Analytical Chemistry Cumulative - October 2011 by Yoshitaka Ishii

Total 113 points. The pass line is ~70 points. Points may be scaled by an adequate scaling function. Unless otherwise mentioned, answer each question concisely using no more than one paragraph and 5 equations.

1. Basic NMR Questions. Total 46 points. Answer the following questions briefly. (a-f) 6 points each (g) 10 points

(a) Write a diagram of the energy due to the interaction between the spin magnetic moment $\mu = \gamma\hbar\mathbf{I}$ and a magnetic field $\mathbf{B}_0$ (assume that B_0 is applied along the z axis) for a spin-half system ($I_z = ½$ or -1/2). Explain how the NMR transition energy is affected by B_0 and the type of nuclei.

(b) What is "shim" or "shimming" used in NMR? Explain its main functions, and describe how it works.

(c) What is "sensitivity"? Explain how is this related to "S/N" and "experimental time".

(d) Bloch equation describes a motion of a magnetic moment $\mathbf{M}(t)$ in a magnetic field $\mathbf{B}(t)$. The equation is given by $(d\mathbf{M}(t)/dt) = \mathbf{M}(t) \times \gamma\mathbf{B}(t)$. What is the expected motion of $\mathbf{M}(t)$ under the following $\mathbf{B}$ and $\mathbf{M}(0)$ defined by $-\gamma\mathbf{B} = [0, \omega_1, 0]$ $\mathbf{M}(0) = [0, 0, M_0]$?

(e) Explain how an NMR spectrum is obtained in FT NMR? Use terms such as FID, FT, pulse, and rf.

(f) Explain how an NMR spectrum is obtained in cw NMR? Why was cw NMR replaced by FT NMR. List two answers.

(g) Draw a diagram of a typical hardware for a NMR spectrometer and explain how the instrument works with explanation for, at least, 5 elements of the instrument.

2. Basic Quantum Mechanics & Spin Operators. Total 35 points. (a-e) 5 each & (f) 10 points. Assume spin operator matrixes I_X, I_Y, I_Z are given by

$$I_X = \begin{pmatrix} 0 & 1/2 \\ 1/2 & 0 \end{pmatrix} I_y = \begin{pmatrix} 0 & -i/2 \\ i/2 & 0 \end{pmatrix} I_z = \begin{pmatrix} 1/2 & 0 \\ 0 & -1/2 \end{pmatrix}, E = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

(a) Prove $[I_Z, I_Y] = -iI_X$, where $[A,B] = AB - BA$.

(b) What are eigen values a_n for I_z? Write an eigen ket $|\psi_n\rangle$ in a vector form for each of eigen value?

(c) Probe $I_X I_Y = [I_Z, I_Y]/2$ and $Tr(I_X I_Y) = 0$, where Tr(A) is the sum of the diagonal elements of A.

(d) Calculate $[I_X, I_X^2 + I_Y^2 + I_Z^2]$ in the matrix representation.

(e) Prove $(I_Y)^{2m} = (1/2)^{2m}E$ and $(I_Y)^{2m+1} = (1/2)^{2m+1}(2I_Y)$, where m is an integer number (m = 0, 1, 2, ...)

(f) Probe $\exp(-i\phi I_Y) = E\cos(\phi/2) - i(2I_Y)\sin(\phi/2)$,
where $\exp(A) = \Sigma(A)^n/n!$. Hint: use (c) and $\exp(-i\phi/2) = \cos(\phi/2) - i\sin(\phi/2)$

3. Fourier Transform Total 26 points. (a, b) 10 points (c) 6 point

Fourier transform (FT) of a time signal s(t) is given by

$$f(\omega) = \int_0^\infty dt s(t) \exp(i\omega t).$$

(a) When s(t) = exp(-iΩt)exp(-λt), prove that

$$f(\omega) = \frac{\lambda}{(\Omega-\omega)^2+\lambda^2} + i\frac{(\Omega-\omega)}{(\Omega-\omega)^2+\lambda^2},$$

where exp(-λt) denotes a decay of a signal and λ denotes a relaxation rate.

(b) Draw an approximate graph of A(ω) = Real[f(ω)] and D(ω) = Imag[f(ω)], which represent real and imaginary component of f(ω), respectively. Use λ = 20 Hz, Ω = 100 Hz from 0 Hz ≤ ω ≤ 200 Hz.

(c) Explain what is discrete Fourier transform (or FT for discretely sampled data). Discuss what is "Nyquist frequency" in discrete FT?

4. Novel Prize in Chemistry 6 points

Who received the Novel Prize in Chemistry this year? What is his contribution to the field?