Comment on "Intermolecular translational-rotational contribution to nuclear-spin relaxation in liquids"

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A recent theoretical treatment of intermolecular nuclear-spin relaxation that incorporates the effect of molecular rotation [K. Lendi, Phys. Rev. A **45**, 7906 (1992)] is shown to be based on what appears to be a mistaken assignment of Euler angles. In particular, the conditional probability for reorientation of the intermolecular vector due to molecular rotation seems to be given incorrectly. Unsolvable integrals that are examined by Lendi are derived without considering the reflecting wall boundary conditions that are requisite for the problem of translational diffusion. [S1050-2947(96)09906-4]

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Recently, Lendi [1] proposed a formalism aimed at incorporating the rotational motion of molecules into the theory of intermolecular NMR relaxation [2]. As shown below, his method rests on what appears to be an incorrect assignment of the Euler angles inherent to this problem. The Hamiltonian of the intermolecular dipole-dipolar interaction is

$$H_{DD}^{IS}(\mathbf{r},\Omega) = -\frac{\mu_0}{4\pi}\gamma_I\gamma_S\hbar r_{IS}^{-3}\sqrt{24\pi/5}\sum_{m=-2}^{2}$$
$$\times(-1)^m Y_{2,-m}(\Omega)A_{2,m}(\mathbf{I},\mathbf{S}), \qquad (1)$$

where $A_{2,m}(\mathbf{I},\mathbf{S})$ are the standard second-rank spin operators, whereas $Y_{2,-m}(\Omega)$ are the spherical harmonics. The angle Ω refers to orientation of the internuclear vector $\mathbf{r}$ in the laboratory frame (see Fig. 1). The choice of laboratory frame is dictated here by the fact that spins $\mathbf{I}$ and $\mathbf{S}$ are quantized along the z axis associated with an external magnetic field. With this, the relaxation rates, T_1^{-1}, T_2^{-1}, can be appropriately defined [2].

In order to account for the rotational motion of molecules, an alternative identification of Ω has been suggested by Lendi [1]. In this interpretation Ω refers to the angular coordinates of $\mathbf{r}$ in the molecular frame and changes through the rotational diffusion of the molecule relative to the intermolecular vector $\mathbf{R}$. Consequently, the conditional probability density associated with this rotational motion is specified [1] as

$$p_{\text{rot}}(\hat{\Omega},t|\hat{\Omega}_0) = \frac{1}{8\pi^2}\sum_{l=0}^{\infty}\sum_{m,n=-l}^{l}(2l+1)D_{mn}^{(l)*}(\hat{\Omega}_0)D_{mn}^{(l)}(\hat{\Omega})$$
$$\times\exp(-\epsilon_{lm}t), \qquad (2)$$

where $D_{mn}^{(l)}(\hat{\Omega})$ are Wigner rotation matrices. This conditional probability function is related to isotropic diffusion of symmetric-top molecules with

$$\epsilon_{lm} = D_\perp l(l+1) + (D_\parallel - D_\perp)m^2, \qquad (3)$$

where $D_\perp$ and $D_\parallel$ are principal components of the diffusion tensor.

In the following analyses, the spherical harmonics of Eq. (1), as well as the symmetric-top functions of Eq. (2), are utilized for calculation of the spectral densities [1].

This approach may be flawed since the two definitions of Ω invoked in Lendi's analysis are, in fact, incompatible. The focusing point of this controversy is the conditional probability function (2), which is in contradiction with the physical picture. Specifically, the reorientation of internuclear vector $\mathbf{r}$ due to molecular rotation is different from the isotropic diffusion contrary to what Eq. (2) suggests (see Fig. 1). Rotational diffusion represented by Eqs. (2) and (3) is relevant for stochastic motion of radial vector ρ_I, but it does not describe adequately the modulation of $\mathbf{r}$ by molecular rotation.

In terms of the physical picture, Lendi's formalism suggests that, in addition to the usual translational motion, two molecules also form a virtual rigid rotator, involved in rotational motion. The latter process, characterized by standard diffusion constants $D_\perp, D_\parallel$, obviously has no physical relevance. The manifestations of this mistaken analysis is the absence of eccentricity parameters, characterizing the off-center location of spins, in Lendi's results. Obviously, the rotational motion modulates intermolecular interactions only for molecules with off-center location of spin sites.

Rigorous and elegant analytic treatment of the same problem posed by Lendi can be found in the work of Ayant, Belorizky, Fries, and Rosset [3], followed by an interpretation of the experimental data [4]. Molecular dynamics studies have been performed by Westlund and Lynden-Bell [5].
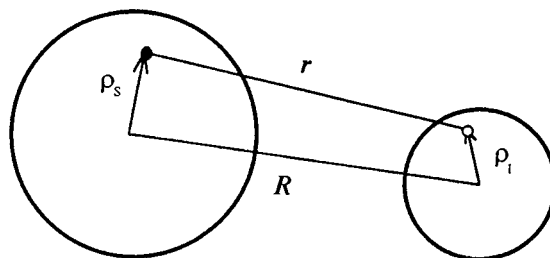

FIG. 1. The set of pointing vectors essential for the description of intermolecular dipole-dipole relaxation.

It should be noted also that the analysis of Lendi is largely devoted to finding analytic approximations for the integrals arising in his consideration, which are similar in structure to the one considered in Ref. [2]. However, as shown by two independent studies [6], integrals of this type arise due to incorrect boundary conditions that do not take account of excluded volume. Proper formulation of the boundary conditions leads to a closed analytic solution for the integrals involved [3]. Finally, the significance of nontrivial pair correlation functions for the problem in question has been demonstrated by the authors of Ref. [6].

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