Chapter 27

Early Quantum Theory and Models of the Atom
Units of Chapter 27

Origins of the Quantum theory…….

- Discovery and Properties of the Electron
- Planck’s Quantum Hypothesis; Blackbody Radiation
- Photon Theory of Light and the Photoelectric Effect
- Energy, Mass, and Momentum of a Photon
- Photon Interactions; Pair Production
- Wave Nature of Matter
- Electron Microscopes
- Early Models of the Atom
- Atomic Spectra: Key to the Structure of the Atom
- The Bohr Model
- de Broglie’s Hypothesis Applied to Atoms
27.1 Discovery and Properties of the Electron

In the late 19th century, discharge tubes were made that emitted “cathode rays.” Cathode rays are called electrons.
27.1 J.J Thomson’s 1890 apparatus to measure the charge/mass ratio (e/m)

- Cathode rays could be deflected by electric or magnetic fields.
- Measuring the angle of deflection gave e/m
- But finding e and m separately proved elusive
27.1 Discovery and Properties of the Electron

By accelerating cathode rays through a known potential and then measuring the radius of their curved path in a known magnetic field, the charge to mass ratio could be measured:

\[ v = \frac{E}{B} \]

\[ \frac{e}{m} = \frac{E}{B^2r} \]  \hspace{1cm} (27-1)

The result is \( e/m = 1.76 \times 10^{11} \text{ C/kg} \)

Cathode rays are called electrons.
27.1 Discovery and Properties of the Electron

Millikan devised an experiment to measure the charge on the electron by measuring the electric field needed to suspend an oil droplet of known mass between parallel plates.

The mass and charge of each oil droplet were measured; careful analysis of the data showed that the charge was always an integral multiple of a smallest charge, $e$.

Knowing $e$ allows the electron mass to be calculated:

$$e = 1.602 \times 10^{-19} \text{ C}$$

$$m_e = 9.11 \times 10^{-31} \text{ kg}$$
Design of the e/m experiment

- Accelerate a beam of electrons through a known potential difference so they gain a known kinetic energy \( E = qV \) and speed.
- Direct the beam through a known magnetic field, so the beam bends into a circle.
- Measure the radius of the circular path.
- Equate the centripetal force to the magnetic force.

Voltage to Accelerate electrons
Current to coils, to provide magnetic field
27.2 Planck’s Quantum Hypothesis; Blackbody Radiation

Blackbody radiation curves for three different temperatures.

**Wien’s Law:**
\[ \lambda_p \ T = k = 2.9 \times 10^{-3} \text{ m.K} \]

Radiation and Temperature

Heated bodies generally radiate across the entire electromagnetic spectrum. There is one particular wavelength, \( \lambda_p \), at which the radiation is most intense.
27.2 Planck’s Quantum Hypothesis; Blackbody Radiation

This spectrum could not be reproduced using 19th-century physics.

All attempts were either purely descriptive (like Wien’s law), or led to the so-called “ultraviolet catastrophe” - failure to derive the decline in flux at short wavelengths, leading to unrealistic prediction of limitless radiation in the UV.

A solution was proposed by Max Planck in 1900:

The atoms are all radiating, absorbing and redistributing energy between themselves. Each behaves as a harmonic oscillator with discrete modes.

The distribution of atomic oscillator energies leads to the black-body spectrum.

The oscillations within atoms can only occur at discrete frequencies that are multiples of a certain minimum value. (like modes on a string, or in a pipe)

Introduced a new fundamental constant of nature: Plank’s Constant: $h$

Many including Planck viewed this model as purely a mathematical device.

Today we view it as the first physically correct model in quantum physics!
27.2 Planck’s Quantum Hypothesis; Blackbody Radiation

Planck found the value of his constant by fitting blackbody curves:  

$$h = 6.626 \times 10^{-34} \text{ J} \cdot \text{s}$$

Planck’s proposal was that the energy of an oscillation had to be an integer multiple of $hf$. This is called the quantization of energy.

\[ E = hf \]

\[ E = nhf \quad \text{with} \quad n = 1, 2, 3, \ldots \]
27.3 Photon Theory of Light and the Photoelectric Effect

Einstein (1905) suggested that, given the success of Planck’s theory, light must be emitted in small energy packets:

\[ E = hf \]  

These tiny packets, or particles, are called photons.

