Lecture Notes: January 10, Thurs, Lecture 2

Schrodinger Equation Expressions for a Particle in 1-D Infinite and 3-D Infinite Potential Wells andHydrogen Atom in 3D

Objectives:

- Express Schrodinger Equations for a particle at bound states in 1D (x) and 3D (x, y, z) infinite wells. Describe quantized energy states and wave functions for infinite potential wells. Understand energy degeneracies.
- Express the time independent Schrodinger Equation for the hydrogen atom in (r, θ, ϕ)
- Apply the separation of variables method to come up with three equations.

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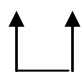
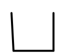
We have the time-independent Schrodinger Equation:

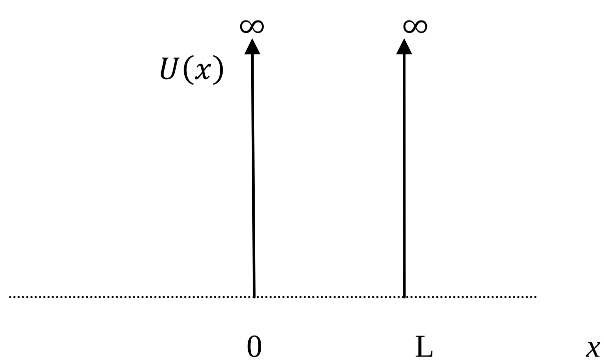
$$\frac{-\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} + U(x)\,\psi(x) = \mathrm{E}\,\psi(x) \qquad \text{(e2.1)}$$

Bound States represent cases when a particle's wave function is limited to a finite region of space by the potential energy, $U(x)$. We will consider wave functions and energies three such cases:

- Infinite Well $where\ U(x)$ = 
- Finite Well $where\ U(x)$ = 

A Particle with E in a 1 Dimensional Infinite Well

$$U(x) = \begin{cases} \infty & x \le 0 \\ 0 & 0 < x < L \\ \infty & x \ge L \end{cases}$$



Where $x \le 0$, wave functions CANNOT exist since the potential is infinity. → $\psi_{x\le 0}(x) = 0$

Where $x \ge L$, wave functions CANNOT exist since the potential is infinity → $\psi_{x\ge L}(x) = 0$

Where $0 < x < L$, put $U(x) = 0$ into the time-independent Schrodinger Equation (e2.1),

$$\frac{-\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} = \mathrm{E}\,\psi(x) \qquad \text{(e2.2)}$$

$$\frac{\partial^2\psi(x)}{\partial x^2} = \frac{-2m\,E}{\hbar^2}\psi(x) = -\,k^2\,\psi(x) \quad \text{where } k = \sqrt{\frac{2mE}{\hbar^2}} \qquad \text{(e2.3)}$$

Since the wave function has to be confined inside the infinite well, we can consider $\sin(kx)$ *or* $\cos(kx)$ that satisfy (e2.2) as $\psi_{0<x<L}(x)$.

BUT, since $\psi(x)$ needs to be continuous which means

- $\psi_{x\le 0}(x=0) = 0$ → We take only $\sin(kx)$ for $\psi_{0<x<L}(x)$ (drop $\cos(kx)$)
- $\psi_{x\ge L}(x=0) = 0$ → $\psi_{0<x<L}(x=L) = \sin(kL) = 0$ gives energy quantization rules

$$kL = \sqrt{\frac{2mE}{\hbar^2}}\,L = n\pi \qquad \text{where n =1, 2, 3, etc.} \qquad \text{(e2.4)}$$

$$E = \frac{n^2\,\pi^2\,\hbar^2}{2mL^2} \qquad \text{Energy quantization} \quad \text{(e2.5)}$$

