H}_0$ the local magnetic which is seen by a nuclear spin at a given site is not usually equal to the external field. This shielding effect is mainly due to the motions of electrons in the molecule induced by the external field. Besides this direct effect the external field can indirectly change the electronic states via the nuclear spin-electron spin coupling, thus giving an additional shielding effect.

This induced magnetic field is usually expressed up to the first order of the external magnetic field $\vec{H}_0$ in a manner like

$$\vec{H}_{ind} = - \underset{\frown}{\sigma} \cdot \vec{H}_0 \quad , \tag{2.6-1}$$

where $\underset{\frown}{\sigma}$ is called the magnetic shielding tensor for a given nuclear spin.

In order to formulate the idea described above mathematically let us write the total Zeeman energy of a given nuclear spin denoted by K as

$$\begin{aligned} E_K &= -\vec{\mu}_K \cdot \vec{H}_0 + \vec{\mu}_K \cdot \underset{\frown}{\sigma}(K) \cdot \vec{H}_0 \\ &= -\vec{\mu}_K(\underset{\frown}{1} - \underset{\frown}{\sigma}(K)) \cdot \vec{H}_0 \quad , \end{aligned} \tag{2.6-2}$$

where the term $\vec{\mu}_K \cdot \underset{\frown}{\sigma}(K) \cdot \vec{H}_0$ can be regarded as a correction to the Zeeman energy of bare nuclear spin due to the magnetic shielding effect, and it is expected that an analytical expression may be obtained by studying this energy correction.

The Hamiltonian for this problem may be written

$$\begin{aligned} \mathcal{H} = \mathcal{H}_0 &- \sum_K \vec{\mu}_K \cdot \vec{H}_0 + \frac{|e|}{mc} \sum_k \frac{\hbar}{i} \vec{A}_k \cdot \vec{\nabla}_k \\ &+ \frac{e^2}{2mc^2} \sum_k \vec{A}_k^2 \quad , \end{aligned} \tag{2.6-3}$$

where $\mathcal{H}_0$ is the unperturbed Hamiltonian for the system in the absence of external magnetic field, $\vec{A}_k$ and $\vec{\nabla}_k$ are the vector potential and the gradient operator at the position of k-th electron, respectively, and

m = mass of electron,

e = charge of electron,

and

$$c = \text{velocity of light.}$$

If we pick the origin at an arbitrary point O, $\vec{A}_k$ may be written

$$\vec{A}_k = (1/2)(\vec{H}_0 \times \vec{r}_{0k}) + \sum_K (\vec{\mu}_K \times \vec{r}_{Kk})/r_{Kk}^3 \quad , \tag{2.6-4}$$

where $\vec{r}_{0k}$ is the position vector of k-th electron with respect to the origin O while $\vec{r}_{Kk}$ is the position vector of the same electron referred to the K-th nucleus. The first term on the right-hand side of (2.6-4) is the vector potential associated with a constant field $\vec{H}_0$ and the second term is that due to nuclei in the molecule.

Then, $\frac{|e|}{mc} \sum_k \frac{\hbar}{i} \vec{A}_k \cdot \vec{\nabla}_k$ and $e^2/2mc^2 \sum_k \vec{A}_k^2$ may be rewritten as follows:

$$\frac{|e|}{mc} \sum_k \frac{\hbar}{i} \vec{A}_k \cdot \vec{\nabla}_k$$

$$= \frac{|e|}{2mc} \sum_k \vec{\ell}_{0k} \cdot \vec{H}_0 + \frac{|e|}{mc} \sum_K \sum_k \frac{\vec{\mu}_K}{r_{Kk}^3} \cdot \vec{\ell}_{Kk} \tag{2.6-5}$$

where

$$\vec{\ell}_{0k} \equiv \frac{\hbar}{i} \vec{r}_{0k} \times \vec{\nabla}_k \tag{2.6-6}$$

and

$$\vec{\ell}_{Kk} \equiv \frac{\hbar}{i} \vec{r}_{Kk} \times \vec{\nabla}_k \quad , \tag{2.6-7}$$

and

$$\frac{e^2}{2mc^2}\sum_k \vec{A}_k^{\,2} = \frac{e^2}{8mc^2}\sum_k (\vec{H}_0 \times \vec{r}_{0k})^2$$

$$+ \frac{e^2}{2mc^2}\sum_{K,k}\ \sum_{g,g'} \frac{(\vec{\mu}_K)_g(\vec{H}_0)_{g'}[(\vec{r}_{0k})_g(\vec{r}_{Kk})_{g'}\delta_{gg'} - (\vec{r}_{0k})_g(\vec{r}_{Kk})_{g'}}{r_{Kk}^3}$$

$$+ \frac{e^2}{2mc^2}\sum_k \sum_K \sum_{K'} \frac{(\vec{\mu}_K \times \vec{r}_{Kk}) \cdot (\vec{\mu}_{K'} \times \vec{r}_{K'k})}{r_{Kk}^3\, r_{K'k}^3} \quad \circ \qquad (2.6\text{-}8)$$

$\vec{\ell}_{0k}$ and $\vec{\ell}_{Kk}$ can be considered as the angular momentum of k-th electron about the origin O and the K-th nucleus, respectively.

Now, let

$$\mathcal{H}'(H_0) = \frac{|e|}{2mc}\sum_k \vec{\ell}_{0k} \cdot \vec{H}_0 \quad , \qquad (2.6\text{-}9)$$

$$\mathcal{H}'(H_0^2) = \frac{e^2}{8mc^2}\sum_k (\vec{H}_0 \times \vec{r}_{0k})^2 \quad , \qquad (2.6\text{-}10)$$

$$\mathcal{H}'(\mu_K) = \frac{|e|}{mc}\sum_k \sum_K \frac{\vec{\ell}_{Kk}}{r_{Kk}^3} \cdot \vec{\mu}_K \quad , \qquad (2.6\text{-}11)$$

$$\mathcal{H}'(\mu_K^2) = \frac{e^2}{2mc^2}\sum_k \sum_K \sum_{K'} \frac{(\vec{\mu}_K \times \vec{r}_{Kk}) \cdot (\vec{\mu}_{K'} \times \vec{r}_{K'k})}{r_{Kk}^3\, r_{K'k}^3} \quad , \qquad (2.6\text{-}12)$$

and

$$\mathcal{H}'(\mu_K H_0) = \frac{e^2}{2mc^2}$$

$$\times \sum_K \sum_k \sum_g \sum_{g'} \frac{(\vec{\mu}_K)_g(\vec{H}_0)_{g'}[(\vec{r}_{0k})_g(\vec{r}_{Kk})_{g'}\delta_{gg'} - (\vec{r}_{0k})_g(\vec{r}_{Kk})_{g'}]}{r_{Kk}^3} \qquad (2.6\text{-}13)$$

$$\mathcal{H} = \mathcal{H}_0 - \sum_K \vec{\mu}_K \cdot \vec{H}_0 + \mathcal{H}'(H_0) + \mathcal{H}'(H_0^2)$$

$$+ \mathcal{H}'(\mu_K) + \mathcal{H}'(\mu_K^2) + \mathcal{H}'(\mu_K H_0) \quad . \qquad (2.6\text{-}14)$$

To evaluate the energy correction we assume that the wave function takes the form

$$\psi = \psi_0 + \vec{\psi}_1 \cdot \vec{H}_0 \quad , \qquad (2.6\text{-}15)$$

which has been used by Tillieu and Guy.[22-25]

One may also adopt the wave function ψ of the form[26,27]

$$\psi = \psi_0 + \vec{\psi}_1 \cdot \vec{H}_0 + \vec{\psi}_2 \cdot \vec{\mu}_K \quad , \qquad (2.6\text{-}16)$$

but if $\vec{H}_0 \cdot \vec{\psi}_1$ satisfies the first-order perturbation equation

$$(\mathcal{H}_0 - W^{(0)})|\vec{H}_0 \cdot \vec{\psi}_1\rangle = -\mathcal{H}'(H_0)|\psi_0\rangle \qquad (2.6\text{-}17)$$

and if we are interested in terms which are bilinear with respect to $\vec{\mu}_K$ and $\vec{H}_0$, it can be shown that we may drop the $\vec{\psi}_2 \cdot \vec{\mu}_K$ term safely.

Replacing (2. 6-15) in the formula

$$W = \langle\psi|\mathcal{H}|\psi\rangle / \langle\psi|\psi\rangle \quad ,$$

we obtain the following expression for the energy correction ΔE:

$$\Delta E = \frac{e^2}{2mc^2} \sum_g \sum_{g'} \sum_K (\vec{\mu}_K)_g (\vec{H}_0)_{g'} \langle\psi_0 | \sum_k \{(\vec{r}_{0k})_g (\vec{r}_{Kk})_{g'} \delta_{gg'}$$

$$- (\vec{r}_{0k})_g (\vec{r}_{Kk})_{g'}\} / r_{Kk}^3 |\psi_0\rangle$$

$$+\frac{2|e|}{mc}\ \mathrm{Re}\Big\{\sum_{g}\sum_{g'}\sum_{K}(H_0)_{g'}(\vec{\mu}_K)_g$$

$$\times\langle\psi_0|\sum_{k}\frac{(\vec{\ell}_{Kk})_g}{r_{Kk}^3}|\psi_{1g'}\rangle\Big\}\quad, \qquad (2.6\text{-}18)$$

where we retained only the terms which are bilinear with respect to μ_K and H_0.

By comparing Eq. (2.6-18) with

$$\Delta E = \sum_{K}\vec{\mu}_K\cdot\underset{\sim}{g}(K)\cdot\vec{H}_0$$

we obtain

$$\sigma(K)_{gg'} = \frac{e^2}{2mc^2}\langle\psi_0|\sum_{k}\frac{\vec{r}_{0k}\cdot\vec{r}_{Kk}\,\delta_{gg'}-(\vec{r}_{0k})_g(\vec{r}_{Kk})_{g'}}{r_{Kk}^3}|\psi_0\rangle$$

$$+\frac{2|e|}{mc}\mathrm{Re}\langle\psi_0|\sum_{k}\frac{(\vec{\ell}_{Kk})_g}{r_{Kk}^3}|\psi_{1g'}\rangle\quad. \qquad (2.6\text{-}19)$$

Since ψ_{1g} is a solution to the first order perturbation equation given by (2.6-17), we have

$$\psi_{1g}(0) = \sum_{n\neq 0}\frac{\langle\psi_n|\frac{|e|}{2mc}\sum_{k}(\ell_{0k})_g|\psi_0\rangle}{W_0^{(0)}-W_n^{(0)}}\psi_n\quad, \qquad (2.6\text{-}20)$$

where 0 in $\psi_{1g}(0)$ indicates the choice of origin since $\psi_{1g}(O)$ depends on gauge transformations.

Replacing (2.6-20) in (2.6-19) and noting

$$\vec{r}_{0k} = \vec{r}_{0K}+\vec{r}_{Kk}\quad,$$

we obtain

$$\sigma(K)_{gg'} = \frac{e^2}{2mc^2}\langle\psi_0|\sum_k \frac{\vec{r}_{Kk}^{\,2}\delta_{gg'} - (\vec{r}_{Kk})_g(\vec{r}_{Kk})_{g'}}{r_{Kk}^3}|\psi_0\rangle$$

$$+ \frac{e^2}{2mc^2}\langle\psi_0|\sum_k \frac{\vec{r}_{0K}\cdot\vec{r}_{Kk}\delta_{gg'} - (\vec{r}_{0K})_g(\vec{r}_{Kk})_{g'}}{r_{Kk}^3}|\psi_0\rangle$$

$$+ \frac{|e|}{mc}\,\mathrm{Re}\sum_{n\neq 0}\frac{\langle 0|(\vec{\pi}_K)_g|n\rangle\langle n|L_{g'}|0\rangle}{W_0^{(0)} - W_n^{(0)}}\ , \qquad (2.6\text{-}21)$$

where $\vec{L}\ (\equiv \sum_k \vec{l}_{0k})$ is the total electronic orbital angular momentum and $\vec{\pi}_k$ has been previously defined by (2.4-26).

Application of the Hellmann-Feynman theorem (2.4-24) to Eq. (2.6-21) gives us

$$\sigma(K)_{gg'} = \frac{e^2}{2mc^2}\langle\psi_0|\sum_k \frac{\vec{r}_{Kk}^{\,2}\delta_{gg'} - (\vec{r}_{Kk})_g(\vec{r}_{Kk})_{g'}}{r_{Kk}^3}|\psi_0\rangle$$

$$- \frac{e^2}{2mc^2}\sum_{K'(\neq K)}\frac{Z_{K'}}{r_{KK'}^3}\{\vec{r}_K\cdot(\vec{r}_K - \vec{r}_{K'})\delta_{gg'} - (\vec{r}_K)_g(\vec{r}_K - r_{K'})_{g'}\}$$

$$+ \frac{1}{2Z_K mc^2}\{\vec{r}_K\cdot\vec{F}_K\delta_{gg'} - (\vec{r}_K)_g(\vec{F}_K)_{g'}\}$$

$$+ \frac{|e|}{mc}\,\mathrm{Re}\sum_{n\neq 0}\frac{\langle 0|(\vec{\pi}_K)_g|n\rangle\langle n|L_{g'}|0\rangle}{W_0^{(0)} - W_n^{(0)}}\ . \qquad (2.6\text{-}22)$$

When we pick the origin at the site of nucleus K, we see that Eq. (2.6-22) is reduced to the Ramsey formula.[28]

The first term on the right-hand side of (2.6-22) is known to be responsible for diamagnetic shielding while the remaining terms are considered to give the effect of paramagnetic shielding. Thus we write for convenience

$$\sigma(K)^{d}_{gg'} = \frac{e^2}{2mc^2} \langle \psi_0 | \sum_{k} \frac{\vec{r}^{\,2}_{Kk}\delta_{gg'} - (\vec{r}_{Kk})_g(\vec{r}_{Kk})_{g'}}{r^3_{Kk}} | \psi_0 \rangle \tag{2.6-23}$$

and

$$\begin{aligned} \sigma(K)^{P}_{gg'} = & -\frac{e^2}{2mc^2} \sum_{K'(\neq K)} \frac{Z_{K'}}{r^3_{KK'}} \{(\vec{r}_K - \vec{r}_{K'})\delta_{gg'} - (\vec{r}_K)_g(\vec{r}_K - \vec{r}_{K'})_{g'}\} \\ & + \frac{1}{2Z_K mc^2} \{\vec{r}_K \cdot \vec{F}_K \delta_{gg'} - (\vec{r}_K)_g (\vec{F}_K)_{g'}\} \\ & + \frac{|e|}{mc} \operatorname{Re} \sum_{n\neq 0} \frac{\langle 0 | (\pi_K)_g | n \rangle \langle n | L_{g'} | 0 \rangle}{W^{(0)}_0 - W^{(0)}_n} \ . \end{aligned} \tag{2.6-24}$$

Nonempirical calculation of the term

$$\operatorname{Re} \sum_{n\neq 0} \frac{\langle 0 | (\pi_K)_g | n \rangle \langle n | L_{g'} | 0 \rangle}{W^{(0)}_0 - W^{(0)}_n} \tag{2.6-25}$$

requires the knowledge of electronically excited states which is, in general, not available. Therefore, the theoretical calculations of either $C(K)_{gg'}$ or $\sigma(K)_{gg'}$ cannot help relying on some approximate or semiempirical means. Though there have been several recent successful attempts at the calculation of proton and fluorine chemical shifts employing variational procedures[29] and the perturbed

Hartree-Fock method,[30, 31] the evaluation of term (2.6-25) still remains formidable. Therefore, where feasible, a direct experimental determination of either $C(K)_{gg'}$ or $\sigma(K)_{gg'}$ is desirable.

In this connection it is of great interest to relate $\sigma(K)_{gg'}$ to $C(K)_{gg'}$ since an experimental determination of either $\sigma(K)_{gg'}$ or $C^{(J)}(K)_{gg'}$ enables us to evaluate the other.

From (2.4-39) to (2.6-24) we obtain

$$\begin{aligned}
\sigma(K)^{P}_{gg'} = & -\frac{e^2}{2mc^2} \sum_{K'(\neq K)} \frac{Z_{K'}}{r^{3}_{KK'}} \Biggl\{ \Bigl(r_K - \frac{I_{g'}}{I_g} r_{K'} \Bigr) \cdot (\vec{r}_K - \vec{r}_{K'}) \delta_{gg'} \\
& \qquad - (\vec{r}_K - \vec{r}_{K'})_g (\vec{r}_K - \vec{r}_{K'})_{g'} \Biggr\} \\
& + \frac{|e|}{2mc} \frac{I_{g'} C^{(J)}(K)_{gg'}}{g_K \beta_N} + \frac{1}{2 Z_K mc^2} \Biggl\{ \vec{r}_K \cdot \vec{F}_K \\
& \times \Bigl(1 - \frac{1}{\beta_K} \frac{I_{g'}}{I_g} \Bigr) \delta_{gg'} - (\vec{r}_K)_g (\vec{F}_K)_{g'} \Bigl(1 - \frac{1}{\beta_K} \Bigr) \Biggr\} \quad . \qquad (2.6\text{-}26)
\end{aligned}$$

Obviously, the relation (2.6-26) enables us to evaluate $C^{(J)}(K)_{gg'}$ (or $\sigma(K)^{P}_{gg'}$) if the molecular structure, internal rotational barrier, and $\sigma(K)^{P}_{gg'}$ (or $C^{(J)}(K)_{gg'}$) are known.

When averaged over the internal rotation, Eq. (2.6-26) may be written for diagonal elements

$$\langle\sigma(K)_{gg}^{P}\rangle_{int} = -\frac{e^2}{2mc^2}\sum_{K'(\neq K)}\left\{\left\langle\frac{Z_{K'}}{r_{KK'}}\right\rangle_{int} - \left\langle\frac{Z_{K'}(\vec{r}_K-\vec{r}_{K'})_g^2}{r_{KK'}^3}\right\rangle_{int}\right\}$$

$$+\frac{|e|}{2mc}\,\frac{I_g C_{gg}^{(J)}}{g_K\beta_N} + \frac{1}{2Z_K mc^2}\left(1-\frac{1}{\beta_K}\right)$$

$$\times\{\langle\vec{r}_K\cdot\vec{F}_K\rangle_{int} - \langle(\vec{r}_K)_g(\vec{F}_K)_g\rangle_{int}\} \quad , \qquad (2.6\text{-}27)$$

where $\langle\quad\rangle_{int}$ indicates the average over internal angle and $C_{gg}^{(J)}$'s are defined by (2.5-3).

For molecules like φ-CF_3 we can readily show that

$$\langle\vec{r}_K\cdot\vec{F}_K\rangle_{int} = \langle(\vec{r}_K)_g(\vec{F}_K)_g\rangle_{int} = 0 \quad .$$

Therefore, for fluorine spins in φ-CF_3 we may write

$$\langle\sigma^{P}(K)_{gg}\rangle_{int} = -\frac{e^2}{2mc^2}\sum_{K'(\neq K)}\left\{\left\langle\frac{Z_{K'}}{r_{KK'}}\right\rangle_{int} - \left\langle\frac{Z_{K'}(\vec{r}_K-\vec{r}_{K'})_g^2}{r_{KK'}^3}\right\rangle_{int}\right\}$$

$$+\frac{|e|}{2mc}\,\frac{I_g C_{gg}^{(J)}}{g_K\beta_N} \quad . \qquad (2.6\text{-}28)$$

Thus, experimental measurements of $\langle\sigma(K)_{gg}\rangle_{int}$ enables us to evaluate $C_{gg}^{(J)}$ if all other relevant knowledge is available.

In nuclear magnetic resonance of liquid or gaseous phase we are concerned only with the averaged value of $\underset{\frown}{\sigma}(K)$ defined as

$$\bar{\sigma}(K)_{av} = \tfrac{1}{3}\,\mathrm{Tr}\langle\underset{\frown}{\sigma}(K)\rangle_{int}$$

$$= \tfrac{1}{3}\sum_{g}\langle\sigma(K)_{gg}\rangle_{int} \quad , \qquad (2.6\text{-}29)$$

since the anisotropy effect is largely smoothed out due to incessant molecular tumblings.

Thus we obtain from (2. 6-23) and (2. 6-27)

$$\begin{aligned}\bar{\sigma}(K)_{av} &= \frac{e^2}{3mc^2}\left\langle \psi_0 \left| \sum_k \frac{1}{r_{Kk}} \right| \psi_0 \right\rangle - \frac{e^2}{3mc^2} \sum_{K'(\neq K)} \left\langle \frac{Z_{K'}}{r_{KK'}} \right\rangle_{int} \\ &+ \frac{|e|}{6mc} \frac{\sum_g I_g \langle C^{(J)}(K)_{gg} \rangle_{int}}{g_K \beta_N} \\ &+ \frac{1}{3Z_K mc^2}\left(1 - \frac{1}{\beta_K}\right) \langle \vec{r}_K \cdot \vec{F}_K \rangle_{int} \qquad (2.6\text{-}30)\end{aligned}$$

A relation similar to Eq. (2. 6-30) was first derived by Schwartz[32] for the case of rigid molecules. Comparing Eq. (2. 6-20) with that derived by Schwartz, we see that we have an extra term, $\frac{1}{3Z_K mc^2}(1 - \frac{1}{\beta_K})\langle \vec{r}_K \cdot \vec{F}_K \rangle_{int}$, which takes into account any internal rotational degree of freedom. This term is generally nonvanishing unless molecules are symmetric about their axes of internal rotation. In cases where the molecules are symmetric about its axis of internal rotation, as in φ-CF_3 and CF_3NO_2, this term vanishes since the position vector $\vec{r}_K$ is always perpendicular to the Hellmann-Feynman force, $\vec{F}_K$, acting on the nucleus K. In this case Eq. (2. 6-30) is reduced to an equivalent form of the Schwartz relation if we remember that all the terms involved in this relation are to be averaged over the internal angle.

It is needless to say that nuclear magnetic shielding and spin-rotation constants provide an important probe for approximate electronic wavefunctions obtained by the variational method.

However, we are not going into further details of this problem, since they can be found elsewhere.[33-35] Finally, we would like to conclude this section by noting that the magnetic shielding tensor of a nucleus on the internal rotor is related to the spin-total-angular-momentum coupling tensor rather than the spin-internal-rotation coupling tensor.

2.7 ^{19}F Spin-Lattice Relaxation in Benzotrifluoride

Recently some people[19, 36, 37, 38] have published their experimental results on the F^{19} spin relaxation in benzotrifluoride. In the pure liquid[36, 37] it was found that the F^{19} spin-lattice relaxation time decreases slowly from 3.2 seconds at -20° C to about 0.5 second at 300° C, just below the critical temperature. Green and Powles[36] concluded that the relaxation in the liquid arises mainly from the motion of the CF_3 top. On the other hand Faulk and Eisner[37] assumed that the internal rotation does not alter the correlation time very much and they interpreted their results in terms of the spin-overall-rotation coupling.

However, as pointed out in the first chapter of this thesis, such an assumption can be a serious mistake in the extreme case that the phenyl ring is stationary while the CF_3 group is rotating. In solid benzotrifluoride[19] second moment and T_1 measurements indicate that while the phenyl ring is stationary the CF_3 group is freely rotating and, in fact, serves as a spin sink for the protons. Thus we infer that even in the liquid state the CF_3 group is much more mobile than the phenyl ring, since the temperature dependence of T_1 for the ring protons is quite different from that for the protons on the CH_3 top in toluene. The ring protons show us a typical example of the spin relaxation via the magnetic dipole-dipole interactions.

Thus the entire thing seems to depend on whether the molecule or internal top on which spins under consideration are located maintains its rotational motion long enough to produce appreciable effects on the spin relaxation. If the rotational angular momentum of any molecule quenches so fast that the spin-rotation interaction can last only for very short time ($\lesssim 10^{-15}$ sec), the spin-rotation interaction is relatively ineffective as a spin relaxation mechanism compared with dipole-dipole interactions whose correlation times are of the order of 10^{-12} sec in many liquids.

Therefore, at low temperatures, where the angular momentum which a molecule can gain from other molecules in the collision processes is very small and the frictional force which can quench the thus obtained angular momentum is very large, the spin-rotation interaction is considered to have little effect on the spin relaxation process, thus leaving the dipole-dipole interaction as a dominant relaxation mechanism in these cases. However, as temperature rises, intermolecular collisions become more and more energetic and the frictional force which restricts the rotation of a molecule smaller and smaller. Consequently, the amount of angular momentum which a molecule obtains in the collision processes increases and the molecule can rotate more and more freely. Therefore, at high temperatures we may expect the importance of spin-rotation interaction as a relaxation mechanism to be appreciable. This has, in particular, been proven in many fluorine compounds.[36, 39, 40]

Though we have no intention to discuss the details of molecular dynamics in this section, we will mention the problem of F^{19} spin relaxation in benzotrifluoride to demonstrate the importance of spin-internal-rotation interaction as a spin relaxation mechanism.

Burke[21] has estimated that the contribution of intramolecular dipole-dipole interaction to $(1/T_1)_{intra}$ in φ-CF_3 is approximately 10% at 240° K and we expect that this contribution will become less appreciable as temperatures rise. Thus, we may safely assume that $(1/T_1)_{intra}$ in φ-CF_3 is entirely due to the spin-rotation interaction.

Imagine a nuclear spin ($I = \frac{1}{2}$) on the internal rotor, and let the Hamiltonian of the problem be written

$$\mathcal{H}^I = \mathcal{H}_0^I + \mathcal{H}_1^I \quad , \tag{2.7-1}$$

where

$$\mathcal{H}_0^I = g_I \beta_N \vec{I} \cdot \vec{H}_0 \tag{2.7-2}$$

$$\mathcal{H}_0^I = -g_I \beta_N \vec{I} \cdot (\vec{H}_J + \vec{H}_j) \tag{2.7-3}$$

with

$$\vec{H}_J = -\frac{1}{g_I \beta_N} \underset{\wedge}{C}^{(J)} \cdot \vec{J} \tag{2.7-4}$$

and

$$\vec{H}_j = -\frac{1}{g_I \beta_N} D_\alpha^{(j)} \vec{j} \quad . \tag{2.7-5}$$

Time-dependent perturbation theory gives us[41, 42, 43]

$$\frac{1}{T_1} = \frac{2}{\hbar^2} \int_{-\infty}^{\infty} \overline{\langle\beta|\mathcal{H}_1^I(t+\tau)|\alpha\rangle\langle\alpha|\mathcal{H}_1^I(t)|\beta\rangle}\; e^{-i\omega_I\tau}\, d\tau \qquad (2.7\text{-}6)$$

for the spin-lattice relaxation time, T_1, where the solid line over the integrand means that we take the average over an equilibrium ensemble and $|\alpha\rangle$, $|\beta\rangle$ are the spin states due to $\mathcal{H}_0^I$ (the Zeeman levels).

Similar formula may be obtained for T_2, the spin-spin relaxation time,[43] though not explicitly given here. It goes without saying that these perturbation formulas apply only if the local field is reasonably small, so that both relaxation times are long compared with the period of the spin precession $(2\pi/\omega_I)$.

Now, rewrite $\mathcal{H}_1^I$ in the component form as

$$\mathcal{H}_1^I = -\, g_I\beta_N \sum_q I_q \{(H_J)_q + (H_j)_q\} \qquad (2.7\text{-}7)$$

and substitute this into Eq. (2.7-6). Then we obtain

$$\frac{1}{T_1} = \frac{2}{\hbar^2}\, g_I^2\beta_N^2 \sum_{q,q'} \langle\alpha|I_{q'}|\beta\rangle\langle\beta|I_q|\alpha\rangle$$

$$\times \int_{-\infty}^{\infty} \overline{H_{q'}(t+\tau)H_q(t)}\; e^{-i\omega_I\tau}\, d\tau \quad , \qquad (2.7\text{-}8)$$

where

$$H_q = (\vec{H}_J)_q + (\vec{H}_j)_q \quad .$$

Evaluation of the correlation functions

requires a detailed knowledge of molecular dynamics which is unavailable at present.

Therefore, we assume as usual that

$$\overline{H_J(t)_q H_J(t+\tau)_{q'}} = \delta_{qq'} \overline{H_J(t)_q^2}\, e^{-|\tau|/\tau_J} \tag{2.7-10}$$

and

$$\overline{H_j(t)_q H_j(t+\tau)_{q'}} = \delta_{qq'} \overline{H_j(t)_q^2}\, e^{-|\tau|/\tau_j} \ , \tag{2.7-11}$$

Burke[21] has assumed that there is no cross correlation between $\vec{H}_J$ and $\vec{H}_j$, that is,

$$\overline{H_J(t)_q H_j(t+\tau)_{q'}} = 0 \quad . \tag{2.7-12}$$

Then, from Eq. (2.7-8) we have

$$\frac{1}{T_1} = A\tau_J + B\tau_j \tag{2.7-13}$$

with

$$A = g_I^2 \beta_N^2 \left(\overline{H_J(t)_X^2} + \overline{H_J(t)_Y^2}\right) \tag{2.7-14}$$

and

$$B = g_I^2 \beta_H^2 \left(\overline{H_j(t)_X^2} + \overline{H_j(t)_Y^2}\right) \quad . \tag{2.7-15}$$

where we have assumed

$$\omega_I^2 \tau_J^2 , \quad \omega_I^2 \tau_j^2 \ll 1 \quad . \tag{2.7-16}$$

Noting that

$$\overline{H^2_{JX}} = \overline{H^2_{JY}} = \overline{H^2_{JZ}} = \tfrac{1}{3}\,\overline{H^2_J}$$

and

$$\overline{H^2_{jX}} = \overline{H^2_{jY}} = \overline{H^2_{jZ}} = \tfrac{1}{3}\,\overline{H^2_j} \quad ,$$

Eq. (2.7-13) may be written

$$\frac{1}{T_1} = \tfrac{2}{3}\,\overline{(\underset{\frown}{C}^{(J)}\cdot\vec{J})^2}\,\tau_J + \tfrac{2}{3}\,D^{(j)^2}_{\alpha}\,\overline{j^2}\,\tau_j \quad . \tag{2.7-17}$$

Thus in the presence of internal rotation we see that unlike the case of usual spin-rotation relaxation we have an additional correlation time, τ_j, which is not necessarily equal to τ_J.

Since the effective coupling tensor $\underset{\frown}{C}^{(J)}$ is approximately diagonal, we may rewrite Eq. (2.7-17) as

$$\frac{1}{T_1} \approx \tfrac{2}{3}\left(C^{(J)^2}_{xx}\,\overline{J^2_x} + C^{(J)^2}_{yy}\,\overline{J^2_y} + C^{(J)^2}_{zz}\,\overline{J^2_z}\right)\tau_J$$

$$+ \tfrac{2}{3}\,D^{(j)^2}_{\alpha}\,\overline{j^2}\,\tau_j \tag{2.7-18}$$

where we have assumed that the cross terms like $\overline{J_xJ_y}$, etc. are negligible.

Substituting

$$\overline{J^2_x} = \frac{I_xkT}{\hbar^2} \tag{2.7-19}$$

$$\overline{J^2_y} = \frac{I_ykT}{\hbar^2} \tag{2.7-20}$$

$$\overline{J_z^2} = \frac{I_z kT}{\hbar^2} \qquad (2.7\text{-}21)$$

and

$$\overline{j^2} = \frac{1}{1 - (I_\alpha / I_z)} \frac{I_\alpha kT}{\hbar^2} \qquad (2.7\text{-}22)$$

into Eq. (2.7-18), we obtain

$$\frac{1}{T_1} \approx \frac{2}{3\hbar^2} (C_{xx}^{(J)^2} I_x + C_{yy}^{(J)^2} I_y + C_{zz}^{(J)^2} I_z) \, kT \, \tau_J$$

$$+ \frac{2}{3\hbar^2} \frac{D_\alpha^{(j)^2} I_\alpha}{1 - (I_\alpha / I_z)} kT \, \tau_j \quad . \qquad (2.7\text{-}23)$$

If we assume that the rotation of the CF_3 top is inertial while the overall rotation of the entire molecule is diffusional, we expect that

$$\tau_J \propto (1/\eta) \qquad (2.7\text{-}24)$$

and

$$\tau_j \propto \tau_c \propto (1/kT)^{\frac{1}{2}} \quad , \qquad (2.7\text{-}25)$$

where τ_c is the mean collision time, and η is the viscosity of solution.

In fact in accordance with (2.7-23) through (2.7-25) Burke found that experimental data for T_1 of the F^{19} spin in φ-CF_3 obtained by Greene and Powles can be excellently described by the relation

$$\frac{1}{T_1} = 5.75 \times 10^{11} \left(\frac{T}{298}\right) \tau_J'$$

$$+ 4.29 \times 10^{11} \left(\frac{T}{298}\right) \tau_j' \quad , \qquad (2.7\text{-}26)$$

where

$$\tau_J{}' = \bar{I}/6kT\,\tau_\theta \quad ,$$

$$\tau_j{}' = (1.48 \times 10^{-38}/kT)^{\frac{1}{2}} \quad ,$$

$$\bar{I} = 7.44 \times 10^{-38} \quad ,$$

$$\tau_\theta = \frac{4\pi(3.01 \times 10^{-8})^3}{3 \times 6.125 \times 10^{-16} T}\,\eta$$

and

$$\eta = \rho \cdot (2.155 \times 10^{-4}/1.1772)\exp\left(\frac{967}{T}\right)$$

with the density of φ-CF$_3$, ρ, being given by

$$\rho = 1.1772\exp\{-107 \times 10^{-5}\,(T - 298) - 0.40 \times 10^{-5}[(T^2 - 298^2) - 273\,(T - 298)]\} \quad .$$

Though Eq. (2.7-18) gives more accurate description of the F^{19} spin-lattice relaxation in φ-CF$_3$, there is an alternative but simpler approach to the problem.

For the convenience of discussion let us define

$$D_\alpha^{(j)} = C_\alpha(1 - I_\alpha/I_z) \quad . \qquad (2.7\text{-}27)$$

C_α is what Dubin and Chan[38] have named the spin-internal-rotation coupling constant though $D_\alpha^{(j)}$ could more appropriately be given this name.

In terms of C_α $\mathcal{H}_{S-R}$ may be rewritten as

$$\mathcal{H}_{S-R} = -\vec{F}\cdot \underset{\frown}{C}^{(J)}\cdot\vec{J} + C_\alpha(I_\alpha/I_z)F_zJ_z$$

$$-C_\alpha\vec{F}\cdot\vec{j}_\alpha \tag{2.7-27}$$

where $\vec{j}_\alpha$ is the total rotational angular momentum of the internal top.

To a good approximation the second term in Eq. (2.7-27) cancels part of the first term, since $C^{(J)}_{zz} \approx (I_\alpha/I_z)C_\alpha$. If we now assume that $C^2_\alpha \gg C^{(J)^2}_{xx} \approx C^{(J)^2}_{yy}$, which is a good approximation for φ-CF_3 because $I_\alpha \ll I_x \approx I_y$, then the spin-lattice relaxation is dominated by fluctuations of the term $-C_\alpha\vec{F}\cdot\vec{j}_\alpha$.

According to Abragam[41] we can write for this case

$$\frac{1}{T_1} \approx \frac{2C^2_\alpha}{3\hbar^2}\overline{j^2_\alpha}\,\tau_{j_\alpha}\ , \tag{2.7-28}$$

where τ_{j_α} is the correlation time characteristic of the modulation of $\vec{j}_\alpha$.

A more rigorous derivation of the relaxation time formulas will be given in Chapter III, and we will see that we obtain a formula slightly different from (2.7-23). However so far as the temperature dependence of relaxation times is concerned, two formulas do not show any difference at all.

2.8 F^{19} Spin-Lattice Relaxation in Halogen Derivatives of Benzotrifluoride and Effect of Internal Barrier on Relaxation Time

So far we have been emphasizing the fact that the spin-internal-rotation interaction plays a crucial role in the F^{19} spin relaxation in

φ-CF_3 and it is expected that the importance of this spin-internal-rotation interaction will diminish with increasing barrier height since the internal barrier more or less hinders the effective fluctuations of $\vec{j}$. To substantiate this idea Dubin and Chan[38] have measured the spin-lattice relaxation times of F^{19} spin for ortho-, meta-, para-chloro-, bromo-, and iodobenzotrifluoride.

We attribute the significant increase in the relaxation time with ortho-substitution to the alteration of the height and symmetry of the internal barrier. However, it is also observed that there is not much change in the relaxation time with meta- and para-substitutions. The small meta- and para- effects on the F^{19} spin relaxation time may be attributed to molecular inertial changes since τ_J is proportional to the mean moment of the molecule.[44]

In this connection we will discuss some relations between orientational and angular momentum correlation times. In the Debye limit Hubbard[44] showed that for a spherical molecule τ_2, the correlation time for orientational modulations, and τ_1, the correlation time for angular momentum modulations, satisfy the relation

$$\tau_1 \tau_2 = \frac{I}{6kT} \quad , \qquad (2.8\text{-}1)$$

where I is the moment of inertia of the molecule. In fact a relation similar to this can be obtained from a more general consideration.[45] The correlation time for the orientational fluctuation due to jumping from one potential well over to another can be expressed by the rate process theory[46] as

$$\tau_2 = \tau_2^0 \exp(V_0/kT) \quad , \tag{2.8-2}$$

where V_0 is the height of internal barrier. Using the relations (2. 8-1) and (2. 8-2), we can take τ_1 as proportional to $\tau_\alpha^0(I/kT) \exp(-V_0/kT)$. Although the temperature dependence of the factor $\tau_\alpha^0(I/kT)$ is not known, previous discussions of F^{19} spin relaxation in φ-CF_3 allow us to assume that this factor be proportional to $(I/kT)^{\frac{1}{2}}$. In fact in the studies of dielectric relaxation there have been similar reports.[47]

Since the effect of ortho-substitution is considered to be caused by the appreciable change of the correlation time τ_j due to the internal barrier, the application of the formula

$$\frac{1}{T_1} = \frac{1}{T_2} = A' kT \eta^{-1} + B' T(I_\alpha/kT)^{\frac{1}{2}} \exp(-V_0/kT) \tag{2.8-3}$$

is plausible, where A', B', and V_0 are all adjustable parameters. In particular the value of V_0 will directly or indirectly reflect the height of internal barrier. Therefore it is desirable that Eq. (2. 8-3) be tested for several appropriate compounds in which the internal barrier is not too low and the spin-rotation interaction is the dominant relaxation mechanism.

2.9 Conclusion

We have shown that for a nuclear spin on an internal rotor the conventional form of spin-rotation interaction should be modified so that the spin-internal-rotation interaction is included. In case the fast internal rotation is present, the resulting Hamiltonian of the spin-rotation interaction is averaged over the internal angle.

The spin-internal-rotation interaction is shown to be an important (often dominating) spin relaxation mechanism and should not be ignored.

In the case of benzotrifluoride it is supposed that between two successive intermolecular collisions the CF_3 top rotates with relatively definite angular momentum with respect to the phenyl ring and the internal rotation can be treated in the inertial limit. On the other hand the end-over-end overall rotation of the molecule should be treated in the Debye limit because of the severe frictional forces which the φ-CF_3 molecule suffers when it rotates in liquid phases.

In the inertial limit the correlation time of the angular momentum may be assumed to be proportional to $(kT)^{-\frac{1}{2}}$ while in the Debye limit the correlation time is usually related to the bulk viscosity via the Debye-Stokes-Hubbard relation.

A qualitative theory accounting for the effect of internal barrier on the spin relaxation time is discussed.

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CHAPTER III

NUCLEAR SPIN RELAXATION IN THE PRESENCE OF INTERNAL ROTATION

3.1 Introduction

In the last two chapters we have presented a considerable amount of discussions about the spin-internal-rotation interaction and its important role in the process of nuclear spin relaxation.

In this chapter in order to shed more light on this problem we are going to review the theory of nuclear spin relaxation and show how we have to take into account the spin-internal-rotation interaction in the derivation of formulas of the spin relaxation times. As we shall see later, discussions given here in this chapter will become an important prelude to the problems of molecular dynamics in liquids and gases which will be considered in the next chapter.

In liquids and gases there exist a variety of molecular random motions and it is the time-dependent spin perturbations produced by these random motions which are responsible for nuclear spin relaxation. These motions include, for example, rotational reorientation of individual molecules, relative translational motion of molecules, chemical exchange of atoms, and anisotropic chemical shift effects. Bloembergen, Purcell, and Pound[1] proposed that these molecular motions produced fluctuating magnetic or electric fields at the site of a nuclear spin and that the Fourier spectrum of the fluctuating field contained nonvanishing components at the precise frequencies required to induce transitions between states of the spin system. This brings the spin system into thermal equilibrium with other degrees of freedom in the system, namely, the 'lattice'. Therefore, it is quite natural to say that by studying the rate at which the spin system approaches to the equilibrium with the lattice a certain aspect of the molecular dynamics will be elucidated.

