Solutions to End-of-Chapter Exercises
Chapter 7

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

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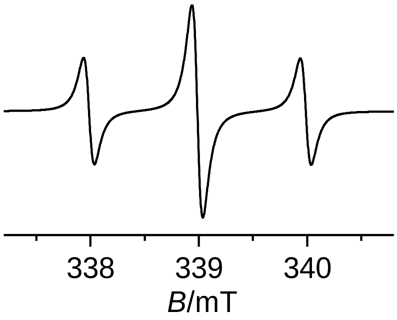
Exercise 7.1) Open a triplet spectrum at www.EPRsimulator.org and measure *D* (and *E*, if appropriate) values. Express your answer in energy units.

ANSWER
An example of how *D* and *E* values can be measured in magnetic field units from a triplet spectrum is shown in Fig. 7.13. The values in the field units can be converted into frequency units using equations in Appendix A (the *g* value should be calculated from the position of the centre of the spectrum). They can be further converted into energy units using equation $E = h\nu$. For instance, in Fig. 7.13b (recorded at 9.5 GHz frequency), the separation between the lines $2D$ is 183 mT, and separation between the lines $3E$ is 38 mT. Hence *D* and *E* are 91.5 and 12.7 mT, respectively. The *g* (e.g., read as a centre of $2D$ separation) is at *ca*. 310 mT which corresponds to the value of 2.190. Hence *D* and *E* in frequency units are *ca*. 2800 and 390 MHz, respectively, or in energy units 1.9×10^{-24} and 2.6×10^{-25} J, respectively. *D* and *E* values are often reported in wavenumber units, e.g., 0.093 and 0.013 cm^{-1}, respectively.

Exercise 7.2) Sketch the EPR spectrum of a fluid solution of the diradical in Fig. 7.2 with both nitrogen atoms replaced by the ^{15}N isotope. Pay particular attention to the number of lines, their relative intensity, and the distance between the lines.

ANSWER
The EPR spectrum of the radical in Fig. 7.2 is similar to the bottom spectrum in Fig. 7.3, i.e., a 1:2:3:2:1 quintet with the separation between the lines equal $a/2$. A typical hyperfine value for nitroxides is *ca*. 1.5 - 1.7 mT, hence the separation between the lines in the spectrum should be around 0.8 mT.

In the ^{15}N-substituted radical, the pattern will be different, as $I(^{15}\text{N}) = ½$. Coupling to two equivalent $I = ½$ nuclei gives a 1:2:1 triplet. The nuclear g_N factor for ^{15}N is ca. 40% greater than that for ^{14}N; hence the EPR spectrum of the ^{15}N-substituted radical will show a 1:2:1 triplet with the separation between the lines up to 40% greater than 0.8 mT (depending on the distribution of unpaired electron density between the N and O atoms of the nitroxide), e.g., around 1.1 mT.



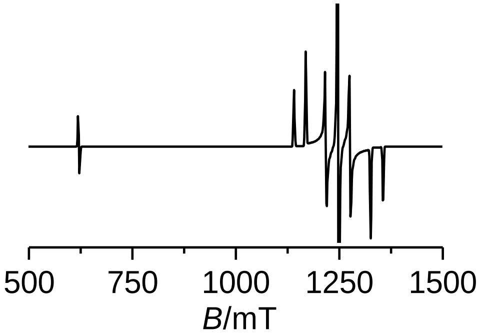
Exercise 7.3) Fig. 7.21 shows an expansion of the EPR spectra of a dilute solution of TEMPO in acrylic acid (only one peak is shown) which was oxygen-saturated, deoxygenated or contains an unknown concentration of oxygen. Estimate the concentration of oxygen (in g/mL) in the unknown sample, assuming that the solubility of oxygen in acrylic acid is 1.5 g/mL.

ANSWER
The peak-to-peak linewidths of the spectra a, b and c in Fig. 7.21 can be measured directly from the spectra as 0.33, 0.13 and 0.20 mT, respectively. The linewidth ΔB_{pp} is linearly proportional to the concentration of oxygen (section 7.2), i.e., $\Delta B_{pp} = x[O_2]+y$, where *x* and *y* are constants. Spectrum b is completely deoxygenated, hence $[O_2] = 0$ and $\Delta B_{pp} = y = 0.13$

mT. Spectrum a corresponds to the oxygen-saturated sample ($[O_2]$ = 1.5 g/mL), for this spectrum $\Delta B_{pp} = 0.33$ mT = $1.5x + 0.13$ mT and hence $x = 0.13$. For the unknown sample, $\Delta B_{pp} = 0.2$ mT = $0.13[O_2] + 0.13$ mT. Rearranging this equation, we get $[O_2] = 0.54$ g/mL.

Exercise 7.4) Sketch the EPR spectrum expected from the naphthalene-d_8 triplet state (see Fig. 7.15) at Q-band

ANSWER
Just like hyperfine constants, the values of *D* and *E* are constant in energy or frequency units, and hence the separation between the lines in the field units do not depend on spectrometer frequency (equations in Appendix A show that conversion of hyperfine values from the field to the frequency units does not include spectrometer frequency or field). Hence the triplet spectrum at Q-band (35 GHz) will look similar to that of X-band. The distance between the main spectrum and the $\Delta m_S = \pm 2$ peak, however, will increase significantly. The spectrum below shows the triplet spectrum at Q-band and includes contributions from a double photon transition and unidentified organic mono-radicals, like in Fig. 7.15.



Exercise 7.5) A colleague asks your advice on recording an EPR spectrum of a V(III) complex. Discuss the feasibility of this experiment, what information can be obtained from the experiment, and how to determine the best conditions for recording the spectrum.

ANSWER
V(III) is a d^2 system which has $S = 1$. The energy levels for this system arrange in non-Kramers doublets, and many transitions may be outside the spectral window. The peaks may be very broad or even too broad to be observed. The advice would be to use high frequency/high field spectrometers, go down to low temperature (liquid He) and use very large sweep width, large modulation amplitude and high power. The spectra are likely to be dominated by the zero-field splitting interaction.