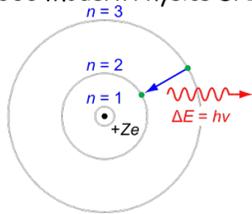


PH300 Modern Physics SP11



Some people say, "How can you live without knowing?" I do not know what they mean. I always live without knowing. That is easy. How you get to know is what I want to know.  
- Richard Feynman

3/1 Day 13:

Questions?  
Balmer Series  
Bohr Atomic Model  
deBroglie Waves

Thursday:

Experiments with atoms:  
Stern-Gerlach

Last time:

- Photons, atomic spectra & lasers

Today:

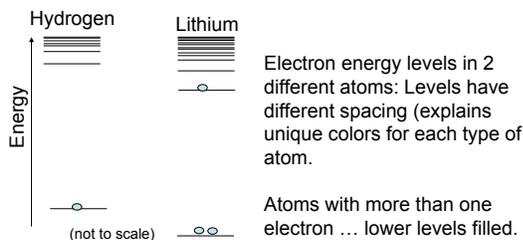
- Balmer formula and ideas about atoms
- Bohr model of hydrogen
- de Broglie waves

Thursday:

- Reading on Blackboard before class
- Magnetic moments and atomic spin
- Stern-Gerlach experiments

Summary of important Ideas

- 1) Electrons in atoms are found at specific energy levels
- 2) Different set of energy levels for different atoms
- 3) One photon emitted per electron jump *down* between energy levels. Photon color determined by energy difference.
- 4) If electron not bound to an atom: Can have any energy. (For instance free electrons in the PE effect.)



Now we know about the energy levels in atoms. But how can we calculate/predict them?

→ Need a model

- Step 1: Make precise, quantitative observations!
- Step 2: Be creative & come up with a model.
- Step 3: Put your model to the test.

**Balmer series:**  
A closer look at the spectrum of hydrogen

410.3 486.1 656.3 nm  
434.0

Balmer (1885) noticed wavelengths followed a progression

$$\lambda = \frac{91.19\text{nm}}{\frac{1}{2^2} - \frac{1}{n^2}} \quad \text{where } n = 3, 4, 5, 6, \dots$$

As n gets larger, what happens to wavelengths of emitted light?

→ λ gets smaller and smaller, but it approaches a limit.

**Balmer series:**  
A closer look at the spectrum of hydrogen

410.3 486.1 656.3 nm  
434.0

Balmer (1885) noticed wavelengths followed a progression

So this gets smaller  $\lambda = \frac{91.19\text{nm}}{\frac{1}{2^2} - \frac{1}{n^2}}$  where n = 3, 4, 5, 6, ...

Balmer correctly predicted yet undiscovered spectral lines. gets smaller as n increases

gets larger as n increases, but no larger than 1/4

$$\lambda_{\text{limit}} = 4 * 91.19\text{nm} = 364.7\text{nm}$$

λ gets smaller and smaller, but it approaches a limit

### Hydrogen atom – Rydberg formula

Does generalizing Balmer's formula work?  
 Yes! → It correctly predicts additional lines in **HYDROGEN**.

**Rydberg's general formula**

$$\lambda = \frac{91.19\text{nm}}{\frac{1}{m^2} - \frac{1}{n^2}}$$

Predicts  $\lambda$  of  $n \rightarrow m$  transition:

$n$  ——— (n>m)  
 |  
 m ——— (m=1,2,3..)

Hydrogen energy levels

∞ ← 0eV  
 6  
 5  
 4  
 3  
 2  
 1

IR  
 Paschen series  
 Balmer series  
 Lyman series  
 UV

$m=1, n=2$

### Hydrogen atom – Lyman Series

**Rydberg's formula**

$$\lambda = \frac{91.19\text{nm}}{\frac{1}{m^2} - \frac{1}{n^2}}$$

Predicts  $\lambda$  of  $n \rightarrow m$  transition:

$n$  ——— (n>m)  
 |  
 m ——— (m=1,2,3..)

Hydrogen energy levels

∞ ← 0eV  
 6  
 5  
 4  
 3  
 2  
 1

UV  
 m=1

Can Rydberg's formula tell us what ground state energy is?

