

Magnetic Resonance

Hilary 2018

Due: 5pm Thursday Week 3

1. Shielding and Chemical Shift

- 1.a Discuss the influence of local diamagnetic and paramagnetic shielding effects on the chemical shift of a magnetic nucleus.
- 1.b Using the Lamb formula for diamagnetic shielding in atoms, explain why the screening constant obtained for ^3He is 59.94×10^{-6} or 59.94 part per million whilst that for ^{21}Ne is 547 ppm.
- 1.c The figure below shows the chemical shift of $^{103}\text{Rh}(\text{I})(\text{hfacac})(\text{alkene})_2$ where the (alkene) is ethylene (lowest shift), cis-butene, and trans-butene (highest shift), plotted against the wavelengths of two UV-vis absorption bands (■, □). Interpret the data with reference to the schematic MO diagram devised for these complexes.

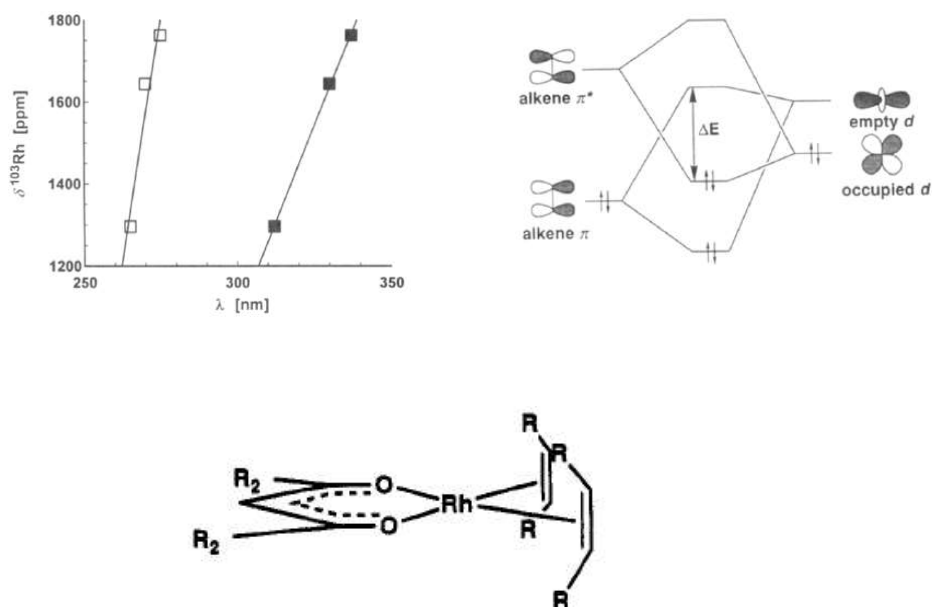


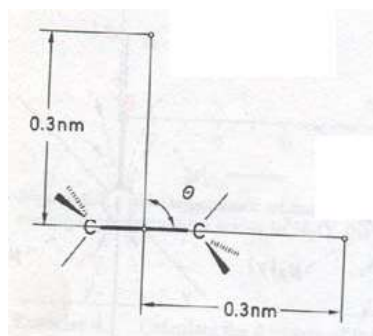
Figure 1: Structure of $^{103}\text{Rh}(\text{I})(\text{hfacac})(\text{alkene})_2$, $\text{R}_2 = \text{CF}_3$.

- 1.d The effects a neighbouring group X exerts on a nucleus A are relatively straightforward to understand if the charge distribution has axial symmetry so that χ_{\parallel} and χ_{\perp} define the susceptibilities parallel and perpendicular to the bond axis. Importantly, if the magnetic moment induced in the neighbouring group is then treated simply as a point dipole, the contribution to the chemical shift of the affected nucleus (of a molecule in solution tumbling rapidly) is simply given by,

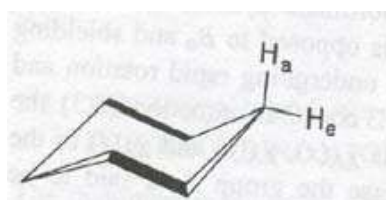
$$\Delta\sigma = \frac{1}{12\pi R^3} (\chi_{\parallel} - \chi_{\perp}) (1 - 3 \cos^2 \theta),$$

where R is the distance between the nucleus under consideration and the centre of the point dipole and θ is the angle between the axis of symmetry (χ_{\parallel}) and the connecting line nucleus-centre.

