Modern methods in experimental physics:
site-directed spin labeling EPR

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Problem Set 3

Questions

a) What is the relation between the *Schrödinger* equation and the *Liouville-von-Neumann* equation?

b) What are the eigenvalues of an operator and what is the expectation value of an observable?

c) What is the dimension of the Hilbert space for a spin 3/2 system? And for a 2-spin 1/2 system (consider the two spin operators S and I)? Give an example for a basis of the Hilbert space.

d) Give the density matrix for an ensemble of spins where all spins are in the α-state.

e) Write the thermal equilibrium density matrix for a spin 1/2 system describing the non zero matrix elements. Why is the high-temperature approximation of the density matrix feasible in NMR and EPR spectroscopy?

Problem 1: Density operator and equilibrium spin density

1.1 How are the density operator $\hat{\rho}$ and the state function ψ related?

1.2 The full equilibrium SPIN density operator $\hat{\sigma_0}$ gives the Boltzmann distribution of the spin populations in the sample when an external magnetic field is applied. Calculate the full equilibrium spin density operator for a non-interacting proton spin system ($\gamma_{free\ ^1H} = 26.752 \cdot 10^7\ rad\ T^{-1}s^{-1}$) and for an electron spin system $\gamma_{free\ e^-} = -1.761 \cdot 10^{11}\ rad\ T^{-1}s^{-1}$) in a magnet with 18.8 T field ($\vec{B_0} = 18.8\ T\ \cdot \vec{e_z}$) and a temperature of 303 K.

1.3 Evaluate the expectation values of $\langle \hat{I}_x \rangle, \langle \hat{I}_y \rangle$ and $\langle \hat{I}_z \rangle$.

1.4 In magnetic resonance only the deviation from an evenly distributed population over all energy levels is of interest and is described by $\hat{\sigma}_0^{'}$, which is directly proportional to $\hat{I}_z$ or $-\hat{S}_z$.

$$\hat{\sigma}_0 = \frac{\hat{1}}{Tr\{\hat{1}\}} - \frac{\hbar \hat{H}}{kT \cdot Tr\{\hat{1}\}} \cong -\frac{\hbar \hat{H}}{kT \cdot Tr\{\hat{1}\}} = \hat{\sigma}_0^{'} \qquad (1)$$

The operator $\hat{\sigma}_0^{'}$ is traceless, and strictly speaking not a density operator (!). Usually the dash is left away in the calculations. Calculate $\hat{\sigma}_0^{'}$ for a non-interacting proton and electron spin system using the same parameters as in 1.2.

1.5 What is the ratio of electron and proton spins that are oriented parallel (α) and antiparallel (β) to the external magnetic B_0-field? What do you conclude?

1.6 In NMR and EPR we aim to get the maximum signal of a sample within a restricted amount of time. How is it possible to increase the signal? Discuss or show analytically which parameter would increase the signal, i.e. increase $\hat{\sigma}_0^{'}$ in 1.4?