

ANISOTROPY OF THE SPIN-LATTICE RELAXATION OF THE DIPOLAR ENERGY OF TWO, THREE AND FOUR SPINS*

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Abstract: The anisotropy of the Slichter Ailion order parameter was calculated for a few groups of two, three and four spins $1/2$ which undergo reorientations. This anisotropy is typically $\sim 50\%$, and in special cases much larger. It makes the relaxation time of the dipolar reservoir anisotropic, which is convenient for the analysis of very slow reorientations.

1. Introduction

Some ten years ago Slichter and Ailion (SA) developed the strong collision theory of nuclear spin relaxation¹⁾. This theory, which uses the sudden approximation method, is applicable to spin relaxation caused by very slow atomic motion. The SA theory made it possible to study the correlation times up to the limit imposed by T_1 , the spin-lattice relaxation time, thus extending the range of the correlation times that can be studied by the NMR technique by some four orders of magnitude.

The use of sudden approximation in the development of this theory implies that the motions which can be studied should occur suddenly on the scale of the Larmor precession period. It is known that most atomic reorientations in solids are abrupt, and occur in $\sim 10^{-12}$ s. In addition, the SA theory requires that between any two successive changes in the atomic coordination enough time must

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be allowed to establish the spin temperature in the system. This is equivalent to saying that the correlation time, τ , for the motion should be larger than T_2 . This condition is usually satisfied, depending on the activation energy, some 20–30 degrees below the temperature at which the NMR absorption line width attains its rigid-lattice value.

The SA theory has been found to be most useful in the study of the relaxation generated by slow translational diffusion²⁾ in solids. The slow reorientations have been studied only in one case³⁾. The present calculations were made to investigate in some simple cases the magnitude of the anisotropy of nuclear spin relaxation by slow reorientation.

2. The anisotropy of the Slichter-Ailion parameter and discussion

The SA relaxation of the dipolar energy by slow reorientations is given by $\frac{1}{T_{1D}} = \frac{1-p}{\tau}$, where p is the SA order parameter¹⁾, and τ is the correlation time for the reorientation. In the following, the results of a calculation of the anisotropy of p are given for groups of two, three and four spins 1/2. The geometries are shown at Fig. 1.

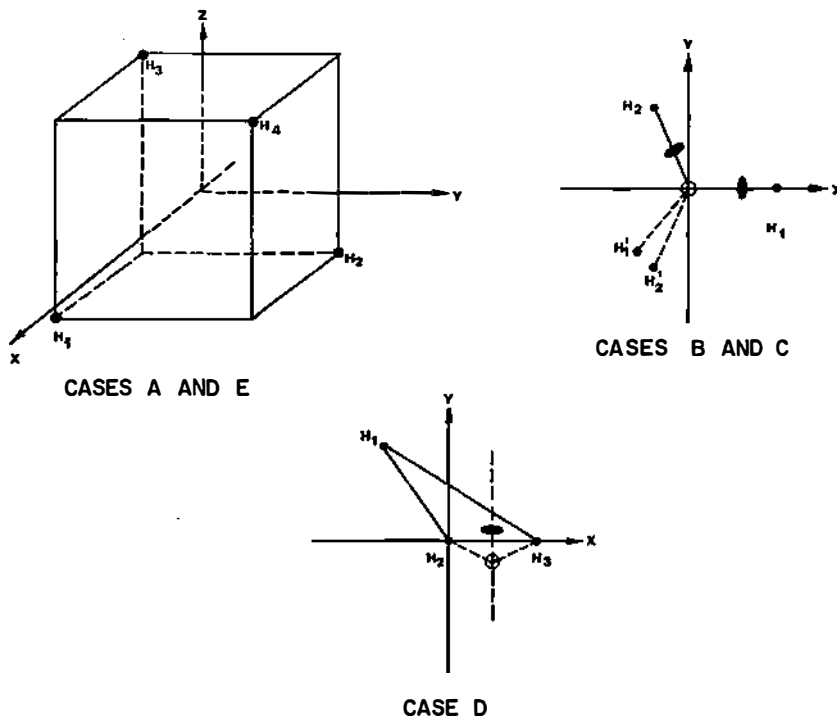


Fig. 1. Spin 1/2 geometries for which the Slichter-Ailion order parameter p was calculated

