Chapter 7   Quantum Theory and Electronic Structure of Atoms

Light and the Electromagnetic Spectrum

The Wave Nature of Light

electromagnetic radiation

wavelength

frequency

speed of light, c, 3.00×10^{8} m/s

Calculate the wavelength, in meters, of radiation with a frequency of $1.18 \times 10^{14}\ s^{-1}$. What region of the electromagnetic spectrum is this?

Particlelike Properties of Electromagnetic Radiation: The Planck Equation

Quantized Energy Levels

$E = h\nu$

Planck's constant, h = 6.626×10^{-34} Js

Determine the energy emitted in the above example.

Photoelectron effect

$$KE\left(\tfrac{1}{2}mv^2\right) = h\nu - \Phi$$

Wavelike Properties of Matter: the de Broglie Equation

The Wave Behavior of Matter

$E = mc^2$ $\qquad$ $E = h\nu = h\frac{c}{\lambda}$

$mc^2 = \frac{hc}{\lambda}$ $\qquad$ $\lambda = \frac{hc}{mc^2} = \frac{h}{mc}$

DeBroglie (pronounced de Broy) wavelength, $\lambda = \frac{h}{m\text{v}}$

What velocity must an electron (mass = 9.11×10^{-31} kg) need for its de Broglie wavelength to be 590 nm?

Quantum Mechanics and the Heisenberg Uncertainty Principle

Bohr's model

$$E_n = (-R_H)\left(\frac{1}{n^2}\right) \qquad n = 1,\ 2,\ 3,\ 4,\ \ldots$$

R_H, the Rydberg constatn. $R_H = 2.18x10^{-18}$ J

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

$$\Delta E = E_f - E_i = h\nu = (R_H)\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

$$\nu = \frac{\Delta E}{h} = \left(\frac{R_H}{h}\right)\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

Electromagnetic Radiation and Atomic Spectra

Line spectra – series of discrete lines (or wavelengths) separated by blank areas.

Calculate the wavelength of light emitted when an electron falls from the n = 6 to the n = 4 level in the hydrogen atom.

Schrödinger – quantum mechanical model **–** electron's wavelike properties.

Heisenberg

It is inherently impossible to know simultaneously both the exact momentum (mv) of the electron and its exact location (x) in space.

$\Delta x \Delta mv \geq \frac{h}{4\pi}$

Wave Functions and Quantum Numbers

Quantum Mechanics and Atomic Orbitals

Schrödinger's wave equation $\hat{H}\psi = E\psi$

Wavefunctions are usually represented by the symbol ψ

probability

Probability density, ψ^2, at a given point in space represents the probability that the electron will be found at that location.

Electron density: regions where there is a high probability of finding the electron are said to be regions of high electron density.

Orbitals and Quantum Numbers

The complete solution to Schrodinger's equation for *the hydrogen atom* yields a set of wave equations and corresponding energies. These wavefunctions are called orbitals.

An atomic orbital is a mathematical function that describes the wavelike behavior of an electron in an atom.

Quantum mechanics uses three quantum numbers n, *l*, and m_l, to describe an orbital.

1. **principal quantum number, n**, can have integral values of 1, 2, 3.and so forth. As n increases the orbital becomes larger and increases in energy.

2. **azimuthal quantum number,** *l*, can have values from 0 to n–1 for each value of n. This quantum number gives the orbital its shape. Also known as the *angular momentum quantum number*.

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

3. **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.

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

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

Each subshell is designated by a number (the value of n) and a letter (s, p, d, or f, corresponding to the value of *l*)

ex: 2s subsehll n = 2, *l* = 0

3f subshell n = 3, *l* = 3.

Restrictions on the possible values of the quantum numbers.

1. The shell with the principal quantum number n will consist of exactly n subshells.

n = 1	1 subshell
n = 2	2 subshells
n = 3	3 subshells
n = 4	4 subshells

2. Each subshell consists of a specific number of orbitals. Each orbital corresponds to a different allowed value of m_l.

