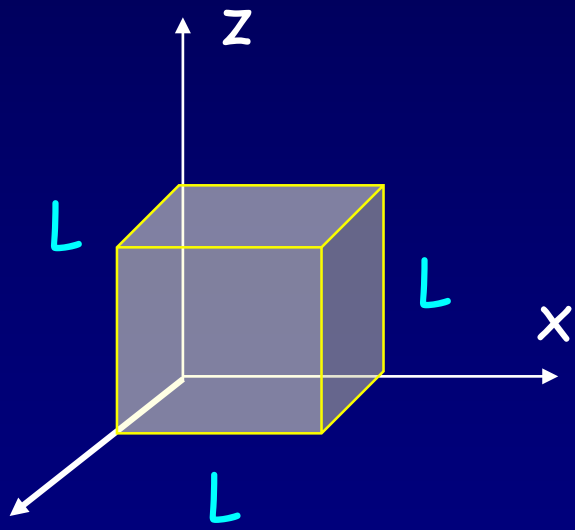
Lecture 16:
3D Potentials and the Hydrogen Atom

3D infinite potential well (cubic)

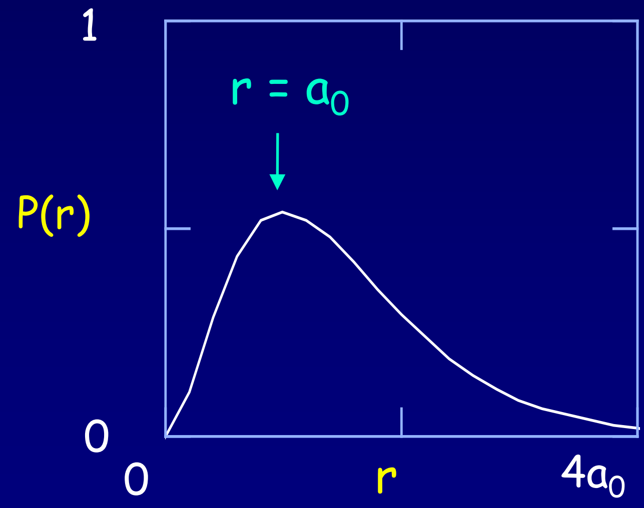
$$\psi(x,y,z)=\varphi(x)\varphi(y)\varphi(z)$$



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

3D Coulomb potential well (hydrogen)

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



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

Today

3-Dimensional Potential Well:

- Separable → Product wave functions
- Degeneracy
- Probability density and normalization

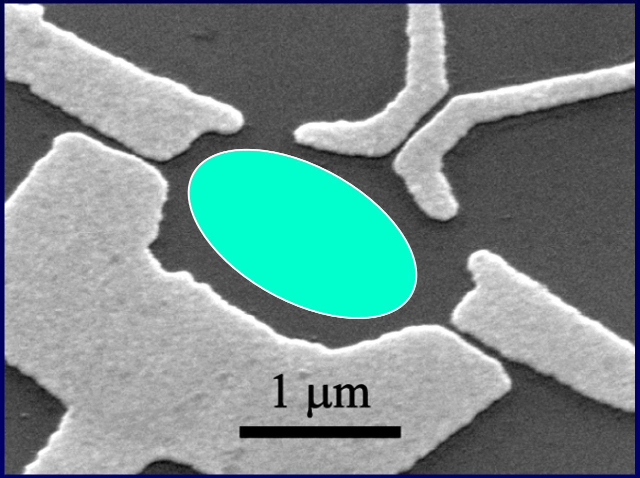
The Hydrogen Atom:

- Early experiments
- Semi-quantitative picture from uncertainty principle
- Hydrogenic ions
- Next time: Separable → Product wave functions

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)

