

"Anyone who can contemplate quantum mechanics without getting dizzy hasn't understood it."

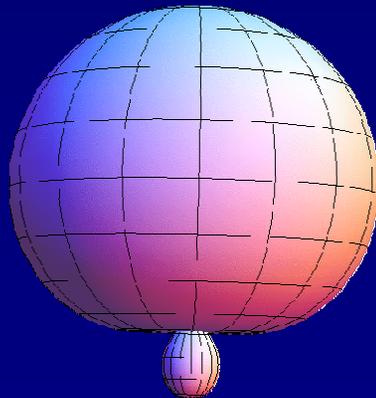
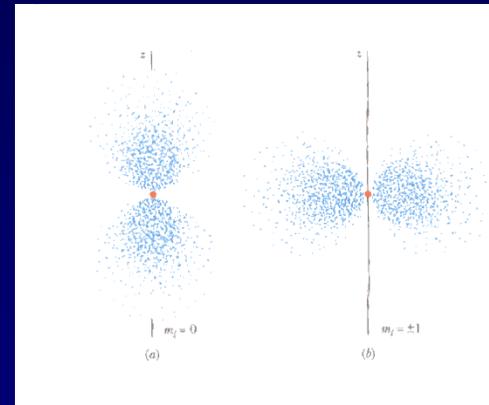
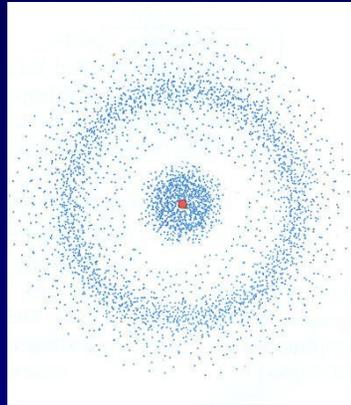
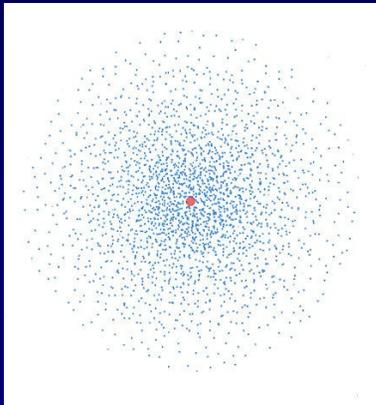
--Niels Bohr

Special (Optional) Lecture

“Quantum Information”

- One of the most modern applications of QM
 - quantum computing
 - quantum communication – cryptography, teleportation
 - quantum metrology
- Prof. Kwiat will give a special 214-level lecture on this topic
 - Sunday, Feb. 24
 - 3 pm, 141 Loomis
- Attendance is optional, but encouraged.

Lecture 17: Atomic States, Angular Momentum & Selection Rules



Today

Schrödinger's Equation for the Hydrogen Atom

- Radial wave functions

Angular Momentum

- Quantization of L_z and L^2

Potential Energy in the Hydrogen Atom

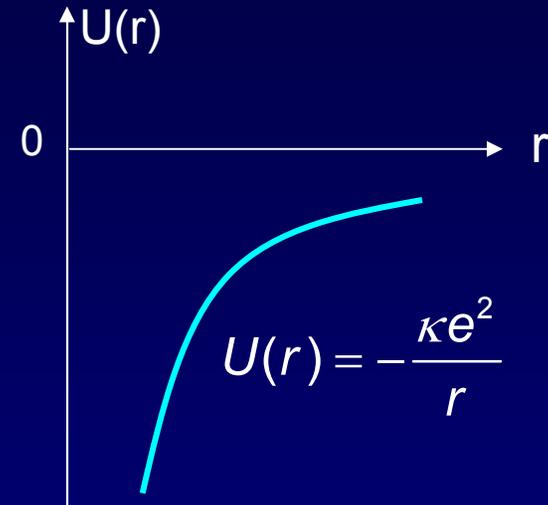
To solve this problem, we must specify the potential energy of the electron. In an atom, the **Coulomb force** binds the electron to the nucleus.

This problem does not separate in Cartesian coordinates, because we cannot write $U(x,y,z) = U_x(x) + U_y(y) + U_z(z)$. However, we can separate the potential in **spherical coordinates** (r, θ, ϕ) , because:

$$U(r, \theta, \phi) = U_r(r) + U_\theta(\theta) + U_\phi(\phi)$$
$$\frac{-\kappa e^2}{r} \quad 0 \quad 0$$

Therefore, we will be able to write:

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



$$\kappa = \frac{1}{4\pi\epsilon_0} = 9 \times 10^9 \text{ Nm}^2/\text{C}^2$$

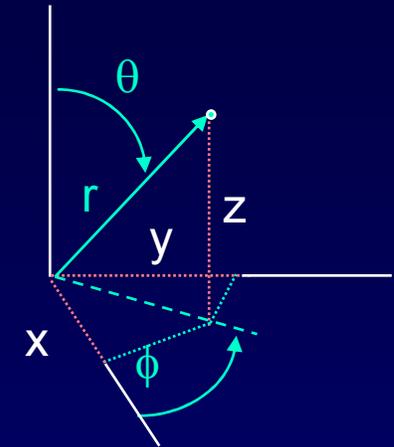
Question:

How many quantum numbers will be needed to describe the hydrogen wave function?

Wave Function in Spherical Coordinates

We saw that because U depends only on the radius, the problem is separable. The hydrogen SEQ can be solved analytically (but not by us). Here we show the solutions and their physical significance.

We can write: $\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_{lm}(\theta, \phi)$



There are three quantum numbers:

- n “principal” ($n \geq 1$)
- l “orbital” ($0 \leq l < n-1$)
- m “magnetic” ($-l \leq m \leq +l$)

What before we called
 $\Theta(\theta)\Phi(\phi)$

The Y_{lm} are called “spherical harmonics.”

First, we will only consider $l = 0$ and $m = 0$.

