

Chapter 11 – Modern Atomic Theory

- 0) This chapter is a continuation of our discussions from Chapter 3 during which we saw how atoms, electrons, protons, and neutrons were discovered. I am going to assume that you remember Dalton, J. J. Thomson, Lord Kelvin, Roentgen, and Rutherford from that chapter.

This chapter will bring us from the early 1900's to current times in looking at the atom and atomic structure.

1) Sec 11.1 – Rutherford's Atom

- 1) An atom contains a nucleus which has a very small volume compared to the volume of the atom, but almost all of the mass of the atom is in the nucleus. The nucleus contains the protons (+1 charge, mass = 1.0 amu) and neutrons (no charge, mass = 1.0 amu). Electrons have -1 charge, 0.00055 amu.

$$\text{Atomic Number} = \# \text{ of protons} \quad \text{Mass Number} = \# \text{ of protons} + \# \text{ of neutrons}$$

- 2) The number of electrons in a neutral atom is the same as the number of protons.
- 3) Rutherford thought that the electrons might move around the nucleus somewhat like the planets move around our sun, but he could not explain how this happened nor why the electrons were not drawn into the nucleus.

2) Sec 11.2 – Energy and Light

The work that led to the development of the modern model of the atom grew out of the study of light. Remember that the people who discovered the protons, neutrons and electrons began by studying electricity and energy. Light is only a small part of the entire thing that is called **electromagnetic energy or radiation**.

- a) Electromagnetic Energy (Light waves) is the energy carried through space by means of wavelike oscillations. The oscillations are systematic fluctuations in the intensities of very tiny electrical and magnetic forces. Electromagnetic radiation has a **wavelength** (λ) and a velocity (c) which is 3.0×10^8 m/sec. The **frequency** (ν , ν) refers to the number of waves that pass a given point in a certain amount of time. The unit of frequency is the Hertz (Hz = cycles/sec). We can relate these things in the following expression:

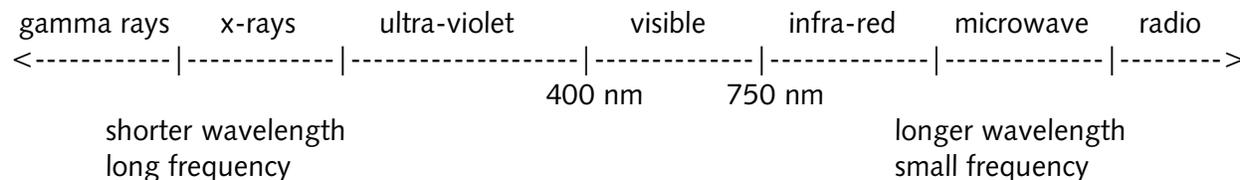
$$\nu = \frac{c}{\lambda} = \frac{\text{m/sec}}{\text{m}} = \frac{1}{\text{s}} ; \text{ therefore Hertz} = \text{s}^{-1} = \text{Hz}$$

- b) Visible light covers a small part of the total spectrum. For most people, light is visible if it has a wavelength between 400 nm (violet) and 750 nm (red).

$$1 \text{ \AA} = 1 \times 10^{-10} \text{ m}$$

$$1 \text{ nm} = 1 \times 10^{-9} \text{ m}$$

The Spectrum



Examples

1) What is the frequency in hertz of violet light?

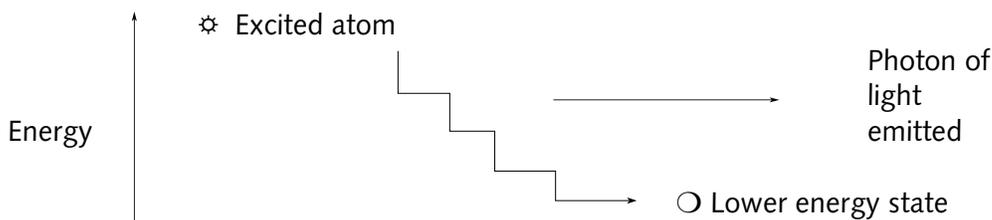
2) What is the wavelength of radio waves that have a frequency of 1240 kHz?

c) Often we can look at the energy that is involved with all of these as packets of energy, distinct units, which are often called **photons**.

