

Handed Out: Friday 2015/03/13
 Due: Tuesday 2015/03/24 (before class)

INSTRUCTIONS

When solving the problems on this exam, you are to work alone. You may refer only to your own notes, this year's problem set solutions, and the class texts. You may not discuss exam questions with anyone except me.

Before beginning this exam, you will read carefully the Cornell Code of Academic Integrity,

<http://cuinfo.cornell.edu/aic.cfm>.

The code is short and clear but a too long to memorize. The Caltech honor code nicely summarizes how I expect you to behave. Paraphrased for Cornell, it reads

No member of the Cornell community shall take unfair advantage of any other member of the Cornell community.

Kindly commit this one-line honor code to memory.

You may now begin the exam. Please give all answers in SI-mks, not cgs, units.

I. MAGNETIC RESONANCE SIGNAL FROM ^{14}N , A SPIN $I = 1$ NUCLEUS

Most of the nuclear spins that chemists encounter in magnetic resonance experiments have a total angular momentum of $I = 1/2$: ^1H , ^{13}C , and ^{19}F , for example. One exception is ^{14}N , the primary isotope of nitrogen ($I = 1$; abundance = 99.6%); because of its presence in proteins, ^{14}N is an important nuclear spin to know about. Step outside of organic chemistry and into materials science, and you are confronted with the fact that *most* nuclei in the period table have total angular momentum $I \geq 1$ [[link](#)].

An applied magnetic field splits the nuclear spin energy levels of all spins (the Zeeman interaction). Spins with $I \geq 1$ experience an additional splitting from *electric field gradients* that arise from an asymmetry in the electronic charge in the vicinity of the nucleus (the quadrupole interaction). The objective of this problem is to understand the nuclear magnetic resonance signal arising from a spin $I = 1$ nucleus whose energy levels are perturbed by the Zeeman and quadrupole interactions.

A spin $I = 1$ particle like ^{14}N has three nuclear-spin energy levels. In the few-tesla magnetic fields used in modern

magnetic resonance experiments, the energy levels are primarily governed by the Zeeman interaction, whose Hamiltonian in the laboratory frame of reference is

$$\mathcal{H}_Z = \gamma B_0 I_z = \omega_0 I_z \quad (1)$$

where γ is the gyromagnetic ratio and ω_0 is the Larmor frequency, respectively, of the nuclear spin. Nuclei with spin $I \geq 1$ have non-spherically-symmetric charge distributions. As a result, the so-called quadrupole interaction between the spin $I \geq 1$ nucleus and an electric field gradient at the site of the nucleus will perturb the spin energy levels. In the rotating frame of reference defined by the radiation-interaction representation, the Zeeman plus quadrupole interaction takes the form

$$\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_Q = \Delta\omega I_z + \omega_Q(3I_z^2 - \mathbf{I} \cdot \mathbf{I}) \quad (2)$$

where $\Delta\omega = \omega_0 - \omega$ is the resonance offset and ω_Q is the quadrupole coupling constant, which depends on the electric quadrupole moment of the nucleus, the total angular momentum quantum number I of the nuclear spin, and the local electric field gradient.

We want to understand the time evolution of the magnetization of an $I = 1$ (e.g., three level) nuclear spin described by Eq. 2. We will consider magnetization evolution following a $\pi/2$ pulse (free evolution) and the evolution during the application of radiofrequency irradiation (transient nutation).

1. Write down the 3×3 spin angular momentum matrices for I_x , I_y , and I_z for an $I = 1$ nucleus.
2. Consider evolution of the spin's density operator ρ under the Hamiltonian of Eq. 2 following a $(\pi/2)_y$ pulse. Write down an expression — don't try to carry out the unitary rotations analytically — for ρ at time t after the pulse. Take the initial density operator prior to the pulse to be I_z and take signal to be

$$S(t) = e^{-t/T_2} \text{Tr}[\rho(t)(I_x + iI_y)] \quad (3)$$

where T_2 is a damping parameter, which we introduce here *ad hoc* in order to yield a finite-width spectrum. Calculate the signal numerically from time $t_{\text{init}} = 0$ to $t_{\text{final}} = 2$ s in steps of $\Delta t = 0.001$ s. Take

$$\Delta\omega = 2\pi \times 200 \text{ Hz}$$

$$\omega_Q = 2\pi \times 25 \text{ Hz}$$

$$T_2 = 0.20 \text{ s}$$

Plot $\text{Re}[S]$ and $\text{Im}[S]$ versus time t [s].

3. Take the numerical Fourier transform of the free-evolution signal to get a free-evolution spectrum $\hat{S}(f)$. Plot $\text{Abs}[S]$ versus frequency f [Hz]. Rationalize the presence of the doublet in the spectrum, explaining both the center frequency of the doublet and the line splitting. What is the line splitting and how is it related to ω_Q ?

