Chapter 4

Quantum Mechanics in Three Dimension

Wavefunction in 3-D

Given a potential in 3D form

$\boldsymbol{r} = (x, y, z)$ or (r, θ, ϕ)

we seek the total solution as a linear combination of the stationary states

to the 3D time-independent SE

Central potential

- We will consider only central potential in ZCT 205:

$$V(\boldsymbol{r}) = V(r)$$

- The value of potential at the 3D location $\boldsymbol{r} = r\,\hat{r}$ depends only on *r* but not on $\hat{r}$ (direction)
- In other words, V(*r*) is angular independent.
- It depends only on the radial distance *r* of the location ***r*** from the origin.

Spherical coordinates

- Due to the radial symmetry of the potential V(*r*), it would be most convenient to solve the SE in spherical coordinates:

$$\boldsymbol{r} = (r, \theta, \phi)$$

$$x = r\cos\theta\cos\phi$$

$$y = r\cos\theta\sin\phi$$

$$z = r\sin\theta$$

Spherical coordinates: radius r; polar angle θ, azimuthal angle ϕ

The Laplacian

← SE in 3D

- ∇^2, pronounced as “nabla-squared”, is known as Laplacian
- It is the 3D generalisation of the second-order partial derivative operator wrp to an independent coordinate.
- In Cartesian coordinates,

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

Laplacian in spherical coordinates

Do you know how this formula comes about? It can be derived from the transformation rules relating $\{x, y, z\}$ to $\{r, \theta, \phi\}$

Refer to Murray Spiegel, Vector analysis (Schaum's series) for the derivation.

Check these out if interested

Laplacian in Spherical Co-ordinates Derivation – YouTube, www.youtube.com/watch?v=5Uebg4AxkFo

http://planetmath.org/derivationofthelaplacianfromrecta

http://skisickness.com/2009/11/20/

http://www.gsjournal.net/old/physics/arife7.pdf

TISE in spherical coordinates

We are seeking the solution

Separation of variables method (1)

Separation of variables method (2)

only *r*-dependent

$= -$

only angular-dependent

Radial equation

We set the separation constant to be

The RHS becomes

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}(V(\mathbf{r}) - E) = \ell(\ell+1)$$

Angular equation

The LHS becomes

Solving the angular equation

$$Y = Y(\theta, \phi)$$

$$\sin\theta \frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial Y}{\partial\theta}\right) + \frac{\partial^2 Y}{\partial\phi^2} = -\ell(\ell+1)\sin^2\theta Y$$

Apply a separation of variable method to obtain the angular solution *Y*, where $Y = Y(\theta, \phi)$

Separation of angular variables

$$\sin\theta \frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial Y}{\partial\theta}\right) + \frac{\partial^2 Y}{\partial\phi^2} = -\ell(\ell+1)\sin^2\theta Y$$

$$Y(\theta,\phi) = \Theta(\theta)\Phi(\phi)$$

$$\left\{\frac{1}{\Theta}\left[\sin\theta \frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right)\right] + \ell(\ell+1)\sin^2\theta\right\} = -\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}$$

Show this

θ and ϕ equations

We set the separable constant as m^2

$$\frac{1}{\Theta}\left[\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)\right]+\ell(\ell+1)\sin^2\theta=m^2$$

$$(\theta \text{ equation })$$

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}=-m^2 \qquad (\phi \text{ equation })$$

Solution to ϕ equation

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -m^2$$

$$\Phi(\phi) = e^{im\phi}$$

m is known as **magnetic quantum number**

m covers both positive and negative values

Boundary condition on the ϕ solution

$$\Phi(\phi) = e^{im\phi}$$

$$\Phi(\phi + n2\pi) = \Phi(\phi)$$ *n* any integer

$$\exp(2\pi i m) = 1$$

m must be an integer

$$m = 0, \pm 1, \pm 2, \cdots$$

Solution to θ equation

$$\frac{1}{\Theta}\left[\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)\right]+\ell(\ell+1)\sin^2=m^2$$

The solution is non-trivial

$$\Theta(\theta)=AP_\ell^m(\cos\theta),$$ *A* normalisation constant

$$P_\ell^m(x)=(1-x^2)^{|m|/2}\left(\frac{d}{dx}\right)^{|m|}P_\ell(x),$$ x = cos θ

associated Legendre function

Notice that $P_\ell^m(x)=P_\ell^{-m}(x)$

Solution to θ equation (cont.)

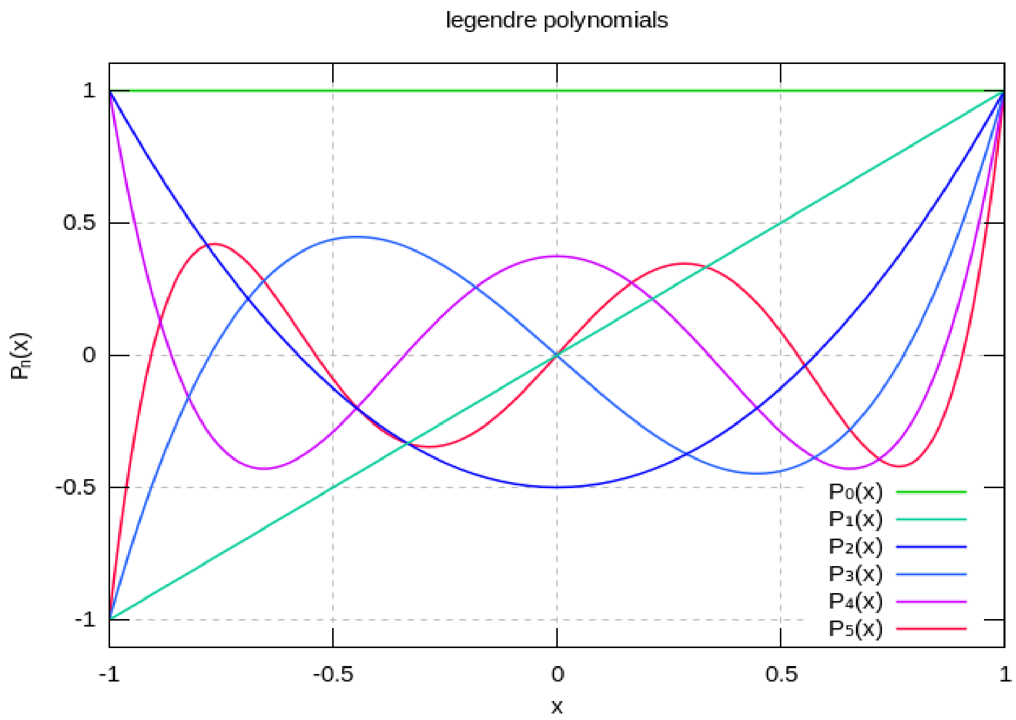
$$P_\ell^m(x) = (1-x^2)^{|m|/2}\left(\frac{d}{dx}\right)^{|m|} P_\ell(x)$$

$P_\ell(x)$ is the ℓth **Legendre polynomial**

$$P_\ell(x) = \frac{1}{2^\ell \ell!}\left(\frac{d}{dx}\right)^\ell (x^2-1)^\ell.$$

Rodrigues formula:

The first few Legendre polynomials



n	$P_n(x)$
0	1
1	x
2	$\frac{1}{2}(3x^2-1)$
3	$\frac{1}{2}(5x^3-3x)$
4	$\frac{1}{8}(35x^4-30x^2+3)$
5	$\frac{1}{8}(63x^5-70x^3+15x)$
6	$\frac{1}{16}(231x^6-315x^4+105x^2-5)$
7	$\frac{1}{16}(429x^7-693x^5+315x^3-35x)$
8	$\frac{1}{128}(6435x^8-12012x^6+6930x^4-1260x^2+35)$
9	$\frac{1}{128}(12155x^9-25740x^7+18018x^5-4620x^3+315x)$
10	$\frac{1}{256}(46189x^{10}-109395x^8+90090x^6-30030x^4+3465x^2-63)$

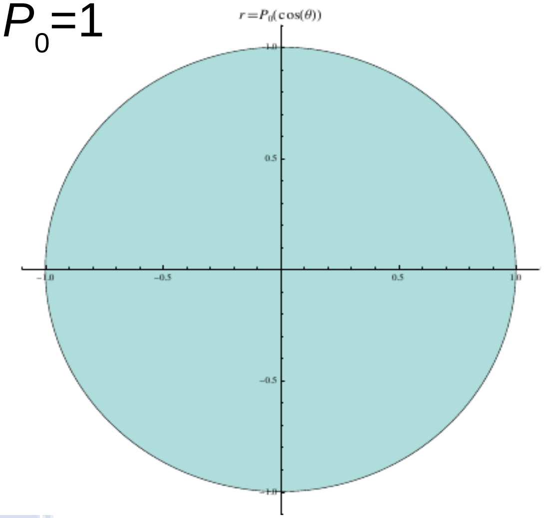
Polar plot of Legendre polynomial

http://demonstrations.wolfram.com/PolarPlotsOfLegendrePolynomials/

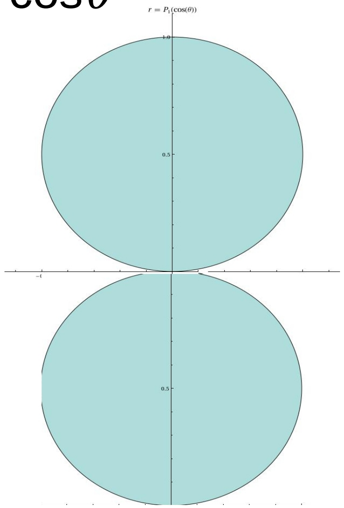
In these plots r (i.e., the length of a point on the plot from the origin) tells you the magnitude of the function in direction θ

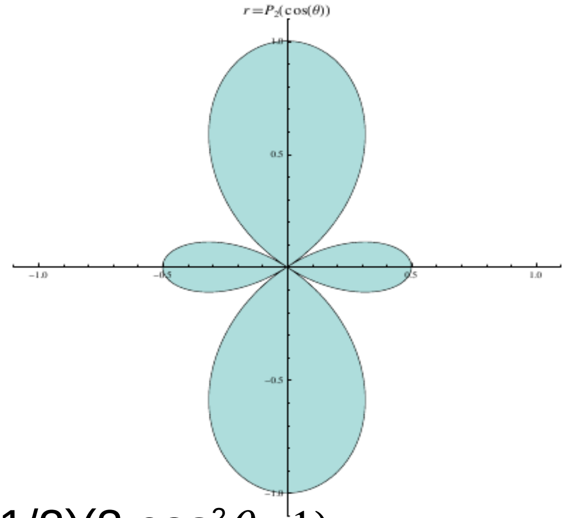
Note: set $x = \cos\theta$ as the argument in the expression of $P_\ell(x)$

$P_0=1$



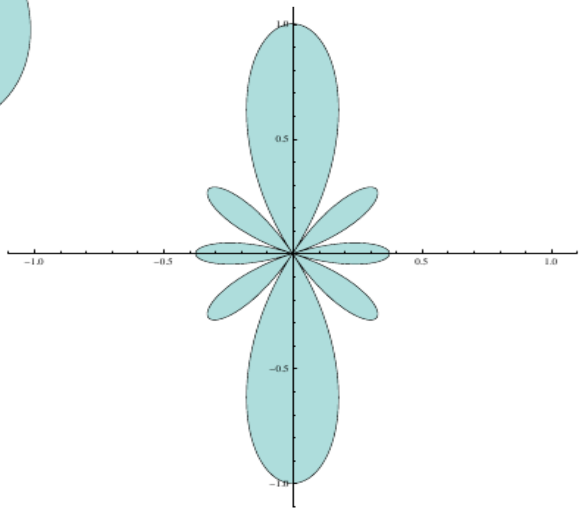
$P_1=\cos\theta$





$P_2=(1/2)(3\cos^2\theta-1)$

$P_4(\cos\theta)$



$P_4=(1/8)(35\cos^4\theta-30\cos^2\theta+3)$

PolarPlotsOfLegendrePolynomials.nb

$$P_\ell(x) = \frac{1}{2^\ell \ell!} \left(\frac{d}{dx}\right)^\ell (x^2 - 1)^\ell.$$

$P_l(x)$ is a polynomial (of degree l) in x, and is even or odd according to the parity of l

