

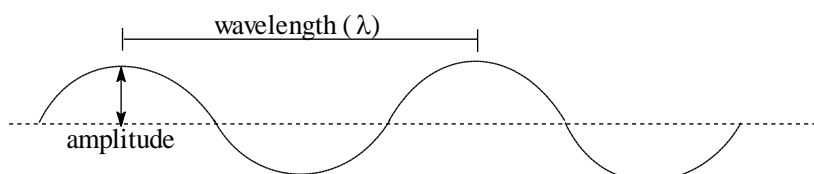
Modern Atomic Theory and the Periodic Table

Ultimately, an understanding of chemistry requires an understanding of the basic physics of atoms and how those atoms interact with each other. In Chapter 5, you learned the basic composition and structure of atoms. Chapters 4 and 8 discussed energy changes in reactions. We will close this course by starting to look at how these topics are connected and why they are important.

10.1 Electromagnetic Radiation

Electromagnetic radiation carries energy through space and is sometimes called radiant energy. There are a number of different kinds of such energy including: visible light, X-rays, and radio waves, as well as the infrared radiation coming from the fire. These labels categorize the waves according to how quickly they carry energy from a source to a target, but qualitatively, the waves are the same. A way to think about this is that all electromagnetic radiation travels as sine waves, but how elongated the waves are determines how quickly they transfer energy. They all share the property of traveling in waves at 3.00×10^8 m/s in a vacuum (memorize this value).

Consider the electromagnetic wave:



Waves have two attributes that concern us: wavelength and amplitude. Wavelength, λ , is the distance between successive peaks. Amplitude is the distance from the center point to the top of the wave crest. The distance covered by one wavelength is sometimes called a wave cycle or more simply, a cycle. The (wave)cycle is frequently used as a counting term. Amplitude is a measure of the intensity of the wave. Wavelength is an indirect measure of how much energy is carried by the wave. Thus, intensity and energy are not directly related. While a sound wave

isn't electromagnetic radiation, this analogy works. The amplitude of a sound wave is how loud it is, while its wavelength is an indirect measure of its pitch. Finally, waves interact with the environment through complete wave cycles. Partial absorption isn't possible. For example, the picture above shows two full wave cycles. Either or both might be absorbed, but not any fraction.

Returning to the first paragraph, the labels we use for electromagnetic radiation, e.g. visible light, X-rays, radio waves, etc. arbitrarily divide the entire spectrum into ranges of wavelengths which have common features which the names suggest. [You should know the ordering of the labels, but not the specific wavelengths, except for visible light which is 400-700 nm.](#)

10.2 The Bohr Atom

In Chapter 5 (section 4), the planetary model of the atom was introduced. In it, electrons travel in circular orbits around a massive nucleus housing all of the atom's protons. Beginning in the 1860's and extending into the 1910's, physicists studying light found something unexpected. When light typically found in nature (e.g. sunlight, firelight, etc.) is passed through a prism, a broad spectrum of colors emerges. A rainbow is a classic example of this phenomenon. The new discovery was that when light was emitted from heated elements, that light appeared as a series of lines (p. 210 textbook), rather than as a continuum (p. 208 textbook).



A series of scientists examining the line spectra of hydrogen found a mathematical relationship between all of the lines.

A third, then separate, area of physics was developing relating to the transfer of energy between objects. Our everyday experience tells us that energy transfer is continuous. For example, a pot of water on a stove warms and cools in a gradual way, rather than jumping from one temperature to another. Also, a ball rolls down a smooth slope and releases its potential

energy continuously. By around 1900, there was mounting evidence that for very small systems, the energy changes were actually punctuated/discontinuous (i.e. occurred as jumps/steps). Max Planck proposed the existence of energy quanta (plural of quantum) as a way to explain these phenomena, including line spectra. A quantum is a small, discrete packet of energy. This tied together the two threads of line spectra and energy steps.

Niels Bohr's great accomplishment was tying Planck's quantum theory to atomic structure. At the time quantum theory was introduced, recall that the atom was thought of as being a blob of positive charge with embedded electrons. When Rutherford proposed the planetary model of the atom, Niels Bohr recognized that quantum theory goes a long way to explaining that model.

