# Notes on Pulsed $\beta$-NMR

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## Abstract

The use of pulsed RF for measuring $\beta$-NMR resonances is examined. There are many advantages, the most important being that systemtatic variations in the resonance signal are greatly reduced.

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## I. INTRODUCTION

After several years of doing $\beta$-NMR we are still facing problems with systematic errors in measuring resonances witha continuous beam. Typically the systematic errors dominate because the sweep rate is limited by the $^8$Li lifetime, $\tau$. Sweeping fast minimizes systematic problems but distorts the line shape due to memory effects. In our conventional CW mode, which we perform slow enough to avoid distortions, it takes several minutes to make one scan of the resonance. Unfortunately the beam is seldom constant on this time scale leading to glitches in measuring quantity– the $\beta$ decay asymmetry versus RF frequency $A(\omega)$. The worst of these appears to be changes in the stopping distribution (i.e. a small fraction of the beam landing in the cryostat radiation shield) which result in a time dependent change in the baseline asymmetry (i.e. count rate asymmetry with zero polarization) that cannot be distinquished from a change in the polarization induced by the RF field. There are other sources of systematic errors- e.g. variations in the beam rate, beam polarization etc. All the beam related systematic effects lead an unwanted time dependence to $A(t)$ that interferes with a measurement of the resonance lineshape. Fortunately the systematic time variations in $A(t)$ all occur on time scale of $\tau$ (1s) or longer due to the lifetime averaging or memory effect. (We are assuming for the moment there is no $T_1$ spin relaxation)

Pulsed RF methods should significantly reduce our sensitivity to such systematics since changes in $A$ can be induced on a short time scale (10-50 ms) which is much less than $\tau$ and thus the time scale for systematic variations. There are several different schemes. The simplest of these is as follows: The beam is continuous and short RF $\pi$ pulses are applied periodically. There appear to be two natural pulse repetition rates. In the low rep rate mode the time between RF pulses $\Delta t$ is chosen to be somewhat longer than $\tau$ (e.g. $3\tau$). In the high rep rate mode $\Delta t$ is much less than $\tau$. For simplicity we assume the RF pulse is shaped to flip all the spins in frequency interval $\Delta\omega$ centered at $\omega$. The discontinuity in $A(t)$ induced by the RF pulse is proportional to the number of spins in that interval. The functional form for $A(t)$ before and after the RF pulse is easily derived for both the low and high rep rate modes. The objective is to determine the size of the RF induced discontinuity in $A$ as function of RF frequency. In some cases (e.g.low rep rates) the discontinuity can be determined from the average value of $A(t)$ before and after the RF pulse and taking the difference. In general it is better to perform a simple fit in the time region $(-\Delta t, +\Delta t)$

around the pulse to determine the discontinuity. Although slightly more complicated such fitting gives a signal which is free of any history depedendence and has the added advantage of being able to assess if there is a problem with any given point. For high resolution the pulse width (which scales as $1/\Delta\omega$) may not be negligable compared to $\Delta t$ or even $\tau$. In fact these are not really 'pulses' per se. In this case it may be necessary to fit $A(t)$ during the pulse as well. In general high resolution will be much more difficult due to the long pulses required.

The main advantages of the pulsed method are:

**1**. Reduced sensitivity to small systematic variations in the beam properties. The RF induced disconinuity is proportional to the number of spins in a given frequency interval and is insensitive to small variations in the beam properties. For example a small change in the beam position has minimal affect on the RF induced step in $A$ whereas in our conventional CW node it would corrupt the whole scan.

**2**. There is no baseline asymmetry to subtract off or to fit. Thus there is no need to scan well off resonance to find the baseline. This eliminates an important parameter in the resonance fitting and will reduce the necessary range of the scan, which in turn allows for more averaging. This advantage is particularly important when the resonance is broad. (e.g. superconductors).

**3**. The figure of merit $A^2N$ (signal/statistical noise) is in general 4 times greater since a $\pi$ pulse reverses the polarization rather than destroying it. At low rep rates the efficiency is slightly lower since some waiting is required. However the figure of merit is still always higher in the pulsed mode.

**4**. There are no broadening effects (distortions) due to spin diffusion whereby spins from one frequency bin move into another, The RF pulse determines the frequency bin width but doesn't broaden the lineshape provided the bin frequency width is not greater than the step size. Thus one actually measures the quantity of interest (the lineshape) rather than the lineshape convolved with other effects.

**5**. At low rep rates there is minimal RF heating since the RF is on for only a small fraction of the time. At higher rep rates the RF heating will be similar to conventional mode.

## II. THEORY

Before discussing the effect of RF pulses on $A(t)$ is important to understand some of the systematic variations in $A(t)$ from beam instability.

### A. Instability of the Beam Position

Suppose at $t = 0$ there is a sudden variation in the stopping distribution such that a small fraction of the beam ($\delta$) lands at the edge of the beam entry hole of the cryostat. For simplicity we assume the following (i) the solid angle for the forward and back detector rates are equal for the fraction $1 - \delta$ of Li landing in sample (ii) the solid angle for the back detector is unchanged but is zero for the F detector for the small faction $\delta$ in the cryostat entry hole (iii) the polarization $p_0$ for the fraction $\delta$ in the cryostat is zero and (iv) the rates before the beam change and with no polarization equals $N$ for both detectors. If $A_0$ is the maximum experimental asymmetry determined by the solid angle of the detectors and the properties of $^8$Li then for $t > \tau$ the detectors record:

$$\begin{aligned} F &= [1-\delta]N[1-p_0A_0] \\ B &= [1-\delta]N[1+p_0A_0] + \delta N \end{aligned}$$

whereas the asymmetry

$$\begin{aligned} A &= (B-F)/(F+B) \\ &= [2(1-\delta)p_0A_0 + \delta]/[2(1-\delta)+\delta] \\ &\approx p_0A_0(1-\delta/2) + \delta/2 \end{aligned}$$