This theory won Einstein the Nobel Prize.

He had resurrected Newton’s 400 yr old idea of light as a stream of particles.
27.3 Photon Theory of Light and the Photoelectric Effect

The photoelectric effect:

If light strikes a metal, electrons are emitted.

\[ hf = KE_{\text{max}} + W_0 \]

\[ KE_{\text{max}} = eV_0 \]

The effect does not occur if the frequency of the light is too low.
If light is a stream of particles, one predicts:

- Increasing intensity increases number of electrons but not energy
- Above a minimum energy required to break atomic bond, kinetic energy will increase linearly with frequency
- There is a cutoff frequency below which no electrons will be emitted, regardless of intensity
27.3 Photon Theory of Light and the Photoelectric Effect

The particle theory assumes that an electron absorbs a single photon.

Plotting the kinetic energy vs. frequency:

\[ KE_{\text{max}} = e \cdot V_0 = hf - W_0 \]

This shows clear agreement with the photon theory, and not with wave theory.
27.3 Photon Theory of Light and the Photoelectric Effect

The photoelectric effect is how “electric eye” detectors work. It is also used for movie film soundtracks.

Photoelectric Effect also occurs in Nature - e.g. Photosynthesis, Sunburn
27.4 Energy, Mass, and Momentum of a Photon

- A photon must travel at the speed of light.
- Quantum theory (photoelectric effect) says
  \[ \text{Kinetic energy} = E_{\text{photon}} = hf \]
- Look at the relativistic equation for momentum:
  \[ E^2 = p^2c^2 + m^2c^4 \]
- The photon has no mass, so this reduces to
  \[ E_{\text{photon}} = pc \]
- We combine these equations and find that a photon **must** carry momentum!

\[ p = \frac{E}{c} = \frac{hf}{c} = \frac{h}{\lambda} \]  
\[ (27-6) \]
27.5 Compton Effect

This is another effect that is correctly predicted by the photon model and not by the wave model.

Before Collision

- Incident photon ($\lambda$)
- Electron at rest

After Collision

- Scattered photon ($\lambda'$)
- $\lambda' > \lambda$

Diagram showing a collision between an electron at rest and an incident photon, resulting in a scattered photon with a longer wavelength.
In pair production, energy, electric charge, and momentum must all be conserved.

Energy will be conserved through the mass and kinetic energy of the electron ($e^-$) and positron ($e^+$); their opposite charges conserve charge; and the interaction must take place in the electromagnetic field of a nucleus, which can contribute momentum.
27.8 de Broglie and the Wave Nature of Matter

• Louis de Broglie, arguing from the idea of *symmetry* in nature discovered the following:
  • Just as light sometimes behaves as a particle, matter sometimes behaves like a wave.
  • The wavelength of a particle of matter is:

\[ \lambda = \frac{h}{p} \]  \hspace{1cm} (27-8)

This wavelength is extraordinarily small.

De Broglie wavelength depends on the particle’s momentum.
27.9 Electron Microscopes

The wavelength of electrons will vary with energy, but is still quite short. This makes electrons useful for imaging – remember that the smallest object that can be resolved is about one wavelength. Electrons used in electron microscopes have wavelengths of about 0.004 nm.

All the properties of optics apply to particles! If we use the appropriate de Broglie wavelength!
27.9 Electron Microscopes

- Transmission electron microscope – the electrons are focused by magnetic coils
- The magnetic coils act as lenses to focus the electron beam
- The resolution limit \( (1.22\lambda/D) \) still applies
- Electron wavelength is tiny compared to that of light \( 0.004\text{nm vs 500nm} \)
- So much smaller details can be seen
27.9 Scanning Electron Microscope

Scanning electron microscope – the electron beam is scanned back and forth across the object to be imaged.
27.10 Early Models of the Atom

It was known that atoms were electrically neutral, but that they could become charged, implying that there were positive and negative charges and that some of them could be removed.

