CHEM6155 – Problem Set 1
Math Foundations, Isotopes, Mathematica

DUE: FRIDAY of Week 3

1 Mathematical Foundations

The following problems are roughly aligned with the indicated chapters of Steiner, The Chemistry Maths Book, 2nd Edition, Oxford University Press 2008. If you have difficulty with any of these problems, please read the corresponding chapter. If that is not sufficient to help you solve it, please contact one of the module instructors for help. Some of the problems require you to use *Mathematica*, which is available to Students from the University. Install a copy of it on your computer. To get started, there are many tutorials and videos available online. *Mathematica* is highly complex, and like most powerful tools requires patience and practice to master. If you run into problems, seek help from the module instructors.

1.1 Functions, Differentiation, and Integration

1. Define the following properties of functions $y = f(x)$, and provide an example for each. You may have to look up the definitions; if so, provide the source.

   - monotonic
   - bounded
   - divergent
   - continuous
   - differentiable
   - periodic

2. Indicate which of the above properties the following functions satisfy (state your reasoning):

   - $f(x) = x^2\, e^{-x}$
   - $f(x) = \tan(1/x)$
   - $f(x) = \cos\frac{2\pi x}{L} + 2\sin\frac{6\pi x}{L}$
   - $f(x) = x^3 - 4x^2 - 11x + 30$
   - $f(x) = \dfrac{x^3 - 4x^2 - 11x + 30}{x^3 - 6}$

3. Plot the above functions using *Mathematica*. Indicate the approximate positions of roots, stationary points and poles in the plots.

4. Find the exact locations of the stationary points in these functions. Try to verify your answers using *Mathematica*. You may need to use the derivative function `D[f[x],x]` and the equation solver `Solve[f[x]==0,x]`

5. Evaluate the definite integral (you may assume $R_2 > 0$:

$$\int_0^\infty e^{-i\omega t}\, e^{(i\omega_0 - R_2)t}\, \mathrm{d}t$$

6. Plot the real and imaginary parts of $e^{(i\omega_0 - R_2)t}$ as a function of t for specific values of ω_0 and R_2 with *Mathematica*. What does a 3D plot (complex plane vs time) of this curve look like?

7. In NMR spectroscopy, resonance lines often take the shape of the absorption mode Lorentzian function

$$g(\omega) = \frac{1}{\pi} \frac{T}{1 + T^2(\omega - \omega_0)^2}$$

   - Plot this function for various choices of the parameters T and ω_0. What role do these parameters play?
   - Find the integral $\int_{-\infty}^{\infty} g(\omega)\,\mathrm{d}\omega$ as a function of the parameters ω_0 and T. Comment on your finding.

1.2 Algebraic Equations and Complex Numbers

8. Provide brief explanations for the following terms and expressions (z is a complex number)

   - complex conjugate, z^*
   - modulus, $|z|$
   - argument, $\arg z$

9. find all complex solutions to the following equations:

   - $z^5 + 1 = 0$
   - $z^3 + 2z^2 + 3z = 0$
   - $\cos \frac{2\pi z}{L} + \frac{i}{2} = 0$

10. Plot the locations of the following complex numbers in the complex plane, and compute their conjugate, modulus, and arguments:

   - $\exp(\pi i)$
   - $1 + \pi i$
   - $\exp(\frac{\pi}{2} i)$
   - $1 + \frac{1}{i}$
   - $\exp(2 + \frac{\pi}{4} i)$
   - $\frac{1}{1-3i}$
   - $\frac{\sqrt{2}}{2}(1 + i)$

1.3 Trigonometric Functions and Euler's Formula

11. Prove the following identities. You may need to use Euler's formula, $\exp i\phi = \cos\phi + i\sin\phi$.

    - $\sin(\alpha\pm\beta) = \sin\alpha\cos\beta \pm \sin\beta\cos\alpha$
    - $\cos(\alpha\pm\beta) = \cos\alpha\cos\beta \mp \sin\beta\sin\alpha$
    - $\cos i\beta = \cosh\beta$
    - $\sin i\beta = -i\sinh\beta$
    - $\sin\frac{\alpha}{2}\cos\frac{\alpha}{2} = \frac{1}{2}\sin\alpha$
    - $\sin(\alpha\pm i\beta) = \sin\alpha\cosh\beta \mp i\sinh\beta\cos\alpha$
    - $\sin\frac{k\pi x}{a}\sin\frac{l\pi x}{a} = \cos\frac{(k-l)\pi x}{a} - \cos\frac{(k+l)\pi x}{a}$

1.4 Operators and Hilbert Spaces

12. Over the space of functions $f(x)$ defined on the interval $x\in[-\pi,\pi]$ a scalar product $\langle f|g\rangle$ is defined as

$$\langle f|g\rangle = \int_{-\pi}^{\pi} f(x)^* g(x)\,\mathrm{d}x,$$

    where the asterisk marks the complex conjugate. Compute the scalar products of all pairs of the following functions:

    - $\sin x$
    - $\cos^2 x$
    - $\exp(i\omega)$

13. A linear operator $\hat{O}$ maps any function $f(x)$ onto another one $g(x)$:

$$\hat{O} : f(x) \longrightarrow g(x)$$

    Linearity means that

$$\hat{O}(f(x)+g(x)) = \hat{O}f(x) + \hat{O}g(x) \quad \forall f(x), g(x).$$

    Which of the following transformations represent linear operators?

