

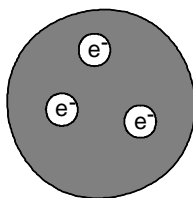
V. Structure of the Atom

A) Early Models of the Atom

By the begin of the twentieth century experimental evidence indicated that the atom was composed of positive and negative electricity. Most of the mass of the atom is associated with the positive electricity. The negative electricity was found to be composed of negative charged particles. The charge on one particle was determined to be $1.60 \cdot 10^{-19}$ coulombs or $4.80 \cdot 10^{-10}$ esu (electrostatic units) and the mass of one particle was found to be $9.1 \cdot 10^{-28}$ g. These particles were named *electrons*.

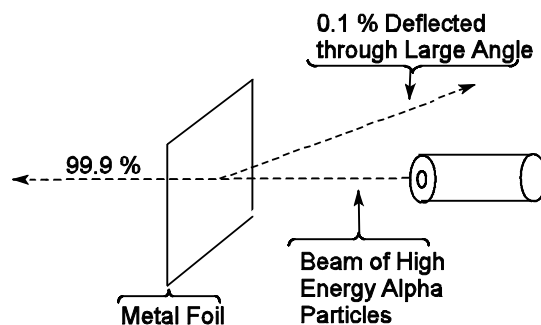
1) Thomson Model, 1904

A spherical sea of positive electricity in which a sufficient number of electrons are embedded to neutralize the positive charge.



Thomson suggested that high energy α particles (He^{2+}) upon striking an atom would pass through the atom rather than be deflected.

2) Geiger-Marsden Experiment, 1911



The 0.1 % of the α particles that were deflected through large angles encountered centers of high positive charge.

3) Rutherford (Planetary) Model, 1911

- Most of the atom is empty space.
- Positive electricity is concentrated in a very small volume called the *nucleus*.

- Electrons sufficient in number to equal the positive charge on the nucleus reside around the nucleus and determine the effective volume of the atom.
- The unit of positive charge on the nucleus is called a *proton*. The number of protons on the nucleus is equal to the *atomic number* of the element.

Element	Atomic No.	No. of Protons	No. of Electrons
H	1	1	1
B	5	5	5
Cl	17	17	17

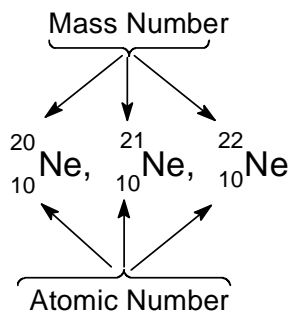
The protons account for only about half the mass of the atom. Most of the remaining mass is associated with the neutrons. A *neutron* is a neutrally charged particle on the nucleus.

The mass number of an atom is the sum of the number of protons and the number of neutrons.

$$\text{Mass Number of an Atom} = \text{Atomic Number of the Element} + \text{Number of Neutrons}$$

Atoms of the same element with different masses are called *isotopes*.

Example: Some Isotopes of Neon



The atomic weights (molar masses) listed in the periodic table are the weighted average of the masses of the various isotopes.

Example: Atomic Weight of Chlorine

Isotope	*Natural Abundance	AW (g/mole)
³⁵ Cl	75.4	34.97
³⁷ Cl	24.6	36.97

*The natural abundance is the percentage of the natural occurring atoms of an element that are this isotope.

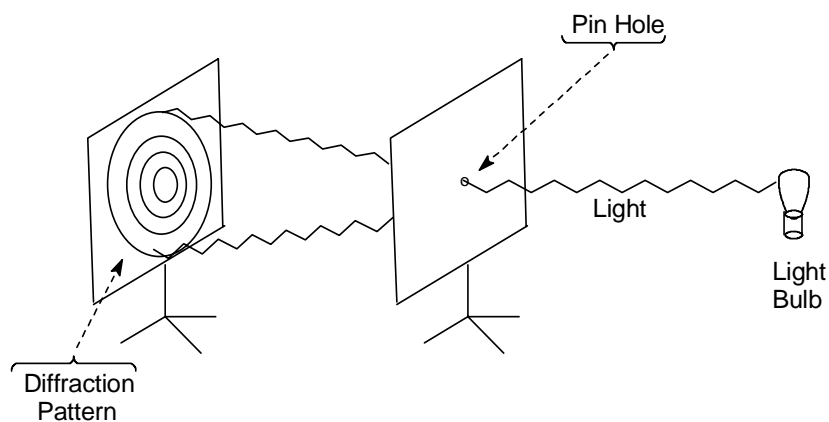
$$AW_{average} = \left[\frac{75.4\%}{100} \right] \left(34.97 \frac{g}{mole} \right) + \left[\frac{24.6\%}{100} \right] \left(36.97 \frac{g}{mole} \right) = 35.45 \frac{g}{mole}$$