One popular atomic model was the “plum-pudding” model:
Rutherford’s Experiment

- Rutherford in 1911 did an experiment that showed that the positively charged nucleus must be extremely small compared to the rest of the atom, and contain essentially all of the mass.

- He directed alpha particles (emitted by some radioactive elements) at a thin metal foil and observed the scattering angle.

- Rutherford found that a tiny fraction of these “bullets” bounced right back!

- Meaning they had hit something massive, yet tiny.

- The atom was mostly empty space!
Rutherford’s Experiment

The only way to account for the large angles was to assume that all the positive charge was contained within a tiny volume – now we know that the radius of the nucleus is 1/10000 that of the atom.
In Rutherford’s model, the electron(s) orbit the nucleus like planets in the solar system.

Held in place by Coulomb force (instead of gravity).


If the electron loses potential energy it falls closer to the nucleus.....

So this electron would spiral into the nucleus immediately.

Niels Bohr suggested the Quantum nature of light could make the atom stable.
An atomic spectrum is a line spectrum – only certain frequencies appear.

If white light passes through such a gas, it absorbs at those same frequencies.

Each line is due to photons with a specific energy

What if these energies correspond to special “allowed” level inside the atom?
27.11 Atomic Spectra: Key to the Structure of the Atom

A very thin gas heated in a discharge tube emits light only at characteristic frequencies.
The wavelengths of electrons emitted from hydrogen have a regular pattern:

\[ \frac{1}{\lambda} = R \left( \frac{1}{2^2} - \frac{1}{n^2} \right), \quad n = 3, 4, \ldots \]  

(27-9)

This is called the **Balmer series**. *R* is called the Rydberg constant:

\[ R = 1.0974 \times 10^7 \text{ m}^{-1} \]

- A spectral line occurs for each value of *n*.
- There are 5 visible lines in the Balmer series: Hα (red), Hβ, Hγ, Hδ, Hε
- This is a ‘phenomenological’ or ‘empirical’ theory - it is very accurate but explains nothing. The constant “R” is easily measured with a spectroscope (basically a prism or a diffraction grating)
- But we are still at “WHY?”
Other series include the Lyman series (in the Ultraviolet):

\[ \frac{1}{\lambda} = R \left( \frac{1}{1^2} - \frac{1}{n^2} \right), \quad n = 2, 3, \ldots \]

And the Paschen series (in the Infrared):

\[ \frac{1}{\lambda} = R \left( \frac{1}{3^2} - \frac{1}{n^2} \right), \quad n = 4, 5, \ldots \]

Note the series differ only in this number
27.11 Atomic Spectra: Key to the Structure of the Atom

A portion of the complete spectrum of hydrogen is shown here. The lines cannot be explained by the Rutherford theory.

[Diagram of atomic spectrum with labeled wavelengths and series: Lyman series, Balmer series, Paschen series, UV, Visible light, IR]
Niels Bohr proposed that the possible energy states for atomic electrons were quantized – only certain values were possible. Then the spectrum could be explained as transitions from one level to another.

\[ hf = E_u - E_l \]
27.12 The Bohr Atom

After trying various ideas....

Bohr found that the angular momentum was quantized:

\[ L = mvr_n = n \frac{h}{2\pi}, \quad n = 1, 2, 3, \ldots \] (27-11)

It worked perfectly!

But there was still no physical motivation.....
27.12 The Bohr Atom

An electron is held in orbit by the Coulomb force:

\[ F = k \frac{(Ze)(e)}{r^2} \]

So you can calculate the radii of the “orbit” responsible for each spectral line.

