Chem 532: Problem Set #2

Due by 5pm: Friday, Sept. 23rd

(1) The energy states for a particle in a 3-dimensional box with lengths L_1, L_2, and L_3 are

given by $E(n_1,n_2,n_3)=\frac{h^2}{8m}\left[\left(\frac{n_1}{L_1}\right)^2+\left(\frac{n_2}{L_2}\right)^2+\left(\frac{n_3}{L_3}\right)^2\right]$

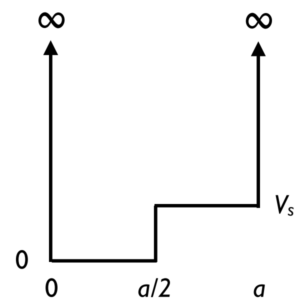
These energy levels are sometimes used to model the motion of electrons in a central metal atom that is surrounded by six ligands.

a) Show that the lowest energy level is nondegenerate and the 2nd level is triply degenerate if the box is cubical. Label the states by their quantum numbers n_1, n_2, n_3.

b) Consider a box of volume V = $L_1L_2L_3$ with 3 electrons inside (2 in the lowest energy level, 1 in the next). Show that the total energy in this case is equal to $E=\frac{h^2}{8m}\left(\frac{12}{L_1^2}\right)$ if L_1=L_2=L_3.

c) A lower total energy results upon rectangular distortion (L_1=L_2≠L_3) at constant volume, $E=\frac{h^2}{8m}\left(\frac{6}{L_1^2}+\frac{6}{L_3^2}\right)$ (assuming L_3>L_1), Show that the ratio of L_3 to L_1 that minimizes the total energy is equal to $\sqrt{2}$. This problem is related to Jahn-Teller distortions in molecules.

(2) Consider a 1-dimensional-box potential such that the bottom of the box has a step at the midpoint, where the step height is V_S and the two sides have infinite potential. Use solutions of the trigonometric variety throughout this problem.



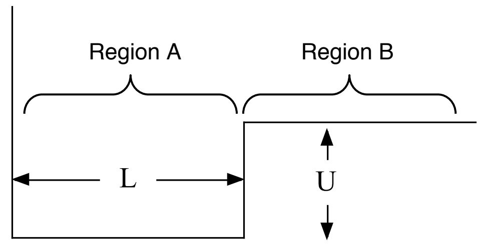
(a) What boundary conditions must be applied to the solutions of the Schrödinger equation at x=0, x=a, and x=a/2 ?

(b) What is the solution of the Schrödinger equation for x<a/2 that satisfies the x=0 boundary condition, but not that at x=a/2?

(c) What is the solution of the Schrödinger equation for x>a/2 that satisfies the x=a boundary condition, but not that at x=a/2? Assume that E>V_S.

~~**(d)** Take the solutions from (b) and (c) and apply the boundary conditions appropriate for x=a/2. It should be possible to manipulate the resulting equations into a single equation that determines the eigenvalues. What is the equation? It is not necessary to~~ solve it.

(3) In class we considered an electron in a simple square-well potential of depth U and width L



It is convenient to chose "atomic units" (a.u.) in which $\hbar = e = m = 1$. Suppose that the well is 2 Å wide (L = 3.781 a.u.) and 54.4 eV deep (U = 2.0 a.u.). Consider the solutions of the wave equation in the "continuum" region $E > U$ (i.e., $E > 2.0$ a.u.), where the electron is classically free to move over both regions A and B (i.e., through the entire space $0 < x < \infty$). As discussed in class, the continuum ("scattering state") wave function for energy E may be written in the two regions in the form

$$\psi_A(x) = A \sin k_A x \qquad\qquad \psi_B(x) = B \sin\left(k_B x + \delta\right)$$

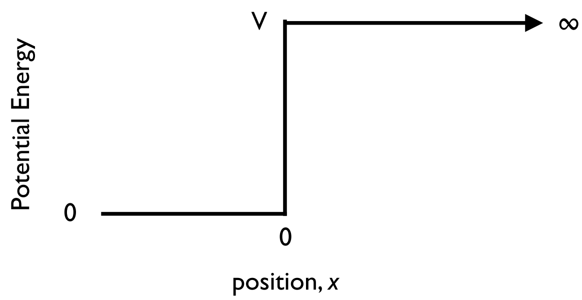
where $k_A = \sqrt{\dfrac{2mE}{\hbar^2}}$ and $k_B = \sqrt{\dfrac{2m\left(E - U\right)}{\hbar^2}}$

(a) Using appropriate matching conditions at $x = L$, determine an expression for the phase shift δ and then show that the ratio of amplitudes must be

$$\frac{A}{B} = \frac{\sin\left[\tan^{-1}\left(\dfrac{k_B}{k_A}\tan k_A L\right)\right]}{\sin k_A L}$$

(b) At any given E, the quantity $\left(\dfrac{A}{B}\right)^2$ is a measure of the relative probability of finding the electron inside the well. It is equally a measure of the time that particles incident from the right spend "above" the well (i.e., in the region A of lower potential energy), as compared to an interval of equal length on region B. For certain special energy values E, a quantum particle spends an unusually long period of time "trapped" in the well. This phenomenon is known as a <u>resonance</u>, and manifests itself as a peak in the quantum probability ratio $\left(\dfrac{P_A}{P_B}\right)_{\text{quantum}} = \left(\dfrac{A}{B}\right)^2$, plotted as a function of E. The <u>width</u> of the resonance peak is a measure of the "lifetime" of the trapped particle in the well, with narrower resonances corresponding to longer-lived states. Evaluate $(A/B)^2$ as a function of E from 2.05 to 12.00 a.u. in 0.05 a.u. steps. Plot up the results and see if you observe any resonances (note their energies if you observe any).

(4) Consider an electron incident from the left on a potential energy barrier of finite height (V) with infinite thickness



(a) The general solutions of the time independent Schrödinger equation in Zone I ($x < 0$) and in Zone II ($x > 0$) are

$$\psi_I = Ae^{ikx} + Be^{-ikx}$$
$$\psi_{II} = A'e^{ik'x} + B'e^{-ik'x}$$

What are the forms of the Hamiltonians in these two zones and the definitions of k and k' in terms of E and V?

(b) For a total energy below the barrier ($E < V$), show that the solution in Zone II is given by $\psi_{II} = A'e^{-\kappa x}$, where $\kappa = \sqrt{\frac{2m(V-E)}{\hbar^2}}$. Justify and explain your answer.

(c) The reflection probability for the incident electron is given by $R = \frac{|B|^2}{|A|^2}$. Use the proper continuity conditions that are imposed on ψ_1 and ψ_2 at x=0 to obtain expressions for R for the cases of $E \leq V$ and $E > V$. For electrons incident on a metal surface, V = 10 eV. Evaluate and plot R as a function of E.