

Problem Set PS08
ISSUED: 10/26/00 **Due: 11/2/00**

Prof. Darin J. Ulness

Name _____

Instructions. Complete all questions before class on the due date. You are encouraged to work together. Be sure to struggle with the problem before seeking help. Many of the exercises are very similar to problems in the book. Understanding the solution to these problems will be helpful in completing the assigned exercises.

Mathematical Exercises

1. The trace of a matrix M (written $\text{Tr}[M]$) is simply the sum of the diagonal elements of M . By diagonal one means top left to bottom right. Evaluate the trace for the following matrices.

(a)

$$M = \begin{bmatrix} 4 & 5 & 6 \\ 1 & 2 & 3 \\ 7 & 8 & 9 \end{bmatrix}$$

(b)

$$M = \begin{bmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{bmatrix}$$

2. Associated with matrices are eigenvectors and eigenvalues. These are analogues of the eigenfunctions and eigenvalues we have worked with for operators. That is, the column vector V is an eigenvector of the matrix M corresponding to the eigenvalue λ if

$$MV = \lambda V.$$

We will not learn how to calculate eigenvectors and eigenvalues in this course (if you had linear algebra you did quite a lot of this), but MATHEMATICA can quickly calculate eigenvectors and eigenvalues. Use MATHEMATICA to determine the eigenvectors and eigenvalues of the following matrices. Comment on your answer for (b) also compare the sum of the eigenvalues for parts (a) and (b) to the answers you got for the traces in the preceding problem.

(a)

$$M = \begin{bmatrix} 4 & 5 & 6 \\ 1 & 2 & 3 \\ 7 & 8 & 9 \end{bmatrix}$$

(b)

$$M = \begin{bmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{bmatrix}$$

3. The geometric series is defined as

$$\sum_{n=0}^{\infty} x^n = 1 + x + x^2 + x^3 + \dots$$

This series can, in fact, be written in *closed form* as

$$\sum_{n=0}^{\infty} x^n = \frac{1}{1-x}.$$

(a) For what values of x is this series valid?

(b) Write

$$f(r) + f(r)r + f(r)r^2 + f(r)r^3 + \dots,$$

where $f(r)$ is some arbitrary function of r , in closed form and in series notation (i.e., \sum notation).

(c) Write

$$1 + \cos x + (\cos x)^2 + (\cos x)^3 + \dots$$

in closed form and in series notation.

(d) Write

$$1 + e^{-\beta x} + e^{-2\beta x} + e^{-3\beta x} + \dots$$

in closed form and in series notation.

Exercises

4. A vial containing 10^{20} iodine molecules is at 300K. How many molecules are in each of the first four vibrational states assume the harmonic oscillator model applies. (The stretching mode of iodine is 200cm^{-1}). Note we will often need to know the so-called thermal energy (kT) in units of wavenumbers. You may want to download my kT calculator from the “files to download” section of the PChem website.
5. Derive the closed form canonical partition function for an ensemble of harmonic oscillators,

$$q_{HO} = \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}},$$

from the series representation. Also show $q_{HO} = \frac{1}{2 \sinh \frac{1}{2}\beta\hbar\omega}$. Note: Eq. (4.32) in the notes should have a factor of 2 in the denominator. Finally separately plot q_{HO} as a function of temperature and then as a function of frequency. What do each of these plots mean physically? (It might be helpful to check out Castro’s legacy project from two years ago)

6. Later on we will derive a relation between pressure, P , and the partition function to be

$$P = \frac{1}{\beta} \left(\frac{\partial \ln Q}{\partial V} \right)_{n,\beta}.$$

For an ideal monatomic gas we have to worry only about translation of the gas in its container (volume V). Thus the partition function is

$$Q = q_{\text{mol}}^N = q_{\text{trans}}^N.$$

Using the translational partition function given on p70 of the notes, derive the ideal gas law. Note: the gas constant $R = N_A k$ where N_A is Avogadro's number. Also the number of moles is $n = N/N_A$.

7. Consider a very intense laser excitation of matter such that the light-matter interaction is nonlinear: $\mu(t) = \alpha(t)E(t)^3$. If no Raman modes are active then $\alpha(t) = \alpha_0$ (a constant). Derive a nonlinear scattering equation analogous to Eq. (5.4) of the notes for the case when $\alpha(t) = \alpha_0$. Use trig identities to simplify the expression such that all the scattering frequencies are easily identified. These scattered frequencies are called third order processes. A number of processes occur at third order. These include (i) third harmonic generation, (iii) degenerate four wave mixing Use your intuition to assign each of your derived frequencies to one of these processes.

