2.

$$E = \frac{n^2h^2}{8mL^2} \qquad E_2 - E_1 = \frac{3h^2}{8mL^2}$$

$m(O_2) = 32 \times 1.66 \times 10^{-27}$ kg ; $L = 5$cm $= 5 \times 10^{-2}$m

$$\therefore \quad E_2 - E_1 = \frac{3 \times (6.626 \times 10^{-34}\ \mathrm{Js})^2}{8 \times 32 \times 1.66 \times 10^{-27}\,\mathrm{kg} \times (5 \times 10^{-2}\,\mathrm{m})^2}$$

$$= \underline{1.24 \times 10^{-39}\ \mathrm{J}}$$

For the second part of the problem we set

$E = \frac{n^2h^2}{8mL^2} = \frac{1}{2} kT$ and solve for n

$k = 1.381 \times 10^{-23}$ JK^{-1}

$$\underline{\underline{n = 2.2 \times 10^9}}$$

3. (a) Right-half of the box :

$$\int_{L/2}^{L} \left(\frac{2}{L}\right) \sin^2 \frac{n\pi x}{L}\, dx$$

$$= \frac{2}{L} \int_{L/2}^{L} \sin^2 \frac{n\pi x}{L}\, dx$$

[Using $\int \sin^2 (by)\, dy = \frac{y}{2} - \frac{1}{4b}(\sin 2by)$]

$$= \frac{2}{L}\left[\left[\frac{x}{2}\right]_{L/2}^{L} - \frac{1}{4 \cdot \frac{n\pi}{L}} \left[\sin \frac{2n\pi}{L} x\right]_{L/2}^{L} \right]$$

$$= \frac{2}{L}\left[\left(\frac{L}{2} - \frac{L}{4}\right) - \frac{L}{4n\pi} \left\{ \sin \frac{2n\pi}{L} \cdot L - \sin \frac{2n\pi}{L} \cdot \frac{L}{2} \right\} \right]$$

$$= \frac{2}{L}\left[\frac{L}{4} - \frac{L}{4n\pi} \{ \underset{0}{\sin 2n\pi} - \underset{0}{\sin n\pi} \} \right]$$

$$= \frac{2}{L} \cdot \frac{L}{4} = \frac{1}{2}$$

$$= \frac{1}{2}$$ ⟸ makes sense

(b) central third of the box :

$$P = \frac{2}{L}\int_{L/3}^{2L/3} \sin^2\left(\frac{n\pi x}{L}\right) dx$$

$$= \frac{2}{L}\left\{ \left[\frac{x}{2}\right]_{L/3}^{2L/3} - \frac{1}{4\cdot\frac{n\pi}{L}}\left[\sin\frac{2n\pi}{L}x\right]_{L/3}^{2L/3} \right\}$$

$$= \frac{2}{L}\left\{ \left(\frac{2L}{6}-\frac{L}{6}\right) - \frac{L}{4n\pi}\left[\sin\frac{2n\pi}{L}\cdot\frac{2L}{3} - \sin\frac{2n\pi}{L}\cdot\frac{L}{3}\right]\right\}$$

$$= \frac{2}{L}\left\{ \frac{L}{6} - \frac{L}{4n\pi}\left[\sin\frac{4n\pi}{3} - \sin\frac{2n\pi}{3}\right]\right\}$$

$$= 2\left[\frac{1}{6} - \frac{1}{4n\pi}\left(\sin\frac{4n\pi}{3} - \sin\frac{2n\pi}{3}\right)\right]$$

$\underline{\underline{n=1}}$;

$$P = 2\left[\frac{1}{6} - \frac{1}{4\pi}\left(\sin\frac{4\pi}{3} - \sin\frac{2\pi}{3}\right)\right]$$

$$= 2\left[\frac{1}{6} - \frac{1}{4\pi}\left[-\frac{\sqrt{3}}{2} - \frac{\sqrt{3}}{2}\right]\right]$$

$$= 2\left[\frac{1}{6} + \frac{1}{4\pi}\sqrt{3}\right] \approx \underline{\underline{0.61}}$$

subsequently do it for other values of n.