- (i) If we approximate that the C-C single bond has such axial symmetry with $\Delta\chi = \chi_{\parallel} - \chi_{\perp} = 140 \times 10^{-36} \text{ m}^3$, then calculate the contributions of this neighbouring group to $\Delta\sigma$ of two H-atoms placed $R = 0.3 \text{ nm}$ from the centre of the bond as shown below.



- (ii) At which geometric condition do you expect a nodal plane ($\Delta\sigma = 0$)?
- (iii) An experimental verification of your findings is provided if you consider the C-C single bond in cyclohexane at low temperatures at which the chair-chair interconversion is slow on the NMR time scale. Using your findings in (i) predict which of the two protons in the molecule shown below is more strongly shielded.



2. Quantum Mechanical consideration of Magnetic Resonance

- 2.a The spin Hamiltonian for a nuclear spin with spin quantum number I in a magnetic field is $\hat{H} = -\omega_0 \hat{I}_z$. Determine the eigenvalues of \hat{H} and show that

the spacing between adjacent energy levels is independent of l .

- 2.b A molecule contains two coupled protons labelled I and S. In the strong magnetic field of an NMR spectrometer, ν_I and ν_S are the NMR frequencies the two protons would have if they had no spin-spin coupling and J is the spin-spin coupling constant. The eigenstates $|j\rangle$ and corresponding energies ϵ_j of this spin system are,

$$\begin{aligned} |1\rangle &= |\alpha_I\alpha_S\rangle; & \epsilon_1 &= \frac{1}{4}hJ - h\nu \\ |2\rangle &= |\alpha_I\beta_S\rangle \cos\theta + |\beta_I\alpha_S\rangle \sin\theta; & \epsilon_2 &= -\frac{1}{4}hJ - \frac{1}{2}h\sqrt{\delta^2 + J^2} \\ |3\rangle &= -|\alpha_I\beta_S\rangle \sin\theta + |\beta_I\alpha_S\rangle \cos\theta; & \epsilon_3 &= -\frac{1}{4}hJ - \frac{1}{2}h\sqrt{\delta^2 + J^2} \\ |4\rangle &= |\beta_I\beta_S\rangle; & \epsilon_4 &= \frac{1}{4}hJ + h\nu \end{aligned}$$

where,

$$\nu = \frac{1}{2}(\nu_I + \nu_S); \quad \delta = \nu_I - \nu_S; \quad \tan 2\theta = \frac{J}{\delta}.$$

The intensity of an NMR transition between eigenstates $|j\rangle$ and $|k\rangle$ is proportional to,

$$I_{jk} = (n_j - n_k)P_{jk},$$

where n_j is the fractional population of state j and $n_1 + n_2 + n_3 + n_4 = 1$. P_{jk} is the transition probability,

$$P_{jk} = \frac{1}{2} \left| \langle j | \hat{I}_+ + \hat{S}_+ | k \rangle \right|^2.$$

Matrix elements of the operator $(\hat{I}_+ + \hat{S}_+)$ in the basis $|\alpha_I\alpha_S\rangle$, $|\alpha_I\beta_S\rangle$, $|\beta_I\alpha_S\rangle$, $|\beta_I\beta_S\rangle$ are as follows:

	$ \alpha_I\alpha_S\rangle$	$ \alpha_I\beta_S\rangle$	$ \beta_I\alpha_S\rangle$	$ \beta_I\beta_S\rangle$
$ \alpha_I\alpha_S\rangle$	0	1	1	0
$ \alpha_I\beta_S\rangle$	1	0	0	1
$ \beta_I\alpha_S\rangle$	1	0	0	1
$ \beta_I\beta_S\rangle$	0	1	1	0

