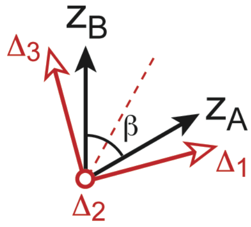
Problem Set: Dynamics from SSNMR

1. The difference tensor $\Delta=\sigma_A - \sigma_B$ plays an important role in the dependence of the stimulated echo and CODEX signals on the reorientation angle. The directions of the principal axes of the difference tensor between two uniaxial tensors are shown below:



(a) Generally, how does the n^{th} (n = 1, 2, 3) principal value of an NMR interaction tensor, ω_n, relate to the frequency measured when the B_0 field points along the n^{th} principal axis?

They are equal.

(b) Calculate the frequencies $\omega_{A,n}$ and $\omega_{B,n}$ for the B_0 field pointing along the n^{th} principal axis of the difference tensor. Express the frequencies in terms of the reorientation angle β, assumed to be < 90˚. Use the result in (a) to calculate the principal values ω_n^Δ of the difference tensor from the difference of these frequencies $\omega_{A,n} - \omega_{B,n}$.

Given the orientations of the difference tensor principal axes in the figure,

For Z_A :

$$\omega_{A,2} = \frac{1}{2}\delta\left(3\cos^2 90° - 1\right) = -\frac{1}{2}\delta$$
$$\omega_{A,1} = \frac{1}{2}\delta\left(3\cos^2\left(45° - \beta/2\right) - 1\right)$$
$$\omega_{A,3} = \frac{1}{2}\delta\left(3\cos^2\left(45° + \beta/2\right) - 1\right)$$

For Z_B

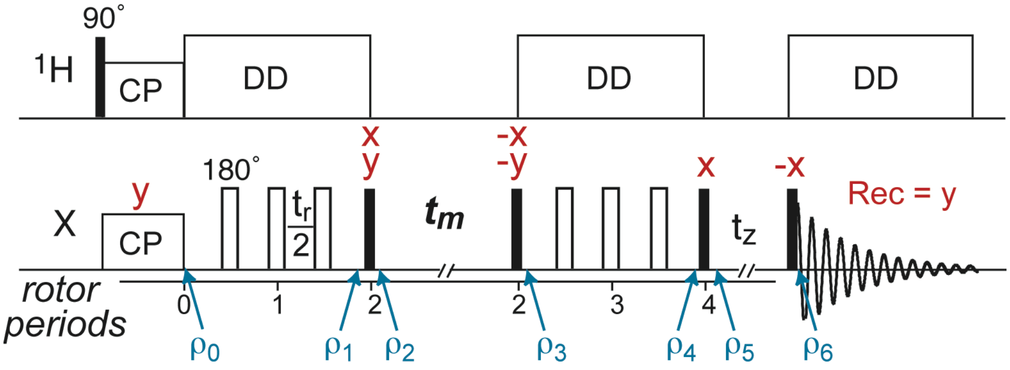
$$\omega_{B,2} = \frac{1}{2}\delta\left(3\cos^2 90° - 1\right) = -\frac{1}{2}\delta$$
$$\omega_{B,1} = \frac{1}{2}\delta\left(3\cos^2\left(45° + \beta/2\right) - 1\right)$$
$$\omega_{B,3} = \frac{1}{2}\delta\left(3\cos^2\left(45° - \beta/2\right) - 1\right)$$

So :

$$\omega_2^\Delta = \omega_{A,2} - \omega_{B,2} = 0$$
$$\omega_1^\Delta = \omega_{A,1} - \omega_{B,1} = \frac{3}{2}\delta \cdot \frac{1}{2}\left[\cos\left(90° - \beta\right) - \cos\left(90° + \beta\right)\right] = \frac{3}{2}\delta\sin\beta$$
$$\omega_3^\Delta = \omega_{A,3} - \omega_{B,3} = \frac{3}{2}\delta \cdot \frac{1}{2}\left[\cos\left(90° + \beta\right) - \cos\left(90° - \beta\right)\right] = -\frac{3}{2}\delta\sin\beta$$

