

ISOTROPIC NMR SHIFTS IN THE 'SOLID' AND 'LIQUID' STATES

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ABSTRACT

The derivation of the expressions for the isotropic shift of nmr signals in paramagnetic molecules is reconsidered. It is shown that the reaction of the electronic spin system to the thermal motions of the molecules should be taken into account. This leads to the result that the isotropic shift in liquids is independent of the relative magnitudes of the tumbling time and the electronic relaxation time. Hence, the temperature dependence of the correlation times cannot be responsible for non-Curie behaviour of the shift. For the case of free rotating molecules this result is proved in a way analogous to Van Vleck's treatment of the Langevin-Debye formula of the electric susceptibility. The relation with the phenomenon of motional narrowing is discussed.

I. INTRODUCTION

The shift of magnetic resonance lines of nuclei in paramagnetic molecules can, in most cases, be considered as the sum of two contributions. One is due to the scalar Fermi contact interaction between the unpaired electrons and the nucleus. This shift is called the contact shift and according to McConnell and Robertson¹ it is given by

$$\Delta H_c = -\bar{g} \frac{\beta H_0 S(S+1) A}{3kT} \frac{1}{\hbar\gamma}, \quad (1)$$

where \bar{g} is the rotationally averaged g value of the paramagnetic ion, β is the Bohr magneton, γ is the gyromagnetic ratio of the resonant nucleus, A is the hyperfine coupling constant in energy units, and H_0 is the applied magnetic field.

The second source for the nmr shift is the anisotropic dipole-dipole interaction between the paramagnetic ion and the nucleus. This shift is a function of the orientation of the molecule with respect to the external field. In this paper we are only concerned with the rotational average of the shift, the so called isotropic shift. In a powder this is the centre of gravity of the whole spectral structure. In liquids the molecular tumbling is normally rapid enough to reduce the spectrum to one narrow line positioned at the centre of gravity. Only when the electronic g -tensor is anisotropic the dipolar interaction gives rise to a non-vanishing contribution to the isotropic shift, which is called the pseudo contact shift.

McConnell and Robertson gave a theoretical treatment of the pseudo

contact shift¹. They considered a paramagnetic ion in which the electronic system can be completely described by a spin Hamiltonian consisting of a Zeeman term with an anisotropic g -tensor. The g -tensor was taken to be of cylindrical symmetry and the point-dipole model was assumed. They showed that the shift is given by

$$\Delta H_p = -f(g) \Delta g \frac{\beta^2 H_0 S(S+1) 3 \cos^2 \theta - 1}{3kT r^3}, \quad (2)$$

where $\Delta g = g_{\parallel} - g_{\perp}$; g_{\parallel} and g_{\perp} being the parallel and perpendicular components of the g -tensor, r is the vector connecting the paramagnetic ion and the nucleus, and θ is the angle between r and H_0 . $f(g)$ is some function of the components of the g -tensor. The authors found that $f(g)$ is different for cases of slow and fast tumbling. They distinguished between a 'solid', i.e. when the correlation time τ for the tumbling is $\tau \gg |\hbar/\Delta g \beta H_0|$, and a 'liquid' when $\tau \ll |\hbar/\Delta g \beta H_0|$. It should be noticed that the 'solid' case is also encountered in real liquids. Nevertheless we then still have a sufficiently short τ to establish motional narrowing, such that a single sharp resonance line is observed. A further distinction was made for the 'liquid' case with respect to the order of magnitude of the electron relaxation time T_{1e} . The results are:

$$\text{'solid'}, \quad f(g) = (g_{\parallel} + g_{\perp})/3, \quad (3)$$

$$\text{'liquid'}, \tau \ll T_{1e}, \quad f(g) = (g_{\parallel} + 2g_{\perp})/9, \quad (4)$$

$$\tau \gg T_{1e}, \quad f(g) = (3g_{\parallel} + 4g_{\perp})/15. \quad (5)$$

Jesson² has extended these expressions for the case of thermally populated excited electronic states. He showed that if a state with energy E_i gives rise to a shift ΔH_i , the total shift is given by

$$\Delta H = \sum_i \Delta H_i \exp(-E_i/kT) / \sum_i \exp(-E_i/kT), \quad (6)$$

an expression which is only justified if Zeeman mixing among the levels is negligible.

