University of Washington
Department of Chemistry
Chemistry 453
Winter Quarter 2015

Homework Assignment 1
Due at 5 p.m. on 1/13/14 in Catalyst Drop-In Box..

This homework is worth a total of 10 points. This homework set is intended as a quick and relatively painless way for you to brush up on your math skills, and for me to understand your math background. Questions of these types will appear in lectures and exams.

QUESTION SET A: The Simple Functions of Applied Math & How to Manipulate Them

Properties of exponential functions, factorial functions, and logarithms are widely exploited in Chemistry 453. Product and summation symbols are also widely used in chapters on quantum and statistical mechanics.

1A) Using only the following facts, and not the logarithm keys on your calculator, determine log($4080.^{1/2}$) ~ ?

$$\ln(2) \sim 0.693; \quad \ln(3) \sim 1.099; \quad \ln(5) \sim 1.609; \quad \log_{10} x = \frac{\ln x}{\ln 10};$$

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \ldots$$ if x<<1. Show your reasoning..

2A) This problem deals with significant figures. How many digits can be accepted from your calculator as reliable? To explore this question , without using your calculator, determine the quantity $\sqrt{5.2}$, using the equation $\sqrt{5.2} = 2 + \frac{x}{10}$. Using your two significant figure value for $\sqrt{5.2}$ generalize this approach and calculate $\sqrt{5.20}$ to three significant figures. Compare this answer to what your calculator gives you. Why does the calculator give more digits? Given the information you provided to the calculator, can these extra digitis be accepted as "significant".

3A) In the course of doing calculations even with a calculator, it is necessary to distinguish between exact numbers and numbers that are subject to significant figure rules. The following calculation is a good example. Using only the following facts, and not the exponential key on your calculator, determine $e^{-5010../1000..}$~ ?

$e^{5.000}$~148.4; ln(1±x)~±x if x<<1. Show your reasoning, 4A) The factorial function $n! = n(n-1)(n-2)\cdots 3\bullet 2\bullet 1$ increases so rapidly, that evaluating 100! with your calculator is often impossible because of memory limitations (try it...some calculators can do it, but others cannot). There is an expression called Stirling's Approximation for evaluating factorial expressions: $n! \approx \left(\frac{n}{e}\right)^n \sqrt{2\pi n}$. Use Stirling's Approximation to evaluate ln(100!).

5A) A simpler form of Stirling's Approximation that will be used in this course is $n! \approx \left(\frac{n}{e}\right)^n$. Calculate ln100! using this form of Stirling's Approximation. How well does it agree with the answer in 4A? Calculate 10000! with the two method.s How will the agreement vary between the two methods vary as the number gets larger?

6A) For calculations involving very large numbers, it is best to use the rules of scientific notation and the algebra of logarithms...including Stirling's Approximation. With this in mind calculate the number $\ln\left(\frac{q^N}{N!}\right)$ where q=100 and N=10,000.

QUESTION SET B: Vectors, Matrices, and Determinants

Linear algebra is also used in chemistry 453 so familiarity with vectors, matrices, and determinants is advisable. Many physical properties including forces, particle velocities, electric fields and dipole moments are represented mathematically as vectors. Vectors can be multiplied together to obtain a scalar result (i.e. inner or dot product) or a vector result (i.e. cross or outer product). For example, energy is a scalar and the energy of interaction between a dipole moment and a field is obtained by taking an inner product. Torque is an outer product of two vectors which can be evaluated with a determinant. The reorientation of a vector in space is mathematically represented by multiplying a vector with a matrix. Representing a vector both in Cartesian and spherical coordinate systems is also a necessary skill.

1B) A vector in three dimensional space is designated $\vec{V} = v_x\hat{i} + v_y\hat{j} + v_z\hat{k} = (v_x, v_y, v_z)$ where $\hat{i}$, $\hat{j}$, and $\hat{k}$ are unit vectors in the x, y, and z directions, respectively. Let $\vec{A} = (1,2,3)$ and $\vec{B} = (4,-4,1)$. Calculate the scalar or "dot" product $\vec{A}\bullet\vec{B} = ?$

2B) Let $\vec{A} = (3,4,3)$. Calculate the magnitude (i.e. length) of this vector. Calculate also the angles θ and ϕ that define the orientation of this vector in a spherical coordinate system.

