Chapter 6
Electronic Structure of Atoms
Chapter Outline

- Wave Nature of Light
- Quantized Energy and Photons
- Bohr Model of the Atom
- Wave Behavior of Matter
- Quantum Mechanics / Atomic Orbitals
- Shapes of Orbitals
- Multi-electron Atoms
- Electron configurations and the periodic table
To understand the electronic structure of atoms, one must understand the nature of electromagnetic radiation.

- The height of the wave is **amplitude** (A).

- The distance between corresponding points on adjacent waves is the **wavelength** ($\lambda$, “lambda”), typically in units of meters.
Waves

- The number of waves passing a given point per unit of time is the frequency ($\nu$, “nu”) in units of $s^{-1}$.

- For waves traveling at the same velocity, the longer the wavelength, the smaller the frequency (and vice versa).
• All electromagnetic radiation travels at the same velocity: the speed of light \((c)\), \(3.00 \times 10^8\) m/s.

• Therefore, \(c = \lambda \nu\) or \(\lambda = c/\nu\) or \(\nu = c/\lambda\)
The wave nature of light does not explain how an object can glow when its temperature increases.

Max Planck explained it by assuming that energy comes in packets of matter called quanta.

Max Plank received the Nobel Prize in Physics for the quantum theory in 1918.
Planks proposed a quantum of energy was related to frequency:

\[ E = h\nu \]

- \( h \) = Plank’s constant = \( 6.626 \times 10^{-34} \) Js
- \( \nu \) = frequency (s\(^{-1}\))

The idea is that energy can be emitted or absorbed only in integer multiples of the frequency (\( h\nu, 2h\nu, 3h\nu, etc \))
Einstein used this assumption to explain the photoelectric effect.

He showed photon’s energy is proportional to its frequency:

\[ E = h \nu \]

\[ h = \text{Planck’s constant} = 6.63 \times 10^{-34} \text{ J} \cdot \text{s} \]

(energy is in J)

Albert Einstein received the Nobel Prize in Physics for the photoelectric effect, not for relativity \((E=mc^2)\).
So, if the wavelength of light is known, one can calculate the energy in one photon, or quanta, of that light:

\[ c = \lambda \nu \quad \text{and} \quad E = h \nu \]

\[ E = \frac{hc}{\lambda} \]

Q: But photons have mass, so light a particle or is it a wave?

A: Yes!

This paradox is called wave-particle duality.
Researchers at Ecole Polytechnique Federale de Lausanne (EPFL) have captured light behaving as a wave and a particle at the same time!


https://www.youtube.com/watch?t=46&v=mlaVHxUSiNk
– Calculate the frequency of laser radiation which has a wavelength (\(\lambda\)) of 640.0 nm.

– Calculate the wavelength of radio waves with a frequency of 103.4 MHz (1 MHz = \(1 \times 10^6\) s\(^{-1}\)).
Practice Problems

- What is the energy of one photon of radiation with a frequency of $4.69 \times 10^{14}$ s$^{-1}$?

- What is the total energy of a pulse of $5.0 \times 10^{17}$ photons at this frequency?
More Practice

• If a laser emits $1.3 \times 10^{-2}$ J of energy, how many photons were emitted?
Another mystery involved the emission spectra observed from energy emitted by atoms and molecules.
The Nature of Energy

- White light sources produce a continuous spectrum.
- Atoms and molecules only produce a line spectrum of discrete wavelengths.
Niels Bohr’s explanation:

1. Electrons in an atom can only orbit at certain radii, corresponding to specific energies.

2. Electrons in permitted orbits have specific, “allowed” energies; these energies will not be radiated from the atom.

3. Energy is only absorbed or emitted as an electron moves from one “allowed” energy state to another; the energy is defined by:

\[ E = h\nu \]