    - $f(x) \longrightarrow f(2x)$
    - $f(x) \longrightarrow 2f(x)$
    - $f(x) \longrightarrow f'(x) + f''(x)$
    - $f(x) \longrightarrow (f'(x))^2$
    - $f(x) \longrightarrow \int_0^x f(u)\,\mathrm{d}u$

14. The stationary wave functions of a particle trapped in an infinitely deep rectangular potential well between $x=0$ and $x=a$ are given by

$$\phi_k(x) = \sqrt{\frac{2}{a}}\sin\frac{k\pi x}{a}, \qquad k\in 1,2,\ldots$$

    - Verify that these wave functions are properly normalised, i.e., that $\langle\phi_k|\phi_l\rangle = \delta_{kl}$
    - Find the matrix elements $\langle\phi_k|\hat{A}|\phi_l\rangle$ for the operator

$$\hat{A} = \begin{cases} 1, x < \frac{a}{2} \\ 0, \text{otherwise} \end{cases}$$

    - Find the matrix elements $\langle\phi_k|\hat{x}|\phi_l\rangle$ of the position operator $\hat{x} = x$ for $k,l = 1\ldots3$

1.4 Linear Equation Systems, Matrices and Eigenvalue Problems

15. Find all solutions (x, y, z) of the equation system

$$\begin{aligned} 3x + 6y - 3z &= 0 \\ 2x + y + 5z &= 0 \\ x + 2y - z &= 0 \end{aligned}$$

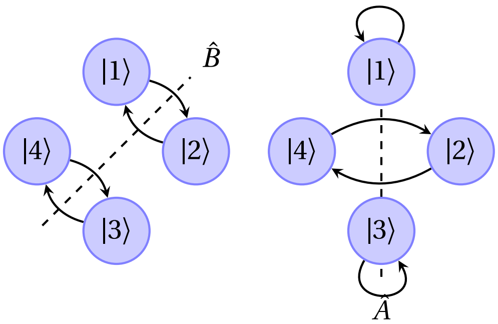
16. Given the following definitions, where b, c_x, c_y, c_x, and d are real numbers,

$$A = \begin{pmatrix} i \\ 2 \\ 3 \end{pmatrix} \quad B = \begin{pmatrix} 0 \\ b \\ -\sqrt{3} \end{pmatrix} \quad C = \begin{pmatrix} 0 & -c_z & c_y \\ c_z & 0 & -c_x \\ -c_y & c_x & 0 \end{pmatrix} \quad D = \begin{pmatrix} 1 & d & 1/d \\ d & -3 & 0 \\ 1/d & 0 & 2 \end{pmatrix}$$

evaluate the matrix products

- $AB^\dagger$
- $A^\dagger B$
- CA
- $B^\dagger C$
- C^2
- $C^\dagger DC$

17. Consider four orthonormal quantum states $|1\rangle \dots |4\rangle$, and two operators $\hat{A}$ and $\hat{B}$ acting on them. These operators interchange the quantum states as indicated by the bent arrows below.



(a) Express $\hat{A}$ and $\hat{B}$ as a superposition of $|n\rangle\langle m|$ operators.

(b) Find their matrix representations in the basis $|1\rangle \dots |4\rangle$.

(c) Find an example of an eigenstate for each of the two operators $\hat{A}$ and $\hat{B}$. What are the associated eigenvalues?

(d) Find a $|n\rangle\langle m|$ representation for the product operator $\hat{A}\hat{B}$. In a diagram similar to the one above, explain what $\hat{A}\hat{B}$ does.

(e) What are the eigenvalues and eigenstates of $\hat{A}\hat{B}$?

18. Assuming A is an $m \times n$ matrix, and B is an $n \times l$ matrix, prove that $(AB)^\dagger = B^\dagger A^\dagger$, where $A^\dagger$ is the conjugate transpose of A.

19. Prove the following theorem:
All eigenvalues of a square, self-adjoint matrix $A = A^\dagger$ are real.

2 Isotopes and Larmor Precession

Isotopomers of Ethanol Ethanol (CH_3CH_2OH) consists of the elements carbon, oxygen, and hydrogen.

1. How many distinct stable (non-radioactive) isotopologues of ethanol exist?
2. Create a table of all isotopomers of ethanol with the sum formula $^{12}C_2\,^2H_3\,^1H_3\,^{18}O$. Indicate which of these (if any) are chiral.
3. Calculate the natural abundances of all possible hydrogen isotopologues of ethanol, assuming that the carbons are all ^{12}C and the oxygen is ^{18}O.

Larmor Precession

4. What are the nuclear Larmor frequencies of ^1H, ^2H, ^{13}C, and ^{29}Si
   (a) in an NMR spectrometer operating at a magnetic field of 7T?
   (b) in the earth's magnetic field?