Chemistry 331 **Problem Set #6** (due Monday 09 November, in class)

1. A particle in a box extending from $x = -L/2$ to $x = L/2$ is described by the wave function
[2] $\psi(x) = A\cos(\pi x/L)$. Show the normalization constant A is $(2/L)^{1/2}$.

2. A free electron with 25.0 eV kinetic energy moving in the positive x-direction hitting an infinitely-wide potential energy barrier $V_0 = 15.0$ eV at $x = 0$ is described by the wave functions

$\psi_I(x) = A\exp(iK_I x) + B\exp(-iK_I x)$	zone I	$x < 0$	$V(x) = 0$
$\psi_{II}(x) = C\exp(iK_{II} x)$	zone II	$x \geq 0$	$V(x) = V_0$

with $K_I = 4.00\ \text{nm}^{-1}$ and and $K_{II} = 1.00\ \text{nm}^{-1}$.

a) Show that the probability distribution function $P_I(x)$ for the electron in zone I is $(A + B)^2$.

b) Show that the probability distribution function $P_{II}(x)$ for the electron in zone II is C^2.

[6] **c)** Use parts **a** and **b** to show $A + B = C$.

d) Calculate the probability the electron is reflected at the barrier.

e) Calculate the electron speed in zone II.

f) Why is the electron speed higher in zone I?

3. **a)** Use the equations copied below to calculate the tunneling probability T for a 1.00 eV electron hitting a 0.100-nm-wide barrier with $V_0 = 5.00$ eV.

$$\beta = \frac{L\sqrt{2m(V_0 - E)}}{\hbar} \qquad T = \left[1 + \frac{V_0^2}{16E(V_0 - E)}\left(e^{\beta} - e^{-\beta}\right)^2\right]^{-1}$$

[2] **b)** Without doing any calculations, why would you expect a much smaller tunneling probability for a 1.00 eV proton hitting the barrier?

4. What is **Very Large Scale Integration** (VLSI)? Why is it important? Quantum mechanical tunneling
[2] places a fundamental limit on VLSI. Explain briefly.

5. Quantum mechanical tunneling is believed to play a key role in the rates of certain biochemical
[2] reactions. Give two examples.

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6. Before exploring quantum mechanical oscillators, this question summarizes the basic features of the classical harmonic oscillation of mass m with displacement

$$x(t) = A\cos(2\pi\nu t)$$

at time t. A and ν are the amplitude and frequency of the oscillation.

a) Use Newton's law ($F = ma$) to show the force acting on the mass is $F(t) = -m(2\pi\nu)^2 x(t)$.

b) Use Hooke's law $F(t) = -kx(t)$ to show the potential energy is $V(t) = kx(t)^2/2$. *Hint*: $F = -\mathrm{d}V/\mathrm{d}x$.

[6] **c)** Show the frequency of the oscillator is $\nu = \dfrac{1}{2\pi}\sqrt{\dfrac{k}{\mu}}$.

d) Show the kinetic energy is $T(t) = \frac{1}{2}\, m(2\pi\nu)^2 \sin^2(2\pi\nu t)$.

e) The potential energy and the kinetic energy of the oscillator are constantly changing. Show, however, the total energy is constant and equal to $kA^2/2$.

$$V(t) + T(t) = kA^2/2$$

Chem 331 **Assignment #6**

Q1 $\psi(x) = A\cos(\pi x/L) \qquad -L/2 \le x \le L/2$

to normalize $\psi(x)$, find the value of A to give:

$$1 = \int_{-L/2}^{L/2} \psi^*(x)\,\psi(x)\,dx = \int_{-L/2}^{L/2} \psi^2(x)\,dx$$