What is the exact nature of light? Does it consist of waves or is it a stream of particles? It seems to be both. This leads to what is called **the wave-particle duality** of the nature of light.

3) Sec 11.3 – Emission of Energy by Atoms

When energy (heat, electrical, or light) is added to a substance, some or all of the energy may be absorbed by the substance which then exists in an excited state. The substance will later become unexcited by losing the energy as a photon of light, which can be observed by a spectroscope.



High-energy photons correspond to short-wavelength light and low-energy photons correspond to long-wavelength light.

Atomic Spectra – We refer to this in terms of atomic spectra – literally, the light from atoms.

- 1) Continuous Spectrum – A spectrum that contains all wavelengths of visible light. When sunlight is passed through a prism, the light is separated into a spectrum.
- 2) Atomic Emission Spectra – The light emitted by elements consists of sharp lines in the visible or near U.V. part of the spectrum.

DEMONSTRATION – Observation of Atomic Emission Spectrum of Selected Elements.

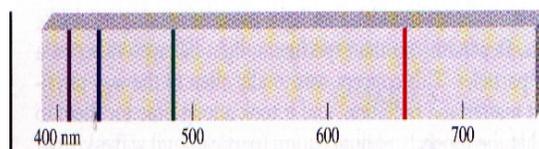
4) Sec 11.4 – The Energy levels of Hydrogen

The hydrogen atom is the simplest system we can look at because it only has one electron to consider. When a hydrogen atom absorbs energy from some outside source, it uses this energy to go to a higher or excited energy state. It can release this excess energy (go to a lower energy state) by emitting a photon of light.

The important thing here is to recognize that the energy contained in the photon corresponds to the change in energy that the atom experiences in going from the excited to the lower energy state.

What we also see, however, is that only certain photons of visible light are emitted. We might have assumed that all wavelengths of light would appear. We do not see all colors.

Hydrogen Spectrum



Atomic Emission Spectrum of Hydrogen – Consists of 4 lines in the visible region of the spectrum (410 nm, 434 nm, 486 nm, 656 nm).

These results tell us that only certain photons are emitted which means that only certain energy changes are occurring. This means that the hydrogen electron can only have certain discrete energy levels. The same colors are always emitted with hydrogen, so we must assume that all hydrogen atoms have the same set of discrete energy levels. This was a change because people expected that atoms could have a continuous set of energy levels rather than only certain values. This discovery greatly changed how people looked at the atom.

5) Sec 11.5 – The Bohr Model of the Atom

In 1913 Niels Bohr proposed that electrons are arranged in concentric circular paths, or orbits, around the nucleus (sometimes referred to as the planetary model). He proposed that electrons in a particular path have a fixed energy. To move from one energy level (orbit) to another, an electron must gain or lose just the right amount of energy. The energy levels in an atom are not equally spaced. They move closer together as we move to higher energy levels. A quantum is the amount of energy required to move an electron from its present energy level to the next higher one. Thus, the energy of the electron is said to be quantized.

Bohr's model gave an excellent explanation of the spectrum of the hydrogen atom but did not work at all with atoms containing more than one electron. However, the ideas of quantum numbers and fixed energy levels were useful in later theories.

6) Sec 11.6 – The Wave (or Quantum) Mechanical Model of the Atom

The modern description of the electrons in atoms derives from the solution to the Schrodinger Equation. This model is primarily mathematical. It has few, if any, analogies in the visible world.

It takes into consideration the possibility that an electron can behave like a wave and not just a particle.

Like the Bohr model, the quantum mechanical model of the atom leads to fixed energy levels for an atom.

Unlike the Bohr model, the quantum mechanical model does not define the exact path an electron takes around the nucleus. The electron does not orbit the nucleus in circles. It does predict the most probable locations of an electron when it is in a certain energy level. This region of a probable location for an electron is called an **orbital**.

