Chapter 6. Electronic Structure of Atoms

This is your first glimpse at the realm of quantum theory in this text. You need to understand that the model has been built up to rationalize experimental data.

I. The Wave Nature of Light

Light is a form of electromagnetic radiation.

Radiation carries energy through space.

Electromagnetic radiation is characterized by its wave nature.

All waves have a characteristic wavelength, $\lambda$, and amplitude, $A$.

The frequency, $\nu$, is a wave is the number of cycles which pass a point in one second.

The units of $\nu$ are Hertz (1 Hz = 1 s$^{-1}$).

The speed of a wave is given by its frequency multiplied by its wavelength.

For light, speed, $c = \lambda \times \nu$

Electromagnetic radiation moves through a vacuum with a speed of $2.99792458 \times 10^8$ m/s.

Electromagnetic waves have characteristic wavelengths and frequencies.

Example: visible radiation has wavelengths between 400 nm (violet) and 750 nm (red).

<table>
<thead>
<tr>
<th>Ultraviolet</th>
<th>Less than 400nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Violet</td>
<td>400-450nm</td>
</tr>
<tr>
<td>Blue</td>
<td>450-490nm</td>
</tr>
<tr>
<td>Green</td>
<td>490-550nm</td>
</tr>
</tbody>
</table>
II. Quantized energy and Photons

Planck: energy can only be absorbed or released from atoms in certain amounts. These amounts are called quanta.

The relationship between energy and frequency is $E=\hbar \nu$ where $\hbar$ is Planck's constant ($6.626 \times 10^{-34}$ J-s).

To understand quantization consider the notes produced by a violin (continuous) and a piano (quantized) a violin can produce any note by placing the fingers anywhere along the string. A piano can only produce notes corresponding to the keys on the keyboard.

A. The Photoelectric Effect

The photoelectric effect provides evidence for the particle nature of light. Einstein assumed that light traveled in energy packets called photons. The energy of one photon: $E = \hbar \nu$.

B. Bohr's Model of the Hydrogen Atom

1. Line Spectra

   Radiation composed of only one wavelength is called monochromatic.
Radiation which spans a whole array of different wavelengths is called continuous.

White light can be separated into a continuous spectrum of colors.

Not all radiation is continuous.

Different gases placed in a partially evacuated tube and subjected to a high voltage produce colored bands of light.

Where do these colored bands come from?

(check out the following site to see some spectra:
http://home.achilles.net/~jtalbot/data/elements/

Rutherford assumed the electrons orbited the nucleus analogous to planets around the sun.
However, a charged particle moving in a circular path should lose energy.

This means that the atom should be unstable according to Rutherford's theory.
Bohr noted the line spectra of certain elements and assumed the electrons were confined to specific energy states. These were called orbits. (energy levels)

Colors from excited gases arise because electrons move between energy states in the atom.
Since the energy states are quantized, the light emitted from excited atoms must be quantized and appear as line spectra.

2. Bohr developed three points

1. Bohr decided zero energy as the point at which the p+ and e- are completely separated. Energy needs to be absorbed to reach this point. This means energies below this point are negative. Hence the minus sign in the equation.
2. In normal hydrogen, the electron at energy level n = 1 is said to be the ground state. As the electron absorbs energy, it moves to a higher, excited state. (n=2,3 ... )
3. When an excited electron gives off energy in the form of light, it drops back down to a lower energy state.

After lots of math, Bohr showed that energy levels have specific energy that can be calculated by

\[ E_n = (-R_H) \left( \frac{1}{n^2} \right) \text{ where } n = 1, 2, 3, 4... \]

where \( n \) is the principal quantum number (i.e. energy level), and \( R_H \) is the Rydberg constant = \( 2.18 \times 10^{-18} \text{ J} \).

The first orbit in the Bohr model has \( n = 1 \) and is closest to the nucleus.

The furthest orbit in the Bohr model has \( n = \infty \) and corresponds to \( E = 0 \). (This may seem strange, but Bohr made the point where the electron is no longer part of the atom an energy of zero and any energy level below infinity, a negative energy.

Electrons in the Bohr model can only move between orbits by absorbing and emitting energy in quanta (Remember: \( E = hv \)).