$\boxed{\psi(x) \text{ is real: } \psi^*(x) = \psi(x)}$

$$= \int_{-L/2}^{L/2} A^2\cos^2(\pi x/L)\,dx = A^2\int_{-L/2}^{L/2}\cos^2(\pi x/L)\,dx$$

$$= A^2\left[\frac{x}{2} + \frac{\sin(2\pi x/L)}{4\pi/L}\right]\Bigg|_{-L/2}^{L/2} \Longleftarrow \left(\text{from a table of integrals}\right)$$

$$= A^2\left[\frac{L}{4} - \left(-\frac{L}{4}\right) + \frac{\overset{0}{\cancel{\sin(\pi)}} - \overset{0}{\cancel{\sin(-\pi)}}}{4\pi/L}\right]$$

$$1 = A^2\frac{L}{2} \qquad \boxed{A = \sqrt{\frac{2}{L}}}$$

Q2 a) probability distribution function $P_I(x)$ in zone I:

$$P_I(x) = \psi_I^*\psi_I = \left(Ae^{-ik_Ix} + Be^{ik_Ix}\right)\left(Ae^{ik_Ix} + Be^{-ik_Ix}\right)$$

$$= A^2e^0 + ABe^{-2ik_Ix} + BAe^{2ik_Ix} + B^2e^0$$

$$= A^2 + AB\left(e^{2ik_Ix} + e^{-2ik_Ix}\right) + B^2$$

$$= A^2 + AB\left[\cos(2k_Ix) + \cancel{i\sin(2k_Ix)} + \cos(-2k_Ix) - \cancel{i\sin(2k_Ix)}\right] + B^2$$

$$= A^2 + AB\left[\cos(2k_Ix) + \cos(2k_Ix)\right] + B^2$$

$$\boxed{P_I(x) = A^2 + B^2 + 2AB\cos(2k_Ix)} \quad \boxed{= (A+B)^2 \text{ at } x = 0}$$

(Q2 cont.)

b) in zone II:

$$P_{II}(x) = \psi_{II}^*(x)\,\psi_{II}(x)$$
$$= (Ce^{-ik_{II}x})(Ce^{ik_{II}x})$$
$$= C^2 e^0$$
$$\boxed{P_{II}(x) = C^2}$$

c) at $x = 0$, $\psi_I(0) = \psi_{II}(0)$ (wave functions must be single-valued)

and $P_I(0) = P_{II}(0)$ (ditto for $P(x)$)

$$A^2 + B^2 + 2AB\underbrace{\cos(0)}_{1} = C^2$$

$$A^2 + B^2 + 2AB = C^2$$

$$(A+B)^2 = C^2 \qquad \boxed{A + B = C}$$

d) reflection probability $R = \dfrac{2\frac{E}{V_0} - 2\sqrt{\frac{E}{V_0}\left(\frac{E}{V_0}-1\right)} - 1}{2\frac{E}{V_0} + 2\sqrt{\frac{E}{V_0}\left(\frac{E}{V_0}-1\right)} - 1}$

$$\frac{E}{V_0} = \frac{25.0\text{ eV}}{15.0\text{ eV}} = \frac{5}{3}$$

$$R = \frac{2\frac{5}{3} - 2\sqrt{\frac{5}{3}\frac{2}{3}} - 1}{2\frac{5}{3} + 2\sqrt{\frac{5}{3}\frac{2}{3}} - 1} = \frac{0.2251}{4.4415}$$

$$\boxed{R = 0.0507}$$

(Q2 cont.)

e) electron speed in zone II ?

the total energy of the electron is 25.0 eV.
→ kinetic + potential energy

in zone II : $E_{II} + V_{II} = 25.0\ eV$

kinetic energy in zone II → $E_{II} = 25.0\,eV - V_0 = (25.0 - 15.0)\,eV$

$$\frac{1}{2} m_e v_{II}^2 = 10.0\,eV = E - V_0$$

$$v_{II} = \sqrt{\frac{2(E-V_0)}{m_e}} = \sqrt{\frac{2\,(10.0\,eV)\;1.602\times10^{-19}\,J\,eV^{-1}}{9.110\times10^{-31}}}$$

$$\boxed{v_{II} = 1.88\times10^{6}\ m\,s^{-1}}$$

f) in zone II, the electron has 10.0 eV kinetic energy

in zone I, it has 25.0 eV kinetic energy
∴ "faster"