These are called “s-states”. This simplifies the problem, because $Y_{00}(\theta, \phi)$ is a constant and the wave function has no angular dependence:

$$\psi_{n00}(r, \theta, \phi) = R_{n0}(r)$$

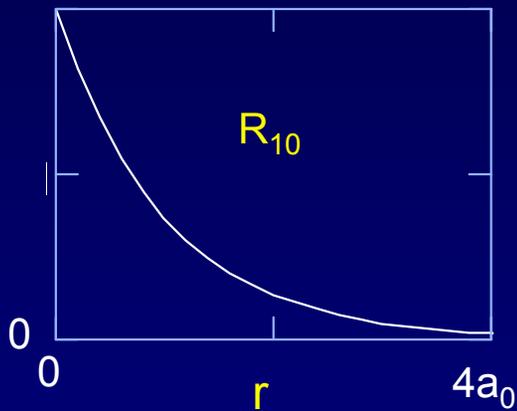
These are states in which the electron has no orbital angular momentum. This is not possible in Newtonian physics. (Why?)

Note:

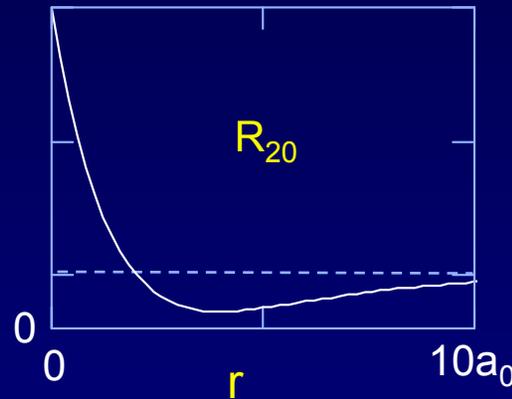
Some of this nomenclature dates back to the 19th century, and has no physical significance.

Radial Eigenstates of Hydrogen

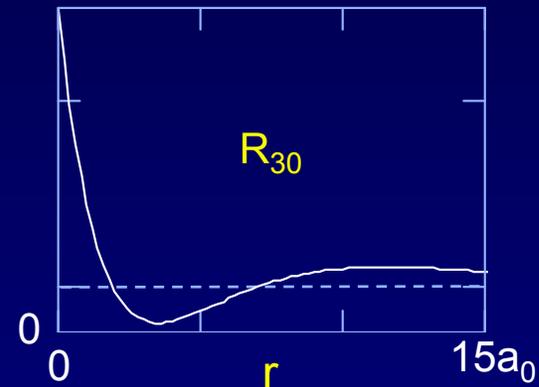
Here are graphs of the s-state wave functions, $R_{n0}(r)$, for the electron in the Coulomb potential of the proton. The zeros in the subscripts are a reminder that these are states with $l = 0$ (zero angular momentum!).



$$R_{1,0}(r) \propto e^{-r/a_0}$$



$$R_{2,0}(r) \propto \left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0}$$



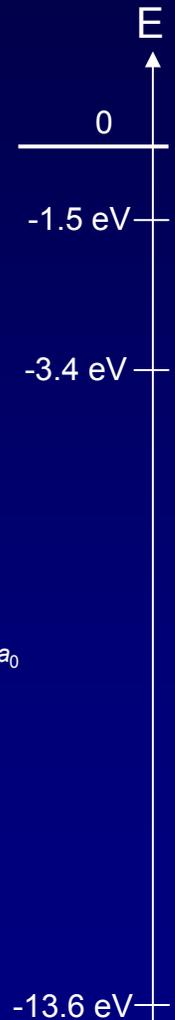
$$R_{3,0}(r) \propto \left(3 - \frac{2r}{a_0} + 2\left(\frac{r}{3a_0}\right)^2\right) e^{-r/3a_0}$$

$$a_0 \equiv \frac{\hbar^2}{m_e \kappa e^2} = 0.053 \text{ nm}$$

$$E_n \equiv \frac{-13.6 \text{ eV}}{n^2}$$

You will not need to memorize these functions.

You can prove these are solutions by plugging into the 'radial SEQ' (Appendix).



ACT 1: Optical Transitions in Hydrogen

An electron, initially excited to the $n = 3$ energy level of the hydrogen atom, falls to the $n = 2$ level, emitting a photon in the process.

1) What is the energy of the emitted photon?

- a) 1.5 eV b) 1.9 eV c) 3.4 eV

2) What is the wavelength of the emitted photon?

- a) 827 nm b) 656 nm c) 365 nm

Solution

An electron, initially excited to the $n = 3$ energy level of the hydrogen atom, falls to the $n = 2$ level, emitting a photon in the process.

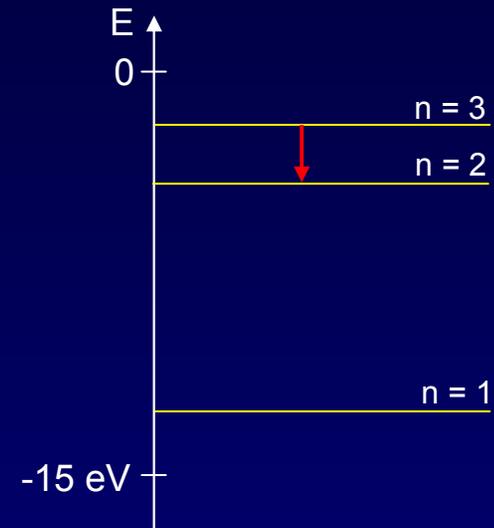
1) What is the energy of the emitted photon?

- a) 1.5 eV **b) 1.9 eV** c) 3.4 eV

$$E_n = \frac{-13.6 \text{ eV}}{n^2}$$
$$\Delta E_{n_i \rightarrow n_f} = -13.6 \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \text{ eV}$$
$$E_{\text{photon}} = \Delta E_{3 \rightarrow 2} = -13.6 \left(\frac{1}{9} - \frac{1}{4} \right) \text{ eV} = 1.9 \text{ eV}$$

2) What is the wavelength of the emitted photon?

