CEM 882 Problem Set 6 – Due Thursday, April 24 – Please email a pdf to weliky@chemistry.msu.edu

1. As discussed in class, crosspeaks mediated by magnetic dipole-dipole coupling between nearby nuclei are the most important observable for molecular structure determination in a NMR experiment. Consider the underlying quantum mechanics of the crosspeaks. Consider: (1) two nuclear spins denoted “1” and “2”; (2) the two spins are the same isotope with $S = ½$; (3) the initial state is $|m_{S1}\rangle|m_{S2}\rangle = |+½\rangle|-½\rangle$; and (4) the final state is $|m_{S1}\rangle|m_{S2}\rangle = |-½\rangle|+½\rangle$. A transition from the initial to the final state can occur during the exchange period of the NMR experiment during which there is no radiation. Consider that the transition rate between the initial and final state follows the same physics as radiative transition rates. In particular the rate $W \propto |\langle -½|\langle +½| -\boldsymbol{\mu}_1 . \boldsymbol{B}_2 |+½\rangle|-½\rangle|^2$ where $\boldsymbol{B}_2$ is the magnetic dipole field of spin 2 experienced by spin 1. Consider the reasonable estimate: $\boldsymbol{B}_2 = (\mu_0/4\pi)(\boldsymbol{\mu}_2/r^3)$ where r is the internuclear distance.

a. (40 points) Evaluate the quantum mechanical form of the operator $-\boldsymbol{\mu}_1 . \boldsymbol{B}_2$. Your final expression should be in terms of $\mu_0/4\pi$, r, $\hbar$, γ, and the operators S_{1x}, S_{2x}, S_{1y}, S_{2y}, S_{1z}, and S_{2z}.

b. (40 points) Transform the **a** result into an expression in terms of $\mu_0/4\pi$, r, $\hbar$, γ, and the operators S_{1+}, S_{2+}, S_{1-}, S_{2-}, S_{1z}, and S_{2z}.

c. (60 points) Use the **b** result to evaluate $\langle -½|\langle +½| -\boldsymbol{\mu}_1 . \boldsymbol{B}_2 |+½\rangle|-½\rangle$ with a final result in terms of $\mu_0/4\pi$, r, $\hbar$, and γ. Operators of spin 1 do not affect wavefunctions of spin 2 and vice-versa. The integrations of spin 1 and spin 2 should be done independently. In addition, $S_{1+}|+½\rangle|\pm½\rangle = 0$, $S_{2+}|\pm½\rangle|+½\rangle = 0$, $S_{1-}|-½\rangle|\pm½\rangle = 0$, and $S_{2-}|\pm½\rangle|-½\rangle = 0$.

d. (40 points) As with the analogous radiative transition rates, the non-radiative rate W depends on the period τ of the time-dependent modulation of $\boldsymbol{B}_2$. Consider the estimates $\tau = 10^{-6}$ s, $\gamma = 2.7 \times 10^8$ Hz/Tesla (for ^{1}H), $r = 5$ Å (typical for a “long-range” crosspeak), and $W = (\tau/\hbar^2) \times |\langle -½|\langle +½| -\boldsymbol{\mu}_1 . \boldsymbol{B}_2 |+½\rangle|-½\rangle|^2$. Use the **c** result to calculate W in units of s^{-1} to two significant figures.

e. (20 points) The typical duration of an exchange period is 10^{-1} s. Use the **d** result to calculate the fraction of spins that make the transition from the initial to the final state during the exchange period. Do you expect or do you not expect to observe a significant long-range crosspeak? Provide a reasoned explanation for your choice.