Homework Assignment 2
Due at 5 p.m. on 1/19/11 at the Catalyst drop box.

This homework is worth a total of 10 points.

1) This problem will give you practice in differentiating sine and cosine functions. You also need to recall how to use the chain rule of differentiation.

The quantum mechanical wave equation (i.e. Schroedinger’s equation) is a differential equation. Differential equations for wave motion are derived from physical models. The quantum mechanical wave equation must be consistent with basic physics and must also include the “new” physical relationships for quantized systems.

- The quantum wave equation must be consistent with the basic energy definition: 
  \[ E = K(p) + V(x) = \frac{p^2}{2m} + V(x) \]
  where K is the kinetic energy, in turn a function of p=mv, the momentum, and V(x) is the potential energy, function of x.

- The quantum wave equation must be consistent with the energy definition from quantum mechanics 
  \[ E = \hbar \omega \]
  and the momentum definition 
  \[ p = \frac{\hbar}{\lambda} = \frac{\hbar}{2\pi} \frac{2\pi}{\lambda} = \frac{\hbar}{\lambda} = \hbar k. \]

  a) Show that \[ \hbar \omega = \frac{\hbar^2 k^2}{2m} + V(x) \]

  b) Assume Schroedinger’s equation is linear so that
  \[ i\hbar \partial \Psi(x,t) = \frac{\hbar^2 k^2}{2m} \Psi(x,t) + V(x) \Psi(x) \]
  \[ \Psi(x,t) = \cos(kx - \omega t) + i \sin(kx - \omega t) \]
  where \( i^2 = -1 \). Show that \[ i\hbar \partial \Psi(x,t) = \hbar \omega \Psi(x,t). \]

  c) Again assuming \( \Psi(x,t) = \cos(kx - \omega t) + i \sin(kx - \omega t) \) show that
  \[ -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x,t)}{\partial x^2} = \frac{\hbar^2 k^2}{2m} \Psi(x,t) \]

  d) Using the results from parts b and c show that the time-dependent Schroedinger’s equation is
  \[ -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x,t)}{\partial x^2} + V(x) \Psi(x,t) = i\hbar \frac{\partial \Psi(x,t)}{\partial t} \]
2) This problem is easier than it seems. It just gives you practice at manipulating wave equations and gives you some experience manipulating partial derivatives. It also clarifies some math in text chapter 13. Follow directions, be careful and you will get through it.

The time-dependent Schrödinger’s equation in problem 1, i.e.
\[-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x,t)}{\partial x^2} + V(x) \Psi(x,t) = i\hbar \frac{\partial \Psi(x,t)}{\partial t}\]
is the analog of the classical wave equation given as equation 13.10 in the text. But the version of the Schrödinger equation given as 13.15 is the stationary wave equation. It is derived as follows.

a) Assume as in text equation 13.9 that the wave function has the form:
\[\Psi(x,t) = f(t)\psi(x)\]
where \(f(t)\) is just a function of time \(t\) and \(\psi(x)\) is just a function of \(x\). Assuming this means that \(\frac{\partial \Psi(x,t)}{\partial t} = \psi(x) \frac{df(t)}{dt}\) and
\[\frac{\partial \Psi(x,t)}{\partial x} = f(t) \frac{d\psi(x)}{dx}\], show that
\[-\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} + V(x) f(t) \psi(x) = i\hbar \frac{\partial f(t)}{\partial t}\]

b) Show that
\[-\frac{\hbar^2}{2m\psi(x)} \frac{\partial^2 \psi(x)}{\partial x^2} + V(x) = \frac{i\hbar}{f(t)} \frac{\partial f(t)}{\partial t}\]

c) Prove that the left hand side and right hand side of the equation in part b have units of energy and so
\[-\frac{\hbar^2}{2m\psi(x)} \frac{\partial^2 \psi(x)}{\partial x^2} + V(x) + \frac{i\hbar}{f(t)} \frac{\partial f(t)}{\partial t} = E\]
where \(E\) is the energy.

d) Using the identities in part c, show that the time dependent Schrödinger equation can be decomposed into two equations:
\[-\frac{\hbar^2}{2m\psi(x)} \frac{\partial^2 \psi(x)}{\partial x^2} + V(x) \psi(x) = E\psi(x)\text{ and } i\hbar \frac{\partial f(t)}{\partial t} = Ef(t)\text{. Note the first equation is identical to text equation 13.15 and so is the stationary Schrödinger equation.}

e) Using the results of part d, show that you can write the wave function as
\[\Psi(x,t) = f(t)\psi(x) = e^{-iEt/\hbar}\psi(x)\text{, where }\psi(x)\text{ is the solution of the stationary Schrödinger equation.}

3) Quantum mechanics may apply to small particles, but its effects can be seen in the macroscopic world if you know where to look. Here you calculate the heat capacity of an ideal diatomic gas classically and quantum mechanically. Look up the heat capacity of oxygen in the back of your text to see which approach is more accurate.
The internal energy of an ideal diatomic gas is given by \( U = U_{\text{trans}} + U_{\text{rot}} + U_{\text{vib}} \), where \( U_{\text{trans}} \) is the internal energy of translation, \( U_{\text{rot}} \) is the internal energy of rotation, and \( U_{\text{vib}} \) is the internal energy due to the bond vibration. Note \( U \) is related to the average mechanical energy by \( \langle E \rangle = \frac{U}{N_A} \).

