PH102, 2014W, Lecture Notes: January 14, Tues, Class 3

Hydrogen Atom in (r, θ, ϕ) coordinates and (l, m_l) orbital quantization

Objectives:

- 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.
- Understand what three quantum numbers $(n, l,\ m_l)$ represent and what combinations of quantum numbers are possible in a given *n* (energy) state.
- Understand the quantization of the angular momentum and the relationship between $l\ and\ m_l$.
- List degeneracies for each n state.

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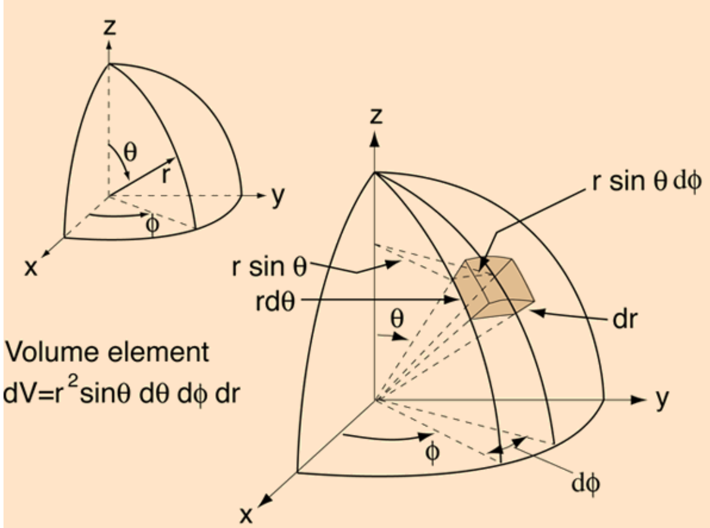
Hydrogen Atom in 3-D

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),

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

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

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

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

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

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

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

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

$$\frac{1}{sin\theta}\frac{\partial}{\partial \theta}\left(sin\theta\frac{\partial}{\partial \theta}\right)\psi + \frac{1}{sin^2\theta}\frac{\partial^2}{\partial \phi^2}\psi = \left[-\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{2mr^2}{\hbar^2}\,(E-U)\right]\psi \qquad \text{(e2.15)}$$

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

$$\frac{1}{sin\theta}\frac{\partial}{\partial \theta}\left(sin\theta\frac{\partial}{\partial \theta}\right)R\Theta\Phi + \frac{1}{sin^2\theta}\frac{\partial^2}{\partial \phi^2}R\Theta\Phi = \left[-\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{2mr^2}{\hbar^2}\,(E-U)\right]R\Theta\Phi$$

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

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

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

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

$$R\Phi\,\frac{1}{sin\theta}\,\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial\Theta}{\partial\theta}\right) + R\Theta\,\frac{1}{sin^2\theta}\,\frac{\partial^2\Phi}{\partial\phi^2} = -\Theta\Phi\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) - \frac{2mr^2}{\hbar^2}\,(E-U)\,R\Theta\Phi \qquad \text{(e2.16)}$$

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

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

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

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

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 $the\ partial\ derivative\ of\ \theta\ and\ that\ of\ \phi$

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

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

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

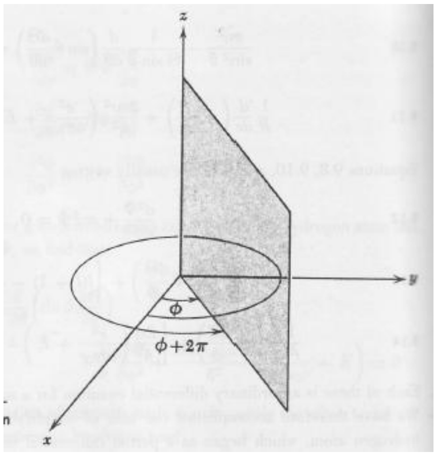
$$\begin{cases} \dfrac{\partial^2\Phi}{\partial\phi^2} = -m_l^2\Phi \\ sin\theta\dfrac{\partial}{\partial\theta}\left(sin\theta\dfrac{\partial\Theta}{\partial\theta}\right) + [l(l+1)sin^2\theta - m_l^2]\Theta = 0 \\ \dfrac{\partial}{\partial r}\left(r^2\dfrac{\partial R}{\partial r}\right) + \dfrac{2mr^2}{\hbar^2}\,\big(E-U(r)\big)R\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

Azimuthal Equation

$$\frac{\partial^2\Phi}{\partial\phi^2} = -m_l^2\Phi$$

Solution: $\Phi(\phi) = A\,e^{im_l\phi}$
Boundary condition: Since $\phi\ and\ \phi + 2\pi$ represent the same meridian plane. Therefore,

$$\Phi(\phi) = \ \Phi(\phi + 2\pi)$$



$$A\,e^{im_l\phi} = A\,e^{im_l(\phi+2\pi)} = Ae^{im_l\phi}e^{i2\pi m_l}$$

$$e^{i2\pi m_l} = 1 = cos2\pi m_l + i\,sin2\pi m_l$$

$$m_l = 0, \pm 1, \pm 2, \pm 3, etc.$$

→ Magnetic quantum number of the hydrogen atom

Polar Equation

$$sin\theta\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial\Theta}{\partial\theta}\right) + [l(l+1)sin^2\theta - m_l^2]\Theta = 0$$

Solutions are called the associated Legendre Functions
The solutions exist only when the constant *l* is an integer equal to or greater than $|m_l|$.

