L-Università ta' Malta

Department of Chemistry
Faculty of Science

B.Sc. (Hons.) Year I

Semester 2 Examination Session

CHE1217: Additional Techniques of Chemical Calculations — 20th June 2022, 08:30–10:35

Instructions

Read the following instructions carefully.

- Attempt only **TWO** questions.
- Each question carries **50** marks. The maximum mark is **100**.
- A list of mathematical formulae is provided on page 2.
- Only the use of non-programmable calculators is allowed.

MATHEMATICAL FORMULÆ

ALGEBRA

Factors

$$a^3 + b^3 = (a+b)(a^2 - ab + b^2)$$
$$a^3 - b^3 = (a-b)(a^2 + ab + b^2)$$

Quadratics

If $ax^2 + bx + c$ has roots α and β,

$$\Delta = b^2 - 4ac$$
$$\alpha + \beta = -\tfrac{b}{a} \qquad \alpha\beta = \tfrac{c}{a}$$

Finite Series

$$\sum_{k=1}^{n} 1 = n \qquad \sum_{k=1}^{n} k = \frac{n(n+1)}{2}$$
$$\sum_{k=1}^{n} k^2 = \frac{k(k+1)(2k+1)}{6}$$
$$(1+x)^n = \sum_{k=0}^{n} \binom{n}{k} x^n$$
$$= 1 + nx + \tfrac{n(n-1)}{2\cdot 1}x^2 + \cdots + x^n$$

GEOMETRY & TRIGONOMETRY

Distance Formula

If $A = (x_1, y_1)$ and $B = (x_2, y_2)$,

$$d(A,B) = \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2}$$
$$= \sqrt{\Delta x^2 + \Delta y^2}$$

Pythagorean Identity

$$\cos^2\theta + \sin^2\theta = 1$$

General Solutions

$$\cos\theta = \cos\alpha \iff \theta = \pm\alpha + 2\pi\mathbb{Z}$$
$$\sin\theta = \sin\alpha \iff \theta = (-1)^n\alpha + \pi n,\ n \in \mathbb{Z}$$
$$\tan\theta = \tan\alpha \iff \theta = \alpha + \pi\mathbb{Z}$$

CALCULUS

Derivatives

$f(x)$	$f'(x)$
x^n	nx^{n-1}
$\sin x$	$\cos x$
$\cos x$	$-\sin x$
$\tan x$	$\sec^2 x$
$\cot x$	$-\operatorname{cosec}^2 x$
$\sec x$	$\sec x \tan x$
$\operatorname{cosec} x$	$-\operatorname{cosec} x \cot x$
e^x	e^x
$\log x$	$1/x$
uv	$u'v + uv'$
u/v	$(u'v - uv')/v^2$

Integrals

$f(x)$	$\int f(x)\,dx$
$x^n\ (n \neq -1)$	$\frac{x^{n+1}}{n+1}$
$\sin x$	$-\cos x$
$\cos x$	$\sin x$
$\tan x$	$\log(\sec x)$
$\cot x$	$\log(\sin x)$
$\sec x$	$\log(\sec x + \tan x)$
$\operatorname{cosec} x$	$\log(\tan\frac{x}{2})$
e^x	e^x
$1/x$	$\log x$
$\frac{1}{a^2+x^2}$	$\frac{1}{a}\tan^{-1}\left(\frac{x}{a}\right)$
$\frac{x}{\sqrt{a^2+x^2}}$	$\sin^{-1}\left(\frac{x}{a}\right)$

Homogeneous Linear Second Order ODEs

If the roots of $ak^2 + bk + c$ are k_1 and k_2, then the differential equation $ay'' + by' + cy = 0$ has general solution

$$y(x) = \begin{cases} c_1 e^{k_1 x} + c_2 e^{k_2 x} & \text{if } k_1 \neq k_2 \\ c_1 e^{kx} + c_2 x e^{kx} & \text{if } k = k_1 = k_2 \\ e^{\alpha x}(c_1 \cos\beta x + c_2 \sin\beta x) & \text{if } k = \alpha \pm \beta i \in \mathbb{C} \end{cases}$$

Infinite Series

$$e^x = \sum_{n=0}^{\infty} \frac{x^n}{n!} = 1 + x + \frac{x^2}{2} + \frac{x^3}{3!} + \frac{x^4}{4!} \cdots$$
$$\cos x = \sum_{\substack{n=0 \\ n \text{ even}}}^{\infty} \frac{(-1)^{\frac{n}{2}}}{n!} x^n = 1 - \frac{x^2}{2} + \frac{x^4}{4!} - \cdots$$
$$\sin x = \sum_{\substack{n=1 \\ n \text{ odd}}}^{\infty} \frac{(-1)^{\frac{n-1}{2}}}{n!} x^n = x - \frac{x^3}{3!} + \frac{x^5}{5!} - \cdots$$
$$\log(1+x) = \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n} x^n = x - \frac{x^2}{2} + \frac{x^2}{3} - \cdots, \quad x \in (-1, 1]$$

⚠ Attempt only **TWO** questions.

