(iii) Estimation of ground state energy of hydrogen atom

Total energy of an electron in an atom is

$$E = \frac{p^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0 r} \qquad [Z=1 \text{ for hydrogen atom}]$$

$$= \frac{p^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r} \longrightarrow (1)$$

But the uncertainty in the measurement of distance is $\Delta x = r$ and in momentum is $\Delta p \simeq p$.

$$\therefore \quad \Delta x \cdot \Delta p \simeq \hbar \qquad \text{or} \qquad \Delta p = \frac{\hbar}{\Delta x} = \frac{h}{2\pi r}$$

Substituting in equ. (1), we get

$$E = \frac{h^2}{4\pi^2 r^2 \cdot 2m} - \frac{e^2}{4\pi\epsilon_0 r} = \frac{h^2}{8\pi^2 m r^2} - \frac{e^2}{4\pi\epsilon_0 r} \longrightarrow (2)$$

For the energy to be minimum, $\frac{dE}{dr} = 0$

$$\therefore \quad \frac{h^2}{8\pi^2 m r^3}(-2) + \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r^2}\right) = 0$$

$$\frac{e^2}{4\pi\epsilon_0 r^2} = \frac{h^2}{4\pi^2 m r^3} \qquad \text{or} \qquad \boxed{r = \frac{h^2\epsilon_0}{e^2\pi m}} = 0.531\,\mathring{A}$$

Substituting for r in equ. (2), we get

$$E = \frac{-me^4}{8\epsilon_0^2 h^2}$$

$$= -\frac{9.1\times10^{-31}\times(1.6\times10^{-19})^4}{8\times(8.854\times10^{-12})^2\times(6.625\times10^{-34})^2} \text{ J}$$

$$= -\frac{59.63776\times10^{-107}}{2.752585\times10^{-96}}$$

$$\simeq -13.6 \text{ eV}$$

This is the ground state energy of the hydrogen atom.

Show that the zero point energy of $\frac{1}{2}\hbar\omega$ of a linear harmonic oscillator is a manifestation of the uncertainity principle.

<u>Ans:</u> For a classical Linear harmonic oscillator,

$\langle x \rangle = 0 \Rightarrow \langle x \rangle^2 = 0$

IIIly $\langle p \rangle = 0 \Rightarrow \langle p_x \rangle^2 = 0 \longrightarrow (1)$

From Standard deviation relation.

$$\Delta x = \left[\langle x^2 \rangle - \langle x \rangle^2\right]^{1/2} = \langle x^2 \rangle^{1/2}$$

IIIly $$\Delta p_x = \left[\langle p_x^2 \rangle - \langle p_x \rangle^2\right]^{1/2} = \langle p_x^2 \rangle^{1/2} \longrightarrow (2)$$

as $\langle x \rangle = 0$ from equ. (1).

The total energy of the Linear harmonic oscillator (classical),

$$E = KE + PE$$

$$\langle E \rangle = \left\langle \frac{p_x^2}{2m} \right\rangle + \frac{1}{2}k\langle x^2 \rangle \longrightarrow (3)$$

According to Heisenberg's uncertainity principle,

$$\Delta p_x \cdot \Delta x \geq \hbar/2$$

Least condition, $\Delta p_x \cdot \Delta x = \hbar/2$.

$$\Delta p_x = \frac{\hbar}{2\Delta x} \quad \text{or} \quad \Delta p_x^2 = \frac{\hbar^2}{4\Delta x^2}.$$

$$\therefore \langle E \rangle = \frac{\hbar^2}{8m(\Delta x)^2} + \frac{1}{2}k\left[(\Delta x)^2\right] \longrightarrow (4)$$

The energy of the LHO in the ground state is minimum, i.e., for the RHS to be minimum, the differential of $\langle E \rangle$ w.r.t. $\langle \Delta x \rangle^2$ must be zero. Therefore. $\langle E \rangle$ = minimum energy $\Rightarrow \frac{\partial \langle E \rangle}{\partial \langle \Delta x \rangle^2} = 0$.

from equ. (4) & $\frac{\partial^2 \langle E \rangle}{\partial^2 \langle \Delta x \rangle^2} = 0$

Let $(\Delta x)^2 = y$

Then $$0 = \frac{\hbar^2}{8m}\left(-1 \cdot y_{min}^{-1-1}\right) + \frac{1}{2}K$$

$$= -\frac{\hbar^2}{8m} y_{min}^{-2} + \frac{1}{2}K.$$

$K = \omega^2 m$.

Substitute for y,

$$\frac{\hbar^2}{8m(\Delta x)^4_{min}} = \frac{K}{2}.$$

$$(\Delta x)^4_{min} = \frac{\hbar^2}{4m^2\omega^2}.$$

$$(\Delta x)^2_{min} = \frac{\hbar}{2m\omega}$$

From equ. 4

$$\langle E \rangle_{min} = \frac{\hbar^2}{8m\left(\frac{\hbar}{2m\omega}\right)} + \frac{1}{2}\omega^2 m \times \frac{\hbar}{2m\omega}$$

$$\Rightarrow \boxed{\langle E \rangle_{min} = \frac{1}{2}\hbar\omega}$$

A $^{200}Hg\,^{35}Cl$ molecule emits a 4.4 cm photon, when it undergoes a rotational transition from $l=1$ to $l=0$. Find the inter-atomic distance in this molecule. Given the masses of ^{200}Hg and ^{35}Cl are 3.32×10^{-25} kg and 5.81×10^{-26} kg respectively.