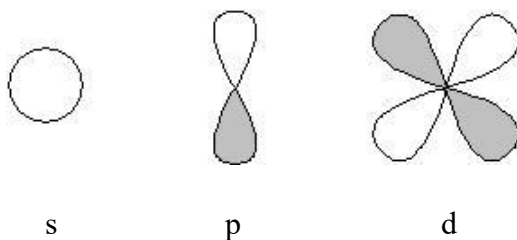
Two fundamental questions left unanswered by Rutherford were the connection between line spectra and his proposed structure and how the orbits worked. Specifically, for the second point, how was it a negatively charged particle could rotate around a positively charged nucleus without spiraling in. What Bohr realized for the hydrogen atom was that the energy of the spectral lines exactly equaled the differences in energy between electrons if their orbits had specific radii. Another way to say this is to imagine a nucleus with two electrons orbiting it at different distances. One can calculate the energy of attraction of each electron to the nucleus based solely on how far the electron is from the nucleus. If one determines the difference in those two energies, it corresponds to one of the wavelengths of light in the hydrogen line spectrum. If there were just four orbits, there would be 6 lines (e.g. $1 \rightarrow 2$, $1 \rightarrow 3$, $1 \rightarrow 4$, $2 \rightarrow 3$, $2 \rightarrow 4$, and $3 \rightarrow 4$). Five orbits would yield 10 lines and six orbits 15 lines. It also explained quantization in the atom because the orbits were fixed, with no intermediate orbits. It also shows bizarre aspects of the quantum world. For example, the electron can be in orbit 1 or 2, but not in between, so how does the electron move from the inner orbit to the outer orbit?

This was explained by Louis de Broglie, who suggested that rather than think of the electron as a particle, think of it as a wave. When that is done only certain wavelengths are possible, which accounts for the specific orbits. We will discuss this in class.

The lowest energy level is called the ground state. All higher energy levels are excited states.

10.3 Energy Levels of Electrons

The book's transition into this section is confusing. Basically, the Bohr atom turns out to be too simplistic. For example, molecules have 3-dimensional shapes and are clearly created by attaching atoms to one another. How does that happen with Bohr atoms? It turns out that the planetary model in any form has to be discarded and replaced with a completely new way of envisioning the atom. In this model (Schrodinger model), electrons are not restricted to 2-dimensional orbits, but rather travel freely, spending their time in regions of space, called orbitals. Three of those orbital types appear below.



In any atom, at any particular energy level, there will be, at most, one *s*, three *p*, five *d*, and seven *f* orbitals. (*f* Orbitals are not pictured because they typically do not engage in bonding.) The different shapes arise because of the wave properties of the electron. On pp. 212-213 of your book, all 9 orbitals are shown and you should be able to sketch each of them with their labels.

There are rules associated with the Schrodinger atom model that are important to remember.

- 1) Each atom has a series of principal energy levels, numbered 1, 2, 3, ... and represented by the letter "*n*."
- 2) Each energy level, *n*, will have associated with it one or more orbitals. For $n = 1$, only a single *s*-orbital exists ($1s$). For $n = 2$, a second *s*-orbital exists as do 3 *p*-orbitals ($2s$, $2p_x$, $2p_y$, and $2p_z$). For $n = 3$, a third *s*-orbital exists, a second set of *p*-orbitals exists, and 5 *d*-orbitals now are possible.

- 3) For the atom as a whole, the number and types of orbitals are additive from the lowest energy up. (i.e. If an atom has electrons in an $n = 3$ level, the $n = 1$ and 2 levels are also present and filled.)
- 4) Each orbital contains at most two electrons. The electrons have a property called spin and if two electrons are in an orbital, they spin in opposite directions: clockwise (\uparrow) and counterclockwise (\downarrow). This is the Pauli exclusion principle.
- 5) As n increases, orbitals of the same type increase in size. i.e. a $2s$ orbital has a larger radius than a $1s$ orbital

10.4 Atomic Structures of the First 18 Elements

Each atom has a unique “electron configuration.” The electron configuration is the set of orbitals on an atom and how they are filled. For example, hydrogen has only one electron and it resides in the $1s$ orbital. Helium has two electrons, with both in the $1s$ orbital, albeit with opposing spins. Lithium has 3 electrons so a second orbital is required, the $2s$. The other atoms follow in a mostly similar fashion.

There are three rules regarding the creation of atomic structures:

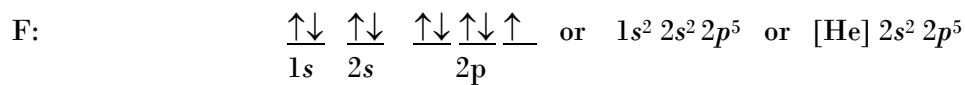
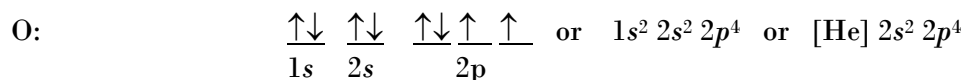
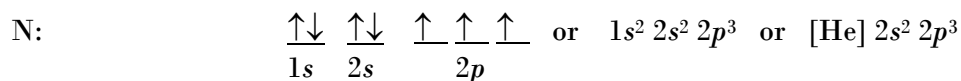
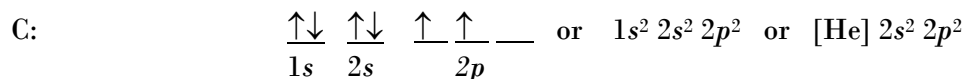
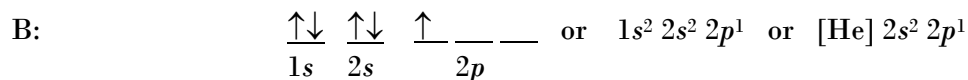
- 1) The Pauli exclusion principle, i.e. at most 2 electrons per orbital.
- 2) Electrons occupy the lowest energy orbital available. Normally, this means filling lower n levels first and s before p before d before f . Energetically, $s < p < d < f$.
- 3) When adding a second electron to an orbital, all other orbitals of that type and energy level must already have one electron in it.

