Chemistry 1410, Hour Exam 2, Nov. 7, 2007.

This exam consists of three (3) problems. Please work them all, and provide brief descriptions of your reasoning as appropriate. GOOD LUCK!

1) [30%] Consider a neutral Helium atom in its ground state electronic configuration. We will use two extreme assumptions to obtain an upper and a lower bound on the binding energy of an electron in the atom. Namely:

(a) i) Assume that the orbit of the electron in question (to be denoted as the "tagged" electron) takes place completely *inside* the other electron. In this situation, the tagged electron sees a bare He^{2+} nucleus (the other electron is "invisible" to it). Calculate the 1s energy level for this electron. [This is approximately the binding energy of the tagged electron when the atom is in its ground state configuration, since it is approximately the energy required to remove the electron from the atom.]

ii) Assume that the orbit of the electron in question takes place completely *outside* the other electron. In this case, the other electron completely screens the tagged electron, which then sees an effective +1 nucleus. Calculate the 1s energy level for this electron.

(b) Give a simple argument why the true binding energy of an electron in the ground electronic state *He* atom should lie between the values obtained in i) and ii) above.

(c) Use the same reasoning to bracket (i.e., determine upper and lower bounds to) the average radial distance from the nucleus $< r >$ of an electron in the ground electronic state of a neutral *He* atom.

2) [35%] The atoms of diatomic molecule, masses m_1, m_2 [hence with reduced mass $\mu = m_1 m_2 /(m_1 + m_2)$], are bound by the central potential $v(r) = \frac{1}{2} k r^2$. Thus, if the molecule is in angular momentum state l (with possible values $l = 0, 1, 2, ...$), the relative motion of the atoms in the molecule is determined by the effective radial potential:

$$v^{eff}(r) = \frac{1}{2} k r^2 + \frac{\hbar^2 l(l+1)}{2\mu r^2}$$

a) Show that the minimum value of $v^{eff}(r)$ occurs precisely at the radius $r_m = \left[\frac{\hbar^2 l(l+1)}{\mu k} \right]^{1/4}$.

b) For nonzero values of l, compute $d^2 v^{eff}(r)/dr^2$ at the value $r = r_m$. [Hint: the answer turns out to be *in*dependent of the value of *l*.]

c) Using the quadratic approximation to $v^{eff}(r)$ obtained by expanding it in a 2nd order Taylor Series about $r = r_m$, calculate the difference between the lowest two quantum mechanical energy eigenvalues corresponding to a given non-zero value of l. [Hints: i) Think "harmonic oscillator"; ii) Again, the answer turns out to be *in*dependent of the value of *l*.]

3) [35%] Consider a particle of mass *m* subjected to the potential energy function $V(x)$ depicted in Fig. 1, namely a box of width a with an infinite potential barrier at $x = 0$ and a finite barrier V_0 for $x > a$. Explicitly:

$$V(x) = \begin{cases} \infty & , x < 0 \\ 0 & , 0 < x < a \\ V_0 & , x > a \end{cases}$$

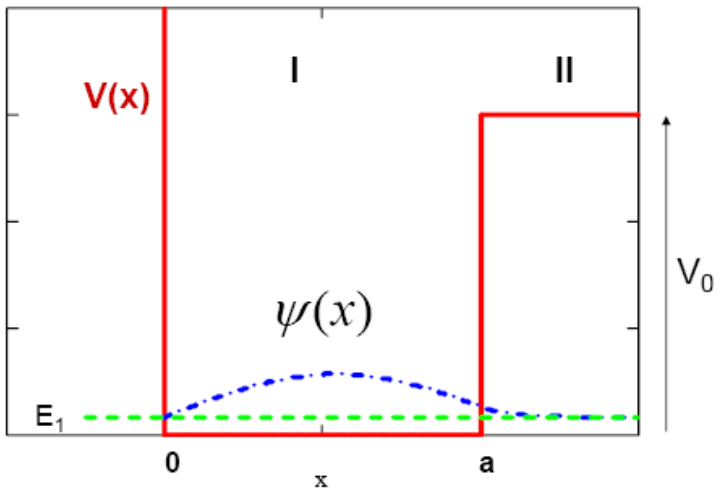

Fig. 1 1D box with infinite wall at *x=0* and finite height wall (potential energy value V_0) at *x=a*: ground state energy eigenfunction and energy level are sketched schematically.

