Supplementary Material

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Schaefer's foresight of pulsed DNP

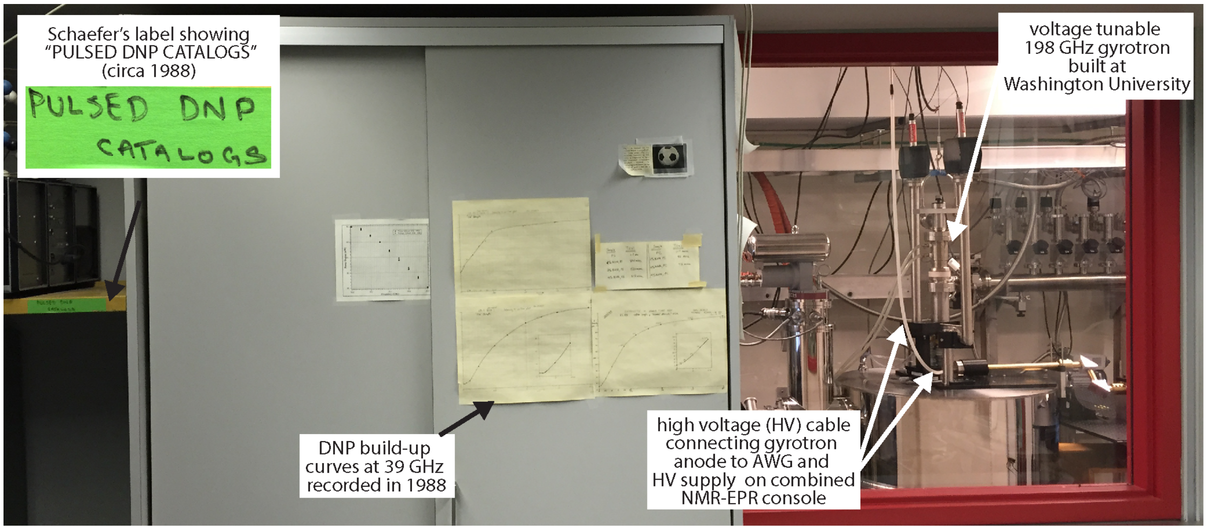

Figure 1: A photograph taken in the laboratory that housed Schaefer's MAS DNP apparatus shows past MAS DNP data and future techonology in the Barnes Lab at Washington University in St. Louis.

As early as in the 1980's, Schaefer was thinking about how to extend continuous wave MAS DNP experiments to pulsed DNP to further improve his success with pulsed MAS NMR. Schaefer's vision of the future of DNP along with his work on establishing REDOR and cross polarization (CP) MAS as gold standard MAS NMR techniques solidify him as a pioneer of solid state NMR.

A photograph (**Figure 1**) taken in the laboratory that housed Schaefer's 39 GHz / 60 MHz MAS DNP apparatus shows past and future DNP. A "PULSED DNP" label (left) and DNP build-up times of 1,3-bis(diphenylene)-2-phenylallyl (BDPA) doped polystyrene recorded with 39 GHz microwave irradiation in 1988 (center). In the adjacent laboratory, a newly constructed 198 GHz voltage tunable gyrotron can be seen through the window (right). Voltage control of the gyrotron anode with an arbitrary waveform generator (AWG) integrated into a combined NMR-EPR console will provide microwave frequency agility to implement the frequency modulated cross effect, EPR spin inversions, and hyperfine decoupling.

Normalized power of gaussian beam

The electric field of a gaussian beam as given in *Infrared and Millimeter Waves* Vol. 6 by Goldsmith,

$$E(r,z) = E_0 \frac{w_0}{w(z)} \exp\left(\frac{-r^2}{w^2(z)}\right) \exp(-ikz) \exp\left(\frac{-i\pi r^2}{\lambda R(z)}\right) \exp(i \arctan \frac{\lambda z}{\pi w_0^2}). \tag{1}$$

The squared magnitude at z=0 is then given by,

$$|E(r,0)|^2 = E_0^2 \exp\left(\frac{-2r^2}{w_0^2}\right). \tag{2}$$

We can relate this to a time RMS intensity profile given that the beam is linearly polarized. The time RMS of the intensity related to the peak field for a plane wave in free space is given by,

$$I_0 = \frac{1}{2}\epsilon_0 c |E_0|^2. \tag{3}$$

Then the intensity profile of the gaussian beam at z=0 can be represented by,

$$I(r,0) = I_0 \exp\left(\frac{-2r^2}{w_0^2}\right). \tag{4}$$

To normalize the total power going through the cross section at z=0 we take an integral over the entire plane,

$$P_0 = \int_0^\infty 2\pi r I_0 \exp\left(\frac{-2r^2}{w_0^2}\right) dr = \frac{1}{2}\pi I_0 w_0^2. \tag{5}$$

From here the equation given in the paper can be found with some basic algebra.