### Balmer-Rydberg formula

$$\lambda = \frac{91.19\text{nm}}{\frac{1}{m^2} - \frac{1}{n^2}}$$

Look at energy for a transition between  $n=\infty$  and  $m=1$

$$E_{\text{final}} - E_{\text{final}} = \frac{hc}{\lambda} = \frac{hc}{91.19\text{nm}} \left( \frac{1}{m^2} - \frac{1}{n^2} \right)$$

$$-E_{\text{final}} = \frac{hc}{91.19\text{nm}} \frac{1}{m^2}$$

$E_m = -13.6\text{eV} \frac{1}{m^2}$

Hydrogen energy levels

∞ ← 0eV  
 6  
 5  
 4  
 3  
 2  
 1

UV  
 -?? eV

The Balmer/Rydberg formula is a mathematical representation of an empirical observation.

It doesn't *explain* anything, really.

How can we calculate the energy levels in the hydrogen atom?

→ A semi-classical explanation of the atomic spectra (*Bohr model*)

Rutherford shot alpha particles at atoms and he figured out that a tiny, positive, hard core is surrounded by negative charge very far away from the core.

- One possible model:  
 Atom is like a solar system:  
 electrons circling the nucleus like planets circling the sun...
- The problem is that accelerating electrons should radiate light and spiral into the nucleus:

**KA-BOOM!**

\*Elapsed time:  $\sim 10^{-11}$  seconds

Nucleus

Electron

Higher Energy

Energy levels

CT: When electron moves to location further from the nucleus,

- energy of electron *decreases* because energy is released as positive and negative charges are separated, and there is a *decrease* in electrostatic potential energy of electron since it is now further away
- energy of electron *increases* because it takes energy input to separate positive and negative charges, and there is an *increase* in the electrostatic potential energy of the electron.
- energy of electron *increases* because it takes energy input to separate positive and negative charges, and there is a *decrease* in the electrostatic potential energy of the electron.

### Electrostatic potential energy

When an electron moves to location farther away from the nucleus its energy increases because energy is required to separate positive and negative charges, and there is an increase in the electrostatic potential energy of the electron.

→ Force on electron is less, but Potential Energy is higher!

→ Electrons at higher energy levels are farther from the nucleus!

### Potential energy of the electron in hydrogen

**We define** electron's PE as 0 when far away from the proton!  
 → Electron's PE = -work done by electric field from  $r_1 = \infty \dots r_2 = D$

Coulomb's constant

$$\int_{\infty}^D \mathbf{F} \cdot d\mathbf{r} = \int_{\infty}^D \frac{kq_{elect}q_{prot}}{r^2} dr$$

$$PE = kq_{elect}q_{prot} \int_{\infty}^D \frac{dr}{r^2} = kq_{elect}q_{prot} \left. \frac{1}{r} \right|_{\infty}^D = -\frac{ke^2}{D}$$

(for hydrogen)

(PE as function of D) =  $-\frac{ke^2}{D}$

Correct answer:  
 PE has 1/D relationship  
 D gets really small.. then PE really large & negative!<sup>5</sup>

### Potential energy of a single electron in an atom

PE of an electron at distance D from the proton is

$$PE = -\frac{ke^2}{D} \quad ke^2 = 1.440\text{eV}\cdot\text{nm}$$

PE =  $-\frac{ke(Ze)}{D}$   
 (For Z protons)

### How can we calculate the energy levels in hydrogen?

$$\lambda = \frac{91.19\text{nm}}{\frac{1}{m^2} - \frac{1}{n^2}}$$

Step 1: Make precise, quantitative observations!  
 Step 2: Be creative & come up with a model.

How to avoid the Ka-Boom?

\*Elapsed time: ~10<sup>-11</sup> seconds

### Bohr Model

- Bohr thought: Everybody's using Planck's constant these days to talk about energy and frequencies. Why not inside atoms themselves, since they interact with quantized light energy?
- The Bohr model has some problems, but it's still useful.
- Why **doesn't** the electron fall into the nucleus?
  - According to classical physics, *It should!*
  - According to Bohr, *It just doesn't.*
  - Modern QM will give a satisfying answer, but you'll have to wait...

Original paper: Niels Bohr: *On the Constitution of Atoms and Molecules*, Philosophical Magazine, Series 6, Volume 26, p. 1-25, July 1913.)

## Bohr's approach:

#1: Treat the mechanics classical (electron spinning around a proton):

- Newton's laws assumed to be valid
- Coulomb forces provide centripetal acceleration.

