

"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

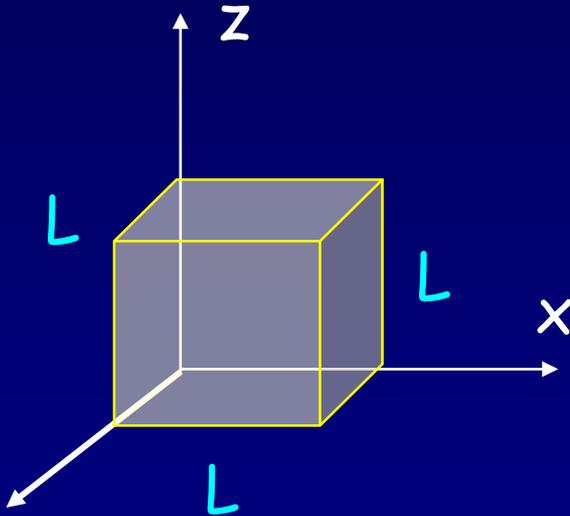
(on the 'discovery'
of the nucleus)

Lecture 16:

3D Potentials and the Hydrogen Atom

3D infinite potential well (cubic)

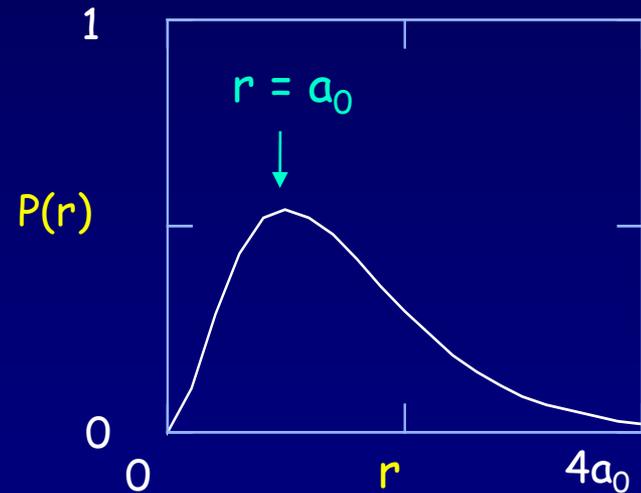
$$\psi(x, y, z) = \varphi(x)\varphi(y)\varphi(z)$$



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

3D Coulomb potential well (hydrogen)

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



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

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, 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. 13

Homework 6: Due Saturday (Oct. 11), 8 am

Today

3-Dimensional Potential Well:

- Separable \rightarrow Product wave functions
- Degeneracy
- Probability density and normalization

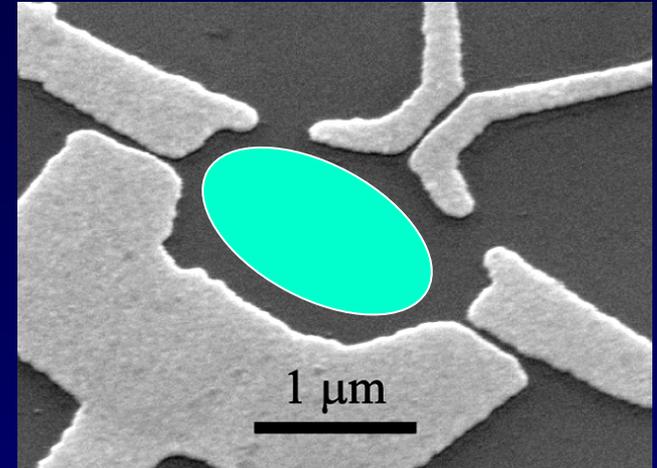
The Hydrogen Atom:

- Early experiments
- Semi-quantitative picture from uncertainty principle
- Hydrogenic ions
- Next time: Separable \rightarrow 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.

