Solutions to End-of-Chapter Exercises
Chapter 3

Fundamental constants & properties of nuclei

$c = 2.997 \times 10^{8}$ m s^{-1}
$e = 1.602 \times 10^{-19}$ C
$k = 1.381 \times 10^{-23}$ J K^{-1}
$h = 6.626 \times 10^{-34}$ J s

Mass

Electron = $9.109\,390 \times 10^{-31}$ kg
Proton = $1.672\,622 \times 10^{-27}$ kg

$\mu_0 = 4\pi \times 10^{-7}$ J s^{2} C^{-2} m^{-1} (= T^{2} J^{-1} m^{3})
$\mu_B = 9.274 \times 10^{-24}$ J T^{-1}
$\mu_N = 5.050\,784 \times 10^{-27}$ J T^{-1}
$g_e = 2.0023\,193$ (electron g factor)
$g_p = 5.585\,694\,7$ (proton g factor)
$\gamma_e = 1.761 \times 10^{11}$ s^{-1} T^{-1}

Properties for other common nuclei

	g_N	ν_N / MHz	γ / 10^{7} s^{-1} T^{-1}
^{1}H	5.5857	14.9021	26.752
^{2}H	0.8574	2.2876	4.107
^{13}C	1.4048	3.7479	6.728
^{14}N	0.4038	1.0772	1.934
^{31}P	2.2632	6.0380	10.839

ν_L (in units of MHz) for $B = 0.35$ T

Exercise 3.1) Using the resonance equation, calculate the *g* and *B* values in the following:

a) ν = 9.486 GHz, *B* = 0.3345 T, *g* = ?

b) ν = 34.86 GHz, *g* = 2.0023, *B* = ?

ANSWER

This is a straight forward use of the resonance eqn 2.9, so that

a) $$g = \frac{(6.626 \times 10^{-34}\ \mathrm{Js}) \times (9.486 \times 10^{9} \mathrm{s}^{-1})}{(9.274 \times 10^{-24}\ \mathrm{JT}^{-1}) \times (3345 \times 10^{-4}\ \mathrm{T})} = 2.0261$$

b) $$B = \frac{(6.626 \times 10^{-34}\ \mathrm{Js}) \times (34.86 \times 10^{9} s^{-1})}{(9.274 \times 10^{-24}\ \mathrm{JT}^{-1}) \times (2.0023)} = 1.2439\ T$$

Exercise 3.2) The centre of the EPR spectrum of atomic hydrogen lies at 329.12 mT in a spectrometer operating at 9.2231 GHz. What is the *g* value of the atom?

ANSWER

$$g = \frac{(6.626 \times 10^{-34}\ \mathrm{Js}) \times (9.2231 \times 10^{9}\ \mathrm{s}^{-1})}{(9.274 \times 10^{-24}\ \mathrm{JT}^{-1}) \times (3291.2 \times 10^{-4}\ \mathrm{T})} = 2.0022$$

Exercise 3.3) The benzene radical anion has a *g* value of 2.0025. At what field should you search for resonance in a spectrometer operating at: a) 9.302 GHz, b) 33.67 GHz?

ANSWER

a) $$g = \frac{(6.626 \times 10^{-34}\ \mathrm{Js}) \times (9.302 \times 10^{9}\ \mathrm{s}^{-1})}{(9.274 \times 10^{-24}\ \mathrm{JT}^{-1}) \times (2.0025)} = 0.3319\ \mathrm{T}\ (or\ 3319\ G)\ \text{at X-band}$$

b) $$g = \frac{(6.626 \times 10^{-34}\ \mathrm{Js}) \times (33.67 \times 10^{9}\ \mathrm{s}^{-1})}{(9.274 \times 10^{-24}\ \mathrm{JT}^{-1}) \times (2.0025)} = 1.2013\ \mathrm{T}\ (or\ 12013\ G)\ \text{at Q-band}$$

Exercise 3.4) At thermal equilibrium (and under the influence of an external magnetic field) the relative difference in population between the two Zeeman energy levels is given by the Maxwell-Boltzman law. Calculate the population ratio between the two levels at the two operating temperatures 298 K and 4 K, for a paramagnetic species at 300 mT and 1300 mT. Comment on the significance of the values for the intensity of the EPR signal.

ANSWER

For the purpose of this question we can assume the g value of the paramagnetic species = 2.0023. Hence using eqn 2.24, we can calculate the population ratio at each temperature (T_S) and each field (*B*) according to:

$$\frac{N_\alpha}{N_\beta} = exp\left(-\frac{\Delta E}{kT_S}\right) = exp\left(-\frac{g\mu_B B}{kT_S}\right)$$

i) $$\frac{N_\alpha}{N_\beta} = exp\left(-\frac{2.0023 \times 9.274 \times 10^{-24}\ \mathrm{JT}^{-1} \times 0.3\ \mathrm{T}}{(1.381 \times 10^{-23}\ \mathrm{JK}^{-1}) \times 298\ K}\right) = 0.9986$$

ii) $$\frac{N_\alpha}{N_\beta} = exp\left(-\frac{2.0023 \times 9.274 \times 10^{-24}\ \mathrm{JT}^{-1} \times 0.3\ \mathrm{T}}{(1.381 \times 10^{-23}\ \mathrm{JK}^{-1}) \times 4\ K}\right) = 0.9041$$

iii) $$\frac{N_\alpha}{N_\beta} = exp\left(-\frac{2.0023 \times 9.274 \times 10^{-24}\ \mathrm{JT}^{-1} \times 1.3\ \mathrm{T}}{(1.381 \times 10^{-23}\ \mathrm{JK}^{-1}) \times 298\ K}\right) = 0.9942$$

iv) $$\frac{N_\alpha}{N_\beta} = exp\left(-\frac{2.0023 \times 9.274 \times 10^{-24}\ \mathrm{JT}^{-1} \times 1.3\ \mathrm{T}}{(1.381 \times 10^{-23}\ \mathrm{JK}^{-1}) \times 4\ \mathrm{K}}\right) = 0.6460$$

From the above calculations of population ratio, the EPR signal intensity may be more intense at lower temperatures and higher fields

Exercise 3.5) For an unpaired electron (*g* = 2.25) interacting with a proton (g_N = 5.58), explain the relative magnitude of the EZ and NZ interactions

ANSWER

From eqn 2.12, $E = g\mu_B B m_S - g_N \mu_N B m_I + a m_S m_I$. Therefore, according to the first two terms in the eqn. the ratio between the electron and nuclear Zeeman interactions (for an $S = I = ½$) spin system is given by:

$$\frac{\text{Electron Zeeman}}{\text{Nucler Zeeman}} = \frac{g \times \mu_B \times \frac{1}{2}}{g_N \times \mu_N \times \frac{1}{2}} = \frac{2.25 \times (9.274 \times 10^{-24}) \times \frac{1}{2}}{5.58 \times (5.051 \times 10^{-27}) \times \frac{1}{2}} = 740$$