Solutions to End-of-Chapter Exercises
Chapter 9

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 9.1) Given that the precession angular frequency for a charged particle in a static magnetic field is ω = γ*B*, calculate the Larmor frequency for an electron and a proton in a field of 1.5 T.

ANSWER

The Larmor frequency $\nu_L = \frac{\omega}{2\pi}$, where the angular frequency ω = γ*B* or generally $\nu_L = \frac{|\gamma|B}{2\pi}$

For an electron, $\gamma_e = -g_e\left(\frac{e}{2m_e}\right)$ = -1.761×10^{11} s^{-1} T^{-1}.

For *B* = 1.5 T then ω = 1.761×10^{11} s^{-1} T^{-1} × 1.5 T = 2.642×10^{11} s^{-1},

Thus $\nu_L = \frac{2.642\times10^{11}}{2\pi}$ = 4.2041×10^{10} s^{-1} (42.041 GHz).

For a proton, $\gamma_N = \left(\frac{e}{2m_e}\right)$ = $+2.675 \times 10^{8}$ s^{-1} T^{-1}.

For *B* = 1.5 T then ω = 2.675×10^{8} s^{-1} T^{-1} × 1.5 T = 4.0125×10^{8} s^{-1},

Thus $\nu_L = \frac{4.0125\times10^{8}}{2\pi}$ = 6.386×10^{7} s^{-1} (63.86 MHz).

Exercise 9.2) For a B_2 RF field of 10 mT, calculate the pulse duration time required to produce a flip angle of 90° and 180° for a proton.

ANSWER

According to eqn 9.5, the tip angle (β) or pulse length is given by $t_p = \frac{\beta}{\gamma_N B_2}$ where β/2 = 90° or β = 180°, γ_N = 2.675×10^{8} s^{-1} T^{-1} for a proton (see Chapter 2, page 8 margin note) and B_2 = 0.01 T.

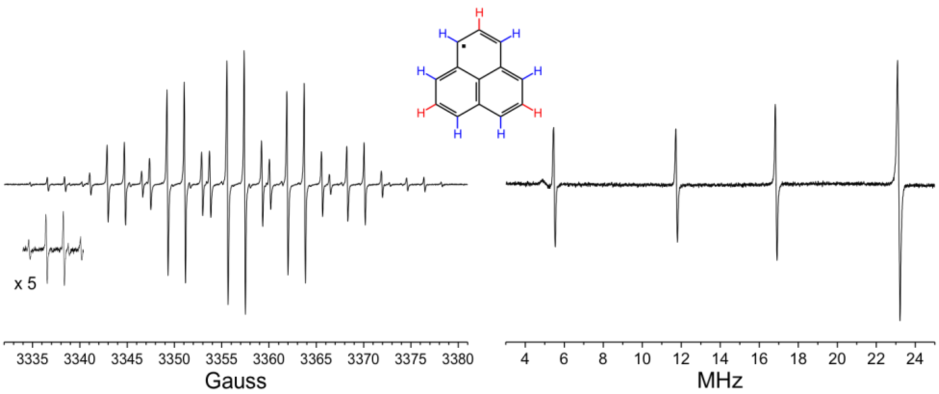
Therefore $t_p = \frac{\beta/2}{(2.675\times10^{8}\ \mathrm{s}^{-1}\mathrm{T}^{-1})\times0.01\ \mathrm{T}} = 5.87 \times 10^{-7}$ s for 90°.

Therefore $t_p = \frac{\beta}{(2.675\times10^{8}\ \mathrm{s}^{-1}\mathrm{T}^{-1})\times0.01\ \mathrm{T}} = 1.17 \times 10^{-6}$ s for 180°.

Exercise 9.3) Calculate the number of lines expected in the EPR and ENDOR spectra of the phenalenyl radical assuming no superposition of overlapping lines (see Fig. 4.22 for radical structure).

ANSWER

According to the structure of the radical (shown in Fig. 4.22, and again highlighted below), the phenalenyl radical has two sets of equivalent protons (shown below in red and blue for clarity). Using the 2*nI* + 1 rule, the three protons in the red set will produce a quartet (1:3:3:1) while the blue set of six equivalent protons will produce a septet (1:6:15:20:15:6:1); the total number of lines in the EPR spectrum will therefore be 4 × 7 = 28.
By comparison, the ENDOR spectrum only produces 4 lines (one pair for each set of equivalent protons) and is therefore considerably easier to interpret.

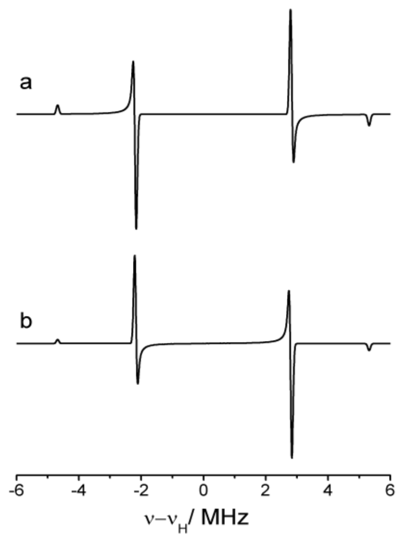


Exercise 9.4) Determine the values of $A_{\|}$ and $A_{\perp}$ in Fig. 9.17(b) and hence sketch the profile of the expected powder hyperfine spectrum for the spin system shown in Fig. 9.16 assuming a quasi isotropic **g** tensor.

ANSWER

It should also be noted, that when the **g** anisotropy is small (ie., assuming a quasi isotropic **g** tensor), then all orientations of ***B*** with respect to *g* are observed simultaneously, resulting in a summed powder hyperfine pattern (as opposed to the 'single crystal like' patterns shown in Fig 9.17).

The numerical values extracted from Fig. 9.17(b) are $A_{\|} = \pm 10$ MHz and $A_{\perp} = \pm 5$ MHz. The resulting profile will depend however on the signs, as shown in the Figure below;



In the case of where *A* is described by [+5, +5, +10] MHz, the powder pattern resembles that shown in a) above. In the case of where *A* is described by [−5, −5, +10] MHz, the powder pattern resembles that shown in b) above. For the purely axial hyperfine shown in this example, the powder hyperfine pattern in b) resembles the Pake pattern shown for a purely dipolar system given in Fig. 5.14(c).

Exercise 9.5) Calculate the frequencies of the two ENDOR transitions shown in Fig. 9.2 for a ^{1}H with a = 10 MHz recorded on a W-band spectrometer (3.4 T).

ANSWER

The Larmor frequency = $\nu_L(\nu_B) = \frac{\nu_{L(ref)}B}{B_{(ref)}} = \frac{14.90212\text{ MHz} \times 3.4\text{ T}}{0.3500\text{ T}} = 144.76$ MHz for ^{1}H at 3.4 T. The two NMR (ENDOR) transitions are centered on ν_L and separated by *a*, therefore transition frequencies occur at $\nu_{N2} = 144.76 + 5 = 149.76$ MHz and $\nu_{N1} = 144.76 - 5 = 139.76$ MHz. This is an example of a *weak coupling* regime.