Chapter 5: Electrons in Atoms

Light (Electromagnetic Radiation)

- Light has the properties of both waves and particles.
- Light waves carry energy through space.

**wavelength** \( (\lambda) \) meters

**frequency** \( (\nu) \) Hz \( (s^{-1}) \)

**amplitude** \( (a) \) intensity

All light travels at the same speed,
\[ c = 2.99792 \times 10^8 \text{ m/sec (vacuum)} \]

The frequency \( (\nu \text{ is pronounced “nu”}) \) is the number of wavelengths that pass a point in a given period of time.
(cycles per second) or \( s^{-1} \) where \( 1 \text{Hz} = 1s^{-1} \)

The wavelength \( (\lambda \text{ is pronounced “lambda”}) \) is the distance between wave crests in meters
\( (m, \text{cm, nm, pm, Å (angstrom, } 10^{-10} \text{ m)}) \)

The product of frequency and wavelength for all forms of electromagnetic radiation (light) is a constant, the speed of light “c”.

\[ \bar{\nu} \times \bar{\lambda} = c \]

\[ \bar{\nu} = \frac{c}{\bar{\lambda}} \quad \text{and} \quad \bar{\lambda} = \frac{c}{\bar{\nu}} \]

**frequency and wavelength** are inversely related:

- high frequency corresponds to short wavelength
- long wavelength corresponds to low frequency
The Electromagnetic Spectrum

Example:
What wavelengths correspond to FM radio (MHz) signals?

\[
\lambda = \frac{3.00 \times 10^8 \text{ m/s}}{93.5 \text{ MHz} \times \frac{10^6 \text{ Hz}}{1 \text{ MHz}} \times \frac{1 \text{ s}^{-1}}{\text{Hz}}} = 3.21 \text{ m}
\]

What frequencies correspond to microwaves?

\[
\delta = \frac{c}{\dot{\delta}} = \frac{3.00 \times 10^8 \text{ m/s}}{1 \text{ m} \times 1 \times 10^{-6} \text{ m}} = 3.00 \times 10^{14} \text{ Hz} = 3.00 \times 10^8 \text{ MHz}
\]
Properties of waves:
(a) **Constructive interference:**
When waves that are in phase interact, they do so such that the amplitudes add in a positive manner.

(b) **Destructive Interference:**
When waves that are out of phase interact, they do so such that the amplitudes cancel one another.

**Light and Energy: Planck’s Law**

**Planck’s Law:** Energy is discontinuous; the transmission of energy can only occur in finite amounts or “**Quanta**”

\[ E_{\text{photon}} = h \nu \quad h = \text{Planck’s constant} = 6.626 \times 10^{-34} \text{ J\cdot s} \]

Planck’s Law is based on the phenomenon known as the **Ultraviolet Catastrophe**

Classically, the intensity of light should increase with decreasing wavelength.

If this were so, the intensity of UV light would go to infinity with decreasing wavelength.

I order to explain the observations of **black-body** radiation, Planck surmised that light is released in defined packets or **quanta**.

![Diagram showing intensity versus wavelength for different temperatures](image)
As the frequency of light increases, the energy **increases**.

As the wavelength of light increases, the energy **decreases**.

\[ E_{\text{photon}} = h \cdot \nu = \frac{hc}{\lambda} \]

**Red Light (650 nm)**

\[ E_{\text{photon}} = \frac{hc}{\nu} = \frac{6.626 \times 10^{-34} \text{Js} \times 3.00 \times 10^8 \text{m/s}}{650 \text{nm} \times \frac{1 \text{m}}{10^9 \text{nm}}} = 3.06 \times 10^{-19} \text{J/photon} \]

**Blue Light (400 nm)**

\[ E_{\text{photon}} = \frac{hc}{\nu} = \frac{6.626 \times 10^{-34} \text{Js} \times 3.00 \times 10^8 \text{m/s}}{400 \text{nm} \times \frac{1 \text{m}}{10^9 \text{nm}}} = 4.97 \times 10^{-19} \text{J/photon} \]

