

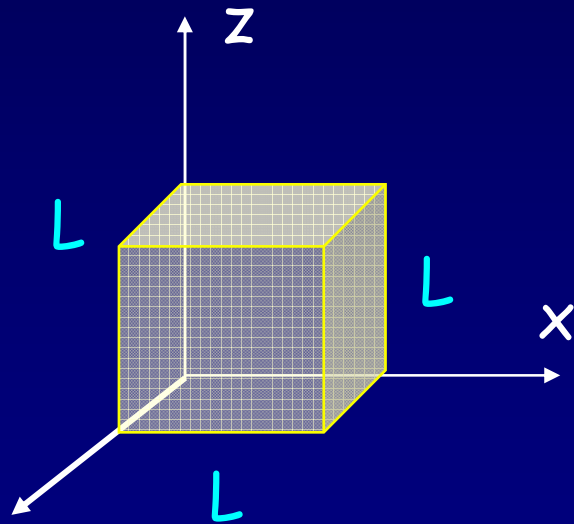
"It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper, and it came back to hit you!"

--E. Rutherford

(on the 'discovery'
of the nucleus)

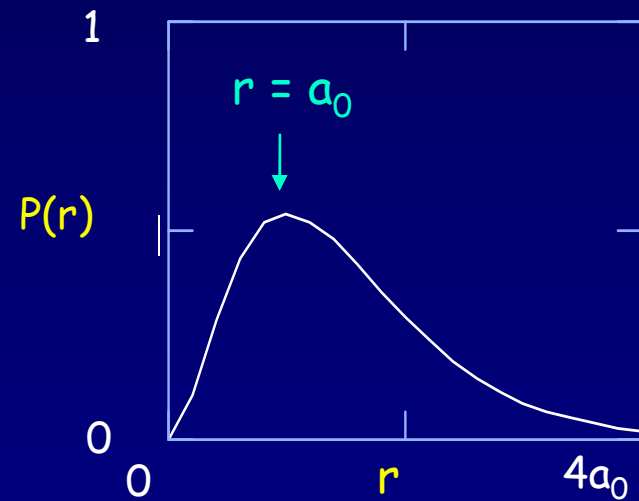
Lecture 16: 3D Potentials and the Hydrogen Atom

$$\psi(x, y, z) = \varphi(x)\varphi(y)\varphi(z)$$



$$E_{n_x n_y n_z} = \frac{h^2}{8mL^2} \cdot (n_x^2 + n_y^2 + n_z^2)$$

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



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

Overview of the Course

Up to now:

- General properties and equations of quantum mechanics
- Time-independent Schrodinger's Equation (SEQ) and eigenstates.
- Time-dependent SEQ, superposition of eigenstates, time dependence.
- Collapse of the wave function
- Tunneling

This week:

- 3 dimensions, angular momentum, electron spin, H atom
- Exclusion principle, periodic table of atoms

Next week:

- Molecules and solids, consequences of Q. M., Schrodinger's cat
- Metals, insulators, semiconductors, superconductors, lasers, . .

Final Exam: Monday, Mar. 4

Homework 6: Due Saturday (March 2), 8 am

Today

3-Dimensional Potential Well:

- Product Wave Functions
- Degeneracy

Schrödinger's Equation for the Hydrogen Atom:

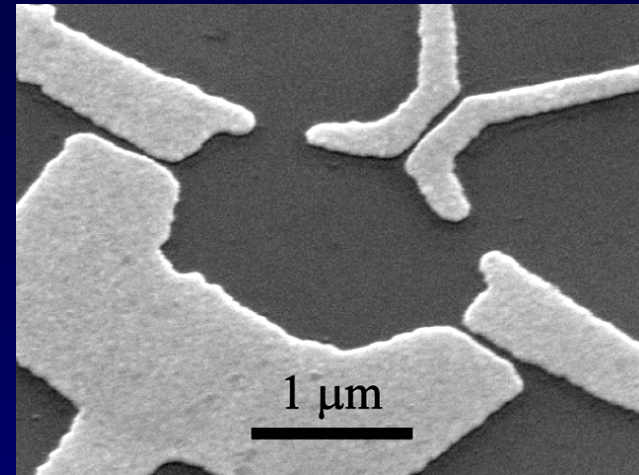
- Semi-quantitative picture from uncertainty principle
- Ground state solution*
- Spherically-symmetric excited states ("s-states")*

*contains details beyond what we expect you to know on exams.

Quantum Particles in 3D Potentials

So far, we have considered quantum particles bound in one-dimensional potentials. This situation can be applicable to certain physical systems but it lacks some of the features of most real 3D quantum systems, such as atoms and artificial structures.

A real (2D) “quantum dot”



<http://pages.unibas.ch/phys-meso/Pictures/pictures.html>

One consequence of confining a quantum particle in two or three dimensions is “degeneracy” -- the existence of several quantum states at the same energy.

To illustrate this important point in a simple system, let's extend our favorite potential - the infinite square well - to three dimensions.

Particle in a 3D Box (1)

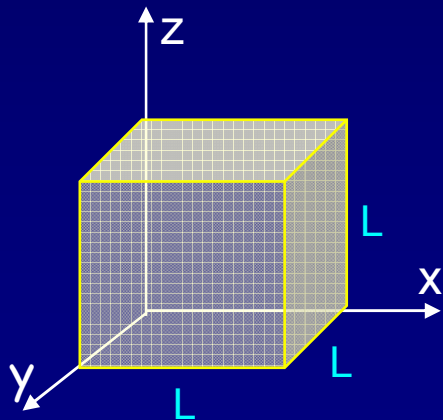
The extension of the Schrödinger Equation (SEQ) to 3D is straightforward in Cartesian (x,y,z) coordinates:

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

where $\psi \equiv \psi(x,y,z)$

Kinetic energy term: $\frac{1}{2m}(p_x^2 + p_y^2 + p_z^2)$

Let's solve this SEQ for the particle in a 3D cubical box:



$$U(x,y,z) = \begin{cases} \infty & \text{outside box, } x \text{ or } y \text{ or } z < 0 \\ 0 & \text{inside box} \\ \infty & \text{outside box, } x \text{ or } y \text{ or } z > L \end{cases}$$

This $U(x,y,z)$ can be “separated”:
 $U(x,y,z) = U(x) + U(y) + U(z)$

$U = \infty$ if any of the three terms = ∞ .

