

**Quantum Mechanics** was developed to account for the behavior of light and atoms. Classical mechanics works very well for macroscopic particles (such as billiard balls, cars, etc.) but fails when applied to atomic particles.

**Composition of Atoms:** The atom (atomic radius  $\approx 1\text{\AA} = 1 \times 10^{-10}$  m) consists of a small dense nucleus containing protons and neutrons (nuclear radius =  $10^{-13}$  to  $10^{-12}$  m) surrounded by electrons.

One proton has one unit of positive charge (+1) The mass of a proton =  $1.67 \times 10^{-27}$  kg

One electron has one unit of negative charge (-1) The mass of an electron =  $9.1 \times 10^{-31}$  kg

The neutron has no charge.

The magnitude of positive charge = the magnitude of negative charge =  $1.602 \times 10^{-19}$  C

In a neutral atom: the number of protons = the number of electrons.

The mass of a proton  $\approx$  the mass of a neutron  $\approx$  2000 times the mass of an electron.

The number of protons in an atom =  $Z$  = atomic number.  $Z$  determines the element and its position in the periodic table.

Generally, as  $Z$  increases the atomic mass increases (some exceptions, e.g. Ar  $\rightarrow$  K, why?)

**Chemical properties of atoms and molecules** are determined by their electronic structure (i.e. the arrangement of the electrons in the atom). Thus, we need to understand electron motion and energy.

### The Rutherford Atom.

Because the mass of protons and neutrons are much greater than the mass of electrons, the nucleus essentially remains stationary relative to the motion of the electrons. Rutherford's "planetary" model of the atom, where the electron orbits the nucleus is not predicted to be stable according to classical electromagnetic theory, which states that an accelerated charged particle radiates energy in the form of electromagnetic waves (light).

In Rutherford's atom, the electron orbiting the nucleus is accelerated (because the velocity vector keeps changing) and, therefore, the electron should lose energy continuously and spiral into the nucleus. This implies that this model of the atom is unstable. Quantum mechanics was developed in the early 1900's to explain the stability of the atom as well as chemical bonding.

**The Nature of light and matter.** Classically light consists of oscillating electric and magnetic fields (waves). However, Planck and Einstein showed that light also consists of discrete particles, photons, of energy  $h\nu$ .

$$E_{\text{photon}} = h\nu = 1 \text{ quantum of energy}$$

$$E = h\nu, \nu = c/\lambda, E = hc/\lambda, \nu = \text{frequency}, \lambda = \text{wavelength}, c = \text{speed of light} = 2.99 \times 10^8 \text{ m/sec}, 1 \text{ J} = 1 \text{ kg m}^2/\text{sec}^2$$

Thus, light is dual in nature: both particle and wave. Similarly, matter is dual in nature: both particle and wave. For billiard balls the wavelength associated with the balls does not effect their behavior. However, for atomic particles, such as electrons, the associated wavelengths are very important. By applying wave mechanics (quantum mechanics) we can understand the nature of atoms and chemical bonding.

**The Bohr Atom** (A model to account for the hydrogen atom emission spectrum).

By assuming quantization of angular momentum of the electron in the hydrogen atom, the energy levels calculated are consistent with the hydrogen atom emission spectrum. In this model the electron orbits the nucleus with angular momentum,  $m_e v r$ . This implies that both the position and the angular momentum of the electron can be determined at a given time. However, as shown below, there is a fundamental limit to how precisely we can determine both the position and the angular momentum of the electron. Even so, the energy levels predicted by the Bohr model are consistent with the observed emission spectrum for the hydrogen atom and for all one-electron atomic ions (e.g.  $\text{He}^+$ ,  $\text{Li}^{2+}$ , etc.)

$$E = - (2.18 \times 10^{-18} \text{ J}) \frac{Z^2}{n^2} \quad \text{or} \quad \Delta E = - (2.18 \times 10^{-18} \text{ J}) \left( \frac{Z^2}{n_{\text{final}}^2} - \frac{Z^2}{n_{\text{initial}}^2} \right)$$

where  $n = 1, 2, 3, 4, \dots, \infty$  and  $Z$  = atomic number = number of protons

$\Delta E < 0 \Rightarrow$  emission of a photon  $\Delta E > 0 \Rightarrow$  absorption of a photon  $|\Delta E| = E_{\text{photon}}$

For  $n = 1$ , the atom is in its ground electronic state (the lowest energy state). For  $n = 2, 3, 4, \dots$  the atom is in an excited electronic state (the electron has excess energy and emits a quantum of energy (a photon) in making a transition to a lower energy state).

It takes energy to remove an electron from an atom because the attractive forces between the positively charged nucleus and negatively charged electron must be overcome.

The **ionization energy** =  $IE$  = the minimum energy required to remove an electron (e.g. For  $\text{H} \rightarrow \text{H}^+ + e^-$ , it is the energy required go from  $n = 1$  (the ground state of the atom) to  $n = \infty$  (electron unbound)).

**Shortcomings of the Bohr theory:**

- 1) Not capable of predicting energy levels and spectra for atoms and ions with more than one electron.
- 2) Can not account for chemical bonds in molecules.

