

## COMMUNICATION

# Effect of Coupling between Rotational and Translational Brownian Motions on NMR Spin Relaxation: Consideration Using Green Function of Rigid Body Diffusion

Igor S. Beloborodov, Vladislav Yu. Orekhov, and Alexander S. Arseniev

*Shemyakin and Ovchinnikov Institute of Bioorganic Chemistry, Russian Academy of Science, ul. Miklukho-Maklaya 16/10, 117871 Moscow, Russia*

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**Using the Green function of arbitrary rigid Brownian diffusion (Goldstein, *Biopolymers* 33, 409–436, 1993), it was analytically shown that coupling between translation and rotation diffusion degrees of freedom does not affect the correlation functions relevant to the NMR intramolecular relaxation. It follows that spectral densities usually used for the anisotropic rotation diffusion (Woessner, *J. Chem. Phys.* 37, 647–654, 1962) can be regarded as exact in respect to the rotation–translation coupling for the spin system connected with a rigid body.** © 1998 Academic Press

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Comprehensive quantum mechanical theory connecting different pathways of the spin relaxation with values of spectral density function at the characteristic frequencies was established long ago (1). There is much confusion, however, regarding the calculation of these spectral densities, because it intrinsically requires a model of the spin motions. Thus relaxation studies in liquids always rely upon some model of molecular Brownian motion. Commonly in the consideration of different relaxation mechanisms either translation (1) or rotation diffusion (2) is taken in to account. It is clear, however, that a body of irregular shape undergoes a coupled translation and rotation diffusion. For example, translation of a screw-shaped particle would lead to rotation and vice versa. Diffusion of a rigid body of arbitrary shape can be rigorously described using  $6 \times 6$  diffusion matrix composed from four  $3 \times 3$  matrixes, which are translation  $\mathbf{D}'$ , and rotation  $\mathbf{D}''$  tensors and tensors  $\mathbf{D}'''$ , and  $\mathbf{D}''''$  describing coupling between rotation and translation degrees of freedom (3). It is not clear, however, whether coupling between rotation and translation diffusion is significant for the calculation of spectral densities. In this communication we show that rotation–translation coupling has no effect on NMR relaxation rates, at least if only intramolecular relaxation mechanisms are concerned.

Equations describing homo- and heteronuclear relaxation rates in terms of values of spectral density function  $J_{qq'}(\omega)$  can be found elsewhere (1). Here,  $J_{qq'}(\omega)$  is a Fourier transform of the relevant correlation function  $\Phi_{qq'}(\tau) = \langle F_q^*(t)F_{q'}(t + \tau) \rangle$ . As usual,  $F(t)$  is the time-dependent part of the interaction causing the relaxation. For the intramolecular relaxation mechanisms  $F(t)$  is not depend explicitly on the coordinates and can be expressed by Wigner matrix components  $D_{q_0}^{(2)}[\Omega_L]$  (4):

$$\Phi_{qq'}(\tau) \sim \langle D_{q_0}^{*(2)}[\Omega_L] \cdot D_{q'_0}^{(2)}[\Omega'_L] \rangle. \quad [1]$$

Here  $\Omega_L$  and  $\Omega'_L$  represent Euler's angles defining orientation of the relevant interaction vector in the laboratory coordinate frame in time  $t$  and  $t + \tau$ , respectively. If intramolecular motions are not regarded, the orientation of the vector in the molecular coordinate system does not depend on time. In this coordinate system

$$\begin{aligned} \Phi_{qq'}(\tau) \sim \sum_{l,l'=-2}^2 \langle D_{q_l}^{*(2)}[\Omega] \cdot D_{q'_l}^{(2)}[\Omega'] \rangle \\ \times D_{l_0}^{*(2)}[\Omega_M] \cdot D_{l'_0}^{(2)}[\Omega_M], \end{aligned} \quad [2]$$

where  $\Omega$  and  $\Omega'$  are Euler's angles defining orientation of the molecular coordinate system with respect to the laboratory coordinate frame in moments  $t$  and  $t + \tau$ , respectively.  $\Omega_M$  are angles of the relevant vector in the molecular coordinate frame. The correlator in Eq. [2] can be calculated using the Green function  $G(\tilde{r}'\Omega'|\tilde{r}\Omega)$ . It provide the probability of finding a rigid body at point  $\tilde{r}'$  with orientation  $\Omega'$  at time  $t + \tau$ , if at time  $t$  it was at point  $\tilde{r}$  with orientation  $\Omega$ :

$$\begin{aligned} \langle D_{q_l}^{*(2)}[\Omega] \cdot D_{q'_l}^{(2)}[\Omega'] \rangle \\ = \frac{1}{8\pi^2} \int D_{q_l}^{*(2)}[\Omega] \cdot D_{q'_l}^{(2)}[\Omega'] G(\tilde{r}'\Omega'|\tilde{r}\Omega) \\ \times d\tilde{r}d\tilde{r}' d\Omega d\Omega'. \end{aligned} \quad [3]$$