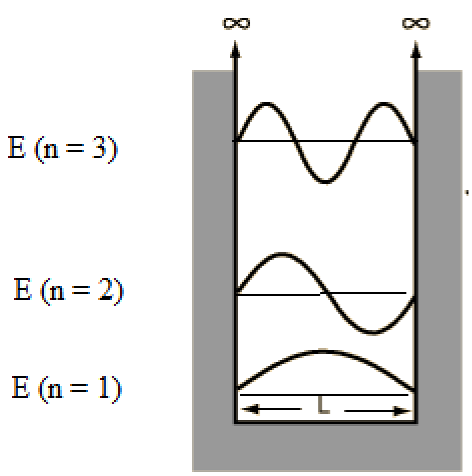
- Normalization

$$\psi_{0<x<L}(x) = A\sin(kx) = \mathrm{A}\sin(\frac{n\pi x}{L})$$

$$\int_0^L |\psi_{0<x<L}(x)|^2 = 1 = \mathrm{A}^2\int_0^L \sin\left(\frac{n\pi x}{L}\right)^2 dx = \mathrm{A}^2\,\frac{\mathrm{L}}{2} \;\rightarrow\; \mathrm{A} = \sqrt{\frac{2}{L}} \quad \text{(e2.6)}$$

THEREFORE,

- Wave function: $\psi_{0<x<L}(x) = \sqrt{\frac{2}{L}}\,\sin(\frac{n\pi x}{L})$
- Energy $E = \frac{n^2\,\pi^2\,\hbar^2}{2mL^2}$



$$E\ (n=3) = 9\,\frac{\pi^2\,\hbar^2}{2mL^2}$$

$$E\ (n=2) = 4\,\frac{\pi^2\,\hbar^2}{2mL^2}$$

$$E\ (n=1) = 1\,\frac{\pi^2\,\hbar^2}{2mL^2}$$

Schrodinger Equation in three dimensions using (x, y, z) coordinates

$$\frac{-\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2} + U(x)\Psi(x,t) = i\hbar\,\frac{\partial\,\Psi(x,t)}{\partial t} \rightarrow \frac{-\hbar^2}{2m}\nabla^2\,\Psi\,(\vec{x}\,,t) + U(\vec{x})\Psi\,(\vec{x}\,,t) = i\hbar\,\frac{\partial\,\Psi\,(\vec{x}\,,t)}{\partial t}$$

In (x, y, z) coordinates, $\vec{x} = (x, y, z)$, $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$
The time-dependent Schrodinger Equation is:

$$\frac{-\hbar^2}{2m}\nabla^2\,\Psi\,(\vec{x}\,,t) + U(\vec{x})\Psi\,(\vec{x}\,,t) = i\hbar\,\frac{\partial\,\Psi\,(\vec{x}\,,t)}{\partial t} \qquad \text{(e2.7)}$$

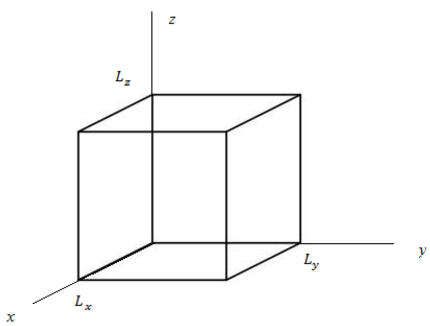
$$\text{Normalization: } \int \;|\Psi\,(\vec{x},t)|^2\,dV = 1$$

The time-independent Schrodinger Equation is:

$$\frac{-\hbar^2}{2m}\nabla^2\,\psi\,(\vec{x}) + U(\vec{x})\psi\,(\vec{x}) = E\,\psi(\vec{x}) \qquad \text{(e2.8)}$$

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi\,(x,y,z) = -\frac{2m}{\hbar^2}(E - U(x,y,z))\psi\,(x,y,z)$$

A particle with E in a 3 Dimensional Infinite Well



$$U(\vec{x}) = \begin{cases} 0 & 0 < x < L_x\,, 0 < y < L_y\,.\, 0 < z < L_z \\ \infty & otherwise \end{cases}$$