In 1946 Bloch[2] postulated the following phenomenological equations describing the nuclear magnetic relaxation of an ensemble of spins:

$$\frac{d\vec{M}}{dt} = \gamma \vec{M} \times \vec{H} - \vec{i} M_x/T_2 - \vec{j} M_y/T_2 - \vec{k}(M_z - M_0)/T_1 \qquad (3.1\text{-}1)$$

with

$$\vec{H} = \vec{k} H_0 + \vec{H}_1(t) \quad , \qquad (3.1\text{-}2)$$

where $\vec{M}$ is the magnetization of an ensemble of spins, $\vec{i}$, $\vec{j}$, and $\vec{k}$ are the unit vectors of the laboratory frame of reference, and $\vec{H}$ is the total externally applied magnetic fields which consist of a static magnetic field $\vec{H}_0$ along the $\vec{k}$ axis and a sinusoidally oscillating magnetic field $\vec{H}_1(t)$ which is perpendicular to $\vec{H}_0$.

Equation (3.1-1) means that starting with arbitrary magnitude and direction, the z-component of $\vec{M}$ will, in the absence of $\vec{H}_1$, reach the value of M_0 exponentially with a time constant T_1, the longitudinal (or spin-lattice) relaxation time and the x- and y- components will decay exponentially with a time constant T_2, the transverse (or spin-spin) relaxation time. The validity of this phenomenological equation has since been verified.[3,4]

Since the pioneering work of Bloembergen, Purcell, and Pound several classic papers on the microdynamical theory of nuclear spin relaxation have appeared[5-11] and they are well summarized in books by Abragam[12] and Slichter.[13] Hubbard[14] has shown that both quantum mechanical and semi-classical forms of a density operator relaxation theory can be derived from a common formulation.

In fact it is Hubbard's treatment which we describe in the next section on spin relaxation theory.

Two of the most important relaxation mechanisms which concern us here are the dipole-dipole interaction and the spin-rotation interaction. These magnetic interactions fluctuate as molecules rotate and translate relative to each other. When there are internal rotational degrees of freedom, we have another factor which modulates magnetic interactions.

Nuclear magnetic dipole-dipole relaxation in molecules with internal rotation was considered by Woessner[15] and will be reviewed later in this chapter. As for the spin-internal-rotation interaction we are not going to mention it here since fairly lengthy discussions have been given in Chapter II of this thesis.

Now, let us review the theory of nuclear spin relaxation in the next section.

3.2 Theory of Spin Relaxation[14]

In discussing the spin relaxation theory it is usually assumed that the interaction between the spin system and its surroundings is so small that the latter virtually remains undisturbed. Let the Hamiltonian of the spin system and their molecular surroundings be written as

$$\mathcal{H} = \hbar[E^0(s,t) + F(q) + G^0(s,q)] \quad , \qquad (3.2\text{-}1)$$

where $\hbar E^0(s,t)$ is the part of the Hamiltonian that depends only on the spin variables s, $\hbar F(q)$ is the energy of the molecular degrees of freedom q, and $\hbar G^0(s,q)$ is the energy of interaction of the spins and the molecular surroundings.

Let us redefine the spin energy to include the average over an ensemble of baths in thermal equilibrium of the interaction $G^0(q,s)$:

$$E(s,t) \equiv E^0(s,t) + \langle G^0(q,s)\rangle_q \qquad (3.2\text{-}2)$$

and

$$G(q,s) \equiv G^0(q,s) - \langle G^0(q,s)\rangle_q \quad , \qquad (3.2\text{-}3)$$

where

$$\langle G^0(q,s)\rangle_q = \mathrm{Tr}[\rho^T(q) G^0(q,s)] \quad , \qquad (3.2\text{-}4)$$

$$\rho^T(q) \equiv e^{-\beta F}/\mathrm{Tr}[e^{-\beta F}] \quad , \qquad (3.2\text{-}5)$$

and

$$\beta \equiv \hbar/kT \quad . \qquad (3.2\text{-}6)$$

On using Eqs. (3.2-2) and (3.2-1) we may rewrite Eq. (3.2-1) as

$$\mathcal{H} = \hbar[E(s,t) + F(q) + G(q,s)] \quad . \qquad (3.2\text{-}7)$$

All interactions of interest can be written in the form

$$G(q,s) = \sum_k U^k(q)V^k(s) \quad , \qquad (3.2\text{-}8)$$

where $U^k(q)$ and $V^k(s)$ operate, respectively, on variables of the bath and variables of the spin system. Note that $G(q,s)$ must be Hermitian even though $U^k(q)$ and $V^k(s)$ need not be. This can be accomplished by defining U^k and V^k so that

$$U^{-k} = (U^k)^+ \quad , \qquad V^{-k} = (V^k)^+ \quad , \qquad (3.2\text{-}9)$$

the index k being summed over negative as well as positive integers in Eq. (3.2-8).

The density operator is a solution of the equation

$$\begin{aligned} i\hbar(d\rho/dt) &= [\mathcal{H}, \rho] \\ &= [\hbar(E+F+G), \rho] \quad . \qquad (3.2\text{-}10) \end{aligned}$$

Now, unitary spin operators $S^{\pm 1}(t)$ defined as solutions of

$$dS/dt = iSE \quad , \qquad dS^{-1}/dt = -iES^{-1} \quad , \qquad S^{\pm 1}(0) = 1 \quad , \qquad (3.2\text{-}11)$$

are now introduced. A unitary transformation of an operator Q by the $S^{\pm 1}(t)$ produces an operator denoted by $Q'(t)$:

$$Q'(t) = S(t)QS^{-1}(t) \quad . \tag{3.2-12}$$

A unitary transformation of Q by the bath operators exp(±iFt) results in an operator denoted by $\overline{Q}(t)$.

Thus we may write

$$\overline{Q}'(t) = e^{iFt}S(t)QS^{-1}(t)e^{-iFt} \quad . \tag{3.2-13}$$

Application of the transformation (3.2-13) to Eq. (3.2-10) gives us

$$d\overline{\rho}'/dt = -i[\overline{G}'(t), \overline{\rho}'(t)] \quad . \tag{3.2-14}$$

The solution of (3.2-14) for $\overline{\rho}'$ at time $t_1 = t + \Delta t$ in terms of at time t can be obtained by successive approximations, with the result

$$\begin{aligned}\overline{\rho}'(t_1) &= \overline{\rho}'(t) + \sum_{n=1}^{\infty} \Delta n\, \overline{\rho}'(t_1, t) \\ &= \sum_{n=0}^{\infty} \Delta n\, \overline{\rho}'(t_1, t) \quad ,\end{aligned} \tag{3.2-15}$$

where

$$\Delta_0 \overline{\rho}'(t_1, t) = \overline{\rho}'(t) \tag{3.2-16}$$

and, for $n \geq 1$,

$$\Delta n\, \overline{\rho}'(t_1, t) = -i \int_t^{t_1} [\overline{G}'(t'), \Delta n\text{-}1\, \overline{\rho}'(t', t)]\, dt' \quad . \tag{3.2-17}$$

Since the heat capacity of the bath is much greater than that of the spin system, that is, $|F| \gg |E+G|$, to a good approximation the bath can be considered to be independent of the spin system, and can be assumed to be in thermal equilibrium at all times. Thus, we may write

$$\rho(q, s, t) = \sigma(s, t)\rho^T(q) \quad , \tag{3.2-18}$$

where $\rho^T(q)$ is the Boltzmann equilibrium density operator for the bath, given by (3.2-5). The reduced density operator $\sigma(s, t)$ describes the spin system in the sense that the average value over the ensemble of a spin operator $Q(s)$ is given by

$$\langle Q(s) \rangle = \mathrm{Tr}[\,\sigma(s, t)\, Q(s)] \quad , \tag{3.2-19}$$

where the trace may be evaluated using any complete set of spin functions or vectors.

Performing the transformation (3.2-13) on Eq. (3.2-18), we obtain

$$\overline{\rho}'(q, s, t) = \sigma'(s, t)\rho^T(q) \quad . \tag{3.2-20}$$

Substituting (3.2-20) in (3.2-15), and taking the trace over the bath variables, the result can be written

$$\sigma(t_1) = \sigma'(t) + \sum_{n=1}^{\infty} \Delta n\, \sigma'(t_1, t) \quad , \tag{3.2-21}$$

where

$$\Delta n\, \sigma'(t_1, t) = \mathrm{Tr}_q[\Delta n\, \overline{\rho}'(t_1, t)] \quad , \tag{3.2-22}$$

the $\Delta n\, \overline{\rho}'(t, t)$ for $n \geq 1$ being given by (3.2-17) and

$$\Delta_0\, \overline{\rho}'(t_1, t) = \sigma'(s, t)\, \rho^T(q) \quad . \tag{3.2-23}$$

If we take $\Delta t \equiv t - t_1$ sufficiently small, we can make the series in Eq. (3.2-15) rapidly converge. In that case the first two terms in the series (3.2-15) are important and all the higher order terms may be assumed to be negligible for values of Δt for which the first terms are themselves small compared with $\sigma'(t)$.

Then from (3.2-17), (3.2-22), and (3.2-23), the first-order term is

$$\begin{aligned} \Delta_1\sigma'(t_1, t) &= -i \int_t^{t_1} \mathrm{Tr}_q[\, \overline{G}'(t'),\ \sigma'(t)\rho^T(q)]\, dt' \\ &= -i \int_t^{t_1} [\mathrm{Tr}_q[\rho^T(q)\overline{G}'(t')],\ \sigma'(t)]\, dt' \\ &= 0 \quad , \end{aligned} \tag{3.2-24}$$

since σ' does not depend on the bath coordinates q, and, for any time t,

$$\mathrm{Tr}_q[\rho^T(q)\overline{G}'(t')] = 0 \quad . \tag{3.2-25}$$

The second-order term in (3.2-21) is

$$\Delta_2 \sigma'(t_1, t)$$

$$= - \int_t^{t_1} dt' \int_t^{t'} dt'' \, \mathrm{Tr}_q\Big[\overline{G}'(t'), \, [\overline{G}'(t''), \, \sigma'(t)\rho^T(q)]\Big] \quad . \tag{3.2-26}$$

Now, introduce the transformed operators defined as

$$U^k(t) = \exp(iFt) \, U^k \exp(-iFt) \tag{3.2-27}$$

and

$$V^k(t) = S(t) V^k S^{-1}(t) \quad . \tag{3.2-28}$$

Then

$$\overline{G}'(t) = \sum_k \overline{U}^k(t) V^{k'}(t) = \sum_k U^k(t) V^k(t) \quad . \tag{3.2-29}$$

The operator $U^k(t)$ is the Heisenberg time-dependent operator for U^k for a system whose Hamiltonian is $\hbar F(q)$, while $V^k(t)$ is the Heisenberg time-dependent operator for V^k for a system whose Hamiltonian is $\hbar E(s, t)$.

After substitution of (3.2-29) into (3.2-26) and a little rearrangement we obtain

$$\begin{aligned} \Delta_2\sigma'(t_1, t) = - \int_t^{t_1} dt' \int_t^{t'} dt'' \sum_{k\ell} \{ & \mathrm{Tr}_q[\rho^T(q) U^k(t'-t'') U^\ell] \\ & \times [V^k(t'), \, V^\ell(t'')\sigma'(t)] \\ & + \mathrm{Tr}_q[\rho^T(q) U^\ell U^k(t'-t'')][\sigma'(t) V^\ell(t''), \, V^k(t')]\} \quad , \end{aligned} \tag{3.2-30}$$

where we have used the fact that a trace of a product of operators is unchanged by a cyclic permutation of the operators.

It is assumed now that it is possible to expand the time-dependent spin operators $V^k(t)$ in a series or integral of periodic terms. We restrict ourselves here to the case of series only. Thus, let

$$V^k(t) \equiv \sum_r V_r^k \exp(i\omega_r^k t) \quad , \tag{3.2-31}$$

where V_r^k is a time-independent spin operator and ω_r^k is a number. The relation $V^{-k} = (V^k)^+$, which is required to maintain the Hermitian property of $G(q, s)$ [see Eq. (3.2-9)], can be maintained by summing r in (3.2-31) over negative as well as positive values, and requiring that

$$(V_r^k)^+ = V_{-r}^{-k} \qquad \text{and} \qquad \omega_{-r}^{-k} = -\omega_r^k \quad . \tag{3.2-32}$$

Substituting (3.2-21) in (3.2-20), changing the variable of integration t″ to $\tau = t'-t''$, and rearranging the order of integration, we may write

$$\Delta_2\sigma'(t_1, t) = -\sum_{k\ell rs} \int_0^{\Delta t} d\tau \exp(-i\omega_s^\ell \tau)$$

$$\times \int_{t+\tau}^{t+\Delta t} dt' \exp[i(\omega_r^k + \omega_s^\ell)t'] \cdot \{A_{k\ell}(\tau)[V_r^k, V_s^\ell \sigma'(t)]$$

$$+ A_{\ell k}(-\tau)[\sigma'(t)V_s^\ell, V_r^k]\} \quad , \tag{3.2-33}$$

where

$$A_{k\ell}(\tau) \equiv \mathrm{Tr}_q[\rho^T(q)U^k(\tau)U^\ell]$$

$$= \mathrm{Tr}_q[\rho^T(q)e^{iF\tau}U^k e^{-iF\tau}U^\ell] \quad . \qquad (3.2\text{-}34)$$

After the integral over t′ in (3.2-33) is performed, we obtain

$$\Delta_2\sigma'(t_1, t) = -\sum_{k\ell rs} \int_0^{\Delta t} d\tau \exp(-i\omega_s^\ell \tau)$$

$$\times \left\{ \frac{\exp[i(\omega_r^k + \omega_s^\ell)\Delta t] - \exp[i(\omega_r^k + \omega_s^\ell)\tau]}{i(\omega_r^k + \omega_s^\ell)\Delta t} \right\}$$

$$\times \Delta t \exp[i(\omega_r^k + \omega_s^\ell)t] \cdot \{A_{k\ell}(\tau)[V_r^k, V_s^\ell \sigma'(t)]$$

$$+ A_{\ell k}(-\tau)[\sigma'(t)V_s^\ell, V_r^k]\} \quad . \qquad (3.2\text{-}35)$$

The trace occurring in (3.2-35) can be evaluated in any representation, but the most convenient way is to use the representation in which F is diagonal with eigenvalues f. Degenerate states are distinguished by a parameter d:

$$A_{k\ell}(\tau) = \sum_{fd} \sum_{f'd'} P(f) \exp(if\tau) \langle fd|U^k|f'd'\rangle$$

$$\exp(-if'\tau)\langle f'd'|U^\ell|fd\rangle \quad , \qquad (3.2\text{-}36)$$

where

$$P(f) = \exp(-\beta f) / \sum_{f''d''} \exp(-\beta f'') \quad .$$

It can be assumed that the energy levels of the bath are so closely spaced that the sums over the eigenvalues in (3.2-36) can be replaced by integrals:

$$\sum_{fd} \rightarrow \sum_{d} \int_{-\infty}^{\infty} df \ \eta_d(f) \qquad (3.2\text{-}37)$$

where $\eta_d(f)$ is the density of the energy levels of F with degeneracy parameter d. Hence

$$P(f) = \exp(-\beta f) / \sum_{d''} \int_{-\infty}^{\infty} df'' \ \eta_{d''}(f'') \exp(-\beta f'') \quad , \qquad (3.2\text{-}38)$$

and

$$A_{k\ell}(\tau) = \sum_{d, d'} \int_{-\infty}^{\infty} df' \int_{-\infty}^{\infty} df \ \eta_{d'}(f') \, \eta_d(f) \, P(f)$$

$$\times \langle fd | U^k | f'd' \rangle \langle f'd' | U^\ell | fd \rangle \exp(-i(f'-f)\tau) \quad . \qquad (3.2\text{-}39)$$

If the variable of integration f′ in (3.2-39) is changed to ω by the relation $\omega = f' - f$, we may write

$$A_{k\ell}(\tau) = \int_{-\infty}^{\infty} L_{k\ell}(\omega) \exp(-i\omega\tau) \, d\omega \quad , \qquad (3.2\text{-}40)$$

where

$$L_{k\ell}(\omega) = \sum_{d, d'} \int_{-\infty}^{\infty} df \ \eta_{d'}(f+\omega) \, \eta_d(f) \, P(f)$$

$$\times \langle fd | U^k | f+\omega, d' \rangle \langle f+\omega, d' | U^\ell | fd \rangle \quad . \qquad (3.2\text{-}41)$$

Since $P(f+\omega) = P(f) \exp(-\beta\omega)$, it follows from (3.2-41) that

$$L_{\ell k}(-\omega) = L_{k\ell}(\omega) \exp(-\beta\omega) \quad . \tag{3.2-42}$$

From (3.2-40) we see that $A_{k\ell}(\tau)$ is the Fourier transform of $L_{k\ell}(\omega)$. Therefore

$$L_{k\ell}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} A_{k\ell}(\tau) \exp(i\omega\tau)\, d\tau \quad . \tag{3.2-43}$$

Since $L_{k\ell}(\omega)$ may be assumed to be a continuous function of ω,

$$|L_{k\ell}(\omega+\Delta\omega) - L_{k\ell}(\omega)|$$

can be arbitrarily small by choosing $|\Delta\omega|$ sufficiently small. The rate of change of $L_{k\ell}(\omega)$ can be rather loosely characterized by a frequency ω^* such that

$$L_{k\ell}(\omega+\Delta\omega) \approx L_{k\ell}(\omega) \qquad \text{if} \qquad |\Delta\omega| \ll \omega^* \quad . \tag{3.2-44}$$

The reciprocal of the characteristic frequency,

$$\tau_c \equiv (\omega^*)^{-1} \quad , \tag{3.2-45}$$

is called the correlation time of the bath.

Since $A_{k\ell}(\tau)$ and $A_{\ell k}(-\tau)$ are large only for $|\tau| \leq \tau_c$, the integrand is large only for $|\tau| \leq \tau_c$.

Terms in the sums over r, s, k, and l for which

$$|(\omega_r^k + \omega_s^\ell)\Delta t| \leq 1 \tag{3.2-46}$$

have

$$\left|(\omega_r^k + \omega_s^\ell)\tau_c\right| \ll 1 \quad , \tag{3.2-47}$$

so that in these terms $\exp[i(\omega_r^k+\omega_s^\ell)\tau]$ may be replaced by 1. Terms not satisfying (3.2-46) are smaller than the terms that do satisfy this relation because of the factor

$$\left\{\frac{\exp[i(\omega_r^k+\omega_s^\ell)\Delta t] - \exp[i(\omega_r^k+\omega_s^\ell)\tau]}{i(\omega_r^k+\omega_s^\ell)\Delta t}\right\}$$

occurring in (3.2-34). Hence little error is introduced in $\Delta_2\sigma'(t_1, t)$ by replacing $\exp[i(\omega_r^k+\omega_s^\ell)\tau]$ by 1 in all terms. Also, the limit of integration Δt can be extended to infinity without appreciably changing the value of the integral, since the integrand is large only for $|\tau| \ll \Delta t$.

Thus (3.2-34) becomes

$$\Delta_2\sigma'(t_1, t)$$

$$= - \sum_{k\ell rs} \left\{\frac{\exp[i(\omega_r^k+\omega_s^\ell)\Delta t] - 1}{i(\omega_r^k+\omega_s^\ell)}\right\} \exp[i(\omega_r^k+\omega_s^\ell)t]$$

$$\times \int_0^\infty d\tau \exp(-i\omega_s^\ell\tau)\,\{A_{k\ell}(\tau)[V_r^k, V_s^\ell\sigma'(t)]$$

$$+ A_{\ell k}(-\tau)[\sigma'(t)V_s^\ell, V_r^k]\} \quad . \tag{3.2-48}$$

If the expression (3.2-40) for $A_{k\ell}(\tau)$ is substituted into (3.2-48) and the variable of integration ω in $A_{k\ell}(\tau)$ is changed to $\omega' = \omega+\omega_s^\ell$, we obtain

$$\Delta_2\sigma'(t_1, t) = \int_t^{t+\Delta t} \{R'(\sigma'(t), t') + iR''(\sigma'(t), t')\}\, dt' \quad , \tag{3.2-49}$$

where

$$R'(\sigma'(t), t') = \pi \sum_{k\ell rs} \exp[i(\omega_r^k + \omega_s^\ell)t'] \cdot \{L_{k\ell}(-\omega_s^\ell)[V_s^\ell \sigma'(t), V_r^k] + L_{\ell k}(\omega_s^\ell)[V_r^k, \sigma'(t)V_s^\ell]\} \tag{3.2-50}$$

and

$$R''(\sigma'(t), t') = \sum_{k\ell rs} \exp[i(\omega_r^k + \omega_s^\ell)t']\, \mathcal{P}\int_{-\infty}^{\infty} \{L_{k\ell}(\omega' - \omega_s^\ell)[V_r^k, V_s^\ell\sigma'(t)] + L_{\ell k}(-\omega' + \omega_s^\ell)[\sigma'(t)V_s^\ell, V_r^k]\}\, \frac{d\omega'}{\omega'} \quad . \tag{3.2-51}$$

In order to derive (3.2-49) we have used the relation[20]

$$\int_0^\infty e^{-i\omega'\tau}\, d\tau = \pi\delta(\omega') - \mathcal{P}\frac{i}{\omega'} \tag{3.2-52}$$

where $\mathcal{P}$ indicates the principal value is to be taken when (3.2-52) occurs in an integrand.

Expression (3.2-51) can be further simplified in the following manner. Interchange of the summation indices k with ℓ and r with s in the second term in the integrand gives

$$R''(\sigma'(t), t')$$

$$= \sum_{k\ell rs} \exp[i(\omega_r^k + \omega_s^\ell)t'] \, \mathcal{P} \int_{-\infty}^{\infty} \{L_{k\ell}(\omega - \omega_s^\ell)[V_r^k, V_s^\ell \sigma'(t)]$$

$$+ L_{k\ell}(-\omega + \omega_r^k)[\sigma'(t) V_r^k, V_s^\ell]\} \frac{d\omega}{\omega} \quad . \tag{3.2-53}$$

As before, when R'' is integrated with respect to t' over an interval $\Delta t \gg \tau_c$, the terms contributing appreciably to the sum (3.2-53) are those for which $|(\omega_r^k + \omega_s^\ell)| \ll \omega^*$. For these terms ω_r^k and $-\omega_s^\ell$ differ from their mean value $\nu_{rs}^{k\ell} \equiv \frac{1}{2}(\omega_r^k - \omega_s^\ell)$ by a small amount compared to ω^*. Hence, in view of (3.2-44), little error is introduced by replacing $L_{k\ell}(\omega - \omega_s^\ell)$ with $L_{k\ell}(\omega + \nu_{rs}^{k\ell})$ and $L_{k\ell}(-\omega + \omega_r^k)$ with $L_{k\ell}(-\omega + \nu_{rs}^{k\ell})$. If the range of integration is next converted from $(-\infty, \infty)$ to $(0, \infty)$ and the commutators are written out explicitly, it is found that half the terms in the integrand cancel, with the result that

$$R''(\sigma'(t), t') = [\sigma'(t), N'(t')] \quad , \tag{3.2-54}$$

where

$$N'(t') = \sum_{k\ell rs} \exp[i(\omega_r^k + \omega_s^\ell)t'] \, V_r^k V_s^\ell$$

$$\times \int_0^{\infty} \{L_{k\ell}(\nu_{rs}^{k\ell} - \omega) - L_{k\ell}(\nu_{rs}^{k\ell} + \omega)\} \frac{d\omega}{\omega} \quad . \tag{3.2-55}$$

If one combines (3.2-54), (3.2-49), and (3.2-24), the expression (3.2-21) for $\sigma'(t + \Delta t)$ to second order in the interaction G becomes

$$\sigma'(t+\Delta t) = \sigma'(t) + \int_{t}^{t+\Delta t} \{R'(\sigma'(t), t') + i[\sigma'(t), N'(t')]\}\, dt' \quad . \qquad (3.2\text{-}56)$$

We can show that the conditions for which (3.2-56) gives $\sigma'(t+\Delta t)$ to good approximation are

$$\tau_c \equiv (\omega^*)^{-1} \ll \Delta t \ll |R|^{-1},\ |N|^{-1} \quad , \qquad (3.2\text{-}57)$$

where $|R|$ and $|N|$ denote the magnitudes of the operators multiplying σ' in the integrand of (3.2-56).

It is now asserted that the time dependence of σ' can be determined with good approximation from the differential equation

$$d\sigma'(t)/dt = i[\sigma'(t), N'(t)] + R'(\sigma'(t), t) \qquad (3.2\text{-}58)$$

if

$$\tau_c \equiv (\omega^*)^{-1} \ll |R|^{-1},\ |N|^{-1} \quad , \qquad (3.2\text{-}59)$$

where $N'(t)$ and $R'(\sigma'(t), t)$ are given by (3.2-55) and (3.2-50), respectively. The approximate validity of Eq. (3.2-58) can be demonstrated by showing that step-by-step integration of the equation over appropriate time intervals gives the same result predicted by the expression (3.2-56). When the condition (3.2-59) holds, we can choose a Δt that satisfies the condition (3.2-57), so that $\sigma'(t+\Delta t)$ is given accurately in terms of $\sigma'(t)$ by Eq. (3.2-56).

In order to facilitate the derivation of the semiclassical theory we define

$$J_{k\ell}(\omega) \equiv (\pi/2)\,[1 + e^{-\beta\omega}]\, L_{k\ell}(\omega) \quad . \qquad (3.2\text{-}60)$$

From (3.2-42) and (3.2-44) it follows that

$$J_{\ell k}(-\omega) = J_{k\ell}(\omega) \tag{3.2-61}$$

and

$$J_{k\ell}(\omega + \Delta\omega) \approx J_{k\ell}(\omega)$$

if

$$|\Delta\omega| \ll \omega^* \quad . \tag{3.2-62}$$

Substitution of (3.2-60) into (3.2-50) and (3.2-55) gives

$$R'(\sigma'(t), t') = \sum_{k\ell rs} \exp[i(\omega_r^k + \omega_s^\ell)t'] \cdot J_{\ell k}(\omega_s^\ell)$$
$$\left\{\left[[V_s^\ell, \sigma'(t)], V_r^k\right] + \tanh\left(\frac{\beta}{2}\omega_s^\ell\right)\left[V_r^k, [V_s^\ell, \sigma'(t)]_+\right]\right\} \tag{3.2-63}$$

and

$$N'(t) = (2/\pi) \sum_{k\ell rs} \exp[i(\omega_r^k + \omega_s^\ell)t]\; V_r^k V_s^\ell$$
$$\times \int_0^\infty \left\{ \frac{J_{k\ell}(\nu_{rs}^{k\ell} - \omega)}{1 + \exp[-\beta(\nu_{rs}^{k\ell} + \omega)]} - \frac{J_{k\ell}(\nu_{rs}^{k\ell} + \omega)}{1 + \exp[-\beta(\nu_{rs}^{k\ell} + \omega)]} \right\} \frac{d\omega}{\omega} \quad , \tag{3.2-64}$$

where $[A, B]_+$ is the anticommutator bracket defined by

$$[A, B]_+ = AB + BA \quad .$$

Returning to $\sigma(t)$ itself, we can rewrite Eq. (3.2-58) as

$$\frac{d\sigma}{dt} = -i[E+N, \sigma] + R(\sigma) \quad , \tag{3.2-65}$$

where

$$\begin{aligned} R(\sigma) &\equiv S^{-1}R'(\sigma', t)S \\ &= \sum_{k\ell s} \exp(i\omega_s^\ell t)\, J_{\ell k}(\omega_s^\ell) \left\{ \left[[S^{-1}V_s^\ell S, \sigma], V^k\right] \right. \\ &\qquad \left. + \tanh\left(\frac{\beta}{2}\omega_s^\ell\right) \left[V^k, [S^{-1}V_s^\ell S, \sigma]_+\right] \right\} \end{aligned} \tag{3.2-66}$$

and

$$N \equiv S^{-1}N'(t)S \quad . \tag{3.2-67}$$

In semiclassical theory the correlation function $C_{k\ell}(\tau)$ of U^k and U^ℓ is defined as the average over an ensemble of baths in thermal equilibrium of the symmetrized product of the Heisenberg operators $U^k(t+\tau)$ and $U^\ell(t)$:

$$\begin{aligned} C_{k\ell}(\tau) &\equiv \langle\{U^k(t+\tau)U^\ell(t)\}\rangle_q \\ &= \langle\{U^k(\tau)U^\ell(0)\}\rangle_q \end{aligned} \tag{3.2-68}$$

where the braces denote the symmetrized product

$$\{U^k(t+\tau)U^\ell(t)\} \equiv (1/2)[U^k(t+\tau)U^\ell(t) + U^\ell(t)U^k(t+\tau)] \quad . \tag{3.2-69}$$

Thus the correlation function can be written in terms of the function $A_{k\ell}(\tau)$ defined by (3.2-34):

whence $C_{k\ell}(\tau) = C_{\ell k}(-\tau)$.

$C_{k\ell}(\tau)$ and $J_{k\ell}(\omega)$ of (3.2-60) are related to each other via the Fourier transformations

$$C_{k\ell}(\tau) = \frac{1}{\pi} \int_{-\infty}^{\infty} J_{k\ell}(\omega) \exp(-i\omega\tau)\, d\omega \tag{3.2-71}$$

and

$$J_{k\ell}(\omega) = \frac{1}{2} \int_{-\infty}^{\infty} C_{k\ell}(\tau) \exp(i\omega\tau)\, d\tau \quad . \tag{3.2-72}$$

Equation (3.2-65) is the starting point of deriving the relaxation time formulas. When the spin Hamiltonian $\hbar E$ does not depend explicitly on time

$$S^{\pm 1}(t) = \exp(\pm iEt) \quad . \tag{3.2-73}$$

Hence the expression for $V^{\ell}(t) = \exp(iEt)\, V^{\ell} \exp(-iEt)$ can be expanded in the form

$$V^{\ell}(t) = \sum_{s} V_{s}^{\ell} \exp(i\omega_{s}^{\ell} t) \tag{3.2-74}$$

if the frequencies ω_{s}^{ℓ} are chosen to be the differences between the eigenvalues of E, denoted by E_{α},

$$\omega_{s}^{\ell} = E_{\alpha} - E_{\alpha'} \equiv \omega_{\alpha\alpha'} \tag{3.2-75}$$

and the operators V_{s}^{ℓ} are defined by the condition that

$$\langle\alpha|V^{\ell}|\alpha'\rangle \begin{cases} = 0 \text{ for a value of } s \text{ for which } \omega_s^{\ell} \neq E_{\alpha} - E_{\alpha'} \\ = \langle\alpha|V^{\ell}|\alpha'\rangle \text{ for a value of } s \text{ for which } \\ \qquad \omega_s^{\ell} = E_{\alpha} - E_{\alpha'} \quad . \end{cases} \tag{3.2-76}$$

Noting that

$$V^{\ell} = \sum_s V_s^{\ell} \quad ,$$

$$[E, V_s^{\ell}] = \omega_s^{\ell} V_s^{\ell} \quad ,$$

$$S^{-1} V_s^{\ell} S = V_s^{\ell} \exp(-i\omega_s^{\ell} t) \quad ,$$

we obtain from (3.2-66) and (3.2-67)

$$R(\sigma) = \sum_{k\ell s} J_{\ell k}(\omega_s^{\ell}) \left\{ \left[[V_s^{\ell}, \sigma], V^k \right] + \tanh\left(\frac{\beta}{2}\omega_s^{\ell}\right) \left[V^k, [V_s^{\ell}, \sigma]_+ \right] \right\} \tag{3.2-77}$$

and

$$N(t) = \frac{2}{\pi} \sum_{k\ell rs} V_r^k V_s^{\ell} \int_0^{\infty} \left\{ \frac{J_{k\ell}(\nu_{rs}^{k\ell} - \omega)}{1 - \exp[-\beta(\nu_{rs}^{k\ell} - \omega)]} - \frac{J_{k\ell}(\nu_{rs}^{k\ell} + \omega)}{1 + \exp[-\beta(\nu_{rs}^{k\ell} + \omega)]} \right\} \frac{d\omega}{\omega} \quad . \tag{3.2-78}$$

If the temperature is high, that is, for all the frequencies ω_s^{ℓ}

$$|\omega_s^{\ell}|\beta \ll 1 \quad , \tag{3.2-79}$$

where as before $\beta = \hbar/kT$, it can be shown that $R(\sigma)$ takes the form

$$\begin{aligned} R(\sigma) &= R(\sigma - \sigma^T) \\ &= \sum_{k\ell s} J_{\ell k}(\omega_s^\ell) \left[[V_s^\ell, \sigma - \sigma^T], V^k \right] \quad , \qquad (3.2\text{-}80) \end{aligned}$$

where σ^T is given by

$$\sigma^T \equiv \exp(-\beta E)/\mathrm{Tr}\left(\exp(-\beta E)\right) \quad . \qquad (3.2\text{-}81)$$

Usually the nuclear magnetic resonance experiment is performed in the presence of a strong static magnetic field. When this is the case, E is much larger in magnitude than the interaction G so that N is negligible in comparison with E.

Therefore Eq. (3.2-65) is reduced to

$$d\sigma/dt = -i[E, \sigma] + R(\sigma) \quad . \qquad (3.2\text{-}82)$$

If Eq. (3.2-82) is multiplied on the right-hand side by the operator I^ν, and the trace is taken, one obtains

$$\frac{d}{dt} \langle I^\nu \rangle = -i\mathrm{Tr}[E, \sigma]\ I^\nu + \mathrm{Tr}\, R(\sigma) I^\nu \quad . \qquad (3.2\text{-}83)$$

Since $E = -\omega_0 I^0$, where the Larmor frequency of the spin under consideration is denoted by ω_0, and

$$\begin{aligned} i\mathrm{Tr}[E, \sigma] I^\nu &= i\omega_0 \mathrm{Tr}[\sigma, I^0] I^\nu \\ &= i\omega_0 \mathrm{Tr}\sigma[I^0, I^\nu] \quad , \end{aligned}$$

Eq. (3.2-83) may be rewritten as

$$\frac{d}{dt}\langle I^{\nu}\rangle = -i\omega_0 \mathrm{Tr}\sigma[I^0, I^{\nu}] + \mathrm{Tr}R(\sigma)I^{\nu} \quad . \tag{3.2-84}$$

By making use of the commutation rule

$$[I^{\mu}, I^{\nu}] = (-1)^{\mu+\nu}(\mu - \nu)I^{\mu+\nu} \quad , \tag{3.2-85}$$

we finally obtain

$$\frac{d}{dt}\langle I^{\nu}\rangle = i(-1)^{\nu}\, \omega_0 \nu \langle I^{\nu}\rangle + \mathrm{Tr}R(\sigma)I^{\nu} \quad , \tag{3.2-86}$$

where the I^{ν}'s are defined as

$$I^{\pm 1} = I_x \pm iI_y$$

and

$$I^0 = I_z \quad .$$

To express the term $R(\sigma)I^{\nu}$ as a function of $\langle I^{\nu}\rangle$ cannot be done without knowledge of the explicit form of the interaction G. Therefore it must be said that all the relevant information is contained in the interaction G. In the next two sections we discuss the spin relaxation processes via two important mechanisms, intramolecular dipole-dipole interactions and spin-rotation interactions, in the presence of internal rotation. Even though the actual procedure of deriving the relaxation time formulas is rather complicated, the basic principle is fairly simple; first, we analyze the functional form of the interaction G, and then we use Eq. (3.2-82) with the aid of (3.2-76) to obtain the relaxation time formulas.

The above statement will be best justified by an actual derivation of the relaxation time formulas as we shall see in the next two sections.

3.3 Spin Relaxation Via Intramolecular Dipole-Dipole Interaction in the Presence of Internal Rotation

Recently there have been some reports which state that when there is internal rotation the intramolecular dipole-dipole interactions are relatively ineffective in causing the relaxation of nuclear spins in the molecule compared to the intermolecular contribution.[16-18] Woessner[15, 19] considered the case where the internal motion is that of independent jumping of each proton among its three occupation positions in a molecule like ethane which has a three-fold barrier. He concluded that the presence of internal rotation introduces an additional correlation time which makes the overall correlation time shorter.

In view of the importance of spin-internal-rotation interaction we review here the problem of intramolecular dipole-dipole relaxation in the presence of internal rotation and rederive the relaxation time formulas. The intermolecular dipole-dipole relaxation is considered not to be influenced appreciably by the presence of internal rotation and will not be discussed here.

For the case of intramolecular dipole-dipole relaxation the relaxation mechanism $\hbar G$ consists of intramolecular magnetic dipole-dipole couplings between the spins. For convenience, suppose now among N spins in a molecule we have two different kinds of spins, N_i numbers of the i-type spins and N_j numbers of the j-type spins, where $N = N_i + N_j$.

For this case G can be written in the form

$$G = \sum_{i>i'=1}^{N_i} \sum_{k=-2}^{2} U^k_{ii'} V^k_{ii'} + \sum_{j>j'=1}^{N_j} \sum_{k=-2}^{2} U^k_{jj'} V^k_{jj'} + \sum_{i=1}^{N_i} \sum_{j=1}^{N_j} \sum_{k=-2}^{2} U^k_{ij} V^k_{ij} \quad , \qquad (3.3\text{-}1)$$

where U^k_{ij} and V^k_{ij} are given as follows:

$$U^k_{ij} = (6\pi/5)^{\frac{1}{2}} \gamma_i \gamma_j \hbar r_{ij}^{-3} (-1)^k Y_2^{-k}(\theta_{ij}, \varphi_{ij}) \qquad (3.3\text{-}2)$$

and

$$V^0_{ij} = -(8/3)^{\frac{1}{2}} [I_i^0 I_j^0 - (1/4)(I_i^1 I_j^{-1} + I_i^{-1} I_j^1)] \quad , \qquad (3.3\text{-}3a)$$

$$V^{\pm 1}_{ij} = \pm(I_i^0 I_j^{\pm 1} + I_i^{\pm 1} I_j^0) \quad , \qquad (3.3\text{-}3b)$$

$$V^{\pm 2}_{ij} = -I_i^{\pm 1} I_j^{\pm 1} \qquad (3.3\text{-}3c)$$

with the spin operators I^{μ} being defined by

$$I_i^{\pm 1} = I_{ix} \pm iI_{iy} \qquad (3.3\text{-}4a)$$

and

$$I_i^0 = I_{iz} \quad . \qquad (3.3\text{-}4b)$$

In (3.3-2) γ_i and γ_j are the magnetogyric ratio of i-th and j-th spins, and r_{ij} is the length of the vector $\vec{r}_{ij}$ from the j-th to the i-th spin. θ_{ij} and φ_{ij} are the polar angles specifying the direction of $\vec{r}_{ij}$, and the Y_2^k's are normalized spherical harmonics defined as

$$Y_2^0(\theta, \varphi) = -(5/16\pi)^{\frac{1}{2}} (1 - 3 \cos^2 \theta) \quad , \tag{3.3-5a}$$

$$Y_2^{\pm 1}(\theta, \varphi) = \mp(15/8\pi)^{\frac{1}{2}} \cos \theta \sin \theta \exp(\pm i\varphi) \quad , \tag{3.3-5b}$$

$$Y_2^{\pm 2}(\theta, \varphi) = (15/32\pi)^{\frac{1}{2}} \sin^2 \theta \exp(\pm 2i\varphi) \quad , \tag{3.3-5c}$$

which satisfy the relations

$$Y_2^{k*}(\theta, \varphi) = (-1)^k Y_2^{-k}(\theta, \varphi) \quad , \tag{3.3-6}$$

and

$$\int_0^{2\pi} \int_0^{\pi} Y_2^{k*}(\theta, \varphi)\, Y_2^{k'}(\theta, \varphi) \sin \theta \, d\theta d\varphi = \delta_{kk'} \tag{3.3-7}$$

Since $\varphi_{ji} = \varphi_{ij} + \pi$, $\theta_{ji} = \pi - \theta_{ij}$, and $r_{ij} = r_{ji}$,

$$Y_2^k(\theta_{ij}, \varphi_{ij}) = Y_2^k(\theta_{ji}, \varphi_{ji}) \quad , \tag{3.3-8a}$$

and

$$U_{ij}^k = U_{ji}^k \quad . \tag{3.3-8b}$$

The first term on the right-hand side of (3.3-1) represents the dipole-dipole interactions among the i-type spins only, the second term represents the similar interactions among the j-type spins only, and the third term expresses the dipole-dipole interactions between any pairs of spins of different type. The reason why we divide the interaction G into three parts is merely for mathematical convenience as we shall see immediately.

