Time Correlation Functions for Rotational Motion of Molecules

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By use of Green’s functions for the diffusional motion a very concise formulation and computation of correlation functions is possible. For an axially symmetric overall diffusion with internal rotation about one and two axes correlation functions of a second rank spherical tensor are calculated. The results comprise all the solutions of the pertinent problem as given so far and allow the extension of the theory to a wider field of application.

1. Introduction

Nuclear spin relaxation has proved to be a powerful tool for studying molecular motions in liquids. Firstly, valuable information concerning the rotational motions of the molecule to which the nucleus belongs can be obtained. Secondly, internal rotational motions about some fixed molecular axes also have a specific influence on the relaxation behaviour of the nucleus to be considered. This type of rotational motion occurs especially in organic liquids.

The molecular motions enter into the theory of nuclear spin relaxation through the autocorrelation functions. The influence of rotational diffusion on correlation functions has been the subject of several investigations. The paper of HUNTRESS treats the case of internal rotational motions in detail. However, it is restricted to the case of extreme narrowing and furthermore asymmetry parameters as indicated above.

The case of internal rotational motions has been studied as well. Recently WOESSNER has given a rather general formula for magnetic dipole-dipole relaxation. WALLACH treated internal motion in macromolecules but he did not make allowance for any anisotropic rotations of the macromolecule as a whole. For very long molecules this may be a poor approximation. Furthermore he neglected asymmetry parameters as indicated above.

The author of this article wants to show that by use of Green’s functions a very concise formulation of the computation and results is possible. For an overall diffusion of the molecule that is axially symmetric this formulation comprises all the solutions

\[ S_1(A') = 2^{-\frac{1}{2}}(r_1 + r_2), \]
\[ S_2(A') = t, \]
\[ S_3(A') = d, \]
\[ S_4(A') = R\alpha, \]
\[ S_5(A') = (TR/2)^{\frac{1}{2}}(\beta_{11} + \beta_{12}), \]
\[ S_6(A') = (DR/2)^{\frac{1}{2}}(\beta_{21} + \beta_{22}), \]

of the pertinent problem as given so far and allows the extension of the theory to a wider field of application.

2. Green's Functions and Rotational Transformations

For the one-dimensional rotational diffusion we shall use $^{9}$:

$$G(\gamma_0, \varphi_0, \gamma_0, \alpha, \beta, \gamma, t) = \sum_{L=0}^{\infty} \frac{(2L+1)}{8 \pi^2} D_{K,M}^{(L)}(\gamma_0, \beta_0, \gamma_0) \cdot e^{-\frac{(D_1(L+1)+D_2-k)}{2}t}. \quad (1)$$

Here, $D^*$ is the diffusion coefficient for the diffusion about the rotational axis, $\gamma_0$, $\varphi$ are the angles of rotation.

For the three-dimensional motion, we shall restrict ourselves to the case of a diffusion tensor with two equal eigenvalues ($D_1 = D_2$). In this case Green's function $^{9,11}$ may be written in closed form:

$$B_M^{(L)}(z, \beta, \gamma) \cdot e^{-\frac{(D_1(L+1)+D_2-d_k)}{2}t}. \quad (2)$$

spherical tensors in the molecular system $B_M^{(L)}$ $^{10,11}$:

$$B_M^{(L)} = \sum_{M=-2}^{+2} D_{M,K}^{(L)}(\alpha, \beta, \gamma) \cdot B_M^{(L)}(z, \beta, \gamma) \cdot e^{-\frac{(D_1(L+1)+D_2-d_k)}{2}t}. \quad (3)$$

But there exists another point of view. If now we look at the molecular orientation as described by rotations $\Omega_0(a_0, \beta_0, \gamma_0)$ and $\Omega'(\alpha, \beta, \gamma')$ which start in the laboratory system, the same physical situation may be described in the molecular system. As seen from the molecular systems these rotations are $\Omega_0(-\gamma_0, -\beta_0, -\gamma_0)$ and $\Omega(-\gamma, -\beta, -\alpha)$. The physical meaning of our Green's function is: If the orientation at zero time was $\Omega_0[\Omega_0]$ then $G'(\Omega_0', \Omega', t) \left[ G(\Omega_0, \Omega, t) \right]$ is the probability that the orientation will be $\Omega'[\Omega]$ at time $t$. Now these probabilities $G'(\Omega_0', \Omega', t)$ as seen from the laboratory system and $G(\Omega_0, \Omega, t)$ as seen from the molecular system must be equal. Thus we get:

we see that the only difference between the Green's function in the laboratory and the molecular system is the interchange of $K$ and $M$.