The 3D infinite well problem is an extension of the 1D infinite well problem in all three direcitons, because we can separate wave functions as

$$\psi(\vec{x}) = \psi\,(x,y,z) = F(x)G(y)H(z) \qquad \text{(e2.9)}$$

If we put (e2.9) into (e2.8), we get

$$\frac{1}{F(x)}\frac{\partial^2 F(x)}{\partial x^2} + \frac{1}{G(y)}\frac{\partial^2 G(y))}{\partial y^2} + \frac{1}{H(z)}\frac{\partial^2 H(z)}{\partial z^2} = -\frac{2mE}{\hbar^2} \quad \text{(e2.10)}$$

$$\begin{cases} \frac{d\,F(x)}{dx^2} = C_x F(x) \rightarrow F(x) = A_x \sin\frac{n_x \pi x}{L_x} \\ \frac{d\,G(y)}{dy^2} = C_y G(y) \rightarrow G(y) = A_y \sin\frac{n_y \pi y}{L_y} \\ \frac{d\,H(z)}{dz^2} = C_z H(z) \rightarrow H(z) = A_z \sin\frac{n_z \pi z}{L_z} \end{cases} \qquad \text{(e2.11)}$$

Put (e2.11) into (e2.10)

$$-\frac{n_x^2\pi^2}{{L_x}^2}-\frac{n_y^2\pi^2}{{L_y}^2}-\frac{n_z^2\pi^2}{{L_z}^2}=-\frac{2mE}{\hbar^2} \rightarrow E_{(n_x,n_y,n_z)}=\left(\frac{n_x^2}{{L_x}^2}+\frac{n_y^2}{{L_y}^2}+\frac{n_z^2}{{L_z}^2}\right)\frac{\pi^2\hbar^2}{2m} \quad \text{(e2.12)}$$

→ Energy Quantized!

$$\psi\,(x,y,z) = F(x)G(y)H(z) = A\,\sin\frac{n_x\pi x}{L_x}\sin\frac{n_y\pi y}{L_y}\sin\frac{n_z\pi z}{L_z}$$

- Lowest Energy State is $(n_x, n_y, n_z) = (1,1,1)$
  - $E_{(1,1,1)} = \left(\frac{1^2}{{L_x}^2}+\frac{1^2}{{L_y}^2}+\frac{1^2}{{L_z}^2}\right)\frac{\pi^2\hbar^2}{2m}$
  - $\psi_{(1,1,1)} = A\,\sin\frac{\pi x}{L_x}\sin\frac{\pi y}{L_y}\sin\frac{\pi z}{L_z}$

Degeneracy occurs when different wave functions have the same energy.

When $L_x = L_y = L_z = L$

We can see that

- $E_{(1,1,1)} = (2^2 + 1^2 + 1^2)\left(\frac{\pi^2\hbar^2}{2mL^2}\right) = 3\,(\frac{\pi^2\hbar^2}{2mL^2})$ → One wave function $\psi_{(1,1,1)} = A\,\sin\frac{\pi x}{L}\sin\frac{\pi y}{L}\sin\frac{\pi z}{L}$ (nondegenerate)
- $E_{(2,1,1)} = E_{(1,2,1)} = E_{(1,1,2)} = (2^2 + 1^2 + 1^2)\left(\frac{\pi^2\hbar^2}{2mL^2}\right) = 6\,\left(\frac{\pi^2\hbar^2}{2mL^2}\right)$

$$\rightarrow \text{3 wave functions} \begin{cases} \psi_{(2,1,1)} = A\,\sin\frac{2\pi x}{L}\sin\frac{\pi y}{L}\sin\frac{\pi z}{L} \\ \psi_{(1,2,1)} = A\,\sin\frac{\pi x}{L}\sin\frac{2\pi y}{L}\sin\frac{\pi z}{L} \\ \psi_{(1,1,2)} = A\,\sin\frac{\pi x}{L}\sin\frac{\pi y}{L}\sin\frac{2\pi z}{L} \end{cases}$$

(degenerate)

Degeneracy = 3 (# of different wave functions that correspond to the same energy)

Consider an electron in a cubic 3D infinite well of 1 nm at the $E_{(2,1,1)}$ state