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1. Consider the matrix

$$\mathbf{A} = \begin{pmatrix} -3 & 2 & 2 \\ 2 & 0 & -2 \\ -2 & 1 & a \end{pmatrix}.$$

(a) Find the inverse matrix $\mathbf{A}^{-1}$. State the value(s) of a for which your answer is valid.

(b) Consider the system of equations

$$\begin{cases} -3x + 2y + 2z = 1 \\ 2x \qquad\quad - 2z = 4 \\ -2x + \; y + az = b. \end{cases}$$

For what values of a and b does this system have:

(i) a unique solution?

(ii) infinitely many solutions?

(iii) no solutions?

(c) (i) Solve the system in (b) when $a = b = 1$.

(ii) Solve the system in (b) when $a = \frac{3}{2}$ and $b = -\frac{1}{2}$.

(d) For this part of the question, assume that $\mathbf{A}$ has $a = 1$.

(i) Find the eigenvalues of $\mathbf{A}$.

(ii) Hence, determine $\mathbf{P}$ and $\mathbf{D}$ such that $\mathbf{A} = \mathbf{PDP}^{-1}$, where $\mathbf{D}$ is a diagonal matrix. (You don't need to find $\mathbf{P}^{-1}$).

(iii) The functions $x(t)$, $y(t)$ and $z(t)$, are related by the differential equations

$$\begin{cases} x'(t) = -3x(t) + 2y(t) + 2z(t) \\ y'(t) = \;\; 2x(t) - 2y(t) \\ z'(t) = -2x(t) + \; y(t) + \; z(t). \end{cases}$$

Solve for $x(t)$, $y(t)$ and $z(t)$.

[12, 6, 7, 25 marks]

2. (a) The function f three variables x, y and z satisfies

$$\frac{\partial f}{\partial x} = 2xz + 3y \qquad \text{and} \qquad \frac{\partial f}{\partial z} = x^2 - 15y^2z^2.$$

Show that

$$f(x,y,z) = x^2z + 3xy - 5y^2z^3 + c(y),$$

where c is some function in y alone.

(b) (i) Suppose $f(x,y)$ is separable, i.e., we may write express f as a product $f(x,y) = X(x)Y(y)$. Explain why

$$\frac{\partial f}{\partial x} = \frac{dX}{dx}\,Y(y) \qquad \text{and} \qquad \frac{\partial f}{\partial y} = X(x)\,\frac{dY}{dy}.$$

(ii) Suppose f is a function of two variables x and y, and that

$$\frac{\partial f}{\partial x} + x^2\frac{\partial f}{\partial y} = 0.$$

Determine the general solution, assuming it is separable.

(c) (i) If $f(x,y)$ is separable, show that

$$\nabla^2 f = \frac{d^2X}{dx^2}Y(y) + X(x)\frac{d^2Y}{dy^2}.$$

(ii) The Schrödinger equation for a particle of mass m moving in the two-dimensional xy-plane is

$$-\frac{\hbar^2}{2m}\nabla^2\Psi = E\Psi,$$

where $\hbar$ and E are constants, ∇^2 is the Laplacian operator, and $\Psi = \Psi(x,y)$ is the wave function. Assuming the solutions is separable, and that $X(0) = Y(0) = X(a) = Y(b) = 0$, show that

$$\Psi(x,y) = C\sin\left(\frac{m\pi}{a}x\right)\sin\left(\frac{n\pi}{b}y\right),$$

where C is some constant.

[10, 15, 25 marks]

3. (a) The Fibonacci numbers F_n are defined by the recurrence relation

$$\begin{pmatrix} F_{n+1} \\ F_n \end{pmatrix} = \begin{pmatrix} F_n + F_{n-1} \\ F_n \end{pmatrix},$$

where $\binom{F_1}{F_0} = \binom{1}{0}$.

The *golden ratio* φ is the number $\frac{1}{2}(1+\sqrt{5})$.