7) Sec 11.7 – The Hydrogen Orbitals (Atomic Orbitals)

An atomic orbital is a region of space where there is a high probability of finding an electron. Atomic orbitals are characterized by a set of three integer quantum numbers (n , l , and m) that come from the mathematical solution to the Schrodinger equation.

- The principal quantum number, n – determines to a large extent the energy of the electron and is also related to how far from the nucleus we are likely to find the electron. ($n = 1, 2, 3, \text{etc.}$)
- The secondary quantum number, l – describes the shape of the orbit (most probable locations of the electron). It also has some effect on the energy of the electron (sublevels). [$l = 0(s), 1(p), 2(d), 3(f), \text{etc. up to } n-1 \text{ for each } n \text{ value.}$]
- The magnetic quantum number, m – is related to the spacial orientation of the orbitals. It tells how many orbitals there are of a given type. ($m = -l, \dots, -1, 0, +1, \dots, +l \text{ for each } l \text{ value.}$)

d) Summary

n	l	Values of m	Orbitals
1	0	0	1s
2	0	0	2s
	1	-1, 0, +1	2p 2p 2p
3	0	0	3s
	1	-1, 0, +1	3p 3p 3p
	2	-2, -1, 0, +1, +2	3d 3d 3d 3d 3d
4	0	0	4s
	1	-1, 0, +1	4p 4p 4p
	2	-2, -1, 0, +1, +2	4d 4d 4d 4d 4d
	3	-3, -2, -1, 0, +1, +2, +3	4f 4f 4f 4f 4f 4f 4f

The orbitals correspond to the appropriately named regions on the Periodic Table.

Your book (pages 334-336) has pictures showing the relative sizes and shapes of orbitals for hydrogen. You also should have a handout that also shows these orbitals.

8) Sec 11.8 – More on the Model

The model also allows for one more quantum number, most often called the “s” or spin quantum number. It takes into consideration that two electrons must have opposite spins in order to occupy the same orbital. The s quantum number can have values of -1/2 and +1/2. We will see how this works shortly.

9) Sec 11.9 – Electron Arrangements in the First Eighteen Atoms on the Periodic Table

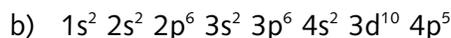
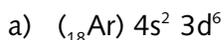
The ways in which electrons are arranged around the nuclei of atoms are called electron configurations. Three rules/principles govern the filling of atomic orbitals.

- The Aufbau Principle – Electrons enter the orbitals of lowest energy first. (See diagram in book on page 345 for order of filling.)
- The Pauli Exclusion Principle – An atomic orbital may contain at most two electrons. To occupy the same orbital, two electrons must have opposite spins (clockwise or counterclockwise). $1s (\uparrow \downarrow)$ [Arrows are sometimes used to indicate the spin of the electron.]
- Hund's Rule – When electrons occupy orbitals of equal energy, one electron enters each orbital until all the orbitals contain one electron with spins parallel.

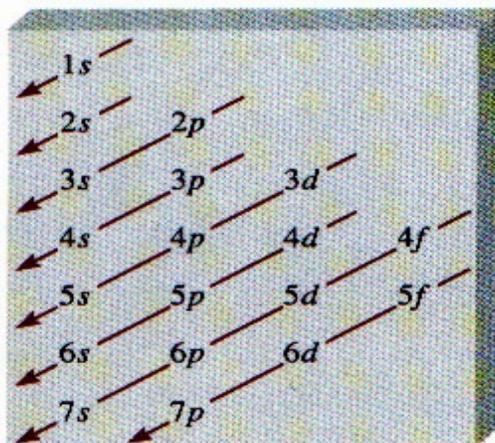
Examples – Give electron configurations of neutral atoms of the following:



Examples – Name the element whose atoms have these electron configurations:



A quick way to remember the order in which orbitals are filled with electrons is to draw the following chart. It is much easier to remember than the one on page 345.