**Bond energies also correspond to the energies of individual photons. The process of light breaking chemical bonds is known as photodissociation.**

Calculate the energy of a mole of photons of 400 nm light.

\[ E_{\text{photon}} = \frac{hc}{\nu} = \frac{6.626 \times 10^{-34} \text{Js} \times 3.00 \times 10^8 \text{m/s}}{400 \text{nm} \times \frac{1 \text{m}}{10^9 \text{nm}}} \times 6.022 \times 10^{23} \text{photons/mole} = 2.99 \times 10^5 \text{J/mole photons} \]

\[ \bar{\epsilon} = \frac{6.626 \times 10^{-43} \text{J} \cdot \text{s} \times 3.00 \times 10^8 \text{ms}^{-1}}{7.24 \times 10^{-19} \text{J/photon}} = 2.75 \times 10^{-7} \text{m} \text{ or } 275 \text{nm} \]
Quantum Theory: Atomic Spectra:

Atomic Spectrum

When a discharge is passed through a tube filled with He, the light emitted spreads into a series of lines rather than a normal spectrum of light.

This indicates that something in the atom is not governed by a continuum…

Something is *Quantized*!

Recall that Quantization was used to explain the “Ultraviolet Catastrophe” (Planck)

Einstein’s work on the “Photoelectric Effect” also contributed to the concept of quantization.

When light strikes the surface of certain metals, electrons may be ejected.

The light must be of a certain frequency (color) in order for this to occur.

The behavior exhibits a threshold effect such that below a minimum energy, no electrons are ejected.
The threshold behavior for the “Photo-electric Effect”

Since \[ E = h\nu \]

Only photons of frequency greater than the minimum frequency \((\nu_0)\) can eject electrons
Any excess energy from the photon goes into the kinetic energy of the electron.

\[ E (\text{electron}) = E (\text{photon}) - \Phi = \frac{1}{2} m_e v^2 \]

\( E (\text{photon}) = h\nu \)

\( m_e = 9.11 \times 10^{-31} \text{ kg} \)

\( \nu = \text{velocity of the ejected electrons} \)

\( \Phi = \text{ejecton threshold “Work function”} \)

\( \nu_0 = \frac{\Phi}{h} \) “Threshold frequency”

If...

\( \nu (\text{photon}) < \nu_0 \) no electrons are ejected

\( \nu (\text{photon}) = \nu_0 \) electrons are removed with no KE

\( \nu (\text{photon}) > \nu_0 \) electrons are ejected

**Example:**

A certain metal has a threshold frequency \((\nu_0)\) of \(3.66 \times 10^{-14} \text{ s}^{-1}\).

Will 532 nm light cause electrons to be ejected?

\[ E (\text{electron}) = E (\text{photon}) - \Phi \]

if \( \nu (\text{photon}) > \nu_0 \) then electrons are ejected

\[ \nu \lambda = c \]

\[ i = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m/s}}{532 \text{ nm} \times \frac{\text{m}}{10^9 \text{ nm}}} = 5.64 \times 14 \text{ s}^{-1} \]

\( \nu (\text{photon}) > \nu_0 \) Electron are ejected

**What is the velocity of the ejected electrons?**

\[ E (\text{electron}) = E (\text{photon}) - \Phi = \frac{1}{2} m_e v^2 \]
The Bohr Atom:

The concept of the atom derived from the Rutherford gold film experiment failed to explain how the electrons orderly themselves about the nucleus.

In 1913, Niels Bohr proposed a model for electron distributions that was a combination of classical and the new emerging quantum theories.

1. Electrons move in circular orbits about the nucleus.
2. These “orbits” are fixed or discrete in terms of allowed energies governed by states of angular momentum.
3. Electrons can only pass between these allowed levels and nowhere in between.

Conclusion: The energy levels of the electrons are quantized!
This explains the observance of line spectra in atom emission.