(i) Show that

$$1-\varphi = -\frac{1}{\varphi} = \frac{1}{2}(1-\sqrt{5}) \qquad \text{and} \qquad 2\varphi - 1 = \sqrt{5}.$$

(ii) If $\mathbf{x}_n = \binom{F_{n+1}}{F_n}$, show that $\mathbf{x}_n = \mathbf{A}\mathbf{x}_{n-1}$ for an appropriate 2×2 matrix $\mathbf{A}$.

(iii) By diagonalising $\mathbf{A}$, solve the recurrence relation and deduce that

$$F_n = \frac{1}{\sqrt{5}}\left(\varphi^n - \left(-\frac{1}{\varphi}\right)^n\right).$$

[Hint: Use φ in your working to keep it simple.]

(iv) Show that

$$\frac{F_{n+1}}{F_n} = \frac{\varphi - \frac{1}{\varphi^n(-\varphi)^{n+1}}}{1 - \frac{1}{\varphi^n(-\varphi)^n}},$$

and deduce that $\frac{F_{n+1}}{F_n} \to \varphi$ as $n \to \infty$.

(b) Let $\mathbf{R}$ be the matrix which rotates vectors in 3D by an anticlockwise rotation of θ around the z-axis.

(i) Find $\mathbf{Ri}$, $\mathbf{Rj}$ and $\mathbf{Rk}$, where $\mathbf{i}$, $\mathbf{j}$ and $\mathbf{k}$ are the unit vectors in the x-, y- and z-directions respectively.

(ii) Hence, show that

$$\mathbf{R} = \begin{pmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

(iii) Show that $\det(\mathbf{R}) = 1$. What does this mean, geometrically?

[35, 15 marks]

Solutions

1. (a) $\mathbf{A}^{-1} = \dfrac{1}{2(2a-3)}\begin{pmatrix} -2 & 2a-2 & 4 \\ 2a-4 & 3a-4 & 2 \\ -2 & 1 & 4 \end{pmatrix}$, valid for when $a \neq \frac{3}{2}$.

   (b) The system is just $\mathbf{A}\mathbf{x} = \mathbf{b}$, where $\mathbf{x} = (x, y, z)$ and $\mathbf{b} = (1, 4, b)$.

   (i) We get a unique solution when $\mathbf{A}$ is invertible, i.e., when $a \neq \frac{3}{2}$. In this case, b can be anything.

   (ii) Infinitely many solutions occur when $\mathbf{A}$ is not invertible, i.e., when $a = \frac{3}{2}$. Doing Gaussian elimination on the augmented matrix $(\mathbf{A} \mid \mathbf{b})$ with $a = \frac{3}{2}$, one possible sequence of steps gives

$$\left(\begin{array}{ccc|c} -3 & 2 & 2 & 1 \\ 2 & 0 & -2 & 4 \\ -2 & 1 & \frac{3}{2} & b \end{array}\right) \xrightarrow[R_3+\frac{1}{4}R_2 \to R_3]{\substack{R_2+\frac{2}{3}R_1 \to R_2 \\ R_3+\left(-\frac{2}{3}\right)R_1 \to R_3}} \left(\begin{array}{ccc|c} -3 & 2 & 2 & 1 \\ 0 & \frac{4}{3} & -\frac{2}{3} & \frac{14}{3} \\ 0 & 0 & 0 & b+\frac{1}{2} \end{array}\right)$$

   The last row corresponds to the equation $0x + 0y + 0z = b + \frac{1}{2}$, which has solutions when $b = -\frac{1}{2}$. Thus, for infinitely many solutions, we need $a = \frac{3}{2}$ and $b = -\frac{1}{2}$.

   (iii) From the previous part, we see that if $a = \frac{3}{2}$ but $b \neq -\frac{1}{2}$, then the system is inconsistent, and we get no solutions.

   (c) (i) When $a = b = 1$, the matrix $\mathbf{A}$ is invertible, so the solution is just $\mathbf{x} = \mathbf{A}^{-1}\mathbf{b} = (-1, 2, -3)$, i.e., $x = -1$, $y = 2$, and $z = -3$.

   (ii) This is the case of infinitely many solutions. With reference to part (b)(ii), we have two restrictions on the three variables x, y and z. Letting $z = \lambda \in \mathbb{R}$, then R_2 gives

$$\frac{4}{3}y - \frac{2}{3}\lambda = \frac{14}{3} \implies y = \frac{7+\lambda}{2},$$

   and then R_1 gives

$$-3x + 2\left(\frac{7+\lambda}{2}\right) + 2\lambda = 1 \implies x = \frac{6+\lambda}{3}.$$

   Therefore, the system has the general solution $x = \frac{1}{3}(6+\lambda)$, $y = \frac{1}{2}(7+\lambda)$, and $z = \lambda$ for any $\lambda \in \mathbb{R}$.

