

NMR Absorption and Tunneling

A. Watton

University of Victoria
British Columbia, Canada

I. INTRODUCTION

The phenomenon of rotational tunneling and its influence on the NMR absorption lineshape have received a good deal of attention in recent years (1-6). The physics of the phenomenon is fairly simple, but tends to be obscured by the mathematical machinery necessary to handle the effect in three-spin (CH_3) and four-spin (NH_4^+) groups. This paper attempts to describe the theory of tunneling first for the conceptually simpler two-spin system. It then shows how the procedures are generalized to the more complicated four-spin system.

II. NMR ABSORPTION IN TWO-SPIN- $1/2$ SYSTEMS

A collection of non-interacting nuclei in a magnetic field \mathcal{H} is described by the Zeeman Hamiltonian

$$\mathcal{H}_z = -\sum_i \vec{\mu}_i \cdot \vec{H} = -\hbar\omega_0 \sum_i I_z^i$$

where $\omega_0 = \gamma\mathcal{H}$ is the Larmor frequency and I_z^i the z component of the spin operator for the i th nucleus.

The spin states for this system are thus labelled by the eigenvalues of I_z^i ; $m_i = \pm 1/2$. For example, for two-spin states $\phi = |m_1, m_2\rangle$

$$\begin{aligned} |++\rangle & E = -\hbar\omega_0 \\ |+-\rangle, |-+\rangle & E = 0, \text{ doubly degenerate} \\ |--\rangle & E = \hbar\omega_0 \end{aligned}$$

It is convenient to form these spin states into symmetric and antisymmetric combinations ϕ_s and ϕ_a .

$$\begin{aligned} \phi_s^{(1)} &= |++\rangle & E &= -\hbar\omega_0 \\ \phi_s^{(0)} &= |+-\rangle + |-+\rangle & E &= 0 \\ \phi_s^{(-1)} &= |--\rangle & E &= \hbar\omega_0 \end{aligned}$$

and

$$\phi_a^{(0)} = |+-\rangle - |-+\rangle \quad E = 0$$

Under spin exchange 1 \leftrightarrow 2 (180° rotation), the ϕ_s states are invariant while the ϕ_a state is negated

$$\begin{aligned} \phi_s(2,1) &= \phi_s(1,2) \\ \phi_a(2,1) &= -\phi_a(1,2) \end{aligned}$$

Now introduce the interaction between nuclei as the secular part of the dipole-dipole interaction

$$\mathcal{H}_D = \gamma^2 \hbar^2 \frac{(1-3\cos^2\theta)}{r^3} [I_z^1 I_z^2 - 1/4(I_x^1 I_x^2 + I_y^1 I_y^2)]$$

where the internuclear vector is of length r and makes an angle θ with the applied magnetic field.

Note that for a two-spin system \mathcal{H}_D is a product of a symmetric spatial and a symmetric spin part. As a

result \mathcal{H}_D can couple only spin states of the same symmetry type. That is

$$\langle \phi_s | \mathcal{H}_D | \Delta \phi_s \rangle = 0$$

The eigenstates ϕ_s and ϕ_a are thus preserved, but the degeneracy in the $E = 0$ level is removed, resulting in a splitting of the NMR absorption line (Figure 1).

