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A Theory for Averaging Anisotropic ESR Parameters

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Abstract

A theoretical treatment was developed for partial averaging of anisotropic ESR parameters arising from the Brownian motion of molecules. The Hamiltonian is divided into the two parts, namely, the time-independent and the time-dependently fluctuating part. The latter was averaged by the aid of the probability density derived from the diffusion equation of the Brownian motion. This method was applied to obtain the average of the anisotropic g factor arising from molecular motion. In the present work each principal value of the g tensor was separately averaged and the results agreed with the experimental findings. And also the results were expressed by the anisotropic part at $t=0$ multiplied by a factor $2/\pi \tan^{-1}(\tau_c/T''_2)$. Our approach is more general than Kneubühl's theory and his results were proved to be an approximation for small anisotropy of the g factor.

Introduction

It is well known that the random Brownian motion of molecules in liquids has an important effect on the relaxation mechanism of ESR. The other effect of the Brownian motion of molecules is the averaging of the anisotropic ESR parameters of the molecules, such as g tensor and the hyperfine coupling constant tensor. If we assume a complete hindrance of molecular motion in a solid phase, the anisotropy should appear in an observation. In liquid, in which molecular motion is sufficiently rapid, the anisotropy is averaged out and the ESR spectrum appears isotropically. In the intermediate case, which sometimes occurs in either polymers or highly viscous liquids, the anisotropy is partly averaged. Hitherto a few work on ESR study of molecular motion based on observation of averaging of the anisotropic ESR parameters were published. If the averaging process of the anisotropic parameters is observable, one can obtain information of the correlation time related to the Brownian motion provided with an appropriate theory. Although Kivelson¹⁾ and Freed²⁾ published a series of papers on the theories in which they studied the effect of the Brownian motion on the relaxation mechanisms in liquid phase where the anisotropy is completely averaged out, there are also a few theoretical studies^{3)~5)} related to the partial averaging of the anisotropic ESR parameters for a system in which the Brownian motion is not sufficiently rapid for complete averaging. It was recently found that the anisotropic g factor gradually changed with rising temperatures and these temperature variations are

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due to the partial averaging of anisotropic g factor caused by the Brownian motions in elevated temperatures⁶⁾. In order to obtain quantitative information on the Brownian motion a theory, by which the experimental results can be analysed, is required and Kneubühl's theory³⁾ is most convenient for the analysis of the experimental results. The authors used Kneubühl's theory for the analysis of their experimental results on the peroxyradicals of polymer⁶⁾ but it was found that the theory has a few defects which should be improved. At first, in Kneubühl's theory, the averaging is done not on the g factor itself but the square of the g factor. On the other hand, the experimentally observed quantity is, of course, the average of the g factor itself. The perturbation due to the Brownian motion is stochastic and therefore the spin Hamiltonian for a molecule fluctuates. Thus, the fluctuating Hamiltonian should be averaged instead of averaging the ESR parameters, which was done after the method of Kneubühl. In this paper the results obtained by Kneubühl on the averaging of the g -anisotropy will be derived from more general assumptions; the time-dependent Hamiltonian and the phenomenological equation of the Brownian motion. And also it will be shown that the theoretical approach can be extended to other anisotropic ESR parameters.

Averaging of the g -anisotropy

For the theoretical approach to partial averaging of the g -anisotropy the following assumptions will be made:

- 1) Only systems with $S=1/2$ will be considered.
- 2) The paramagnetic molecules are randomly oriented.
- 3) No hyperfine splitting is considered.
- 4) The line-shape is mainly determined by the anisotropic g factor.
- 5) The Brownian motion of the paramagnetic molecules in viscous liquids is independent of the magnetic interaction between these magnetic centers and their neighbors or the external field.