For a further facilitation of discussion we define $V_{ij}^k(m, n)$ as

$$V_{ij}^{k}(m,n) = A_{mn}^{k} I_i^m I_j^n \quad , \tag{3.3-9}$$

where

$$A_{mn}^{0} = (-1)^{m+1} (1/2)^{|m|+|n|} (8/3)^{\frac{1}{2}} \quad , \tag{3.3-10a}$$

$$A_{mn}^{\pm 1} = \pm 1 \quad , \tag{3.3-10b}$$

$$A_{mn}^{\pm 2} = -1 \quad , \tag{3.3-10c}$$

and

$$A_{mn}^{k} = 0 \quad \text{unless} \quad k = m+n \quad . \tag{3.3-10d}$$

Integers m and n each run from -1 to +1, and k runs from -2 to +2.

From the definitions (3.3-3) and (3.3-9) we can easily see that

$$V_{ij}^{k} = \sum_{m,n} V_{ij}^{k}(m,n) \quad . \tag{3.3-11}$$

The energy of the spin system for this case may be written as

$$\hbar E = -\hbar\left(\sum_{i}^{N_i} \omega_{0i} I_i^0 + \sum_{j}^{N_j} \omega_{0j} I_j^0\right) \tag{3.3-12}$$

in the magnetic field H_0, where

$$\omega_{0i} = \gamma_i H_0 \tag{3.3-13}$$

and

$$\omega_{0j} = \gamma_j H_0 \quad . \tag{3.3-14}$$

If use is made of the relation

$$\exp(-i\omega_{oi} I_i^0 t) I_i^{\mu} \exp(i\omega_{oi} I_i^0 t) = \exp(-i\mu\omega_{oi} t) I_i^{\mu} \quad , \qquad (3.3\text{-}15)$$

from (3.3-3) and (3.3-11) we obtain

$$\exp(iEt) V_{ij}^k \exp(-iEt) = \sum_{m,n} V_{ij}^k(m,n) \exp[-i(m\omega_{oi} + n\omega_{oj})t] \; . \qquad (3.3\text{-}16)$$

If the i-th and j-th spins are of the same kind, (3.3-16) can be reduced to a simpler form. In this case $\omega_{oi} = \omega_{oj}$, whence

$$\begin{aligned} \exp(iEt) V_{ij}^k \exp(-iEt) &= \sum_{m,n} V_{ij}^k(m,n) \exp[-i(m+n)\omega_{oi} t] \\ &= V_{ij}^k \exp(-ik\omega_{oi} t) \quad , \end{aligned} \qquad (3.3\text{-}17)$$

where we have used the relations (3.3-10d) and (3.3-11). Thus

$$\exp(iEt) V_{ii'}^k \exp(-iEt) = V_{ii'}^k \exp(-ik\omega_{oi} t) \qquad (3.3\text{-}18)$$

and

$$\exp(iEt) V_{jj'}^k \exp(-iEt) = V_{jj'}^k \exp(-ik\omega_{oj} t) \quad . \qquad (3.3\text{-}19)$$

Therefore, $R(\sigma)$ takes the form

$$\begin{aligned} R(\sigma) &= R(\sigma - \sigma^T) \\ &= \sum_{i>i'} \sum_{k=-2}^{2} \sum_{i''>i'''} \sum_{\ell=-2}^{2} J_{(i''i''')(ii')}^{\ell k} (-\ell\omega_{oi}) \\ &\qquad \times \left[[V_{i''i'''}^{\ell}, \sigma - \sigma^T], V_{ii'}^k \right] \end{aligned}$$

$$+ \sum_{j>j'} \sum_{k=-2}^{2} \sum_{j''>j'''} \sum_{\ell=-2}^{2} J^{\ell k}_{(j''j''')(jj')}(-\ell\omega_{oj}) \times \left[[V^{\ell}_{j''j'''}, \sigma - \sigma^T], V^k_{jj'} \right]$$

$$+ \sum_{i,j} \sum_{k=-2}^{2} \sum_{i',j'} \sum_{\ell=-2}^{2} \sum_{m,n=-1}^{1} J^{\ell k}_{(i'j')(ij)}(-m\omega_{oi} - n\omega_{oj}) \times \left[[V^{\ell}_{i'j'}(m,n), \sigma - \sigma^T], V^k_{ij} \right] \quad , \qquad (3.3\text{-}20)$$

where

$$J^{\ell k}_{(i'j')(ij)}(\omega) = \tfrac{1}{2} \int_0^{\infty} [C^{\ell k}_{(i'j')(ij)}(\tau)\, e^{i\omega\tau} + C^{k\ell}_{(ij)(i'j')}(\tau)\, e^{-i\omega\tau}]\, d\tau \qquad (3.3\text{-}21)$$

and

$$C^{\ell k}_{(i'j')(ij)}(\tau) = \langle U^{\ell}_{i'j'}(t+\tau)\, U^k_{ij}(t) \rangle \quad . \qquad (3.3\text{-}22)$$

Suppose, now, we are interested in the relaxation of i-type spins, and let

$$\vec{I}_{(i)} = \sum_i \vec{I}_i \quad . \qquad (3.3\text{-}23)$$

Then, from (3.3-20) we have

$$
\begin{aligned}
&\mathrm{Tr}[R(\sigma) I^{0}_{(i)}] \\
&= \sum_{i>i'} \sum_{k=-2}^{2} \sum_{i''>i'''} \sum_{\ell=-2}^{2} J^{\ell k}_{(i''i''')(ii')}(-\ell\omega_{0i}) \\
&\qquad \times \mathrm{Tr}[V^{\ell}_{i''i'''}, \sigma - \sigma^{T}]\,[V^{k}_{ii'}, I^{(0)}_{(i)}] \\
&+ \sum_{j>j'} \sum_{k=-2}^{2} \sum_{j''>j'''} \sum_{\ell=-2}^{2} J^{\ell k}_{(j''j''')(jj')}(-\ell\omega_{0j}) \\
&\qquad \times \mathrm{Tr}[V^{\ell}_{j''j'''}, \sigma - \sigma^{T}]\,[V^{k}_{jj'}, I^{(0)}_{(i)}] \\
&+ \sum_{i,j} \sum_{k=-2}^{2} \sum_{i',j'} \sum_{\ell=-2}^{2} \sum_{m,n=-1}^{1} J^{\ell k}_{(i'j')(ij)}(-m\omega_{0i} - n\omega_{0j}) \\
&\qquad \times \mathrm{Tr}[V^{\ell}_{i'j'}(m,n), \sigma - \sigma^{T}]\,[V^{k}_{ij}, I^{0}_{(i)}] \quad , \qquad (3.3\text{-}24)
\end{aligned}
$$

where we have used the property

$$\mathrm{Tr}[A, B]C = \mathrm{Tr}A[B, C] \quad . \qquad (3.3\text{-}25)$$

Since

$$[I^{\mu}_{i}, I^{\nu}_{j}] = (-1)^{\mu+\nu}(\mu-\nu)I^{\mu+\nu}_{i}\,\delta_{ij} \quad , \qquad (3.3\text{-}26)$$

we may write

$$[V^{k}_{jj'}, I^{0}_{(i)}] = 0 \quad , \qquad (3.3\text{-}27)$$

$$[V^{k}_{ii'}, I^{0}_{(i)}] = -kV^{k}_{ii'} \quad , \qquad (3.3\text{-}28)$$

and

$$[V_{ij}^{k},\ I_{(i)}^{o}] = \sum_{m,n} (-1)^{m}\, m\, V_{ij}^{k}(m,n) \quad . \tag{3.3-29}$$

It is usually assumed that in dipole-dipole relaxation only the pair correlation functions contribute significantly to the relaxation time. Therefore it may be written

$$C_{(i'j')(ij)}^{\ell k}(\tau) = \delta_{ii'}\,\delta_{jj'}\ C_{(ij(ij)}^{\ell k}(\tau) \quad . \tag{3.3-30}$$

Substituting Eqs. (3.3-27) through (3.3-30) into (3.3-24), we obtain

$$\begin{aligned} &\mathrm{Tr}[\,R(\sigma)I_{(i)}^{o}] \\ &\quad = \sum_{i>i'} \sum_{k=-2}^{2} \sum_{\ell=-2}^{2} kJ_{(ii')(ii')}^{\ell k}(-\ell\omega_{oi})\ \mathrm{Tr}\ \chi[V_{ii'}^{\ell},\ V_{ii'}^{k}] \\ &\quad + \sum_{i,j} \sum_{k=-2}^{2} \sum_{\ell=-2}^{2} \sum_{m,n} \sum_{m',n'} (-1)^{m'+1} m'\ J_{(ij)(ij)}^{\ell k}(-m\omega_{oi} - n\omega_{oj}) \\ &\qquad \times\ \mathrm{Tr}\ \chi[V_{ij}^{\ell}(m,n),\ V_{ij}^{k}(m',n')] \quad , \end{aligned} \tag{3.3-31}$$

where $\chi = \sigma - \sigma^{T}$.

If the nuclei have spins of 1/2, so that the following relation is valid

$$I_{i}^{m} I_{i}^{n} = \tfrac{1}{2}(m-n)(-1)^{m+n} I_{i}^{m+n} + \tfrac{1}{4}\,\delta_{m,\,-n}(1+m^{2}) \quad , \tag{3.3-32}$$

we can show that

$$
\begin{aligned}
&[V^{\ell}_{ij}(m,n),\ V^{k}_{ij}(m',n')] \\
&\quad = A^{\ell}_{mn}A^{k}_{m'n'}\ \{\tfrac{1}{8}\ \delta_{n,\,-n'}(m-m')(-1)^{m+m'}\ I_i^{m+m'}\ (2+n^2+n'^2) \\
&\quad + \ \tfrac{1}{8}\ \delta_{m,\,-m'}\,(n-n')(-1)^{n+n'}\ I_j^{n+n'}\ (2+m^2+m'^2) \\
&\quad + \tfrac{1}{16}\ \delta_{m,-m'}\delta_{n,-n'}(1+m^2)\,(1+n^2) \\
&\quad - \tfrac{1}{16}\ \delta_{m,\,-m'}\,\delta_{n,-n'}\,(1+m'^2)(1+n'^2)\} \quad .
\end{aligned}
\tag{3.3-33}
$$

Hence

$$
[V^{k}_{ij},V^{k}_{ij}] = \sum_{m,n}\ \sum_{m',n'}\ [V^{k}_{ij}(m,n),\ V^{k}_{ij}(m',n')]
$$

$$
= \tfrac{1}{2}\,(-1)^{k} \sum_{\mu=-1,\,0,\,1} \delta_{k,\,-\ell+\mu}(1-\tfrac{1}{2}\,\mu^2)\ A^{\mu}_{-k}(I_i^{\mu}+I_j^{\mu}) \ , \tag{3.3-34}
$$

where A^{μ}_{k}'s are defined by

$$
A^{0}_{k} = k \tag{3.3-35a}
$$

and

$$
A^{\pm 1}_{k} = [(2\mp k)(3\pm k)]^{\frac{1}{2}} \quad . \tag{3.3-35b}
$$

Since the phenomenological equation is linear with respect to the I_i^0's, we have only to concern ourselves with terms in (3.3-31) satisfying the conditions

$$
\mu = 0,\ m+m' = 0,\ \text{and}\ n+n' = 0 \quad .
$$

Then, substitution of (3.3-33), (3.3-34), and (3.3-36) into (3.3-31) gives us

$$\mathrm{Tr}[R(\sigma)I^0_{(i)}] = -\sum_{i>i'} \frac{1}{T_{1ii'}} \{\langle I^0_i + I^0_{i'}\rangle - \langle I^0_i + I^0_{i'}\rangle_T\}$$

$$-\sum_i \frac{1}{T'_{1i}} \{\langle I^0_i\rangle - \langle I^0_i\rangle_T\} - \sum_j \frac{1}{T'_{1j}} \{\langle I^0_j\rangle - \langle I^0_j\rangle_T\} \qquad (3.3\text{-}36)$$

where

$$\frac{1}{T_{1ii'}} = \tfrac{1}{2} \sum_{\ell=-2}^{2} (-1)^{-\ell}\, \ell^2\, J^{\ell,-\ell}_{(ii')(ii')}(-\ell\omega_{0i})$$

$$= -J^{-1,1}_{(ii')(ii')}(\omega_{0i}) + 4\, J^{-2,2}_{(ii')(ii')}(2\omega_{0i}) \quad , \qquad (3.3\text{-}37)$$

$$\frac{1}{T'_{1i}} = \sum_j \{\tfrac{1}{3}\, J^{0,0}_{(ij)(ij)}(\omega_{0i} - \omega_{0j}) - J^{-1,1}_{(ij)(ij)}(\omega_{0i})$$

$$+ 2\, J^{-2,2}_{(ij)(ij)}(\omega_{0i} + \omega_{0j})\} \quad , \qquad (3.3\text{-}38)$$

and

$$\frac{1}{T'_{1j}} = \sum_i \{2\, J^{-2,2}_{(ij)(ij)}(\omega_{0i} + \omega_{0j}) - \tfrac{1}{3}\, J^{0,0}_{(ij)(ij)}(\omega_{0i} - \omega_{0j})\} \quad . \qquad (3.3\text{-}39)$$

Similarly, for $I_i^{\pm1}*$ defined by

$$I_i^{\pm1}* = \exp(-iEt)\, I_i^{\pm1} \exp(iEt) = \exp(\pm i\omega_{0i}t)\, I_i^{\pm1} \quad , \qquad (3.3\text{-}40)$$

we obtain

$$\frac{d}{dt}\langle I^{\pm1}_{(i)}*\rangle = -\sum_{i>i'} \frac{1}{T_{2ii'}} \{\langle I_i^{\pm1}* + I_{i'}^{\pm1}*\rangle - \langle I_i^{\pm1}* + I_{i'}^{\pm1}*\rangle_T\}$$

$$-\sum \frac{1}{T'} \{\langle I_i^{\pm1}*\rangle - \langle I_i^{\pm1}*\rangle_T\} \quad . \qquad (3.3\text{-}41)$$

where

$$\frac{1}{T_{2ii'}} = \frac{3}{2} J^{0,0}_{(ii')(ii')}(0) - \frac{5}{2} J^{-1,1}_{(ii')(ii')}(\omega_{oi}) + J^{-2,2}_{(ii')(ii')}(2\omega_{oi}) \qquad (3.3\text{-}42)$$

and

$$\frac{1}{T'_{2i}} = \sum_j \{\frac{2}{3} J^{0,0}_{(ij)(ij)}(0) + \frac{1}{6} J^{0,0}_{(ij)(ij)}(\omega_{oi} - \omega_{oj}) - \frac{1}{2} J^{-1,1}_{(ij)(ij)}(\omega_{oi})$$

$$- J^{-1,1}_{(ij)(ij)}(\omega_{oj}) + J^{-2,2}_{(ij)(ij)}(\omega_{oi} + \omega_{oj})\} \quad . \qquad (3.3\text{-}43)$$

From (3.3-36) through (3.3-43) we can see that when there are several different kinds of nuclear spins on a molecule the relaxation of these different kinds of spins is coupled to each other in a complicated manner, and therefore the relaxation of any spin cannot be described by a single parameter T_1. For example, for a molecule which contains only two spins of different kinds, as in HF, Eq. (3.3-36) takes the form

$$\frac{d}{dt}\langle I_z\rangle = -\frac{1}{T_1^{II}}(\langle I_z\rangle - \langle I_z\rangle_T) - \frac{1}{T_1^{IS}}(\langle S_z\rangle - \langle S_z\rangle_T) \qquad (3.3\text{-}44)$$

and

$$\frac{d}{dt}\langle S_z\rangle = -\frac{1}{T_1^{SI}}(\langle I_z\rangle - \langle I_z\rangle_T) - \frac{1}{T_1^{SS}}(\langle S_z\rangle - \langle S_z\rangle_T) \quad , \qquad (3.3\text{-}45)$$

with

$$\frac{1}{T_1^{II}} = \frac{1}{3} J^{0,0}(\omega_{0I} - \omega_{0S}) - J^{-1,1}(\omega_{0I}) + 2\, J^{-2,2}(\omega_{0I} + \omega_{0S}) , \qquad (3.3\text{-}46)$$

$$\frac{1}{T_1^{IS}} = 2\, J^{-2,2}(\omega_{0I} + \omega_{0S}) - \tfrac{1}{3}\, J^{0,0}(\omega_{0I} - \omega_{0S}) \quad , \qquad (3.3\text{-}47)$$

and similar equations for T_1^{SS} and T_1^{SI} are obtained by interchanging the indices I and S.

However, when all the spins on a molecule are equivalent, as protons in C_2H_6, the cross relaxation terms disappear and the longitudinal relaxation process can be well described by a single parameter T_1.[21] In a molecule like toluene, however, the CH_3 protons and ring protons will have different relaxation times and in this case we have to use the coupled relaxation equations. Here for the convenience of discussion we treat the ethane molecule. In the absence of internal rotation the internuclear distances, r_{ij}, and polar angles, θ_{ij} and φ_{ij}, do not change with time in the body-fixed coordinates. Thus in this case we have only to study the rotation of the body-fixed frame with respect to the space-fixed frame.[22, 23] However, in the presence of internal rotation internuclear distances and polar angles do not necessarily remain constant even in the body-fixed frame, thus the situation becomes more complicated than in the case of no internal rotation.

Since the correlation functions (3.3-22) can be more readily evaluated in the body-fixed coordinates, we have to transform U_{ij}^{k} so that they can be expressed in terms of polar angles of $\vec{r}_{ij}$ with respect to the body-fixed coordinates. We take the body-fixed frame (x, y, z) in such a way that the z-axis coincides with the molecular symmetry axis and the other two axes are perpendicular to the symmetry axis. Let the radii of circles traced by the protons when two CH_3 groups

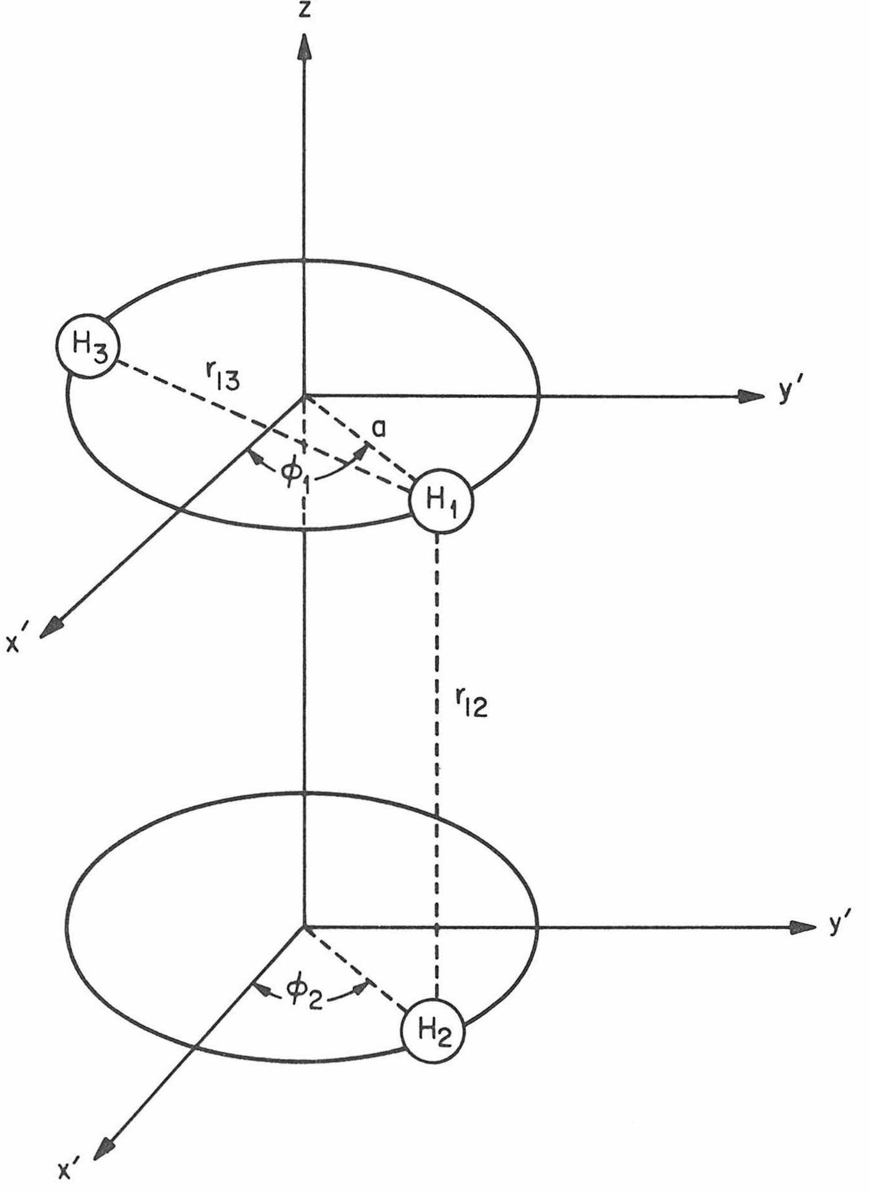

Fig VI Basic Geometry of Ethane Molecule undergo internal rotation with respect to the body-fixed frame be a and let the distance between two circles be b.

Since all the protons in an ethane molecule are equivalent, we may write from (3.3-36) through (3.3-43)

$$\frac{1}{T_1} = \frac{2}{T_1'} + \frac{3}{T_1''} \qquad (3.3\text{-}48)$$

and

$$\frac{1}{T_2} = \frac{2}{T_2'} + \frac{3}{T_2''} \quad , \qquad (3.3\text{-}49)$$

where

$$\frac{1}{T_1'} = - J^{-1,1}_{(13)(13)}(\omega_0) + 4 J^{-2,2}_{(13)(13)}(2\omega_0) \quad , \qquad (3.3\text{-}50)$$

$$\frac{1}{T_1''} = - J^{-1,1}_{(12)(12)}(\omega_0) + 4 J^{-1,1}_{(12)(12)}(2\omega_0) \quad , \qquad (3.3\text{-}51)$$

$$\frac{1}{T_2'} = \frac{3}{2} J^{0,0}_{(13)(13)}(0) - \frac{5}{2} J^{-1,1}_{(13)(13)}(\omega_0) + J^{-2,2}_{(13)(13)}(2\omega_0) \quad . \qquad (3.3\text{-}53)$$

and

$$\frac{1}{T_2''} = \frac{3}{2} J^{0,0}_{(12)(12)}(0) - \frac{5}{2} J^{-1,1}_{(12)(12)}(\omega_0) + J^{-2,2}_{(12)(12)}(2\omega_0) \quad . \qquad (3.3\text{-}53)$$

Let us denote the three Euler angles, which determine the orientation of body-fixed frame with respect to the space-fixed frame, by Θ, Φ, and Ψ, and let θ and ϕ be the polar angles of a point on a unit sphere in terms of the laboratory coordinate system and θ' and ϕ' be the coordinates in terms of the body-fixed coordinate system. Then it may be shown that[24]

$$Y_\ell^m(\theta, \phi) = \sum_n \mathcal{D}^{\ell}_{mm}(\Omega)\, Y_\ell^n(\theta', \phi') \quad , \qquad (3.3\text{-}54)$$

where $\mathscr{D}^{\ell}_{nm}(\Omega)$ are elements of the Wigner rotation matrix and are also functions of the rotation $\Omega = (\Phi, \Theta, \Psi)$. Therefore

$$U^{k}_{ij}(\theta_{ij}, \varphi_{ij}) = \sum_{n} \mathscr{D}^{(2)*}_{nk}(\Omega)\, U^{n}_{ij}(\theta'_{ij}, \varphi'_{ij}) \quad , \tag{3.3-55}$$

where

$$U^{k}_{ij}(\theta_{ij}, \varphi_{ij}) = (6\pi/5)^{\frac{1}{2}}\, \gamma_i \gamma_j\, \hbar r_{ij}^{-3} (-1)^{k}\, Y_2^{-k}(\theta_{ij}, \varphi_{ij}) \tag{3.3-56}$$

and

$$U^{n}_{ij}(\theta'_{ij}, \varphi'_{ij}) = (6\pi/5)^{\frac{1}{2}}\, \gamma_i \gamma_j\, \hbar r_{ij}^{-3} (-1)^{n}\, Y_2^{-n}(\theta'_{ij}, \varphi'_{ij}) \quad . \tag{3.3-57}$$

From (3.3-55) we have

$$\begin{aligned} &\langle [U^{k'}_{ij}(\theta_{ij}, \varphi_{ij})]_{t+t_0} [U^{k}_{ij}(\theta_{ij}, \varphi_{ij})]_{t_0} \rangle \\ &= \sum_{n} \sum_{n'} \langle [\mathscr{D}^{(2)}_{n'k'}{}^{*}(\Omega)\, U^{n'}_{ij}(\theta'_{ij}, \varphi'_{ij})_{t+t_0} [\mathscr{D}^{(2)}_{nk}{}^{*}(\Omega)\, U^{n}_{ij}(\theta'_{ij}, \varphi'_{ij})]_{t_0} \rangle \quad . \end{aligned} \tag{3.3-58}$$

If we may assume that molecular chaos in gaseous or liquid state is such that the overall rotational motion is uncorrelated with the internal rotation, (3.3-58) may be written

$$\begin{aligned} &\langle [U^{k'}_{ij}(\theta_{ij}, \varphi_{ij})]_{t+t_0} [U^{k}_{ij}(\theta_{ij}, \varphi_{ij})]_{t_0} \rangle \\ &\quad = \sum_{n} \sum_{n'} \langle [\mathscr{D}^{(2)}_{nk}{}^{*}(\Omega)]_{t+t_0} [\mathscr{D}^{(2)}_{nk}{}^{*}(\Omega)]_{t_0} \rangle \\ &\qquad \times \langle [U^{n'}_{ij}(\theta'_{ij}, \varphi'_{ij})]_{t+t_0} [U^{n}_{ij}(\theta'_{ij}, \varphi'_{ij})]_{t_0} \rangle \quad . \end{aligned} \tag{3.3-59}$$

In the next chapter it will be shown that if the rotational motion of the body-fixed frame with respect to the space-fixed frame can be described by the diffusion model we have

$$\langle [\mathscr{D}^{(2)}_{n'k'}{}^{*}(\Omega)]_{t+t_0} [\mathscr{D}^{(2)}_{nk}{}^{*}(\Omega)]_{t_0} \rangle = (-1)^{k'-n} \delta_{-k'k} (1/5)\, I^{(2)}_{n',\,-n}(t) \ , \qquad (3.3\text{-}60)$$

where

$$I^{(2)}_{n',\,-n}(t) = \int \mathscr{D}^{(2)}_{n',\,-n}(\Omega')\ P(\vec{\Omega}', \vec{0};\ t)\, d'\Omega' \qquad (3.3\text{-}61)$$

and $P(\vec{\Omega}', \vec{0};\ t)$ is the probability density that there is a rotation through Euler angles Ω' in time t. Since $P(\vec{\Omega}', \vec{0};\ t)$ is an even function of Ω', $I^{(2)}_{n',\,-n}(t)$ vanishes unless $n'-n$ is an even number (see Chapter IV).

Evaluation of a correlation function of the type

$$\langle [U^{n'}_{ij}(\theta'_{ij}, \varphi'_{ij})]_{t+t_0} [U^{n}_{ij}(\theta'_{ij}, \varphi'_{ij})]_{t_0} \rangle \qquad (3.3\text{-}62)$$

depends on the details of internal rotational motion in a molecule as we shall see in what follows.

In a molecule like ethane we can express r_{12}, θ'_{12}, φ'_{12}, r_{13}, θ'_{13}, and φ'_{13} in terms of a, b, ϕ_1, and ϕ_2 as follows (see Fig. 6):

$$r_{12} = \{2a^2[1 - \cos(\phi_2 - \phi_1)] + b^2\}^{\frac{1}{2}} \ ,$$

$$\sin\theta'_{12} = \left\{\frac{2a^2[1 - \cos(\phi_2 - \phi_1)]}{2a^2[1 - \cos(\phi_2 - \phi_1)] + b^2}\right\}^{\frac{1}{2}} \ ,$$

$$\cos\theta'_{12} = \left\{\frac{b^2}{2a^2[1 - \cos(\phi_2 - \phi_1)] + b^2}\right\}^{\frac{1}{2}} \ ,$$

$$\varphi'_{12} = \frac{\pi}{2} + \frac{1}{2}(\phi_2 + \phi_1) \ , \qquad (3.3\text{-}63)$$

and

$$r_{13} = \sqrt{3}\,a, \quad \theta'_{13} = \frac{\pi}{2}, \quad \varphi'_{13} = \pi + \left(\phi_1 + \frac{\pi}{6}\right) \quad . \tag{3.3-64}$$

Let us define

$P_1(\phi_1^0)$ = probability that the first methyl group is found to be rotated away from the origin by an angle ϕ_1^0 at $t = 0$,

$P_2(\phi_2^0)$ = probability that the second methyl group is found to be rotated away from the origin by an angle ϕ_2^0 at $t = 0$,

$P_1(\phi_1; t)$ = probability that the angle ϕ of the first methyl group takes the value ϕ_1 at time t when we know that it takes the value 0 at $t = 0$,

$P_2(\phi_2; t)$ = probability that the angle ϕ of the second methyl group takes the value ϕ_2 at time t when we know that it takes the value 0 at $t = 0$,

$P_1(\phi_1^0, \phi_1'; t)$ = probability that the angle ϕ of the first methyl group takes the value ϕ_1^0 at $t = 0$ and ϕ_1' at time t,

$P_2(\phi_2^0, \phi_2'; t)$ = probability that the angle ϕ of the second methyl group takes the value ϕ_2^0 at $t = 0$ and ϕ_2' at time t,

and

$P(\phi_1^0, \phi_1', \phi_2^0, \phi_2'; t)$ = probability that the first and second methyl groups are found at ϕ_1^0 and ϕ_2^0 at $t = 0$ and at ϕ_1' and ϕ_2' after time t, respectively.

Here we have tacitly assumed that the process of molecular reorientation is stationary (see Chapter IV). According to the definition of the correlation function we may write

$$\langle G\left[\phi_1(t), \phi_2(t)\right] \; F\left[\phi_1(0), \phi_2(0)\right]\rangle$$

$$= \iiiint P(\phi_1^0, \phi_1', \phi_2^0, \phi_2'; t) \; F(\phi_1^0, \phi_2^0) \; G(\phi_1', \phi_2') \, d\phi_1^0 d\phi_2^0 d\phi_1' d\phi_2' \quad ,(3.3\text{-}65)$$

when ϕ_1 and ϕ_2 vary continuously from 0 to 2π, and

$$\langle G\left[\phi_1(t), \phi_2(t)\right] \cdot F\left[\phi_1(0), \phi_2(0)\right] \rangle$$

$$= \sum_{\phi_2'} \sum_{\phi_1'} \sum_{\phi_2^0} \sum_{\phi_1^0} P(\phi_1^0, \phi_1', \phi_2^0, \phi_2'; t) \; F(\phi_1^0, \phi_2^0) \; G(\phi_1', \phi_2') \qquad (3.3\text{-}66)$$

when ϕ_1 and ϕ_2 can take only some discrete values between 0 and 2π.

If the internal rotation of one methyl group with respect to the body-fixed frame may be assumed to be independent of that of the other methyl group, we may write

$$P(\phi_1^0, \phi_1', \phi_2^0, \phi_2'; t) = P_1(\phi_1^0, \phi_1'; t) \; P_2(\phi_2^0, \phi_2'; t) \quad . \qquad (3.3\text{-}67)$$

Moreover, from the definitions of $P_1(\phi_1^0, \phi_1'; t)$ and $P_2(\phi_2^0, \phi_2'; t)$ it follows that

$$P_1(\phi_1^0, \phi_1'; t) = P_1(\phi_1^0) \; P_1(\phi_1' - \phi_1^0; t) \quad . \qquad (3.3\text{-}68)$$

Substitution of (3.3-67) through (3.3-69) in (3.3-65) and (3.3-66) gives us

$$\langle G\left[\phi_1(t), \phi_2(t)\right] \cdot F\left[\phi_1(0), \phi_2(0)\right] \rangle$$

$$= \iint F(\phi_1^0, \phi_2^0) \; P_1(\phi_1^0) \; P_2(\phi_2^0) \, d\phi_1^0 d\phi_2^0$$

$$\times \iint G(\phi_1', \phi_2') \; P_1(\phi_1' - \phi_1^0; t) \; P_2(\phi_2' - \phi_2^0; t) \, d\phi_1' d\phi_2' \qquad (3.3\text{-}70)$$

when ϕ_1 and ϕ_2 vary continuously, and

$$\langle G\left[\phi_1(t),\ \phi_2(t)\right] \cdot F\left[\phi_1(0),\ \phi_2(0)\right]\rangle$$

$$= \sum_{\phi_2^0} \sum_{\phi_1^0} F(\phi_1^0, \phi_2^0)\ P_1(\phi_1^0)\ P_2(\phi_2^0)$$

$$\times \sum_{\phi_2'} \sum_{\phi_1'} G(\phi_1', \phi_2')\ P_1(\phi_1' - \phi_1^0;\, t)\ P_2(\phi_2' - \phi_2^0;\, t) \quad , \qquad (3.3\text{-}71)$$

when ϕ_1 and ϕ_2 can take some discrete values only.

$P_1(\phi_1' - \phi_1^0;\, t)$ and $P_2(\phi_2' - \phi_2^0;\, t)$ depend on the dynamics of internal rotation and thus on the inter- and intramolecular forces. Since we do not have much knowledge available about the effect of intermolecular forces on the dynamics of intramolecular reorientation, a general approach to this problem cannot be given in the present time. Therefore, we shall be satisfied by considering only a few limiting cases. If the internal reorientation process can be described by a diffusion model, ϕ_1 and ϕ_2 can be considered to vary continuously. Therefore, in this case correlation functions like $\langle [r_{12}^{-3}\ Y_2^0(\theta_{12}', \varphi_{12}')]_t \times [r_{12}^{-3}\ Y_2^0(\theta_{12}', \varphi_{12}')]_0 \rangle$ involve integrals which approach the complete elliptic integral at long correlation times. The complexity of integrals appearing in (3.3-70) prevents us from obtaining an explicit expression for the correlation functions when ϕ_1 and ϕ_2 vary continuously.

However, the evaluation of correlation functions is relatively easy if the internal reorientation process is such that ϕ_1 and ϕ_2 can take some discrete values only. If the internal motion is that of independent jumping of each proton among its three occupation positions as it is in ethane, the occupation probabilities for the proton 1 in its three possible positions are

$$P_1(\phi_1' - \phi_1^0;\, t) = \tfrac{1}{3} + \tfrac{2}{3}\exp(-t/\tau_i) \qquad \text{for} \qquad \phi_1' - \phi_1^0 = 0 \tag{3.3-73}$$

and

$$P_1(\phi_1' - \phi_1^0;\, t) = \tfrac{1}{3} - \tfrac{1}{3}\exp(-t/\tau_i) \qquad \text{for} \qquad \phi_1' - \phi_1^0 = \pm\frac{2\pi}{3}\ . \tag{3.3-74}$$

The independent motion of proton 2 is similarly described by probabilities in terms of ϕ_2' and τ_i.

By making use of (3.3-5), (3.3-64), (3.3-71), (3.3-73), and (3.3-74) we can show that for this model

$$\langle [r_{13}^{-3} Y_2^0(\theta_{13}', \varphi_{13}')]_t\, [r_{13}^{-3} Y_2^0(\theta_{13}', \varphi_{13}')]_0 \rangle = \frac{5}{16\pi} \cdot \frac{1}{27a^6}\ , \tag{3.3-75a}$$

$$\langle [r_{13}^{-3} Y_2^{\pm 2}(\theta_{13}', \varphi_{13}')]_t\, [r_{13}^{-3} Y_2^{\mp 2}(\theta_{13}', \varphi_{13}')]_0 \rangle$$

$$= \frac{15}{32\pi}\, \frac{1}{27a^6}\, \frac{1}{3} \exp(-t/\tau_i)\ , \tag{3.3-75b}$$

$$\langle [r_{12}^{-3} Y_2^0(\theta_{12}', \varphi_{12}')]_t\, [r_{12}^{-3} Y_2^0(\theta_{12}', \varphi_{12}')]_0 \rangle$$

$$= \frac{5}{72\pi}\, [Q_0'' \exp(-2t/\tau_i) + Q_0]\ , \tag{3.3-75c}$$

$$\langle [r_{12}^{-3} Y_2^{\pm 1}(\theta_{12}', \varphi_{12}')]_t\, [r_{12}^{-3} Y_2^{\mp 1}(\theta_{12}', \varphi_{12}')]_0 \rangle$$

$$= -\frac{15}{72\pi}\, [Q_1'' \exp(-2t/\tau_i) + Q_1' \exp(-t/\tau_i) + Q_1]\ , \tag{3.3-75d}$$

and

$$\langle [r_{12}^{-3} Y_2^{\pm 2}(\theta_{12}', \varphi_{12}')]_t\, [r_{12}^{-3} Y_2^{\mp 2}(\theta_{12}', \varphi_{12}')]_0 \rangle$$

$$= \frac{5}{96\pi}\, [Q_2'' \exp(-2t/\tau_i) + Q_2' \exp(-t/\tau_i)]\ , \tag{3.3-75e}$$

where

$$Q_0'' = [r_s^{-5}(a^2-2b^2) - 2r_\ell^{-5}(2a^2-b^2)]^2 \quad ,$$

$$Q_0 = 2[r_s^{-5}(a^2-2b^2) + r_\ell^{-5}(2a^2-b^2)]^2 \quad ,$$

$$Q_1'' = 2a^2b^2[r_s^{-10} - 4r_\ell^{-5}r_s^{-5} + 2r_\ell^{-10}] \quad ,$$

$$Q_1' = 8a^2b^2(r_s^{-5} + r_\ell^{-5})^2 \quad ,$$

$$Q_1 = -a^2b^2(r_s^{-10} - 8r_\ell^{-5}r_s^{-5}) \quad ,$$

$$Q_2'' = 4a^4(r_s^{-5} + 2r_\ell^{-5})^2 \quad ,$$

and

$$Q_2' = 2a^4(r_s^{-5} - 4r_\ell^{-5})^2 \quad , \tag{3.3-76}$$

with

$$r_s^2 = a^2 + b^2 \qquad \text{and} \qquad r_\ell^2 = 4a^2 + b^2 \quad .$$

Also we can see that

$$\langle [r_{12}^{-3} Y_2^m(\theta_{12}', \varphi_{12}')]_t \, [r_{12}^{-3} Y_2^{m'}(\theta_{12}', \varphi_{12}')]_0 \rangle = 0 \tag{3.3-77a}$$

and

$$\langle [r_{13}^{-3} Y_2^m(\theta_{13}', \varphi_{13}')]_t \, [r_{13}^{-3} Y_2^{m'}(\theta_{13}', \varphi_{13}')]_0 \rangle = 0 \quad , \tag{3.3-77b}$$

unless $m = -m'$.