\( h = \) Planck’s constant
\( \nu = \) frequency of radiation
Energy that’s absorbed (promotion) or emitted (demotion) can be calculated by the Rydberg equation:

$$\Delta E = -\frac{hcR_H}{n_f^2 - n_i^2}$$

$$\Delta E = \left(-2.18 \times 10^{-18}\right)\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

$R_H = \text{Rydberg constant, } 1.097 \times 10^7 \text{ m}^{-1}$

$h = \text{Planck’s constant; } c = \text{speed of light}$

$n_i = \text{initial energy level of electron}$

$n_f = \text{final energy level of the electron}$
The Nature of Energy: The Hydrogen Atom

Section 6.3

Ground State = lowest energy state

Excited State = higher energy state

\[ \Delta E = -hcR_H \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \]

- Moving from high n to lower n
  - \( n_f < n_i \) so \( \Delta E < 0 \)
  - Emits energy

- Moving from low n to higher n
  - \( n_f > n_i \) so \( \Delta E > 0 \)
  - Absorbs energy
Bohr Model: Strengths and Limitations

- **Strengths of the Bohr model:**
  - Electrons have discrete energies
  - Energy is absorbed or radiated when electrons are moved between discrete levels

- **Limitations of the model**
  - Designed to work for hydrogen atom only. Other elements/substances are much more complicated
  - Electrons are not merely particles circling the nucleus of atoms, they exhibit wave-like properties
• Do the following transitions represent absorption of energy or emission of energy:
  
  – $n = 3$ to $n = 1$?
  
  – $n = 2$ to $n = 4$?
The Wave Nature of Matter

- Louis de Broglie suggested that if light (photons) has material properties, then matter should exhibit wave properties.

- DeBroglie Equation: Relationship between mass and wavelength:

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

\( \lambda \) = wavelength (meters)
\( h \) = Planck’s constant \((6.63 \times 10^{-34} \text{ J} \cdot \text{s})\)
\( m \) = mass (kg)
\( v \) = velocity (meters/s)

Reminder: 1 J = 1 kg·m²/s²
Practice Problems

- Calculate the velocity of a neutron whose de Broglie wavelength is 500 pm.
  (Neutron mass = $1.675 \times 10^{-24}$ g)
The (Heisenberg) Uncertainty Principle

• The **more** precisely the momentum ($\Delta mv$) of a particle is known, the **less** precisely its position ($\Delta x$) is known (and *vice versa*):

$$ (\Delta x)(\Delta mv) \geq \frac{h}{4\pi} $$

• The uncertainty of an electron’s position can be greater than the size of the atom! (see pg 225!)
Camera Analogy to Heisenberg’s Uncertainty Principle

- Use a camera to photograph a car in motion.
- Short exposure shot: good idea of the car’s position, but not of it’s speed
- Long exposure shot: good idea of speed, but position is blurry
The (Heisenberg) Uncertainty Principle

- Doesn’t apply to large objects (e.g. a tennis balls or people) because $(\Delta x)(\Delta mv)$ is much smaller than the size of the object.

Baseball (d=0.075m) at 90 mph with an uncertainty of 2 mph:

$$\Delta x = \frac{h}{4\pi m\Delta v} = \frac{6.626 \times 10^{-34} \text{ Js}}{4\pi (0.145 \text{ kg})(0.894 \text{ m/s})} = 4.06 \times 10^{-34} \text{ m}$$

Electron at (d=<10^{-10}m) at a bit over 1million mph with uncertainty of a bit over 100,000 mph:

$$\Delta x = \frac{h}{4\pi m\Delta v} = \frac{6.626 \times 10^{-34} \text{ Js}}{(9.109 \times 10^{-31} \text{ kg})(5 \times 10^{4} \text{ m/s})} = 1 \times 10^{-9} \text{ m}$$
Quantum mechanics - mathematical treatment into which both the wave and particle nature of matter is incorporated

Developed by Erwin Schrödinger

As we delve deeper into the atom, it actually becomes less tangible and more mathematical.
The “wave” equation is designated with a lower case Greek \( \psi \).