a) The energy eigenfunctions have the form:

$$\psi_I(x) = \sin(kx)$$

$$\psi_{II}(x) = Ae^{-\kappa x}$$

with $k(E) \equiv \sqrt{2mE}/\hbar$ and $\kappa(E) \equiv \sqrt{2m(V_0 - E)}/\hbar$. [Note: as indicated in Fig. 1, regions *I,II* cover *0<x<a ,x>a*, respectively.]

Briefly explain why the energy eigenfunctions have this functional form.

b) Show that applying the usual matching conditions at *x=a* leads to the following *quantization condition* for the energy *E*:

$$\cot\left(\frac{\sqrt{2mE}a}{\hbar}\right) = -\sqrt{\frac{V_0 - E}{E}} \qquad [1]$$

c) To analyze this equation further, we introduce dimensionless versions of the system energy and the barrier height. In particular, let $\varepsilon \equiv E / E_{gs}^{\infty}$ and $v_0 = V_0 / E_{gs}^{\infty}$, where E_{gs}^{∞} is the ground state energy eigenvalue of a particle in an infinitely deep box of width *a*, namely $E_{gs}^{\infty} = \frac{\hbar^2 \pi^2}{2ma^2}$. Substituting into Eq. 1 yields the equivalent equation:

$$-\cot(\pi\sqrt{\varepsilon}) = \sqrt{\frac{v_0 - \varepsilon}{\varepsilon}} \qquad [2]$$

In Fig. 2, we plot the left hand side of Eq. 2 vs. the right hand side of Eq. 2 on the same graph for the case that $v_0 = 15$.

i) How many bound-state energy eigenfunctions are there in a box characterized by this value of v_0?

ii) Estimate (roughly) from Fig. 2 the energy eigenvalue corresponding to the <u>third</u> state in this box (labeling the ground state as state 1); state your answer in units of E_{gs}^{∞}. What would its energy be if $V_0 = \infty$ (i.e., for a standard [infinitely deep] box of width *a*)?

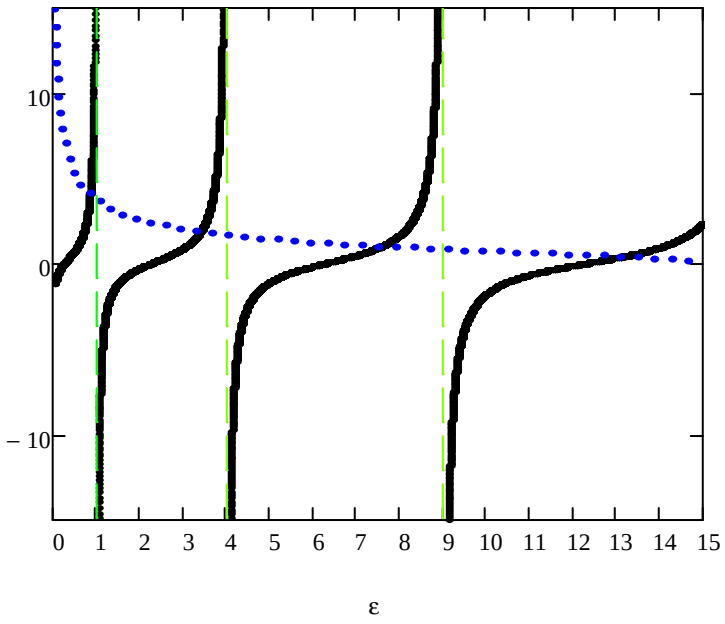

Fig. 2 Left hand side of Eq. 2 = solid line; right hand side of Eq. 2 = dotted line. [Vertical dashed lines indicate the values of $\varepsilon = 1, 4, 9$.] Here $v_0 = 15$.