Atomic Structure and Periodicity

Electromagnetic radiation

Electromagnetic radiation is the emission and transmission of energy in the form of electromagnetic waves. Electromagnetic waves travel 3.00×10^8 meters per second, or 186,000 miles per second, in a vacuum. This speed does differ from one medium to another, but not enough to distort our calculations significantly. By convention, we use the symbol c for the speed of electromagnetic waves, or as it is more commonly called, the speed of light. The wavelength of electromagnetic waves is usually given in nanometers (nm).

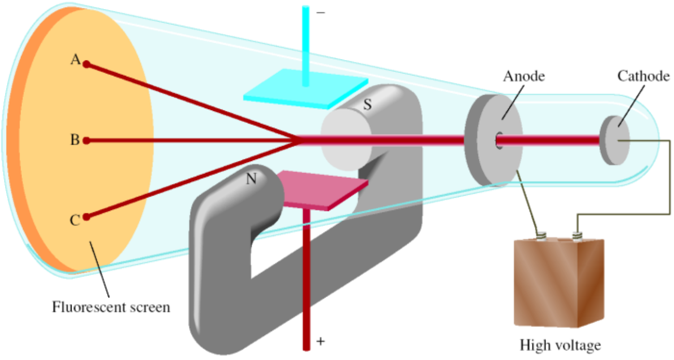


Figure : Cathode Ray Tube

Milican Oil Experiment

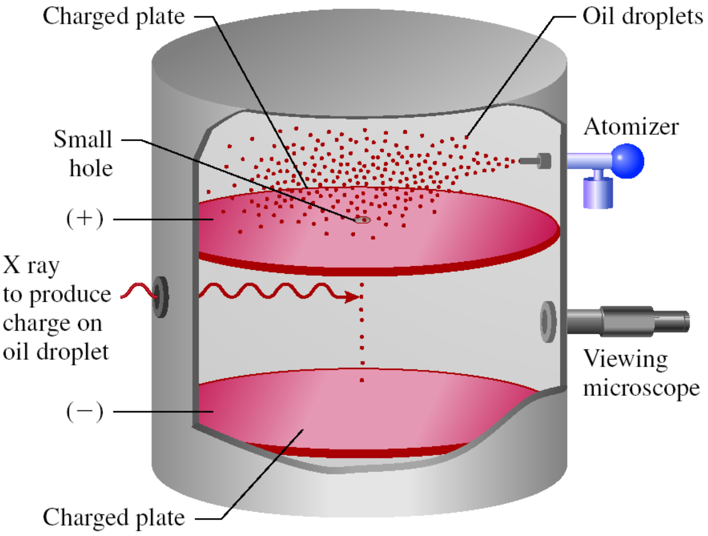
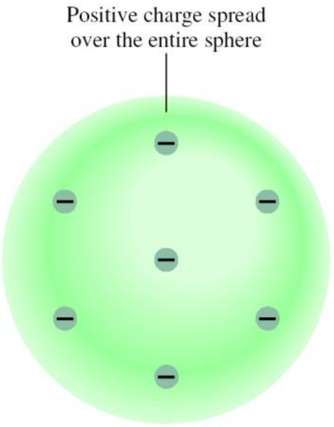


