Solutions to End-of-Chapter Exercises
Chapter 5

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

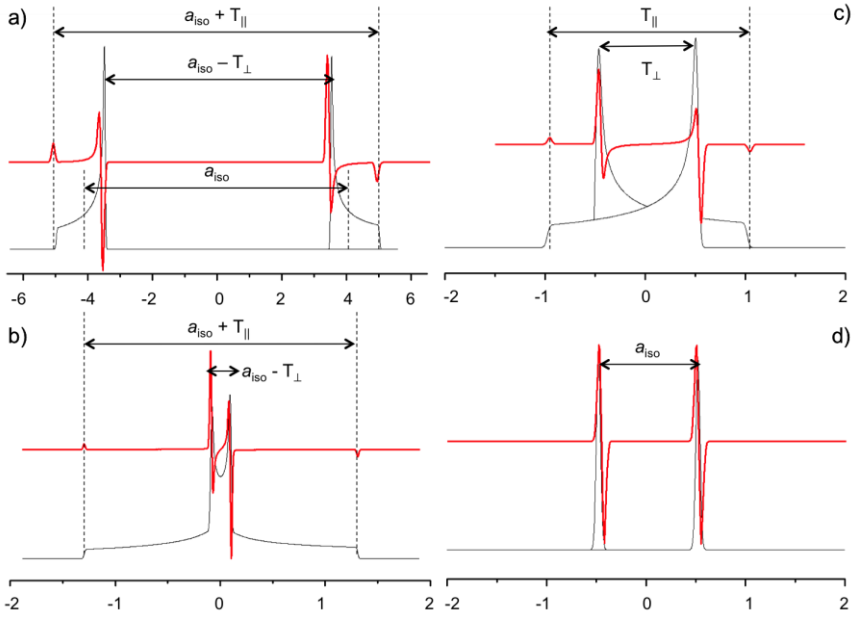
	g_N	ν_N / MHz	γ / 10^7 s^{-1} T^{-1}
^{1}H	5.5857	14.9021	26.752
^{2}H	0.8574	2.2876	4.107
^{13}C	1.4048	3.7479	6.728
^{14}N	0.4038	1.0772	1.934
^{31}P	2.2632	6.0380	10.839

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

Exercise 5.1) Sketch the expected first derivative profiles of the resultant powder EPR spectra for the idealised hyperfine patterns shown in Fig. 5.14.

ANSWER

These spectra were shown in Fig. 5.14 in absorption mode (eg., as would be observed in a pulsed ENDOR spectrum). However, the anisotropic profile with derivative lineshape may also be observed in CW mode, so the resultant spectra are shown below (red trace). Notice the similarity in profiles for a)-c), with the major differences arising from the spacings:



Exercise 5.2) A 2 × 2 matrix, labelled **M**, is given below. Find the determinant (*det*(**M**)), the transpose ($\mathbf{M}^T$) and the inverse ($\mathbf{M}^{-1}$) of the matrix. Briefly explain how the diagonal of the matrix can be determined, and therefore why **g** (and **A** or **D**, see Chapter 8) is expressed as a diagonal matrix.

ANSWER

Throughout this book, several matrices (eg. g, A or P) are presented. It is necessary to be able to manipulate and transform these matrices:

$$\mathbf{M} = \begin{bmatrix} 4 & 3 \\ 2 & -5 \end{bmatrix}$$

i) The determinant of M, written *det*(**M**) = (4 × –5) – (3 × 2) = –26

ii) The transpose $\mathbf{M}^T$, written $\begin{bmatrix} 4 & 3 \\ 2 & -5 \end{bmatrix}^T = \begin{bmatrix} 4 & 2 \\ 3 & -5 \end{bmatrix}$

iii) The inverse $\mathbf{M}^{-1}$, written $\begin{bmatrix} 4 & 3 \\ 2 & -5 \end{bmatrix}^{-1} = \begin{bmatrix} \frac{5}{26} & \frac{3}{26} \\ \frac{1}{13} & \frac{-2}{13} \end{bmatrix}$

Therefore in the above case, $= \frac{1}{-26} \times \begin{bmatrix} -5 & -3 \\ -2 & 4 \end{bmatrix} = \begin{bmatrix} \frac{5}{26} & \frac{3}{26} \\ \frac{1}{13} & \frac{-2}{13} \end{bmatrix}$

In may cases, the values of *g* and *A* determined experimentally will not be the principle values of **g** or **A** (such as g_{xx}, g_{yy}, g_{zz}). Diagonalisation of an experimentally determined set of values must therefore be performed. For the *A* values this is written as $A_{exp} = P^{-1}\,\mathbf{A}_{diag}\,P$.