We may also give an equivalent formula for the transformation of spherical tensors like (3), if the rotations are looked at from the laboratory system:

$$B_M^{(L)} = \sum_{M'} D_M^{(L)}(\Omega) \cdot B_M^{(L)}(z, \beta, \gamma) \cdot e^{-\frac{(D_1(L+1)+D_2-d_k)}{2}t}. \quad (2a)$$

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Now the calculation of correlation functions may be performed in the molecular system with (2) and (3) or in the laboratory system with (2a) and (3a). Because of the more complex structure of (3a) in this paper it will be carried out in the molecular system. We mention, however, that by use of (2a) and (3a) the same results can be obtained.

$^{9}$ A. R. Edmonds, Angular Momentum in Quantum Mechanics, German translation, Bibliographisches Institut, Mannheim 1964.

3. Calculation of Correlation Functions

When dealing with dipole-dipole interaction one is interested in the correlation functions of the spherical harmonics \( y_m^L (\Theta, \Phi) \) \((\Theta, \Phi)\) are spherical coordinates). The more general correlation function of any second rank spherical tensor \( B_m^{(2)} \) (for which in short-hand notation we write \( B_m \)) will be used in quadrupole — and anisotropic chemical shift relaxation \(^1\).

The correlation functions we want to calculate are of the form:

\[
g_{(m)}(t) = \int dR_0 \int dR B^*(R) B_m (R_0) \cdot p \cdot P (R_0, R, t).
\]

(4)

The rotations \( R_0, R \) now are taken to describe not only the orientation of the molecule but also the internal degrees of freedom.

If the overall orientation at zero time was \( R_0 \) then the probability that the orientation will be \( R \) at time \( t \) is \( P (R_0, R, t) \). \( p \) is the a priori probability for any orientation \( R_0 \).

Now we shall decompose the orientation \( R \) at time \( t \) into rotations \( \Omega, \Omega' \) and \( \Omega'' \). Each of these rotations leads from one coordinate system of physical significance to another.

By use of Eq. (3) we can write for \( g^{(m)}(t) \) as given by Eq. (4):

\[
g^{(m)}(t) = \int dR_0 \int dR \sum_{n=-2}^{+2} D_{nm}^{(2)} (\Omega_0) B^n \cdot \sum_{l=-2}^{+2} D_{lm}^{(2)*} (\Omega) B^l \cdot p \cdot P (R_0, R, t)
\]

\[
= \int dR_0 \int dR \sum_{n=-2}^{+2} D_{nm}^{(2)} (\Omega_0) \sum_{j=-2}^{+2} D_{jn}^{(2)*} (\Omega_0') B'^j \cdot \sum_{l=-2}^{+2} D_{lm}^{(2)*} (\Omega) \sum_{k=-2}^{+2} D_{lk}^{(2)*} (\Omega') B''^k \cdot p \cdot P (R_0, R, t)
\]

\[
= \int dR_0 \int dR \sum_{n=-2}^{+2} D_{nm}^{(2)} (\Omega_0) \sum_{j=-2}^{+2} D_{jn}^{(2)*} (\Omega_0') \sum_{k=-2}^{+2} D_{lk}^{(2)*} (\Omega_0'') B''^k \cdot p \cdot P (R_0, R, t).
\]

(5)

Next we must consider the form of the function \( P (R_0, R, t) \). The rotational diffusion of the whole molecule is described by the rotations \( \Omega_0, \Omega \) and therefore the Green’s function for the three-dimensional motion has to be used. The a priori probability for an orientation \( \Omega_0 \) is \( 1/8 \pi^2 \). The internal rotational motion about the axis \( z'' \) is taken to follow the one-dimensional Green’s function with the a priori probability \( 1/2 \pi \).

For \( p \cdot P (R_0, R, t) \) \( dR_0 dR \) in (5) we write, using Eqs. (1) and (2):

\[
p \cdot P (R_0, R, t) = \frac{1}{8 \pi^2} G (\Omega_0, \Omega, t) \frac{1}{8 \pi^2} G (\Omega_0, \Omega, t) \frac{1}{8 \pi^2} G (\Omega_0, \Omega, t) \frac{1}{8 \pi^2} G (\Omega_0, \Omega, t)
\]

\[
= \frac{1}{2 \pi} \sum_{j=-\infty}^{+\infty} e^{j(\chi - \chi')} \cdot e^{-p p' t} \frac{1}{8 \pi^2} \sum_{L, K, M} \frac{(2L+1)}{8 \pi^2} \frac{(2L+1)}{8 \pi^2} D_{K,n}^{(L)} (\Omega_0) D_{K,m}^{(L)} (\Omega)
\]

\[
\cdot e^{-\langle d_l L(L+1) + (d_l - d_0) K \rangle^2 t}.
\]
The angles \( \chi_0, \chi \) which measure the internal rotation are of the form:

\[
\chi_0 = \gamma'' + \alpha_0; \quad \chi = \gamma'' + \alpha
\]

