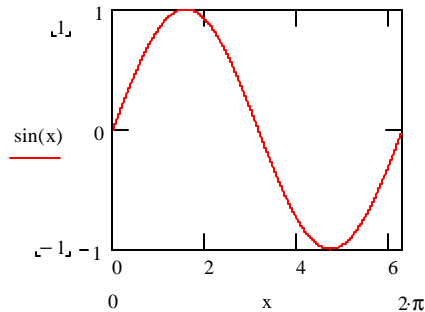


Light, Quantum Mechanics and the Atom

Light

Light is something that is familiar to most of us. It is the way in which we are able to see the world around us. Light can be thought of as a wave and, as a consequence, has two numbers that can be used to characterize it. The first is the **wavelength, λ** , which is the distance between any two corresponding points on the wave. In the graph of the so-called “sine wave” below, the wavelength is the distance across the graph from 0 to 2π .



The second number used to characterize a wave is the **frequency, ν** . This is how many wave pass a given point in a given amount of time, usually 1 second. Wavelength has units of meters and frequency has units of s^{-1} , or Hz. The two numbers for any wave are related to each other by the expression

$$c = \lambda \nu$$

where c is the speed of the wave. For light c is $2.998 \times 10^8 \text{ m s}^{-1}$.

Early Quantum Mechanics

The first use of quantum mechanics was by Max Planck in the late 1800s. He was attempting to reconcile the experimental data in the black body experiments with the theoretical data, which was clearly not right. In order to get the theory to work right, he made the assumption that the energy could only be emitted in discrete amount called **quanta**. Mathematically this is stated as

$$E = n h \nu$$

where n is a positive integer, h is a constant called **Planck's constant** and has a value of $6.626 \times 10^{-34} \text{ J s}$, and ν is the frequency of the emitted radiation.

Later, Einstein picked up on this idea to explain the photoelectric effect, which is the effect where light of certain colors will cause electrons to leave the surface of a metal. Einstein made the statement that the energy of a photon (or a particle of light) is equal to

the frequency of the light times Planck's constant. This allowed some of the information about the photoelectric effect to be better understood.

Up to this point in time, light could be thought of as a wave or as a particle. The way you think about it depends on how you are measuring it. No one thought about particles though until Louis deBroglie's Ph.D. dissertation on treating particles as waves. Niels Bohr picked up on this idea to explain the spectrum of hydrogen.

Atomic spectra

When energy is added to an atom, that atom releases that energy to get back to the lowest energy state. This energy leaves the atom as light of varying wavelengths or "colors." If we take the light that comes from the atom and pass it through a prism or a diffraction grating the light is separated into its component colors.

Bohr used the ideas first proposed by Planck to explain this. First, he proposed a postulate that the energy of the electron in the Hydrogen atom was quantized. The electron can have only specific value for energy or be in specific **energy levels**. These energy levels have the following form

$$E = -\frac{R_H}{n^2}$$

where n is a positive integer. This relation holds only for the Hydrogen atom. Second, he proposed that the electron can change energy only by going from one energy level to another. It cannot have an energy that is between two levels because there is no energy level there. The electron will then return to a lower energy level and give up some energy in the process. This energy is emitted as light. The energy of the emitted photon is the same as the difference in the energy levels. We can calculate the wavelength of the light from this relationship.

$$\begin{aligned}\Delta E &= E_i - E_f = h\nu = \frac{hc}{\lambda} \\ \frac{hc}{\lambda} &= \left(-\frac{R_H}{n_i^2}\right) - \left(-\frac{R_H}{n_f^2}\right) = R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \\ \frac{1}{\lambda} &= \frac{R_H}{hc} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)\end{aligned}$$

This relationship is for the Hydrogen atom only. We can modify it for an ion that looks like the Hydrogen atom (i.e., it has only one electron) by multiplying the right side by Z^2 .

$$\frac{1}{\lambda} = \frac{Z^2 R_H}{hc} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

This relationship can be used to calculate the spectrum of any atom or ion that has only one electron. The equations are known that will allow us to calculate the spectrum of an atom or ion with more than one electron but the problem is so complicated that it cannot be solved exactly, approximations must be made. The equations that describe this situation are the laws and equations of quantum mechanics.