2. The CODEX pulse sequence with the basic two-step phase cycle is shown below. Calculate the density operator or magnetization direction, along with its frequency modulation factor, at the points specified below. Do this for the two scans separately, and show that the detected signal after two scans is modulated by $\cos\Phi_1\cos\Phi_2-\sin\Phi_1\sin\Phi_2$, where Φ_1 and Φ_2 are the MAS phases accumulated in the first and second π-pulse trains, respectively,

$$\Phi_1 = N\int_0^{t_r/2}\omega_1(t)dt, \quad \Phi_2 = -N\int_0^{t_r/2}\omega_2(t)dt.$$



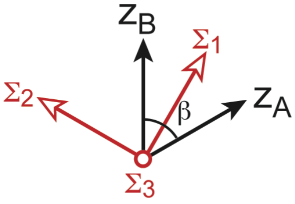
scan 1	scan 2
$\rho_0 = S_y$	$\rho_0 = S_y$
$\rho_1 = S_y\cos\Phi_1 + S_x\sin\Phi_1$	$\rho_1 = S_y\cos\Phi_1 + S_x\sin\Phi_1$
$\rho_2 = -S_z\cos\Phi_1 + S_x\sin\Phi_1$	$\rho_2 = S_y\cos\Phi_1 + S_z\sin\Phi_1$
$\rho_3 = S_y\cos\Phi_1$	$\rho_3 = S_x\sin\Phi_1$
$\rho_4 = S_y\cos\Phi_1\cos\Phi_2$ $+ S_x\cos\Phi_1\sin\Phi_2$	$\rho_4 = S_x\sin\Phi_1\cos\Phi_2$ $- S_y\sin\Phi_1\sin\Phi_2$
$\rho_5 = -S_z\cos\Phi_1\cos\Phi_2$ $+ S_x\cos\Phi_1\sin\Phi_2$	$\rho_5 = S_x\sin\Phi_1\cos\Phi_2$ $- S_z\sin\Phi_1\sin\Phi_2$
$\rho_6 = S_y\cos\Phi_1\cos\Phi_2$	$\rho_6 = -S_y\sin\Phi_1\sin\Phi_2$

detect S_y for both scans, so the accumulated modulation factor is:

$$\cos\Phi_1\cos\Phi_2 - \sin\Phi_1\sin\Phi_2 = \cos(\Phi_1+\Phi_2)$$

3. Consider fast trans-gauche isomerization of a C-D bond between two sites (e.g. t and g+) at equal population. The jump angle is 109.5˚. As a good approximation η = 0 for the rigid-limit ^{2}H quadrupolar interaction.

(a) Calculate the three principal values of the motionally averaged quadrupolar interaction. Sketch the resulting ^{2}H spectrum.



$$\Sigma_3 \text{ axis}: 90^\circ \text{ from both } Z_A \text{ and } Z_B,\ \overline{\omega}_3 = \frac{1}{2}\delta\left(3\cos^2 90^\circ - 1\right) = -\frac{1}{2}\delta$$

$$\Sigma_2 \text{ axis}: \beta/2 \text{ from both } Z_A \text{ and } Z_B,\ \overline{\omega}_2 = \frac{1}{2}\delta\left(3\cos^2\frac{109°5}{2} - 1\right) = \frac{1}{2}\delta\left(3\cdot\frac{1}{3} - 1\right) = 0$$

$$\Sigma_1 \text{ axis}: 90^\circ \pm \beta/2 \text{ from both } Z_A \text{ and } Z_B,\ \overline{\omega}_1 = \frac{1}{2}\delta\left(3\cos^2\left(90^\circ \pm \frac{109°5}{2}\right) - 1\right)$$

