"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!"

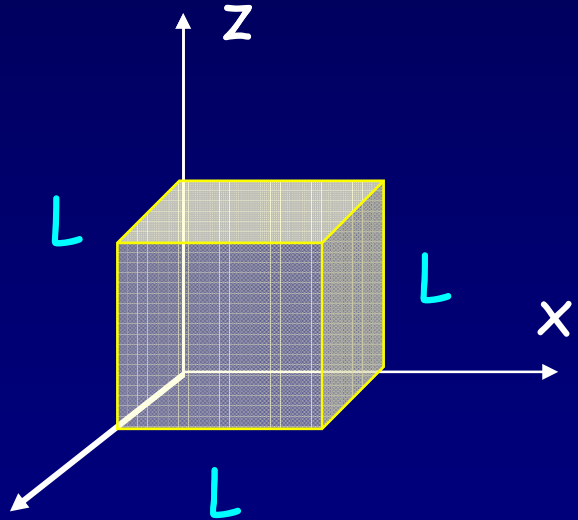
--E. Rutherford

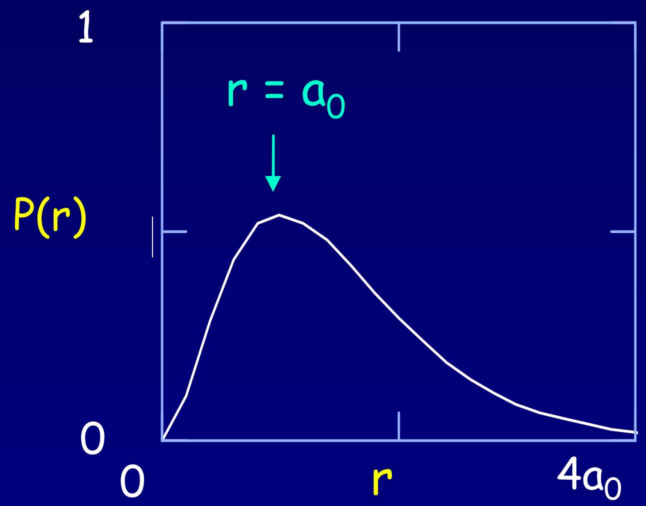
(on the 'discovery' of the nucleus)

Lecture 16:
3D Potentials and the Hydrogen Atom

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

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





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

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

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, H atom
- Angular momentum, electron spin

Next week:

- Exclusion principle, periodic table of atoms, molecules
- Solids, Metals, insulators, semiconductors
- Consequences of Q. M., Schrodinger's cat, superconductors, lasers, . .

Final Exam: Monday, Oct. 14
Homework 6: Due Saturday (Oct. 12), 8 am

Today

3-Dimensional Potential Well:

- Product wave functions
- Degeneracy
- Probability density and normalization

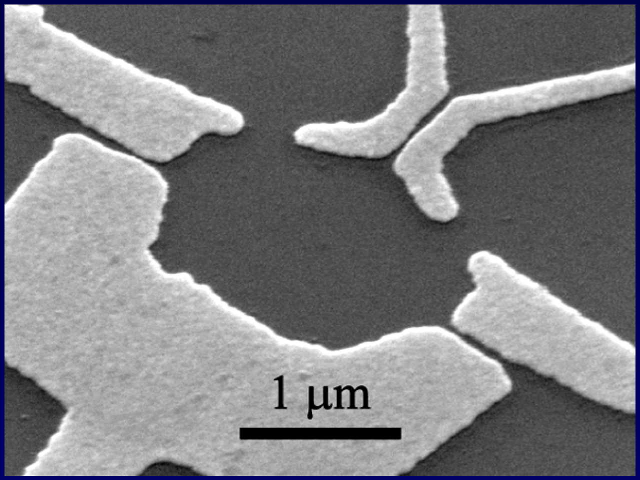
The Hydrogen Atom:

- Early experiments
- Semi-quantitative picture from uncertainty principle
- Hydrogenic ions

