The Photoelectric Effect

- Light can strike the surface of some metals causing an electron to be ejected.

- No matter how brightly the light shines, electrons are ejected only if the light has sufficient energy (sufficiently short wavelength).

- After the necessary energy is reached, the current (# electrons emitted per second) increases as the intensity (brightness) of the light increases.

- The current, however, does not depend on the wavelength.
The Photoelectric Effect

- 1905 - Albert Einstein
  Explained photoelectric effect
  (Nobel prize in physics in 1921)

- Light consists of photons, each with a particular amount of energy, called a quantum of energy
- Upon collision, each photon can transfer its energy to a single electron
- The more photons strike the surface of the metal, the more electrons are liberated and the higher is the current
Emission and Absorption Spectra

- When electric current passes through a sample of gas at very low pressure, light is emitted.
- The picture obtained is called an emission spectrum.
- An absorption spectrum is formed by shining a beam of white light through a sample of gas.
- Every element has a unique emission or absorption spectrum.
Balmer-Rydberg Equation

- An empirical equation that relates the wavelengths of the lines in the hydrogen spectrum

\[ \frac{1}{\lambda} = R \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad (n_1 < n_2) \]

\[ R = 1.097 \times 10^7 \text{ m}^{-1} \] - the Rydberg constant

- n’s refer to the numbers of the energy levels in the emission spectrum of hydrogen

- Balmer-Rydberg equation suggested that atoms have more complex underlying structure
Rydberg Equation: Example

- What is the wavelength of light emitted when the hydrogen atom’s energy level changes from $n = 4$ to $n = 2$?
Bohr’s Atom

- Rydberg equation suggested that atoms have more complex underlying structure

- 1913 - Neils Bohr
  Applied Planck’s quantum theory to explain the hydrogen spectrum
  (Nobel prize in physics in 1921)
Postulates of Bohr’s theory

- Atom has a number of discrete energy levels (orbits) in which an electron may revolve without emitting or absorbing electromagnetic radiation. As the orbital radius increases so does the energy of the electron.
Postulates of Bohr’s theory

- An electron may move from one energy level (orbit) to another, but, in so doing, monochromatic radiation is emitted or absorbed in accordance with the following equation

\[ E_2 - E_1 = \Delta E = h \nu = \frac{hc}{\lambda} \]

\[ E_2 > E_1 \]
Atomic Spectra and the Bohr Atom

- Light of a characteristic wavelength (and frequency) is emitted when the electron moves from higher energy level (larger $n$) to lower energy level (smaller $n$)
  - This is the origin of emission spectra

- Light of a characteristic wavelength (and frequency) is absorbed when the electron moves from lower energy level (smaller $n$) to higher energy level (larger $n$)
  - This is the origin of absorption spectra
Postulates of Bohr’s theory

- An electron revolves in a circular orbit about the nucleus and its motion is governed by the ordinary laws of mechanics and electrostatics, with the restriction that its angular momentum is quantized (can only have certain discrete values)

\[ \text{angular momentum} = m \cdot v \cdot r = \frac{nh}{2\pi} \]

- \( m \) = mass of electron
- \( v \) = velocity of electron
- \( r \) = radius of orbit
- \( n = 1, 2, 3, 4, \ldots \) (energy levels)
- \( h \) = Planck’s constant
Bohr’s Theory

- Bohr’s theory correctly explained the hydrogen emission spectrum.
- The theory failed for all other elements with more than 1 electron.
- Bohr’s theory attempted to use classical mechanics to solve a problem that could not be solved by classical mechanics.
Wave Nature of the Electron

- 1925 - Louis de Broglie
  (Nobel prize in physics in 1929)
  - Not only electromagnetic waves can be sometimes considered as particles (photons)
  - Very small particles (electrons) might also behave as waves under the proper circumstances

\[ \lambda = \frac{h}{mv} \]

Planck’s constant
mass and velocity of the particle
Wave Nature of the Electron

- How to prove this experimentally?
  - Every wave should exhibit the phenomena of interference and diffraction
Wave Nature of the Electron

- De Broglie’s assertion was verified by Davisson & Germer within two years:
  - They demonstrated that a beam of electrons can diffract through a crystal of nickel

- Today we now know that electrons (in fact - all particles) have both particle- and wave-like character
  - This wave-particle duality is a fundamental property of submicroscopic particles.
Determine the wavelength, in m, of an electron, with mass $9.11 \times 10^{-31}$ kg, having a velocity of $5.65 \times 10^7$ m/s.
Wave-Particle Duality

Determine the wavelength, in m, of a 0.22 caliber bullet, with mass $3.89 \times 10^{-3}$ kg, having a velocity of 395 m/s
Heisenberg Uncertainty Principle

- 1927 - Werner Heisenberg (Nobel prize in physics in 1932)
- Developed the concept of the Uncertainty Principle
  - It is impossible to determine simultaneously both the position and momentum of an electron (or any other small particle)
Schrödinger Equation

- 1926 - Erwin Schrödinger (Nobel prize in physics in 1933)
- Demonstrated that the small particles should be described in terms of probability theory

\[
-\frac{\hbar^2}{8\pi^2m} \left( \frac{\partial^2 \Psi}{\partial^2 x} + \frac{\partial^2 \Psi}{\partial^2 y} + \frac{\partial^2 \Psi}{\partial^2 z} \right) + V\Psi = E\Psi
\]

- We cannot determine precisely the position of the electron but we can determine the probability of electron being present in certain region of space
Electrons can occupy only discrete energy levels with certain amount of energy.

When an electron changes its energy state, it must emit or absorb just enough energy to bring it to the new energy state (the quantum condition).

\[ \Delta E = E_2 - E_1 = h \nu = \frac{hc}{\lambda} \]
The allowed energy states of atoms and molecules can be described by sets of numbers called quantum numbers.

Quantum numbers emerge from the solutions of the Schrödinger equation.

Four quantum numbers are necessary to describe energy states of electrons in atoms:

\[ n \quad \ell \quad m_\ell \quad m_s \]
Quantum Numbers

- $n$ - the principal quantum number
  - Allowed values
    - $n = 1, 2, 3, 4, \ldots$ “shells”
    - $n = K, L, M, N, \ldots$

- $\ell$ - the angular momentum quantum number
  - Allowed values
    - $\ell = 0, \ldots, n - 1$ “subshells”
    - $\ell = s, p, d, f, \ldots$
Quantum Numbers and Orbitals

- $n + \ell$
  - Define the energy of the electron

- $\ell$
  - Defines the shape of the orbital

- Orbital
  - The volume around the nucleus where the electron appears 90-95% of the time.
Quantum Numbers

- $m_l$ - the magnetic quantum number
  - Allowed values
    
    \[ m_l = -\ell, -\ell + 1, -\ell + 2, \ldots, \ell - 2, \ell - 1, \ell \]
  
    - Defines the orientation of the orbital
Quantum Numbers

- $m_s$ - the spin quantum number
  - Allowed values
    - $m_s = -\frac{1}{2}, +\frac{1}{2}$
  - Defines the orientation of the magnetic field generated by the electron

- 1925 - Wolfgang Pauli
  - (Nobel prize in physics in 1945)
- Formulated Pauli Exclusion Principle
  - Any electron can have only one unique set of the four quantum numbers
$s$ orbital ($\ell = 0$)
$p$ orbital ($\ell = 1$)

- There are 3 $p$ orbitals per $n$ level
- They are named $p_x$, $p_y$, and $p_z$
$d$ orbital ($\ell = 2$)

- There are 5 $d$ orbitals per $n$ level
There are 7 \( f \) orbitals per \( n \) level