- (i) Explain the significance of α_I , β_I , α_S , and β_S .
- (ii) a. Use the Boltzmann distribution to show that the fractional populations of the eigenstates at thermal equilibrium when $k_B T \gg h\nu \gg h|\delta|$ and $h|J|$ are approximately

$$\frac{j}{n_j} \left| \begin{array}{cccc} 1 & 2 & 3 & 4 \\ \frac{1}{4}(1 + \Delta) & \frac{1}{4} & \frac{1}{4} & \frac{1}{4}(1 - \Delta) \end{array} \right.$$

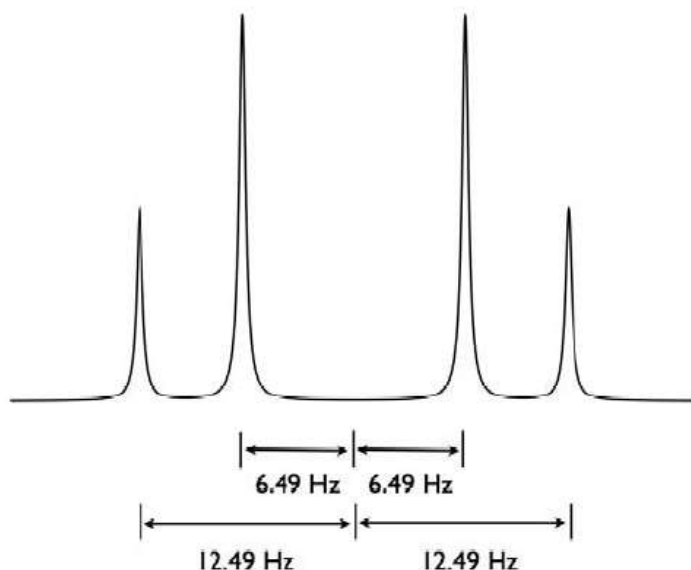
where $\Delta = h\nu/K_B T$.

- b. How does Δ vary with the strength of the magnetic field of the NMR spectrometer?

- (iii) a. Show that the transition probabilities are as follows:

j, k	1,2	3,4	1,3	2,4
P_{jk}	$\frac{1}{2}(1 + \sin 2\theta)$	$\frac{1}{2}(1 - \sin 2\theta)$	$\frac{1}{2}(1 - \sin 2\theta)$	$\frac{1}{2}(1 + \sin 2\theta)$

- b. Explain why it is not necessary to consider the transitions 1,4 and 2,3.
- (iv) Using the information given above and your answers to (ii) and (iii), account for the appearance of the ^1H NMR spectrum shown below of a molecule containing two *inequivalent* protons with $J > 0$. [Note: $\sin 2\theta = -J/\sqrt{\delta^2 + J^2}$.]



- (v) Use the data given the spectrum to determine the values of the coupling constant J and the difference in the NMR frequencies of the two nuclei, δ .
- (vi) Use the information given above and your answers to (ii) and (iii) to predict the appearance of the NMR spectrum of two coupled *equivalent* protons.
- (vii) Under what conditions would the spectrum comprise four lines at different frequencies, all with the same intensity?
- 2.c Show that the only transitions between *adjacent* energy states of a spin- I particle in a magnetic field are allowed in a conventional magnetic resonance experiment. Show that the three allowed NMR transitions of a spin- $\frac{3}{2}$ nucleus have transition probabilities in the ratio 3:4:3.

3. Scalar and dipolar couplings between spins

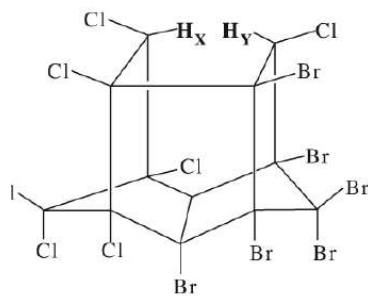
- 3.a Two particles with spin quantum number $I = 1/2$, such as two protons in a molecule, may interact via two mechanisms, namely dipolar coupling and the spin-spin (or scalar) coupling. Discuss the nature of both coupling mechanisms.