B) Dual Nature of Light

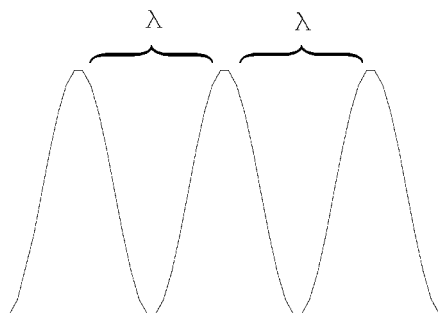
1) Wave

Light is regarded as an electromagnetic wave that travels through space at a constant speed of $c = 2.998 \cdot 10^{10}$ cm/sec.

Diffraction is a wave property and light is diffracted.



Wave



Wavelength, λ , is the distance between the crests of two consecutive waves.

Units: $1 \text{ \AA} \text{ (Angstrom)} = 1 \cdot 10^{-1} \text{ nm (nanometer)} = 1 \cdot 10^{-8} \text{ cm} = 1 \cdot 10^{-10} \text{ m} = 1 \cdot 10^2 \text{ pm (picometer)}$

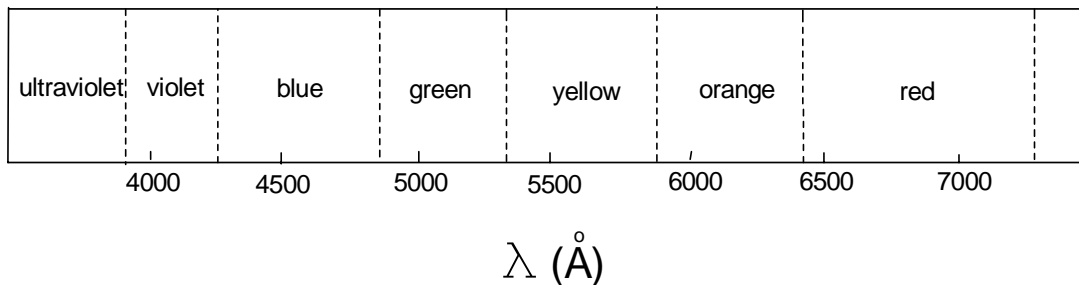
Frequency, ν , is the number of waves that pass a given point in unit time.

Units: 1/sec or 1 Hz (hertz) = one cycle/sec

Since the speed of light is constant

$$c = \nu\lambda = 2.998 \cdot 10^{10} \frac{\text{cm}}{\text{sec}} \quad (1)$$

Visible Spectrum of Light



2) Particle

Monochromatic light is light of a single wavelength λ .

Quantum Theory

- When light interacts with matter, it behaves as if it were composed of discrete units or quanta called *photons*.
- The energy of one photon is

$$E_{\text{photon}} = h\nu = \frac{hc}{\lambda} \quad (2)$$

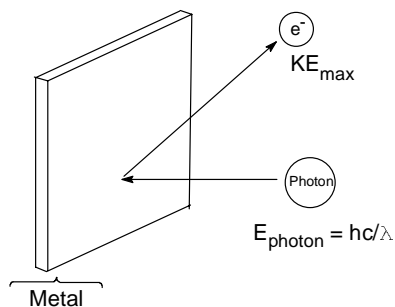
where h (Planck's constant) = $6.626 \cdot 10^{-27}$ erg-sec

Note: 1 erg = 10^{-7} J and erg = g-cm²/sec²

- Only whole numbers of photons are absorbed or emitted by matter.

3) Photoelectric Effect

When monochromatic light of an appropriate wavelength strikes a metal surface, electrons are ejected.



The maximum kinetic energy, KE_{\max} , of the ejected electron was experimentally found to be independent of the intensity (energy/area-time) of the monochromatic light and dependent on the wavelength, λ , of the monochromatic light.

Einstein's explanation

$$E_{\text{photon}} = E_t + KE_{\max} \quad (3)$$

where the threshold energy, E_t , is the minimum energy required to remove the electron from the surface of the metal.