The amount of energy absorbed or emitted on moving between states is given by

\[ \Delta E = E_f - E_i \]

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

* when \( n_i > n_f \) energy is emitted. \( \Delta E = - \)

* When \( n_f > n_i \) energy is absorbed. \( \Delta E = + \)

Bohr used this to predict the spectral lines that would be emitted by the different transitions of the electron. Bohr found the following wavelengths and separated them into series.

1. Balmer: visible spectrum (400-700nm)
2. Lyman series: ultraviolet (<400nm)
3. Paschen series. infrared (>700 nm)
Example: An electron falls from energy level 5 to level 2. Calculate the energy emitted. Will you see a color for this energy emission?

The ionization energy of an electron can be calculated by using $n_f = \infty$ and $n_i$ the energy level the electron is on.

Example 2: What is the ionization energy of the outermost electron in a Lithium atom.

III. The Wave Behavior of Matter

Knowing that light travels in waves, it seems reasonable to ask if matter has a wave nature.

This question was answered by Louis de Broglie.

Wave Particle Duality

Using Einstein’s and Planck’s equations, de Broglie derived:

$\lambda = \frac{h}{mv}$
The momentum, $m \nu$, is a particle property, where as $\lambda$ is a wave property.

Therefore, in one equation de Broglie summarized the concepts of waves and particles as they apply to low mass, high speed objects.

As a consequence of de Broglie’s discovery, we now have techniques such as X-ray diffraction and electron microscopy to study small objects.

*The Uncertainty Principle*

**Heisenberg's Uncertainty Principle:** on the mass scale of atomic particles, we cannot determine the *exactly* the position, direction of motion, and speed simultaneously. For electrons: we cannot determine their momentum and position simultaneously.

**IV. Quantum Mechanics and Atomic Orbitals**

Schrodinger proposed an equation which contains both wave and particle terms. Solving the equation leads to wave functions, $\psi$ (psi)

The wave function gives the shape of the electronic orbital.

The square of the wave function, $\psi^2$, gives the probability of finding the electron.

That is, $\psi^2$, gives the electron density for the atom.

*Orbitals and Quantum Numbers*

If we solve the Schrodinger equation, we get wave functions and energies for the wave functions.

We call $\psi$ **orbitals**.

Schrodinger’s equation requires 3 quantum numbers:

1. **Principal Quantum Number**, $n$. This is the same as Bohr’s $n$. As $n$ becomes larger, the atom becomes larger and the electron is further from the nucleus.

2. **Azimuthal Quantum Number**, $l$. This quantum number depends on the value of $n$. The values of $l$ begin at 0 and increase to $(n - 1)$. We usually use letters for $l$ (s, p, d and f for $l = 0, 1, 2, \text{ and } 3$). Usually we refer to the $s, p, d$ and orbitals.
3. **Magnetic Quantum Number, \( m_l \)** This quantum number depends on \( l \). The magnetic quantum number has integral values between \(-l\) and \(+l\). Magnetic quantum numbers give the 3D orientation of each orbital.

4. A fourth quantum number, \( m_s \) designates spin of electron as \( +1/2, -1/2 \)

Orbitals can be ranked in terms of energy to yield an **Aufbau diagram**.

Note that this Aufbau diagram is for a single electron system. As \( n \) increases note that the spacing between energy levels becomes smaller.

V. Representation of Orbitals

**The s-Orbitals**

All s-orbitals are spherical.

As \( n \) increases, the s-orbitals get larger.

**The p-Orbitals**

There are three p-orbitals: \( p_x, p_y \), and \( p_z \). The letters correspond to allowed values of \( m \), of \(-1, 0, \) and \(+1\). The orbitals are dumb-bell shaped.

As \( n \) increases, the p-orbitals get larger.

All p-orbitals have a node at the nucleus. (a place of zero electron density)

**The d- and f Orbitals**

- There are 5 \( d \) and 7 \( f \) orbitals.
- Three of the d-orbitals lie in a plane bisecting the \( x-, y- \), and \( z- \) axes.
- Two of the d-orbitals lie in a plane aligned along the \( x-, y-, \) and \( z- \) axes. Four of the d-orbitals have four lobes each.
- One d-orbital has two lobes and a collar.