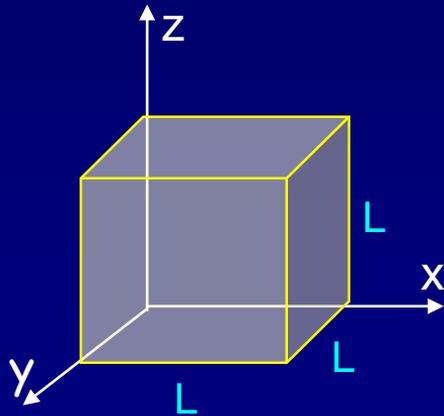
Particle in a 3D Box (1)

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

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

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:

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

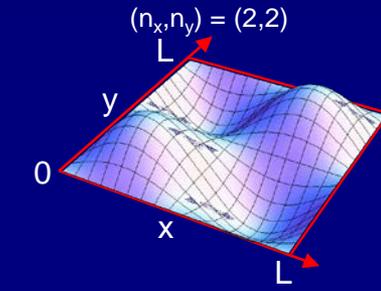
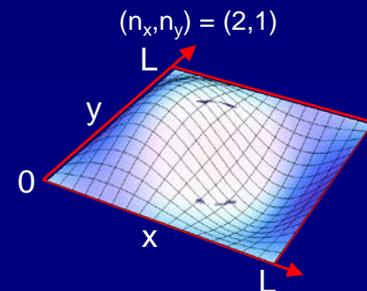
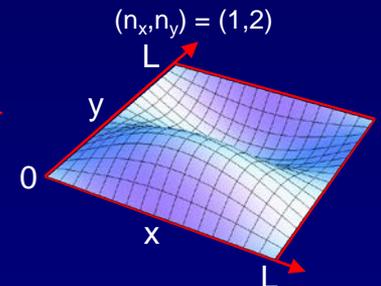
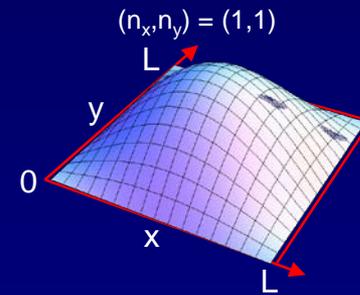
Similarly for y and z .

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

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

2D wave functions:

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



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.

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)

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

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

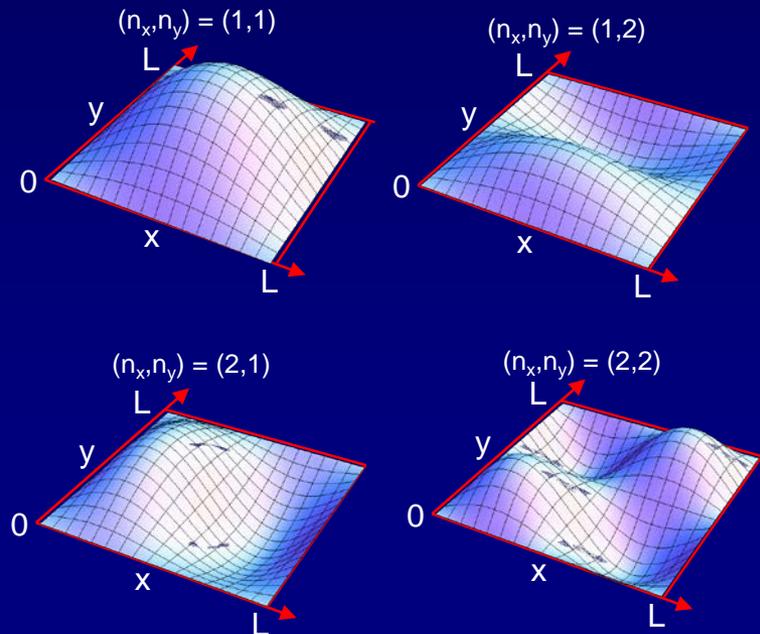
Similarly for y and z .

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

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

2D wave functions:

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

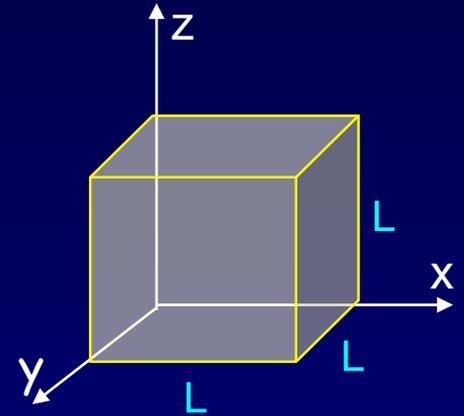


Particle in a 3D Box (3)

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.

