

01) For a 1D system, momentum operator,

$$\hat{p}_x = -i\hbar \frac{\partial}{\partial x}$$

$$\hat{p}_x^2 = -\hbar^2 \frac{\partial^2}{\partial x^2}$$

let  $[\hat{p}_x, \hat{p}_x^2]$  act upon an arbitrary function  $f(x)$

$$[\hat{p}_x, \hat{p}_x^2] f(x) = \hat{p}_x \hat{p}_x^2 f(x) - \hat{p}_x^2 \hat{p}_x f(x)$$

$$= \hat{p}_x \left( -\hbar^2 \frac{\partial^2}{\partial x^2} f(x) \right) - \hat{p}_x^2 \left( -i\hbar \frac{\partial}{\partial x} f(x) \right)$$

$$= -\hbar^2 \left( -i\hbar \frac{\partial}{\partial x} \frac{\partial^2}{\partial x^2} f(x) + i\hbar \left( -\hbar^2 \frac{\partial^2}{\partial x^2} \frac{\partial}{\partial x} f(x) \right) \right)$$

$$[\hat{p}_x, \hat{p}_x^2] f(x) = +i\hbar \frac{\partial^3}{\partial x^3} f(x) - i\hbar^3 \frac{\partial^3}{\partial x^3} f(x) = 0$$

$$\therefore [\hat{p}_x, \hat{p}_x^2] = 0$$

02)  $\langle (B - \langle B \rangle)^2 \rangle = \int \psi^*(x) (B - \langle B \rangle)^2 \psi(x) dx$

$$= \int \psi^*(x) \hat{B}^2 \psi(x) dx + \langle B \rangle^2 \int \psi^*(x) \psi(x) dx - 2\langle B \rangle \int \psi^*(x) \hat{B} \psi(x) dx$$

$$= \langle B^2 \rangle + \langle B \rangle^2 - 2\langle B \rangle \langle B \rangle$$

$$= \underline{\underline{\langle B^2 \rangle - \langle B \rangle^2}}$$

$$(3) \text{ for } n=1 \quad \psi_1 = \left(\frac{4\alpha^3}{\pi}\right)^{1/4} x e^{-\alpha x^2/2}$$

$$\langle x \rangle = \int_{-\infty}^{\infty} \psi_1^* \hat{x} \psi_1 dx$$

$$(1) \langle x \rangle = \left(\frac{4\alpha^3}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} x^3 e^{-\alpha x^2} dx = 0$$

odd function

$$\langle P_n \rangle = \int_{-\infty}^{\infty} \psi_1^* \hat{P}_n \psi_1 dx = \int_{-\infty}^{\infty} \psi_1^* \left(-i\hbar \frac{\partial}{\partial x}\right) \psi_1 dx$$

odd / even = odd = 0

$$(2) \langle P_n \rangle = 0$$

$$\langle x^2 \rangle = \int_{-\infty}^{\infty} \psi_1^* x^2 \psi_1 dx$$

$$= \left(\frac{4\alpha^3}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} x^4 e^{-\alpha x^2} dx$$

$$= \left(\frac{4\alpha^3}{\pi}\right)^{1/2} \times 2 \int_0^{\infty} x^4 e^{-\alpha x^2} dx$$

$$= \left(\frac{4\alpha^3}{\pi}\right)^{1/2} \times 2 \left[ \frac{3}{8\alpha^3} \sqrt{\frac{\pi}{\alpha}} \right]$$

$\int_0^{\infty} x^{2n} e^{-\alpha x^2} dx = \frac{1 \times 3 \times 5 \dots (2n-1)}{2^{n+1} \alpha^n} \sqrt{\frac{\pi}{\alpha}}$

$$(3) \langle x^2 \rangle = \frac{3\hbar^2}{2\alpha} = \frac{3\hbar}{2\sqrt{\mu k}} \rightarrow (n+1) \frac{\hbar}{\sqrt{\mu k}}$$

$$\langle P_n^2 \rangle = -\hbar^2 \left(\frac{4\alpha^3}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} x e^{-\alpha x^2/2} \left(\frac{\partial^2}{\partial x^2}\right) x e^{-\alpha x^2/2} dx$$