Conceptual Problems

8. The thermal de Broglie wavelength is a measure of the “quantumness” of the ensemble. That is how much quantum character is manifest in the macroscopic system. Plot the thermal de Broglie wavelength as a function of temperature. What does this say about the quantumness of the ensemble as a function of temperature? Superfluidity and superconductivity are very quantum in character. Based on you above argument, would you expect (macroscopic) superfluidity or superconductivity at high or low temperatures?
9. Using the classical theory of light scattering (Eq. (5.4) in the notes), sketch the Rayleigh, Stokes and anti-Stokes spectral lines for iodine. Assume iodine has one active mode (200cm^{-1}) and assume the laser light used to do the scattering is at 20000cm^{-1} (this is 500nm —green light).

Computer Problems

10. Consider a linear chain of N atoms. Each of the atoms can be in one of three states A , B , C or D , except that an atom in state A can not be adjacent to an atom in state C and an atom in state B can not be adjacent to an atom in state C or D . Find the entropy per atom for this system as $N \rightarrow \infty$. To solve this problem it is useful to define the set of four dimensional column vectors $V^{(j)}$ such that the four elements are the total number of allowed configurations of a j -atom chain having the j^{th} atom in

state A , B , C , or D . For example,

$$V^{(1)} = \begin{bmatrix} 1 \\ 1 \\ 1 \\ 1 \end{bmatrix}, V^{(2)} = \begin{bmatrix} 3 \\ 2 \\ 2 \\ 3 \end{bmatrix}, V^{(3)} = \begin{bmatrix} 8 \\ 5 \\ 5 \\ 8 \end{bmatrix}, \dots$$

The $V^{(j+1)}$ can be found from the $V^{(j)}$ vector using the matrix equation,

$$V^{(j+1)} = MV^{(j)},$$

where *for this example*

$$M = \begin{bmatrix} 1 & 1 & 0 & 1 \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 1 \\ 1 & 0 & 1 & 1 \end{bmatrix}.$$

The matrix M is the so-called *transfer matrix* for this system. It can be shown that the number of configurations $W = \text{Tr}[M^N]$. Now for large N , $\text{Tr}[M^N] \approx \lambda_{\max}^N$, where λ_{\max} is the largest eigenvalue of M . So

$$W = \lim_{N \rightarrow \infty} \lambda_{\max}^N.$$

- (a) Use M to find $V^{(4)}$
- (b) Verify $V^{(2)}$ explicitly by drawing all the allowed 4-atom configurations.
- (c) Verify $W = \text{Tr}[M^N]$ for $N = 1$ and $N = 2$.
- (d) Use Boltzmann's equation to find the entropy per atom for this chain as N goes to infinity.
- (e) What is the entropy per atom for the case of $N = 4$. How does this compare to the large N answer.
- (f) Think of a real situation that could be modeled by this system.

Reflective Exercises

11. Considering your future career, think of a task you may be called upon to do that will make the PChem oral exams seem trivial (e.g., Ph.D. defense or having to inform a mother that her child has leukemia, etc.). Do you feel that you have the strength to complete the task in a professional manner?

1 a) $Tr[M] = 4 + 2 + 9 = 15$

b) $Tr[M] = \lambda_1 + \lambda_2 + \lambda_3$

2 a) Using Mathematica the eigenvalues are $0, \frac{3}{2}(5 - \sqrt{29}), \frac{3}{2}(5 + \sqrt{29})$

Sum

$0 + \frac{3}{2}(5) - \frac{3}{2}(\sqrt{29}) + \frac{3}{2}(5) + \frac{3}{2}(\sqrt{29})$

$\frac{15}{2} + \frac{15}{2} = 15$ This equals the Trace sum 1 a

b) eigenvalues

$\lambda_1, \lambda_2, \lambda_3$

Sum

$\lambda_1 + \lambda_2 + \lambda_3$ This equals the Trace sum 1 b

5) $q_{HD} = \sum_{n=0}^{\infty} e^{-\beta \epsilon_n} = \sum_{n=0}^{\infty} e^{-\beta \hbar \omega (n + \frac{1}{2})} = \sum_n (e^{-\beta \hbar \omega}) e^{-\beta \frac{\hbar \omega}{2}}$
 $= e^{-\beta \frac{\hbar \omega}{2}} \sum_{n=0}^{\infty} e^{-\beta \hbar \omega n} = e^{-\beta \frac{\hbar \omega}{2}} \sum_{n=0}^{\infty} (e^{-\beta \hbar \omega})^n$
 $= \frac{e^{-\beta \frac{\hbar \omega}{2}}}{1 - e^{-\beta \hbar \omega}}$ ✓
 $= \frac{1}{e^{\beta \frac{\hbar \omega}{2}} (1 - e^{-\beta \hbar \omega})} = \frac{1}{e^{\beta \frac{\hbar \omega}{2}} - e^{-\beta \frac{\hbar \omega}{2}}} = \frac{1}{2 \sinh \frac{\beta \hbar \omega}{2}}$ *got 4*

