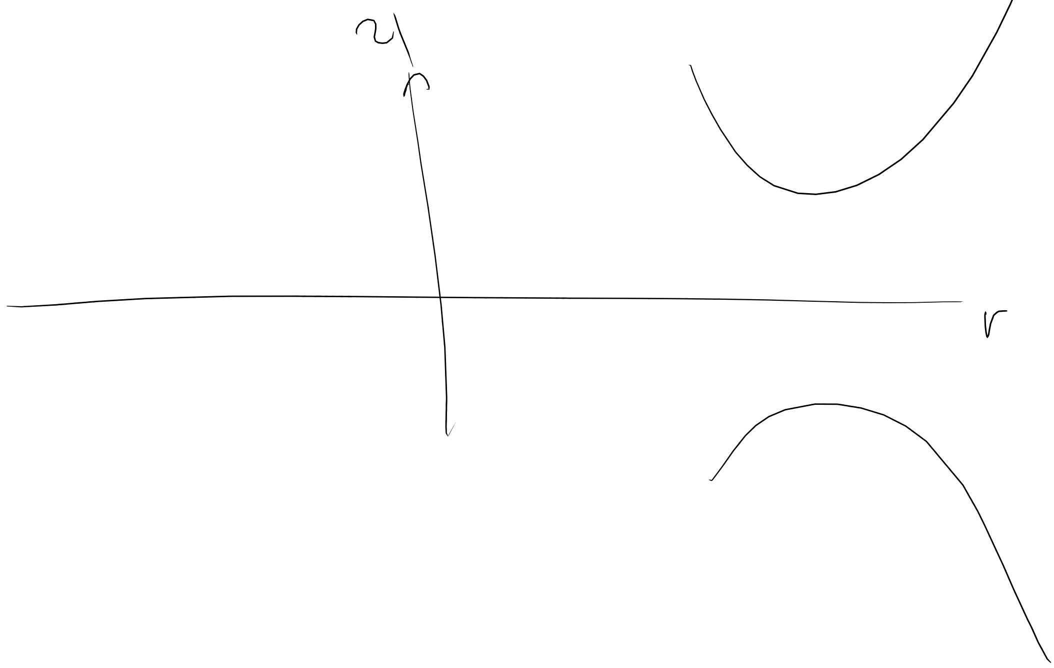
$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2 \psi + V(\vec{r})\psi$$

$$E\psi = -\frac{\hbar^2}{2m}\nabla^2\psi + V(\vec{r})\psi \Leftarrow$$

$$E < \lim_{r\to\infty} V(\vec{r})$$



Example Free Particle in 3D

$$H = \frac{\vec{p}^{\,2}}{2m}$$

$$[p_i, H] = 0$$

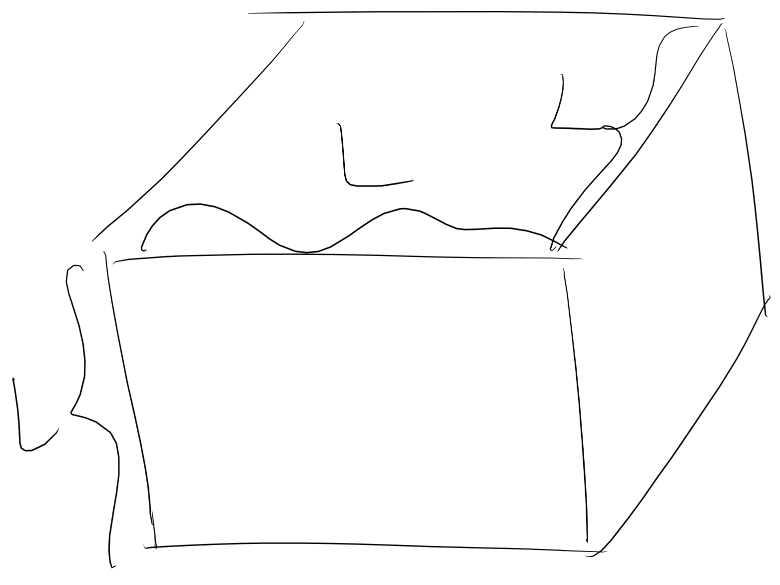
$$-i\hbar \frac{\partial \psi(\vec{r})}{\partial x_i} = p_i \psi \quad \text{(no sum over } i\text{)}$$