In high magnetic fields, the dipolar coupling results in a splitting of the protons' resonance signals by the amount

$$\Delta B = 3\mu(3\cos^2\theta - 1)r^{-3}(\mu_0/4\pi), \quad (1)$$

where μ is the magnetic moment of the proton, r the interproton distance and θ the angle between the applied magnetic field, \mathbf{B} , and the interspin vector, \mathbf{r} .

- 3.b (i) Produce a diagrammatic sketch relating \mathbf{B} , \mathbf{r} and θ .
 (ii) Which approximation has been used to derive equation (1).
 (iii) Determine the angle, θ_{MA} , for which the splitting in the protons' resonance signal disappears.
- 3.c Consider a molecule containing two dipolar coupled protons, tumbling rapidly in solution. Taking into account the appropriate weighting factor for a molecule with no preferred orientation ($\sin\theta$), prove that the dipolar coupling as defined in equation (1) does not contribute to the NMR splitting patterns of dipolar coupled protons in liquids.
- 3.d The figure below shows a molecule in which two protons are highlighted.
- (i) Explain why there is no coupling to the Cl or BR nuclei. The spin quantum number of both Cl and BR is equal to $3/2$.
 (ii) Predict the appearance of the NMR spectra of the two protons H_x and H_y in liquid solution giving your reasons.
 (iii) Assuming isotropic chemical shifts for all nuclei, predict the NMR spectrum of proton X in a single crystal of the molecule below at $\theta = 0, \pi/4, \theta_{\text{MA}}, \pi/2$.

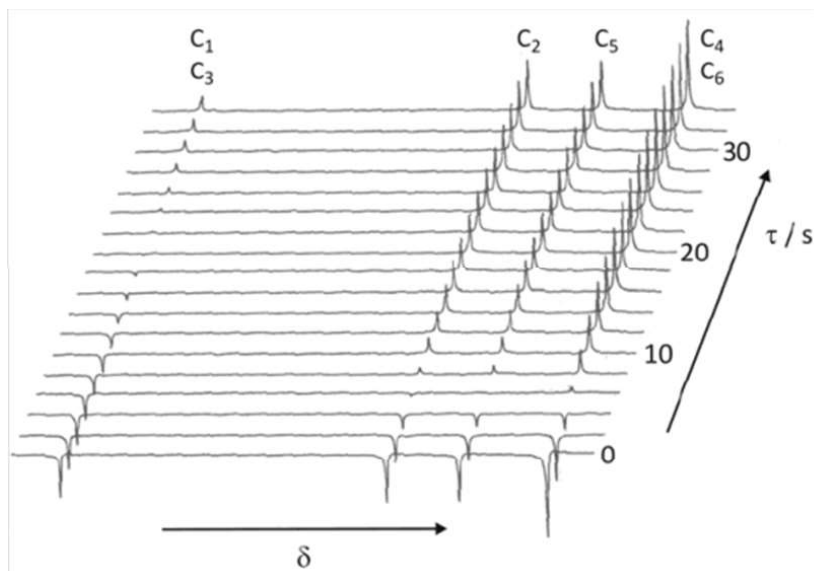


4. Relaxation phenomena

Relaxation processes are fundamental to the phenomenon of Magnetic Resonance and can be broadly divided into two types: (i) Spin-lattice (or longitudinal) relaxation and (ii) spin-spin (or transverse) relaxation.

- 4.a Briefly discuss the origin of both phenomena including the terms 'spectral density' and 'rotational correlation time' and, using the vector model, outline experiments which are employed to measure the spin-spin and spin-lattice relaxation time.

- 4.b The figure below illustrates the results of an inversion recovery experiment for the aromatic region of the ^{13}C NMR spectrum of a conformer of Xylene. Using the spectrum below explain why this conformer must be m-Xylene.



- 4.c Assuming exponential relaxation, the magnetization in such an inversion recovery experiment can be described by,

$$M_z(\tau) = M_0 [1 - 2 \exp(-\tau/T_1)].$$

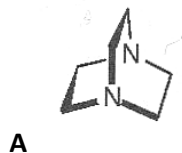
- (i) Define the parameter T_1 in this expression.
 (ii) using values in the table below determine the relaxation times of the aromatic $^{13}\text{C}_4$ and $^{13}\text{C}_6$ nuclei in m-Xylene.