The most complete discussion of the isotropic shift, applicable to cases where one or more of the customarily assumed restrictions cannot be made, was recently given by Kurland and McGarvey.³ However, only the case of slow tumbling was treated and the problems connected with fast tumbling still remained untreated. The contact contribution of spin-only paramagnetic molecules exhibits Curie behaviour, according to equation 1. Equations 2 to 5 show that the pseudo contact shift also behaves proportionally to $1/T$ as long as τ remains in the domain of either the 'solid' or the 'liquid' case. Anomalous temperature dependence was observed in several cases. This behaviour was considered by Golding⁴, Jesson², La Mar and Van Hecke⁵, and McGarvey⁶. These authors considered the presence of low lying excited levels as the origin of deviations from Curie's law. However, as pointed out by Reuben and Fiat⁷, the following possibility should also be considered.

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Since τ depends exponentially on T we expect to find many examples of transitions between the 'solid' and 'liquid' states (equations 3 to 5), and thus a sharp drop in $f(g)$ when the temperature is increased. It is clear that this effect should be allowed for in the explanations of anomalous temperature behaviour.

Another striking consequence of equations 2 to 5 is the nonlinear H_0 -dependence: a sample which behaves as a 'solid' under normal experimental conditions, can in principle be changed into a 'liquid' by decreasing H_0 sufficiently.

Finally we observe that this is an example of an average spectral *shift* which is dependent on the correlation times, whereas in most other theories of the effect of random motions on spectral features, it is just the *line shape* which is determined by the nature of the motion.

The work reported in this paper was undertaken in order to study these properties of the isotropic shift in more detail. In particular it was hoped to be able to calculate the shift for the intermediate τ region. In fact, we came to the conclusion that there is no τ dependence at all, as will be explained in the following sections.

II. THE STEADY STATE OF THE ELECTRONIC SYSTEM

In nmr experiments on paramagnetic molecules it is the nuclear system which is directly disturbed by the r.f. field, and since the interaction between the nuclei and the electrons is only a small perturbation of the electronic Hamiltonian, the effect of the r.f. field on the behaviour of the electrons is negligible. Thus, the nuclei feel the influence of the electrons which are in thermal equilibrium, i.e. the determination of isotropic nmr shifts is essentially the measurement of a property of the electron system in equilibrium. This in contradistinction to an esr measurement on the same molecule, where we measure the response of the system to a time dependent force which removes the system from equilibrium. Thus the first step in the calculation of isotropic shifts is the determination of the equilibrium density matrix of the electronic system.

To begin with a powder is considered. We specify the orientation of a molecule by the Eulerian angles, Ω . The electronic Hamiltonian, \mathcal{H}_e , is in general a function of Ω , and the equilibrium density matrix for all the molecules with the same Ω is

$$\rho(\Omega) = \exp[-\mathcal{H}_e(\Omega)/kT] / \text{tr} \exp[-\mathcal{H}_e(\Omega)/kT]. \quad (7)$$

The nmr shift is essentially the z -component of the local magnetic field at the site of the nucleus. This is a physically observable quantity, which is represented quantum mechanically by an operator \mathbf{P} . This operator also depends on the orientation of the molecule. The shift of the molecules with orientation Ω is now given by $\text{tr}[\rho(\Omega)\mathbf{P}(\Omega)]$ and the isotropic shift by

$$\Delta H = \frac{1}{8\pi^2} \int d\Omega \text{tr}[\rho(\Omega)\mathbf{P}(\Omega)]. \quad (8)$$