To explain the spectral line puzzle, Bohr came up with a radical model of the atom, which had electrons orbiting around a nucleus.

Because of these "signature colors" or emission lines, Bohr stated that electrons had to exist in discrete orbits or "quantized" levels and that the spectral lines occurred when the electron jumped between the allowed levels.

Each level is designated by a “Quantum Number”, \( n \)

\[ n = 1, 2, 3, 4, \ldots \text{ infinity} \]

the radius of each orbit is given by:

\[ r_n = n^2 a_o \quad \text{The Bohr radius} \quad a_o = 0.53 \text{ Å or 53 pm} \]
The energy of each level is given by:

\[ E_n = -\frac{Z^2R_H}{n^2} \]

Where \( R_H = 2.179 \times 10^{-18} \) J

The Bohr Model:
\( r_n = n^2a_0 \)
\( n = 1, 2, 3, 4… \)

The Energy Levels:
\[ E_n = -\frac{Z^2R_H}{n^2} \]

The Lowest energy level corresponds to \( n = 1 \)

Where,  
\( n = 1 \) “Ground State”
\( n = 2 \) “1\(^{st}\) excited state”
\( n = 3 \) “2\(^{nd}\) excited state”
\( n = n-1 \) “\( n \)\(^{th}\) excited state”
Absorption and Emission

When an electron jumps from a lower state to a higher state, Energy (light) is absorbed.

When an electron jumps from a higher state to a lower state, Energy is (light) emitted

Emission of Light:

Electrons move from a higher level (state) to a lower level (state)

Absorption of Light:

Electrons move from a lower level (state) to a higher level (state)

\[ E_n = \frac{-Z^2 R_H}{n^2} \quad \text{for} \quad Z = 1 \]

\[ \Delta E = E_{\text{fin}} - E_{\text{in}} = \frac{-R_H}{n_{\text{fin}}^2} - \frac{-R_H}{n_{\text{in}}^2} = E_{\text{photon}} \]

\[ \Delta E = R_H \times \left( \frac{1}{n_{\text{in}}^2} - \frac{1}{n_{\text{fin}}^2} \right) = h \cdot v = \frac{h \cdot c}{\lambda} \]

\[ \frac{1}{\lambda} = \frac{R_H}{h \cdot c} \times \left( \frac{1}{n_{\text{in}}^2} - \frac{1}{n_{\text{fin}}^2} \right) \]

A negative signs indicates emission, positive absorption.

The Wave-like Nature of a Particle
The Wave Particle Duality:

Louis de Broglie in response to Planck & Einstein’s assertion that light was “particle-like” (photon) stated that small particles moving fast could exhibit a characteristic wavelength.

\[ E = mc^2 \]
\[ h\nu = mc^2 \]

\[ \frac{h\nu}{c} = mc = p \text{ (momentum)} \]

since \[ \frac{\nu}{c} = \frac{1}{c} \]

\[ \frac{h}{\lambda} = p \quad \text{or} \quad \lambda = \frac{h}{p} = \frac{h}{m \cdot u} \quad u = \text{velocity} \]

What is the wavelength associated with an 80g tennis ball (d = 8 cm) moving at 115 miles per hour? Compare that to an electron moving at 1/100 the speed of light.

\[ \lambda_{\text{(tennis ball)}} = 2 \times 10^{-34} \text{ m} \quad \frac{\lambda}{d} \times 100 = 2 \times 10^{-31} \% \]

\[ \lambda_{\text{(electron)}} = 2 \times 10^{-10} \text{ m} \quad \frac{\lambda}{d} \times 100 = 70000 \% \]The electron looks like a wave!

Heisenberg Uncertainty Principle:

The more precisely the position is determined, the less precisely the momentum is known in this instant, and vice versa.

\[ \Delta p \Delta x \geq \frac{h}{4\pi} \]

\[ \Delta p = \text{uncertainty in momentum} \]
\[ (\text{velocity}) \]
\[ \Delta x = \text{uncertainty in position} \]

Classically, i.e., in our macroscopic world, I can measure these two quantities to infinite precision (more or less). There is really no question where something is and what its momentum is.