τ/s	$M_z/M_0(\text{C}_4, \text{C}_6)$
0	-1
3	-0.32
6	+0.13
9	+0.43
12	+0.62

- 4.d Obtain a rough estimate of T_1 for $^{13}\text{C}_1/^{13}\text{C}_3$, $^{13}\text{C}_2$ and $^{13}\text{C}_5$ from the data provided in the figure (graphs not required) and comment on the relative values you obtain for the spin-lattice relaxation times of carbons C_1/C_3 vs C_2 , C_5 and C_4/C_6 .
- 4.e Describe an NMR experiment which would allow the measurement of a pure m-Xylene ^{13}C -spectrum in a solution containing 50% benzene and 50% m-Xylene and sketch the 1D spectrum ($T_1(^{13}\text{C})$ of benzene is 23 s) you would obtain.

5. Electron Paramagnetic Resonance

- 5.a What magnetic field would be required to do an EPR experiment on a $g = 2.0$ radical at 250 GHz?
- 5.b Calculate the difference in resonance frequencies of the two radicals CH_2CH_3 ($g = 2.0026$) and CH_2CHO ($g = 2.0045$) in a magnetic field of 0.33 T.
- 5.c The 9.25 GHz EPR spectrum of the radical HO-CH-COOH in aqueous solution comprises four lines at field positions 329.8160 ± 0.0985 mT and 329.8160 ± 0.0725 mT. Explain the appearance of this spectrum by means of an energy level diagram.
- 5.d Explain why the EPR spectrum of the cation radical of the molecule **A** comprises 65 lines whose positions relative to the centre of the spectrum can be predicted by means of just two hyperfine coupling constants. [$I(^{14}\text{N}) = 1$; $I(^1\text{H}) = 1/2$; $I(^{12}\text{C}) = 0$.]



- 5.e Hydrogen atoms in the gas phase can be detected using radiofrequency radiation with a wavelength of 21 cm. Estimate the field positions of the EPR lines of hydrogen atoms in a 9 GHz spectrometer. [Note: The resonance condition for an electron coupled to a nucleus with magnetic quantum number m_I is

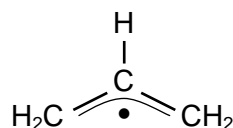
$$\nu = \frac{\gamma_e B}{2\pi} + m_I a,$$

where B is the magnetic field strength, a is the hyperfine coupling constant and ν is the spectrometer frequency.]

- 5.f Comment on the observation that the EPR spectrum of the allyl radical displays hyperfine coupling constants of 1.48 mT (2 protons); 1.39 mT (2 protons); 0.41 mT (1 proton) in the light of the Hückel theory for π -molecular orbitals given below.

$$\frac{1}{2} (\phi_1 \pm \sqrt{2}\phi_2 + \phi_3); \quad \varepsilon = \alpha \pm \sqrt{2}\beta,$$

$$\frac{1}{\sqrt{2}} (\phi_1 - \phi_3); \quad \varepsilon = \alpha.$$



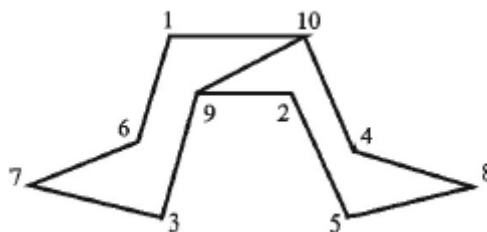
6. Double Resonance Techniques in Magnetic Resonance

- 6.a Basing your discussion on a molecule containing two inequivalent protons explain the physical principles underlying double resonance techniques making reference to both decoupling techniques and the Nuclear Overhauser Effect.
- 6.b Shown below is the ^{31}P spectrum of triethyl phosphate $(\text{CH}_3\text{CH}_2\text{O})_3\text{P}$ obtained without double irradiation. Predict the spectra when a) the methylene protons are irradiated and b) the methyl protons are irradiated.