Note a change in the stopping distribution (e.g. beam landing in the crysotat instead of the sample) produces two separate affects. The largest is the change in the baseline equal to $\delta/2$. In addition there is a smaller term proportional to the polarization ($p_0A_0\delta/2$) arising from the fact that fewer Li are stopping in the sample. Both changes occurs on the scale of $\tau$ for reasons described below. As an example if $\delta = 0.02$ then the baseline would change by 0.01. The resulting glitch will ruin the entire scan using our CW mode. In the pulsed mode, where the signal depends only on RF induced change in polarization, the baseline shift has no affect. The only influence is a slight disconinuity in the signal itself since fewer Li are stopping in the sample. However this is typically two orders of magnitude smaller than the baseline shift. For example if the change in asymmetry induced by the RF in a given frequency interval were 0.01 for $t < 0$ the same signal for $t > \tau$ would be $0.01(1 - \delta/2) = 0.0099$ (i.e. virtually unchanged).

### B. Instability of the Beam Intensity

We start by first examining the polarization with constant beam. Let $R(t')dt'$ be the number of Li arriving in the sample at time $(t', t' + dt')$. Let $N(t', t)dt'$ be the number of Li arriving in the time interval $(t', t' + dt')$ and surviving until time $t$

$$N(t', t)dt' = R(t') \exp[-(t - t')/\tau]dt'$$

The total number of Li in the target at time $t$ averaged over all $t' < t$ is then:

$$\begin{aligned} N(t) &= \int_{-\infty}^{t} R(t') \exp[-(t - t')/\tau]dt' \\ &= R_0 \int_{0}^{\infty} \exp[-t'/\tau]dt' \\ &= R_0\tau \end{aligned}$$

where we have assumed $R_0$ is the time independent incoming Li rate. This is just the equilibrium number long after the beam has been turned on.

Let $p(t', t) = p_0 \exp[-(t-t')/T_1]$ be the polarization of the Li arriving at time $t'$ measured at $t$ where $T_1$ is the relaxation time. Then the polarization of the Li at $t$ averaged over all $t' < t$ is:

$$p(t) = p_0 \frac{\int_{-\infty}^{t} R(t') \exp[-(t - t')/\tau] \exp[-(t - t')/T_1 dt'}{\int_{-\infty}^{t} R(t') \exp[-(t - t')/\tau]dt'}$$

Changing the integration variable from $t'$ to $t - t'$ yields:

$$\begin{aligned} p(t) &= \frac{p_0 R_0 \int_0^\infty \exp[-t'/\tau] \exp[-t'/T_1]dt'}{R_0\tau} \\ &= \frac{p_0 R_0}{R_0\tau[1/\tau + 1/T_1]} \\ &= p_0\tau'/\tau \end{aligned}$$

Where $\tau' = T_1\tau/(T_1 + \tau)$ and $1/\tau' = 1/T_1 + 1/\tau$. As one expects the time averaged polarization to be constant but reduced in amplitude by the $T_1$ spin relaxation.

Now suppose there is a discontinuity in $R(t)$ at time $t = 0$ such that $R(t) = R_0$ for $t < 0$ and $R_1$ for $t > 0$. What affect does this have on the polarization and asymmetry for $t > 0$? The number of Li in the target for $t > 0$ is given by:

$$
\begin{aligned}
N(t) &= R_0 \int_{-\infty}^{0} \exp[-(t+t')/\tau]dt' + R_1 \int_0^t \exp[-(t-t')/\tau]dt' \\
&= R_0 \int_t^{\infty} \exp[-t'/\tau]dt' + R_1 \int_0^t \exp[-t'/\tau]dt' \\
&= \tau[R_1 + (R_0 - R_1)\exp(-t/\tau)]
\end{aligned}
$$

which equals $R_0\tau$ at $t = 0$ and relaxes exponentially to $R_1\tau$ for $t > 0$. Similarly the average polarization is given by:

$$
\begin{aligned}
p(t) &= \frac{R_1 p_0 \int_0^t \exp[-t'/\tau]\exp[-t'/T_1]dt' + R_0 p_0 \int_t^{\infty} \exp[-t'/\tau]\exp[-t'/T_1]}{N(t)} \\
&= p_0 \frac{T_1}{T_1 + \tau} \times \frac{R_1 + (R_0 - R_1)\exp[-t(1/\tau + 1/T_1)]}{R_1 + (R_0 - R_1)\exp[-t/\tau]} \\
&= p_0 \frac{\tau'}{\tau} \times \frac{R_1 + (R_0 - R_1)\exp[-t/\tau']}{R_1 + (R_0 - R_1)\exp[-t/\tau]}
\end{aligned}
$$

As expected the average polarization equals $p_0\tau'/\tau$ and time independent at $t < 0$ and for $t >> \tau'$. However when $T_1$ is finite the polarization is time dependent for times on the scale of $\tau'$ where $1/\tau' = 1/T_1 + 1/\tau$. The maximum deviation depends on $T_1$ and the fractional change in $R(t)$. Contrary to naive expectations this implies our asymmetry $A(t) = A_0 p(t)$ is rate dependent when $T_1$ is finite. Specifically it depends on the magnitude of any changes in the rate. This may explain some of the instability we have seen for resonances in $NbSe_2$ and the Fe multilayer where the relaxation is significant. Basically the average polarization of the Li in the target is time dependent within a time $\tau'$ of a change in beam intensity. Thus it is important not to collect data within several seconds after the beam rate changes. On the other hand the absolute rate doesn't matter so the tolerance can be quite large. It is during the changes that we must avoid taking data. Our DAQ should me modified to reflect this.

