

Chapter 6. Electronic Structure of Atoms

Common Student Misconceptions

This is often students' first glimpse at the realm of quantum theory. They need to understand that the model has been built up to rationalize experimental data. They also need to know that elements of one theory are maintained in the subsequent theory.

Using the unit s^{-1} for frequency makes the units cancel more easily.

Some students will have difficulty in converting between angstroms, nanometers, etc.

Chapter Outline

6.1 The Wave Nature of Light

The electronic structure of an atom refers to the arrangement of electrons.

Visible light is a form of **electromagnetic radiation**, or *radiant energy*.

Radiation carries energy through space.

Electromagnetic radiation is characterized by its wave nature.

All waves have a characteristic **wavelength**, λ (lambda), and amplitude, A .

The **frequency**, ν (nu), of a wave is the number of cycles that pass a point in one second.

The units of ν are Hertz ($1 \text{ Hz} = 1 \text{ s}^{-1}$).

The speed of a wave is given by its frequency multiplied by its wavelength.

For light, speed is $c = \lambda \nu$.

Electromagnetic radiation moves through a vacuum with a speed of $3.00 \times 10^8 \text{ m/s}$.

Electromagnetic waves have characteristic wavelengths and frequencies.

The *electromagnetic spectrum* is a display of the various types of electromagnetic radiation arranged in order of increasing wavelength.

Example: visible radiation has wavelengths between 400 nm (violet) and 750 nm (red).

Sample Problem

1. What is the wavelength of light (in nm) that has a frequency of $3.22 \times 10^{14} \text{ Hz}$? (answer 932 nm)

6.2 Quantized Energy and Photons

Some phenomena cannot be explained using a wave model of light.

Blackbody radiation is the emission of light from hot objects.

The *photoelectric effect* is the emission of electrons from metal surfaces on which light shines.

Emission spectra are the emissions of light from electronically excited gas atoms.

Hot Objects and the Quantization of Energy

Heated solids emit radiation (blackbody radiation)

The wavelength distribution depends on the temperature (i.e., "red hot" objects are cooler than "white hot" objects).

Planck investigated black body radiation.

He proposed that energy can only be absorbed or released from atoms in certain amounts.

These amounts are called quanta.

A **quantum** is the smallest amount of energy that can be emitted or absorbed as electromagnetic radiation.

The relationship between energy and frequency is:

$$E = h\nu$$

where h is **Planck's constant** ($6.626 \times 10^{-34} \text{ J}\cdot\text{s}$).

To understand quantization, consider the notes produced by a violin (continuous) and a piano (quantized).

A violin can produce any note when the fingers are placed at an appropriate spot on the bridge.

A piano can only produce notes corresponding to the keys on the keyboard.

The Photoelectric Effect and Photons

The **photoelectric effect** provides evidence for the particle nature of light.

It also provides evidence for quantization.

Einstein assumed that light traveled in energy packets called **photons**.

The energy of one photon is $E = h\nu$.

Light shining on the surface of a metal can cause electrons to be ejected from the metal.

The electrons will only be ejected if the photons have sufficient energy (*work function*):

Below the threshold frequency no electrons are ejected.

Above the threshold frequency, the excess energy appears as the kinetic energy of the ejected electrons.

Light has wave-like AND particle-like properties.

Sample Problem

2. How much energy is in a mole of red photons which have wavelength of 725 nm? (answer 165 kJ)

6.3 Line Spectra and the Bohr Model

Line Spectra

Radiation composed of only one wavelength is called *monochromatic*.

Radiation that spans a whole array of different wavelengths is called *continuous*.

When radiation from a light source, such as a light bulb, is separated into its different wavelength components, a **spectrum** is produced.

White light can be separated into a **continuous spectrum** of colors.

A rainbow is a continuous spectrum of light produced by the dispersal of sunlight by raindrops or mist.

Note that on the continuous spectrum there are no dark spots, which would correspond to different lines.

Not all radiation is continuous.

A gas placed in a partially evacuated tube and subjected to a high voltage produces single colors of light.

The spectrum that we see contains radiation of only specific wavelengths; this is called a **line spectrum**.



This is the line spectrum of Hydrogen

Bohr's Model

Rutherford assumed that electrons orbited the nucleus analogous to planets orbiting the sun.

However, a charged particle moving in a circular path should lose energy.

This means that the atom should be unstable according to Rutherford's theory.

Bohr noted the line spectra of certain elements and assumed that electrons were confined to specific energy states. These were called orbits.

Bohr's model is based on three postulates:

Only orbits of specific radii, corresponding to certain definite energies, are permitted for electrons in an atom.