The square of this equation, \( \psi^2 \), gives a probability density map.

- This tells us where an electron is statistically likely to be at any given instant.
- More blue dots = more likely to be there
Quantum Numbers

- Solving the wave equation gives a set of wave functions, or orbitals, and their corresponding energies.

- Orbitals describe a spatial distribution of electron density (90% probability of finding a particular electron or electrons).

- Quantum numbers are used to describe each orbital. A total of three quantum numbers is required to describe a specific orbital.
The principal quantum number, \( n \), describes the energy level on which the orbital resides.

- The values of \( n \) are whole numbers > 0.
  - e.g. \( n = 1, \ n = 2, \ n = 3, \) etc
  - Same \( n \) as in the Bohr model
  - \( n \) is equal to the number of the row on the periodic table
Azimuthal Quantum Number, $l$
(aka Angular Quantum Number)

- The azimuthal quantum number, $l$ (“ell”), defines the shape of the orbital.

- Possible values for $l$: integers ranging from 0 to $n-1$.

- Letter designations of $l$ are used to describe the different values (i.e. shapes) of orbitals.

<table>
<thead>
<tr>
<th>Value of $l$</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of orbital</td>
<td>s</td>
<td>p</td>
<td>d</td>
<td>f</td>
</tr>
</tbody>
</table>
The magnetic quantum number, $m_l$, describes the three-dimensional orientation of the orbital.

Possible values are integers ranging from $+l$ to $-l$ (including zero):

$$-l \leq m_l \leq +l$$

Example: $l = 1 \rightarrow m_l = -1, 0, +1$ (3 values)

Therefore, on any given energy level (n), there can be up to:

- 1 $s$ orbital, 3 $p$ orbitals, 5 $d$ orbitals, 7 $f$ orbitals, etc.
  which of these are available depends on $n$ and then $l$. 
Magnetic Quantum Number, $m_l$

- All the orbitals with the same value of $n$ form a shell.
- Different orbital types within a shell are subshells.

<table>
<thead>
<tr>
<th>$n$</th>
<th>Possible Values of $l$</th>
<th>Subshell Designation</th>
<th>Possible Values of $m_l$</th>
<th>Number of Orbitals in Subshell</th>
<th>Total Number of Orbitals in Shell</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>1s</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>2s</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>2p</td>
<td>1, 0, −1</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>3s</td>
<td>0</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>3p</td>
<td>1, 0, −1</td>
<td>3</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>3d</td>
<td>2, 1, 0, −1, −2</td>
<td>5</td>
<td>16</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>4s</td>
<td>0</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>4p</td>
<td>1, 0, −1</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>4d</td>
<td>2, 1, 0, −1, −2</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>4f</td>
<td>3, 2, 1, 0, −1, −2, −3</td>
<td>7</td>
<td>16</td>
</tr>
</tbody>
</table>
A shell with principal quantum number $n$ has exactly $n$ subshells
- $n=2 \rightarrow 2$ subshells ($\ell=0$, $\ell=1$)

Each subshell has $2\ell+1$ orbitals
- $\ell=0 \rightarrow m_\ell=0$
- $\ell=1 \rightarrow m_\ell=1,0,-1$

The total number of orbitals in a shell is $n^2$.
- $n=2 \rightarrow 4$ (count $m_\ell$ values)
Practice Problems

• Predict the number of subshells in the fourth shell \((n=4)\).

• Give the label for each of these subshells.

• How many orbitals are in each of these subshells?
• Value of $l = 0$.

• Spherical in shape.

• Radius of the sphere increases as $n$ increases.
  
  - $r_{n=1} < r_{n=2} < r_{n=3} < \ldots$
The s orbitals possess $n-1$ nodes, or regions where there is zero probability of finding an electron.
$p$ Orbitals

- Value of $l = 1$.
- Two lobes with 1 node between them.
- $m_l = -1, 0, +1$ and thus 3 different spatial orientations.