- a) 827 nm b) 656 nm c) 365 nm



Solution

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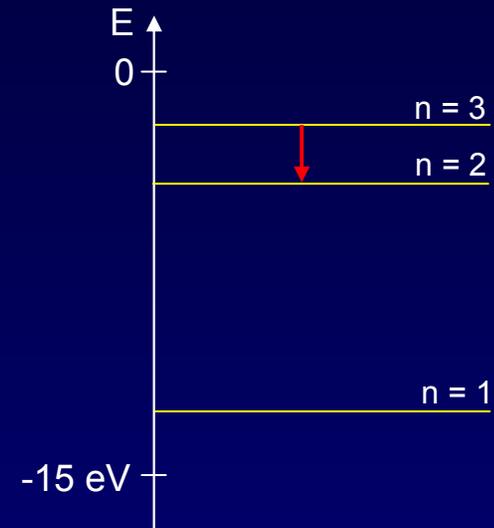
2) What is the wavelength of the emitted photon?

- a) 827 nm **b) 656 nm** c) 365 nm

$$\lambda = \frac{hc}{E_{\text{photon}}} = \frac{1240 \text{ eV} \cdot \text{nm}}{1.9 \text{ eV}} = 656 \text{ nm}$$

You will measure several transitions in Lab.

We'll see next lecture that there are other constraints on which transitions can occur.



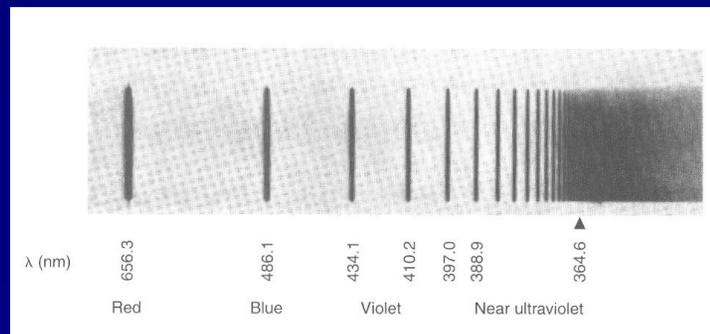
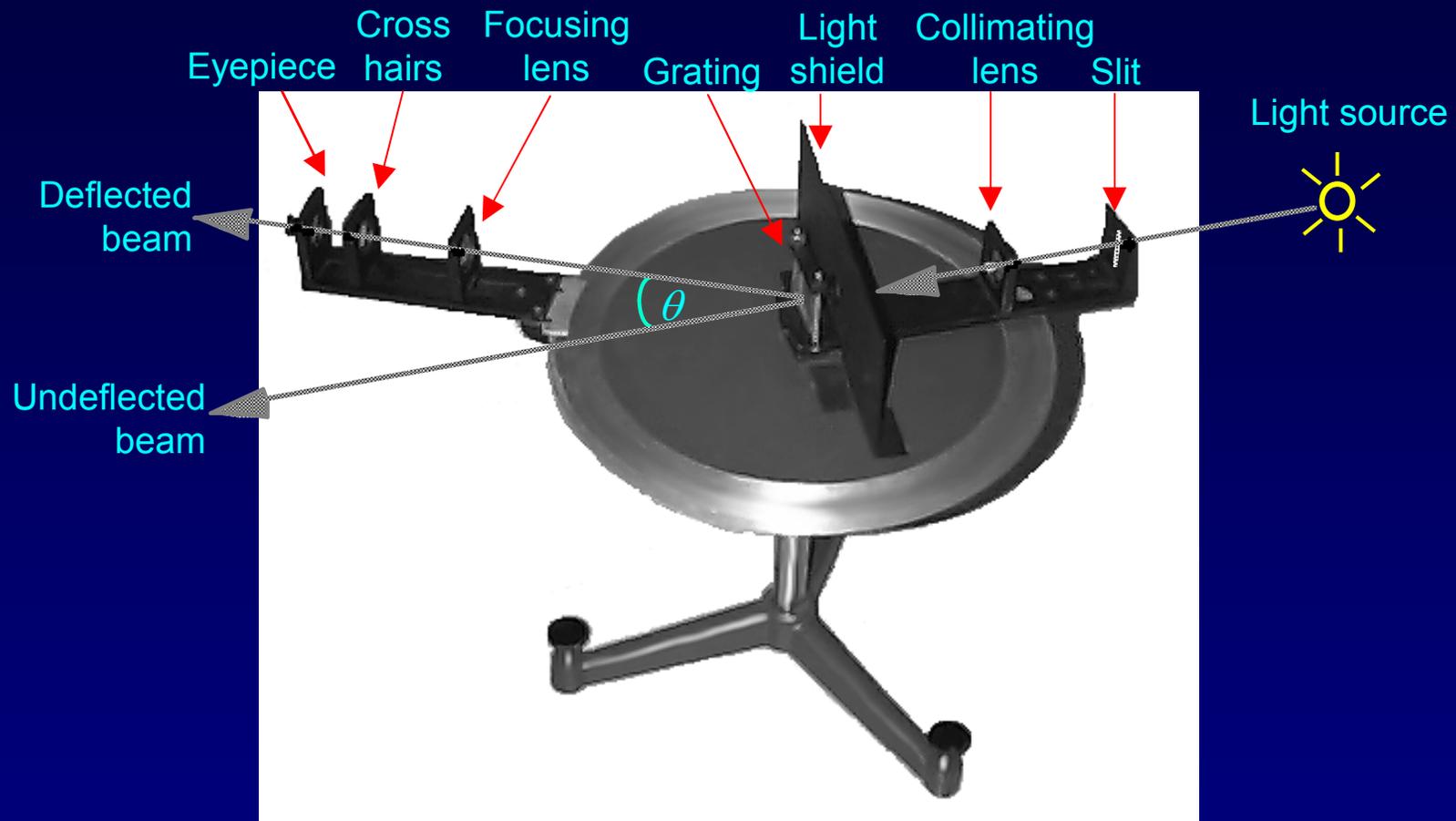
Atomic hydrogen



λ (nm)

Question:
Which transition is this?
($\lambda = 486 \text{ nm}$)