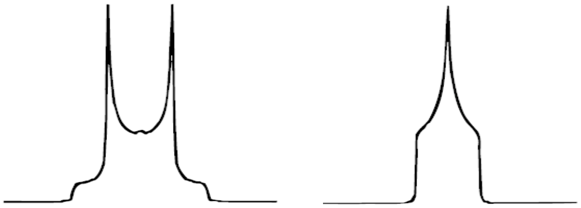
$$= \frac{1}{2}\delta\left[3\sin^2\left(\frac{109°5}{2}\right) - 1\right] = \frac{1}{2}\delta\left[3\cdot\frac{2}{3} - 1\right] = \frac{1}{2}\delta$$

(b) What is the $\overline{\eta}$ of the averaged lineshape?

Since $\overline{\omega}_3 = -\overline{\omega}_1$ and $\overline{\omega}_2 = 0$, $\overline{\eta} = 1$.

(c) What is the ratio between $\overline{\delta}$ and δ?

$\overline{\delta} = \overline{\omega}_1 - \overline{\omega}_{iso} = \frac{1}{2}\delta - 0 = \frac{1}{2}\delta$, so the ratio between $\overline{\delta}$ and δ is $\frac{1}{2}$.



4. Consider a C-H vector held rigidly in a peptide that undergoes fast uniaxial rotation around the lipid bilayer normal.
(a) What is the rigid limit coupling? Use a C-H bond length of 1.10 Å.

Rigid limit C-H dipolar coupling is 22.7 kHz.

(b) If the C-H vector is 90˚ from the bilayer normal, what is the averaged coupling? What is the order parameter?

90˚ from the motional axis: $\bar{\delta} = \delta \cdot \left\langle \frac{1}{2}\left(3\cos^2 90° - 1\right)\right\rangle = -\frac{1}{2}\delta \quad \Rightarrow S = -\frac{1}{2}$

(c) If the C-H vector is 35˚ from the bilayer normal, what is the averaged coupling? What is the order parameter?

35˚ from the motional axis: $\bar{\delta} = \delta \cdot \left\langle \frac{1}{2}\left(3\cos^2 35° - 1\right)\right\rangle = \frac{1}{2}\delta \quad \Rightarrow S = \frac{1}{2}$

(d) What is the $\bar{\eta}$ of the averaged coupling?

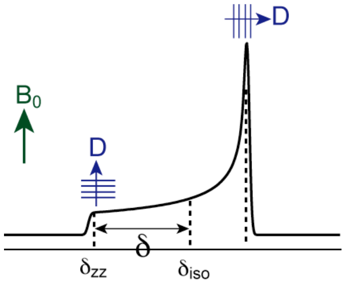
$\bar{\eta} = 0$ for both (b) and (c) due to uniaxiality of motion.

5. Consider the equation $\sigma_{zz}^{L} = \bar{\delta} \cdot \frac{1}{2}\left(3\cos^2\Phi_{zz} - 1\right) + \sigma_{iso}$ for the measured NMR frequency of a powder sample with uniaxial rotational mobility.

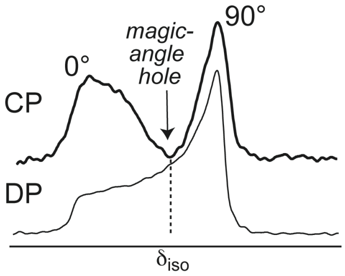
(a) What is the definition of the angle Φ_{zz}? Be specific about the two axes.

Φ_{zz} is the angle between the magnetic field B_0 and the local motional axis.

(b) Sketch the static CSA lineshape of this system measured by direct polarization. Indicate $\bar{\delta}$ in your sketch.



(c) If you measure the static CP spectrum, how will the lineshape be different from the DP spectrum? (Hint: consider how the motionally averaged X-H dipolar tensor and the motionally averaged CSA tensor are related).