Figure : Schematic indication of Thomson’s Model



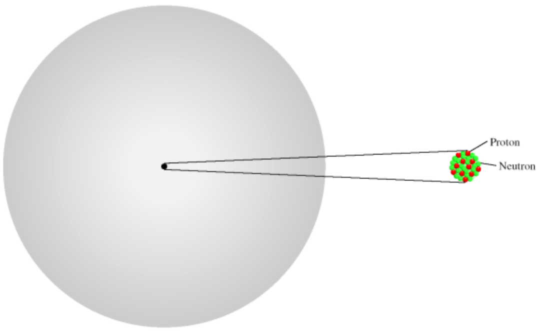
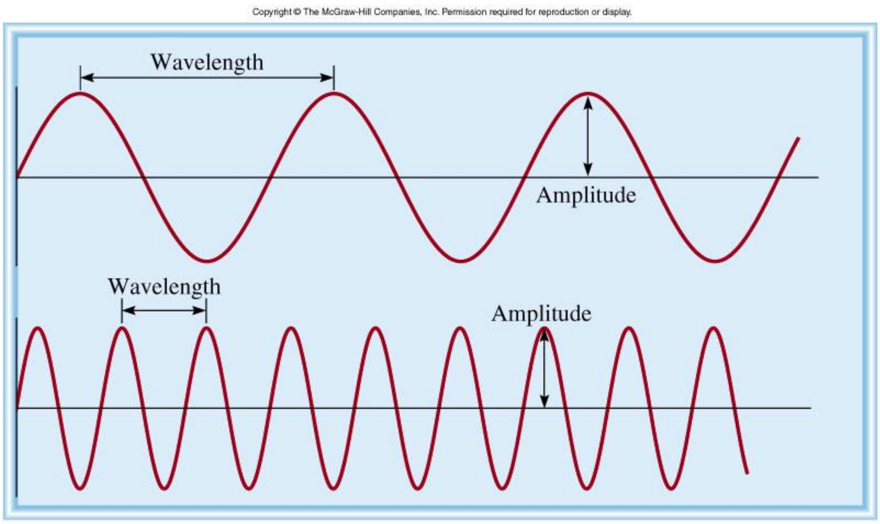


Figure : Schematic expression of Rutherford’s Model of the Atom

Properties of Waves



(b)

Figure : Showing of electromagnetic wave properties

All electromagnetic radiation provide as follow equation

$$\lambda \times \nu = c$$

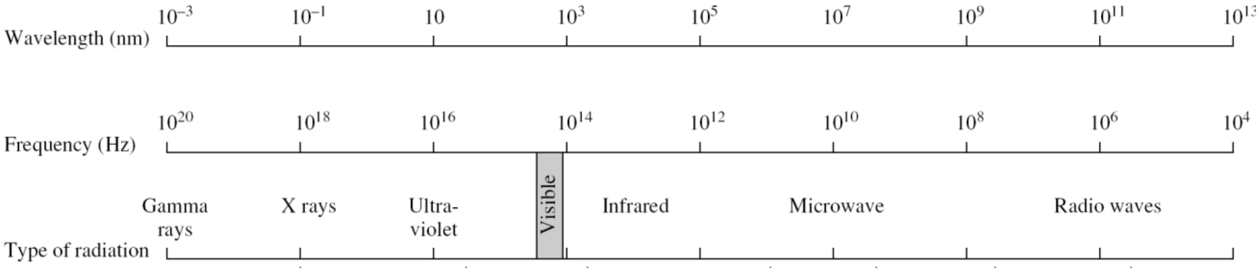


Figure shows various types of electromagnetic radiation, which differ from one another in wavelength and frequency. The long radio waves are emitted by large antennas, such as those used by broadcasting stations. The shorter, visible light waves are produced by the motions of electrons within atoms and molecules. The shortest waves, which also have the highest frequency, are associated with gamma) rays, which result from changes within the nucleus of the atom. As we will see shortly, the higher the frequency, the more energetic the radiation. Thus, ultraviolet radiation, X rays, and gamma rays are high-energy radiation.

Planck gave the name **quantum** to the smallest quantity of energy that can be emitted (or absorbed) in the form of electromagnetic radiation. The energy E of a single quantum of energy is given by equation

$$E = h \times \nu$$

where h is called Planck's constant and ν is the frequency of radiation. The value of Planck's constant is 6.63×10^{-34} J s. According to quantum theory, energy is always emitted in multiples of hn; for example, hn, 2 hn, 3 hn, . . . , but never, for example, 1.67 hn or 4.98 hn. At the time

Planck presented his theory, he could not explain why energies should be fixed or quantized in this manner. Starting with this hypothesis, however, he had no trouble correlating the experimental data for emission by solids over the entire range of wavelengths; they all supported the quantum theory. The idea that energy should be quantized or "bundled" may seem strange, but the concept of quantization has many analogies. For example, an electric charge is also quantized; there can be only whole-number multiples of e, the charge of one electron. Matter itself is quantized because the numbers of electrons, protons, and neutrons and the numbers of atoms in a sample of matter must also be integers.

