University of Washington
Department of Chemistry
Chemistry 453
Winter Quarter 2015

Homework Assignment 6; Due at 5p.m. on 2/25/15

1) The Schroedinger wave equation for the particle in a 1D box is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x) \text{ where } \hbar = \frac{h}{2\pi} = 1.05\times10^{-34}\,Js$$

(a) Show that $\psi(x) = A\sin\left(\frac{\sqrt{2mE}}{\hbar}x\right) + B\cos\left(\frac{\sqrt{2mE}}{\hbar}x\right)$ is a solution for the Schroedinger equation for a particle in a 1D box.

(b) Show that if $\psi(0) = 0$ then B=0 and the solution to Schroedinger's equation is now $\psi(x) = A\sin\left(\frac{\sqrt{2mE}}{\hbar}x\right)$.

(c) Show that if $\psi(L) = 0$ then $\frac{\sqrt{2mE}}{\hbar} = \frac{n\pi}{L}$ where n=1, 2, 3...and the solution to Schroedinger's equation is now $\psi_n(x) = A\sin\left(\frac{n\pi x}{L}\right)$.

(d) The accepted interpretation of the wave function is that $\left|\psi^2(x)\right|dx$ is the probability of the particle occurring between x and x+dx. Therefore the wave function has the property: $\int_0^L \left|\psi_n^2(x)\right|dx = 1$. From this integral and using the definition from part c $\psi_n(x) = A\sin\left(\frac{n\pi x}{L}\right)$, show that $A = \sqrt{\frac{2}{L}}$. Hint: Use the standard integral: $\int \sin^2(ax)\,dx = \frac{x}{2} - \frac{1}{4a}\sin 2ax + \text{constant}$.

2) Although the Heisenberg Uncertainty Principle $\Delta x \Delta p_x \geq h$ prevents us from determining simultaneously the exact location and momentum of a particle, we can calculation the average position $\langle x\rangle$ and average momentum $\langle p\rangle$ of a particle.

(a) The average position of a particle in the nth energy state of a 1D box is defined by the integral $\langle x_n\rangle = \int_0^L x\psi_n^2(x)\,dx$. Using your expression for the wave function $\psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$, determine $\langle x_n \rangle$. Does the average position depend on the value of n. Explain. Hint: You will need the integral:

$$\int x\sin^2(ax)dx = \frac{x^2}{4} - \frac{x}{4a}\sin(2ax) - \frac{1}{8a^2}\cos(2ax) + \text{constant}$$

(b) The average momentum for a particle in the nth energy state of a 1D box is defined as: $\langle p_n \rangle = \int_0^L \psi_n(x)\left[-i\hbar\frac{d\psi_n(x)}{dx}\right]dx$. Calculate $\langle p_n \rangle$. Explain this result. Hint: You will need the integral:

$$\int \sin(ax)\cos(ax)\,dx = \frac{1}{2a}\sin^2(ax) + \text{constant}$$

(c) Suppose an electron is confined to a box of length L=5x10^{-11}m. Suppose we know the position of the particle in this box to an accuracy of 1%, i.e. $\frac{\Delta x}{L} = 0.01$. Calculate the uncertainty of the momentum Δp. and the uncertainty of the velocity Δv. How accurately do we know the velocity of the electron in this box?

3) This problem deals with calculating the entropy of an ideal monatomic gas:

a) Calculate the single particle partition function q for neon gas under standard conditions i.e. T=298K and V=22.4L. Assume translational motion in a 3D box so that

$$q_{trans} = q_X q_Y q_Z$$

b) Calculate the molar translational internal energy and the molar entropy for neon gas under standard conditions.

c) Calculate the entropy change if the temperature increases to T=500K and the volume doubles.

4) In this problem we will treat the bond vibrations of diatomic molecules as the motions of quantized linear harmonic oscillators.

a) For ^{1}H^{35}Cl the bond force constant is $\kappa = 480Nm^{-1}$. Calculate the reduced mass of HCl i.e. calculate $\mu_{HCl} = \frac{m_H m_{Cl}}{m_H + m_{Cl}}$ and calculate the bond vibration frequency $\nu_{HCl} = \frac{1}{2\pi}\sqrt{\frac{\kappa_{HCl}}{\mu_{HCl}}}$

b) For a harmonic oscillator, on average the kinetic energy K and the potential energy V are equal. This means that for every quantum number n: $\langle K_n \rangle = \langle V_n \rangle = \frac{E_n}{2}$ where $E_n = h\nu\left(n+\frac{1}{2}\right)$. Using the fact that $\langle K_n \rangle = \langle V_n \rangle = \frac{E_n}{2}$, calculate $\langle x_n^2 \rangle$ and $\langle p_n^2 \rangle$ for HCl.

c) Calculate the vibrational partition function for HCl at T=300K. Also, calculate the vibrational heat capacity for HCl at this temperature.

d) $^{127}I_2$ has a much smaller bond vibrational frequency than $^{1}H^{35}Cl$. For ^{127} I_2 $\nu_{I_2} \approx \frac{\nu_{HCl}}{14}$. Repeat the calculations in part c for I_2 and explain the differences in the results.

5) Assume vibrational motion of $^{12}C^{16}O$ can be treated as a quantum mechanical harmonic oscillator. It is conventional to report the rate of bond vibrations in units of wave numbers (cm^{-1}): $\varpi = \frac{1}{\lambda} = \frac{\nu}{c}$ where c is the speed of light c=3x10^{10} cm s^{-1}. The $^{12}C^{16}O$ bond has a vibrational frequency $\varpi = 2057cm^{-1}$.

a) Assuming T=1000K, calculate the vibrational partition function for $^{12}C^{16}O$ in the gas phase.

b) Using your result from part a, calculate the fraction of molecules in the vibrational ground state and the first and second excited states.

c) Suppose $^{12}C^{16}O$ binds to a Hb protein with the oxygen fixed to the protein and the carbon free to vibrate. Assuming the bond spring constant κ does not change, calculate the vibrational frequency ϖ for $^{12}C^{16}O$ attached to Hb.

d) Using your result from part c, calculate the vibrational partition function for $^{12}C^{16}O$ attached to Hb.