1. The Steady-State Density Matrix $\sigma_0$

Given a time independent Hamiltonian, $\hat{H}$ with non-degenerate eigenvalues $e_i$ and eigenvectors $|i\rangle$, i.e.

$$\hat{H}|i\rangle = e_i|i\rangle,$$

a) Show that in steady-state conditions, the diagonal elements of $\sigma_0$ (expressed in terms of the eigenvectors of $\hat{H}$) are constants.

b) Show that in steady-state conditions the off-diagonal elements of $\sigma_0$ (expressed in terms of the eigenvectors of $\hat{H}$) are zero.

c) For a two-spin system of spin 1/2 nuclei I and S, the steady-state density operator, $\hat{\sigma}_0$, can be expressed as a linear combination of the following four product operators:

$$\hat{E}, \hat{I}_z, \hat{S}_z, \text{ and } 2\hat{I}_z\hat{S}_z$$

Why don’t we need any of the other twelve 2-spin product operators?
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d. Given: $\hat{H}_0 = -\gamma I B_0 \hat{I}_z - \gamma S B_0 \hat{S}_z + 2\pi J (\hat{I} \cdot \hat{S})$,
the Boltzmann distribution yields the follow expression for $\hat{\sigma}_0$

$$\hat{\sigma}_0 = \frac{1}{Z} e^{-\frac{\hbar \hat{H}_0}{kT}} \quad \text{and} \quad Z = \text{Tr}\left(e^{-\frac{\hbar \hat{H}_0}{kT}}\right).$$

Ignoring the standard high temperature approximation, show

$$\hat{\sigma}_0 = \alpha_0 \frac{1}{2} \hat{E} + \alpha_1 \hat{I}_z + \alpha_2 \hat{S}_z + \alpha_3 2\hat{I}_z \hat{S}_z$$

where

$$\alpha_0 = \frac{1}{2}$$

$$\alpha_1 \approx \frac{1}{2} \tanh \left( \frac{\hbar \gamma I B_0}{2kT} \right)$$

$$\alpha_2 \approx \frac{1}{2} \tanh \left( \frac{\hbar \gamma S B_0}{2kT} \right)$$

$$\alpha_3 \approx \frac{1}{2} \tanh \left( \frac{\hbar \gamma I B_0}{2kT} \right) \tanh \left( \frac{\hbar \gamma S B_0}{2kT} \right)$$

Hint: you may safely assume $\gamma I B_0, \gamma S B_0 \gg J$. 

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This text contains a mathematical problem involving quantum mechanics, specifically dealing with the Boltzmann distribution in the context of quantum systems. The problem requires the use of approximations and calculations to determine the expression for the spin susceptibility in the context of a specific Hamiltonian. It involves understanding the Boltzmann distribution and its implications for quantum states at high temperatures, as well as applying specific approximations to simplify the calculation.
2. **J-coupling**
Consider a homonuclear two-spin system with a J-coupling of \( J = 16 \) Hz, \( T_2 = 100 \) ms, and chemical shift difference between the two spins equal to \( \Delta \Omega \). Using the full density matrix, simulate (e.g. using Matlab) the series of spectra generated by the 90-acquire sequence shown below with \( \Delta \Omega / J \) ranging from 0 to 10. Account for the effect of \( T_2 \) by assuming the signal following the 90\(^0\) excitation is weighted by a factor of \( e^{-t/T_2} \).

![90y acquire t time diagram](image)

3. **Dipolar-coupling**
Consider a homonuclear two-spin system from an anisotropic material with J=0 but a residual dipole coupling of \( d = 16 \) Hz. Assume a \( T_2 = 100 \) ms and a chemical shift difference between the two spins equal to \( \Delta \Omega \). Using the full density matrix, simulate (e.g. using Matlab) the series of spectra generated by the 90-acquire sequence shown above with \( \Delta \Omega / d \) ranging from 0 to 10. Use the secular approximation to the dipolar coupling spin Hamiltonian. Account for the effect of \( T_2 \) by assuming the signal following the 90\(^0\) excitation is weighted by a factor of \( e^{-t/T_2} \).

Comments on the differences between the results found in Problems 2 and 3.
4. **Creatine in skeletal muscle.**

The methyl group (-CH$_3$) of creatine, a metabolite involved in cellular energetics, gives rise to a single peak at 3.0 ppm in an *in vivo* $^1$H-MRS brain spectrum (note, creatine is found in the body in the form of both creatine [Cr] and phosphocreatine [PCr], hence the peak is often labeled “total creatine” [tCr]).

However, the same compound, when measured in skeletal muscle, gives rise to a triplet.

a) Suggest an explanation for this effect,
b) How might you test your hypothesis?