Homework Set #1
Chem 544

All homework is “open book”: any book or web resource you want. Solve them alone or in groups, as long as what you turn in reflects YOUR OWN final answer. You’re welcome to double-check any of your answers using Matlab/Mathematica, but whip out the pencil first!

This problem set has you do some stuff related to the math quiz. “Appendix A” has man of the answers.

1. The first two problems familiarize you with Jacobians. They are the way to deal with iffy partial derivatives. The Jacobian \( \frac{\partial(u,v)}{\partial(x,y)} \) is defined as the determinant

\[
\begin{vmatrix}
\frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} \\
\frac{\partial v}{\partial x} & \frac{\partial v}{\partial y}
\end{vmatrix}.
\]

Use the properties of determinants to show

\[
\frac{\partial(u,v)}{\partial(x,y)} = \frac{\partial(u,v)}{\partial(s,t)} \frac{\partial(s,t)}{\partial(x,y)} \quad \text{and that} \quad \frac{\partial(u,v)}{\partial(x,y)} = -\frac{\partial(v,u)}{\partial(x,y)}.
\]

2. Also show that

\[
\frac{\partial(x,v)}{\partial(u,v)} = \left( \frac{\partial x}{\partial u} \right)_v.
\]

This relates any partial derivative to a Jacobian. The results of problems 1 and 2 are the basic tool for thermodynamic calculations.

3. Use the logarithm function to split the complex number 7+7i into its magnitude and phase parts. (See App. A p. 2)

4. Consider a system with two nearby energy levels, \( E_i(x) = E_0 + a(x-x_0) \) and \( E_j(x) = E_0 - a(x-x_0) \). An example would be two intersecting electronic potential surfaces. Plot both energies from \( x=0 \) to \( x=2x_0 \). Now assume that the two levels are coupled by a coupling of strength \( V \). Assuming \( E_0 = 0 \), \( a=1 \), \( x_0=1 \), \( V=0.1 \), diagonalize the resulting 2x2 matrix, obtaining eigenvalues \( \lambda(x) \). Then plot the energies from \( x=0 \) to \( 2 \). Label the part of the plot that is called an “avoided crossing” (compare to the crossing in your first plot). This is a common situation for electronic states, whose potential curves usually refuse to intersect unless \( V=0 \) by symmetry (called a “conical intersection”).

5. Calculate the Fourier transform \( Y(k) \) of the gaussian \( y(x) = \exp[-x^2/a^2] \). To do the integral, complete a square in the exponent to get rid of the linear term in \( xk \). Then make an argument that the left-over integral provides only a normalization factor.

6. Two dice are rolled repeatedly, yielding \( j \) dots each time. Calculate the probability density \( \rho = P(j) \) as a function of \( j \) from \( j=2 \) to 12; sketch \( P \) on a normalized scale from \( x=0 \) to 1 (\( j=2 \) scales to 0, \( j=12 \) to 1), and also \( \ln(P) \). Then do the analogous problem for 5 dice, from \( j=5 \) to 30, with a scaling from \( x=0 \) to 1 again. Compare the two curves (they should peak near \( x=1/2 \)), and comment on why macroscopic (many particle) systems can be characterized by average properties, usually without the need to know about deviations from the average.

7. Compute the first and second moment of the Lorentzian probability distribution \( L(x) \sim a/[a^2+(x-x_0)^2] \), after first properly normalizing the probability distribution over the range \( x = -\infty \) to \( \infty \). Are you finding the second moment problematic? What does this say about the probability of getting outliers from this distribution, compared to a “normal” (= Gaussian) distribution? Could we successfully do any experiments if the Central Limit Theorem produced \( L \) instead of a Gaussian as its limiting distribution?
8. Rewrite the time-dependent Schrödinger equation explicitly in terms of real and imaginary parts using \( \Psi = \Psi_r + i\Psi_i \). Then insert into the Schrödinger equation, split it into its separate real and imaginary parts, and write down the equations of motion for \( \Psi_r \) and \( \Psi_i \) to show that the Schrödinger equation has a structure analogous to Hamilton’s equations, as stated in Chapter 1 of the “Survey” notes.

9. In cartesian coordinates, use the definition of force \( F_i = -\partial V / \partial x_i \) (force “i” is the change of potential energy of a particle upon displacement in direction \( x_i \)) and the definition of acceleration \( a = \partial v / \partial t = (\partial p / \partial t) / m \), where \( m \) is the particle mass, to prove starting with Hamilton’s equations that \( F = ma \).

10. Prove that if \( Y(k) \) is the Fourier transform of \( y(x) \), then the Fourier transform of \( y'(x) = \partial y / \partial x \) is simply \( i k Y(k) \). Fourier transformation turns derivatives into simple multiplication. What would be the Fourier transform of \( \partial^n y / \partial x^n \)? (See appendix A.2; note: there the F.T. and inverse F.T.l are defined with a \( 1/\sqrt{2\pi} \) factor, so the conventional normalization is split. Likewise, you’ll see the \( \pm i \) in the F.T. transform swapped depending on what text you read.)