Example: When monochromatic light of 4500 \AA strikes the surface of metallic sodium, electrons with $KE_{\max} = 3.36 \cdot 10^{-12} \text{ erg}$ are ejected. What is the threshold energy for sodium?

Unknown: E_t for sodium

Knowns: $\lambda = 4500 \text{ \AA}$ and $KE_{\max} = 3.36 \cdot 10^{-12} \text{ erg}$

Concepts: Quantum theory, photoelectric effect

$$\text{Relationships: } E_{\text{photon}} = \frac{hc}{\lambda} \quad \text{and} \quad E_{\text{photon}} = E_t + KE_{\max}$$

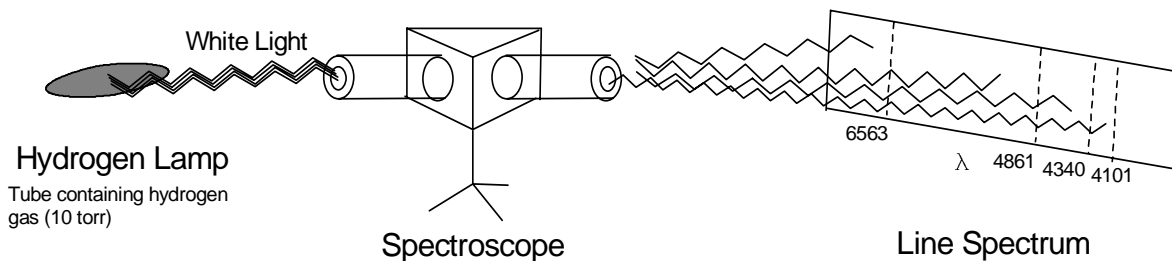
$$\frac{hc}{\lambda} = E_t + KE_{\max}$$

$$\frac{(6.626 \cdot 10^{-27} \text{ erg-sec})(2.998 \cdot 10^{10} \frac{\text{cm}}{\text{sec}})}{(4500 \text{ \AA})(\frac{10^{-8} \text{ cm}}{1 \text{ \AA}})} = E_t + 3.36 \cdot 10^{-12} \text{ erg}$$

$$E_t = 1.05 \cdot 10^{-12} \text{ erg}$$

C) Line Spectra of the Elements

When an electric current is passed through a discharge tube that contains hydrogen gas (10 torr), a white light is emitted. Analysis of the white light reveals that only certain wavelengths of light are emitted.



Conclusion: atoms emit only certain, discrete energies.

Spectroscope is an instrument that analyzes white light by separating it into its various wavelengths.

Line spectrum consists of a limited number of lines and each line corresponds to a different wavelength of light.

A mathematical equation that predicts the wavelengths of the bands in the hydrogen line spectrum was developed by J. J. Balmer.

$$\nu = \frac{c}{\lambda} = (3.289 \cdot 10^{15} \text{ sec}^{-1}) \left[\frac{1}{(n_1)^2} - \frac{1}{(n_2)^2} \right] \quad (4)$$

where n_1 and n_2 are dimensionless integers, i.e. $n = 1, 2, 3, 4, 5, \dots$ and $n_2 > n_1$.

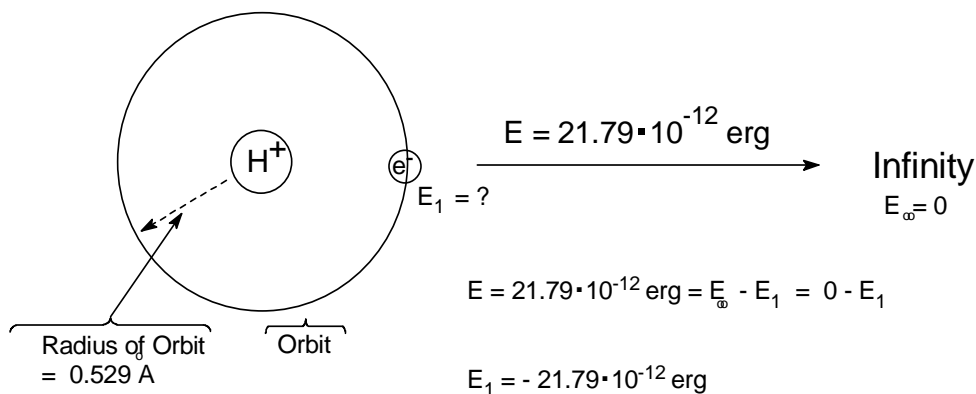
Example: Calculate the wavelength of light in the hydrogen line spectrum that corresponds to $n_1 = 2$ and $n_2 = 6$.