Let three principal values of the diffusion tensor of the molecule be D_x, D_y, D_z, and also define (see Chapter IV)

$$\alpha^+ = 2\Delta + 3(D_z - D) \quad ,$$

$$\alpha^- = 2\Delta - 3(D_z - D) \quad ,$$

$$\Delta = (D_x^2 - D_y^2 + D_z^2 - D_xD_y - D_yD_z - D_xD_x)^{\frac{1}{2}} \quad ,$$

$$D = \tfrac{1}{3}(D_x + D_y + D_z) \quad ,$$

and

$$\frac{1}{\tau_1} = 3(D+D_x) \, , \quad \frac{1}{\tau_2} = 3(D+D_y) \, , \quad \frac{1}{\tau_3} = 3(D+D_z) \, ,$$

$$\frac{1}{\tau_+} = 6D + 2\Delta \quad , \quad \frac{1}{\tau_-} = 6D - 2\Delta \quad . \tag{3.3-78}$$

Furthermore, we introduce new correlation times defined by

$$\frac{1}{\tau_1'} = \frac{1}{\tau_i} + \frac{1}{\tau_1} \, , \quad \frac{1}{\tau_2'} = \frac{1}{\tau_i} + \frac{1}{\tau_2} \, , \quad \frac{1}{\tau_3'} = \frac{1}{\tau_i} + \frac{1}{\tau_3} \quad ,$$

$$\frac{1}{\tau_+'} = \frac{1}{\tau_i} + \frac{1}{\tau_+} \, , \quad \frac{1}{\tau_-'} = \frac{1}{\tau_i} + \frac{1}{\tau_-} \quad , \tag{3.3-79}$$

and

$$\frac{1}{\tau_1''} = \frac{2}{\tau_i} + \frac{1}{\tau_1} \, , \quad \frac{1}{\tau_2''} = \frac{2}{\tau_i} + \frac{1}{\tau_2} \, , \quad \frac{1}{\tau_3''} = \frac{2}{\tau_i} + \frac{1}{\tau_3} \quad ,$$

$$\frac{1}{\tau_+''} = \frac{2}{\tau_i} + \frac{1}{\tau_+} \, , \quad \frac{1}{\tau_-''} = \frac{2}{\tau_i} + \frac{1}{\tau_-} \quad . \tag{3.3-80}$$

Then from (3.3-59), (3.3-60), (3.3-75), (3.3-78), (3.3-79), and (3.3-80) we obtain

$$\begin{aligned} & \langle [U_{13}^{-1}(\theta_{13}, \varphi_{13})]_{t+t_0} \, [U_{13}^{1}(\theta_{13}, \varphi_{13})]_{t_0} \rangle \\ & \quad = - \langle [U_{13}^{0}(\theta_{13}, \varphi_{13})]_{t+t_0} \, [U_{13}^{0}(\theta_{13}, \varphi_{13})]_{t_0} \rangle \\ & \quad = - \langle [U_{13}^{-2}(\theta_{13}, \varphi_{13})]_{t+t_0} \, [U_{13}^{2}(\theta_{13}, \varphi_{13})]_{t_0} \rangle \end{aligned}$$

$$= - C_+ \exp(-t/\tau_+) - C_- \exp(-t/\tau_-) - C'_+ \exp(-t/\tau'_+)$$
$$- C'_- \exp(-t/\tau'_-) - C'_3 \exp(-t/\tau'_3) \qquad (3.3\text{-}81)$$

and

$$\langle [U^{-1}_{12}(\theta_{12}, \varphi_{12})]_{t+t_0} \, [U'_{12}(\theta_{12}, \varphi_{12})]_{t_0} \rangle$$
$$= - \langle [U^0_{12}(\theta_{12}, \varphi_{12})]_{t+t_0} \, [U^0_{12}(\theta_{12}, \varphi_{12})]_{t_0} \rangle$$
$$= - \langle [U^{-2}_{12}(\theta_{12}, \varphi_{12})]_{t+t_0} \, [U^2_{12}(\theta_{12}, \varphi_{12})]_{t_0} \rangle$$
$$= - D_1 \exp(-t/\tau_1) - D_2 \exp(-t/\tau_2) - D_+ \exp(-t/\tau_+)$$
$$- D_- \exp(-t/\tau_-) - D'_1 \exp(-t/\tau'_1) - D'_2 \exp(-t/\tau'_2)$$
$$- D'_3 \exp(-t/\tau'_3) - D'_+ \exp(-t/\tau'_+) - D'_- \exp(-t/\tau'_-)$$
$$- D''_1 \exp(-t/\tau''_1) - D''_2 \exp(-t/\tau''_2) - D''_3 \exp(-t/\tau''_3)$$
$$- D''_+ \exp(-t/\tau''_+) - D''_- \exp(-t/\tau''_-) \qquad (3.3\text{-}82)$$

where

$$C_+ = \frac{\gamma^2\hbar}{360a^2}\frac{\alpha^-}{4\Delta}, \quad C_- = \frac{\gamma^2\hbar}{360a^2}\frac{\alpha^+}{4\Delta}, \quad C'_+ = \frac{\gamma^2\hbar}{360a^2}\frac{\alpha^+}{8\Delta},$$

$$C'_- = \frac{\gamma^2\hbar}{360a^2}\frac{\alpha^-}{8\Delta}, \quad C'_3 = \frac{\gamma^2\hbar}{720a^2}, \quad D_1 = \frac{Q_1}{20}, \quad D_2 = \frac{Q_1}{20},$$

$$D_+ = \frac{Q_0\alpha^-}{240\Delta}, \quad D_- = \frac{Q_0\alpha^+}{240\Delta}, \quad D'_1 = \frac{Q'_1}{20}, \quad D'_2 = \frac{Q'_1}{20}, \quad D'_3 = \frac{Q'_2}{80},$$

$$D'_+ = \frac{Q'_2\alpha^+}{320\Delta}, \quad D'_- = \frac{Q'_2\alpha^-}{320\Delta}, \quad D''_1 = \frac{Q''_1}{20}, \quad D''_2 = \frac{Q''_1}{20}, \quad D''_3 = \frac{Q''_2}{80},$$

$$D''_+ = -\left(\frac{Q''_0\alpha^-}{240\Delta} + \frac{Q''_2\alpha^+}{320\Delta}\right), \quad D''_- = -\left(\frac{Q''_0\alpha^+}{240\Delta} + \frac{Q''_2\alpha^-}{320\Delta}\right) . \qquad (3.3\text{-}83)$$

From the definitions of $J^{\ell k}_{(ij)(ij)}(\omega_0)$ and Eqs. (3.3-50) through

(3.3-53) we can easily obtain $(1/T_1')$, $(1/T_1'')$, $(1/T_2')$, and $(1/T_2'')$. In the limit that $\omega_0^2\tau^2 \ll 1$ for all the correlation times involved in (3.3-81) and (3.3-82) we may write

$$\frac{1}{T_1'} = \frac{1}{T_2'} = 5C_+\tau_+ + 5C_-\tau_- + 5C'_+\tau'_+ + 5C'_-\tau'_- + 5C_3'\tau_3' \qquad (3.3\text{-}84)$$

and

$$\begin{aligned}\frac{1}{T_1''} = \frac{1}{T_2''} = {} & 5D_1\tau_1 + 5D_2\tau_2 + 5D_+\tau_+ + 5D_-\tau_- + 5D_1'\tau_1' + 5D_2'\tau_2' \\ & + 5D_3'\tau_3' + 5D'_+\tau'_+ + 5D'_-\tau'_- + 5D_1''\tau_1'' + 5D_2''\tau_2'' \\ & + 5D_3''\tau_3'' + 5D''_+\tau''_+ + 5D''_-\tau''_- \quad . \qquad (3.3\text{-}85)\end{aligned}$$

Since the internal motion decreases the values of τ''s and τ'''s in (3.3-84) and (3.3-85), the overall relaxation times due to the dipole-dipole interaction increase for all rates of internal motion. Consequently, internal molecular motion causes the intramolecular dipole-dipole relaxation in liquid to decrease in relative importance compared to the intermolecular contribution. Actually, the intramolecular relaxation time in ethane is longer than we expect.[25] This prediction is also coincident with results observed by Richards.[16, 17]

However, the above statement is not valid when it comes to the spin-rotational relaxation. As we have already seen in the previous chapters, an additional term called the spin-internal-rotation interaction appears in the spin-rotation Hamiltonian in the presence of internal rotation, and this spin-internal-rotation interaction contributes appreciably to the overall relaxation rate. In the next section we discuss the contribution of spin-internal-rotation interaction to the relaxation rate of spins on an internal rotor.

3.4 Spin Relaxation via Spin-Rotation Interaction in the Presence of Internal Rotation

In Chapter II we have shown that for three equivalent fluorine spins in φ-CF_3 the spin-rotation interaction can then be expressed as

$$\mathcal{H}_{S-R} = -\vec{F}\cdot\underset{\wedge}{C}^{(J)}\cdot\vec{J} - D_{\alpha}^{(j)}\vec{F}\cdot\vec{j} \quad , \tag{3.4-1}$$

where $\underset{\wedge}{C}^{(J)}$ and $D_{\alpha}^{(j)}$ are the spin-overall-rotation interaction tensor and spin-internal-rotation interaction constant, respectively, properly averaged over the internal angle. For this case the relaxation mechanism can be expressed as

$$\begin{aligned}\hbar G(q, s) &\equiv \mathcal{H}_{S-R} \\ &= \sum_{K, K'} A_{KK'}J_{K'}F_K + \sum_{K} B_K j_K F_K \quad , \end{aligned} \tag{3.4-2}$$

in the molecular frame in which $\underset{\wedge}{C}^{(J)}$ is diagonal, where

$$A_{00} = -C_{zz}^{(J)}, \quad A_{11} = A_{-1-1} = -\tfrac{1}{2}\left(C_{xx}^{(J)} - C_{yy}^{(J)}\right),$$

$$A_{1-1} = A_{-11} = \tfrac{1}{2}\left(C_{xx}^{(J)} + C_{yy}^{(J)}\right), \quad B_0 = -D_{\alpha}^{(j)} \quad ,$$

and $$B_1 = B_{-1} = 0 \tag{3.4-3}$$

with $A_{KK'}$ vanishing unless $|K| = |K'|$.

J_K, j_K, and F_K are components of first-rank spherical tensors J, j, and F, respectively, defined by

$$J_0 = J_z \ , \qquad J_{\pm 1} = \mp \frac{1}{\sqrt{2}} (J_x \pm iJ_y) \quad , \qquad (3.4\text{-}4a)$$

$$j_0 = j_z \ , \qquad j_{\pm 1} = \mp \frac{1}{\sqrt{2}} (j_x \pm ij_y) \quad , \qquad (3.4\text{-}4b)$$

and

$$F_0 = F_z \ , \qquad F_{\pm 1} = \mp \frac{1}{\sqrt{2}} (F_x \pm iF_y) \quad . \qquad (3.4\text{-}4c)$$

In the expression (3.4-2) both the nuclear spin vectors and the rotational angular momenta are expressed in the body-fixed frame where $\underset{\frown}{C}^{(J)}$ is diagonal. However, the resonance experiment is performed in a space-fixed frame that is determined by the direction of the externally applied magnetic field. The two frames are related by a rotation which can be defined by the set of Euler angles $\Omega \equiv (\alpha, \beta, \gamma)$. It is necessary, therefore, to relate the Hamiltonian to the space-fixed frame at least inasmuch as the components of the spins are concerned, and it may also prove convenient to refer the components of the molecular rotation similarly.[26, 27] These transformations may be effected if the Wigner rotation matrices, $\underset{\frown}{\mathcal{D}}^{(n)}(\Omega)$, are employed[28] as in Eq. (3.3-54), and following Atkins[27] we will henceforth refer to the Hamiltonian in which only the spin has been transformed as the K-representation Hamiltonian and to the doubly transformed Hamiltonian as being in the M-representation. This nomenclature has been adopted by Atkins because in the K-representation we shall be concerned with the correlation of the components of $\vec{J}$ and $\vec{j}$ in the molecular frame, the z-component of $\vec{J}$ then being expressed in terms of the quantum number K for symmetric top molecules, and because in the M-representation the letter M normally denotes the Z-component of $\vec{J}$ in the space-fixed frame.

Since F_K, J_K, and j_K transform according to[28]

$$T_K = \sum_{q=-1}^{1} \mathscr{D}^{(1)}_{qK}{}^{*}(\Omega)\ T_q \quad , \tag{3.4-5}$$

we may rewrite (3.4-2) as

$$\begin{aligned} \mathscr{H}_{S-R} &= \sum_{KK'q} A_{KK'} J_{K'} \mathscr{D}^{(1)}_{qK}{}^{*}(\Omega)\ F_q \\ &\qquad + \sum_{K'q} B_K j_K \mathscr{D}^{(1)}_{qK}{}^{*}(\Omega)\ F_q \\ &\equiv \vec{\mathscr{R}}^{(K)} \cdot \vec{\mathscr{F}} \end{aligned} \tag{3.4-6}$$

in the K-representation, and

$$\begin{aligned} \mathscr{H}_{S-R} &= \sum_{KK'qq'} A_{KK'} \mathscr{D}^{(1)}_{q'K'}{}^{*}(\Omega) \mathscr{D}^{(1)}_{qK}{}^{*}(\Omega)\ J_{q'} F_q \\ &\qquad + \sum_{Kqq'} B_K \mathscr{D}^{(1)}_{q'K}{}^{*}(\Omega) \mathscr{D}^{(1)}_{qK}{}^{*}(\Omega)\ j_{q'} F_q \\ &\equiv \vec{\mathscr{R}}^{(M)} \cdot \vec{\mathscr{F}} \end{aligned} \tag{3.4-7}$$

in the M-representation, where $\vec{\mathscr{F}}$ is a vector whose component is represented by F_q, and

$$\mathscr{R}^{(K)}_q = \sum_{K,K'} A_{KK'} \mathscr{D}^{(1)}_{qK}{}^{*}(\Omega)\ J_{K'} + \sum_{k} B_K \mathscr{D}^{(1)}_{qK}{}^{*}(\Omega)\ j_K \tag{3.4-8}$$

and

$$\mathcal{R}_q^{(M)} = \sum_{KK'q'} A_{KK'} \mathcal{D}^{(1)}_{q'K'}{}^*(\Omega)\, \mathcal{D}^{(1)}_{qK}{}^*(\Omega) J_{q'} + \sum_{K,q'} B_K \mathcal{D}^{(1)}_{q'K}{}^*(\Omega)\, \mathcal{D}^{(1)}_{qK}{}^*(\Omega) j_{q'} \quad . \qquad (3.4\text{-}9)$$

Now, for a moment let us digress to derive the relaxation time formulas for the case of spin-rotational relaxation. Noting the relation

$$\exp(-i\omega_0 F_0 t) F_q \exp(i\omega_0 F_0 t) = \exp(-iq\omega_0 t) F_q \quad , \qquad (3.4\text{-}10)$$

we can write from (3.2-76)

$$\mathrm{Tr}[R(\chi)F_\nu] = \sum_{k=-1}^{1} \sum_{\ell=-1}^{1} J_{\ell k}(-\ell\omega_0)\, \mathrm{Tr}\left\{\left[[F_\ell, \chi], F_k\right] F_\nu\right\} \quad , \qquad (3.4\text{-}11)$$

where

$$\chi = \sigma - \sigma^T$$

and ω_0 is the Larmor frequency of nuclear spins under consideration.

After a little rearrangement similar to those used to obtain Eq. (3.3-24) we obtain

$$\mathrm{Tr}[R(\chi)F_\nu] = \sum_{k=-1}^{1} \sum_{\ell=-1}^{1} J_{\ell k}(-\ell\omega_0)\, A^\nu(1,k)\, \mathrm{Tr}\,\chi[F_\ell, F_{k+\nu}] \quad , \qquad (3.4\text{-}12)$$

where we have used the relation

$$[F_\nu, F_k] = A^\nu(1,k) F_{k+\nu} \qquad (3.4\text{-}13)$$

with $A^\nu(1,k)$ being given by

$$A^0(K,k) = k \qquad (3.4\text{-}14a)$$

and

$$A^{\pm 1}(K,k) = [(K \mp k)(K \pm k+1)]^{\frac{1}{2}} \quad . \qquad (3.4\text{-}14b)$$

If we assume that the macroscopic relaxation equation can be replaced by the corresponding microscopic one, we arrive at the equation

$$\frac{d}{dt}\langle F_\nu\rangle + i(-1)^\nu \nu\omega_0\langle F_\nu\rangle$$

$$= \sum_{k=-1}^{1}\sum_{\ell=-1}^{1} J_{\ell k}(-\ell\omega_0)\, A^\nu(1,k)\cdot \{\langle[F_\ell, F_{k+\nu}]\rangle$$

$$- \langle[F_\ell, F_{k+\nu}]\rangle_0\} \quad . \qquad (3.4\text{-}15)$$

For $\nu = 0$, Eq. (3.3-15) may be written

$$\frac{d}{dt}\langle F_z\rangle = \sum_{k=-1}^{1}\sum_{\ell=-1}^{1} J_{\ell k}(-\ell\omega_0)\, k\{\langle[F_\ell, F_k]\rangle$$

$$- \langle[F_\ell, F_k]\rangle_0\} \quad . \qquad (3.4\text{-}16)$$

Assume the phenomenological equation takes the form

$$\frac{d}{dt}\langle F_z\rangle = -\frac{1}{T_1}\{\langle F_z\rangle - \langle F_z\rangle_0\} \quad . \qquad (3.4\text{-}17)$$

Then, in order that Eq. (3.4-16) coincide with (3.4-17) we require that

$$J_{\ell k}(-\ell\omega_0) = 0 \qquad (3.4\text{-}18)$$

unless $k = -\ell$. Therefore,

$$\frac{1}{T_1} = -[J_{1,-1}(-\omega_0) + J_{-1,1}(\omega_0)] \quad . \qquad (3.4\text{-}19)$$

In a similar manner we can derive the formula for T_2, the spin-spin relaxation time. The result is

$$\frac{1}{T_2} = J_{0,0}(0) - J_{1,-1}(-\omega_0) \quad . \tag{3.4-20}$$

Now, let us return to Eqs. (3.4-8) and (3.4-9). Edmonds[29] gives us two relations which are very useful for our purpose. They are

$$\mathcal{D}^{(j)}_{m'm}{}^*(\Omega) = (-1)^{m'-m} \mathcal{D}^{(j)}_{-m',-m}(\Omega) \tag{3.4-21}$$

and

$$\mathcal{D}^{(j_1)}_{m_1'm_1}(\Omega)\, \mathcal{D}^{(j_2)}_{m_2'm_2}(\Omega) = \sum_{jm'm} (2j+1) \begin{pmatrix} j_1 & j_2 & j \\ m_1' & m_2' & m' \end{pmatrix} \mathcal{D}^{(j)}_{m'm}{}^*(\Omega) \begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m \end{pmatrix}, \tag{3.4-22}$$

where $\begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m \end{pmatrix}$ is a Wigner 3-j symbol. For a further convenience we introduce new constants defined by

$$C = \tfrac{1}{3} \operatorname{Tr} \underset{\frown}{C}^{(J)} \quad ,$$

$$\Delta C = C^{(J)}_{zz} - \tfrac{1}{2} (C^{(J)}_{xx} + C^{(J)}_{yy}), \qquad \text{and}$$

$$\delta C = C^{(J)}_{xx} - C^{(J)}_{yy} \quad . \tag{3.4-23}$$

In terms of these constants $\mathcal{R}^{(K)}_q$ of (3.4-8) can be rewritten as

$$\mathcal{R}^{(K)}_q = \sum_K \left[(-1)^{K+1} C - \tfrac{2}{3} \Delta C \left(\tfrac{1}{2}\right)^{|K|} \right] \mathcal{D}^{(1)}_{qK}{}^*(\Omega)\, J_{-K}$$

$$- \tfrac{1}{2} \delta C \sum_K |K|\, \mathcal{D}^{(1)}_{qK}{}^*(\Omega)\, J_K - D^{(j)}_{\alpha}\, \mathcal{D}^{(1)}_{q0}{}^*(\Omega)\, j_0 \tag{3.4-24}$$

Also, substitution of (3.4-22) and (3.4-23) into (3.4-9) gives us

$$
\begin{aligned}
\mathcal{R}_q^{(M)} &= (-1)^{q+1} (C_{zz}^{(J)} - \Delta C)\, J_{-q} + (-1)^{q+1} (\Delta C - \tfrac{1}{2}\,\delta C) \sum_{q'} (-1)^{q'} J_{q'} \\
&\times \sum_{\ell m m'} (2\ell+1) \begin{pmatrix} 1 & 1 & \ell \\ 0 & 0 & m' \end{pmatrix} \mathcal{D}_{m'm}^{(\ell)}{}^*(\Omega) \begin{pmatrix} 1 & 1 & \ell \\ -q' & -q & m \end{pmatrix} \\
&\quad + (-1)^{q+1} \tfrac{1}{2}\,\delta C \sum_{q'} (-1)^{q'} J_{q'} \sum_{q''=-1}^{1} \sum_{\ell m' m} (2\ell+1) \begin{pmatrix} 1 & 1 & \ell \\ -q'' & -q'' & m' \end{pmatrix} \\
&\times \mathcal{D}_{m'm}^{(\ell)}{}^*(\Omega) \begin{pmatrix} 1 & 1 & \ell \\ -q' & -q & m \end{pmatrix} + (-1)^{q+1} D_{\alpha}^{(j)} \sum_{q'} (-1)^{q'} j_{q'} \\
&\times \sum_{\ell m' m} (2\ell+1) \begin{pmatrix} 1 & 1 & \ell \\ 0 & 0 & m' \end{pmatrix} \mathcal{D}_{m'm}^{(\ell)}{}^*(\Omega) \begin{pmatrix} 1 & 1 & \ell \\ -q' & -q & m \end{pmatrix} \quad .
\end{aligned}
\tag{3.4-25}
$$

Now, we note that the 3-j symbols satisfy the following relations:

(1) $$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = \begin{pmatrix} j_k & j_\ell & j_m \\ m_k & m_\ell & m_m \end{pmatrix}$$

for (k, ℓ, m), an even permutation of (1, 2, 3), and

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_1+j_2+j_3} \begin{pmatrix} j_k & j_\ell & j_m \\ m_k & m_\ell & m_m \end{pmatrix}$$

for (k, ℓ, m), an odd permutation of (1, 2, 3):

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

Since $\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = 0$ unless $m_i = -(m_j + m_k)$, where (i, j, k)

= (1, 2, 3) in any order, we can simplify (3.4-24) to

$$
\begin{aligned}
\mathcal{R}_q^{(M)} = {} & (-1)^{q+1} (C_{zz}^{(J)} - \Delta C)\, J_{-q} - (\Delta C - \tfrac{1}{2}\delta C) \sum_{q'=-1}^{1} J_{q'} \sum_{\ell=0}^{2} \sum_{q''=-\ell}^{\ell} (2\ell+1) \\
& \times \begin{pmatrix} 1 & 1 & \ell \\ 0 & 0 & 0 \end{pmatrix} \mathcal{D}_{0q''}^{(\ell)}(\Omega) \begin{pmatrix} 1 & 1 & \ell \\ q & q' & q'' \end{pmatrix} \\
& - \tfrac{1}{2}\delta C \sum_{q'=-1}^{1} J_{q'} \sum_{\ell=0}^{2} \sum_{q''=-\ell}^{\ell} \sum_{p=-1}^{1} (2\ell+1) \begin{pmatrix} 1 & 1 & \ell \\ p & p & -2p \end{pmatrix} \mathcal{D}_{-2p,q''}^{(\ell)}(\Omega) \begin{pmatrix} 1 & 1 & \ell \\ q & q' & q'' \end{pmatrix} \\
& - D_\alpha^{(j)} \sum_{q'=-1}^{1} j_{q'} \sum_{\ell=0}^{2} \sum_{q''=-\ell}^{\ell} (2\ell+1) \begin{pmatrix} 1 & 1 & \ell \\ 0 & 0 & 0 \end{pmatrix} \mathcal{D}_{0q''}^{(\ell)}(\Omega) \begin{pmatrix} 1 & 1 & \ell \\ q & q' & q'' \end{pmatrix} \quad .
\end{aligned}
\tag{3.4-26}
$$

By making use of the values of the 3-j symbols tabulated by Rotenberg et al.[30] (3.4-26) can be further simplified to

$$
\begin{aligned}
\mathcal{R}_q^{(M)} = {} & (-1)^{q+1} (C_{zz}^{(J)} - \Delta C)\, J_{-q} + (1/3)^{\frac{1}{2}} \Delta C \sum_{q'=-1}^{1} J_{q'} \begin{pmatrix} 1 & 1 & 0 \\ q & q' & 0 \end{pmatrix} \\
& - (10/3)^{\frac{1}{2}} \Delta C \sum_{q'=-1}^{1} J_{q'} \sum_{q''=-2}^{2} \mathcal{D}_{0q''}^{(2)}(\Omega) \begin{pmatrix} 1 & 1 & 2 \\ q & q' & q'' \end{pmatrix} \\
& - (5)^{\frac{1}{2}}/2\, \delta C \sum_{q'=-1}^{1} J_{q'} \sum_{q''=-2}^{2} \{\mathcal{D}_{2q''}^{(2)}(\Omega) + \mathcal{D}_{-2q''}^{(2)}(\Omega)\} \begin{pmatrix} 1 & 1 & 2 \\ q & q' & q'' \end{pmatrix} \\
& + (1/3)^{\frac{1}{2}} D_\alpha^{(j)} \sum_{q'=-1}^{1} j_{q'} \begin{pmatrix} 1 & 1 & 0 \\ q & q' & 0 \end{pmatrix} \\
& - (10/3)^{\frac{1}{2}} D_\alpha^{(j)} \sum_{q'=-1}^{1} j_{q'} \sum_{q''=-2}^{2} \mathcal{D}_{0q''}^{(2)}(\Omega) \begin{pmatrix} 1 & 1 & 2 \\ q & q' & q'' \end{pmatrix} \quad .
\end{aligned}
\tag{3.4-27}
$$

Since

$$
\begin{pmatrix} 1 & 1 & 0 \\ q & q' & 0 \end{pmatrix} = (-1)^{q+1} \; (1/3)^{\frac{1}{2}} \; \delta_{q_1 -q'} \quad . \tag{3.4-28}
$$

we finally obtain

$$\begin{aligned}\mathcal{R}_q^{(M)} &= (-1)^{q+1}\, C\, J_{-q} - (10/3)^{\frac{1}{2}}\, \Delta C \sum_{q'=-1}^{1} J_{q'} \sum_{q''=-2}^{2} \mathcal{D}^{(2)}_{0q''}(\Omega) \begin{pmatrix} 1 & 1 & 2 \\ q & q' & q'' \end{pmatrix} \\ &\quad - (5/4)^{\frac{1}{2}}\, \delta C \sum_{q'=-1}^{1} J_{q'} \sum_{q''=-2}^{2} \{\mathcal{D}^{(2)}_{2q''}(\Omega) + \mathcal{D}^{(2)}_{-2q''}(\Omega)\} \begin{pmatrix} 1 & 1 & 2 \\ q & q' & q'' \end{pmatrix} \\ &\quad + (1/3)(-1)^{q+1}\, D_\alpha^{(j)}\, j_{-q} - (10/3)^{\frac{1}{2}}\, D_\alpha^{(j)} \sum_{q'=-1}^{1} j_{q'} \sum_{q''=-2}^{2} \mathcal{D}^{(2)}_{0q''}(\Omega) \begin{pmatrix} 1 & 1 & 2 \\ q & q' & q'' \end{pmatrix}\end{aligned} \tag{3.4-29}$$

Since the inverses of relaxation times can be expressed in terms of the Fourier transforms of correlation functions of either $\mathcal{R}_q^{(K)}$ or $\mathcal{R}_q^{(M)}$, we concern ourselves here with a correlation matrix of the form

$$\underset{\sim}{G}(\tau) \equiv \| \langle \mathcal{R}_{q'}(t+\tau)\, \mathcal{R}_q(t) \rangle \| \quad . \tag{3.4-30}$$

In evaluating the matrix elements of $\underset{\sim}{G}(\tau)$ either $\mathcal{R}_q^{(K)}$ or $\mathcal{R}_q^{(M)}$ may be used. However, in the body-fixed frame it is easier to treat $\mathcal{R}_q^{(K)}$, and therefore we consider $\mathcal{R}_q^{(K)}$ first.

Using the expression (3.4-24), we may write

$$\begin{aligned}&\langle \mathcal{R}_{q'}^{(K)}(t+\tau)\, \mathcal{R}_q^{(K)}(t) \rangle \\ &\quad = \sum_K \sum_{K'} \{(-1)^{K'+1} C - (2/3)\, \Delta C\, (1/2)^{|K'|}\} \{(-1)^{K+1} C - (2/3)\, \Delta C\, (1/2)^{|K|}\} \\ &\qquad \times \langle [\mathcal{D}^{(1)*}_{q'K'}(\Omega)\, J_{-K'}]_{t+\tau}\, [\mathcal{D}^{(1)*}_{qK}(\Omega)\, J_{-K}]_t \rangle \\ &\quad - \tfrac{1}{2}\, \delta C \sum_{K'} \sum_{K} |K|\, \{(-1)^{K'+1} C - (2/3)\, \Delta C\, (1/2)^{|K'|}\} \\ &\qquad \times \langle [\mathcal{D}^{(1)*}_{q'K'}(\Omega)\, J_{-K'}]_{t+\tau}\, [\mathcal{D}^{(1)*}_{qK}(\Omega)\, J_K]_t \rangle\end{aligned}$$

$$
\begin{aligned}
&- \tfrac{1}{2}\,\delta C \sum_{K'}\sum_{K} |K'|\, \{(-1)^{K+1}\, C - (2/3)\,\Delta C\,(1/2)^{|K|}\} \\
&\qquad \times \langle [\mathcal{D}^{(1)}_{q'K'}{}^{*}(\Omega)\, J_{K'}]_{t+\tau}\, [\mathcal{D}^{(1)}_{qK}{}^{*}(\Omega)\, J_{-K}]_{t} \rangle \\
&+ \tfrac{1}{4}\,(\delta C)^{2} \sum_{K}\sum_{K'} |K'|\cdot|K|\, \langle [\mathcal{D}^{(1)}_{q'K'}{}^{*}(\Omega)\, J_{K'}]_{t+\tau}\, [\mathcal{D}^{(1)}_{qK}{}^{*}(\Omega)\, J_{K}]_{t} \rangle \\
&- D^{(j)}_{\alpha} \sum_{K'} \{(-1)^{K'+1}\, C - (2/3)\,\Delta C\,(1/2)^{|K'|}\} \\
&\qquad \times \langle [\mathcal{D}^{(1)}_{q'K'}{}^{*}(\Omega)\, J_{-K'}]_{t+\tau}\, [\mathcal{D}^{(1)}_{q0}{}^{*}(\Omega)\, j_{0}]_{t} \rangle \\
&- D^{(j)}_{\alpha} \sum_{K} \{(-1)^{K+1}\, C - (2/3)\,\Delta C\,(1/2)^{|K|}\} \\
&\qquad \times \langle [\mathcal{D}^{(1)}_{q'0}{}^{*}(\Omega)\, j_{0}]_{t+\tau}\, [\mathcal{D}^{(1)}_{qK}{}^{*}(\Omega)\, J_{-K}]_{t} \rangle \\
&+ \tfrac{1}{2}\, D^{(j)}_{\alpha}\, \delta C \sum_{K'} |K'|\, \langle [\mathcal{D}^{(1)}_{q'K'}{}^{*}(\Omega)\, J_{K'}]_{t+\tau}\, [\mathcal{D}^{(1)}_{q0}{}^{*}(\Omega)\, j_{0}]_{t} \rangle \\
&+ \tfrac{1}{2}\, D^{(j)}_{\alpha}\, \delta C \sum_{K} |K|\, \langle [\mathcal{D}^{(1)}_{q'0}{}^{*}(\Omega)\, j_{0}]_{t+\tau}\, [\mathcal{D}^{(1)}_{qK}{}^{*}(\Omega)\, J_{K}]_{t} \rangle \\
&+ D^{(j)^{2}}_{\alpha}\, \langle [\mathcal{D}^{(1)}_{q'0}{}^{*}(\Omega)\, j_{0}]_{t+\tau}\, [\mathcal{D}^{(1)}_{q0}{}^{*}(\Omega)\, j_{0}]_{t} \rangle \quad . \qquad\qquad (3.4\text{-}31)
\end{aligned}
$$

We assume that molecular motions in liquids are such that the following separability approximations are valid:

$$
\begin{aligned}
&\langle [\mathcal{D}^{(1)}_{q'k'}{}^{*}(\Omega)\, J_{K'}]_{t+\tau}\, [\mathcal{D}^{(1)}_{qK}{}^{*}(\Omega)\, J_{K}]_{t} \rangle \\
&\qquad \approx \langle [\mathcal{D}^{(1)}_{q'K'}{}^{*}(\Omega)]_{t+\tau}\, [\mathcal{D}^{(1)}_{qK}{}^{*}(\Omega)]_{t} \rangle\, \langle [J_{K'}]_{t+\tau}\, [J_{K}]_{t} \rangle \quad , \\
&\langle [\mathcal{D}^{(1)}_{q'K'}{}^{*}(\Omega)\, J_{K'}]_{t+\tau}\, [\mathcal{D}_{q0}{}^{*}(\Omega)\, j_{0}]_{t} \rangle \\
&\qquad \approx \langle [\mathcal{D}^{(1)}_{q'K'}{}^{*}(\Omega)_{t+\tau}\, [\mathcal{D}_{q0}{}^{*}(\Omega)]_{t} \rangle\, \langle [J_{K'}]_{t+\tau}\, [j_{0}]_{t} \rangle \quad , \\
&\langle [\mathcal{D}^{(1)}_{q0}{}^{*}(\Omega)\, j_{0}]_{t+\tau}\, [\mathcal{D}^{(1)}_{q'K'}{}^{*}(\Omega)\, J_{K'}]_{t} \rangle \\
&\qquad \approx \langle [\mathcal{D}^{(1)}_{q0}{}^{*}(\Omega)]_{t+\tau}\, [\mathcal{D}^{(1)}_{q'K'}{}^{*}(\Omega)]_{t} \rangle\, \langle [j_{0}]_{t+\tau}\, [J_{K'}]_{t} \rangle \quad ,
\end{aligned}
$$

and

$$\langle [\mathscr{D}^{(1)}_{q'K'}{}^{*}(\Omega)\, j_{K'}]_{t+\tau}\; [\mathscr{D}^{(1)}_{qK}{}^{*}(\Omega)\, j_K]_t \rangle$$

$$\approx \langle [\mathscr{D}^{(1)}_{q'K'}{}^{*}(\Omega)]_{t+\tau}\; [\mathscr{D}^{(1)}_{qK}{}^{*}(\Omega)]_t \rangle \cdot \langle [j_{K'}]_{t+\tau} [j_K]_t \rangle \quad . \tag{3.4-32}$$

Then, with the aid of these separability approximations and the fact that $\langle [\mathscr{D}^{(j)}_{q'K'}{}^{*}(\Omega)]_{t+\tau}\, [\mathscr{D}^{(j)}_{qK}{}^{*}(\Omega)]_t \rangle$ vanishes unless $K' = -K$, Eq. (3.4-31) can be simplified to

$$\begin{aligned}
&\langle \mathcal{R}^{(K)}_{q'}(t+\tau)\, \mathcal{R}^{(K)}_{q}(t) \rangle \\
&= \sum_K \{(-1)^{K+1}\, C - (2/3)\, \Delta C\, (1/2)^{|K|}\}^2 \\
&\quad \times \langle [\mathscr{D}^{(1)}_{q',-K}{}^{*}(\Omega)]_{t+\tau}\, [\mathscr{D}^{(1)}_{qK}{}^{*}(\Omega)]_t \rangle\, \langle [J_K]_{t+\tau} [J_{-K}]_t \rangle \\
&\quad - \tfrac{1}{2}\, \delta C \sum_K |K|\, \{(-1)^{K+1}\, C - (2/3)\, \Delta C\, (1/2)^{|K|}\} \\
&\quad \times \langle [\mathscr{D}^{(1)}_{q',-K}{}^{*}(\Omega)]_{t+\tau}\, [\mathscr{D}^{(1)}_{qK}{}^{*}(\Omega)]_t \rangle\, \langle [J_K]_{t+\tau} [J_K]_t + [J_{-K}]_{t+\tau} [J_{-K}]_t \rangle \\
&\quad + \tfrac{1}{4}\, (\delta C)^2 \sum_K |K^2|\, \langle [\mathscr{D}^{(1)}_{q'-K}{}^{*}(\Omega)]_{t+\tau}\, [\mathscr{D}^{(1)}_{qK}{}^{*}(\Omega)]_t \rangle\, \langle [J_{-K}]_{t+\tau} [J_K]_t \rangle \\
&\quad + D^{(j)}_{\alpha}\, (C + \tfrac{2}{3}\, \Delta C) \langle [\mathscr{D}^{(1)}_{q'0}{}^{*}(\Omega)]_{t+\tau}\, [\mathscr{D}^{(1)}_{q0}{}^{*}(\Omega)]_t \rangle\, \langle [J_0]_{t+\tau} [j_0]_t + [j_0]_{t+\tau} [J_0]_t \rangle \\
&\quad + D^{(j)^2}_{\alpha}\, \langle [\mathscr{D}^{(1)}_{q0}{}^{*}(\Omega)]_{t+\tau}\, [\mathscr{D}^{(1)}_{q0}{}^{*}(\Omega)]_t \rangle\, \langle [j_0]_{t+\tau} [j_0]_t \rangle \quad .
\end{aligned} \tag{3.4-33}$$

For convenience let us define

$$f^{(1)}_{\ell k}(\tau) = \langle J_\ell(t+\tau)\, J_k(t) \rangle \quad ,$$

$$f^{(2)}_{\ell k}(\tau) = \langle J_\ell(t+\tau)\, j_k(t) \rangle \quad ,$$

$$f^{(3)}_{\ell k}(\tau) = \langle j_\ell(t+\tau)\, J_k(t) \rangle \quad , \qquad \text{and}$$

$$f^{(4)}_{\ell k}(\tau) = \langle j_\ell(t+\tau)\, j_k(t) \rangle \quad . \tag{3.4-34}$$

From (3.4-33), (3.4-34), and the relation

$$\langle [\mathcal{D}^{(j)}_{ik}(\Omega)]_{t+\tau}\, [\mathcal{D}^{(j)}_{\ell m}(\Omega)]_{t} \rangle = (-1)^{-k-\ell}\, \delta_{-k,\, m}\, \frac{1}{2j+1}\, I^{(j)}_{i,\, -\ell}(\tau) \;, \qquad (3.4\text{-}35)$$

where

$$I^{(j)}_{ik}(\tau) = \int \mathcal{D}^{(j)}_{ik}(\Omega')\, P(\Omega', 0; \tau)\, d^3\Omega' \quad , \qquad (3.4\text{-}36)$$

$$\begin{aligned}
&\langle \mathcal{R}^{(K)}_{q}(t+\tau)\, \mathcal{R}^{(K)}_{q}(t) \rangle \\
&= \frac{1}{3} \sum_{K} (-1)^{K+q} \{(-1)^{K+1}\, C - (2/3)\, \Delta C\, (1/2)^{|K|}\}^{2}\, I^{(1)}_{q',\, -q}(\tau)\, f^{(1)}_{K,\, -K}(\tau) \\
&- \frac{1}{3}\, \delta C \sum_{K} (-1)^{K+q}\, |K|\, \{(-1)^{K+1}\, C - (2/3)\, \Delta C\, (1/2)^{|K|}\}\, I^{(1)}_{q',\, -q}(\tau)\, f^{(1)}_{K,\, K}(\tau) \\
&+ \frac{1}{12} (\delta C)^{2} \sum_{K} (-1)^{K+q}\, |K^{2}|\, I^{(1)}_{q',\, -q}(\tau) \cdot f^{(1)}_{K,\, K}(\tau) \\
&+ \frac{1}{3}\, D^{(j)}_{\alpha}\, (C + \tfrac{2}{3}\, \Delta C)\, (-1)^{q}\, I^{(1)}_{q',\, -q}(\tau)\, \{f^{(2)}_{0,\, 0}(\tau) + f^{(3)}_{0,\, 0}(\tau)\} \\
&+ \frac{1}{3}\, D^{(j)^{2}}_{\alpha}\, (-1)^{q}\, I^{(1)}_{q',\, -q}(\tau)\, f^{(4)}_{0,\, 0}(\tau) \quad . \qquad (3.4\text{-}37)
\end{aligned}$$

In addition we introduce a new component of angular momentum defined by

$$\mathcal{J}_{z} = J_{z} + \frac{D^{(j)}_{\alpha}}{C^{(J)}_{zz}}\, j \quad , \qquad (3.4\text{-}38)$$

in terms of which we may obtain

$$\begin{aligned}
&\langle \mathcal{R}^{(K)}_{q'}(t+\tau)\, \mathcal{R}^{(K)}_{q}(t) \rangle \\
&= \tfrac{1}{3}\, (-1)^{q}\, I^{(1)}_{q',\, -q}(\tau)\, \{C^{(J)^{2}}_{xx}\, \langle J_{x}(t+\tau)\, J_{x}(t) \rangle \\
&+ C^{(J)^{2}}_{yy}\, \langle J_{y}(t+\tau)\, J_{y}(t) \rangle + C^{(J)^{2}}_{zz}\, \langle \mathcal{J}_{z}(t+\tau)\, \mathcal{J}_{z}(t) \rangle\} \quad , \qquad (3.4\text{-}39)
\end{aligned}$$

where we have assumed that the cross correlations among three different components, J_x, J_y, and $\mathcal{J}_z$ are negligible. Thus, in the extreme narrowing limit we have

$$\begin{aligned}\frac{1}{T_1} &= \frac{1}{3} C_{xx}^{(J)^2} \langle J_x^2 \rangle \left(\tau^{(1)}_{1, J_x} + \tau^{(1)}_{-1, J_x} \right) \\ &+ \frac{1}{3} C_{yy}^{(J)^2} \langle J_y^2 \rangle \left(\tau^{(1)}_{1, J_y} + \tau^{(1)}_{-1, J_y} \right) \\ &+ \frac{1}{3} C_{zz}^{(J)^2} \langle \mathcal{J}_z^2 \rangle \left(\tau^{(1)}_{1, \mathcal{J}_z} + \tau^{(1)}_{-1, \mathcal{J}_z} \right) \qquad (3.4\text{-}40)\end{aligned}$$

and

$$\begin{aligned}\frac{1}{T_2} &= \frac{1}{6} C_{xx}^{(J)^2} \langle J_x^2 \rangle \left(2\tau^{(1)}_{0, J_x} + \tau^{(1)}_{1, J_x} + \tau^{(1)}_{-1, J_x} \right) \\ &+ \frac{1}{6} C_{yy}^{(J)^2} \langle J_y^2 \rangle \left(2\tau^{(1)}_{0, J_y} + \tau^{(1)}_{1, J_y} + \tau^{(1)}_{-1, J_y} \right) \\ &+ \frac{1}{6} C_{zz}^{(J)^2} \langle \mathcal{J}_z^2 \rangle \left(2\tau^{(1)}_{0, \mathcal{J}_z} + \tau^{(1)}_{1, \mathcal{J}_z} + \tau^{(1)}_{-1, \mathcal{J}_z} \right) , \qquad (3.4\text{-}41)\end{aligned}$$

where τ_{J_x}, τ_{J_y}, and $\tau_{\mathcal{J}_z}$ are the correlation times for the autocorrelation functions of J_x, J_y, and $\mathcal{J}_z$, respectively, and

$$\tau_{1,1}^{-1} = D_x + D_z , \quad \tau_{1,-1}^{-1} = D_y + D_z , \quad \tau_{1,0}^{-1} = D_x + D_y ,$$

$$\tau^{(1)\,-1}_{n, J_x} = \tau_{1,n}^{-1} + \tau_{J_x}^{-1} , \quad \tau^{(1)\,-1}_{n, J_y} = \tau_{1,n}^{-1} + \tau_{J_y}^{-1} ,$$

$$\tau^{(1)\,-1}_{n, \mathcal{J}_z} = \tau_{1,n}^{-1} + \tau_{\mathcal{J}_z}^{-1} , \quad \text{etc.}$$

Since (3.4-40) and (3.4-41) have been derived in the limit that the separability approximations (3.4-32) are valid, we can further approximate (3.4-40) and (3.4-41) to

$$\frac{1}{T_1} \approx \frac{1}{T_2} \approx \tfrac{2}{3}\, C_{xx}^{(J)^2} \langle J_x^2 \rangle\, \tau_{J_x} + \tfrac{2}{3}\, C_{yy}^{(J)^2} \langle J_y^2 \rangle\, \tau_{J_y} + \tfrac{2}{3}\, C_{zz}^{(J)^2} \langle \mathcal{J}_z^2 \rangle\, \tau_{\mathcal{J}_z} \quad , \tag{3.4-42}$$

In Chapter IV we will show how we obtain τ_{J_x}, τ_{J_y}, τ_{J_z}, and other relevant correlation times in terms of macroscopic quantities like the viscosity of medium using the theory of rotational Brownian motion.[31-34]

Using the definition of C_α previously introduced by Dubin and Chan[35] and noting that for a molecule like benzotrifluoride $C_\alpha \cong (I_z/I_\alpha) C_{zz}^{(J)}$, we may write

$$\mathcal{J}_z = (I_z/I_\alpha) j_\alpha = J_z + \frac{I_z - I_\alpha}{I_\alpha}\, j \quad . \tag{3.4-43}$$

Substitution of the relation (3.4-43) into (3.4-42) gives us

$$\frac{1}{T_1} \approx \frac{1}{T_2} \approx \tfrac{2}{3}\, C_{xx}^{(J)^2} \langle J_x^2 \rangle\, \tau_{J_x} + \tfrac{2}{3}\, C_{yy}^{(J)^2} \langle J_y^2 \rangle\, \tau_{J_y} + \tfrac{2}{3}\, C_\alpha^2 \langle j_\alpha^2 \rangle\, \tau_{j_\alpha} \quad . \tag{3.4-44}$$

Considering the fact that in benzotrifluoride $C_\alpha^2 \gg C_{xx}^{(J)^2}, C_{yy}^{(J)^2}$, the formula (3.4-44) coincides with the formula (2.7-28) originally derived by Dubin and Chan. Though the formula (3.4-44) is formally correct, it may not be the best form for practical purposes since τ_{j_α}

depends not only on the end-over-end molecular rotation but also on the rotation of internal rotor itself. Only when the internal rotational barrier is completely (or almost completely) zero and thus the rotation of internal rotor is not influenced by end-over-end molecular rotation about the z-axis, this formula is a useful form. In such a situation the relaxation rates are determined by the behavior of internal top alone. From now on let us express this extreme case using the terminology "j_α-limit". In the j_α-limit if the internal top rotates almost freely between two successive intermolecular collisions which change j_α in a random manner, then we can take τ_{j_α} as proportional to τ_c, the characteristic time for intermolecular collisions which deprive dynamical coherences of j_α, which in turn is known to be proportional to $(I_\alpha/kT)^{\frac{1}{2}}$. If the change of j_α occurs mainly because of frictional forces due to neighboring molecules, we may take τ_{j_α} as inversely proportional to the viscosity of medium.