In the Quantum Mechanical world, the idea that we can measure things exactly breaks down, i.e. there is a limit to the precision.

This uncertainty leads to many strange things.

For example, in a Quantum Mechanical world, I cannot predict where a particle will be with 100% certainty. I can only speak in terms of probabilities.

A consequence of the Quantum Mechanical nature of the world is that particles can appear in places where they have no right to be (from an ordinary, common sense [classical] point of view)!
The results state that there is a “probability” of finding the particle in space at position “x” with an uncertainty of $\Delta x$.

The location of a particle is given by a localized increase in the amplitude of the wave at position x.

**Probability Distributions:**

The *mental picture* of an electron corresponds to a wave superimposed upon the radial trajectory of a particle orbiting the nucleus.

The position of an electron is best described by the image of a dart board: As the *Schrödinger Wave Equation* is solved time and time again, the position of an electron is found such that each “hit” builds up a pattern.

The build up of “hits” yields the probability in 3-dimensions for the likelihood of finding an electron about the nucleus.

- It is these *probability functions* that give rise to the familiar hydrogen-like orbitals that electrons occupy.

**Quantum numbers and Electron Orbitals**

Quantum Numbers are terms that were developed to aid in describing electron behavior according to the Schrödinger equation.

**Principal Quantum Number**

$n$

$n = 1, 2, 3, 4…$ up to infinity

**Azimuthal or Angular Quantum Number**

$l$

$l = 0, 1, 2, 3…$ up to a maximum of “n – 1”

**Magnetic Quantum Number**

$m_l$

$m_l$ may take on the value an integer from $-l$ to $+l$

**Spin Quantum Number**

$m_s$

$m_s \pm 1/2$

The *Quantum numbers* give information about the location of an electron, like an address.

The *principal* quantum number indicates the “state” where the electron is located, the *angular momentum* quantum number indicates the town, the *magnetic* QN is the street address and the *spin* quantum number corresponds to the right or left side of a duplex.
Each n-level defines a **principle energy level** or **shell**.

\[ E_n = -\frac{Z^2 \text{R}_\text{H}}{n^2} \]

Z = atomic number of the nucleus and \( \text{R}_\text{H} = \text{Rydberg constant.} \)

Each “l” within an “n-level” represents a **subshell**.

- \( l = 0 \) “s” subshell
- \( l = 1 \) “p” subshell
- \( l = 2 \) “d” subshell
- \( l = 3 \) “f” subshell

Each subshell is divided into \( m_l \) orbitals, where \( m_l \) designates the spatial orientation of each orbital. (Cartesian coordinates, x, y & z)

Each orbital can hold **2 electrons**, one designated by \( m_l = + \frac{1}{2} \) and one by \( m_l = - \frac{1}{2} \)

### Atomic structure

<table>
<thead>
<tr>
<th>Shell</th>
<th>( n = 1 )</th>
<th>( n = 2 )</th>
<th>( n = 3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Subshell</td>
<td>1s</td>
<td>2s</td>
<td>3s</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2p</td>
<td>3p</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3d</td>
</tr>
</tbody>
</table>

for \( l = 0 \) \( m_l = 0 \) (no orientation)

for \( l = 1 \) \( m_l = -1 \ -1 \ 0 \ +1 \)

\( p_x \ p_y \ p_z \)

for \( l = 2 \)

\( m_l = -2 \ -1 \ 0 \ +1 \ +2 \)
Electron Configurations: Multi-electron atoms

The ideas presented thus far have focused on the H-atom, a one-electron system.

What happens when there are two or more electrons in an atom?

The diagram to the right explains:

- The innermost electrons screen or “shield” the nucleus from the view of the outer electrons.
- The outermost electrons in effect see a charge that is less than the actual charge on the nucleus, Z.

