Chemistry 331 **Tutorial #4**

1. Show that the average position, average position squared, and the variance for a particle in a box of width L are

$$<x> = L/2$$

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

$$\sigma_x^2 = <x^2> - <x>^2 = \left(\frac{L}{2\pi n}\right)^2\left(\frac{\pi^2 n^2}{3} - 2\right)$$

Notice that the standard deviation in x for a particle in a box is less than the box width, L, and increases with n. Can you account for this behavior?

Useful integrals:

$$\int_0^L \sin^2 \frac{n\pi x}{L} dx = \frac{L}{2}$$

$$\int_0^L x \sin^2 \frac{n\pi x}{L} dx = \frac{L^2}{4}$$

$$\int_0^L x^2 \sin^2 \frac{n\pi x}{L} dx = \left(\frac{L}{2\pi n}\right)^3\left(\frac{4\pi^3 n^3}{3} - 2\pi n\right)$$

2. Operate on the particle-in-a-box wavefunction

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

with the momentum operator

$$-\frac{ih}{2\pi}\frac{\partial}{\partial x}$$

Note that this result is not an eigenvalue equation. This means that the momentum of a particle in a box does not have well defined values. Does this make sense?

3. Show that the average momentum, average momentum squared, and the variance in the momentum for a particle in a box are

$$\langle p_x \rangle = 0 \qquad \text{(does this make sense?)}$$

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

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

4. Use the results from questions 1 and 3 to demonstrate Heisenberg's Uncertainty Principle:

$$\sigma_x \sigma_{px} > h/4\pi$$

for a particle in a box.

5. Calculate the ground state (n = 1) energy (in Joules and in eV) for an electron confined within a one-dimensional box of width 10^{-14} m, the typical width of an atomic nucleus. Are electrons likely to be found in atomic nuclei under ambient conditions?

6. To a crude first approximation, a π electron in a linear polyene may be considered to be a particle in a one-dimensional molecular box. The polyene β-carotene contains 22 conjugated carbon atoms. The average carbon-carbon distance is 0.140 nm. In the ground state, each energy level up to n = 11 is occupied by two electrons of opposite spin (the Pauli Exclusion Principle we will talk about later). Calculate

a) the difference between the ground state energy and the energy of the first excited state in which one electron occupies the n = 12 level

b) the wavelength of radiation required to produce a transition between these two states.

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

(Q1.) $$\langle x \rangle = \int_0^L \psi^*(x)\, x\, \psi(x)\, dx$$

$$= \frac{2}{L}\int_0^L x \sin^2\left(\frac{n\pi x}{L}\right) dx = \frac{2}{L}\frac{L^2}{4} = \boxed{\frac{L}{2}}$$

$$\langle x^2 \rangle = \int_0^L \psi^*(x)\, x^2\, \psi(x)\, dx = \frac{2}{L}\int_0^L x^2 \sin^2\left(\frac{n\pi x}{L}\right) dx$$

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

$$\sigma_x^2 = \langle x^2\rangle - \langle x\rangle^2 = \frac{L^2}{(2\pi n)^2}\left(\frac{4\pi^2 n^2}{3} - 2\right) - \frac{L^2}{4}$$

$$= \frac{L^2}{3} - \frac{2L^2}{(2\pi n)^2} - \frac{L^2}{4} = \frac{L^2}{12} - \frac{2L^2}{(2\pi n)^2}$$

$$= \frac{L^2}{(2\pi n)^2}\left[-2 + (2\pi n)^2\frac{1}{12}\right] = \boxed{\left(\frac{L}{2\pi n}\right)^2\left[\frac{\pi^2 n^2}{3} - 2\right]}$$

$\underline{\underline{n=1}}$ $$\sigma_x^2 = L^2\left(\frac{1}{12} - \frac{1}{2\pi^2}\right) \approx L^2\, 0.0326 \qquad \sigma_x \cong 0.181\, L$$

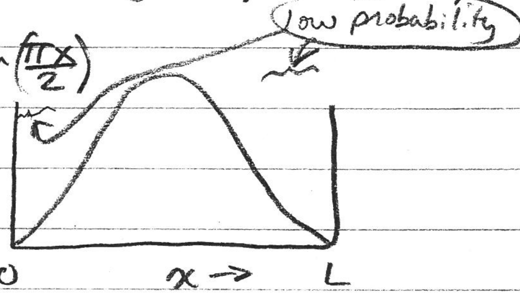
$\underline{\underline{n=\infty}}$ $$\sigma_x^2 = \frac{L^2}{12} \qquad \sigma_x = \frac{L}{\sqrt{12}} \cong 0.289\, L$$

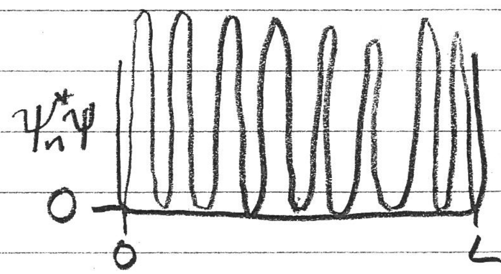
(Q1 cont.) the particle must be located between $x=0$ and $x=L$, so σ_x should be less than L

as n increases, the particle is more likely to be found near the edges of the box, so σ_x increases