However, it is supposed that in actual molecular systems such a situation is very rare since the internal barrier is seldom zero (though low in some molecules) and thus the rotational motion of internal top is more or less related to the rotation of remaining parts of the molecule. In this situation we have to transform Eq. (3.4-44) into a new form in which correlation times have more or less direct physical meanings. In one extreme case in which the variation of j is completely controlled by the internal torque $-\nabla_\alpha V(\alpha)$ between two successive random changes due to the external torque and the end-over-end molecular rotation about the z-axis is diffusional, J_z and j are considered to te uncorrelated to each other and (3.4-42) becomes

$$\frac{1}{T_1} \approx \frac{1}{T_2} \approx \tfrac{2}{3}\, C_{xx}^{(J)^2} \langle J_x^2 \rangle\, \tau_{J_x} + \tfrac{2}{3}\, C_{yy}^{(J)^2} \langle J_y^2 \rangle\, \tau_{J_y}$$

$$+ \tfrac{2}{3}\, C_{zz}^{(J)^2} \langle J_z^2 \rangle\, \tau_{J_z} + \tfrac{2}{3}\, D_\alpha^{(j)^2} \langle j^2 \rangle\, \tau_j \quad . \tag{3.4-45}$$

("j-limit")

In the j-limit τ_j, instead of τ_{j_α}, is considered to be proportional to $(I_\alpha/kT)^{\frac{1}{2}}$, thus giving us the formula used by Burke.

Though it is not necessary here, for reference we derive $\langle \mathcal{R}_{q'}^{(M)}(t+\tau) \cdot \mathcal{R}_q^{(M)}(t) \rangle$ in the M-representation. From (3.4-29) it follows that

$$\begin{aligned}
&\langle \mathcal{R}_{q'}^{(M)}(t+\tau)\ \mathcal{R}_q^{(M)}(t) \rangle \\
&= (-1)^{q+q'}\, C^2 \langle [J_{-q'}]_{t+\tau} [J_{-q}]_t \rangle + (-1)^{q+q'}\, (1/9)\, D_\alpha^{(j)^2} \langle [j_{-q'}]_{t+\tau} [j_{-q}]_t \rangle \\
&+ (10/3)\, (\Delta C)^2 \sum_{n,n'=-1}^{1} \sum_{p,p'=-2}^{2} \begin{pmatrix} 2 & 1 & 1 \\ p & q & n \end{pmatrix} \begin{pmatrix} 2 & 1 & 1 \\ p' & q' & n' \end{pmatrix} \langle [J_{n'} \mathcal{D}_{0p'}^{(2)}(\Omega)]_{t+\tau} [J_n \mathcal{D}_{0p}^{(2)}(\Omega)]_t \rangle \\
&+ (10/3)\, D_\alpha^{(j)^2} \sum_{n,n'=-1}^{1} \sum_{p,p'=-2}^{2} \begin{pmatrix} 2 & 1 & 1 \\ p & q & n \end{pmatrix} \begin{pmatrix} 2 & 1 & 1 \\ p' & q' & n' \end{pmatrix} \langle [j_{n'}\, \mathcal{D}_{0p'}^{(2)}(\Omega)]_{t+\tau} [j_n\, \mathcal{D}_{0p}^{(2)}(\Omega)]_t \rangle \\
&+ (5/4)(\delta C)^2 \sum_{n,n'=-1}^{1} \sum_{p,p'=-2}^{2} \begin{pmatrix} 2 & 1 & 1 \\ p & q & n \end{pmatrix} \begin{pmatrix} 2 & 1 & 1 \\ p' & q' & n' \end{pmatrix} \langle [J_{n'}\, \{\mathcal{D}_{2p'}^{(2)}(\Omega) + \mathcal{D}_{-2p'}^{(2)}(\Omega)\}]_{t+\tau} \\
&\times [J_n \{\mathcal{D}_{2p}^{(2)}(\Omega) + \mathcal{D}_{-2p}^{(2)}(\Omega)\}]_t \rangle + \text{cross terms} \quad .
\end{aligned} \tag{3.4-46}$$

We assume that the separability approximations similar to (3.4-32) are also valid in the M-representation and that at any instant the orientation of a molecule is independent of its angular momentum. From these assumptions it follows that

$$\langle [J_{-q'}]_{t+\tau}\, [J_q \mathscr{D}^{(2)}_{np}(\Omega)]_t \rangle$$

$$\approx \langle [J_{-q'}]_{t+\tau}\, [J_q]_t \rangle \langle [\mathscr{D}^{(2)}_{np}(\Omega)]_t \rangle = 0 \qquad (3.4\text{-}47)$$

since $\langle [\mathscr{D}^{(2)}_{np}(\Omega)]_t \rangle = 0$.

Because of (3.4-47) and relations similar to this some cross terms in (3.4-46) are vanishing. Taking all these facts into consideration, we obtain

$$\begin{aligned}
&\langle \mathcal{R}^{(M)}_{q'}(t+\tau)\, \mathcal{R}^{(M)}_{q}(t) \rangle \\
&= (-1)^{q+q'} C^2 g^{(1)}_{-q',-q}(\tau) + (-1)^{q+q'} (1/9) D^{(j)2}_{\alpha}\, g^{(4)}_{-q',-q}(\tau) \\
&\quad + (2/3)(\Delta C)^2 I^{(2)}_{0,0}(\tau) \sum_{n,n'=-1}^{1} \sum_{p=-2}^{2} (-1)^p \begin{pmatrix} 2 & 1 & 1 \\ p & q & n \end{pmatrix} \begin{pmatrix} 2 & 1 & 1 \\ -p & q' & n' \end{pmatrix} g^{(1)}_{n',n}(\tau) \\
&\quad + (2/3)\, D^{(j)2}_{\alpha}\, I^{(2)}_{0,0}(\tau) \sum_{n,n'=-1}^{1} \sum_{p=-2}^{2} (-1)^p \begin{pmatrix} 2 & 1 & 1 \\ p & q & n \end{pmatrix} \begin{pmatrix} 2 & 1 & 1 \\ -p & q' & n' \end{pmatrix} g^{(4)}_{n',n}(\tau) \\
&\quad + (1/2)(\delta C)^2 \{ I^{(2)}_{2,2}(\tau) + I^{(2)}_{2,-2}(\tau) \} \\
&\quad \times \sum_{n,n'=-1}^{1} \sum_{p=-2}^{2} (-1)^p \begin{pmatrix} 2 & 1 & 1 \\ p & q & n \end{pmatrix} \begin{pmatrix} 2 & 1 & 1 \\ -p & q' & n' \end{pmatrix} g^{(1)}_{n',n}(\tau) \\
&\quad + (1/3)(-1)^{q+q'} C \cdot D^{(j)}_{\alpha} \{ g^{(2)}_{-q',-q}(\tau) + g^{(3)}_{-q',-q}(\tau) \} \\
&\quad + (8/3)^{\frac{1}{2}} \Delta C \cdot \delta C\, I^{(2)}_{2,0}(\tau) \sum_{n,n'=-1}^{1} \sum_{p=-2}^{2} (-1)^p \begin{pmatrix} 2 & 1 & 1 \\ p & q & n \end{pmatrix} \begin{pmatrix} 2 & 1 & 1 \\ -p & q' & n' \end{pmatrix} g^{(1)}_{n',n}(\tau) \\
&\quad + (2/3)\, \Delta C \cdot D^{(j)}_{\alpha} I^{(2)}_{0,0}(\tau) \sum_{n,n'=-1}^{1} \sum_{p=-2}^{2} (-1)^p \begin{pmatrix} 2 & 1 & 1 \\ p & q & n \end{pmatrix} \begin{pmatrix} 2 & 1 & 1 \\ -p & q' & n' \end{pmatrix} \\
&\quad \times \{ g^{(2)}_{n',n}(\tau) + g^{(3)}_{n',n}(\tau) \} \\
&\quad + (8/3)^{\frac{1}{2}} \delta C \cdot D^{(j)}_{\alpha} I^{(2)}_{2,0}(\tau) \sum_{n,n'=-1}^{1} \sum_{p=-2}^{2} (-1)^p \begin{pmatrix} 2 & 1 & 1 \\ p & q & n \end{pmatrix} \begin{pmatrix} 2 & 1 & 1 \\ -p & q' & n' \end{pmatrix} \\
&\quad \times \{ g^{(2)}_{n',n}(\tau) + g^{(3)}_{n',n}(\tau) \} \quad , \qquad (3.4\text{-}48)
\end{aligned}$$

where we have used the relation (3.4-35) and $g^{(n)}_{p,q}(\tau)$'s have been defined as

$$g^{(1)}_{p,q}(\tau) = \langle J_p(t+\tau)\, J_q(t)\rangle \ , \quad g^{(2)}_{p,q}(\tau) = \langle J_p(t+\tau)\, j_q(t)\rangle \ ,$$

$$g^{(3)}_{p,q}(\tau) = \langle j_p(t+\tau)\, J_q(t)\rangle \ , \quad \text{and}$$

$$g^{(4)}_{p,q}(\tau) = \langle j_p(t+\tau)\, j_q(t)\rangle \tag{3.4-49}$$

in the M-representation.

When the angular momentum correlation functions are more easily obtainable in the M-representation than in the K-representation, Eq. (3.4-48) will serve better than Eq. (3.4-37) in obtaining the relaxation time formulas. Hubbard[26] has used M-representation for derivation of the relaxation time formula for spherical molecules. In fact if we let $C = \frac{1}{3}(C_{//} + 2C_{\perp})$, $\Delta C = C_{//} - C_{\perp}$, $\delta C = 0$, and $D^{(j)}_{\alpha} = 0$, Eq. (3.4-49) reduces to the case which Hubbard has already treated. However, when a molecule is not spherical, the angular momentum correlation functions can be more conveniently evaluated in the K-representation and therefore in this situation (3.4-37) is more desirable for our purpose than (3.4-49).

3.5 Conclusion

We have discussed the spin relaxation phenomenon both via dipole-dipole and spin-rotation interaction in the presence of internal rotation. In the presence of internal rotation we see that the relative importance of intramolecular dipole-dipole relaxation decreases compared to that of intermolecular dipole-dipole relaxation. On the other hand, when it comes to the spin-rotational relaxation, the presence of internal rotation gives an additional contribution through the spin-internal-rotation interaction. We have derived the formulas for spin-rotational relaxation times in the presence of internal rotation in the K-representation, and confirmed that these formulas are reduced to those derived by Hubbard in case the entire molecule is spherical and there is no internal rotation. In order to obtain an explicit form of T_1 we have considered two extreme cases, j_α-limit and j-limit. In the j_α-limit the fluctuation of j_α is supposed to depend only on the motion of internal top and thus relaxation times are determined by the rotational motion of internal top alone--independent of the motion of other parts of the molecule. On the other hand, in the j-limit the relative motion of internal top with respect to the molecule fixed frame is completely controlled by internal rotational barrier and thus the relaxation time depends on the correlation time of j rather than j_α. For reference we have also given the derivation of T_1 and T_2 in the M-representation.

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CHAPTER IV

DYNAMICS OF MOLECULAR ROTATIONS IN CONDENSED PHASES

4.1 Introduction

In order to elucidate molecular motions in a wide variety of physical systems several experimental methods have been applied. The absorption of radio frequency, microwave, infrared, and ultrasonic waves, Raman scattering and fluorescent scattering of light, magnetic and microwave resonance, and double resonance experiments are all yielding new and more detailed information on the dynamics of molecular collisions.[1] When information of this sort has been fully interpreted, we will understand a great deal about the shape or angle dependence of intermolecular forces. The traditional sources of information about intermolecular forces, such as viscosity and virial coefficients, are largely insensitive to the angle dependence of intermolecular forces. In contrast to this, many of the spectroscopic effects, such as pressure broadening and narrowing of rotational lines, occur because of intermolecular torques, and would vanish for spherical intermolecular forces. Therefore, spectroscopic methods are most valuable in probing the nonspherical shape of intermolecular forces--especially for dilute gases.

The interpretation of these experiments requires us to express the basic macroscopic quantity being measured as an explicit function of the microscopic molecular motion. Time-dependent correlation functions provide the most convenient mathematical form in which to express these relations. Then these correlation functions should be calculated for the molecular motion. Unfortunately, no exact method of evaluating these correlation functions is known, since we have not yet been able to find exact solutions to the quantum equations of motion for an N-particle system. Therefore, numerous approximate methods have been used[2, 3, 4] to evaluate correlation functions of some molecular properties. Recently the correlation functions of permanent electric dipole in carbon monoxide molecules[1] and the correlation functions of anisotropy of polarizability tensor of N_2 and liquid CH_4[5] have been evaluated from the vibration-rotation bands of infrared spectra and the Raman spectra, respectively. The observed time dependence differs substantially from the simple exponential form usually assumed in nuclear resonance problems. Usually the phenomenological interpretation of several experiments for the molecular rotational study has been based almost universally on a diffusion equation. When the molecular reorientation takes place through small angular steps, a rotational diffusion equation should be a reasonable basis for the discussion of such experiments. Solutions to rotational diffusion equations were given by Debye[6] and Furry[7] for spherical molecules and by Perrin[8] and Favro[9] for nonspherical molecules. Gordon[1, 10] has argued that while the rotational diffusion model appears plausible when applied to large molecules in liquids, the assumption of small angular steps is not obviously applicable to small molecules. He has eliminated the assumption of small-angle diffusion and has proposed a generalized model of rotational diffusion process. His model has given a reasonable interpretation of the correlation function of electric dipole moment in CO experimentally determined from infrared spectra. Independently of this Shimizu[11] has approached the problem of molecular reorientation from two limiting cases--the Debye limit and the inertial limit. In the Debye limit molecules are assumed to be immersed in a continuous homogeneous medium which gives a negative torque to the rotation of the molecules through a contact friction between the medium and the surface of molecules. Because of this torque molecules are supposed to rotate by very small angle at one time. On the other hand, in the inertial limit all molecules are supposed to rotate with relatively definite angular momenta between intermolecular collisions. Therefore, in the Debye limit, molecular states are well characterized in terms of the molecular orientations with respect to a space fixed coordinate system, while the angular momenta must be used in the inertial limit. Shimizu has discussed the molecular reorientational process in both limits and expressed the correlation functions for intermediate cases as a linear combination of correlation functions for two limiting cases. However, time-dependence of coefficients in this linear combination should be studied and theorized in a more detailed and systematic manner. As for large molecules like benzotrifluoride we simply presume that the assumption of small-angle diffusion is valid in their liquid state so that the Perrin-Favro rotational diffusion equation is applicable. Correlation functions involving the molecular orientation alone can be calculated by making use of this equation as we shall see later. Now, what about the correlation functions involving angular momenta or both angular momenta and molecular orientation?

An intuitive idea that comes into our attention is that we may be able to apply a Langevin-type equation[12, 13] to the molecular reorientation process. However, there are some troubles we encounter if we try to apply the translational Brownian motion theory to the rotational case. In the translational case the velocity $\vec{v}$ of a particle is the derivative with respect to time of its position. However, the angular velocity (or momentum) of a molecule, $\vec{\omega}$ (or $\vec{J}$), is not the derivative of a vector that can be used to specify the orientation of the molecule, as is well known.[14] For the convenience of discussion let us define conditional probability densities as follows:

$W(\vec{v}, \vec{r}, t; \vec{v}_0, \vec{r}_0, t_0)$ = probability density that a particle has velocity $\vec{v}$ and position $\vec{r}$ at time t if it has velocity $\vec{v}_0$ and position $\vec{r}_0$ at time t_0 , (4.1-1)

and

$W(\vec{J}, \vec{\Omega}, t; \vec{J}_0, \vec{\Omega}_0, t_0)$ = probability that a particle has angular momentum $\vec{J}$ and orientation $\vec{\Omega}$ at time t if it has angular momentum $\vec{J}_0$ and orientation $\vec{\Omega}_0$ at time t_0 . (4.1-2)

In the case of translational Brownian motion it has been shown that $W(\vec{v}, \vec{r}, t; \vec{v}_0, \vec{r}_0, t_0)$ can be obtained from the Fokker-Planck equation with the aid of the Langevin equation.[12, 13] However, in the rotational case it is not possible to obtain $W(\vec{J}, \vec{\Omega}, t; \vec{J}_0 , \vec{\Omega}_0, t_0)$ in a similar manner, since as we have already mentioned $\vec{\Omega}$ is not related to $\vec{J}$ as $\vec{r}$ does to $\vec{v}$. As we have seen in Chapter III, by adopting the separability approximation which requires

$$W(\vec{J}, \vec{\Omega}, t; \vec{J}_0, \vec{\Omega}_0, t_0) = W(\vec{J}, t; \vec{J}_0, t_0)\, W(\vec{\Omega}, t; \vec{\Omega}_0, t_0) \tag{4.1-3}$$

we can get out of dilemma, where $W(\vec{J}, t; \vec{J}_0, t_0)$ and $W(\vec{\Omega}, t; \vec{\Omega}_0, t_0)$ are the conditional probabilities corresponding to the change of $\vec{J}$ and $\vec{\Omega}$, respectively. In fact, Hubbard[14] and Atkins[15] have used the separability approximation to evaluate terms like (3.4-42). The validity of this approximation is assured if the correlation time for the change of angular momentum is much different from that for the orientational change, that is, $\tau_J \ll \tau_\Omega$ or $\tau_J \gg \tau_\Omega$. In the limit of small-angle diffusion (Debye limit) τ_J is much shorter than τ_Ω. In many molecules it is known that τ_J is of the order of 10^{-14} sec while τ_Ω is of the order of 10^{-12} sec in their liquid states far below critical temperature. As temperature rises, molecules rotate more and more freely so that τ_J increases. On the other hand if the angular momentum is maintained for a longer time, then the molecular orientation changes in a shorter time, i.e., τ_Ω decreases. Hubbard[14] showed that τ_J and τ_Ω are related to each other by the relation

$$\tau_J \tau_\Omega = \frac{I}{6kT} \tag{4.1-4}$$

for a spherical molecule, where I is the moment of inertia of the molecule. The relation (4.1-4) is valid only under the condition $\tau_J \ll \tau_\Omega$, and its validity is doubtful if the condition $\tau_J \ll \tau_\Omega$ fails. Actually as the critical temperature is approached, τ_J and τ_Ω become comparable so that the relation (4.1-4) is no longer valid. In this situation molecular reorientation processes deviate appreciably from the character of Brownian motion, and the Langevin-type equation no longer works. For the case of dilute hydrogen gas Bloom and Oppenheim[16-19] has developed a detailed theory and expressed τ_J and τ_Ω in terms of intermolecular forces. No theory so far has been proposed to evaluate the correlation functions involving angular momentum or molecular orientation or both in the region where the condition $\tau_J \ll \tau_\Omega$ or $\tau_J \gg \tau_\Omega$ fails, and this question will still remain formidable even in the future. In this chapter we restrict ourselves to the case where the condition $\tau_J \ll \tau_\Omega$ is valid so that the Brownian motion theory can be applied to the molecular reorientational process in the liquid state. One more important thing we have to note here is that for molecules like φ-CF_3 molecular reorientational process is no longer isotropic. In this case we cannot use the isotropic Langevin equation to evaluate the angular momentum correlation functions since a molecule suffers anisotropic frictional torque when it rotates. In this chapter we generalize and extend the Langevin equation of motion so that we can take into account not only the anisotropy of overall rotation but also the internal rotation. Recently experimental evidences of anisotropic molecular reorientational process in liquid phase have been accumulated,[20-23] and their interpretations are all based on the anisotropic rotational diffusion equation. For this reason we will review and discuss the Perrin-Favro anisotropic rotational diffusion equation of Brownian motion. Before going into further detail we review and introduce some stochastic concepts for better understanding of the problem of molecular dynamics.

4.2 Markov Process and Fokker-Planck Equation[13]

(a) Markov process.

A random process, $y(t)$, defines a variable y which does not depend in a completely definite way on the independent argument, t. The representation of the process is the set of states available to the process for each value of the independent variable (argument). Thus, the process is said to be discrete if the set of states can be put into one to one correspondence with the positive integers, and continuous if it cannot. The independent variable may also assume discrete, or continuous values. The order of a random process is a measure of its complexity. In general, the random process is completely specified by set of probability distributions: $P_1(y_1 t_1)\, dy_1$ is the probability that y is found in the range (y_1, y_1+dy_1) at time t_1, where $y_n = y(t_n)$, $P_2(y_1, t_1; y_2, t_2)\, dy_1 dy_2$ is the joint probability that y is found in the range (y_1, y_1+dy_1) at t_1 and in the range (y_2, y_2+dy_2) at t_2, $P_3(y_1, t_1; y_2 t_2; y_3 t_3)\, dy_1 dy_2 dy_3$ is the joint probability that y is found in the range (y_1, y_1+dy_1) at t_1, in (y_2, y_2+dy_2) at t_2, and in (y_3, y_3+dy_3) at t_3, and so on.

These probability distributions must satisfy the following conditions:

(a) $P_n \geq 0$,

(b) $P_n(y_1 t_1; \ldots ; y_n t_n)$ is a symmetric function of the set of variables $y_1, \ldots, y_n$, and

(c) $P_k(y_1 t_1; \ldots ; y_k t_k) = \int \ldots \int P_n(y_1, t_1; \ldots y_n t_n)\, dy_{k+1} \ldots dy_n$, since each function P_n must imply all the reduced functions $P_k (k < n)$. (4.2-1)

The process may be called a pure random, or completely random process if $P_2(y_1t_1;y_2t_2) = P_1(y_1t_1)P_1(y_2t_2)$, because the successive values of y are not correlated. Thus, in the case of a pure random process all the information about the process is contained in P_2. If all the information is contained in P_2, the process is called a Markov process. For a Markov process it is convenient to introduce the conditional probability $K_1(y_1t_1|y_2t_2)dy_2$ that y is found in the range (y_2, y_2+dy_2) at t_2, if y had the value y_1 at t_1. Accordingly one has

$$P_2(y_1t_1;y_2t_2) = P_1(y_1t_1)K_1(y_1t_1|y_2t_2) \quad . \tag{4.2-2}$$

K_1 must obviously fulfill the relations

$$\begin{aligned} &K_1(y_1t_1|y_2t_2) \geq 0 \quad , \\ &\int K_1(y_1t_1|y_2t_2)dy_2 = 1, \qquad \text{and} \\ &\int P_1(y_1t_1)\, K_1(y_1t_1|y_2t_2)dy_1 = P_1(y_2t_2) \quad . \end{aligned} \tag{4.2-3}$$

If the statistical character of the process is invariant to a change of the origin of the time or to a translation in time, that is, for example

$$\begin{aligned} &P_1(y_1t_1) = P_1(y_1) \ , \\ &P_2(y_1t_1;y_2t_2) = P_2(y_1, y_2; t_2-t_1) \quad , \end{aligned} \tag{4.2-4}$$

etc., the process may be called a stationary process.

The first moments of a Markov process are defined by

$$\langle y_1 \rangle = \iint y_1\, P_2(y_1t_1;y_2t_2)dy_1dy_2$$

and

$$\langle y_2 \rangle = \iint y_2\, P_2(y_1t_1;y_2t_2)dy_1dy_2 \quad . \tag{4.2-5}$$

If the process is stationary then by Eq. (4.2-4) $\langle y_1 \rangle = \langle y_2 \rangle$.

The second moments are

$$\mu_{jk}^{(2)} = \iint (y_1 - \langle y_1 \rangle)^j \, (y_2 - \langle y_2 \rangle)^k \, P_2(y_1 t_1 ; y_2 t_2) dy_1 dy_2$$
$$(j+k = 2) \qquad (4.2\text{-}6)$$

There are three second moments. The moments $\mu_{20}^{(2)}$ and $\mu_{02}^{(2)}$ are the mean-square deviations, and are equal if the process is stationary. The moment $\mu_{11}^{(2)}$ is related to the autocorrelation function of y, $\psi(t_1, t_2)$, by

$$\psi(t_1, t_2) = \mu_{11}^{(2)} / (\mu_{20}^{(2)} \, \mu_{02}^{(2)})^{\frac{1}{2}} \quad . \qquad (4.2\text{-}7)$$

If the process is stationary, Eq. (4.2-7) simplifies to

$$\psi(t_2 - t_1) = \frac{\mu_{11}^{(2)}}{\mu_{20}^{(2)}} = \frac{\mu_{11}^{(2)}}{\mu_{02}^{(2)}} \quad . \qquad (4.2\text{-}8)$$

Consider a special case of Eq. (4.2-1) for which n = 3, that is,

$$P_2(y_1 t_1 ; y_3 t_3) = \int P_3(y_1 t_1 ; y_2 t_2 ; y_3 t_3) dy_2 \quad . \qquad (4.2\text{-}9)$$

If y is a Markov process, then by definition we have

$$\begin{aligned} P_3(y_1 t_1 ; y_2 t_2 ; y_3 t_3) &= P_1(y_1 t_1) \, K_1(y_1 t_1 | y_2 t_2) \, K_2(y_1 t_1 ; y_2 t_2 | y_3 t_3) \\ &= P_1(y_1 t_1) \, K_1(y_1 t_1 | y_2 t_2) \, K_1(y_2 t_2 | y_3 t_3) \quad , \qquad (4.2\text{-}10) \end{aligned}$$

and substitution of this in Eq. (4.2-10), followed by cancellation of $P_1(y_1 t_1)$ from both sides, yields

$$K_1(y_1t_1|y_3t_3) = \int K_1(y_1t_1|y_2t_2)\, K_1(y_2t_2|y_3t_3)dy_2 \quad . \qquad (4.2\text{-}11)$$

Equation (4.2-11) is Markov's integral equation, sometimes referred to as the Chapman-Kolmogorov equation. If the process is stationary, Eq. (4.2-11) may then be simplified to

$$K_1(y_1|y;t) = \int K_1(y_1|y_0;t_0)\, K_1(y_0|y;t-t_0)dy_0 \quad . \qquad (4.2\text{-}12)$$

Equation (4.2-12) expresses the fact that the probability that the variable is in the state y at time t is the sum of the probabilities that it was in state y_0 at some time $t_0 (< t)$ and underwent a transition from y_0 to y in the interval $(t-t_0)$. Such a statement is, of course, true of any random process. The Markovian nature of the process is expressed in the assumed form of K_1. Then, let us consider the passage of (4.2-12) to a differential equation which governs the time variation of distribution functions.

(b) Fokker-Planck equation.

Continuous Markov processes occurring in physical systems often fall into one of two limiting cases. They may be subjected to frequent small changes or to large discontinuous changes. In the small change case a differential equation for the distribution function is obtained in the following way. We suppose that the changes in the variable occur at intervals of the order of τ_c, while the distribution function changes in times of the order of τ_r. If the changes of the variables are very small compared to typical values of the variable, and if the changes are very rapid, then we may assume that these two time scales to be widely separated; in other words we may expect that a time τ exists which satisfies the inequalities

$$\tau_c \ll \tau \ll \tau_r \quad . \tag{4.2-13}$$

With these restrictions in mind, we may write Markov integral equation for a stationary process as

$$K_1(y_1|y;t+\tau) = \int K_1(y_1|y_0;t)\, K_1(y_0|y;\tau)dy_0 \quad . \tag{4.2-14}$$

The assumption of small changes in the variable during τ may be exploited by writing $y - y_0 = \Delta y$ and changing the variable of integration in Eq. (4.2-14) to Δy. The negative sign arising in the relation between the differentials $dy_0 = -d\Delta y$ is included in an inversion of the limits, and we obtain

$$K_1(y_1|y;t+\tau) = \int K_1(y_1|y-\Delta y;t)\, \Psi(y-\Delta y|\Delta y;\tau)d\Delta y \quad , \tag{4.2-15}$$

where we have introduced the notation

$$\Psi(y-\Delta y|\Delta y;\tau) = K_1(y-\Delta y|y;\tau) \quad . \tag{4.2-16}$$

$\Psi(y-\Delta y|\Delta y;\tau)$ can be regarded as the probability that y will undergo a transition Δy in an interval τ starting from $y - \Delta y$.

$K_1(y_1|y;t+\tau)$ is now expanded in a Taylor series in powers of τ about $K_1(y_1|y;t)$; by virtue of the right-hand inequality (4.2-13) the expansion may be truncated after the second term. We also expand $K_1(y_1|y-\Delta y;t)\, \Psi(y-\Delta y|\Delta y;\tau)$ in powers of Δy about $K_1(y_1|y;t)$ $\Psi(y|\Delta y;\tau) = K_1\Psi$, and we obtain

$$K_1 + \tau \frac{\partial K_1}{\partial t} + \ldots$$

$$= \int [\, K_1\Psi - \Delta y \frac{\partial}{\partial y}(K_1\Psi) + \tfrac{1}{2}(\Delta y)^2 \frac{\partial^2}{\partial y^2}(K_1\Psi) + \ldots \,]\, d\Delta y$$

$$= K_1 - \frac{\partial}{\partial y}(K_1\langle\Delta y\rangle_1) + \tfrac{1}{2}\frac{\partial^2}{\partial y^2}(K_1\langle(\Delta y)^2\rangle_1) + \ldots \quad , \qquad (4.2\text{-}17)$$

where we have used

$$\int \Psi(y\,|\,\Delta y;\tau)\,d\Delta y = 1 \quad , \qquad (4.2\text{-}18)$$

and $\langle\cdots\rangle_1$ is the average of the enclosed variable conditional upon the given initial value of y:

$$\langle(\Delta y)^n\rangle_1 = \int (\Delta y)^n\, \Psi(y\,|\,\Delta y;\tau)\,d\Delta y \quad . \qquad (4.2\text{-}19)$$

In order that Eq. (4.2-17) be of use, τ cannot appear explicitly. The time τ will not appear in the equation when the first n moments are proportional to τ, while all other moments are proportional to τ^2 or some higher power of τ; the constant of proportionality in the preceding is of order τ_r^{-1}, so that high-order moments are at least of order $(\tau/\tau_r) \ll 1$ in relation to the first n terms. Writing,

$$\lim_{\substack{\tau\to 0\\ (\tau\gg\tau_c)}} \frac{\langle\Delta y\rangle_1}{\tau} = a^{(1)}(y)$$

and

$$\lim_{\substack{\tau\to 0\\ (\tau\gg\tau_c)}} \frac{\langle(\Delta y)^2\rangle_1}{\tau} = a^{(2)}(y), \text{ etc.} \quad , \qquad (4.2\text{-}20)$$

Eq. (4.2-17) becomes

$$\frac{\partial K_1}{\partial t} = -\frac{\partial}{\partial y}(a^{(1)}K_1) + \frac{1}{2}\frac{\partial^2}{\partial y^2}(a^{(2)}K_1) + \dots \quad . \tag{4.2-21}$$

If y has more than one component, Eq. (4.2-21) takes the form

$$\frac{\partial K_1}{\partial t} = -\vec{\nabla}_y \cdot (\vec{a}^{(1)}K_1) + \frac{1}{2}\vec{\nabla}_y\vec{\nabla}_y : (\underset{\frown}{a}^{(2)}K_1) + \dots \quad , \tag{4.2-22}$$

where $\vec{\nabla}_y$ is the gradient operator in y space, and $\vec{a}^{(1)}$, and $\underset{\frown}{a}^{(2)}$ are the first and second moments of Ψ, respectively. Equations (4.2-21) and (4.2-22) are known as the Fokker-Planck equations; their solutions are the transition probabilities K_1, but they may also be written in terms of the absolute probability $P_1(\vec{y};t)$, by using the relation

$$P_1(\vec{y};t) = \int P_1(\vec{y}_1;t_1)\, K_1(\vec{y}_1|\vec{y};t-t_1)d\vec{y}_1 \quad , \tag{4.2-23}$$

for then

$$\frac{\partial P_1}{\partial t} = -\vec{\nabla}_y \cdot (\vec{a}^{(1)}P_1) + \frac{1}{2}\vec{\nabla}_y\vec{\nabla}_y : (\underset{\frown}{a}^{(2)}P_1) \quad , \tag{4.2-24}$$

with the initial condition $P_1(y;0) = \delta(\vec{y}-\vec{y}_1)$.

If the system is not subject to external forces (or other constraints), the first moment may be assumed to vanish in many cases. For example, if Δy indicates the displacement of a Brownian particle, $\langle\Delta y\rangle_1$, the average displacement, vanishes without any external forces. Moreover, if $\langle(\Delta y\Delta y)\rangle_1$ is proportional to τ over a range of τ sufficiently large that the quotient

$$\underset{\frown}{D} = \frac{1}{2}\,\frac{\langle(\Delta\vec{y}\Delta\vec{y})\rangle_1}{\tau} \qquad (4.2\text{-}25)$$

can be said to be sensibly independent of τ, we see that Eq. (4.2-44) becomes a diffusion equation

$$\frac{\partial P_1}{\partial t} = \vec{\nabla}_y\vec{\nabla}_y : (\underset{\frown}{D}P_1) \quad . \qquad (4.2\text{-}26)$$

All the diffusion equations (translational or rotational) are nothing but a special form of Eq. (4.2-26). For example, the Perrin-Favro rotational diffusion equation which is going to be discussed in the next section can be derived from Eq. (4.2-26) by replacing $\vec{y}$ by $\vec{\Omega}(=\theta,\phi,\psi)$ where θ, ϕ, and ψ are the Euler angles which specify a body-fixed frame with respect to the stationary (or laboratory) frame.

Thus we have seen that in the small change case the differential equation (4.2-22) determines the distribution function. The opposite limiting case, in which large discontinuous changes in the variable take place, can sometimes be included in the Fokker-Planck scheme if the moments behave suitably. This is not usually the case, however. If we assume that a time interval τ_c exists, which is the time between the transitions undergone by the variable, but during which the change in $K_1(y_1|y;t)$ is small, then we can immediately write down a master equation. Since $K_1(y|y_0;\tau)$ is normalized in y_0, we have upon expanding $K_1(y_1|y;t+\tau)$ in a Taylor series about $K_1(y_1|y;t)$ to first order in τ,

$$\frac{\partial K_1}{\partial t} = \int [K_1(y_1|y_0;t)\,\Phi(y_0|y) - K_1(y_1|y;t)\,\Phi(y|y_0)]\,dy_0 \ , \qquad (4.2\text{-}27)$$

where
$$\Phi(y_0\,|y) = \lim_{\substack{\tau\to 0\\(\tau\gg\tau_c)}} \frac{1}{\tau} K_1(y_0\,|y;\tau) \tag{4.2-28}$$

is the number of transitions from $y_0 \to y$ in unit time. The normalization of $K_1(y_0|y;\tau)$ now requires

$$\int \Phi(y_0\,|y)dy = \lim_{\tau\to\tau_c} \frac{1}{\tau} = \frac{1}{\tau_c} \quad ,$$

so that the total transition rate out of y_0 is simply the inverse of the time between transitions τ_c. Multiplication of equation (4.2-27) by $P_1(y_1;t_1)$ and use of Eq. (4.2-23) leads to

$$\frac{\partial P_1(y;t)}{\partial t} = \int [P_1(y_0;t)\,\Phi(y_0\,|y) - P_1(y;t)\,\Phi(y\,|y_0)]\,dy_0 \ . \tag{4.2-29}$$

In developing Eqs. (4.2-23) and (4.2-29) the conjectured characteristics of the two processe imposed conditions on the transition probability $\Psi(y\,|\Delta y;\tau)$ and transition rate $\Phi(y_0\,|y)$, respectively. Thus, $\Psi(y\,|\Delta y;\tau)$ is assumed to be sharply peaked about $\Delta y = 0$, and to be negligibly small for values of Δy comparable with $\langle y\rangle$ (or with $\langle y^2\rangle^{\frac{1}{2}}$ if $\langle y\rangle = 0$), while $\Phi(y_0\,|y)$ is not sharply peaked but is approximately uniform over a range of $(y-y_0)$ comparable to $\langle y^2\rangle^{\frac{1}{2}}$. The treatment for the two limiting cases may be easily extended to include processes which exhibit both types of behavior, provided that the underlying mechanisms of the two types of transition occur on the same or similar, time scales. In fact we can show that

$$\frac{\partial P_1}{\partial t} = \int [P_1(y_0;t)\,\Phi(y_0\,|y) - P_1(y;t)\,\Phi(y\,|y_0)]\,dy_0$$
$$-\frac{\partial}{\partial y}\,(a^{(1)}P_1) + \tfrac{1}{2}\,\frac{\partial^2}{\partial y^2}\,(a^{(2)}P_1) \quad . \qquad (4.2\text{-}30)$$

We must emphasize that Eq. (4.2-30) is only applicable to a process in which P_1 changes by only negligible amounts during a transition. The three special cases discussed here exclude a large class of processes of interest; namely, those in which P_1 changes sufficiently fast so that, for instance, $\tau_c(\partial^2 P_1/\partial t^2)$ cannot be neglected in comparison with $(\partial P_1/\partial t)$. In the next section we restrict our attention to the case in which Eq. (4.2-26) is valid.