Associated Legendre polynomials

$P_0^0(x) = 1$

$P_1^{-1}(x) = -\frac{1}{2}P_1^1(x)$

$P_1^0(x) = x$

$P_1^1(x) = -(1-x^2)^{1/2}$

$P_2^{-2}(x) = \frac{1}{24}P_2^2(x)$

$P_2^{-1}(x) = -\frac{1}{6}P_2^1(x)$

$P_2^0(x) = \frac{1}{2}(3x^2-1)$

$P_2^1(x) = -3x(1-x^2)^{1/2}$

$P_2^2(x) = 3(1-x^2)$

$P_3^{-3}(x) = -\frac{1}{720}P_3^3(x)$

$P_3^{-2}(x) = \frac{1}{120}P_3^2(x)$

$P_3^{-1}(x) = -\frac{1}{12}P_3^1(x)$

$P_3^0(x) = \frac{1}{2}(5x^3-3x)$

$P_3^1(x) = -\frac{3}{2}(5x^2-1)(1-x^2)^{1/2}$

$P_3^2(x) = 15x(1-x^2)$

$P_3^3(x) = -15(1-x^2)^{3/2}$

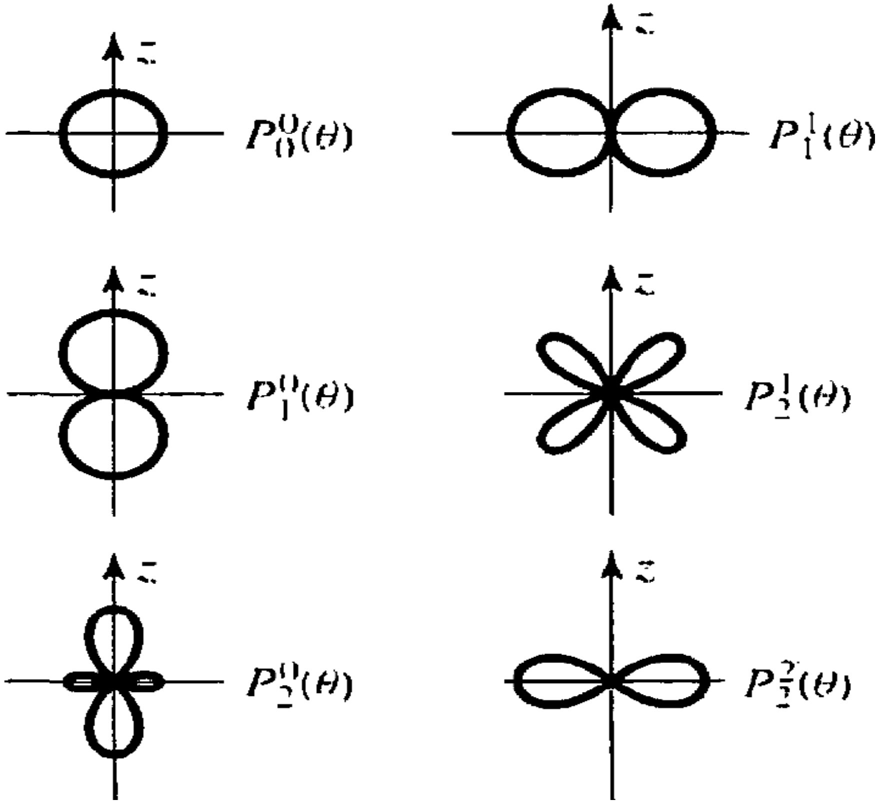
$$P_\ell^m(x) = (1-x^2)^{|m|/2}\left(\frac{d}{dx}\right)^{|m|}P_\ell(x)$$

$$P_\ell(x) = \frac{1}{2^\ell \ell!}\left(\frac{d}{dx}\right)^\ell (x^2-1)^\ell.$$

Some associated Legendre polynomials and polar plots

Note: set *x* = cos θ as the argument in the expression of $P_\ell^m(x)$

$P_0^0 = 1$	$P_2^0 = \frac{1}{2}(3\cos^2\theta - 1)$
$P_1^1 = \sin\theta$	$P_3^3 = 15\sin\theta(1-\cos^2\theta)$
$P_1^0 = \cos\theta$	$P_3^2 = 15\sin^2\theta\ \cos\theta$
$P_2^2 = 3\sin^2\theta$	$P_3^1 = \frac{3}{2}\sin\theta(5\cos^2\theta - 1)$
$P_2^1 = 3\sin\theta\ \cos\theta$	$P_3^0 = \frac{1}{2}(5\cos^3\theta - 3\cos\theta)$



$P_l^m(x)$ is not, in general, a polynomial

It is only if *m* is even

Allowed values of ℓ and m

- $$P_\ell(x) = \frac{1}{2^\ell \ell!}\left(\frac{d}{dx}\right)^\ell (x^2-1)^\ell.$$
- ℓ must be a non-negative integer

- $$P_\ell^m(x) = (1-x^2)^{|m|/2}\left(\frac{d}{dx}\right)^{|m|} P_\ell(x)$$

$(\frac{d}{dx})^{|m|} P_\ell(x)$ vanish if $|m| > \ell$

- $P_\ell^{|m|}(x)$ is non-zero only if
- $|m| \le \ell \Rightarrow m = 0, \pm 1, \pm 2, \cdots, \pm \ell$
- for a given ℓ (non-negative integer)

Notice that for a given ℓ, there are $2\ell + 1$ values of allowed m

Allowed values of ℓ and *m*

Notice that for a given ℓ, there are $2\ell + 1$ values of allowed m

$$P_\ell^m(x) = (1 - x^2)^{|m|/2} \left(\frac{d}{dx}\right)^{|m|} P_\ell(x)$$

$$l = 0,\ 1,\ 2, \ldots ;$$

$$m = -l,\ -l+1,\ \ldots,\ -1,\ 0,\ 1,\ \ldots,\ l-1,\ l.$$

-
- For example,
- $$P_2^3(x), P_0^1(x), P_1^{-2}(x), P_0^{-1}(x)$$
-

where $|m| > \ell$ are not allowed

Exercise

Derive the first 3 non-zero Legendre polynomial based on the Rodrigues formula.

$$P_\ell(x) = \frac{1}{2^\ell \ell!} \left(\frac{d}{dx} \right)^\ell (x^2 - 1)^\ell.$$

Exercise

Derive the associated Legendre function

$$P_2^0(x),\ P_2^1(x),\ P_2^2(x)$$

based on the $P_2(x)$ that your have derived in previous exercise.

Normalisation of $\Psi(\boldsymbol{r})$

Solution to the 3D TISE with a central potential

$$\psi(r,\theta,\phi)=R(r)\Phi(\phi)\Theta(\theta)=R(r)Y(\phi,\theta)$$

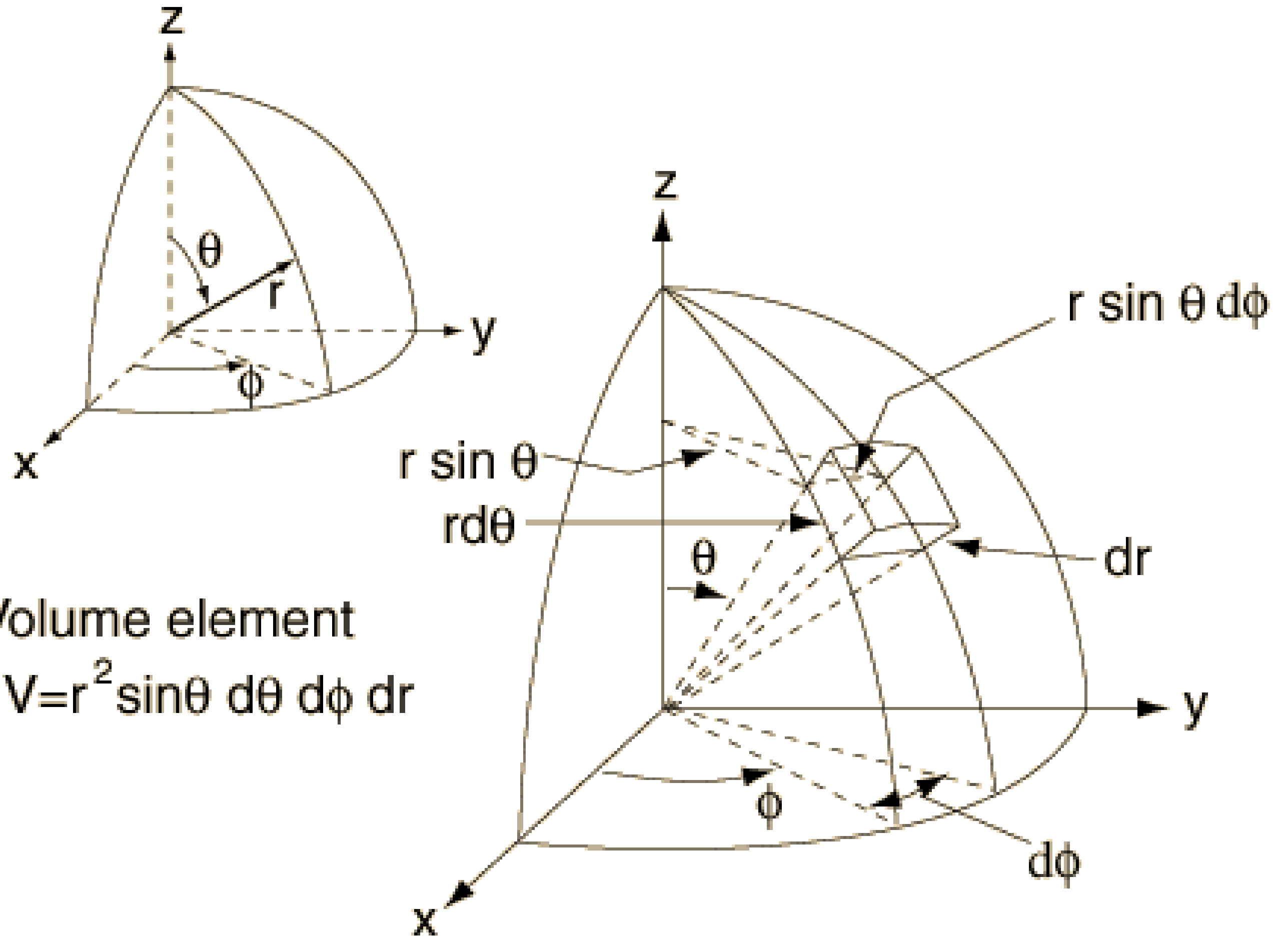
$$\begin{aligned} Y \equiv Y(\theta,\phi) &= \Phi(\phi)\cdot\Theta(\theta) \\ &\equiv \Phi(\phi)\cdot A P_\ell^m(\theta) \end{aligned}$$

$\Psi(\boldsymbol{r})$ has to be normalised:

$$\int_{all\;space} |\psi(r,\theta,\phi)|^2 dV = 1$$

Volume element in spherical coordinates

$$dV = d^3\mathbf{r} = r^2 \sin\theta dr d\theta d\phi$$



Volume element

$dV=r^2\sin\theta\, d\theta\, d\phi\, dr$

Normalisation of $\Psi(\boldsymbol{r})$ in spherical coordinates

$$dV = d^3\mathbf{r} = r^2 \sin\theta \, dr\, d\theta\, d\phi$$

$$\int_{all\,space} |\psi(r,\theta,\phi)|^2 dV =$$

$$= \int_{r=0}^{r\to\infty} \int_{\theta=0}^{\theta=\pi} \int_{\phi=0}^{\phi=2\pi} |\psi(r,\theta,\phi)|^2 r^2 \sin\theta \, dr\, d\theta\, d\phi =$$

$$\underbrace{\int_{r=0}^{r\to\infty} r^2 R(r)^2 dr}_{1} \cdot \underbrace{\int_{\phi=0}^{\phi=2\pi} \int_{\theta=0}^{\theta=\pi} |Y(\theta,\phi)|^2 \sin\theta \, d\theta\, d\phi}_{1} = 1$$

Normalisation of angular solution in spherical coordinates

$$\int_{\phi=0}^{\phi=2\pi} \int_{\theta=0}^{\theta=\pi} \left|Y(\theta,\phi)\right|^2 \sin\theta \, d\theta \, d\phi = 1$$

The normalised angular wavefunctions are called spherical harmonics:

$$Y(\theta,\phi) = A P_\ell^m(\cos\theta) e^{im\phi} \equiv Y_\ell^m(\theta,\phi)$$

$$= \epsilon \sqrt{\frac{(2\ell+1)(\ell-|m|)!}{4\pi(\ell+|m|)}} e^{im\phi} P_\ell^m(\cos\theta)$$

$$\epsilon = (-1)^m \text{ for } m \geq 0 \text{ and } \epsilon = 1 \text{ for } m \leq 0$$

The first few spherical harmonics $Y_\ell^m(\theta, \phi)$

$l = 0,\ 1,\ 2, \ldots;$

$m = -l,\ -l+1,\ \ldots,\ -1,\ 0,\ 1,\ \ldots,\ l-1,\ l.$

$$Y_0^0 = \left(\frac{1}{4\pi}\right)^{1/2}$$

$$Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$$

$$Y_1^{\pm 1} = \mp\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{\pm i\phi}$$

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

$$Y_2^{\pm 1} = \mp\left(\frac{15}{8\pi}\right)^{1/2} \sin\theta\cos\theta e^{\pm i\phi}$$

$$Y_2^{\pm 2} = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta e^{\pm 2i\phi}$$

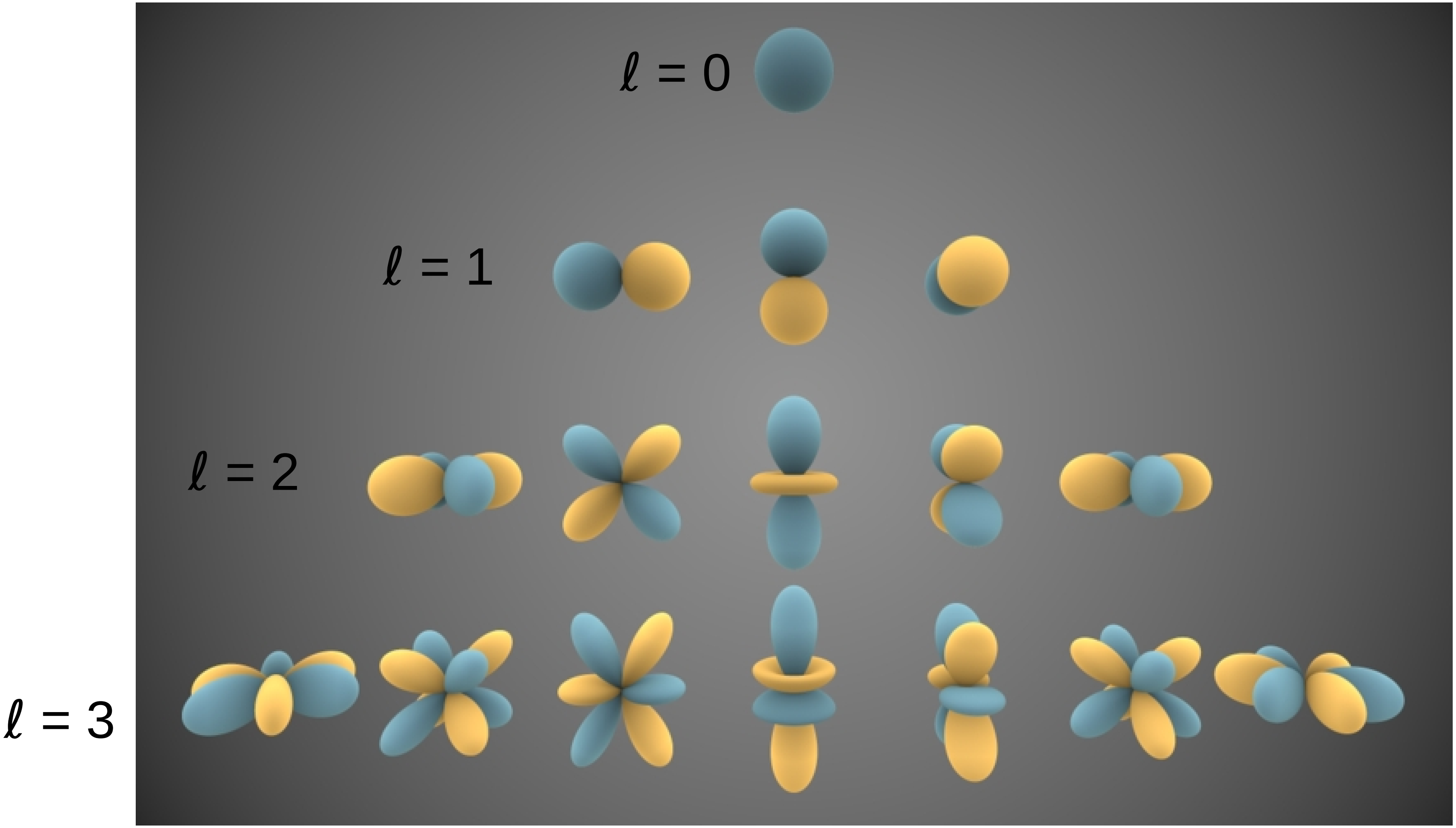
$$Y_3^0 = \left(\frac{7}{16\pi}\right)^{1/2} (5\cos^3\theta - 3\cos\theta)$$