$$= -\hbar^2 \left(\frac{4\alpha^3}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} x e^{-\alpha x^2/2} \frac{\partial}{\partial x} \left[ e^{-\alpha x^2/2} + \alpha x^2 e^{-\alpha x^2/2} \right] dx$$

$$= -\hbar^2 \left(\frac{4\alpha^3}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} x e^{-\alpha x^2/2} \left[ -\alpha x e^{-\alpha x^2/2} - \alpha [2x e^{-\alpha x^2/2} - \alpha x^3 e^{-\alpha x^2/2}] \right] dx$$

$$= -\hbar^2 \left(\frac{4\alpha^3}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} -\alpha x^2 e^{-\alpha x^2} - 2\alpha x^2 e^{-\alpha x^2} + \alpha^2 x^4 e^{-\alpha x^2} dx$$

(3) Contd. ....

$$= -\hbar^2 \left( \frac{4\alpha^3}{\kappa} \right)^{\frac{1}{2}} \int_{-\infty}^{\infty} (\alpha^2 x^4 - 3\alpha x^2) e^{-\alpha x^2} dx.$$

$$= -\hbar^2 \left( \frac{4\alpha^3}{\kappa} \right)^{\frac{1}{2}} \times 2 \int_0^{\infty} (\alpha^2 x^4 - 3\alpha x^2) e^{-\alpha x^2} dx.$$

$$= -\hbar^2 \left( \frac{4\alpha^3}{\kappa} \right)^{\frac{1}{2}} \times 2 \left\{ \alpha^2 \left[ \frac{3}{8\alpha^2} \sqrt{\frac{\kappa}{\alpha}} \right] - 3\alpha \left[ \frac{1}{4\alpha} \sqrt{\frac{\kappa}{\alpha}} \right] \right\}$$

$$= 3\hbar^2 \alpha - \frac{3}{2}\hbar^2 \alpha = \frac{3}{2}\hbar^2 \alpha.$$

$$\therefore \langle \hat{P}_n^2 \rangle = \frac{3}{2}\hbar^2 \alpha = \frac{3}{2}\hbar \sqrt{\mu k} \quad \rightsquigarrow (n+1)\hbar \sqrt{\mu k}$$

Using  $\langle x^2 \rangle$  &  $\langle \hat{P}_n^2 \rangle$

$$\sigma_{\hat{P}_n}^2 \sigma_x^2 = \langle \hat{P}_n^2 \rangle \langle x^2 \rangle = \left( \frac{3}{2}\hbar \sqrt{\mu k} \right) \left( \frac{3}{2}\hbar \sqrt{\mu k} \right).$$

$$\langle \hat{P}_n^2 \rangle \langle x^2 \rangle = \left( \frac{3}{2} \right)^2 \hbar^2$$

$$\therefore \langle \hat{P}_n \rangle \langle x \rangle = \frac{3}{2}\hbar^2 \geq \frac{\hbar}{2}$$

In accord with the Heisenberg uncertainty principle.

$$(04). \quad \psi_2 = \left(\frac{\alpha}{\pi}\right)^{1/4} (2\alpha x^2 - 1) e^{-\alpha x^2/2}$$

$$\psi_2 = A_0 (2\alpha x^2 - 1) e^{-\alpha x^2/2}$$

$$-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial x^2} A_0 (2\alpha x^2 - 1) e^{-\alpha x^2/2} + \frac{1}{2} kx^2 A_0 (2\alpha x^2 - 1) e^{-\alpha x^2/2}$$

$$-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial x^2} [2\alpha x^2 A_0 e^{-\alpha x^2/2} - A_0 e^{-\alpha x^2/2}] + \frac{1}{2} kx^2 A_0 (2\alpha x^2 - 1) e^{-\alpha x^2/2}$$

$$-\frac{\hbar^2}{2\mu} \frac{\partial}{\partial x} [2\alpha A_0 [2x e^{-\alpha x^2/2} - \alpha x^3 e^{-\alpha x^2/2}] - A_0 [-\alpha x e^{-\alpha x^2/2}]] + \frac{1}{2} kx^2 A_0 (2\alpha x^2 - 1) e^{-\alpha x^2/2}$$

