# Section 5: The Hydrogen Atom

In these slides we will cover:

- The 3D Schrödinger equation
- Particle in a box and degenerate quantum states
- Radial and angular solutions for central potentials
- Identification of the angular piece with the angular momentum eigenfunctions (spherical harmonics)
- Infinite spherical well
- Solution of the radial equation for the Coulomb potential
- Eigenfunctions of the hydrogen atom
- Quantum numbers of the hydrogen atom

# Particle in a box

## The 3D Schrödinger Equation

- We now move from particles in 1D space, to 3D space
- The derivative in 1 dimension, $\frac{d^2}{dx^2}$, is replaced by its 3D equivalent, the "Laplacian" operator $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$
- The **3D time-independent Schrödinger equation** for the energy eigenfunctions $\psi(x, y, z)$ and eigenvalues $E$ is hence:

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

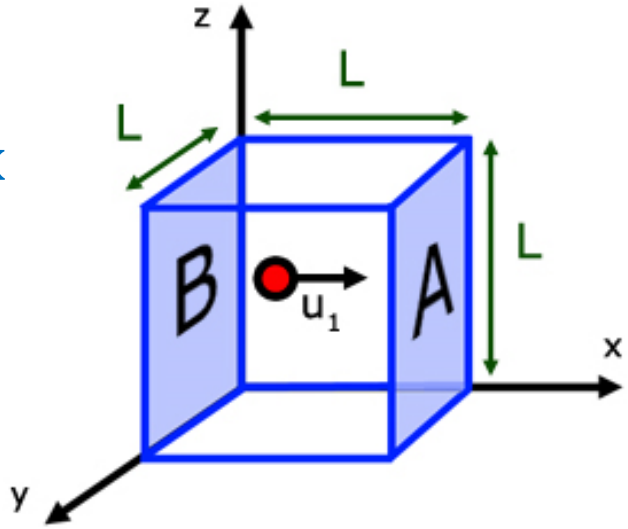
- The **normalisation condition** for the 3D wavefunction is $\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz\, |\psi(x, y, z)|^2 = 1$

# Particle in a box

**Particle in a box**

- A good example is a "particle in a box" with potential

$$V(x) = \begin{cases} 0, & |x| < L, |y| < L, |z| < L \\ \infty, & \text{outside the box} \end{cases}$$




- We look for a separable solution

$$\psi(x, y, z) = f(x)\, g(y)\, h(z)$$

- We find, by substituting this trial solution in the 3D Schrödinger equation and re-arranging,

$$-\frac{\hbar^2}{2m}\left[\frac{1}{f(x)}\frac{d^2 f}{dx^2} + \frac{1}{g(y)}\frac{d^2 g}{dy^2} + \frac{1}{h(z)}\frac{d^2 h}{dz^2}\right] = E$$

# Particle in a box

**Particle in a box**

- That last equation again:

$$-\frac{\hbar^2}{2m}\left[\frac{1}{f(x)}\frac{d^2f}{dx^2}+\frac{1}{g(y)}\frac{d^2g}{dy^2}+\frac{1}{h(z)}\frac{d^2h}{dz^2}\right]=E$$

- We can solve this equation using a nice piece of logic:
  - each term in the squared bracket only depends on 1 variable ($x$, $y$ or $z$)
  - each of those variables is free to vary independently from the others
  - in this case, the only way to make the terms always sum to a constant is if each individual term in the squared bracket is separately a constant
- We find that each separate function $f, g, h$ satisfies the 1D Schrödinger equation for the infinite potential well. We multiply them together for the total solution, $\psi = f \cdot g \cdot h$

# Particle in a box

**Particle in a box**

- Summarising, the particle in a box has energy eigenfunctions labelled by **three quantum numbers** $(n_x, n_y, n_z)$

$$\psi^{3D}(x,y,z) = \psi^{1D}_{n_x}(x)\,\psi^{1D}_{n_y}(y)\,\psi^{1D}_{n_z}(z)$$

- $\psi^{1D}_n(x)$ are the different states $n$ which are solutions of the 1D infinite potential well