An electron in a permitted orbit has a specific energy and is an "allowed" energy state.

Energy is only emitted or absorbed by an electron as it moves from one allowed energy state to another.

The energy is gained or lost as a photon.

The Energy States of the Hydrogen Atom

Colors from excited gases arise because electrons move between energy states in the atom.

Since the energy states are quantized, the light emitted from excited atoms must be quantized and appear as line spectra.

Bohr showed mathematically that

$$E = -(hcR_H)\left(\frac{1}{n^2}\right) = (-2.18 \times 10^{-18} \text{ J})\left(\frac{1}{n^2}\right)$$

where n is the *principal quantum number* (i.e., $n = 1, 2, 3, \dots$) and R_H is the Rydberg constant.

The product $hcR_H = 2.18 \times 10^{-18} \text{ J}$.

The first orbit in the Bohr model has $n = 1$ and is closest to the nucleus.

The furthest orbit in the Bohr model has $n = \infty \dots$ and corresponds to $E = 0$.

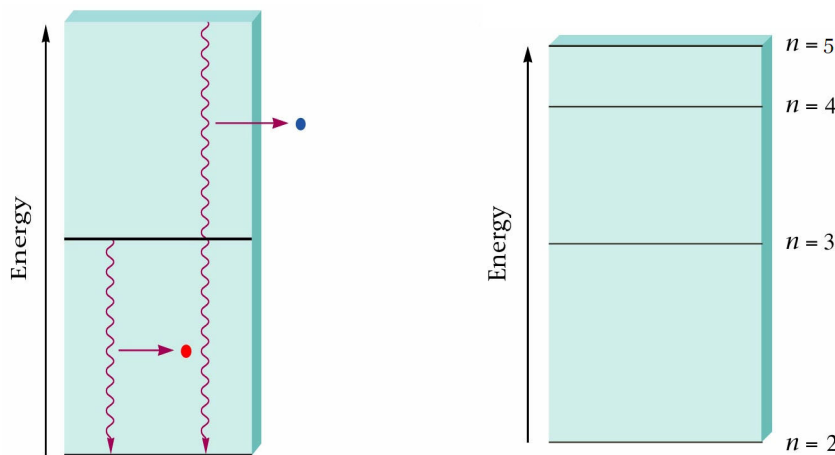
Electrons in the Bohr model can only move between orbits by absorbing and emitting energy in quanta ($E = h\nu$).

The **ground state** = the lowest energy state.

An electron in a higher energy state is said to be in an **excited state**.

The amount of energy absorbed or emitted by moving between states is given by

$$\Delta E = E_f - E_i = h\nu = 2.18 \times 10^{-18} \text{ J} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$



These are two of the visible transitions in the hydrogen atom

Sample Problem

3. When the electron in a hydrogen atom moves from $n = 6$ to $n = 2$, what is the wavelength of the light emitted? (answer 411 nm)

Limitations of the Bohr Model

The Bohr Model has several limitations:

It cannot explain the spectra of atoms other than hydrogen.

Electrons do not move about the nucleus in circular orbits.

However, the model introduces two important ideas:

The energy of an electron is quantized: electrons exist only in certain energy levels described by quantum numbers.

Energy gain or loss is involved in moving an electron from one energy level to another.

6.4 The Wave Behavior of Matter

Knowing that light has a particle nature, it seems reasonable to ask whether matter has a wave nature.

This question was answered by Louis de Broglie.

Using Einstein's and Planck's equations, de Broglie derived:

$$\lambda = h/mv$$

The **momentum**, mv , is a particle property, whereas λ is a wave property.

Matter waves is the term used to describe wave characteristics of material particles.

Therefore, in one equation de Broglie summarized the concepts of waves and particles as they apply to low-mass, high-speed objects.

As a consequence of de Broglie's discovery, we now have techniques such as X-ray diffraction and electron microscopy to study small objects.

The Uncertainty Principle

Heisenberg's uncertainty principle: we cannot determine the *exact* position, direction of motion, and speed of subatomic particles simultaneously.

For electrons: we cannot determine their *momentum* and *position* simultaneously.

6.5 Quantum Mechanics and Atomic Orbitals

Schrödinger proposed an equation containing both wave and particle terms.

Solving the equation leads to **wave functions**, Ψ

The wave function describes the electron's matter wave.

The square of the wave function, Ψ^2 , gives the probability of finding the electron.

That is, Ψ^2 gives the electron density for the atom.

Ψ^2 is called the **probability density**.

Electron density is another way of expressing probability.

A region of high electron density is one where there is a high probability of finding an electron.

Orbitals and Quantum Numbers

If we solve the Schrödinger equation we get wave functions and energies for the wave functions.