$$\psi(\vec{r}) = N e^{\frac{i}{\hbar} p_i x_i}$$

a sum over i is implied

$$\boxed{\psi(\vec{r}) = N e^{\frac{i}{\hbar} \vec{p} \cdot \vec{r}}}$$

$$H\psi(\vec{r}) = \frac{\vec{p}^2}{2m} \psi(\vec{r})$$



$L \to \infty$

$$\int d^3\vec{r} \, |\psi|^2 = 1$$

$$\psi = N e^{\frac{i}{\hbar} \vec{p} \cdot \vec{r}}$$

$$|\psi|^2 = |N|^2$$

$$\underbrace{\int d^3\vec{r} \, |N|^2}_{|N|^2 L^3} = 1$$

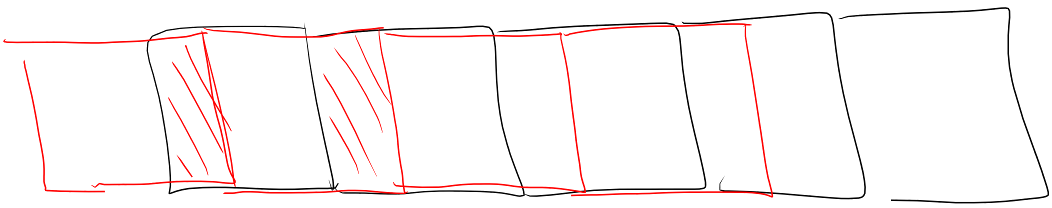
$$|N|^2 L^3 = 1 \to N = \frac{1}{\sqrt{L^3}}$$

$$\boxed{\psi(\vec{r}) = \frac{1}{\sqrt{L^3}}\, e^{\frac{i}{\hbar}\vec{p}\cdot\vec{r}}}$$

$\psi(\vec{r}) = 0$ on the boundary of the box

$$\psi\left[\vec{r} + (n_x\hat{x} + n_y\hat{y} + n_z\hat{z})L\right] = \psi(\vec{r})$$

periodic boundary condition.



$$\psi(\vec{r}) = \frac{1}{\sqrt{L^3}}\, e^{\frac{i}{\hbar}\vec{p}\cdot\vec{r}}$$

$$\psi(\vec{r} + \vec{n}L) = \psi(\vec{r})$$

$\vec{n} = n_x\hat{x} + n_y\hat{y} + n_z\hat{z}$

$n_x, n_y, n_z \in \{0, 1\}$

$$\Rightarrow \boxed{e^{\frac{i}{\hbar}\vec{p}\cdot\vec{n}L} = 1}$$

$\vec{p} \cdot \vec{n} L \frac{1}{\hbar} = (n_x p_x + n_y p_y + n_z p_z) \frac{L}{\hbar}$ = multiple of 2π

$\forall \; n_x, n_y, n_z \in \{0, 1\}$ $\quad n_x + n_y + n_z = 1$

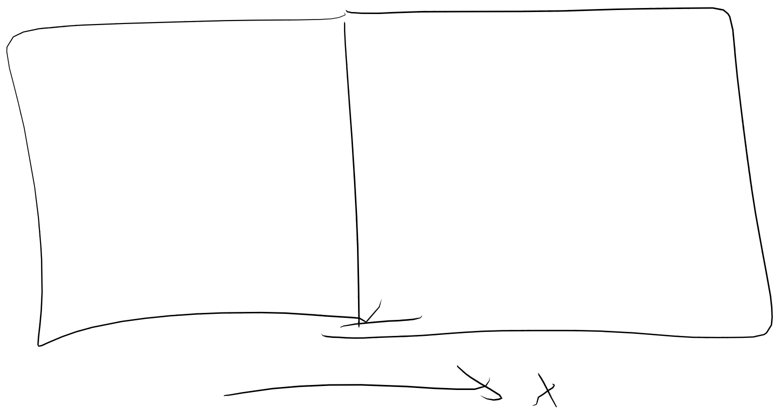
$\vec{n} = (1, 0, 0)$ $\quad p_x \frac{L}{\hbar} = 2\pi m_x \Rightarrow p_x = \frac{2\pi\hbar}{L} m_x$