As an example of the rate induced change in polarization consider the extreme case where the beam rate $R = 0$ for $t < 0$ and constant at $R_1$ for $t > 0$.

$$p_{step}(t) \;=\; p_0\frac{\tau'}{\tau}\times\frac{1-\exp[-t/\tau']}{1-\exp[-t/\tau]}$$

In the limit $t \to 0$ :

$$\begin{aligned} p_{step}(t) &\approx p_0\left[\frac{1-t/\tau'}{1-t/\tau}\right] \\ &\approx p_0\left[1-t/T_1...\right]. \end{aligned}$$

As one would expect the polarization starts off at its maximum $p_0$ and relaxes towards its equilibrium value of $p_0\tau'/\tau$ on the time scale of $T_1$. If the beam goes off the polarization will relax from that value with a relaxation time $T_1$. Thus in a $T_1$ measurement with a beam pulse width $\Delta$ we expect the following form:

$$\begin{aligned} p_{pulse}(t) &= p_{step}(t) && for\ 0 < t < \Delta \\ &= p_{step}(\Delta)\exp[-(t-\Delta)/T_1] && for\ t > \Delta \end{aligned}$$

Clearly the polarization relaxes exponentially with at a rate $1/T_1$ after the pulse but the amplitude depends on the pulse width $\Delta$. In the future we should fit all $T_1$ data to the above form, including during the pulse, to get the right initial amplitude. It should be possible to derive a similar expression for multi-exponential relaxation.

### C. Pulsed RF mode at low repetition rates

Now suppose the beam rate is constant and an RF pulse is applied at $t = 0$ which reverses a fraction of the spins, $S_n = f(\omega_n)\Delta\omega$, where $f(\omega)$ is the resonance lineshape and $\Delta\omega$ the frequency bin width affected by the $nth$ RF pulse. Low rep rates correspond to when the time interval between RF pulses is comparable to or longer than the recovery time $\tau'$. In this case the polarization is close to the equilibrium value of $p_0\tau'/\tau$ prior to the RF pulse and independent of the previous pulse history. At $t = 0$ we assume the polarization of the spins in the frequency interval $\omega_n, \omega_n + \Delta\omega$ are reversed. As long we are considering times $t > 0$ (i.e. after the RF pulse) this is equivalent to having the spins in this frequency interval enter the sample with a polarization with $-p_0$ for $t' < 0$ and $+p_0$ for $t' > 0$. The polarization from spins in this interval is :

$$
\begin{aligned}
p(n,t) &= p_0 \frac{\int_0^t \exp[-t'/\tau]\exp[-t'/T_1]dt' - \int_t^\infty \exp[-t'/\tau]\exp[-t'/T_1]dt'}{\tau} \\
&= p_0 \frac{\tau'}{\tau} \times [1 - 2\exp(-t/\tau')]
\end{aligned}
$$

whereas outside this interval the polarization remains at the equilibrium value. The total polarization from all frequencies is then :

$$
p(t) = S_n p(n,t) + (1 - S_n) p_0 \tau'/\tau
$$

The quantity of interest $S_n$ can be extracted from the average of $p(t)$ measured in the time interval $(-T, 0)$ (i.e. before the the RF) minus the average $p(t)$ in the time interval $(0, T)$ (just after the RF pulse). All the time independent terms in $p(t)$ cancel out leaving:

$$
\begin{aligned}
p^+ - p^- &= -p_0 S_n \frac{\tau'}{\tau} \times \frac{2\int_0^T \exp[-t/\tau']}{T} \\
&= -p_0 S_n \frac{2\tau}{T} \left(\frac{\tau'}{\tau}\right)^2 (1 - \exp[-T/\tau'])
\end{aligned}
$$

Choosing the integration time $T = \tau'$ we get a change in average asymmetry equal to :

$$
A^+ - A^- = -2p_0 A_0 S_n \frac{\tau'}{\tau} [1 - 1/e]
$$

The observed signal in the asymmetry:

$$
\begin{aligned}
\mathcal{A}_n &\equiv p_0 A_0 S_n \\
&= -\frac{(A^+ - A^-)\tau}{2[1 - 1/e]\tau'}
\end{aligned}
$$

is proportional to the difference in average asymmetries before and after the pulse with no memory effects. The amplitude of $\mathcal{A}_n$ is about 1.26 times the value of the asymmetry signal $S_n A_0 p_0 \tau'/\tau$ expected in a conventional CW mode. The statistical uncertainty in measuring an average asymmetry between two detectors with similar rates equals $1/\sqrt{N}$ where $N$ is the total number of counts. If the total beta rate is $R_\beta$ then the uncertainty in $\mathcal{A}_n$ equals:

$$
\Delta\mathcal{A}_n = 1/\sqrt{2R_\beta\tau'}
$$

If the time between RF pulses is chosen to be about $3\tau'$ then we are using only betas in the time interval $(-\tau, \tau')$ (i.e. 2/3 the total beta rate) whereas in the conventional mode all the betas are being used. This means the figure of merit $A^2N$ for low rep rates will be about $(1.27)^2 0.666 = 1.06$ times that of a CW conventional mode. Although the statistical uncertainty in measuring the resonance is about the same for both methods, the systematic errors in the pulsed mode are greatly reduced.

