# 1.3: ELECTRONIC STRUCTURE (REVIEW)

The primary skills needed are the ability to determine the electron configurations of elements following the concepts of "aufbau" or "build up", Hund's Rule, and the Pauli Exclusion Principle, as well as visualizing the orbitals, subshells, and shells spatially and energetically. Converting electron configurations to orbital diagrams is a useful skill as we transition to organic chemistry. These skills are practiced in the next section.

## THE WAVE NATURE OF LIGHT

A wave is a periodic oscillation by which energy is transmitted through space. All waves are periodic, repeating regularly in both space and time. Waves are characterized by several interrelated properties.

- **Electronic structure**: arrangement of electrons in atoms
- **Electromagnetic radiation**: aka **radiant energy**; form of energy that has wave characteristics and carries energy through space. *All types of electromagnetic radiation move through a vacuum at a speed of 3.00 X $10^8$ m/s (speed of light).*
- **Wavelength**: the distance between identical points on successive waves
- **Frequency**: the number of complete wavelengths that pass a given point in 1s

$$\nu\lambda = c \tag{1.3.1}$$

where $\nu$ = frequency, $\lambda$= wavelength, and $c$ = speed of light

Wavelength is expressed in units of length.

- **Electromagnetic spectrum**: various types of electromagnetic radiations arranged in order of increasing wavelength.

Frequency is expressed in Hertz (Hz), also denoted by $s^{-1}$ or /s

Quantum Effects and Photons

- **Quantum**: smallest quantity of energy that can be emitted or absorbed as electromagnetic radiation

$$E = hv \tag{1.3.2}$$

where $E$ = energy, $h$ = Planck's constant, $\nu$ = frequency

*Planck's constant = 6.63 X $10^{-34}$ J/s*

According to Planck's theory, energy is always emitted or absorbed in whole-number multiples of *hv*, for example, *hv, 2hv, 3hv,* and so forth. We say that the allowed energies are *quantized* (that is, their values are restricted to certain quantities).

## QUANTIZED ENERGY AND PHOTONS

Blackbody radiation is the radiation emitted by hot objects and could not be explained with classical physics. Max Planck postulated that energy was quantized and may be emitted or absorbed only in integral multiples of a small unit of energy, known as a quantum. The energy of a quantum is proportional to the frequency of the radiation; the proportionality constant h is a fundamental constant (Planck's constant). Albert Einstein used the quantization of energy to explain the photoelectric effect

- The photoelectric effect: when photons of sufficiently high energy strike a metal surface, electrons are emitted from the metal. The emitted electrons are drawn toward the other electrode, which is a positive terminal. As a result, current flows in a circuit.
- **Photon**: smallest increment (a *quantum*) of radiant energy; a photon of light with frequency v has an energy equal to *hv*.
- When a photon strikes the metal, its energy is transferred to an electron in the metal. A certain amount of energy is required for the electron to overcome the attractive forces that hold it within the metal. If the photons have less energy that this energy threshold, the electrons cannot escape from the metal surface. If a photon has sufficient energy, an electron is emitted. If the photon has more energy than necessary, the excess appears as kinetic energy of the emitted electron.

## LINE SPECTRA AND THE BOHR MODEL

There is an intimate connection between the atomic structure of an atom and its spectral characteristics. Most light is polychromatic and contains light of many wavelengths. Light that has only a single wavelength is monochromatic and is produced by devices called lasers,

which use transitions between two atomic energy levels to produce light in a very narrow range of wavelengths. Atoms can also absorb light of certain energies, resulting in a transition from the ground state or a lower-energy e

### Line Spectra

Radiation composed of a single wavelength is said to be *monochromatic*.

- **Spectrum**: distribution among various wavelengths of the radiant energy emitted or absorbed by an object
- **Continuous spectrum**: rainbow of colors, containing light of all wavelengths. *Not all radiation sources produce a continuous spectrum*
- **Line spectrum**: spectrum containing radiation of only specific wavelengths

$$v = C \left( \frac{1}{2^2} - \frac{1}{n^2} \right) \tag{1.3.3}$$

with $n$ = 3, 4, 5, 6, and $C = 3.29 \times 10^{15}\, s^{-1}$ (constant)

### Bohr's Model

Electrons in a permitted orbit have a specific energy and are said to be in an "allowed" energy state. An electron in an allowed energy state will not radiate energy and therefore will not spiral into the nucleus.

$$E_n = -R_H \frac{1}{n^2} \tag{1.3.4}$$

- $R_H$ = Rydberg constant: 2.18 X $10^{-18}$ J
- $n$ = principal quantum number, corresponds to the different allowed orbits for the electron

*All energies given by this equation will be negative. The lower (more negative) the energy is, the more stable the atom is. The lowest energy state is that for which n=1.*