We call ψ^2 **orbitals**.

Schrödinger's equation requires three quantum numbers:

Principal quantum number, n . This is the same as Bohr's n value.

As n becomes larger, the atom becomes larger and the electron is further from the nucleus.

Azimuthal quantum number, l . This quantum number depends on the value of n .

The values of l begin at 0 and increase to $n - 1$.

We usually use letters for l (s , p , d and f for $l = 0$, 1, 2, and 3, respectively).

This quantum number defines the **shape** of the orbital.

Magnetic quantum number, m_l .

This quantum number depends on l .

The magnetic quantum number has integer values between $-l$ and $+l$.

Magnetic quantum numbers give the three-dimensional **orientation** of each orbital.

A collection of orbitals with the same value of n is called an **electron shell**.

A set of orbitals with the same n and l is called a **subshell**.

Each subshell is designated by a number and a letter. For example, $3p$ orbitals have $n = 3$ and $l = 1$.

Orbitals can be ranked in terms of energy to yield an Aufbau diagram.

Note that this Aufbau diagram is for a single electron system.

As n increases note that the spacing between energy levels becomes smaller.

6.6 Representations of Orbitals

The s Orbitals

All s orbitals are spherical.

As n increases, the s orbitals get larger.

As n increases, the number of **nodes** increases.

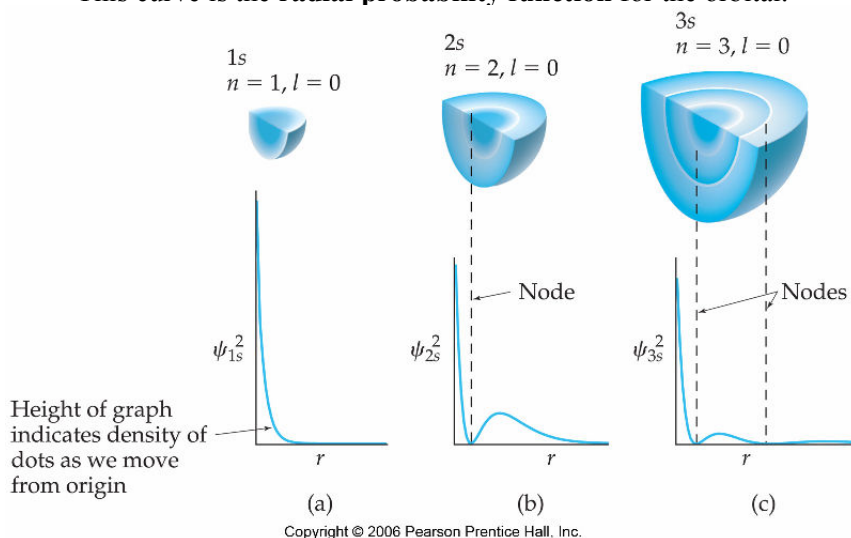
A node is a region in space where the probability of finding an electron is zero.

$$\psi^2 = 0 \text{ at a node.}$$

For an s orbital the number of nodes is given by $n - 1$.

We can plot a curve of *radial probability density* vs. distance (r) from the nucleus.

This curve is the **radial probability function** for the orbital.



The p Orbitals

There are three p orbitals: p_x , p_y and p_z .

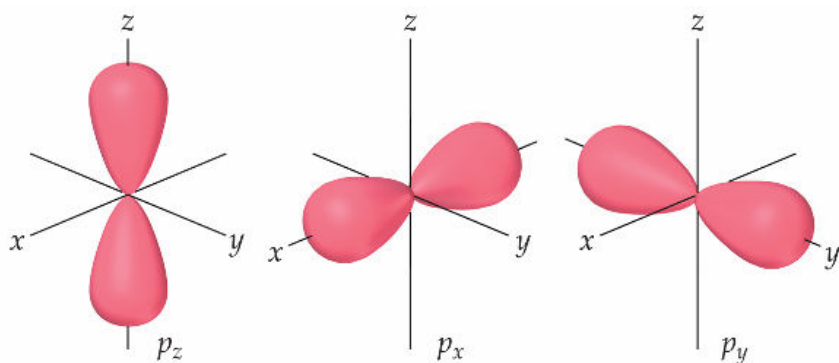
The three p orbitals lie along the x -, y -, and z -axes of a Cartesian system.

The letters correspond to allowed the values of m_l of -1 , 0 , and $+1$.

The orbitals are dumbbell shaped; each has two *lobes*.

As n increases, the p orbitals get larger.

All p orbitals have a node at the nucleus.