$$\begin{aligned} \nu &= \frac{c}{\lambda} = (3.289 \cdot 10^{15} \text{ sec}^{-1}) \left[\frac{1}{(n_1)^2} - \frac{1}{(n_2)^2} \right] \\ \frac{2.998 \cdot 10^{10} \frac{\text{cm}}{\text{sec}}}{\lambda} &= (3.289 \cdot 10^{15} \text{ sec}^{-1}) \left[\frac{1}{(2)^2} - \frac{1}{(6)^2} \right] \left[\frac{10^{-8} \text{ cm}}{1 \text{ \AA}} \right] \\ \lambda &= 4102 \text{ \AA} \end{aligned}$$

D) Bohr Model of the Hydrogen Atom

- The electron revolves around the nucleus with a fixed energy and does not emit or absorb energy spontaneously.

For the hydrogen atom in its ground state, the energy of the electron is E_1 .

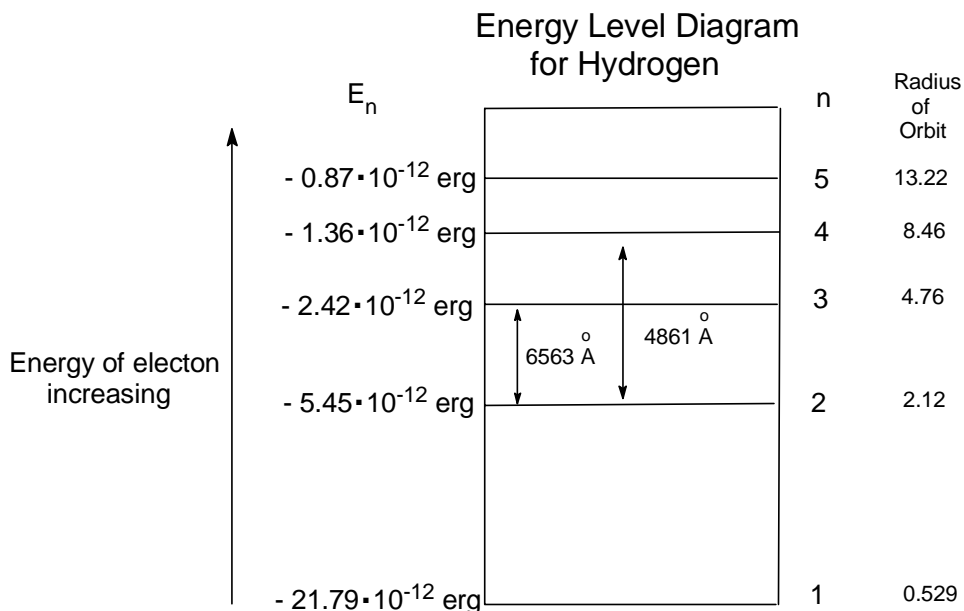


where E_{∞} is the energy of the electron at an infinite distance from the nucleus.

- The electron in the hydrogen atom may have other possible energies, namely

$$E_n = \frac{-21.79 \cdot 10^{-12} \text{ erg}}{n^2} \quad (5)$$

where n called the Principal quantum number is a dimensionless integer i.e. 1, 2, 3, 4, ...



- Absorption of energy by the hydrogen atom corresponds to the transition of the electron from a lower energy level E_{n_1} with quantum number n_1 to a higher energy level E_{n_2} with quantum number n_2 . Emission of energy by the hydrogen atom corresponds to the transition of the electron from a higher energy level E_{n_2} with quantum number n_2 to a lower energy level E_{n_1} with quantum number n_1 .

$$E(\text{energy emitted or absorbed}) = E_{n_2} - E_{n_1} \quad (6)$$

where $n_2 > n_1$

Note: The energy emitted or absorbed by an atom must equal the difference in energies of two energy levels.