Shielding of Electrons:

The further out an electron exists from the nucleus, the greater the effect of shielding. (There are more electrons to screen the nucleus charge)

Since the s-orbitals have no nodal properties at the nucleus, they can penetrate more effectively.

This increase in the ability to penetrate magnifies the ability to screen.

s-orbitals > p or d-orbitals

Increasing Screening

The effect of Shielding:

In a hydrogen atom, the orbitals are arranged as a function of “n” only.

For each value of n, the l-sub shells are degenerate (of the same energy).

Shielding brought upon by the presence of more than one electron causes the orbital energies to split.

<table>
<thead>
<tr>
<th>Shell</th>
<th>n = 3</th>
<th>3s</th>
<th>3p</th>
<th>3d</th>
</tr>
</thead>
<tbody>
<tr>
<td>n = 2</td>
<td>E</td>
<td>2s</td>
<td>2p</td>
<td></td>
</tr>
<tr>
<td>n = 1</td>
<td></td>
<td>1s</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Subshell

Each subshell is made up of \((2l + 1)\) orbitals.
The electrons of a many-electron atom occupy the orbitals in accordance with a series of rules.

The Pauli Exclusion Principle:

*Only two electrons with opposite spin can occupy an atomic orbital.*

Stated another way, no two electrons have the same 4 quantum numbers \( n, l, m, m_s \).

In applying this rule, you should realize that an atomic orbital is an energy state.

Hund’s rule:

*Electrons prefer parallel spins in separate orbitals of sub shells.*

Electrons will fill across a set of degenerate orbitals until forced to pair with opposite spins.

The Aufbau (Building up) Principle:

*Electrons fill from the lowest energy states (orbitals) up.*

The Aufbau procedure (filling order of atomic orbitals) is used to work out the electron configurations of all atoms.
Electron Configurations of the 1st and 2nd Period:

H = 1s\(^1\)  
He = 1s\(^2\)  
Li = 1s\(^2\) 2s\(^1\)  
Be = 1s\(^2\) 2s\(^2\)  
B = 1s\(^2\) 2s\(^2\) 2p\(^1\)  
O = 1s\(^2\) 2s\(^2\) 2p\(^4\)  
N = 1s\(^2\) 2s\(^2\) 2p\(^3\)  
F = 1s\(^2\) 2s\(^2\) 2p\(^5\)  
Ne = 1s\(^2\) 2s\(^2\) 2p\(^6\)
Valence Electon Blocks:

Electron Configurations continued:

Electrons in the outermost shell are called **valence electrons**.

- It is the **valence electrons** determine an atom’s chemical properties.
- Electrons in the inner shells are inner electrons or **core electrons**.
- Regions in periodic table are designated as the **s-block, p-block, d-block** and the **f-block**.

---

![Periodic Table Diagram](image-url)
Core Notation:

- Sc: \([\text{Ar}]\)  
- Ti: \([\text{Ar}]\)  
- V: \([\text{Ar}]\)  
- Cr: \([\text{Ar}]\)  
- Mn: \([\text{Ar}]\)  
- Fe: \([\text{Ar}]\)  
- Co: \([\text{Ar}]\)  
- Ni: \([\text{Ar}]\)  
- Cu: \([\text{Ar}]\)  
- Zn: \([\text{Ar}]\)

For \(d^4\) and \(d^9\) elements, an s-electron can jump over to create a \(\frac{1}{2}\) filled \((d^5)\) or completely filled \((d^{10})\) d-orbital.

This lowers the overall energy of the atom.

Some anomalies in filling are seen in the \(d\)-elements.