By equating centripetal force and coulomb force
27.12 The Bohr Atom

Using the Coulomb force, we can calculate the radius of 1\textsuperscript{st} orbit (n=1) orbit for hydrogen (Z=1):

\[ r_1 = \frac{\hbar^2}{4\pi^2 m e^2} = 0.529 \times 10^{-10} \text{ m} \quad (27-13) \]

Radius of n\textsuperscript{th} orbit:

\[ r_n = \frac{n^2 \hbar^2}{4\pi^2 m k Z e^2} = \frac{n^2}{Z} r_1 \quad (27-12) \]

The equation above comes from equating the centripetal force needed to balance the coulomb force. -a type of calculation you are all familiar with.

The resulting levels are not evenly spaced in radius- just like the spectral lines are not evenly spaced, but follow a distinct pattern.
27.12 The Bohr Atom

For Hydrogen (Z=1)

• Lowest energy (n=1) → ground state energy:
  \[ E_1 = -13.6 \text{ eV} \]

• Higher energy states → excited states:
  \[ E_n = -\frac{13.6 \text{ eV}}{n^2}, \quad n = 2, 3, 4 \ldots \]

• Ionization energy or binding energy → Minimum energy required to remove an electron from the ground state
  • Requires +13.6eV to remove an electron from the ground state (n=1) for hydrogen.
27.12 The Bohr Atom

- The lowest energy level is called the ground state; the others are excited states.
- Notice how the levels are not evenly spaced in energy or in radius.

Each series of lines corresponds to electron transitions landing on a specific level.

\[
\frac{1}{\lambda} = R \left( \frac{1}{2^2} - \frac{1}{n^2} \right), \quad n = 3, 4, \ldots \quad (27-9)
\]

\[R = 1.0974 \times 10^7 \text{ m}^{-1}\]
Summary of Chapter 27

- Planck’s hypothesis: molecular oscillation energies are quantized
  \[ E = n hf \quad n = 1, 2, 3, \ldots \]
- Light can be considered to consist of photons, each of energy \[ E = hf \]
- Photoelectric effect: incident photons knock electrons out of material
- Compton effect and pair production also support photon theory
- Wave-particle duality – both light and matter have both wave and particle properties
- Wavelength of an object: \[ \lambda = \frac{h}{p} \]
- Principle of complementarity: both wave and particle properties are necessary for complete understanding
- Rutherford showed that atom has tiny nucleus
- Line spectra are explained by electrons having only certain specific orbits
Summary of Chapter 27

• Ground state \((n = 1)\) has the lowest energy of \(-13.6\) eV; the others are called excited states. For Hydrogen \((Z = 1)\)

\[
E_n = \frac{-13.6 \text{ eV}}{n^2} \quad n = 2, 3, 4 \ldots
\]

• Wavelength emitted for hydrogen:
  - Balmer series (in the visible)
    \[
    \frac{1}{\lambda} = R \left( \frac{1}{2^2} - \frac{1}{n^2} \right), \quad n = 3, 4, \ldots
    \]
  - Lyman series (in the ultraviolet)
    \[
    \frac{1}{\lambda} = R \left( \frac{1}{1^2} - \frac{1}{n^2} \right), \quad n = 2, 3, \ldots
    \]
  - Paschen series (in the infrared)
    \[
    \frac{1}{\lambda} = R \left( \frac{1}{3^2} - \frac{1}{n^2} \right), \quad n = 4, 5, \ldots
    \]

• Rydberg constant: \(R = 1.0974 \times 10^7 \text{ m}^{-1}\)
ConcepTest 27.1 Photons

Which has more energy, a photon of:

1) red light
2) yellow light
3) green light
4) blue light
5) all have the same energy
The photon with the highest frequency has the most energy because $E = hf = hc/\lambda$ (recall that $c = f\lambda$). So a higher frequency corresponds to a lower wavelength. The highest energy of the above choices is blue.

ConcepTest 27.1: Photons

Which has more energy, a photon of:

1) red light
2) yellow light
3) green light
4) blue light
5) all have the same energy