For a given value of ***l*** there are 2***l*** + 1 allowed values for m_l, ranging from ***l*** to –***l***.

each s (***l*** = 0) subshell consists of one orbital	(2(0)+1)=1
each p (***l*** = 1) subshell consists of three orbitals	(2(1)+1)=3
each d (***l*** = 2) subshell consists of five orbitals	(2(2)+1)=5

3. The total number of orbitals in a shell is n^2, where n is the principle quantum number of the shell.

n	1	2	3	4
n^2 orbitals in a shell	1	4	9	16
elements in a row	2	8	18	32

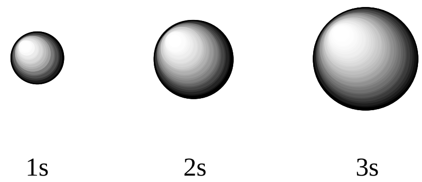
The Shapes of Orbitals: Representations of Orbitals

The s orbitals

- spherically symmetrical.
- probability function approaches zero as the distance, r, from the nucleus increases.
- 2s orbital has a node. Regions where the probability, ψ^2, goes to zero.

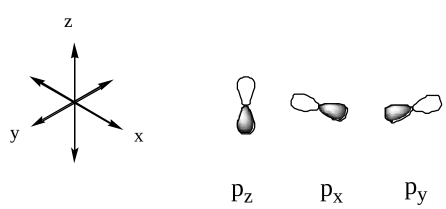
- 3s orbital has two nodes.
- As n increases, the electron is more likely to be farther from the nucleus. The size of the orbital increases as n increases.

Contour representations: give relative sizes of orbitals.



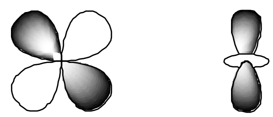
The p orbitals

- not spherically symmetrical
- all p orbitals have nodes at the nucleus
- on either side of the node there are lobes
- n = 2 has three p orbitals; all the same size, but one oriented along each axis: p_x, p_y, p_z.
- p orbitals increase in size as n increases.



d orbitals

- four of d (*l* = 2) orbitals have "four-leaf clover" shapes.
- lie primarily in a plane: d_{xy}, d_{xz}, d_{yz}, with lobes between axes. the $d_{x^2-y^2}$ lies in the x-y plane along the axes.
- the d_z2 orbital has two lobes along the z axis and a "doughnut" in the xy plane. It has the same energy as the other four d orbitals.



d_{xy}, d_{xz}, d_{yz}, $d_{x^2-y^2}$ d_{z^2}

The f orbitals (l = 3) are more complicated than the d orbitals.

Quantum Mechanics and Atomic Spectra

Electron Spin and the Pauli Exclusion Principle

Electron Spin

How do electrons populate the available orbitals?

A new quantum number, $\mathbf{m_s}$, is introduced.

It has two possible values: +1/2 and –1/2 (often referred to as spin up and spin down)

The **Pauli exclusion principle** states that no two electrons can have the same set of four quantum numbers n, l, m_l, and m_s.

An orbital can hold a maximum of two electrons, and they must have opposite spins.

Diamagnetism and Paramagnetism

Paramagnetism - parallel or unpaired spins; attracted by a magnet

Diamagnetism - antiparallel or paired spins; slightly repelled by a magnet.

Orbital Energy Levels in Many-Electron Atoms

We can describe many-electron atoms in terms of orbitals like those for hydrogen.

In hydrogen the energy levels in a subshell have the same energy.

In many-electron atoms, the energy levels can differ.

ex: 2s subshell is lower than the 2p subshell

Effective Nuclear Charge and Shielding

Any electron density between the nucleus and the electron of interest will reduce the nuclear charge acting on that electron. The net positive charge attracting the electron is called the effective nuclear charge, Z_{eff}. $Z_{eff} = Z - S$

Z - number of protons in nucleus

S - the average number of electrons between the nucleus and the electron in question.

s > p > d > f

Energies of Orbitals

In a many-electron atom, for a given value of n, Zeff 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*.

s < p < d

Orbitals of a subshell have the same energy.