- Calculate the $E_{(2,1,1)}$ value
  - $E_{(2,1,1)} = 6\,\left(\frac{\pi^2\hbar^2}{2mL^2}\right) = (2^2 + 1^2 + 1^2)\frac{\pi^2(1.055\text{ x }10^{-34}\text{ J sec})^2}{2(9.11\text{ x }10^{-31}\text{kg})(10^{-9}\text{ m})^2}$

    $= 3.62\text{ x }10^{-19}\text{ J} = 2.26\text{ eV}$ (the same as $E_{(1,2,1)} = E_{(1,1,2)}$)

$$\text{Where} \begin{cases} \text{electron mass} = 9.11 \text{ x } 10^{-31}\text{kg} \\ h = 1.055 \text{ x } 10^{-34} \text{ J sec} \\ L = 10^{-9} \text{ m} \end{cases} \quad \text{and 1 eV = 1.602 x } 10^{-19} \text{ J}$$

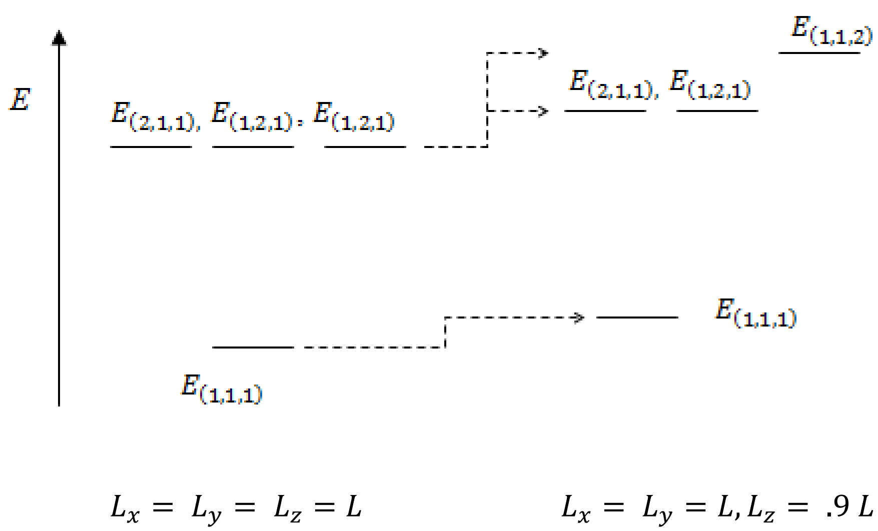
- Probability density
  - $|\psi_{(2,1,1)}|^2 = A^2 \left(\sin\frac{2\pi x}{L}\right)^2 \left(\sin\frac{\pi y}{L}\right)^2 \left(\sin\frac{\pi z}{L}\right)^2$

    Since the value of $(sin\theta)^2$ *is highest when* $\theta = \frac{1}{2}\pi, \frac{3}{2}\pi, etc.$, the probability density will be highest when $\begin{cases} x = \frac{L}{4}, \frac{3L}{4} \\ y = \frac{L}{2} \\ z = \frac{L}{2} \end{cases}$

Consider $L_x = L_y = L,\ L_z = .9\,L$ (that is, a slightly nonsymmetric box along the z axis)

- With the perfect symmetry ($L_x = L_y = L_z = L$), $E_{(2,1,1)} = E_{(1,2,1)} = E_{(1,1,2)}$
- With the change in symmetry,
  - $E_{(1,1,1)} = \left(\frac{1^2}{L^2} + \frac{1^2}{L^2} + \frac{1^2}{.9^2L^2}\right)\left(\frac{\pi^2\hbar^2}{2m}\right) = (1 + 1 + 1.23)\left(\frac{\pi^2\hbar^2}{2mL^2}\right) = 3.23\left(\frac{\pi^2\hbar^2}{2mL^2}\right)$
  - $E_{(2,1,1)} = E_{(1,2,1)} = \left(\frac{2^2}{L^2} + \frac{1^2}{L^2} + \frac{1^2}{.9^2L^2}\right)\left(\frac{\pi^2\hbar^2}{2m}\right) = (4 + 1 + 1.23)\left(\frac{\pi^2\hbar^2}{2mL^2}\right) = 6.23\left(\frac{\pi^2\hbar^2}{2mL^2}\right)$
  - $E_{(1,1,2)} = \left(\frac{1^2}{L^2} + \frac{1^2}{L^2} + \frac{2^2}{.9^2L^2}\right)\left(\frac{\pi^2\hbar^2}{2m}\right) = (1 + 1 + 4.92)\left(\frac{\pi^2\hbar^2}{2mL^2}\right) = 6.92\left(\frac{\pi^2\hbar^2}{2mL^2}\right)$