For the discussion of rotating molecules in liquids we write $\mathcal{H}_e(\Omega)$ as the

sum of an isotropic and an anisotropic part,

$$\mathcal{H}_e(\Omega) = \overline{\mathcal{H}}_e + \mathcal{H}'_e(\Omega), \quad (9)$$

$$\overline{\mathcal{H}}_e = \frac{1}{8\pi^2} \int \mathcal{H}_e(\Omega) d\Omega. \quad (10)$$

It is well known, that in an esr experiment on fast tumbling molecules the measured spectrum is almost completely determined by $\overline{\mathcal{H}}_e$, whereas $\mathcal{H}'_e(\Omega)$ acts only as a small time-dependent perturbation. This effect of motional narrowing is usually explained by saying that the spins are unable to follow the rapid changes in the Hamiltonian and therefore only its time average is observed⁸. If we apply this type of reasoning to the description of the spin system in equilibrium, this will mean that the density matrix of all molecules with the same momentary orientation Ω , is given by equation 7, but with $\overline{\mathcal{H}}_e$ substituted for $\mathcal{H}_e(\Omega)$.

However, as we already indicated, the isotropic shift and esr experiments are fundamentally different and we may therefore doubt the validity of this conclusion. Indeed, there is another approach to this problem which leads to a different conclusion, as we will clarify in the following simple model. Consider a set of molecules, each containing a nucleus of spin $\frac{1}{2}$, which jump randomly between two sites a and b , occupied with equal *a priori* probability.

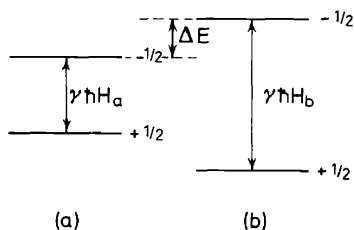


Figure 1. Energy level scheme of a spin $\frac{1}{2}$ jumping between two sites of different magnetic fields.

The magnetic fields H_a and H_b at the two sites are different. Figure 1 shows the energy-level scheme. If the jump rate is slow, the joint probability to find a molecule in site i and its spin in state m is in the high temperature limit,

$$p(i, m) = \frac{1}{4} \left(1 - \frac{\gamma \hbar H_i m}{kT} \right). \quad (11)$$

It is easily seen that this distribution is established, when the time τ between jumps is much longer than the relaxation time T_1 . Alexander and Tzalmona⁹ pointed out that equation 11 also holds for $\tau \ll T_1$ in the slow jump case ($\tau \gg \Delta E/\hbar$). To understand this we consider a molecule with its spin for a relatively long time in state m . This molecule as a whole jumps randomly between two sites with potential energies $\gamma \hbar H_a m$ and $\gamma \hbar H_b m$. Hence, the molecules with spin state m are distributed over a and b with the appropriate Boltzmann factor. In the high temperature approximation this leads to

$p(i, m)$ as given by equation 11. Apparently, the reaction of the spin system to the thermal motion of the molecules prevents the populations from becoming equal in the two sites. The motion is no longer completely random, but rather correlated to the actual spin state. The question now arises if there is any reason why this type of argument would not hold in the fast jump case. If it were valid under all circumstances, then the populations of the levels in equilibrium would remain unaffected by the relative magnitudes of τ and T_1 .

In our case this would mean that $\rho(\Omega)$ is always prescribed by the full Ω -dependent Hamiltonian, and that the isotropic shift is independent of τ and T_1 . It is clear that both approaches to the problem of the 'liquid' case are not free of uncertainties. Fortunately, as we shall see in Section IV, the problem can be solved for a set of molecules which undergo free rotations, as in a gas. This solution is important for the understanding of what occurs in liquids, because, as Frenkel¹⁰ pointed out, the states of slow diffusion and free rotation are the limits of the molecular motion in liquids.

III. NO ROTATION

Before we treat the free rotation case we derive a few expressions for the solid state, in order to compare the two.