Emission Spectrum of the Hydrogen Atom

In 1913, not too long after Planck’s and Einstein’s discoveries, a theoretical explanation of the emission spectrum of the hydrogen atom was presented by the Danish physicist Niels Bohr. Bohr’s treatment is very complex and is no longer considered to be correct in all its details. Thus, we will concentrate only on his important assumptions and final results, which do account for the spectral lines.

According to the laws of classical physics, an electron moving in an orbit of a hydrogen atom would experience an acceleration toward the nucleus by radiating away energy in the form of electromagnetic waves. Thus, such an electron would quickly spiral into the nucleus and annihilate itself with the proton. To explain why this does not happen, Bohr postulated that the electron is allowed to occupy only certain orbits of specific energies. In other words, the energies of the electron are quantized. An electron in any of the allowed orbits will not radiate energy and therefore will not

Bohr’s Theory of the Hydrogen Atom

$$E_n = -R_{\mathrm{H}}\left(\frac{1}{n^2}\right)$$

where R_H, the Rydberg constant has the value J. The number n is an integer called the principal quantum number; it has the values n = 1, 2, 3, ...
The negative sign in Equation is an arbitrary convention, signifying that the

energy of the electron in the atom is lower than the energy of a free electron, which is an electron that is infinitely far from the nucleus. The energy of a free electron is arbitrarily assigned a value of zero.

The most negative value, then, is reached when n = 1, which corresponds to the most stable energy state. We call this the **ground state,** or the **ground level,** which refers to the lowest energy state of a system. The stability of the electron diminishes for n = 2, 3, ... Each of these levels is called an **excited state,** or **excited level,** which is higher in energy than the ground state. A hydrogen electron for which n is greater than 1 is said to be in an excited state. The radius of each circular orbit in Bohr’s model depends on n2. Thus, as n increases from 1 to 2 to 3, the orbit radius increases very rapidly. The higher the excited state, the farther away the electron is from the nucleus (and the less tightly it is held by the nucleus).

Bohr’s theory enables us to explain the line spectrum of the hydrogen atom. Radiant energy absorbed by the atom causes the electron to move from a lower-energy state to a higher-energy state. Conversely, radiant energy is emitted when the electron moves from a higher-energy state to a lower-energy state. The quantized movement of the electron from one energy state to another is analogous to the movement of a tennis ball either up or down a set of stairs. The ball can be on any of several steps but never between steps. The journey from a lower step to a higher one is an energy-requiring process, whereas movement from a higher step to a lower step is an energy-releasing process. The quantity of energy involved in either type of change is determined by the distance between the beginning and ending steps. Similarly, the amount of energy needed to move an electron in the Bohr atom depends on the difference in energy levels between the initial and final states.

To apply to the emission process in a hydrogen atom, let us suppose that the electron is initially in an excited state characterized by the principal quantum number ni. During emission, the electron drops to a lower energy state characterized by the principal quantum number nf (the subscripts i and f denote the initial and final states, respectively). This lower energy state may be either a less excited state or the ground state. The difference between the energies of the initial and final states is

$$\Delta E = E_\mathrm{f} - E_\mathrm{i}$$

$$E_\mathrm{f} = -R_\mathrm{H}\left(\frac{1}{n_\mathrm{f}^2}\right)$$

$$\Delta E = R_\mathrm{H}\left(\frac{1}{n_\mathrm{i}^2} - \frac{1}{n_\mathrm{f}^2}\right)$$

Quantum Numbers

In quantum mechanics, three **quantum numbers** are required to describe the distribution of electrons in hydrogen and other atoms. These numbers are derived from the mathematical solution of the Schrödinger equation for the hydrogen atom. They are called the principal quantum number, the angular momentum quantum number, and the magnetic quantum number. These quantum numbers will be used to describe atomic orbitals and to label electrons that reside in them. A fourth quantum number— the spin quantum number—describes the behavior of a specific electron and completes the description of electrons in atoms.