Substituting eq 5 into eq 6 yields the following equation for the **hydrogen atom**.

$$E(\text{energy emitted or absorbed}) = (-21.79 \cdot 10^{-12} \text{ erg}) \left[\frac{1}{(n_2)^2} - \frac{1}{(n_1)^2} \right] \quad (7)$$

where $n_2 > n_1$

Example: What wavelength of light will be emitted when an electron in a hydrogen atom drops

from the energy level with $n = 5$ to the level with $n = 2$?

Unknown: Wavelength, λ , of light emitted

Knowns: Since $n_2 > n_1$, then $n_2 = 5$ and $n_1 = 2$.

Concepts: Bohr model of the hydrogen atom, quantum theory

$$\text{Relationships: } E_{\text{photon}} = \frac{hc}{\lambda} \text{ and } E = (-21.79 \cdot 10^{-12} \text{ erg}) \left[\frac{1}{(n_2)^2} - \frac{1}{(n_1)^2} \right]$$

$$\frac{hc}{\lambda} = (-21.79 \cdot 10^{-12} \text{ erg}) \left[\frac{1}{(n_2)^2} - \frac{1}{(n_1)^2} \right]$$

$$\frac{(6.626 \cdot 10^{-27} \text{ erg-sec})(2.998 \cdot 10^{10} \frac{\text{cm}}{\text{sec}})}{\lambda} = (-21.79 \cdot 10^{-12} \text{ erg}) \left[\frac{1}{(5)^2} - \frac{1}{(2)^2} \right] \left[\frac{10^{-8} \text{ cm}}{1 \text{ \AA}} \right]$$

$$\lambda = 4341 \text{ \AA}$$

E) Matter Waves

1) de Broglie, 1924

Proposed that particles such as electrons may have wave character. Particles with wave character are called *matter waves*.

The momentum, mv , of the photon or electron is related to the wavelength, λ , by the eq 8.

$$\lambda = \frac{h}{mv} \quad (8)$$

where m = mass, v = velocity ($p = mv$ = momentum), and h is Planck's constant.

Example: Calculate the wavelength of an electron ($m = 9.1 \cdot 10^{-28}$ g) that has a velocity of $5.9 \cdot 10^8$ cm/sec.

$$\lambda = \frac{h}{mv} = \left[\frac{6.626 \cdot 10^{-27} \text{ erg-sec}}{(9.1 \cdot 10^{-28} \text{ g})(5.9 \cdot 10^8 \frac{\text{cm}}{\text{sec}})} \right] \left[\frac{1 \text{ \AA}}{10^{-8} \text{ cm}} \right] = 1.2 \text{ \AA}$$

2) Heisenberg's Uncertainty Principle

It is impossible to know simultaneously both the position and momentum of a particle with wave character.

$$\Delta x \Delta p_x \geq \frac{h}{4\pi} \quad (9)$$

where Δx is the uncertainty in the position, x , of the particle and Δp_x is the uncertainty of the momentum in the x direction of the particle.

F) Quantum Mechanics

The electron is considered to be a wave as well as a particle and the energy of the electron is given by the Schrödinger wave equation.

Schrödinger wave equation for one dimension (x)

$$\frac{d^2 \psi}{dx^2} + \left[\frac{8\pi^2 m}{h^2} \right] (E - V) \psi = 0 \quad (11)$$

where

h is Planck's constant,

m is the mass of the electron,

x is the coordinate (position) of the electron,

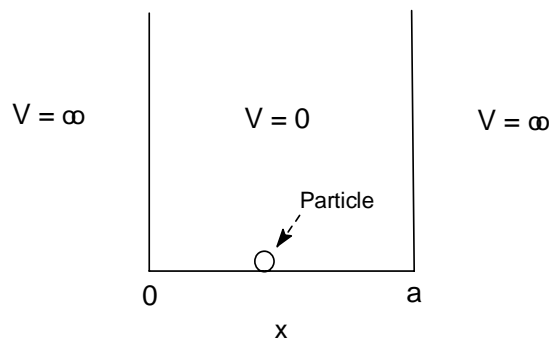
E is the total energy of the electron,

V is the potential energy,

ψ is the solution (a mathematical equation that depends on the coordinate x) to the differential equation and is called the *wave function*, and

d^2/dx^2 is a mathematical operator.

To illustrate some of the features of the Schrödinger wave equation, we consider the following problem. Calculate the allowed energies of a particle ($m = 9.1 \cdot 10^{-28}$ g) constrained to a one-dimensional box of length $a = 2.5 \cdot 10^{-8}$ cm.