- **Ground state:** lowest energy state of an atom, $n = 1$
- **Excited state:** when the electron is in higher energy orbit (less negative), n=2 or higher

*If n becomes infinitely large (∞), the electron is completely separated from the nucleus:*

$$E_\infty = \left( -2.18 \times 10^{-18}\, J \right) \left( \frac{1}{\infty^2} \right) = 0 \tag{1.3.5}$$

*Thus, the state in which the electron is removed from the nucleus is the reference, or zero-energy, state of the hydrogen atom. It is important to remember that this zero-energy state is higher in energy than the states with negative energies*

Electrons can change from one energy state to another by absorbing or emitting radiant energy. Radiant energy must be absorbed for an electron to move to a higher energy state, but is emitted when the electron moves to a lower energy state. .

$$\Delta E = E_f - E_i \tag{1.3.6}$$

- If $n_f > n_i$, then ΔE is positive, radiant energy is absorbed
- If $n_f < n_i$, then ΔE is negative, radiant energy is emitted

## THE WAVE BEHAVIOR OF MATTER

An electron possesses both particle and wave properties. Louis de Broglie showed that the wavelength of a particle is equal to Planck's constant divided by the mass times the velocity of the particle. The electron in Bohr's circular orbits could thus be described as a standing wave, one that does not move through space. Werner Heisenberg's uncertainty principle states that it is impossible to precisely describe both the location and the speed of particles that exhibit wavelike behavior.

- **Momentum**: the product of the mass, *m*, and the velocity, *v*, of a particle
- **Matter waves**: term used to describe the wave characteristics of a particle

$$\lambda = \frac{h}{mv} \tag{1.3.7}$$

where $\lambda$ is the wavelength, $h$ is Planck's constant, $m$ is the particle mass, and $v$ is the velocity

The Uncertainty Principle

- **Uncertainty principle**: theory first put forth by Heisenberg, states that is it impossible to determine both the exact momentum of the electron and its exact location.

## QUANTUM MECHANICS AND ATOMIC ORBITALS

There is a relationship between the motions of electrons in atoms and molecules and their energies that is described by quantum mechanics. Because of wave–particle duality, scientists must deal with the probability of an electron being at a particular point in space. To do so required the development of quantum mechanics, which uses wavefunctions to describe the mathematical relationship between the motion of electrons in atoms and molecules and their energies.

- **Wave functions**: represented by $\psi$, square of wave function, $\psi^2$, provides information about an electron's location when it is in an allowed energy state.
- **Probability density**: represented by $\psi^2$, value that represents the probability that an electron will be found at a given point in space
- **Electron density**: the probability of finding and electron at any particular point in an atom. Equals $\psi^2$.

Orbitals and Quantum Numbers

-**Orbital**: allowed energy state of an electron in the quantum-mechanical model of the atom; also used to describe the spatial distribution of an electron. Defined by the value of 3 quantum numbers; *n, l, and $m_l$.*

| Value of l | 0 | 1 | 2 | 3 |
|---|---|---|---|---|
| Letter used | s | p | d | f |

1. The principal quantum number, *n*, can have integral values of 1, 2, 3 and so forth. As *n* increases, the orbital becomes larger; the electron has a higher energy and is farther away from the nucleus.
2. The second quantum number, *l*, can have integral values from 0 to $n-1$ for each value of *n*. This quantum number defines the shape of the orbital. Generally designated by the letters *s, p, d,* and *f*. These correspond to values ranging from 0 to 3.
3. The magnetic quantum number, $m_l$, can have integral values between *l* and –*l*, including zero. This quantum number describes the orientation of the orbital in space.

**Electron shell**: collection of orbitals with the same value of *n*

**Subshell**: one or more orbitals with the same set of *n* and *l* values

1. Each shell is divided into the number of subshells equal to the principal quantum number, *n*, for that shell. The first shell consists of only the 1s subshell; the second shell consists of two subshells, 2s and 2p; the third of three subshell, 3s, 3p and 3d, and so forth.
2. Each subshell is divided into orbitals. Each *s* subshell consists of one orbital; each *p* subshell of three orbitals, each *d* subshell of five, and each *f* subshell of seven orbitals.

## 3D REPRESENTATION OF ORBITALS

Orbitals with l = 0 are s orbitals and are spherically symmetrical, with the greatest probability of finding the electron occurring at the nucleus. Orbitals with values of n > 1 and l = 0 contain one or more nodes. Orbitals with l = 1 are p orbitals and contain a nodal plane that includes the nucleus, giving rise to a dumbbell shape. Orbitals with l = 2 are d orbitals and have more complex shapes with at least two nodal surfaces. l = 3 orbitals are f orbitals, which are still more complex.

**The s Orbitals:** 1s orbital: most stable, spherically symmetric, figure indicates that the probability decreases as we move away from the nucleus. ALL *s* ORBITALS ARE SPHERICALLY SYMMETRIC.