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

$$= \frac{2}{L}\left[\left\{ \frac{x}{2} \right\}_0^{L/n} - \frac{1}{\frac{4n\pi}{L}} \left\{ \sin\left(\frac{2n\pi}{L}\cdot x\right) \right\}_0^{L/n} \right]$$

$$= \frac{2}{L}\left[\frac{L}{2n} - \frac{L}{4n\pi} \left\{ \sin \frac{2n\pi}{L}\cdot\frac{L}{n} - 0 \right\} \right]$$

$$= 2\left[\frac{1}{2n} - \frac{L}{4n\pi} \underbrace{\sin 2\pi}_{0} \right]$$

$$= \frac{1}{n}$$

Hence P does depend upon 'n'.

4.

$$\psi_3(x) = \sqrt{\frac{2}{L}} \sin \frac{3\pi x}{L}$$

$$\text{Prob} = \int_0^{L/6} \left[\sqrt{\frac{2}{L}} \sin \frac{3\pi x}{L} \right]^2 dx$$

$$= \frac{2}{L} \int_0^{L/6} \sin^2 \frac{3\pi x}{L} \, dx$$

[Using the integral $\int \sin^2(by)\,dy = \frac{y}{2} - \frac{1}{4b}\sin(2by)$]

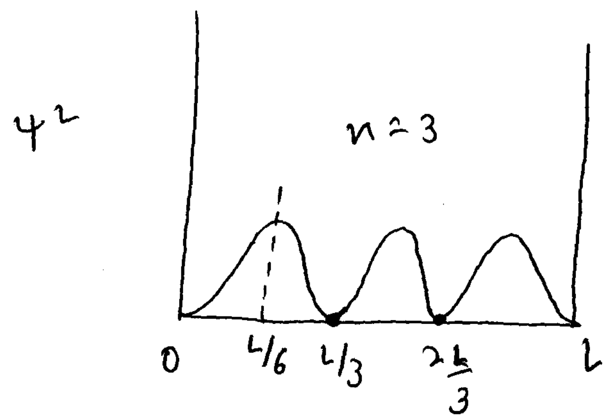
$$= \frac{2}{L}\left[\left\{ \frac{x}{2} \right\}_0^{L/6} - \frac{1}{4.\frac{3\pi}{L}} \left\{ \sin \frac{2.3\pi}{L} x \right\}_0^{L/6} \right]$$

$$= \frac{2}{L}\left[\frac{L}{12} - \frac{L}{12\pi} \left\{ \sin \frac{6\pi}{L}.\frac{L}{6} - \sin 0 \right\} \right]$$

$$= \frac{2}{L}\left[\frac{L}{12} - \frac{L}{12\pi} \sin\pi \right]$$

$$= \frac{2}{L}.\frac{L}{12} = \frac{1}{6}$$

To explain qualitatively even without calculating



← symmetric probability distribution

Since it is a symmetric distribution, each waveform ($\frown$) contributes to $\frac{1}{3}$ of the probability since

$$\text{Prob} = \underbrace{\int_0^{L/3} \psi^2\,dx + \int_{L/3}^{2L/3} \psi^2\,dx + \int_{2L/3}^{L} \psi^2\,dx}_{\text{equal to each other } = \frac{1}{3}} = 1$$

Hence $\int_0^{L/6} \psi^2\,dx = \frac{1}{6}$

6.

(i) 22 conjugated carbon atoms and avg. internuclear distance $\approx 140\,pm$

$$\underbrace{C-C \;\cdots\; C-C}_{L}$$

$L = 21 \text{ (bonds)} \times 140\,pm$

$= 2940\,pm$

$= 2940 \times 10^{-12}\,m$

HOMO $\rightarrow$ corresponds to $n = 11$

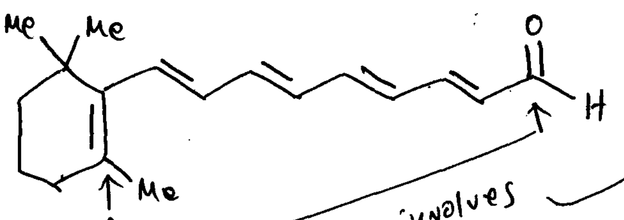
LUMO $\rightarrow$ " " $n = 12$

(a) $\Delta E = E_{12} - E_{11} = \dfrac{h^2}{8mL^2}(12^2 - 11^2) \approx 1.6 \times 10^{-19}\,J$

$[\, m = 9.11 \times 10^{-31}\,kg \;;\; L = 2940 \times 10^{-12}\,m \,]$

(b) $\Delta E = h\nu \quad \therefore \nu = 2.41 \times 10^{14}\,s^{-1}$

(ii) $\Delta E = \dfrac{h^2(7^2 - 6^2)}{8mL^2}$; $L = 11 \times 140\,pm$



conjugation involves the O atom too

$\Delta E = 3.3 \times 10^{-19}\,J$

$\nu = 4.95 \times 10^{-14}\,s^{-1}$

Comment: Absorption spectrum shifts to ~~lower~~ lower frequency for a linear polyene as the number of conjugated atoms increases.

