Quantum Mechanics I
Physics 325

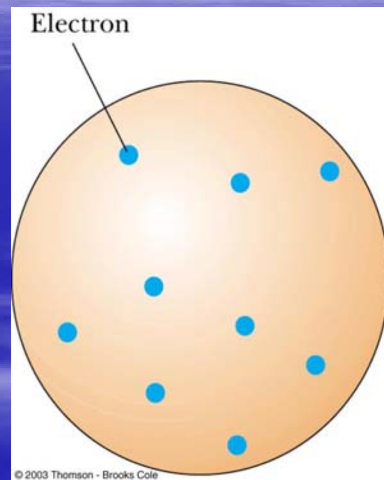
Atomic spectra and Atom Models

Importance of Hydrogen Atom

- Hydrogen is the simplest atom
- The quantum numbers used to characterize the allowed states of hydrogen can also be used to describe (approximately) the allowed states of more complex atoms
  - This enables us to understand the periodic table
- The hydrogen atom is an ideal system for performing precise comparisons of theory and experiment
  - Also for improving our understanding of atomic structure
- Much of what we know about the hydrogen atom can be extended to other single-electron ions
  - For example, He^{+} and Li^{2+}

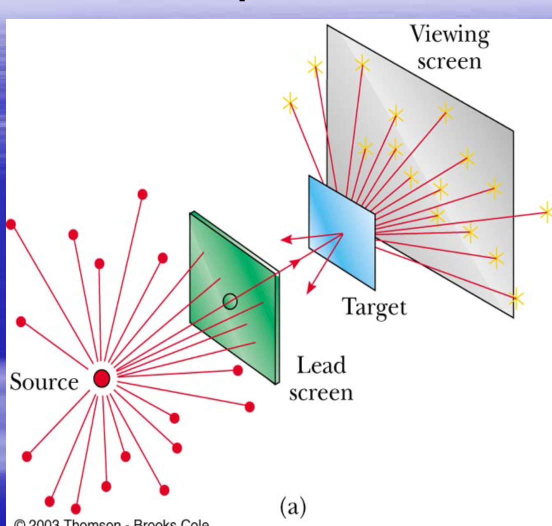
Early Models of the Atom

- J.J. Thomson's model of the atom
  - A volume of positive charge
  - Electrons embedded throughout the volume
- A change from Newton's model of the atom as a tiny, hard, indestructible sphere



"watermelon" model

Experimental tests



Expect:

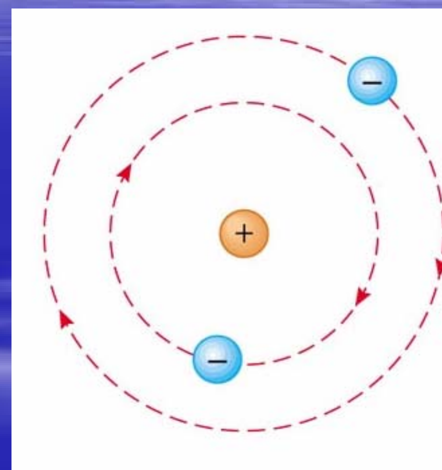
1. Mostly small angle scattering
2. No backward scattering events

Results:

1. Mostly small scattering events
2. <u>Several backward scatterings!!!</u>

Early Models of the Atom

- Rutherford's model
  - Planetary model
  - Based on results of thin foil experiments
  - Positive charge is concentrated in the center of the atom, called the *nucleus*
  - Electrons orbit the nucleus like planets orbit the sun

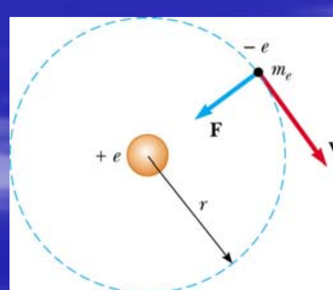


Rutherford's model

The "size" of the *atom* in Rutherford's model is about 1.0×10^{-10} m.