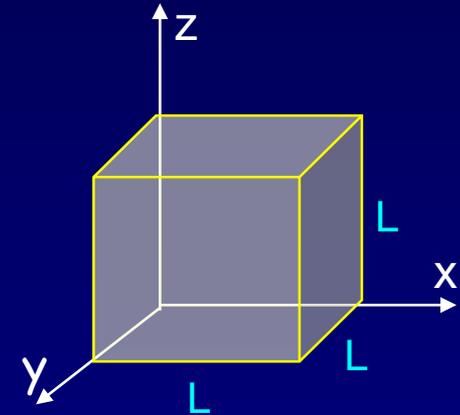
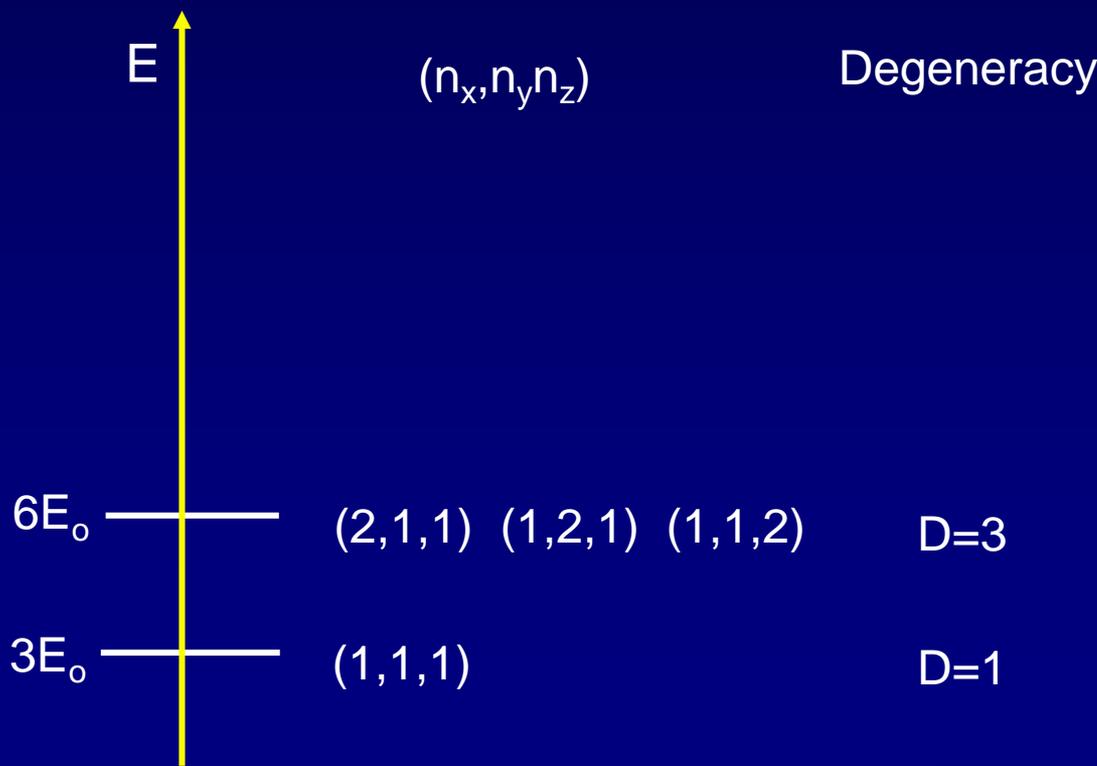
Cubical Box Exercise

Consider a 3D 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 $E_0 = h^2/8mL^2$.

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

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



Solution

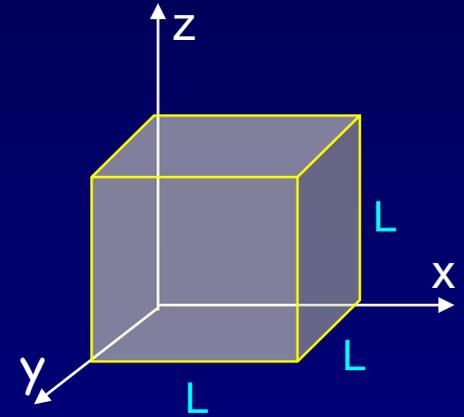
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E	(n_x, n_y, n_z)	Degeneracy
$12E_0$	$(2, 2, 2)$	$D=1$
$11E_0$	$(3, 1, 1)$ $(1, 3, 1)$ $(1, 1, 3)$	$D=3$
$9E_0$	$(2, 2, 1)$ $(2, 1, 2)$ $(1, 2, 2)$	$D=3$
$6E_0$	$(2, 1, 1)$ $(1, 2, 1)$ $(1, 1, 2)$	$D=3$
$3E_0$	$(1, 1, 1)$	$D=1$

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

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



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

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).