7. $\psi_3 = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{3\pi x}{L}\right)$

$P(x) \propto \psi_3^2 \propto \sin^2\left(\frac{3\pi x}{L}\right)$

$\frac{dP(x)}{dx} = 0$ ← maxima and minima

$\frac{dP(x)}{dx} \propto 2\sin\left(\frac{3\pi x}{L}\right)\cos\left(\frac{3\pi x}{L}\right) \propto \sin\left(\frac{6\pi x}{L}\right)$

[$2\sin x\cos x = \sin 2x$]

$\sin\left(\frac{6\pi x}{L}\right) = 0 \quad \therefore \quad \frac{6\pi x}{L} = n\pi \quad , \quad n = 0, 1, 2, \ldots$

$\therefore \quad x = \frac{nL}{6} \qquad n \leq 6$

$n = 0, 2, 4$ and 6 correspond to minima in ψ_3

example: $\underline{n=2}$, $\sin\left(\frac{6\pi x}{L}\right) = \sin\left(\frac{6\pi}{L}\cdot\frac{2L}{6}\right) = \sin(2\pi) = 0$

hence $n = 1, 3$ and 5 should correspond to the maxima that is

$x = \frac{L}{6}, \frac{3L}{6}\left(\frac{L}{2}\right), \frac{5L}{6}$

8. From Heisenberg's uncertainty principle we know that

$$\sigma_x \sigma_p \geq \frac{\hbar}{2} \quad \cdots (1)$$

Where σ_x and σ_p are the uncertainties respectively in position and momentum.

Also for a particle in a box of length 'L', $\sigma_x \leq L$: (2)

Using (1) and (2) we have

$$\frac{\hbar}{2\sigma_p} \leq \sigma_x \leq L$$

$$\therefore \frac{\hbar}{2\sigma_p} \leq L \quad \text{or} \quad \frac{\hbar}{2L} \leq \sigma_p$$

$$\therefore \frac{\hbar^2}{4L^2} \leq \sigma_p^2$$

Now $\sigma_p^2 = \langle p_x^2 \rangle - \underset{\substack{\uparrow \\ 0}}{\langle p_x \rangle^2} = \langle p_x^2 \rangle$

$$\therefore \frac{\hbar^2}{4L^2} \leq \langle p_x^2 \rangle \quad \text{or} \quad \frac{\hbar^2}{4L^2} \leq 2m\langle E \rangle$$

$$\left[\because \langle E \rangle = \frac{\langle p_x^2 \rangle}{2m}\right]$$

$$\therefore \frac{\hbar^2}{8mL^2} \leq \langle E \rangle$$

$$\text{or} \quad \langle E \rangle \geq \frac{\hbar^2}{8mL^2}$$

9. $\psi(x) = D\cos kx + C\sin kx$

Boundary conditions $\psi(-L) = \psi(+L) = 0$

$\psi(-L) = D\cos(-kL) + C\sin(-kL)$

$\psi(-L) = D\cos kL - C\sin kL = 0 \quad \ldots (1)$

also $\psi(L) = D\cos kL + C\sin kL = 0 \quad \ldots (2)$

Adding (1) to (2), we have $2D\cos kL = 0$ or $D\cos kL = 0$

Subtracting (2) from (1), we have $2C\sin kL = 0$ or $C\sin kL = 0$

The general soln. to these set of equations is to set

$$k = \frac{n\pi}{2L} \leftarrow$$ [2L is the actual length of this box]

$n = 1, 2, 3, 4 \ldots$

to satisfy the boundary conditions one has to understand that one cannot make both sin and cos zero for a given value of E.