- **Nodal surfaces (nodes)**: intermediate regions where $\psi^2$ goes to zero. The number of nodes increases with increasing value for the principal quantum number, *n*.

**The *p* Orbitals:** Electron density is concentrated on two sides of the nucleus, separated by a node at the nucleus. The orbitals of a given subshell have the same size and shape but differ from each other in orientation. The axis along which the orbital is oriented is not related to $m_l$.

## MANY-ELECTRON ATOMS

In addition to the three quantum numbers $(n, l, m_l)$ dictated by quantum mechanics, a fourth quantum number is required to explain certain properties of atoms. This is the electron spin quantum number $(m_s)$, which can have values of +½ or −½ for any electron, corresponding to the two possible orientations of an electron in a magnetic field. This is important for chemistry because the Pauli exclusion principle implies that no orbital can contain more than two electrons (with opposite spin).

Although the shapes of the orbitals for many-electron atoms are the same as those for hydrogen, the presence of more than one electron greatly changes the energies of the orbitals. In hydrogen, the energy of an orbital depends only on its principal quantum number, however, in many-electron atoms, electron-electron repulsions cause different subshells to be at different energies

**Effective Nuclear Charge**

- *Effective nuclear charge*: net positive charge attracting electrons

$$Z_{eff} = Z - S \tag{1.3.8}$$

where $Z_{eff}$ is the effective nuclear charge, $Z$ is the number of protons in the nucleus, and $S$ is the average number of electrons between the nucleus and electron in question.

- *Screening effect*: effect of inner electrons in decreasing the nuclear charge experienced by outer electrons

**Energies of Orbitals**

The extent to which an electron will be screened by the other electrons depends on its electron distribution as we move outward from the nucleus.

- *In a many-electron atom, for a given value of n, $Z_{eff}$ decreases with increasing value of l.*
- *In a many-electron atom, for a given value of n, the energy of an orbital increases with increasing value of l.*

**Degenerate**: orbitals that have the same energy

Electron Spin and the Pauli Exclusion Principle

- **Electron spin**: property of the electron that makes it behave as though it were a tiny magnet. The electron behaves as if it were spinning on its axis; electron spin is quantized.
- **Electron spin quantum number**: denoted as $m_s$. It can only have two possible values, +½ and –½, which we can interpret as indicating the two opposite directions in which the electron can spin.
- **Pauli exclusion principle**: states that no two electrons in an atom can have the same set of four quantum numbers $n$, $l$, $m_l$, $m_s$. This means that if we wish to put two electrons in an orbital and satisfy Pauli's exclusion principle, our only choice is to assign different $m_s$ values to the electrons. Because there are only two values, *we can conclude that an orbital can hold a maximum of two electrons and they must have opposite spins*.

## ELECTRON CONFIGURATIONS

Based on the Pauli principle and a knowledge of orbital energies obtained using hydrogen-like orbitals, it is possible to construct the periodic table by filling up the available orbitals beginning with the lowest-energy orbitals (the aufbau principle), which gives rise to a particular arrangement of electrons for each element (its electron configuration). Hund's rule says that the lowest-energy arrangement of electrons is the one that places them in degenerate orbitals with parallel spins.

- **Electron configuration**: the way in which the electrons are distributed among the various orbitals. The most stable, or ground, electron configuration of an atom is that in which the electrons are in the lowest possible energy level
- **Orbital diagram**: representation of electron configuration in which each orbital is represented by a box and each electron by a half-arrow. A half-arrow pointing upward represents an electron with positive spin; one pointing downward represents an electron with a negative spin.

Writing Electron Configurations

- **Hund's rule**: rule stating that electrons occupy degenerate orbitals in such a way as to maximize the number of electrons with the same spin. In other words, each orbital has one electron placed in it before paring of electron in orbitals occurs. Note that this rule applies to orbitals that are *degenerate*, which means that they have the same energy.
- **Valence electrons**: electrons in the outer shells
- **Core electrons**: electrons in the inner shells
- **Transition elements**: aka **Transition metals**; elements of the *d* orbitals
- **Lanthanide elements**: aka **Rare-earth elements**; 14 elements of the 4f orbitals, # 58-71
- **Actinide elements**: 14 elements of 5f orbitals, # 90-103. Most are not found in nature.

## ELECTRON CONFIGURATIONS AND THE PERIODIC TABLE

The arrangement of atoms in the periodic table results in blocks corresponding to filling of the ns, np, nd, and nf orbitals to produce the distinctive chemical properties of the elements in the s block, p block, d block, and f block, respectively.

- **Main group elements**: aka **Representatives**; *s* and *p* block elements
- **F-block metals**: 28 elements located below the table, *f* block elements

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