The expression that was used to calculate the order parameter p for a dipolar system is given by²⁾

$$p = \frac{\sum_i \sum_f \sum_{l < j} A_{i,l} A_{f,l} P_{if}}{\sum_i \sum_{l < j} A_{i,l}^2}, \quad (1)$$

where

$$A_{i,l} = (1 - 3 \cos^2 \alpha_{i,l}) r_{i,l}^{-3};$$

$\alpha_{i,l}$ is the angle between the vector $\vec{r}_{i,l}$ connecting the spins l and j in the initial configuration, and the external magnetic field \vec{H}_0 . P_{if} is the element of the transition probability matrix³⁾. The sums in equation (1) are over all distinct spin pairs in all initial and final configurations.

The relation between α and the polar coordinates of $\vec{r}_{i,l}$ ($\vartheta_{i,l}, \varphi_{i,l}$) and H_0 (Θ, Φ) is given by

$$\cos \alpha = \cos \Theta \cos \vartheta + \sin \Theta \sin \vartheta \cos (\Phi - \varphi).$$

A. Two tetrahedrally coordinated protons. If two protons, which are tetrahedrally coordinated, Fig. 1, are allowed to jump randomly between any two corners of a tetrahedron, then, for each initial state, 5 final states are possible. For such a system³⁾, p is equal to -0.2 and is isotropic (independent of Θ, Φ).

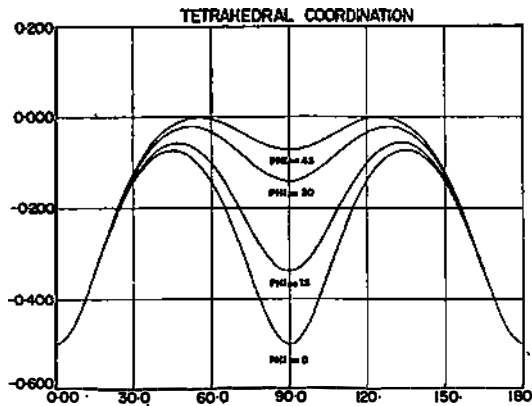


Fig. 2. Case A: The dependence of the parameter p (along the y -axis) on the angle Θ for two tetrahedrally coordinated protons.

Since a simultaneous jump of two protons, a two-axis reorientation, is less likely to occur, the above case was considered with the restriction that $P_{if} = 0$ for all final states which are generated from any initial state by a simultaneous jump

of two protons. As a result, for each initial state there are only four final states. With this restriction the parameter p becomes anisotropic. The results are given in Fig. 2, where p is plotted as a function of θ for different values of Φ . The polar coordinates θ and Φ are defined in a coordinate system where the tetrahedral sites are on the corners of a cube. The results for $\Phi > 45^\circ$ can be obtained from the following relations: $p(\Phi) = p(90^\circ + \Phi)$ and $p(45^\circ + \Phi) = p(45^\circ - \Phi)$.

B. *Two (water) protons, two rotational axes.* The values of p for a water molecule in an environment such that both O — H bonds are 180° symmetry axes are given in Fig. 3. For each initial state there are two final states. Each final state corresponds to a 180° rotation of one of the O-H bonds around the other one. θ and Φ are defined in a coordinate system where one O-H bond is along the x axis and the second

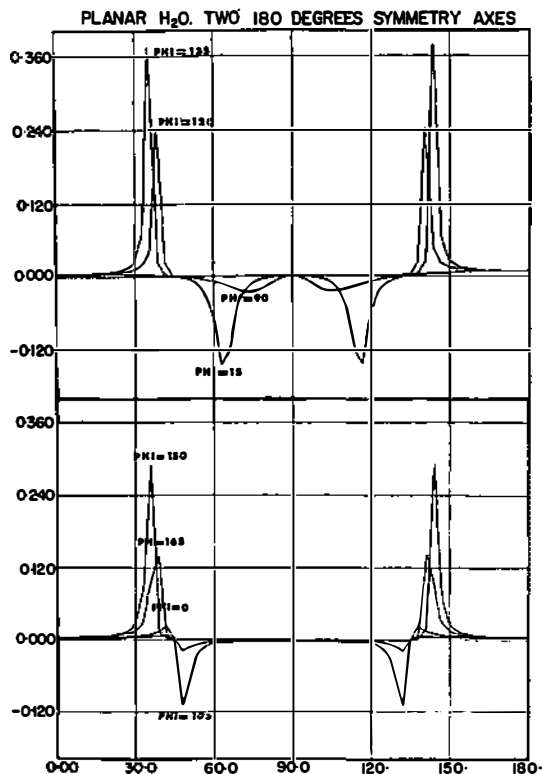


Fig. 3. Case B: The dependence of the parameter p on the angle θ for two protons having two 180° symmetry axes.