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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 $E = 62E_0$.

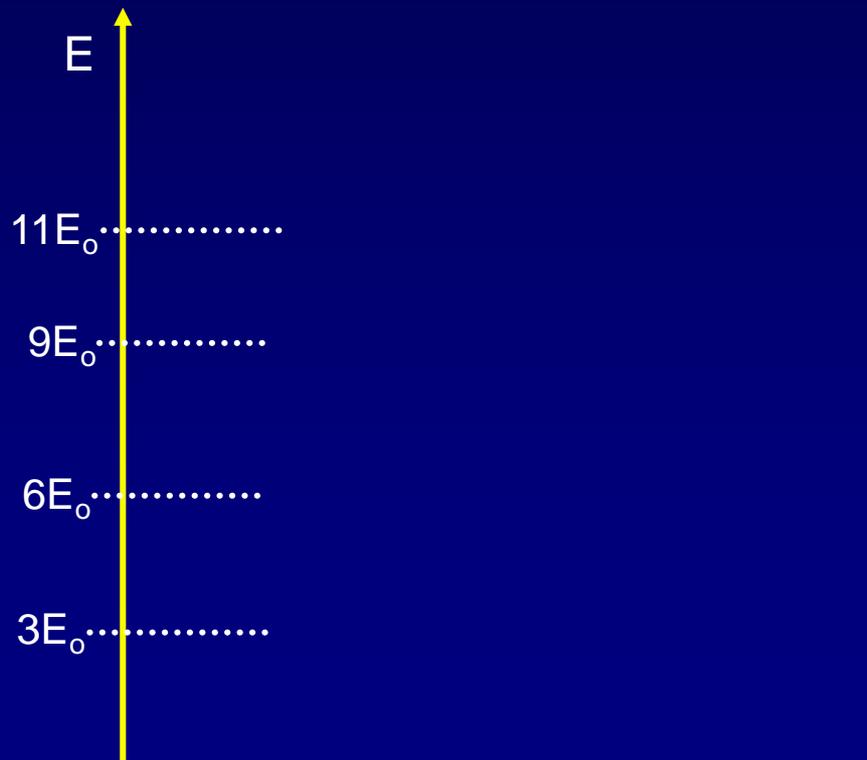
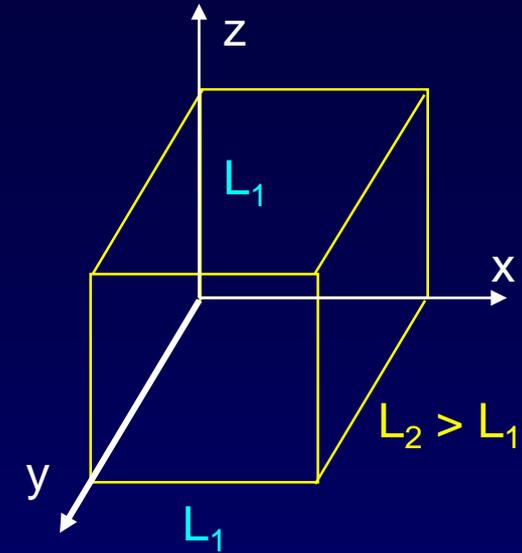
Non-cubic Box

Consider a non-cubic box:

The box is stretched along the y-direction.

What will happen to the energy levels?