For molecules with only one thermally populated energy level, describable by a single spin Hamiltonian \mathcal{H}_z , we have for the isotropic nuclear shift

$$\Delta H = - \frac{\int d\Omega \sum_M \langle M | P(\Omega) \mathcal{H}_z(\Omega) | M \rangle}{8\pi^2 kT (2S + 1)}, \quad (12)$$

which follows directly from equation 8 and where M runs over the components of the $(2S + 1)$ -times degenerate ground level.

In McConnell and Robertson's example¹,

$$\mathcal{H}_z(\Omega) = \beta S \cdot \hat{g} \cdot \mathbf{H}_0. \quad (13)$$

For the contact shift (equation 1),

$$P(\Omega) = (A/\hbar\gamma) S \cdot \mathbf{h}_0, \quad (14)$$

and for the pseudo contact shift (equations 2 and 3),

$$P(\Omega) = \beta S \cdot \hat{g} \cdot \hat{T} \cdot \mathbf{h}_0. \quad (15)$$

When thermally populated excited states are present, we follow the procedure of Kurland and McGarvey⁴ and make use of the following theorem proved by Karplus and Schwinger¹¹:

Let $|i\rangle$ and E_i denote the eigenstates of \mathcal{H}_0 , and let $|\mathcal{H}_1| \ll kT$, then

$$\langle i | \exp [-(\mathcal{H}_0 + \mathcal{H}_1)/kT] - f \rangle \simeq \exp(-E_i/kT) \exp(-E_i/kT) \delta_{if} + \dots + Q_{if} \langle i | \mathcal{H}_1 | f \rangle, \text{ where} \quad (16)$$

$$Q_{if} = \begin{cases} [\exp(-E_i/kT) - \exp(-E_f/kT)] / (E_i - E_f) & \text{if } E_i \neq E_f \\ -\exp(-E_i/kT)/kT & \text{if } E_i = E_f. \end{cases} \quad (17)$$

In our case \mathcal{H}_0 is the Hamiltonian of the paramagnetic molecule in the absence of a field and \mathcal{H}_z is the interaction with the field. Thus, from equation 8,

$$\Delta H = \frac{1}{8\pi^2 Z} \sum_{if} \int d\Omega Q_{if} \langle i | \mathcal{H}_z(\Omega) | f \rangle \langle f | P(\Omega) | i \rangle, \quad (18)$$

where $Z = \sum_i \exp(-E_i/kT) [1 - \langle i | \mathcal{H}_z | i \rangle / kT] = \sum_i \exp(-E_i/kT)$, under the assumption that \mathcal{H}_z is traceless within each degenerate manifold of \mathcal{H}_0 .

Equation 18 reduces to equations 12 and 6 in the cases of spin-only behaviour and no Zeeman mixing, respectively, for in these cases only the second line of equation 17 is relevant.

Note also that for $|E_i - E_f| \ll kT$ we can write approximately

$$Q_{if} \simeq -\exp(-E_i/kT)/kT. \quad (19)$$

IV. FREE ROTATION

The difficulty encountered in Section II is closely related to the following problem raised by Van Vleck in his theory of electric susceptibilities¹². The polarizability of a gas of N molecules possessing a permanent dipole moment μ is given by the Langevin-Debye formula,

$$\chi = N \left(\frac{\mu^2}{3kT} + \alpha \right). \quad (20)$$

The $1/T$ term in this equation was originally explained by assuming a Boltzmann distribution over the angles θ between the dipolar axis and the electric field \mathbf{E} ,

$$p(\theta) \propto \exp(E\mu \cos \theta/kT). \quad (21)$$

Van Vleck remarked, that this proof cannot be regarded as satisfactory, since the kinetic energies of rotation and vibration were entirely omitted from the Hamiltonian in forming the Boltzmann distribution factor. Instead, he derived equation 20 under fairly general assumptions, taking the kinetic energy into account¹³. We will use the same ideas in order to arrive at an expression for the isotropic shift in free rotating molecules.