$$Y_3^{\pm 1} = \mp\left(\frac{21}{64\pi}\right)^{1/2} \sin\theta\,(5\cos^2\theta - 1)e^{\pm i\phi}$$

$$Y_3^{\pm 2} = \left(\frac{105}{32\pi}\right)^{1/2} \sin^2\theta\cos\theta e^{\pm 2i\phi}$$

$$Y_3^{\pm 3} = \mp\left(\frac{35}{64\pi}\right)^{1/2} \sin^3\theta e^{\pm 3i\phi}$$

Visualisaion of SH



Visual representations of the first few spherical harmonics. Blue portions represent regions where the function is positive, and yellow portions where the it is negative.

http://en.wikipedia.org/wiki/Spherical_harmonics

Orthonormality of spherical harmonics

The spherical harmonics are automatically orthogonal

$$\int_0^{2\pi} \left\{ \int_0^{\pi} [Y_\ell^m(\theta,\phi)]^* \left[Y_{\ell'}^{m'}(\theta,\phi) \right] \sin\theta d\theta \right\} d\phi = \delta_{\ell\ell',mm'}$$

Show that the spherical harmonics

$$Y_0^0,\ Y_2^1$$

are normalised and orthogonal.

Radial equation

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}(V(\mathbf{r}) - E) = \ell(\ell+1)$$

Let $R = u(r)/r$

$$\frac{dR}{dr} = \frac{r\frac{du}{dr} - u}{r^2} \rightarrow r^2\frac{dR}{dr} = r\frac{du}{dr} - u$$

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) = r\frac{d^2u}{dr^2} + \cancel{\frac{du}{dr}} - \cancel{\frac{du}{dr}} = r\frac{d^2u}{dr^2}$$

Radial equation in terms of *u*(*r*)

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}(V(\mathbf{r}) - E) = \ell(\ell+1)$$

In terms of $u(r) \equiv r\,R(r)$

$$r\frac{d^2u}{dr^2} - \frac{2mr^2}{\hbar^2}[V(r) - E]\frac{u}{r} = \ell(\ell+1)\frac{u}{r}$$

rearrange

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[V(r) + \frac{\hbar^2}{2mr^2}\ell(\ell+1)\right]u = Eu$$

Effective potential

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2}+\left[V(r)+\frac{\hbar^2}{2mr^2}\ell(\ell+1)\right]u=Eu$$

$$V_{eff}=V(r)+\frac{\hbar^2}{2mr^2}\ell(\ell+1)$$

ℓ-dependent centrifugal term

Given $V_{eff}(r)$, find the solutions $u(r)$ which has a ℓ-dependence.

Normalisation of the radial solution

$$\int_0^\infty R^2 r^2 dr = \int_0^\infty u(r)^2 dr = 1$$

Infinite spherical potential well

$$V(\mathbf{r}) = \begin{cases} 0, & \text{if } r \leq a \\ \infty, & \text{if } r > a \end{cases}$$

Analogy: a spherical hollow hole in a large solid of ice.

What is its wavefunction and the allowed energy?

$$\Psi(\mathbf{r}, t) = R(r) Y_\ell^m(\theta, \phi) e^{-iEt/\hbar}$$

R(*r*) is different for a different *V*(*r*)

The angular solutions are the same even for different *V*(*r*)

TISE for infinite spherical potential well in terms of *u*(*r*)

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2}+\left[V(r)+\frac{\hbar^2}{2mr^2}\ell(\ell+1)\right]u=Eu$$

$$k \equiv \sqrt{\frac{2mE}{\hbar^2}}$$

$$V(\mathbf{r}) = \begin{cases} 0, & \text{if } r \leq a \\ \infty, & \text{if } r > a \end{cases}$$

$$\frac{d^2u}{dr^2}=\left[\frac{\ell(\ell+1)}{r^2}-k^2\right]u\,, \quad r \leq a$$

Solution to $\frac{d^2u}{dr^2} = \left[\frac{\ell(\ell+1)}{r^2} - k^2\right] u$

$$u(r) = Ar j_\ell(kr) + Br n_\ell(kr)$$

spherical Bessel function of order ℓ

spherical Neumann function of order ℓ

(Bessel functions of the second kind)

$$j_\ell(x) = (-x)^\ell \left(\frac{1}{x}\frac{d}{dx}\right)^\ell \frac{\sin x}{x},$$

$$n_\ell(x) = -(-x)^\ell \left(\frac{1}{x}\frac{d}{dx}\right)^\ell \frac{\cos x}{x}$$

The first few spherical Bessel and Neumann functions,

$$j_0 = \frac{\sin x}{x} \qquad n_0 = -\frac{\cos x}{x}$$

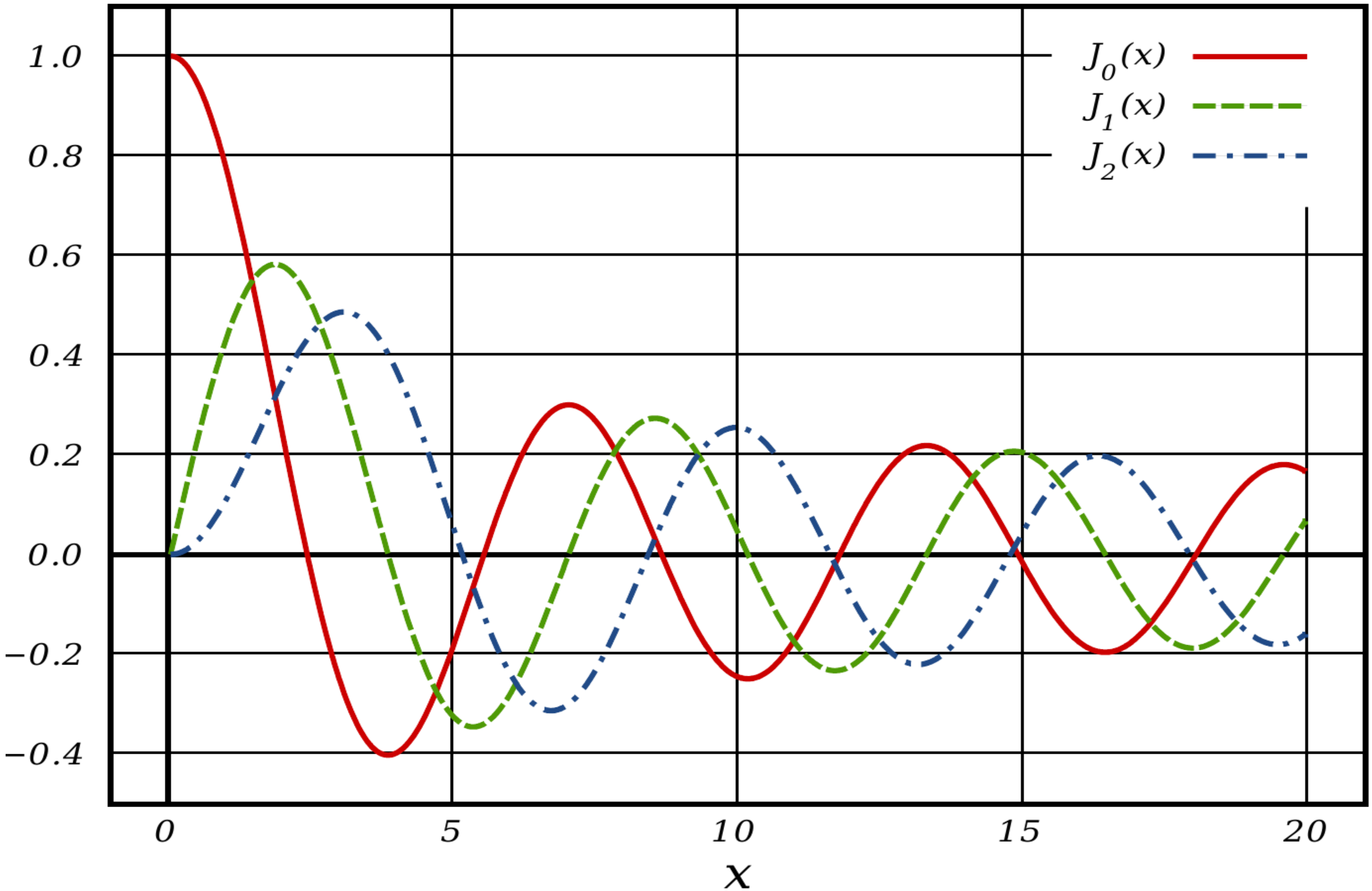
$$j_1 = \frac{\sin x}{x^2} - \frac{\cos x}{x} \qquad n_1 = -\frac{\cos x}{x^2} - \frac{\sin x}{x}$$

$$j_2 = \left(\frac{3}{x^3} - \frac{1}{x}\right)\sin x - \frac{3}{x^2}\cos x \qquad n_2 = -\left(\frac{3}{x^3} - \frac{1}{x}\right)\cos x - \frac{3}{x^2}\sin x$$

$$j_l \to \frac{2^l l!}{(2l+1)!}x^l, \qquad n_l \to -\frac{(2l)!}{2^l l!}\frac{1}{x^{l+1}}, \quad \text{for } x \ll 1.$$

ℓ must be a non-zero integer, $\ell = 0, 1, 2, \cdots$.

The graphs of the first three Bessel function



Exercise

Derive $n_0(x)$, $n_1(x)$, $j_0(x)$, $j_1(x)$.

Do you think the Neumann function a physically acceptable solution?

Explain.

Boundary conditions on the radial solution

$$u(r) = A\,r\,j_l(kr) + B\,r\,n_l(kr)$$

1. $R\ (r \to 0)$ must be finite.
2. $R\ (r = a) = 0$ (wavefunction must vanish at the boundary of the infinite well)

First BC on the radial solution

1. R ($r \rightarrow 0$) must be finite.

$$u(r) = Arj_\ell(kr) + \cancel{Brn_\ell(kr)}$$

The BC leads to the dropping of the Neumann function from the solution.

