Chapter 5
Modern Atomic Theory
The beautiful color of fireworks comes from the particular elements used. The colors are characteristic of the elements and can be used to understand their properties.
Emission spectra of atoms

- When atoms are excited (like in a flame) they emit discrete wavelengths of light, not a continuum.
- Shown below is the visible light range at the top, the emission spectrum of Na in the middle and the emission spectrum of H at the bottom.
Measuring the emission spectrum of atoms

- The atoms in the gas discharge tube are excited by electricity.
- The light produced is separated by the prism.
Light

- Electromagnetic energy
- Travels at $3.0 \times 10^{10}$ cm/s
- White light is a continuous spectrum of light (all energies represented) and can be separated
Properties of light

- Light has intensity, which is termed amplitude
- Light is characterized by its wavelength, which is given the symbol $\lambda$ (lambda)
- Wavelength is the distance between two adjacent peaks
Wavelength and energy

Wavelength and energy have an inverse relationship, as shown below

- $h$ is Planck’s constant ($6.626 \times 10^{-34}$ J·s)
- $c$ is the speed of light

$$c = \lambda \nu \quad \frac{c}{\lambda} = \nu \quad E = h\nu$$
Energy range of light

- Infrared light is lower energy than visible light.
- Ultraviolet light is higher energy than visible light. (Some of the ultraviolet range is of high enough energy to damage living tissue.)
- X-rays and gamma rays are even higher energy forms of light. (There are especial hazards associated with this type of radiation.)
Visible light

- Visible light comprises only a small fraction of the electromagnetic spectrum (400-800 nm)
- Ultraviolet and infrared light cannot be seen with the unaided eye, but are quite important
Atoms (and many molecules) emit discrete wavelengths of light

- The H$_2$ in the gas discharge tube is excited by electricity (discharge produces excited H atoms)
- The light produced is separated by the prism
A model for the electrons in the atom

A model is a description or analogy used to help visualize a phenomenon or entity.

Bohr proposed a model that violated classical physics, but started a new way of looking at atomic and molecular structure.

The central concept of this model is that the properties of atoms and electrons do not behave in a continuous fashion.
The Bohr atom

- Electrons revolve around the nucleus in stable orbits

- Each orbit is quantized
  - the electron is a discrete distance from the nucleus
  - the orbit has a discrete energy

- These orbits are referred to as energy levels
The energy levels are characterized by an integral number called the principle quantum number, n.

n has discrete values of 1, 2, 3,…

The Bohr atom (con’t.)
Quantized energy levels

- Only one idea remains from the Bohr model

- Quantized energy levels are like the steps of a staircase

- An electron can have one energy or another, but not an energy in between (can you stand between two steps?)
States of the atom

- **Ground state**
  - the lowest energy state

- **Excited state**
  - all states that have higher energies
  - atoms and molecules have many excited states but only one ground state
Modern atomic theory

- Modern theory is a complex mathematical description.
- Takes into account that atomic sized things behave more like waves than particles.
Wave mechanics

We treat electrons as waves, since we cannot precisely determine the location of the electrons.

Electrons are said to be described by orbitals, which are regions in space where there is a significant probability of finding the electron.
Wave mechanics reveals that the energy levels (sometimes called shells) have sublevels. The sublevels are designated by letters $s, p, d, f$. The sublevels increase in energy as $s < p < d < f$. Each sublevel has one or more orbitals.
Orbitals

- The orbital is best thought of as an electron cloud.
- The picture below is the density diagram for an s orbital.
- It indicates the probability of an electron being located in a particular location near the nucleus.
Representing orbitals

- We often represent orbitals as spherical volume of probability (volume in which the electron is found 90% of the time)
- The orbitals of the s sublevel are shown below
$p$ orbitals

- There are three orbitals in the $p$ sublevel.
- One is aligned along each of the Cartesian coordinates around the nucleus.
- Orientation is indicated by a right subscript.
There are five orbitals in the d-sublevel.

They are important to understanding the behavior of the transition metals.
The orbitals you need to know

The third shell ($n=3$)

- $3s$
- $3p$
- $3d$

$d$ subshell

- $d_{x^2-y^2}$
- $d_{xz}$
- $d_{yz}$

$p$ subshell

- $p_x$
- $p_y$
- $p_z$
Shell designation

The shell is indicated by the principle quantum number $n$ (Bohr orbit idea)
Shell designation

- The shell is indicated by the principle quantum number $n$ (*Bohr orbit idea*)
- The subshell is indicated by the letter $(s, p, d, f)$
Shell designation

- The shell is indicated by the principle quantum number $n$ (*Bohr orbit idea*)
- The subshell is indicated by the letter ($s, p, d, f$)
- The number of electrons in the subshell is indicated by a right superscript

For example, $4p^3$ (4th shell, p subshell, three electrons)
Electronic configurations

- The electrons in the atom are indicated by an electron configuration.
- We use only as many subshells and shells as are needed for the number of electrons.
- The number of available subshells depends on the shell that is being filled.
  - $n = 1$ only has an $s$ subshell (only 1 type of $s$ orbital).
  - $n = 2$ has $s$ and $p$ subshells (3 $p$ orbitals, $p_x$, $p_y$, $p_z$).
  - $n = 3$ has $s$, $p$ and $d$ subshells (5 $d$ orbitals, $d_1$, $d_2$, $d_3$, $d_4$, $d_5$).
The $n = 3$ shell
The *aufbau* Principle