Inside the box $V = 0$ and thus

$$\frac{d^2 \psi}{dx^2} + \left[\frac{8\pi^2 m}{h^2} \right] (E - 0) \psi = 0$$

It can be shown that the solution to this second order, homogeneous, linear differential

equation has the form

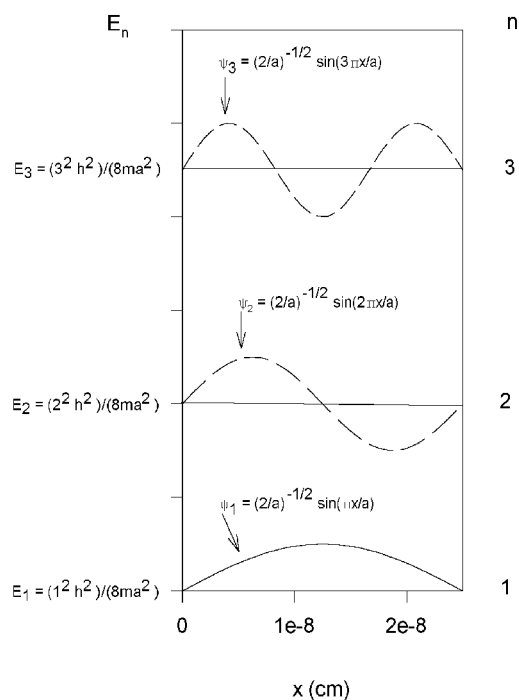
$$\psi = A \sin(\alpha x)$$

where A and α are constants. The constraint that the particle must be inside the box is used to evaluate the constants and the solutions take the form

$$\psi_n = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \quad \text{and} \quad E_n = \frac{n^2 h^2}{8ma^2}$$

where n , called the quantum number, is an integer, i.e. $n = 1, 2, 3, 4, 5, 6, \dots$

Energy Level Diagram for Particle in the Box and Plot of ψ_n versus x



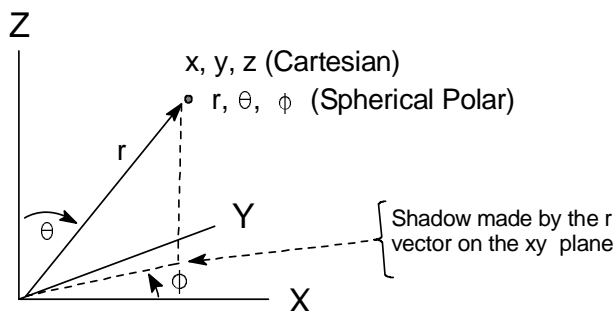
Observations:

- For each ψ_n (solution to the wave equation) there is a corresponding E_n .
- Only certain discrete values of the energy for the particle are possible, namely $E_n = n^2 h^2 / 8ma^2$.
- The energy of the particle, E_n , is independent of the particle's position, x .

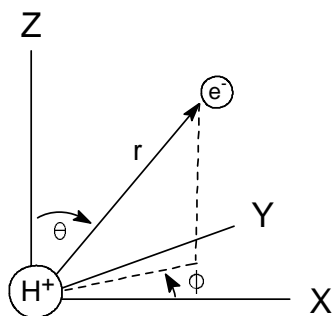
The number of different types of quantum numbers is a consequence of the number of coordinates.

Coordinates	Quantum Numbers
x	n
x, y, z	n, l , m_l
x, y, z, time	n, l , m_l , m_s

Spherical Polar Coordinates



G) Hydrogen Atom (Quantum Mechanical Model)



$$V = -\frac{Ze^2}{r}$$

Z = charge on nucleus (+1 for H)

e = charge on electron (4.8×10^{-10} esu)

1) Solutions to the Schrödinger wave equation for the hydrogen atom have the following features.

- The wave functions are characterized by four quantum numbers n, l , m_l , and m_s .
- Acceptable solutions, ψ , are obtained only when n, l , m_l , and m_s have the following values.