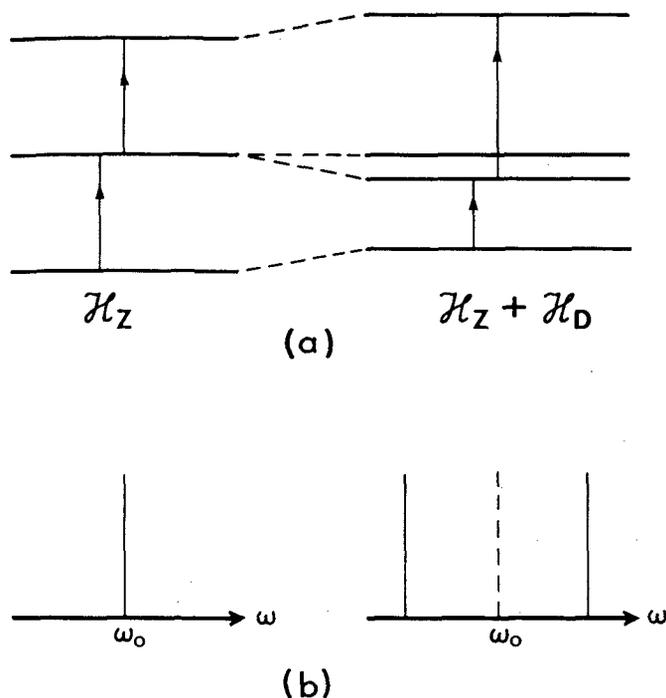


Figure 1. (a) Energy level scheme for two-spin- $1/2$ system. (b) Splitting of NMR absorption line by \mathcal{H}_D .

However, not all compounds exhibit the full lineshape at rigid lattice temperatures expected from the above considerations. For example, some methyl (CH_3) and ammonium (NH_4^+) compounds and solid methane (CH_4) exhibit considerably narrowed lineshapes at liquid helium temperatures. It becomes necessary then to consider the other molecular coordinates, for example, the orientation or rotational coordinates.

A more complete Hamiltonian for the system would be

$$\mathcal{H} = \mathcal{H}_R + \mathcal{H}_Z + \mathcal{H}_D$$

where the rotational Hamiltonian is

$$\mathcal{H}_R = \frac{1}{2} I \omega^2 + V(\phi, \theta, \psi)$$

$V(\phi, \theta, \psi)$ specifies the potential energy of the nuclear group in the local crystal field.

If we suppose the temperature to be low enough for only ground vibrational and electronic states to be occupied, we can ignore their associated coordinates.

Since \mathcal{H}_D is a small perturbation on $\mathcal{H}_R + \mathcal{H}_Z$, the total wave function can be represented as a product of space (rotational) and spin parts

$$\Psi = \psi(\text{space})\phi(\text{spin})$$

For example, if V is small, ψ free rotor state; if V is large, ψ torsional oscillator state.

The two-spin system has 180° (spin exchange) symmetry. There are therefore two degenerate spatial states ψ_1 and ψ_2 ; $\psi_2(r_1, r_2) = \psi_1(r_2, r_1)$. From these we can form symmetric and antisymmetric combinations as for ϕ .

$$\begin{aligned} \psi_s &= \psi_1 + \psi_2 \\ \psi_a &= \psi_1 - \psi_2 \end{aligned}$$

which are degenerate if V is large enough for there to be no overlap, $\langle \psi_1 | \psi_2 \rangle = 0$. If V is decreased, the overlap splits the spatial states apart so that $E_s > E_a$. This is referred to as tunneling.

A. Spin Statistics

Since protons are fermions, the total wavefunction Ψ is antisymmetric under proton exchange (180° rotation). This restricts the combinations of ψ and ϕ states allowed to

$$\Psi = \psi_s \phi_s \text{ or } \psi_a \phi_a$$

i.e., the symmetry requirement associates ψ and ϕ states of opposite symmetry only.

The splitting of the spatial states resulting from the overlap of ψ_1 and ψ_2 (tunneling) therefore leads to a splitting of the associated spin states. This splitting is of the order $\langle \psi | \mathcal{H}_R | \Delta \psi \rangle$ and may be much less than, of the order of, or much greater than the dipolar splitting, depending on whether V is large or small. The overall energy level scheme, as various parts of the Hamiltonian are introduced, is shown in Figure 2.

The NMR absorption is observed by exciting the system with an RF field \mathcal{H}_1 along the x axis. The perturbing Hamiltonian