$$p_x = \frac{\hbar}{L} 2\pi m_x$$

$m_x, m_y, m_z = 0, \pm 1, \pm 2, \dots$

$$p_y = \frac{2\pi\hbar}{L} m_y$$

$$p_z = \frac{2\pi\hbar}{L} m_z$$



$\psi(x, y, z)$

$\psi(x+L, y, z) = \psi(x, y+L, z) = \psi(x, y, z+L)$

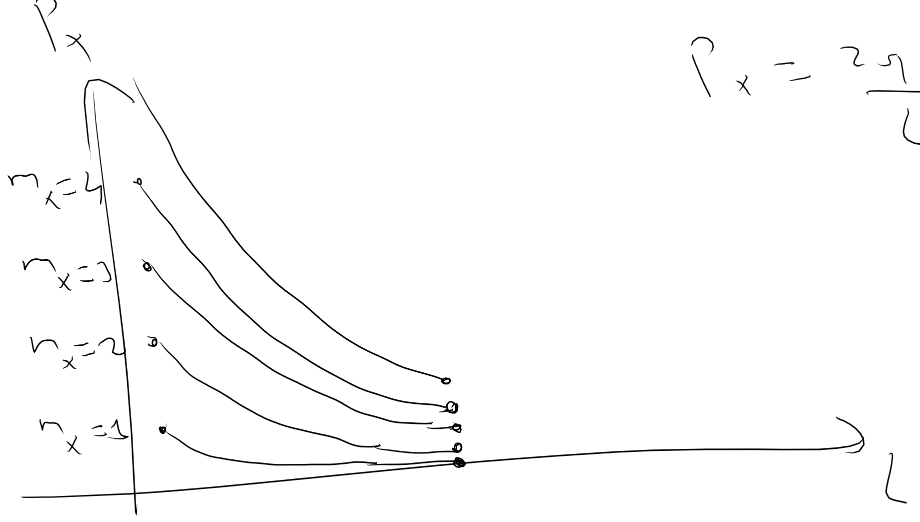
$= \psi(x, y, z)$

$$\psi_{\vec{p}}(\vec{r}) = \frac{1}{\sqrt{L^3}} e^{\frac{i}{\hbar}\vec{p}\cdot\vec{r}}$$

$$\vec{p} = \frac{2\pi\hbar}{L}\left(n_x \hat{x} + n_y \hat{y} + n_z \hat{z}\right)$$

$$\Delta p_x = \frac{2\pi\hbar}{L}(n_x+1) - \frac{2\pi\hbar}{L} n_x = \frac{2\pi\hbar}{L} \xrightarrow[L\to\infty]{} 0$$

$$p_x = \frac{2\pi\hbar}{L} n_x$$



$$\Delta E = \frac{1}{2m}\left(\frac{2\pi\hbar}{L}\right)^2 \left(\vec{n}'^2 - \vec{n}^2\right) \xrightarrow[L\to\infty]{} 0$$

$$\vec{n} = n_x \hat{x} + n_y \hat{y} + n_z \hat{z}$$
$$\vec{n}' = n'_x \hat{x} + n'_y \hat{y} + n'_z \hat{z}$$

