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Problem Set #5

Rad 226

1. **Two-spin Operators**

For a single spin-1/2 nucleus, matrices corresponding to the spin operators are identity plus the 2x2 Pauli matrices:

$$\underline{I}_x = \tfrac{1}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad \underline{I}_y = \tfrac{1}{2}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \quad \underline{I}_z = \tfrac{1}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \quad \underline{E} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

If we now consider *pairs* of spins, e.g. I and S, the two-spin operators needed to describe the system correspond to 4 x4 matrices are are calculated using the <u>matrix direct product</u> (also known as the Kronecker product, tensor product, or outer product):

$$\begin{bmatrix} a & b \\ c & d \end{bmatrix} \underset{\text{Direct product}}{\otimes} \begin{bmatrix} \alpha & \beta \\ \gamma & \delta \end{bmatrix} = \begin{bmatrix} a\begin{bmatrix} \alpha & \beta \\ \gamma & \delta \end{bmatrix} & b\begin{bmatrix} \alpha & \beta \\ \gamma & \delta \end{bmatrix} \\ c\begin{bmatrix} \alpha & \beta \\ \gamma & \delta \end{bmatrix} & d\begin{bmatrix} \alpha & \beta \\ \gamma & \delta \end{bmatrix} \end{bmatrix} = \begin{bmatrix} a\alpha & a\beta & b\alpha & b\beta \\ a\gamma & a\delta & b\gamma & b\delta \\ c\alpha & c\beta & d\alpha & d\beta \\ c\gamma & d\delta & d\gamma & d\delta \end{bmatrix}$$

a. Find the matrices corresponding to these two-spin operators:

$$\underbrace{\underline{I}_x}_{\text{two-spin operator}} = \underbrace{\underline{I}_x \otimes \underline{E}}_{\text{one-spin operators}} = ? \qquad \underline{S}_x = ?$$

$$2\underline{I}_z\underline{S}_z = ? \qquad 2\underline{I}_y\underline{S}_z = ?$$

b. Show $2\hat{I}_z\hat{S}_z$, $\hat{I}_x$, and $2\hat{I}_y\hat{S}_z$ cyclically commute.

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2. **The Steady-State Density Matrix** $\underline{\sigma}_0$

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

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

a) Show that in steady-state conditions, the diagonal elements of $\underline{\sigma}_0$ (expressed in terms of the eigenkets of $\hat{H}$) are constants.

b) Show that in steady-state conditions the off-diagonal elements of $\underline{\sigma}_0$ (expressed in terms of the eigenkets 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: $\hat{H}_0 = -\gamma_I B_0 \hat{I}_z - \gamma_S B_0 \hat{S}_z + 2\pi J(\hat{\vec{I}} \cdot \hat{\vec{S}})$,

the Boltzmann distribution yields the follow expression for $\hat{\sigma}_0$

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

Ignoring the standard high temperature approximation, show

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

where

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

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

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

$$\alpha_3 \approx \tfrac{1}{2} \tanh\left(\frac{\hbar \gamma_I B_0}{2kT} \right) \tanh\left(\frac{\hbar \gamma_S B_0}{2kT} \right)$$

Hint: you may safely assume $\gamma_I B_0,\ \gamma_S B_0 >> J$.

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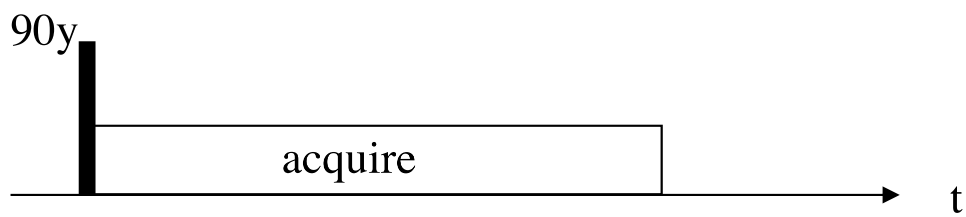
3. **J-coupling**

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 $e^{-t/T2}$.



4. **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 $e^{-t/T2}$.

Comments on the differences between the results found in Problems 2 and 3.