Chapter 7: The Quantum-Mechanical Model of the Atom

**Homework:** Read Chapter 7. Work out sample/practice exercises

*Check for the MasteringChemistry.com assignment and complete before due date*

**Earlier we learned:**

*Dalton’s Indivisible Atom* explained the Law of Constant Composition and the Law of Conservation of Mass and led to the Law of Multiple Proportions.

*J.J. Thomson*, through Cathode Ray Tube experiments, discovered that electrons are small negatively charged particles inside a divisible atom and came up with the *Plum Pudding Model* of the atom.

*Rutherford* came up with the gold foil experiment shooting alpha particles through thin gold foil to test the Plum Pudding Model and discovered that some alpha particles were deflected. This led to *Rutherford’s Nuclear Model* of the atom in which a heavy positive nucleus is surrounded by a cloud of electrons.

Now we will further our knowledge of the atom by describing how electrons behave inside the atom.

**Important Constants and Equations:**

Below are several terms, constants and important equations for this section.

\[ c = \lambda \nu; \]

- wavelength (\(\lambda\)), frequency or hertz (\(\nu\)), speed of light (\(c=3.00 \times 10^8 \text{ m/s}\))

  *sidenote: sound waves move about 340 m/s*

\[ E = h\nu; \]

- Planck’s constant (\(h=6.6262 \times 10^{-34} \text{ J s}\))

\[ \frac{1}{\lambda} = R \left[ \frac{1}{n_{\text{final}}^2} - \frac{1}{n_{\text{initial}}^2} \right] \]

- Rydberg’s constant (\(R = 1.097 \times 10^7 \text{ m}^{-1}\))

Energy of a Bohr Hydrogen orbit (\(E_n = -B/n^2\))

- Bohr’s constant (\(B = 2.179 \times 10^{-18} \text{ J}\))

De Broglie equation wavelength is Planck’s constant over momentum (\(\lambda = h/(mv)\))

- Mass of an electron (\(m_e = 9.11 \times 10^{-31} \text{ kg}\))

Heisenberg’s Uncertainty Principle (\(\Delta x \cdot \Delta (mv) \geq h/(4\pi)\))
Quantum Mechanics:

Explains the behavior of the electrons inside atoms and leads to the explanation of the periodic law and chemical bonding

Electrons are very small.
Electron behavior determines much of the behavior of atoms
Directly observing electrons is impossible; observing an electron would change its behavior

Nature of Light:

Electromagnetic radiation (also called Light) is wave-like:

speed of light = (wavelength)(frequency); \(c = \lambda \nu\) speed of light \((c = 3.00 \times 10^8 \text{ m/s})\)

Electromagnetic radiation has a magnetic field component and perpendicular to that an electric field component.
The electromagnetic spectrum is continuous starting with the low energy, long wavelength, low frequency radio waves and increasing in energy through microwaves, IR, VIS (ROYGBIV), UV, Xrays, and gamma rays which are high energy, short wavelength, high frequency).

The color of light is determined by its wavelength: Visible light: 750nm-400nm

Example 1:

\[ c = \lambda \nu; \]

wavelength (\( \lambda \)), frequency or hertz (\( \nu \)), speed of light (\( c=3.00 \times 10^8 \text{m/s} \))

\[ E = h \nu; \]

Planck’s constant (\( h=6.6262 \times 10^{-34} \text{ J s} \))

a) Solve for the frequency of green light with a wavelength of 540nm.

b) Solve for the wavelength of a radio signal whose frequency is 100.7MHz. \( \text{Hz} = \text{s}^{-1} \)

c) Solve for the energy of a photon with a frequency of \( 2.55 \times 10^{14} \text{s}^{-1} \).
The interaction between waves is called **interference**

- When waves interact so that they add to make a larger wave it is called **constructive interference**: waves are in-phase

![Waves in phase and constructive interference](image1)

- When waves interact so they cancel each other it is called **destructive interference**: waves are out-of-phase

![Waves out of phase and destructive interference](image2)

**Diffraction:**

- When traveling waves encounter an obstacle or opening in a barrier that is about the same size as the wavelength, they bend around it – this is called **diffraction**

- The diffraction of light through two slits separated by a distance comparable to the wavelength results in an interference pattern of the diffracted waves

- An interference pattern is a characteristic of all light waves; traveling particles do not diffract
Light is particle-like ($E = h\nu$ or $E = \frac{hc}{\lambda}$). Light has photons of quantized energy. Quantized energy can explain the emission of light from hot bodies, the emission of electrons from metal surfaces on which light shines (the photoelectric effect).

**Photoelectric Effect:** Many metals emit electrons when light (photons) shines on their surface. It was observed that a minimum frequency (called threshold frequency) is needed before electrons would be emitted from the surface of a metal. Greater intensity or brightness of light only increased the current once the minimal frequency was met. In 1905, Albert Einstein published a paper explaining experimental data from the photoelectric effect as the result of light energy in **discrete quantized packets**. This led to the quantum revolution. Einstein was awarded the Nobel Prize in 1921 for "his discovery of the law of the photoelectric effect".