- *Energy Split*

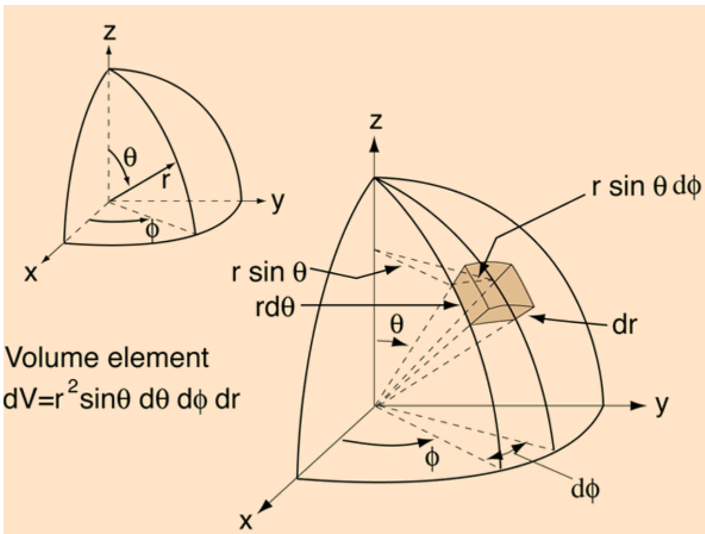


Hydrogen Atom in 3-D

The potential energy of the electron in the hydrogen atom (= Coulomb potential energy between two charges: (+*e*) of the proton and (-*e*) of the electron separated by *r*).

$$U(r) = \frac{1}{4\pi\varepsilon_0}\frac{-e^2}{r} \qquad \text{(e2.13)}$$

Since this potential has a spherical symmetry, to make solving the Schrodinger Equation easier, we choose the spherical polar coordinate system.



$$(x, y, z) \quad \leftrightarrow \quad (r, \theta, \phi)$$

$$\begin{cases} r = \sqrt{x^2 + y^2 + z^2} \\ \phi = tan^{-1}\dfrac{y}{x} \\ \theta = cos^{-1}\dfrac{z}{r} \end{cases}$$

$$\begin{cases} x = rsin\theta cos\phi \\ y = r\, sin\theta sin\,\phi \\ z = rcos\theta \end{cases}$$

The time independent Schrodinger Equation for the hydrogen atom (an electron + a proton)

$$\frac{-\hbar^2}{2m}\nabla^2\psi(\vec{x}) + U(\vec{x})\psi(\vec{x}) = E\,\psi(\vec{x}) \qquad \text{(e2.14)}$$

∇^2 can be expressed as follows:

In (x, y, z),

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

In (r, θ, ϕ),

$$\nabla^2 = \frac{1}{r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + csc\theta\,\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial}{\partial\theta}\right) + csc^2\theta\,\frac{\partial}{\partial\phi^2}\right]$$
$$= \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2 sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2 sin^2\theta}\frac{\partial}{\partial\phi^2}$$

In (x, y, z), the time independent Schrodinger Equation (e2.14) becomes

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi(x, y, z) + U(x, y, z)\psi(x, y, z) = -\frac{2mE}{\hbar^2}\psi(x, y, z)$$

In (r, θ, ϕ), the time independent Schrodinger Equation (e2.14) becomes

$$\frac{-\hbar^2}{2m}\frac{1}{r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + csc\theta\ \frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial}{\partial\theta}\right) + \ csc^2\theta\frac{\partial^2}{\partial\phi^2}\right]\psi(r,\theta,\phi) + U(r)\ \psi(r,\theta,\phi) = E\ \psi(r,\theta,\phi)$$