4.3 Rotational Brownian Motion of an Asymmetric Rotor

As in the case of translational Brownian motion[13] we adopt two different approaches to the problem of rotational Brownian motion. One approach is to obtain the probability distribution function from Eq. (4.2-26) and evaluate the displacement of particle orientation; the other is to start from an equation of rotational motion similar to that of the Langevin equation for translational cases. The first approach is very convenient for evaluation of the correlation functions involving only the orientation of a particle while the second method is more adequate for evaluation of the correlation functions involving angular momenta only. As we have mentioned earlier, the separability approximation is helpful to evaluate the correlation functions involving both orientation and angular momenta of the particle under consideration. In the final stage two approaches are made connected to each other via

Stokes-Debye-Einstein relations. The relation (4.1-4) is nothing but a result from this connection between these two different approaches. In this section we shall discuss both approaches and show how to evaluate the correlation functions involving $\vec{\Omega}$, or $\vec{J}$, $\vec{j}$, or both.

(a) Perrin-Favro rotational diffusion equation and orientation correlation functions.

The dynamics of rotational Brownian motion of a sphere around a given axis has been discussed briefly by Einstein in one of his early papers.[24] As we have previously mentioned, solutions to rotational diffusion equations were given by Debye[6] and Furry[7] for spherical molecules and by Perrin[8] and Favro[9] for nonspherical molecules. Here we will reconsider the anisotropic rotational Brownian motion which Perrin and Favro treated; however, we will not duplicate the derivation of rotational diffusion equation for nonspherical molecules, but directly start from Perrin's diffusion equation for a nonspherical rigid rotor

$$\frac{\partial P}{\partial t} = \frac{1}{4} \sum_{i} \sum_{\lambda\mu} D_i [(g^{\frac{1}{2}})^{-1} (\partial/\partial q_\lambda) \, g^{\frac{1}{2}} a_i^\lambda a_i^\mu (\partial/\partial q_\mu)] \, P \quad , \qquad (4.3\text{-}1)$$

where $\vec{q}(q_1, q_2, q_3)$ is the coordinate which describes the rotation, P is the probability density of the diffusion, a_i^λ is the transformation coefficient from the infinitesimal rotation $\frac{1}{2} \Delta\xi_i$ around the principal axis x_i to q_λ, $g^{\frac{1}{2}}$ is the volume element of the coordinates, i.e., $[\det(g_{\lambda\mu})]^{\frac{1}{2}}$, where the symbol $g_{\lambda\mu}$ is the line element defined by

$$\sum_i d(\tfrac{1}{2}\Delta\xi_i)^2 = \sum_{\lambda\mu} g_{\lambda\mu}\, dq_\lambda dq_\mu \quad , \qquad (4.3\text{-}2)$$

and D_i is the diffusion constant for the rotational Brownian motion about the principal axis x_i and is related to f_i, the friction coefficient about x, via

$$D_i = kT/f_i \quad . \qquad (4.3\text{-}3)$$

We have to note here that Eq. (4.3-1) has been derived under the assumption of small-angle jump and is nothing but a special form of Eq. (4.2-26).

In terms of the Euler angles (θ, ϕ, ψ), which specify the body-fixed frame in which the diffusion tensor $\underset{\frown}{D}$ takes a diagonal form with respect to a space-fixed frame (Eq. (4.3-1) may be rewritten as

$$\frac{\partial}{\partial t} P = -(D_1 P_1^2 + D_2 P_2^2 + D_3 P_3^2)P \quad , \qquad (4.3\text{-}4)$$

where the operators, P_1, P_2, and P_3, are defined as*

$$P_1 = \sin\psi \cdot P_\theta - \frac{\cos\psi}{\sin\theta} P_\phi - \cot\theta \cos\psi\, P_\psi \quad , \qquad (4.3\text{-}5a)$$

$$P_2 = \cos\psi \cdot P_\theta + \frac{\sin\psi}{\sin\theta} P_\phi + \cot\theta \sin\psi\, P_\psi \quad , \qquad (4.3\text{-}5b)$$

and

$$P_3 = P_\psi \qquad (4.3\text{-}5c)$$

---

*Note: Definition of the Euler angles which we adopt here is that listed in Tinkham,[25] thus differing from that described by Goldstein.

with

$$P_\theta = -i\frac{\partial}{\partial\theta}\ , \quad P_\phi = -i\frac{\partial}{\partial\phi}\ , \quad \text{and} \quad P_\psi = -i\frac{\partial}{\partial\psi}\ . \qquad (4.3\text{-}6)$$

Favro has expressed Eq. (4.3-4) in terms of the Cayley-Klein parameters[21] rather than the Euler angles. Coincidence of the Euler angle expression with that of the Cayley-Klein parameters can be seen if we note that (Appendix II)

$$\begin{aligned}
\Gamma &= \cos\frac{\theta}{2}\cos\frac{\psi+\phi}{2}\ ,\\
\Omega_X &= \sin\frac{\theta}{2}\sin\frac{\psi-\phi}{2}\ ,\\
\Omega_Y &= \sin\frac{\theta}{2}\cos\frac{\psi-\phi}{2}\ , \quad \text{and}\\
\Omega_Z &= \cos\frac{\theta}{2}\sin\frac{\psi-\phi}{2}\ ,
\end{aligned} \qquad (4.3\text{-}7)$$

where Γ, Ω_X, Ω_Y, and Ω_Z are the Cayley-Klein parameters associated with the given rotation.

Comparison of Eq. (4.3-4) with the time-dependent Schrödinger equation for the rotational motion of an asymmetric rotor (without any internal rotational degree of freedom)

$$i\hbar\frac{\partial\Psi}{\partial t} = \mathcal{H}\Psi = (AP_x^2 + BP_y^2 + CP_z^2)\Psi \qquad (4.3\text{-}8)$$

enables us to understand that $P(\vec{\Omega};t)$ takes the form

$$P(\vec{\Omega};t) = \sum_n a_n\varphi_n(\vec{\Omega})\exp(-W_n t)\ , \qquad (4.3\text{-}9)$$

where $\varphi_n(\vec{\Omega})$ and W_n are, respectively, the eigenfunction and corresponding eigenvalue of the operator

$$\hat{\mathscr{D}} \equiv D_1P_1^2 + D_2P_2^2 + D_3P_3^2 \quad . \tag{4.3-10}$$

Let us assume that all the eigenfunctions $\varphi_n(\vec{\Omega})$ of $\hat{\mathscr{D}}$ have already been orthonormalized, and let the initial condition be

$$P(\vec{\Omega};t=0) = \delta(\vec{\Omega}) \quad . \tag{4.3-11}$$

Then, we have

$$P(\vec{\Omega},\vec{0};t) = \sum_n \varphi_n{}^*(\vec{0})\,\varphi_n(\vec{\Omega})\exp(-W_n|t|) \tag{4.3-12}$$

where we have inserted $\vec{0}$ in $P(\vec{\Omega};t)$ to indicate that at $t=0$ $\vec{\Omega}$ takes the orientation $\vec{0}(\equiv \theta, \phi, \psi = 0)$. P_1, P_2, and P_3 can be seen to play the same role as the angular momentum operators in the rotational Hamiltonian for an asymmetric rotor. Let us introduce a new operator defined by

$$P^2 = P_1^2 + P_2^2 + P_3^2 \tag{4.3-13}$$

and a new notation given by

$$D^{\pm} = \tfrac{1}{2}(D_1 \pm D_2) \quad . \tag{4.3-14}$$

Then, $\hat{\mathscr{D}}$ may be rewritten as

$$\hat{\mathscr{D}} = D^+P^2 + (D_3 - D^+)P_3^2 + D^-(P_1^2 - P_2^2) \quad . \tag{4.3-15}$$

As in the case of asymmetric rotor problems, we introduce an additional angular momentum operator P_Z defined by

$$P_Z = -i(\partial/\partial\phi) \quad . \tag{4.3-16}$$

The operator set (P^2, P_3, P_Z) will provide the complete description of the system, and the eigenvalues associated with the set are given by

$$\begin{aligned} P^2 &\longrightarrow j(j+1) \;, && j = 0, 1, 2, 3, \ldots, \infty \\ P_3 &\longrightarrow m \;, && m = -j, -j+1, \ldots, j-1, j \\ P_Z &\longrightarrow n \;, && n = -j, -j+1, \ldots, j-1, j \;, \end{aligned} \qquad (4.3\text{-}17)$$

and the eigenfunctions corresponding to the set of eigenvalues are complete and nondegenerate.

Now, let us introduce a new set of variables defined as

$$\rho = (\Omega_X^2 + \Omega_Y^2)^{\frac{1}{2}} \;, \qquad \Theta = \tan^{-1}(\Omega_Z/\Gamma) \;, \qquad \text{and}$$

$$\Phi = \tan^{-1}(\Omega_X/\Omega_Y) \;, \qquad (4.3\text{-}18)$$

in terms of which we obtain

$$P^2 = -\tfrac{1}{4}\left[(1-\rho^2)\frac{\partial^2}{\partial\rho^2} + \frac{1}{\rho}(1-3\rho^2)\frac{\partial}{\partial\rho} + (1-\rho^2)\frac{\partial^2}{\partial\Theta^2} + \frac{1}{\rho^2}\frac{\partial^2}{\partial\Phi^2}\right] \;, \qquad (4.3\text{-}19)$$

$$P_3 + P_Z = -i\frac{\partial}{\partial\Phi} \;, \qquad (4.3\text{-}20)$$

and

$$P_3 - P_Z = i\frac{\partial}{\partial\Theta} \;. \qquad (4.3\text{-}21)$$

The raising and lowering operators defined as

$$P^{\pm} = P_1 \pm iP_2 \qquad (4.3\text{-}22)$$

and

$$P'^{\pm} = P_X \pm iP_Y \;, \qquad (4.3\text{-}23)$$

are now introduced, where P_X and P_Y are the components of the vector $\vec{P}(P_1, P_2, P_3)$ along the X and Y axes in the space-fixed coordinates system, respectively, and let the eigenvalues of the operators $P_3 + P_Z$ and $P_3 - P_Z$ be given as

$$(P_3 + P_Z) \longrightarrow \mu \ , \qquad \mu = m + n$$

and

$$(P_3 - P_Z) \longrightarrow \nu \ , \qquad \nu = m - n \ . \tag{4.3-24}$$

Operators $P^{\pm}$ and $P'^{\pm}$, when applied to an eigenfunction $\psi_j^{m;n}$ of (4. 3-17), produce the following results:

$$P^{\pm} \psi_j^{m;n} = [(j \mp m)(j \pm m + 1)]^{\frac{1}{2}} \psi_j^{m\pm1;n} \tag{4.3-25}$$

and

$$P'^{\pm} \psi_j^{m;n} = [(j \mp n)(j \pm n + 1)]^{\frac{1}{2}} \psi_j^{m;n\pm1} \ . \tag{4.3-26}$$

Now, putting $\psi_j^{m;n} = w_j^{\mu;\nu}$, we obtain from (4. 3-17), (4. 3-19), (4. 3-20), and (4. 3-21)

$$w_j^{\mu;\nu} = g_j^{\mu;\nu}(\rho) \exp(-i\nu\Theta) \exp(i\mu\Phi) \ , \tag{4.3-27}$$

where $g_j^{\mu-\nu}(\rho)$ is the solution of

$$[(1-\rho^2)\frac{\partial^2}{\partial\rho^2} + \frac{1}{\rho}(1-3\rho^2)\frac{\partial}{\partial\rho} - \frac{\mu^2}{\rho^2} - \frac{\nu^2}{1-\rho^2}$$

$$+ 4j(j+1)] \cdot g_j^{\mu;\nu} = 0 \ . \tag{4.3-28}$$

Equation (4. 3-28) can be converted into a more easily recognized form by making the substitution

$$\xi = \rho^2 \,, \qquad \text{and} \qquad g_j^{\mu;\nu}(\rho) = (1-\xi)^{\frac{1}{2}|\nu|}\, \xi^{\frac{1}{2}|\nu|}\, f_j^{\mu;\nu} \quad . \tag{4.3-29}$$

Substitution of (4.3-29) in (4.3-28) gives us

$$\left\{(1-\xi)\,\xi\,\frac{\partial^2}{\partial\xi^2} + [c - (a+b+1)\xi]\,\frac{\partial}{\partial\xi} - ab\right\} f_j^{\mu;\nu} = 0 \quad , \tag{4.3-30}$$

where

$$a = [(|\mu| + |\nu|)/2 + j + 1] \quad , \quad b = [(|\mu| + |\nu|)/2 - j] \quad ,$$

and

$$c = (|\mu| + 1) \quad .$$

Equation (4.3-30) is the well-known hypergeometric equation satisfied by the hypergeometric function

$$F(a,b,c;\xi) = \sum_{k=0}^{\infty} \frac{(a+k-1)!}{(a-1)!}\,\frac{(b+k-1)!}{(b-1)!}\,\frac{(c-1)!}{(c+k-1)!}\,\frac{\xi^k}{k!} \quad . \tag{4.3-31}$$

Thus, the function $g_j^{\mu;\nu}$ may be rewritten as

$$\begin{aligned} g_j^{\mu;\nu} = A_j^{\mu;\nu}(1-\rho^2)^{\frac{1}{2}|\nu|}\,\rho^{|\mu|}\,F([\tfrac{1}{2}(|\mu| + |\nu|) + j + 1]\,; \\ [\tfrac{1}{2}(|\mu| + |\nu|) - j]\,; (|\mu| + 1)\,; \rho^2) \quad . \end{aligned} \tag{4.3-32}$$

The nonvanishing constants $A_j^{\mu;\nu}$ may be determined by normalizing one function, say $g_j^{2j;0}$, and then using (4.3-25) and (4.3-26) to determine the ratios of the various constants by direct application of $P^{\pm}$ and $P'^{\pm}$ to (4.3-32). The result has been given by Favro as

$$\begin{aligned} A_j^{\mu;\nu} = \left(\frac{-\mu}{|\mu|}\right)^{\mu} e^{i\nu\pi/2}\,\frac{(2j+1)^{\frac{1}{2}}}{\pi\,|\mu|!} \\ \times \left(\frac{[j+\frac{1}{2}(|\mu| + |\nu|)]!\;[j+\frac{1}{2}(|\mu| - |\nu|)]!}{[j-\frac{1}{2}(|\mu| + |\nu|)]!\;[j-\frac{1}{2}(|\mu| - |\nu|)]!}\right)^{\frac{1}{2}} \quad . \end{aligned} \tag{4.3-33}$$

Therefore, when $D_1 = D_2$, we can write

$$P(\Omega, 0; t)\Big|_{D_1=D_2} = \pi^{-1} \sum_{j=0}^{\infty} (2j+1)^{\frac{1}{2}} \sum_{m=-j}^{j} (-1)^m w_j^{0;2m}$$

$$\times \exp\{-[D^+ j(j+1) + (D_3-D^+)m^2]t\} \quad . \qquad (4.3\text{-}34)$$

The expression (4.3-34) is exact since $w_j^{\mu;\nu}$ is available in analytical form when $D_1 = D_2$. What if $D_1 \neq D_2$? In this case P_3 does not commute with $\hat{\mathcal{D}}$, and therefore $\psi_j^{m;n}$ is no longer an eigenfunction of $\hat{\mathcal{D}}$. In fact, a complete set of eigenfunctions of $\hat{\mathcal{D}}$ is not available in any analytical form if $D_1 \neq D_2$. However, in many cases one needs only those eigenfunctions with low values of j. Those eigenfunctions and corresponding eigenvalues may be obtained by diagonalizing $\hat{\mathcal{D}}$ directly with $\psi_j^{m;n}$ as the unperturbed basic set of functions. In the $\psi_j^{m;n}$ representation the matrix elements of $\hat{\mathcal{D}}$ take the form

$$\langle j\,m\,n|\hat{\mathcal{D}}|j\,m\,n\rangle = D^+ j(j+1) + (D_3-D^+)m^2 \qquad (4.3\text{-}35)$$

and

$$\langle j\,m\,n|\hat{\mathcal{D}}|j\,m{\pm}2\,n\rangle = -\tfrac{1}{2} D^- \{[j(j+1)-m(m\pm1)]$$

$$\times [j(j+1)-(m\pm1)(m\pm2)]\}^{\frac{1}{2}} \quad . \qquad (4.3\text{-}36)$$

Expressions (4.3-35) and (4.3-36) show that $\hat{\mathcal{D}}$ never mixes even and odd values of m so that the secular equation may be factored into an even and odd part by separating these values in the secular determinant. A further factorization may be effected by introducing a new set of basis functions defined as

$$\Psi_j^{m;n} = \frac{1}{\sqrt{2}} (\psi_j^{m;n} + \psi_j^{-m;n}) , \qquad m > 0$$

$$\Psi_j^{m;n} = \frac{1}{\sqrt{2}} (\psi_j^{-m;n} - \psi_j^{m;n}) , \qquad m < 0$$

and

$$\Psi_j^{0;n} = \psi_j^{0;n} \quad . \tag{4.3-37}$$

It is then observed that there are no matrix elements connecting positive values of m with negative values of m in the $\Psi_j^{m;n}$ representation. This, combined with the even-odd factorization, produces a four-fold factorization of the secular equation. For even j there are three factors of degree j/2 and one of (j/2 + 1) while for odd j there are three factors of degree (j + 1)/2 and one of degree (j - 1)/2. This factorization makes the solution of the secular equation relatively easy for low values of j. The eigenfunctions and eigenvalues thus obtained can then be substituted into the expression (4.3-12) to obtain an approximate expression for $P(\vec{\Omega}, \vec{0}; t)$. Functions $\Psi_j^{m;n}$, eigenfunctions and eigenvalues of the operator $\hat{\mathcal{D}}$, and $P(\vec{\Omega}, \vec{0}; t)$ up to j=3 are tabulated in Table V, VI, and VII, respectively. Wigner matrix elements $\mathcal{D}_{MN}^{(J)}(\Omega)$ can be expanded in terms of $\Psi_j^{m;n}$ and this is also tabulated in Table VIII. The expanded form of $\mathcal{D}_{MN}^{(J)}$ does not involve any term of $\Psi_j^{m;n}$ in which $j > J$. Therefore, we need terms up to j=2 to expand $\mathcal{D}_{MN}^{(2)}$ in terms of $\Psi_j^{m;n}$.

Now, we consider how to evaluate the correlation function of the form

$$\langle [\mathcal{D}_{M'N'}^{(J')}(\vec{\Omega})]_{t+t_0} \, [\mathcal{D}_{MN}^{(J)}(\vec{\Omega})]_{t_0} \rangle \quad .$$

Consider a reference frame S′ fixed on the molecule containing the spin (or spins) under consideration, and let the orientation of S′ with respect to the laboratory coordinate system S be specified by the Euler angles $\vec{\Omega}_0(\equiv \phi_0, \theta_0, \psi_0)$ at t = 0 and by another set of Euler angles $\vec{\Omega}(\equiv \phi, \theta, \psi)$ at a later time t. The Euler angles specifying S′ at time t with respect to S′ at t = 0 are $\vec{\Omega}'(\equiv \phi', \theta', \psi')$. Then it follows from properties of $\underset{\sim}{\mathcal{D}}(\vec{\Omega})$ matrix[27] that

$$\mathcal{D}^{(J)}_{M'N}(\vec{\Omega}) = \sum_{M''} \mathcal{D}^{(J)}_{M'M''}(\Omega')\mathcal{D}^{(J)}_{M''N}(\Omega_0) \quad , \qquad (4.3\text{-}38)$$

so that

$$\begin{aligned}\langle[\mathcal{D}^{(J)}_{M'N'}(\vec{\Omega})]_t\,[\mathcal{D}^{(J)}_{MN}(\vec{\Omega})]_0\rangle \\ = \sum_{L} \{\int \mathcal{D}^{(J)}_{M'L}(\vec{\Omega}')\; P(\vec{\Omega}', \vec{0};t)d^3\Omega'\} \\ \times \{\int \mathcal{D}^{(J)}_{LN'}(\vec{\Omega}_0)\mathcal{D}^{(J)}_{MN}(\vec{\Omega}_0)\;\rho(\vec{\Omega}_0)d^3\Omega_0\} \quad , \qquad (4.3\text{-}39)\end{aligned}$$

where $\rho(\vec{\Omega}_0)$ is the probability density that S′ has the orientation $\vec{\Omega}_0$ at time t = 0. If all the orientations are assumed to be equally probable at a given time, $\rho(\vec{\Omega}_0)$ may be written as

$$\rho(\vec{\Omega}_0)d^3\Omega_0 = \frac{1}{8\pi^2}\, d\phi \sin\theta \; d\theta d\psi \quad . \qquad (4.3\text{-}40)$$

Substitution of (4.3-40) in (4.3-39) and use of two relations

$$\mathcal{D}^{(J)}_{MN}(\vec{\Omega}) = (-1)^{M-N}\mathcal{D}^{(J)}_{-M,\,-N}{}^*(\vec{\Omega})$$

and

TABLE V. Expressions for $\Psi_j^{m;n}$

$j=0$	$\Psi_0^{0;0}$	$= (\pi)^{-1}$
$j=1$	$\Psi_1^{1;\pm1}$	$= (\pi)^{-1}(3/2)^{\frac{1}{2}}[\rho^2 e^{\pm2i\Phi} - (1-\rho^2)\, e^{\pm2i\Theta}]$
	$\Psi_1^{1;0}$	$= -(\pi)^{-1}(3)^{\frac{1}{2}}\, i\rho(1-\rho^2)^{\frac{1}{2}}[e^{i(\Phi-\Theta)} - e^{-i(\Phi-\Theta)}]$
	$\Psi_1^{0;\pm1}$	$= (\pi)^{-1}(\mp1)(6)^{\frac{1}{2}}\, i\rho\,(1-\rho^2)^{\frac{1}{2}}\, e^{\pm i(\Phi+\Theta)}$
	$\Psi_1^{0;0}$	$= (\pi)^{-1}(3)^{\frac{1}{2}}\,(1-2\rho^2)$
	$\Psi_1^{-1;\pm1}$	$= (\pi)^{-1}(\pm1)(3/2)^{\frac{1}{2}}[\rho^2 e^{\pm2i\Phi} + (1-\rho^2)\, e^{\pm2i\Theta}]$
	$\Psi_1^{-1;0}$	$= -(\pi)^{-1}(3)^{\frac{1}{2}}\, i\rho(1-\rho^2)^{\frac{1}{2}}[e^{i(\Phi-\Theta)} + e^{-i(\Phi-\Theta)}]$
$j=2$	$\Psi_2^{2;\pm2}$	$= (\pi)^{-1}(5/2)^{\frac{1}{2}}[\rho^4 e^{\pm4i\Phi} + (1-\rho^2)^2\, e^{\pm4i\Theta}]$
	$\Psi_2^{2\pm1}$	$= (\pi)^{-1}(5/2)^{\frac{1}{2}}\, i(1-\rho^2)^{\frac{1}{2}}\, \rho[(1-\rho^2)\, e^{\mp i(\Phi-3\Theta)} - \rho^2\, e^{\pm i(3\Phi-\Theta)}]$
	$\Psi_2^{2;0}$	$= -(\pi)^{-1}(15)^{\frac{1}{2}}\,(1-\rho^2)\, \rho^2[e^{2i(\Phi-\Theta)} + e^{-2i(\Phi-\Theta)}]$
	$\Psi_2^{1;\pm2}$	$= (\pi)^{-1}(5/2)^{\frac{1}{2}}\, i(1-\rho^2)^{\frac{1}{2}}\, \rho[\rho^2\, e^{\pm i(3\Phi+\Theta)} - (1-\rho^2)\, e^{\pm i(\Phi+3\Theta)}]$
	$\Psi_2^{1;\pm1}$	$= (\pi)^{-1}(5/2)^{\frac{1}{2}}[(3-4\rho^2)\, \rho^2\, e^{\pm2i\Phi} - (1-4\rho^2)(1-\rho^2)\, e^{\pm2i\Theta}]$
	$\Psi_2^{1;0}$	$= -(\pi)^{-1}(15)^{\frac{1}{2}}\, i(1-\rho^2)^{\frac{1}{2}}\, \rho(1-2\rho^2)[e^{i(\Phi-\Theta)} + e^{-i(\Phi-\Theta)}]$
	$\Psi_2^{0;\pm2}$	$= -(\pi)^{-1}(30)^{\frac{1}{2}}\,(1-\rho^2)\, \rho^2\, e^{\pm2i(\Phi+\Theta)}$
	$\Psi_2^{0;\pm1}$	$= (\pi)^{-1}(30)^{\frac{1}{2}}\, i(1-\rho^2)^{\frac{1}{2}}\, \rho(1-2\rho^2)\, e^{\pm i(\Phi+\Theta)}$
	$\Psi_2^{0;0}$	$= (\pi)^{-1}(5)^{\frac{1}{2}}\,(1-6\rho^2+6\rho^4)$
	$\Psi_2^{-1;\pm2}$	$= (\pi)^{-1}(\pm1)(5/2)^{\frac{1}{2}}\, i(1-\rho^2)^{\frac{1}{2}}\, \rho[\rho^2\, e^{\pm i(3\Phi+\Theta)} + (1-\rho^2)\, e^{\pm i(\Phi+3\Theta)}]$
	$\Psi_2^{-1;\pm1}$	$= (\pi)^{-1}(\pm1)(5/2)^{\frac{1}{2}}[(3-4\rho^2)\, \rho^2\, e^{\pm2i\Phi} + (1-\rho^2)(1-4\rho^2)\, e^{\pm2i\Theta}]$
	$\Psi_2^{-1;0}$	$= -(\pi)^{-1}(15)^{\frac{1}{2}}\, i(1-\rho^2)^{\frac{1}{2}}\, \rho(1-2\rho^2)[e^{i(\Phi-\Theta)} - e^{-i(\Phi-\Theta)}]$

TABLE V. (Continued)

$$\Psi_2^{-2;\pm2} = (\pi)^{-1}(\pm1)(5/2)^{\frac{1}{2}}\,[\rho^4\, e^{\pm4i\Phi} - (1-\rho^2)^2\, e^{\pm4i\Theta}]$$

$$\Psi_2^{-2;\pm1} = (\pi)^{-1}(\mp1)(5/2)^{\frac{1}{2}}\, i(1-\rho^2)^{\frac{1}{2}}\, \rho[\rho^2\, e^{\pm i(3\Phi-\Theta)} + (1-\rho^2)\, e^{\mp i(\Phi-3\Theta)}]$$

$$\Psi_2^{-2;0} = -(\pi)^{-1}(15)^{\frac{1}{2}}\,(1-\rho^2)\,\rho^2[e^{2i(\Phi-\Theta)} - e^{-2i(\Phi-\Theta)}]$$

$$j=3 \qquad \Psi_3^{3;\pm3} = (\pi)^{-1}(7/2)^{\frac{1}{2}}\,[\rho^6\, e^{\pm6i\Phi} - (1-\rho^2)^3\, e^{\pm6i\Theta}]$$

$$\Psi_3^{3;\pm2} = -(\pi)^{-1}(21)^{\frac{1}{2}}\, i(1-\rho^2)^{\frac{1}{2}}\,\rho[\rho^4\, e^{\pm i(5\Phi-\Theta)} + (1-\rho^2)^2\, e^{\mp i(\Phi-5\Theta)}]$$

$$\Psi_3^{3;\pm1} = -(\pi)^{-1}(105/2)^{\frac{1}{2}}\,(1-\rho^2)\,\rho^2[\rho^2\, e^{\pm2i(2\Phi-\Theta)} - (1-\rho^2)\, e^{\mp2i(\Phi-2\Theta)}]$$

$$\Psi_3^{3;0} = (\pi)^{-1}(70)^{\frac{1}{2}}\, i(1-\rho^2)^{\frac{3}{2}}\,\rho^3[e^{3i(\Phi-\Theta)} + e^{-3i(\Phi-\Theta)}]$$

$$\Psi_3^{2;\pm3} = (\pi)^{-1}(21)^{\frac{1}{2}}\, i(1-\rho^2)^{\frac{1}{2}}\,\rho[\rho^4\, e^{\pm i(5\Phi+\Theta)} + (1-\rho^2)^2\, e^{\pm i(\Phi+5\Theta)}]$$

$$\Psi_3^{2;\pm2} = (\pi)^{-1}(7/2)^{\frac{1}{2}}\,[\rho^4(5-6\rho^2)\, e^{\pm4i\Phi} + (1-\rho^2)^2\,(1-6\rho^2)\, e^{\pm4i\Theta}]$$

$$\begin{aligned}\Psi_3^{2;\pm1} = {} & -(\pi)^{-1}(35)^{\frac{1}{2}}\, i(1-\rho^2)^{\frac{1}{2}}\,\rho[\rho^2(2-3\rho^2)\, e^{\pm i(3\Phi-\Theta)} \\ & - (1-\rho^2)(1-3\rho^2)\, e^{\mp i(\Phi-3\Theta)}]\end{aligned}$$

$$\Psi_3^{2;0} = -(\pi)^{-1}(105)^{\frac{1}{2}}\,(1-\rho^2)\,\rho^2(1-2\rho^2)[e^{2i(\Phi-\Theta)} + e^{-2i(\Phi-\Theta)}]$$

$$\Psi_3^{1;\pm3} = -(\pi)^{-1}(105/2)^{\frac{1}{2}}\,(1-\rho^2)\,\rho^2[\rho^2\, e^{\pm2i(2\Phi+\Theta)} - (1-\rho^2)\, e^{\pm2i(\Phi+2\Theta)}]$$

$$\begin{aligned}\Psi_3^{1;\pm2} = {} & (\pi)^{-1}(35)^{\frac{1}{2}}\, i(1-\rho^2)^{\frac{1}{2}}\,\rho[\rho^2(2-3\rho^2)\, e^{\pm i(3\Phi+\Theta)} \\ & - (1-\rho^2)(1-3\rho^2)\, e^{\pm i(\Phi+3\Theta)}]\end{aligned}$$

$$\begin{aligned}\Psi_3^{1;\pm1} = {} & (\pi)^{-1}(7/2)^{\frac{1}{2}}\,[\rho^2(6-20\rho^2+15\rho^4)\, e^{\pm2i\Phi} \\ & -(1-\rho^2)(1-10\rho^2+15\rho^4)\, e^{\pm2i\Theta}]\end{aligned}$$

$$\Psi_3^{1;0} = -(\pi)^{-1}(42)^{\frac{1}{2}}\, i(1-\rho^2)^{\frac{1}{2}}\,\rho(1-5\rho^2+5\rho^4)[e^{i(\Phi-\Theta)} + e^{-i(\Phi-\Theta)}]$$

$$\Psi_3^{0;\pm3} = -(\pi)^{-1}2(35)^{\frac{1}{2}}\, i(1-\rho^2)^{\frac{3}{2}}\,\rho^3\, e^{\pm3i(\Phi+\Theta)}$$

$$\Psi_3^{0;\pm2} = -(\pi)^{-1}(210)^{\frac{1}{2}}\,(1-\rho^2)\,\rho^2(1-2\rho^2)\, e^{\pm2i(\Phi+\Theta)}$$

TABLE V. (Continued)

$$
\begin{aligned}
\Psi_3^{0;\pm1} &= (\pi)^{-1} 2(21)^{\frac{1}{2}}\, i(1-\rho^2)^{\frac{1}{2}}\, (1-5\rho^2+5\rho^4)\, \rho\, e^{\pm i(\Phi+\Theta)} \\
\Psi_3^{0;0} &= (\pi)^{-1}(7)^{\frac{1}{2}}\, (1-12\rho^2+30\rho^4-20\rho^6) \\
\Psi_3^{-1;\pm3} &= (\pi)^{-1}(\mp1)(105/2)^{\frac{1}{2}}\, (1-\rho^2)\, \rho^2[\rho^2\, e^{\pm2i(2\Phi+\Theta)} \\
&\qquad + (1-\rho^2)\, e^{\pm2i(\Phi+2\Theta)}] \\
\Psi_3^{-1;\pm2} &= (\pi)^{-1}(\pm1)(35)^{\frac{1}{2}}\, i(1-\rho^2)^{\frac{1}{2}}\, \rho[\rho^2(2-3\rho^2)\, e^{\pm i(3\Phi+\Theta)} \\
&\qquad + (1-\rho^2)(1-3\rho^2)\, e^{\pm i(\Phi+3\Theta}] \\
\Psi_3^{-1;\pm1} &= (\pi)^{-1}(\pm1)(7/2)^{\frac{1}{2}}\, [\rho^2(6-20\rho^2+15\rho^4)\, e^{\pm2i\Phi} \\
&\qquad + (1-\rho^2)(1-10\rho^2+15\rho^4)\, e^{\pm2i\Theta}] \\
\Psi_3^{-1;0} &= -(\pi)^{-1}(42)^{\frac{1}{2}}\, i(1-\rho^2)^{\frac{1}{2}}\, \rho(1-5\rho^2+5\rho^4)\, [e^{i(\Phi-\Theta)} - e^{-i(\Phi-\Theta)}] \\
\Psi_3^{-2;\pm3} &= (\pi)^{-1}(\pm1)(21)^{\frac{1}{2}}\, i(1-\rho^2)^{\frac{1}{2}}\, \rho[\rho^4\, e^{\pm i(5\Phi+\Theta)} - (1-\rho^2)^2\, e^{\pm i(\Phi+5\Theta)}] \\
\Psi_3^{-2;\pm2} &= (\pi)^{-1}(\pm1)(7/2)^{\frac{1}{2}}[\rho^4(5-6\rho^2)\, e^{\pm4i\Phi} - (1-\rho^2)^2\, (1-6\rho^2)\, e^{\pm4i\Theta}] \\
\Psi_3^{-2;\pm1} &= (\pi)^{-1}(\mp1)(35)^{\frac{1}{2}}\, i(1-\rho^2)^{\frac{1}{2}}\, \rho[\rho^2(2-3\rho^2)\, e^{\pm i(3\Phi-\Theta)} \\
&\qquad + (1-\rho^2)\, (1-3\rho^2)\, e^{\mp i(\Phi-3\Theta)}] \\
\Psi_3^{-2;0} &= -(\pi)^{-1}(105)^{\frac{1}{2}}(1-\rho^2)\, \rho^2(1-2\rho^2)[\, e^{2i(\Phi-\Theta)} - e^{-2i(\Phi-\Theta)}] \\
\Psi_3^{-3;\pm3} &= (\pi)^{-1}(\pm1)(7/2)^{\frac{1}{2}}\, [\rho^6\, e^{\pm6i\Phi} + (1-\rho^2)^3\, e^{\pm6i\Theta}] \\
\Psi_3^{-3;\pm2} &= (\pi)^{-1}(\mp1)(21)^{\frac{1}{2}}\, i(1-\rho^2)^{\frac{1}{2}}\, \rho[\rho^4\, e^{\pm i(5\Phi-\Theta)} - (1-\rho^2)^2\, e^{\mp i(\Phi-5\Theta)}] \\
\Psi_3^{-3;\pm1} &= (\pi)^{-1}(\mp1)(105/2)^{\frac{1}{2}}\, (1-\rho^2)\, \rho^2[\rho^2\, e^{\pm2i(2\Phi-\Theta)} \\
&\qquad + (1-\rho^2)\, e^{\mp2i(\Phi-2\Theta)}] \\
\Psi_3^{-3;0} &= (\pi)^{-1}(70)^{\frac{1}{2}}\, i(1-\rho^2)^{\frac{3}{2}}\, \rho^3[e^{3i(\Phi-\Theta)} - e^{-3i(\Phi-\Theta)}]
\end{aligned}
$$

---

*Note the following property of $\Psi_j^{m;n}$:

$$\Psi_j^{m;n*} = \frac{m}{|m|}(-1)^{m-n}\, \Psi_j^{m;-n} \quad .$$

TABLE VI. Eigenfunctions and Eigenvalues of $\hat{\mathcal{D}}$ up to $j = 3$

	Eigenfunctions	Eigenvalues
$j = 0$	$\Psi_0^{0;0}$	0
$j = 1$	$\Psi_1^{1;\pm n}$	$D_2 + D_3$
	$\Psi_1^{-1;\pm n}$	$D_1 + D_3$
	$\Psi_1^{0;\pm n}$	$D_1 + D_2$
$j = 2$	$a_1^+ \Psi_2^{2;\pm n} + a_2^+ \Psi_2^{0;\pm n}$	$6D + 2\Delta$
	$a_1^- \Psi_2^{2;\pm n} + a_2^- \Psi_2^{0;\pm n}$	$6D - 2\Delta$
	$\Psi_2^{-2;\pm n}$	$3(D + D_3)$
	$\Psi_2^{1;\pm n}$	$3(D + D_2)$
	$\Psi_2^{-1;\pm n}$	$3(D + D_1)$
$j = 3$	$\Psi_3^{-2;\pm n}$	$12D$
	$b_1^{\prime +} \Psi_3^{-3;\pm n} + b_2^{\prime +} \Psi_3^{-1;\pm n}$	$D' + 2\Delta'$
	$b_1^{\prime -} \Psi_3^{-3;\pm n} + b_2^{\prime -} \Psi_3^{-1;\pm n}$	$D' - 2\Delta'$
	$b_1^{\prime\prime +} \Psi_3^{1;\pm n} + b_2^{\prime\prime +} \Psi_3^{3;\pm n}$	$D'' + 2\Delta''$
	$b_1^{\prime\prime -} \Psi_3^{-1;\pm n} + b_2^{\prime\prime -} \Psi_3^{3;\pm n}$	$D'' - 2\Delta''$
	$b_1^{\prime\prime\prime +} \Psi_3^{0;\pm n} + b_2^{\prime\prime\prime +} \Psi_3^{2;\pm n}$	$D''' + 2\Delta'''$
	$b_1^{\prime\prime\prime -} \Psi_3^{0;\pm n} + b_2^{\prime\prime\prime -} \Psi_3^{2;\pm n}$	$D''' - 2\Delta'''$

*In the above table the following notations are adopted:

$D = \frac{1}{3}(D_1+D_2+D_3)$, $\Delta = (D_1^2+D_2^2+D_3^2-D_1D_2-D_2D_3-D_1D_3)^{\frac{1}{2}}$, $\alpha^{\pm} = 2\Delta \pm 3(D_3-D)$,

TABLE VI. (Continued)

$a_1^{\pm} = (\alpha^{\mp}/4\Delta)^{\frac{1}{2}}$, $a_2^{\pm} = \pm(\alpha^{\pm}/4\Delta)^{\frac{1}{2}}$, $D' = 3(5D-D_2)$, $D'' = 3(5D-D_1)$,
$D''' = 3(5D-D_3)$, $\Delta' = (4D_1^2+D_2^2+4D_3^2-D_1D_2-D_1D_3-7D_2D_3)^{\frac{1}{2}}$, $\Delta'' = (D_1^2+4D_2^2$
$+4D_3^2-D_1D_2-D_2D_3-7D_1D_3)^{\frac{1}{2}}$, $\Delta''' = (4D_1^2+4D_2^2+D_3^2-D_1D_2-D_2D_3-7D_1D_2)^{\frac{1}{2}}$,
$\beta'^{\pm} = [(3D^{+}+9D_3) - (D'\pm2\Delta')]/\sqrt{15}\ D^{-}$, $\beta''^{\pm} = [(11D^{+}+D_3-6D^{-}) - (D''\pm2\Delta'')]/$
$\sqrt{15}\ D^{-}$, $\beta'''^{\pm} = [12D^{+}-(D'''\pm2\Delta''')]/2\sqrt{15}\ D^{-}$, $b_1'^{\pm} = \left(\frac{1}{1+\beta'^{\pm2}}\right)^{\frac{1}{2}}$,
$b_2'^{\pm} = \pm\left(\frac{\beta'^{\pm2}}{1+\beta'^{\pm2}}\right)^{\frac{1}{2}}$, $b_1''^{\pm} = \left(\frac{1}{1+\beta''^{\pm2}}\right)^{\frac{1}{2}}$, $b_2''^{\pm} = \pm\left(\frac{\beta''^{\pm2}}{1+\beta''^{\pm2}}\right)^{\frac{1}{2}}$,
$b_1'''^{\pm} = \left(\frac{1}{1+\beta'''^{\pm2}}\right)^{\frac{1}{2}}$, $b'''^{\pm} = \pm\left(\frac{\beta'''^{\pm2}}{1+\beta'''^{\pm2}}\right)^{\frac{1}{2}}$.