$$-\frac{\hbar^2}{2\mu} \frac{\partial}{\partial x} [4\alpha x A_0 e^{-\alpha x^2/2} - 2\alpha^2 x^3 A_0 e^{-\alpha x^2/2} + A_0 \alpha x e^{-\alpha x^2/2}] + \frac{1}{2} kx^2 A_0 (2\alpha x^2 - 1) e^{-\alpha x^2/2}$$

$$-\frac{\hbar^2}{2\mu} [4\alpha A_0 (e^{-\alpha x^2/2} - \alpha x^2 e^{-\alpha x^2/2}) - 2\alpha^2 A_0 (3x^2 e^{-\alpha x^2/2} - \alpha x^4 e^{-\alpha x^2/2}) + A_0 \alpha [e^{-\alpha x^2/2} - \alpha x^2 e^{-\alpha x^2/2}]] + \frac{1}{2} kx^2 A_0 (2\alpha x^2 - 1) e^{-\alpha x^2/2}$$

$$-\frac{\hbar^2}{2\mu} [4\alpha A_0 e^{-\alpha x^2/2} - 4\alpha^2 x^2 A_0 e^{-\alpha x^2/2} - 6x^2 \alpha^2 A_0 e^{-\alpha x^2/2} + 2\alpha^3 x^4 A_0 e^{-\alpha x^2/2} + \alpha A_0 e^{-\alpha x^2/2} - \alpha^2 x^2 A_0 e^{-\alpha x^2/2}] + \frac{1}{2} kx^2 A_0 (2\alpha x^2 - 1) e^{-\alpha x^2/2}$$

$$-\frac{\hbar^2}{2\mu} [5\alpha A_0 e^{-\alpha x^2/2} - 4\alpha^2 x^2 A_0 e^{-\alpha x^2/2} + 2\alpha^3 x^4 A_0 e^{-\alpha x^2/2} - \alpha^2 x^2 A_0 e^{-\alpha x^2/2}] + \frac{1}{2} kx^2 A_0 (2\alpha x^2 - 1) e^{-\alpha x^2/2}$$

$$-\frac{\hbar^2}{2\mu} [-5\alpha A_0 (2\alpha x^2 - 1) e^{-\alpha x^2/2} + \alpha^2 x^2 A_0 (2\alpha x^2 - 1) e^{-\alpha x^2/2}] + \frac{1}{2} kx^2 A_0 (2\alpha x^2 - 1) e^{-\alpha x^2/2}$$

$$= \frac{5\hbar^2}{2\mu} \alpha A_0 (2\alpha x^2 - 1) e^{-\alpha x^2/2} - \frac{1}{2} \frac{\hbar^2}{\mu} \alpha^2 x^2 A_0 (2\alpha x^2 - 1) e^{-\alpha x^2/2} + \frac{1}{2} kx^2 A_0 (2\alpha x^2 - 1) e^{-\alpha x^2/2}$$

$$E_2 \psi_2 = \frac{5\hbar^2}{2\mu} \alpha \psi_2 - \frac{\hbar^2}{2\mu} \alpha^2 x^2 \psi_2 + \frac{1}{2} kx^2 \psi_2$$

$$E_2 \psi_2 = \frac{5\hbar^2}{2\mu} \alpha \psi_2 + \frac{1}{2} x^2 \psi_2 \left(k - \frac{\hbar^2 \alpha^2}{\mu}\right)$$

$$\alpha = \sqrt{\frac{\mu k}{\hbar^2}}$$

$$E_2 \psi_2 = \frac{5\hbar^2}{2\mu} \alpha \psi_2$$

$$\therefore E_2 = \frac{5\hbar^2}{2\mu} \alpha = \frac{5\hbar}{2} \sqrt{\frac{k}{\mu}}$$

(5)

$${}^1\text{H}^{127}\text{I} \quad k = 314 \text{ Nm}^{-1} \quad r = 160.92 \times 10^{-12} \text{ m}$$

$$1 \text{ amu} = 1.66 \times 10^{-24} \text{ g}$$

$$\mu = \frac{m_{\text{H}} m_{\text{I}}}{m_{\text{H}} + m_{\text{I}}} = \frac{(1 \times 127) \text{ amu}^2}{(128) \text{ amu}} = 1.647 \times 10^{-24} \text{ g}$$

