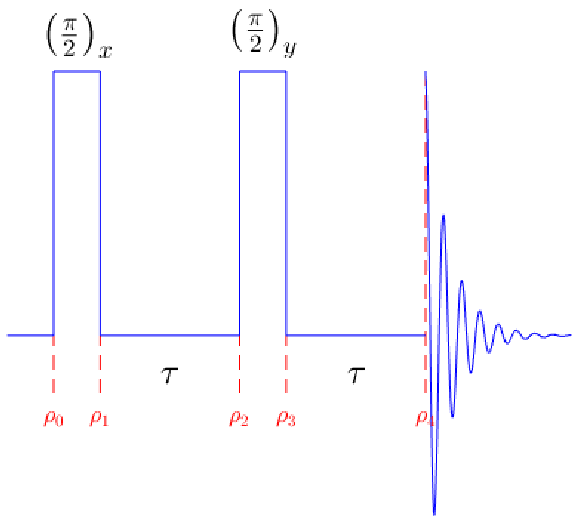
February 2023 NMR Topic of the Month: The Solid Echo



How is that an echo?

In John Waugh's Gitte Vold Memorial Lecture (circa 2004) he tore apart the picture of isochromats that diffuse and coalesce as you probably heard the Hahn echo described. So open your mind a little when it comes to echoes. The picture above is the solid (quadrupolar) echo, and it refocuses bilinear homonuclear terms in the Hamiltonian rather than chemical shift terms.

When is this echo important?

This echo is particularly important when looking at deuterium signals in (semi-) rigid environments.

How does the solid echo work?

Product-operators cannot explain this experiment, but a quick examination of the propagator does. Between the initial $\frac{\pi}{2}$ pulse and acquisition the magnetization undergoes: free evolution for τ, a $\frac{\pi}{2}$ pulse phase shifted from the initial pulse by 90°, and a second free evolution for τ. The propagator for these three steps is:

$$U(2\tau) = exp\left[-\omega_\theta\left(3I_z^aI_z^b - I^a\cdot I^b\right)\tau\right]exp\left[i\frac{\pi}{2}I_y\right]exp\left[-\omega_\theta\left(3I_z^aI_z^b - I^a\cdot I^b\right)\tau\right]$$

If to the right side we multiply by $1 = exp\left[-i\frac{\pi}{2}I_y\right]exp\left[i\frac{\pi}{2}I_y\right]$, then the final evolution term above is rotated about the $\hat{y}$-axis by $\frac{\pi}{2}$. The resulting propagator may then be further simplified (note the $I_z^aI_z^b$ and $I_x^aI_x^b$ terms commute):

$$U(2\tau) = exp\left[-\omega_\theta\left(3I_z^aI_z^b - I^a\cdot I^b\right)\tau\right]exp\left[-\omega_\theta\left(3I_x^aI_x^b - I^a\cdot I^b\right)\tau\right]exp\left[i\frac{\pi}{2}I_y\right] = exp\left[-\omega_\theta\left(3I_y^aI_y^b - I^a\cdot I^b\right)\tau\right]exp\left[i\frac{\pi}{2}I_y\right]$$

Following the initial $\frac{\pi}{2}$ pulse the magnetization is along I_y, so this propagator does not affect it.

References

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2. J.H. Davis, K.R. Jeffrey, M. Bloom, M.I. Valic, and T.P. Higgs, *Chem. Phys. Lett.* **42**(2), 390-394 (1976).
3. K. Schmidt-Rohr and H.W. Spiess, *Multidimensional Solid-State NMR and Polymers [Section 2.6.4]*, Academic Press, New York (1996).
4. M.H. Levitt, *Spin Dynamics [Section 13.1.10],* 2nd ed., John Wiley & Sons, New Jersey (2012).