Principal Quantum Number, n	$n = 1, 2, 3, 4, 5, 6, \dots$
Azimuthal Quantum Number, l	$l = 0, 1, 2, 3, \dots, n - 1$
Magnetic Quantum Number, m_l	$m_l = l, \dots, 3, 2, 1, 0, -1, -2, -3, \dots, -l$
Spin Quantum Number, m_s	$m_s = \frac{1}{2}, -\frac{1}{2}$

2) Solution, $\psi_{n, l, m}$, when $n = 1$, $l = 0$, $m_l = 0$

$$\Psi_{1,0,0} = \Psi_{1s} = R\Theta\Phi = \left[2\left(\frac{1}{a_0}\right)^{\frac{3}{2}} \exp\left(\frac{-r}{a_0}\right) \right] \left[\frac{1}{\sqrt{2}} \right] \left[\frac{1}{\sqrt{2\pi}} \right]$$

$$E_{1s} = -21.79 \cdot 10^{-12} \text{ erg}$$

where $a_0 = 0.529 \text{ \AA}$; R , called the radial part, is the part of ψ that depends on r ; $\Theta\Phi$, called the angular part, is the part of ψ that depends on $\theta\phi$.

Note: the angular part of ψ_{1s} is a constant.

If the electron is in state ψ_{1s} , then it will have energy E_{1s} irrespective of its position in space, i.e. r may be any value from 0 to ∞ . We know the energy of the electron exactly but we do not know its position (r, θ, ϕ) in space.

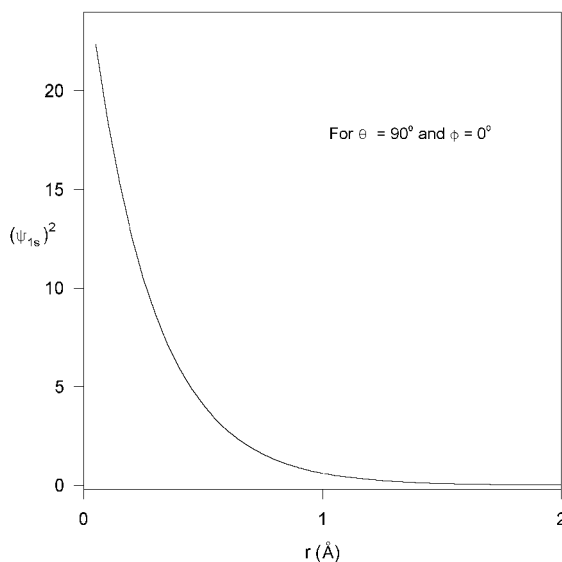
3) Probability

Electron density, $(\Psi_{n,l,m})^2$, is proportional to the probability per unit volume of finding the electron at a point r, θ, ϕ in space. Units of $(\Psi_{n,l,m})^2$: $(\text{volume})^{-1}$

Graphical Representations of Probability

a) Plot of ψ^2 versus r with θ and ϕ fixed

Plot of $(\Psi_{1s})^2$ Versus r



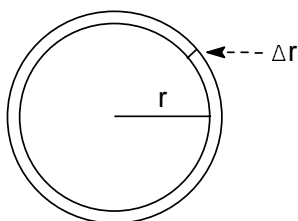
Points on the curve represent the probability of finding the electron at distance r from the nucleus.

b) Radial Distribution Function

What is the probability of finding the electron in a spherical shell of thickness Δr and radius r ?

$$\text{Probability} = (\text{Probability per unit volume}) \times (\text{volume of spherical shell})$$

Cross Section of
a Spherical Shell



When Δr is very small, the volume of the spherical shell is approximately

$$\text{Volume of Spherical Shell} \approx 4\pi r^2 \Delta r$$

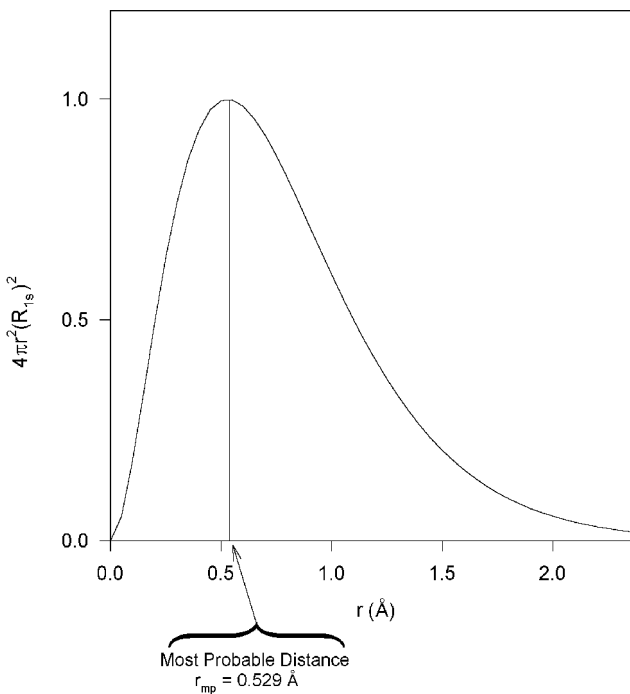
and

$$\text{Probability} = (R^2)(4\pi r^2 \Delta r)$$

where R is the radial part of ψ .