- The energy eigenvalues are then the sum of the corresponding eigenvalues for the 1D infinite potential well,

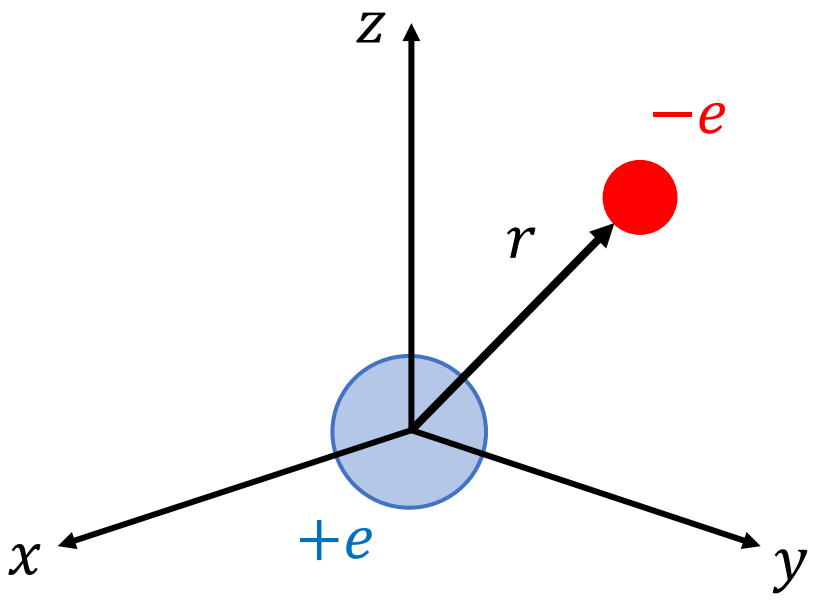
$$E(n_x, n_y, n_z) = \frac{\pi^2\hbar^2}{8mL^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

- We notice here that distinct eigenfunctions can have the same energy (**degenerate states**), e.g. (2,1,1), (1,2,1) and (1,1,2)

# Central potentials

**Radial and angular solutions for central potentials**

- A **central potential** depends only on the distance from the origin, $V(x, y, z) = V(r)$. An important example is, the potential around a hydrogen nucleus (proton) at the origin




*(Sorry for the illustration with classical point particles. They are of course probability clouds in QM!)*

# Central potentials

**Radial and angular solutions for central potentials**

- A **central potential** depends only on the distance from the origin, $V(x, y, z) = V(r)$. An important example is, the potential around a hydrogen nucleus (proton) at the origin

- These problems are best treated using spherical polar co-ordinates, $(r, \theta, \phi)$

- Non-examinable: we need the expression for the Laplacian in spherical polar co-ordinates (ouch!):

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

# Central potentials

## Radial and angular solutions for central potentials

- Non-examinable: We again look for a separable solution for the energy eigenfunctions,

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

Switching to using $\mu$ for mass, since $m$ is about to mean something else

- Substituting this in the 3D Schrödinger equation and re-arranging, we find:

$$-\frac{\hbar^2}{Y}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right] = \frac{\hbar^2}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + 2\mu[E-V(r)]\,r^2$$

- By a similar logic to the cubical box solution … the left-hand side of this equation is a function of $(\theta,\phi)$ only and the right-hand side is a function of $r$ only. But they must remain equal as $(r,\theta,\phi)$ vary independently. So they must both be equal to the same constant, let's call it $\lambda$

# Central potentials

**Radial and angular solutions for central potentials**

- The left-hand side of this equation becomes,

$$-\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]Y(\theta,\phi)=\lambda\,Y(\theta,\phi)$$

- **Aha!** The left-hand side is just the operator for the total angular momentum, $\hat{L}^2$, from the previous Section:

$$\hat{L}^2\,Y=l(l+1)\hbar^2\,Y$$

- Hence, the angular piece of the energy eigenfunctions for a central potential is just the spherical harmonic functions $Y_{lm}(\theta,\phi)$ where $\lambda=l(l+1)\hbar^2$ – that's convenient