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)

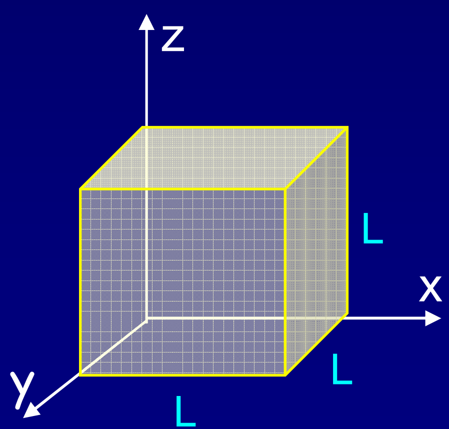
The extension of the Schrödinger Equation (SEQ) to 3D is straightforward in Cartesian (x,y,z) coordinates:

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

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:



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

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:

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

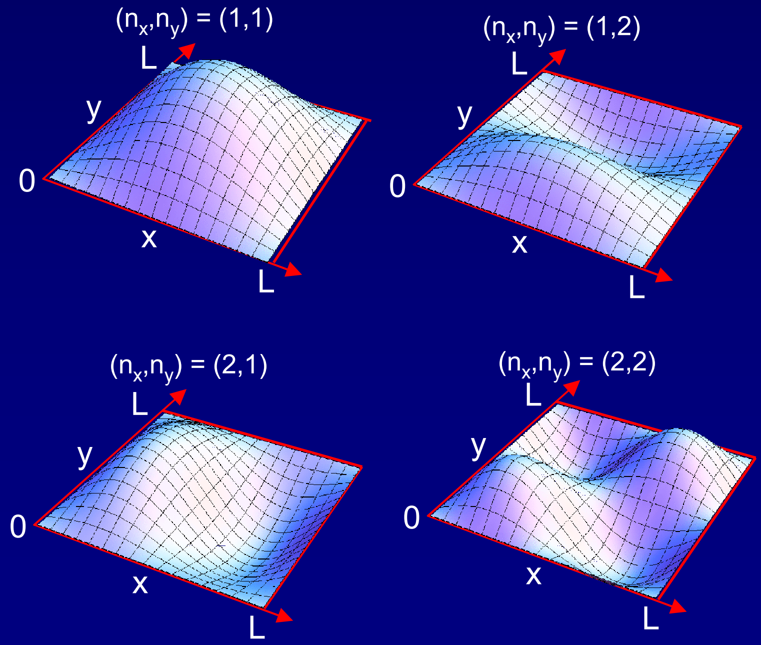
Similarly for y and z.

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

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

2D wave functions:

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



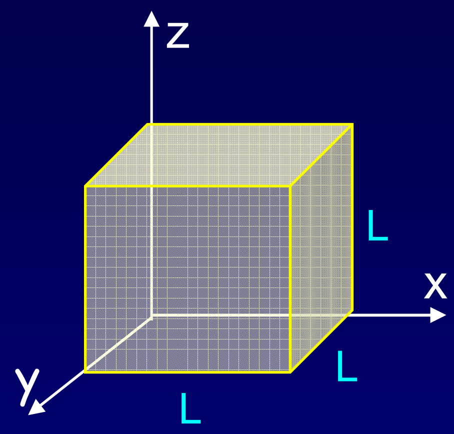
http://www.falstad.com/qm2dbox/

Particle in a 3D Box (3)

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

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

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



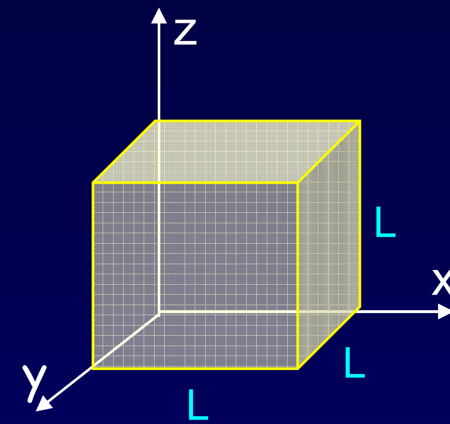
This problem illustrates two important points:

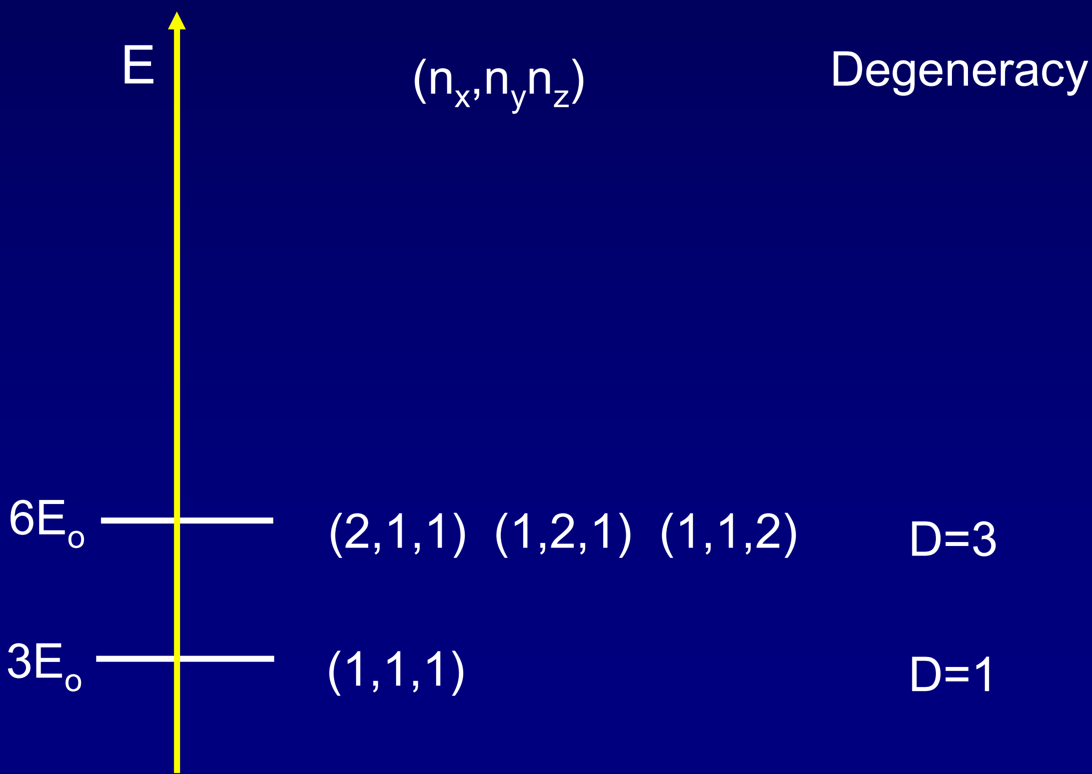
- Three quantum numbers (n_x,n_y,n_z) are needed to identify the state of this three-dimensional system.
  That is true for every 3D system.
- More than one state can have the same energy: "Degeneracy".
  Degeneracy reflects an underlying symmetry in the problem.
  3 equivalent directions, because it's 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 $E_o = h^2/8mL^2$.





Solution

Consider a 3D cubic box:

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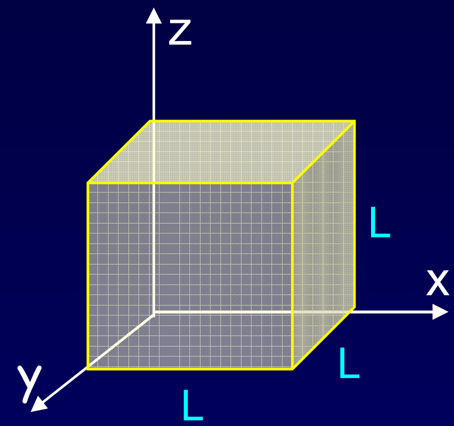

E	(n_x,n_y,n_z)	Degeneracy
$12E_o$	(2,2,2)	D=1
$11E_o$	(3,1,1) (1,3,1) (1,1,3)	D=3
$9E_o$	(2,2,1) (2,1,2) (1,2,2)	D=3
$6E_o$	(2,1,1) (1,2,1) (1,1,2)	D=3
$3E_o$	(1,1,1)	D=1

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

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

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. $\boxed{14E_0}$ 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?