That is, any given *l*, $m_l = 0, \pm 1, \pm 2, \dots \pm l$

- *l* is called "orbital quantum number"

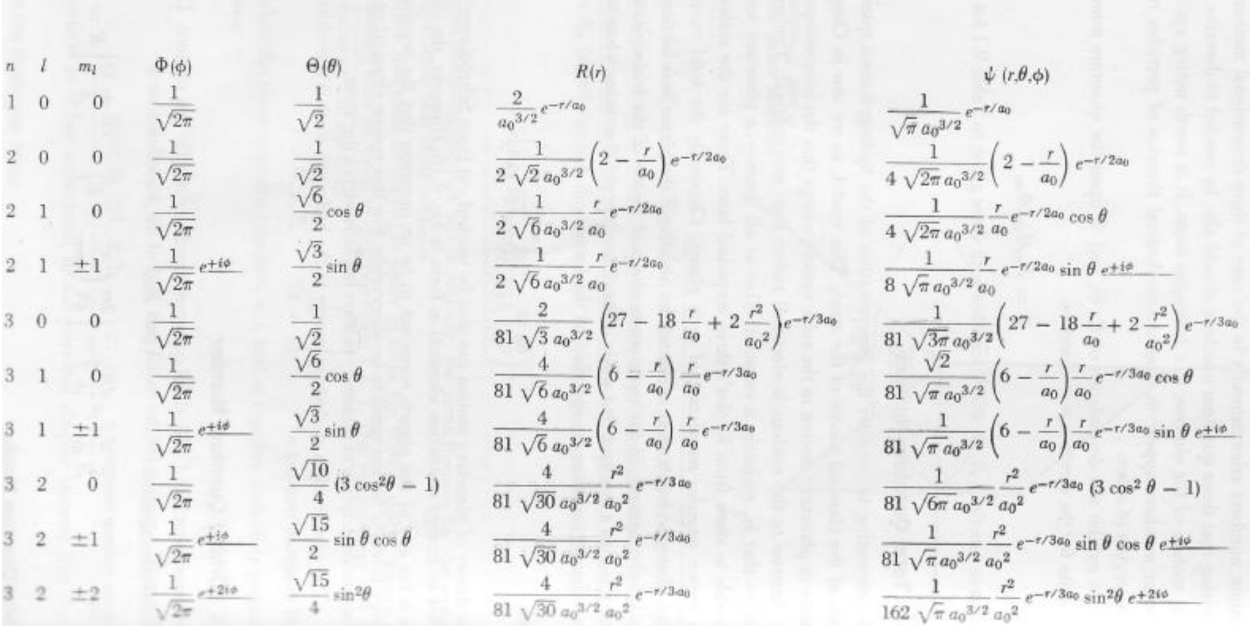
Radial Equation
Solutions are called the associated Laguerre functions

- Solutions can be solved only when E is positive or has one of the following energy values

$E_n = -\frac{me^4}{32\pi\varepsilon_0^2\hbar^2}(\frac{1}{n^2})$ where *n* is an integer

→n is called the principal quantum number
This is the same as Bohr's energy levels for the hydrogen atom.

- Another condition that should be obeyed is n should be equal to or greater than *l* + 1.
  l = 0, 1, 2, …(*n*-1)