The only terms which do not vanish after integration over \( \Omega_3, \Omega \) because of orthogonality relations are those for which:

\[
L = 2, \quad M = m, \quad K = n = l.
\]

The integration over \( \chi_0, \chi \) leads to:

\[
J = k = j.
\]

So we get:

\[
g^{(m)}(t) = \sum_{n, j, l} \left| \sum_{l''} D_{2n}^{(2)}(\alpha'', \beta'', l) D_{2j}^{(2)}(0, \beta', 0) B^{0j''} \cdot e^{-\left(6D_1 + (D_2 - D_3)\right) t} \cdot e^{-P^{**} t} \right|^2.
\]

In this expression the product \( D_{2n}^{(2)}(0, \beta', 0) \cdot D_{2j}^{(2)}(0, \beta', 0) \) occurs which means that \( g^{(m)}(t) \) is independent of \( \gamma' \). As our final result we write

\[
g^{(m)}(t) = \sum_{n, j} \left| \sum_{l''} D_{2n}^{(2)}(\alpha'', \beta'', l) D_{2j}^{(2)}(0, \beta', 0) B^{0j''} \cdot e^{-\left(6D_1 + (D_2 - D_3)\right) t} \cdot e^{-P^{**} t} \right|^2.
\]

4. Dipole-Dipole Relaxation

\[ B^{0j''} = y^{(2)}(\Theta'', \Phi''). \]

In the principle axis-system \( \Theta'' = 0, \Phi'' = 0 \) which means:

\[ B^{0j''} = \delta_{j, 0} \cdot \sqrt{5/4 \pi}. \]

Now \( g^{(m)}(t) \) is independent of \( \alpha'' \) and by the use of the relation

\[ D_{0m}^{(1)}(\alpha, \beta, \gamma) = \sqrt{\frac{4 \pi}{2l + 1}} \cdot y^{(l)}(\beta, \gamma) \]

we get:

\[
g^{(m)}(t) = \sum_{l''} \left| \sum_{l''} D_{2n}^{(2)}(\alpha'', \beta'', l) D_{2j}^{(2)}(0, \beta', 0) \right|^2 \cdot e^{-\left(6D_1 + (D_2 - D_3)\right) t} \cdot e^{-P^{**} t}.
\]

This result has been derived recently in a different manner.

5. Quadrupole Relaxation and Anisotropic Chemical Shift Relaxation

The second rank tensor of interest for quadrupole relaxation is the field gradient tensor \(^1\):

\[
B^{00} = \frac{1}{2} q; \quad B^{0\pm 1} = 0; \quad B^{0\mp 2} = \frac{1}{216} q \eta;
\]

\[ q = V_{z^0 z} = \frac{3}{2} \text{ is the field gradient in the } z^0 \text{ direction,} \]

\[ \eta = \frac{V_{z^0 z} - V_{y^0 y}}{V_{z^* z^*}} \text{ is the asymmetry parameter of the field gradient (} V_{x^0 x} \text{ and } V_{y^0 y} \text{ are the field gradients in the directions } x^0 \text{ and } y^0 \text{).} \]

For the anisotropic chemical shift tensor one gets \(^1\):

\[
B^{00} = \frac{1}{2} \gamma \delta_{z^0}; \quad B^{0\pm 1} = 0; \quad B^{0\mp 2} = \frac{1}{216} \gamma \delta_{z^0} \eta;
\]
γ is the gyromagnetic ratio, δρ is the chemical shift in the z° direction. η is given by η = (δρ - δρν)/δρν.

Here δρ and δρν are the chemical shifts in the directions x° and y° respectively.

It is not necessary to write down formulas for the most general case of Eq. (6) since this is straight forward but rather lengthy. Instead, we shall discuss some cases of special interest. By simplifying assumptions we also shall get results which have been discussed earlier. We give them in the same compact formulation as Eq. (6).

1) A first simplification of Eq. (1) arises if one takes η = 0. Then j = 0 and the result becomes independent of x°.

\[
g(m)(t) = \frac{1}{2} \sum_{n,j=-2}^{+2} D_{0,j}^{(2)}(0, \beta'', 0) D_{j,n}^{(2)}(0, \beta', 0) B_{00}^{2} \cdot e^{-(6D_1 + (D_1 - D_2)\eta^2)t} \cdot e^{-jD_\perp t}.
\]  

This formula can be used for the calculation of relaxation rates for long molecules with internal motions, when the asymmetry parameter is to be neglected.