Exercise 5.3) Using eqn. 5.12, derive an expression for g^2 when the single crystal containing a paramagnetic centre is rotated in the *YZ* and *XY* plane, given the corresponding direction cosines are (l_x = 0, l_y = sinθ, l_z = cosθ) and (l_x = cosϕ, l_y = sinϕ, l_z = 0) respectively, and where θ is the angle between ***B*** and the z-axis.

ANSWER
According to eqn. 5.12:

$$g^2 = [l_x \quad l_y \quad l_z]\begin{bmatrix}(\mathbf{gg})_{xx} & (\mathbf{gg})_{xy} & (\mathbf{gg})_{xz}\\ (\mathbf{gg})_{xy} & (\mathbf{gg})_{yy} & (\mathbf{gg})_{yz}\\ (\mathbf{gg})_{xz} & (\mathbf{gg})_{yz} & (\mathbf{gg})_{zz}\end{bmatrix}\begin{bmatrix}l_x\\ l_y\\ l_z\end{bmatrix}$$

By inserting the values of the direction cosines into the above equation for the two YZ and XY planes, we must then find the product of the row vector multiplied by a square matrix multiplied by a column vector.

In the *YZ* plane

$$g^2 = [0 \quad \sin\theta \quad \cos\theta]\begin{bmatrix}(\mathbf{gg})_{xx} & (\mathbf{gg})_{xy} & (\mathbf{gg})_{xz}\\ 0 & (\mathbf{gg})_{yy} & (\mathbf{gg})_{yz}\\ 0 & 0 & (\mathbf{gg})_{zz}\end{bmatrix}\begin{bmatrix}0\\ \sin\theta\\ \cos\theta\end{bmatrix}$$

giving $g^2 = (\mathbf{gg})_{yy}\sin^2\theta + 2(\mathbf{gg})_{yz}\sin\theta\cos\theta + (\mathbf{gg})_{zz}\cos^2\theta$

In the *XY* plane

$$g^2 = [\cos\phi \quad \sin\phi \quad 0]\begin{bmatrix}(\mathbf{gg})_{xx} & (\mathbf{gg})_{xy} & (\mathbf{gg})_{xz}\\ 0 & (\mathbf{gg})_{yy} & (\mathbf{gg})_{yz}\\ 0 & 0 & (\mathbf{gg})_{zz}\end{bmatrix}\begin{bmatrix}\cos\phi\\ \sin\phi\\ 0\end{bmatrix}$$

giving $g^2 = (\mathbf{gg})_{xx}\cos^2\phi + 2(\mathbf{gg})_{xy}\sin\phi\cos\phi + (\mathbf{gg})_{yy}\sin^2\phi$

Exercise 5.4) Using a suitable graphics programme, calculate the angular dependency curve and resonant field position for an *S* = ½ spin system with axial symmetry where $g\perp$ = 2.000 and $g_{\|}$ = 1.950 (given ν = 9.5 GHz).

ANSWER
For a system with axial symmetry, the angular dependency of g was given by eqn. 5.11. Simple algebraic manipulation of this equation gives an explicit expression of the angle θ between ***B*** and the molecular z axis as:

$$\theta = \cos^{-1}\left[\frac{g^2(\theta)-g_\perp^2}{g_\|^2-g_\perp^2}\right]^{1/2} \qquad \text{(page 49)}$$

Given that $B(\theta) = \frac{h\nu}{\mu_B g(\theta)}$, then two possible algorithms can be used to solve for θ.

1. Fixing an array θ so that $0 < \theta < \frac{\pi}{2}$ and then calculating $B(\theta)$ with equations 5.11 and the above eqn. in series;
2. Fixing an array g so that $g_1 < g < g_2$, in this case $g_\| < g < g_\perp$, and then calculating θ with the above eqn. and $B(\theta)$ with the eqn. $B(\theta) = \frac{h\nu}{\mu_B g(\theta)}$ independently.

