First Steps in Tensor Polarization Measurement using the DMR Lineshape

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The first steps to investigate the tensor polarization measurement with uncertainty is outlined. The objective is to look into possible measurements of the deuteron alignment given an arbitrary lineshape that was distorted by a modulated RF field of known frequency range with respect to each absorption line.

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1. The DMR lineshape

1.1. *The Basis Distribution*

The deuteron and other nuclear species with the spin quantum number of one or higher have a non-spherically symmetric electric charge distribution leading to a dependence in electric energy on its orientation within the existing fields. The addition of this structure means that the electron electric fields will interact with the nuclear electric charge such that spatial variations of the electric field will couple to the charge distribution giving rise to the quadrupolar nucleus. The result is a change in the energy level in addition to the Zeeman effect. The large nature of the quadrupole interaction allows one to incorporate this effect to just the first order. These first order interactions have an angular dependency with respect to the magnetic field of $(3 \cos^2 \theta - 1)$, the P2 Legendre polynomial. The θ is the polar angle between the axis given by the deuteron bond and the holding field H_0 .

In the DMR signal all the orientations of θ will be present. The absorption spectrum will then be a superposition of lines and the Fourier transform of the local

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frequency distribution is the corresponding superposition of cosines. The resonance frequencies are $\omega = \omega_0 + \Delta$, where the relation between the frequency offset Δ and the pair orientation θ may be written from the expression for the absorption consisting of a pair of lines either side of the free-spin resonance,

$$w = w_0 \pm \frac{\mu_0}{4\pi} \frac{3}{2} \frac{\hbar\gamma^2}{2r^3} (1 - 3\cos^2\theta) \pm w_0 \pm \frac{\mu_0}{4\pi} \frac{3}{2} \frac{\hbar\gamma^2}{2r^3} (1 - 3\cos^2\theta) = w_0 \pm \delta(1 - 3\cos^2\theta). \quad (1)$$

Since θ varies between 0 and π , the range of Δ is $-2\delta \leq \Delta \leq \delta$. Here the effects that arise when the electric field gradient is not symmetric about the bond axis are left out for simplicity. Given the distribution $p(\theta)$ of angles θ it is relevant to denote the corresponding distribution of offset frequencies Δ as $P(\Delta)$. This implies the same interval in terms of either angle or frequency,

$$p(\theta)d\theta = P(\Delta)d\Delta.$$

The frequency distribution is then expressed as,

$$P(\Delta) = p(\theta) \frac{d\theta}{d\Delta}. \quad (2)$$

Using the distribution of orientations θ and the relation between Δ and θ , one can obtain the distribution for frequency deviations Δ which lead to the absorption lineshape.

Differentiating $\Delta(\theta)$ leads to,

$$\frac{d\theta}{d\Delta} = 6\delta \cos\theta \sin\theta.$$

Normalizing the probability $p(\theta)$ to 1 results in $p(\theta) = \frac{1}{2} \sin\theta$ which leads to

$$P(\Delta) = \frac{1}{12\delta \cos\theta} = \frac{1}{2\delta[12(1 - \Delta/\delta)]^{1/2}} = \frac{1}{2\delta[12(1 - R)]^{1/2}}. \quad (3)$$

This expression gives the distribution of frequency offsets of one of the lines, as expressed in Eq. 1. There is an additional resonance line symmetrically placed from ω_0 . The final lineshape is the sum of both. More information can be found in the standard treatment of the topic.¹⁻³

1.2. Homogeneous Broadening

The dominating aspects of the shape described in Eq. 4 depend on the nature of random orientations and do not directly give information about the spin-temperature state of the system. This generalized shape maybe relevant for a number of equilibrium and non-equilibrium states. A description of the moments gives information on the shape of the resonance curve. Lines broadened by strong collisions have been shown to be well described by the Lorentz shape.¹ The shape seen in the DMR line is rooted in NMR dipolar broadened response to the isotropic reorientations which have a time-correlation function unique to the normalized $Y_{2,0}$ spherical harmonics. The corresponding spectral densities are Lorentzian so that the lineshape contains

information from the probability density as well as the moments of the frequency deviations and so that aspects of broadening come from changes to the Lorentzian part. Information about the degree of spin-temperature equilibrium can be associated to the lineshape only under strict parametrization of the full expression.