(a) Determine the attractive electrical force between an electron and a proton separated by this distance.

(b) Determine (in eV) the electrical potential energy of the atom.



The “size” of the *atom* in Rutherford’s model is about 1.0 × 10^{-10} m. (a) Determine the attractive electrical force between an electron and a proton separated by this distance. (b) Determine (in eV) the electrical potential energy of the atom.

Given:

r = 1.0 × 10^{-10} m

Find:

(a) F = ?
(b) PE = ?

Electron and proton interact via the Coulomb force

$$F = k_e \frac{|q_1 q_2|}{r^2} = \frac{\left(8.99\times10^9\, N\cdot m^2/C^2\right)\left(1.60\times10^{-19}\, C\right)^2}{\left(1.0\times10^{-10}\, m\right)^2}$$

$$= 2.3\times10^{-8}\, N$$

Potential energy is

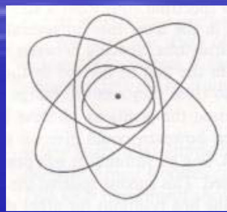
$$PE = k_e \frac{q_1 q_2}{r} = -2.3\times10^{-18}\, J\left(\frac{1eV}{1.6\times10^{-19}\, J}\right) = -14\text{ eV}$$

Difficulties with the Rutherford Model

- Atoms emit certain discrete characteristic frequencies of electromagnetic radiation
  - The Rutherford model is unable to explain this phenomena
- Rutherford’s electrons are undergoing a centripetal acceleration and so should radiate electromagnetic waves of the same frequency
  - The radius should steadily decrease as this radiation is given off
  - The electron should eventually spiral into the nucleus
    - It doesn’t

How to explain the hydrogen spectra?

Hydrogen consists of a nucleus (proton) and an electron. According to Rutherford, the negative electron orbits around the positive nucleus like a planet.



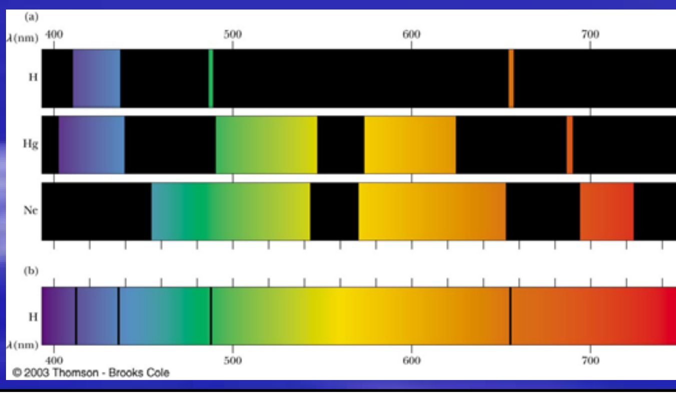
Rutherford model of the atom.

Unstable!!!

According to classical physics, an electron accelerating around its orbit should emit radiation. This loss of energy should be accompanied by a decrease in orbit speed and **a spiraling of the electron into the nucleus!**

Emission Spectra

- A gas at low pressure has a voltage applied to it
- A gas emits light characteristic of the gas
- When the emitted light is analyzed with a spectrometer, a series of discrete bright lines is observed



-This series of lines is called an *emission spectrum*

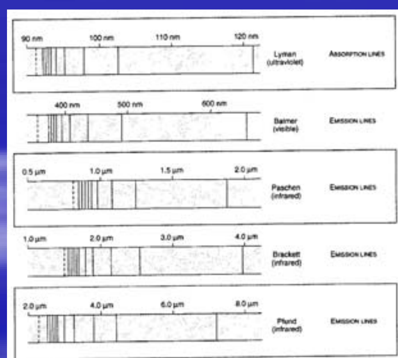
-Each line has a different

Particles behaving as waves : Atomic Spectra

A major area where classical physics break down was the area of atomic physics. The simplest example is hydrogen atom that can adsorbs and emit electromagnetic radiation. Both the adsorption emission spectra consist of series of sharp lines i.e. discrete wavelengths (frequencies), according to

$$\frac{1}{\lambda} = R(\frac{1}{n_f^{\ 2}} - \frac{1}{n_i^{\ 2}})$$

where R=1.0973732 x 10^7 m^{-1}, n_f and n_i are integers.