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Solution

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

2. What is the degeneracy of this energy level?

a. 2 **b. 4** **$\boxed{\text{c. } 6}$**

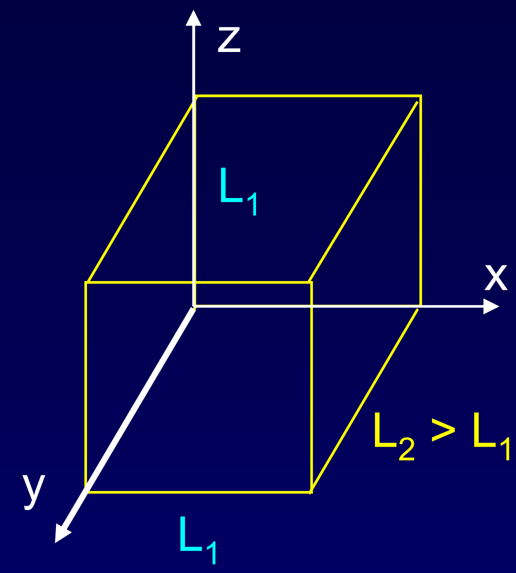
Any ordering of the three numbers will give the same energy.
Because they are all different (distinguishable), the answer is 3! = 6.

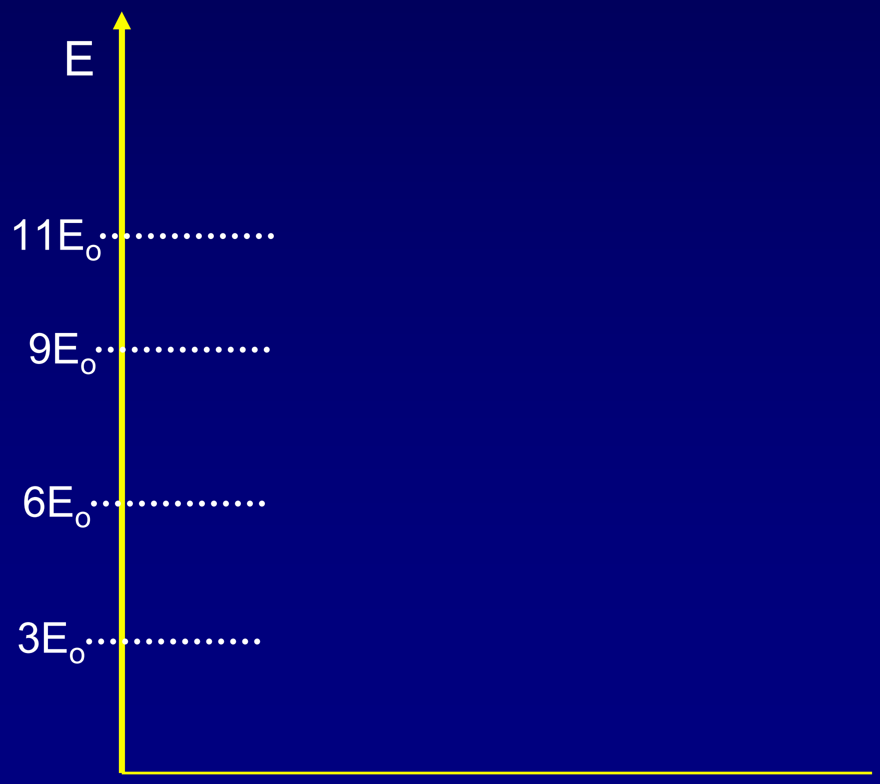
Question:
Is it possible to have D > 6?
Hint: Consider E = $62E_0$.