Decomposition of Linear Oscillating field into two counter-rotating vectors

Consider a linearly oscillating field with a magnetic field,

$$\mathbf{B} = B_0 cos(wt)\mathbf{j}. \tag{6}$$

The electric component is then,

$$\mathbf{E} = cB_0 cos(wt)\mathbf{i}. \tag{7}$$

We can decompose the magnetic field into two components that rotate with exactly opposite frequencies.

$$\mathbf{B}_+ = \frac{1}{2}B_0\cos(wt)\mathbf{j} + \frac{1}{2}B_0\sin(wt)\mathbf{i} \tag{8}$$

$$\mathbf{B}_- = \frac{1}{2}B_0\cos(-wt)\mathbf{j} + \frac{1}{2}B_0\sin(-wt)\mathbf{i} \tag{9}$$

From energy conservation we expect that half of the power of the linearly oscillating wave goes into each component and we show that here.

Consider the Poynting vector given by,

$$\mathbf{S} = \frac{1}{\mu_0}\mathbf{E}\times\mathbf{B}. \tag{10}$$

The magnitude of the Poynting vector represents the intensity of the field. For the linearly polarized wave this gives,

$$\mathbf{S} = \frac{c}{\mu_0}B_0^2\cos^2(\omega t)\mathbf{k} = \epsilon_0 c|E_0|^2\cos^2(\omega t)\mathbf{k}. \tag{11}$$

Remember that the time averaged intensity is then given by equation (3). The Poynting vector for one of the components is

$$\frac{c}{2\mu_0}B_0^2\cos^2(wt)(\mathbf{i}\times\mathbf{j}) = \frac{c}{2\mu_0}B_0^2\cos^2(wt)\mathbf{k} \tag{12}$$

$$\frac{c}{2\mu_0}B_0^2\cos(wt)\sin(wt)(\mathbf{i}\times\mathbf{i}) = 0. \tag{13}$$

So the intensity of one of the circularly polarized components holds half of the power of the original linearly polarized light.

Stator cavity schematic used in HFSS simulations

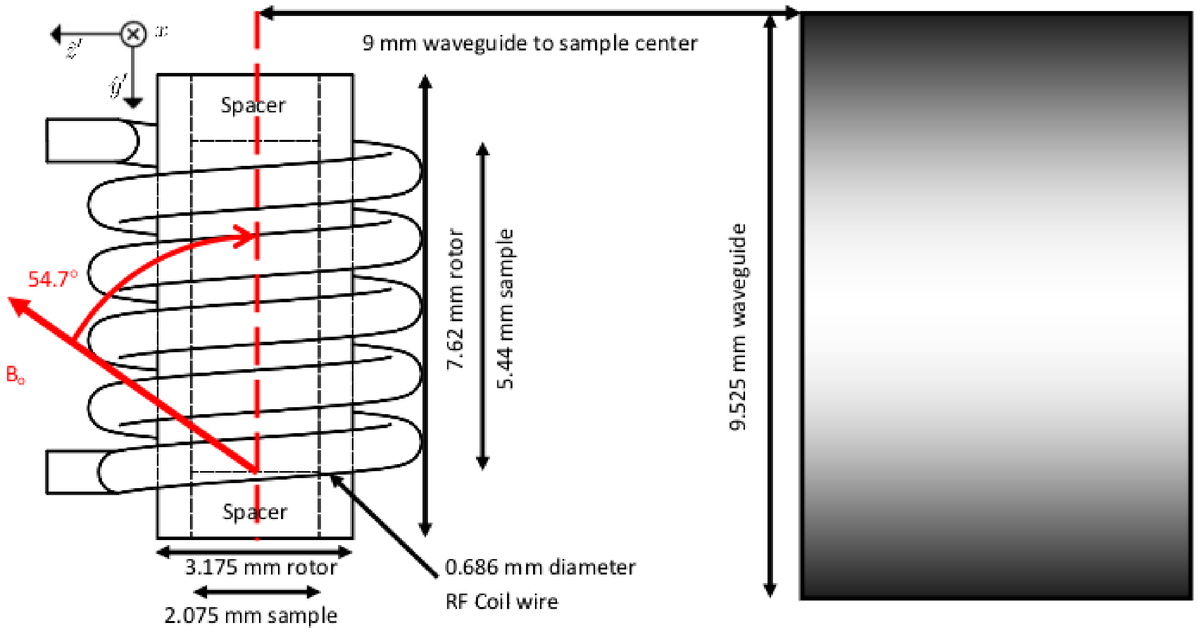

Figure 2: A picture of the fields calculator with the operations outlined in the paper