The approach starts from the Hamiltonian which is fluctuating because of the Brownian motion of a molecule in a viscous liquid or polymers. In such systems the molecular motion may be considered to be so rapid that the anisotropy of ESR parameters are affected. Thus, it is desirable and more general if the average is taken over the Hamiltonian itself instead of the weighted average of the g factor, which was done in Kneubühl's theory. In a similar manner to Freed's theory⁷⁾ on the line shape, the Hamiltonian is divided into two parts.

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

A part of the Hamiltonian $\mathcal{H}_0$, which is related to the isotropic part of the g tensor, is time independent and is described as

$$\mathcal{H}_0 = g_0 \beta H \cdot S \quad (2)$$

where H , S and β represent the applied magnetic field, the spin operator and the Bohr magneton, respectively, and g_0 is the average of the principal values of the

g -tensor :

$$g_0 = \frac{1}{3}(g_x + g_y + g_z) \quad (3)$$

On the other hand the other part of the Hamiltonian $\mathcal{H}_1(t)$ is a contribution from the anisotropic part and a fluctuating perturbation, which is averaged out in a case of sufficiently rapid molecular motion. This part of the Hamiltonian is given by Eq.(4) in reference to the molecular coordinates, in which the static magnetic field is explicitly time-dependent.

$$\mathcal{H}_1(t) = \beta S \tilde{g}' H(t) \quad (4)$$

$$\tilde{g}' \equiv \begin{pmatrix} g'_x & 0 & 0 \\ 0 & g'_y & 0 \\ 0 & 0 & g'_z \end{pmatrix} \equiv \begin{pmatrix} g_x - g_0 & 0 & 0 \\ 0 & g_y - g_0 & 0 \\ 0 & 0 & g_z - g_0 \end{pmatrix}$$

Since only rotational motion of a molecule is effective in averaging the anisotropic ESR parameters, such as the g -factor, the equation of angular diffusion, which is the phenomenological equation of the rotational Brownian motion, is taken as the fundamental equation which governs the probability density $P_\tau(\alpha, \beta, \gamma)$, which is the probability density to find a molecule at the time τ an orientation described by Eulerian angles, α, β, γ , defined in Fig. 1.

$$\frac{\partial P_\tau}{\partial \tau} = D \Delta_{\alpha\beta\gamma} P \quad (5)$$

where D is the angular diffusion coefficient. Since the two angles, α and β , defined in Fig. 1, determine the magnetic energy with reference to the static magnetic field H along the Z axis of the laboratory coordinates, the average is taken over the two angles α and β .

With the initial condition

$$P(\alpha_0, \beta_0, \tau, \alpha, \beta)_{\tau=0} = \delta(\alpha - \alpha_0, \beta - \beta_0) \quad (6)$$

equation (5) is solved and a solution, which is the probability density P_τ determined by Eq.(5), is obtained and expressed as a spherical harmonic function,

$$P_\tau(\alpha_0, \beta_0, \tau, \alpha, \beta) = \sum_l \exp \left[-l(l+1) \tau / 6\tau_c \right] \sum_m Y_l^m(\alpha_0, \beta_0) Y_l^{m*}(\alpha, \beta) \quad (7)$$

On the other hand, the average of any function $f(\alpha, \beta)$ expressed by the spherical harmonic function as shown in Eq.(8)

$$f(\alpha, \beta) = \sum_m a_m Y_l^m(\alpha, \beta) \quad (8)$$

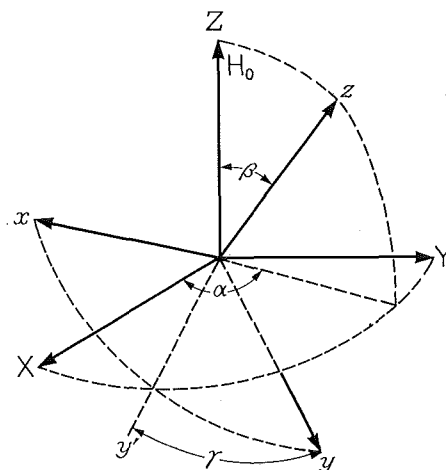


Fig. 1. XYZ: Laboratory coordinates
xyz: Molecular coordinates

is taken making use of the probability density of Eq. (7), as follows,

$$\langle f(\alpha, \beta) \rangle_{Av} = \iint f(\alpha, \beta) P_\tau \sin \beta \, d\beta \, d\alpha = \exp[-l(l+1)\tau/6\tau_c] f(\alpha_0, \beta_0) \quad (9)$$