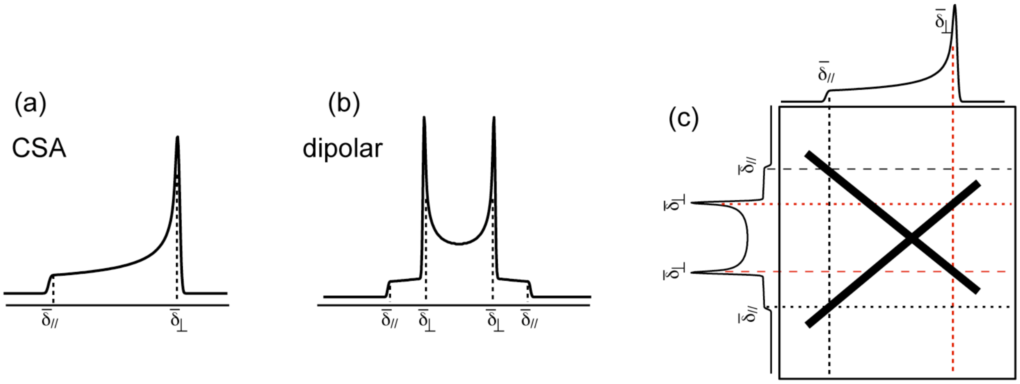


Anisotropic chemical shift

The CP lineshape in (c) is due to the fact that the X-H dipolar coupling is also averaged by motion to be uniaxial, so that the motionally averaged CSA and the dipolar interactions are parallel to each other in each molecule (see problem #6). The isotropic shift position originates from molecules whose motional axis is at the magic angle from B_0. These molecules have their averaged dipolar tensor also at the magic angle from B_0, thus they have a coupling strength of 0, thus giving no CP intensity. The rest of the powder lineshape is similarly modulated by the motionally averaged dipolar coupling. The 90˚ intensity in the CP spectrum relative to the DP spectrum is reduced by a factor of two compared to the 0˚ intensity.

6. Consider a non-spinning sample of a singly ^{15}N-labeled helical peptide in the lipid membrane. The peptide undergoes uniaxial rotation around the membrane normal.
(a) Sketch the 1D static ^{15}N chemical shift spectrum of the peptide. Indicate the frequency positions at which the bilayer normal is
(i) perpendicular to B_0, (ii) parallel to B_0.
(b) Sketch the 1D motionally averaged N-H dipolar spectrum of the same sample. Indicate the frequency positions at which the bilayer normal is
(i) perpendicular to B_0, (ii) parallel to B_0.
(c) If you measure the 2D dipolar-chemical shift correlation spectrum of this peptide under the non-spinning condition, what is the expected lineshape? Sketch the 2D contour spectrum.

Spectra:



7. The ^{1}H-decoupled T_2 relaxation rate of an X spin depends on τ_c as: $R_{2,X} = \frac{\omega_{Hx}^2}{5}\frac{\tau_c}{1+\omega_{1,H}^2\tau_c^2}$,

where ω_{HX} is the dipolar coupling strength, and $\omega_{1,H}$ is the ^{1}H decoupling field strength.
(a) Calculate the τ_c at which R_2 is at the maximum (i.e. at T_2 minimum).

$$\frac{dR_{2,X}}{d\tau_c} = \frac{\omega_{Hx}^2}{5}\left[\frac{1}{1+\omega_{1,H}^2\tau_c^2} - \frac{\tau_c\cdot 2\omega_{1,H}^2\tau_c}{\left(1+\omega_{1,H}^2\tau_c^2\right)^2}\right] = \frac{\omega_{Hx}^2}{5}\cdot\frac{1-\omega_{1,H}^2\tau_c^2}{\left(1+\omega_{1,H}^2\tau_c^2\right)^2}\overset{!}{=}0$$

$$\Rightarrow\ 1-\omega_{1,H}^2\tau_c^2 = 0 \qquad \Rightarrow \tau_c = 1/\omega_{1,H}$$