Screenshot of HFSS fields calculator

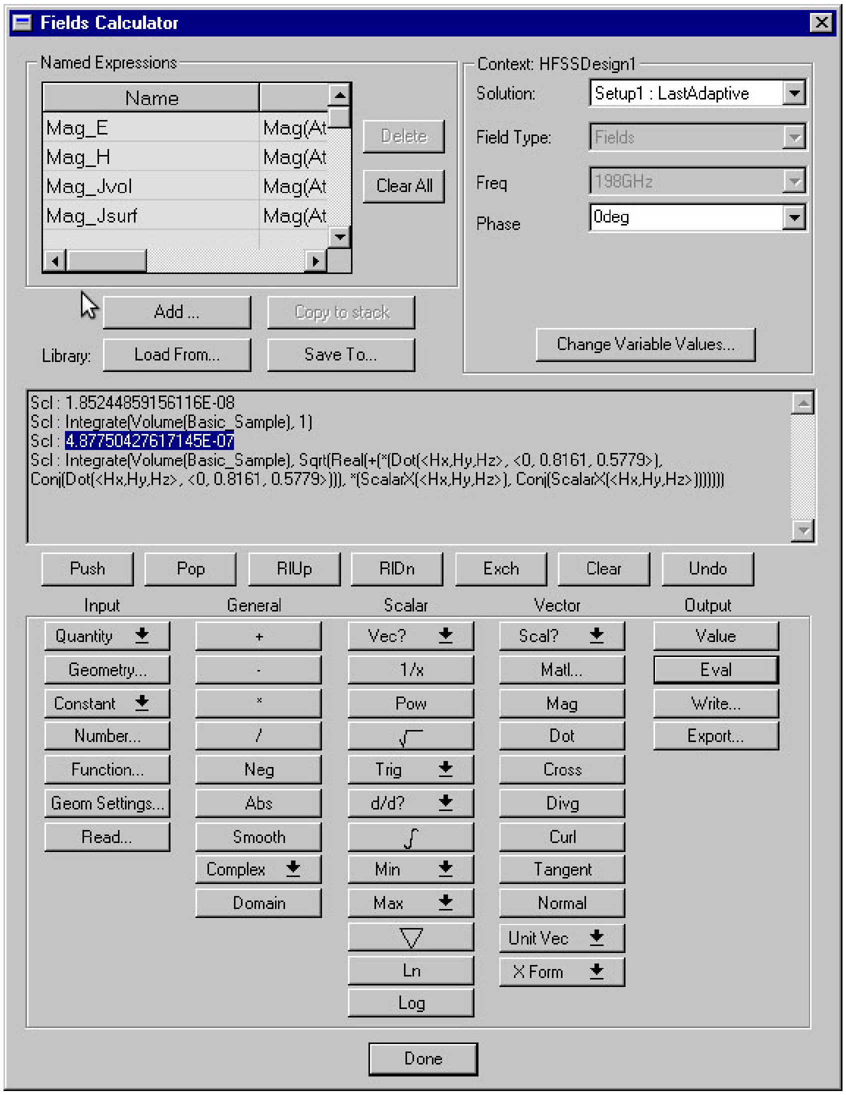

Figure 3: A picture of the fields calculator with the operations outlined in the paper

The image shown is from our high density mesh simulation of our 198GHz system. The top number corresponds to the volume of the sample. The second one is the integral outlined in the paper.To convert these numbers to a $\gamma_e B_{1S}$ we have,

$$\gamma_e B_{1S} = \frac{1}{2} \times 28024.95 \frac{\text{MHz}}{\text{Tesla}} \times 1.257 \times 10^{-6} \frac{\text{Henries}}{\text{meter}} \times \frac{4.877 \times 10^{-7}\ \text{Tesla}}{18.5\ \mu\text{L}} = 0.46\ \text{MHz}. \tag{14}$$

The 1/2 acconuts for the light being linearly polarized.