# Central potentials

**Radial and angular solutions for central potentials**

- Substituting $\lambda = l(l+1)\hbar^2$ in the radial piece, we find

[Again, $\mu$ =mass]

$$-\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\left[V(r)+\frac{l(l+1)\hbar^2}{2\mu r^2}\right]R = E\,R$$

- A useful change of variables is to substitute $u(r) = r \cdot R(r)$ [i.e. $R = u/r$]. In this case,

$$-\frac{\hbar^2}{2\mu}\frac{d^2u}{dr^2}+\left[V(r)+\frac{l(l+1)\hbar^2}{2\mu r^2}\right]u = E\,u$$

Note: this equation depends on the angular momentum state, through $l$

- We note that this looks just like a 1D Schrödinger equation, except the usual potential has been replaced by an **"effective potential"** $V(r)+\frac{l(l+1)\hbar^2}{2\mu r^2}$

# Central potentials

## Infinite spherical well

- A good example of this is a "particle in a sphere", where

$$V(r) = \begin{cases} 0, & r < a \\ \infty, & r > a \end{cases}$$

- In this case, the energy eigenfunctions $u_n(r)$ at $r < a$ satisfy

$$-\frac{\hbar^2}{2\mu}\frac{d^2u_n}{dr^2} + \left[\frac{l(l+1)\hbar^2}{2\mu r^2}\right]u_n = E\,u_n$$

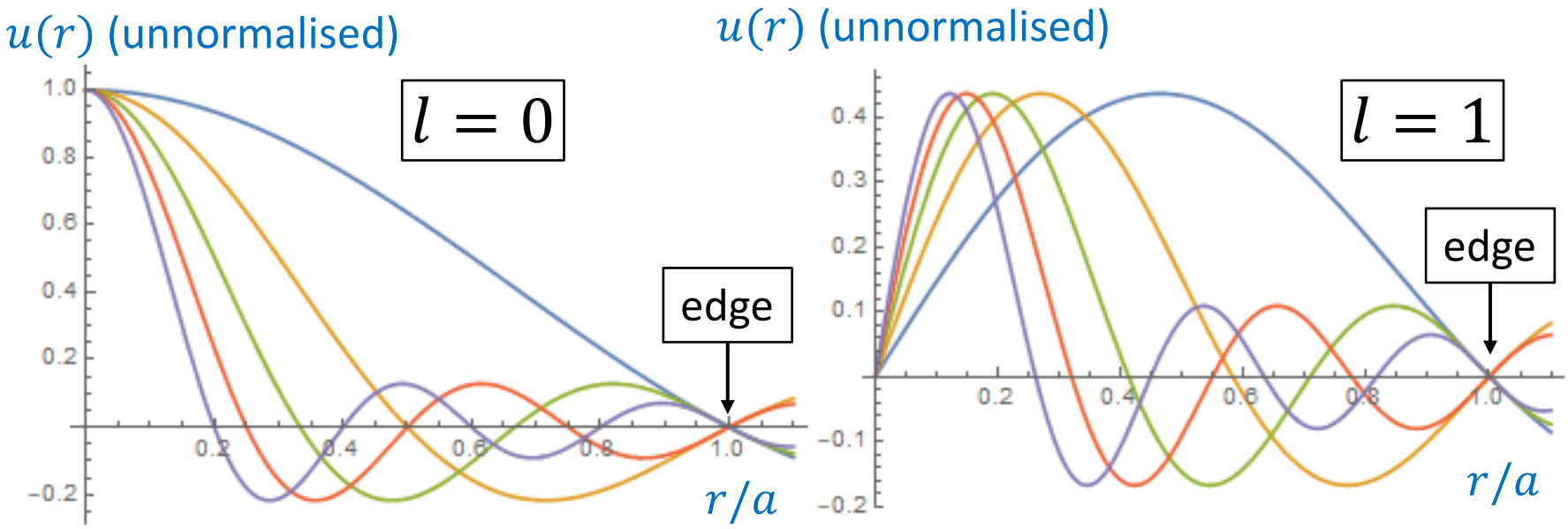
- Boundary condition is $u = 0$ at $r = a$. The first eigenfunctions are $u \propto \sin kr$ for $l = 0$ and $u \propto \left(\frac{\sin kr}{kr} - \cos kr\right)$ for $l = 1$