At low rep rates it seems most reasonable to record one multiscaler event for each frequency point. It would be best to perform an analysis on the fly so that any bad points (with large $\chi^2$) can be repeated. As before it would be best to take all the points on a scan with one helicity before reversing the polarization direction. Otherwise one would have to use a much larger time between RF pulses. A 40 point frequency scan at 5 s a point will take about 200 s which is similar to a conventional scan. Although the signal averaging is not any better this may not be so critical since most the largest systematic effects will be greatly reduced.

The main application of this mode is likely to be for high resolution (less than 100 Hz frequency bins) since then pulse lengths of 100-1000ms are needed. In this case we should probably fit the entire spectrum even during the RF pulse.

### D. High Rep Rates

The pulsed mode can also be applied at higher repetition rates and thus higher frequency sweep rates. The advantages are a higher figure of merit and better signal averaging. The disadvantages are somewhat more RF heating and one additional parameter in the fits needed to describe the time dependence of the polarization from previous pulses. In particular at high rep rates we expect a history dependent linear term in $A(t)$. However, the signal itself (the RF induced step in $A(t)$) is not history dependent.

In the high rep rate mode the time between RF pulses $\Delta t$ is short compared to the recovery time $\tau'$ but the sweep time $N\Delta t$ is long compared to $\tau'$ where $N$ is the number of pulses in the sweep. The first condition implies the polarization function $p(t)$ can be approximated by a simple linear function of time before and after the RF pulse. The latter condition ensures all the spins in a given frequency interval have had a chance to relax back to equilibrium before the next RF pulse is applied to that same interval. For example, at a rep rate of 5Hz and a frequency bin width of 500 Hz would cover 20kHz frequency range in 8s.

We assume at the beginning of the scan the polarization is in equilibrium at $p'_0 = p_0\tau'/\tau$. If $t = 0$ is defined as when the $nth$ RF pulse occurs then the polarization just before the $nth$ pulse for times between $-\Delta t$ and 0 is given by:

$$\begin{aligned} p^-(t) &= p'_0 \left[1 - 2\sum_{m=1}^{n-1} S_m \exp[-(t + (n-m)\Delta t)/\tau']\right] \\ &= p'_0 \left[1 - a_{n-1} \exp[-(t+\Delta t)/\tau']\right] \\ &= p'_0[1 - a_{n-1} + a_{n-1}(t+\Delta t)/\tau']; \quad\quad \Delta t << \tau' \\ &= p'_0[1 - a_{n-1}(1 - \Delta t/\tau') + a_{n-1}t/\tau'] \\ &= p'_0[\alpha_n + \beta_n t] \end{aligned}$$

where

$$\begin{aligned} \alpha_n &= 1 - a_{n-1}(1 - \Delta t/\tau') \\ \beta_n = &= a_{n-1}/\tau' \\ a_{n-1} &= 2\sum_{m=1}^{n-1} S_m \exp[-(n-1-m)\Delta t/\tau'] \end{aligned}$$

Note $a_{n-1}$ is the contribution to the polarization at $t = -\Delta t$ from the previous $n-1$ pulses. Immediately after the $nth$ pulse for times $0 < t < +\Delta t$ the polarization is approximately given by:

$$\begin{aligned} p^+(t) &= p'_0[1 - a_{n-1}(1 - \Delta t/\tau') + a_{n-1}t/\tau' - 2S_n[1 - t/\tau'] \\ &= p'_0[1 - a_{n-1}(1 - \Delta t/\tau') - 2S_n + (a_{n-1} + 2S_n)t/\tau'] \end{aligned}$$

where the signal $S_n = f(\omega_n)\Delta\omega$ is the fraction of spins flipped by the $nth$ RF pulse. The best way to determine $S_n$ is to fit the asymmetry to the following linear form valid when $\Delta t << \tau'$:

$$\begin{aligned} A(t) &= p'_0 A_0[\alpha_n + \beta_n t] \;\;;\;\; for \;\; -\Delta t < t < 0 \\ &= p'_0 A_0[\alpha_n - 2S_n + (\beta_n + 2S_n/\tau')t] \;\;;\;\; for \;\; 0 < t < +\Delta t \end{aligned}$$

where $p'_0 A_0$ and $\tau'$ are constants which are common to all frequencies. It would be most convenient to add up many scans and then perform a simple three parameter fit for each frequency. $p'_0 A_0 \beta_n = dA/dt$ is the slope of $A(t)$ just before the $nth$ pulse, $p'_0 A_0 \alpha_n$ is the value of $A(t)$ just before the $nth$ pulse, and $2p'_0 A_0 S_n$ is the step in $A(t)$ after the $nth$ pulse.

Note $\beta_n$ and $\alpha_n$ are related and determined by the previous pulses and $\tau'$. They may vary as a result of systematic variations in the beam and thus should not be constrained. $S_n$ on the other hand is insensitive to both pulse history and beam variations.

In principle the figure of merit in the high rep rate mode should be about four times greater than the conventional method as a result of the $\pi$ pulse. However extracting the signal from a three parameter fit may lead to some additional uncertainty in the signal due to correlations. The figure of merit should at least be comparable to the conventional CW mode and the low rep rate mode. However the signal averaging and thus control over systematics will be highest with this mode.

One could estimate $S_n$ from the difference of the average polarization just before and after the RF pulse $\mathcal{A}$, analogous to the slow rep rate case. However, unless the integration time $T < 0.01\tau'$ the time variation in the polarization ($\approx \beta_n T$), cannot be neglected compared to the signal $2S_n$ and thus $\mathcal{A}$ would be history dependent. Since rep rates of 100 Hz or higher are probably not practical given the RF pulse widths are at least 10 ms, fitting is a safe way to determine $S_n$.