4. Consider the evolution of the equilibrium density operator I_z under irradiation with on-resonance rf in the presence of a non-zero quadrupole coupling. The relevant rotating-frame Hamiltonian on resonance is

$$\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_Q + \mathcal{H}_{\text{rf}} = \omega_1 I_x + \omega_Q(3I_z^2 - \mathbf{I} \cdot \mathbf{I}) \quad (4)$$

Taking $\omega_1 = 2\pi \times 250$ Hz and the other parameters as above, numerically calculate the signal

$$S(t) = e^{-t/T_2} \text{Tr} [\rho(t) I_y] \quad (5)$$

Plot $S(t)$ and $\hat{S}(f)$. Rationalize the doublet center frequency. How is the splitting in this spectrum related to ω_Q ?

II. RELAXATION OF ELECTRONIC EXCITED STATES INDUCED BY SOLVENT FLUCTUATIONS

An aromatic molecule absorbs light and an electron in the molecule is promoted from a π to a π^* orbital. As estimated in class following our discussion of the Einstein coefficients, the electron in the π^* orbital will radiatively decay to the ground-state π orbital in a few nanoseconds typically. In a polar solvent, however, the decay can be accelerated by stochastic electric fields arising from fluctuations in the positions and angles of the surrounding solvent molecules.

The goal of the following calculation is to develop an approximate formula for estimating the solvent-induced non-radiative decay time. To estimate the order of magnitude of the effect and its dependence on solvent polarity and the radius of the π conjugated molecule, we will model the solvent as a collection of electrostatic dipoles fixed in space, undergoing rotational diffusion.

To begin, consider an aromatic molecule with a (ground state) highest occupied molecular orbital (HOMO) described in Dirac notation by the ket $|g\rangle$ and an (excited state) lowest unoccupied molecular orbital (LUMO) described by the ket $|e\rangle$. The energy levels are described by the empirical Hamiltonian

$$\mathcal{H}_0 = (\omega_e - \omega_g) I_z \quad (6)$$

where

$$I_z = \frac{1}{2} (|e\rangle\langle e| - |g\rangle\langle g|). \quad (7)$$

Here $\hbar\omega_g$ is the energy of the HOMO and $\hbar\omega_e$ is the energy of the LUMO. The interaction of these two levels with the environment may be described by the Hamiltonian

$$\mathcal{H}_{\text{int}} = -\frac{\mathbf{E} \cdot \boldsymbol{\mu}_{ge}}{\hbar} I_x \quad (8)$$

where

$$I_x = \frac{1}{2} (|e\rangle\langle g| + |g\rangle\langle e|). \quad (9)$$

Here \mathbf{E} is the electric field, $\boldsymbol{\mu}_{ge} = -q_e \langle g | \mathbf{r} | e \rangle$ the molecule's transition dipole, q_e is the charge of the electron, and \mathbf{r} is the position operator of the electron. The transition dipole is a triple of numbers which depends on the details of the ground and excited-state wavefunctions as well as on the orientation of the molecule.

Let us model the aromatic molecule as a sphere of radius r_0 located at the origin. Take the molecule's transition dipole moment to be oriented along the z axis: $\boldsymbol{\mu}_{ge} = \mu_{ge} \hat{z}$, with p the magnitude of the transition dipole.

An applied electric field oscillating at the resonance frequency $\omega_e - \omega_g$ can be used to induce transitions between the HOMO and the LUMO levels in the same way that an oscillating magnetic field is employed to induce transitions between energy levels in the spin-1/2 two-level system. Suppose that the aromatic molecule has been prepared in the excited state. A *fluctuating* electric field due to the molecule's environment, by analogy with spin-lattice relaxation, will cause the aromatic molecule to return to the (thermal equilibrium) ground state. The goal of this problem is to calculate the $|e\rangle \rightarrow |g\rangle$ relaxation rate for an aromatic solute molecule interacting with a surrounding bath of polar solvent molecules.

We will model the solvent as a continuum of "wiggling" electric dipoles. Consider first a single solvent dipole, located at a distance r from the aromatic solute molecule (which is at the origin). Let the direction of \mathbf{r} be described by the polar angles (θ, ϕ) . The solvent dipole \mathbf{p} has magnitude p and an orientation described by the polar angles (θ', ϕ') . The electric field seen by the solute molecule due to the solvent molecule at \mathbf{r} is

$$\mathbf{E} = \frac{1}{4\pi\epsilon_0\epsilon_s} \frac{3(\mathbf{p} \cdot \hat{\mathbf{r}})\hat{\mathbf{r}} - \mathbf{p}}{r^3} \quad (10)$$

with ϵ_0 the permittivity of free space and ϵ_s the relative dielectric constant of the solvent. Here

$$\mathbf{p} = p (\sin \theta' \cos \phi', \sin \theta' \sin \phi', \cos \theta') \quad (11)$$

$$\hat{\mathbf{r}} = (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta) \quad (12)$$

Since the solute's transition dipole is taken to lie along the z axis, we are only interested in E_z .