For convenience we place the lobes along the $x, y$ and $z$ axes.
• Value of $l$ is 2; five values of $m_l$ (+2, +1, 0, −1, −2)
• Four of the five orbitals have 4 lobes; the other resembles a $p$ orbital with a ring around the center.
Energies of Orbitals

- For a one-electron hydrogen atom, orbitals on the same energy level have the same energy (degenerate).

- But this is only theory, what we observe is…
As the number of electrons increases, so does the repulsion between them.

In many-electron atoms, orbitals in the same energy level are no longer degenerate.

Specific orbitals are described by $n$, $l$ and $m_l$, but 2 electrons can be located in an orbital. How can we distinguish them?
In the 1920s, it was found that two electrons in the same orbital do not have exactly the same energy.

The “spin” of an electron describes its magnetic field, which affects its energy.

This led to a 4th quantum number, the spin quantum number, $m_s$.

The spin quantum number has only 2 allowed values:
- $m_s = +\frac{1}{2}$ or $m_s = -\frac{1}{2}$. 
Pauli Exclusion Principle

- No two electrons in the same atom can have exactly the same energy.
- No two electrons in the same atom can have four identical quantum numbers.
- Each orbital can only hold two electrons (and they must have opposite spins, $m_s = +\frac{1}{2}, -\frac{1}{2}$).
- Each electron’s “address” is a unique combination of the 4 quantum numbers.
## Summary of Quantum Numbers

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Name</th>
<th>Description</th>
<th>Values</th>
<th>Misc. notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$</td>
<td>principal</td>
<td>Energy level of orbital</td>
<td>Integers &gt; 0</td>
<td>$n$ corresponds to a row on periodic table</td>
</tr>
<tr>
<td>$l$</td>
<td>azimuthal (angular)</td>
<td>Shape of orbital</td>
<td>Integers 0 to $n-1$</td>
<td>$0 = s$, $1 = p$, $2 = d$, $3 = f$</td>
</tr>
<tr>
<td>$m_l$</td>
<td>Magnetic</td>
<td>3D orientation of orbital</td>
<td>Integers $-l$ to $+l$</td>
<td>Gives number of orbitals for different values of $l$</td>
</tr>
<tr>
<td>$m_s$</td>
<td>Spin</td>
<td>Electron spin</td>
<td>+½, −½</td>
<td>Only describes electrons, not orbitals</td>
</tr>
</tbody>
</table>

No two **orbitals** can have the exact same $n$, $l$, and $m_l$ values! No two **electrons** can have the exact same $n$, $l$, $m_l$, and $m_s$ values!
Electron Configurations

- Tally of where each electron is in an atom.

- Consists of
  - Number denoting the energy level.
    - Corresponds to principle QN, n
  - Letter denoting the type of orbital.
    - Corresponds to azimuthal QN, l
  - Superscript denoting the number of electrons in those orbitals.

\[ 4p^5 \]
Practice Problems

- What is the designation for the subshell with \( n=5 \) and \( l=1 \)?

- How many orbitals are in this subshell?

- Indicate the values for \( m_l \) for each of these orbitals.
Practice Problems

- Write the electron configuration for Li atom.
Each box represents one orbital.

Half-arrows represent the electrons.

The direction of the arrow represents the spin of the electron.

Orbital diagrams represent the “ground state” or most stable electron configuration.
“For degenerate orbitals, the lowest energy is attained when the number of electrons with the same spin ($m_s$) is maximized.”

Don’t pair up electrons until after you’ve half-filled a subshell.

Nitrogen has 7 electrons:
• Draw the orbital diagram for the electron configuration of oxygen (atomic number 8).

• How many unpaired electrons does an oxygen atom have?
Practice Problems

• Write the full electron configuration for P, element 15.

