Chemistry 331 **Problem Set #5** (due Monday 02 November, in class)

1. It is useful to normalize the wave functions used in quantum mechanics. Why? [1]

2. Can the following wave functions be normalized? If so, calculate the normalization factor.

a) $\psi(x) = \sin(\pi x/L)$ on the interval $-\infty < x < +\infty$

[4] **b)** $\psi(x) = \sin(\pi x/L)$ on the interval $0 < x < L$

c) $\psi(x) = e^{-i\theta}$ on the interval $0 < \theta < 2\pi$

Hint: A table of integrals might be useful to answer this question. See **http://integral-table.com/**

3. Solving Schrodinger's equation $\hat{H}\psi_n(x) = E_n\psi(x)$ for a particle in a box gives the wave functions

$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$$

The particle is clearly *moving* back and forth in the box, but $\psi_n(x)$ is a **stationary wave** that is *not moving*! Are we missing something here? *Yes*!

Use the **time-dependent Schrodinger equation**

$$\hat{H}\Psi_n(x,t) = i\hbar\left(\frac{\partial\Psi(x,t)}{\partial t}\right)_x$$

[3] to show the complete wave function for the particle in a box is

$$\Psi_n(x,t) = \psi_n(x)e^{-iE_nt/\hbar}$$

Hints: Because the Hamiltonian operator is a function of x, but not t, $\Psi_n(x,t)$ can be expressed as the product $\psi_n(x)f(t)$ of the function $\psi_n(x)$ that depends only on x and the function $f(t)$ that depend only on t. Use the method of **separation of variables** (recall Assignment #3) to show

$$f(t) = e^{-iE_nt/\hbar}$$

4. For a particle in a box of width L:

$$<x> = \frac{L}{2} \qquad <x^2> = L^2\left(\frac{1}{3} - \frac{1}{2\pi^2n^2}\right) \qquad <p_x> = 0 \qquad <p_x^2> = \frac{n^2h^2}{4L^2}$$

[3] Prove the particle obeys the **Heisenberg Uncertainty Principle** $\sigma_x\sigma_{px} \geq h/4\pi$.

5. This question refers to a <u>classical</u> particle in a box extending from $x = 0$ to $x = L$.

a) A classical particle is equally likely to be anywhere in the box, so the probability distribution function $P(x)$ is a constant. Use the normalization requirement

$$1 = \int_0^L P(x)\mathrm{d}x$$

to show $P(x) = 1/L$.

b) Use $P(x)$ to derive expressions for $<x>$, $<x^2>$ and σ_x for a classical particle.

[6] **c)** Show σ_x for a classical particle in a box equals σ_x for a quantum particle in a box (see Question 4) in the limit $n \to \infty$.

d) Part **c** illustrates an important principle of quantum mechanics. Explain.

6. **a)** An electron with kinetic energy 9.50 eV hits a 10.0 eV potential energy barrier. Calculate the penetration depth.

[2] **b)** The penetration depth is nonclassical. Why?

7. **a)** An electron with kinetic energy 11.0 eV hits a 10.0 eV potential energy barrier. Calculate the probability the electron will be reflected by the barrier.

[2] **b)** The reflection of the electron is nonclassical. Why?

Chem 331 Assignment #5

(Q1) Quantum mechanical wave functions are normalized

[for example: $\int \psi^*(x)\,\psi(x)\,dx = 1$]

so that $\psi^*\psi$ is a probability distribution

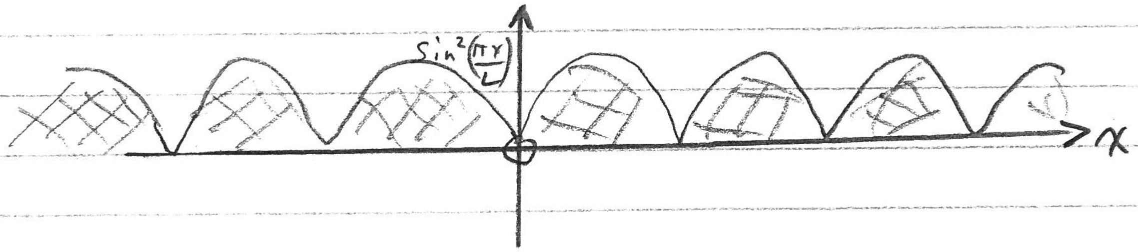
suitable for calculating average $\langle x\rangle, \langle x^2\rangle, \langle p_x\rangle, \langle E\rangle, ..$ values

[for example: $\langle x\rangle = \int \psi^*(x)\, x\, \psi(x)\,dx$]

(Q2) a) can $\psi(x) = \sin(\pi x/L)$ be normalized on the interval $-\infty < x < \infty$?

$\boxed{\text{Nope!}}$ $\int_{-\infty}^{\infty} \psi^*(x)\,\psi(x)\,dx = \int_{-\infty}^{\infty} \sin^2(\pi x/L)\,dx = \infty$

a graph of $\sin^2(\pi x/L)$:



b) can $\psi(x) = \sin(\pi x/L)$ be normalized on the interval $0 < x < L$?