The Green function of a rigid particle diffusion in liquid, which rigorously accounts for the translation and rotation coupling, was recently obtained by Goldstein (5):

$$G(\tilde{r}'\Omega'|\tilde{r}\Omega) = \sum_{J,n,J',n',m} \int \frac{dp_z}{2\pi} e^{ip_z(r'_z-r_z)} \Psi_{nm}^J(\Omega) \Psi_{n'm}^{*J'}(\Omega') \\ \times \exp\{-(p_z^2 D_0 + E_{Jn} + p_z^2 V_{Jn}^{(2)})\tau\} \\ \times \langle 0|\hat{T}a_{Jnm} \exp\left\{\int_0^t H_I(t')dt'\right\} a_{J'n'm}^+ |0\rangle. \quad [4]$$

Here  $p_z$  is the  $z$  projection of the molecular momentum in laboratory system coordinate frame;  $\tilde{r}$  is the molecular coordinate system origin;  $E_{Jn}$  and  $\Psi_{nm}^J(\Omega)$  are the eigenvalues and eigenfunctions of the anisotropic rotator, respectively;  $D_0 = \text{trace}(\mathbf{D}^t)/3$ ;  $V_{Jn}^{(2)} = \langle \Psi_{nm}^J | V^{(2)} | \Psi_{nm}^J \rangle$  is the matrix element of the  $V^{(2)}$  operator in Goldstein's (5) notation;  $\hat{T}$  is the operator of chronological order;  $H_I$  is the off-diagonal part of the Green function evolution operator in the interaction representation and representation of secondary quantification, where raising and destroying operators  $a^+$  and  $a$  obey the following rules:  $a_{Jnm} |\Psi_{nm}^J(\Omega)\rangle = |0\rangle$  and  $a_{Jnm}^+ |0\rangle = |\Psi_{nm}^J(\Omega)\rangle$ . It should be noted that there is a misprint in Eq. [26] of Goldstein's work (5). Namely, the term in the second line of the equation  $2D_{zz}^t D_{00}^1 L_z$  must be replaced with  $2D_{zz}^t D_{00}^1 L_z$ .

From Eqs. [3] and [4] after the integration on coordinates  $\tilde{r}$  and  $\tilde{r}'$  one can get

$$\langle D_{q_l}^{*(2)}[\Omega] \cdot D_{q_l'}^{(2)}[\Omega'] \rangle \\ = \frac{1}{8\pi^2} \int D_{q_l}^{*(2)}[\Omega] \cdot D_{q_l'}^{(2)}[\Omega'] d\Omega d\Omega' \\ \times \sum_{J,n,J',n',m} \int dp_z \delta(p_z) \Psi_{nm}^J(\Omega) \Psi_{n'm}^{*J'}(\Omega') \\ \times \exp\{-(p_z^2 D_0 + E_{Jn} + p_z^2 V_{Jn}^{(2)})\tau\} \\ \times \langle 0|\hat{T}a_{Jnm} \exp\left\{\int_0^t H_I(t')dt'\right\} a_{J'n'm}^+ |0\rangle. \quad [5]$$

If  $p_z = 0$ ,  $H_I$  is also zero (see Eq. [31] in (5)) and consequently matrix element  $\langle 0|\dots|0\rangle$  in Eqs. [4] and [5] reduces to  $\delta_{JJ'}\delta_{mm'}$ . Finally, after integration on  $p_z$ , Eq. [5] transforms to

$$\langle D_{q_l}^{*(2)}[\Omega] \cdot D_{q_l'}^{(2)}[\Omega'] \rangle \\ = \frac{1}{8\pi^2} \int D_{q_l}^{*(2)}[\Omega] \cdot D_{q_l'}^{(2)}[\Omega'] d\Omega d\Omega' G_R(\Omega|\Omega'). \quad [6]$$

Here  $G_R(\Omega|\Omega')$  is the Green function of rotation diffusion without coupling with translation:

$$G_R(\Omega|\Omega') = \sum_{J,n,m} \Psi_{nm}^J(\Omega) \Psi_{nm}^{*J'}(\Omega') \exp\{-(E_{Jn})\tau\}. \quad [7]$$

The same form of the Green function for the rotation diffusion without translations was obtained by Favro (6).

It follows from Eqs. [2], [6] that coupling between translation and rotation diffusion degrees of freedom does not effect the correlation functions relevant to the NMR intramolecular relaxation. It can be shown that spectral densities calculated using Eqs. [6], [7] are the same as those obtained without accounting for translation-rotation coupling by Woessner (2). Thus Woessner's spectral densities can be regarded as exact with respect to the rotation-translation coupling for the spin system connected with a rigid body. It is notable, however, that the results presented have been proved in this paper only for the intramolecular relaxation mechanisms, which are not connected with the displacement of molecular origin during Brownian motion.

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