$\psi_1 = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{2}\right)$

$\psi_1^* \psi_1$





(Q2.)

$$\hat{p}_x \psi(x) = \frac{-ih}{2\pi} \frac{\partial}{\partial x} \psi(x) = \frac{-ih}{2\pi} \frac{\partial}{\partial x} \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

$$\hat{p}_x \psi(x) = -\frac{ih}{2\pi}\sqrt{\frac{2}{L}} \frac{n\pi}{L} \cos\left(\frac{n\pi x}{L}\right) = \frac{-nih}{2L}\sqrt{\frac{2}{L}} \cos\left(\frac{n\pi x}{L}\right)$$

$$\hat{p}_x \psi(x) = \hat{p}_x\left[\sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}\right] = \text{constant} \cdot \cos\left(\frac{n\pi x}{L}\right) \neq \text{constant } \psi(x)$$

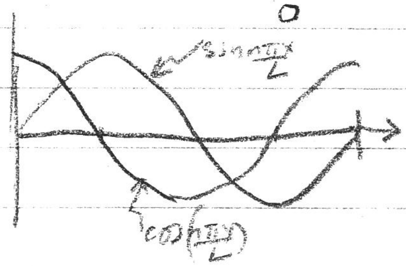
p_x can be positive (if $v_x > 0$) or negative (if $v_x < 0$) for a particle moving back and forth in a box

no fixed value for p_x, or eigenvalue

(Q3.)

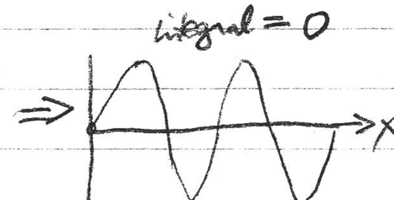
average momentum $\langle p_x \rangle = \int_0^L \psi^*(x)\, \hat{p}_x\, \psi(x)\, dx = \frac{-nih}{2L} \frac{2}{L} \int_0^L \sin\left(\frac{n\pi x}{L}\right) \cos\left(\frac{n\pi x}{L}\right) dx$

the integral of the product of an even and odd function



⇒

integral = 0



$$\boxed{\langle p_x \rangle = 0}$$

(Q3 cont.) $$\langle p_x^2 \rangle = \int_0^L \psi(x)^* \hat{p}_x^2 \psi(x)\, dx$$

$$\langle p_x^2 \rangle = \int_0^L \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)\left[\left(-\frac{ih}{2\pi}\frac{\partial}{\partial x}\right)^2 \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)\right] dx$$

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

$$= \cancel{\frac{2}{L}} \frac{h^2}{4\pi^2} \frac{n^2\pi^2}{L^2} \cancel{\frac{L}{2}} = \boxed{\frac{n^2h^2}{4L^2}}$$

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

Q4.

$$\sigma_x \sigma_{p_x} = \sqrt{\sigma_x^2}\sqrt{\sigma_{p_x}^2} = \underbrace{\sqrt{L^2\left(\frac{1}{12} - \frac{2}{(2\pi n)^2}\right)}}_{Q1}\underbrace{\sqrt{\frac{n^2h^2}{4L^2}}}_{Q3}$$

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

$$= \frac{nh}{4\pi} 2\pi \left(\frac{1}{12} - \frac{1}{2\pi^2 n^2}\right)^{1/2}$$

$$\geqslant \frac{nh}{4\pi}\frac{2\pi}{\sqrt{12}}$$

$$\geqslant \frac{nh}{4\pi} 1.814$$

$$\boxed{\sigma_x \sigma_{p_x} > \frac{nh}{4\pi}}$$

Q5 $E_n = \dfrac{n^2h^2}{8mL^2}$ $n = 1$, $L = 10^{-14}\ m$

$$= \frac{1^2(6.626\times10^{-34}\ J\cdot s)^2}{8(9.109\times10^{-31}\ kg)(10^{-14}\ m)^2} = 0.602\times10^{-9}\ J$$

$$= (0.602\times10^{-9}\ J)(1.602\times10^{-19}\ J\ eV) = 3.76\times10^{9}\ eV$$

$$= 3.62\times10^{14}\ J\ mol^{-1}$$

$$= 3.76\ GeV \text{ per electron}$$

would need to have "super-high" energy electrons to enter nucleus ($e^- + p^+ \rightarrow$ neutron)

Q6 a) $E_n = \dfrac{n^2h^2}{8mL^2}$ $L = 2.94\ nm = 21(0.140\ nm)$

$$E_{12} - E_{11} = \frac{(12^2 - 11^2)(6.626\times10^{-34}\ J\cdot s)^2}{8(9.109\times10^{-31}\ kg)(2.94\times10^{-9}\ m)^2} = 1.60\times10^{-19}\ J$$

b) $E_{12} - E_{11} = h\nu$ $\nu = 2.42\times10^{14}\ s^{-1}$

$\lambda = c/\nu = 1239\ nm$ (infrared)