Particle in a 3D Box (2)

Whenever $U(x,y,z)$ can be written as the sum of functions of the individual coordinates, we can write some wave functions as products of functions of the individual coordinates: (see the supplementary slides)

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

For the 3D square well, each function is simply the solution to the 1D square well problem:

$$f_{n_x}(x) = N \sin\left(\frac{n_x \pi}{L} x\right) \quad E_{n_x} = \frac{h^2}{2m} \cdot \left(\frac{n_x}{2L}\right)^2$$

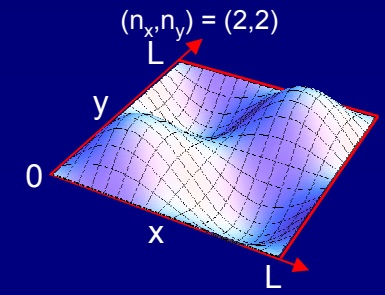
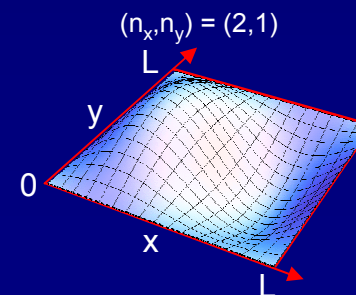
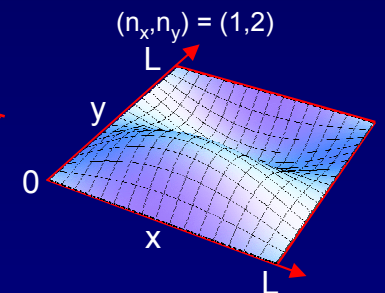
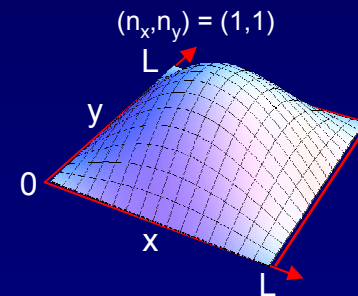
Similarly for y and z .

Each function contributes to the energy. The total energy is the sum:

$$E_{\text{total}} = E_x + E_y + E_z$$

2D wave functions:

$$\sin\left(\frac{n_x \pi}{L} x\right) \sin\left(\frac{n_y \pi}{L} y\right)$$

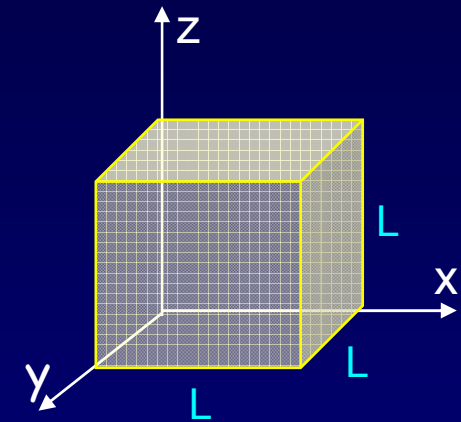


Particle in a 3D Box (3)

The energy eigenstates and energy values in a 3D cubical box are:

$$\psi = N \sin\left(\frac{n_x \pi}{L} x\right) \sin\left(\frac{n_y \pi}{L} y\right) \sin\left(\frac{n_z \pi}{L} z\right)$$
$$E_{n_x n_y n_z} = \frac{h^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2)$$

where $n_x, n_y,$ and n_z can each have values 1,2,3,.....



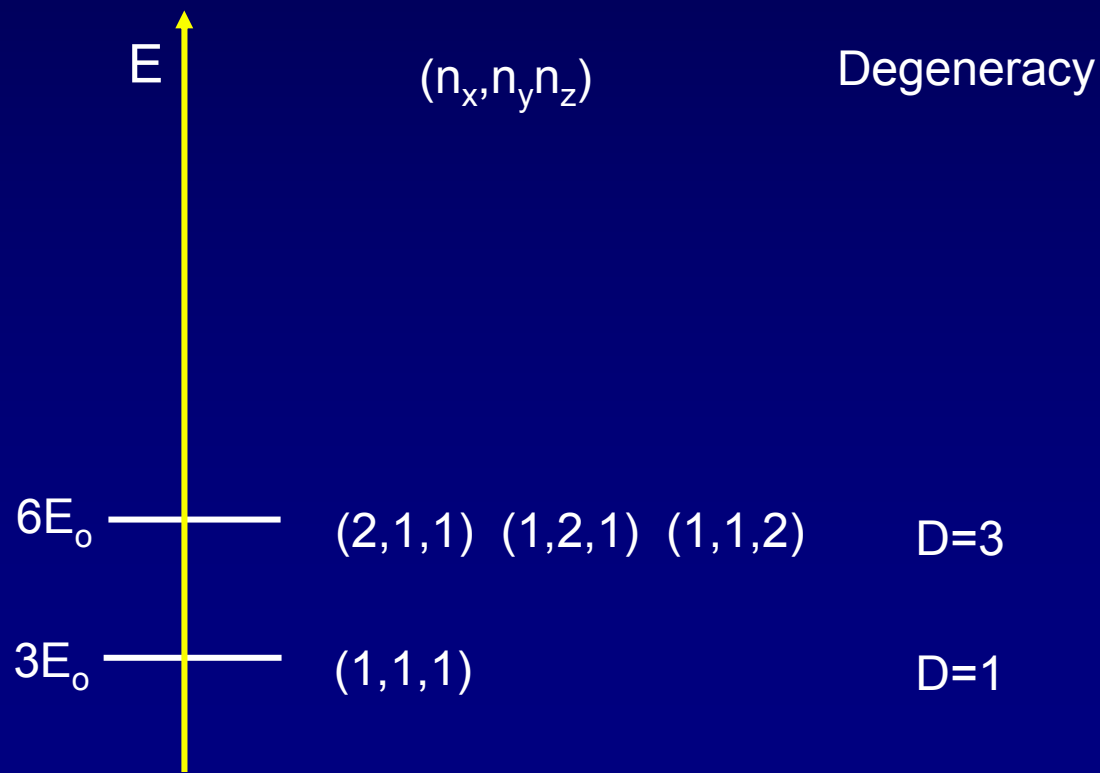
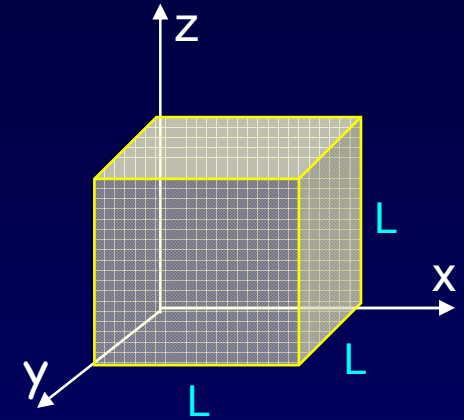
This problem illustrates two important points:

- Three quantum numbers (n_x, n_y, n_z) are needed to identify the state of this three-dimensional system.
That is true for every 3D system.
- More than one state can have the same energy: “Degeneracy”.
Degeneracy reflects an underlying symmetry in the problem.
3 equivalent directions, because it’s a cube, not a rectangle.

Cubical Box Exercise

Consider a 3D cubical box:

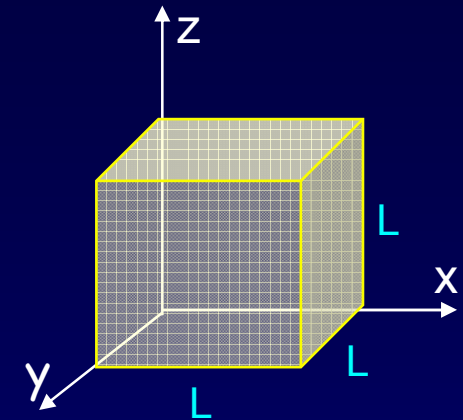
Show energies and label (n_x, n_y, n_z) for the first 11 states of the particle in the 3D box, and write the degeneracy, D , for each allowed energy. Define $E_0 = h^2/8mL^2$.



Solution

Consider a 3D cubic box:

Show energies and label (n_x, n_y, n_z) for the first 11 states of the particle in the 3D box, and write the degeneracy, D , for each allowed energy. Define $E_0 = h^2/8mL^2$.



E	(n_x, n_y, n_z)	Degeneracy
$12E_0$	$(2, 2, 2)$	$D=1$
$11E_0$	$(3, 1, 1)$ $(1, 3, 1)$ $(1, 1, 3)$	$D=3$
$9E_0$	$(2, 2, 1)$ $(2, 1, 2)$ $(1, 2, 2)$	$D=3$
$6E_0$	$(2, 1, 1)$ $(1, 2, 1)$ $(1, 1, 2)$	$D=3$
$3E_0$	$(1, 1, 1)$	$D=1$

$$E_{n_x n_y n_z} = \frac{h^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2)$$

$$n_x, n_y, n_z = 1, 2, 3, \dots$$

Act 1

For a cubical box, we just saw that the 5th energy level is at $12 E_0$, with a degeneracy of 1 and quantum numbers (2,2,2).

1. What is the energy of the next energy level?

- a. $13E_0$ b. $14E_0$ c. $15E_0$

2. What is the degeneracy of this energy level?

- a. 2 b. 4 c. 6

Solution

For a cubical box, we just saw that the 5th energy level is at $12 E_0$, with a degeneracy of 1 and quantum numbers (2,2,2).

1. What is the energy of the next energy level?

- a. $13E_0$ **b. $14E_0$** c. $15E_0$

$$E_{1,2,3} = E_0 (1^2 + 2^2 + 3^2) = 14 E_0$$

2. What is the degeneracy of this energy level?

- a. 2 **b. 4** c. 6

Solution

For a cubical box, we just saw that the 5th energy level is at $12 E_0$, with a degeneracy of 1 and quantum numbers (2,2,2).

1. What is the energy of the next energy level?

- a. $13E_0$ **b. $14E_0$** c. $15E_0$

$$E_{1,2,3} = E_0 (1^2 + 2^2 + 3^2) = 14 E_0$$

2. What is the degeneracy of this energy level?

- a. 2 b. 4 **c. 6**

Any ordering of the three numbers will give the same energy. Because they are all different (distinguishable), the answer is $3! = 6$.

Question:

Is it possible to have $D > 6$?

Hint: Consider $E = 62E_0$.

Another 3D System: The Atom

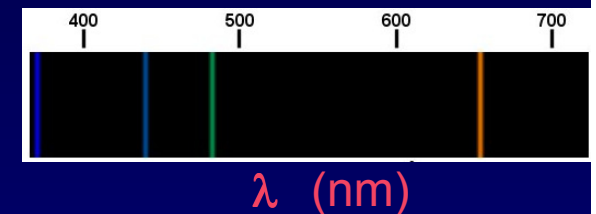
-electrons confined in Coulomb field of a nucleus

Early hints of the quantum nature of atoms:

Discrete Emission and Absorption spectra

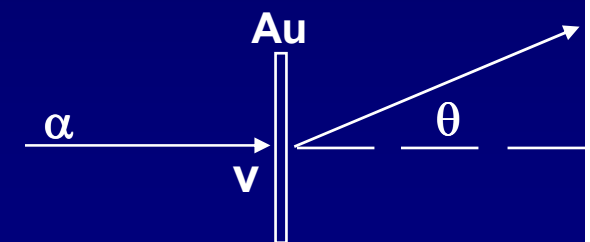
- When excited in an electrical discharge, atoms emit radiation only at discrete wavelengths
- Different emission spectra for different atoms

Atomic hydrogen



Geiger-Marsden (Rutherford) Experiment (1911):

- Measured angular dependence of a particles (He ions) scattered from gold foil.
- Mostly scattering at small angles \rightarrow supported the "plum pudding" model. But...
- Occasional scatterings at large angles \rightarrow Something massive in there!