To show that this extremem is a maximum in $R_{2,X}$,

$$\frac{d^2R_{2,X}}{d\tau_c{}^2} = \frac{\omega_{Hx}^2}{5}\cdot\left[\frac{-2\omega_{1,H}^2\tau_c}{\left(1+\omega_{1,H}^2\tau_c^2\right)^2} - \frac{4\omega_{1,H}^2\tau_c\left(1-\omega_{1,H}^2\tau_c^2\right)}{\left(1+\omega_{1,H}^2\tau_c^2\right)^3}\right] = \frac{\omega_{Hx}^2\cdot 2\omega_{1,H}^2\tau_c}{5\left(1+\omega_{1,H}^2\tau_c^2\right)^3}\cdot\left[-1-\omega_{1,H}^2\tau_c^2-2+2\omega_{1,H}^2\tau_c^2\right]$$

$$= \frac{\omega_{Hx}^2 2\omega_{1,H}^2\tau_c}{5\left(1+\omega_{1,H}^2\tau_c^2\right)^3}\left[-3+\omega_{1,H}^2\tau_c^2\right]\xrightarrow{\omega_{1H}\tau_c<3} <0 \quad \Rightarrow \text{maximum at } \omega_{1,H}\tau_c = 1.$$

(b) Calculate the slope of the $\log R_2$ versus $\log\tau_c$ curve for $\tau_c << \omega_{1,H}^{-1}$.

When $\tau_c << \omega_{1,H}^{-1}$.

$$R_{2,X} = \frac{\omega_{Hx}^2}{5}\frac{\tau_c}{1+\omega_{1H}^2\tau_c^2} \overset{\tau_c<<\omega_{1H}^{-1}}{\approx} \frac{\omega_{Hx}^2}{5}\tau_c \quad\Rightarrow\quad \log R_{2,X} = \log\left(\frac{\omega_{Hx}^2}{5}\right)+\log\tau_c.$$

So the slope of the $\log R_2$ versus $\log\tau_c$ curve is 1.

(c) Calculate the slope of the $\log R_2$ versus $\log\tau_c$ curve for $\tau_c >> \omega_{1,H}^{-1}$.

$$R_{2,X} = \frac{\omega_{Hx}^2}{5}\frac{\tau_c}{1+\omega_{1H}^2\tau_c^2} \overset{\tau_c>>\omega_{1H}^{-1}}{\approx} \frac{\omega_{Hx}^2}{5}\frac{1}{\omega_{1,H}^2\tau_c} \quad\Rightarrow\quad \log R_{2,X} = \log\left(\frac{\omega_{Hx}^2}{5\omega_{1H}^2}\right)-\log\tau_c.$$

So the slope of the $\log R_2$ versus $\log\tau_c$ curve is –1.

8. An activated motional process is characterized by $\tau_c = \tau_0 e^{E_a/RT}$. You conduct a variable-temperature experiment to measure R_2 under ^{1}H decoupling. Suppose the mechanism of relaxation is dipolar coupling between ^{1}H and the observed X spin.
(a) What is the slope of the $\log R_2$ versus 1/T curve in the extreme narrowing limit?
(b) What does the above answer mean in terms of how to determine E_a?
(c) How can you obtain τ_0?

(a) In the extreme narrowing limit $\tau_c << \omega_{1,H}^{-1}$.

$$\log R_{2,X} = \log\left(\frac{\omega_{Hx}^2}{5}\right) + \log\tau_c = \log\left(\frac{\omega_{Hx}^2}{5}\right) + \log\left(\tau_0 e^{E_a/RT}\right) = \log\left(\frac{\omega_{Hx}^2}{5}\right) + \log\tau_0 + \frac{1}{2.303}\frac{E_a}{RT},$$

So the slope of the $\log R_2$ versus 1/T curve is $\frac{1}{2.303}\frac{E_a}{R}$.

(b) E_a can be obtained from the slope of the $\log R_2$ versus 1/T plot.

(c) τ_0 can be obtained from the intercept of the $\log R_2$ versus 1/T plot as long as the dipolar coupling strength ω_{Hx} is known.