n	l	m_l	$\Phi(\phi)$	$\Theta(\theta)$	$R(r)$	$\psi(r,\theta,\phi)$
1	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{a_0^{3/2}} e^{-r/a_0}$	$\frac{1}{\sqrt{\pi}\, a_0^{3/2}} e^{-r/a_0}$
2	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{2\sqrt{2}\, a_0^{3/2}}\left(2-\frac{r}{a_0}\right) e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi}\, a_0^{3/2}}\left(2-\frac{r}{a_0}\right) e^{-r/2a_0}$
2	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2}\cos\theta$	$\frac{1}{2\sqrt{6}\, a_0^{3/2}}\frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi}\, a_0^{3/2}}\frac{r}{a_0} e^{-r/2a_0}\cos\theta$
2	1	±1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{3}}{2}\sin\theta$	$\frac{1}{2\sqrt{6}\, a_0^{3/2}}\frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{8\sqrt{\pi}\, a_0^{3/2}}\frac{r}{a_0} e^{-r/2a_0}\sin\theta\, e^{\pm i\phi}$
3	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{81\sqrt{3}\, a_0^{3/2}}\left(27-18\frac{r}{a_0}+2\frac{r^2}{a_0^2}\right) e^{-r/3a_0}$	$\frac{1}{81\sqrt{3\pi}\, a_0^{3/2}}\left(27-18\frac{r}{a_0}+2\frac{r^2}{a_0^2}\right) e^{-r/3a_0}$
3	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2}\cos\theta$	$\frac{4}{81\sqrt{6}\, a_0^{3/2}}\left(6-\frac{r}{a_0}\right)\frac{r}{a_0} e^{-r/3a_0}$	$\frac{\sqrt{2}}{81\sqrt{\pi}\, a_0^{3/2}}\left(6-\frac{r}{a_0}\right)\frac{r}{a_0} e^{-r/3a_0}\cos\theta$
3	1	±1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{3}}{2}\sin\theta$	$\frac{4}{81\sqrt{6}\, a_0^{3/2}}\left(6-\frac{r}{a_0}\right)\frac{r}{a_0} e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi}\, a_0^{3/2}}\left(6-\frac{r}{a_0}\right)\frac{r}{a_0} e^{-r/3a_0}\sin\theta\, e^{\pm i\phi}$
3	2	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{10}}{4}(3\cos^2\theta-1)$	$\frac{4}{81\sqrt{30}\, a_0^{3/2}}\frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{81\sqrt{6\pi}\, a_0^{3/2}}\frac{r^2}{a_0^2} e^{-r/3a_0}(3\cos^2\theta-1)$
3	2	±1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{15}}{2}\sin\theta\cos\theta$	$\frac{4}{81\sqrt{30}\, a_0^{3/2}}\frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi}\, a_0^{3/2}}\frac{r^2}{a_0^2} e^{-r/3a_0}\sin\theta\cos\theta\, e^{\pm i\phi}$
3	2	±2	$\frac{1}{\sqrt{2\pi}} e^{\pm 2i\phi}$	$\frac{\sqrt{15}}{4}\sin^2\theta$	$\frac{4}{81\sqrt{30}\, a_0^{3/2}}\frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{162\sqrt{\pi}\, a_0^{3/2}}\frac{r^2}{a_0^2} e^{-r/3a_0}\sin^2\theta\, e^{\pm 2i\phi}$

Three Quantum Numbers that describe the Hydrogen Atom:

- Principal quantum number, $n = 1, 2, 3, \ldots$
- Orbital quantum number, $l = 0, 1, 2, \ldots (n-1)$ where l =1*(s)*, =2*(p)*, =3*(d)*, =4*(f)*, *etc.*
- Magnetic quantum number, $m_l = 0, \pm1, \pm2, \ldots \pm l$

Wave function = $\psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi) = R_{n,l}\Theta_{l,m_l}\Phi_{m_l}$

where $\Theta_{l,m_l}\Phi_{m_l} = \mathbf{Y}_l^{m_l}$ (Spherical harmonics)

Symbolic designation of atomic states in hydrogen

	s *l = 0*	*p* *l =1*	*d* *l =2*	*f* *l =3*	*g* *l = 4*	*h* *l =5*
n = 1	*1s*					
n = 2	*2s*	*2p*				
n = 3	*3s*	*3p*	*3d*			
n = 4	*4s*	*4p*	*4d*	*4f*		
n = 5	*5s*	*5p*	*5d*	*5f*	*5g*	
n = 6	*6s*	*6p*	*6d*	*6f*	*6g*	*6h*

Degeneracies in the Hydrogen Atom

According to the rules related to the three quantum numbers above, the following states (wave functions) are possible in each energy level:

n	l	m_l	E_n(eV)	$\lvert L\rvert$	L_z	ψ_{n,l,m_l} =	$R_{n,l}\mathbf{Y}_l^{m_l}$	degeneracies	Orbital name
1	0	0	-13.6	0	0	ψ_{100}	$R_{10}\mathbf{Y}_0^0$	Non-degenerate	1s
2	0	0	-3.40	0	0	ψ_{200}	$R_{20}\mathbf{Y}_0^0$	4 (=2^2)	2s
	1	-1		$\sqrt{2}\hbar$	$-\hbar$	ψ_{21-1}	$R_{21}\mathbf{Y}_1^{-1}$		2p
		0			0	ψ_{210}	$R_{21}\mathbf{Y}_1^0$		
		1			$+\hbar$	ψ_{211}	$R_{21}\mathbf{Y}_1^{+1}$		
3	0	0	-1.51	0	0	ψ_{300}	$R_{30}\mathbf{Y}_0^0$	9 (=3^2)	3s
	1	-1		$\sqrt{2}\hbar$	$-\hbar$	ψ_{31-1}	$R_{31}\mathbf{Y}_1^{-1}$		3p
		0			0	ψ_{310}	$R_{31}\mathbf{Y}_1^0$		
		1			$+\hbar$	ψ_{311}	$R_{31}\mathbf{Y}_1^1$		
	2	-2		$\sqrt{6}\hbar$	$-2\hbar$	ψ_{32-2}	$R_{32}\mathbf{Y}_2^{-2}$		3d
		--1			$-\hbar$	ψ_{32-1}	$R_{32}\mathbf{Y}_2^{-1}$		
		0			0	ψ_{320}	$R_{32}\mathbf{Y}_2^0$		
		1			$+\hbar$	ψ_{321}	$R_{32}\mathbf{Y}_2^1$		
		2			$+2\hbar$	ψ_{322}	$R_{32}\mathbf{Y}_2^2$		

Therefore, in the hydrogen atom, there are n^2degenerate wave functions associated with each E_n.