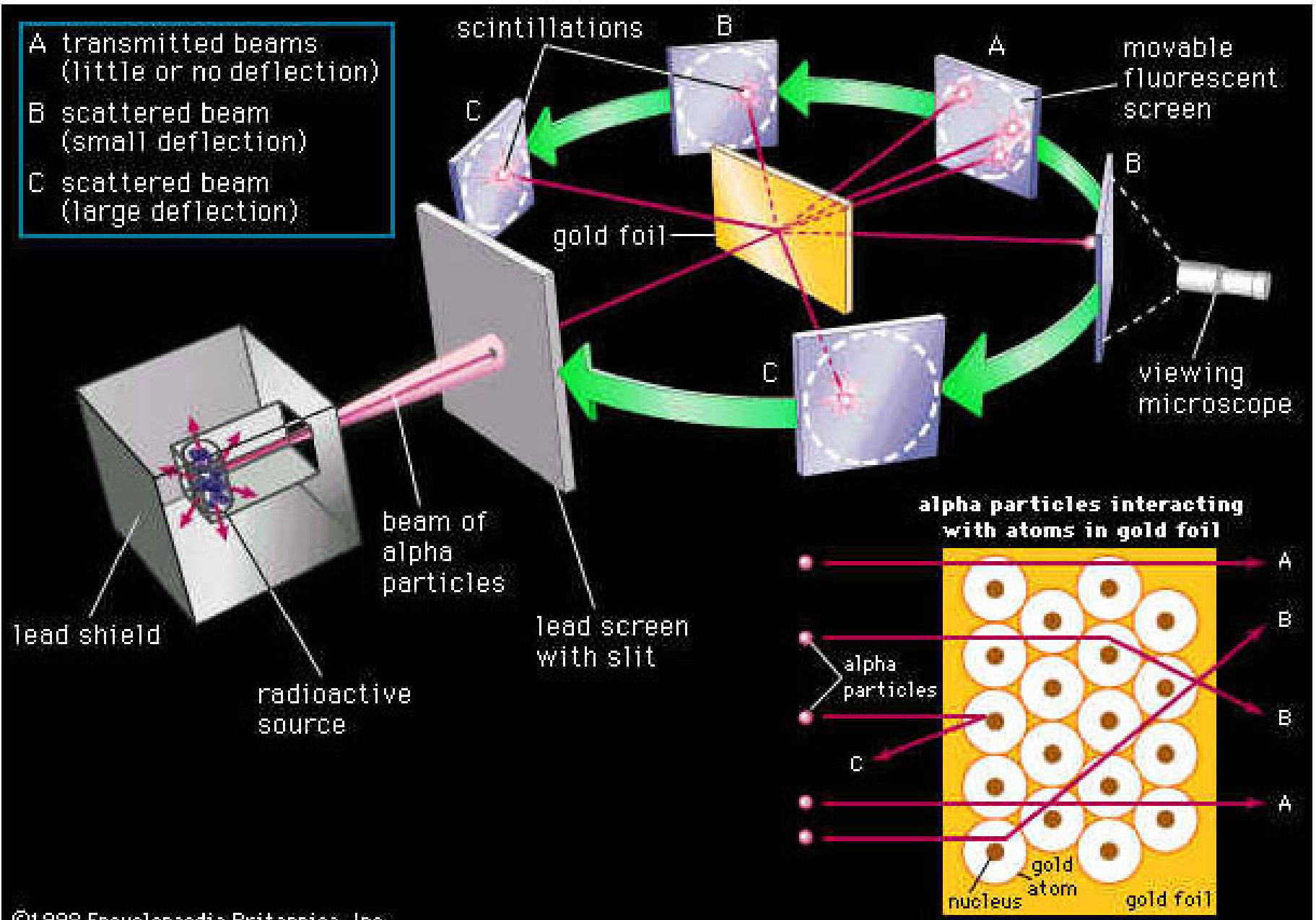


- **Conclusion:** Most of atomic mass is concentrated in a small region of the atom

\rightarrow a nucleus!

Rutherford Experiment

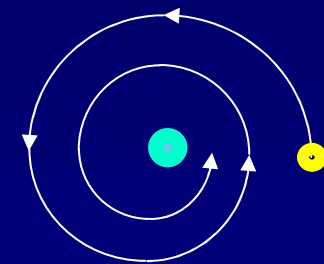
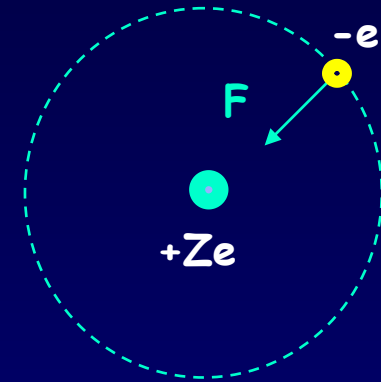
- A transmitted beams (little or no deflection)
- B scattered beam (small deflection)
- C scattered beam (large deflection)



Atoms: Classical Planetary Model

(An early model of the atom)

- **Classical picture:** negatively charged objects (electrons) orbit positively charged nucleus due to Coulomb force.
- There is a **BIG PROBLEM** with this:
 - As the electron moves in its circular orbit, it is **ACCELERATING**.
 - As you learned in Physics 212, accelerating charges radiate electromagnetic energy.
 - Consequently, an electron would continuously lose energy and spiral into the nucleus in about 10^{-9} sec.