- Note that the full energy eigenfunction also includes the angular piece, $\psi(r, \theta, \phi) = [u_n(r)/r]\, Y_{lm}(\theta, \phi)$ – the state of the particle is characterised by 3 quantum numbers $n, l, m$

# Central potentials

## Infinite spherical well

- Here are the first few radial eigenfunctions for two values of $l$:

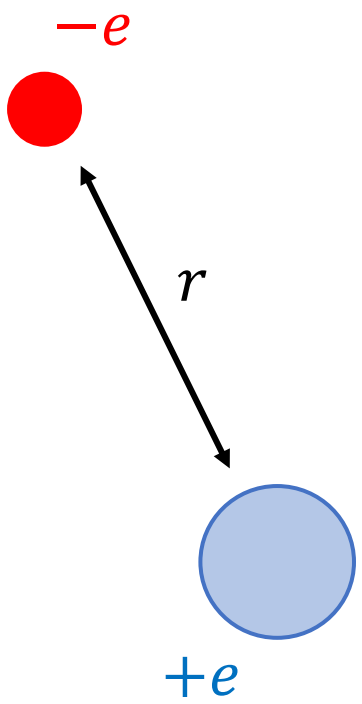



- The probability of finding the particle between $r$ and $r + dr$ is given by $r^2|\psi|^2 \propto r^2|R|^2 \propto |u|^2$ – the extra factor of $r^2$ is appearing because of the volume element in spherical polars

# Eigenfunctions of the hydrogen atom

**Solution of radial equation for Coulomb potential**

- However, the most important example of a central potential is **an electron in a hydrogen atom orbiting around a nucleus**, which follows the Coulomb potential energy, $V(r) = -\frac{e^2}{4\pi\varepsilon_0 r}$




- In this case the radial equation becomes (where $a = 4\pi\varepsilon_0\hbar^2/\mu e^2$),

$$-\frac{d^2u_n}{dr^2} + \left[-\frac{2}{ar} + \frac{l(l+1)}{r^2}\right]u_n = \frac{2\mu E}{\hbar^2}\,u_n$$

*(Sorry for the illustration with classical point particles. They are of course probability clouds in QM!)*

# Eigenfunctions of the hydrogen atom

**Solution of radial equation for Coulomb potential**

- We can solve this equation by considering two limits …
- If $r \to \infty$, we have $-\frac{d^2u}{dr^2} = \frac{2\mu E}{\hbar^2}u$. We recognise this equation as having solution $u(r) \propto e^{-r/a}$, where $E = -\frac{\hbar^2}{2\mu a^2}$
- If $r \to 0$, we have $-\frac{d^2u}{dr^2} + \frac{l(l+1)}{r^2}u = 0$. This equation has a solution $u(r) \propto r^{l+1}$
- This logic motivates that the complete solution is a **polynomial multiplied by an exponential**, depending on the value of $l$

# Eigenfunctions of the hydrogen atom

**Eigenfunctions for hydrogen atom**

- The textbook explains [we won't give the derivation here since it's a bit involved…] that the energy eigenvalues $E_n$ can be characterised by a single quantum number $n$, and a given energy has $n$ degenerate eigenfunctions $u_{nl}(r)$ given by $l = 0,1, \ldots, n-1$

- Here are some solutions for $R_{nl}(r) = u_{nl}(r)/r$ corresponding to the first two values of $n = 1,2$ and the allowed values of $l$:

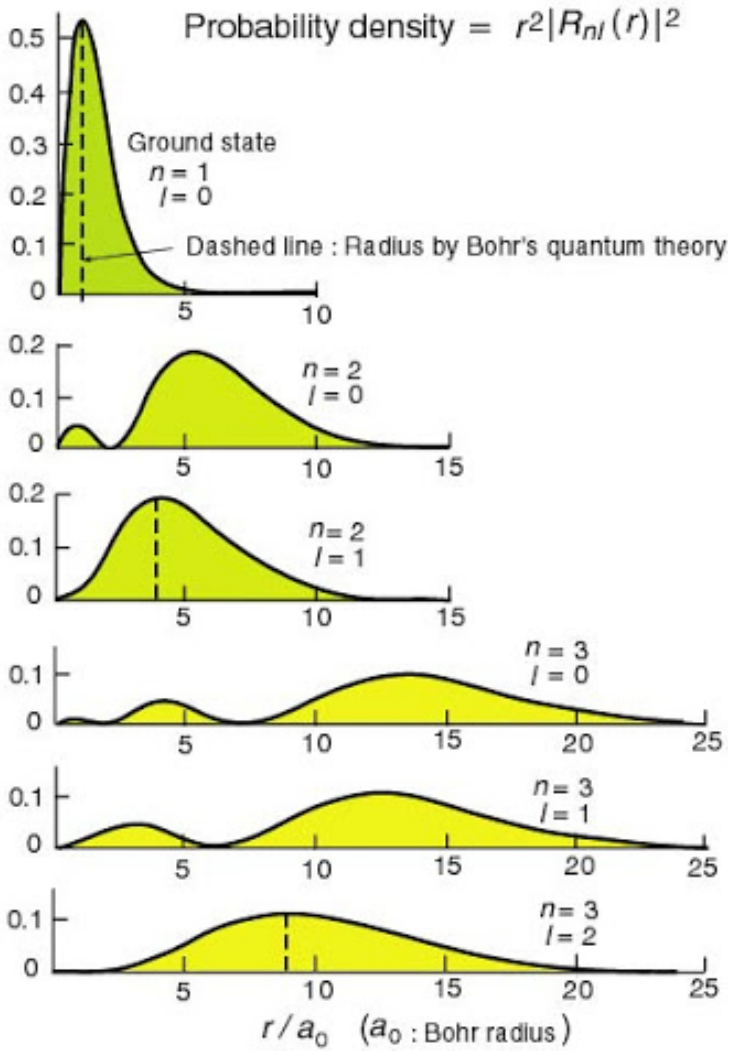
| | $n = 1$ | $n = 2$ |
|---|---|---|
| $l = 0$ | $R_{10} = \frac{2}{a^{3/2}} e^{-r/a}$ | $R_{20} = \frac{1}{\sqrt{2}\, a^{3/2}} \left(1 - \frac{r}{2a}\right) e^{-r/2a}$ |
| $l = 1$ | (not allowed) | $R_{21} = \frac{1}{2\sqrt{6} a^{3/2}} \left(\frac{r}{a}\right) e^{-r/2a}$ |

# Eigenfunctions of the hydrogen atom

**Eigenfunctions for hydrogen atom**

- The radial extent of the eigenfunctions are characterised by the parameter $a = \frac{4\pi\varepsilon_0\hbar^2}{\mu e^2} = 5.3\times10^{-11}\ m$ known as the **Bohr radius**

- Here are the first few radial eigenfunctions, plotted as a probability density $|u_{nl}|^2 = r^2|R_{nl}|^2$



# Eigenfunctions of the hydrogen atom

**Energy levels and quantum numbers of hydrogen atom**

- The textbook shows that the energy eigenvalues only depend on $n$, and are given by $E_n = -E_1/n^2$, where $E_1 = \frac{\mu}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2$. This is the famous **Bohr formula** for the hydrogen energy levels