The Hamiltonian in the absence of the field is \mathcal{H}_0 . It contains both the rotational kinetic energy and the electronic interactions. The eigenstates are $|\alpha\rangle$ with energies E_α . The interaction with the magnetic field is \mathcal{H}_z , and the isotropic shift operator is P . Note that \mathcal{H}_z and P now operate in the combined space of rotational and electronic degrees of freedom. Since $|\mathcal{H}_z| \ll kT$, we have, as in the foregoing section,

$$\Delta H = \frac{1}{Z} \sum_{\alpha\beta} Q_{\alpha\beta} \langle \alpha | \mathcal{H}_z | \beta \rangle \langle \beta | P | \alpha \rangle. \quad (22)$$

If we first confine our discussion to molecules with only one populated electronic level, then \mathcal{H}_0 contains only the rotational kinetic energy and \mathcal{H}_z is the spin Hamiltonian. Van Vleck's basic assumption is that¹³

$$\langle \alpha | \mathcal{H}_z | \beta \rangle = 0, \text{ unless } |E_\alpha - E_\beta| \ll kT. \quad (23)$$

This assumption expresses the fact that selection rules ensure that only close lying rotational states are mixed by \mathcal{H}_z . With equation 19 we then have

$$\Delta H = -\frac{1}{kTZ} \sum_{\alpha} \langle \alpha | \mathcal{H}_z P | \alpha \rangle \exp(-E_{\alpha}/kT), \quad (24)$$

which can be considered as Van Vleck's equation 25¹³ in generalized form[†].

Now we have to evaluate the right hand side of equation 24. This can easily be done if the molecules have three equal moments of inertia. The unperturbed wave functions are then $|lkmM\rangle$, where lkm denote the normalized Wigner matrix elements $[(2l+1)/8\pi^2]^{\frac{1}{2}} D_{km}^l(\Omega)$, which are the eigenfunctions of the rotational kinetic energy operator^{14,15}, and M runs over the $(2S+1)$ components of the degenerate electronic ground level. The energy of the state $|lkmM\rangle$ depends only on l .

The operator product $P\mathcal{H}_z$ can be written as a sum of products of functions $F_q(\Omega)$ and spin operators A_q

$$P\mathcal{H}_z = \sum_q F_q(\Omega) A_q. \quad (25)$$

Thus,

$$\Delta H = -\frac{1}{kT} \frac{\sum_{lkm} \sum_M \sum_q \{(2l+1)/(8\pi^2)\} D_{km}^{l*} F_q D_{km}^l d\Omega \langle M | A_q | M \rangle \exp(-E_l/kT)}{\sum_l (2l+1)^2 (2S+1) \exp(-E_l/kT)} \quad (26)$$

$$= -\frac{\int d\Omega \sum_M \langle M | P(\Omega) \mathcal{H}_z(\Omega) | M \rangle}{8\pi^2 kT (2S+1)}, \quad (27)$$

where use is made of the unitarity of the Wigner matrices

$$\sum_{km} D_{km}^{l*}(\Omega) D_{km}^l(\Omega) = 2l+1. \quad (28)$$

Equation 27 is exactly the same as equation 12 for the solid case. For molecules with unequal moments of inertia the k -degeneracy is lifted¹⁴⁻¹⁶. But because of the small energy differences between adjacent levels, only a negligible error is introduced if we replace E_{lkm} by E_l ¹⁷, such that equation 26 is valid for aspherical molecules as well.