(d) (i) We have the characteristic polynomial

$$\chi_{\mathbf{A}}(\lambda) = \det(\lambda \mathbf{I} - \mathbf{A}) = \lambda^3 + 2\lambda^2 - 2\lambda - 2 = (\lambda - 1)(\lambda + 1)(\lambda + 2),$$

so the eigenvalues are $\lambda = \pm 1, -2$.

(ii) We determine corresponding eigenvectors for each eigenvalue:

For $\lambda = 1$, $\mathbf{x} = (1, 2, 0)$,

For $\lambda = -1$, $\mathbf{x} = (1, 0, 1)$,

For $\lambda = -2$, $\mathbf{x} = (4, -1, 3)$.

Thus if we define $\mathbf{P} = \begin{pmatrix} 1 & 1 & 4 \\ 2 & 0 & -1 \\ 0 & 1 & 3 \end{pmatrix}$, we get

$$\mathbf{A} = \mathbf{P} \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -2 \end{pmatrix} \mathbf{P}^{-1}.$$

(iii) The given differential equations are equivalent to the matrix equation $\mathbf{\Omega} = \mathbf{A}\mathbf{x}$, where $\mathbf{x} = \mathbf{x}(t) = (x(t), y(t), z(t))$.

Using the diagonalised form, this is $\mathbf{\Omega} = \mathbf{P}\mathbf{D}\mathbf{P}^{-1}\mathbf{x}$, equivalently, $\mathbf{P}^{-1}\mathbf{\Omega} = \mathbf{D}\mathbf{P}^{-1}\mathbf{x}$. If we let $\mathbf{u} = \mathbf{P}^{-1}\mathbf{x}$, then this is $\mathbf{\Omega} = \mathbf{D}\mathbf{u}$, i.e.,

$$\begin{pmatrix} x'(t) \\ y'(t) \\ z'(t) \end{pmatrix} = \begin{pmatrix} x(t) \\ -y(t) \\ -2z(t) \end{pmatrix}.$$

In general, the differential equation $f'(t) = af(t)$ is equivalent to $\frac{f'(t)}{f(t)} = a$, and integrating both sides with respect to t, we get $\log(f(t)) = at + \log c$, i.e., $f(t) = c\, e^{at}$. So the vector differential equation above becomes

$$\begin{pmatrix} x(t) \\ y(t) \\ z(t) \end{pmatrix} = \begin{pmatrix} Ae^{t} \\ Be^{-t} \\ Ce^{-2t} \end{pmatrix},$$

and thus we've determined the solution $\mathbf{u}(t)$ of $\mathbf{\Omega} = \mathbf{D}\mathbf{u}$. Now to translate this into the desired solution $\mathbf{x}(t)$ of the original equation, we use the fact that $\mathbf{x} = \mathbf{P}\mathbf{u}$:

$$\mathbf{x}(t) = \mathbf{P}\mathbf{u}(t) = \begin{pmatrix} Ae^t + Be^{-t} + 4Ce^{-2t} \\ 2Ae^t \qquad\qquad - Ce^{-2t} \\ \qquad Be^{-t} + 3Ce^{-2t} \end{pmatrix},$$

i.e., the solution is

$$\begin{cases} x(t) = Ae^t + Be^{-t} + 4Ce^{-2t} \\ y(t) = 2Ae^t \qquad\quad - Ce^{-2t} \\ z(t) = \qquad\quad Be^{-t} + 3Ce^{-2t}. \end{cases}$$

2. (a) Integrating both derivatives gives the result.

(b) (i) By the product rule,

$$\begin{aligned} \frac{\partial f}{\partial x} &= \frac{\partial}{\partial x}\big(X(x)Y(y)\big) \\ &= \frac{\partial X}{\partial x}Y(y) + X(x)\frac{\partial Y}{\partial y} = \frac{dX}{dx}Y(y), \end{aligned}$$

and similarly for $\frac{\partial f}{\partial y}$.

(ii) Assuming $f = XY$, differential equation is

$$\frac{dX}{dx}Y + x^2X\frac{dY}{dy} = 0,$$

which rearranges into

$$\frac{1}{x^2X}\frac{dX}{dx} + \frac{1}{Y}\frac{dY}{dy} = 0,$$

and so we must have

$$\frac{1}{x^2X}\frac{dX}{dx} = C \qquad \text{and} \qquad \frac{1}{Y}\frac{dY}{dy} = -C$$

for some constant C.