or

$$\langle Y_l^m \rangle_{Av} = \iint P_\tau Y_l^m(\alpha, \beta) \sin \beta \, d\beta \, d\alpha = Y_l^m(\alpha_0, \beta_0) \exp[-l(l+1)\tau/6\tau_c] \quad (10)$$

One can regard this average as the time average of the magnetic interaction by the fluctuating molecular motion described by Eq. (5). And $\langle Y_l^m \rangle_{Av}$ is also expressed as the Fourier expansion as shown in Eq. (11)

$$\langle Y_l^m \rangle_{Av} = \int_{-\infty}^{\infty} a(\alpha_0, \beta_0, \nu) \exp(i2\pi\nu\tau) \, d\nu \quad (11)$$

In a similar manner to Kneubühl's approach only the time interval which is shorter than the inverse of the line-width T_2' is taken into account as a good approximation. Since the time dependent Hamiltonian, Eq. (4), is expressed as the second rank of the spherical harmonics as shown in Eq. (27) in the next section, the average of this Hamiltonian can be taken by the aid of P_τ , which is governed by the rotational diffusion equation, Eq. (5). And the integration will be performed with the above mentioned approximation, and the following equation, Eq. (12), will be obtained.

$$\langle \mathcal{H}_1 \rangle_{Av} = \int_{-1/\tau T_2'}^{1/\tau T_2'} a(\alpha_0, \beta_0, \nu) \exp(i2\pi\nu\tau) \, d\nu = \mathcal{H}_1(0) \frac{2}{\pi} \tan^{-1}(\tau_c/T_2') \quad (12)$$

Taking Eq. (4) into account the average of the anisotropic g factor is obtained

$$\langle \mathcal{H}_1 \rangle_{Av} = \beta(g_x' H_x + g_y' H_y + g_z' H_z) \frac{2}{\pi} \tan^{-1}(\tau_c/T_2') \quad (13)$$

Therefore the average of the total Hamiltonian is expressed as

$$\begin{aligned} \langle \mathcal{H} \rangle_{Av} &= \mathcal{H}_0 + \langle \mathcal{H}_1 \rangle_{Av} \\ &= \left\{ g_0 + g_x' (2/\pi) \tan^{-1}(\tau_c/T_2') \right\} \beta H_x \\ &\quad + \left\{ g_0 + g_y' (2/\pi) \tan^{-1}(\tau_c/T_2') \right\} \beta H_y \\ &\quad + \left\{ g_0 + g_z' (2/\pi) \tan^{-1}(\tau_c/T_2') \right\} \beta H_z \\ &= \langle g_x \rangle_{Av} \beta H_x + \langle g_y \rangle_{Av} \beta H_y + \langle g_z \rangle_{Av} \beta H_z \end{aligned} \quad (14)$$

where

$$\begin{aligned} \langle g_x \rangle_{Av} &= g_0 + g_x' (2/\pi) \tan^{-1}(\tau_c/T_2') \\ \langle g_y \rangle_{Av} &= g_0 + g_y' (2/\pi) \tan^{-1}(\tau_c/T_2') \\ \langle g_z \rangle_{Av} &= g_0 + g_z' (2/\pi) \tan^{-1}(\tau_c/T_2') \end{aligned} \quad (15)$$

Eq. (15) indicates that each principal value of the g tensor is separately averaged and this theoretical conclusion of the separate averaging agrees with what was found in the experiment⁶⁾. Comparing one component of Eq. (15), for example $\langle g_x \rangle$, with the experimental values of g_x at various temperatures one can estimate

the correlation time τ_c at the temperatures provided with the known line-width $T_2'^{6)}$.