Finally we consider molecules with low lying excited levels. The unperturbed Hamiltonian is now the sum of a rotational part \mathcal{H}_R and an electronic part \mathcal{H}_E . We denote the eigenstates and eigenvalues of \mathcal{H}_R and \mathcal{H}_E by Greek and Latin letters, respectively. Equation 22 becomes

$$\Delta H = \frac{1}{Z} \sum_{i\alpha, f\beta} Q_{i\alpha, f\beta} \langle i\alpha | \mathcal{H}_z | f\beta \rangle \langle f\beta | P | i\alpha \rangle, \quad (29)$$

[†] In the case of electric susceptibility, ΔH stands for the average electric dipole moment per molecule, $\mathcal{H}_z = \boldsymbol{\mu} \cdot \mathbf{E}$, and $P = \boldsymbol{\mu} \cdot \mathbf{e}$, where \mathbf{e} is the unit vector along \mathbf{E} .

where

$$Q_{i\alpha, f\beta} = \frac{\exp [-(E_i + E_\alpha)/kT] - \exp [-(E_f + E_\beta)/kT]}{(E_i + E_\alpha) - (E_f + E_\beta)}. \quad (30)$$

Again we assume that only closely spaced rotational levels are connected by \mathcal{H}_z . This allows the simplification

$$Q_{i\alpha, f\beta} \simeq Q_{if} \exp(-E_\alpha/kT), \quad (31)$$

for $|E_\alpha - E_\beta| \ll kT$. Following the same procedure as outlined in equations 25–27 it can be shown that the expression for ΔH reduces to equation 28 for the no rotation case.

One remark remains to be made. Throughout this section we assumed tacitly that the wave functions in the absence of the field were direct products of rotational and electronic parts, thus excluding the possibility of spin-rotation interaction. However, since this interaction is both smaller than kT and obeys the selection rules required for equation 23¹⁸, we are allowed to consider it as a part of \mathcal{H}_z . Since the shift vanishes at $H_0 = 0$, we conclude that its effect on the isotropic shift is of no importance.

V. CONCLUSION AND DISCUSSION

We saw that the expressions for the isotropic shift for the states of no rotation and free rotation are equal, at least to first order in H_0/kT . Since the tumbling of molecules in liquids can be considered as an intermediate type of rotational motion between these two extremes, we conclude that the same expressions also hold for the liquid state. Consequently, the pseudo contact shift is independent of τ and $T_{1\rho}$, such that no contribution to non-Curie behaviour is expected due to temperature dependence of the correlation times.

The underlying reason for this result is clearly the fact that $\rho(\Omega)$ is unaffected by the nature of the random tumbling. This favours the second type of approach to the liquid state problem mentioned in Section II, i.e. the reaction of the spin system to the random motions of the molecules is effective, also in the fast tumbling case.

In a forthcoming paper we will discuss these conclusions in more detail. In particular it will be shown, that the theory of Brownian motion provides evidence for the validity of our results in the case of diffusional motion.

Let us return to the subject of motional narrowing. For simplicity we consider again the example of nuclei which jump between two sites (*Figure 1*). The general conclusion of this paper suggests that the populations of the levels in the two sites remain undisturbed, also in the case of very short τ . That this does not contradict the phenomenon of motional narrowing, can be understood in the following way.

In thermal equilibrium the number of molecules in a certain state is constant in time, but the individual molecules jump rapidly back and forth. In a resonance experiment we measure the Larmor frequency of the nuclei. This frequency becomes practically equal for all nuclei if the jump rate becomes faster than the difference in the local Larmor frequencies. If we now

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take the reaction of the spin system into account, there will be small changes in the lifetimes of the different sites, but the individual spins remain jumping at a high rate, and hence they still precess at one uniform Larmor frequency. On the other hand, if we performed an experiment in which we could measure the magnetizations in the two sites separately, we would find that M_a and M_b remain 'unmixed' by the rapid jumps. The difference from the resonance experiment is that here we do not follow the dynamic behaviour of the individual spins, but rather count the instantaneous number of molecules which find themselves in a certain state.

Pseudo contact shift is an example of this last type of measurement. It measures the dipolar field generated by the paramagnetic ion, i.e. a quantity which is directly related to the magnetization of the ion. Moreover, it is just the part of the magnetization which depends on the orientation of the molecule that gives rise to a pseudo contact shift. This is the reason why the present considerations are of practical importance, primarily in the theory of isotropic shifts.

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