a) According to the Principle of Equipartition of classical mechanics, 
\[ \langle E \rangle = \text{dof} \times \frac{k_B T}{2} \], where dof is the number of degrees of freedom,
\[ k_B = \frac{R}{N_A} \], and \( T \) is the temperature. For a diatomic molecule like \( \text{O}_2 \), there are three degrees of translational freedom, two degrees of rotational freedom, and two degrees of vibrational freedom. Using the Equipartition Principle, calculate \( U = U_{\text{trans}} + U_{\text{rot}} + U_{\text{vib}} \) in terms of \( RT \).

b) Using your result in part a, calculate the heat capacity \( C_v = \left( \frac{\partial U}{\partial T} \right)_v \) and \( C_p \). Assume ideal gas behavior.

c) Now assume that the vibrational energy is quantized such that \( E_{\text{vib}} = n\hbar \nu \), \( n=0,1,2,3 \ldots \) and so the average vibrational energy is \( \langle E_{\text{vib}} \rangle = \frac{\hbar \nu}{e^{\hbar \nu/k_B T} - 1} \). Using \( C_v = \left( \frac{\partial U}{\partial T} \right)_v \) and \( \langle E_{\text{vib}} \rangle = \frac{\hbar \nu}{e^{\hbar \nu/k_B T} - 1} = \frac{U_{\text{vib}}}{N_A} \), obtain an expression for the vibrational heat capacity.

d) Assume a \( \text{O}_2 \) bond vibrates at a frequency of \( \nu = 5 \times 10^{13} \text{ s}^{-1} \). Calculate the vibrational heat capacity at \( T=298\text{K} \).

e) Assume at \( T=298\text{K} \) the translational and rotational heat capacities can be calculated using the equipartition principle as in parts a and b, but the quantum mechanical expression from parts c and d must be used for the vibrational heat capacity. Calculate the total heat capacity \( C_V \) for \( \text{O}_2 \) and assuming \( \text{O}_2 \) behaves ideally, calculate also \( C_p \).

f) Look up the value for \( C_p \) for \( \text{O}_2 \) in the back of your text. Compare this value to your calculated results in parts b and e. Neglecting non-ideal behavior, are quantum effects important for the vibration of the \( \text{O}_2 \) bond at \( T=298\text{K} \)? Explain.

4) Here you calculate just how unstable hydrogen is predicted to be if you not quantize the electron orbital radii.

According to the nuclear model for the hydrogen atom, the condition for orbital stability is the Coulombic force \( -\frac{Ze^2}{4\pi\varepsilon_0 R^2} \) must be balanced by the centripetal force \( \frac{mv^2}{R} \) associated with the electron’s orbital motion. See Lecture 2. \( Z=1 \) is the atomic
number of hydrogen, e is the electron charge in Coulombs C, m is the mass of the electron in kilograms kg, \( \varepsilon_0 \) is the free space permittivity with units \( C^2 J^{-1} m^{-1} \), R is the radius of a circular orbit in units of meters, and v is the orbital velocity of the electron in units of m s\(^{-1} \).

a) Assuming the electron in hydrogen occupies an orbit of radius \( R=0.53 \times 10^{-10} \) m, and assuming the Coulombic force is exactly equal to the centripetal force as given by equation 2.2 in the notes, calculate the orbital velocity v of the electron.

b) Calculate the centripetal acceleration of the electron described in part a.

c) Larmor’s equation gives the rate of energy loss P by an accelerating electron charge e: \( P = \frac{e^2 a^2}{6\pi\varepsilon_0 c^3} \) where a is the acceleration of the electron in units of m s\(^{-2} \), c is the speed of light in units of m s\(^{-1} \), and P has units of J s\(^{-1} \). Using the acceleration calculated in part b, calculate the rate of energy loss P by the electron.

d) Assume the electron in hydrogen has an energy \( 2.18 \times 10^{-18} \) J. Using your result from part c, calculate the amount of time it will take for the electron to lose this energy and collide with the nucleus.

e) This atom can be saved by quantizing the angular momentum of the electron and thus the orbital radii as shown in lecture 2. Calculate the wavelength of the electron, given the orbital velocity that you calculated in part a. About how many electron wavelengths occur in the orbit described in part a?

5) This problem explores when you do and do not have to quantize motions.

Assume a large number of particles exist in a one dimensional box. Each particle has a mass of \( M=2 \times 10^{-27} \) kg and the length of the box is \( L=0.01 \) m.

a) Assume the pressure is low enough that each particle translates freely in one dimension and does not interact in any way with the other particles. Calculate the average one dimensional translational kinetic energy of the particles, assuming \( T=300 \) K.

b) Assume each particle energy can be expressed by the quantized particle-in-a-box equation, given in Ch. 14. For what value of n does the single particle energy equal the average energy calculated in part a?

c) Calculate the translational energy level separation \( \Delta E = E_{n+1} - E_n \), where n is the value determined in part b. How large is this separation compared to \( k_B T \), for \( T=300 \) K?

d) Repeat the calculations in parts b and c only assume the length of the box is \( L=0.01 \) nm (nm=nanometer=\( 10^{-9} \) m). How is the importance of quantization, i.e. the size of \( \Delta E \) compared to \( k_B T \), dependent on the size of the box?