2 classes of solution are possible:

n is an odd integer

setting $C = 0$ and $\cos kx = 0$

" $D = 0$ and $\sin kx = 0$

$\rightarrow kL = \frac{n\pi}{2}$

n is even integer

Hence $\quad \psi_n(x) = C \sin \frac{n\pi}{2L} x \qquad \underline{n = \text{even}}$

$\qquad\qquad = D \cos \frac{n\pi}{2L} x \qquad \underline{n = \text{odd}}$

$\underline{n = \text{even}} = 2, 4, 6, \cdots$

$$\left.\begin{array}{l} n=2 \rightarrow \quad \psi_n(L) = C \sin\left(\frac{2\pi}{2L} \cdot L\right) = C \sin(\pi) = 0 \\ n=4 \rightarrow \quad \psi_n(L) = C \sin\left(\frac{4\pi}{2L} \cdot L\right) = C \sin(2\pi) = 0 \end{array}\right\} \underline{\sin n\pi = 0}$$

$\underline{n = \text{odd}} = 1, 3, 5$

$n=1, \quad \psi_n(L) = D \cos\left(\frac{\pi}{2L} \cdot L\right) = D \cos\left(\frac{\pi}{2}\right) = 0$

$n=3, \quad \psi_n(L) = D \cos\left(\frac{3\pi}{2L} \cdot L\right) = D \cos\left(\frac{3\pi}{2}\right) = 0$

Since $\cos x = 0$ when $x = \frac{\pi}{2}, \frac{3\pi}{2}, \frac{5\pi}{2} \cdots$

If you carry out normalization, you will find

that $\underline{C = D = \frac{1}{L^{1/2}}}$

Also, $$k^2 = \frac{2mE}{\hbar^2}$$

$$\therefore \frac{n^2\pi^2}{2L^2} = \frac{2mE}{\hbar^2}$$

$$\therefore E = \frac{\hbar^2 n^2 \pi^2}{4mL^2} = \left(\frac{h}{2\pi}\right)^2 \frac{n^2\pi^2}{2m.(2L)^2}$$

$$= \frac{n^2h^2}{8m\underbrace{(2L)}_{\text{Total length of box}}^2} = \frac{n^2h^2}{32mL^2}$$

and is equivalent to Energy for a particle in a box within boundary $x=0$ to $x=2L$

How we define our coordinate system changes the way we express the wave function mathematically.

No experimentally observable properties depend upon how we define our coordinate system.

Q15

Consider a particle in a one-dimensional box defined by $V(x)=0,\ a>x>0$ and $V(x)=\infty,\ x\geq a,\ x\leq 0$. Explain why each of the following unnormalized functions is or is not an acceptable wave function based on criteria such as being consistent with the boundary conditions, and with the association of $\psi^*(x)\psi(x)dx$ with probability.

a) $A\cos\frac{n\pi x}{a}$ b) $B(x+x^2)$ c) $Cx^3(x-a)$ d) $\frac{D}{\sin\frac{n\pi x}{a}}$

a) $A\cos\frac{n\pi x}{a}$ is not an acceptable wave function because it does not satisfy the boundary condition that $\psi(0)=0$.

b) $B(x+x^2)$ is not an acceptable wave function because it does not satisfy the boundary condition that $\psi(a)=0$.

c) $Cx^3(x-a)$ is an acceptable wave function. It satisfies both boundary conditions and can be normalized.

d) $\frac{D}{\sin\frac{n\pi x}{a}}$ is notan acceptable wave function. It goes to infinity at $x=0$ and cannot be normalized in the desired interval.

Q17

Are the eigenfunctions of $\hat{H}$ for the particle in the one-dimensional box also eigenfunctions of the position operator $\hat{x}$? Calculate the average value of x for the case where $n=3$. Explain your result by comparing it with what you would expect for a classical particle. Repeat your calculation for $n=5$ and, from these two results, suggest an expression valid for all values of n. How does your result compare with the prediction based on classical physics?

No, they are not eigenfunctions because multiplying the function by x does not return the function multiplied by a constant.

