CHM 6480 – Problem Set 3
Due date: Sunday, September 20th (by 11:59pm)
Do all of the following problems. Show your work.

1) For the solutions to the TISE for a particle in a one dimentional finite box of dimensions $-b < x < b$, we showed in class that

$$\frac{C}{D} = -\frac{(K + ik)}{(K - ik)}\exp(2ikb) \tag{1.1}$$

where

$$K = [\,2m(V_0 - E)/\hbar^2]^{1/2} \qquad k = [\,2mE/\hbar^2]^{1/2} \tag{1.2}$$

For the even solutions (corresponding to $D = C$), we showed that starting from eq 1.1 the following relationship can be obtained

$$\beta = \alpha \tan(\alpha) \qquad \alpha = kb \qquad \beta = Kb \tag{1.3}$$

Starting with eq 1.1, derive the following equation for the odd solutions to the above TISE (that is, the solutions corresponding to $D = -C$)

$$\beta = -\alpha \cot(\alpha) \tag{1.4}$$

2) Using the definitions for α, β, k, and K given in the previous problem, derive the following equation

$$\alpha^2 + \beta^2 = \frac{2mV_0b^2}{\hbar^2} \tag{2.1}$$

3) The particle in a three dimensional box TISE is a model for the translational energy of a molecule in an ideal gas. In this problem we explore this idea.

Consider a nitrogen molecule (N_2, MW = 28.0 g/mol) in a cubic box of dimensions $\ell = 1.00$ m. Using the equipartition theorem, the average kinetic energy for an N_2 molecule for motion in the x-direction is

$$E_{K,x} = \tfrac{1}{2} k_BT \tag{3.1}$$

where k_B, the Boltzmann constant hasa value $k_B = 1.381 \times 10^{-23}$ J/K.

a) Based on the above information, find the value for n_x, the quantum number for motion of a nitrogen molecule in the x-direction, at T = 300.0 K, and assuming the molecule possesses the average value for kinetic energy predicted from the equipartition theorem. Note that since we defined the particle in a one dimensional box problem as having V = 0 for $-b < x < b$, it follows that $\ell = 2b$. As discussed in class, for a particle in an infinite one dimensional box, the energies for the bound states are

$$E_n = \frac{n^2h^2}{32mb^2} \qquad n = 1, 2, 3, \ldots \tag{3.2}$$

b) Based on your answer in a, find the value for ΔE_{nx}, defined as

$$\Delta E_{nx} = E_{nx+1} - E_{nx} \tag{3.3}$$

for a nitrogen molecule in the above box and having the average value for kinetic energy for motion in the x-direction. Note that ΔE_{nx} represents the difference in energy between the n_x and n_{x+1} energy levels.

c) Based on your answers above, is it a good approximation to treat the molecules of an ideal gas classically for conditions similar to those in this problem? Why or why not?

4) One interesting application to the particle in a box model is for the observed first wavelength of light absorption for a molecule containing conjugated single and double carbon bonds. Consider the following molecules:

ethane	(CH_2=CH_2)	λ = 162. nm
1,3 butadiene	(CH_2=CH-CH=CH_2)	λ = 217. nm
1,3,5 hexatriene	(CH_2=CH-CH=CH-CH=CH_2)	λ = 247. nm

The particle in a box model can be used as a crude approximation for the energy levels for the pi-electrons in the above molecule.

a) Using the one dimensional particle in an infinite box TISE, find the values for energy for the n = 1, 2, 3, and 4 levels for electrons in ethane, 1,3 butadiene, and 1,3,5 hexatriene. For the size of the box for these molecules use $\ell = 2b = 2n_d$ (0.144 nm) , where n_d = number of double bonds and 0.144 nm represents the average value for the bond length for a C-C and C=C bond.

b) The number of pi-electrons in a conjugated system is $2n_d$, where n_d is as defined above. Since an energy level can hold two electrons, the lowest energy electronic transition will be $n_d \rightarrow n_d+1$. Using your results in a, predict the wavelength (in nm) for the lowest energy electronic transition for the pi-electrons in ethane, 1,3 butadiene, and 1,3,5 hexatriene.

c) How does the values predicted for the wavelength for the lowest energy transition for the pi-electrons compare to the observed values? Is the trend in wavelengths the same? Are the predicted wavelengths close to the experimental wavelengths?

5) Unlike the particle in a one dimensional infinite box, there are only a finite number of bound solutions for the particle in a finite box TISE. The number of bound states (n*) is the smallest positive integer satisfying the relationship

$$n^* > [32mV_0b^2/h^2\ ]^{1/2} \qquad (5.1)$$

a) Find the number of bound states for the case of an electron ($m_e = 9.11 \times 10^{-31}$ kg) in a one dimensional box of length $\ell = 2b = 0.400$ nm, with $V_0 = 4.00 \times 10^5$ cm^{-1} (1 $cm^{-1} = 1.986 \times 10^{-23}$ J, h = 6.626×10^{-34} J•s).

b) Find the value for E_n for all of the bound states (n = 1 to n = n*) for the electron in part a of this problem. Give your final answers in units of J and in units of cm^{-1} (cm^{-1} is a more convenient unit in spectroscopy, which is one of the main areas of application for quantum chemistry). This will have to be done iteratively by trial and error. One way to proceed is as follows:

i.) Pick a value for n (quantum number). For this value, we know $(n - 1)\pi/2 < \alpha < n\pi/2$ must be true (see Fig 2.4.1 of Handout 2).

ii.) Pick a trial value for α

iii.) Calculate the corresponding value for β in the following two ways:

Using eq 2.1 $\quad \beta = [\ (2mV_0b^2/\hbar^2) - \alpha^2\ ]^{1/2} \qquad (5.2)$

Using either eq 1.3 $\quad \beta = \alpha \tan(\alpha) \quad$ for n = 1, 3, 5, … $\qquad (5.3)$

or eq 1.4 $\quad \beta = - \alpha \cot(\alpha) \quad$ for n = 2, 4, 6, … $\qquad (5.4)$

iv.) For the correct value for α, the value for β calculated by eq 5.2 and either eq 4.3 (for n = 1, 3, 5, …) or eq 5.4 (for n = 2, 4, 6) should be the same. If they are not, pick a new trial value for α.

v.) Repeat steps i.-iv. above until a sufficiently precise value for α is found. Use that value to find the corresponding value for E (in J and in cm^{-1}). Find your values for energy to three significant figures.

c) Find the values for E_n for n = 1 to n = n*) for the case $V_0 = \infty$ (corresponding to the electron being treated as a particle in a one dimensional infinite box – see eq 3,2 above). Compare these results to those found in part b for the electron in a fiite box. Are the results surprising? Why or why not?