$$\mu = 1.647 \times 10^{-27} \text{ kg}$$

The lowest energy vibrational transitions,

$$P=0 \rightarrow P=1$$

$$E_p = (P + \frac{1}{2}) \hbar \sqrt{\frac{k}{\mu}}$$

$$\hbar = \frac{h}{2\pi} = 1.054 \times 10^{-34} \text{ J}\cdot\text{s}$$

$$\therefore E_1 - E_0 = \Delta E = \hbar \sqrt{\frac{k}{\mu}} \left( \frac{3}{2} - \frac{1}{2} \right)$$

$$\Delta E_p = 1.0545 \times 10^{-34} \text{ J}\cdot\text{s} \sqrt{\frac{314 \text{ Nm}^{-1}}{1.647 \times 10^{-27} \text{ kg}}}$$

$$\Delta E_p = 4.60 \times 10^{-20} \text{ J}$$

$$\Delta E_p = h\nu_p$$

$$\nu_p = \frac{4.60 \times 10^{-20} \text{ J}}{6.626 \times 10^{-34} \text{ J}\cdot\text{s}} = 6.9488 \times 10^{13} \text{ Hz} = 6.95 \times 10^{13} \text{ Hz} \Rightarrow \text{IR region.}$$

The lowest energy rotational transition,

$$E_{l,ml} = l(l+1) \frac{\hbar^2}{2\mu r^2}$$

$$\Delta E_{l,ml} = \frac{2\hbar^2}{2\mu r^2} - 0 = \frac{\hbar^2}{\mu r^2} = \frac{(1.0545 \times 10^{-34} \text{ J}\cdot\text{s})^2}{(1.647 \times 10^{-27} \text{ kg})(160.92 \times 10^{-12} \text{ m})^2} = 2.607 \times 10^{-22} \text{ J}$$

$$\Delta E_{l,ml} = 8.935 \times 10^{11} \text{ Hz}$$

$$\Delta E_{l,ml} = h\nu$$

$$\nu = \frac{2.607 \times 10^{-22} \text{ J}}{6.626 \times 10^{-34} \text{ J}\cdot\text{s}} = 3.935 \times 10^{11} \text{ Hz} \Rightarrow \text{Microwave region.}$$

$$(06) \quad Y_2^0(\theta, \phi) = \left(\frac{5}{16}\right)^{1/2} (3\cos^2\theta - 1),$$

$$\int_0^{2\pi} \int_0^{\pi} Y_2^0 Y_2^0 \sin\theta d\theta d\phi = 1$$

$$\left(\frac{5}{16\pi}\right) \int_0^{2\pi} d\phi \int_0^{\pi} (3\cos^2\theta - 1)^2 \sin\theta d\theta = 1$$

$$\left(\frac{5}{16\pi}\right) \times 2\pi \left[ - \int_0^{\pi} (3\cos^2\theta - 1)^2 d\cos\theta \right] = 1$$

$$\left(\frac{5}{16\pi}\right) 2\pi \left[ - \int_0^{\pi} (9\cos^4\theta + 1 - 6\cos^2\theta) d\cos\theta \right] = 1$$

$$\left(\frac{5}{16\pi}\right) 2\pi \left[ - 9 \int_0^{\pi} \cos^4\theta d\cos\theta - \int_0^{\pi} d\cos\theta + 6 \int_0^{\pi} \cos^2\theta d\cos\theta \right] = 1$$

$$\left(\frac{5}{16\pi}\right) (2\pi) \left[ - \frac{9}{5} \cos^5\theta \Big|_0^{\pi} - \cos\theta \Big|_0^{\pi} + \frac{6}{3} \cos^3\theta \Big|_0^{\pi} \right] = 1$$

$$\left(\frac{5}{16\pi}\right) (2\pi) \left[ - \frac{9}{5} (-1-1) - (-1-1) + \frac{6}{3} (-1-1) \right] = 1$$

$$\left(\frac{5}{16\pi}\right) (2\pi) \left[ \frac{18}{5} + 2 - 4 \right] = 1$$

$$\frac{5}{16\pi} \times 2\pi \times \left[ \frac{18}{5} - 2 \right] = 1$$

$$\frac{5}{16\pi} \times 2\pi \times \left[ \frac{18}{5} - \frac{10}{5} \right] = 1$$

$$\frac{5}{16\pi} \times 2\pi \times \frac{8}{5} = 1$$

$$1 = 1$$

$\therefore Y_2^0(\theta, \phi) = \left(\frac{5}{16}\right)^{1/2} (3\cos^2\theta - 1)$  is normalized over the interval  $0 \leq \theta \leq \pi$  and  $0 \leq \phi \leq 2\pi$ .