Next week: Laboratory 4



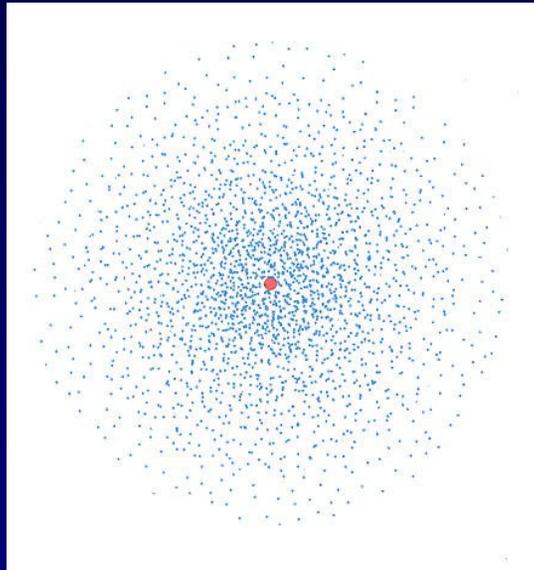
$$E_n = \frac{-13.6\text{eV}}{n^2}$$

Probability Density of Electrons

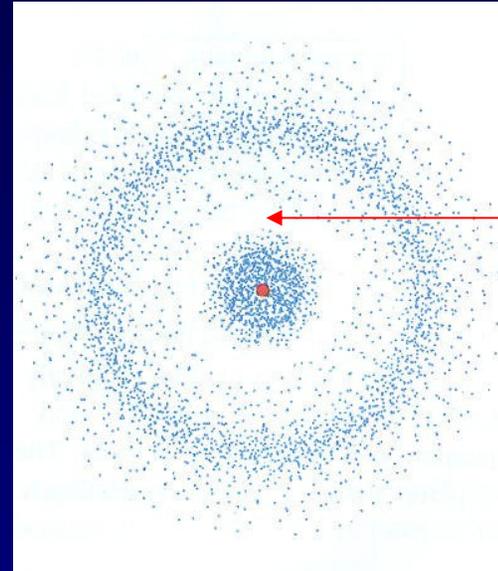
$|\psi|^2 = \text{Probability density} = \text{Probability per unit volume} \propto R_{n0}^2$ for s-states.

The density of dots plotted below is proportional to R_{n0}^2 .

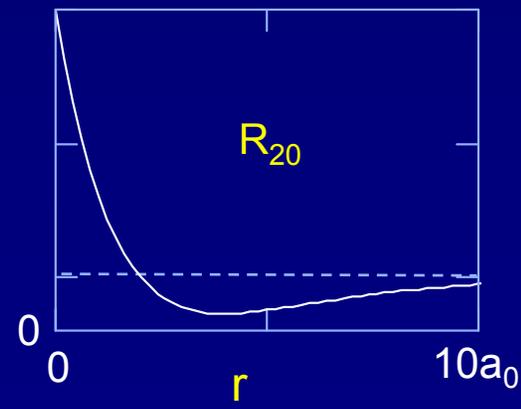
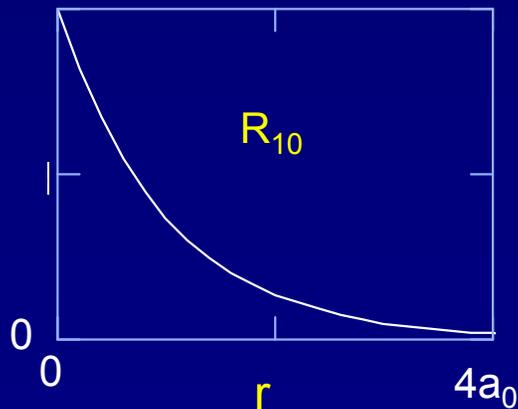
1s state



2s state

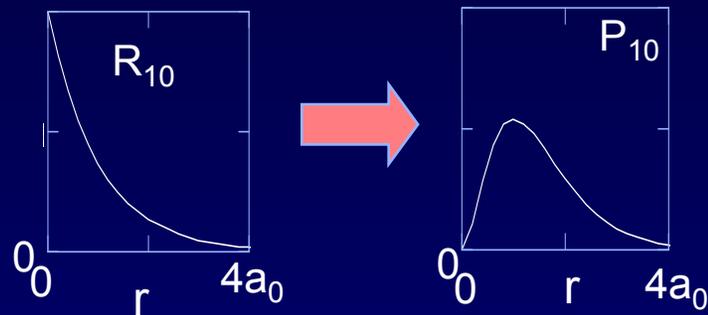


A node in the radial probability distribution.



Radial Probability Densities for S-states

Summary of wave functions and radial probability densities for some s-states.



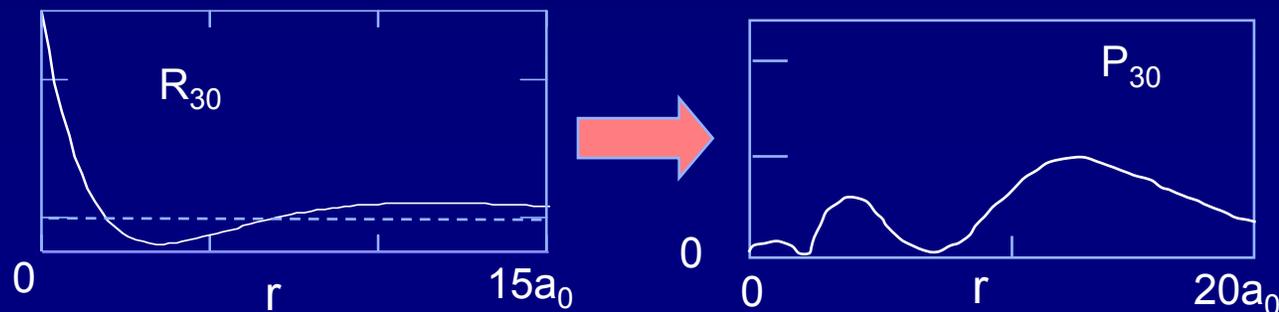
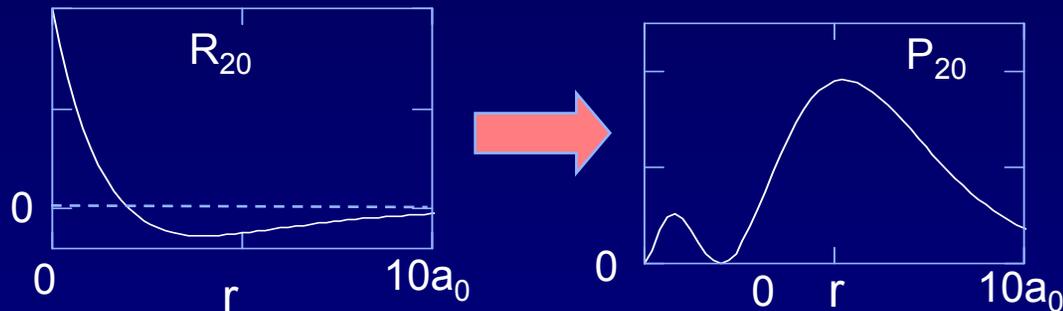
The radial probability density has an extra factor of r^2 because there is more volume at large r . That is, $P_{n0}(r) \propto r^2 R_{n0}^2$.