TABLE VII. Terms Appearing in $P(\vec{\Omega}, \vec{0}; t)$ Up to $j = 3$

$j = 0$	$(\pi)^{-1}\,\Psi_0^{0;0}$
$j = 1$	$-\,(\pi)^{-1}(3/2)^{\frac{1}{2}}\,(\Psi_1^{1;1} + \Psi_1^{1;-1})e^{-(D_2+D_3)t}$
	$(\pi)^{-1}(3/2)^{\frac{1}{2}}\,(\Psi_1^{-1;1} - \Psi_1^{-1;-1})\,e^{-(D_1+D_3)t}$
	$(\pi)^{-1}(3)^{\frac{1}{2}}\,\Psi_1^{0;0}\;e^{-(D_1+D_2)t}$
$j = 2$	$(4\pi\Delta)^{-1}(5)^{\frac{1}{2}}\,\alpha^{\mp}\,\Psi_2^{0;0}\;e^{-(6D\pm 2\Delta)t}$
	$(4\pi\Delta)^{-1}(5/2)^{\frac{1}{2}}\,\alpha^{\pm}\,(\Psi_2^{2;2} + \Psi_2^{2;-2})\;e^{-(6D\pm 2\Delta)t}$
	$\mp\,(4\pi\Delta)^{-1}(15)^{\frac{1}{2}}\,(D_1 - D_2)\;\Psi_2^{2;0}\;e^{-(6D\pm 2\Delta)t}$
	$\mp\,(4\pi\Delta)^{-1}(15/2)^{\frac{1}{2}}\,(D_1 - D_2)(\Psi_2^{0;2} + \Psi_2^{0;-2})\;e^{-(6D\pm 2\Delta)t}$
	$-\,(\pi)^{-1}(5/2)^{\frac{1}{2}}\,(\Psi_2^{-2;2} - \Psi_2^{-2;-2})\;e^{-3(D+D_3)t}$
	$-\,(\pi)^{-1}(5/2)^{\frac{1}{2}}\,(\Psi_2^{1;1} + \Psi_2^{1;-1})\;e^{-3(D+D_2)t}$
	$(\pi)^{-1}(5/2)^{\frac{1}{2}}\,(\Psi_2^{-1;1} - \Psi_2^{-1;-1})\;e^{-3(D+D_1)t}$
$j = 3$	$(\pi)^{-1}(7/2)^{\frac{1}{2}}\,b_1'^{\pm 2}\,(\Psi_3^{-3;3} - \Psi_3^{-3;-3})\;e^{-(D'\pm 2\Delta')t}$
	$(\pi)^{-1}(7/2)^{\frac{1}{2}}\,b_1'^{\pm}\,b_2'^{\pm}\,(\Psi_3^{-1;3} - \Psi_3^{-1;-3})\;e^{-(D'\pm 2\Delta')t}$
	$(\pi)^{-1}(7/2)^{\frac{1}{2}}\,b_1'^{\pm}\,b_2'^{\pm}\,(\Psi_3^{-3;1} - \Psi_3^{-3;-1})\;e^{-(D'\pm 2\Delta')t}$
	$(\pi)^{-1}(7/2)^{\frac{1}{2}}\,b_2'^{\pm 2}\,(\Psi_3^{-1;1} - \Psi_3^{-1;-1})\;e^{-(D'\pm 2\Delta')t}$
	$-\,(\pi)^{-1}(7/2)^{\frac{1}{2}}\,b_1''^{\pm 2}\,(\Psi_3^{1;1} + \Psi_3^{1;-1})\;e^{-(D''\pm 2\Delta'')t}$
	$-\,(\pi)^{-1}(7/2)^{\frac{1}{2}}\,b_1''^{\pm}b_2''^{\pm}\,(\Psi_3^{3;1} + \Psi_3^{3;-1})\;\;e^{-(D''\pm 2\Delta'')t}$
	$-\,(\pi)^{-1}(7/2)^{\frac{1}{2}}\,b_1''^{\pm}b_2''^{\pm}\,(\Psi_3^{1;3} + \Psi_3^{1;-3})\;e^{-(D''\pm 2\Delta'')t}$
	$-\,(\pi)^{-1}(7/2)^{\frac{1}{2}}\,b_2''^{\pm 2}\,(\Psi_3^{3;3} + \Psi_3^{3;-3})\;e^{-(D''\pm 2\Delta'')t}$

TABLE VII. (Continued)

$$(\pi)^{-1}(7)^{\frac{1}{2}}\, b_1^{\prime\prime\prime\pm 2}\, \Psi_3^{0;0}\; e^{-(D^{\prime\prime\prime}\pm 2\Delta^{\prime\prime\prime})t}$$

$$(\pi)^{-1}(7/2)^{\frac{1}{2}}\, b_2^{\prime\prime\prime\pm 2}\, (\Psi_3^{2;2}+\Psi_3^{2;-2})\quad e^{-(D^{\prime\prime\prime}\pm 2\Delta^{\prime\prime\prime})t}$$

$$(\pi)^{-1}(7/2)^{\frac{1}{2}}\, b_1^{\prime\prime\prime\pm}\, b_2^{\prime\prime\prime\pm}\, (\Psi_3^{0;2}+\Psi_3^{0;-2}+\sqrt{2}\,\Psi_3^{2;0})\; e^{-(D^{\prime\prime\prime}\pm 2\Delta^{\prime\prime\prime})t}$$

$$-\;(\pi)^{-1}(5/2)^{\frac{1}{2}}\, \Psi_3^{-2;2}\; e^{-12Dt}$$

$$(\pi)^{-1}(5/2)^{\frac{1}{2}}\, \Psi_3^{-2;-2}\; e^{-12Dt}$$

TABLE VIII. $\mathcal{D}^{(J)}_{MN}(\Omega)$'s in Terms of $\Psi_j^{m;n}{}_*$

j = 1	$\mathcal{D}^{(1)}_{11} = -\frac{\pi}{\sqrt{6}} (\Psi_1^{1;1*} - \Psi_1^{-1;1*})$
	$\mathcal{D}^{(1)}_{10} = -\frac{\pi}{\sqrt{6}} i (\Psi_1^{1;0*} - \Psi_1^{-1;0*})$
	$\mathcal{D}^{(1)}_{1-1} = \frac{\pi}{\sqrt{6}} (\Psi_1^{1;-1*} - \Psi_1^{-1;-1*})$
	$\mathcal{D}^{(1)}_{01} = \frac{\pi}{\sqrt{3}} i \Psi_1^{0;1*}$
	$\mathcal{D}^{(1)}_{00} = \frac{\pi}{\sqrt{3}} \Psi_1^{0;0*}$
	$\mathcal{D}^{(1)}_{0-1} = \frac{\pi}{\sqrt{3}} i \Psi_1^{0;-1*}$
	$\mathcal{D}^{(1)}_{-11} = \frac{\pi}{\sqrt{6}} (\Psi_1^{1;1*} + \Psi_1^{-1;1*})$
	$\mathcal{D}^{(1)}_{-10} = \frac{\pi}{\sqrt{6}} i (\Psi_1^{1;0*} + \Psi_1^{-1;0*})$
	$\mathcal{D}^{(1)}_{-1-1} = -\frac{\pi}{\sqrt{6}} (\Psi_1^{1;-1*} + \Psi_1^{-1;-1*})$
j = 2	$\mathcal{D}^{(2)}_{22} = \frac{\pi}{\sqrt{10}} (\Psi_2^{2;2*} - \Psi_2^{-2;2*})$
	$\mathcal{D}^{(2)}_{21} = \frac{2\pi}{\sqrt{10}} i (\Psi_2^{2;1*} - \Psi_2^{-2;1*})$
	$\mathcal{D}^{(2)}_{20} = -\frac{\pi}{\sqrt{10}} (\Psi_2^{2;0*} - \Psi_2^{-2;0*})$
	$\mathcal{D}^{(2)}_{2-1} = \frac{2\pi}{\sqrt{10}} i (\Psi_2^{2;-1*} - \Psi_2^{-2;-1*})$
	$\mathcal{D}^{(2)}_{2-2} = \frac{\pi}{\sqrt{10}} (\Psi_2^{2;-2*} - \Psi_2^{-2;-2*})$
	$\mathcal{D}^{(2)}_{12} = \frac{2\pi}{\sqrt{10}} i (\Psi_2^{1;2*} - \Psi_2^{-1;2*})$
	$\mathcal{D}^{(2)}_{11} = -\frac{\pi}{\sqrt{10}} (\Psi_2^{1;1*} - \Psi_2^{-1;1*})$

TABLE VIII. (Continued)

$$\mathscr{D}^{(2)}_{10} = -\frac{\pi}{\sqrt{10}}\, i\, (\Psi_2^{1;0*} - \Psi_2^{-1;0*})$$

$$\mathscr{D}^{(2)}_{1-1} = \frac{\pi}{\sqrt{10}}\, (\Psi_2^{1;-1*} - \Psi_2^{-1;-1*}) + \frac{\pi}{\sqrt{6}}\, (\Psi_1^{1;-1*} - \Psi_1^{-1;-1*})$$

$$\mathscr{D}^{(2)}_{1-2} = -\frac{2\pi}{\sqrt{10}}\, i\, (\Psi_2^{1;-2*} - \Psi_2^{-1;-2*})$$

$$\mathscr{D}^{(2)}_{02} = -\frac{\pi}{\sqrt{5}}\, \Psi_2^{0;2*}$$

$$\mathscr{D}^{(2)}_{01} = \frac{\pi}{\sqrt{5}}\, i\, \Psi_2^{0;1*}$$

$$\mathscr{D}^{(2)}_{00} = \frac{\pi}{\sqrt{5}}\, \Psi_2^{0;0*}$$

$$\mathscr{D}^{(2)}_{0-1} = -\frac{\pi}{\sqrt{5}}\, i\, \Psi_2^{0;-1*}$$

$$\mathscr{D}^{(2)}_{0-2} = -\frac{\pi}{\sqrt{5}}\, \Psi_2^{0;-2*}$$

$$\mathscr{D}^{(2)}_{-12} = \frac{2\pi}{\sqrt{10}}\, i\, (\Psi_2^{1;2*} + \Psi_2^{-1;2*})$$

$$\mathscr{D}^{(2)}_{-11} = \frac{\pi}{\sqrt{10}}\, (\Psi_2^{1;1*} + \Psi_2^{-1;1*}) + \frac{\pi}{\sqrt{6}}\, (\Psi_1^{1;1*} + \Psi_1^{-1;1*})$$

$$\mathscr{D}^{(2)}_{-10} = \frac{\pi}{\sqrt{10}}\, i\, (\Psi_2^{1;0*} + \Psi_2^{-1;0*})$$

$$\mathscr{D}^{(2)}_{-1-1} = -\frac{\pi}{\sqrt{10}}\, (\Psi_2^{1;-1*} + \Psi_2^{-1;-1*})$$

$$\mathscr{D}^{(2)}_{-1-2} = -\frac{2\pi}{\sqrt{10}}\, i\, (\Psi_2^{1;-2*} + \Psi_2^{-1;-2*})$$

$$\mathscr{D}^{(2)}_{-22} = \frac{\pi}{\sqrt{10}}\, (\Psi_2^{2;2*} + \Psi_2^{-2;2*})$$

$$\mathscr{D}^{(2)}_{-21} = -\frac{2\pi}{\sqrt{10}}\, i\, (\Psi_2^{2;1*} + \Psi_2^{-2;1*})$$

TABLE VIII. (Continued)

$$\mathcal{D}^{(2)}_{-20} = -\frac{\pi}{\sqrt{10}} \left(\Psi_2^{2;0\,*} + \Psi_2^{-2;0\,*}\right)$$

$$\mathcal{D}^{(2)}_{-2-1} = -\frac{\pi}{\sqrt{10}}\, i \left(\Psi_2^{2;-1*} + \Psi_2^{-2;-1*}\right)$$

$$\mathcal{D}^{(2)}_{-2-2} = \frac{\pi}{\sqrt{10}} \left(\Psi_2^{2;-2*} + \Psi_2^{-2;-2*}\right)$$

$$\frac{1}{8\pi^2}\int_0^{2\pi}\int_0^{\pi}\int_0^{2\pi}\mathcal{D}^{(J_1)}_{M_1'M_1}{}^*(\phi\theta\psi)\mathcal{D}^{(J_2)}_{M_2'M_2}(\phi\theta\psi)d\phi\sin\theta\, d\theta d\psi$$

$$= \delta_{M_1'M_2'}\delta_{M_1M_2}\delta_{J_1J_2}\cdot\frac{1}{2J_1+1}$$

yield

$$\langle[\mathcal{D}^{(J)}_{M'N'}(\vec{\Omega})]_t\,[\mathcal{D}^{(J)}_{MN}(\vec{\Omega})]_0\rangle$$

$$= (-1)^{-M-N'}\,\delta_{-N',N}\,\frac{1}{2J+1}\cdot I^{(J)}_{M',-M}(t)\quad ; \tag{4.3-41}$$

where

$$I^{(J)}_{M',-M}(t) = \int\mathcal{D}^{(J)}_{M',-M}(\vec{\Omega}')\,P(\vec{\Omega}',\vec{0};t)d^3\Omega' \quad . \tag{4.3-42}$$

In molecules without any element of symmetry it is possible that the principal axes of the diffusion tensor $\underset{\frown}{\mathcal{D}}$ may not be equivalent to those of the momentum ellipsoid of the molecule. In order to take this case into consideration let us define for convenience

S' = frame in which the inertia tensor takes a diagonal form,

S'' = frame in which the diffusion tensor takes a diagonal form,

$\vec{\Omega}_0$ = orientation of S' with respect to S, the space-fixed frame, at time 0,

$\vec{\Omega}$ = orientation of S' with respect to S at time t,

$\vec{\Omega}_1$ = orientation of S' at time t with respect to S' at time 0,

$\vec{\Omega}_0'$ = orientation of S'' with respect to S at time 0,

$\vec{\Omega}'$ = orientation of S'' with respect to S at time t,

and

$\vec{\Omega}_1'$ = orientation of S'' at time t with respect to S'' at time 0.

Also we assume that S″ is rotated away from S′ by $\Delta\vec{\Omega}$, that is,

$$\Delta\vec{\Omega} = \vec{\Omega}_0' - \vec{\Omega}_0 = \vec{\Omega}' - \vec{\Omega} \ .$$

Obviously, $\vec{\Omega}_1' = \vec{\Omega}_1$. Therefore, from the relation (4.3-38) we may write

$$\mathcal{D}^{(J)}_{MN}(\vec{\Omega}) = \sum_{L,\,L'} \mathcal{D}^{(J)}_{LL'}(\vec{\Omega}_0')\,\mathcal{D}^{(J)}_{L'N}(\Delta\vec{\Omega})\,\mathcal{D}^{(J)}_{ML}(\vec{\Omega}_1) \ . \qquad (4.3\text{-}43)$$

Substituting (4.3-43) in (4.3-41) and making use of the properties of $\mathcal{D}(\vec{\Omega})$ matrix, it may be shown that

$$\langle[\mathcal{D}^{(J')}_{M'N'}(\vec{\Omega})]_t\,[\mathcal{D}^{(J)}_{MN}(\vec{\Omega})]_0\rangle$$

$$= \sum_{L'} (-1)^{M-L'}\,\delta_{J'J}\,\frac{1}{2J+1}\,\mathcal{D}^{(J)}_{-L'N}(\Delta\vec{\Omega})\,\mathcal{D}^{(J)}_{L'N'}(\Delta\vec{\Omega})\,I^{(J)}_{M',\,-M}(t) \ . \qquad (4.3\text{-}44)$$

Note that when S′ and S″ coincide, that is, $\Delta\vec{\Omega} = 0$, Eq. (4.3-44) is reduced to (4.3-41). Integrals $I^{(J)}_{M',\,M}(t)$ can be readily evaluated if we use the results tabulated in Table VII and VIII and note the orthonormalization condition

$$\int \Psi^{m';n'\,*}_{j'}(\vec{\Omega})\,\Psi^{m;n}_{j}(\vec{\Omega})\,d^3\Omega = \delta_{jj'}\delta_{mm'}\delta_{nn'} \ . \qquad (4.3\text{-}45)$$

Thus we find the integrals $I^{(J)}_{MN}(t)$ are given as follows:

$$I^{(1)}_{11}(t) = \tfrac{1}{2}\{e^{-(D_1+D_3)|t|} + e^{-(D_2+D_3)|t|}\} \ ,$$

$$I^{(1)}_{1,-1}(t) = \tfrac{1}{2}\{e^{-(D_1+D_3)|t|} - e^{-(D_2+D_3)|t|}\} \ ,$$

$$I^{(1)}_{0\,0}(t) = e^{-(D_1+D_2)|t|}$$

$$I^{(2)}_{22}(t) = \frac{1}{8\Delta}\{\alpha^+ e^{-(6D+2\Delta)|t|} + \alpha^- e^{-(6D-2\Delta)|t|}\} + \tfrac{1}{2}\,e^{-3(D+D_3)|t|} \ ,$$

$$I^{(2)}_{20}(t) = \frac{1}{4\Delta}\left(\frac{3}{2}\right)^{\frac{1}{2}}(D_1 - D_2)\left\{e^{-(6D+2\Delta)|t|} - e^{(6D-2\Delta)|t|}\right\} ,$$

$$I^{(2)}_{2-2}(t) = \frac{1}{8\Delta}\left\{\alpha^+ e^{-(6D+2\Delta)|t|} + \alpha^- e^{-(6D-2\Delta)|t|}\right\} - \tfrac{1}{2} e^{-3(D+D_3)|t|} ,$$

$$I^{(2)}_{11}(t) = \tfrac{1}{2}\left\{e^{-3(D+D_1)|t|} + e^{-3(D+D_2)|t|}\right\} ,$$

$$I^{(2)}_{1-1}(t) = \tfrac{1}{2}\left\{e^{-3(D+D_1)|t|} - e^{-3(D+D_2)|t|}\right\}$$

$$+ \tfrac{1}{2}\left\{e^{-(D_1+D_3)|t|} - e^{-(D_2+D_3)|t|}\right\} ,$$

and

$$I^{(2)}_{00}(t) = \frac{1}{4\Delta}\left\{\alpha^- e^{-(6D+2\Delta)|t|} + \alpha^+ e^{-(6D-2\Delta)|t|}\right\} .$$

All the other $I^{(1)}_{ij}$ and $I^{(2)}_{ij}$'s are obtained from the relation

$$I^{(J)}_{ij}(t) = I^{(J)}_{ji}(t) = I^{(J)}_{-i-j} .$$

In case $D_1 = D_2$, $I^{(J)}_{ij}(t)$ is zero unless $i = j$.

(b) Langevin equation and angular momentum correlation functions.

The use of a Langevin-type equation for evaluating angular momentum correlation functions was first suggested by Hubbard,[28] and actually he has used the equation[14]

$$I\frac{d\vec{\omega}}{dt} = -\beta\vec{\omega} + \vec{A}(t) \tag{4.3-46}$$

to evaluate the correlation functions of angular velocity $\vec{\omega}$ for a spherical particle, where I is the moment of inertia of the particle and $-\beta\vec{\omega}$ and $\vec{A}$ are the frictional and fluctuating part of the torque suffered by the particle, respectively. However, in a molecule like ϕ-CF_3 we are confronted by two tough tasks which have not been considered by Hubbard. First problem is 'how can we extend Eq. (4.3-46) so that the anisotropy in rotational Brownian motions can be taken into account?', and the second question is 'how can we include the internal rotation in this Langevin formalism?' In order to find the equations which can give answers to these questions we go back to the classical equations of motion

$$\frac{d\vec{J}}{dt} = \vec{N}(t) \quad \text{and} \quad \frac{d\vec{j}_\alpha}{dt} = \vec{n}(t) \quad , \tag{4.3-47}$$

where $\vec{J}$ and $\vec{j}_\alpha$ are the total rotational angular momentum of the entire molecule and of the internal top only, respectively, and $\vec{N}(t)$ and $\vec{n}(t)$ are the corresponding torques. In a body-fixed frame rotating with an angular velocity $\vec{\omega}$, which is the angular velocity of end-over-end molecular rotation, with respect to the laboratory coordinate system, Eq. (4.3-47) may be written in the component form as

$$\frac{dJ_x}{dt} = -(\omega_y J_z - \omega_z J_y) + N_x(t) \quad ,$$

$$\frac{dJ_y}{dt} = -(\omega_z J_x - \omega_x J_z) + N_y(t) \quad ,$$

$$\frac{dJ_z}{dt} = -(\omega_x J_y - \omega_y J_x) + N_z(t) \quad ,$$

and

$$\frac{dj_\alpha}{dt} = n_z(t) \quad . \tag{4.3-48}$$

It is well known that it is not possible to solve Eq. (4.3-48) analytically if the nonlinear term $(\vec{\omega} \times \vec{J})$ does not vanish. Therefore we assume that $\vec{\omega}$ is so small that the nonlinear term may be ignored. This assumption is well compatible with the assumption of small-angle rotation for end-over-end molecular rotation. If the end-over-end rotation of entire molecule can be described by the rotational diffusion process, the term $(\vec{\omega} \times \vec{J})$ may well be ignored. As in the traditional Langevin formalism, $N_x(t)$ and $N_y(t)$ may be assumed to take the form

$$N_x = - f_x \omega_x + A_x(t)$$

and

$$N_y = - f_y \omega_y + A_y(t) \quad , \tag{4.3-49}$$

where f_x and f_y are friction coefficients about x- and y-axes, respectively, and $A_x(t)$ and $A_y(t)$ are the corresponding randomly fluctuating torques.

In the presence of internal rotation it is not easy to assume appropriate forms of N_z and n_z. In the j_α-limit j_α is supposed to fluctuate independently of J_x and J_y and moreover j_α is not considered to be correlated to the z-component of $\vec{\omega}$. Thus, in the j_α-limit we formally write

$$n_z = - g(\omega_z + \dot{\alpha}) + a_z(t) \quad , \tag{4.3-50}$$

where $a_z(t)$ is the fluctuating torque exerted on the internal top and g is the damping factor which eliminates the dynamical coherence of j_α. If the change of j_α is due to frictional forces from neighboring molecules, we may assume that g is proportional to the viscosity of medium. On the other hand, if the random change of j_α mainly arises from intermolecular collisions, we will assume that g is inversely proportional to τ_c, the mean collision time.

On the other hand, in the j-limit the fluctuation of j is controlled by the internal torque between two successive intermolecular collisions which randomly change j. Therefore, in this case j is supposed to be uncorrelated to J_z, while J_z is changed by the external torque alone. Thus, in the j-limit it is convenient if we assume

$$\frac{dJ_z}{dt} = -f_z\dot{\varphi} + A_z(t) \quad , \qquad (4.3\text{-}51)$$

where

$$\dot{\varphi} = \omega_z + (I_\alpha/I_z)\dot{\alpha} \quad . \qquad (4.3\text{-}52)$$

As for the autocorrelation function of j (or j_α) we may use a method similar to that described by Rice.[38] Suppose a sequence of events, in which j loses its dynamical coherence with previous values, occurs at random, separated by an average time τ_j; if the probability P that n events occur in a time interval of length τ is given by the Poisson distribution

$$P(n,\tau) = (1/n!)(\tau/\tau_j)^n \exp(-|\tau|/\tau_j) \quad , \qquad (4.3\text{-}53)$$

then we have

$$\begin{aligned} \langle j(t+\tau)\, j(t)\rangle &= \langle j^2\rangle \; P(0,\tau) \\ &= \langle j^2\rangle \; \exp(-|\tau|/\tau_j) \quad . \qquad (4.3\text{-}54) \end{aligned}$$

The same procedure can be applied for evaluating the autocorrelation function of j_α in the j_α-limit.

In the j-limit we obtain from (4.3-49)

$$J_x(t) = J_x(0)\exp(-f'_x t) + \exp(-f'_x t)\int_0^t \exp(f'_x \xi)\, A_x(\xi)d\xi \ ,$$

$$J_y(t) = J_y(0)\exp(-f'_y t) + \exp(-f'_y t)\int_0^t \exp(f'_y \xi)\, A_y(\xi)d\xi \ . \qquad (4.3\text{-}55)$$

In the j-limit we need $\langle J_z(t+\tau)\, J_z(t)\rangle$, too. Therefore, we also obtain from (4.3-51)

$$J_z(t) = J_z(0)\exp(-f'_z t) + \exp(-f'_z t)\int_0^t \exp(f'_z \xi)\, A_z(\xi)d\xi \ . \qquad (4.3\text{-}56)$$

In (4.3-55) and (4.3-56) f'_x, f'_y, and f'_z are defined by

$$f'_x = f_x/I_x \ , \quad f'_y = f_y/I_y \ , \quad \text{and} \quad f'_z = f_z/I_z \ . \qquad (4.3\text{-}57)$$

In order to evaluate the various correlation functions we make the following assumptions for the components of torques $\vec{A}(t)$ as in the theory of translational Brownian motion:

(1) The average values of $A_i(t)$ at a given time over an ensemble of particles are zero, that is,

$$\langle A_i(t)\rangle = 0 \ ; \qquad (4.3\text{-}58)$$

(2) $A_i(t)$ fluctuates so fast that all the relevant components of rotational angular momentum at a given time are not correlated with $A_i(t)$ at a later time, that is,

$$\langle J_i(t)\, A_j(t')\rangle = 0 \qquad (i, j = x, y, z) \qquad (4.3\text{-}59)$$

for all time $t < t'$.

With the aid of these assumptions we obtain from (4.3-55) and (4.3-56)

$$\langle J_x(t)\, J_x(0)\rangle = \langle J_x^2\rangle \exp(-f'_x|t|) \quad ,$$

$$\langle J_y(t)\, J_y(0)\rangle = \langle J_y^2\rangle \exp(-f'_y|t|) \quad , \quad \text{and}$$

$$\langle J_z(t)\, J_z(0)\rangle = \langle J_z^2\rangle \exp(-f'_z|t|) \quad , \qquad (4.3\text{-}60)$$

where the third expression is valid only in the j-limit.

Use of the Stokes hydrodynamic approach yields the friction coefficients in a medium of viscosity η,[8, 9] as

$$f_x = 16\pi\eta(b^2+c^2)/[3(b^2Q+c^2R)] \quad ,$$

$$f_y = 16\pi\eta(c^2+a^2)/[3(c^2R+a^2P)] \quad , \quad \text{and}$$

$$f_z = 16\pi\eta(a^2+b^2)/[3(a^2P+b^2Q)] \quad , \qquad (4.3\text{-}61)$$

where P, Q, and R are the elliptical integrals

$$P = \int_0^\infty (a^2+r)^{-3/2}\,(b^2+r)^{-1/2}\,(c^2+r)^{-1/2}\,dr \quad ,$$

$$Q = \int_0^\infty (b^2+r)^{-3/2}\,(c^2+r)^{-1/2}\,(a^2+r)^{-1/2}\,dr \quad , \quad \text{and}$$

$$R = \int_0^\infty (c^2+r)^{-3/2}\,(a^2+r)^{-1/2}\,(b^2+r)^{-1/2}\,dr \quad . \qquad (4.3\text{-}62)$$

Therefore, if the viscosity data of the medium are available, we can calculate the correlation times τ_{J_x} and τ_{J_y} in the j_α-limit and the correlation times τ_{J_x}, τ_{J_y}, and τ_{J_z} in the j-limit.

4.4 Some Criticisms about the Application of Theory of Rotational Brownian Motion to the Actual Molecular Reorientation Processes

So far we have been emphasizing the application of rotational Brownian motion model to the actual molecular reorientation processes.

However, as we have pointed out in the introductory section of this chapter, there are many questions about the applicability of Brownian motion theory to the molecular reorientation processes in condensed phases. As is well known, the theory of Brownian motion was proposed to explain the motion of a Brownian particle which is much larger in magnitude than molecules of the medium in which it is suspended. Therefore, a Brownian particle supposedly suffers a tremendous number of collisions (10^{21} collisions per second) with molecules of the medium, whence it travels infinitesimal distance between two successive collisions so that the diffusion equation can be valid. The same thing can be said for the rotational Brownian motion. We know that in many solutions solute molecules have about the same size as solvent molecules. Now, we question ourselves 'Can the rotational Brownian motion be applied to the reorientation of solute molecules surrounded by solvent molecules or to the reorientation of molecules in pure liquids?' Obviously, we shall hesitate to answer 'Yes'. Long time ago Kauzmann[30] has questioned the validity of the concept of a rotational friction coefficient based on a diffusion model of infinitesimal reorientations. He has contended that the temperature dependence observed in dielectric relaxation indicates that reorientation most likely proceeds by discrete jumps between stable orientations separated by a potential barrier. One of the points of recent arguments about the applicability of rotational Brownian motion is the relative magnitudes of dielectric and NMR (dipolar) correlation times. Since the electric dipole moment vector is a first-rank tensor and magnetic dipolar coupling tensor is second-rank, dielectric correlation time, τ_μ, and NMR correlation time τ_2, are given by

$$\tau_\mu = (2D)^{-1} \qquad \text{and} \qquad \tau_2 = (6D)^{-1} \qquad (4.4\text{-}1)$$

for the case of isotropic diffusion (see Sec. 4.3(a)), where D is the isotropic diffusion coefficient. Therefore, if molecular reorientation proceeds by the isotropic diffusion, the condition $\tau_2 = \frac{1}{3}\tau_\mu$ should be satisfied. When molecular reorientation proceeds by large-angle jumps, the relation $\tau_2 = \frac{1}{3}\tau_\mu$ is not valid;[31] instead we expect that $\tau_\mu \approx \tau_2$. Powles[32] has pointed out that many liquids, including highly associated liquids such as water, reorient by small-angle jumps and the relation $\tau_\mu/\tau_2 \approx 3$ is satisfied. However, this conclusion can hardly be said to be universally acceptable, since the interpretation of infrared band shape due to Gordon,[1,10] as we have previously mentioned, indicates that the assumption of small-angle jumps is hardly acceptable for small molecules even in liquid phases. Waugh[33] has also suggested that a water molecule might jump through a large angle, breaking one set of hydrogen bonds and making another while there might be co-operative motions of molecular aggregates that might involve smaller angles. This question has arisen not only in the distribution function approach to the rotational Brownian motion but also in the Langevin approach. Mori[34] and Kubo[35] have contended that if the particle under consideration is not necessarily heavier than neighboring particles with which it interacts the classical Langevin equation should be modified to

$$\frac{dv}{dt} = -\int_{t_0}^{t} \gamma(t-t')\, v(t')dt' + R(t)/m \ , \qquad t > t_0 \qquad (4.4\text{-}2)$$

where the function $\gamma(t)$ represents a retarded effect of the frictional force and R(t) is the random force. Likewise for the rotational motion we can say that if the moment of inertia of the particle is not necessarily larger than that of neighboring particles Eq. (4.3-46) may be generalized to

$$I \frac{d\vec{\omega}}{dt} = - \int_{t_0}^{t} \beta(t-t') \, \vec{\omega}(t')dt' + \vec{A}(t) \quad . \qquad (4.4\text{-}3)$$

Application of Eq. (4.4-2) for obtaining the velocity correlation function has been given by Kubo[36] and the same method was employed by Rigny and Virlet[37] to obtain the angular momentum correlation function for spherical molecules. However, because of mathematical difficulty we could not be successful to extend the application of an equation similar to (4.4-3) to the case of anisotropic rotational diffusion. For the present there will be many questions unanswered about the molecular reorientation process. It is needless to say that a more complete answer should come from the solution of quantum equations of motion for an N-particle system.

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APPENDIX I

Let P_1, P_2, and P_3 be probabilities that we find a particular proton at three distinguishable sites 1, 2, and 3, respectively, and also let W be the transition rate per unit time between sites. Then, the following master equations will hold:

$$\frac{dP_1}{dt} = -2WP_1 + W(P_2 + P_3) \quad , \tag{AI-1}$$

$$\frac{dP_2}{dt} = -2WP_2 + W(P_1 + P_3) \quad , \tag{AI-2}$$

and

$$\frac{dP_3}{dt} = -2WP_3 + W(P_1 + P_2) \quad . \tag{AI-3}$$

Suppose at $t = 0$ we know that $P_1 = 1$ and $P_2 = P_3 = 0$. Since the sites 2 and 3 are equivalent, the symmetry condition $P_2 = P_3$ will be maintained even after the elapse of an arbitrary amount of time, say τ. Thus, with the aid of this condition we obtain from (AI-1) and (AI-2)

$$\frac{d}{dt}(P_1 - P_2) = -3W(P_1 - P_2)$$

and

$$\frac{d}{dt}(P_1 + 2P_2) = 0 \quad ,$$

of which the second relation indicates nothing but the fact that the total probability $P_1 + P_2 + P_3$ should be conserved. Therefore we obtain

$$P_1(\tau) = \tfrac{1}{3} + \tfrac{2}{3}\exp(-3W\tau)$$

and

$$P_2(\tau) = P_3(\tau) = \tfrac{1}{3} - \tfrac{1}{3}\exp(-3W\tau) \quad . \tag{AI-4}$$

APPENDIX II

In the Cayley-Klein representation any vector $\vec{A}$ is replaced by a 2×2 matrix $\vec{\sigma} \cdot \vec{A}$, where $\vec{\sigma}$ indicates the three Pauli spin matrices, that is,

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \text{and} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} .$$

The components of $\vec{A}$ in one coordinate system are then obtained from the components in the other by performing a unitary transformation on $\vec{\sigma} \cdot \vec{A}$. Thus

$$(\vec{\sigma} \cdot \vec{A})_{\text{body}} = \underset{\sim}{Q} \cdot (\vec{\sigma} \cdot \vec{A})_{\text{lab}} \, \underset{\sim}{Q}^{\dagger} \quad . \qquad \text{(AII-1)}$$

The transformation matrix Q is given by

$$\underset{\sim}{Q} = Q_{\psi} Q_{\theta} Q_{\phi}$$

where

$$Q_{\psi} = \begin{pmatrix} e^{i\psi/2} & 0 \\ 0 & e^{-i\psi/2} \end{pmatrix}, \quad Q_{\theta} = \begin{pmatrix} \cos\frac{\theta}{2} & \sin\frac{\theta}{2} \\ -\sin\frac{\theta}{2} & \cos\frac{\theta}{2} \end{pmatrix}$$

and

$$Q_{\phi} = \begin{pmatrix} e^{i\phi/2} & 0 \\ 0 & e^{i\phi/2} \end{pmatrix} \quad . \qquad \text{(AII-2)}$$

On the other hand if the body-fixed coordinate system is rotated away from the laboratory coordinates through an angle α about the axis specified by the unit vector $\hat{n}$, then

$$\underset{\sim}{Q} = e^{i\hat{n}\alpha \cdot \vec{\sigma}/2} = \Gamma \, \underset{\sim}{1} + i\vec{\sigma} \cdot \vec{\Omega} \quad , \qquad \text{(AII-3)}$$

where $\Gamma = \cos(\alpha/2)$, $\vec{\Omega} = \hat{n} \sin(\alpha/2)$, and $\underset{\frown}{1}$ is a unit matrix.

Equating two different expressions for $\underset{\frown}{Q}$, we obtain

$$\begin{aligned}
\Gamma &= \cos(\alpha/2) = \cos\frac{\theta}{2}\cos\frac{\psi+\phi}{2} \quad , \\
\Omega_X &= n_X \sin(\alpha/2) = \sin\frac{\theta}{2}\sin\frac{\psi-\phi}{2} \quad , \\
\Omega_Y &= n_Y \sin(\alpha/2) = \sin\frac{\theta}{2}\cos\frac{\psi-\phi}{2} \quad , \qquad \text{and} \\
\Omega_Z &= n_Z \sin(\alpha/2) = \cos\frac{\theta}{2}\sin\frac{\psi+\phi}{2} \quad .
\end{aligned}$$

PROPOSITIONS

PROPOSITION I

It is proposed that the intermolecular potential function of the exp-6 type had better be used than that of the Lennard-Jones type in order to interpret the proton T_1 data in gaseous molecular hydrogen on the basis of Bloom-Oppenheim theory.

Recently Bloom and Oppenheim[1-3] have developed a theory in which the correlation time for molecular rotation can be expressed in terms of the intermolecular force. To demonstrate the usefulness of their theory Bloom, Oppenheim, and their co-workers[4] have evaluated the proton spin-lattice relaxation time in gaseous molecular hydrogen assuming that the r-dependent part of intermolecular force can be represented by the Lennard-Jones type potential function and obtained seemingly excellent results. In the meantime Christensen[5] has measured the spin-lattice relaxation time of proton in gaseous HD and found that the proton T_1 in HD is much longer than that in H_2. A crude evaluation due to Christensen indicates that the potential function of the Lennard-Jones type may not adequately represent the isotropic part of intermolecular force in gaseous molecular hydrogen and therefore its contribution to the anisotropic part of intermolecular force in HD gas may be too small.

Thus, it is proposed that we have to test the exp-6 type intermolecular force to interpret the proton T_1 data in both H_2 and HD. The observed relaxation rate can be written as

$$\frac{1}{T_1} = \sum_J P_J \left(\frac{1}{T_1}\right)_J \quad , \tag{I-1}$$

where P_J is the probability at thermal equilibrium that the J-state is occupied and $(1/T_1)_J$ represents the spin relaxation rate within a given J-manifold. Abragam[6] shows that

$$\left(\frac{1}{T_1}\right)_J = \frac{2\gamma^2 H'^2 J(J+1)}{3}\, \tau_1^J + \frac{6\gamma^2 H''^2 J(J+1)}{(2J-1)(2J+3)}\, \tau_2^J \quad , \qquad \text{(I-2)}$$

where τ_1^J and τ_2^J are, respectively, angular momentum and orientational correlation times within a given J-manifold, and $H'(= 26.752 \pm 0.007$ gauss) and $H''(= 33.862 \pm 0.015$ gauss) are the spin-rotation and dipole-dipole coupling constants in a H_2 molecule.