You can also use the Periodic Table to do the same thing if you remember certain basic things that you have to consider. (Again, remember that the model helps to explain the Periodic Table. The Table does not depend on the model.)

10) Sec 11.10 – Electron Configurations and the Periodic Table

The standard system for determining electronic configurations works through the elements up to atomic number 21. After that there are some special configurations that occur which do not follow the general rules. It is most important to remember the general rules and then learn the exceptions if and when needed.

For the higher numbered elements, the Nobel gas abbreviation is often used to make writing the electron configurations easier.

11) The Quantum Concept – Max Planck proposed that electromagnetic radiation is carried by tiny packets of energy called photons. These are the same “photons” mentioned earlier. Planck proposed and Einstein confirmed that the energy of the radiation was proportional to its frequency and not to its intensity or brightness. The energy of one photon is called one quantum.

$$E = h * \nu$$

$$E = \underline{hc} \quad h = 6.62 \times 10^{-34} \text{ Joules-sec} \quad c = 3.0 \times 10^8 \text{ m/sec}$$

Example: Calculate the energy of a photon of violet light ($\lambda = 400 \text{ nm}$) in joules.

12) An Explanation of Atomic Spectra

Bohr's application of the quantum theory to the energy levels of the electrons in atoms resulted in an explanation of the hydrogen spectrum. Each of the lines in the hydrogen spectrum is a result of movements of electrons from higher to lower energy levels. Bohr was able to derive an equation from which the energy and wavelengths of the lines in the hydrogen spectrum could be obtained.

$$E = \frac{-B}{n^2} \quad B = 2.18 \times 10^{-18} \text{ J}$$

$$E_{\text{light emitted}} = E_{\text{H.L.}} - E_{\text{L.L.}}$$

Thus, the energy of light can be calculated:

$$E_{\text{light emitted}} = \frac{-B}{n_{\text{H.L.}}^2} + \frac{B}{n_{\text{L.L.}}^2}$$

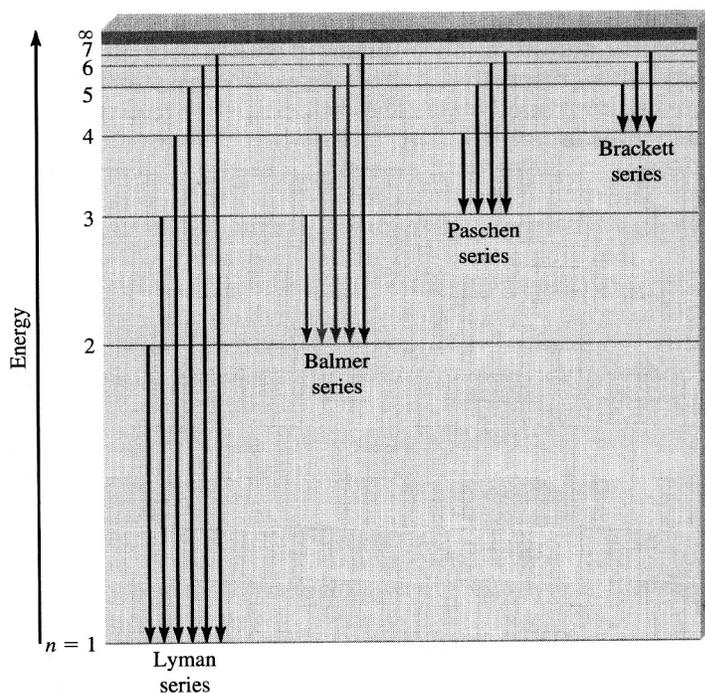
And, further, the wavelength of that light from:

$$E_{\text{light emitted}} = E = \frac{hc}{\lambda} \quad \text{or} \quad \lambda = \frac{hc}{E_{\text{light emitted}}}$$

Example – Calculate the energy of the light and the wavelength in nm of the light emitted when a hydrogen electron drops from level 3 to level 2.