Hence, $B = 0$

$$R(r) = \frac{u(r)}{r} = A\, j_l(kr)$$

Second BC on the radial solution

2. R (r = a) = 0 (wavefunction must vanish at the boundary of the infinite well)

$$R(r) = A\, j_l(kr)$$

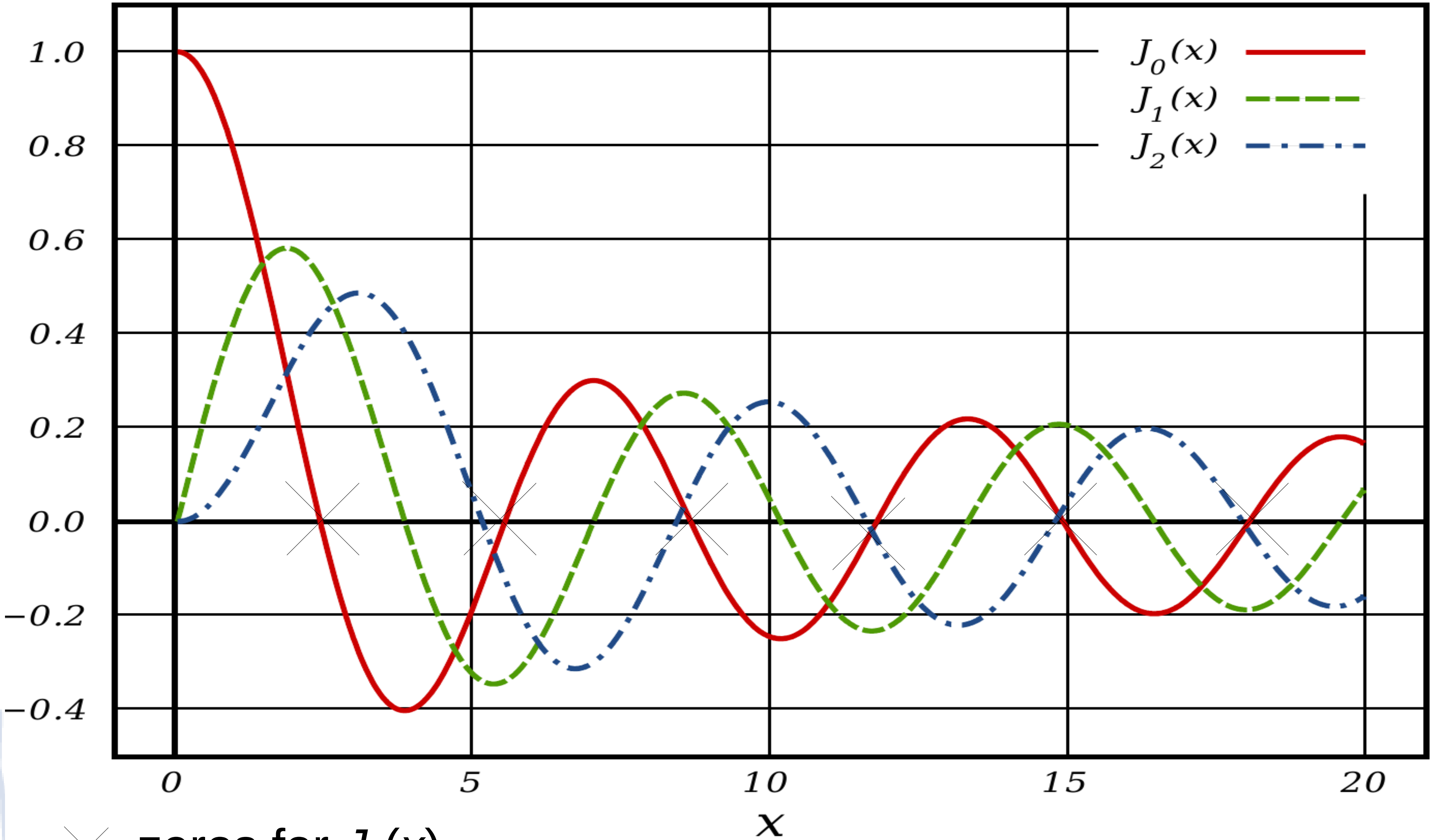
↓

$$R(r=a) = A\, j_l(ka) = 0$$

ka is a zero of the ℓth-order spherical Bessel function

they have to be solved numerically

Examples of zeros in the spherical Bessel functions

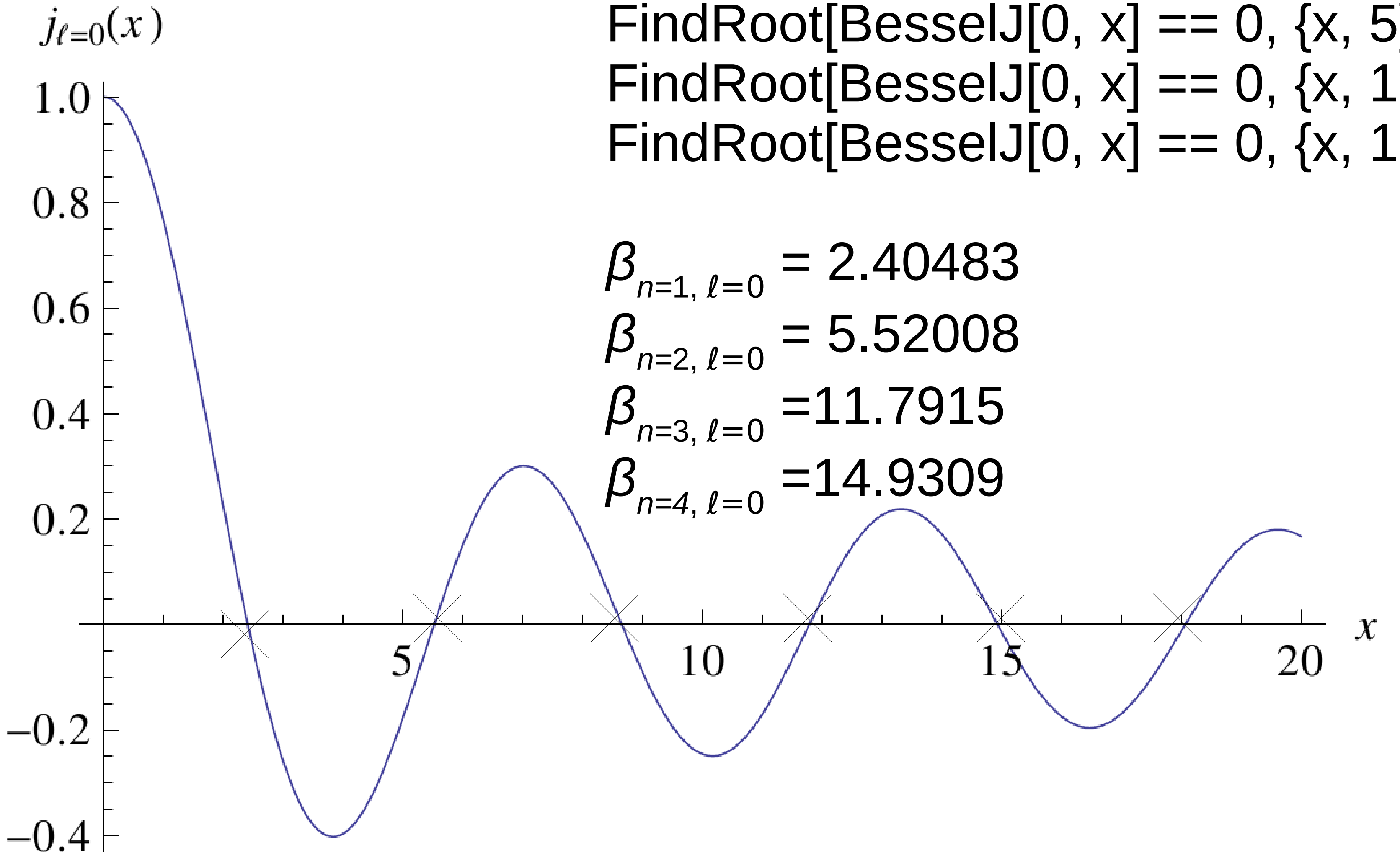


zeros for $J_0(x)$

Zeros

- The zeros in the spherical Bessel functions of order ℓ occurs at discrete points along the x-axis.
- For a fixed ℓ, the zeros are labeled $\beta_{n\ell}$, n=1,2,3,...
- These zeros are to be found numerically.
- The Mathematica code shows you how to solve for these zeros numerically
- BesselFunctionoftheFirstKind.nb

Numerical results of the zeros $\beta_{n,\ell=0}$




```
FindRoot[BesselJ[0, x] == 0, {x, 2}]
FindRoot[BesselJ[0, x] == 0, {x, 5}]
FindRoot[BesselJ[0, x] == 0, {x, 12}]
FindRoot[BesselJ[0, x] == 0, {x, 15}]
```

$\beta_{n=1,\,\ell=0} = 2.40483$

$\beta_{n=2,\,\ell=0} = 5.52008$

$\beta_{n=3,\,\ell=0} = 11.7915$

$\beta_{n=4,\,\ell=0} = 14.9309$

Quantisation of energy

Hence we arrive at the quantisation of energy

$$ka = \beta_{n\,\ell}$$

$n = 1, 2, 3, \ldots;\ \ell = 0, 1, 2, 3, \ldots$

$\beta_{n\,\ell}$ is the n-th zero of the ℓ spherical Bessel function.

$$k^2 a^2 = (\beta_{n\,\ell})^2$$

$$[(2mE)/\hbar^2]\, a^2 = (\beta_{n\,\ell})^2$$

$$E \equiv E_{n\,\ell} = (\beta_{n\,\ell})^2 \hbar^2/(2ma)$$

The stationary solution

$$\psi(\mathbf{r}) = \psi_{nlm}(r,\theta,\phi)$$
$$= A\, j_l(k r) Y_l^m(\theta,\phi)$$
$$= A\, j_l\left(\frac{r\beta_{nl}}{a}\right) Y_l^m(\theta,\phi);$$
$$k \equiv k_{nl} = \frac{\beta_{nl}}{a}$$

- Each stationary solution is specified by a set of three quantum number, $\{n, \ell, m\}$.

- Each stationary solution $\psi_{n,\ell,m}$ with a set of distinct quantum number $\{n, \ell, m\}$ is referred to as a

'state'.

Example

What is the solutions and allowed energies for $\ell = 0$?

- Solutions:
- For $\ell = 0$ the allowed values for n is $n = 1, 2, \cdots$; and the allowed value for m is $m=0$.
- The solutions are $\psi_{n,\ell=0,\, m=0}$, $n = 1, 2, 3, \cdots$

Allowed energies are

$$E_{n\,\ell} = (\beta_{n\,\ell})^2\hbar^2/(2ma),\ n = 1, 2, 3, \cdots$$

$$E_{n=1,\,\ell=0} = (\beta_{n=1,\,\ell=0})^2\hbar^2/(2ma)=2.40483\hbar^2/(2ma)$$

$$E_{n=2,\,\ell=0} = (\beta_{n=2,\,\ell=0})^2\hbar^2/(2ma)=5.52008\hbar^2/(2ma)$$

$$E_{n=3,\,\ell=0} = (\beta_{n=3,\,\ell=0})^2\hbar^2/(2ma)=11.7915\hbar^2/(2ma),$$

...

$E_{n\ell}$ is $2\ell+1$ degenerate

$$E_{n\ell} = (\beta_{n\,\ell})^2\hbar^2/(2ma)$$

- For a given set of $\{n,\ell\}$, the energy is given by $E_{n\ell}$.
- The energy is dependent on both discrete number n and ℓ but not on m.
- Each energy level $E_{n\ell}$ is $(2\ell + 1)$-fold degenerate, since there are $(2\ell + 1)$ different values of m for each value of ℓ.
- In other words, there are $2\ell+1$ stationary states that carry the same energy $E_{n\ell}$.

Example of energy degeneracy

The 3 states, each with a common ℓ=1 and n=1,

$$\psi_{1,1,-1},\ \psi_{1,1,0},\ \psi_{1,1,1}$$

bears the same energy

$$E_{n=1,\ \ell=1}=(\beta_{11})^2\hbar^2/(2ma)$$

In this example, ℓ=1, the the number of degeneracy is $2\ell+1=3$.

Normalisation of the radial function

$$\int_0^\infty A_{n\ell}^2 j_\ell(\frac{r\beta_{n\ell}}{a})^2 r^2 dr = 1$$

The normalisation $A_{n\ell}$ are complicated to derive.

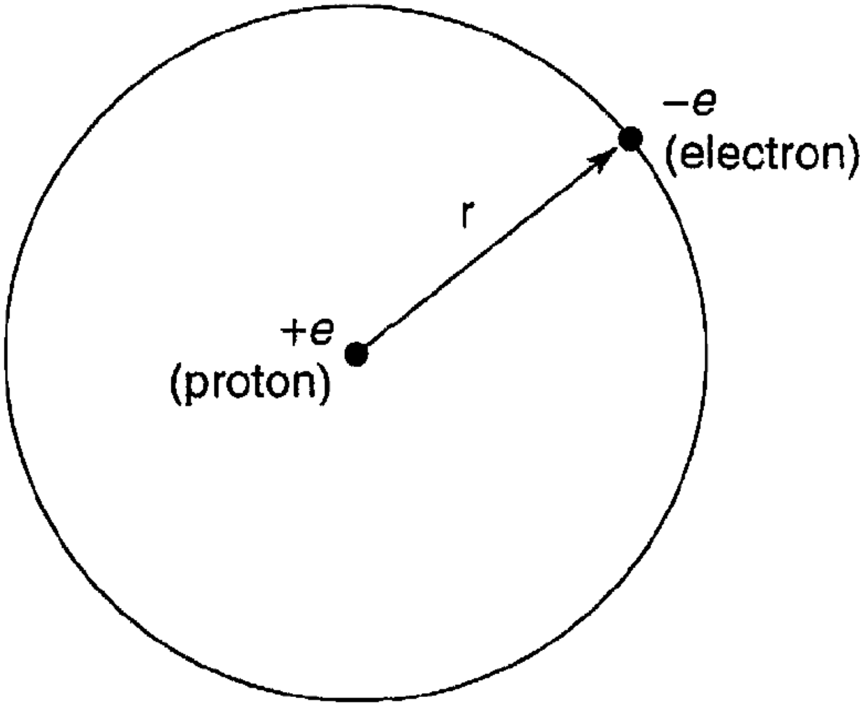
$A_{n\ell}$ are n, ℓ dependent

Hydrogen atom

$$V(\mathbf{r}) = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}$$

$M_{\text{proton}} \gg m_e$ so that the nucleus is "integrated out" from the picture

Note: $V(r) < 0$, bound state



TISE for hydrogen atom in terms of *u*(*r*)

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2}+\left[V(r)+\frac{\hbar^2}{2mr^2}\ell(\ell+1)\right]u=Eu$$

$$\downarrow \quad V(\mathbf{r}) = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}$$

$$-\frac{\hbar}{2m}\frac{d^2u}{dr^2}+\left[-\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}+\frac{\hbar}{2mr^2\ell(\ell+1)}\right]u=Eu$$

Solving the radial equation (1)

$$-\frac{\hbar}{2m}\frac{d^2u}{dr^2} + \left[-\frac{e^2}{4\pi\epsilon_0}\frac{1}{r} + \frac{\hbar}{2mr^2\ell(\ell+1)}\right]u = Eu$$

$$\kappa = \frac{\sqrt{-2mE}}{\hbar}$$

$$\frac{1}{\kappa^2}\frac{d^2u}{dr^2} = \left[1 - \frac{me^2}{2\pi\epsilon_0\hbar^2\kappa}\frac{1}{\kappa r} + \frac{\ell(\ell+1)}{(\kappa r)^2}\right]u$$

$$\rho \equiv \kappa r \quad \rho_0 \equiv \frac{me^2}{2\pi\epsilon_0\hbar^2\kappa}$$

Show this $$\frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{\ell(\ell+1)}{\rho^2}\right]u$$

Solving the radial equation (2)

$$\frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{\ell(\ell+1)}{\rho^2}\right] u$$

$$\kappa = \frac{\sqrt{-2mE}}{\hbar}$$

$$\rho_0 \equiv \frac{me^2}{2\pi\epsilon_0\hbar^2\kappa}$$

$$\rho \equiv \kappa r$$

Solution in the limit $\rho \longrightarrow \infty$:

$$\frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{\ell(\ell+1)}{\rho^2}\right] u$$