Atomic hydrogen spectra.
Lyman series: n_f=1;
Balmer series: n_f=2;
Paschen series: n_f=3;
.....

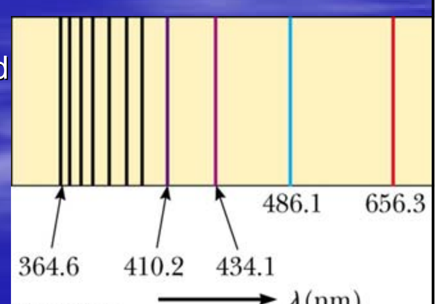
Emission Spectrum of Hydrogen

- The wavelengths of hydrogen's spectral lines can be found from

$$\frac{1}{\lambda} = R_H\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$$

  – R_H is the *Rydberg constant*
    - R_H = 1.0973732 x 10^7 m^{-1}

  – n is an integer, n = 1, 2, 3, …
  – The spectral lines correspond different values of n
- A.k.a. *Balmer series*
- Examples of spectral lines
  – n = 3, λ = 656.3 nm
  – n = 4, λ = 486.1 nm



Absorption Spectra

- An element can also absorb light at specific wavelengths
- An absorption spectrum can be obtained by passing a continuous radiation spectrum through a vapor of the gas
- The absorption spectrum consists of a series of dark lines superimposed on the otherwise continuous spectrum
  – The dark lines of the absorption spectrum coincide with the bright lines of the emission spectrum

Applications of Absorption Spectrum

- The continuous spectrum emitted by the Sun passes through the cooler gases of the Sun's atmosphere
  – The various absorption lines can be used to identify elements in the solar atmosphere
  – Led to the discovery of helium

Difficulties with the Rutherford Model

- Cannot explain emission/absorption spectra
- Rutherford's electrons are undergoing a centripetal acceleration and so should radiate electromagnetic waves of the same frequency, thus leading to electron "falling on a nucleus" in about 10^{-12} seconds!!!

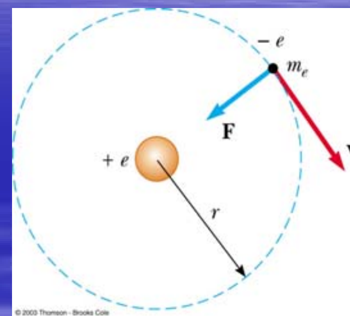
Bohr's model addresses those problems

The Bohr Theory of Hydrogen

- In 1913 Bohr provided an explanation of atomic spectra that includes some features of the currently accepted theory
- His model includes both classical and non-classical ideas
- His model included an attempt to explain why the atom was stable

Bohr's Assumptions for Hydrogen

- The electron moves in circular orbits around the proton under the influence of the Coulomb force of attraction
  - The Coulomb force produces the centripetal acceleration
- Only certain electron orbits are stable
  - These are the orbits in which the atom does not emit energy in the form of electromagnetic radiation
  - Therefore, the energy of the atom remains constant and classical mechanics can be used to describe the electron's motion
- Radiation is emitted by the atom when the electron "jumps" from a more energetic initial state to a lower state
  - The "jump" cannot be treated classically



$$E_i - E_f = hf$$

Bohr's Assumptions

- More on the electron's "jump":
  - The frequency emitted in the "jump" is related to the change in the atom's energy
  - It is *generally not the same as the frequency of the electron's orbital motion*

$$E_i - E_f = hf$$

- The size of the allowed electron orbits is determined by a condition imposed on the electron's orbital angular momentum

$$m_e v r = n\left(\frac{h}{2\pi}\right), \quad n = 1, 2, 3, \ldots$$

Results

- The total energy of the atom

$$E = KE + PE = \frac{1}{2} m_e v^2 - k_e \frac{e^2}{r}$$

- Newton's law $F = m_e a \quad or \quad k_e \frac{e^2}{r^2} = m_e \frac{v^2}{r}$
- This can be used to rewrite kinetic energy as

$$KE \equiv \frac{mv^2}{2} = k_e \frac{e^2}{2r}$$

- Thus, the energy can also be expressed as

$$E = -\frac{k_e e^2}{2r}$$

How to explain the hydrogen spectra?