- The electrons are added to the atom beginning with the lowest energy level.
- As the sublevels and levels are filled, electrons are added to the next higher energy level.
- Each orbital can hold two electrons, so each sublevel can hold twice as many electrons as there are orbitals.
The aufbau principle

- electrons occupy the available orbitals in the subshells of lowest energy
- The electronic configuration of an element is the assignment of all the electrons of the atom into shells and subshells
Order of filling of orbitals

1s  2s  2p  3s  3p  3d  4s  4p  4d  5s  5p  5d  6s  6p  6d  7s  7p  7d  7f...
Electronic configurations

- The levels increase in energy.
- Within the levels, the sublevels also increase (recall $s<p<d<f$).
- Recall that the electrons go into the lowest orbital first (1s, then 2s, etc.)
Consider S

Sulfur has 16 electrons

Electronic configuration is therefore

$1s^22s^22p^63s^23p^4$

$d$ and $f$ subshells are used for heavier elements
Core and valence shells

Chemically, we find that the electrons in the shell with the highest value of $n$ are the ones involved in chemical reactions.

This shell is termed the valence shell.

Electrons in shells with lower $n$ values are chemically unreactive because they are of such low energy.

These shells are grouped together as the core.
Abbreviated electron configurations

- We develop a shorthand for the electron configuration by noting that the core is really the same as the electron configuration for the noble gas that occurs earlier in the periodic table.

- E.g. for S (1s²2s²2p⁶3s²3p⁴), the core is 1s²2s²2p⁶ which is the same as the electron configuration for Ne.

- Abbreviated form is [Ne]3s²3p⁴.
Electron configuration shorthand

- We note that the valence shell electron configuration has the same pattern for elements in the same group.
- All elements in the same column as S have the valence electron configuration \([\text{core}]ns^2np^4\).
- This is the secret to the structure of the periodic table.
Representative elements

Representative elements have the general electron configuration \([\text{NG}]ns^x np^y\) (NG represents noble gas)

Each representative element has one more electron in the valence shell than the previous element
Representative elements

• $[\text{NG}] ns^1$ - alkali metals
• $[\text{NG}] ns^2$ - alkaline earths
• $[\text{NG}] ns^2 np^5$ - halogens
• $[\text{NG}] ns^2 np^6$ - noble gases
Transition elements

[NG]$ns^2(n-1)d^y$ - Transition elements

[NG]$ns^2(n-1)d^1(n-2)f^z$ - Inner transition elements
Electrons act as if they are little magnets due to a property called *spin*, and they can have a spin up (↑) or spin down (↓).

**The Pauli Exclusion Principle** - two electrons can occupy an orbital if they have different spins.

Practically, if two electrons are in the same orbital, they have opposite spins.

**Hund’s Rule** - when filling a subshell, electrons will avoid entering an orbital that already has an electron in it until there is no other alternative.
Represent the orbitals of the subshells as boxes and electrons as arrows.

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<td>N</td>
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<th></th>
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<td>Ne</td>
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Orbital diagrams
Dorm room analogy

- We can think of the levels as dorm rooms.
- A student will choose the dorm that is closest to the campus and on the lowest floor.
Dorm room analogy, con’t

- The dorms correspond to the shells
- The floors correspond to the subshells
Shell, subshell and orbitals
Periodic trends

Atomic radius is the distance from the nucleus to the outermost electrons

- Atomic radii decrease across a period
- Atomic radii increase down a group

The decrease from left to right in a period results from adding electrons to the same outer shell while protons are being added to the nucleus

All of the outer electrons are drawn closer to the nucleus
Atomic radii
**Ionization energy**

- The energy required to remove an electron from a gaseous atom to form a gaseous ion
- 1st ionization energy (IE$_1$)
  
  \[ M_{(g)} \rightarrow M^{+}_{(g)} + e^- \]

- Ionization energies increase across a period  
  (Increased nuclear charge and size)

- Ionization energies decrease down a group  
  (Increased distance from nucleus)

- Smaller atoms have higher ionization energies  
  (small atoms hold their electrons more tightly)
Ionization energies

- Metals are characterized by the relative ease that electrons are removed from them.
- Atoms can lose more than one electron:
  \[ M^+(g) \rightarrow M^{2+}(g) + e^- \]  
  \[ I_{E_2} \]
- Note that \( I_{E_2} \) for Na, \( I_{E_3} \) for Mg, \( I_{E_4} \) for Al are all very large compared to the preceding (\( I_E \); see Table 5-3).
When atoms lose electrons, the remaining electrons are more strongly attracted to the nucleus, hence cations are smaller than the atom.

Anions hold the electrons less tightly, so they are larger.
Core vs valence electrons

- To remove an electron from an inner shell is energetically very costly.
- Removing electrons from the valence shell requires quite a bit less energy.
- This will have consequences for the formation of compounds.