Define $E_0 = h^2/8mL_1^2$



Solution

Consider a non-cubic box:

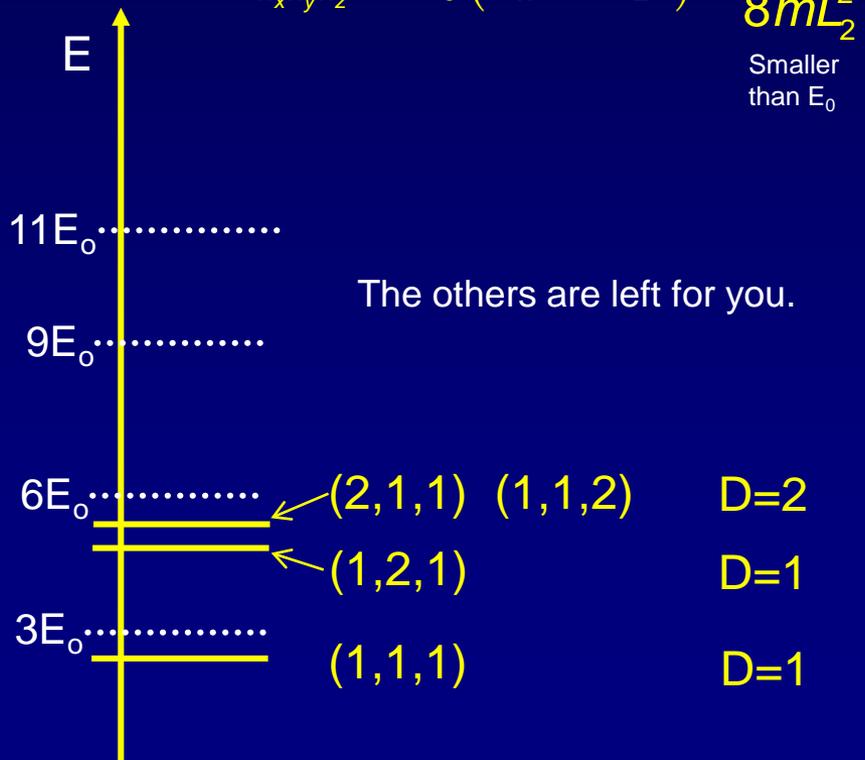
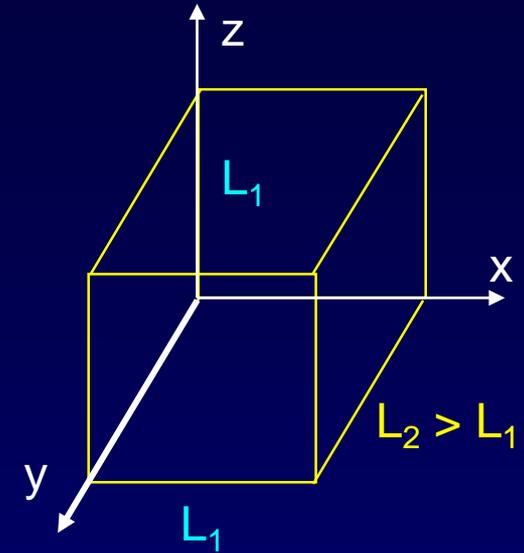
The box is stretched along the y-direction.

What will happen to the energy levels?

Define $E_0 = h^2/8mL_1^2$

$$E_{n_x n_y n_z} = E_0 (n_x^2 + n_z^2) + \frac{h^2}{8mL_2^2} (n_y^2)$$

Smaller than E_0



- 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. $E_{(1,3)} = E_{(3,1)}$

c. $E_{(1,3)} > E_{(3,1)}$

Solution

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c. $E_{(2,2)} < E_{(1,3)} = E_{(3,1)}$

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

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

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

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

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a. $E_{(1,3)} < E_{(3,1)}$

b. $E_{(1,3)} = E_{(3,1)}$

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: $L_x = \frac{1}{2}$, $L_y = 1$:

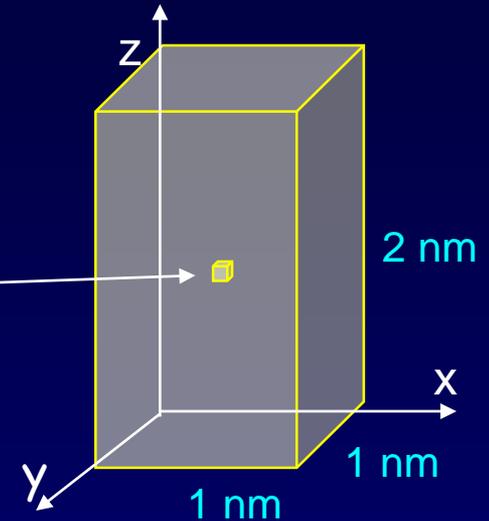
$$E_{(1,3)} \propto 4 \times 1^2 + 1 \times 3^2 = 13$$

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

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.