$\boxed{\text{Yes!}}$

(Q2 b cont.) $\left(\text{look up: } \int \sin^2(ax)\,dx = \frac{x}{2} - \frac{\sin(2ax)}{4a}\right)$

$$\int_0^L \psi^*(x)\,\psi(x)\,dx = \int_0^L \sin\left(\frac{\pi x}{L}\right)\sin\left(\frac{\pi x}{L}\right)dx$$

$$= \int_0^L \sin^2\left(\frac{\pi x}{L}\right)dx = \left(\frac{x}{2} - \frac{\sin(2\pi x/L)}{4\pi/L}\right)\Bigg|_0^L$$

$$= \left(\frac{x}{2} - \cancelto{0}{\frac{\sin(2\pi)}{4\pi/L}}\right)\Bigg|_0^L = \frac{L}{2} - 0 = \frac{L}{2}$$

To give a normalized wave function, use

$$\boxed{\underset{(\text{normalized})}{\psi(x)} = \sqrt{\frac{2}{L}}\,\sin\left(\frac{\pi x}{L}\right)}$$

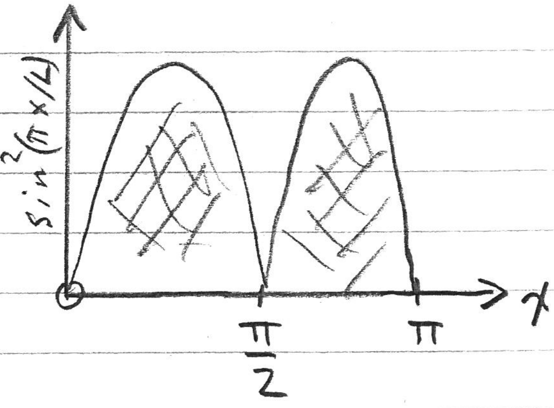
with normalization factor $\sqrt{\frac{2}{L}}$, then

$$\underset{\text{normalized}}{\int \psi^*(x)\,\psi(x)\,dx} \quad \int_0^L \sqrt{\frac{2}{L}}\sin\left(\frac{\pi x}{L}\right)\sqrt{\frac{2}{L}}\sin\left(\frac{\pi x}{L}\right)dx$$

$$= \frac{2}{L}\int_0^L \sin^2\left(\frac{\pi x}{L}\right)dx$$

$$= \frac{2}{L}\,\frac{L}{2}$$

$$= 1$$



(Q2 cont.)

c) can $\psi(\theta) = e^{-i\theta}$ be normalized on the interval $0 < \theta < 2\pi$? $\boxed{\text{Yes!}}$

$$\int_0^{2\pi} \psi^*(\theta)\,\psi(\theta)\,d\theta = \int_0^{2\pi} e^{i\theta} e^{-i\theta}\,d\theta = \int_0^{2\pi} e^{i\theta - i\theta}\,d\theta$$

$$= \int_0^{2\pi} e^{0}\,d\theta = \int_0^{2\pi} 1\,d\theta = 2\pi$$

the normalization factor here is $\boxed{\sqrt{\frac{1}{2\pi}}}$

$$\psi(\theta)_{\text{normalized}} = \sqrt{\frac{1}{2\pi}}\; e^{-i\theta}$$

(Q3) time-dependent Schrodinger equation:

$$\hat{H}\Psi(x,t) = i\hbar\left(\frac{\partial \Psi(x,t)}{\partial t}\right)_x$$

using separation of variables: $\Psi(x,t) = \psi(x) f(t)$ and

$$\hat{H}[\psi(x) f(t)] = i\hbar\left(\frac{\partial}{\partial t}\psi(x) f(t)\right)_x$$

$$f(t)\hat{H}\psi(x) = f(t) E \psi(x) = i\hbar\,\psi(x)\left(\frac{\partial f(t)}{\partial t}\right)_x$$

$$E f(t) = i\hbar \frac{df(t)}{dt}$$

$$\frac{E}{i\hbar} = \frac{1}{f(t)}\frac{d f(t)}{dt} = \frac{d \ln f(t)}{dt} \Longrightarrow f(t) = e^{Et/i\hbar}$$

$$f(t) = e^{iEt/ii\hbar} = e^{-iEt/\hbar}$$

Q4 $\sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2$ (the variance of x)

$$= L^2\left(\frac{1}{3} - \frac{1}{2\pi h^2}\right) - \left(\frac{L}{2}\right)^2$$

$$= L^2\left(\frac{1}{3} - \frac{1}{2\pi n^2} - \frac{1}{4}\right)$$

$$\left(\frac{1}{3} - \frac{1}{4} = \frac{4}{12} - \frac{3}{12} = \frac{1}{12}\right)$$