The interaction of each spin with the surrounding spins results in a dipolar broadening characterized by the Lorentzians in a signal envelope. The lineshape can be approximated with a convolution of the basis distribution and a Lorentzian leading to,

$$f_{\pm} = \frac{B}{2\pi\rho} \left[2\nu(R) \left(\arctan \frac{3 - \rho^2}{2\sqrt{3}\rho\nu'(R)} + \frac{\pi}{2} \right) + \nu'(R) \ln \left(\frac{3 + \rho^2 + 2\sqrt{3}\rho\nu(R)}{3 + \rho^2 - 2\sqrt{3}\rho\nu(R)} \right) \right] \quad (4)$$

where $\rho = (A^2 + [1 \pm R])^{1/4}$, $\nu(R) = (1 + [1 \pm R]/\rho^2)^{1/4}/2$, and $\nu'(R) = (1 - [1 \pm R]/\rho^2)^{1/4}/2$. The values A , B and the asymmetry parameter η (left out) are just constants and become the fitting parameters. The parameter A is related to the dipolar effects at each point in the signal envelope and when consistent through the frequency range implies homogeneous broadening throughout the line and represents the width Γ of the Lorentzian in the convolution. The parameter B relates to the overall magnitude. This function is easily used to fit the curve of a DNP enhanced signal for a system with small quadrupole broadening in which the energy states are populated in a Boltzmann distribution.

2. Pumping with Modulated RF

2.1. Inhomogeneous Broadening

Applying a modulated RF magnetic field at select frequencies allows DMR line manipulation by disturbing the natural distribution creating inhomogeneous broadening. At a temperature of ~ 1 K, there are little relevant molecular dynamics except for the tunneling processes. Rotations are mostly quenched by lockup from intermolecular bonding.⁴ This leads to cross-relaxation being the most critical aspect of this effect. The spatial inhomogeneity comes from local gradients in the external and local fields in the sample. The spin populations that vary in space can come into equilibrium by spin diffusion which is a relatively slow process with respect to the dominating relaxation pathways at the modulated RF frequencies.

Outside of dipolar broadening and CW NMR resolution, the width also has effects from additional local variations of nuclear spin arrangements such as further hyperfine structure and distribution of crystal field parameters. A leading component of inhomogeneous broadening comes from adjacent spins with unassociated resonant frequencies. The energy absorbed at a local frequency can be spread over the DMR line by spin diffusion in the frequency domain.

In the system of interest the deuterons are at high field relative to the quadrupole Hamiltonian, so the Zeeman contribution dominates the axis of quantization, which leads to an angular dependence to the deuteron-deuteron dipole-dipole coupling.

By driving RF induced excitations at different positions in the line, one selects different angles of the inter moment vector relative to the applied holding field, leading to an angular dependence of the cross-relaxation rate. The moments in NMR are essentially parallel, which yield the Legendre relation in $\cos\theta$. This relation persists during RF irradiation. The deuteron moment is small implying that the rates are small and are on the scale of many seconds to minutes or longer at 1 K, depending on material. The paramagnets in the system for the DNP effect (quicken) the spin-lattice relaxation rates, leading to further overall contributions to the rates depending on the concentration of paramagnetic impurities.

The fundamental rate constant for the deuterons in a particular relaxation pathway is the same for all spins in the sample that experience the same temperature environment. However, the effective rate is the product of the rate constant and the population. The effective rate constant in the solid is a function of the angle that the inter moment vector makes with the field. For liquids, this would be averaged over all orientations and disappears leaving the same rate constant for all spins. But for the system of interest at 1 K the population seen at a particular θ plays a critical role in the observed dynamical rates.^{1,4}

The application of the modulated RF at a given θ or R of one transition pumps the other transition at the same θ . This pumping occurs at a rate related to the energy from the RF and the effective rate constant seen for the irradiated location in the DMR line. The three dominating relaxation pathways are the cross-relaxation to the other transition at the same θ , the cross-relaxation to other transition through adjacent spins with unassociated resonant frequency, and the spin-lattice relaxation. Using the solid effect there are just two additional terms in the rate equations from the RF field, cross-relaxation and the additional relaxation to the lattice. The latter is likely where the greatest losses in magnetization come from while driving with RF irradiation. Losses are expected to generally occur by leakage to the lattice from interaction of the phonon modes in the solid imposed by the RF. Spectral diffusion can also occurs by molecular motions that change the angle of the inter moment vectors, but it is likely a much small component than leakage to the lattice at this temperature.

Irradiation at a frequency where the two absorption lines are overlapping results in a pumping from both transitions to the opposing transitions at the same θ with a rate proportional to the population in each case. As an example, when an overlapping region (i.e. the smaller peak in the doublet seen for positive vector polarization) is irradiated, because the population is much greater for $(0 \rightarrow -1)$ than $(1 \rightarrow 0)$ at this region, there will be enhancement at the opposing peak predominately from $(0 \rightarrow -1)$ at a rate equal to the population at the location in the line being irradiated times the rate constant. There would also be enhancement at the same place from the $(1 \rightarrow 0)$ but at a slower rate (due to smaller population) until the two transitions had the same population at which point the spin flips occur at the same rate from each transition. The process that takes place after irradiation is also a cross-relaxation which will continue until it recovers the Boltzmann distribution.