Quantum Mechanics

Quantum mechanics is the field of physics that deals with the energies and motions of sub-microscopic particles. Every particle has associated with it a wavefunction, ψ . This wavefunction will give all of the information you need about the particle. But, it does so as probabilities (technically it's ψ^2 that gives the probability). These probabilities have been verified by experiment. If we calculate the most probable place for an electron to be around an atom we come up with some places that are more likely than others based on the energy of that electron. The calculations from quantum mechanics show us that Bohr was only partially correct. For each energy level, there are 1 or more sublevels. These sublevels are then broken down into orbitals, each of which can hold only two electrons. The number of sublevels in a given energy level is given by the quantum number, n , from Bohr's formula. So, the first energy level has one sublevel, the second energy level has two sublevels, and so on. So we have the following table.

Energy level	Number of Sublevels	Sublevel name	Number of orbitals	Sublevel name	Number of orbitals	Sublevel name	Number of orbitals	Sublevel name	Number of orbitals
1	1	s	1						
2	2	s	1	p	3				
3	3	s	1	p	3	d	5		
4	4	s	1	p	3	d	5	f	7

The orbitals associated with the sublevels have particular shapes. s orbitals are spherical, p orbitals are "dumb-bell" shaped. These shapes represent the volume where we are most likely to find an electron.

It turns out that the quantum mechanical calculations also predict another property of electrons that has been observed. It is called "spin." The electron is not actually spinning. It is merely acting as if it is spinning. The spin can have one of two values, $\pm \frac{1}{2}$

This has implications about the atom that are revealed in the periodic table. The electrons are arranged about the atom in the energy levels and sublevels. These can be seen in the layout of the periodic table. The first energy level has only one sublevel with one orbital. This orbital can hold only two electrons. The s sublevels is also present in every other energy level. This is shown in the periodic table by the first two columns. Every energy level from the second on has a p sublevel which has 3 orbitals. These three orbitals can hold six electrons. This is shown in the table by the last six columns. The d sublevel is present in every energy level from three up. It has 5 orbitals that can hold 10 electrons.

There are 10 columns in the transition metals. The fourth energy level and higher has f sublevels with 7 orbitals holding 14 electrons. The lanthanides and actinides comprise 14 columns in the periodic table.

We can use this information and the periodic table to come up with the **electron configurations** for the elements. This is a way of showing how many electrons are in each energy level and sublevel. Hydrogen has the simplest configuration with $1s^1$. One electron is the first energy level and the s sublevel. Helium is $1s^2$. Two electrons in the first energy level and s sublevel. The electron configurations can be read directly from the periodic table following the **Aufbau principle** or **building-up principle**. This states that the electrons will fill into the atoms in the order specified by the periodic table.

Some electron configurations from the periodic table:

Carbon	$1s^2 2s^2 2p^2$
Silver	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^9$

Note that the 3d comes after the 4s. The first energy level with a d sublevel is the 3rd. So the first d sublevel we come to is the 3d. There is a shorter way of doing this. We can realize that the noble gases are at the end of each period. They all have electron configurations that end in $s^2 p^6$. We can then use the noble gas at the end of the period above the element we are looking at as the “core electrons.” The outermost electrons are the “valence electrons.” Silver then becomes

Silver	$[Kr] 5s^2 4d^9$
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Using the knowledge of the number of orbitals in each sublevel and a couple of guiding rules we can also write **orbital diagrams**. These will show which orbitals the electrons are in and with what spin. The orbital diagram for carbon would look like