Table 9.2: Electron Configurations of Some Groups of Elements

<table>
<thead>
<tr>
<th>Group</th>
<th>Element</th>
<th>Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>1s(^1)</td>
</tr>
<tr>
<td></td>
<td>Li</td>
<td>[He]2s(^2)</td>
</tr>
<tr>
<td></td>
<td>Na</td>
<td>[Ne]3s(^1)</td>
</tr>
<tr>
<td></td>
<td>K</td>
<td>[Ar]4s(^1)</td>
</tr>
<tr>
<td></td>
<td>Rb</td>
<td>[Kr]5s(^1)</td>
</tr>
<tr>
<td></td>
<td>Cs</td>
<td>[Xe]6s(^1)</td>
</tr>
<tr>
<td></td>
<td>Fr</td>
<td>[Rn]7s(^1)</td>
</tr>
<tr>
<td>17</td>
<td>F</td>
<td>[He]2s(^2)p(^2)</td>
</tr>
<tr>
<td></td>
<td>Cl</td>
<td>[Ne]3s(^2)p(^3)</td>
</tr>
<tr>
<td></td>
<td>Br</td>
<td>[Ar]3d(^{10})4s(^2)p(^5)</td>
</tr>
<tr>
<td></td>
<td>I</td>
<td>[Kr]4d(^{10})5s(^2)p(^5)</td>
</tr>
<tr>
<td></td>
<td>At</td>
<td>[Xe]4f(^{14})5d(^{10})6s(^2)p(^5)</td>
</tr>
<tr>
<td>18</td>
<td>He</td>
<td>1s(^2)</td>
</tr>
<tr>
<td></td>
<td>Ne</td>
<td>[Ne]2s(^2)p(^6)</td>
</tr>
<tr>
<td></td>
<td>Ar</td>
<td>[Ne]3s(^2)3p(^6)</td>
</tr>
<tr>
<td></td>
<td>Kr</td>
<td>[Ar]3d(^{10})4s(^2)p(^6)</td>
</tr>
<tr>
<td></td>
<td>Xe</td>
<td>[Kr]4d(^{10})5s(^2)p(^6)</td>
</tr>
<tr>
<td></td>
<td>Rn</td>
<td>[Xe]4f(^{14})5d(^{10})6s(^2)p(^6)</td>
</tr>
</tbody>
</table>

What is the electron configuration of the element as shown on the right?

Which electrons are the valence electrons and which are the core electrons?

Answers:

\(1s^22s^22p^63s^23p^6\) P (phosphorous)
Electron Configurations of ions:

When an atom gains or loses electrons it becomes an ion.

Loss of electrons: Cation  Gain of electrons: Anion

(+)

(-)

Atoms of group 1, 2 and the non-metals will lose or gain electrons to attain the electron configuration of a Noble gas \((\text{ns}^2\text{np}^6)\).

Example: Sodium forming sodium ion:

\[
\text{Na: } 1s^22s^22p^63s^1 \\
\text{Na}^+: [\text{Ne}] 1s^22s^22p^6
\]

All group 1 cations (+1) will have the electron configuration of the previous Noble gas.

The formation of the phosphide ion:

\[
P \quad (1s^22s^22p^63s^33p^3) \quad \text{P}^3- \quad (1s^22s^22p^63s^33p^6) = [\text{Ar}]
\]

All group 5 (15) anions (-3) will have the electron configuration of the next Noble gas.

Electron configurations of Transition Metal Ions:

The charge states on most transition metals cannot be equated to the electron configurations of the Noble gases. You will see why in chem. 2C (ch. 24 and 25)

The electron configurations of transition metal cations must be determined from the charge state.

\[
\text{Fe}^{3+} \ldots 3 \text{ electrons lost} \quad \text{Ni}^{2+} \ldots 2 \text{ electrons lost and so on.}
\]

- When transition metals ionize, they lose the s-electrons first.
- This may seem odd as it is opposite to the filling order.
- From a stability argument, the removal of the s-electrons first results in lower energy configuration when we take into account ionization energies of s vs. p and d electrons.

Examples:

\[
\text{Sc: } [\text{Ar}] \quad \text{[Ar]3d}^14s^2
\]

\[
\text{Sc}^{3+}: [\text{Ar}] \quad \text{[Ar]3d}^1
\]
Electron Configurations: Excited States

Which of the electron configurations to the right corresponds to phosphorous?

Answer: c
The rest are excited states of phosphorous.