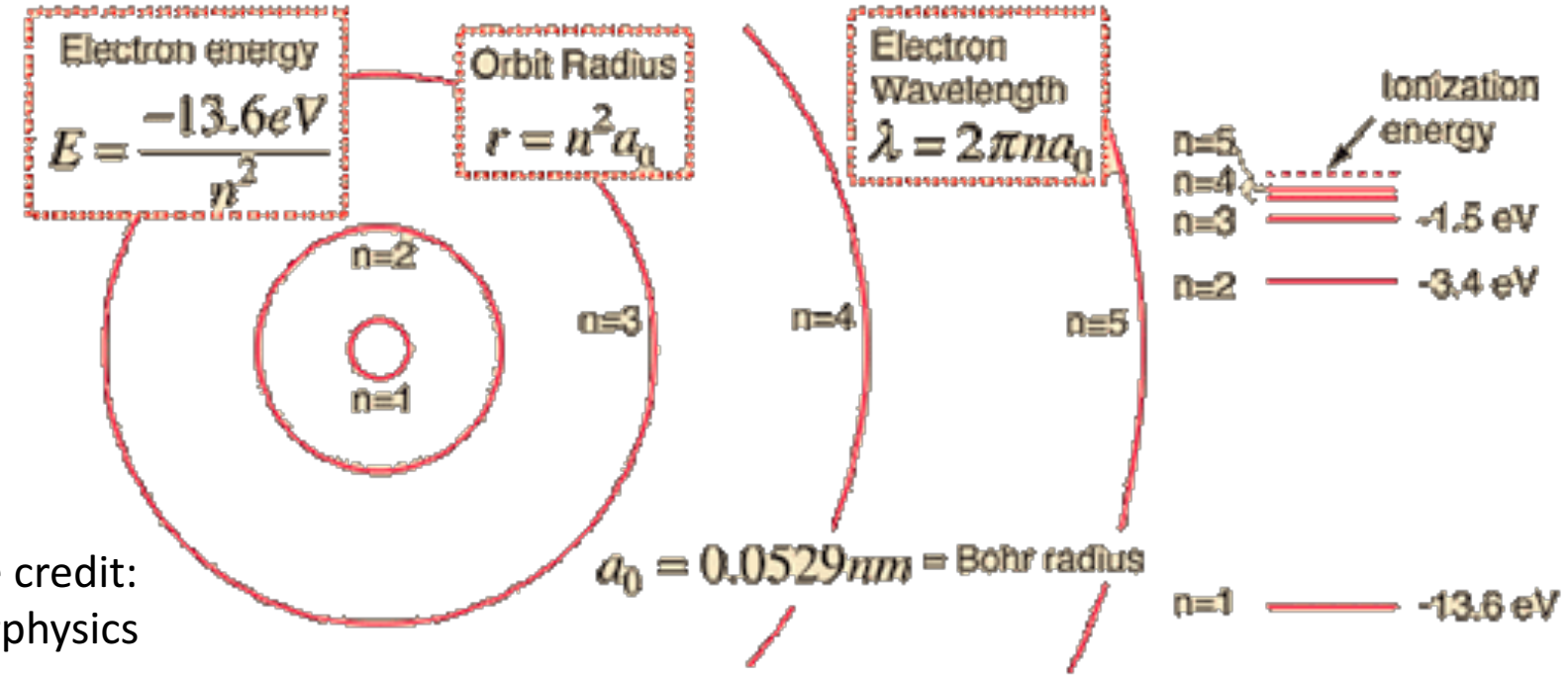



Image credit: Hyperphysics

# Eigenfunctions of the hydrogen atom

## Energy levels and quantum numbers of hydrogen atom

- Let's recap the full argument:

1. The Schrödinger equation for a central potential always has separable solutions $\psi(r,\theta,\phi) = R_{nl}(r)\, Y_{lm}(\theta,\phi)$, where $Y_{lm}$ are the spherical harmonics and $R_{nl}$ satisfies a radial equation

2. Hence, these are automatically eigenfunctions of angular momentum, with $L^2 = l(l+1)\hbar^2$ and $L_z = m\hbar$ $(-l \leq m \leq +l)$