This means that:

The most likely r is not 0 !!!

Even though that's where $|\psi(r)|^2$ is largest.

This is always a confusing point. See the supplementary slide for more detail.



radial wave functions

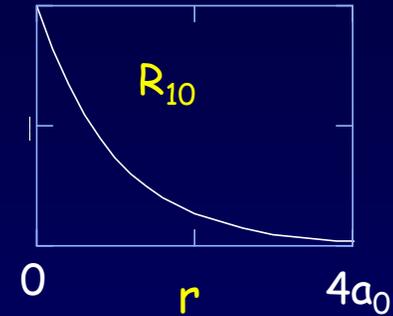
radial probability densities, $P(r)$

<http://www.falstad.com/qmatom/>

Wave Function Normalization

What is the normalization constant for the hydrogen atom ground state?

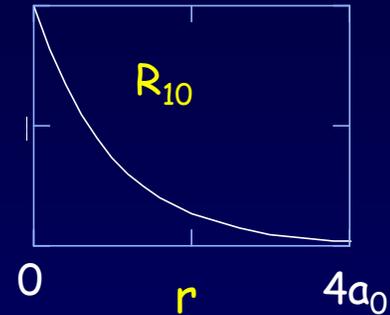
$$\psi_{100}(r, \theta, \phi) = NR_{10}(r) = Ne^{-r/a_0}$$



Solution

What is the normalization constant for the hydrogen atom ground state?

$$\psi_{100}(r, \theta, \phi) = NR_{10}(r) = Ne^{-r/a_0}$$



The probability density is $|\psi|^2 = N^2 \exp(-2r/a_0)$.
In 3D, this means “probability per unit volume”.

We require that the total probability = 1: $\int |\psi|^2 dV = 1$

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

With spherical symmetry, the angular integrals give 4π , so we are left with:

$$4\pi N^2 \int_0^{\infty} r^2 e^{-2r/a_0} dr = 1 \Rightarrow N^2 = \frac{1}{\pi a_0^3}$$

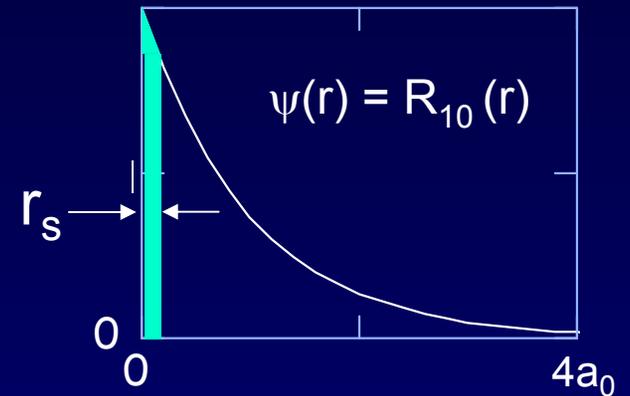
“You can look it up!”

$$\psi_{100}(r) = \sqrt{\frac{1}{\pi a_0^3}} e^{-r/a_0}$$

Normalized ground-state wave function of hydrogen

Probability Calculation

Estimate the probability of finding the electron within a small sphere of radius $r_s = 0.2 a_0$ at the origin.



$$\psi(r) = Ne^{-r/a_0}$$

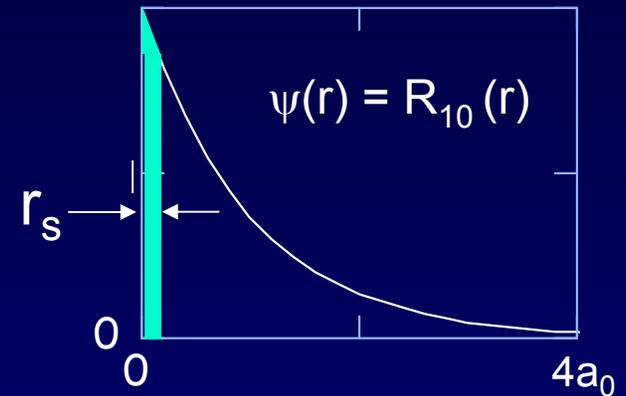
Solution

Estimate the probability of finding the electron within a small sphere of radius $r_s = 0.2 a_0$ at the origin.

If it says “estimate”, don’t integrate.

The wave function is nearly constant near $r = 0$:

$$\psi(0) = \sqrt{\frac{1}{\pi a_0^3}} e^{-0/a_0} = \sqrt{\frac{1}{\pi a_0^3}}$$



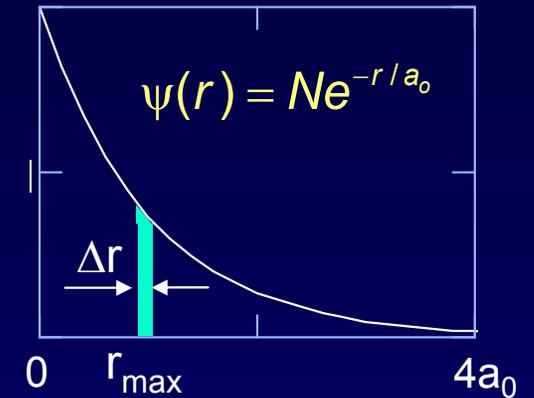
$$\psi(r) = Ne^{-r/a_0}$$

Simply multiply $|\psi|^2$ by the volume $\Delta V = (4/3)\pi r_s^3$:

$$\text{Probability} = |\psi(0)|^2 \Delta V = \frac{4}{3} \left(\frac{r_s}{a_0} \right)^3 \approx 0.01$$

Maximum Radial Probability

At what radius are you most likely to find the electron?