6) $P = \frac{1}{\beta} \frac{\partial \ln Q}{\partial V}$ $Q = \sum_{trans}^N$ so $\ln Q = \ln \sum_{trans}^N = N \ln \sum_{trans}$
 $P = \frac{N}{\beta} \frac{\partial \ln \sum_{trans}}{\partial V} = \frac{N}{\beta} \frac{\partial \ln \left[\frac{V}{\Lambda^3} \right]}{\partial V}$ $\sum_{trans} = \frac{V}{\Lambda^3}$
 $= \frac{N}{\beta} \left(\frac{\partial \ln V}{\partial V} - \frac{\partial \ln \Lambda^3}{\partial V} \right) = \frac{N}{\beta} \frac{1}{V}$

$P = \frac{NkT}{V} = \frac{N}{N_A} \frac{N_A kT}{V} = \frac{nRT}{V}$

$\Rightarrow PV = nRT$ ✓

3 a) $|x| < 1$

b) $f(x) + f(x)r + f(x)r^2 + f(x)r^3 + \dots$
 $= f(x) [1 + r + r^2 + r^3 + \dots]$
 $= \frac{f(x)}{1-r}$

c) $1 + \cos x + (\cos x)^2 + (\cos x)^3 + \dots = \sum_{n=0}^{\infty} (\cos x)^n$
 $= \frac{1}{1 - \cos x}$

d) $1 + e^{-\beta x} + e^{-2\beta x} + e^{-3\beta x} + \dots = \sum_{n=0}^{\infty} e^{-n\beta x}$
 $= \sum_{n=0}^{\infty} (e^{-\beta x})^n = \frac{1}{1 - e^{-\beta x}}$

4) $n=0$ $(2 \sinh \frac{1}{2} \frac{200}{208}) (e^{-\frac{1}{2} \frac{200}{208}}) (10^{20}) = 6.18 \times 10^{19}$
 $n=1$ $(e^{-\frac{1}{2} \frac{200}{208}}) (10^{20}) = 2.37 \times 10^{19}$
 $n=2$ $(e^{-\frac{1}{2} \frac{200}{208}})^2 (10^{20}) = 9.09 \times 10^{18}$
 $n=3$ $(e^{-\frac{1}{2} \frac{200}{208}})^3 (10^{20}) = 3.48 \times 10^{18}$

7) $N(x) = d_0 \epsilon_0^3 \cos^3 \omega t \cos \omega t \cos \omega t$

$\cos \omega t \cos \omega t = \frac{\cos 2\omega t + 1}{2}$
 $(\frac{\cos 2\omega t + 1}{2}) \cos \omega t = \frac{\cos 3\omega t + \cos \omega t}{4}$

So $N(x) = \frac{d_0 \epsilon_0^3}{3} \cos 3\omega t + \frac{3d_0 \epsilon_0^3}{4} \cos \omega t$
 Third harmonic generation degenerate four wave mixing

8)

See last year's set

States	Rayleigh	Anti-Stokes
Raman		Raman
19,800 cm ⁻¹	20,000 cm ⁻¹	20,200 cm ⁻¹

9) $\sqrt{10} = \begin{bmatrix} 11 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 1 \end{bmatrix} \begin{bmatrix} 3 \\ 8 \\ 5 \end{bmatrix} = \begin{bmatrix} 21 \\ 13 \\ 21 \end{bmatrix}$ b)

AA	AB	AC	AD
BA	BB	BC	BD
CA	CB	CC	CD
DA	DB	DC	DD

c) $Tr[M] = 4$ ✓ $Tr[M.M] = 10$ ✓

d) $\lambda_{max} = \frac{1}{2}(3 + \sqrt{5})$ (from Mathematica) $S = k \ln W \approx k \ln \lambda_{max}$
 $S = N k \ln \lambda_{max}$ $\frac{S}{N} = k \ln \lambda_{max} = k \ln \left(\frac{1}{2}(3 + \sqrt{5}) \right)$

e) $W = Tr[M^4] = 36$ $W \approx \lambda_{max}^4 = 46.97$

$\frac{S}{N} = k \ln 36 = 3.58k$ $\frac{S}{N} \approx k \ln 46.97 = 3.84k$ $\frac{3.84k - 3.58k}{3.58k} \times 100\% = 7.4\%$ rel error