Bohr Model of Atom: Like Rutherford's plant model, the electrons orbit around the nucleus, but the electrons can only go around in orbits in which **the angular momentum is an integral multiple of** $\hbar$ or

$$mvr = n\hbar$$

Where n=1, 2, 3, … , m is the mass of electron, v is the orbital velocity and r the orbital radius of the electron. Using this postulate, Bohr was able to fit the hydrogen spectra and explain why the electron does not radiate continuously and collapse into the nucleus - **the electron cannot radiate unless it jumps from allowed orbit to another.**

A quantitative description of Bohr's model:

$$F = ma_c$$

$$\frac{1}{4\pi\varepsilon_0} \frac{e^2}{r^2} = m \frac{v^2}{r}$$

$$\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r} = mv^2$$

The kinetic energy is: $KE = \frac{1}{2}mv^2 = \frac{1}{8\pi\varepsilon_0}\frac{e^2}{r}$

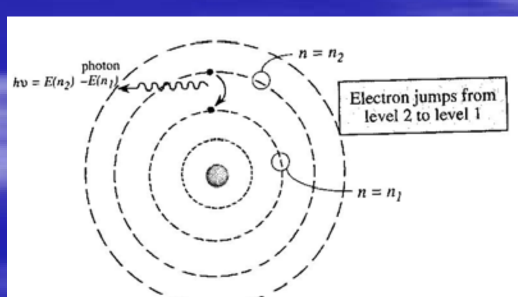
The potential energy is the electrostatic energy: $U = -\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}$

The total energy is: $E = KE + U = -\frac{1}{8\pi\varepsilon_0}\frac{e^2}{r}$

According to Bohr's postulation, $mvr = n\hbar$

$$r_n = \frac{4\pi\varepsilon_0}{me^2}(n\hbar)^2 = n^2 a_0 \text{ where } a_0 = \frac{4\pi\varepsilon_0}{me^2}\hbar^2 = 0.053\ nm.$$

$$E_n = -\frac{me^4}{32\pi^2\varepsilon_0{}^2\hbar^2}\frac{1}{\mathrm{n}^2} = -\frac{13.6\mathrm{eV}}{\mathrm{n}^2}.$$



Discrete spectral lines are explained by transitions of the electron from one level to another.

Bohr Radius

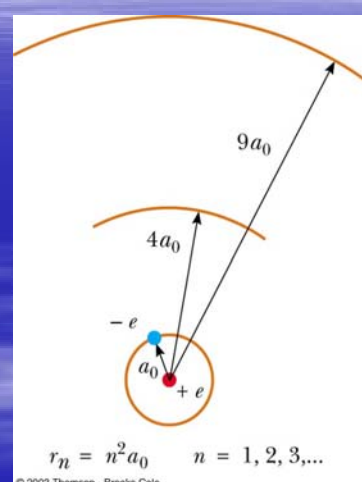
- The radii of the Bohr orbits are quantized

$$r_n = \frac{n^2 \hbar^2}{m_e k_e e^2} \qquad n = 1, 2, 3, \ldots$$

  - This shows that the *electron can only exist in certain allowed orbits determined by the integer n*
    - When n = 1, the orbit has the smallest radius, called the *Bohr radius*, a_o
    - $a_o = 0.0529$ nm

