# Problem Set

## High Frequency Dynamic Nuclear Polarization

**Problem 1 – Nuclear and Electron Spin Polarizations**

(a) Derive the formula for the polarization in a magnetic resonance experiment for I=1/2

$$P = \tanh\left(\frac{\gamma\hbar B_0}{2kT}\right)$$

(b) Show that in the high temperature limit

$$P = \frac{\gamma\hbar B_0}{2kT}$$

(c) Calculate the polarization for an ensemble of $^1$H's at 1T, 10 T and 100 T at 100 K and 1K

(d) Calculate the polarization for an ensemble of e's at 1T, 10T, and 100 T at 100 K and 1 K

(e) Using your favorite math program (MatLab, Mathematica, etc.) plot log (P) vs. log (T). for $^1$H Larmor frequencies of 100, 500 and 1000 MHz and for electrons at the same magnetic fields

**Problem 2 – Instrumentation for DNP**

(a) Outline the additional instrumentation required for microwave driven DNP experiments.

(b) What alternative microwave sources are possible for DNP experiments

(c) What is the difference between a slow wave and fast wave microwave source and what is the advantage/disadvantage of each ?

**Problem 3 – EPR Spectra**

(a) What is the breadth of the EPR spectrum of BDPA, trityl, and a nitroxide radical at 5 T (140 GHz for $e^-$ /211 MHz for $^1$H).

**(b)** What is required for the EPR spectrum to yield a solid effect, thermal mixing effect or a cross effect.

**(c)** What is the magnitude of the $e^-$-$e^-$ dipole coupling for a solution of TEMPO at 40 mM concentration.

**(d)** Suppose that you tether two radicals together at a distance of ~10-15 Å, What is the size of the $e^{-}$-$e^{-}$ dipole coupling ?

**Problem 4 – Solid Effect**

(a) Sketch and energy level diagram that arises when the EPR linewidth is small compared to the nuclear Larmor frequency.

(b) label the energy levels associates with the product spin wavefunctions and show that the terms associated the electron-nuclear ZQ and DQ polarization process. Show that these are forbidden transitions.

(c) Show that state mixing occurs and this leads to the wavefunctions.

$$|\alpha\alpha\rangle + q^{*}|\alpha\beta\rangle$$
$$|\alpha\beta\rangle + q|\alpha\alpha\rangle$$
$$|\beta\alpha\rangle + q^{*}|\beta\beta\rangle$$
$$|\beta\beta\rangle + q|\alpha\beta\rangle$$

where

$$q_{ij} = -\frac{3}{4}\frac{\gamma_e \gamma_n \hbar}{\omega_n}\frac{1}{r_{ij}^3}\sin\theta_{ij}\cos\theta_{ij}e^{i\varphi_{ij}}$$

(d) Show that the transition probability goes as $4q^2$. What is the dependence on the Larmor field ?

(e) Calculate the Boltzmann populations for each of the four levels.

(f) Calculate the difference in populations between the transitions corresponding to the NMR transitions and therefore the NMR signal intensity

(g) Assume that the ZQ and DQ transitions are saturated with high power microwave irradiation that equalizes the populations of the energy levels. Calculate the change in polarization and the change in the NMR signal intensity.