BCMB/CHEM 8190
ANSWERS TO PROBLEM SET 5

1) The splitting will be equal to the actual coupling for an AB system. The center of the down field doublet will be further downfield than the true chemical shift.

2)

$\hat{I}_x$ for $I = 1$ nucleus - like ^2H

$$\hat{I}_x = \frac{\hat{I}_+ + \hat{I}_-}{2}, \quad I_+ |\psi\rangle_{I,m} = \sqrt{I(I+1) - m(m+1)}\ \psi_{I,m+1}$$

$$I_- |\psi_{I,m}\rangle = \sqrt{I(I+1) - m(m-1)}\ \psi_{I,m-1}$$

$$I_+ |\psi_{1,1}\rangle = 0, \quad I_- |\psi_{1,1}\rangle = \sqrt{2-0}\ \psi_{1,0}$$

$$\langle \psi_{1,1} | \tilde{I}_x | \psi_{1,1} \rangle = \frac{1}{2}\left(0 + \sqrt{2}\langle \psi_{1,1} | \psi_{1,0}\rangle\right) = 0$$

$$\langle \psi_{1,0} | \tilde{I}_x | \psi_{1,1} \rangle = \frac{1}{2}\left(0 + \sqrt{2}\langle \psi_{1,0} | \psi_{1,0}\rangle\right) = \sqrt{2}/2$$

$$\tilde{I}_x = \frac{\sqrt{2}}{2}\begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix}$$

1a) $$\sigma_{eq} = \begin{bmatrix} 2\delta & & \\ & 0 & \\ & & -2\delta \end{bmatrix}$$

b) $$M_z = Tr\left(\sigma_{eq} \cdot \gamma I_{z\,tot}\right) = Tr\left(\sigma_{eq} \cdot \gamma (I_{zA} + I_{Bz})\right)$$

$$= Tr \begin{bmatrix} 2\delta & & \\ & 0 & \\ & & -2\delta \end{bmatrix} \cdot \begin{bmatrix} 1 & & \\ & 0 & \\ & & -1 \end{bmatrix} \gamma\hbar$$

$$= \gamma\hbar 4\delta$$

c) $$\sigma_{12}(t) = \exp\left(-\tfrac{i}{\hbar}\mathcal{H}_{11}t\right)\sigma_{12}(0)\exp\left(\tfrac{i}{\hbar}\mathcal{H}_{22}t\right)$$

$$= \exp\left(\tfrac{i}{\hbar}(\mathcal{H}_{22} - \mathcal{H}_{11})t\right)\sigma(0)$$

$$-i\gamma B_0\left(\frac{\Delta\sigma_A}{2} - \frac{\Delta\sigma_x}{2} + \frac{\Delta\sigma_A}{2} + \frac{\Delta\sigma_x}{2}\right)$$

$$-\Delta\omega_A t$$

d) $$\sigma_{14}(t) = \exp\left(\tfrac{i}{\hbar}(\mathcal{H}_{44} - \mathcal{H}_{11})t\right)\sigma(0)$$

$$-(\Delta\omega_A + \Delta\omega_x)$$