Radii and Energy of Orbits

- A general expression for the radius of any orbit in a hydrogen atom is
  - $r_n = n^2 a_o$
- The energy of any orbit is
  - $E_n = -13.6 \text{ eV}/n^2$
- The lowest energy state is called the *ground state*
  - This corresponds to n = 1
  - Energy is –13.6 eV
- The next energy level has an energy of –3.40 eV
  - The energies can be compiled in an *energy level diagram*
- The *ionization energy* is the energy needed to completely remove the electron from the atom
  - The ionization energy for hydrogen is 13.6 eV

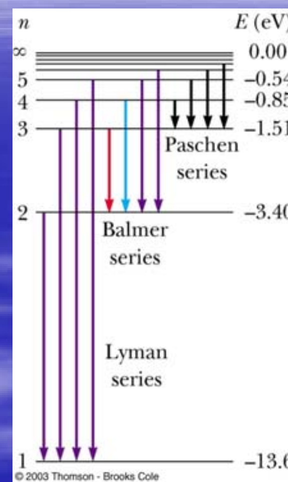


Energy Level Diagram

- The value of R_H from Bohr's analysis is in excellent agreement with the experimental value
- A more generalized equation can be used to find the wavelengths of any spectral lines

$$\frac{1}{\lambda} = R_H\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

  - For the Balmer series, $n_f = 2$
  - For the Lyman series, $n_f = 1$
- Whenever a transition occurs between a state, n_i and another state, n_f (where $n_i > n_f$), a photon is emitted
  - The photon has a frequency f = (Ei – Ef)/h and wavelength λ



Transitions in the Bohr's model

A photon is emitted as a hydrogen atom undergoes a transition from the $n = 6$ state to the $n = 2$ state. Calculate the energy and the wavelength of the emitted photon.

A photon is emitted as a hydrogen atom undergoes a transition from the $n = 6$ state to the $n = 2$ state. Calculate the energy and the wavelength of the emitted photon.

Given:

$n_i = 6$
$n_f = 2$

Find:

(α) $\lambda = ?$
(b) $E_\gamma = ?$

From $\frac{1}{\lambda} = R_H\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$,

or $\lambda = \frac{1}{R_H}\left(\frac{n_i^2 n_f^2}{n_i^2 - n_f^2}\right)$ with $n_i = 6$ and $n_f = 2$

$$\lambda = \frac{1}{1.09737 \times 10^7 \text{ m}^{-1}}\left[\frac{(36)(4)}{36-4}\right] = 4.10 \times 10^{-7} \text{ m} = \boxed{410 \text{ nm}}$$

Photon energy is

$$E = \frac{hc}{\lambda} = \frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{410 \times 10^{-9} \text{ m}} = 4.85 \times 10^{-19} \text{ J} = \boxed{3.03 \text{ eV}}$$

Bohr's Correspondence Principle

- Bohr's *Correspondence Principle* states that quantum mechanics is in agreement with classical physics when the energy differences between quantized levels are very small
  - Similar to having Newtonian Mechanics be a special case of relativistic mechanics when v << c

Successes of the Bohr Theory

- Explained several features of the hydrogen spectrum
  - Accounts for Balmer and other series
  - Predicts a value for R_H that agrees with the experimental value
  - Gives an expression for the radius of the atom
  - Predicts energy levels of hydrogen
  - Gives a model of what the atom looks like and how it behaves
- Can be extended to "hydrogen-like" atoms
  - Those with one electron
  - Ze^2 needs to be substituted for e^2 in equations
    - Z is the atomic number of the element