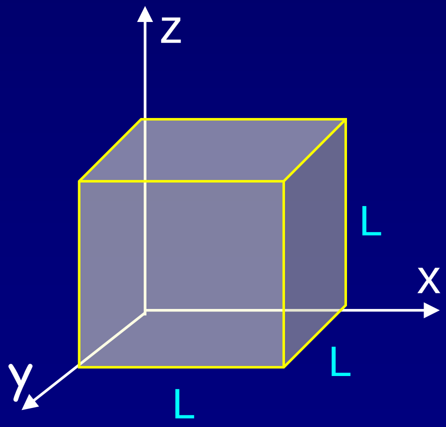
The extension of the Schrödinger Equation (SEQ) to 3D is straightforward in Cartesian (x,y,z) coordinates:

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

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

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

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 = ∞ 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:

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

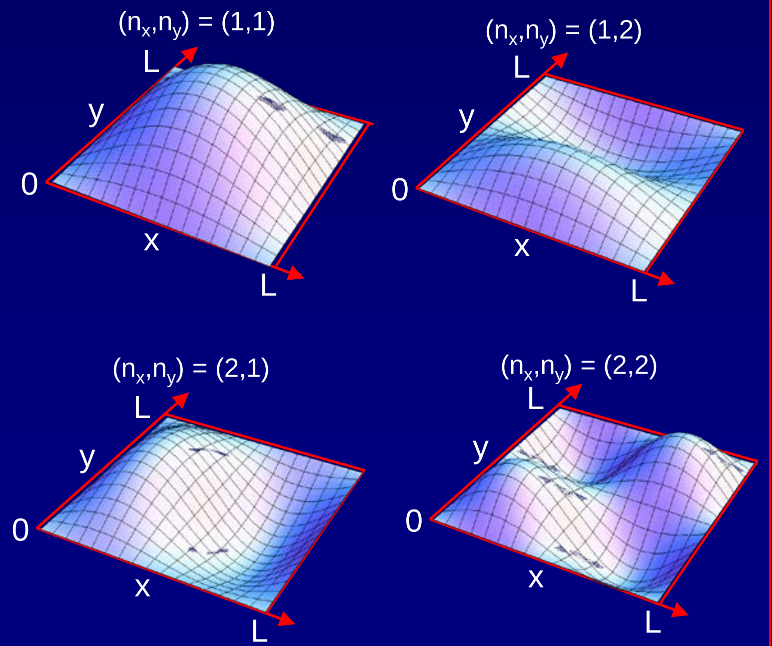
Similarly for y and z.

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

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

2D wave functions:

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



http://www.falstad.com/qm2dbox/

Supplement: Separation of Variables (1)

In the 3D box, the SEQ is:

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

NOTE:
Partial derivatives.

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

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

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

NOTE:
Total derivatives.

Divide by fgh:

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

Supplement: Separation of Variables (2)

Regroup:

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

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:

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

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

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

$$E_x+E_y+E_z=E$$

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

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:

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

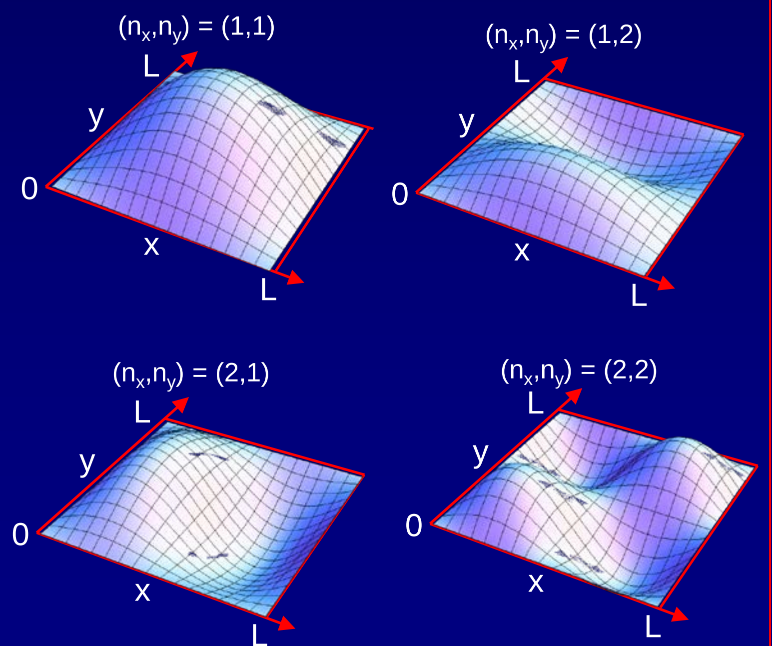
Similarly for y and z.