For on-line resonance viewing it is possible to extract the signal $S_n$ by coarsely binning the data around the the RF pulse and measuring the average polarization in those time bins. Since at high rep rates $p(t)$ is a linear function of time (outside the RF pulse) one only needs two points to characterize $p(t)$ before and after the pulse and thereby determine $S_n$.

For example suppose the RF pulse is centered at $t = 0$ and has a width $t_p$. Let $p_1^+$, $p_2^+$ be the average polarization in two time bins $(t_p/2, t_p/2 + T)$ and $(t_p/2 + T, t_p/2 + 2T)$ respectively. Similarly let $p_1^-$, $p_2^-$ be the average polarization in time bins $(-t_p/2, -t_p/2 - T)$ and $-t_p/2 - T, -t_p/2 - 2T)$ just before the nth RF pulse. let $A_1^+, A_2^+, A_1^-, A_2^-$ be the corresponding average asysmmtries in the four time bins. If the bin width $T = 50ms$ then the rep rate is about 5 Hz. The slopes in $p(t)$ just before and after the RF pulse are given respectively by:

$$
\begin{aligned}
p_0'\beta^- &= (p_1^- - p_2^-)/T \\
p_0'\beta^+ &= (p_2^+ - p_1^+)/T
\end{aligned}
$$

Extrapolating these polarization functions before and after the RF pulse ($p^-(t)$ and $p^+(t)$

respectively) to $t = 0$ gives intercepts:

$$\begin{aligned} p^-(0) &= p_1^- + p_0'\beta^-(t_p + T)/2 \\ p^+(0) &= p_1^+ - p_0'\beta^+(t_p + T)/2 \end{aligned}$$

The difference is proportional to the signal:

$$\begin{aligned} p_0'S_n &= \frac{1}{2}[p^+(0) - p^-(0)] \\ &= \frac{1}{2}(p_1^+ - p_1^-) - \frac{1}{4}p_0'(\beta^+ + \beta^-)(t_p + T) \\ &= \frac{1}{2}(p_1^+ - p_1^-) - \frac{1}{4}(p_2^+ - p_1^+ + p_1^- - p_2^-)(1 + t_p/T) \\ &= \frac{3}{4}(p_1^+ - p_1^-)(1 + t_p/3T) + \frac{1}{4}(p_2^- - p_2^+)(1 + t_p/T) \end{aligned}$$

Then the signal in terms of the asymmetry:

$$\mathcal{A}_n = \frac{3}{4}(A_1^+ - A_1^-)(1 + t_p/3T) + \frac{1}{4}(A_2^- - A_2^+)(1 + t_p/T)$$

Let $\Delta A$ be the statistical uncertainty in the average asymmetry for each of the four time bins. Then the uncertainty in $\mathcal{A}_n$ is just the quadratic sum of the individual errors for the four terms in $\mathcal{A}_n$ :

$$\Delta\mathcal{A}_n = \frac{1}{4}\left[18(1 + t_p/3T)^2 + 2(1 + t_p/T)^2\right]^{1/2}\Delta A$$

As an example is $t_p = 10\,ms$ and $T = 50\,ms$ then $\Delta\mathcal{A}_n \approx 1.2\Delta A$. This imlies the uncertainty in the signal is about the same as in a conventional scan where the signal is just equal to the asymmetry. This is understandable since $\mathcal{A}_n$ requires measurements of the asymmetry in four time bins. This leads to an additional uncertainty which is compenstated by using a $\pi$ pulse. Both the statistical and systematic uncertainty will be reduced if one fits $A(t)$ before and after the pulse with $\mathcal{A}_n$ as a parameter, since one can impose a relationship between the slopes $dA/dt$ before and after the RF pulse and use the $\chi^2$ to decide if the point is good.

$\mathcal{A}_n$ can also be determined from the discontinuity in $dA/dt$ at the RF pulse but the uncertainty is much larger.

$$\begin{aligned} \mathcal{A}_n &= \frac{1}{2}p_0'A_0(\beta^+ - \beta^-)\tau' \\ &= \frac{\tau'}{2T}(A_2^+ - A_1 - A_1^- + A_2^-) \end{aligned}$$

with an uncertainty:

$$\Delta\mathcal{A}_n = \Delta A\tau'/T$$

Since $\tau'/T \approx 10$ the uncertainty in $S_n$ determined this way is much larger than getting it directly from the discontinuity in $A(t)$. It could be used as a consistency check.

To get an idea of how small a signal we can measure one can use the relationship $\Delta A = [\sqrt{N}]^{-1}$ where $N$ is the total number of counts in the detectors in the time bin being considered. Using the beta rate $R = 2 \times 10^6/s$, $T = 50ms$, and cycle rate of 0.1 Hz after an hour we obtain an uncertainty $\Delta\mathcal{A}_n = 2 \times 10^{-4}$.

### E. High Rep Rate with Double Pulses

It is possible to reduce the history depedendence of $A(t)$ before the $nth$ RF pulse by applying the $nth$ and $(n+1)th$ pulses at the same frequency. The role of the second pulse is to "undo" the effects of the first pulse and thereby return the polarization in frequency interval $\omega_n, \omega_n + \Delta\omega$ back to its equilibrium value or close to it. A disadvantage is that it requires two RF pulses per frequency point and thus the sweep rate will be reduced by a factor of two. The advantage is that $A(t)$ before the $nth$ RF pulse is less sensitive to pulse history. In this way it may be possible to get a good estimate of the signal $S_n$ simply from the difference in $A(t)$ measured before and after the nth RF pulse.