Q3 a) $$\beta = \frac{L\sqrt{2m(V_0 - E)}}{h/2\pi}$$ $V_0 = 5.00\ eV$, $E = 1.00\ eV$

$$\beta = \frac{(0.100\times10^{-9}\,m)\sqrt{2\,(9.110\times10^{-31}\,kg)(4.00\times1.602\times10^{-19})\,J}}{(6.626\times10^{-34}\,Js)/2\pi}$$

$$\boxed{\beta = 1.024}$$

(Q3 a cont.)

tunneling probability $T = \left[1 + \frac{V_0^2}{16E(V_0-E)}(e^{\beta} - e^{-\beta})^2\right]^{-1}$

$= \left[1 + \frac{5.00^2}{16(1.00)4.00}(e^{1.024} - e^{-1.024})^2\right]^{-1}$

$\boxed{T = 0.303}$

b) a proton is $\approx$ 2000 times heavier than an electron, making β much larger, and therefore T much smaller

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Q4 VLSI : manufacturing integrated circuits with millions or even billions of diodes, transistors, resistors, capacitors on a single semiconductor chip

as the density of the cirnit elements increases, the circuit elements get so close together that electrons can tunnel to places they shouldn't be, causing errors in device performance

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Q5 photosynthesis — higher efficiency electron transfer

enzyme reactions — transfer electrons at higher rates

vision — faster conversion of photon energies to chromaphore reactions

(Q6) mass m oscillates classically with

displacement $x(t) = A\cos(2\pi\nu t)$

a) force = (mass)(acceleration)

$$= m\frac{dv}{dt} = m\frac{d}{dt}\frac{dx}{dt} = m\frac{d^2x}{dt^2}$$

$$= m\frac{d^2}{dt^2}A\cos(2\pi\nu t)$$

$$\frac{d^2\cos(at)}{dt^2} = -a^2\cos(at)$$

$$= -m(2\pi\nu)^2 A\cos(2\pi\nu t)$$

$$F = -m(2\pi\nu)^2 x(t)$$

b) Hooke's law $F = -k\,x(t)$

compare to $F = -m(2\pi\nu)^2 x(t)$

find force constant $k = m(2\pi\nu)^2$

$$F = -\frac{\partial V}{\partial x} = -kx$$

$$\int_{V(0)}^{V(x)} dV = k\int_0^x x\,dx = k\frac{x^2}{2}\Bigg|_0^x = \frac{kx^2}{2}$$

c) from $k = m(2\pi\nu)^2$

get $\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$

(here mass m = reduced mass μ (only one mass))

d) kinetic energy: $T = \frac{1}{2} m v_x^2$

$$= \frac{1}{2} m \left(\frac{dx}{dt}\right)^2$$

$$= \frac{1}{2} m \left(\frac{d}{dt} A\cos(2\pi\nu t)\right)^2$$

$$= \frac{1}{2} m \left[(-2\pi\nu) A \sin(2\pi\nu t)\right]^2$$

$$= \frac{1}{2} m (2\pi\nu)^2 A^2 \sin^2(2\pi\nu t)$$

e) total energy $= T + V$

$$= \frac{1}{2} m v_x^2 + \frac{1}{2} k x^2$$

$$= \frac{1}{2} \overbrace{m (2\pi\nu)^2}^{=k} A^2 \sin^2(2\pi\nu t) + \frac{1}{2} k A^2 \cos^2(2\pi\nu t)$$

$$= \frac{1}{2} k A^2 \sin^2(2\pi\nu t) + \frac{1}{2} k A^2 \cos^2(2\pi\nu t)$$

$$= \frac{1}{2} k A^2 \underbrace{\left(\sin^2(2\pi\nu t) + \cos^2(2\pi\nu t)\right)}_{=1}$$

$$\boxed{T + V = \frac{1}{2} k A^2}$$