# of states
that have
energy in the
interval (5eV, 5.1eV)

$$\sum_{\text{states}} f(E)$$

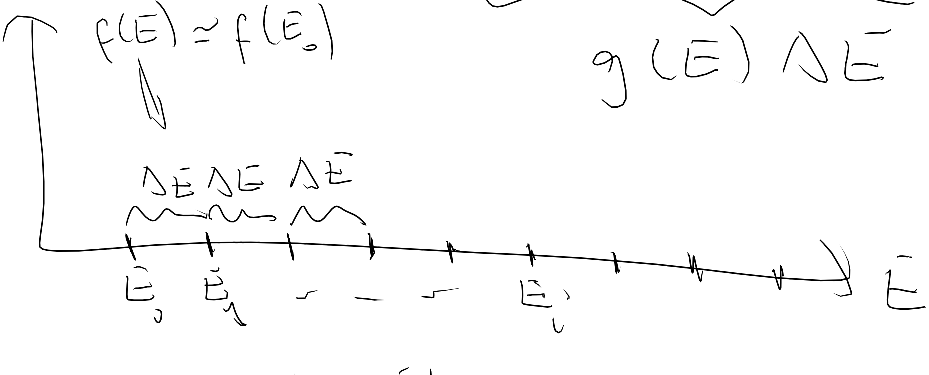
$$= \sum_{\substack{\text{energies}\\ E}} f(E) \sum_{\substack{\text{states}\\ \text{that have}\\ \text{energy } E}} 1$$

$E, \; E+dE$ $\qquad$ $f(E)$ is constant

$$= \sum_{\substack{\text{energies}\\ E}} f(E) \left(\begin{array}{l} \#\text{ of states} \\ \text{having energy } E \end{array} \right)$$

$$\approx$$

$$= \sum_{\substack{\text{discrete}\\ \text{energies}\\ E_i}} f(E_i) \underbrace{\left(\begin{array}{l} \#\text{ of states} \\ \text{having energy} \\ \text{in the interval} \\ (E_i, E_i + \Delta E) \end{array} \right)}_{g(E)\,\Delta E}$$



$g(E)$: density of states.

$$\sum_{\text{states}} f(E) = \sum_{E_i} f(E_i)\, g(E_i)\, \Delta E$$

$$\xrightarrow[\Delta E \to 0]{} \int dE\, f(E)\, g(E)$$

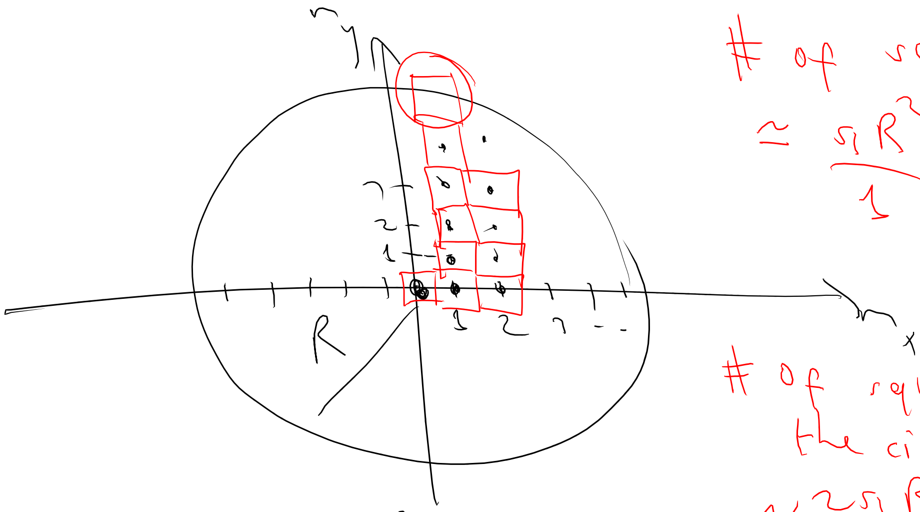
<u>Example</u> Density of states for a free particle.