$$\boxed{\sigma_x^2 = L^2\left(\frac{1}{12} - \frac{1}{2\pi h^2}\right)}$$

$$\sigma_{p_x}^2 = \langle p_x^2 \rangle - \langle p_x \rangle^2 = \frac{n^2 h^2}{4L^2} - 0$$

$$\boxed{\sigma_{p_x}^2 = \frac{n^2 h^2}{4L^2}}$$

$$\sigma_x \sigma_{p_x} = \sqrt{\cancel{L^2}\left(\frac{1}{12} - \frac{1}{2\pi n^2}\right)}\ \sqrt{\frac{n^2 h^2}{4\cancel{L^2}}}$$

$$= \sqrt{\frac{1}{12} - \frac{1}{2\pi n^2}}\ \frac{nh}{2}$$ (multiply and divide by 2π)

$$= \sqrt{\frac{4\pi^2}{12} - \frac{4\pi^2}{2\pi n^2}}\ \frac{nh}{2}\ \frac{1}{2\pi}$$

$$= \sqrt{\frac{\pi^2}{3} - \frac{2}{n^2}}\ n\frac{\hbar}{2}$$ minimum value for $n = 1$

$$= \sqrt{\frac{\pi^2}{3} - 2}\ \frac{\hbar}{2}$$ for $n = 1$

$$\boxed{\overset{\text{min.}}{\sigma_x \sigma_{p_x}} = 1{\cdot}135\ \frac{\hbar}{2} > \frac{\hbar}{2}}$$

Q5 a) $P(x) = k$ (a constant)

$$1 = \int_0^L P(x)\,dx = \int_0^L k\,dx = k\int_0^L dx = kL$$

$$k = \frac{1}{L} \qquad \boxed{P(x) = \frac{1}{L}}$$

b) average x value $\langle x \rangle = \int_0^L x\,P(x)\,dx$

$$\langle x \rangle = \int_0^L x\,\frac{1}{L}\,dx = \frac{1}{L}\int_0^L x\,dx = \frac{1}{L}\,\frac{x^2}{2}\Big|_0^L$$

$$= \frac{1}{L}\left(\frac{L^2}{2} - 0\right) = \boxed{\frac{L}{2}}$$

average x^2 value $\langle x^2 \rangle = \int_0^L x^2 P(x)\,dx = \frac{1}{L}\int_0^L x^2 dx = \frac{1}{L}\,\frac{x^3}{3}\Big|_0^L$

$$= \frac{1}{L}\left(\frac{L^3}{3} - 0\right) = \boxed{\frac{L^2}{3}}$$

variance of x $\sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2 = \frac{L^2}{3} - \left(\frac{L}{2}\right)^2$

$$= \frac{L^2}{3} - \frac{L^2}{4} = \boxed{\frac{L^2}{12}}$$

Standard deviation of x $= \sqrt{\sigma_x^2} = \boxed{\sigma_x = \frac{L}{\sqrt{12}}}$

(Q5 cont.)

c) for a quantum mechanical particle in the box

variance (quantum) $$\sigma_x^2 = L^2\left[\frac{1}{12} - \frac{1}{2\pi n^2}\right]$$

standard deviation (quantum) $$\sigma_x = L\sqrt{\frac{1}{12} - \frac{1}{2\pi n^2}}$$

$n \to \infty$

as $n \to \infty$ (very large quantum numbers)

$$\boxed{\text{notice} \quad \underset{(\text{quantum})}{\sigma_x} \; \lim_{n\to\infty} = L\sqrt{\frac{1}{12}}}$$

$$= \underset{(\text{classical})}{\sigma_x} = \frac{L}{\sqrt{12}}$$

d) part c illustrates the Correspondence Principle:

as quantum numbers get very large, many energy levels are populated, and the discrete quantum energy levels become continuous (classical)

Q6 a) a $\overset{(E)}{9.50}$ eV electron hits a $\overset{(V_0)}{10.0}$ eV barrier.

penetration depth $D_p = \dfrac{h/2\pi}{\sqrt{(V_0 - E)\,2m}}$

$$= \frac{6.626\times10^{-34}/2\pi}{\sqrt{(10.0-9.50)(1.602\times10^{-19})\,2\;9.110\times10^{-31}}}$$

$$= 2.76\times10^{-10}\ \text{m} \qquad \boxed{0.276\ \text{nm}}$$

b) classically, the electron has insufficient kinetic energy to penetrate the barrier, and $D_p = 0$

Q7 an electron with $\overset{(E)}{11.0}$ eV hits a $\overset{(V_0)}{10.0}$ eV barrier

a)

$$R = \text{probability of reflection} = \frac{2y - 2\sqrt{y(y-1)} - 1}{2y + 2\sqrt{y(y-1)} - 1} \qquad \left(y = \frac{E}{V_0} = 1.10 \right)$$

$$R = \frac{2(1.10) - 2\sqrt{1.10(.10)} - 1}{2(1.10) + 2\sqrt{1.10(.10)} - 1} = \frac{0.536}{1.863}$$

$$\boxed{R = 0.288}$$

b) classically, for $E > V_0$, the probability of reflection is zero