Solution

At what radius are you most likely to find the electron?

Looks like a no-brainer. $r = 0$, of course!

Well, that's not the answer.

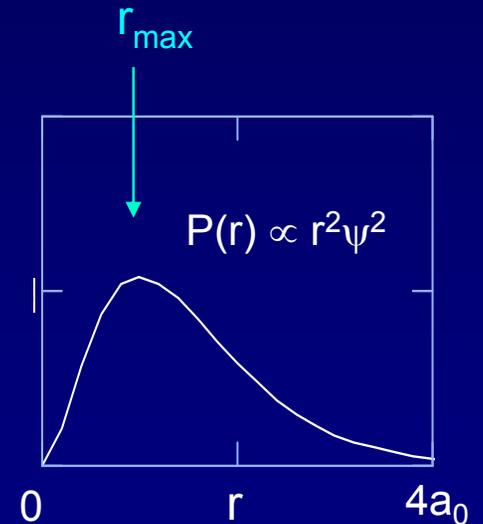
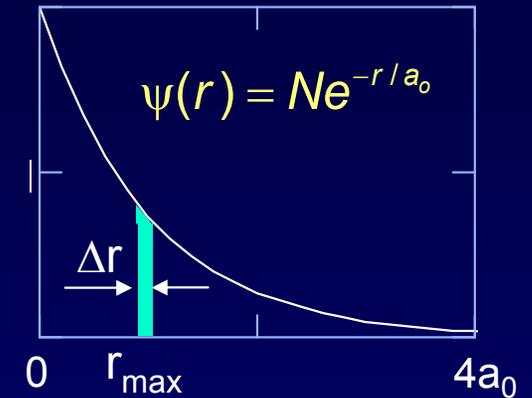
You must find the probability $P(r)\Delta r$ that the electron is in a shell of thickness Δr at radius r . For a given Δr the volume, ΔV , of the shell increases with radius.

The radial probability has an extra factor of r^2 :

$$P(r)\Delta r = |\psi(r)|^2 \Delta V = Cr^2 e^{-2r/a_0} \Delta r$$

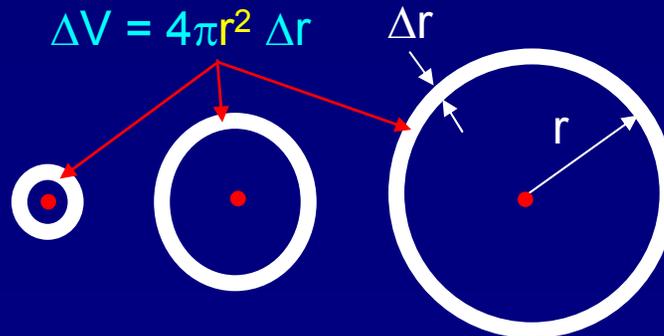
Set $dP/dr = 0$ to find:

$$r_{\max} = a_0 !$$



More volume
at larger r .

No volume
at $r = 0$.



Summary of S-states of H-atom

The “s-states” ($l=0, m=0$) of the Coulomb potential have no angular dependence. In general:

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_{lm}(\theta, \phi)$$

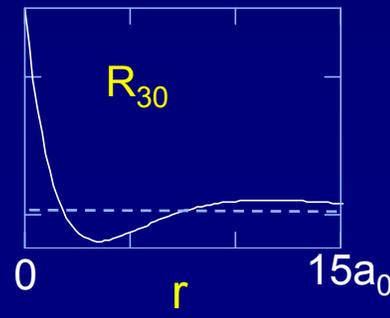
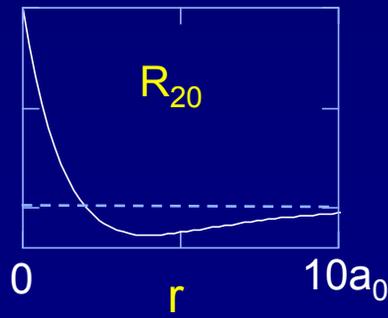
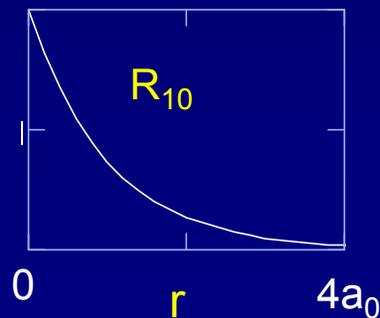
but:

$$\psi_{n00}(r, \theta, \phi) \propto R_{n0}(r)$$

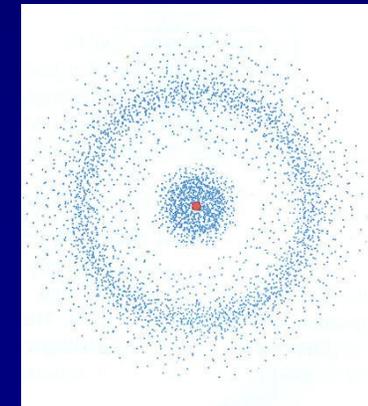
because $Y_{00}(\theta, \phi)$ is a constant.

S-state wave functions are spherically symmetric.