$\rho \longrightarrow \infty$:

$$\frac{d^2u}{d\rho^2} = u$$

$$u(\rho) = Ae^{-\rho} + Be^{\rho}$$

Drop e^{ρ} term so that $u(\rho)$ is finite in the limit $\rho \rightarrow \infty$

$$u(\rho) \sim Ae^{-\rho} \text{ when } \rho \longrightarrow \infty$$

Solution in the limit $\rho \to 0$

$$\frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{\ell(\ell+1)}{\rho^2}\right] u$$

$\rho \to 0$

$$\frac{d^2u}{d\rho^2} = \frac{\ell(\ell+1)}{\rho^2} u$$

$$u(\rho) = C\rho^{\ell+1} + D\rho^{-\ell}$$

Drop $\rho^{-\ell}$ term so that $u(\rho)$ is finite in the limit $\rho \to 0$

$$u(\rho) \sim C\rho^{\ell+1} \text{ when } \rho \to 0.$$

Exercise

Check that

$$u(\rho) = C\rho^{\ell+1} + D\rho^{-\ell}$$

is indeed the solution to

$$\frac{d^2u}{d\rho^2} = \frac{\ell(\ell+1)}{\rho^2}u$$

Patching up the limiting solutions

$u(\rho) \sim C\rho^{\ell+1}$ when $\rho \to 0$

$u(\rho) \sim Ae^{-\rho}$ when $\rho \to \infty$

$$u(\rho) = \rho^{\ell+1} e^{-\rho} v(\rho)$$

for all ρ

$$\frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{\ell(\ell+1)}{\rho^2}\right] u$$

Casting the equation in terms of $\upsilon(\rho)$

$$\frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{\ell(\ell+1)}{\rho^2}\right] u$$

$$u(\rho) = \rho^{\ell+1} e^{-\rho} \upsilon(\rho)$$

Show this step

$$\rho \frac{d^2\upsilon}{d\rho^2} + 2(\ell + 1 - \rho)\frac{d\upsilon}{d\rho} + [\rho_0 - 2(\ell+1)]\, \upsilon = 0$$

Seeking the solution via power series method

$$\rho \frac{d^2 v}{d\rho^2} + 2(\ell + 1 - \rho)\frac{dv}{d\rho} + [\rho_0 - 2(\ell + 1)]\, v = 0$$

$$\frac{dv}{d\rho} = \sum_{j=0}^{\infty} j c_j \rho^{j-1} = \sum_{j=0}^{\infty} (j+1) c_{j+1} \rho^j$$

$$\frac{d^2 v}{d\rho^2} = \sum_{j=0}^{\infty} j(j+1) c_{j+1} \rho^{j-1}$$

$$v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j$$

$$\sum_{j=0}^{\infty} j(j+1) c_{j+1} \rho^j + 2(l+1) \sum_{j=0}^{\infty} (j+1) c_{j+1} \rho^j$$

$$-2 \sum_{j=0}^{\infty} j c_j \rho^j + [\rho_0 - 2(l+1)] \sum_{j=0}^{\infty} c_j \rho^j = 0.$$

Seeking the solution via power series method (cont.)

$$\sum_{j=0}^{\infty} j(j+1)c_{j+1}\rho^j + 2(l+1)\sum_{j=0}^{\infty}(j+1)c_{j+1}\rho^j$$
$$-2\sum_{j=0}^{\infty} jc_j\rho^j + [\rho_0 - 2(l+1)]\sum_{j=0}^{\infty} c_j\rho^j = 0.$$

Equating the coefficients of like powers yields the recurrent formula

$$j(j+1)c_{j+1} + 2(l+1)(j+1)c_{j+1} - 2jc_j + [\rho_0 - 2(l+1)]c_j = 0$$

Recurrent formula

$$c_{j+1} = \left\{ \frac{2(j+\ell+1) - \rho_0}{(j+1)(j+2\ell+2)} \right\} c_j$$

All c_j, $j > 1$, can be expressed in terms of the “seed” coefficient c_0, an overall constant which would be fixed by normalisation.

$$v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j$$

$$= c_0 + c_1 \rho + c_2 \rho^2 + c_3 \rho^3 + \ldots$$

Divergence of the series

BUT the series is divergent

$$v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j \qquad = c_0 + c_1\rho + c_2\rho^2 + c_3\rho^3 + \ldots \to \infty$$

where $$c_{j+1} = \left\{ \frac{2(j+\ell+1) - \rho_0}{(j+1)(j+2\ell+2)} \right\} c_j$$

For the proof, see the textbook.

The need for the existence of j_{max}

The infinite series

$$v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j$$

causes u (ρ) to diverge at large value of ρ (see text book for technical detail)

$$u(\rho) \sim c_0 \rho^{l+1} e^{\rho}$$

unless the summation is truncated beyond some integer j_{max}.

This is an "existence" requirement.

For the series to converge, there must exist an integer j_{max} such that $c_j = 0$ for all $j > j_{max}$

Truncating the series

In order to make $c_j = 0$ for all $j > j_{max}$, we look at the recurrence formula:

$$c_{j+1} = \left\{ \frac{2(j+\ell+1)-\rho_0}{(j+1)(j+2\ell+2)} \right\} c_j$$

One finds that if there exists an integer j_{max} such that

$$2(j_{\text{max}}+\ell+1) = \rho_0$$

then $c_j = 0$ for all $j > j_{max}$

Termination of the series for $j > j_{max}$

$$2(j_{\max} + \ell + 1) = \rho_0$$

All coefficients c_j with $j > j_{max}$ in the series vanishes

$$c_{j+1} = \left\{ \frac{2(j + \ell + 1) - \rho_0}{(j+1)(j + 2\ell + 2)} \right\} c_j$$

$$\Rightarrow c_{j_{max}+1} = \left\{ \frac{2\left(j_{max} + l + 1\right) - \rho_0}{\left(j_{max}+1\right)\left(j_{max} + 2l + 2\right)} c_{j_{max}} \right\} = 0$$

Convergence of the series

As a result of the existence of j_{max}, whe $2(j_{\max} + \ell + 1) = \rho_0$

the series is truncated up to the j_{max} terms

$$\sum_{j=0}^{j\to\infty} c_j \rho^j$$

$$= \sum_{j=0}^{j=j_{max}} c_j \rho^j$$

$$= c_0 + c_1\rho + c_2\rho^2 + c_3\rho^3 + \ldots + c_{j_{max}}\rho^{j_{max}}$$

An as a result, the function

$$u(\rho) = \rho^{\ell+1} e^{-\rho} v(\rho)$$

becomes finite for all values of ρ.

(The rigorous proof of the convergence of $u(\rho)$ for all values of ρ is not discussed here.)

j_{max}

The possible values of j_{max} are

$$j_{max} = 0, 1, 2, 3, \ldots$$

How to see this? From

$$\sum_{j=0}^{j=j_{max}} c_j \rho^j$$

$$= c_0 + c_1 \rho + c_2 \rho^2 + c_3 \rho^3 + \ldots + c_{j_{max}} \rho^{j_{max}}$$

The smallest possible value for j_{max} is 0. In this case, the series just "summed up" to a value of c_0

Principal quantum number *n*

We need a j_{max} to exist for the series to converge.

The particular values of j_{max} is to be specified by a pair of quantum numbers, namely, $\{n, \ell\}$

$$n \equiv j_{\max} + \ell + 1$$

The principal quantum number *n* is an independent, non-zero integer (because both j_{max} and ℓ are non-negative integers)

The possible values of *n*

The possible values of *n* are

$$n = 1, 2, 3, \ldots,$$

- The principle quantum number is more important than the other quantum numbers, ℓ,*m*, and has to be specified first.
- Once *n* is specified, the possible values of ℓ must be consistent with the definition
-
$$n \equiv j_{\max} + \ell + 1$$
-
-

The smallest value of ℓ is 0

What are the possible values for ℓ?

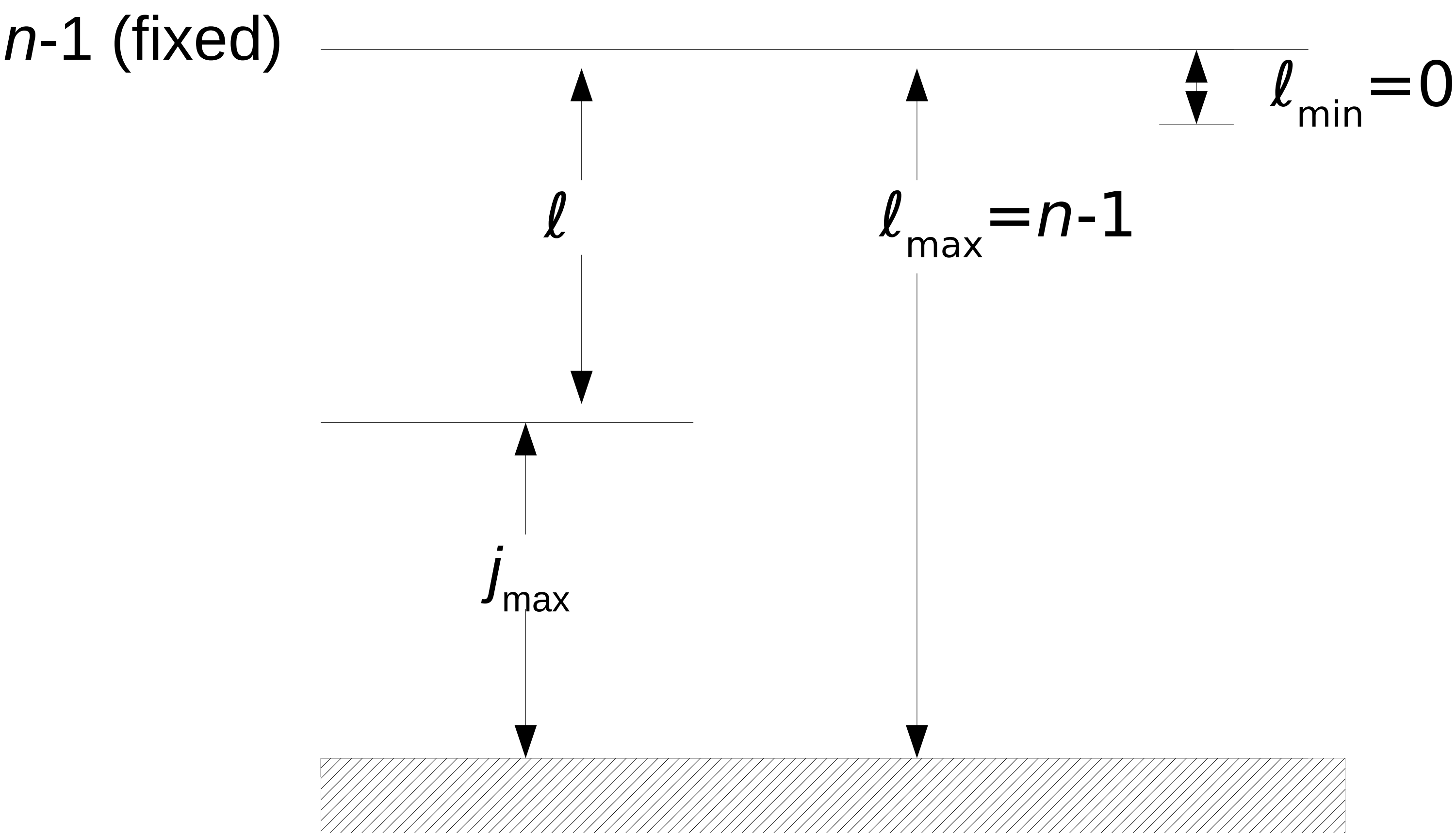
1. ℓ must be non-negative integers (as it specifies the "order" of a Legendre polynomial, as in P_ℓ)
2. The smallest value for ℓ is 0, independent of *n*.
3. But the maximal value of ℓ, ℓ_{max} is *n*-dependent. Once the value of *n* is fixed, what is the maximal value of ℓ, ℓ_{max}?

$$\ell = 0, 1, 2, ..., \ell_{max}$$

The largest possible value of ℓ

$$n \equiv j_{\mathrm{max}} + \ell + 1$$

j_{max} is not to be specified independently. It is to be specified in terms of ℓ and n.



Hence, the possible value of ℓ (for a fixed *n*)

The possible values of ℓ for a fixed *n* is

$$\ell = 0, 1, 2, \ldots, n-1$$

Count the number of ℓ states corresponds to a given *n* state:

There are *n* ℓ-state corresponds to fixed *n*

The possible value of j_{max}

j_{max} is a **dependent** variable of ℓ and n.

$j_{max} = j_{max}(\ell, n)$

$= n - \ell - 1$

For a fixed value of n, the value of j_{max} values depends on ℓ.

Since $\ell =$ 0, 1, 2, ... , n-1

$j_{max} = n-1, n-2, n-3, \ldots, 0$

Quantisation of energy

$$2(j_{\max} + \ell + 1) = \rho_0 \qquad n \equiv j_{\max} + \ell + 1$$

$$2n = \rho_0 \Rightarrow E = -\frac{\hbar^2\kappa^2}{2m} = -\frac{me^2}{8\pi^2\epsilon_0^2\hbar^2\rho_0^2}$$

$$\rho_0 \equiv \frac{me^2}{2\pi\epsilon_0\hbar^2\kappa} \qquad \kappa = \frac{\sqrt{-2mE}}{\hbar}$$

Bohr formula for quantised energies

The energy of a hydrogen eigenstate with *n*=1, irrespective of ℓ and m, is given by

$$E_n = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2} = \frac{E_1}{n^2},$$

Bohr formula.