The photoelectric effect experiment shown below led to photons and $E = h\nu$

Planck’s constant $(h = 6.6262 \times 10^{-34} \text{ J s})$
**Emission Spectra:** the emission of light (waves) from excited gas atoms. When atoms or molecules absorb energy, that energy is often released as light energy. The spectrum is noncontinuous (quantized) and can be used to identify the material.
Emission Spectra are like fingerprints, each element or compound has a unique emission spectrum. This allows scientists to investigate what matter makes up our sun, the stars or the planet Mars without the necessity to bring back material samples to earth for testing.

![Helium spectrum](image1)

![Barium spectrum](image2)

![White light spectrum](image3)

**Johannes Rydberg (1854–1919)** analyzed the spectrum of hydrogen and found that a mathematical equation could describe the lines...

\[
1/\lambda = R\left[1/n_{\text{final}}^2 - 1/n_{\text{initial}}^2\right]
\]

Rydberg’s constant (R = 1.097 x 10⁷ m⁻¹)

*This equation only works for hydrogen*

**Example 2:**

Solve for the wavelength that is emitted as an electron jumps from level 5 to level 2.

\[n_{\text{initial}} = 5 \text{ and } n_{\text{final}} = 2\]

**Problems with Rutherford’s nuclear atom:**

- Electrons are moving charged particles
- According to classical physics, moving charged particles give off energy
- Therefore electrons should constantly be giving off energy; they should glow!
- The electrons should lose energy, crash into the nucleus, and the atom should collapse; but it doesn’t!
Neils Bohr (1885–1962)

1913 Bohr’s Model (electrons move around the nucleus in circular orbits):

Emission spectra of hydrogen gave experimental evidence of quantized energy states for electrons within an atom.

Quantum Theory:

- Explains the emission and absorption spectra
- 1. An electron moves in circular orbits at a fixed distance from the nucleus. The energy of the electron is proportional to that distance from the nucleus.
- 2. Therefore, energy of the electron is quantized. An atom has discrete energy levels (orbits) where $e^-$ may exist without emitting or absorbing electromagnetic radiation.
- 3. An electron may jump from one orbit to another. By doing so the electromagnetic radiation is absorbed (jumps farther from nucleus) or emitted (jumps closer to the nucleus and a photon of light is produced).

Emission Spectra of Hydrogen explained by the Bohr Model.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>434</td>
<td>Violet</td>
</tr>
<tr>
<td>486</td>
<td>Blue-green</td>
</tr>
<tr>
<td>657</td>
<td>Red</td>
</tr>
</tbody>
</table>

Bohr’s mathematically equations are limited to one electron systems such as Hydrogen
**Hydrogen Series:**
- $n_{\text{final}} = 1$, Lyman series (UV)
- $n_{\text{final}} = 2$, Balmer series (Visible)
- $n_{\text{final}} = 3$, Paschen series (IR)
- $n_{\text{final}} = 4$, Brackett series (IR)
- $n_{\text{final}} = 5$, Pfund series

**Example 3:** Solve for the energy value of orbits $n = 1, 2, 3, 4, 5$

Energy of a Bohr Hydrogen orbit ($E_n = -\frac{B}{n^2}$)

Bohr’s constant ($B = 2.179 \times 10^{-18} \text{ J}$)

**Example 4:** Solve for the wavelength emitted for a jump from $n = 4$ to $n = 1$

a) Using Rydberg’s equation: $\frac{1}{\lambda} = R\left[\frac{1}{n_{\text{final}}^2} - \frac{1}{n_{\text{initial}}^2}\right]$; ($R = 1.097 \times 10^7 \text{ m}^{-1}$)

b) Using $\Delta E = \frac{hc}{\lambda}$

(h=$6.6262 \times 10^{-34} \text{ J s}$)

**Problem:** Bohr’s theory only worked for spectra with only one electron.
**Louis de Broglie (1892–1987)**

- de Broglie proposed that particles could have wave-like character
- the wavelength of a particle was inversely proportional to its momentum
  \[ \lambda = \frac{h}{mv} \]

  \[ \lambda(m) = \frac{\hbar}{\text{mass}(kg) \cdot \text{velocity}(m \cdot s^{-1})} \]

- Because it is so small, (mass of an electron; \( m_e = 9.11 \times 10^{-31} \) kg), the wave character of electrons is significant

**Electrons** have both particle and wave like properties just as light does. Proof of the wave-like properties came when an experiment demonstrated that beams of electrons passing between slits had interference patterns. If electrons behave only like particles there should be only two bright lines.