Some s-state wave functions (radial part):



$|\psi_{20}(r, \theta, \phi)|^2$:

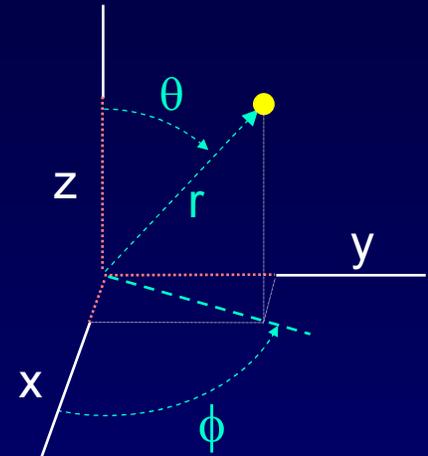


Total Wave Function of the H-atom

We will now consider non-zero values of the other two quantum numbers: l and m .

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_{lm}(\theta, \phi)$$

- n “principal” ($n \geq 1$)
 - l “orbital” ($0 \leq l < n-1$)
 - m “magnetic” ($-l \leq m \leq +l$)
- } *



The $Y_{lm}(\theta, \phi)$ are known as “spherical harmonics”.

They are related to the angular momentum of the electron.

* The constraints on l and m come from the boundary conditions one must impose on the solutions to the Schrodinger equation. We'll discuss them briefly.

Quantized Angular Momentum

Linear momentum depends on the wavelength ($k=2\pi/\lambda$):

$$p = \hbar k \text{ where } \psi(x) \propto e^{ikx}$$

Angular momentum depends on the tangential component of the momentum. Therefore L_z depends on the wavelength as one moves around a circle in the x-y plane. Therefore, a state with L_z has a similar form:

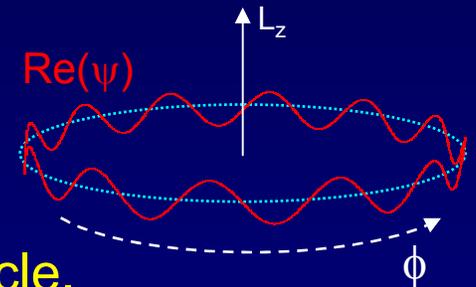
$$L_z = m\hbar \text{ where } \psi(\vec{r}) \propto Y_{lm}(\theta, \phi) \propto e^{im\phi}$$

We're ignoring $R(r)$ for now.

An important boundary condition:

An integer number of wavelengths must fit around the circle.

Otherwise, the wave function is not single-valued.



Reminder:

$$e^{im\phi} = \cos(m\phi) + i \sin(m\phi)$$

This implies that $m = 0, \pm 1, \pm 2, \pm 3, \dots$

and $L_z = 0, \pm\hbar, \pm 2\hbar, \pm 3\hbar, \dots$

Angular momentum is quantized!!

The l Quantum Number

The quantum number m reflects the component of angular momentum about a given axis.

$$L_z = m\hbar \text{ where } m = 0, \pm 1, \pm 2, \dots$$

In the angular wave function $\psi_{lm}(\theta, \phi)$ the quantum number l tells us the total angular momentum L .

$L^2 = L_x^2 + L_y^2 + L_z^2$ is also quantized. The possible values of L^2 are:

$$L^2 = l(l+1)\hbar^2 \text{ where } l = 0, 1, 2, \dots$$

Wave functions can be eigenstates of both L^2 and L_z .

For spherically symmetric potentials, like H-atom, they can also be eigenstates of E . Such states are called “orbitals”.

Summary of quantum numbers for the H-atom orbitals:

Principal quantum number:	$n = 1, 2, 3, \dots$
Orbital quantum number:	$l = 0, 1, 2, \dots, n-1$
Orbital ‘magnetic’ quantum number:	$m = -l, -(l-1), \dots, 0, \dots, (l-1), l$

Angular Momentum & Uncertainty Principle

Note that $L^2 = l(l+1)\hbar^2$ not $(l\hbar)^2$

Also, we describe angular momentum using only two numbers, l and m .

Q: Why can't we specify all three components (e.g., $L = (0,0,l)$) so that $L^2 = l^2$?

A: The uncertainty principle doesn't allow us to know that both $L_x = 0$ and $L_y = 0$ unless $L_z = 0$ also.

Proof by contradiction: Assume $L = (0,0,l)$.

$\vec{L} = \vec{r} \times \vec{p}$, so if L points along the z-axis, both r and p lie in the x-y plane. This means that $\Delta z = 0$ and $\Delta p_z = 0$, violating the uncertainty principle.

Thus, L must have a nonzero L_x or L_y , making L^2 somewhat larger.

We can't specify all three components of the angular momentum vector.

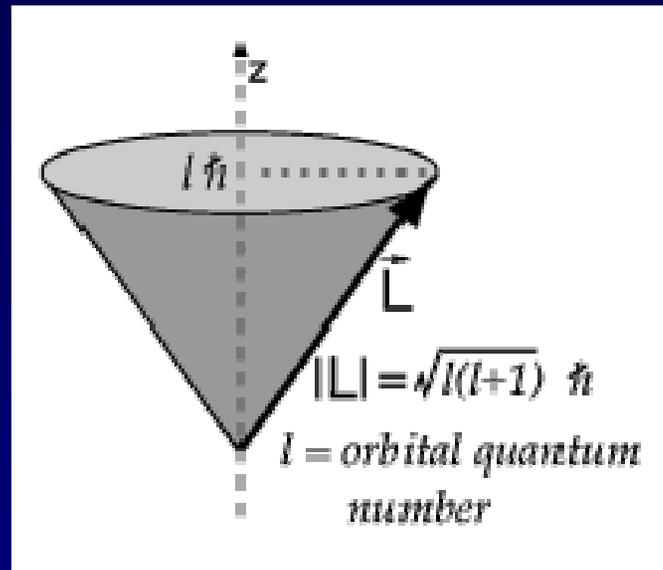
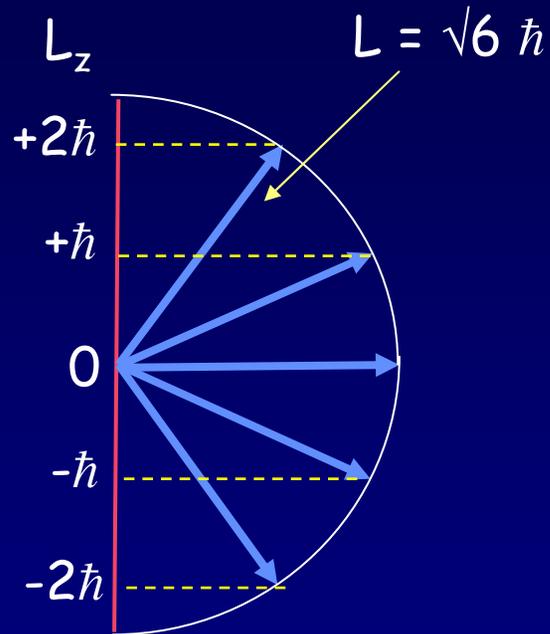
This logic only works for $L \neq 0$. $L = (0,0,0)$ is allowed. It's the s-state.

