Prof. Thomas Prisner, Dr. Deniz Sezer

Theorie der EPR Spektroskopie mit Übungen

Übungsblatt 2

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1 Electron g-factor and EPR resonance lines

In the first exercise sheet from last week (i.e., Übungsblatt 1), you calculated the magnitude of the spin magnetic moment using the expression

$$\mu_S = \gamma_{\mathrm{e}}\, \hbar\, S. \tag{1}$$

(Recall that $S = 1/2$ for an electron.) As you know from the lectures, the same magnetic moment can alternatively be written in terms of the electron g-factor (or g value) as

$$\mu_S = -g\, \mu_{\mathrm{B}}\, S. \tag{2}$$

In addition to the g-factor, this expression also contains the Bohr magneton,

$$\mu_{\mathrm{B}} = \frac{e\hbar}{2m_{\mathrm{e}}}, \tag{3}$$

where e is the elementary charge (i.e., the electric charge of a single proton, or the magnitude of the negative electric charge of a single electron) and m_{e} is the electron (rest) mass.

From eqs. (1) and (2), we see that

$$\gamma_{\mathrm{e}} = -g\, \frac{e}{2m_{\mathrm{e}}}, \tag{4}$$

which relates the gyromagnetic ratio of the electron to its g-factor.

In a magnetic field, the energies of the spin states α and β due to the interaction with the magnetic field are different. The energy difference

$$\Delta E = E_\alpha - E_\beta \tag{5}$$

is proportional to the magnitude of the magnetic field. For the electron, which is a particle with

$S = 1/2$, the proportionality is

$$\Delta E = -\gamma_{\mathrm{e}}\, \hbar\, B_0 = g\, \mu_{\mathrm{B}}\, B_0. \tag{6}$$

The (angular) Larmor frequency that corresponds to this energy difference is

$$\omega_{\mathrm{L}} = \frac{\Delta E}{\hbar} = -\gamma_{\mathrm{e}} B_0 = \frac{g\mu_{\mathrm{B}}}{\hbar} B_0. \tag{7}$$

This is the frequency at which a resonance phenomenon will be observed.

a) Calculate the numerical value of the Bohr magneton <u>in units of J/T</u>, given that

$$e = 1.602\,177 \times 10^{-19}\,\mathrm{C}, \qquad m_{\mathrm{e}} = 9.109\,384 \times 10^{-31}\,\mathrm{kg}, \qquad \hbar = 1.054\,572 \times 10^{-34}\,\frac{\mathrm{J\,s}}{\mathrm{rad}}. \tag{8}$$

b) Using eq. (4) and the gyromagnetic ratio of the electron,

$$\gamma_{\mathrm{e}} = -1.760\,860 \times 10^{11}\,\frac{\mathrm{rad}}{\mathrm{s T}}, \tag{9}$$

calculate the electron g-factor. What are its units?

c) For a free radical <u>molecule</u> in a magnetic field of strength $B_0 = 0.335\,\mathrm{T}$, resonance is observed at the frequency $\nu = 9.415\,\mathrm{GHz}$. What is the g-factor of this molecule?

d) Imagine that the EPR experiment is carried out at a constant (microwave) frequency of $\nu = 9.415\,\mathrm{GHz}$ and the strength of the magnetic field is varied around the resonance condition of $B_0 = 0.335\,\mathrm{T}$. If the molecule that you identified in part **c)** is a *nitroxide* free radical, there will be additional resonance lines when the magnetic field is equal to

$$B = B_0 \pm \Delta B \tag{10}$$

with $\Delta B = 1.5\,\mathrm{mT}$. As was explained in the lecture, these lines are due to the interaction between the spin of the unpaired electron on the nitroxide molecule and the nuclear spin of the nitrogen atom on the nitroxide. The value of ΔB reflects the strength of this, so called, *hyperfine* interaction. The interaction strength is typically reported in units of MHz.

Calculate the frequency

$$\Delta\nu = \frac{g\mu_{\mathrm{B}}}{h}\Delta B \tag{11}$$

that corresponds to the difference ΔB. Report this value in units of MHz.

2 Pauli spin matrices

The Pauli spin matrices are

$$\hat{S}_x = \frac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad \hat{S}_y = \frac{1}{2}\begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}, \qquad \hat{S}_z = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{12}$$

They constitute the x, y and z components of the spin vector operator $\hat{\vec{S}}$.

(Note that the actual Pauli matrices are denoted by the letter σ and do not have the prefactor $\frac{1}{2}$.)

A commutator of two matrices A and B is another matrix, C, which is defined as

$$C = [A, B] = AB - BA. \tag{13}$$

If two quantum operators commute (i.e., their commutator equals zero), their corresponding properties can be measured at the same time. If they do not commute (i.e., their commutator is not equal to zero), their corresponding properties cannot be measured simultaneously.

a) What are the eigenvalues of the spin matrices $\hat{S}_x$, $\hat{S}_y$, and $\hat{S}_z$?
(Recall that the eigenvalues of a quantum mechanical operator give the values that would actually be measured.)

b) Calculate the matrix for the operator $\hat{S}^2$, which corresponds to the "squared length" of the spin vector operator $\hat{\vec{S}}$, and is given by

$$\hat{S}^2 = \hat{\vec{S}} \cdot \hat{\vec{S}} = \hat{S}_x\hat{S}_x + \hat{S}_y\hat{S}_y + \hat{S}_z\hat{S}_z = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2. \tag{14}$$

What are the eigenvalues of this matrix?

c) Calculate the commutators of $\hat{S}^2$ with the three spin matrices.

$$[\hat{S}^2, \hat{S}_x] = ?, \qquad [\hat{S}^2, \hat{S}_y] = ?, \qquad [\hat{S}^2, \hat{S}_z] = ?. \tag{15}$$

d) Show that the following commutation relations between the spin matrices hold:

$$[\hat{S}_x, \hat{S}_y] = \mathrm{i}\hat{S}_z, \qquad [\hat{S}_y, \hat{S}_z] = \mathrm{i}\hat{S}_x, \qquad [\hat{S}_z, \hat{S}_x] = \mathrm{i}\hat{S}_y. \tag{16}$$

e) Show that

$$[A, B] = -[B, A]. \tag{17}$$

3 Spin Hamiltonian

In quantum mechanics, the energy is represented by the Hamiltonian operator. The Hamiltonian describing the interaction between the magnetic moment of a spin and a magnetic field vector is

$$\hat{\mathcal{H}} = -\hat{\vec{\mu}} \cdot \vec{B}, \tag{18}$$

where the dot indicates the scalar product of the two vectors. The magnetic moment vector of the electron is

$$\hat{\vec{\mu}}_S = \gamma_{\mathrm{e}} \hbar \hat{\vec{S}} = \gamma_{\mathrm{e}} \hbar \begin{pmatrix} \hat{S}_x \\ \hat{S}_y \\ \hat{S}_z \end{pmatrix}. \tag{19}$$

Let the x, y, z components of the magnetic field vector be

$$\vec{B} = \begin{pmatrix} B_x \\ B_y \\ B_0 \end{pmatrix}. \tag{20}$$

Then the Hamiltonian operator in eq. (18) becomes

$$\hat{H} = -\gamma_{\mathrm{e}} \hbar \left(B_x \hat{S}_x + B_y \hat{S}_y + B_0 \hat{S}_z \right). \tag{21}$$

Using the Pauli spin matrices in (12), write down this Hamiltonian as a 2×2 matrix.