E_1 (= -13.6 eV) is the ground state energy

Bohr radius

$$a = \frac{4\pi\epsilon_0\hbar^2}{me^2} = 0.529 \times 10^{-10} \text{ m}$$

In terms of Bohr radius, $\rho = \rho_n = \frac{r}{an}$

The eigenfunction in full expression

$$\psi_{n,\ell,m}(r,\theta,\phi) = R_{n\ell} Y_\ell^m(\theta,\phi),$$

$$R_{n\ell} = \frac{1}{r}\rho^{\ell+1} e^{-\rho} v(\rho)$$

$v(\rho)$ a polynomial of degree $j_{\max} = n - \ell - 1$ in ρ

whose coefficients are determined by the recursion formula

$$c_{j+1} = \left\{ \frac{2(j+\ell+1) - \rho_0}{(j+1)(j+2\ell+2)} \right\} c_j$$

Ground state

- GS corresponds to $n=1$.
- The largest allowed value of $\ell = n-1 = 0$
- The smallest value of $\ell = 0$.
- Hence, $\ell = 0$.
- The number of allowed values of m is $= 2\ell+1=1$, i.e., $m=0$.
- Hence, the set of quantum numbers characterising the GS is

$$\{n,\ell,m\}=\{1,0,0\}$$

Explicit expression for the GS eigenfunction

$$\psi_{100}(r,\theta,\phi) = R_{10}(r)Y_0^0(\theta,\phi)$$

$$R_{10}(r) = \frac{c_0}{a}e^{-r/a}, Y_0^0 = \frac{1}{\sqrt{4\pi}}$$

$$\int_{r=0}^{\infty} R_{10}^2 r^2 dr = 1 \Rightarrow c_0 = 2/\sqrt{a}$$

$$\psi_{100}(r,\theta,\phi) = \frac{1}{\sqrt{\pi a^3}}e^{-r/a}$$

$$E_{n=1} = -\frac{13.6\mathrm{eV}}{1^2} = 13.6\mathrm{eV}$$

First excited state

- It corresponds to n=2.
- The largest allowed value of $\ell = n$-1 = 1
- The smallest value of $\ell = 0$.
- Hence, the possible values for ℓ are $\{0,1\}$.
- The number of allowed values of m for $\ell=0$ is $2\ell+1=1$, i.e., $m=0$.
- The number of allowed values of m for $\ell=1$ is $2\ell+1=3$, i.e., $m=1,0,-1$.
- Hence, the set of quantum numbers characterising the first excited state is

$$\{n,\ell,m\}=\{\{2,1,1\},\{2,1,-1\},\{2,1,0\};\ \{2,0,0\}\}$$

Explicit expression for the first excited state eigenfunction

$$\rho_2 = \frac{r}{2a}$$

For $\ell = 1$ $\quad j_{max} + \ell = n - 1 = 1$

$$R_{21}(r) = \left(\frac{1}{r}{\rho_2}^2 e^{-\rho_2}\right) \sum_{j=0}^{j=j_{max}=0} c_j \rho_2^j$$

$$= \left(\frac{r}{4a^2} e^{\frac{-r}{2a}}\right)\left(c_0 \rho_2^0\right) = \frac{c_0}{4a^2} r e^{-\frac{r}{2a}}$$

Explicit expression for the first excited state eigenfunction

$$\text{For } \ell = 0 \ (j_{max} + \ell = n - 1 = 1 \Rightarrow j_{max} = 1)$$

$$R_{20}(r) = \left(\frac{1}{r}{\rho_2}^2 e^{-\rho_2}\right) \sum_{j=0}^{j=j_{max}=1} c_j \rho_2^j$$

$$= \left(\frac{r}{4a^2} e^{\frac{-r}{2a}}\right) (c_0 \rho_2^0 + c_1 \rho_2^1)$$

$$= \cdots = \frac{c_0}{2a}(1 - \frac{r}{2a})e^{-r/2a}$$

Show the last step

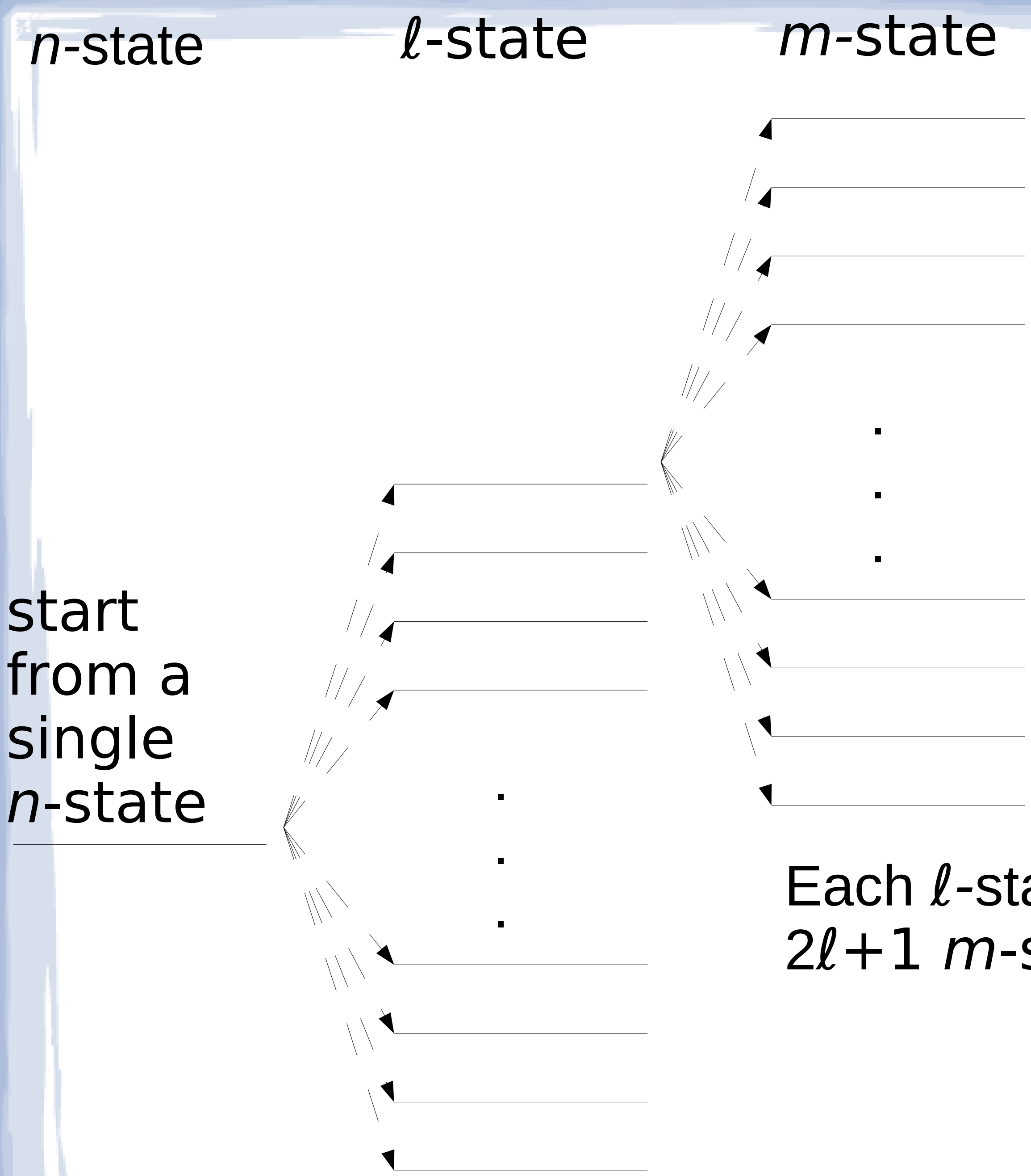
Counting the degeneracy of E_n

For a fixed *n*-state:

Sum over all allowed ℓ corresponds to the fixed *n*

$$\sum_{l=0}^{l=n-1} (2l+1) = n^2$$

the number of allowed *m* at a fixed ℓ



$$\sum_{l=0}^{l=n-1}(2l+1)=n^{2}$$

Each *ℓ*-state splits into 2*ℓ*+1 *m*-state

Each *n*-state splits into *n* *ℓ*-state

The number of degeneracy for n=2

- The number of degeneracy of $E_{n=2}$ hence is n^2=4
- 4 is the total number of states with principle quantum number n=2.
- Each of the $\{n,\ell,m\}=\{\{2,1,1\},\{2,1,-1\},\{2,1,0\};\ \{2,0,0\}\}$ states share the same energy, E_2.

Exercise

Count the total number of degenerate states corresponds to the quantum number n=3. List down all of these state, $\psi_{n,\,\ell,\,m}$, one by one

ANS:

There are n^2=9 states correspond to quantum number n=2.

ℓ=0,1,2.

For ℓ=0, m= 0

For ℓ=1, m=0,$\mp$1

For ℓ=2, m=0,$\mp$1,$\mp$2

The states correspond to n=3

$\Psi_{3,0,0}$,

$\Psi_{3,1,0}, \Psi_{3,1,-1}, \Psi_{3,1,1}$,

$\Psi_{3,2,0}, \Psi_{3,2,-2}, \Psi_{3,2,-1}, \Psi_{3,2,1}, \Psi_{3,2,2}$

All these 9 states share the same energy E_3 = $-13.6\text{eV}/3^2 = -1.511\text{eV}$

Associated Laguerre polynomial

The truncated series, $\upsilon(\rho)$, apart from the overall normalisation constant, is a special function known as associated Laguarre polynomial

$$\upsilon(\rho)=\sum_{j=0}^{j=j_{max}=n-l-1} c_j \rho^j$$

$$=c_0+c_1\rho+c_2\rho^2+c_3\rho^3+\ldots+c_{n-l-1}\rho^{n-l-1}$$

$$=c_0\left(1+\frac{c_1}{c_0}\rho+\frac{c_2}{c_0}\rho^2+\frac{c_3}{c_0}\rho^3+\ldots+\frac{c_{n-l-1}}{c_0}\rho^{n-l-1}\right)$$

$$=c_0\left(1+c_1'\rho+c_2'\rho^2+c_3'\rho^3+\ldots+c_{n-l-1}'\rho^{n-l-1}\right)$$

$$=c_0 L_{n-l-1}^{2l+1}(2\rho)$$

Associated Laguerre polynomial

$$L^q_{q-p}(x) \equiv (-1)^p \left(\frac{d}{dx}\right)^p L_q(x)$$

$$L_q(x) \equiv e^x \left(\frac{d}{dx}\right)^q (e^{-x} x^q)$$

the qth **Laguerre polynomial**

The first few associated Lagerrer polynomial

$$L_0^0 = 1$$

$$L_1^0 = -x + 1$$

$$L_2^0 = x^2 - 4x + 2$$

$$L_0^1 = 1$$

$$L_1^1 = -2x + 4$$

$$L_2^1 = 3x^2 - 18x + 18$$

$$L_0^2 = 2$$

$$L_1^2 = -6x + 18$$

$$L_2^2 = 12x^2 - 96x + 144$$

$$L_0^3 = 6$$

$$L_1^3 = -24x + 96$$

$$L_2^3 = 60x^2 - 600x + 1200$$

The first few Laguerre polynomial

$$L_0 = 1$$

$$L_1 = -x + 1$$

$$L_2 = x^2 - 4x + 2$$

$$L_3 = -x^3 + 9x^2 - 18x + 6$$

$$L_4 = x^4 - 16x^3 + 72x^2 - 96x + 24$$

$$L_5 = -x^5 + 25x^4 - 200x^3 + 600x^2 - 600x + 120$$

$$L_6 = x^6 - 36x^5 + 450x^4 - 2400x^3 + 5400x^2 - 4320x + 720$$

The normalised hydrogen eigenfunctions are

$$\psi_{n,\ell,m}(r,\theta,\phi) = R_{n\ell} Y_\ell^m(\theta,\phi),$$

$$R_{nl} = \frac{1}{r}\rho^{l+1} e^{-\rho} \cdot c_0 L_{n-l-1}^{2l+1}(2\rho); \rho = \frac{r}{na}$$

$$= \frac{1}{r}\left(\frac{r}{an}\right)^{l+1} e^{-\left(\frac{r}{na}\right)} \cdot c_0 L_{n-l-1}^{2l+1}\left(\frac{2r}{na}\right)$$

$$= \frac{c_0}{2^l an}\left(\frac{2r}{an}\right)^l e^{-\left(\frac{r}{na}\right)} L_{n-l-1}^{2l+1}\left(\frac{2r}{na}\right)$$

$$= A_{nl}\left(\frac{2r}{an}\right)^l e^{-\left(\frac{r}{na}\right)} L_{n-l-1}^{2l+1}\left(\frac{2r}{na}\right)$$

Orthogonality of the eigenfunctions

The wave functions are mutually orthogonal:

$$\int \psi^*_{n'\ell'm'} \psi_{n\ell m} r^2 \sin\theta \, dr \, d\phi = \delta_{nn'} \delta_{\ell\ell'} \delta_{mm'}$$

The normalisation constant $A_{n\ell}$

$$R_{nl} = A_{nl} \left(\frac{2r}{an}\right)^{l} e^{-\left(\frac{r}{na}\right)} L_{n-l-1}^{2l+1}\left(\frac{2r}{na}\right)$$

$$A_{nl} = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-\ell-1)!}{2n[(n+\ell)!]^3}}$$

$$R_{10} = 2a^{-3/2} \exp(-r/a)$$

$$R_{20} = \frac{1}{\sqrt{2}} a^{-3/2} \left(1 - \frac{1}{2}\frac{r}{a}\right) \exp(-r/2a)$$

$$R_{21} = \frac{1}{\sqrt{24}} a^{-3/2} \frac{r}{a} \exp(-r/2a)$$

$$R_{30} = \frac{2}{\sqrt{27}} a^{-3/2} \left(1 - \frac{2}{3}\frac{r}{a} + \frac{2}{27}\left(\frac{r}{a}\right)^2\right) \exp(-r/3a)$$

$$R_{31} = \frac{8}{27\sqrt{6}} a^{-3/2} \left(1 - \frac{1}{6}\frac{r}{a}\right)\left(\frac{r}{a}\right) \exp(-r/3a)$$

$$R_{32} = \frac{4}{81\sqrt{30}} a^{-3/2} \left(\frac{r}{a}\right)^2 \exp(-r/3a)$$

$$R_{40} = \frac{1}{4} a^{-3/2} \left(1 - \frac{3}{4}\frac{r}{a} + \frac{1}{8}\left(\frac{r}{a}\right)^2 - \frac{1}{192}\left(\frac{r}{a}\right)^3\right) \exp(-r/4a)$$