All physical quantities are subject to uncertainty relations, not just position and momentum.

Classical Picture of L-Quantization

e.g., $l = 2$

$$L = \sqrt{l(l+1)\hbar^2} = \sqrt{2(2+1)\hbar^2} = \sqrt{6}\hbar$$



$$\vec{L} = \vec{r} \times \vec{p}$$

Act 2

We've just seen that we cannot have the total orbital angular momentum vector of an atom pointing definitely along the z-axis.

If we measure $L_z = \hbar$, what can we say about L_x , the x-component of the angular momentum?

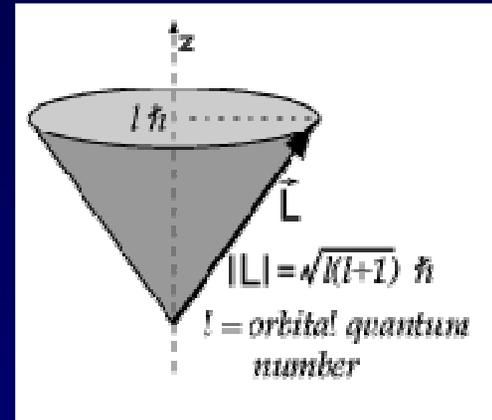
- a) $L_x = 0$
- b) $L_x = \hbar$
- c) $L_x = -\hbar$
- d) any of the above
- e) none of the above

Solution

We've just seen that we cannot have the total orbital angular momentum vector of an atom pointing definitely along the z-axis.

If we measure $L_z = \hbar$, what can we say about L_x , the x-component of the angular momentum?

- a) $L_x = 0$
- b) $L_x = \hbar$
- c) $L_x = -\hbar$
- d) any of the above**
- e) none of the above



As soon as we determine the angular momentum projection along one axis, we lose definite knowledge of its value along any perpendicular axis. We will again find $L_x = m \hbar$, but we don't know what m is until we do the measurement. And if we find $m = 1$, i.e., $L_x = m \hbar$, then we won't know anything about L_z except that $L_z = m \hbar$, where again we don't know m .

Next Time

Electron orbitals in atoms

Electron 'spin' and the Stern-Gerlach experiment

Next Week

Multi-electron atoms

Covalent bonds in molecules

Electron energy bands in solids

QM in everyday life

Supplement: Why Radial Probability Isn't the Same as Volume Probability

Let's look at the $n=1, l=0$ state (the "1s" state): $\psi(r,\theta,\phi) \propto R_{10}(r) \propto e^{-r/a_0}$.

So, $P(r,\theta,\phi) = \psi^2 \propto e^{-2r/a_0}$.

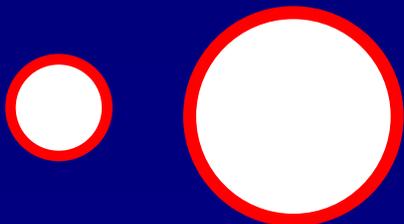
This is the volume probability density.

If we want the radial probability density, we must remember that:

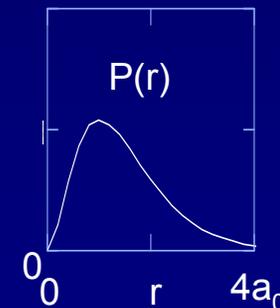
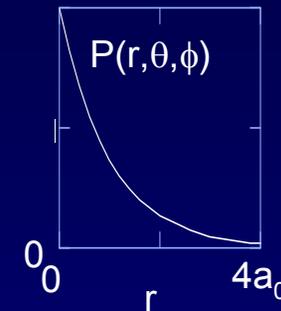
$$dV = r^2 dr \sin\theta d\theta d\phi$$

We're not interested in the angular distribution, so to calculate $P(r)$ we must integrate over θ and ϕ . The s-state has no angular dependence, so the integral is just 4π . Therefore, $P(r) \propto r^2 e^{-2r/a_0}$.

The factor of r^2 is due to the fact that there is more volume at large r . A spherical shell at large r has more volume than one at small r :



Compare the volume of the two shells of the same thickness, dr .



Appendix: Solving the 'Radial' SEQ for H --deriving a_0 and E

- Substituting $R(r) = Ne^{-\alpha r}$ into $\left(\frac{-\hbar^2}{2m} \frac{1}{r} \frac{\partial^2}{\partial r^2} r - \frac{\kappa e^2}{r} \right) R(r) = ER(r)$, we get:

$$\frac{-\hbar^2}{2m} \frac{1}{r} \left(-2\alpha e^{-\alpha r} + \alpha^2 r e^{-\alpha r} \right) - \frac{\kappa e^2}{r} e^{-\alpha r} = E e^{-\alpha r}$$

- For this equation to hold for all r , we must have:

$$\frac{\hbar^2 \alpha}{m} = \kappa e^2 \quad \text{AND} \quad \frac{-\hbar^2 \alpha^2}{2m} = E$$



$$\alpha = \frac{m \kappa e^2}{\hbar^2} \equiv \frac{1}{a_0} \quad \longrightarrow \quad E = \frac{-\hbar^2}{2m a_0^2}$$

- Evaluating the ground state energy:

$$E = \frac{-\hbar^2}{2m a_0^2} = \frac{-\hbar^2 c^2}{2m c^2 a_0^2} = \frac{-(197)^2}{2(51)(10^6)(.053)^2} = -13.6 \text{ eV}$$