NMR Meets Biology: Tutorial/Basics of Solid-State NMR

1. In the lecture, for spins-$\frac{1}{2}$, we extensively worked out the spin-echo and solid-echo schemes. Whilst the former refocuses interactions that are linear in I_z (I standing for a particular nuclear spin), the latter refoucses interactions that are bilinear in the same spin operators, like $I_{1z}I_{2z}$ (homonuclear dipole-dipole coupling between two spins). How will you design an echo scheme that can refocus both the interactions at the same time? Sketch the appropriate pulse scheme.

2. We presented the rotation matrices in the lecture. For the Pauli spin matrix, $A=\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$, find $\exp(i\theta B)$ and show that your result is a rotation matrix. Repeat the calculation for $\exp(-i\theta B)$.

3. In the lecture, we saw the set of matrices (Pauli) for spin-$\frac{1}{2}$. From first principles, derive the same, S_x, S_y, S_z, for spin-1 matrix. These will be useful in dealing with quadrupole spins, such as, ^{14}N, ^{2}H, and ^{6}Li.

4. The expression for the interaction energy, in classical electrodynamics, between two point–magnetic dipoles μ_j and μ_k separated by a distance r_{jk} is given by

$$U = \left\{ \frac{\mu_j \cdot \mu_k}{r_{jk}^3} - 3\frac{(\mu_j.r)(\mu_k.r)}{r_{jk}^5} \right\} \frac{\mu_0}{4\pi} \tag{1}$$

Substituting for $\mu = \gamma\hbar I$, we get the expression for the dipole-dipole Hamiltonian between I_j and I_k as

$$\mathcal{H}_{jk}^{DD} = -\left(\frac{\mu_0}{4\pi}\right)\gamma_j\gamma_k\hbar\left(\frac{I_j \cdot I_k}{r_{jk}^3} - 3\frac{(I_j.r)(I_k.r)}{r_{jk}^5}\right) \tag{2}$$

This dipole-dipole Hamiltonian may be expressed, in the dipolar alphabet form as seen in the lecture, as:

$$\mathcal{H}_{IS} = -\frac{\mu_0}{4\pi}\frac{\gamma_I\gamma_S\hbar}{r^3}[A + B + C + D + E + F] \tag{3}$$

with

$$A = I_{jz}I_{kz}(3\cos^2\theta - 1)$$

$$B = -\frac{1}{4}(I_{j+}I_{k-} + I_{j-}I_{k+}))(3\cos^2\theta_{jk} - 1)$$

$$C = \frac{3}{2}(I_{jz}I_{k+} + I_{j+}I_{kz})\sin\theta_{jk}\cos\theta_{jk}e^{-i\phi}$$

$$D = \frac{3}{2}(I_{jz}I_{k-} + I_{j-}I_{kz})\sin\theta_{jk}\cos\theta_{jk}e^{i\phi}$$

$$E = \frac{3}{4}(I_{j+}I_{k+})\sin^2\theta_{jk}e^{-2i\phi}$$

$$F = \frac{3}{4}(I_{j-}I_{k-})\sin^2\theta_{jk}e^{2i\phi} \tag{4}$$

(a) Derive the form for A, B, C, D, E, F.

(b) Why is the A term retained for the heteronclear case and both A and B terms retained for the homonuclear case under secular approximation?

(c) Why are the other letters in the dipolar alphabet neglected under secular approximation?

5. In the lecture, we outlined the principle of solid-echo formation for a two-spin homonuclear dipole-dipole coupled spin pair. Many steps were missing in the lecture though. Work out the entire derivation and show that $\rho(2\tau)=\rho(0)$.

6. Suppose one has two spin-$\frac{1}{2}$ particles, with their individual spin operators $\mathbf{I_1}$ and $\mathbf{I_2}$. Obtain the eigenstates of $\mathbf{I^2}$ and $\mathbf{I_z}$ operators, where $\mathbf{I} = \mathbf{I_1} + \mathbf{I_2}$, by constructing the $\mathbf{I^2}$ operator in the uncoupled basis, and diagonalising it. (Note that this can be done, more elegantly perhaps, making use of the Clebsch-Gordan coefficients.)

7. In the lecture, we worked out in detail the effect of Lee-Goldburg irradiation on the homonuclear dipole-dipole interaction. What will happen to the isotropic chemical-shift interaction under an LG irradiation?

8. The rank of spin components and spatial components under an appropriate rotation (under RF pulses and MAS respectively) is given in the table below. How do you justify the various ranks?

Table: Rotational signatures of the internal spin Hamiltonians:

Interaction	Space rank	Spin rank
Iso-CS	0	0
CSA	2	1
J	0	0
Hetero-DD	2	1
Homo-DD	2	2

9. Refer to the figure depicting the so-called CP fingers. Explain the spectra in both (a) and (b) plots, especially the origin of the so-called CP fingers in (b) which has probably one finger missing.
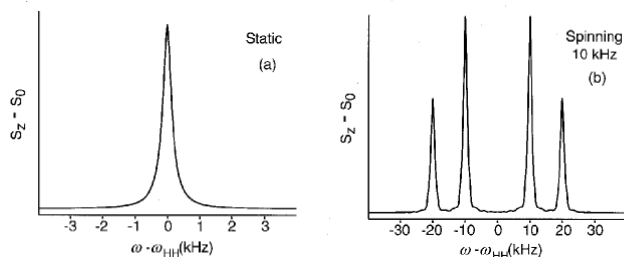

Figure 1:

Plot of the intensity of ^{13}C ($\mathbf{S}$) spectrum as a function of the mismatch of the Hartmann-Hahn match, i.e, the difference in the nutation frequencies of the CP spin-lock pulses applied on the ^{13}C and ^{1}H spins. (a) depicts the static case and (b) shows the MAS case with $\nu_r = 10$ kHz.

10. Advanced question: In the part of the lecture on CW decoupling, we mentioned that one should avoid conditions, such as, $\nu_1 = n\nu_r$. Here, ν_r is the MAS frequency and ν_1 is the nutation frequency of the RF employed for decoupling on the ^{1}H channel whilst observing the dipole coupled ^{13}C spectrum. What happens when this condition is met, the so-called R^3, rotary-resonance condition? Work out using the STO formalism to understand this effect.