The Principal Quantum Number (n)

The principal quantum number (n) can have integral values 1, 2, 3, and so forth; it corresponds to the quantum number. In a hydrogen atom, the value of n determines the energy of an orbital. As we will see shortly, this is not the case for a many electron atom. The principal quantum number also relates to the average distance of the electron from the nucleus in a particular orbital. The larger n is, the greater the average distance of an electron in the orbital from the nucleus and therefore the larger the orbital.

The Angular Momentum Quantum Number (l)

The angular momentum quantum number (l) tells us the "shape" of the orbitals. The values of l depend on the value of the principal quantum number, n. For a given value of n, l has possible integral values from 0 to (n - 1). If n - 1, there is only one possible value of l; there are two values of l, given by 0 and 1. If n = 3, there are three values of l, given by 0, 1,and 2. Name of orbital**,** s p d f g h.

A collection of orbitals with the same value of n is frequently called a shell. One or more orbitals with the same n and l values are referred to as a subshell. For example, the shell with n = 2 is composed of two subshells, l = 0 and 1). These subshells are called the 2s and 2p subshells where 2 denotes the value of n, and s and p denote the values of l.

The Magnetic Quantum Number (m)

The magnetic quantum number (m) describes the orientation of the orbital in space. Within a subshell, the value of m depends on the value of the angular momentum quantum number.

$$-\ell,\ (-\ell + 1), \ldots 0, \ldots (+\ell - 1),\ +\ell$$

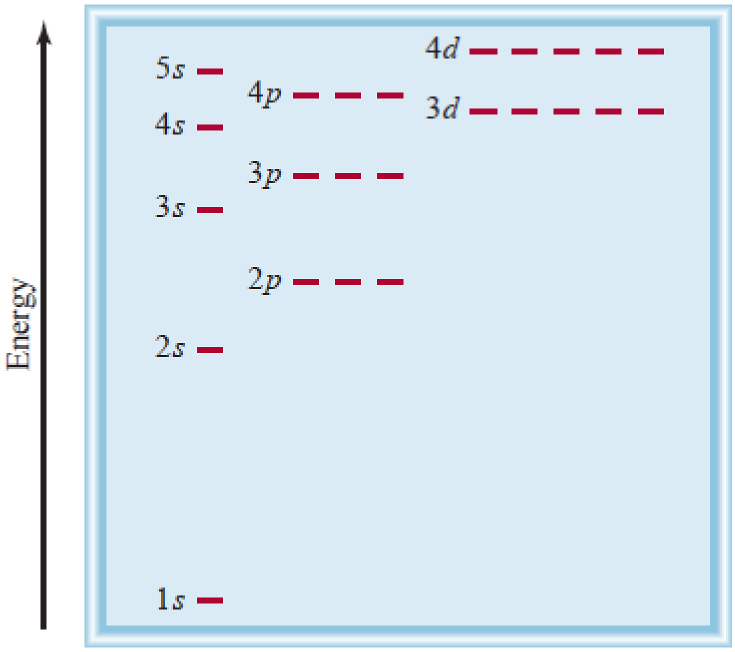
The Electron Spin Quantum Number (ms)

The emission spectra of hydrogen and sodium atoms indicated that lines in the emission spectra could be split by the application of an external magnetic field. The only way physicists could explain these results was to assume that electrons act like tiny magnets. According to electromagnetic theory, a spinning charge generates a magnetic field, and it is this motion that causes an electron to behave like a magnet.

To take the electron spin into account, it is necessary to introduce a fourth quantum number, called the electron spin quantum number (ms), which has a value of or.