3B) Determine the vector that results from the operation: $\begin{pmatrix} 1 & 3 & -4 \\ 8 & 2 & 2 \\ -6 & 2 & 1 \end{pmatrix}\begin{pmatrix} 3 \\ -2 \\ 1 \end{pmatrix} = ?$

4B) Determine the matrix that results from the product: $\begin{pmatrix} -1 & 2 \\ 4 & -5 \end{pmatrix}\begin{pmatrix} 6 & 9 \\ -2 & -1 \end{pmatrix} = ?$

5B) Evaluate the determinant of the matrix $\begin{pmatrix} 1 & 3 & -4 \\ 8 & 2 & 2 \\ -6 & 2 & 1 \end{pmatrix}$

6B) Solve the determinant equation for x: $\begin{vmatrix} 1-x & 0 & -2 \\ 0 & -x & 0 \\ -2 & 0 & 4-x \end{vmatrix} = 0$

QUESTION SET C: Derivatives and their Applications
The derivative is the calculus operation used most frequently in this course. Derivatives are used generally throughout mechanics. Derivatives are used in Taylor expansions to approximate values of functions and are used to find the minima and maxima of functions. Derivatives are fundamental components of differential equations. Differential equations are used to solve mechanical problems.

1C) $f(\theta) = 2\cos\theta\sin\theta \qquad \frac{df}{d\theta} = ?$

2C)
$f(x) = (1 - x^4)/x \qquad \frac{df}{dx} = ?$

3C)

4C) $\frac{\partial}{\partial x}\left(2x^4y^6+\frac{3}{x^2}\right)=?$ $\frac{\partial}{\partial y}\left(2x^4y^6+\frac{3}{x^2}\right)=?$

5C) Using a Taylor expansion show that close to 1, ln(x) ≈ x -1. Use a Taylor expansion to approximate ln(1.05) = ? to first order. Recall the Taylor Series has the form: f(x) = f(a) + (x-a)f'(a) +(1/2!)(x-a)^{2}f''(a)…

6C) Find the local maximum and minimum of the equation f(x) = x^3 – 27x (ignore any max or min at ± ∞)

QUESTION SET D: Integrals and their Applications

Integrals and derivatives go hand-in-hand in mechanics courses. In Chemistry 453 integrals are commonly used to calculate averages of various types. Although we expect you to be able to perform simple integrations from scratch, it is far more often the case that you are required to evaluate an integral that has standard form. Standard form means the integral has a form with a generally recognized answer, which you can find in books or on the Web. In Chemistry 453 very often the challenge is to correctly frame a physical problem in terms of an integral with standard form.

1D) Evaluate the integral; $\frac{2}{L}\int_{L/3}^{2L/3}\sin^2\left(\frac{\pi x}{L}\right)dx$ where L is a constant, using the standard form $\int \sin^2 ax\,dx=\frac{x}{2}-\frac{1}{4a}\sin 2ax+C$, where a and C are constants.

2D) Evaluate the integrals $\int_{-\infty}^{+\infty} e^{-\kappa x^2/2kT}dx$ and $\int_{-\infty}^{+\infty} e^{-p^2/2mkT}dp$ using the standard form integral: $\int_0^{\infty} e^{-cx^2}dx=\left(\frac{\pi}{4c}\right)^{1/2}$. Note κ, k, T, and m are constants. In the standard form c indicates a constant. Note the function being integrated is an even function: f(x)=f(-x).

3D) The average kinetic energy of a very small spherical particle moving in one dimension is: $\langle E\rangle=\frac{1}{\sqrt{2\pi mkT}}\int_{-\infty}^{+\infty}\frac{p^2}{2m}e^{-p^2/2mkT}dp$, where m is the mass, k=R/N_A,is Boltzmann's constant, and T is the temperature. Assume m, k, and T are constants. Calculate $\langle E\rangle$ using the standard form: $\int_0^{\infty} x^{2n}e^{-ax^2}dx=\frac{1\cdot3\cdot5\cdots(2n-1)}{2^{n+1}a^n}\sqrt{\frac{\pi}{a}}$, where n is a positive integer and a is a constant greater than zero. Note the function being integrated is even.