If furthermore the overall diffusion is isotropic (D_3 = D_1) the summation over n may be carried out with the result:

\[
g(m)(t) = \frac{1}{4} \sum_{j=-2}^{+2} D_{0,j}^{(2)}(0, \beta'', 0) B_{00}^{2} \cdot e^{-(6D_1 + (D_1 - D_2)\eta^2)t} \cdot e^{-jD_\perp t}.
\]  

(10a)

Functions like this were derived by WALLACH. We also mention the more general case of isotropic overall diffusion of the molecule (D_3 = D_1) with η ≠ 0. Now in Eq. (6) we may take β' = 0 and get:

\[
g(m)(t) = \frac{1}{4} \sum_{n,j=-2}^{+2} D_{0,j}^{(2)}(0, \beta'', 0, 0) B_{00}^{2} \cdot e^{-(6D_1 + (D_1 - D_2)\eta^2)t} \cdot e^{-jD_\perp t}.
\]  

(11)

2) Eq. (6) must give the results for anisotropic rotational motion if there is no internal motion. In Eq. (6) now D_3 = 0 and the summation over j may be carried out. The angles β'' and β' must be added. For β'' + β' we again write β'':

\[
g(m)(t) = \frac{1}{4} \sum_{n=-2}^{+2} D_{0,n}^{(2)}(0, \beta'', 0, 0) B_{00}^{2} \cdot e^{-(6D_1 + (D_1 - D_2)\eta^2)t} \cdot e^{-jD_\perp t}.
\]  

(12)

This result may be used if one deals with non-vanishing η. But the orientation of the principle axis system of the second rank tensor relative to the diffusion tensor must be known.

The correlation function (12) simplifies further if η = 0.

By use of: B_{0j}^{j} = 0j • B_{00} one finds for g(m)(t):

\[
g(m)(t) = \frac{1}{4} \sum_{n=-2}^{+2} D_{0,n}^{(2)}(0, \beta', 0) B_{00}^{2} \cdot e^{-(6D_1 + (D_1 - D_2)\eta^2)t}.
\]  

(12 a)

This formula has been derived earlier by SHIMIZU.

As is well known, the relaxation rates 1/T_1 and 1/T_2 are certain linear combinations of the Fourier transforms of the correlation functions given here. Thus, because of the rather complicated form of Eqs. (6), (7), (10), (11) and (12) the expressions for 1/T_1, 1/T_2 or line width will also be complicated. With the formulation of the correlation functions given here it will be easy to write computer programs for evaluating experimental data.

6. Appendix

Another model for the internal axial motion is the stepwise reorientation through an angle of 2π/3. Each orientation 0, 2π/3, 4π/3 has an a priori probability p = 1/3. We assume that the mean lifetime in each site is τ_x. Then the probability that no rotation has taken place until time t is (1 + 2 exp(-t/τ_x))
and the probability that a rotation has taken place to one of the other two orientations is
\[ g(\chi_0, \chi, t) = \left( \frac{1}{3} - \frac{1}{3} \exp\left(-t/\tau_r\right) \right). \]

The probability \(g(\chi_0, \chi, t)\) may be given in terms of these two expressions.

\[ g(\chi_0, \chi, t) = (\frac{1}{3} + \frac{2}{3} e^{-t/\tau_r}) \left\{ \delta(\chi_0) \delta(\chi) + \delta(\chi_0 - \frac{2\pi}{3}) \delta\left(\chi - \frac{2\pi}{3}\right) + \delta(\chi_0 - \frac{4\pi}{3}) \delta\left(\chi - \frac{4\pi}{3}\right) \right\} \]
\[ + \left( \frac{1}{3} - \frac{1}{3} e^{-t/\tau_r} \right) \left\{ \delta(\chi_0) \delta(\chi) + \delta(\chi_0 - \frac{2\pi}{3}) \delta\left(\chi - \frac{2\pi}{3}\right) \right. \]
\[ \left. + \delta(\chi_0 - \frac{4\pi}{3}) \delta(\chi) + \delta(\chi_0 - \frac{2\pi}{3}) \delta\left(\chi - \frac{2\pi}{3}\right) \right\}. \]

\(\delta\) is Dirac's delta function.

Now the integration over \(\chi_0, \chi\) which leads to Eq. (6) can be again carried out. Except for the time dependence one gets the same result. The time dependent factor in Eq. (6) becomes:
\[ e^{-(6D_0 + (D_0 - D) n^2)t} e^{-t/\tau_j}. \]

Here \(1/\tau_j\) is given by:
\[ \frac{1}{\tau_j} = \begin{cases} 0 & \text{if } j = 0, \\ \frac{1}{\tau_r} & \text{if } j = \pm 1 \pm 2. \end{cases} \]

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