Time differential ALC - experiments, simulations and benefits

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Abstract. Traditional muon avoided-level-crossing measurements use “integral counting” analysis, which results in a simple 1-D spectrum with resonance lines. At pulsed muon facilities, the time spectrum (TD-ALC) is available “for free” so it should be analysed to extract all relevant information. An ALC line corresponds to resonant transfer of polarisation back and forth between the muon and the other spins in a radical, and this oscillation is often at a convenient frequency of order 1 MHz. Following the oscillation frequency through just one \( \Delta m = 0 \) line can give the hyperfine constants for both the muon and nucleus and the gyromagnetic ratio for that nucleus.

1. Introduction
Muons often form muonated radicals via muonium addition when implanted into molecular solids, liquids, solutions or gases[1]. Measurements can give the hyperfine coupling constants between the unpaired electron and the nuclei in the molecule (including the muon itself which behaves chemically like another hydrogen atom). In addition, dynamics such as electron spin exchange and molecular reorientation will be observed.

A number of variations of the muon technique can be used to measure radicals and muonium. The simplest is repolarisation, where we scan the magnetic field from zero up to typically 0.5 T and measure the average longitudinal asymmetry. This gives a characteristic step at a field proportional to the hyperfine coupling and so gives a quick and simple confirmation of the presence of radicals. However it is unable to resolve distinct radicals with similar hyperfine constants, as may be expected in complex or low symmetry molecules, and is affected by dynamics and anisotropic interactions.

Muon spin rotation spectra taken in a sufficiently high transverse field will give two lines corresponding to the unpaired electron spin being parallel or antiparallel to the applied field, and with spacing equal to the muon’s hyperfine constant. Multiple radicals are easily identified. At lower fields, the lines may split if the electron also interacts with other nuclei. However this technique fails if there is a large anisotropy in a powder sample, if the formation of the radicals is slow and the muons dephase, as may happen in a dilute solution, or if there is strong relaxation.

Radio-frequency resonance can be used, with the longitudinal field scanned to bring different transitions into resonance. This is similar to the rotation measurement, where in high fields and frequencies only the muon hyperfine constant is relevant, and low fields show splitting from other nuclei. It is not affected by slow formation, and in some cases can measure the timescale of such dynamics.
Avoided level crossing is where the longitudinal magnetic field is scanned and at certain fields the levels will cross. Usually the levels interact so that they “avoid” each other with a small gap of order 1 MHz. At this point — assuming the two levels concerned have different values of the muon polarisation — the muon spin will oscillate or precess giving a lower average polarisation.

Traditional muon avoided-level-crossing measurements [2, 3] use “integral counting” analysis, which results in a simple 1-D spectrum with resonance lines. It requires only simple instrumentation and can take advantage of high rates on continuous muon sources. The resonance spectra can be fitted to give the central field, linewidth, and in some cases a line shape resulting from dipolar coupling.

At pulsed muon facilities, the time spectrum is available “for free” so it should be analysed to extract all relevant information. A $\Delta m = 1$ ALC line corresponds to the muon spin precessing around an off-axis internal field, while a $\Delta m = 0$ line corresponds to resonant transfer of polarisation back and forth between the muon and another nucleus [5]. These oscillations are often at a convenient frequency of order 1 MHz. The oscillation may still be observable if the radical formation is too slow to obtain a precession spectrum in high transverse field (for example in dilute solutions). The damping rates can be very low in liquids and single crystals, and the oscillation is even seen in powder samples at certain magic fields.

![Figure 1](image1.png)

**Figure 1.** Experimental $\Delta m = 0$ level crossing in liquid benzene at 300 K, as a 2-D plot.

![Figure 2](image2.png)

**Figure 2.** Integral asymmetry (upper) and the on-resonance time spectrum (lower) from figure 1.

2. Sharp lines

Figure 1 shows one of the $\Delta m = 0$ ALC lines for the cyclohexadienyl radical in liquid benzene measured on the HiFi instrument at ISIS [4], presented as a 2D intensity plot versus time and magnetic field. Figure 2 shows the integral asymmetry which would be obtained from this data (before background subtraction), and one of the individual time spectra. In addition to the line centre position and width, it is clear that there is an oscillation which has a minimum frequency on-resonance and increases when further away, while the amplitude decreases.