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

$$\text{Etotal} = E_x + E_y + E_z$$

2D wave functions:

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



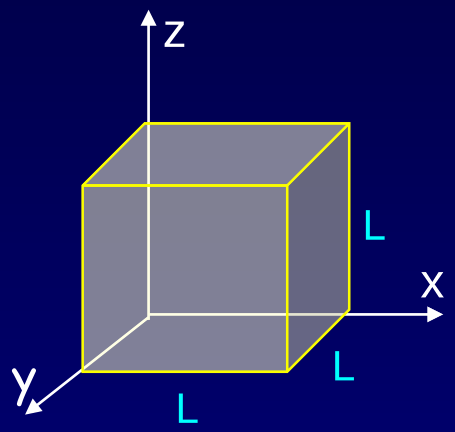
http://www.falstad.com/qm2dbox/

Particle in a 3D Box (3)

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

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

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.

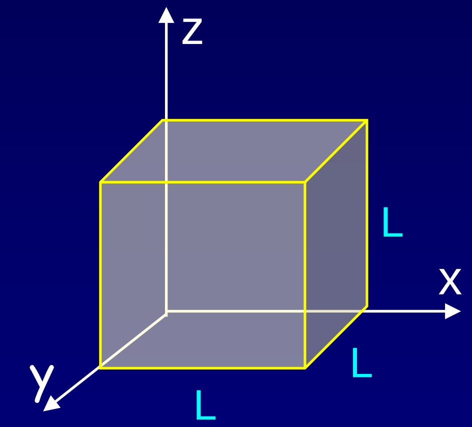
Cubical Box Exercise

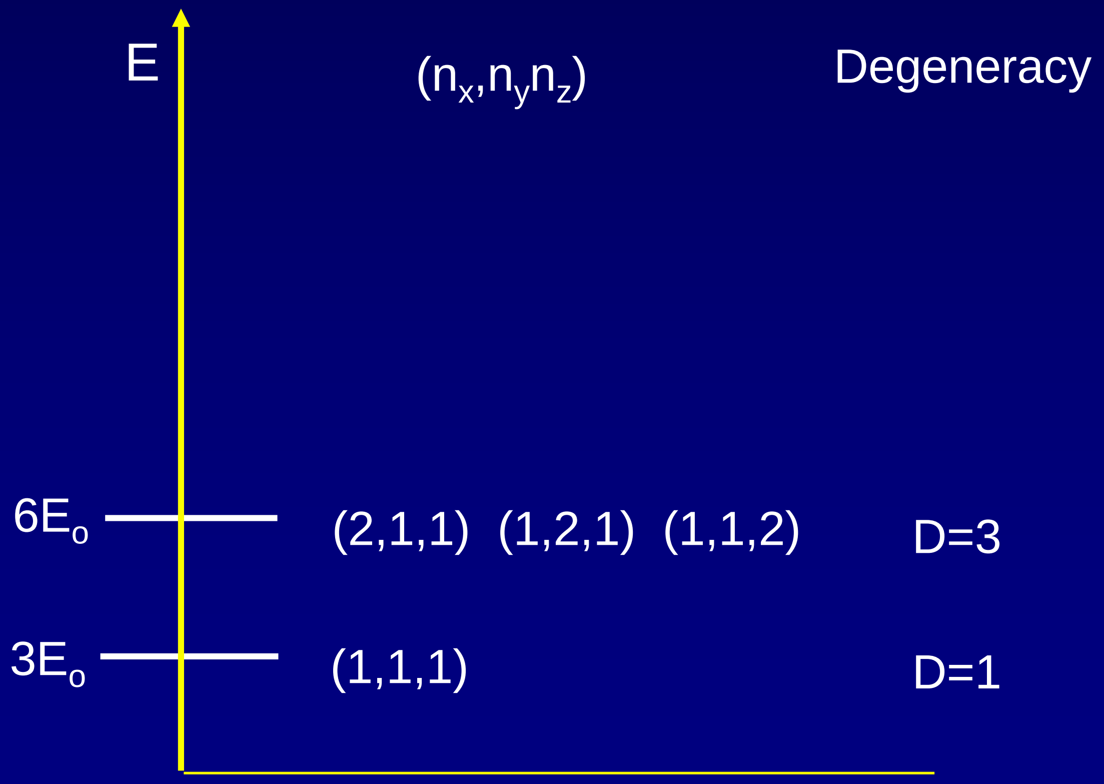
Consider a 3D cubic box:

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 $E_o = h^2/8mL^2$.

$$\psi = N \sin\left(\frac{n_x \pi}{L} x\right) \sin\left(\frac{n_y \pi}{L} y\right) \sin\left(\frac{n_z \pi}{L} z\right)$$

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





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

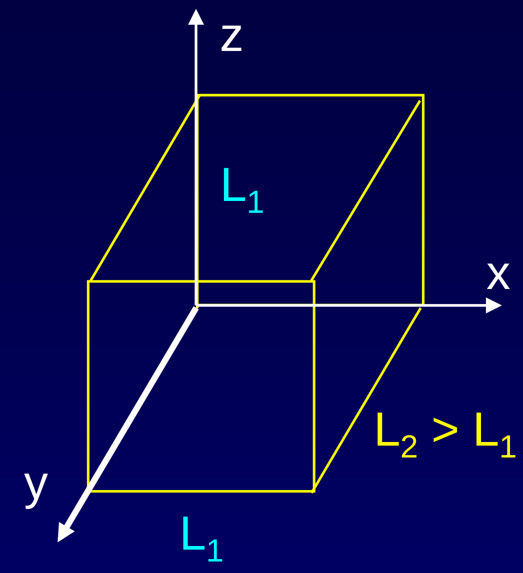
Non-cubic Box

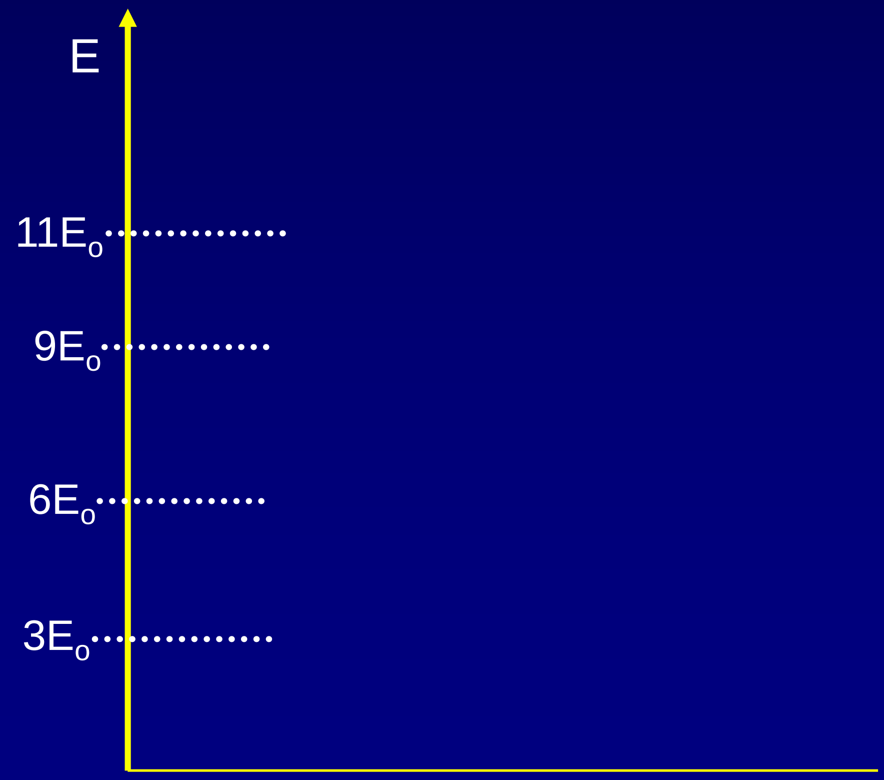
Consider a non-cubic box:

The box is stretched along the y-direction.

What will happen to the energy levels?

Define $E_o = h^2/8mL_1^2$





Act 2

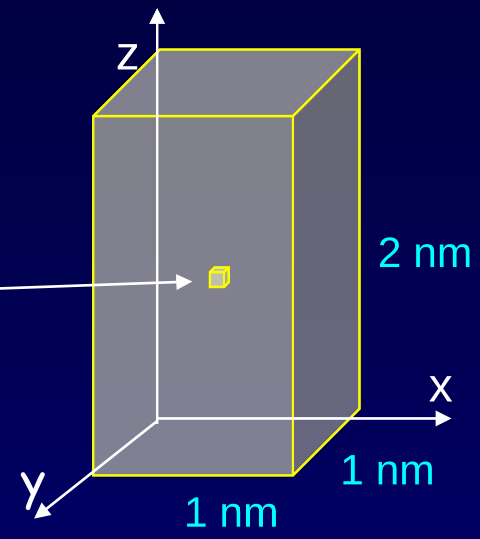
Consider a particle in a 2D well, with $L_x = L_y = L$.

1. Compare the energies of the (2,2), (1,3), and (3,1) states?
   a. $E_{(2,2)} > E_{(1,3)} = E_{(3,1)}$
   b. $E_{(2,2)} = E_{(1,3)} = E_{(3,1)}$
   c. $E_{(2,2)} < E_{(1,3)} = E_{(3,1)}$

2. If we squeeze the box in the x-direction (*i.e.*, $L_x < L_y$) compare $E_{(1,3)}$ with $E_{(3,1)}$.
   a. $E_{(1,3)} < E_{(3,1)}$
   b. $E_{(1,3)} = E_{(3,1)}$
   c. $E_{(1,3)} > E_{(3,1)}$

Probability Exercise

Consider an electron in a 3D rectangular box of size 1 x 1 x 2 nm. Assuming the electron is in the lowest energy state, what is the (approximate) probability to find it at the center of the box, within a region 0.1 x 0.1 x 0.1 nm?



Just as in 1D problems, the probability to find a particle is given by the integral of the probability density ($\equiv |\psi|^2$) over the region of interest.

We properly normalize ψ by forcing the integral of $|\psi|^2$ over all space = 1.

For an infinite 3D well, we have

$$\boxed{\psi = \sqrt{\frac{2}{L_x}}\sqrt{\frac{2}{L_y}}\sqrt{\frac{2}{L_z}}\sin(k_x x)\sin(k_y y)\sin(k_z z)}$$

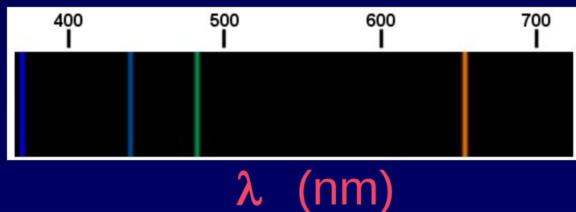
Another 3D System: The Atom
-electrons confined in Coulomb field of a nucleus

Early hints of the quantum nature of atoms:

Discrete Emission and Absorption spectra

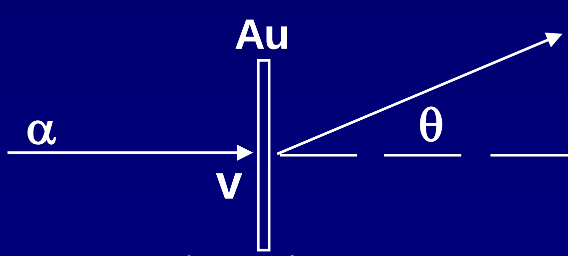
- When excited in an electrical discharge, atoms emit radiation only at discrete wavelengths
- Different emission spectra for different atoms

Atomic hydrogen



Geiger-Marsden (Rutherford) Experiment (1911):

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



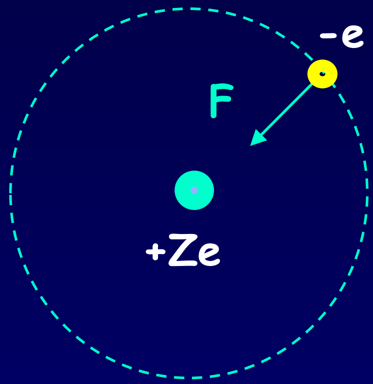
- Conclusion: Most of atomic mass is concentrated in a small region of the atom

a nucleus!

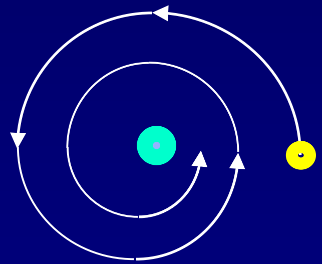
Atoms: Classical Planetary Model

(An early model of the atom)

- Classical picture: negatively charged objects (electrons) orbit positively charged nucleus due to Coulomb force.

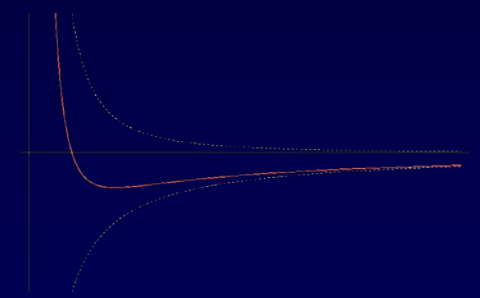


- There is a BIG PROBLEM with this:
  - As the electron moves in its circular orbit, it is ACCELERATING.
  - As you learned in Physics 212, accelerating charges radiate electromagnetic energy.
  - Consequently, an electron would continuously lose energy and spiral into the nucleus in about 10^{-9} sec.



⇨ 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): $U = -\frac{\kappa e^2}{r}$
- However, as it becomes more and more confined, its kinetic energy increases: $p \approx \frac{\hbar}{r} \Rightarrow KE \approx \frac{\hbar^2}{2mr^2}$

Therefore, the total energy is: $E = KE + PE \approx \frac{\hbar^2}{2mr^2} - \frac{\kappa e^2}{r}$

E has a minimum at: $\boxed{r \approx \frac{\hbar^2}{m\kappa e^2} \equiv a_0 = 0.053\text{ nm}}$ The "Bohr radius" of the H atom.

At this radius, $\boxed{E \approx -\frac{m\kappa^2 e^4}{2\hbar^2} = -13.6\text{ eV}}$ The ground state energy of the hydrogen atom.

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

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

Act 3

Consider an electron around a nucleus that has two protons, like an ionized Helium atom.

1. Compare the "effective Bohr radius" $a_{0,He}$ with the usual Bohr radius for hydrogen, a_0:

   a. $a_{0,He} > a_0$

   b. $a_{0,He} = a_0$

   c. $a_{0,He} < a_0$

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

The "Bohr radius" of the H atom.

2. What is the ratio of ground state energies $E_{0,He}/E_{0,H}$?

   a. $E_{0,He}/E_{0,H} = 1$

   b. $E_{0,He}/E_{0,H} = 2$

   c. $E_{0,He}/E_{0,H} = 4$

Next Lectures

Angular momentum → atomic orbitals

“Spin” → Pauli Exclusion Principle