In the orientation shown in Fig. 1, g^2 is expressed as follows.

$$g^2 = g_x^2 \sin^2 \beta_0 \sin^2 \alpha_0 + g_y^2 \sin^2 \beta_0 \cos^2 \alpha_0 + g_z^2 \cos^2 \beta_0$$

In a similar way, the square of the averaged g factor is obtained as

$$\begin{aligned} \langle g^2 \rangle_{Av} = & \left\{ g_0 + g_x' (2/\pi) \tan^{-1} (\tau_c/T_2') \right\}^2 \sin^2 \beta_0 \sin^2 \alpha_0 \\ & + \left\{ g_0 + g_y' (2/\pi) \tan^{-1} (\tau_c/T_2') \right\}^2 \sin^2 \beta_0 \cos^2 \alpha_0 \\ & + \left\{ g_0 + g_z' (2/\pi) \tan^{-1} (\tau_c/T_2') \right\}^2 \cos^2 \beta_0 \end{aligned} \quad (16)$$

On the other hand the average of the square of the g tensor was derived by Kneubühl [3] in the following expression.

$$\begin{aligned} \langle g^2 \rangle_{Av} = & \left\{ s + (g_x^2 - s) (2/\pi) \tan^{-1} (\tau_c/T_2') \right\} \sin^2 \beta_0 \sin^2 \alpha_0 \\ & + \left\{ s + (g_y^2 - s) (2/\pi) \tan^{-1} (\tau_c/T_2') \right\} \sin^2 \beta_0 \cos^2 \alpha_0 \\ & + \left\{ s + (g_z^2 - s) (2/\pi) \tan^{-1} (\tau_c/T_2') \right\} \cos^2 \beta_0 \\ s = & \frac{1}{3} (g_x^2 + g_y^2 + g_z^2) \end{aligned} \quad (17)$$

If the difference of the principal values are small enough in comparison with g , that is $4g \ll g$,

$$g_x^2 - s \doteq g_x^2 - g_0^2 = (g_x - g_0)(g_x + g_0) \doteq g_x' 2g_0$$

and

$$(g_0 + g_x' 2/\pi \tan^{-1} \tau_c/T_2')^2 \doteq s + (g_x^2 - s) 2/\pi \tan^{-1} (\tau_c/T_2') \quad (18)$$

Since each component of Eq. (16) is equal to the corresponding one of Eq. (17) in the case of small anisotropy, it is verified that the Kneubühl's result is an approximation of the average obtained from the averaging of the perturbing Hamiltonian in the case of a smaller anisotropy of the g factor.

Averaging of other anisotropic ESR parameters

The method of average, developed in the last section, is readily extended to averaging other anisotropic ESR parameters, such as hyperfine coupling tensor and the quadrupole interaction, if one takes the Hamiltonian which includes these interactions. The total Hamiltonian is also divided into the two parts, the time-independent part and the dependent one.

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1(t) \quad (19)$$

The time-independent part $\mathcal{H}_0$ consists of the Zeemann term and the isotropic hyperfine interaction term.

$$\mathcal{H}_0 = g_0 \beta H \cdot S + \sum_{i=1}^n a_i I_i \cdot S \quad (20)$$

The anisotropic parts of the interactions contribute to the time-dependent Hamiltonian which stochastically fluctuates, because only the anisotropic part of the interactions are influenced by the Brownian motion of a molecule. This time-dependent Hamiltonian is divided into three different interactions

$$\mathcal{H}_1(t) = \mathcal{H}^{(g)}(t) + \mathcal{H}^{(D)}(t) + \mathcal{H}^{(Q)}(t) \quad (21)$$

where $\mathcal{H}^{(g)}$ is the Zeemann splitting related to the anisotropic part of the g factor, which was discussed in the last section, $\mathcal{H}^{(D)}$ is the anisotropic hyperfine splitting, and $\mathcal{H}^{(Q)}$ is the quadrupole interaction. The spin Hamiltonian is expressed in general form as follows with reference to the molecular coordinates system. [7]