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

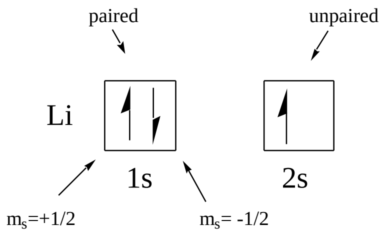
Electron Configurations of Multielectron Atoms

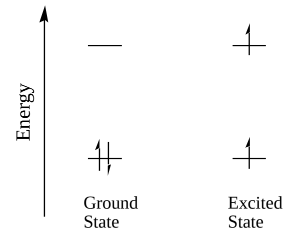
The way in which the electrons are distributed among the various orbitals of an atom are called its **electron configuration**.

orbital diagram: each orbital is represented by a box and each electron is represented by a half arrow.

Electrons having opposite spins are paired when they are in the same orbital.

The most stable, or ground, electron configuration of an atom is that in which the electrons are in the lowest possible energy states.

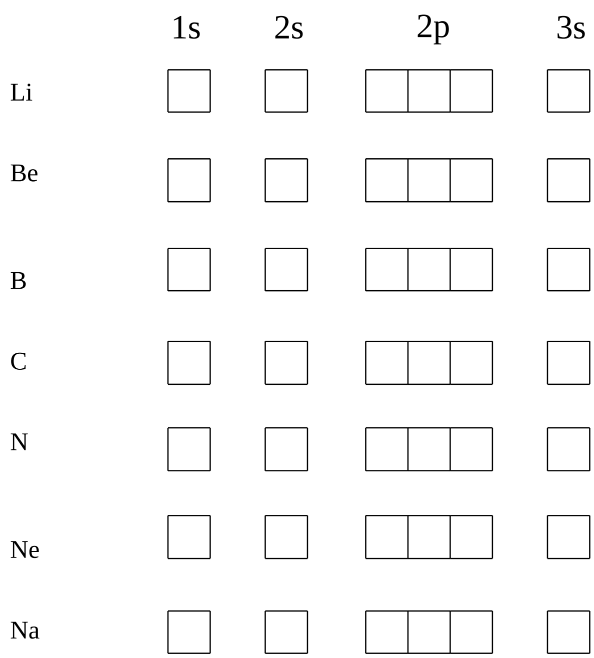




Periods 1, 2, and 3

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

Orbitals of a subshell will fill with electrons with the same spin first then with electrons of opposite spin.



The filling of the 2p subshell is complete at neon, which has a stable configuration with eight electrons (an octet) in the outermost shell.

Sodium has a single electron beyond the stable configuration of neon. We abbreviate the electron configuration of sodium as follows:

Na $[Ne]3s^1$ $1s^2 2s^2 2p^6 3s^1$

$[Ne] = 1s^2 2s^2 2p^6$

Li $[He]2s^1$

Electrons in subshells not occupied in the nearest noble-gas element of lower atomic number are referred to as outer-shell electrons, or **valence electrons**.

The electrons in the inner shells are the **core electrons**.

Period 4 and Beyond

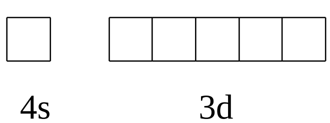
Ar $1s^2 2s^2 2p^6 3s^2 3p^6$

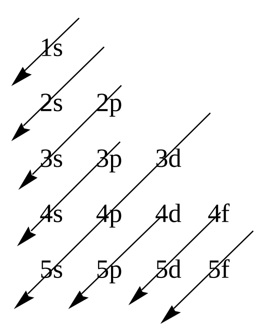
K $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$?

K has properties similar to Na. This suggests that the electron is in an s orbital.

K $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$

The 4s orbital is lower in energy than the 3d.





Electron Configurations and the Periodic Table

The periodic table is your best guide to the order in which orbitals are filled.

See fig 7.26

1s		1s
2s		2p
3s		3p
4s	3d	4p
5s	4d	5p
6s	5d	6p
7s	6d	

4f
5f

Some Anomalous Electron Configurations

Exceptions: $Cr \quad [Ar]4s^1 3d^5$

$Cu \quad [Ar]4s^1 3d^{10}$

Trends

1. Within each column (group) the atomic radius tends to increase as we proceed from top to bottom

2. Within each row (period) the atomic radius tends to decrease as we move from left to right.

- orbitals increase in size with increasing principle quantum number, n.
- The effective nuclear charge increases moving from left to right but the principle quantum number stays the same.
- The effective nuclear charge remains relatively constant while the principle quantum number increases.