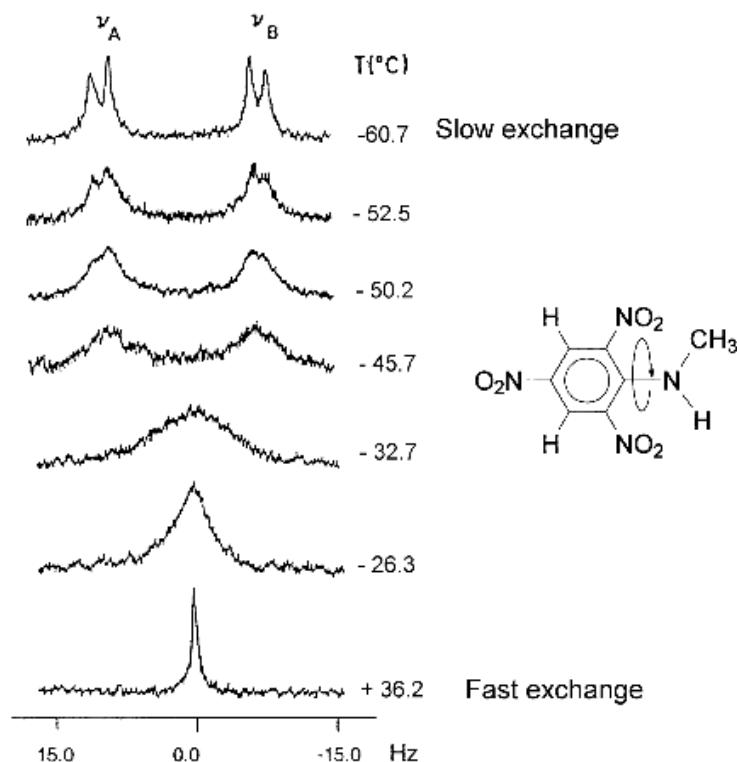
7. Chemical Exchange

- 7.a $\text{C}_{10}\text{H}_{18}$ (cis-decalin) undergoes flips between two degenerate conformations by chair-to-chair inversions in both rings at high temperatures.



^{13}C spectra taken below 240 K consist of five lines of equal intensity but when the temperature is elevated to 320 K, only three lines appear in the spectrum with one of the lines unaffected by the temperature rise. The ^{13}C spectra were recorded in a proton-decoupled mode so that the splittings due to the protons are not observed.

- Account for the fact that only five lines are observed at low temperatures and that three are observed at higher temperatures.
 - Predict how the line positions and linewidths observed in the NMR spectrum vary over this temperature range?
 - How would the chemical shifts, transition frequencies, and the temperature dependence be affected as the spectrometer frequency is increased by a factor of 10?
- 7.b Consider the spectra of the aromatic protons in *N*-methyl-2,4,6-trinitroaniline recorded at a number of different temperatures:



Discuss the appearance of the spectra in terms of an exchange process in this molecule.

- 7.c The following data give the observed ^{31}P chemical shift of phosphate ions involved in the reaction $\text{H}_2\text{PO}_4^-(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{HPO}_4^{2-}(\text{aq})$. Determine the acid dissociation constant of H_2PO_4^- . Assume all activity coefficients are equal to unity. $\delta(\text{H}_2\text{PO}_4^-) = 3.41$ ppm, $\delta(\text{HPO}_4^{2-}) = 5.82$ ppm.

pH	7.00	6.70	6.30	6.00
δ/ppm	4.33	3.98	3.67	3.55

- 7.d (i) Explain why the NMR lines of ^{13}C atoms bonded to the halogen atoms Cl, Br, and I, are affected in frequency but not by split by spin-spin coupling although all common isotopes of these halogens have non-zero nuclear spin.
- (ii) Explain why the ^1H spectrum of the NH_4^+ ion in solution shows splitting into three lines by the ^{14}N nucleus but spectra of primary amines show no such splitting for protons bonded to the nitrogen atoms.