$$\mathcal{H}_1(t) = \sum_{m, \mu, i} F_{\mu, i}^{(2, m)} A_{\mu, i}^{(2, -m)} \quad (22)$$

where μ specifies the specific interaction, i specifies the different nucleus, $A_{\mu, i}^{(2, -m)}$ is the irreducible tensor with the rank 2, and the component of $-m$. $F_{\mu, i}$ can be calculated by the electron wave function and remains unchanged while the Eulerian angles $(\alpha\beta\gamma)$ change due to the Brownian motion. On the other hand $A_{\mu, i}$ depends on the Eulerian angle $(\alpha\beta\gamma)$. $F_{\mu, i}$ is expressed in the coordinate system of the principal axis of the g tensor, and $A'_{\mu, i}$ described in a frame fixed in space. Taking advantage of the Wigner matrix, $D_{-m, m'}^{(2)}$, the equation expressed with the molecular coordinate system is transformed to those with the space coordinate $A'_{\mu, i}^{(2, m)}$

$$A_{\mu, i}^{(2, -m)} = \sum_{m'} D_{-m, m'}^{(2)}(\alpha, \beta, \gamma) A'_{\mu, i}^{(2, m')} \quad (23)$$

where α, β, γ are Eulerian angles.

Thus

$$\mathcal{H}_1(t) = \sum_{m, \mu, i} \sum_{m'} D_{-m, m'}^{(2)}(\alpha, \beta, \gamma) A'_{\mu, i}^{(2, m')} F_{\mu, i}^{(2, m')} \quad (24)$$

The concrete descriptions of $A'_{\mu, i}^{(2, m)}$ and $F_{\mu, i}^{(2, m')}$ for the three interactions are given as follows

1) Anisotropic g effect ($\mu=1, L=2$)

$$\begin{aligned} & A'_{1, i}^{(2, m)} \\ m=0 & -2(2/3)^{1/2} H_0 S_z \\ m=\pm 1 & \pm H_0 S_{\pm} \\ m=\pm 2 & 0 \end{aligned} \quad (25)$$

$$\begin{aligned} F_1^{(2, 0)} &= -\frac{1}{2} (-1)^m \beta_e \hbar^{-1} 6^{-1/2} [2g_z - (g_x + g_y)] \\ F_1^{(2, \pm 1)} &= 0 \\ F_1^{(2, \pm 2)} &= -\left(\frac{1}{2}\right)^2 (-1)^m \beta_e \hbar^{-1} (g_x - g_y) \end{aligned} \quad (26)$$

2) d - d interaction ($\mu=2, L=2$)

$$\begin{aligned}
 & A'_{2,\delta}^{(2,m)} \\
 m=0 & \quad -2\left(\frac{2}{3}\right)^{1/2} \left[I_{\delta z} S_z - \frac{1}{4} (I_{\delta+} S_- + I_{\delta-} S_+) \right] \\
 m=\pm 1 & \quad \pm (I_{\delta\pm} S_z + I_{\delta z} S_{\pm}) \\
 m=\pm 2 & \quad -I_{\delta\pm} S_{\pm} \\
 F_{2,\delta}^{(2,m)} & = (-1)^m \gamma_e \gamma_\delta \hbar^{-1} (6\pi/5)^{1/2} \langle \phi | r_\delta^{-3} Y_{2m}(\theta_\delta, \phi_\delta) | \phi \rangle
 \end{aligned} \tag{27}$$