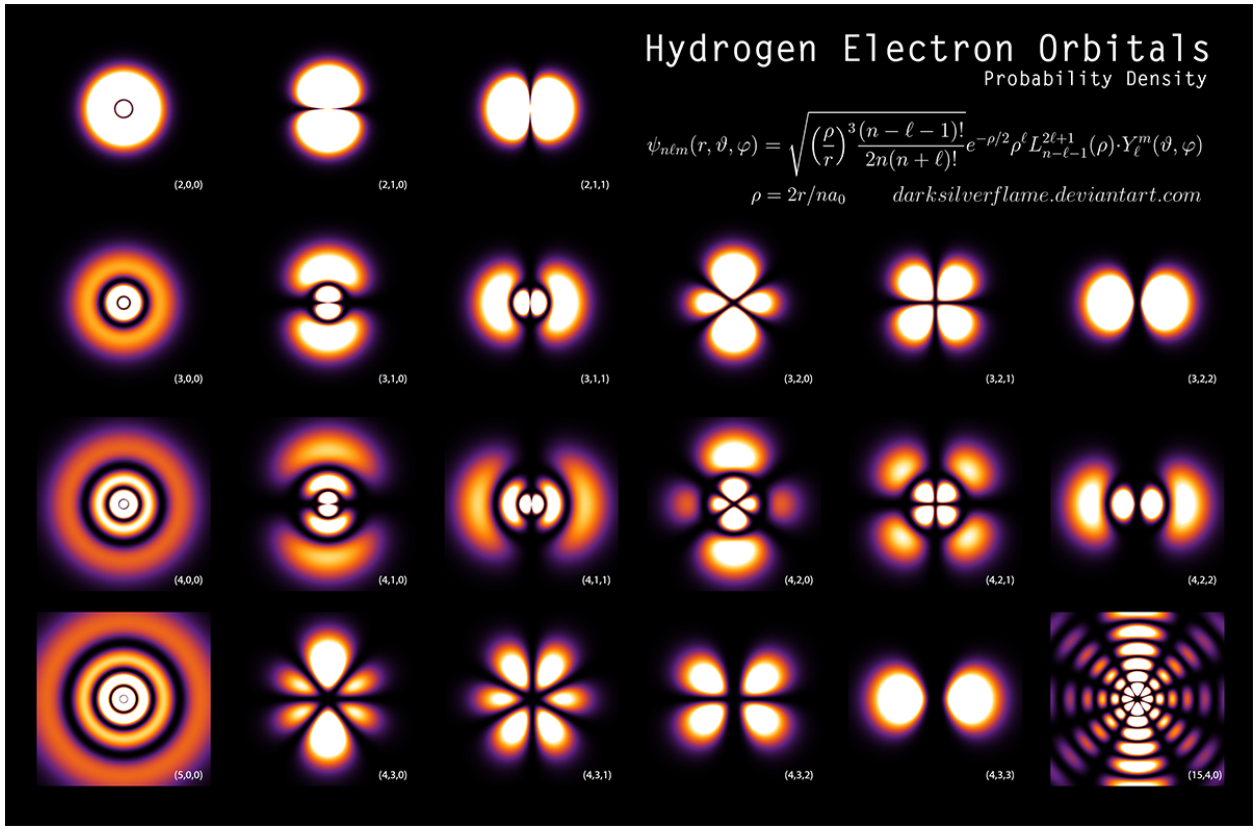
3. For a Coulomb potential in particular, the energy eigenvalues do not depend on $l$, but only on a single quantum number $n$, $E_n = -E_1/n^2$, with the restriction $0 \leq l \leq n-1$

4. There are hence 3 quantum numbers which characterise the hydrogen atom: total energy ($n$), total angular momentum ($l$) and the $z$-component of angular momentum ($m$)