These are separable first order ODEs, which have solutions $X = Ae^{Cx^3/3}$ and $Y = Be^{-Cy}$ respectively. Thus we obtain the general solution $f = XY = ABe^{C(x^3/3-y)}$, or, if we relabel the constants,

$$f(x,y) = Ae^{C\left(\frac{x^3}{3}-y\right)}.$$

(c) (i) Similar to (b)(i), using the product rule twice.

(ii) By part (i), assuming $\Psi = XY$, the equation is just

$$\frac{d^2X}{dx^2}Y + X\frac{d^2Y}{dy^2} = -\frac{2mE}{\hbar^2}\Psi,$$

and dividing through by $\Psi = XY$, we get

$$\frac{1}{X}\frac{d^2X}{dx^2} + \frac{1}{Y}\frac{d^2Y}{dy^2} = -\frac{2mE}{\hbar^2}.$$

Thus we have

$$\frac{1}{X}\frac{d^2X}{dx^2} = -C_1 \qquad \text{and} \qquad \frac{1}{Y}\frac{d^2Y}{dy^2} = -C_2$$

where $C_1 + C_2 = 2mE/\hbar^2$. In other words,

$$X'' + C_1X = 0 \qquad \text{and} \qquad Y'' + C_2Y = 0.$$

These are second order differential equations with constant coefficients, and they have solutions

$$X = A\sin(\sqrt{C_1}x) \qquad \text{and} \qquad Y = B\sin(\sqrt{C_2}y)$$

respectively (notice the boundary conditions $X(0) = Y(0) = 0$ give the forms above).

Moreover, since $X(a) = 0$, we have $\sin(\sqrt{C_1}a) = 0$, so we must have $\sqrt{C_1}a = m\pi$ for some m, i.e., $\sqrt{C_1} = m\pi/a$. Similarly, since $Y(b) = 0$, we get that $\sqrt{C_2} = n\pi/b$ for some integer n.

Thus, relabelling AB with C, we get

$$\Psi = XY = C\sin\left(\frac{m\pi}{a}x\right)\sin\left(\frac{n\pi}{b}y\right).$$

3. (a) (i) Simple algebra.

(ii) We have

$$\mathbf{x}_n = \begin{pmatrix} 1 & 1 \\ 1 & 0 \end{pmatrix} \mathbf{x}_{n-1}.$$

(iii) The diagonalisation is

$$\mathbf{A} = \frac{1}{\sqrt{5}} \begin{pmatrix} \varphi & 1-\varphi \\ 1 & 1 \end{pmatrix} \begin{pmatrix} \varphi & 0 \\ 0 & 1-\varphi \end{pmatrix} \begin{pmatrix} 1 & \varphi - 1 \\ -1 & \varphi \end{pmatrix},$$

and since $\mathbf{x}_n = \mathbf{A}^n \mathbf{x}_0$, where $\mathbf{x}_0 = \binom{F_1}{F_0} = \binom{1}{0}$, we get

$$\begin{aligned} \mathbf{x}_n &= \frac{1}{\sqrt{5}} \begin{pmatrix} \varphi & 1-\varphi \\ 1 & 1 \end{pmatrix} \begin{pmatrix} \varphi^n & 0 \\ 0 & (1-\varphi)^n \end{pmatrix} \begin{pmatrix} 1 & \varphi - 1 \\ -1 & \varphi \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \\ \implies \begin{pmatrix} F_{n+1} \\ F_n \end{pmatrix} &= \frac{1}{\sqrt{5}} \begin{pmatrix} \varphi^{n+1} - (1-\varphi)^{n+1} \\ \varphi^n - (1-\varphi)^n \end{pmatrix}, \end{aligned}$$

and comparing the bottom entries gives the required formula.

(iv) This part is just a matter of simplifying the expression F_{n+1}/F_n using the formula. When $n \to \infty$, the terms in n go to zero, and we get that $F_{n+1}/F_n \to \varphi/1 = \varphi$.

(b) (i) For this question, a quick sketch or verbal argument suffices to obtain these coordinates.

$\mathbf{Ri} = (\cos\theta, \sin\theta, 0)$

$\mathbf{Rj} = (-\sin\theta, \cos\theta, 0)$

$\mathbf{Rk} = (0, 0, 1)$.

(ii) The matrix is just the images of $\mathbf{i}, \mathbf{j}, \mathbf{k}$ in its columns.

(iii) The proof involves the Pythagorean identity for simplification. It means that the volume of any regions which we apply R to remains unchanged (it will be multiplied by 1).