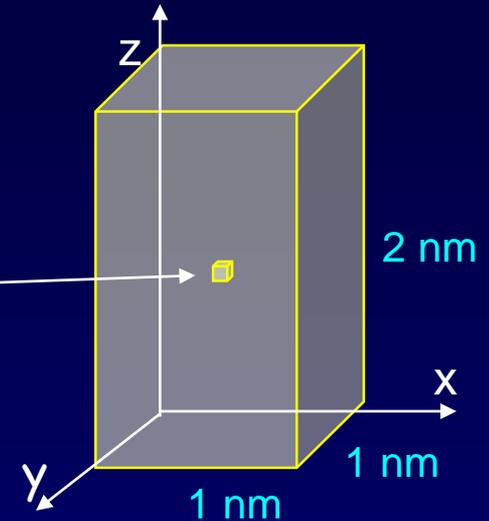
We properly normalize ψ by forcing the integral of $|\psi|^2$ over all space = 1.

For an infinite 3D well, we have

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

Probability Exercise - Solution

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

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

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

Exact solution = 0.00393

Another 3D System: The Atom

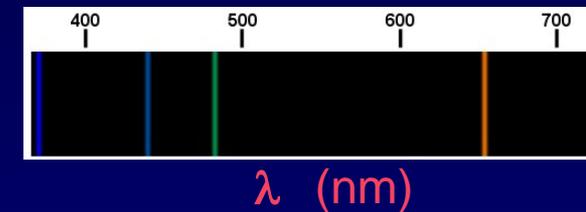
-electrons confined in Coulomb field of a nucleus

Early hints of the quantum nature of atoms:

Discrete Emission and Absorption spectra

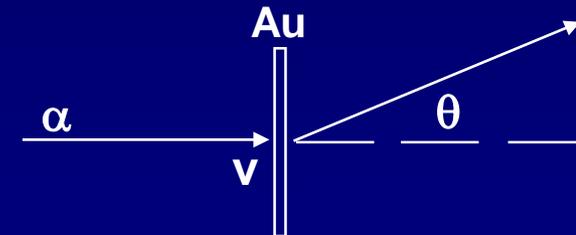
- When excited in an electrical discharge, atoms emit radiation only at discrete wavelengths
- Different emission spectra for different atoms

Atomic hydrogen



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!