Non-cubic Box

Consider a non-cubic box:

The box is stretched along the y-direction.
What will happen to the energy levels?
Define $E_o = h^2/8mL_1^2$





Solution

Consider a non-cubic box:

The box is stretched along the y-direction.

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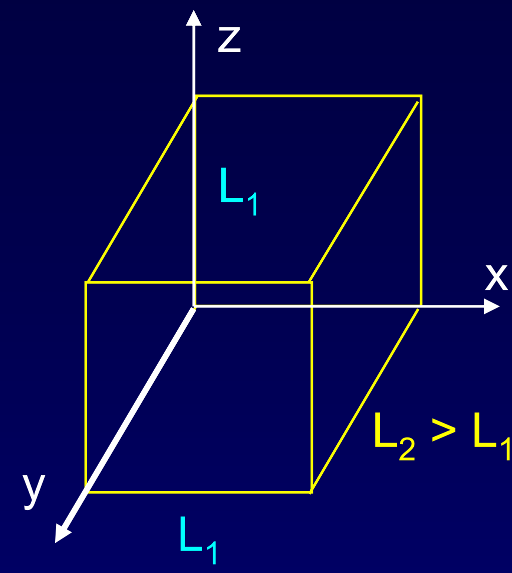
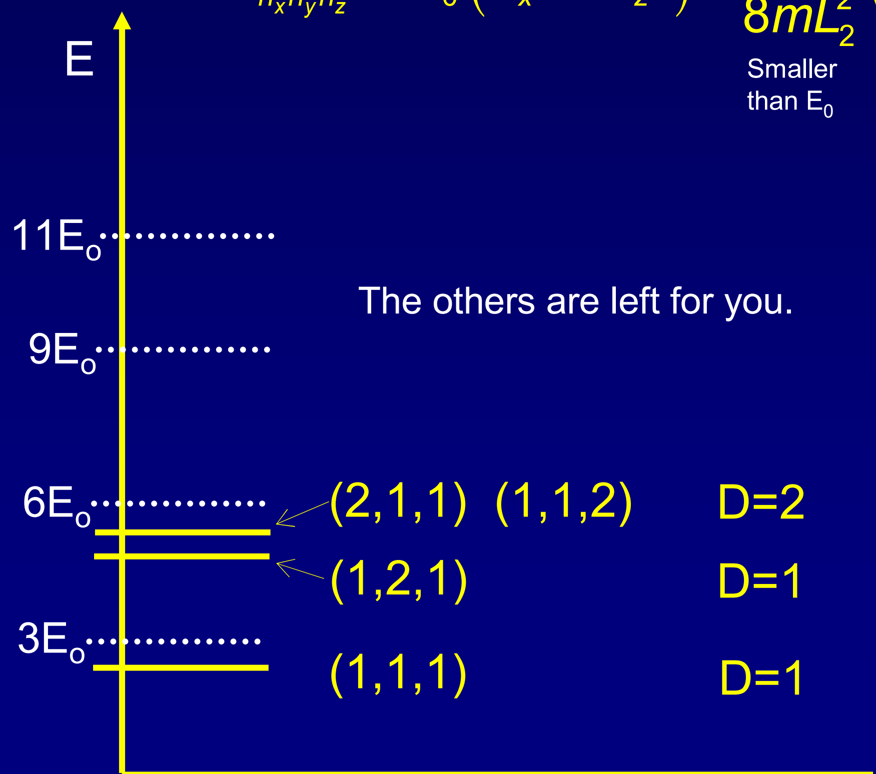


$$E_{n_x n_y n_z} = E_0\left(n_x^2 + n_z^2\right) + \underbrace{\frac{h^2}{8mL_2^2}}_{\text{Smaller than } E_0}\left(n_y^2\right)$$



1: The symmetry is "broken" for y, so the 3-fold degeneracy is lowered. A 2-fold degeneracy remains, because x and z are still symmetric.