proton is in the second quadrant. The HOH angle was taken to be the tetrahedral angle, Fig. 1. The plots of p for $\Phi = 30^\circ, 45^\circ, 60^\circ, 75^\circ$ are not shown because of the very small values of p ($|p| < 0.005$).

C. *Two (water) protons, one rotational axis.* If only one O-H bond of the water molecule is a 180° symmetry axis, the parameter p is shown in Fig. 4. The 180° symmetry axis (the O-H bond) is along the x -axis, Fig. 1. For each initial state there is only one final state. The plots of p for $\Phi = 45^\circ, 60^\circ, 75^\circ, 90^\circ$ are not given because of the very small values of p .

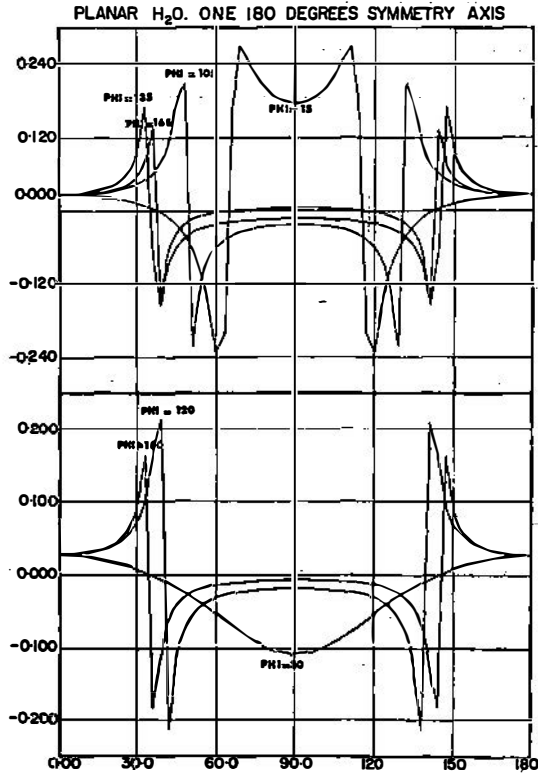


Fig. 4. Case C: The dependence of the parameter p on the angle θ for two protons having one 180° symmetry axis.

D. *Three protons.* The symmetric arrangement of 3 protons around a 3-fold symmetry axis was treated by SA¹⁾. For the present model one H₂O molecule in which the two water protons exchange sites, and one OH group, were used. The inter-proton distances correspond to the colemanite⁴⁾ structure; the water protons are 1.70\AA apart and the hydroxyl proton is 2.34\AA and 3.66\AA distant from the water protons, Fig. 1. Since for each initial state there is only one final state, we get

$$p = \frac{2A_{1,12}A_{1,13} + (A_{1,23})^2}{(A_{1,12})^2 + (A_{1,13})^2 + (A_{1,23})^2} \quad (2)$$