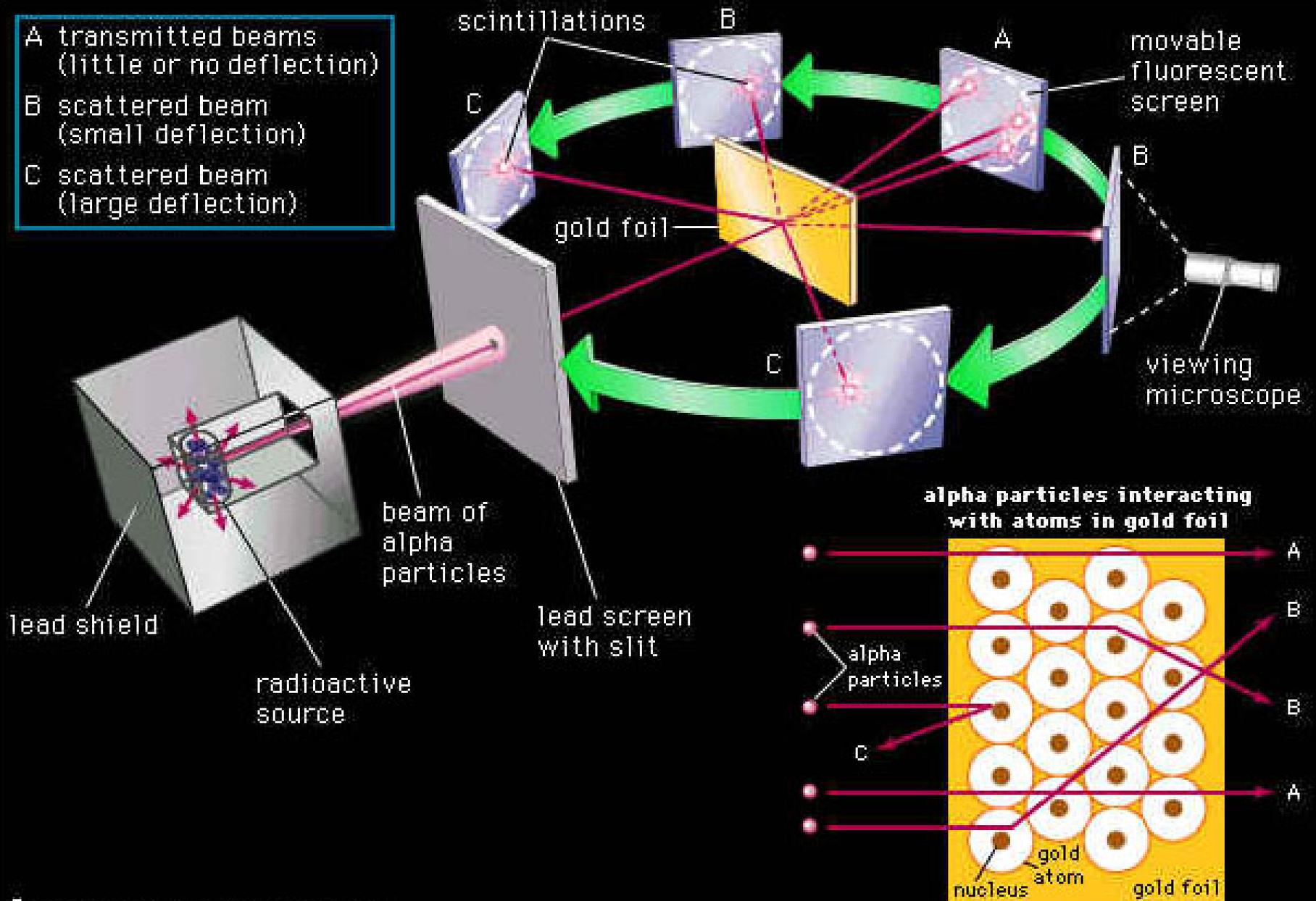


- **Conclusion:** Most of atomic mass is concentrated in a small region of the atom

\rightarrow a nucleus!

Rutherford Experiment

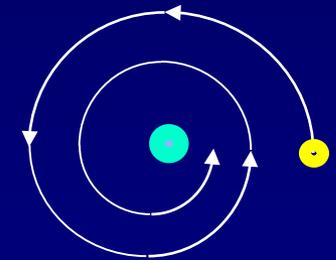
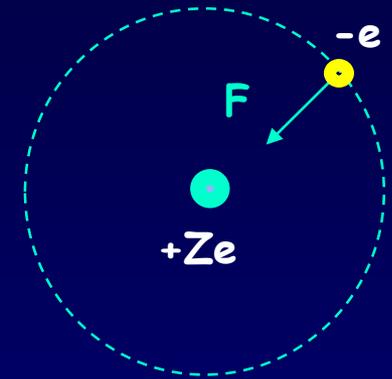
- A transmitted beams (little or no deflection)
- B scattered beam (small deflection)
- C scattered beam (large deflection)



Atoms: Classical Planetary Model

(An early model of the atom)

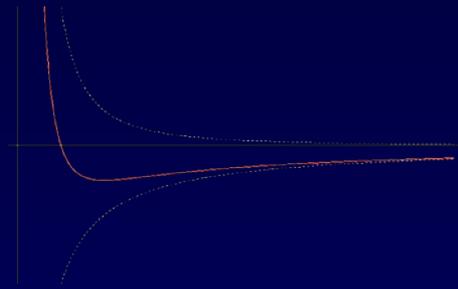
- **Classical picture:** negatively charged objects (electrons) orbit positively charged nucleus due to Coulomb force.
- There is a **BIG PROBLEM** with this:
 - As the electron moves in its circular orbit, it is **ACCELERATING**.
 - As you learned in Physics 212, accelerating charges radiate electromagnetic 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):

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

- 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.

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.

Act 3

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

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

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

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

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

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

The “Bohr radius”
of the H atom.

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

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

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

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

Solution

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

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

Look at how a_0 depends on the charge:

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

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

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

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

This should make sense:

more charge \rightarrow stronger attraction

\rightarrow electron sits closer to the nucleus

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

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

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

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

Next Lectures

Angular momentum → atomic orbitals

“Spin” → Pauli Exclusion Principle