$N(E) = \#$ of states having energy less then E

$$\begin{pmatrix} \text{\# of states} \\ \text{having energy} \\ \text{in the interval} \\ E,\, E+\Delta E \end{pmatrix} = N(E+\Delta E) - N(E)$$

$$\equiv g(E)\, \Delta E$$

$$g(E) = \lim_{\Delta E \to 0} \frac{N(E+\Delta E) - N(E)}{\Delta E} = \frac{\partial N(E)}{\partial E}$$

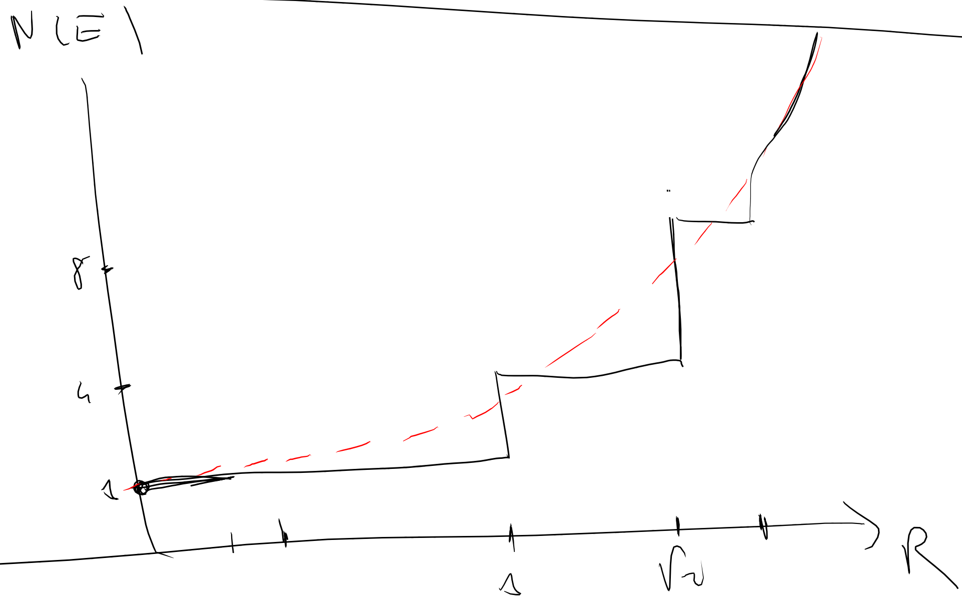


\# of squares $\simeq \frac{\pi R^3}{1}$

\# of squares on the circumference $\sim \frac{2\pi R}{1}$

$$\frac{1}{2m}\left(\frac{2\pi\hbar}{L}\right)^2 (n_x^2+n_y^2) \leq E$$

$$\boxed{n_x^2+n_y^2 \leq 2m\left(\frac{L}{2\pi\hbar}\right)^2 E = R^2}$$



in 3D

$$n_x^2+n_y^2+n_z^2 \leq 2m\left(\frac{L}{2\pi\hbar}\right)^2 E = R^2$$

$$N(E) = \left(\frac{4}{3}\pi R^3\right)\frac{1}{1} = \frac{4}{3}\pi\left[2m\left(\frac{L}{2\pi\hbar}\right)^2 E\right]^{3/2}$$

$$\boxed{g(E) = \frac{4}{3}\pi\left[2m\left(\frac{L}{2\pi\hbar}\right)^2\right]^{3/2}\frac{3}{2}E^{1/2}}$$

$$g(E) \propto L^3$$

$$\int d^3r\, \psi^*_{\vec{p}}(\vec{r})\, \psi_{\vec{p}\,'}(\vec{r})$$

$$= \int_{-L/2}^{L/2} dx \int_{-L/2}^{L/2} dy \int_{-L/2}^{L/2} dz\, \frac{e^{-\frac{i}{\hbar}(\vec{p}-\vec{p}\,')\cdot\vec{r}}}{L^3} = \delta_{n_x n_x'}\,\delta_{n_y n_y'}\,\delta_{n_z n_z'}$$