2: There is an overall lowering of energies due to decreased confinement along y.

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. $E_{(1,3)} = E_{(3,1)}$
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$E_{(1,3)} = E_{(3,1)} = E_0\,(1^2 + 3^2) = 10\,E_0$

$E_{(2,2)} = E_0\,(2^2 + 2^2) = 8\,E_0$

$$E_0 \equiv \frac{h^2}{8mL^2}$$

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   a. $\boxed{E_{(1,3)} < E_{(3,1)}}$
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   c. $E_{(1,3)} > E_{(3,1)}$

Because $L_x < L_y$, for a given n, E_0 for x motion is larger than E_0 for y motion. The effect is larger for larger n. Therefore, $E_{(3,1)} > E_{(1,3)}$.

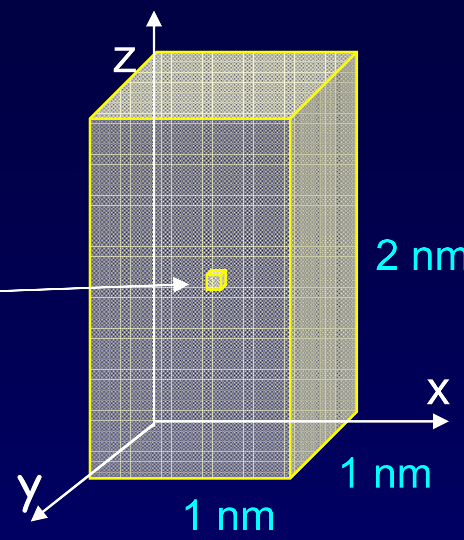
Example: $L_x = ½$, $L_y = 1$:

$E_{(1,3)} \propto 4\times1^2 + 1\times3^2 = 13$
$E_{(3,1)} \propto 4\times3^2 + 1\times1^2 = 37$

We say "the degeneracy has been lifted."

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

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

Probability Exercise -Solution

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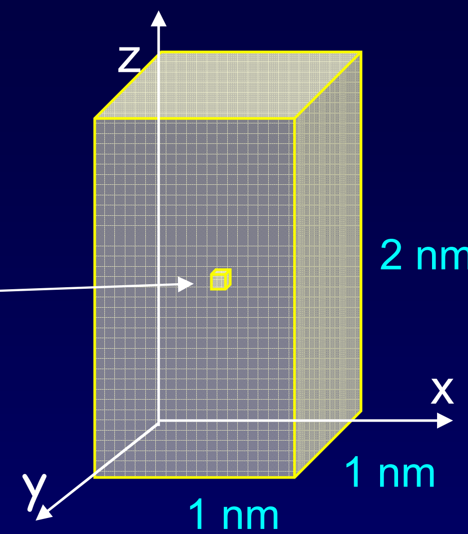

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$$\psi = \sqrt{\frac{2}{L_x}}\sqrt{\frac{2}{L_y}}\sqrt{\frac{2}{L_z}}\sin(k_x x)\sin(k_y y)\sin(k_z z)$$

Since the region in question is very small (i.e., ψ is nearly constant), we can approximate the integral:

$$\boxed{\int_{0.45}^{0.55}\int_{0.45}^{0.55}\int_{0.95}^{1.05}|\psi|^2\,dxdydz \approx |\psi(0.5,0.5,1|^2 \times dvol = \left(\sqrt{\frac{2}{1\text{ nm}}}\sqrt{\frac{2}{1\text{ nm}}}\sqrt{\frac{2}{2\text{ nm}}}\right)^2 (0.1\text{ nm})^3 = 0.004}$$

