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

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Solution Problem Set 3

Answers

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

Both, the time-dependent Schrödinger equation and the Liouville-von-Neumann-Equation describe the time evolution of a quantum system. The Schrödinger equation describes a closed quantum system by a wave function $|\psi(t)\rangle$ according to

$$i\hbar\frac{d}{dt}|\psi(t)\rangle = \hat{H}|\psi(t)\rangle. \tag{1}$$

The Liouville-von-Neumann-Equation defines the state of a quantum system by a density operator $\hat{\rho}(t)$ according to

$$\frac{d}{dt}\hat{\rho}(t) = -\frac{i}{\hbar}[\hat{H}, \hat{\rho}(t)]. \tag{2}$$

For pure states, both the state function $|\psi(t)\rangle$ and the density operator $\hat{\rho}(t)$ contain the same information. However, in contrast to the the Schrödinger equation that can be used only for the characterization of a pure spin system, the density operator $\hat{\rho}(t)$ allows the characterization of the evolution of an ensembles of spins.

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

The eigenvalues of a Hamilton operator $\hat{H}$ are the solutions E_k of the time-independent *Schrödinger* equation:

$$\hat{H}|\Psi_k\rangle = E_k|\Psi_k\rangle \tag{3}$$

The expectation value of an observable A is represented by an operator $\hat{A}$ in a quantum system characterized by the state function $|\Psi(t)\rangle$ and it is defined by:

$$\langle\hat{A}\rangle(t) = \frac{\langle\Psi(t)|\hat{A}|\Psi(t)\rangle}{\langle\Psi(t)|\Psi(t)\rangle} \tag{4}$$

c) What is the dimension for the Hilbert Space for a spin 3/2 system? Give an example for a basis of the Hilbert Space.

The Hilbert space dimension for a spin system with $I = \frac{3}{2}$ is $D = 2I + 1 = 4$. An example of an appropriate vector basis given is by $|+3|2\rangle$, $|+1|2\rangle$, $|-1|2\rangle$ and $|-3|2\rangle$, which are the common eigenvectors of the operators $\hat{I}^2$ with the eigenvalue 15/4 and $\hat{I}_z$ with the eigenvalues +3/2, +1/2, -1/2, -3/2, respectively. For a two-spin 1/2 system (I and S) the Hilbert space will have a dimension 4 (see direct produc for creation of matrix representtaion of the 16 operators).

d) Give the density matrix for an ensemble of spins where all spins are in the α-state. An ensemble of spin systems in which all spins are in the same state is called a pure state. In such a state only one element of the density matrix is unequal zero. In the case where all spins are in the α-state, only the first element in the density matrix ρ is unequal zero.

$$\rho = \begin{pmatrix} 1 & 0 & \dots & 0 \\ 0 & 0 & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & 0 \end{pmatrix}$$

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?

In the eigenbasis $\{\phi_1, \dots, \phi_{D_H}\}$ of the Hamiltonian $\hat{H}$ in the thermal equilibrium density operator is diagonal and given by:

$$(\sigma_0)_{kl} = \frac{exp\{-\frac{E_k}{kT}\}}{\sum_l exp\{-\frac{E_l}{kT}\}} \cdot \delta_{kl} \tag{5}$$

in matrix form the density operator is:

$$(\sigma_{\mathbf{0}}) = \begin{pmatrix} p_1 & 0 & 0 \\ 0 & p_2 & 0 \\ 0 & 0 & \dots \end{pmatrix}$$

where D_H is the dimension of the *Hilbert* space and E_l , E_k are the eigenvalues. When $E_{k/l} \ll kT$ one can neglect higher order terms in the power expansion of the exponential, then

$$\hat{\sigma}_0 = \frac{\hat{1}}{Tr\{\hat{1}\}} - \frac{\hbar\hat{H}}{kT \cdot Tr\{\hat{1}\}} \cong -\frac{\hbar\hat{H}}{kT \cdot Tr\{\hat{1}\}} \tag{6}$$

The first term is dropped because the $\hat{1}$ operator remains unchanged during the pulse sequence and is destroyed at the detection, i.e. $Tr\{\hat{S}_x \cdot (\hat{1} + \hat{\sigma})\} = 0 + Tr\{\hat{S}_x \cdot \hat{\sigma}\}$.