## **Quantum Mechanics** (Wave Mechanics) DeBroglie, Heisenberg, Schrodinger, and others.

Light and particles are dual in nature: both particle and wave

Focus on wave properties of electron:

$$\lambda = h/mv \quad (\text{DeBroglie's wave equation})$$

$$\lambda = h/p \quad \text{or} \quad p = h/\lambda \quad \text{where } p = mv = \text{momentum}$$

**Macroscopic Particles:** The position and velocity (or momentum) describe the behavior of macroscopic particles.

**Atomic Particles:** There is a fundamental limit to how precisely we can know both the position and the momentum of a particle at a given time. This limit is imposed by the measurement of the position and momentum of a microscopic particle, because the measurement changes the particle's trajectory.

For example: The position of an electron can be determined by scattering photons off the electron. However, this involves a collision between the photon and the electron. The photon (of wavelength,  $\lambda$ , and momentum,  $h/\lambda$ ) will transfer some unknown fraction of momentum to the electron in the photon-electron collision. Thus, locating the position of the electron to within a distance,  $\Delta x \approx \pm \lambda$ , produces an uncertainty in its momentum  $\Delta p \approx h/\lambda$ . Thus,  $\Delta x \Delta p \approx \lambda h/\lambda$  or  $\Delta x \Delta p \approx h$ .

More rigorously:  $\Delta x \Delta p \geq h/4\pi$  This is the **Heisenberg Uncertainty Principle**, which indicates that the more precisely we know a particle's position (when  $\Delta x$  is small) the less precisely we can know its momentum (when  $\Delta p$  is large), and vice versa (when  $\Delta x$  is large,  $\Delta p$  must be small). An uncertainty in momentum corresponds to an uncertainty in velocity since the mass,  $m$ , is constant and  $\Delta p = m\Delta v$ . This means that we cannot simultaneously be certain of an electron's position and velocity.

**DeBroglie's wave equation.**  $\lambda = h/p$ , is the basis for predicting the behavior of freely moving particles. Schrödinger generalized this expression so as to apply it to bound particles such as electrons in atoms. For the motion of one particle in the x-direction, the Schrödinger wave equation is:

$$-\frac{\hbar^2}{8\pi^2m} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x)$$

where  $m$  = the mass of particle,  $V(x)$  = the potential energy as a function of the particle's position.  $\Psi(x)$  = the wave function and  $E$  = the total energy.  $\Psi(x)$  and  $E$  are determined by solving the Schrödinger equation.  $d^2\Psi(x)/dx^2$  = the rate of change of  $\Psi(x)/dx$  which equals the rate of change of  $\Psi(x)$ .

### **The Schrodinger wave equation applied to the hydrogen atom.**

The Schrödinger wave equation can not be solved unless the energy  $E$  takes on certain values which are related by integers. Thus, quantized energy and quantum numbers are an automatic consequence of the Schrödinger equation.

**What is  $\Psi$ ?**  $\Psi(x,y,z)$  is the amplitude of the wave at the point in space defined by the set of coordinates  $(x,y,z)$ . The amplitude can be positive or negative, i.e.  $\Psi$  can be positive or negative. The points at which the wave function passes through zero and changes sign are called nodes.

The absolute value of  $\Psi$  squared,  $|\Psi|^2$  = the probability of finding a particle in a given place (probability density). In other words,  $\Psi^2(x,y,z)\Delta x\Delta y\Delta z$  is the probability that the particle will be found in a small volume  $\Delta x\Delta y\Delta z$  about the point  $(x,y,z)$ . In the hydrogen atom  $\Psi^2(x,y,z)\Delta x\Delta y\Delta z$  is the probability of finding the electron in a given space outside the nucleus.

**The Hydrogen Atom.** In order to understand the periodicity of atomic properties and the nature of chemical bonding, it is necessary to thoroughly understand the behavior of the electron in the hydrogen atom.

**Three quantum numbers**,  $n$ ,  $l$ ,  $m$ , are an automatic consequence of mathematics. The spin quantum number,  $s$ , was determined experimentally. There are a total of four quantum numbers associated with each electron.

$$n = 1, 2, 3, \dots, \infty \quad n = \text{principal quantum number}$$

The principle quantum number  $n$  is related to size and energy of the orbital. As  $n$  increases, the orbital becomes larger and the electron spends more time farther from the nucleus. Thus, as the value of  $n$  increases the energy of the electron increases.

$$l = 0, 1, 2, 3, \dots, \leq n - 1 \quad l = \text{angular momentum quantum number}$$

The amount of angular momentum or kinetic energy of angular motion is limited by the total energy of the electron => restriction on  $l$  according to the value of  $n$ . The dependence of the wave function on  $l$  determines the shapes of the atomic orbitals.

$$m = 0, \pm 1, \pm 2, \pm 3, \dots, \pm l \quad m = \text{magnetic quantum number } (m_l \text{ in your text})$$

The angular momentum of the electron induces a magnetic field. The observed magnetism is determined by the value of  $m$  and is limited by the angular momentum quantum number  $l$ .

$$s = \pm 1/2 \quad s = \text{spin quantum number } (m_s \text{ in your text})$$

The electron itself has an intrinsic magnetic property. A charged particle spinning about its own axis behaves like a small magnet. Therefore, the electron is said to have spin associated with it.