Orbitals of the same energy are said to be degenerate. If you want to check out what \( f \) and even \( g \) orbitals look like go to [http://www.d.umn.edu/~pkiprof/chemweb/AOs/ao5.html](http://www.d.umn.edu/~pkiprof/chemweb/AOs/ao5.html) OR [http://www.chem.ufl.edu/~chm2040/Notes/Chapter_9/Coolstuff/forb.html](http://www.chem.ufl.edu/~chm2040/Notes/Chapter_9/Coolstuff/forb.html)
Effective Nuclear Charge

- Effective nuclear charge is the charge experienced by an electron on a many-electron atom.
- The effective nuclear charge is not the same as the charge on the nucleus because of the effect of the inner electrons. The electron is attracted to the nucleus, but repelled by the electrons which shield or screen it from the full nuclear charge.
- The nuclear charge experienced by an electron depends on its distance from the nucleus and the number of electrons in the spherical volume out to the electron in question.
- As the average number of screening electrons (S) increases, the effective nuclear charge ($Z_{\text{eff}}$) decreases.
- As the distance from the nucleus increases, S increases and $Z_{\text{eff}}$ decreases.

Electron Spin and the Pauli Exclusion Principle

Line spectra of many electron atoms show each line as a closely spaced pair of lines. Stem and Gerlach designed an experiment to determine why.

A beam of atoms was passed through a slit and into a magnetic field and the atoms were then detected. Two spots were found: one with the electrons spinning in one direction and one with the electrons spinning in the opposite direction.

Since electron spin is quantized, we define $m_s =$ spin quantum number = $\pm 1/2$.

Pauli's Exclusions Principle: no two electrons can have the same set of 4 quantum numbers.

Therefore, two electrons in the same orbital must have opposite spins.

Electron Configurations

Electron configurations tells us in which orbitals the electrons for an element are located. There is a great application program from TI website that will do electron configurations.

Three rules:
1. electrons fill orbitals starting with lowest \( n \) and moving upwards;

2. no two electrons can fill one orbital with the same spin (Pauli);

3. for degenerate orbitals, electrons fill each orbital singly before any orbital gets a second electron. (Hund’s rule)

\[ \uparrow \uparrow \uparrow \]

An arrow pointing upwards has \( m_s = +1/2 \) (spin up).

An arrow pointing downwards has \( m_s = -1/2 \) (spin down).

There is a shorthand way of writing electron configurations:

Write the **core electrons** corresponding to the filled noble gas in square brackets.

Write the **valence electrons** explicitly.

Example:

P: \( 1\,s^2\,2s^2\,2p^6\,3s^2\,3p^3 \)

but, Ne: \( ls^2\,2s^2\,2p^6 \)

Therefore, P: \([\text{Ne}]\,3s^2\,3p^3\)

**Periods 1, 2, and 3**

**Valence electrons**: electrons in the outer-shell. These electrons are gained and lost in reactions.

**Core electrons**: electrons in the inner shells. (Generally not involved in bonding.)

**Period 4 and Beyond**

After Ar the \( d \) orbitals begin to fill.

After the \( 3d \) orbitals are full the \( 4p \) orbitals begin to fill.

The ten elements between Ti and Zn are called the transition metals.

From Ce onwards the \( 4f \) orbitals begin to fill.

Note: La: \([\text{Xe}]6s^2\,5d^1\,4f^0\)
Elements Ce - Lu have the 4f orbitals filled and are called **lanthanides**.

Elements Th - Lr have the 5f orbitals filled and are called **actinides**.
Most actinides are not found in nature.

**Electron Configurations and the Periodic Table**

The periodic table can be used as a guide for electron configurations.

The period number is the value of $n$.
Groups 1 A and 2A have the s-orbital filled.
Groups 3A - 8A have the p-orbital filled.
Groups 3B - 2B (transition elements) have the d-orbital filled.

The lanthanides and actinides have the f-orbital filled.
Note that the 3d orbital fills **after the** 4s orbital. Similarly, the 4f orbital fills after the 5d orbital.

**Some important notes**

- $d^4$ and $d^9$
- $f^6$ and $f^{13}$
- Ion formation and bonding in the transition metals