The d and f Orbitals

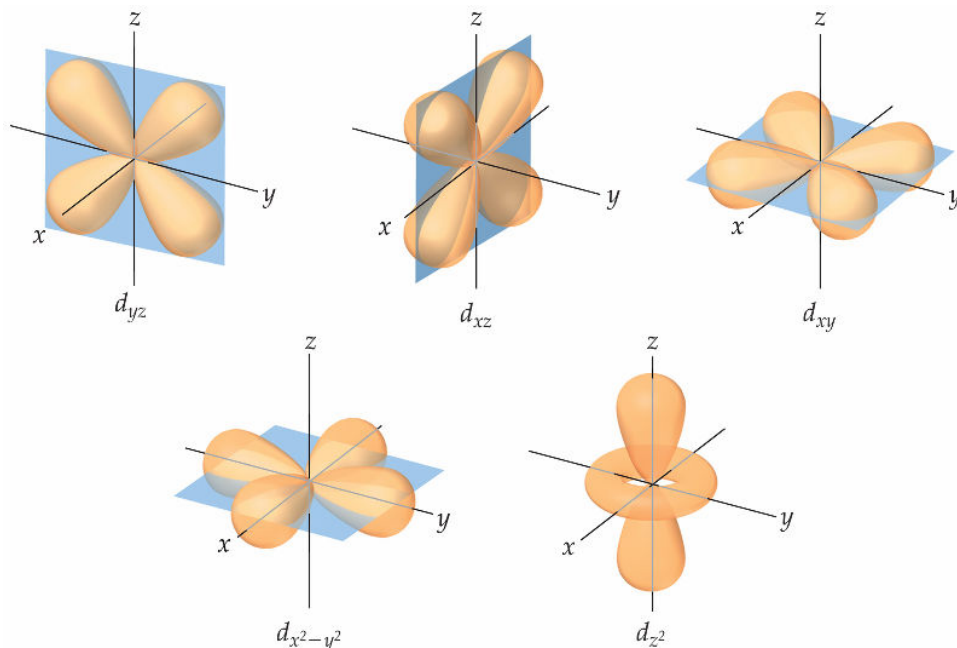
There are five d and seven f orbitals.

Three of the d orbitals lie in a plane bisecting the x -, y -, and z -axes.

Two of the d orbitals lie in a plane aligned along the x -, y -, and z -axes.

Four of the d orbitals have four lobes each.

One d orbital has two lobes and a collar.



6.7 Many-Electron Atoms

Orbitals and Their Energies

In a many-electron atom, for a given value of n , the energy of an orbital increases with increasing value of l .

Orbitals of the same energy are said to be **degenerate**.

For $n = 2$, the s and p orbitals are no longer degenerate.

Therefore, the Aufbau diagram looks slightly different for many-electron systems.

Electron Spin and the Pauli Exclusion Principle

Line spectra of many-electron atoms show each line as a closely spaced pair of lines.

Stern and Gerlach designed an experiment to determine why.

A beam of atoms was passed through a slit and into a magnetic field and the atoms were then detected.

Two spots were found: one with the electrons spinning in one direction and one with the electrons spinning in the opposite direction.

Since **electron spin** (electron as a tiny sphere spinning on its own axis) is quantized,

we define $m_s =$ **spin magnetic quantum number** $= \pm \frac{1}{2}$.

Pauli's exclusion principle states that no two electrons can have the same set of four quantum numbers.

Therefore, two electrons in the same orbital must have opposite spins.

6.8 Electron Configurations

Electron configurations tell us how the electrons are distributed among the various orbitals of an atom.

The most stable configuration, or ground state, is that in which the electrons are in the lowest possible energy state.

When writing ground-state electronic configurations:

electrons fill orbitals in order of increasing energy with no more than two electrons per orbital.

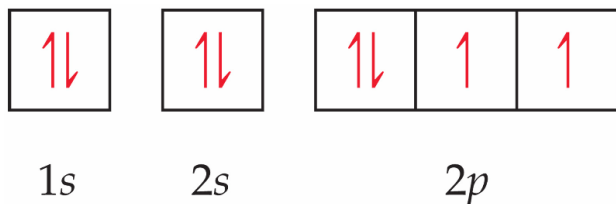
no two electrons can fill one orbital with the same spin (Pauli).

for degenerate orbitals, electrons fill each orbital singly before any orbital gets a second electron.

How do we show spin?

An arrow pointing upwards has $m_s = +\frac{1}{2}$ (spin up).

An arrow pointing downwards has $m_s = -\frac{1}{2}$ (spin down).



Sample Problems

- How many unpaired electrons does oxygen have?
- Write 4 quantum numbers to represent chlorine's unpaired electron.