The electron configurations are important because they play a major role in understanding chemical bonding, which is at the heart of chemical reactivity. With a few exceptions, only one of which is important for you to remember, electron configurations follow a predictable pattern. So, hydrogen is the first element and so has only one electron. It goes into the $1s$ orbital yielding an electron configuration of $1s^1$. Helium has two valence electrons and so the second electron goes into the $1s$ orbital as well (from the rules) to yield $1s^2$ as its electron configuration. Lithium

has 3 valence electrons, with the 1s filled, the next lowest energy orbital is 2s, yielding an electron configuration of $1s^2 2s^1$.

When continuing further into the periodic table, pictures can help show what happens in subshells (groups of orbitals at the same principal quantum number, but different shapes).

Shells are groups of orbitals with the same principal quantum number.



In these pictures, the application of the third rule may be seen in a way not possible with the simple text description (e.g. $1s^2 2s^2 2p^1$). You will see a shorthand at the far right of each line. Once all of the orbitals for a principal quantum number are filled, the orbitals may be replaced by the noble gas to which it corresponds. For helium, this won't seem like a big deal, but for lead (element 82) it saves a considerable amount of writing and with it, many chances to make errors. Pb: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 5d^{10} 4f^{14} 6p^2$ vs. [Kr] $6s^2 5d^{10} 4f^{14} 6p^2$

Electrons in the outer (valence) shell are referred to as valence electrons. Once a shell is completed, the electrons are referred to as core electrons (except the outermost electrons in the noble gases and anions, which are still valence electrons). Valence electrons are the chemically active electrons, while core electrons are chemically inert.

10.5 Electron Structures and the Periodic Table

Like much of modern chemistry, the periodic table was created/discovered in the late 1800's. It was proposed independently by Dmitri Mendeleev and Lothar Meyer in the same year (1869). Mendeleev has generally been credited with the discovery because he spent most of the rest of his career advocating for it, while Meyer published his idea and largely didn't pursue it further. The name "periodic table" of the elements is important because it speaks to the central idea in its creation, a regularity in the placement of the elements. There are systematic and regular changes in the properties of the elements that lead to their placement on the chart. We will discuss some of them now.

Prior to the proposed periodic table, scientists had long known that relationships between elements existed. This was borne out in their names. Two examples will illustrate this. Sodium and potassium were both first identified from the residue of burned plants (soda ash and potash, respectively). Lithium was first extracted from rocks (lithos from the Greek for stone). Also, a Johan Dobereiner observed for some sets of three elements with similar physical and chemical properties (e.g. chlorine, bromine, and iodine), one element (bromine here) had an atomic weight and density close to the average of the other two. What Mendeleev and Meyer were able to do was resolve all of the major discrepancies that existed in all of these models. Notably, Amazingly, Mendeleev even was able to predict the existence, properties, and location on the periodic table of four then unknown elements: scandium, gallium, technetium and germanium. All were found later, with properties close to those predicted.

The periodic table has a few structures within it. For example, the first two and last six columns (also called groups or families) are collectively called the representative elements. The 10-column block in the center are the transition metals. The top 14-element row (called a period) below the main part of the periodic table are the lanthanide elements and the 14-element period beneath it are the actinide elements.

From the electron configurations introduced in the previous section, the first two groups are sometimes called the *s*-block elements, the last six groups are the *p*-block elements, the transition metals are the *d*-block elements, and, collectively, the lanthanides and actinides are called the *f*-block elements.

Some groups also have names that are important. For example, the first column holds the alkali metals, while the second column are the alkaline earth metals. Column 17 (7A) are the halogens, column 16 are the chalcogens. Finally, one column (which is it?) are the coinage metals. A few other columns have names, but they are obscure and rarely used anymore.

There are some rules with respect to groups and periods.

- 1) Periods are numbered 1 – *n*, where *n* is a whole number. The *n* corresponds to the principal quantum number of the *s* orbital beginning that period. E.g. Period 1 corresponds to the 1 in $1s^1$ of hydrogen.
- 2) There are 3 systems of numbering groups. The modern system is 1-18, with the number determined by counting from left to right the total number of columns. (The book says, incorrectly, that it corresponds to the number of valence electrons, but that is not always true (e.g. fluorine has 7 valence electrons, but is in group 17). There is another system that was used for decades using a 1-8 A/B system that you may encounter if you are a chemistry major.
- 3) The elements in a group have the same or similar electron configurations, except for the principal quantum numbers. E.g. $H = 1s^1$, $Li = [He] 2s^1$ (again the book's statement is not technically correct).

August 26, 2024