Electron Configuration

The four quantum numbers n, l, m and ms enable us to label completely an electron in any orbital in any atom. In a sense, we can regard the set of four quantum numbers as the “address” of an electron in an atom.

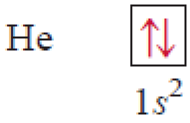


The hydrogen atom is a particularly simple system because it contains only one electron. The electron may reside in the 1s orbital of the ground state, or it may be found in some higher-energy orbital (an excited state). For many-electron atoms, however, we must know the **electron configuration** of the atom, that is, how the electrons are distributed among the various atomic orbitals, in order to understand electronic behavior. We will use the first 10 elements to illustrate the rules for writing electron configurations for atoms in the ground state.

The Pauli Exclusion Principle

For many-electron atoms it is used the **Pauli exclusion principle** to determine electron configurations. This principle states that no two electrons in an atom can have the same four quantum numbers. If two electrons in an atom should have the same n, l, and m values, then they must have different values of ms. In other words, only two electrons may occupy the same atomic orbital, and these electrons must have opposite spins. Consider the helium atom, which has two electrons.

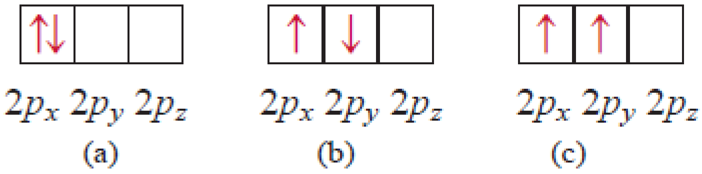
The three possible ways of placing two electrons in the 1s orbital are as follows:

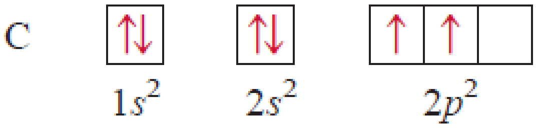


Hund's Rule

The electron configuration of carbon (Z=6) is $1s^2 2s^2 2p^2$. The following are different ways of distributing two electrons among three p orbitals:

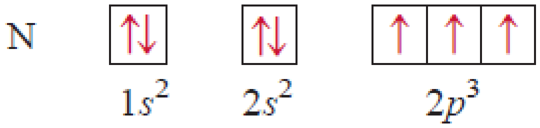
None of the three arrangements violates the Pauli exclusion principle, so we must determine which one will give the greatest stability. The answer is provided by **Hund's rule**, which states that the most stable arrangement of electrons in subshells is the one with the greatest number of parallel spins. The arrangement shown in (c) satisfies this condition. In both (a) and (b) the two spins cancel each other. Thus, the orbital diagram for carbon is

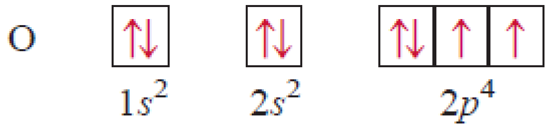




Qualitatively, we can understand why (c) is preferred to (a). In (a), the two electrons are in the same 2px orbital, and their proximity results in a greater mutual repulsion than when they occupy two separate orbitals, say 2px and 2py. The choice of (c) over (b) is more subtle but can be justified on theoretical grounds. The fact that carbon atoms contain two unpaired electrons is in accord with Hund's rule.

The electron configuration of nitrogen (Z = 7) is $1s^2 2s^2 2p^3$:





General Rules for Assigning Electrons to Atomic Orbitals

Based on the preceding examples we can formulate some general rules for determining the maximum number of electrons that can be assigned to the various subshells and orbitals for a given value of n:

1. Each shell or principal level of quantum number n contains n subshells. For example, if n = 2, then there are two subshells (two values of l) of angular momentum quantum numbers 0 and 1.

2. No more than two electrons can be placed in each orbital. Therefore, the maximum number of electrons is simply twice the number of orbitals that are employed.

3. A quick way to determine the maximum number of electrons that an atom can have in a principal level n is to use the formula $2n^2$.