$$\psi_{\vec{p}}(\vec{r}) = \frac{e^{\frac{i}{\hbar}\vec{p}\cdot\vec{r}}}{\sqrt{L^3}}$$

$$L^3 \int_{-L/2}^{L/2}\!dx\int_{-L/2}^{L/2}\!dy\int_{-L/2}^{L/2}\!dz\ \frac{e^{-\frac{i}{\hbar}(\vec{p}-\vec{p}\,')\cdot\vec{r}}}{L^3} = L^3\delta_{n_x n_x'}\,\delta_{n_y n_y'}\,\delta_{n_z n_z'}$$

$$\int_{-L/2}^{L/2} dx \int_{-L/2}^{L/2} dy \int_{-L/2}^{L/2} dz\ e^{-\frac{i}{\hbar}(\vec{p}-\vec{p}\,')\cdot\vec{r}}$$

$$= L^3\,\delta_{n_x n_x'}\,\delta_{n_y n_y'}\,\delta_{n_z n_z'}$$

$$\Rightarrow$$

$$\lim_{L\to\infty} \int_{-L/2}^{L/2} dx \int_{-L/2}^{L/2} dy \int_{-L/2}^{L/2} dz\ e^{-\frac{i}{\hbar}(\vec{p}-\vec{p}\,')\cdot\vec{r}} = (2\pi\hbar)^3\,\delta^{(3)}(\vec{p}-\vec{p}\,')$$

$L\to\infty$

$$\psi_{\vec{p}}(\vec{r}) = \frac{1}{\sqrt{(2\pi\hbar)^3}}\,e^{-\frac{i}{\hbar}\vec{p}\cdot\vec{r}}$$

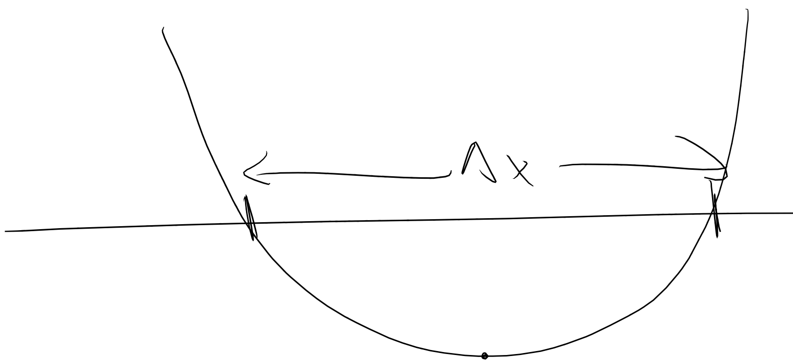
$$\boxed{\int d^3r\ \psi^*_{\vec{p}}(\vec{r})\,\psi_{\vec{p}\,'}(\vec{r}) = \delta^{(3)}(\vec{p}-\vec{p}\,')}$$

Free particle

$H = \frac{\vec{p}^2}{2m}$ $\quad E_{min} = 0 \quad \Delta x = \infty \quad p \sim \Delta p = 0$

1D Harmonic Oscillator

$H = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2 \quad E_{min} = \frac{\hbar\omega}{2}$



$\Delta x < \infty$

$p \sim \Delta p > 0$

1D Harmonic Oscillator

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2} m\omega^2 x^2 \psi = E\psi$$

Switch to dimensionless units.

$$\left[\frac{\hbar^2}{\cancel{2}mx^2}\right] = \left[\frac{1}{\cancel{2}} m\omega^2 x^2\right]$$

$$\frac{\hbar^2}{m^2\omega^2} = [x^4] \qquad x_0 = \sqrt{\frac{\hbar}{m\omega}}$$

$$x = x_0 y$$

$$-\frac{\hbar^2}{2mx_0^2}\frac{d^2\psi}{dy^2} + \frac{1}{2}m\omega^2 x_0^2 y^2\psi = E\psi$$