For $n=3$,

$$\langle x\rangle=\int_0^a\psi^*(x)\,x\,\psi(x)\,dx=\frac{2}{a}\int_0^a x\sin^2\left(\frac{3\pi x}{a}\right)dx$$

Using the standard integral $\int x\sin^2(bx)\,dx=\frac{x^2}{4}-\frac{\cos(2bx)}{8b^2}-\frac{x\sin(2bx)}{4b}$

$$\langle x\rangle=\frac{2}{a}\left[\frac{x^2}{4}-\frac{\cos\left(\frac{6\pi x}{a}\right)}{8\left(\frac{3\pi x}{a}\right)^2}-\frac{x\sin\left(\frac{6\pi x}{a}\right)}{4\left(\frac{3\pi x}{a}\right)}\right]_0^a$$

$$\langle x\rangle=\frac{2}{a}\left[\frac{a^2}{4}-\frac{\cos(6\pi)}{72\pi^2}-\frac{a\sin(6\pi)}{12\pi}+\frac{\cos(0)}{72\pi^2}-\frac{0\sin(0)}{12\pi}\right]=\frac{2}{a}\left[\frac{a^2}{4}-\frac{1}{72\pi^2}-0+\frac{1}{72\pi^2}-0\right]=\frac{a}{2}$$

For $n=5$,

$$\langle x\rangle = \int_0^a \psi^*(x)\, x\, \psi(x)\, dx = \frac{2}{a}\int_0^a x\sin^2\left(\frac{5\pi x}{a}\right) dx$$

Using the standard integral $\int x\sin^2(bx)\,dx = \frac{x^2}{4} - \frac{\cos(2bx)}{8b^2} - \frac{x\sin(2bx)}{4b}$

$$\langle x\rangle = \frac{2}{a}\left[\frac{x^2}{4} - \frac{\cos\left(\frac{10\pi x}{a}\right)}{8\left(\frac{5\pi x}{a}\right)^2} - \frac{x\sin\left(\frac{10\pi x}{a}\right)}{4\left(\frac{5\pi x}{a}\right)}\right]_0^a$$

$$\langle x\rangle = \frac{2}{a}\left[\frac{a^2}{4} - \frac{\cos(10\pi)}{200\pi^2} - \frac{a\sin(10\pi)}{20\pi} + \frac{\cos(0)}{200\pi^2} - \frac{0\sin(0)}{20\pi}\right] = \frac{2}{a}\left[\frac{a^2}{4} - \frac{1}{200\pi^2} - 0 + \frac{1}{200\pi^2} - 0\right]$$

$$= \frac{a}{2}$$

The general expression valid for all states is $\langle x\rangle = \frac{a}{2}$. Classical physics gives the same result because the particle is equally likely to be at any position. The average of all these values is the midpoint of the box.

P4.10) Are the eigenfunctions of $\hat{H}$ for the particle in the one-dimensional box also eigenfunctions of the momentum operator $\hat{p}_x$? Calculate the average value of p_x for the case $n = 3$. Repeat your calculation for $n = 5$ and, from these two results, suggest an expression valid for all values of n. How does your result compare with the prediction based on classical physics?

For $n = 3$,

$$\langle p\rangle = \int_0^a \psi^*(x)\left(-i\hbar\frac{d}{dx}\right)\psi(x)\, dx = \frac{-2i\hbar}{a}\frac{3\pi}{a}\int_0^a \sin\left(\frac{3\pi x}{a}\right)\cos\left(\frac{3\pi x}{a}\right) dx$$

Using the standard integral $\int \sin(bx)\cos(bx)\,dx = \frac{\cos^2(bx)}{2b}$

$$\langle p\rangle = \frac{-2i\hbar}{a}\frac{3\pi}{a}\left[\frac{\cos^2(3\pi)}{2b} - \frac{\cos^2(0)}{2b}\right] = \frac{-2i\hbar}{a}\frac{3\pi}{a}\left[\frac{1}{2b} - \frac{1}{2b}\right] = 0$$

For $n = 5$,

$$\langle p\rangle = \int_0^a \psi^*(x)\left(-i\hbar\frac{d}{dx}\right)\psi(x)\, dx = \frac{-2i\hbar}{a}\frac{5\pi}{a}\int_0^a \sin\left(\frac{5\pi x}{a}\right)\cos\left(\frac{3\pi x}{a}\right) dx$$

Using the standard integral $\int \sin(bx)\cos(bx)\,dx = \frac{\cos^2(bx)}{2b}$

$$\langle p\rangle = \frac{-2i\hbar}{a}\frac{5\pi}{a}\left[\frac{\cos^2(5\pi)}{2b} - \frac{\cos^2(0)}{2b}\right] = \frac{-2i\hbar}{a}\frac{5\pi}{a}\left[\frac{1}{2b} - \frac{1}{2b}\right] = 0$$