This process follows the same relaxation pathways but at a different fundamental rate constant. The effective rate is the rate constant times the population at the enhance location in the DMR line. This results in the higher population transition at the overlapping region to deplete quicker during the RF pumping but to also re-populate quicker once the RF is off.

2.2. Inhomogenous Fitting

When the energy states are in a natural Boltzmann distribution it is convenient to talk about intensity of magnetization in the longitudinal direction as the height of each peak in the DMR line. In fact the normal fitting⁵ procedure would fix parameters A and η having to do with the material, field and thermodynamic conditions while leaving B , the magnitude or height of the peak, as the single free parameter in the fit. Still, the intensity of magnetization is truly represented by the area, and the qualifier for fitting the height alone is that the distribution must satisfy the Boltzmann relation. For the purposes of fitting outside this qualifier, it is necessary to focus on the integrated area of each peak.

The total DMR signal, consisting of the output voltage integrated over the frequency, is the total area under the sum of two separate peaks I_+ and I_- that originate from the $(1 \rightarrow 0)$ and $(0 \rightarrow -1)$ transitions, respectively. Each intensity is proportional to the differences of the level populations through that transition such that $I_+ = C(a_+ - a_0)$ and $I_- = C(a_0 - a_-)$ where a_m is normalized to the sample population and C is the calibration constant. The calibration constant can be determined from a measurement with the spin system in thermal equilibrium with the lattice or using the fitting procedure before disturbing the Boltzmann distribution, but ideally both to reduce systematic uncertainty. The vector polarization is then, $P \times C = I_+ + I_-$ and the tensor polarization is, $P_{zz} \times C = I_+ - I_-$. So given the area of each absorption line, P and P_{zz} can be easily calculated where the dominate error comes from the error in the area for each peak and the error in the calibration constant. Understanding how the RF modulation affects the rates and the spectral density, it is always possible to fit the area of an arbitrarily disturbed distribution within the uncertainty of the effective relaxation rates at the excited regions of the DMR line. The pumping rate during RF modulation is directly dependent on the energy absorbed at that frequency range which is a function of the RF power and the sweep rate. For a non-steady-state dynamic a large portion of the uncertainty in the lineshape comes from the measurement of the RF power.

The cross-relaxation terms of the Bloch equations show up as simultaneous loss from one equation leading to a gain in another and vice versa. This is particularly important for the spins in separate transitions at the same θ . Once the system has been brought to a steady-state using the DNP process the dominating dynamics once the modulated RF has been turned on is the cross-relaxation pathway being pumped by saturation of the sublevels in one of the transtions. This rate is intrinsically dependent on the Hamiltonian contribution pertaining to the oscillator

magnetic field strength so the RF power is a direct control to this fundamental rate constant of the saturating RF.

2.3. *Non-Equilibrium Fitting*

One method to create a measurable steady state is to irradiate just one pedestal. The area of the pedestal is dominated by only one transition as there is minimal area under each pedestal from the opposite transition, due to dipolar broadening in the form of a Lorentzian like tail. It is then straight forward to irradiate one pedestal completely to achieve full saturation at that frequency range leading to enhancement at the opposite pedestal.

Another plausible method is to establish a semi-saturated condition on an overlapping region of the DMR line. Each transition has the same fundamental rate constant imposed by the RF irradiation which implies that each transition absorbs energy at the same rate. It is possible to analyze the DMR line height at the point of irradiation when the power from the RF has been saturated and can not fully deplete the magnetization at that frequency. Done strategically, approximate equalization of the intensities from each transition can be achieved, obtaining additional constraints for the line fitting.

Using the absorption line intensity at a particular point in the DMR line prior to irradiation one can calculate the RF threshold summed population level for equalization as twice the intensity of the lower overlapping transition. When RF is applied and the DMR line drops slightly below this threshold and power saturates then the RF will reach a steady state with equal population in both transitions. Knowing this allows for additional fitting constraints that eliminate the need for a power measurement or a reliance on the rate equations.

The overall uncertainty comes from the total error from the calibration constant,⁶ the fitting error from the covariance matrix of the non-constrained parameters, as well as the systematic error from the variation in area imposed by time dependent deviation from the hypothesis of the lineshape. The total error is largely dependent on the set of constraints that are relevant for a particular degree of RF saturation.

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