Then, put the partial derivertivees in θ *and* ϕ on one side and the radial partial derivertive on the other side of the equation:

$$csc\theta\ \frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial}{\partial\theta}\right)\psi + \ csc^2\theta\frac{\partial^2}{\partial\phi^2}\psi = \ \left[-\ \frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \ \frac{2mr^2}{\hbar^2}\ (E - U(r))\right]\psi \qquad \text{(e2.15)}$$

Separation of variables

$\psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi)$ → for shorthand $\psi = R\Theta\Phi$

$$\frac{\partial\psi}{\partial r} = \ \Theta\Phi\frac{\partial R}{\partial r}$$

$$\frac{\partial\psi}{\partial\theta} = R\Phi\frac{\partial\Theta}{\partial\theta}$$

$$\frac{\partial^2\Phi}{\partial\phi^2} = R\Theta\frac{\partial^2\Phi}{\partial\phi^2}$$

After substituting $\psi(r,\theta,\phi) with\ R(r)\Theta(\theta)\Phi(\phi)$, (e2.15) becomes:

$$R\Phi\ csc\theta\ \frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial\Theta}{\partial\theta}\right) + R\Theta csc^2\theta\frac{\partial^2\Phi}{\partial\phi^2} = \ -\Theta\Phi\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) - \frac{2mr^2}{\hbar^2}\ (E - U(r))\ R\Theta\Phi \qquad \text{(e2.16)}$$

Divide (e2.16) by $R\Theta\Phi$

$$\frac{1}{\Theta}\ csc\theta\ \frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \ \frac{1}{\Phi}csc^2\theta\frac{\partial^2\Phi}{\partial\phi^2} = \ -\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) - \frac{2mr^2}{\hbar^2}\ (E - U(r)) = C\ \text{(Constant)} \quad \text{(e2.17)}$$

Consider C is $-l(l+1)$**, then each side of the equation (e2.17) should be the same constant of** $-l(l+1)$**.**

$$\begin{cases} -\dfrac{1}{R}\dfrac{\partial}{\partial r}\left(r^2\dfrac{\partial R}{\partial r}\right) - \dfrac{2mr^2}{\hbar^2}\ \left(E - U(r)\right) = C = \ -l(l+1) \rightarrow (e2.18)a \\ \dfrac{1}{\Theta}\ csc\theta\ \dfrac{\partial}{\partial\theta}\left(sin\theta\dfrac{\partial\Theta}{\partial\theta}\right) + \dfrac{1}{\Phi}csc^2\theta\dfrac{\partial^2\Phi}{\partial\phi^2} = C = -l(l+1) \rightarrow (e2.18)b \end{cases}$$

Divide both sides of (e2.18)b by $csc^2\theta\ (or\ multiply\ sin^2\theta\ since\ csc\theta = \frac{1}{sin\theta})$

$$\frac{1}{\Theta}sin\theta\ \frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2} = -l(l+1)\ sin^2\theta \qquad \text{(e2.19)}$$

Arrange (e2.19) to separate *the partial derivative of θ and that of ϕ*

$$\frac{1}{\Theta} sin\theta \ \frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial\Theta}{\partial\theta}\right) + l(l+1)sin^2\theta = -\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2} \qquad \text{(e2.20)}$$

$$= \boldsymbol{m_l^2} \text{ (another constant)}$$

Three equations can be derived from the time independent Schrodinger Equation (e2.14)

$$\begin{cases} \dfrac{\partial^2\Phi}{\partial\phi^2} = -m_l^2\Phi \\ sin\theta\dfrac{\partial}{\partial\theta}\left(sin\theta\dfrac{\partial\Theta}{\partial\theta}\right) + [l(l+1)sin^2\theta - m_l^2]\Theta = 0 \\ \dfrac{\partial}{\partial r}\left(r^2\dfrac{\partial R}{\partial r}\right) + \dfrac{2mr^2}{\hbar^2}\left(E - U(r)\right)R - l(l+1)R = 0 \end{cases}$$