Consider the polarization from a given frequency interval $f(\omega_n)\Delta\omega$ in the time interval $(-\Delta t, \infty)$ where the $nth$ pulse is applied at t=0 and the second pulse at that same frequency is applied at $t = \Delta t$. Then

$$\begin{aligned}
p_n(t) &= p_0' \quad ; for \quad -\Delta t < t < 0 \\
&= p_0'[1 - 2S_n \exp(-t/\tau')] \quad ; for \quad 0 < t < \Delta t \\
&= p_0'[1 - 2S_n[1 - \exp(-\Delta t/\tau')] \exp(-t/\tau')] \quad ; for \quad t > \Delta t \\
&\approx p_0'[1 - 2S_n \Delta t/\tau' \exp(-t/\tau')]
\end{aligned}$$

Note the effect of the second $\pi$ pulse is to reduce the amplitude of the polarization at later times by a factor of $\Delta t/\tau'$. Thus the amplitude at $t = -\Delta$ from a string of $n-1$ prior pulses is also reduced by a factor $\Delta t/\tau'$ compared with the mode where a single pulse is applied:

$$a'_{n-1} = 2\frac{\Delta t}{\tau'} \sum_{m=1\ odd}^{n-1} S_m \exp[-(n-1-m)\Delta t/\tau']$$

The difference in the average polarization from before the $nth$ pulse and after the $nth$ pulse averaged over a time $\Delta t$ equals:

$$\hat{p^-} - \hat{p^+} = p'_0[2S_n(1-\Delta t/\tau') - a'_{n-1}\Delta t/\tau']$$

The last term is history dependent but is smaller by a factor $\Delta t/\tau'$ compared to the normal high rep rate mode. Clearly this method would require careful tuning of the RF pulse. Even then spin diffusion and the finite size of $\Delta t$ means there will be some residual history dependence in $A(t)$. Depending on the required length of the RF pulse and the degree of spin diffusion between the two pulses double pulsing may or may not be useful.

### F. Syd's Random Pulse Sequence

Random pulse sequencing is likely a better way to minimize any history depedence in $A(t)$ before the RF pulse. After many scans with random sampling $A(t)$ and $dA(t)/dt$ are almost independent of frequency just prior to the RF pulse. There will be some residual frequency dependence since the previous history excludes the frequency bin about to be excited. As long as the signal from this frequency bin is only a small fraction of the total signal the frequency dependence in $A(t)$ prior to the RF pulse is small. In any event the signal extracted from a two point measurement of the asymmetry (i.e. before and after the pulse) has no history dependence. This means the statistical error bars will in general be a factor of two smaller than in a four point measurement described above. The only disadvantage is that there is additional error in the signal due to the random sampling, which after a sufficently large number of scans becomes small. This additional error should decrease as $1/\sqrt{M}$ where M is the number of scans. There is no decrease in the signal amplitude $S_n$.

The derivation for the $A(t)$ just before and after the RF pulse is similar to the high rep rate case except we need to lablel each RF pulse in the scan by both a frequency index $i$ and a pulse sequence number $n$. The frequency bin being irradiated starts at $\omega_0 + i\Delta\omega$ where $\omega_0$ is the start frequency and $\Delta\omega$ is the frequency bin width. If the pulse sequence number is $n$, then $n-1$ is the number of RF pulses which have preceeded the frequency bin $i$ about to be irradiated. If $N$ is the total number of frequency bins in a scan then $n$ must lie the range $(1, N)$.

Assume a large number of scans with random sequencing. Consider all the pulses with the same $i$ and $n$. The average amplitude from the $n-1$ prior pulses at a time $t = -\Delta t$ relative the $nth$ pulse in frequency bin $i$ is:

$$\begin{aligned}\langle a_{i,n}\rangle &= 2\sum_{m=0}^{n-2}\langle S_{j\neq i}\rangle \exp[-m\Delta t/\tau'] \quad ; for \quad 1 < \; n \; \leq \; N \\ &= 0 \;\; ; \;\; n = 1\end{aligned}$$

where we have replaced $S_m$ inside the sum by $\langle S_{j\neq i}\rangle$ defined as the average of all the signal amplitudes but excluding $S_i$. Since $\langle S_{j\neq i}\rangle$ is independent of $m$ it can be pulled outside the sum. If $\langle S\rangle$ is the average signal over all $N$ frequencies then is easy to show:

$$\langle S_{j\neq i}\rangle = \frac{N\langle S\rangle - S_i}{N-1}$$

The probability, $p_n$,that any given pulse has index $n$ (i.e.preceeded by $n-1$ pulses) is independent of $n$ and equals $1/N$. If we only specify $i$ then $\langle a_{i,n}\rangle$ must be averaged over all possible values of $n$ is just:

$$\begin{aligned}\langle a_i\rangle &= \sum_{n=1}^{N} p_n\langle a_{i,n}\rangle \\ &= 2\frac{\langle S_{j\neq i}\rangle}{N}\sum_{n=2}^{N}\sum_{m=0}^{n-2}\exp[-m\Delta t/\tau'] \\ &= 2\frac{\langle S_{j\neq i}\rangle}{N}\sum_{m=0}^{N-2}(N-1-m)\exp[-m\Delta t/\tau'] \\ &= 2\langle S_{j\neq i}\rangle\left[\frac{N-1}{N}\sum_{0}^{N-2}\exp[-m\Delta t/\tau'] - \frac{1}{N}\sum_{0}^{N-2} m\exp[-m\Delta t/\tau']\right] \\ &= 2\langle S_{j\neq i}\rangle f\end{aligned}$$