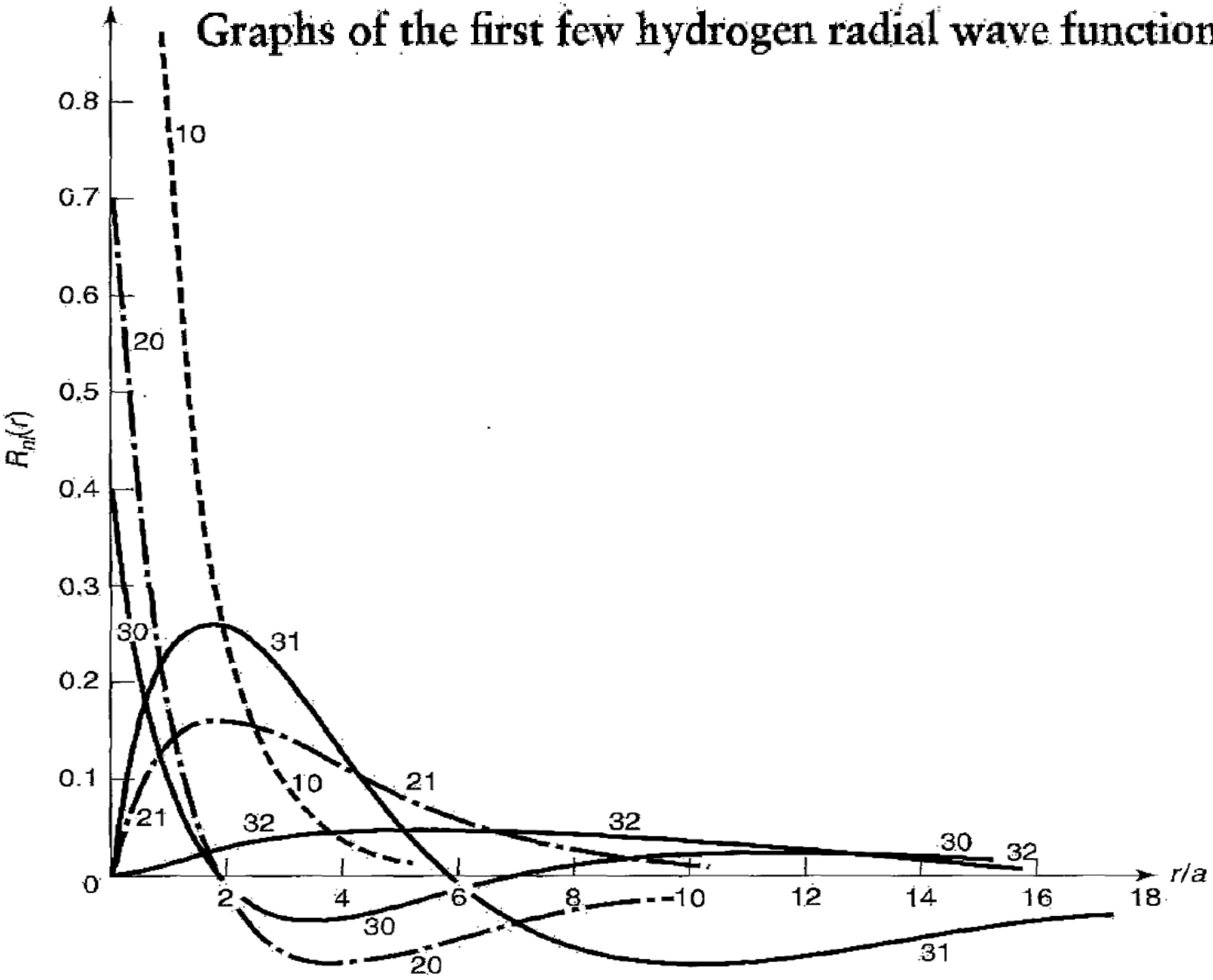
$$R_{41} = \frac{\sqrt{5}}{16\sqrt{3}} a^{-3/2} \left(1 - \frac{1}{4}\frac{r}{a} + \frac{1}{80}\left(\frac{r}{a}\right)^2\right) \frac{r}{a} \exp(-r/4a)$$

$$R_{42} = \frac{1}{64\sqrt{5}} a^{-3/2} \left(1 - \frac{1}{12}\frac{r}{a}\right)\left(\frac{r}{a}\right)^2 \exp(-r/4a)$$

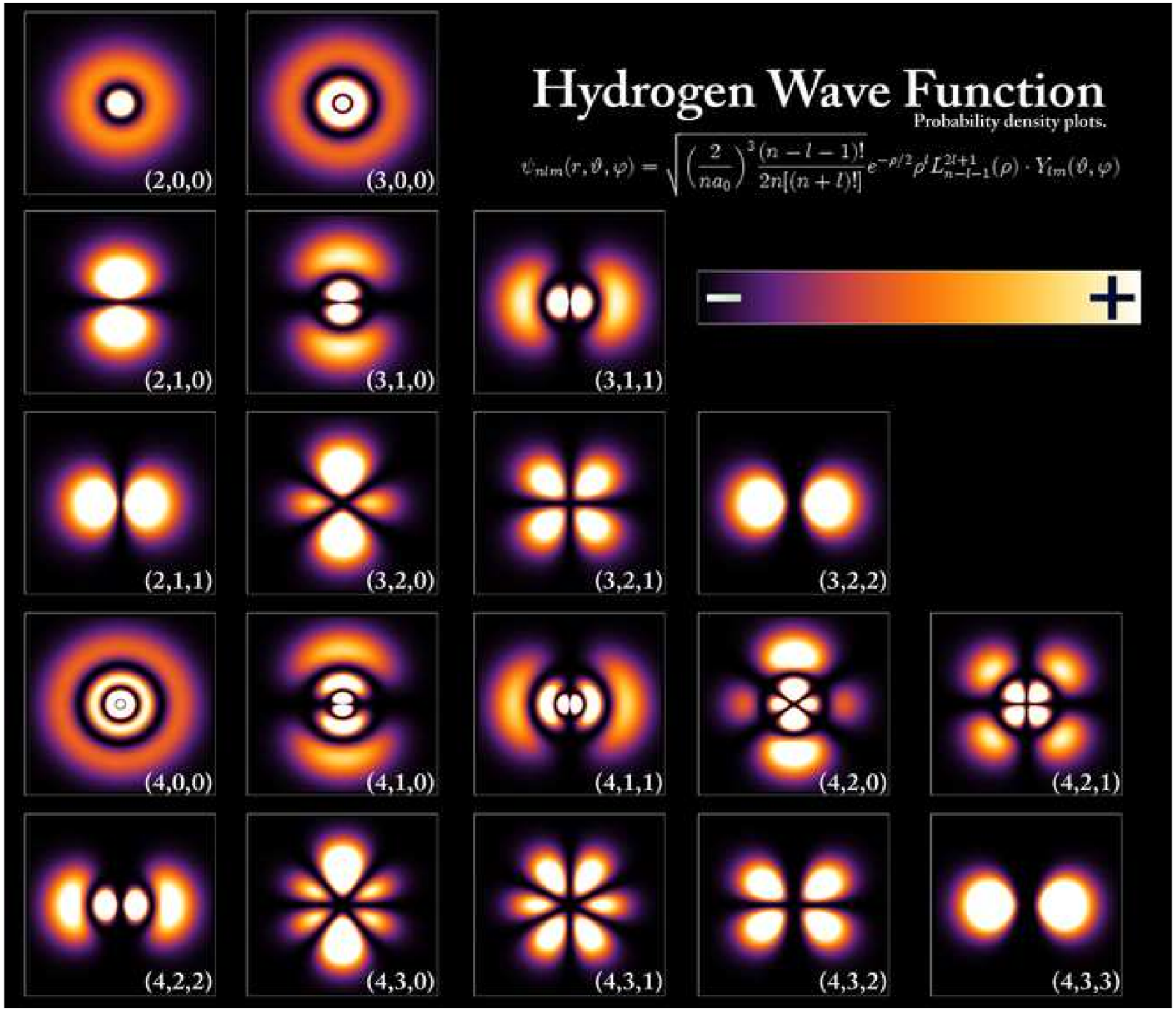
$$R_{43} = \frac{1}{768\sqrt{35}} a^{-3/2} \left(\frac{r}{a}\right)^3 \exp(-r/4a)$$

The first few normalised radial functions

Graphs of the first few hydrogen radial wave functions, $R_{nl}(r)$



Density plots of the 3D WF projected on the 2D cross-sectional area going through the origin



What is the most probably value of *r* in the ground state of the hydrogen?

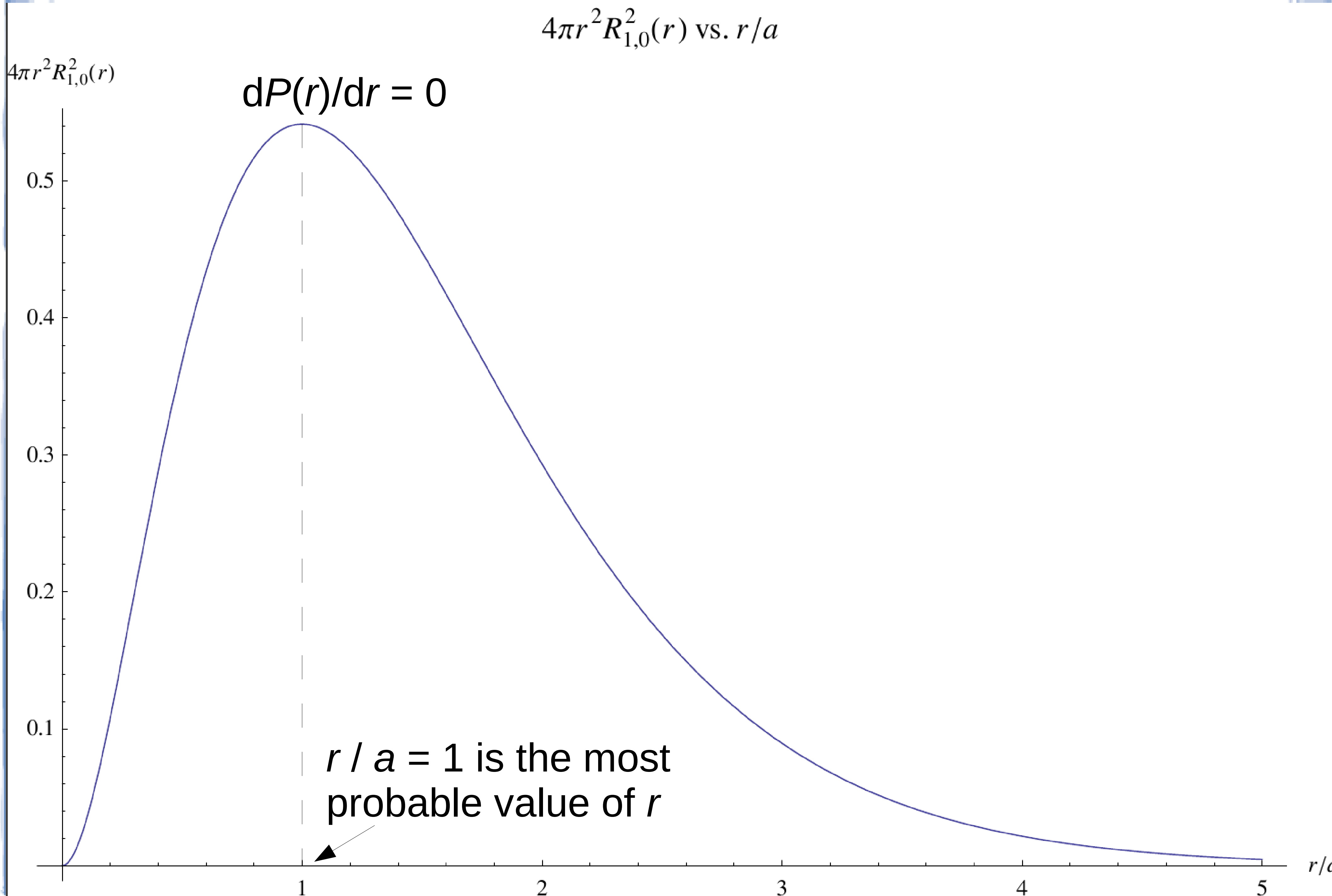
See solution in the main.pdf notes.

dP(r)/dr = 0, where P(r) the probability density for at location r.

$$P(r) = 4\pi r^2 R^2_{n,\ell}(r)$$

At the ground state, n=1, ℓ=0 $$R_{n=1,\ell=0} = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}$$

Setting dP(r)/dr = 0 leads to $r=r_{max}= a$



$4\pi r^2 R_{1,0}^2(r)$ vs. r/a
$4\pi r^2 R_{1,0}^2(r)$
$dP(r)/dr = 0$
0.5
0.4
0.3
0.2
0.1
1
2
3
4
5
r/a
$r / a = 1$ is the most probable value of r

Exercise

Find $\langle r \rangle$ and $\langle r^2 \rangle$ for an electron in the ground state of hydrogen atom.

$$\langle \hat{Q} \rangle = \int \int \int \psi^*_{n,\ell,m} \hat{Q} \psi_{n,\ell,m} r^2 dr \sin\theta d\theta d\phi$$

Here $\hat{Q} = r$ and $\hat{Q} = r^2$

$$\psi_{n,\ell,m} = \psi_{1,0,0} = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}$$

Solution (1)

$$\langle \hat{Q} \rangle = \int \int \int \psi^*_{n,\ell,m} \hat{Q} \psi_{n,\ell,m} r^2 dr \sin\theta d\theta d\phi.$$