The wave and particle nature of the electron are **complementary properties**

As you know more about one you know less about the other

**Example 5:** Calculate the wavelength of an electron traveling at \( 2.75 \times 10^6 \) m/s
Heisenberg’s Uncertainty Principle:

The product of the uncertainties in both the position and speed of a particle was inversely proportional to its mass…

\[ \Delta x \cdot (m \Delta v) \geq \frac{h}{4\pi} \]

\( x \) = position, \( \Delta x \) = uncertainty in position
\( v \) = velocity, \( \Delta v \) = uncertainty in velocity
\( m \) = mass

This means that the more accurately you know the position of a small particle, such as an electron, the less you know about its speed and vice-versa.

Example 6:

a) Calculate the uncertainty in position for an electron in a hydrogen atom if the electron velocity is known to be within 10% of \( 2.2 \times 10^6 \) m/s.
\( m_e = 9.11 \times 10^{-31} \) kg

b) Given that the diameter of a hydrogen atom is 240 pm = \( 2.4 \times 10^{-10} \) m, how does the uncertainty of position compare to the diameter of H?

Bohr’s atomic theory only worked for 1 electron systems, to explain further the next theory involves orbitals not orbits...

Quantum Mechanical Model of the Atom (orbitals):

Electrons can be treated as waves or particles (just as in light)
Weakness: Heisenberg’s Uncertainty Principle. It is impossible to determine both the momentum and position of an electron simultaneously; \( \Delta x \cdot \Delta (mv) \geq \frac{h}{4\pi} \).

Use 90% probability maps (orbitals not orbits) volume of space.

1. Electrons have quantized energy states (orbitals).
2. Electrons absorb or emit electromagnetic radiation when changing energy states.
3. Allowed energy states are described by four quantum numbers: \( n, l, m_l, m_s \), which describe size, shape, position and spin respectively.
The 2s and 3s Orbitals

2s (n = 2, l = 0)

3s (n = 3, l = 0)

Density of dots proportional to probability density ($\psi^2$).

Height of curve proportional to probability density ($\psi^2$).
All the orbitals exist in one atom surrounding one nucleus. The orbitals are each quantized, but it does look a bit like Rutherford’s nuclear model with a cloud of electrons taking up most of the space.

**Orbitals:** 90% probability map for electron location

Shapes and amounts within an energy level

- s-1 spherical shape
- p-3 dumbell shapes on x, y, z
- d-5 shaped
- f-7 shapes

Maximum 2 electrons in any one orbital (must have opposite spins),

Maximum 2n² electrons for any n level

i.e. n= 1, 2 electrons in 1s²; n = 2, 8 electrons 2s²2p⁶, n = 3, 18 e⁻⁻⁻ 3s²3p⁶3d¹⁰

Electron configuration of atoms and ions

Aufbau Principle

Hund’s Rule of multiplicity

Pauli’s Exclusion Principle

Long (Complete) and Condensed Configurations. Energy vs Size order.

Core, pseudocore, and valence electron

Some exceptions (s¹d⁵, s¹d¹⁰).

Cations lose valence p,s orbital electrons before d orbital electrons.

Ground state electrons fill lowest energy and up, excited state electrons are in higher energy orbits.

**Paramagnetic** (weakly attracted to a magnetic field): The electron configuration has unpaired electrons.

**Diamagnetic:** All electrons are paired. (weakly repelled by a magnetic field)

**Isoelectronic:** Atoms and ions having the same number of electrons.

**Orbital diagram:** Drawing the electron configuration with arrows in each orbital
**Quantum Numbers** \((n, l, m_l, m_s)\)

**Size:** \(n\)
- \(1, 2, 3, 4, 5, 6, 7\) for \(s, p\) orbital \(n = \) period number
- \(n-1\) of period for \(d\) orbitals
- \(n-2\) of period for \(f\) orbitals

**Shape:** \(\ell\)
- \(0, 1, 2, 3\)
- \(s = 0, p = 1, d = 2, f = 3\)

**Orientation:** \(m_\ell\)
- \(-\ell \ldots +\ell\)
- \(s = 0, p = -1, 0, +1, d = -2, -1, 0, +1, +2, f = -3, -2, -1, 0, +1, +2, +3\)

**Spin:** \(m_s\)
- \(-1/2, +1/2\)

**Ions and their Electron Configurations:**

**Metals:** *Give up electrons and become positive cations*

**Nonmetals:** *Accept electrons and become negative anions*

**Main group atoms** give up or accept electrons toward the goal of establishing a core (noble gas) electron configuration. Metals will first lose the valence \(p\) electrons before the valence \(s\) electrons.

**Transition metals and Inner Transition metals** first lose the largest \(s\) electrons, then the \(d\) electrons and for inner transitions last are the \(f\) electrons.

**Example 7:** Predict the ground state short electron configuration for each.

**Ba**
- \(\text{Ba}^{+2}\)

**I**
- \(\text{I}^-\)