To a rough approximation, for most sharp avoided level crossings (and RF resonances) we have:

$$P(t) = (1 - A(B)) + A(B) \cos(\omega(B)t)$$  \hspace{1cm} (1)

with:

$$A(B) = \frac{1}{2} \frac{\omega_0^2}{\omega_0^2 + [\gamma_{\text{eff}}(B - B_0)]^2}$$  \hspace{1cm} (2)
\[ \omega(B) = \sqrt{\omega_0^2 + \gamma_{\text{eff}}(B - B_0)} \]  
\[ \omega_0 = \frac{A_\mu - A_X}{2(\gamma_\mu - \gamma_X)} \]  
\[ \gamma_{\text{eff}} = (\gamma_\mu - \gamma_X) \]

For an isotropic \( \Delta m = 0 \) line, a rough approximation is that the Zeeman splitting for each of the muon and nucleus adds to (or subtracts from) its hyperfine splitting until the two spins have the same energy difference and can exchange polarisation:

\[ B_0 = \frac{A_\mu - A_X}{2(\gamma_\mu - \gamma_X)} \]  
\[ \gamma_{\text{eff}} = (\gamma_\mu - \gamma_X) \]

The polarisation is transferred via the electron so the oscillation frequency depends on the coupling of the muon and nucleus to it, versus the field keeping the electron fully aligned:

\[ \omega_0 = \frac{A_\mu A_X}{2\gamma B_0} \]

Therefore, by fitting the whole data set, we should be able to extract values for \( A_\mu, A_X \) and \( \gamma_X \). Usually the last of these is known (e.g. \( X = \) hydrogen) and fixing it will help improve the accuracy of the fit. If there are several species which might give rise to lines then we may be able to identify them unambiguously.

For accurate fitting, the full Hamiltonian is solved numerically rather than using these approximations (which will serve to give a starting point for the fit). Fit parameters \( A_\mu - A_X \) and \( A_\mu + A_X \) are used, with these being converted internally back to \( A_\mu \) and \( A_X \) for the simulation, to avoid instability due to the correlation between them.

3. Broadened lines

In an anisotropic environment the behaviour is more complex and the integral line deviates from the simple Lorentzian shape. However, for an axial \( \Delta m = 1 \) line an oscillation appears near the line centre. The local field seen by an individual muon is \( B_\mu = B + (A \cdot S / \gamma_\mu) \) and in high field the electron spin \( S \) is parallel or antiparallel to \( B \). If we work in coordinates where the hyperfine tensor is diagonal, and an arbitrary field direction \((\theta, \phi)\), and consider only that electron spin direction giving the crossing, \( B_\mu = (B - A_{\perp}/2\gamma_\mu) \hat{x} \sin \theta \cos \phi + (B - A_{\perp}/2\gamma_\mu) \hat{y} \sin \theta \sin \phi + (B - A_{\parallel}/2\gamma_\mu) \hat{z} \cos \theta \). When \( B = (A_{\parallel} + A_{\perp})/4\gamma_{\text{Mu}} \), the magnitude of \( B_\mu \) is independent of \( \theta \) and \( \phi \) giving \( \omega_\mu = \gamma_\mu |B_\mu| = \frac{1}{2}|A_{\parallel} - A_{\perp}| \). Away from this magic field the frequencies spread out so the oscillation disappears by its damping rate increasing and only a small change in the average frequency.

A non-axial hyperfine tensor does not show a single magic field, but if statistics are sufficient, three fields each give rise to weak oscillations when all field orientations perpendicular to one principal axis have the same frequency.

Figure 3 shows ALC resonances in solid benzene just below the melting point where the \( \Delta m = 1 \) line and one of the \( \Delta m = 0 \) lines are both visible. The different characters of the lines are apparent. The \( \Delta m = 1 \) line (figure 4, lower) has a strongly damped oscillation of about 1.5 MHz indicating anisotropy \( |A_{\parallel} - A_{\perp}| = 6 \) MHz. At this temperature the benzene molecules are rotating about their 6-fold axes so the radical also averages out most of the dipolar interaction by “magic angle spinning” leaving an approximately axial component with the same symmetry. Residual non-axial asymmetry (the molecules are not at high symmetry points in the lattice) and dynamics may contribute to the loss of the longer-lived oscillations sometimes seen.

The \( \Delta m = 0 \) line at higher field (figure 4, upper) has a frequency 0.6 MHz very similar to that in the liquid, since the isotropic hyperfine couplings are similar. The increase in frequency when off-resonance is now damped out by the anisotropy.
Single crystal $\Delta m = 1$ ALCs should show oscillating polarisation in the transverse directions, especially for lower symmetry crystal structures with few molecules per unit cell. Positron spiralling may result in the measured transverse polarisation being rotated compared to that seen with small transverse fields.

4. Implementation
The simulation package “Quantum” is now integrated with the data analysis framework “Mantid” so that the results of simulations can be converted back to experimental format, or used in fitting.