1. Give an expression for E_z .
2. Now let the solvent dipole "wobble" about its equilibrium orientation,

$$\theta' \rightarrow \theta'(t) = \theta'_{\text{eq}} + \delta\theta'(t) \quad (13)$$

$$\phi' \rightarrow \phi'(t) = \phi'_{\text{eq}} + \delta\phi'(t) \quad (14)$$

where θ'_{eq} and ϕ'_{eq} determine the equilibrium orientation of the solute dipole and $\delta\theta'(t)$ and $\delta\phi'(t)$ represent fluctuations in the orientation of the solvent's electric dipole moment. Expand E_z in a Taylor series to first order about $\delta\theta' = 0$ and $\delta\phi' = 0$. Write the expansion as

$$E_z(t) = e_0 + e_\theta \delta\theta'(t) + e_\phi \delta\phi'(t) \quad (15)$$

where e_θ and e_ϕ are functions of θ , ϕ , θ'_{eq} , and ϕ'_{eq} . Give formulas for e_θ and e_ϕ .

3. Inserting this stochastic electric field into Eq. 8 will yield a fluctuating interaction Hamiltonian that can drive relaxation of the electron from the π^* to the π orbital. In the interaction representation, the resulting stochastic Hamiltonian is

$$\tilde{\mathcal{H}}_{\text{int}} = \frac{E_z(t)\mu_{ge}}{\hbar} (I_x \cos(\omega_0 t) + I_y \sin(\omega_0 t)) \quad (16)$$

where $\omega_0 = \omega_e - \omega_g$. Use BPP theory to derive

$$\frac{d}{dt} \langle I_z \rangle = -k_1 (\langle I_x \rangle - \langle I_z \rangle_{\text{eq}}) \quad (17)$$

and give an equation for $k_1 [\text{s}^{-1}]$ due to a single solvent molecule in terms of

- μ_{ge} and \hbar ;
 - the correlation functions $C_{\delta\theta'}(\tau)$ and $C_{\delta\phi'}(\tau)$, ω_0 , and τ ; and
 - e_θ and e_ϕ .
4. Derive an expression for e_θ^2 and e_ϕ^2 due to a shell of randomly-oriented solvent molecules located at a distance r from the solute by integrating θ over $(0, \pi)$, θ'_{eq} over $(0, \pi)$, ϕ over $(0, 2\pi)$, and ϕ'_{eq} over $(0, 2\pi)$.
5. Use this result to write down an equation for k_1 due to a shell of solvent molecules in terms of
- μ_{ge} , \hbar , p , ϵ_0 , and r ; and
 - the correlation functions $C_{\delta\theta'}(\tau)$ and $C_{\delta\phi'}(\tau)$, ω_0 , and τ .
6. Finally, integrate the above k_1 (weighted by the number of molecules in each shell) over r from r_0 (the solute radius) to ∞ . Note that the number of molecules in each shell is $r^2 dr [\text{m}^3]$ times the density of molecules per shell, $\rho_{\text{molec}} [\text{m}^{-3}]$. The resulting k_1 is the $|e\rangle \rightarrow |g\rangle$ decay rate due relaxation from a continuum of wiggling solvent dipoles. Be sure to check that the units work in your expression for k_1 .
7. Let the rotational correlation time of the solvent be τ_c . Assuming for the sake of simplicity large-angle motions, the angle correlation functions may be written

approximately as

$$C_{\delta\theta'}(\tau) \approx \pi^2 e^{-\tau/\tau_c} \quad (18)$$

$$C_{\delta\phi'}(\tau) \approx 4\pi^2 e^{-\tau/\tau_c} \quad (19)$$

Substitute these correlation functions into your expression for k_1 above and simplify the result. Report an answer for the non-radiative decay rate k_1 in terms of the solvent rotational correlation time τ_c .

8. Propose experiments to test the predicted decay rate.

MATHEMATICA TIPS

- In evolving the density matrix numerically, use the function `MatrixExp[]` to exponentiate $\pm i\mathcal{H}t$. Do not use `Exp[]`.
- The command `Table[]` is useful for generating a list of numerical data that can be plotted using the command `ListPlot[]`. If you want the data to be joined by a line, use the option `Joined -> True`; another useful option is `PlotMarkers`. Please label your axes using the `ListPlot` option `AxesLabel`.
- The function `Fourier[]` will compute the numerical Fourier transform of a list of numbers. The numbers are however returned in a funny order. The $f = 0$ point is the first point in the returned list, for example. The function `RotateLeft[]` is helpful for reordering the transformed data to run from negative frequency to positive frequency, with the zero-frequency point in the middle of the spectrum.
- The function `Ordering[]` can be used to help pick out the peaks in a spectrum.