Magic Angle Spinning PhL 3.31.08

Consider two **arbitrarily located** spins in our cylinder which is rotating with axis at the magic angle. But make the cylinder axis be $\hat{\mathbf{z}}$ and so $\mathbf{B}_0$ is then pointing off axis by the magic angle. Imagine two spins in our rotating sample located arbitrarily in the sample. We can express the position of each spin in cylindrical coordinates as follows:

$$\mathbf{r}_1 = z_1\hat{\mathbf{z}} + \rho_1 C_{\theta 1}\,\hat{\mathbf{x}}' + \rho_1 S_{\theta 1}\hat{\mathbf{y}}'$$
$$\mathbf{r}_2 = z_2\hat{\mathbf{z}} + \rho_2 C_{\theta 2}\,\hat{\mathbf{x}}' + \rho_2 S_{\theta 2}\hat{\mathbf{y}}'$$

where due to our spin we have

$$\hat{\mathbf{x}}' = C_{\omega t}\hat{\mathbf{x}} + S_{\omega t}\hat{\mathbf{y}}$$
$$\hat{\mathbf{y}} = -S_{\omega t}\hat{\mathbf{x}} + C_{\omega t}\hat{\mathbf{y}}$$

Therefore, the vector **e** which connects the two spins is given by:

$$\mathbf{e} \sim \mathbf{r}_1 - \mathbf{r}_2 = (z_1-z_2)\,\hat{\mathbf{z}} + (\rho_1 C_{\theta 1} - \rho_2 C_{\theta 2})\,\hat{\mathbf{x}}' + (\rho_1 S_{\theta 1} - \rho_2 S_{\theta 2})\,\hat{\mathbf{y}}'$$

$$= (z_1-z_2)\,\hat{z} + (\rho_1 C_{\theta 1} - \rho_2 C_{\theta 2})\,(C_{\omega t}\hat{\mathbf{x}} + S_{\omega t}\hat{\mathbf{y}}) + (\rho_1 S_{\theta 1} - \rho_2 S_{\theta 2})\,(-S_{\omega t}\hat{\mathbf{x}} + C_{\omega t}\hat{\mathbf{y}})$$

I think we have that

$$e^2 = (z_1-z_2)^2 + [\,\rho_1^2 + \rho_2^2 - 2\,\rho_1\rho_2\cos(\theta_1 - \theta_2)\,]$$

Now let's put B_o in the x-z plane arbitrarily so we have

$$\mathbf{B}_0 = B_0\,(\sin\theta_m\,\hat{x} + \cos\theta_m\,\hat{z})/\sqrt{2}$$

Method #1 (no good)

What is the angle between this B field and our e direction?

$$\cos\theta = e \bullet (\sin\theta_m\,\hat{x} + \cos\theta_m\,\hat{z}) / |e|$$

Then,

$$|e|\cos\theta = (z_1-z_2)\cos\theta_m + \{(\rho_1 C_{\theta 1} - \rho_2 C_{\theta 2})\,C_{\omega t} - (\rho_1 S_{\theta 1} - \rho_2 S_{\theta 2})\,S_{\omega t}\}\sin\theta_m$$

$$|e|^2\cos^2\theta = (z_1-z_2)^2\cos^2\theta_m + \text{"the rest"}$$

If we time average, the cross term $\cos\theta_m \sin\theta_m$ will average to zero, and the cross term of the second term will also average to zero, but there is a piece which does average away this, so we get

$$|e|^2\langle\cos^2\theta\rangle = (z_1-z_2)^2\cos^2\theta_m + (1/2)[\,\rho_1^2 + \rho_2^2 - 2\rho_1\rho_2\cos(\theta_1-\theta_2)\,]\sin^2\theta_m$$

Now I am lost. I was hoping to find that $\langle\cos^2\theta\rangle = \cos^2\theta_m$, but this does not seem possible.

Method #2 (gives the desired result)

If we do a time average, we get $\langle C_{\omega t}\rangle = \langle S_{\omega t}\rangle = 0$ so our result is

$$\langle \mathbf{e}\rangle \sim (z_1-z_2)\,\hat{\mathbf{z}}$$

So the average value of the e-vector (for an arbitrary pair of spins) is strictly along the axis of the cylinder. For d-d coupling we know that

$$H'(t) \sim (1/2)(3\cos^2\theta(t) - 1)$$

We now have to make a tricky argument: if the angle $\theta(t)$ of our dipole pair axis against the B_0 field direction varies rapidly relative to the d-d relaxation time frame, then we can replace $\theta(t)$ by $\langle\theta\rangle$. We are not averaging the secular Hamiltonian, we are averaging the parameter that goes into it, as was done in the case of libration. Assuming this is justified, we get

$$H'(t)_{MAS} \sim (1/2)(3\cos^2\langle\theta\rangle - 1)$$

If we set the cylinder at θ_{magic} relative to B, then we have

$H'(t)_{MAS} \sim 0$ *for any pair of spins* which have a dipole-dipole coupling.

Comment: To the extent that this coupling causes line broadening due to dipole-dipole relaxation [the main source of relaxation in spin-1/2 systems says Malcolm] doing this spinning action removes this relaxation mechanism from the effective Hamiltonian, so the line broadening goes away and you can see fine peaks again!