Analytical Chemistry Cumulative --- March 2016
by Yoshitaka Ishii

Total 100 points. The pass line is ~70 points. Points may be scaled by an adequate scaling function. Unless specified, answer each question concisely using no more than one paragraph and 5 equations.

1. **FT NMR and cw NMR**

(a) 9 points, (b) 9 points, (c) 7 points

(a) Explain the principle of cw NMR. How is the experiment performed? List three key elements.
(b) Explain the principle of FT NMR. What kind of experimental requirements that are not found in cw NMR are demanded in the FT NMR experiment? List three elements and explain the principle.
(c) Explain why FT NMR nearly completely replaced cw NMR. List two reasons.

2. Bloch equation in a rotating frame

(a) 6 points, (b) 6 points, (c) 6 points, (d) 7 points.

The Bloch equation describes a motion of a magnetic moment $\mathbf{M}$(t) in an effective magnetic field $\mathbf{B}_{\mathbf{eff}}$(t) in a rotating frame as follows: $(d\mathbf{M}(t)/dt) = \mathbf{M}(t) \times \gamma\mathbf{B}_{\mathbf{eff}}(t)$. What is the expected motion of $\mathbf{M}$(t) under the following $\mathbf{B}_{\mathbf{eff}}$ and $\mathbf{M}$(0) defined in (a-d)? Explain the motions with equations and draw a vector motion.

(a) $-\gamma\mathbf{B}_{\mathbf{eff}} = [0, 0, \Omega]$ & $\mathbf{M}(0) = [0, 0, M_0]$

(b) $-\gamma\mathbf{B}_{\mathbf{eff}} = [0, 0, \Omega]$ & $\mathbf{M}(0) = [M_0, 0, 0]$

(c) $-\gamma\mathbf{B}_{\mathbf{eff}} = [\omega_1, 0, 0]$ & $\mathbf{M}(0) = [0, 0, M_0]$

(d) $-\gamma\mathbf{B}_{\mathbf{eff}} = [0, 0, \Omega]$ & $\mathbf{M}(0) = [M_1, M_2, M_3]$

3. Quantum mechanical rotating operator

(a) 9 points, (b) 9 points, (c) 7 points

Suppose that $\exp(\lambda A) = \sum_{n=0}^{\infty} \frac{\lambda^n}{n!} A^n$ for a matrix A and a complex number λ, and

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

(a) Confirm that the following equation is correct with a proof.

$$\exp(-i\alpha I_Y) = E\cos(\alpha/2) - i2I_Y\sin(\alpha/2),$$

where α is a real number denoting an angle.

(b) Answer whether the following equation is correct or not. If it is correct, prove that it is correct. If not, derive a correct equation with a proof. You can use the results of (a).

$$\exp(-i\alpha I_Y)\, I_Z \exp(i\alpha I_Y) = I_z\cos\alpha - I_X\sin\alpha$$

(c) Prove

$$\exp(-i\alpha I_Z)\, I_X \exp(i\alpha I_Z) = I_X\cos\alpha + I_Y\sin\alpha$$

4. Unitary transformation of a system in quantum mechanics and transformation of Hamiltonian

(a) 9 points, (b) 9 points, (c) 7 points.

A unitary transformation U from a laboratory frame to a new rotating frame on a state ket is given by

$$|\psi(t)^R> = U|\psi(t)> , \qquad [1]$$

where $|\psi(t)^R>$ and $|\psi(t)>$ denote state kets in the rotating frame and laboratory frame, respectively.

Now, Liouville-von Neuman equation for the density operator in the laboratory frame is given by

$$d\sigma(t)/dt = i[\sigma(t),\ H] \qquad [2]$$

with

$$\sigma(t) = |\psi(t)><\psi(t)|,$$

The corresponding equation for the rotating frame is given by

$$d\sigma^R(t)/dt = i[\sigma^R(t),\ H_e], \qquad [3]$$

where

$$\sigma^R(t) = |\psi(t)^R><\psi(t)^R|. \qquad [4]$$

The effective Hamiltonian in the rotating frame is give by

$$H_e = U(t)HU^{-1}(t) - iU(t)\{dU^{-1}(t)/dt\}. \qquad [5]$$

Now, suppose U denotes a rotation along the z-axis at an angular frequency of ω_{RF} as

$$U(t) = R_Z(t) = \exp(i\omega_{RF}I_Z t) \qquad [6]$$

$$U^{-1}(t) = R_Z^{-1}(t) = \exp(-i\omega_{RF}I_Z t) \qquad [7]$$

(a) Prove $iU(t)\{dU^{-1}(t)/dt\} = \omega^{RF}I_Z$.
(b) When $H= \omega_0 I_Z$, calculate H_e using eq. [5] and the results of (a).
(c) When $H = \omega_0 I_z + 2\omega_1 I_x\cos(\omega_{rf}t)$, derive a static (time-independent) part of the Hamiltonian for H_e.

Hint: You can use $2\omega_1 I_x\cos(\omega_{rf}t) = \omega_1\{R_Z(t)I_X R_Z^{-1}(t) + R_Z^{-1}(t)I_X R_Z(t)\}$
where $R_Z^{-1}(t) = U^{-1}(t)= \exp(-i\omega_{RF}I_Z t)$.

A few useful relationships:

- For a real number a

$$\exp(ia)=\sum_{n=0}^{\infty}\frac{(ia)^n}{n!}=\sum_{m=0}^{\infty}\frac{(ia)^{2m}}{2m!}+\frac{(ia)^{2m+1}}{(2m+1)!}=\sum_{m=0}^{\infty}(-1)^m\frac{(a)^{2m}}{2m!}+i\sum_{m=0}^{\infty}(-1)^m\frac{(a)^{2m+1}}{(2m+1)!}=\cos(a)+i\sin(a)$$

- An arbitarary unitary operator P is given by P = exp(-iA), where A is an Hermitian operator.
$P^{-1} = \exp(iA)$. $PP^{-1} = P^{-1}P = E$

- When f(A) is a polynomial of A, [A, f(A)] = 0, where [A, B] = AB – BA.