Ans:. Given, transition from $l=1$ to $l=0$

wavelength of emitted photon, $\lambda = 4.4\times10^{-2}$ m.

Mass of $^{200}Hg = m_1 = 3.32\times10^{-25}$ kg.

Mass of $^{35}Cl = m_2 = 5.81\times10^{-26}$ kg.

$$\text{Reduced mass, } \mu = \frac{m_1 m_2}{(m_1+m_2)} = \frac{(33.2\times5.81)\times(10^{-26})^2}{(33.2+5.81)\times10^{-26}}$$

$$= \frac{192.892}{39.01} \doteq 4.94468\times10^{-26}\text{ kg.}$$

The inter-atomic distance in the molecule is given by.

$$r_e^2 = \frac{\hbar\lambda}{2\pi c\mu} \quad \text{where } c = \nu\lambda$$

$$r_e = \sqrt{\frac{\hbar\lambda}{2\pi c\mu}} = \sqrt{\frac{1.054\times10^{-34}\times4.4\times10^{-2}}{2\times3.14\times3\times10^{8}\times4.94\times10^{-26}}}$$

or $r_e = 2.232\times10^{-10}$ m.

$$\boxed{r_e = 2.232\ \text{Å}}$$

Show that for a linear harmonic oscillator in the ground state, the probability of find the particle outside the classical limits is approximately 16%.

Ans: The energy of the oscillator in the ground state

$$E_0 = \frac{1}{2}\hbar\omega \longrightarrow ①$$

$\left[\because E_n = (n+\frac{1}{2})\hbar\omega\right.$

Classically, the total energy of the oscillator is

$$E_0 = \frac{1}{2} m\omega^2 A^2 \longrightarrow ②$$ Where A is the amplitude of motion

Comparing equ ① & ②,

$$A^2 = \frac{\hbar}{m\omega} \implies A = \pm\sqrt{\frac{\hbar}{m\omega}}$$

In the normal state of the oscillator, the probability of finding the particle in classical region is

$$P = \int_{-\infty}^{\infty} \psi_0^* \psi_0 \, dx \longrightarrow ③$$

The ground state wave function of the oscillator is

$$\psi(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega x^2}{2\hbar^2}}, \quad \text{let } \frac{m\omega}{\hbar} = \beta.$$

$$= \left(\frac{\beta}{\pi}\right)^{1/4} e^{-\frac{\beta x^2}{2}}$$

Substituting in equ. ③, we have

$$P = \int_{-\infty}^{\infty} |\psi_0|^2 dx = \left(\frac{\beta}{\pi}\right)^{1/2} \int_{-A}^{A} e^{-\frac{y^2}{2}x^2} dx \longrightarrow ④$$

Where $y = \sqrt{\beta}\, x$

$y^2 = \beta x^2$

$\frac{dy}{dx} = \sqrt{\beta}\, dx$

$dx = \sqrt{\frac{1}{\beta}}\, dy$

or $dx = \left(\frac{\hbar}{m\omega}\right)^{1/2} dy.$

$\therefore$

Substituting in eqn. (4)

$$P = \left(\frac{m\omega}{\hbar\pi}\right)^{1/2} \int_{-A}^{A} e^{-y^2} \left(\frac{\hbar}{m\omega}\right)^{1/2} dy.$$

$$= \pi^{-1/2} \int_{-1}^{+1} e^{-y^2}\, dy$$

→ As P vanishes between the limits $-A$ and A, therefore, the limit -1 and $+1$. as $y = \pm 1$

$$P = 2\pi^{-1/2} \int_{0}^{1} e^{-y^2}\, dy.$$

$$= 2\pi^{-1/2} \int_{0}^{1} \left(1 - y^2 + \frac{y^4}{2!} - \frac{y^6}{3!} + \frac{y^8}{4!} - \cdots\right) dy.$$

[But $n! = n(n-1) \times (n-2) \times \cdots \cdots [n-(n-1)]$

Eg: $5! = 5(5-1) \times (5-2) \times (5-3) \times (5-4)$ —

$= 5 \times 4 \times 3 \times 2 \times 1$.]

$$\therefore P = 2\pi^{-1/2}\left[y - \frac{y^3}{3} + \frac{y^5}{10} - \frac{y^7}{42} + \frac{y^9}{216} - \cdots\right]_0^1$$

$$= 2\pi^{-1/2}\left[1 - 0.333 + 0.1 - 0.024 + 0.004 - \cdots\right]$$

$= 0.84 = 84\%$ inside the classical limits.

Therefore, the probability of finding the particle outside the classical limits would be 16%