where the term in square brackets $f$ is a number in the range $(1, N-1)$. Note $f$ depends on $\tau'$, $\Delta t$ and $N$ but is independent of the resonance signals. $f$ can be estimated in a continuum approximation where $x = m\Delta t/\tau'$ and $dx = \Delta t/\tau'$

$$\begin{aligned}
f &\approx \frac{\tau'}{\Delta t}\left[\frac{N-1}{N}\int_0^{x_2}\exp(-x)dx - \frac{\tau'}{N\Delta t}\int_0^{x_2} x\exp(-x)dx\right] \\
&= \frac{\tau'}{\Delta t}\left[\frac{N-1}{N}[1-\exp(-x_2)] - \frac{\tau'}{N\Delta t}[1-(1+x_2)\exp(-x_2)]\right] \\
&\approx \frac{\tau'}{\Delta t}\left[\frac{N-1}{N} - \frac{\tau'}{N\Delta t}\right]
\end{aligned}$$

where the last step assumes $x_2 = (N-2)\Delta t/\tau'$ is large or that the time range of a scan is several $\tau'$. The main point here is that the average $\langle a_i \rangle$ is proportional to $\langle S_{j\neq i}\rangle = \frac{N\langle S\rangle - S_i}{N-1}$ with no history dependence and only a weak frequency dependence (assuming the frequency bin is much smaller than the line width). Thus on average $p(t)$ just before and just after the RF is applied to frequency bin $i$ depends only on the signal $S_i$.

As before one can determine the signal $S_i$ from the average polarization $p^-(t)$ and $p^+(t)$ just before and after the RF pulse. One can use a 4 bin measurement described above for fast pulsing if there is an insufficient number of scans to remove the noise in $p^-(t)$ and $p^+(t)$ generated by random sequencing. In this case the main advantage of the random sequence is to reduce any possible correlation between the extracted signal and the otherwise history dependent slope in $p(t)$. When there is a sufficient number of scans it is possible to extract the signal from the average polarization in two time bins $(-t_p/2, -t_p/2-T)$ and $(t_p/2, t_p+T)$ just before and after the RF pulse at $t=0$. In principle this should reduce the statistical uncertainty in a measurement of the signal by about a factor of two relative to the four point measurement as mentioned before. The scan averaged slope $\beta_i$ just before the $ith$ frequency is given by:

$$\begin{aligned}
\langle \beta_i \rangle &= \langle a_i \rangle/\tau' \\
&= \frac{fN\langle S\rangle}{\tau'(N-1)} - \frac{fS_i}{\tau'(N-1)}
\end{aligned}$$

For example if the entire signal were in frequency bin $i$ then $S_i = N\langle S\rangle$ and $\langle \beta_i\rangle = 0$. This is reasonable since the signals from all the previous pulses must be zero. The mean value of $\langle \beta_i \rangle$ averaged over all $i$ is

$$\begin{aligned}
\langle \beta \rangle &= \frac{1}{N}\sum_{i=1}^{N}\left[\frac{fN\langle S\rangle}{\tau'(N-1)} - \frac{fS_i}{\tau'(N-1)}\right] \\
&= \frac{f\langle S\rangle}{\tau}
\end{aligned}$$

The scan averaged polarization function just before and after an RF pulse applied to frequency bin $i$ are respectively:

$$\begin{aligned}\langle p_i^-(t)\rangle &= p_0'[\langle\alpha_i\rangle + \langle\beta_i\rangle t]\\ \langle p_i^+(t)\rangle &= p_0'[\langle\alpha_i\rangle - 2S_i + [\langle\beta_i\rangle + (2S_i/\tau')t]\end{aligned}$$

The time averaged polarization in the two bins is then:

$$\begin{aligned}p_1^- &= p_0'[\langle\alpha_i\rangle - \langle\beta_i\rangle(t_p+T))]\\ p_1^+ &= p_0'[\langle\alpha_i\rangle - 2S_i + (\langle\beta_i\rangle + 2S_i/\tau')(t_p+T)]\end{aligned}$$

Taking the difference we obtain:

$$\begin{aligned}p_1^+ - p_1^- &= 2p_0'\left[-S_i\left[1-\frac{(t_p+T)}{\tau'}\right] + \langle\beta_i\rangle(t_p+T)\right]\\ &= 2p_0'\left[-S_i\left[1-\frac{(t_p+T)}{\tau'}\right] + \left(\frac{fN\langle S\rangle}{\tau'(N-1)} - \frac{fS_i}{\tau'(N-1)}\right)(t_p+T)\right]\\ &= 2p_0'\left[-S_i\left[1-\frac{(t_p+T)}{\tau'}(1-\frac{f}{N-1})\right] + \frac{fN\langle S\rangle}{\tau'(N-1)}(t_p+T)\right]\end{aligned}$$

Solving for $p_0'S_i$ and multiplying by the maximum asymmetry $A_0$ we obtain the observed signal in terms of the time averaged asymmetries in the two time bins $\mathcal{A}_+$ and $\mathcal{A}_-$, the mean slope $\langle dA/dt\rangle = p_0A_0\langle\beta\rangle$ and known parameters.

$$\begin{aligned}A_0p_0'S_i &= \left[-\frac{A_0(p_1^+-p_1^-)}{2} + \frac{fN\langle S\rangle A_0p_0'(t_p+T)}{2\tau'(N-1)}\right]\times\left[1-\frac{(t_p+T)}{2\tau'}\left(1-\frac{f}{N-1}\right)\right]^{-1}\\ \mathcal{A}_i &= \left[-\frac{(\mathcal{A}^+-\mathcal{A}^-)}{2} + \frac{N\langle dA/dt\rangle(t_p+T)}{2(N-1)}\right]\times\left[1-\frac{(t_p+T)}{\tau'}\left(1-\frac{f}{N-1}\right)\right]^{-1}\end{aligned}$$

The first term in square brackets is the dominant term which determines the statistical uncertainty. If $\Delta A$ is the statistical uncertainty in the average asymmetry for one time bin then the uncertainty in $\mathcal{A}_i$ is about $\Delta A/\sqrt{2}$. This is about half that of the four point measurement, taking into consideration that the time bins will be twice as long compared to the four point measurement. Overall the figure of merit should higher by a factor of 4. This an upper limit since it assumes an infinite number of scans and no random scan noise.