$$+\frac{d^2\psi}{dy^2} - \underbrace{\frac{m^2\omega^2}{\hbar^2}x_0^2}_{1} y^2\psi = \underbrace{-\frac{2mx_0^2}{\hbar^2}}_{-\varepsilon}E\psi$$

$$+\varepsilon = +\frac{2mx_0^2}{\hbar^2}E = 2\cancel{m}\frac{\cancel{\hbar}}{\cancel{m}\omega}\frac{1}{\hbar^{\cancel{2}}}E$$

$$\boxed{\varepsilon = \frac{2}{\hbar\omega}E} \qquad \boxed{E = \frac{\hbar\omega}{2}\varepsilon}$$

$$\boxed{\frac{d^2\psi}{dy^2} + (\varepsilon - y^2)\psi = 0}$$

$\psi \to 0$ as $y \to \infty$

as $y \to \infty$

$$\frac{d^2\psi}{dy^2} - y^2\psi = 0$$

$$\boxed{\psi \sim e^{\mp y^2/2}\psi_0}$$

$$\frac{d\psi}{dy} \sim \mp y\psi$$

$$\frac{d^2\psi}{du^2} \sim \mp\psi \pm u\left(\mp u\psi\right)$$

$$\frac{d^2\psi}{du^2} \sim u^2\psi$$

$$\psi = e^{-u^2/2}\,\phi(u)$$

$$\frac{d\psi}{du} = -u e^{-u^2/2}\phi + e^{-u^2/2}\frac{d\phi}{du}$$

$$\frac{d^2\psi}{du^2} = -e^{-u^2/2}\phi + u^2 e^{-u^2/2}\phi - u e^{-u^2/2}\frac{d\phi}{du}$$

$$- u e^{-u^2/2}\frac{d\phi}{du} + e^{-u^2/2}\frac{d^2\phi}{du^2}$$

$$0 = \left[\frac{d^2\psi}{du^2} + (\varepsilon - u^2)\psi\right]e^{u^2/2}$$

$$= -\phi - 2u\frac{d\phi}{du} + \frac{d^2\phi}{du^2} + \varepsilon\phi$$

$$\boxed{\frac{d^2\phi}{du^2} - 2u\frac{d\phi}{du} + (\varepsilon - 1)\phi = 0}$$

Assume

$$\phi(u) = \sum_{n=0}^{\infty} a_n u^n$$

$$\sum_{n=0}^{\infty} a_n \, n(n-1) \, u^{n-2} - 2 \sum_{n=0}^{\infty} a_n n u^n$$
$$+ \sum_{n=0}^{\infty} (\varepsilon - 1) a_n u^n = 0$$

Coefficient of u^m $m = 0, 1, \ldots$

$$a_{m+2} (m+2)(m+1) - 2 a_m m + (\varepsilon - 1) a_m = 0$$

$$\boxed{a_{m+2} = \frac{(2m + 1 - \varepsilon) a_m}{(m+1)(m+2)}}$$

$$\phi(u) = a_0 \sum_{m \text{ even}} \left(\frac{a_m}{a_0}\right) u^m$$
$$+ a_1 \sum_{m \text{ odd}} \left(\frac{a_m}{a_1}\right) u^m$$

For large m,
$$a_{m+2} \simeq 2 \frac{a_m}{m}$$

$$a_{2n} \simeq \frac{\cancel{2}}{\cancel{2}n} a_{2n-2} \simeq \frac{1}{n(n-1)} a_{2n-4}$$

$$a_{2n} \simeq \frac{1}{n!} a_0$$

$$\sum_{m \text{ even}} \left(\frac{a_m}{a_0}\right) u^m = \sum_n \left(\frac{a_{2n}}{a_0}\right) u^{2n}$$

$$= \sum_n \frac{1}{n!} (u^2)^n$$

$$= \exp(u^2)$$

For the series to terminate

$\varepsilon = 2m_0 + 1$ for some integer m_0

$$\Rightarrow \boxed{E_{m_0} = \frac{\hbar w}{2} (2m_0 + 1)}$$