ADVANCED CHEMISTRY

QUANTUM MECHANICS - WINTER - WEEK 3

Chapter 9

(13) $[\hat{x}, \hat{P}_x]\phi = (\hat{x}\hat{P}_x - \hat{P}_x\hat{x})\phi$

$$= \hat{x}\hat{P}_x\phi - \hat{P}_x\hat{x}\phi$$

$$= x\left(-i\hbar\frac{\partial}{\partial x}\right)\phi - \left(-i\hbar\frac{\partial}{\partial x}\right)(x)\phi$$

$$= -i\hbar\, x\frac{\partial\phi}{\partial x} + i\hbar\frac{\partial}{\partial x}(x\phi)$$

$$= -i\hbar\, x\frac{\partial\phi}{\partial x} + i\hbar\left[x\frac{\partial\phi}{\partial x} + \phi\frac{\partial x}{\partial x}\right]$$

$$= \cancel{-i\hbar\, x\frac{\partial\phi}{\partial x}} + \cancel{i\hbar\, x\frac{\partial\phi}{\partial x}} + i\hbar\phi$$

$$= i\hbar\phi \neq 0$$

$\therefore$ $\hat{x}$ and $\hat{P}_x$ do not commute

$\underline{[\hat{x}, \hat{P}_x] = i\hbar}$ $\quad \left\{\text{or } [\hat{P}_x, \hat{x}] = -i\hbar\right\}$

(14) (a) Probability that the particle is in the right hand half of the box $= \int_{a/2}^{a} \phi^*\phi\, dx$

$$= \int_{a/2}^{a} \sqrt{\frac{2}{a}}\sin\left(\frac{\pi x}{a}\right)\sqrt{\frac{2}{a}}\sin\left(\frac{\pi x}{a}\right)dx$$

$$= \left(\frac{2}{a}\right) \int_{a/2}^{a} \sin^2\left(\frac{\pi x}{a}\right) dx \qquad \cos 2\alpha = 1 - 2\sin^2\alpha$$

$$= \left(\frac{2}{a}\right) \frac{1}{2} \int_{\frac{a}{2}}^{a} \left(1 - \cos \frac{2\pi x}{a}\right) dx$$

$$= \frac{1}{a}\left[\int_{a/2}^{a} dx - \int_{a/2}^{a} \cos\left(\frac{2\pi x}{a}\right) dx\right]$$

$$= \frac{1}{a}\left\{ \left(x\right)_{a/2}^{a} - \left(\frac{a}{2\pi}\right)\left[\sin\left(\frac{2\pi x}{a}\right)\right]_{a/2}^{a} \right\}$$

$$= \frac{1}{a}\left\{ \left(a - \frac{a}{2}\right) - \frac{a}{2\pi}\left[\sin \frac{2\pi}{a}.a - \sin \frac{2\pi}{a} \cdot \frac{a}{2}\right]\right\}$$

$$= \frac{1}{a}\left\{ \frac{a}{2} - \frac{a}{2\pi}\left(\underbrace{\sin 2\pi - \sin \pi}_{=0}\right)\right\} = \frac{1}{a} \cdot \frac{a}{2}$$

$$= \frac{1}{2}$$

(b) Probability that the particle is in the middle third of the box $\Big\} = \int_{a/3}^{2a/3} \phi^* \phi \, dx$

$$= \int_{a/3}^{2a/3} \sqrt{\frac{2}{a}} \sin \frac{\pi x}{a} \sqrt{\frac{2}{a}} \sin \frac{\pi x}{a} \, dx$$

$$= \frac{1}{a}\left\{ \left(x\right)_{a/3}^{2a/3} - \frac{a}{2\pi}\left[\sin \frac{2\pi x}{a}\right]_{a/3}^{2a/3} \right\}$$ by analogy from part (a)

$$= \frac{1}{a}\left\{ \left(\frac{2a}{3} - \frac{a}{3}\right) - \frac{a}{2\pi}\left[\sin \frac{2\pi}{a} \cdot \frac{2a}{3} - \sin \frac{2\pi}{a} \cdot \frac{a}{3}\right]\right\}$$

$$= \frac{1}{a}\left\{\frac{a}{3} - \frac{a}{2\pi}\left(\sin\frac{4\pi}{3} - \sin\frac{2\pi}{3}\right)\right\}$$

$$= \frac{1}{a}\left\{\frac{a}{3} - \frac{a}{2\pi}\left(-0.867 - 0.867\right)\right\}$$

$$= \frac{1}{3} + \frac{1}{2\pi}\left(1.734\right) = \frac{1}{3} + \frac{0.867}{\pi} = \underline{\underline{0.609}}$$