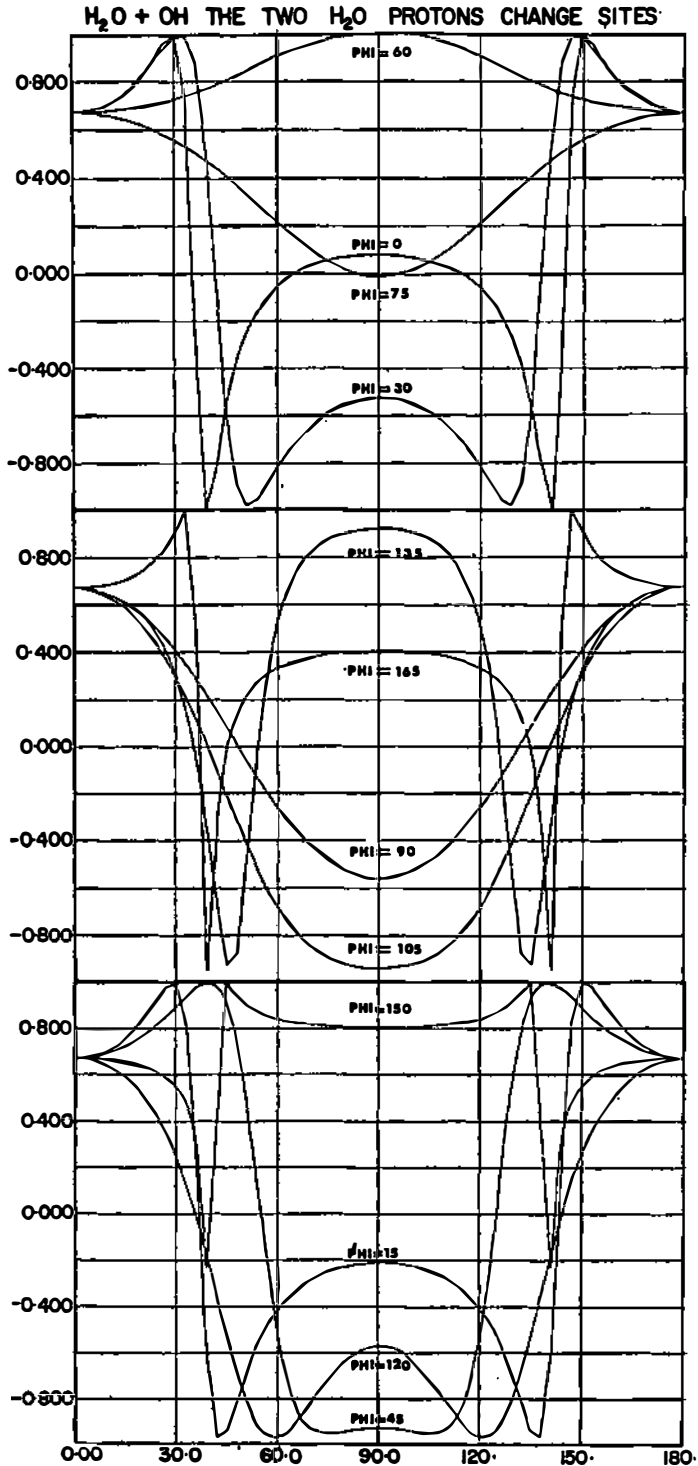


Fig. 5. Case D: The dependence of the parameter p on the angle θ for three protons. The geometry corresponds to one water molecule and one hydroxyl group in the mineral colemanite⁴⁾.

where the proton pair 23 is the water pair. This expression is obtained by using the relation $A_{1,12} = A_{2,13}$ and $A_{1,13} = A_{2,12}$. The values of p are shown in Fig. 5. The polar co-ordinates Θ and Φ are defined in a coordinate system where the water proton pair lies along the x -axis and the hydroxyl proton is in the second quadrant, Fig. 1.

E. *Four tetrahedrally coordinated protons*. In this case, all pairs are equivalent and the sum over all pairs is reduced to a sum over one pair multiplied by the number of pairs. Since the number of pairs appears both in the numerator and denominator of the equation (1), the parameter p is -0.2 , the same as in case A.

In order to study the molecular dynamics through the anisotropy of p , T_{1D} must be measured accurately. The best methods are the $90 - 45 - 45$ pulse sequence of Jeener and Broekaert and the ADRF²⁾. When the condition for the SA relaxation of the dipolar energy is met, T_1 is normally very long (100 s and more) and T_{1D} is quite short. For example, in a hydrate with T_2 of $\sim 5 \mu\text{s}$, if the p -anisotropy is studied at $\tau \sim 10 \cdot T_2$, the calculated variation of T_{1D} is typically from 100 to $50 \mu\text{s}$. In the geometry of case D the anisotropy becomes exceptionally large. If τ is $50 \mu\text{s}$ then T_{1D} changes from 1,000 to $25 \mu\text{s}$ as the crystal is rotated in the magnetic field. However, if the neighbouring spins are included in the calculation, the anisotropy becomes smaller in general but is still large enough to make the study of the anisotropy of T_{1D} in crystals an effective method for the analysis of very slow reorientations.

References

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