### Possible combinations of quantum numbers:

Lowest energy state:  $n = 1, l = 0, m = 0, s = \pm 1/2$  Thus, there are two ways for the hydrogen atom to be in its ground state:  $n = 1, l = 0, m = 0, s = + 1/2$  and  $n = 1, l = 0, m = 0, s = - 1/2$

Other combinations of quantum numbers lead to excited electronic states of the hydrogen atom.

If the electron is excited to the energy corresponding to  $n = 2$  then  $l = 0$  or  $l = 1$ . For  $n = 2$  and  $l = 0, m = 0$  and  $s = \pm 1/2$ . For  $n = 2$  and  $l = 1, m = -1, 0, +1$  and  $s = \pm 1/2$ . Thus, there are 8 ways for the electron to be in the H atom in the  $n = 2$  state.

The total picture of the probability of finding an electron at various points in space is called an orbital. Orbitals are classified according to the values of  $n$  and  $l$  associated with them. The larger the value of  $n$ , the larger the orbital. To avoid confusion by having two numbers in sequence, the numerical values of  $l$  are replaced by letters.

<u>Letter designation (orbital)</u>		
$l = 0$	s	electrons in orbitals with $l = 0$ are called s-electrons
$l = 1$	p	p-electrons
$l = 2$	d	d-electrons
$l = 3$	f	f-electrons
$l = 4$	g	g-electrons etc.

For the ground state hydrogen atom ( $n = 1, l = 0$ ) we have a 1s electron, that is, the electron moves in a 1s-orbital.

Possible combinations of quantum numbers and the orbitals are summarized as follows:

$n$	$l$	orbital	$m$	$s$	Number of Combinations
1	0	1s	0	$\pm 1/2$	2
2	0	2s	0	$\pm 1/2$	2
2	1	2p	+1, 0, -1	$\pm 1/2$	6
3	0	3s	0	$\pm 1/2$	2
3	1	3p	+1, 0, -1	$\pm 1/2$	6
3	2	3d	+2, +1, 0, -1, -2	$\pm 1/2$	10
4	0	4s	0	$\pm 1/2$	2
4	1	4p	+1, 0, -1	$\pm 1/2$	6
4	2	4d	+2, +1, 0, -1, -2	$\pm 1/2$	10
4	3	4f	+3, +2, +1, 0, -1, -2, -3	$\pm 1/2$	14

Each set of quantum numbers is associated with a different type of electronic motion.

**Summary of the hydrogen atom:** In the quantum mechanical model the electron is described as a wave. Solving the Schrödinger equation leads to a series of electronic wave functions (orbitals) that describe the possible energies and spatial distributions available to the electron. The square of the wave function,  $|\Psi|^2$ , represents the probability distribution of the electron in that orbital. This approach allows us to picture orbitals in terms of probability distributions, or electron density maps. The size of an orbital is arbitrarily defined as the surface that contains 90% of the total electron probability. The hydrogen atom has many types of orbitals. In the ground state the single electron resides in the 1s orbital. The electron can be excited to higher-energy orbitals if the atom absorbs energy.

The shapes of the orbitals are very important in chemical bonding, both in the energy of the bond formed and the structure (geometry) of the molecule. See Figs. 12.18 – 12.22 for the shapes of the s, p, d, and f orbitals, pg. 542 – 544 text.

**Atoms with more than one electron.** The Schrodinger equation can be solved exactly for the hydrogen atom. For many electron atoms the Schrodinger equation can not be solved exactly. However, we can use the hydrogen atom orbitals as a template. The hydrogen atom has only one electron and the orbitals with the same principle quantum number are degenerate (they have the same energy). For many electron atoms the orbital energies with the same principle quantum number do not necessarily have the same energy due to electron-electron repulsion and relative electron penetration of the various orbitals. For example, in many electron atoms the 2s orbital fills before the 2p orbital because the 2s orbital is lower in energy than the 2p orbital. Similarly, the 4s orbital fills before the 3d orbital because the 4s orbital is lower in energy than the 3d orbital. As a result, the electron configuration for potassium is  $[\text{Ar}]4s^1$  not  $[\text{Ar}]3d^1$ . The 4s and 3d orbitals are close in energy, however, as seen in the valence electron configuration for the transition metals, Cr  $4s^1 3d^5$  and Cu  $4s^1 3d^{10}$ .

**Pauli exclusion principle:** In a given atom no two electrons can have the same set of four quantum numbers ( $n, l, m$ , and  $s$ ). Since electrons in the same orbital have the same values of  $n, l$ , and  $m$ , this postulate requires that they have different values of  $s$ . Because only two values of  $s$  are allowed it implies that an orbital can hold only two electrons, and they must have opposite spin.

**Hund's rule:** The lowest-energy configuration for an atom is the one having a maximum number of unpaired electrons in a particular set of degenerate orbitals allowed by the Pauli exclusion principle.