Classical: equally likely to be moving in $+x$ or $-x$ directions, average velocity $= 0$, average momentum $= 0$

Q16

[redacted]) The function $\psi(x) = Ax\left(1-\frac{x}{a}\right)$ is an acceptable wave function for the particle in the one dimensional infinite depth box of length a. Calculate the normalization constant A and the expectation values $\langle x\rangle$ and $\langle x^2\rangle$.

$$1 = A^2\int_0^a\left[x\left(1-\frac{x}{a}\right)\right]^2 dx = A^2\int_0^a\left[\frac{x^4}{a^2}-2\frac{x^3}{a}+x^2\right]dx$$

$$1 = A^2\left[\frac{x^5}{5a^2}-\frac{x^4}{2a}+\frac{x^3}{3}\right]_0^a = A^2\left[\frac{a^3}{5}-\frac{a^3}{2}+\frac{a^3}{3}\right]_0^a = A^2\frac{a^3}{30}$$

$$A = \sqrt{\frac{30}{a^3}}$$

$$\langle x\rangle = \int_0^a \psi^*(x)\,x\,\psi(x)\,dx = \frac{30}{a^3}\int_0^a x\left[x\left(1-\frac{x}{a}\right)\right]^2 dx$$

$$= \frac{30}{a^3}\left[\frac{x^4}{4}-\frac{2x^5}{5a}+\frac{x^6}{6a^2}\right]_0^a = \frac{30}{a^3}\left[\frac{a^4}{6}-\frac{2a^4}{5}+\frac{a^4}{4}\right] = \frac{30}{a^3}\frac{a^4}{60} = \frac{a}{2}$$

$$\langle x^2\rangle = \int_0^a \psi^*(x)\,x^2\,\psi(x)\,dx = \frac{30}{a^3}\int_0^a x^2\left[x\left(1-\frac{x}{a}\right)\right]^2 dx$$

$$= \frac{30}{a^3}\left[\frac{x^5}{5}-\frac{x^6}{3a}+\frac{x^7}{7a^2}\right]_0^a = \frac{30}{a^3}\left[\frac{a^5}{5}-\frac{a^5}{3}+\frac{a^5}{7}\right] = \frac{30}{a^3}\frac{a^5}{105} = \frac{2a^2}{7}$$

Q18

[redacted]) Derive an equation for the probability that a particle characterized by the quantum number n is in the first quarter ($0 \le x \le \frac{a}{4}$) of an infinite depth box. Show that this probability approaches the classical limit as $n \to \infty$.

Using the standard integral $\int \sin^2(by)\,dy = \frac{y}{2} - \frac{1}{4b}\sin(2by)$

$$P = \frac{2}{a}\int_0^{0.25a}\sin^2\left(\frac{n\pi x}{a}\right)dx = \frac{2}{a}\left[\frac{x}{2}-\frac{a}{4n\pi}\sin\left(\frac{2n\pi x}{a}\right)\right]_0^{0.25a}$$

$$= \frac{2}{a}\left[\frac{a}{8}-\frac{a}{4n\pi}\sin\left(\frac{n\pi}{2}\right)-\frac{0}{2}+\frac{a}{4n\pi}\sin(0)\right] = \frac{1}{4}-\frac{1}{2n\pi}\sin\left(\frac{n\pi}{2}\right)$$

← Note that probability depends on quantum number 'n'

As $n \to \infty$, the second term goes to zero, and the probability approaches $\frac{1}{4}$.
This is the classical value, because the particle is equally likely to be found anywhere in the box.