There are advantages to measure four points rather than two. With four points one has the option to calculate the signal both ways and decide which is best. In general a four point calculation will be better for short runs whereas two points should give better results for long runs. Also the second term in square brackets is proportional to the mean value of the slope of $A(t)$ between pulses ($\langle dA/dt \rangle$). In a four point measurement this is measured separately from all the slopes. In a two point measurement this term can only be determined by going well off resonance which is problematic for broad lines and leads to uncertainty in the other resonance parameters. Double pulsing in a two point will reduce the offset but will not remove it.

The second term in the denominator originates from the discontinuity in $dA/dt$ and its correlation with the signal $S_i$. However it is just a simple scaling factor.

The signal can also be obtained from a single point measurement as in current version of mode 2a. In this case the single observable is the time averaged asymmetry $A_1$ in the time bin $(t_p/2, t_p/2+T)$ after the RF pulse.

$$
\begin{aligned}
A_1 &= p_0' A_0 \left[ \langle \alpha_i \rangle - 2S_i + (\langle \beta_i \rangle + 2S_i/\tau')(t_p+T) \right] \\
&= p_0' A_0 \left[ -2S_i \left( 1 - \frac{(t_p+T)}{\tau'} \right) + \langle \alpha_i \rangle + \langle \beta_i \rangle \frac{(t_p+T)}{\tau'} \right] \\
&= p_0' A_0 \left[ -2S_i \left( 1 - \frac{(t_p+T)}{\tau'} \right) + 1 - \langle a_i \rangle \left( 1 - \frac{(\Delta t + t_p + T)}{\tau'} \right) \right] \\
&= p_0' A_0 \left[ -2S_i \left[ 1 - \frac{(t_p+T)}{\tau'} - \frac{f}{N-1} \left( 1 - \frac{\Delta t + t_p + T)}{\tau'} \right) \right] + 1 - \frac{2fN\langle S \rangle}{N-1} \left( 1 - \frac{(\Delta t + t_p + T)}{\tau'} \right) \right] \\
&= p_0' A_0 \left[ -2S_i(1-\delta_1) + 1 - \delta_2 \right]
\end{aligned}
$$

where $\delta_1$ and $\delta_2$ are constants less than one given by:

$$
\begin{aligned}
\delta_1 &= \frac{(t_p+T)}{\tau'} + \frac{f}{N-1} \left( 1 - \frac{\Delta t + t_p + T)}{\tau'} \right) \\
\delta_2 &= \frac{2fN\langle S \rangle}{N-1} \left( 1 - \frac{(\Delta t + t_p + T)}{\tau'} \right)
\end{aligned}
$$

The signal in the asymmetry ( $\mathcal{A}_i \equiv p_0 A_0 S_i$ )is then:

$$
\mathcal{A}_i = \frac{-A_1/2 + p_0' A_0 (1-\delta_2)}{1-\delta_1}
$$

Note this signal is directly sensitive to variations in the stopping distribution since there is a term proportional to $\langle \alpha_i \rangle$. This is different than the two and four point neasurements where the terms involving $\langle \alpha_i \rangle$ cancel out. Also $\delta_2$ is generally not much less than 1. Consequently for single scan there is an offset and random scatter in the baseline which is much bigger than the resonance amplitude. This can be suppressed by having a scan range much larger than the resonance width or by double pulsing but this will increase the scan time. My guess is that a one point signal will be substantially noisier than the two and four point signals, especially when the beam is not steady.

In the current version of mode 2a there is a single time bin for each resonance frequency. One can still make a two point measurement by defining a signal as the difference between the asymmetry just before and after the RF pulse:

$$\mathcal{A}_i \equiv A_{i,n} - A_{j,n-1} \quad ; \quad j \neq i$$

where the first index of the average asymmetry $A_{i,n}$ labels the frequency and the second index in the sequence number. Eventually the mode should be modified so that one can record data in $m$ time bins (e.g. only apply the RF pulse every $mth$ time bin).

## III. CONCLUSIONS

A RF pulsed mode of operation has significant advantages over our conventional CW mode of scanning a resonance. The statistical uncertainties in the determining the lineshape should be similar or better. The main advantage is that systematic effects can be reduced significantly since it allows for must faster scanning. Furthermore, in many cases the baseline is automatically subtracted so there is one less parameter to fit. Together this means the quality of information should be much higher in any of pulsed modes discussed above. Simple fitting of $A(t)$ in the region of the RF pulse is likely the best way to extract the signal $S_n$ and it is free of any history dependence. Furthermore the $\chi^2$ can be used to judge if there is problem with any given data point.

Syd's random sampling has many advantages and should reduce or eliminate history dependence in the $A(t)$ before the pulse (as advertised). In this case the signal can be extracted from measurements of the asymmetry in 1, 2 or 4 time bins in the region of the RF pulse. Four time bins is best since one then has the option to calculate the signal in different ways and compare. This can be done on line without fitting.