➔ The planetary model doesn't lead to stable atoms.

Hydrogen Atom - Qualitative

Why doesn't the electron collapse into the nucleus, where its potential energy is lowest?

We must balance two effects:

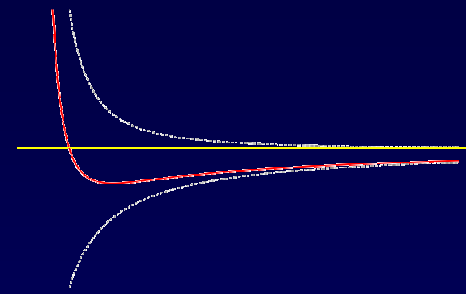
- As the electron moves closer to the nucleus, its potential energy decreases (more negative):
- However, as it becomes more and more confined, its kinetic energy increases:

$$U = -\frac{\kappa e^2}{r}$$

$$p \approx \frac{\hbar}{r} \Rightarrow KE \approx \frac{\hbar^2}{2mr^2}$$

Therefore, the total energy is:

$$E = KE + PE \approx \frac{\hbar^2}{2mr^2} - \frac{\kappa e^2}{r}$$



E has a minimum at:

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

The "Bohr radius" of the H atom.

At this radius,

$$E \approx -\frac{m\kappa^2 e^4}{2\hbar^2} = -13.6 \text{ eV}$$

The ground state energy of the hydrogen atom.

Heisenberg's uncertainty principle prevents the atom's collapse.

One factor of e or e^2 comes from the proton charge, and one from the electron.

Potential Energy in the Hydrogen Atom

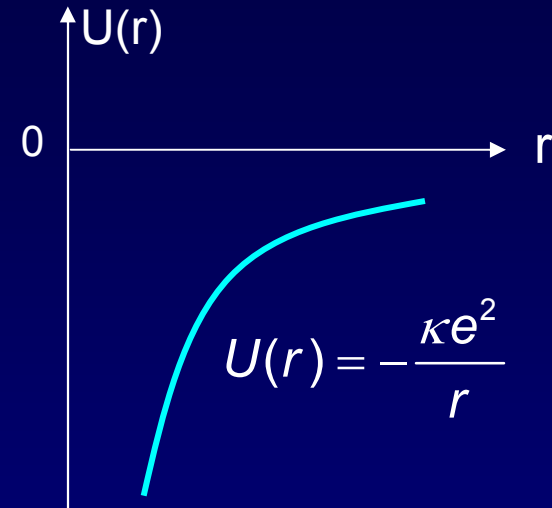
To solve this problem, we must specify the potential energy of the electron. In an atom, the **Coulomb force** binds the electron to the nucleus.

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:

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



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

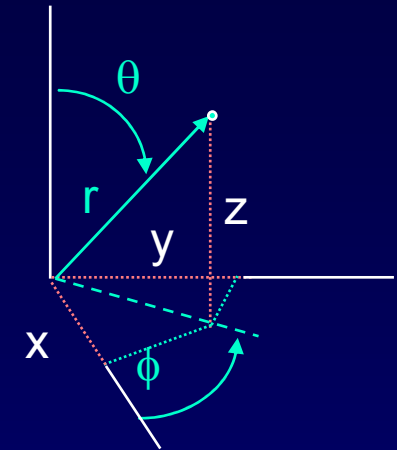
Question:

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). We will show you the solutions and discuss 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.”

Today, 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:

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

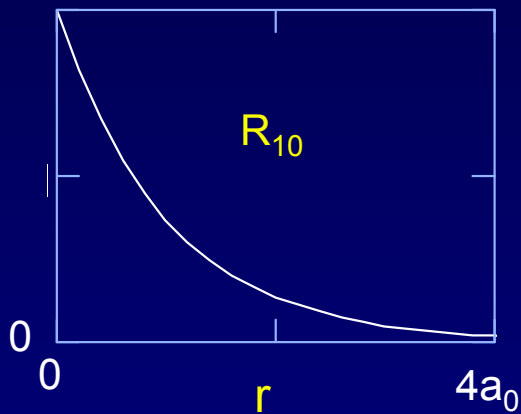
These are states in which the electron has no orbital angular momentum. This is not possible in Newtonian physics. (Why?)

Note:

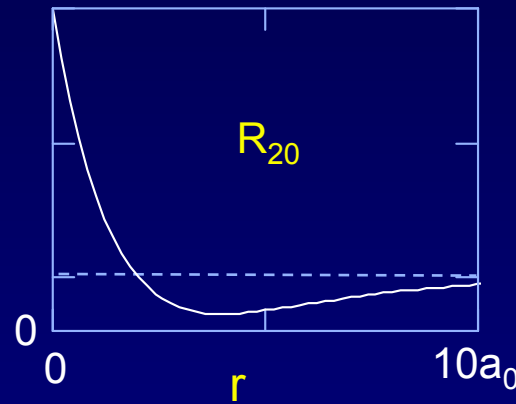
Some of this nomenclature dates back to the 19th century, and has no physical significance.

Radial Eigenstates of Hydrogen

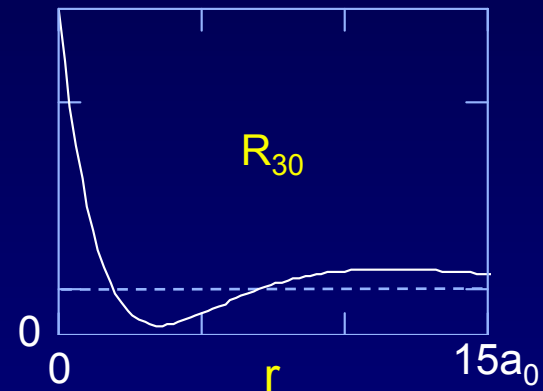
Here are graphs of the s-state wave functions, $R_{n0}(r)$, for the electron in the Coulomb potential of the proton. The zeros in the subscripts are a reminder that these are states with $l = 0$ (zero angular momentum!).