8. [Based on PART IB 2012]

The shielding of the nucleus by the local electronic environment is quantified in a shielding constant, σ , which has contributions from both local diamagnetic and local paramagnetic shielding (σ_d^{loc} and σ_p^{loc} , respectively) as well as shielding due to

remote currents (σ'), such that,

$$\sigma = \sigma_{\text{d}}^{\text{loc}} + \sigma_{\text{p}}^{\text{loc}} + \sigma'. \quad (2)$$

NMR resonances are conventionally expressed in term of chemical shifts, δ , a unitless parameter which accounts for the relative shielding of a particular nucleus compared with that of a reference nucleus,

$$\delta = \frac{\sigma_{\text{ref}} - \sigma}{1 - \sigma_{\text{ref}}} \times 10^6.$$

- (a) Explain whether the $\sigma_{\text{d}}^{\text{loc}}$ and $\sigma_{\text{p}}^{\text{loc}}$ terms in eq. (2) are positive or negative and hence describe how these contributions affect the chemical shifts in an NMR spectrum. **[5]**
- (b) For spherically symmetrical charge distributions, the local diamagnetic shielding can be calculated explicitly as,

$$\sigma_{\text{d}}^{\text{loc}} = \frac{e^2 \mu_0}{2m_e} \int_0^\infty r \rho(r) dr,$$

where $\rho(r) = \psi^2$ is the electron density at a radical distance r from the nucleus and μ_0 is the magnetic constant ($= 4\pi \times 10^{-7} \text{ J s}^2 \text{ C}^{-2} \text{ m}^{-1}$).

- i. Using the H-atom 1s wavefunction, $\psi_{1s}(r) = (1/[\pi a_0^3])^{1/2} e^{-r/a_0}$, in which a_0 is the Bohr radius ($= 0.529 \times 10^{-10} \text{ m}$), calculate the shielding constant for the proton in the free H atom. **[8]**

Note:

$$\int_0^\infty x^n e^{-bx} dx = \frac{n!}{b^{n+1}}; \quad (n \geq 0, b > 0).$$

- ii. The shielding constants, σ , for the free atoms ^3He , ^{21}Ne , and ^{129}Xe are 60, 547, and 6938 ppm, respectively. Account qualitatively for this trend. **[3]**

The local paramagnetic contribution to shielding takes the form

$$\sigma_{\text{p}}^{\text{loc}} = \frac{b}{\Delta E} \langle r^{-3} \rangle,$$

in which b is a constant and ΔE is the HOMO-LUMO energy gap. Against a reference of $[\text{Ru}(\text{CN})_6]^{4-}$, the ^{99}Ru chemical shifts for a series of octahedral low-spin d^6 ruthenium complexes are given in the table below with the $^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$ transition energies, ΔE .

Complex ion	δ/ppm	$\Delta E/10^3 \text{ cm}^{-1}$
$[\text{Ru}(\text{OH}_2)_6]^{2+}$	16050	18.9
$[\text{Ru}(\text{NH}_2)_6]^{2+}$	7820	25.6
$[\text{Ru}(\text{en})_3]^{2+}$	6600	27.0
$[\text{Ru}(\text{CN})_6]^{4-}$	0	40.0

- (c) i. Explain briefly why the paramagnetic shielding is inversely proportional to the HOMO-LUMO energy gap. [3]
- ii. Graphically, or otherwise, show that the chemical shift of the ^{99}Ru complexes is dominated by the paramagnetic contributions to shielding. [6]

9. [Based on PART IB 2015]

- (a) Define the chemical shift in the context of proton NMR-spectroscopy of molecular species in solution and discuss its physical origins. [5]
- (b) What is the ring current effect? Illustrate your answer with one or more example(s), discussing both shielding and deshielding effects. [4]
- (c) Discuss the physical origins of spin-spin coupling in proton NMR. [4]
- (d) Sketch the proton NMR spectrum for $\text{CH}_3\text{CH}_2\text{CH}_2\text{NO}_2$, identifying the key features. [4]
- (e) What are the advantages of using a large applied magnetic field in NMR? [4]
- (f) Explain spin-lattice relaxation. Comment on the observation that the ^1H spin-lattice relaxation time of liquid water increases with increasing temperature. [4]