3) Nuclear quadrupole interaction ($\mu=3, L=2$)

$$\begin{aligned}
 & A'_{3,\delta}^{(2,m)} \\
 m=0 & \quad -\left(\frac{2}{3}\right)^{1/2} \left\{ 3 I_{\delta z}^2 - I_\delta(I_\delta + 1) \right\} \\
 m=\pm 1 & \quad \pm (I_{\delta\pm} I_{\delta z} + I_{\delta z} I_{\delta\pm}) \\
 m=\pm 2 & \quad -I_{\delta\pm}^2
 \end{aligned} \tag{28}$$

$$\begin{aligned}
 & F_{3,\delta}^{(2,m)} \\
 (-1)^m & \left[e Q_\delta \hbar^{-1} \left\{ 4 I_\delta (2 I_\delta - 1) \right\}^{-1} \right] (V_\varepsilon)_\delta^{(m)} \\
 (V_\varepsilon)_\delta^{(0)} & = -(3/2)^{1/2} \langle \phi | V_{zz}(i) | \phi \rangle \\
 (V_\varepsilon)_\delta^{(\pm 1)} & = \pm \langle \phi | V_{xz}(i) \pm i V_{yz}(i) | \phi \rangle \\
 (V_\varepsilon)_\delta^{(\pm 2)} & = -\frac{1}{2} \langle \phi | V_{xx}(i) - V_{yy}(i) \pm 2i V_{xy}(i) | \phi \rangle
 \end{aligned} \tag{29}$$

Since the directions of the principal axes differ from one interaction to the other, the Eulerian angles of the principal axes of each interaction are specified with suffix, μ . In the above expression term $D_{-m,m'}^{(2)}$, fluctuates time-dependently and is expressed with the second order of the spherical harmonic function. This fluctuating term is averaged by the aid of P_r ,

$$\begin{aligned}
 & \int D_{-m,m'}^{(2)}(\alpha, \beta, \gamma) P_r(\alpha_0 \beta_0 \gamma_0, \tau, \alpha, \beta, \gamma) d\Omega \\
 & = D_{-m,m'}^{(2)}(\alpha_0 \beta_0 \gamma_0) \exp(-\tau/\tau_c)
 \end{aligned} \tag{30}$$

Therefore,

$$\begin{aligned}
 \langle \mathcal{H}_1 \rangle_{Av} & = \sum_{m,\mu,\delta} \sum_{m'} D_{-m,m'}^{(2)}(\alpha_0 \beta_0 \gamma_0)_\mu A'_{\mu,\delta}^{(2,m')} F_{\mu,\delta}^{(2,m)} \exp(-\tau/\tau_c) \\
 & = \mathcal{H}_1(0) \exp(-\tau/\tau_c) \\
 & = \int_{-\infty}^{\infty} a(\alpha_0, \beta_0, \gamma_0, \nu) \exp(i2\pi\nu\tau) d\nu
 \end{aligned} \tag{31}$$

In a similar way to the averaging of g developed in the last section

$$\langle \mathcal{H}_1 \rangle_{Av} = \int_{-1/\pi T_2}^{1/\pi T_2} a(\alpha_0, \beta_0, \gamma_0) \exp(i2\pi\nu\tau) d\nu \tag{32}$$

$$\langle \mathcal{H}_1 \rangle_{Av} = \mathcal{H}_1(0) \frac{2}{\pi} \tan^{-1} \left(\frac{\tau_c}{T_2} \right) \tag{33}$$

$$\langle \mathcal{H} \rangle_{Av} = \mathcal{H}_0 + \mathcal{H}_1(0) 2/\pi \tan^{-1}(\tau_c/T'_2) \quad (34)$$

That is, the average of any anisotropic ESR parameter is given as a product of $\mathcal{H}_1(0)$ and $\tan^{-1}(\tau_c/T'_2)$.

Conclusion

The averaging of the anisotropy due to the rotational Brownian motion was considered. Starting from the separation of the time-independent part and the dependent one of the Hamiltonian it was deduced that the average Hamiltonian is obtained by adding the isotropic part to the anisotropic one at $t=0$ multiplied by a factor $2/\pi \tan^{-1}(\tau_c/T'_2)$. This result involves Kneubühl's result as the approximation permitted for small g anisotropy. Our result can be applied to the anisotropic ESR parameters, such as the g factor, hyperfine coupling, which have an even larger anisotropy.

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