$$\mathcal{H}_1 = -\gamma \hbar \mathcal{H}_1 I_x$$

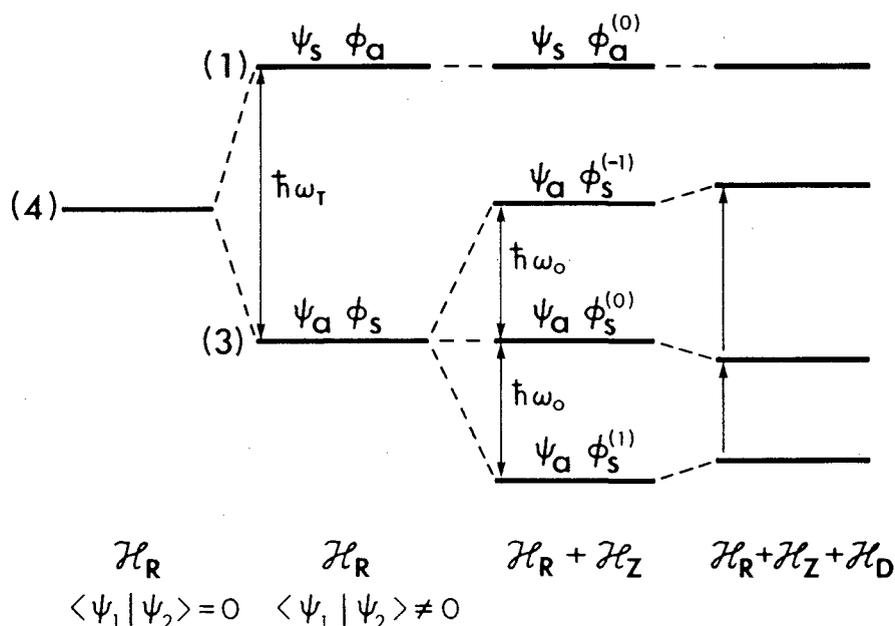


Figure 2. Energy level scheme for two-spin- $\frac{1}{2}$ system as each contribution is added to the total Hamiltonian.

induces transitions between levels for which $\Delta m = \pm 1$. However, since \mathcal{H}_C is completely symmetric under spin exchange, it couples only spin states of the same symmetry. Therefore, only transitions between the s states are induced and the effects of tunneling are not observed by absorption in the two-spin system.

vastly more energy than rotation, we can restrict our consideration to the tetrahedral rotation group T , consisting of the elements E (identity), $4C_3$ (four 120° rotation axes), $4C_2$ (four 240° rotation axes), and $3C_2$ (three 180° rotation axes). Two of the elements are illustrated in Figure 3.

III. TETRAHEDRAL FOUR-SPIN- $\frac{1}{2}$ SYSTEM (NH_4^+)

In a four-spin- $\frac{1}{2}$ system there are 16 spin states $\phi = |m_1 m_2 m_3 m_4\rangle$, where $m_i = \pm \frac{1}{2}$.

No. of States	m	States	E
1	2	$ ++++\rangle$	$-2\hbar\omega_0$
4	1	$ - + + + \rangle, + \text{ perms}$	$-\hbar\omega_0$
6	0	$ -- + + \rangle, + \text{ perms}$	0
4	-1	$ + --- \rangle, + \text{ perms}$	$\hbar\omega_0$
1	-2	$ ---- \rangle$	$2\hbar\omega_0$

For a tetrahedral arrangement of spins, as in NH_4^+ , we must consider the molecular symmetry. However, since molecular inversion would require

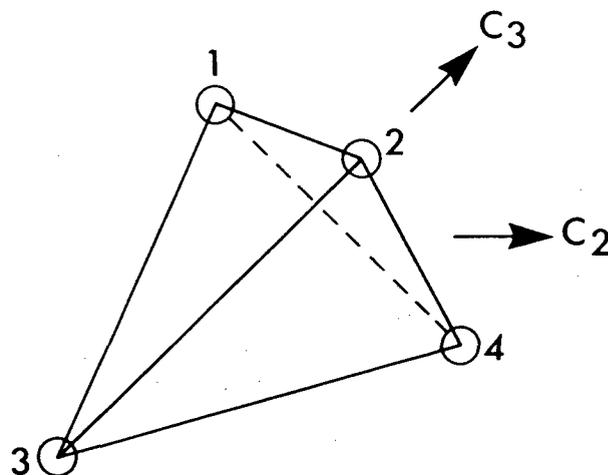


Figure 3. A C_2 and a C_3 rotation axis of the tetrahedral four-spin system.