Exact solution = 0.00393

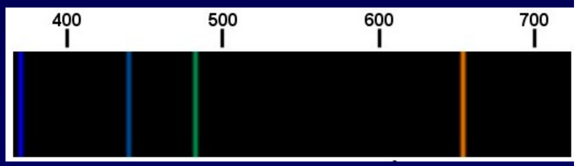
Another 3D System: The Atom
-electrons confined in Coulomb field of a nucleus

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

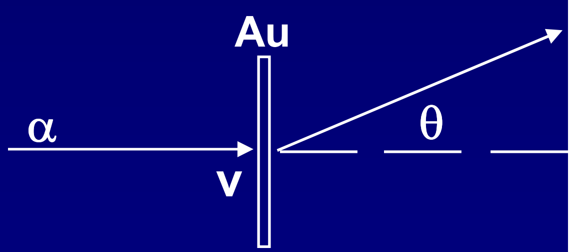
Atomic hydrogen



λ (nm)

Geiger-Marsden (Rutherford) Experiment (1911):

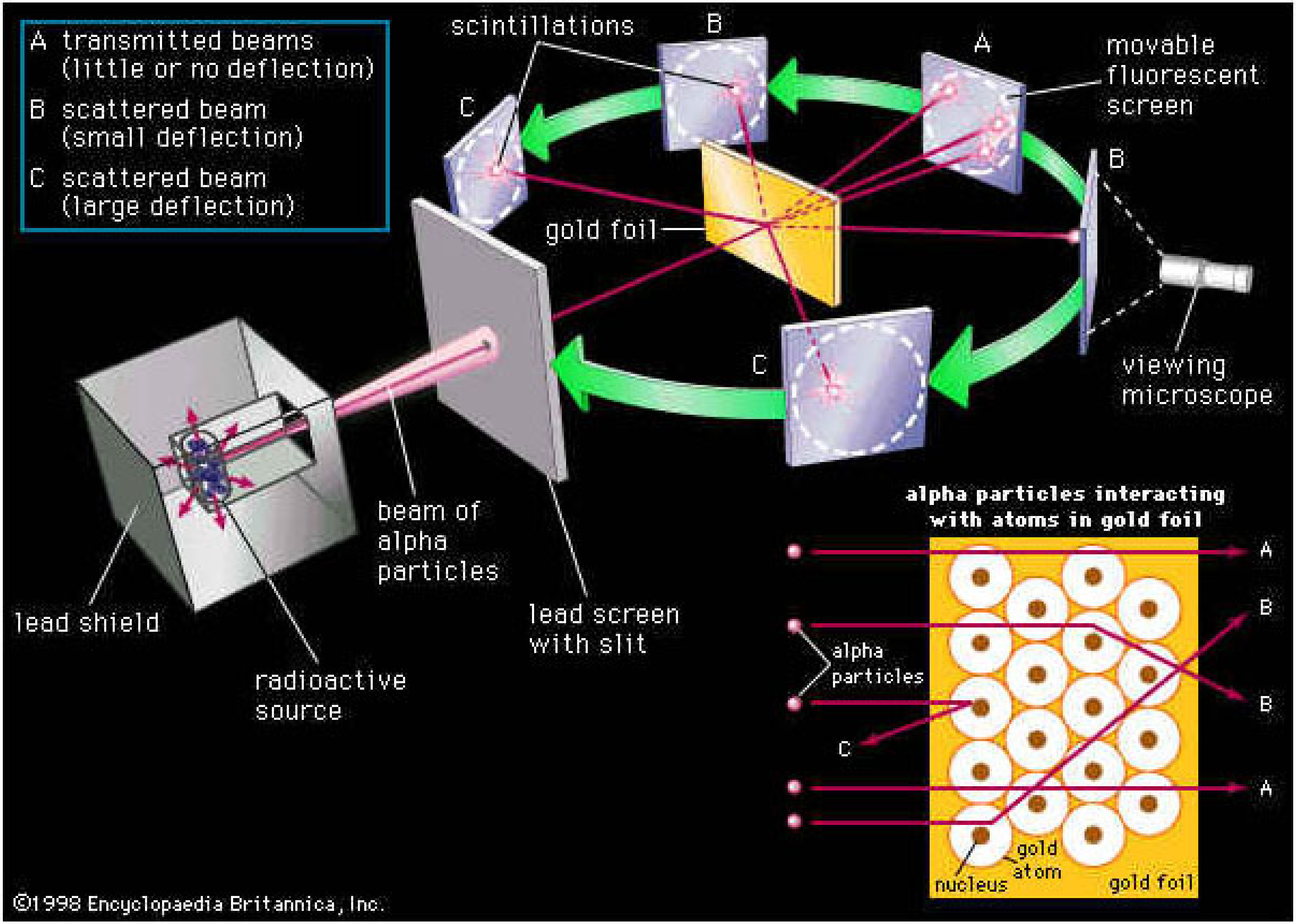
- *Measured angular dependence of a particles (He ions) scattered from gold foil.*
- *Mostly scattering at small angles → supported the "plum pudding" model. But…*
- *Occasional scatterings at large angles →Something massive in there!*