As $E_k/k \approx 1mK$ ($\approx 1K$) for a nuclear spin (electron spin) this approximation is even a good one for experiments at very low temperatures.

1 Problem 1: Density Operator

1.1 How are the density operator ρ and wave function ψ related?

The relation between the density operator and the wave function is given by

$$\hat{\rho}(t) = |\psi(t)\rangle\langle\psi(t)| = \sum_i \sum_j c_i(t) c_j(t)^*(t) |\phi_i\rangle\langle\phi_j| \tag{7}$$

In the case of an ensemble of spins, the system is not necessarily described by a single wave or pure state function, $|\psi(t)\rangle$. Instead the system is in a mixed state and is described by a set of possible wave functions, $|\psi_k(t)\rangle$, and their associated probabilities, P_k. In this case the density operator is defined as:

$$\hat{\rho}(t) = \sum_k P_k |\psi(t)\rangle\langle\psi(t)| = \sum_i \sum_j \overline{c_i(t) c_j^*(t)} |\phi_i\rangle\langle\phi_j|, \tag{8}$$

where the overbar denotes the weighted sum over all wave functions or the ensemble average.

1.2 Calculate the full equilibrium spin density operator $\hat{\sigma}_0$ for a non-interacting proton spin system.

Here a list of the values that are given:

- $\gamma_{free\ ^1H} = 26.752 \cdot 10^7 rad\ T^{-1} s^{-1}$
- $\gamma_{free\ e} = -1.761 \cdot 10^{11} rad\ T^{-1} s^{-1}$
- $B_0 = 18.8T$
- $T = 303K$
- $\kappa_B = 1.3806 \cdot 10^{-23} J\ K^{-1}$
- $\hbar = 1.0545 \cdot 10^{-34} Js$
- $I_z = \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix}$

we also know:

$$\hat{\sigma}_0 = \frac{\hat{1}}{Tr\{\hat{1}\}} - \frac{\hbar \hat{\mathscr{H}}}{\kappa_B T \cdot Tr\{\hat{1}\}} \tag{9}$$

$$Tr\{\hat{1}\} = Tr \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = 2 \tag{10}$$

To derive $\hat{\sigma}_0$, we first need to calculate the Hamiltonian for the electron and proton spin system. The interaction of a spin system with the external magnetic field, also known as *Zeeman interaction* can be described classically by

$$\mathscr{H} = \frac{1}{\hbar}\mathscr{H}^S = \mathscr{H}_z = -\gamma\vec{\hat{I}}\vec{B_0} \tag{11}$$

As the magnetic field is in the z-direction, we assume $\vec{B_0} = (0, 0, B_0)$ and can write

$$\hat{\mathscr{H}_z} = -\gamma \hat{I}_z B_0 = \omega_0 I_z \tag{12}$$

$$\hat{\mathscr{H}}_{ze} = -\gamma_e \hat{I}_z B_0 \tag{13}$$

$$= 1.761 \cdot 10^{11} rad\ T^{-1} s^{-1} \cdot \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix} \cdot 18.8T \tag{14}$$

$$= \underline{\underline{3.3106 \cdot 10^{12} rad\ s^{-1} \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix}}} \tag{15}$$

$$\hat{\mathscr{H}}_{zH} = -\gamma_H \hat{I}_z B_0 \tag{16}$$

$$= -26.752 \cdot 10^{7} rad\ T^{-1} s^{-1} \cdot \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix} \cdot 18.8T \tag{17}$$

$$= \underline{\underline{-5.0294 \cdot 10^{9} rad\ s^{-1} \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix}}} \tag{18}$$