Both algorithms implemented in MATLAB are given on the next page:

MATLAB SOLUTION 1

Implementing the following code in a *.m file:

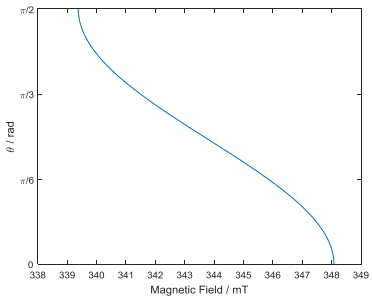
```
h = 6.62607004e-34; % Planck constant in Kg*m^2*s^-1, equivalent to J*s
freq = 9.5e9; % X-band microwave frequency in Hertz, i.e s^-1
bohr_mag = 9.27400968e-24; % Bohr magneton in A*m^2, equivalent to J*T^-1

theta = 0:0.01:pi/2; % array containing the angular domain. use a sufficiently high number of points. in this case (pi/2-0)/0.01 + 1 = 158
g_para = 1.950; % numerical value of g parallel
g_perp = 2.000; % numerical value of g perpendicular
B = h*freq/bohr_mag*(1./sqrt((g_para^2-g_perp^2).*(cos(theta)).^2+g_perp^2))*1000; % angular dependency of the resonant field position

plot(B,theta)

% Graph formatting code
ylim([0 pi/2]) % lower and upper limits of the y-axis
xlim([338 349]) % left and right limits of the x-axis
set(gca,'ytick',0:pi/6:pi/2) % numerical values to be displayed
set(gca,'yticklabel',{'0','\pi/6','\pi/3','\pi/2'})
xlabel('Magnetic Field / mT') % x-axis label
ylabel('\theta / rad') % y-axis label
```

The following figure should be obtained:



MATLAB SOLUTION 2

Implementing the following code in a *.m file:

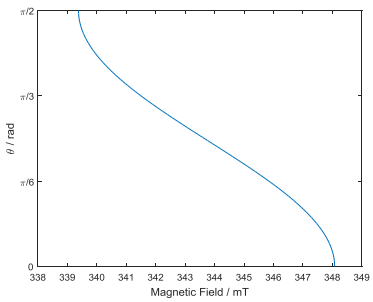
```
h = 6.62607004e-34; % Planck constant in Kg*m^2*s^-1, equivalent to J*s
freq = 9.5e9; % X-band microwave frequency in Hertz, i.e s^-1
bohr_mag = 9.27400968e-24; % Bohr magneton in A*m^2, equivalent to J*T^-1

g_para = 1.950; % numerical value of g parallel
g_perp = 2.000; % numerical value of g perpendicular
g = g_para:0.0001:g_perp; % array containing values of g € (g_para; g_perp)
B = h*freq./(g*bohr_mag)*1000; % resonant field position
theta = acos(sqrt((g.^2-g_perp^2)./(g_para^2-g_perp^2))); % angle  between B0 and the molecular z-axis

plot(B,theta)

% Graph formatting code
ylim([0 pi/2]) % lower and upper limits of the y-axis
xlim([338 349]) % left and right limits of the x-axis
set(gca,'ytick',0:pi/6:pi/2) % numerical values to be displayed
set(gca,'yticklabel',{'0','\pi/6','\pi/3','\pi/2'})
xlabel('Magnetic Field / mT') % x-axis label
ylabel('\theta / rad') % y-axis label
```

The following figure should be obtained:



Exercise 5.5) The CW powder EPR spectrum for an S = ½ spin system with an isotropic g value and a purely axial hyperfine interaction to a proton (I = ½), is shown in Fig. 5.16. Determine the axial hyperfine values, in units of MHz, and hence by applying the point-dipole approximation:

$$T = \frac{\mu_0}{4\pi h} g_e \mu_B g_N \mu_N \frac{3\cos^2\theta - 1}{r^3}$$

calculate the electron-proton distance r. What are the limitations of this approach for the determination of r?

ANSWER

Because the hyperfine is purely axial, the $T_{\|}$ and $T_{\perp}$ components can be extracted directly from the EPR spectrum (shown below), giving $T_{\|}$ = 2 G and $T_{\perp} = -1$ G. In frequency units this gives $T_{\|}$ = 5.6 MHz. Substituting for the values of μ_o, g_e, μ_B, g_N, μ_N into the above eqn gives:

$$T_{||} = \frac{\mu_0}{4\pi h}(g_e \mu_B g_N \mu_N)\frac{3\cos^2\theta - 1}{r^3} = 1.509 \times 10^{26}(5.2390 \times 10^{-49})\frac{3\cos^2\theta - 1}{r^3}$$

Simplifying this gives $5.6 \times 10^{6} = 7.9068 \times 10^{-23} \times \frac{3\cos^2\theta - 1}{r^3}$

Hence $7.0825 \times 10^{28} = \frac{2}{r^3}$, therefore this gives a values of $r = 3.05 \times 10^{-10}$ m.

Note if we use the value for $T_{\perp} = -2.8$ MHz, then the term $3\cos^2\theta - 1 = -1$, and one obtains the same answer for r. However, it is important to note, that although the point-dipole approximation is frequently used in EPR investigations, the above formula is only valid when g is isotropic, and when the distance is greater than *ca*. 2.0×10^{-10} m.