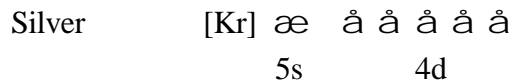
Carbon	\uparrow	\uparrow	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$
	1s	2s	2p		

Here we have 2 electrons in the 1s orbital, 2 electrons in the 2s orbital and one electron in each of 2 of the 3 2p orbitals. This requires the rules. The first rule is the **Pauli Exclusion Principle**. It states that no two electrons in the same orbital can have the same spin. The second rule is **Hund’s Rule**. It states that the lowest energy arrangement of electrons in a sublevel is given by putting electrons in separate orbitals with the same spin before pairing them up.

Silver would look like:

Silver	$[Kr] \uparrow$	\uparrow	\uparrow	\uparrow	\uparrow	\uparrow	\uparrow	\uparrow	\uparrow
		5s	4d						

There are some exceptions to this rule. For instance, silver would actually look like



This happens because of energy considerations. The arrangement above is more stable than that given by the Aufbau principle.

Magnetism and atoms

By magnetism we do not mean ferromagnetism, like in a permanent magnet. This is a much more subtle effect. There are two kinds of magnetism, **paramagnetism** and **diamagnetism**. Paramagnetism arises from the presence of unpaired electrons and results in the atom or molecule being slightly attracted to a magnetic field. Diamagnetism arises when all the electrons are paired and results in the atom or molecule being slightly repelled by a magnetic field or the field doesn't affect it. Most of the elements are paramagnetic. Only the elements with completely filled sublevels will be diamagnetic.

Quantum numbers

For any given electron in an atom there are 4 quantum numbers. We have seen two of them already. The first is the **principal quantum number, n**. It is the number that tells what energy level the electron is in. The second quantum number is the **angular momentum quantum number, l**. It tells us what sublevels the electron is in. The third quantum number is the **magnetic quantum number, m_l**. This tells us what orbital the electron is in. The last quantum number is the **spin quantum number, m_s**. It shows the electrons spin ("up" or "down"). There are numerical relationships between these quantum numbers.

n is any positive integer	$n = 1, 2, 3, 4, \dots, \infty$
l is any integer between 0 and n	$l = 0, 1, 2, \dots, n$
m _l is any integer between l and -l	$m_l = -l, -l+1, \dots, l-1, l$
m _s is one of two values + 1/2 or - 1/2	$m_s = \pm 1/2$

The Pauli exclusion principle can be restated; any two electrons in an atom cannot have the same set of quantum numbers.

The correspondence between the l value and the sublevel is given by:

l	sublevel
0	s
1	p
2	d
3	f

If an electron is in the 4d sublevel its first two quantum numbers are 4 and 2. The last two will depend on the orbital the electron is in and its spin.

Periodic properties

Atomic Radius

As we move across the periodic table the atoms get smaller. This is because the valence electrons feel a stronger “effective” nuclear charge as the atomic number increases in a period. They are pulled more strongly toward the nucleus and the atom gets smaller. As we move down a group the atoms increase in size because the electrons are in higher energy levels and are farther from the nucleus.

Ionization energy

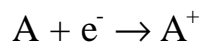
For the reaction



An atom is losing an electron. The ionization energy is the energy needed to remove an electron from an atom. As we move across a period the atom holds the electrons more tightly. This results in more energy being needed to remove the electron from the atom. So ionization energies will increase as we move across a period. As we move down a group the electrons are in higher energy levels. This makes it easier to remove them. The ionization energies will decrease as we move down a group.

Electron affinity energy

For the reaction



$$\Delta H < 0 \text{ (usually)}$$

An atom is gaining an electron. These energies are usually negative. The electron affinity energy is the energy released when an electron is added to an atom. As we move across a period, the electron will release more energy to get into the atom. This is a larger negative number, which means that the electron affinity energy is decreasing. As we move down a group the electron does not have as far to go. This means that there is less energy released. The electron affinity energy increases.