13) Emission Spectrum of the Hydrogen Atom

The emission spectrum of hydrogen covers a wide range of wavelengths from the infrared to the ultraviolet. The table below lists the series of transitions in the hydrogen spectrum; they are named after their discoverers. The Balmer series was particularly easy to study because a number of the lines fall within the visible range.



Series	n_{low}	n_{high}	Spectrum region
Lyman	1	2, 3, 4, ...	Ultraviolet
Balmer	2	3, 4, 5, ...	Visible and ultraviolet
Paschen	3	4, 5, 6, ...	Infrared
Brackett	4	5, 6, 7, ...	Infrared

14) The Wave Motion of Matter and Quantum Mechanics

- a) Very small particles show properties that we identify with waves. Louis de Broglie suggested that small bits of matter, such as electrons, behave like waves. In 1927 Davisson and Germer conducted experiments which involved the "shooting" of electrons at a sample of nickel. To their amazement, they obtained diffraction patterns similar to those obtained when x-rays (a form of light) are diffracted by a crystal. Furthermore, the experimentally determined wavelength agreed with the value calculated by using the deBroglie equation.

$$\lambda = \frac{h}{mv} \quad \text{where } m = \text{mass of particle and } v = \text{its velocity}$$

- b) Practical use of the wave character of the electron is shown in the operation of the electron microscope. This instrument uses a beam of electrons rather than light waves to produce the image of an object being viewed. The wavelength of "electron-waves" is much smaller than that of visible light waves. Therefore, the electron microscope has a much greater resolving power than an ordinary microscope.
- c) Current theories of electronic structure (the Schrodinger Equation) are based on the wave properties of the electron. This theory is called wave mechanics or quantum mechanics.
- d) Another feature of quantum mechanics that is not found in classical mechanics (study of normal size objects) is the Uncertainty Principle. The Heisenberg Uncertainty Principle states that it is impossible to know exactly BOTH the velocity and the position of a particle at the same time. The principle is extremely important when dealing with a small particle like the electron. This is the reason we can only predict the most probable locations of an electron and not its path.

15) Sec 11.11 – Atomic Properties and the Periodic Table

With all these special calculations and theories trying to make models that match reality, we must not forget that chemistry still depends upon observed properties of substances. The modern atomic theory is really just an attempt to help us to explain WHY things happen and to help us possibly predict what might happen in a new situation.

- a) As one moves down a group on the Periodic Table, atoms get bigger. As one moves left to right across a period, the atoms get smaller.

We can understand the increase in size as one moves down the group if we remember that with each period, the principle energy level increases and that means that the average distance of the outer electrons from the nucleus also increases.

The decrease in size requires a little more thought. If the outer electrons are all in the same principle energy level as one moves left to right across a period, then you might think that the size should remain the same. But also remember that the nucleus is also increasing in protons as one moves from left to right. Therefore, the pull on the electrons from the nucleus is increasing and has a tendency to draw the electrons closer to the nucleus.

- b) As size increases, the tendency for an atom to lose an electron increases. That is, as you

move down a group, the atoms are more likely to lose electrons. This tendency to lose electrons is called **ionization energy**. As you move from left to right across a period, atoms are less likely to lose electrons, because the atoms are getting smaller.

Ionization energy is the energy it takes to remove an electron from a neutral atom.

Ionization energy **decreases** as you go down a group and **increases** as you go left to right across a period. [As you move from metals to non-metals across a period, the ionization energy increases so much that not only do the electrons not leave, the atoms actually attract other electrons.

EXTRA PROBLEMS

- 1) Calculate the energy and wavelength (in nm) of the light emitted when a hydrogen electron drops from the higher to the lower energy level given below. What region of the spectrum is the light emitted in (visible, U.V., or I.R.)?
a) 5 to 2 b) 5 to 1 c) 5 to 3
- 2) The spectral lines of hydrogen in the visible range represent electron transitions from a higher energy level back to the 2nd energy level. In what energy level was the electron if the spectral line of 410 nm is emitted? (You must show your calculations to support your answer.)