Now we have all values to calculate $\hat{\sigma}_0$ for ^1H and the free electron:

$$\hat{\sigma}_0(^1H) = \frac{\hat{1}}{Tr\{\hat{1}\}} - \frac{\hbar \hat{\mathscr{H}}_{zH}}{\kappa_B T \cdot Tr\{\hat{1}\}} \tag{19}$$

$$= \frac{\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}}{2} - \frac{\hbar \cdot -5.0294 \cdot 10^9 \cdot \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix}}{\kappa_B \cdot 303 \cdot 2} \tag{20}$$

$$= \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & \frac{1}{2} \end{pmatrix} + 6.3 \cdot 10^{-5} \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix} \tag{21}$$

$$= \underline{\underline{\begin{pmatrix} 0.500032 & 0 \\ 0 & 0.499968 \end{pmatrix}}} \tag{22}$$

$$\hat{\sigma}_0(e) = \frac{\hat{1}}{Tr\{\hat{1}\}} - \frac{\hbar \hat{\mathscr{H}}_{ze}}{\kappa_B T \cdot Tr\{\hat{1}\}} \tag{23}$$

$$= \underline{\underline{\begin{pmatrix} 0.479137 & 0 \\ 0 & 0.520863 \end{pmatrix}}} \tag{24}$$

From the results we see that more electrons than nuclei are in the β state at 303K and 18.8T, and consequently less in the α state. The bigger difference in α to β electrons, shows that more signal from electrons can be acquired compared to nuclei (EPR is more sensitive than NMR). Remark: For a negative γ, the β state is energetically lower and for a positive γ the α state is energetically lower state, respectively.

1.3 Evaluate the expectation values I_x , I_y and I_z for electrons and protons.

Using the Pauli matrices for spin 1/2

- $\hat{I}_x = \begin{pmatrix} 0 & \frac{1}{2} \\ \frac{1}{2} & 0 \end{pmatrix}$
- $\hat{I}_y = \begin{pmatrix} 0 & \frac{-i}{2} \\ \frac{-i}{2} & 0 \end{pmatrix}$
- $\hat{I}_z = \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix}$

the expectation value of an operator can be calculated:

$$< \hat{I}_x > = Tr\{\hat{\sigma}_0 \cdot I_x\} \tag{25}$$

$$< \hat{I}_{xH} > = \underline{\underline{0}} \tag{26}$$

$$< \hat{I}_{xe} > = \underline{\underline{0}} \tag{27}$$

$$\tag{28}$$

the expectation values for I_y is the same as for I_x.

$$< \hat{I}_z > = Tr\{\hat{\sigma}_0 \cdot I_z\} \tag{29}$$

$$< \hat{I}_{zH} > = \underline{\underline{3.16951 \cdot 10^{-5}}} \tag{30}$$

$$< \hat{I}_{ze} > = \underline{\underline{-0.0208633}} \tag{31}$$

1.4 We reveal the deviation from the equipopulation calculating $\hat{\sigma}'_0$ for protons and electrons .

$$\hat{\sigma}'_0(^1H) = \hat{\sigma}_0(^1H) - \frac{\hat{1}}{Tr\{\hat{1}\}} = -\frac{\hbar\hat{\mathscr{H}}_{zH}}{\kappa_B T \cdot Tr\{\hat{1}\}} \tag{32}$$

$$= \underline{\underline{\begin{pmatrix} 3.16951 \cdot 10^5 & 0 \\ 0 & -3.16951 \cdot 10^5 \end{pmatrix}}} \tag{33}$$

$$\hat{\sigma}'_0(e) = \hat{\sigma}_0(e) - \frac{\hat{1}}{Tr\{\hat{1}\}} = -\frac{\hbar\hat{\mathscr{H}}_{ze}}{\kappa_B T \cdot Tr\{\hat{1}\}} \tag{34}$$

$$= \underline{\underline{\begin{pmatrix} -0.0208633 & 0 \\ 0 & 0.0208633 \end{pmatrix}}} \tag{35}$$

1.5 Spin-up vs Spin-down population

The spin up and spin down population is represented in $\vec{\hat{\sigma}}_0$ in $(\hat{\sigma}_0)_{11}$ and $(\hat{\sigma}_0)_{22}$, respectively.