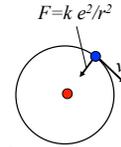
#2: Bohr's hypothesis (Bohr had no proof for this; he just assumed it – leads to correct results!):

- The angular momentum of the electrons is quantized in multiples of  $\hbar$ .
- The lowest angular momentum is  $\hbar$ .

$$\hbar = \frac{h}{2\pi}$$

## Bohr Model. # 1: Classical mechanics

The centripetal acceleration  $a = v^2/r$  is provided by the coulomb force  $F = k \cdot e^2/r^2$ .



Newton's second law  $\rightarrow mv^2/r = k \cdot e^2/r^2$   
or:  $mv^2 = k \cdot e^2/r$

The electron's kinetic energy is  $KE = \frac{1}{2} m v^2$   
The electron's potential energy is  $PE = -k e^2/r$   $\rightarrow E$   
 $\rightarrow E = KE + PE = -\frac{1}{2} k e^2/r = \frac{1}{2} PE$

Therefore: If we know  $r$ , we know  $E$  and  $v$ , etc...

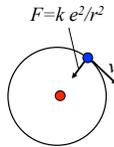
## Bohr Model. #2: Quantized angular momentum

Bohr assumed that the angular momentum of the electron could only have the quantized values of:

$$L = n\hbar$$

And therefore:  $mvr = n\hbar$ , ( $n=1,2,3\dots$ )

$$\text{or: } v = n\hbar/(mr)$$



Substituting this into  $mv^2 = k \cdot e^2/r$  leads to:

$$r_n = r_B n^2, \text{ with } r_B = \frac{\hbar^2}{k e^2 m} = 52.9 \text{ pm}, r_B: \text{ Bohr radius}$$

$$E_n = -E_R / n^2, \text{ with } E_R = \frac{m(k e^2)^2}{2\hbar^2} = 13.6 \text{ eV}, E_R: \text{ Rydberg Energy}$$

## Bohr Model. Results

$$r = r_B n^2, \text{ with } r_B = \frac{\hbar^2}{k e^2 m} = 52.9 \text{ pm}, r_B: \text{ Bohr radius}$$

$$E_n = -E_R / n^2, \text{ with } E_R = \frac{m(k e^2)^2}{2\hbar^2} = 13.6 \text{ eV}, E_R: \text{ Rydberg Energy}$$

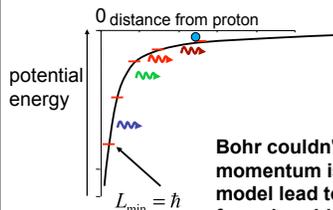
The Bohr model not only predicts a reasonable atomic radius  $r_B$ , but it also predicts the energy levels in hydrogen to 4 digits accuracy!

Possible photon energies:

$$E_\gamma = E_n - E_m = E_R \left( \frac{1}{m^2} - \frac{1}{n^2} \right) \quad (n > m)$$

$\rightarrow$  The Bohr model 'explains' the Rydberg formula!!

Only discrete energy levels possible. Electrons hop down towards lowest level, giving off photons during the jumps. Atoms are stable in lowest level.



Bohr couldn't explain *why* the angular momentum is quantized but his model lead to the Rydberg-Balmer formula, which matched to the experimental observations very well!

He also predicted atomic radii reasonably well and was able to calculate the Rydberg constant.

## Which of the following principles of classical physics is violated in the Bohr model?

- Opposite charges attract with a force inversely proportional to the square of the distance between them.
- The force on an object is equal to its mass times its acceleration.
- Accelerating charges radiate energy.
- Particles always have a well-defined position and momentum.
- All of the above.

Note that both A & B are used in derivation of Bohr model.

## Successes of Bohr Model

- 'Explains' source of Balmer formula and predicts empirical constant  $R$  (Rydberg constant) from fundamental constants:  $R = 1/91.2 \text{ nm} = mk^2e^4/(4\pi ch^3)$   
Explains why  $R$  is different for different single electron atoms (called *hydrogen-like ions*).
- Predicts approximate size of hydrogen atom
- Explains (sort of) why atoms emit discrete spectral lines
- Explains (sort of) why electron doesn't spiral into nucleus

## Shortcomings of the Bohr model:

- Why is angular momentum quantized yet Newton's laws still work?
- Why don't electrons radiate when they are in fixed orbitals yet Coulomb's law still works?
- No way to know *a priori* which rules to keep and which to throw out...
- Can't explain shapes of molecular orbits and how bonds work
- Can't explain doublet spectral lines

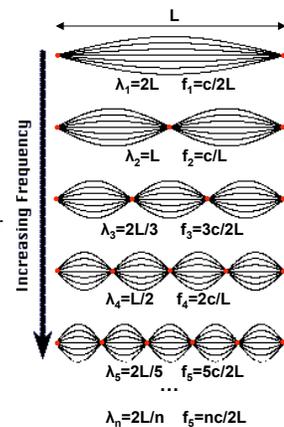
Questions?