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



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



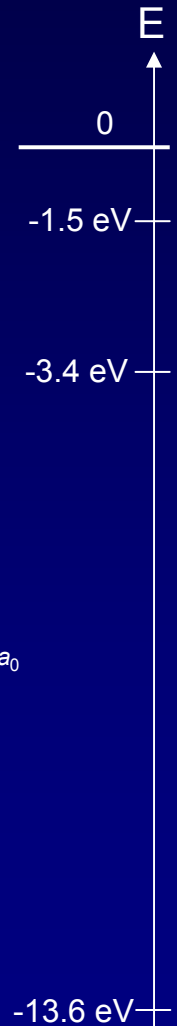
$$R_{3,0}(r) \propto \left(3 - \frac{2r}{a_0} + 2\left(\frac{r}{3a_0}\right)^2\right) e^{-r/3a_0}$$

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

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

You will not need to memorize these functions.

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



ACT 2: 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.

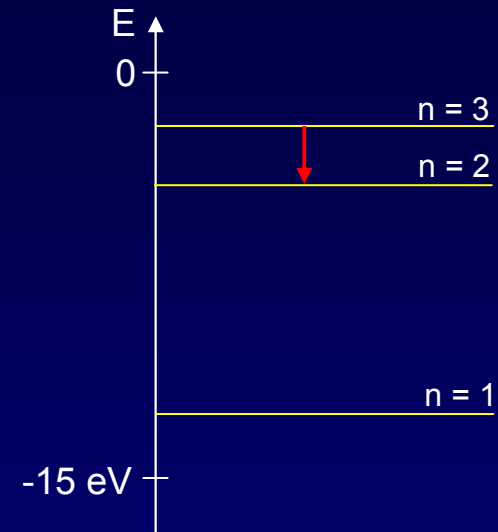
1) What is the energy of the emitted photon?

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

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

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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.

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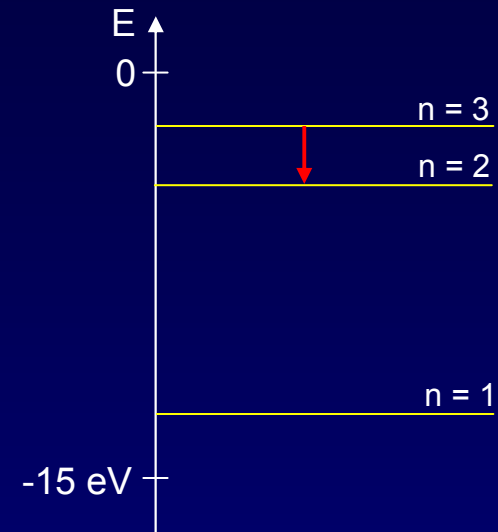
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2) What is the wavelength of the emitted photon?

- 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.

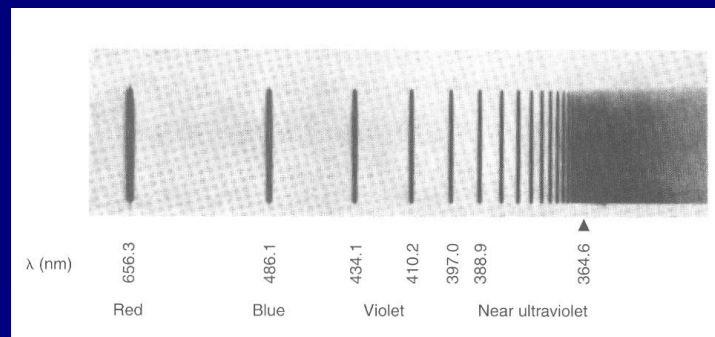
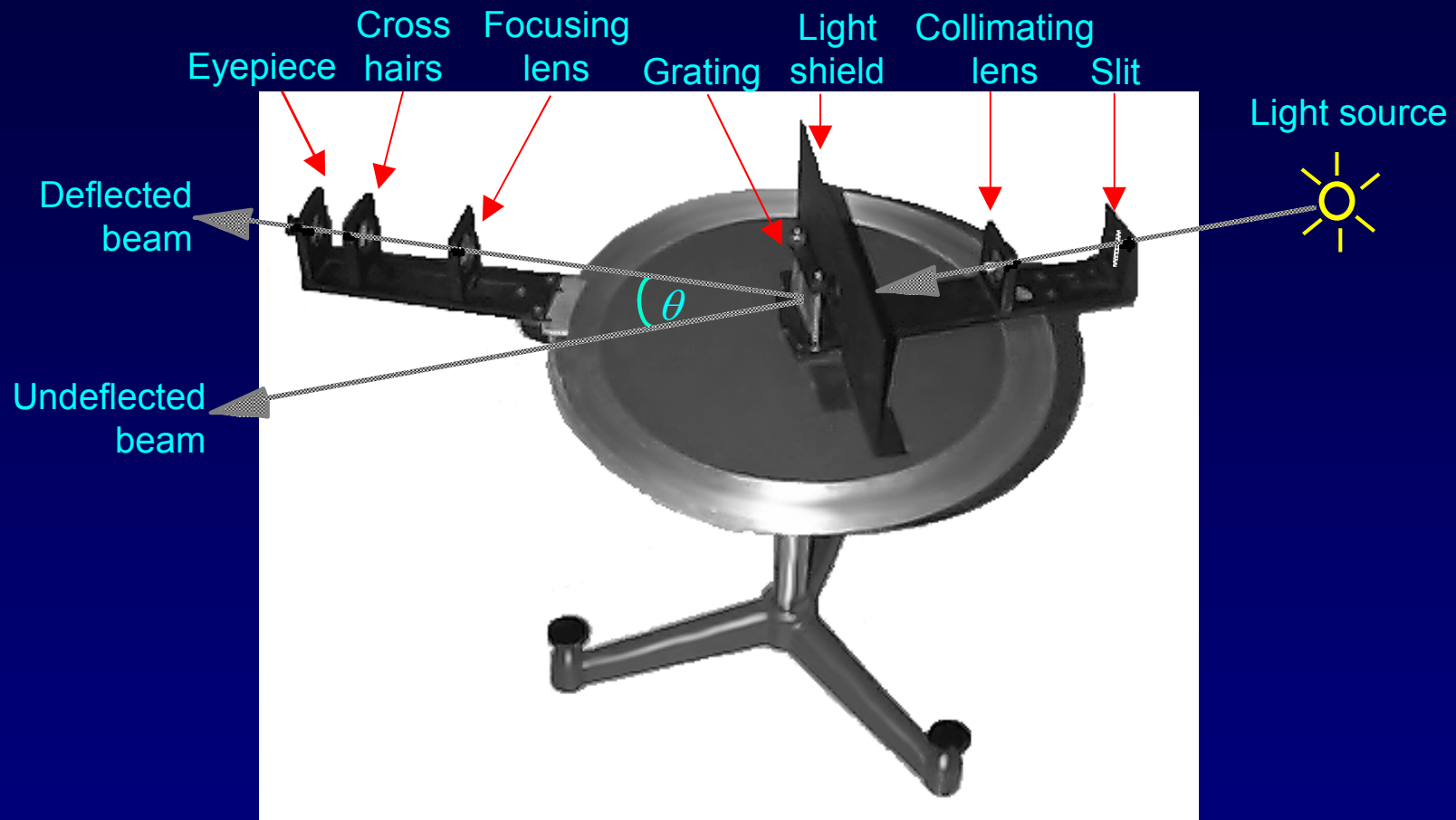