• How many unpaired electrons does a P atom possess?
• Fill orbitals in increasing order of energy
• Rows correspond to principal quantum numbers
• Groups correspond to different electron configurations.
Alternate Depiction of Filling up Orbitals

Same order as previous slide
Elements with orbitals in lighter shade aren’t known (yet!)

Filling from lowest to highest energy level is called the Aufbau Principle
Aufbau Principle

- Not sure which orbitals are lowest energy?
  - Fill lowest sum of $n+l$ first
  - Ties go to lower $n$

- What order should we fill
  - Check $n+l$ → what order should we fill 3d, 4s & 4p?
    - 3d: $n=3$, $l=2$ → $n+l = 5$
    - 4s: $n=4$, $l=0$ → $n+l = 4$
    - 4p: $n=4$, $l=1$ → $n+l = 5$
  - Fill order: 4s, 3d, 4p
Condensed Electron Configurations

- Group 8A elements are said to have “filled shells”.

- Filled shell electrons are called “core electrons” and do not participate in making bonds or redox reactions.

- Electrons in the “outer shell” are “valence electrons” and do participate in bonding and redox reactions.

- We write condensed electron configurations by writing the next lowest noble gas configuration (the core electrons) plus the valence electrons.

- Examples: P – \(1s^22s^22p^63s^23p^3\) \(\rightarrow\) [Ne]\(3s^23p^3\)

  Ge – \(1s^22s^22p^63s^23p^34s^23d^{10}\) \(4p^2\) \(\rightarrow\) [Ar]\(4s^23d^{10}\)\(4p^2\)
More Practice Problems

- Write the condensed electron configuration for Te (element 52).
More Practice Problems

- Which element has an electron configuration of [Kr]5s^2 4d^3?

- How many unpaired electrons are there in this element?
For predicting reactivity, the valence shell configuration is most important.

- We don’t usually consider electrons in completely filled d or f subshells
More Practice Problems

• What family of elements is characterized by an \( ns^2np^2 \) electron configuration in the outermost occupied shell?

• What family of elements is characterized by an \( ns^2np^5 \) electron configuration in the outermost occupied shell?
Some Anomalies

- 4s and 3d orbitals are very close in energy
- Energetically favorable to half-fill or fully fill the d orbitals

Similar logic also applies to the f-block

Order of orbital stability
1. Full or empty subshell
2. Half–filled
3. Everything else

If the energy cost very low, re-arrange to make more stable subshells
Chromium: $[\text{Ar}] \ 4s^13d^5$
not $[\text{Ar}] \ 4s^23d^4$

Copper: $[\text{Ar}] \ 4s^13d^{10}$
not $[\text{Ar}] \ 4s^23d^9$

4s 3d
Full + Random

½ Full + Full
More Stable
Summary of Electron Configurations

- When writing electron configurations remember:
  1. Fill lowest energy levels first (Aufbau Principle)
     - Lowest sum of n+l goes first
     - Ties go to the lowest n
  2. Limited to 2 electrons per orbital so
     - s subshell gets 2 max
     - p subshell gets 6 max
     - d subshell gets 10 max
     - f subshell get 14 max
  3. Be aware of anomalies
     - Above 4s, bump an electron up to the d or f subshell if doing so will create a combination of full, empty or half-filled shells.
Key Concepts

- Calculations involving $E$, $l$, $n$, $m$ and $v$
- Bohr hydrogen atom model
  - Electron transitions and Rydberg equation
  - Energy states
  - Strengths and limitations of the model
- DeBroglie equation, uncertainty principle (define and calculate)
- What are orbitals and probability densities?
Key Concepts

- Quantum numbers, orbital shapes, shells, subshells, and nodes
- Ordering of orbitals: degenerate vs non-degenerate, Pauli exclusion principle
- Writing electron configurations, Hund’s rule, condensed electron configurations, electron configurations of groups on periodic table