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

→ **a nucleus!**

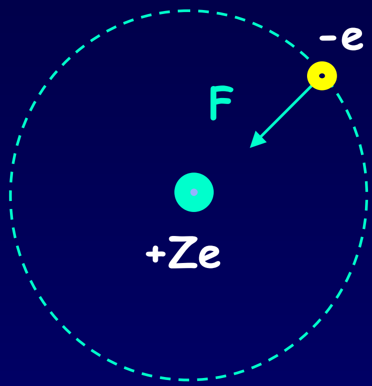
Rutherford Experiment



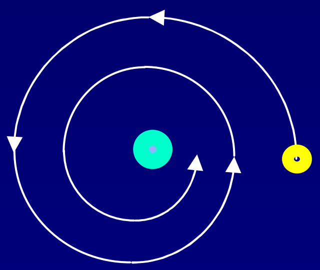
Atoms: Classical Planetary Model

(An early model of the atom)

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



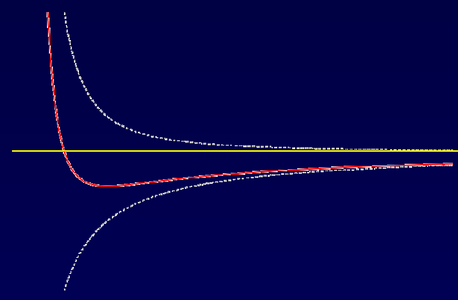
- There is a BIG PROBLEM with this:
  - As the electron moves in its circular orbit, it is ACCELERATING.
  - As you learned in Physics 212, accelerating charges radiate electromagnetic energy.
  - Consequently, an electron would continuously lose energy and spiral into the nucleus in about 10^{-9} sec.



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

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.

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

Solution

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

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

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

Look at how a_0 depends on the charge:

$$a_0 \equiv \frac{\hbar^2}{m\kappa e^2} \Rightarrow a_{0,He} \equiv \frac{\hbar^2}{m\kappa(2e)e} = \frac{a_0}{2}$$

This should make sense:
more charge → stronger attraction
→ electron sits closer to the nucleus

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

Clearly the electron will be more tightly bound, so $|E_{0,He}| > |E_{0,H}|$. How much more tightly? Look at E_0:

$$E_{0,H} = -\frac{m\kappa^2 e^4}{2\hbar^2} \quad \Rightarrow \quad E_{0,He} = \frac{-m\kappa^2 (2e)^2 e^2}{2\hbar^2} = 4E_{0,H}$$

In general, for a "hydrogenic" atom (only one electron) with Z protons:

$$\boxed{E_{0,Z} = Z^2 E_{0,H}}$$

Next Lectures

Angular momentum → atomic orbitals

"Spin" → Pauli Exclusion Principle

Supplement: Separation of Variables (1)

In the 3D box, the SEQ is:

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

NOTE:
Partial derivatives.

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

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

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

NOTE:
Total derivatives.

Divide by fgh:

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

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.