An explicit form of the intermolecular force between two interacting hydrogen molecules is given by Nakamura[7] and Moriya and Motizuki.[8] Using this intermolecular potential function we can obtain from the Bloom-Oppenheim theory

$$\frac{1}{\tau_1^J} = \frac{(\pi\beta M)^{\frac{1}{2}}\,\rho}{(2J-1)(2J+3)\hbar^2} \left[\int_0^\infty F(u)\,du + \frac{2}{15}\,\xi \int_0^\infty K(u)\,du\right] \qquad \text{(I-3)}$$

and

$$\frac{1}{\tau_2^J} = \frac{3(4J^2+4J-7)}{(2J-1)(2J+3)}\,\frac{1}{\tau_1^J} \quad , \qquad \text{(I-4)}$$

where

$$F(u) = \frac{4\pi}{5}\left\{\int_0^\infty [g(r)]^{\frac{1}{2}}\, r^{\frac{3}{2}}\, f(r)\, J_{\frac{5}{2}}(ur)\,dr\right\}^2 \quad , \qquad \text{(I-5)}$$

$$K(u) = \frac{4\pi}{175}\left\{7\left[\int_0^\infty [g(r)]^{\frac{1}{2}}\, r^{\frac{3}{2}}\, X(r)\, J_{\frac{1}{2}}(ur)\,dr\right]^2\right.$$

$$\left. + 10\left[\int_0^\infty [g(r)]^{\frac{1}{2}}\, r^{\frac{3}{2}}\, Y(r)\, J_{\frac{5}{2}}(ur)\,dr\right]^2\right.$$

$$+ 2 \left[\int_0^{\infty} [g(r)]^{\frac{1}{2}} r^{\frac{3}{2}} Z(r)\, J_{\frac{9}{2}}(ur)\, dr \right]^2 \Bigg\} \qquad \text{(I-6)}$$

along with

$$f(r) = A \exp(-r/r_0) + (2Q-4R/3)/r^6 \ ,$$

$$X(r) = A' \exp(-r/r_0) - R/r^6 \ ,$$

$$Y(r) = A' \exp(-r/r_0) + R/r^6 \ , \quad \text{and}$$

$$Z(r) = 3A' \exp(-r/r_0) - 18R/r^6 + (105/2)(e^2 \mu_Q^2/r^5) \ . \qquad \text{(I-7)}$$

$g(r)$ is the radial distribution function, $J_n(x)$ represents the n-th order Bessel function, μ_Q is the quadrupole moment of H_2 molecule, and A, A′, Q, R, P, and r_0 are all known (or at least empirically determined) parameters.

ξ is the ensemble average of $\{J(J+1)/(2J-1)(2J+3)\}$ and ρ is the density of gas.

In order to determine the radial distribution function $g(r)$ we use the exp-6 potential function

$$V(r) = B \exp(-r/r_0) - (2P/3)/r^6 \ . \qquad \text{(I-8)}$$

However, this isotropic potential function is not adequate for determining $g(r)$, since it does not behave properly about $r = 0$. Since contributions from this very short distance to integrals in Eq. (I-5) and (I-6) are completely negligible, we can replace the lower limit of integrals by a small number ϵ for which we may assume

$$V(r) = +\infty \qquad \text{for} \quad r < \epsilon$$

and

$$V(r) = B \exp(-r/r_0) - (2P/3)/r^6 \qquad \text{for} \quad r \geq \epsilon \ . \qquad \text{(I-9)}$$

The radial distribution function for dilute gases can be written as

$$g(r) = \exp[-\beta V(r)] \quad , \tag{I-10}$$

where

$$\beta = \frac{1}{kT} \quad .$$

If the density of the gas is not too low, we have to add the density correction to g(r). The first density correction to the radial distribution function is given by Oppenheim and Mazur[9] as

$$g(r) = \exp[-\beta V(r)] \ \{1+\rho\gamma(r)\} \quad , \tag{I-11}$$

where

$$\begin{aligned}\gamma(r) = & \int \{\exp[-\beta(V_{13}+V_{23})] - 1\} d\vec{r_3} \\ & - 2 \int \{\exp(-\beta V_{12}) - 1\} d\vec{r_2} \quad .\end{aligned} \tag{I-12}$$

It is desirable that after evaluating integrals (I-5) and (I-6) results should be applied to the case of HD.

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PROPOSITION II

Recently, H. Eyring, T. Ree, and their collaborators[1] proposed the so-called "Significant Structure Theory" of liquid, applied their theory to many examples and have successfully explained many thermodynamic properties of such liquids that expand in volume by ca. 12% on melting. Such liquids will be referred to as normal liquids from now on.

The Significant Structure Theory is based on the assumption that many holes ("vacant sites") are introduced when solid melts into liquid, and in liquid phase each molecule can have both the solid-like and gas-like degrees of freedom. Even though the mathematical approach due to Mayer, Kirkwood and many other people is logically beautiful, at present it cannot give us much result because of mathematical difficulties involved in it. On the other hand, starting from somewhat intuitive and daring assumptions, the Significant Structure Theory has so far provided simple ways of explanation and calculation of thermodynamic properties of many liquids.[2-6]

Application of the SST to the molten state of metals have been attempted by Carlson, Ree, and Eyring.[5] They have assumed that in the molten state of metals the solid-like behaving molecule has the same frequency of oscillation both in the most stable position and in a neighboring vacancy. With this assumption, the partition function can be written as

$$\mathcal{F} = \left[\frac{\exp(E_s/RT)}{(1-e^{-\frac{\theta}{T}})^3}\ \{1+n_h\exp(-\epsilon/kT)\}\right]^{\frac{V_s}{V}N}$$

$$\cdot\left[\frac{(2\pi mkT)^{3/2}\,eV}{Nh^3}\right]^{\frac{V-V_s}{V}N}, \qquad \text{(II-1)}$$

where n_h is the number of holes surrounding the given molecule, ϵ is the strain energy which is required to shift the given molecule from its most favored position to its neighboring vacancy, E_s and θ, though not having such clear meanings as in the solid, are the heat of sublimation and the oscillation frequency of the assumed harmonic oscillator, respectively, and V_s and V are, respectively, molar volumes of solid and liquid. For normal liquids it has been usually assumed that

$$n_h = 12 \cdot \frac{V - V_s}{V} \qquad \text{(II-2)}$$

and the solid-like and the gas-like properties are distributed by factors V_s/V and $(V - V_s)/V$. However, it was found that Eq. (II-2) works poorly for the molten state of metals. Thus Carlson et al. have assumed

$$n_h = n \cdot \frac{V - V_s}{V}, \qquad \text{(II-3)}$$

where n is a parameter to be determined. There are many things in Carlson's work which must be pointed out. First, the meaning of the parameter n is not clear, which was originally interpreted as the maximum number of available sites for a given molecule. Second, to obtain the calculated value which are coincident with experimental data n has to assume values of 25 to 45 which varies from one kind of metal to another. Third, even with those assumed values of n good results could not be obtained for the vapor pressure which is very sensitive to the partition functional form. Therefore, it is natural to look for a more general partition function which include those for normal liquids as special cases.

To begin with, a glance at the partition function (II-1) leads us to the question why a solid-like molecule must have the same frequency both in the most favored site and in its neighboring sites. This is the starting point of new formulation. If we assume that the oscillation frequency in the most favored site is different from those in the neighboring sites, we can write our partition function as

$$\mathcal{F} = \left[\frac{\exp(E_s/RT)}{(1-\exp(-\theta_1/T))^3} \left\{ 1 + n_h \frac{(1-\exp(-\theta_1/T))^3}{(1-\exp(-\theta_2/T))^3} \exp(-\epsilon/RT) \right\} \right]^{\frac{V_s}{V} N} \cdot \left[\frac{(2\pi mkT)^{3/2}\, eV}{N h^3} \right]^{\frac{V-V_s}{V} N} \qquad \text{(II-4)}$$

Carlson has assumed (II-3), but we may assume with our new partition function that (II-2) will be all right.

According to the method of fixing parameters and calculating thermodynamical properties developed by Eyring <u>et al.</u> we can calculate easily the molar volume, vapor pressure and some other equilibrium properties. For example, for the molten state of potassium we obtain the following results:

Molar Volume (cc)

Temp (°K)	$V_{calc.}$	$V_{obs.}$
373.15	47.565	47.736
523.15	48.534	49.931
673.15	49.549	52.337
823.15	50.656	54.987
973.15	52.133	57.834

Vapor Pressure (atm.)

Temp (°K)	$P_{cal.}$	$P_{obs.}$
373.15	2.650×10^{-8}	2.681×10^{-8}
523.15	6.257×10^{-5}	7.111×10^{-5}
673.15	4.188×10^{-3}	5.446×10^{-3}
823.15	6.871×10^{-2}	8.423×10^{-2}
873.15	3.269×10^{-1}	5.509×10^{-1}

Both calculated values of the molar volume and the vapor pressure are smaller than experimental ones. In order to correct this deviation we note the fact that the ionic size is about one-third of the atomic size. Therefore, in this case better results may be obtained by assuming

$$n_h = 12(V - \tfrac{1}{3} V_s)/V \quad . \tag{II-5}$$

More generally we may assume

$$n_h = 12(V - m V_s)/V \quad , \tag{II-6}$$

where m is the parameter which varies from one kind of metal to another.

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PROPOSITION III

The use of nuclear quadrupole relaxation effect for the study of dynamics of internal rotation in a molecule in liquid is proposed.

It is well-known that a nucleus of $I > 1/2$ has nonvanishing electric quadrupole moment due to nonspherical distribution of nuclear charge and this quadrupole moment can interact with the electric field gradient at the site of nucleus. This quadrupole interaction energy fluctuates as the molecule undergoes random rotational motions due to intermolecular collisions in gases and liquids, thus causing the electric quadrupole to relax.

Assuming the axial symmetry of electric field gradient, the quadrupole relaxation time, T_1, for a nucleus of $I = 1$ is given by[1, 2]

$$\frac{1}{T_1} = \frac{9}{32}\left(\frac{e^2qQ}{\hbar}\right)^2 [\, J_1(\omega_0) + J_2(2\omega_0)] \quad , \tag{III-1}$$

where $(e^2qQ/\hbar) = 2\pi$ times the quadrupole coupling constant, ω_0 = the Larmor frequency, and

$$J_n(n\omega_0) = \int_{-\infty}^{\infty} \langle F_n{}^*(t+\tau)\, F_n(t)\rangle \; \exp(in\omega_0\tau)\, d\tau \qquad n = 1, 2 \tag{III-2}$$

with

$$F_1(t) = \sin\theta(t)\cos\theta(t)\exp(i\phi(t))$$

and

$$F_2(t) = \sin^2\theta(t)\exp(2i\phi(t)) \quad . \tag{III-3}$$

θ and ϕ are, respectively, polar and azimuthal angles of the symmetry axis of electric field gradient with respect to a molecule-fixed frame.

For the study of molecular reorientation process in liquids the application of quadrupole relaxation phenomena has in general several advantages over that of nuclear magnetic relaxation phenomenon. In the nuclear relaxation processes which take place in an ensemble of nuclei which have no electric quadrupole moment the magnetic relaxation will be induced mainly via the dipolar interactions among nuclei. Unfortunately, we cannot separate the relaxation induced via the intramolecular interactions from the whole phenomena. The contribution from the intermolecular interactions has, in general, comparable magnitude with that from the intramolecular interactions, and, moreover, estimation of the former contribution is so difficult that we cannot treat it with reasonable rigor.[3] However, if we use the nuclei of $I > 1/2$, this difficulty can be avoided. The magnitude of the magnetic field produced by a point dipole moment of the order of a nuclear magneton, being apart of the order of angstrom, is a few gauss, and the energy of the interaction of a ^{14}N magnetic moment with this field is of the order of 10^{-4} Mc/sec. On the other hand, the interaction of the quadrupole moment of this nucleus with the electric field gradient there yields a potential energy of the order of Mc/sec.[4] Thus, we can safely neglect all the contributions from the dipolar interactions compared with that from the quadrupole interaction, whose randomness depends only on the rotational motion of the molecule under consideration.

When the nucleus under consideration is located on an internal top in the molecule, the quadrupole interaction is modulated not only by end-over-end molecular rotation but also on internal rotation. For an example we take a nucleus of $I = 1$ located on an internal top in the molecule whose shape can be approximated to an ellipsoid, and let us assume that end-over-end molecular rotation in liquid can be described by the anisotropic diffusion equation.[5-8] Then, it can be shown that[9]

$$\langle F_n^*(t+\tau)\, F_n(t)\rangle = \tfrac{1}{2} K_n[B_A \exp(-|\tau|/\tau_A) + B_B \exp(-|\tau|/\tau_B) + B_C \exp(-|\tau|/\tau_C)] \quad , \qquad \text{(III-4)}$$

where $K_1 = 2/15$, $K_2 = 8/15$, $1/\tau_A = 6R_2$, $1/\tau_B = R_1 + 5R_2$, $1/\tau_C = 4R_1 + 2R_2$; R_1 is the rotational-diffusion constant of the ellipsoid about its major axis, R_2 is the rotational-diffusion constant of the ellipsoid about its minor axis, and

$$\begin{aligned} B_A &= \frac{1}{2}\langle[1 - 3\cos^2\theta(t+\tau)]\cdot[1 - 3\cos^2\theta(t)]\rangle \quad , \\ B_B &= \frac{3}{2}\langle\sin 2\theta(t+\tau)\exp[-i\phi(t+\tau)]\ \sin\theta(t)\exp[i\phi(t)]\rangle \quad , \\ B_C &= \frac{3}{2}\langle\sin^2\theta(t+\tau)\exp[-2i\phi(t+\tau)]\ \sin^2\theta(t)\exp[2i\phi(t)]\rangle \quad . \qquad \text{(III-5)} \end{aligned}$$

The correlation functions B_A, B_B, and B_C depend only on the internal reorientation process, and therefore they cannot be evaluated without any knowledge of the dynamics of internal rotation. However, B_A, B_B, and B_C can be reduced to more feasible forms as follows. Let us choose another body-fixed frame (x', y', z') so that the z'-axis coincides with the axis of notation of the internal top, and let the polar and azimuthal angle of the symmetry axis of electric field gradient at the site of nuclear spin with respect to this frame be Δ and $\phi'(t)$. Also let the polar angle of z'-axis with respect to the symmetry axes of ellipsoid be α. Then, it may be shown that[2]

$$B_A = B_{A_1} + B_{A_2}\langle \cos \phi''(t)\rangle + B_{A_3}\langle \cos 2\phi''(\tau)\rangle \quad ,$$

$$B_B = B_{B_1} + B_{B_2}\langle \cos \phi''(\tau)\rangle + B_{B_3}\langle \cos 2\phi''(\tau)\rangle \quad , \quad \text{and}$$

$$B_C = B_{C_1} + B_{C_2}\langle \cos \phi''(\tau)\rangle + B_{C_3}\langle \cos 2\phi''(\tau)\rangle \qquad \text{(III-6)}$$

with

$$\phi''(\tau) = \phi'(t+\tau) - \phi'(t) \quad ,$$

$$B_{A_1} = (1/8)(1-3\cos^2\alpha)^2\,(1-3\cos^2\Delta)^2 \quad ,$$

$$B_{A_2} = (9/16)\sin^2 2\alpha \sin^2 2\Delta, \;\; B_{A_3} = (9/16)\sin^4\Delta \sin^4\alpha \quad ,$$

$$B_{B_1} = (3/8)\sin^2 2\alpha\,(3\cos^2\Delta - 1)^2 \quad ,$$

$$B_{B_2} = (3/4)(\cos^2 2\alpha + \cos^2\alpha)\sin^2 2\Delta \quad ,$$

$$B_{B_1} = (3/4)(\sin^2\alpha + \tfrac{1}{4}\sin^2 2\alpha)\sin^4\Delta \quad ,$$

$$B_{C_1} = (3/8)\sin^4\alpha\,(3\cos^2\Delta - 1)^2 \quad ,$$

$$B_{C_2} = (3/4)(\sin^2\alpha + \tfrac{1}{4}\sin^2 2\alpha)\sin^2 2\Delta$$

and

$$B_{C_3} = (3/16)[(1+\cos^2\alpha)^2 + 4\cos^2\alpha]\sin^4\Delta \quad . \qquad \text{(III-7)}$$

In order to evaluate $\langle \cos \phi''(\tau)\rangle$ and $\langle \cos 2\phi''(\tau)\rangle$ we must assume a model for the time dependence of $\phi''(\tau)$. If the internal reorientation is such that the nucleus jumps among three equivalent sites, as a deuterated terminal methyl group in an n-paraffin molecule probably does, then both $\langle \cos \phi''(\tau)\rangle$ and $\langle \cos 2\phi''(\tau)\rangle$ become $\exp(-R|\tau|)$, where R is (3/2) times the total rate of jumping of a deuterated methyl group from any of its three equivalent orientations. In this case we have from (III-6)

$$B_A = B_{A_1} + (B_{A_2} + B_{A_3}) \exp(-R|\tau|) \quad ,$$

$$B_B = B_{B_1} + (B_{B_2} + B_{B_3}) \exp(-R|\tau|) \quad , \qquad \text{and}$$

$$B \ = B_{C_1} + (B_{C_2} + B_{C_3}) \exp(-R|\tau|) \quad . \tag{III-8}$$

If the functional group does not reorient by random jumps between three equivalent positions, but instead can assume any orientation with equal probability, the time dependence of $\phi''(\tau)$ must be redefined. If we now can assume a stochastic diffusion process in which the time dependence of $\phi''(\tau)$ is defined, so that the probability of finding the internuclear vector at $\phi''(\tau)$ at time $t+\tau$ is given by the Gaussian distribution

$$P[\phi''(\tau), \tau] = \tfrac{1}{2} (\pi D\tau)^{-\frac{1}{2}} \exp[-\phi''^2(\tau)/4D\tau] \quad , \tag{III-9}$$

where D is the rotational-diffusion constant of the functional group with respect to the axis of the ellipsoid, then B_A, B_B, and B_C take the form

$$B_A = B_{A_1} + B_{A_2} \exp(-D|\tau|) + B_{A_3} \exp(-4D|\tau|) \quad ,$$

$$B_B = B_{B_1} + B_{B_2} \exp(-D|\tau|) + B_{B_3} \exp(-4D|\tau|) \quad , \qquad \text{and}$$

$$B_C = B_{C_1} + B_{C_2} \exp(-D|\tau|) + B_{C_3} \exp(-4D|\tau|) \quad . \tag{III-10}$$

The end-over-end molecular rotations can be described fairly well by the rotational Brownian motion when the molecule is not too small,[5-8] and in such a situation the diffusion constants, R_1, R_2, and R_3, can be taken to be proportional to (T/η), where T and η are the temperature and macroscopic viscosity of medium. Therefore, if the temperature dependence of T_1, molecular structure, and viscosity of medium as a function of temperature are known, we can sort out the internal rotational contribution to the total relaxation rate $(1/T_1)$ and consequently can investigate the temperature dependence of either R or D in Eq. (III-8) or (III-10).

Recently, there have been some publications[9-12] which report that in the presence of internal rotation the intramolecular magnetic dipole-dipole interaction is relatively ineffective as a spin relaxation mechanism compared to the intermolecular dipole-dipole interaction. Woessner[13] interprets that the presence of internal rotation shortens the effective correlation time for the modulation of intramolecular dipole-dipole interaction, thus making the intramolecular dipole-dipole relaxation relatively unimportant. However, the study of internal rotation using the magnetic dipole relaxation effect encounters two major difficulties; first, as we have already mentioned, we cannot exactly separate the intramolecular contribution to $(1/T_1)$ from the whole phenomena, and secondly, in the presence of internal rotation even the estimation of intramolecular contribution is not easy. The use of quadrupole relaxation method in this case can eliminate both troubles and thus can give us fairly accurate knowledge about the process of internal reorientation in a molecule in liquid.

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PROPOSITION IV

H. J. Lucas[1] has reported 2-chloro-1-propanol(2ClP) has an anomalously large optical rotatory power compared with other compounds structurally similar to 2C1P. Mizushima[2] has indicated from the study of Raman spectra that it is quite possible to form a hydrogen bond in halogen-containing alcohols. So far many examples for the intramolecular hydrogen bond have been known.[3]

If the prediction of Mizushima is applied to the case of 2ClP, it provides us a means which can determine the intramolecular potential function due to hydrogen bonds in halogen-containing alcohols to measure the specific rotation of those compounds as a function of temperature. Experimentally measured values of the specific rotation are the average values over all rotation and can be expressed as

$$[\alpha]^{T} = \frac{\int_0^{2\pi} \alpha(\theta) \exp\{-V(\theta)/kT\} d\theta}{\int_0^{2\pi} \exp\{-V(\theta)/kT\} d\theta}, \qquad \text{(IV-1)}$$

where $\alpha(\theta)$ is the value of specific rotation for a certain configuration which is characterized by the internal angle θ. Since $\alpha(\theta)$ can be evaluated by making use of the Kirkwood polarizability theory[4] of optical rotatory power, Eq. (IV-1) can give us a means of determining the intramolecular potential function due to the hydrogen bond in halogen-containing alcohols. However, in order to apply the Kirkwood theory to our problem the accurate knowledge of molecular structure is required. Unfortunately, not much of the knowledge about the exact structures and spatial configurations of halogen-containing alcohols have been obtained yet, but we can check our proposal using a rather simple, though approximate, model of 2ClP.

Since $V(\theta)$ is obviously a periodic function of θ with period 2π, we can expand $V(\theta)$ into Fourier series as

$$V(\theta) = V_0 + V_1 \cos\theta + V_2 \cos 2\theta + \cdots$$
$$+ U_1 \sin\theta + U_2 \sin 2\theta + \cdots \quad , \qquad \text{(IV-2)}$$

where it is empirically known that only first few terms are important.

If experimental values of $[\alpha]$ at several different temperatures are available, we can determine a few coefficients in (IV-2).

According to Born[5] the specific rotation for an optically active molecule in a solution state is given by the relation

$$[\alpha]_D = 4.930 \times 10^5 \, (n^2+2) \, g/3M \quad , \qquad \text{(IV-3)}$$

where n is the refractive index of the solution and M is the molecular weight of the optically active molecule. g is the factor of determining the rotatory power which is characteristic of the given molecule. Kirkwood approximates g as

$$g^{(0)} = \frac{1}{6} \sum_{i>k} \alpha_i \alpha_k \beta_i \beta_k G_{ik} \vec{R}_{ik} \cdot (\vec{b}_i \times \vec{b}_k) \quad , \qquad \text{(IV-4)}$$

where

$$G_{ik} = \frac{1}{R_{ik}^3} \left\{ \vec{b}_i \cdot \vec{b}_k - \frac{3(\vec{b}_i \cdot \vec{R}_{ik})(\vec{b}_k \cdot \vec{R}_{ik})}{R_{ik}^2} \right\} , \qquad \text{(IV-5)}$$

$$\vec{R}_{ik} = \vec{R}_k - \vec{R}_i \, , \qquad \text{and}$$

α_i = mean polarizability of the constituents,

β_i = anisotropy ratio of each constituent,

$\vec{R}_i$ = position vector of the center of mass of i-th constituent,

and $\vec{b}_i$ and $\vec{b}_k$ are unit vectors in the directions of optically symmetric axes of the i-th and k-th constituents.

If we use the above formula and the simple structure for 2ClP, we can calculate $[\alpha]_D$ at an arbitrary angle. To obtain the coefficients V_i and U_i we have to pursue the following procedure:

(1) By using a simple molecular model we calculate $[\alpha]_D$ according to Kirkwood polarizability theory. If we select one conformation which will give the dominant effect on $[\alpha]_D$, the calculated value must show the approximate value for $[\alpha]_D$. If the calculated value for one or two dominant conformations agrees approximately with the observed value, we shall proceed to the next step;

(2) We have to obtain the general formula which shows the θ-dependence of $[\alpha]_D$.

(3) Finally, we introduce the Fourier expansion of this formula to calculate V_i's and U_i's.

Obviously if n numbers of experimental values of $[\alpha]_D$ at different temperatures are available, we can calculate n constants, V_i and U_i.

Now, we are going to show how we can use this method for 2C1P. Since the exact spatial structure has not been known well, we may use a simple model shown in Fig. 1 and Fig. 2.

We can express $\vec{b}_i$'s as functions of θ, using this model. Especially when $\theta = \pi/3$, we have

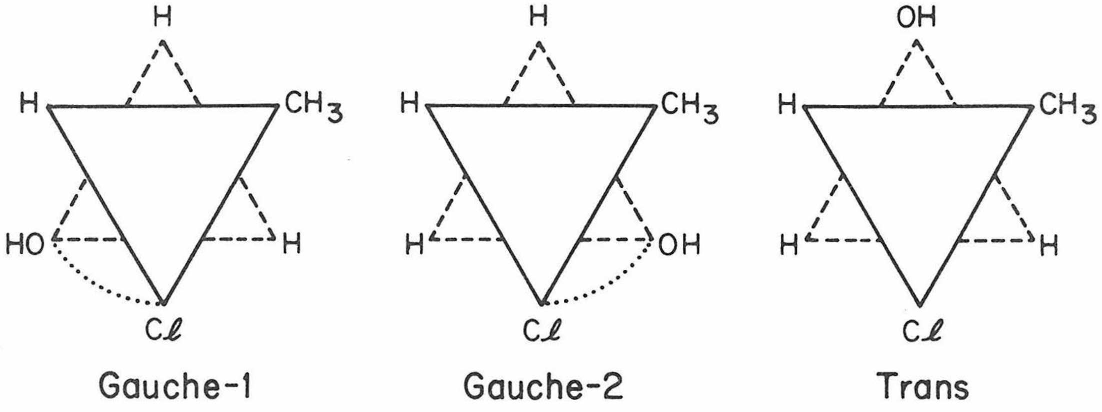

Fig. A Fischer Projection Formula of **L**(+)-2-chloro-1-propanol

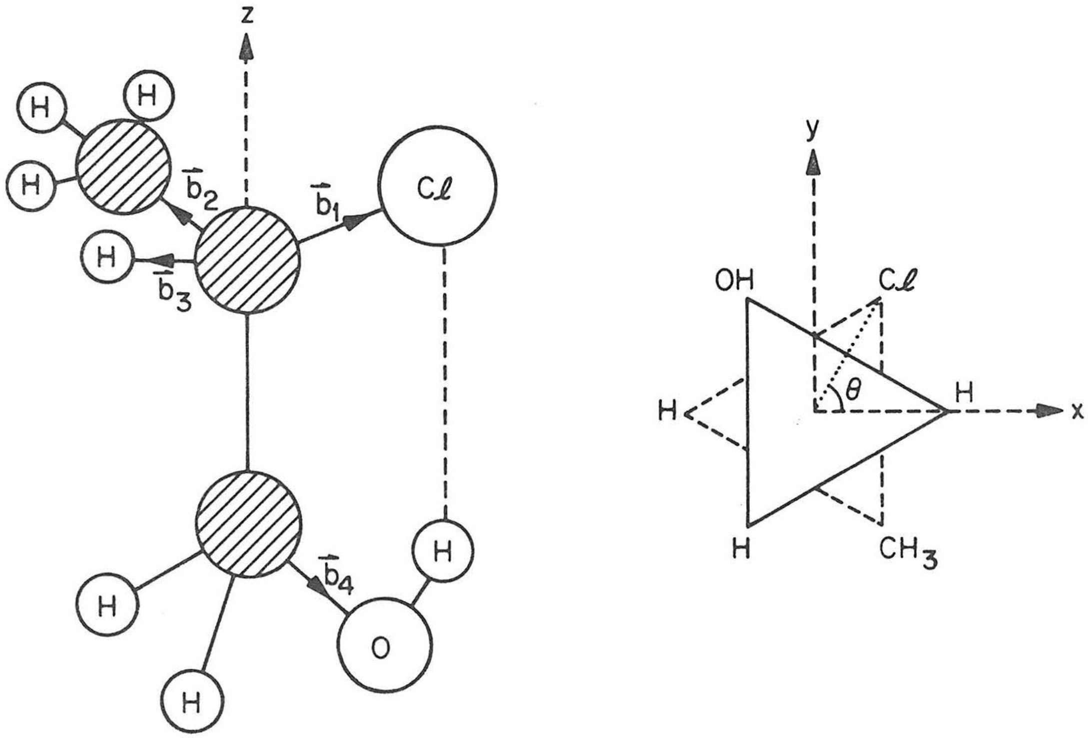

Fig.B Molecular Model of 2C 1P and its coordinates

$$\vec{b}_1 = \tfrac{1}{3}\,(\sqrt{2}\,\vec{i} + \sqrt{6}\,\vec{j} + \vec{k}) \quad ,$$

$$\vec{b}_2 = \tfrac{1}{3}\,(-2\sqrt{2}\,\vec{i} - \vec{k}) \quad ,$$

$$\vec{b}_3 = \tfrac{1}{3}\,(\sqrt{2}\,\vec{i} - \sqrt{6}\,\vec{j} + \vec{k}) \quad ,$$

and

$$\vec{b}_4 = \tfrac{1}{3}\,(2\sqrt{2}\,\vec{i} - \vec{k}) \quad , \tag{IV-6}$$

where we have assumed the tetrahedral structure of carbon sp^3 bonds.

For an arbitrary angle θ, each $\vec{b}_i$ can be expressed as

$$\vec{b}_i' = \begin{pmatrix} \cos(\theta-\pi/3) & -\sin(\theta-\pi/3) & 0 \\ \sin(\theta-\pi/3) & \cos(\theta-\pi/3) & 0 \\ 0 & 0 & 1 \end{pmatrix} \vec{b}_i \tag{IV-7}$$

where $\vec{b}_i$'s are unit vectors at $\theta = \pi/3$.

α_i and β_i are discussed in the original paper of Kirkwood and are calculated and tabulated.

Generally in ethane derivatives it is known that there are three potential minima, one of which corresponds to the trans form and the other two to two different gauche forms. In order to check whether the polarizability theory is useful for this problem we have to calculate the theoretical values of $[\alpha]_D$ and to do this we must first know the potential function $V(\theta)$ because the relative population of each spatial configuration will be proportional to the Boltzmann factor $\exp\{-V(\theta)/kT\}$. However, in order to check the theory crudely we may simply assume that the contribution from trans form can be ignored and only two gauche configurations contribute significantly.

Under these assumptions we may write

$$g^{(0)} \approx \tfrac{1}{2}\left(g_{I}^{(0)} + g_{II}^{(0)}\right) \qquad \text{(IV-8)}$$

and

$$[\alpha]_D \approx \tfrac{1}{2}\left([\alpha_I]_D + [\alpha_{II}]_D\right) \quad , \qquad \text{(IV-9)}$$

where subscripts I and II stand for gauche-1 and gauche-2 configuration, respectively.

If we pick the origin at the asymmetric carbon atom, it follows that

$$g_{I}^{(0)} = K_{34} \cdot F_{34} + K_{14} \cdot F_{14} \qquad \text{(IV-10)}$$

and

$$g_{II}^{(0)} = K_{14} \cdot F_{14} + K_{24} \cdot F_{24} \qquad \text{(IV-11)}$$

where

$$K_{ik} = \frac{1}{6}\alpha_i \alpha_k \beta_i \beta_k \qquad \text{(IV-12)}$$

and

$$F_{ik} = \frac{1}{R_{ik}^3}\left\{\vec{b}_i \cdot \vec{b}_k - \frac{3(\vec{b}_i \cdot \vec{R}_{ik})(\vec{b}_k \cdot \vec{R}_{ik})}{R_{ik}^2}\right\} \vec{R}_{ik} \cdot (\vec{b}_i \times \vec{b}_k)$$

$$\equiv G_{ik}\vec{R}_{ik} \cdot (\vec{b}_i \times \vec{b}_k) \quad . \qquad \text{(IV-13)}$$

In order to derive (IV-10) and (IV-11) we have considered the fact that if $\vec{R}_{ik}$, $\vec{b}_i$, and $\vec{b}_k$ are all on the same plane, $F_{ik} = 0$. If the bond lengths for C-CH_3, C-H, C-Cl, C-CH_2OH, and C-OH are all known for 2C1P, we can easily determine $[\alpha]_D$ by making use of Eqs. (IV-1) through (IV-13). If theoretical values show reasonable agreements with experimental data, we can proceed to calculate $[\alpha]_D$ at arbitrary angles and temperatures to obtain $V(\theta)$ as mentioned earlier.

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PROPOSITION V

It is proposed that the measurement of the spin-lattice relaxation time, T_1, for ${}^{13}C$ spin in φ-C^*F_3 or φ-C^*H_3 may provide an indirect evidence of the presence of spin-internal-rotation interaction.

The only stable isotope of carbon with a nuclear magnetic moment is ${}^{13}C$ ($I = 1/2$), which has a natural abundance of 1.1 per cent, and the spin-lattice relaxation time, T_1, of ${}^{13}C$ spin is known to be long (several minutes in most carbon compounds). This fact and the small magnetogyric ratio of ${}^{13}C$ spin indicate that the contribution of magnetic dipole-dipole interaction to the relaxation rate may be very small and if the spin-rotation constant for ${}^{13}C$ spin is of moderate magnitude the spin-rotation interaction may well be the dominant relaxation mechanism.

The spin-rotation Hamiltonian for the ${}^{13}C$ spin in φ-C^*H_3 or φ-C^*F_3 may be written as[1]

$$\mathcal{H}_{S-R} = -\vec{I}\cdot\underset{\wedge}{C}\cdot\vec{J} - D_\alpha\vec{I}\cdot\vec{j} \quad , \tag{V-1}$$

where D_α and the matrix elements of $\underset{\wedge}{C}$ are given by

$$C_{gg'} = -g_c\beta_N \sum_{K'}{}' \frac{Z_{K'}|e|}{c\, r_{CK'}^3} \left\{ \frac{1}{I_g}(\vec{r}_C - \vec{r}_{K'})\cdot\vec{r}_{K'}\delta_{gg'} - \frac{1}{I_{g'}}(\vec{r}_{K'})_g(\vec{r}_C - \vec{r}_{K'})_{g'} \right\}$$

$$- \frac{2g_c\beta_N}{I_{g'}} \sum_{n\neq 0} \frac{1}{W_n^{(0)} - W_0^{(0)}} \mathrm{Re}\langle 0|\pi_g|n\rangle\langle n|L_{g'}|0\rangle \tag{V-2}$$

and

$$D_\alpha = -g_c\beta_N \sum_{K'}{}'' \frac{Z_{K'}|e|}{c\,r^3_{CK'}} \frac{1}{I_\alpha} \{(\vec{r}_C - \vec{r}_{K'})\cdot\vec{r}_{K'} - (\vec{r}_C - \vec{r}_{K'})_z(\vec{r}_{K'})_z\}$$

$$+ g_c\beta_N \sum_{K'}{}' \frac{Z_{K'}|e|}{c\,r^3_{CK'}} \frac{1}{I_z} \{(\vec{r}_C - \vec{r}_{K'})\cdot\vec{r}_{K'} - (\vec{r}_C - \vec{r}_{K'})_z(\vec{r}_{K'})_z\}$$

$$-2g_c\beta_N \left(\frac{1}{I_\alpha} - \frac{1}{I_z}\right)_n \sum_{n\neq 0} \frac{1}{W_n^{(0)} - W_0^{(0)}}$$

$$\times\ \mathrm{Re}\{\langle 0|\pi_z|n\rangle \langle 0|\ell_z|n\rangle\} \quad . \qquad \text{(V-3)}$$

In (V-2) and (V-3) several signs are defined as follows:

g_c = nuclear g-factor for ^{13}C spin,
β_N = nuclear magneton,
I_g = g-th principal moment of inertia of the entire molecule,
I_α = moment of inertia of the internal top about its symmetry axis,
$\vec{r}_C$ = position vector of the ^{13}C spin with respect to the origin 0 identified as the center of mass of the entire molecule,
$\vec{r}_K$ = position vector of the nucleus K with respect to the origin 0,
$\vec{r}_k$ = position vector of the electron k with respect to the origin 0,
$r_{CK'}$ = distance between the ^{13}C spin and the nucleus K′,
r_{Ck} = distance between the ^{13}C spin and the electron k,

and

$$\vec{\pi} = \sum_k \frac{|e|}{mc} \frac{(\vec{r}_K - \vec{r}_C)\times m\vec{v}_k}{r^3_{Ck}} \quad .$$

Also, $\vec{L}$ and $\vec{\ell}$ are, respectively, the total orbital angular momentum of electrons of the entire molecule and of those electrons localized in the internal top, and the summations $\Sigma'_{K'}$ and $\Sigma''_{K'}$ run over all the nuclei in the molecule and on the internal top, respectively, except the ^{13}C spin in the $-CH_3$ or $-CF_3$ group.

Evaluation of the average spin-rotation constant at the site of ^{13}C spin can be performed with the aid of the Schwartz relation

$$(\sigma_C)_{gg} = \frac{e^2}{2mc^2}\left\{ \langle\psi_0 | \sum_k \frac{r^2_{Ck} - (\vec{r}_{Ck})^2_g}{r^3_{Ck}} | \psi_0\rangle - \Sigma'_{K'} Z_{K'} \frac{r^2_{CK'} - (\vec{r}_{CK'})^2_g}{r^3_{CK'}} \right\} + \frac{e^2}{mc^2}\frac{h}{4M_p g_c \beta^2_N} C_{gg} I_g \qquad \text{(V-4)}$$

where M_p and h are the mass of proton and the Planck constant, respectively. Typically, each term in the curly bracket on the right-hand side of the expression (V-4) is anisotropic, but Chan and Dubin[2] have indicated that the sum of two terms in the curly bracket is nearly independent of chemical environments of the nucleus under consideration and thus, to a good approximation, is isotropic. Therefore, if the components of magnetic shielding and spin-rotation tensor for ^{13}C spin are known in a ^{13}C containing compound are known, we can evaluate the components of spin-rotation tensor for ^{13}C spin in φ-CH_3 or φ-CF_3 provided the components of magnetic shielding tensor for ^{13}C in this compound are available. Even if not all the components of magnetic shielding tensor is known, we can gain some knowledge about several components of spin-rotation tensor. For example, the chemical shift of ^{13}C in benzene is 195. 8 ppm with respect to $^{13}CS_2$ and the chemical shift of ^{13}C in H_2CO is 40 ppm with respect to benzene. Therefore, the chemical shift of ^{13}C in H_2CO is 235.8 ppm with respect to $^{13}CS_2$. If we use the calculated values for σ^P and σ^d in H_2C^*O by Flygare et al.[3] and Dunning et al.,[4] respectively, we obtain

$$\sigma_{^{13}C}(\mathrm{HCHO}) = \sigma^P + \sigma^d$$

$$= -215 \text{ ppm} + 338.1 \text{ ppm} = 123.1 \text{ ppm} \quad . \qquad \text{(V-5)}$$

From the structural data for H_2CO measured by Oka[5, 6] we have calculated three principal moments of inertia. The results are as follows:

$$I_a \approx I_b \approx 23.22 \times 10^{-40} \text{ g cm}^2$$

and

$$I_c = 3.014 \times 10^{-40} \text{ g cm}^2 \quad ,$$

where we have taken the c-axis along the C-O bond and the other two axes perpendicular to this axis.

Flygare[3] has estimated that

$$C_{cc} \approx -135 \text{ kHz}$$

and

$$C_{aa} + C_{bb} \approx -7 \text{ kHz} \quad .$$

By making use of the above data for ^{13}C in H_2CO we find that the sum of the first two terms on the right-hand side of the expression (V-4) is 315.82×10^{-6}. Therefore, we obtain from (V-4)

$$(\sigma^{^{13}C})_{gg} \approx 259.14 \times 10^{-6} + 1.0522 \times 10^{-6}\, C_{gg} I_g \quad , \qquad \text{(V-6)}$$

where C_{gg} and I_g are expressed in units of kHz and 10^{-40} g cm^2, respectively.

If we can assume that the spin-internal-rotation coupling constant C_α in φ-C^*H_3 is equal to the spin-rotation constant C in C^*H_4, we can estimate C_{zz} and D_α as we show in what follows. The chemical shift of ^{13}C in C^*H_4 is known to be 130.8 ppm with respect to benzene and we know that the chemical shift of ^{13}C in H_2CO is 40 ppm with respect to benzene. Using the value of absolute chemical shift for H_2C^*O, we see that

$$\sigma^{^{13}C}(C^*H_4) = 213.9 \text{ ppm} \quad .$$

Since $I_\alpha = 4.482 \times 10^{-40}$ g cm^2, we obtain from (V-6)

$$C_\alpha \approx -9.593 \text{ kHz} \quad .$$

Assuming that $C_{zz}I_z \approx C_\alpha I_\alpha$ in toluene, we also obtain

$$C_{zz} \approx -0.283 \text{ kHz} \quad .$$

Following Dubin and Chan[5] we write

$$\frac{1}{T_1} \approx \frac{8\pi^2 I_\alpha kT}{3\hbar^2} C_\alpha^2 \tau_{j_\alpha} \qquad \text{(V-7)}$$

where C_α is expressed in units of cycle per second. Since $\tau_{j_\alpha} \sim (I_\alpha/kT)^{\frac{1}{2}}$, at 20° C we obtain

$$\frac{1}{T_1} \sim 0.0097 \text{ sec}^{-1}$$

If we let $\tau_{j_\alpha} \approx 3.0 \times (I_\alpha/kT)^{\frac{1}{2}}$, we have

$$\frac{1}{T_1} = 0.029 \text{ sec}^{-1}$$

which is comparable to the dipole-dipole contribution for the case of proton relaxation in toluene.[7] In view of the fact that the magnetogyric ratio of ^{13}C is almost one-fourth of proton magnetogyric ratio we may conclude that the dominant contribution to the relaxation rate of ^{13}C spin in φ-CH_3 comes from the spin-internal-rotation coupling.

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