(15) (a) $a = 0.25\,nm = 0.25 \times 10^{-9}\,m$ $\quad E_n = \frac{n^2h^2}{8ma^2}$

$$E_1 = \frac{h^2}{8ma^2} = \frac{(6.626\times 10^{-34}\,Js)^2}{8(9.109\times 10^{-31}\,kg)(0.25\times 10^{-9}\,m)^2}$$

$$= 9.639\times 10^{-19}\,\frac{J^2 s^2}{kg\,m^2}$$

$$= 9.639\times 10^{-19}\,J \times \frac{kJ}{10^3\,J} \times \frac{6.02\times 10^{23}}{1\,mol}$$

$$E_1 = \underline{\underline{580.31\,kJ/mol}}$$

$$\frac{J^2 s^2}{kg\,m^2} = \frac{(kg\,m^2 s^{-2})^2 s^2}{kg\,m^2} = kg\,m^2 s^{-2} = J$$

$$E_2 = \frac{4h^2}{8ma^2} = 4E_1 = \underline{\underline{2321.23\,kJ/mol}}$$

$$E_3 = \frac{9h^2}{8ma^2} = 9E_1 = \underline{\underline{5222.77\,kJ/mol}}$$

(b) $\Delta E = E_2 - E_1 = (2321.23 - 580.31)\frac{kJ}{mol}$

$$= 1740.92\,\frac{kJ}{mol} \times \frac{mol}{6.02\times 10^{23}} \times \frac{10^3\,J}{1\,kJ}$$

$$= 2.892\times 10^{-18}\,J$$

$$\Delta E = h\nu = \frac{hc}{\lambda} = 2.892 \times 10^{-18}\,J$$

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.626\times10^{-34}\,JS)(2.99\times10^{8}\,ms^{-1})}{(2.892\times10^{-18}\,J)}$$

$$\lambda = 6.851 \times 10^{-8}\,m$$

$$= \underline{\underline{68.51\,nm}}$$

(16) He atom mass $= 4.003\,amu \times \frac{1.661\times10^{-27}\,kg}{1\,amu}$

$$= 6.644 \times 10^{-27}\,kg$$

$$E_n = \frac{3}{2}kT = \frac{3}{2}(1.381\times10^{-23}\,JK^{-1})(298\,K)$$

$$E_n = 6.173\times10^{-21}\,J = \frac{n^2h^2}{8ma^2}$$

$$n^2 = \frac{E_n(8ma^2)}{h^2}$$

(a) $$n^2 = \frac{6.173\times10^{-21}\,J\,(8)(6.649\times10^{-27}\,kg)(1\times10^{-9}\,m)^2}{(6.626\times10^{-34}\,JS)^2}$$

$$= 7.479\times10^{2}$$

$$n = 27.3 \approx \underline{\underline{27}}$$

(b) $$n^2 = \frac{(6.173\times10^{-21}\,J)(8\times6.649\times10^{-27}\,kg)\times(10^{-6}\,m)^2}{(6.626\times10^{-34}\,JS)^2}$$

$$n^2 = 9.999 \times 10^5$$

$$n = 9.999 \times 10^2 = 999.99$$

$$\underline{\underline{n = 1000}}$$

(c) $$n^2 = \frac{(6.173 \times 10^{-21}\ J)(8 \times 6.649 \times 10^{-27}\ kg)(10^{-2}\ m)^2}{(6.626 \times 10^{-34}\ Js)^2}$$

$$n^2 = 9.999 \times 10^{13} \Rightarrow n = 9.999 \times 10^6$$

$$\underline{\underline{n = 1 \times 10^7}}$$

(17) $\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}\right)x$ as n changes the wavefunction changes.

Consider 2 different quantum states with $n = n$ and $n = m$

The corresponding wavefunctions are

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

$$\psi_m(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{m\pi}{a}\right)x$$

Evaluate $\int_0^a \psi_n^*(x)\, \psi_m(x)\, dx$

$$\int_0^a \psi_n^*(x)\, \psi_m(x) dx = \int_0^a \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) \sqrt{\frac{2}{a}} \sin\left(\frac{m\pi x}{a}\right) dx$$

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

$$= \frac{2}{a} \int_0^a \left\{ \left[\frac{1}{2} \left[\cos\left(\frac{n\pi x}{a} + \frac{m\pi x}{a}\right) - \frac{1}{2} \cos\left(\frac{n\pi x}{a} - \frac{m\pi x}{a}\right) \right] \right\} dx$$

$$= \frac{1}{a} \left\{ \int_0^a \cos\left(\frac{(m+n)\pi x}{a}\right) dx - \int_0^a \cos\left(\frac{(n-m)\pi x}{a}\right) dx \right\}$$

$$= \frac{1}{a} \left\{ \frac{a}{(m+n)\pi} \left(\sin\frac{(m+n)\pi x}{a}\right)_0^a - \frac{a}{(n-m)\pi} \left(\sin\frac{(n-m)\pi x}{a}\right)_0^a \right\}$$

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

$$= \frac{1}{(m+n)\pi} \underbrace{\left\{ \sin (m+n)\pi \right\}}_{=0} - \frac{1}{(n-m)\pi} \underbrace{\left\{ \sin (n-m)\pi \right\}}_{=0}$$

$$= \underline{\underline{0}}$$

$\therefore$ $\psi_n(x)$ and $\psi_m(x)$ are orthogonal.