Recall Bohr's Assumptions

- Only certain electron orbits are stable. Radiation is emitted by the atom when the electron "jumps" from a more energetic initial state to a lower state

$$E_i - E_f = hf$$

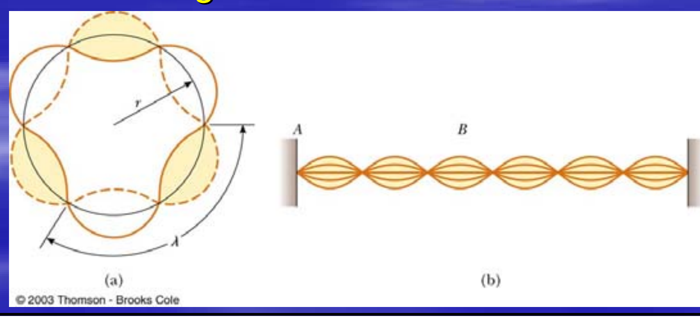
- The size of the allowed electron orbits is determined by a condition imposed on the electron's orbital angular momentum

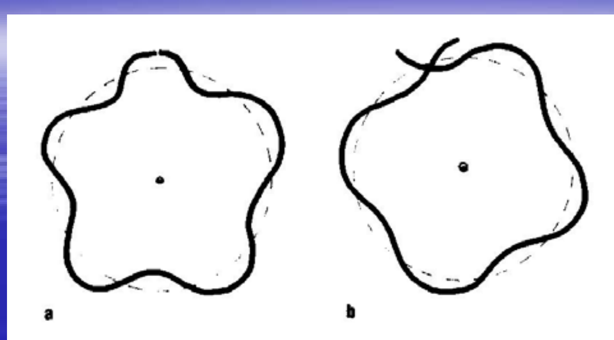
$$m_e vr = n\hbar, \quad n = 1, 2, 3, \ldots$$

Why is that?

de Broglie Waves

- One of Bohr's postulates was the angular momentum of the electron is quantized, but there was no explanation why the restriction occurred
- de Broglie assumed that the electron orbit would be stable only if it contained an integral number of electron wavelengths





(a) Orbit electrons form standing waves only when the circumference of the orbit is equal to an integral number of wavelengths. In (b), the wave does not close in on itself in phase, and therefore it undergoes destructive interference.

$$n\lambda = 2\pi r$$

Since $\lambda = \frac{h}{p}$, we have

$$mvr = n\hbar$$

This is precisely the Bohr postulation!

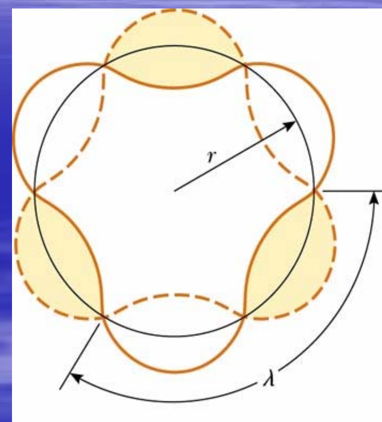
de Broglie Waves in the Hydrogen Atom

- In this example, three complete wavelengths are contained in the circumference of the orbit
- In general, the circumference must equal some integer number of wavelengths

$$2\pi r = n\lambda, \quad \lambda = 1, 2, 3, \ldots$$

but $\lambda = \dfrac{h}{m_e v}$, so

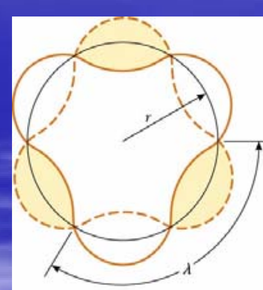
$$m_e v r = n\hbar, \quad n = 1, 2, 3, \ldots$$



This was the first convincing argument that the wave nature of matter was at the heart of the behavior of atomic systems

wavelength of the electron

Determine the wavelength of an electron in the third excited orbit of the hydrogen atom, with *n* = 4.



Determine the wavelength of an electron in the third excited orbit of the hydrogen atom, with $n = 4$.

Given:

n = 4

Find:

λ_e = ?