Atomic hydrogen



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

Next week: Laboratory 4



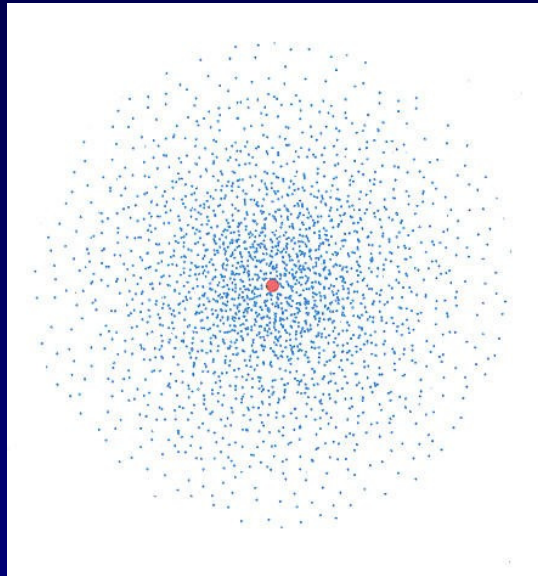
$$E_n = \frac{-13.6\text{eV}}{n^2}$$

Probability Density of Electrons

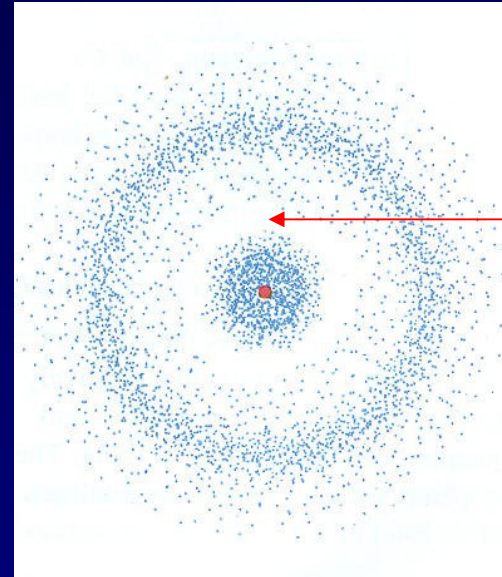
$|\psi|^2 = \text{Probability density} = \text{Probability per unit volume} \propto R_{n0}^2$ for s-states.

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

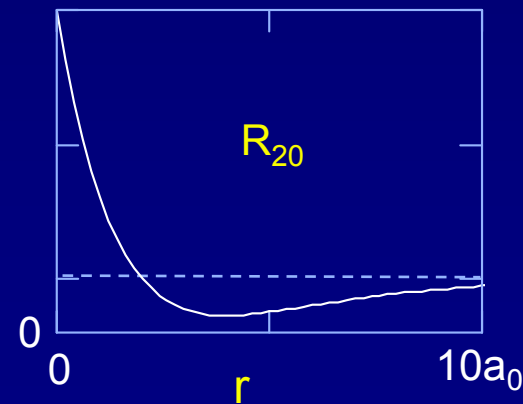
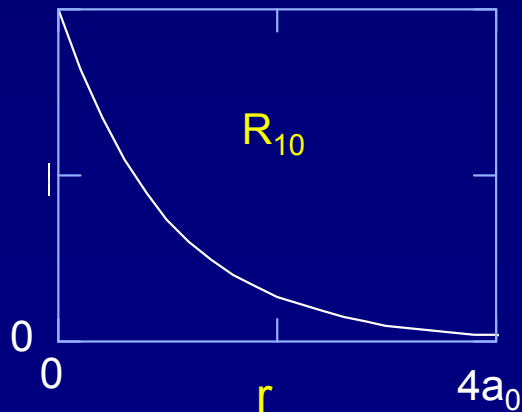
1s state



2s state

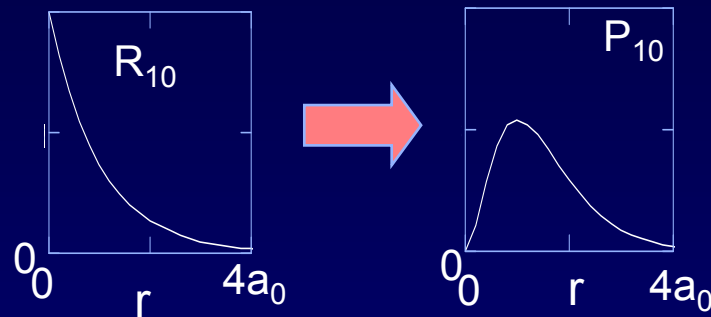


A node in the radial probability distribution.