From the 16 spin states we can form combinations which have definite transformation properties under the operations of T. These are the irreducible representations of T (7), for example, completely symmetric states A

$$\phi_A^{(2)} = | + + + + \rangle \phi_A^{(1)} = \frac{1}{2} [| - + + + \rangle + | + - + + \rangle + | + + - + \rangle + | + + + - \rangle]$$

and so on. In this way we can form five singlet A states ($m = 0, \pm 1, \pm 2$), three triply degenerate F states ($m = 0, \pm 1$), and one doubly degenerate E state ($m = 0$), that is, $5A + 3F + E$. In a similar way, the spatial states can also be classified according to their behaviour under T.

If the crystal field $V(\theta, \phi, \psi)$ is very large, the ψ states are close to torsional oscillator states. These are 12-fold degenerate, corresponding to the 12 equivalent orientations of the tetrahedron, $\psi_2 = C_3, \psi_1$, etc. The 12 degenerate spatial states break down into the combinations $A + E + 3F$, for example,

$$\psi_A = \psi_1 + \psi_2 + \dots + \psi_{12}$$

A. Spin Statistics

A rigid rotation of the molecule is equivalent to an exchange of two pairs of protons, for example, from Figure 3

$$C_2 \equiv (13)(24) \\ C_3 \equiv (134) \equiv (13)(14)$$

Therefore, the total wavefunction Ψ must be completely symmetric under all rotations of T. This means that only spatial ψ and spin ϕ states of the same symmetry type can be combined: $\psi_A \phi_A, \psi_E \phi_E,$ and $\psi_F \phi_F$.

Overlap of the spatial wavefunction splits the 12-fold degenerate spatial states apart (tunneling), so splitting the associated spin states. The level splitting will depend on the symmetry as well as the strength of the crystal field potential $V(\phi, \theta, \psi)$ as shown in Figure 4.

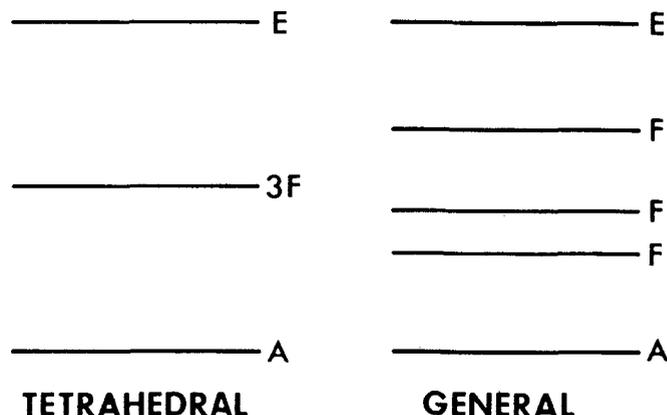


Figure 4. Comparison of the spatial energy level scheme for crystal fields of tetrahedral and of general symmetry.

The dipolar Hamiltonian is invariant under spin and space operations, but not under spin operations alone. \mathcal{H}_D therefore mixes the A, E, and F spin states. The tunneling splits transitions between these mixed levels, thus leading to observable effects in the absorption lineshape. The smaller the crystal field, the larger the spatial overlap and the further certain transitions are removed into the wings of the spectrum, eventually becoming lost in the noise and leaving the remaining observable part considerably narrowed.

REFERENCES

- ¹F. Apaydin and S. Clough, *J. Phys.* **C1**, 972 (1968).
- ²S. Clough, *J. Phys.* **C4**, 1075 (1971).
- ³A. Watton, A.R. Sharp, H.E. Petch, and M.M. Pintar, *Phys. Rev.* **B5**, 4281 (1972).
- ⁴R. Ikeda, and C.A. McDowell, *Mol. Phys.* **25**, 1217 (1973).
- ⁵A. Watton and H.E. Petch, *Phys. Rev.* **B7**, 12 (1973).
- ⁶Z. T. Lalowicz, C.A. McDowell, and R. Raghunathan, *J. Chem. Phys.* **68**, 852 (1978).
- ⁷M. Hamermesh, *Group Theory and its Applications to Physical Problems*, Addison-Wesley, 1962.