For $\hat{Q} = r$

$$\langle \hat{r} \rangle = \int \int \int \frac{1}{\sqrt{\pi a^3}} e^{-r/a} r \frac{1}{\sqrt{\pi a^3}} e^{-r/a} r^2 dr \sin\theta d\theta d\phi$$

$$= 4\pi \frac{1}{\pi a^3} \int_0^\infty e^{-2r/a} r^3 dr = \frac{3a}{2}$$

Solution (2)

$$\langle \hat{Q} \rangle = \int \int \int \psi^*_{n,\ell,m} \hat{Q} \psi_{n,\ell,m} r^2 dr \sin\theta d\theta d\phi.$$

For $\hat{Q} = r^2$

$$\langle \hat{r}^2 \rangle = \int \int \int \frac{1}{\sqrt{\pi a^3}} e^{-r/a} r^2 \frac{1}{\sqrt{\pi a^3}} e^{-r/a} r^2 dr \sin\theta d\theta d\phi$$

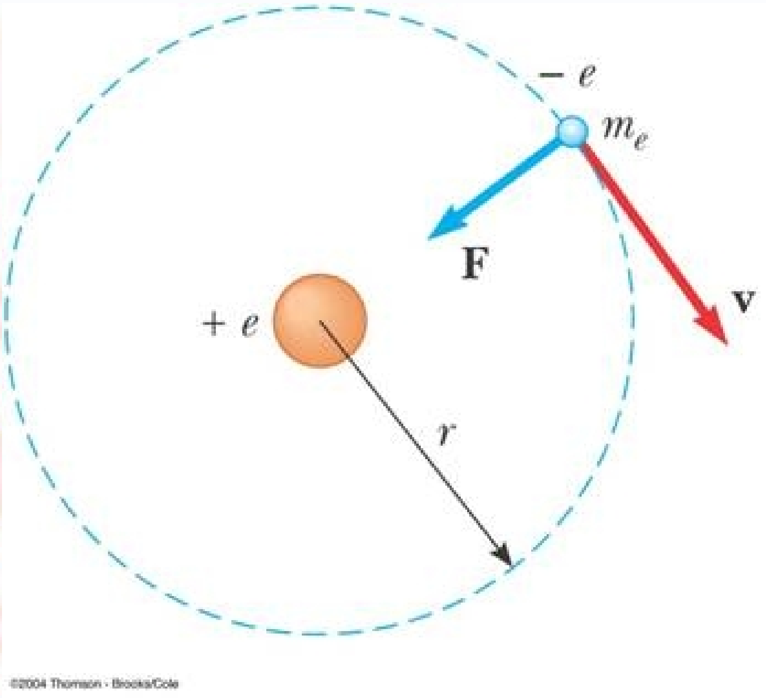
$$= 4\pi \frac{1}{\pi a^3} \int_0^\infty e^{-2r/a} r^4 dr = 3a^2$$

Bohr's hydrogen model (Remember ZCT 104?)

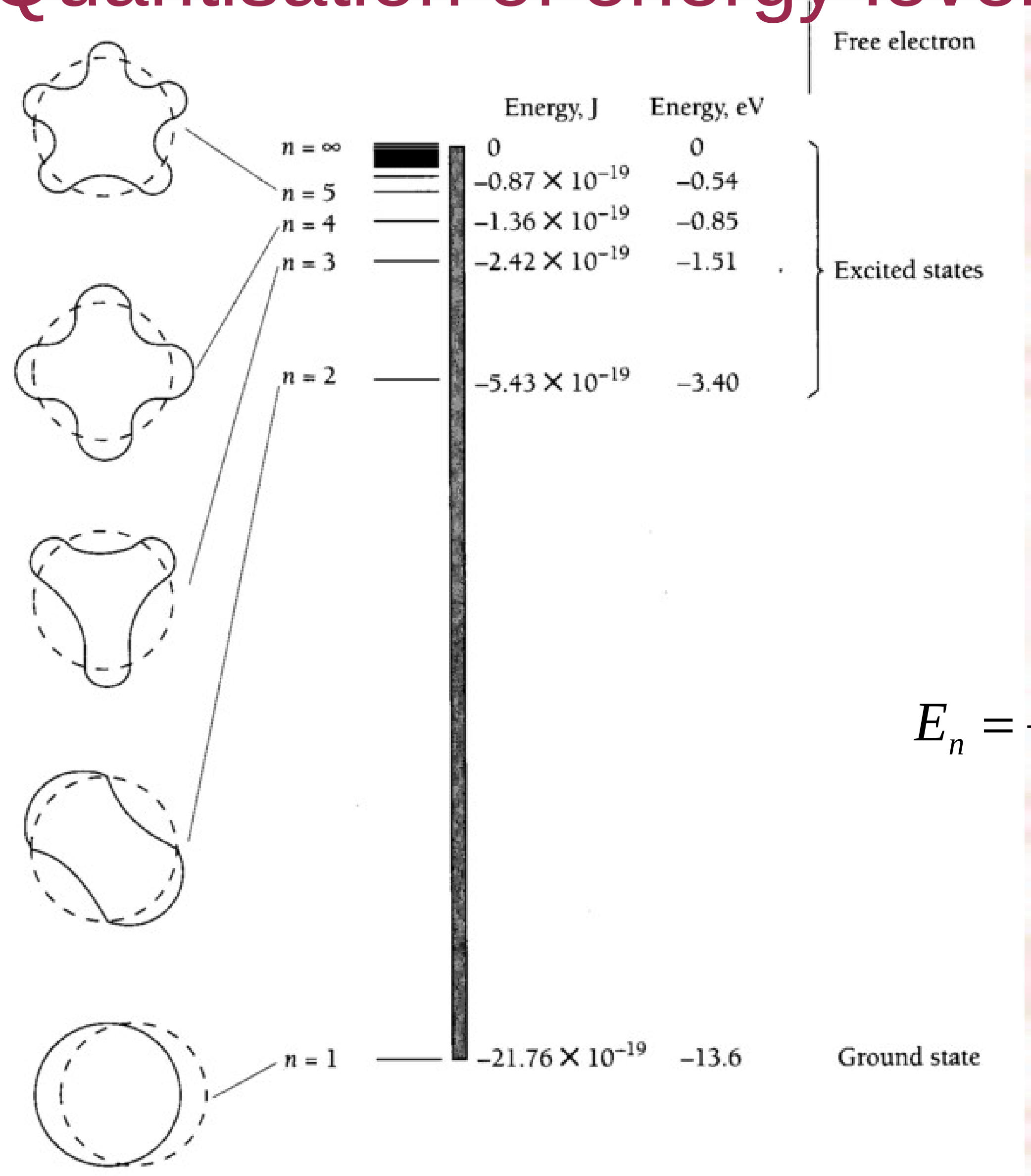
$$\frac{1}{4\pi\varepsilon_0}\frac{(Ze)e}{r^2} = \frac{m_e v^2}{r}$$

$$n\lambda_n = 2\pi\ r_n,\ n = 1,2,3...$$

$+Ze$



Quantisation of energy levels in Bohr's model



$$E_n = \frac{E_0}{n^2} = -\frac{13.6}{n^2}\,\text{eV}$$

Inter-state transition in Bohr's model

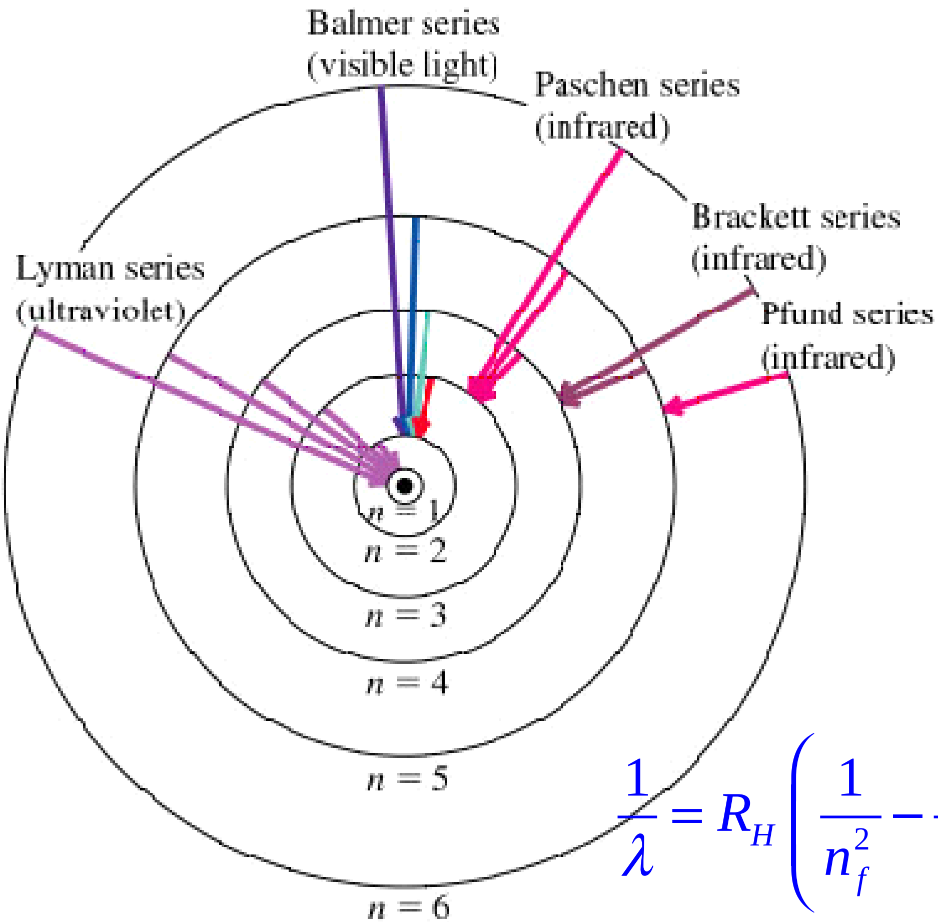
$$\Delta E = E_f - E_i = -13.6 \text{ eV} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

$$E_\gamma = h\nu = \frac{hc}{\lambda}$$

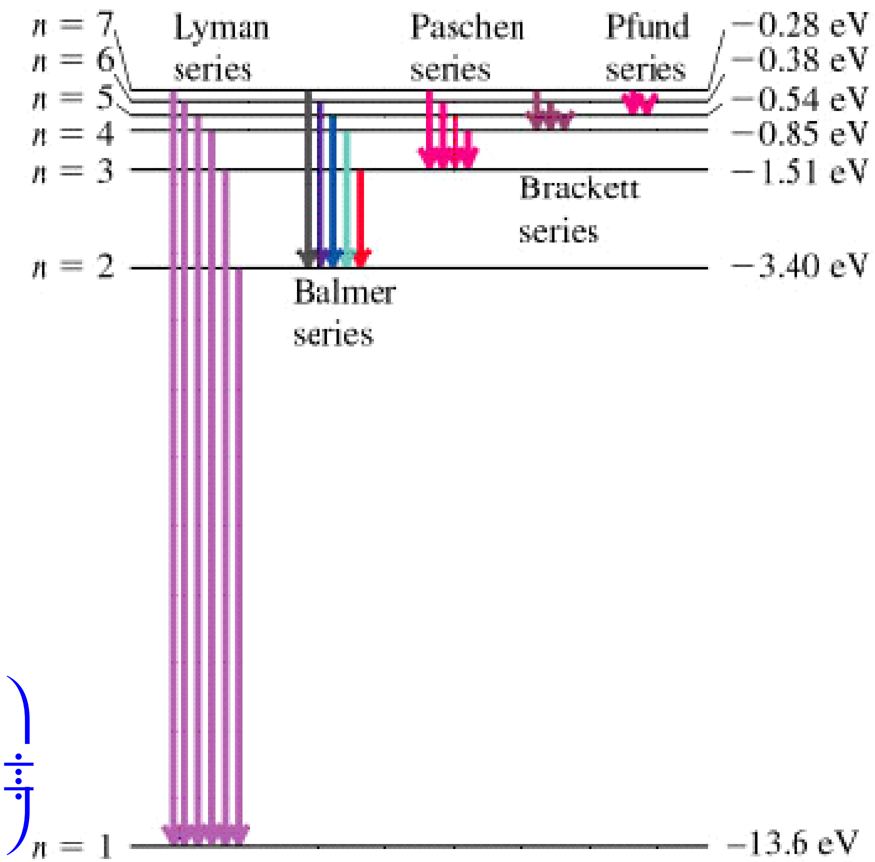
$$\frac{1}{\lambda} = R \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

Rydberg constant,

$$R = \frac{m}{4\pi c\hbar^3} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2$$



(a)



(b)

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

For Lyman series, $n_f = 1,\ n_i = 2, 3, 4, \ldots$

For Balmer series, $n_f = 2,\ n_i = 3, 4, 5\ldots$

For Paschen series, $n_f = 3,\ n_i = 4, 5, 6\ldots$

For Brackett series, $n_f = 4,\ n_i = 5, 6, 7\ldots$

For Pfund series, $n_f = 5,\ n_i = 6, 7, 8\ldots$

What are the differences?

- The energy levels as predicted by Bohr's model is the essentially same as that predicted in the quantum mechanical one, where the energy of each state is characterised by the principal quantum number *n*.
- But in Bohr model it has no *m*, ℓ quantum numbers; only *n.*
- Bohr's model has no degenerate states; unlike in QM model, each energy level *n* is n^2-degenerate.

What are the differences? (cont.)

In Bohr's model, each orbit and state are discrete, both are uniquely characterised by the quantum number n.

- But in the QM model the states are characterised by a set of three quantum number $\{n, \ell, m\}$. Each quantum state is known as an 'orbital'. These orbitals are not discrete circles but a 'cloud' of probability of electrons, $n(\mathbf{r}) = \Psi^*_{n\ell m}(\mathbf{r})\Psi_{n\ell m}(\mathbf{r})$.

What are the differences? (cont.)

Both models are actually derived based on TOTALLY different theoretical basis

- But yet there are so many common features that agree between both.

THINK!

- Can you think of more differences between the old quantum theory of hydrogen atom and the quantum mechanical model?
- Try to think of the fundamental causes that lead to these differences.