12. $\psi(x,y) = \sqrt{\frac{4}{ab}} \sin \frac{n_x \pi}{a} x \sin \frac{n_y \pi}{b} y$

(a) $\hat{X}\hat{P}_y \psi = x\left(-i\hbar \frac{\partial \psi}{\partial y}\right)$

$= -i\hbar \sqrt{\frac{4}{ab}} \frac{n_y \pi}{b} x \sin\left(\frac{n_x \pi}{a} x\right) \cos\left(\frac{n_y \pi}{b} y\right)$

$\hat{P}_y \hat{X} \psi = -i\hbar \frac{\partial}{\partial y}(x\psi)$

$= -i\hbar \sqrt{\frac{4}{ab}} \frac{n_y \pi x}{b} \sin\left(\frac{n_x \pi}{a} x\right) \cos\left(\frac{n_y \pi}{b} y\right)$

Hence $[\hat{X}, \hat{P}_y] = \hat{X}\hat{P}_y - \hat{P}_y \hat{X} = 0$

(b) Similarly $[\hat{X}, \hat{P}_x] = i\hbar$

(c) $[\hat{Y}, \hat{P}_y] = i\hbar$

(d) $[\hat{Y}, \hat{P}_x] = 0$.

19.

position operator in 3D is

$$\hat{R} = \hat{x} i + \hat{y} j + \hat{z} k$$

unit vectors

$$\langle r \rangle = \int_0^a dx \int_0^b dy \int_0^c dz \, \psi^*(x,y,z) \hat{R} \psi(x,y,z)$$

$$= \int_0^a dx \int_0^b dy \int_0^c dz \, \psi^* (\hat{x} i + \hat{y} j + \hat{z} k) \psi$$

$$= \int_0^a dx \, \psi^* \hat{x} i \psi \int_0^b dy \int_0^c dz$$

$$+ \int_0^a dx \int_0^b \psi^* \hat{y} j \psi \, dy \int_0^c dz$$

$$+ \int_0^a dx \int_0^b dy \int_0^c \psi^* \hat{z} k \psi \, dz$$

$$= i\langle x \rangle + j\langle y \rangle + k\langle z \rangle$$

$$\langle x \rangle = \int_0^a \left(\frac{2}{a}\right) x \sin^2 \frac{n_x \pi x}{a} dx \underbrace{\int_0^b \left(\frac{2}{b}\right) \sin^2 \frac{n_y \pi y}{b} dy}_{=1} \quad \leftarrow \text{normalized wavefns}$$

$$\underbrace{\int_0^c \left(\frac{2}{c}\right) \sin^2 \frac{n_z \pi z}{c} dz}_{=1}$$

$$= \frac{a}{2}$$

$\therefore \quad \langle y \rangle = \frac{b}{2}$

$\langle z \rangle = \frac{c}{2}$

$$\langle r \rangle = \frac{a}{2} i + \frac{b}{2} j + \frac{c}{2} k$$

---

20. To prove $\sigma_x \sigma_p \geq \frac{\hbar}{2}$

$$\sigma_x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$$

$$\sigma_p = \sqrt{\langle p^2 \rangle - \langle p \rangle^2}$$

$$\langle x \rangle = \frac{2}{L} \int_0^L x \sin^2\left(\frac{n\pi}{L} x\right) dx = \frac{L}{2} \text{ (for all } n)$$

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

$$= \frac{L^2}{3} - \frac{L^2}{2n^2\pi^2}$$

$$\langle p_x \rangle = \frac{2}{L} \int_0^L \sin\left(\frac{n\pi x}{L}\right) \left(-i\hbar \frac{d}{dx}\right) \sin\left(\frac{n\pi x}{L}\right) dx$$

$$= 0$$

$$\langle p_x^2 \rangle = 2m \langle E \rangle = 2m \frac{n^2 h^2}{8mL^2} = \underset{\sim}{\frac{n^2 h^2}{4L^2}}$$

$$\sigma_p = \sqrt{\langle p_x^2 \rangle - \underset{\substack{\uparrow \\ 0}}{\langle p_x \rangle}} = \sqrt{\frac{n^2 h^2}{4L^2}} = \frac{nh}{2L}$$

$$\sigma_x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = \sqrt{\frac{L^2}{3} - \frac{L^2}{2n^2\pi^2} - \frac{L^2}{4}}$$

$$= \sqrt{\frac{L^2}{12} - \frac{L^2}{2n^2\pi^2}}$$

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

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

$$\sigma_x \sigma_p = \frac{nh}{2L} \frac{L}{2\pi n} \left(\frac{\pi^2 n^2}{3} - 2 \right)^{1/2}$$

$$= \frac{h}{4\pi} \underbrace{\left(\frac{\pi^2 n^2}{3} - 2 \right)}_{\text{value of this is never less than 1}}^{1/2}$$

Hence $\sigma_x \sigma_p > \frac{h}{4\pi}$