Radial Probability Densities for S-states

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



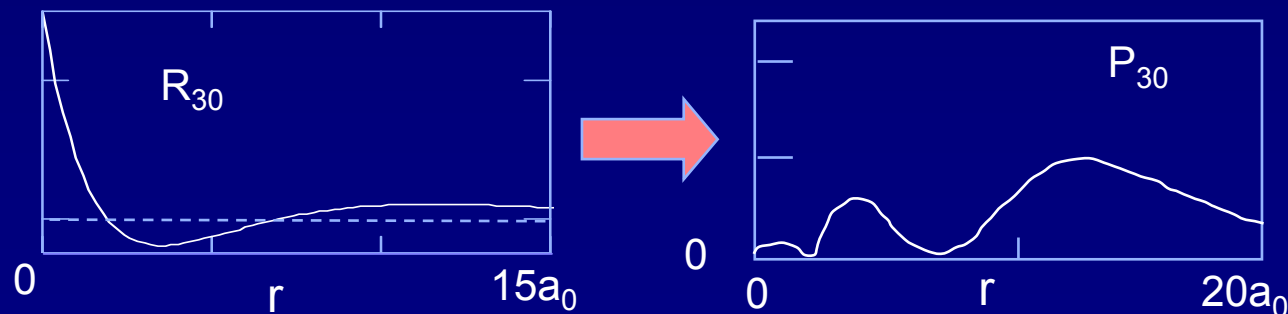
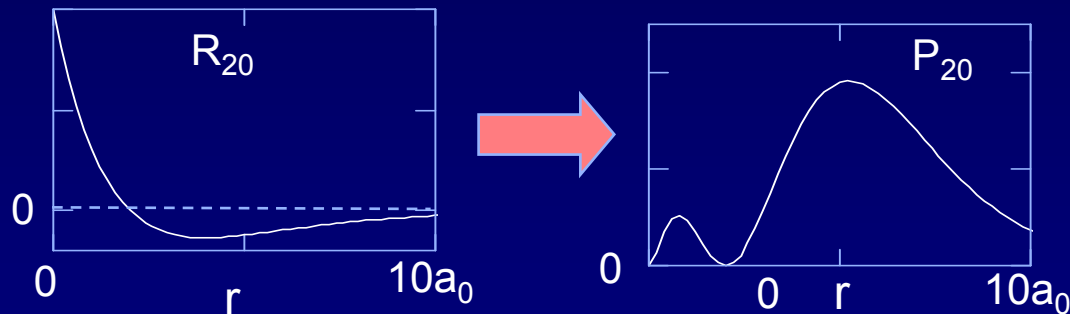
The radial probability density has an extra factor of r^2 because there is more volume at large r . That is, $P_{n0}(r) \propto r^2 R_{n0}^2$.

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/>

Next Lectures

Angular momentum

“Spin”

Nuclear Magnetic Resonance

Supplement: Separation of Variables (1)

In the 3D box, the SEQ is:

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

NOTE:
Partial derivatives.

Let's see if separation of variables works.
Substitute this expression for ψ into the SEQ:

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

$$-\frac{\hbar^2}{2m} \left(gh \frac{d^2 f}{dx^2} + fh \frac{d^2 g}{dy^2} + fg \frac{d^2 h}{dz^2} \right) + (U(x) + U(y) + U(z))fgh = E fgh$$

NOTE:
Total derivatives.

Divide by fgh:

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

Supplement: Separation of Variables (2)

Regroup:

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

A function of x

A function of y

A function of z

We have three functions, each depending on a different variable, that must sum to a constant.

Therefore, each function must be a constant:

$$-\frac{\hbar^2}{2m} \frac{1}{f} \frac{d^2 f}{dx^2} + U(x) = E_x$$

$$-\frac{\hbar^2}{2m} \frac{1}{g} \frac{d^2 g}{dy^2} + U(y) = E_y$$

$$-\frac{\hbar^2}{2m} \frac{1}{h} \frac{d^2 h}{dz^2} + U(z) = E_z$$

$$E_x + E_y + E_z = E$$

Each function, $f(x)$, $g(y)$, and $h(z)$ satisfies its own 1D SEQ.

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

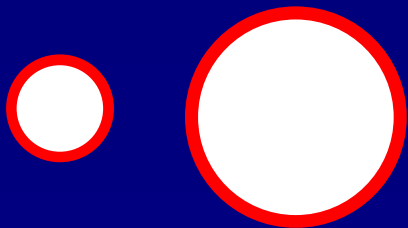
This is the volume probability density.

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

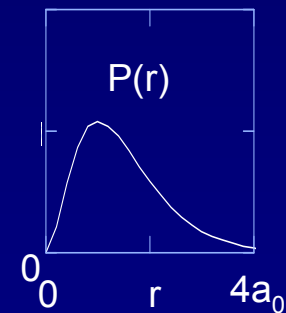
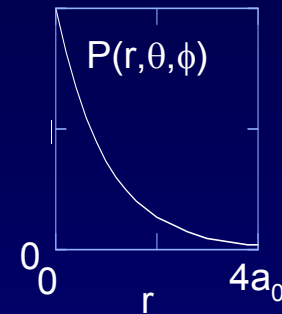
$$dV = r^2 dr \sin\theta d\theta d\phi$$

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:

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