Theorie der EPR Spektroskopie mit Übungen

Übungsblatt 1

(20.10.2021)

Besprechung 26.10.2021

1 Magnetic moment of a spin

A free electron spin has an intrinsic angular momentum (i.e., due to its spin and not due to its motion) equal to $\hbar\,\hat{\vec{S}}$, where the 'hat' above a symbol indicates that the object represented by the symbol is a quantum mechanical operator. This intrinsic angular momentum of the electron results in a magnetic moment

$$\hat{\vec{\mu}}_S = \gamma_\mathrm{e}\,\hbar\,\hat{\vec{S}}. \tag{1}$$

In this expression, the constant

$$\hbar = \frac{h}{2\pi} = 1.0545718 \times 10^{-34}\ \frac{\mathrm{J\,s}}{\mathrm{rad}} \tag{2}$$

is Planck's constant, and the constant

$$\gamma_\mathrm{e} = -1.7608596 \times 10^{11}\,\frac{\mathrm{rad}}{\mathrm{s\,T}} \tag{3}$$

is the gyromagnetic ratio of the electron. [Observe that I have written the gyromagnetic ratio of the electron as a negative number. If you take γ_e to be positive, then you should put the negative sign in eq. (1), as was done in the lecture. You should always be careful because different sources may use different conventions.]

While the magnetic moment is both a vector and a quantum mechanical operator, its magnitude is a regular real number. With μ_S and S denoting the magnitudes of, respectively, the magnetic moment $\hat{\vec{\mu}}_S$ and the vector operator $\hat{\vec{S}}$, we have

$$\mu_S = \gamma_\mathrm{e}\,\hbar\,S \tag{4}$$

from eq. (1).

a) Given that $S = 1/2$ for a free electron, calculate the magnitude of the magnetic moment, μ_S. (Make sure you also work out the units, and not only the number.)

The same equations apply to a nuclear spin, after replacing the spin operator of the electron, $\hat{\vec{S}}$, by the spin operator of the nucleus, $\hat{\vec{I}}$, and the gyromagnetic ratio of the electron by the gyromagnetic ratio of the nucleus. In the case of a proton spin, for example, $I = 1/2$ and

$$\gamma_{\mathrm{p}} = 2.675222 \times 10^8 \, \frac{\mathrm{rad}}{\mathrm{s\,T}}. \tag{5}$$

b) Calculate the magnitude of the magnetic moment of a proton spin, μ_{p}.

2 Energies of a spin in a magnetic field

The magnetic moment of a spin interacts with the magnetic field. Classically, this interaction is expressed by the interaction energy

$$E = -\vec{\mu} \cdot \vec{B}, \tag{6}$$

where $\vec{\mu}$ is the magnetic moment vector, $\vec{B}$ is the magnetic field vector, and the 'dot' symbol between the two vectors denotes their dot product. In quantum mechanics, where the magnetic moment is a quantum mechanical operator, the interaction energy also becomes an operator and eq. (6) is modified to

$$\hat{H} = -\hat{\vec{\mu}} \cdot \vec{B}. \tag{7}$$

Here the symbol E was replaced by H because the operator version of the energy is known as the *Hamiltonian*, which is generally denoted by the letter H.

The Stern-Gerlach experiment revealed that, when placed in a magnetic field, the spin of an electron can be in only two different states. These states are envisioned to correspond to the two possibilities for the magnetic moment to point either in the same direction as the magnetic field or in the opposite direction. When $\vec{\mu}$ and $\vec{B}$ are in the same direction, their dot product is simply μ times B, where μ is the magnitude of $\vec{\mu}$, and B is the magnitude of $\vec{B}$. Hence the energy of this state is

$$E_{\mathrm{same}} = -\mu B. \tag{8}$$

Analogously, the energy of the state in which $\vec{\mu}$ and $\vec{B}$ point in opposite directions is

$$E_{\mathrm{opposite}} = \mu B. \tag{9}$$

a) Calculate the energies E_{same} and E_{opposite} for an electron spin in a magnetic field $B = 1\,\mathrm{T}$. Which state has a lower energy?

b) Calculate these two energies for a proton spin in the same magnetic field. Which state has a lower energy?

EPR spectroscopy relies on the transitions of the electron spins between these two states, and is thus very sensitive to the energy *difference* between them. Let us define ΔE to be the magnitude of this energy difference:

$$\Delta E = |E_{\mathrm{same}} - E_{\mathrm{opposite}}|. \tag{10}$$

In quantum mechanics, every energy difference has a corresponding frequency, with the two being related through the Planck constant:

$$\Delta E = h\nu = \hbar\omega. \tag{11}$$

Here, ν is the frequency in units of cycles per second (or simply Hz), while ω is the angular frequency with units of radians per second.

c) Calculate the frequencies ν and ω for an electron spin in a field $B = 1\,\mathrm{T}$.

Calculate these two frequencies for a proton spin in the same field.

3 Frequencies of EPR spectroscopy

In both EPR and NMR, one typically talks about the frequency of the spectrometer (ν), rather than the strength of the magnetic field at which the spectrometer operates.

Fill out the following table for the operational frequencies of typical EPR spectrometers. In the table, λ is the wavelength of an electromagnetic wave whose frequency is ν, which is used to generate transitions between the two states of the electron spin.

	X band	Q band	W band	J band
frequency, ν (GHz)	9	35	95	260
angular frequency, ω (10^9 rad/s)				
wavelength, λ (mm)				
magnetic field, B_0 (T)				

Clearly, when filling out the table, you will need to perform the same calculations four times. Alternatively, you could write a short computer program to perform these repetitive calculations for you. Write down such a program in any programming language that you feel comfortable with.

4 Spin polarization in EPR and NMR

The energy difference ΔE determines the frequency of the electromagnetic excitation that generates transitions between the two spin states. However, the temperature of the environment also generates such transitions in a random fashion. Assuming Boltzmann statistics, the two spin states will be populated proportionally to their Boltzmann factors. If p_i denotes the probability for a spin to be in state i, where i is either 'same' or 'opposite', then we have

$$p_i = \frac{\mathrm{e}^{-E_i/k_\mathrm{B}T}}{\mathrm{e}^{-E_\mathrm{same}/k_\mathrm{B}T} + \mathrm{e}^{-E_\mathrm{opposite}/k_\mathrm{B}T}}. \tag{12}$$

The numerator of this expression is the Boltzmann factor of state i, with

$$k_\mathrm{B} = 1.380649 \times 10^{-23}\ \frac{\mathrm{J}}{\mathrm{K}} \tag{13}$$

being Boltzmann's constant, and T being the absolute temperature of the environment (in units of Kelvin). The denominator in (12) is chosen such that the probabilities of the two states add to one, i.e., $p_\mathrm{same} + p_\mathrm{opposite} = 1$.

The difference between the probabilities of the two states is known as the spin *polarization*:

$$P = p_\mathrm{same} - p_\mathrm{opposite}. \tag{14}$$

a) For an electron spin in a magnetic field of strength $B = 1\,\mathrm{T}$, calculate the probabilities p_same and p_opposite at $T = 300\,\mathrm{K}$ and $T = 5\,\mathrm{K}$.

b) Calculate the same two probabilities for a proton spin at $T = 300\,\mathrm{K}$ and $T = 5\,\mathrm{K}$ in the same magnetic field.

c) What is the ratio between the polarization of the electron spin and the polarization of the proton spin at $300\,\mathrm{K}$? Is that ratio larger or smaller at $5\,\mathrm{K}$?