## How to resolve these problems?

→ Matter waves

## Waves

- Physicists at this time may have been confused about atoms, but they understood waves really well.
- They understood that for standing waves, boundary conditions mean that waves only have discrete modes.
- e.g., guitar strings

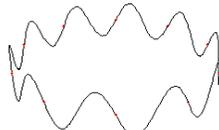


• = node = fixed point that doesn't move

PHE

## Standing Waves on a Ring

Just like standing wave on a string, but now the two ends of the string are joined.

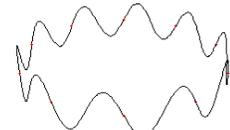


What are the restrictions on the wavelength?

- A.  $r = \lambda$   
 B.  $r = n\lambda$   
 C.  $\pi r = n\lambda$   
 D.  $2\pi r = n\lambda$   
 E.  $2\pi r = \lambda/n$
- $n = 1, 2, 3, \dots$

## Standing Waves on a Ring

- Answer: D.  $2\pi r = n\lambda$



- Circumference =  $2\pi r$
- To get standing wave on ring:  
Circumference =  $n\lambda$   
Must have integer number of wavelengths to get constructive, not destructive, interference.
- $n$  = number of wavelengths

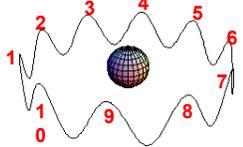
### deBroglie Waves

- deBroglie (French grad student) suggested: maybe electrons are actually little waves going around the nucleus.
- This seems plausible because...
  - Standing waves have quantized frequencies, might be related to quantized energies.
  - Einstein had shown that light, typically thought of as waves, have particle properties. Might not electrons, typically thought of as particles, have wave properties?

### deBroglie Waves

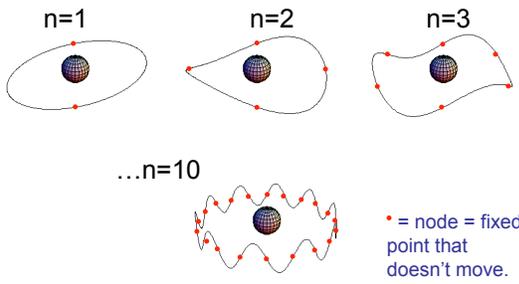
What is n for the 'electron wave' in this picture?

A. 1  
B. 5  
C. 10  
D. 20  
E. Cannot determine from picture



**Answer: C. 10** n = number of wavelengths. It is **also** the number of the energy level  $E_n = -13.6/n^2$ . So the wave above corresponds to  $E_{10} = -13.6/10^2 = -0.136\text{eV}$  (will explain soon)

### deBroglie Waves



• = node = fixed point that doesn't move.

### deBroglie Waves

- If electron orbits are standing waves, there is a relationship between orbital radius and wavelength:  $2\pi r = n\lambda$
- But what is the wavelength of an electron?!
- For photons, it was known that photons have momentum  $E = pc = hc/\lambda$
- $\rightarrow p = h/\lambda \rightarrow \lambda = h/p$
- deBroglie proposed that this is also true for massive particles (particles w/mass)!  $\lambda = h/p = \text{"deBroglie wavelength"}$

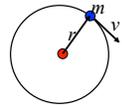


### deBroglie Waves

Given the deBroglie wavelength ( $\lambda = h/p$ ) and the condition for standing waves on a ring ( $2\pi r = n\lambda$ ), what can you say about the angular momentum L of an electron if it is a deBroglie wave?

A.  $L = n\hbar/r$   
B.  $L = n\hbar$   
C.  $L = n\hbar/2$   
D.  $L = 2n\hbar/r$   
E.  $L = n\hbar/2r$   
(Recall:  $\hbar = h/2\pi$ )

L = angular momentum = pr  
p = (linear) momentum = mv



### deBroglie Waves

- Substituting the deBroglie wavelength ( $\lambda = h/p$ ) into the condition for standing waves ( $2\pi r = n\lambda$ ), gives:
 
$$2\pi r = nh/p$$
- Or, rearranging:
 
$$pr = nh/2\pi$$

$$L = n\hbar$$
- deBroglie EXPLAINS quantization of angular momentum, and therefore EXPLAINS quantization of energy!