Recall that de Broglie's wavelength of electron depends on its momentum, $\lambda = h/(m_e v)$. Let us find it,

$$m_e v r_n = n\hbar, \quad so \quad m_e v = \frac{n\hbar}{r_n}$$

Recall that $r_n = n^2 a_0, \quad so \quad m_e v = \frac{h}{(2\pi a_0)n}$

Thus, $\lambda = \frac{h}{m_e v} = (2\pi a_0)n = 8\pi(0.0529nm) = 1.33nm$

Quantum Mechanics and the Hydrogen Atom

- One of the first great achievements of quantum mechanics was the solution of the wave equation for the hydrogen atom
- The significance of quantum mechanics is that the quantum numbers and the restrictions placed on their values arise directly from the mathematics and not from any assumptions made to make the theory agree with experiments

Modifications of the Bohr Theory – Elliptical Orbits

- Sommerfeld extended the results to include elliptical orbits
  - Retained the *principle quantum number*, n
  - Added the *orbital quantum number*, ℓ
    - ℓ ranges from 0 to n-1 in integer steps
  - All states with the same principle quantum number are said to form a *shell*
  - The states with given values of n and ℓ are said to form a *subshell*

Modifications of the Bohr Theory – Zeeman Effect and fine structure

- Another modification was needed to account for the *Zeeman effect*
  - The Zeeman effect is the splitting of spectral lines in a strong magnetic field
  - This indicates that the energy of an electron is slightly modified when the atom is immersed in a magnetic field
  - A new quantum number, m_ℓ, called the *orbital magnetic quantum number*, had to be introduced
    - m_ℓ can vary from - ℓ to + ℓ in integer steps
- High resolution spectrometers show that spectral lines are, in fact, two very closely spaced lines, even in the absence of a magnetic field
  - This splitting is called *fine structure*
  - Another quantum number, m_s, called the *spin magnetic quantum number,* was introduced to explain the fine structure

Quantum Number Summary

TABLE 28.2 Three Quantum Numbers for the Hydrogen Atom

Quantum Number	Name	Allowed Values	Number of Allowed States
n	Principal quantum number	1, 2, 3, . . .	Any number
ℓ	Orbital quantum number	0, 1, 2, . . . , $n-1$	n
m_ℓ	Orbital magnetic quantum number	$-\ell, -\ell+1, \ldots, 0, \ldots, \ell-1, \ell$	$2\ell+1$

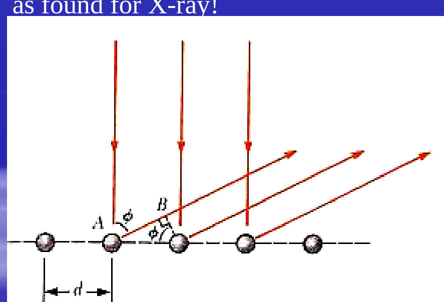
- The values of n can increase from 1 in integer steps
- The values of ℓ can range from 0 to n-1 in integer steps

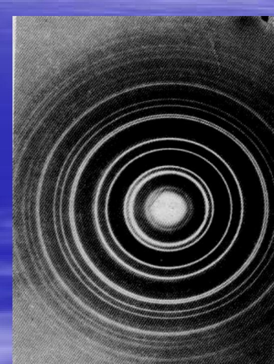
A direct proof electron waves: The Davisson-Germer Experiment

Constructive interference of electrons scattered an array of surface atom at an angle f is described by

dsin(ϕ)=nλ (3.32)

as found for X-ray!





Diffraction of 50 keV electrons from a Cu_3Au alloy film.

Why surface atoms only?

CONCLUSIONS

Light and matter exhibit wave-particle duality

Relation between wave and particle properties given by the de Broglie relations

$$E = h\nu \qquad p = \frac{h}{\lambda}$$

Evidence for particle properties of light
Photoelectric effect, Compton scattering

Evidence for wave properties of matter
Electron diffraction, interference of matter waves (electrons, neutrons, He atoms, C60 molecules)

Heisenberg uncertainty principle limits simultaneous knowledge of conjugate variables

$$\Delta x \Delta p_x \geq \hbar / 2$$
$$\Delta y \Delta p_y \geq \hbar / 2$$
$$\Delta z \Delta p_z \geq \hbar / 2$$