# Eigenfunctions of the hydrogen atom

**Energy levels and quantum numbers of hydrogen atom**

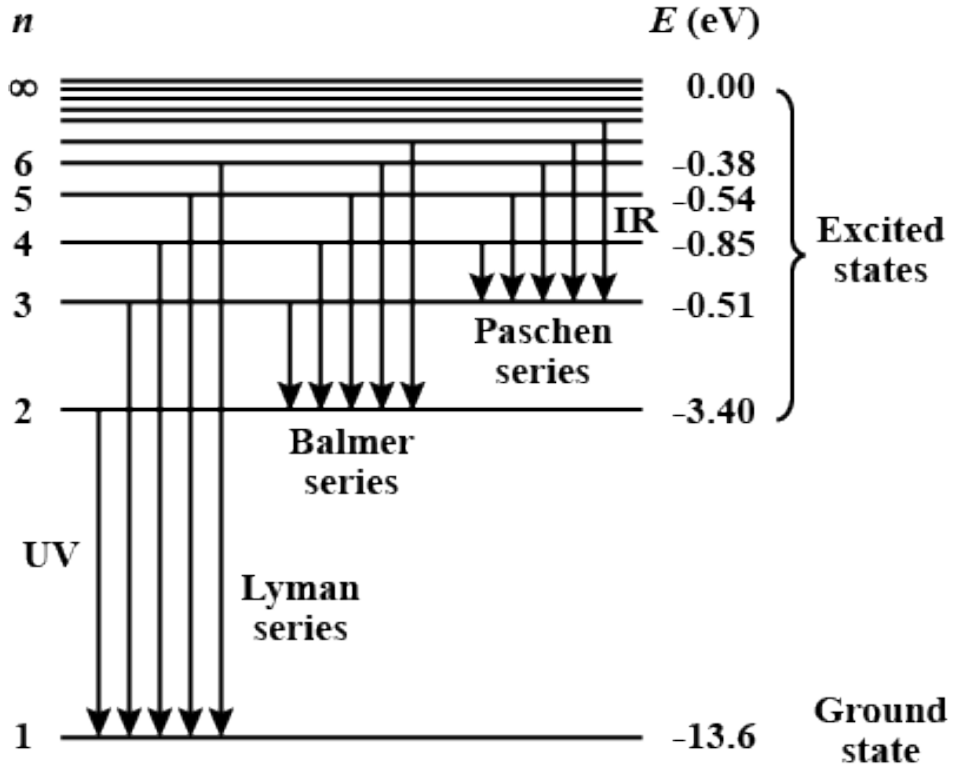
- The full eigenfunctions $\psi(r, \theta, \phi)$ are a combination of the radial eigenfunction and spherical harmonics:



# Eigenfunctions of the hydrogen atom

**Energy levels and quantum numbers of hydrogen atom**

- Counting the **number of distinct eigenstates** associated with a specific energy $n$ …
- There are $n$ possible values of $l$
- For each $l$, there are $(2l + 1)$ allowed values of $m$
- Combining all those, we find $n^2$ distinct states



# Eigenfunctions of the hydrogen atom

**Summary**

- The hydrogen atom has discrete energy levels $E_n = -E_1/n^2$, where $E_1 = \frac{\mu}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2$ and **$n$ is the energy quantum number**
- For each state $n$, there are $n$ different values of $l = (0,1,\dots,n-1)$, where **$l$ is the quantum number for total angular momentum** and $L^2 = l(l+1)\hbar^2$
- For each state $l$, there are $(2l+1)$ different values of $m = (-l,-l+1,\dots,l-1,l)$, where **$m$ is the quantum number for the $z$-component of angular momentum** and $L_z = m\hbar$
- The **energy eigenfunctions** are then $\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)\,Y_{lm}(\theta,\phi) = \frac{u_{nl}(r)}{r}\,Y_{lm}(\theta,\phi)$

# Summary

## Particle in a box

- The 3D time-independent Schrödinger equation is $-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi$, where $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$
- A convenient method of solving is to search for a wavefunction separable in the system co-ordinates
- Different eigenfunctions which have the same energy are called degenerate states

## Central potentials

- If the potential depends only on the radius $r$, then the angular piece of $\psi$ is the angular momentum eigenfunctions, the spherical harmonics $Y_{lm}(\theta, \phi)$
- The radial piece of $\psi$ satisfies the 1D Schrödinger equation for an effective potential, depending on $l$

## Eigenfunctions of the hydrogen atom

- For a Coulomb potential, the radial piece takes the form of a polynomial multiplied by an exponential
- The hydrogen atom is characterised by quantum numbers $(n, l, m)$ for $(E, L^2, L_z)$ where $0 \leq l \leq n-1$ and $-l \leq m \leq l$