A real muon instrument often shows a variable background as a function of field, seen in figure 2, especially at the higher fields where ALC lines are found and with complex or thick walled sample cells. This is because the positrons travel on spiral tracks in the applied field, with radii comparable to the size of the spectrometer and varying with the field magnitude and their remaining momentum after escaping the sample. Fitting only the oscillating part of $P(t)$ allows us to let the constant part of each spectrum be a free parameter in the fit, instead of requiring careful background modelling and subtraction. When following a resonance line as a function of temperature or other parameter there may be no need to measure a large background field range each side of the line. We take advantage of the fact that the polarisation starts at 1.0 at time=0 and only varies away from this as $\cos(\omega t)$.

5. Sensitivity
Simulated data can be fitted and the accuracy of the resulting fits estimated. For this example we used the $\Delta m = 0$ line from a radical with $A_\mu = 520$ MHz and $A_p = 120$ MHz. We generated a series of random data sets with selected spacing and number of field points. Each field has 10 Mevents, full asymmetry of the radical = 5%, and $\alpha = 1.01$.

Table 1 shows the mean error value E reported by the Levenberg-Marquardt fitting routine in Mantid, and the RMS scatter S of the fitted parameter between 50 data sets, for the full time dependent fit and a simple line fit to the integral data.

The 10 kHz accuracy for $A_\mu - A_p$ comes from the line centre position and requires the magnetic field in each measurement to be known to 0.1 mT, probably requiring a NMR measurement rather than relying on the set current in a superconducting magnet. However $A_\mu + A_p$ is a measurement
Table 1. Fitting accuracy

| Parameter | Time Dependent fit | Integral Fits (Lorentzian) |
|-----------|--------------------|---------------------------|
|           | 5 points 50G       | 5 points 50G              |
|           | S                  | E                         |
|           | 15 points 50G      | 30 points 25G             |
|           | S                  | E                         |
| $A_{\mu} + A_p$ / MHz | 0.54 0.89 | – – – – – – – – – – |
| $A_{\mu} - A_p$ / MHz | 0.010 0.015 | 0.016 0.021 0.014 0.021 0.0090 0.0144 |
| Amplitude / % | 0.11 0.19 | 2.8 1.4 0.23 0.32 0.16 0.23 |
| Total Mevents | 50 | 50 150 300 |

of muon oscillation frequency, determined with much lower systematic errors. The integral fit needs a background region in order to get an accurate amplitude while the time dependent fit can work with the oscillations within the line.

When the nuclear hyperfine coupling is small ($\Delta m = 0$) or the hyperfine tensor is nearly isotropic ($\Delta m = 1$), the oscillation frequency may be too small to see a whole cycle within the time scale of the muon measurement, or fit the frequency. In this case the asymmetry still follows a behaviour $a(t) = a_0 \cos(\omega t) \approx a_0 - a_1 t^2$ and if the data is taken in time differential mode a significant improvement over standard integral analysis is still possible with suitable choice of time window or weighting.

6. Dynamics

Observation of the damping of oscillations, and relaxation of the underlying baseline, can allow us to fit the relaxation rates. Different mechanisms may have different relative effects.

As an example we modelled the rapid exchange between two states with hyperfine constants differing by $\pm 2.5\%$ from the values earlier. Again the $\Delta m = 0$ line is studied. Figure 5 shows simulated on-resonance time differential data and figure 6 shows integral data for the same conversion rates. Figure 7 shows the resulting fitted residence time $\tau$ as a function of that used in the simulation, along with the integral asymmetry linewidth. The time dependent fit is able to directly extract much lower times (faster exchange). The residence time can also be extracted from the linewidth but that relies on the width of the static averaged line being known accurately. Each simulation
Figure 7. Fit results for rapid conversion between two radicals, observed by the $\Delta m = 0$ line.

uses 10 Mevents per run. 5 runs at 50 G spacing are used for the time dependent fit, but 61 runs at 25 G for the integral data since a region of background must be measured in order to get an accurate fit of the linewidth. As can be seen in the individual spectra (figure 5), the background of the integral line varies due to relaxation of the non-oscillating component. The increasing errors at large $\tau$ for either analysis method are because the field scans only include the central motionally narrowed line and not the whole field region including the two individual lines.

7. Conclusions
Fitting the time dependent asymmetry is a useful way to extract further information from ALC data, especially when measuring narrow resonances in solution or single crystals. Sharp $\Delta m = 0$ lines start with $P(t = 0) = 1.0$ so can be used to check the instrumental background. However solid powder or polycrystalline samples with large or non-axial anisotropy may not show significant time dependence. Strong dynamics may obscure the oscillations, but the time dependent data may still give useful information.

References
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