- $(\hat{\sigma}_0) = \begin{pmatrix} \alpha & 0 \\ 0 & \beta \end{pmatrix} = \begin{pmatrix} (\hat{\sigma}_0)_{11} & 0 \\ 0 & (\hat{\sigma}_0)_{22} \end{pmatrix}$

$$ratio = \frac{(\hat{\sigma}_0)_{11}}{(\hat{\sigma}_0)_{22}} \tag{36}$$

$$ratio(^1H) = \frac{0.50003}{0.49997} = \underline{\underline{1.00013}} \tag{37}$$

$$ratio(e) = \frac{0.47913}{0.52086} = \underline{\underline{0.91989}} \tag{38}$$

1.6 How is it possible to increase the signal?

As in 1.2 we calculate $\hat{\sigma}_0$ for a higher frequency magnet, here B_0=20T (instead of 18.8T) and at a lower and higher T, and we compare it with that obtained at B_0= 18.8T, T = 303 K:

$$\hat{\sigma}_0(e) = \begin{pmatrix} 0.47915 & 0 \\ 0 & 0.52086 \end{pmatrix} \tag{39}$$

$$ratio = 0.91989. \tag{40}$$

(a)B_0= 20T, T = 303 K

$$\hat{\sigma}_0(e) = \frac{\hat{1}}{Tr\{\hat{1}\}} - \frac{\hbar \hat{\mathscr{H}}_{zH}}{\kappa_B T \cdot Tr\{\hat{1}\}} \tag{41}$$

$$= \frac{\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}}{2} - \frac{\hbar \cdot 3.522 \cdot 10^{12} \cdot \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix}}{\kappa_B \cdot \mathbf{303} \cdot 2} \tag{42}$$

$$= \underline{\underline{\begin{pmatrix} 0.47780 & 0 \\ 0 & 0.52219 \end{pmatrix}}} \tag{43}$$

$$\Rightarrow \underline{ratio = 0.91499} < 0.91989 \tag{44}$$

$\Rightarrow$ With a higher field, we increase the difference in spins occupying the α and β spin states.

(b)B_0= 20T, T = 330 K

$$\hat{\sigma}_0(e) = \frac{\hat{1}}{Tr\{\hat{1}\}} - \frac{\hbar\hat{\mathscr{H}}_{zH}}{\kappa_B T \cdot Tr\{\hat{1}\}} \tag{45}$$

$$= \frac{\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}}{2} - \frac{\hbar \cdot 3.522 \cdot 10^{12} \cdot \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix}}{\kappa_B \cdot \mathbf{330} \cdot 2} \tag{46}$$

$$= \underline{\underline{\begin{pmatrix} 0.47962 & 0 \\ 0 & 0.52038 \end{pmatrix}}} \tag{47}$$

$$\Rightarrow \underline{ratio = 0.92167} > 0.91989 \tag{48}$$

⇒ With a higher field and higher T, we decrease the difference in spins occupying the α and β spin states.

(c)B_0= 20T, T = 290 K

$$\hat{\sigma}_0(e) = \frac{\hat{1}}{Tr\{\hat{1}\}} - \frac{\hbar\hat{\mathscr{H}}_{zH}}{\kappa_B T \cdot Tr\{\hat{1}\}} \tag{49}$$

$$= \frac{\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}}{2} - \frac{\hbar \cdot 3.522 \cdot 10^{12} \cdot \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix}}{\kappa_B \cdot 290 \cdot 2} \tag{50}$$

$$= \underline{\underline{\begin{pmatrix} 0.47681 & 0 \\ 0 & 0.52319 \end{pmatrix}}} \tag{51}$$

$$\Rightarrow \underline{ratio = 0.91135} < 0.91989 \tag{52}$$

⇒ With a higher field and low T, we increase the difference in spins occupying the α and β spin states.