Hund's Rule

Hund's rule: for degenerate orbitals, the lowest energy is attained when the number of electrons with the same spin is maximized.

Thus, electrons fill each orbital singly with their spins parallel before any orbital gets a second electron.

By placing electrons in different orbitals, electron-electron repulsions are minimized.

Condensed Electron Configurations

Electron configurations may be written using a shorthand notation (*condensed electron configuration*):

Write the **valence electrons** explicitly.

Valence electrons are electrons in the outer shell.

These electrons are gained and lost in reactions.

Write the **core electrons** corresponding to the filled noble gas in square brackets.

Core electrons are electrons in the inner shells.

These are generally not involved in bonding.

Example:

P is $1s^2 2s^2 2p^6 3s^2 3p^3$,

but Ne is $1s^2 2s^2 2p^6$.

Therefore, P is $[\text{Ne}]3s^2 3p^3$.

Transition Metals

After Ar the d orbitals begin to fill.

After the $3d$ orbitals are full the $4p$ orbitals begin to fill.

The ten elements between Ti and Zn are called the **transition metals**, or **transition elements**.

The $4f$ orbitals begin to fill with Ce.

Note: The electron configuration of La is $[\text{Xe}]6s^2 5d^1$.

The $4f$ orbitals are filled for the elements Ce – Lu, which are called **lanthanide elements** (or rare earth elements).

The $5f$ orbitals are filled for the elements Th – Lr, which are called **actinide elements**.

Most actinides are not found in nature.

6.9 Electron Configurations and the Periodic Table

The periodic table can be used as a guide for electron configurations.

The period number is the value of n .

Groups 1A and 2A have their s orbitals being filled.

Groups 3A – 8A have their p orbitals being filled.

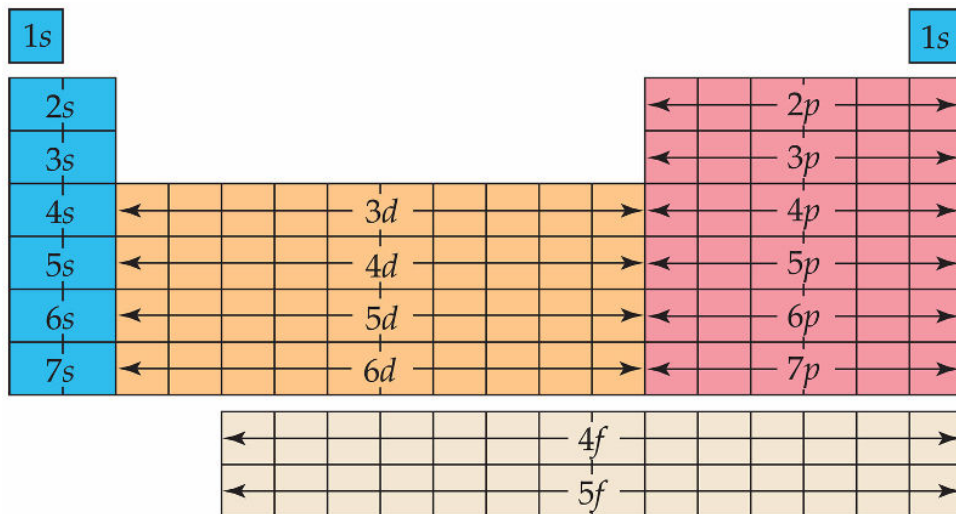
The s -block and p -block of the periodic table contain the representative, or main-group, elements.

Groups 3B – 2B have their d orbitals being filled.

The lanthanides and actinides have their f orbitals being filled.

The actinides and lanthanide elements are collectively referred to as the **f -block metals**.

Note that the $3d$ orbitals fill after the $4s$ orbital. Similarly, the $4f$ orbitals fill after the $5d$ orbitals.



Sample Problems

6. Write the abbreviated electron configuration for Sr^{+2} .

7. Write the full electron configuration for Ni.

Anomalous Electron Configurations

There are many elements that appear to violate the electron configuration guidelines. However, these unusual electron configurations are ground state electron configurations because half filled d shells are particularly stable. This is true for all elements in the column below these elements (Cr group VIB, aka group 6)

Examples:

Chromium is $[\text{Ar}]3d^54s^1$ instead of $[\text{Ar}]3d^44s^2$.

Copper is $[\text{Ar}]3d^{10}4s^1$ instead of $[\text{Ar}]3d^94s^2$.

Sample Problems

8. Write the abbreviated electron configuration for Au.

9. Write the abbreviated electron configuration for Ag^+ . (hint: s block **fills** before d , and electrons **leave** s before d !)