(7)

$$\frac{N_J}{N_0} = (2J+1) \exp\left(-\frac{\hbar^2 J(J+1)}{2\mu r^2 kT}\right)$$

$$\frac{N_{J=2}}{N_{J=0}} = 5 \exp\left(-\frac{\hbar^2}{2\mu r^2 kT}\right) \cdot 6$$

$$\frac{N_{J=2}}{N_{J=0}} = 5 \exp(-0.1 \times 6)$$

$$\frac{N_{J=2}}{N_{J=0}} = 2.74 //$$

$$\frac{N_{J=15}}{N_{J=0}} = 31 \exp(-0.1 \times 240)$$

$$\frac{N_{J=15}}{N_{J=0}} = 1.17 \times 10^{-9} //$$

$$r = 92 \text{ pm}$$

$$\mu = \left(\frac{1 \times 19}{1+20}\right) \times 1.66 \times 10^{-24} \text{ g} = 1.578 \times 10^{-27} \text{ kg}$$

$$\hbar = \frac{h}{2\pi} = 1.0545 \times 10^{-34} \text{ Js}$$

$$r = 92 \times 10^{-12} \text{ m}$$

$$T = 200 \text{ K}$$

$$k = 1.380 \times 10^{-23} \text{ J K}^{-1}$$

$$\frac{\hbar^2}{2\mu r^2 kT} = 0.1$$

$$\left. \begin{array}{l} \\ \\ \\ \end{array} \right\} J(J+1) = 240$$

$$\textcircled{08} \quad -\frac{\hbar^2}{2\mu r^2} \left[ \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left( \sin\theta \frac{\partial}{\partial\theta} Y(\theta, \phi) \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} Y(\theta, \phi) \right] = E Y(\theta, \phi)$$

$$Y(\theta, \phi) = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$$

$$-\frac{\hbar^2}{2\mu r^2} \left[ \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left( \sin\theta \frac{\partial}{\partial\theta} \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1) \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1) \right] = E Y(\theta, \phi)$$

$$-\frac{\hbar^2}{2\mu r^2} \left[ \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left[ -6\pi \left(\frac{5}{16\pi}\right)^{1/2} \sin\theta \cdot \sin\theta \cos\theta \right] \right] = E Y(\theta, \phi)$$

$$-\frac{\hbar^2}{2\mu r^2} \left[ \cancel{11} -6 \left(\frac{5}{16\pi}\right)^{1/2} \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left[ \sin^2\theta \cos\theta \right] \right] = E Y(\theta, \phi)$$

$$+\frac{6\hbar^2}{2\mu r^2} \left(\frac{5}{16\pi}\right)^{1/2} \left[ \frac{1}{\sin\theta} \left[ 2\sin\theta \cos^2\theta - \sin^3\theta \right] \right] = E Y(\theta, \phi)$$

$$\frac{6\hbar^2}{2\mu r^2} \left(\frac{5}{16\pi}\right)^{1/2} \left[ 2\cos^2\theta - \sin^2\theta \right] = E Y(\theta, \phi)$$

$$\frac{6\hbar^2}{2\mu r^2} \left(\frac{5}{16\pi}\right)^{1/2} \left[ 2\cos^2\theta - (1 - \cos^2\theta) \right] = E Y(\theta, \phi)$$

$$\frac{6\hbar^2}{2\mu r^2} \left(\frac{5}{16\pi}\right)^{1/2} \left[ 3\cos^2\theta - 1 \right] = E Y(\theta, \phi)$$

$$\therefore E = \frac{6\hbar^2}{2\mu r^2}$$

$$l = 2$$

$$l(l+1) = \underline{\underline{6}}$$

$$E_l = \frac{6\hbar^2}{2\mu r^2} l(l+1)$$

$$\left. \begin{aligned} \sin^2\theta + \cos^2\theta &= 1 \\ \sin^2\theta &= 1 - \cos^2\theta \end{aligned} \right\}$$