Since Δr is very small and effectively constant, $4\pi r^2 R^2$, called the *radial distribution function*, is plotted as a function of r .

Plot of Scaled Radial Distribution Function Versus r



Points on the curve represent the probability of finding the electron in spherical shell of very small thickness at distance r from the nucleus.

c) Electron Density Cloud

A three-dimensional plot of $(\psi_{n,l,m})^2$ versus r , θ , and ϕ

The density of dots at a specific coordinate (r , θ , and ϕ) is proportional to the probability of finding the electron at that coordinate.

d) Contour Plot

A cross section of the electron density cloud

The symbols which are printed below represent the relative electron densities, $\psi^2/(\psi_{\max})^2$, where $(\psi_{\max})^2$ is the maximum value calculated for ψ^2 .

Range of Electron Dinsity (ED)	Symbol
$ED \leq 0.01$:
$0.01 \leq ED \leq 0.02$	/
$0.02 \leq ED \leq 0.10$	o
$0.10 \leq ED \leq 0.25$	o

$$0.25 \leq ED \leq 0.50$$

+

$$0.50 \leq ED \leq 1.0$$

\$

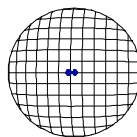
Contour Plot for Hydrogen 1s Atomic Orbital, ψ_{1s}



The printed area represents the region in space in which there is a 99% probability of the finding the electron.

e) Solid Representation

Boundary surface of the electron density cloud for the hydrogen 1s atomic orbital, ψ_{1s}



The enclosed volume represents the region in which there is a 99% probability of

finding the electron.

H) Atomic Orbitals

The one electron wave function, $\Psi_{n,l,m}$, which is identified by the three quantum numbers n , l , and m_l is called an *atomic orbital* (AO).

A number and letter are used to designate the values of the n and l quantum numbers of an AO.

Letter:	s	p	d	f	g
$l = :$	0	1	2	3	4

Example:

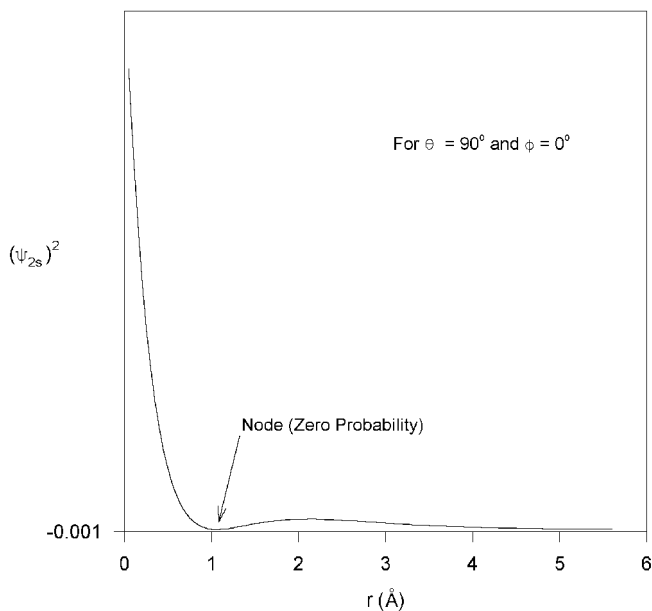
A 3p AO is an AO with $n = 3$ and $l = 1$, i.e. $\Psi_{3,1} = \Psi_{3p}$.

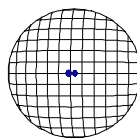
1) 2s AO for Hydrogen ($n = 2$, $l = 0$, $m_l = 0$)

$$\Psi_{2s} = \left[\left(\frac{1}{a_0} \right)^3 \left(2 - \frac{r}{a_0} \right) \exp\left(\frac{-r}{2a_0} \right) \right] \left[\frac{1}{4\sqrt{2\pi}} \right]$$

Graphical Representations

Plot of $(\Psi_{2s})^2$ Versus r



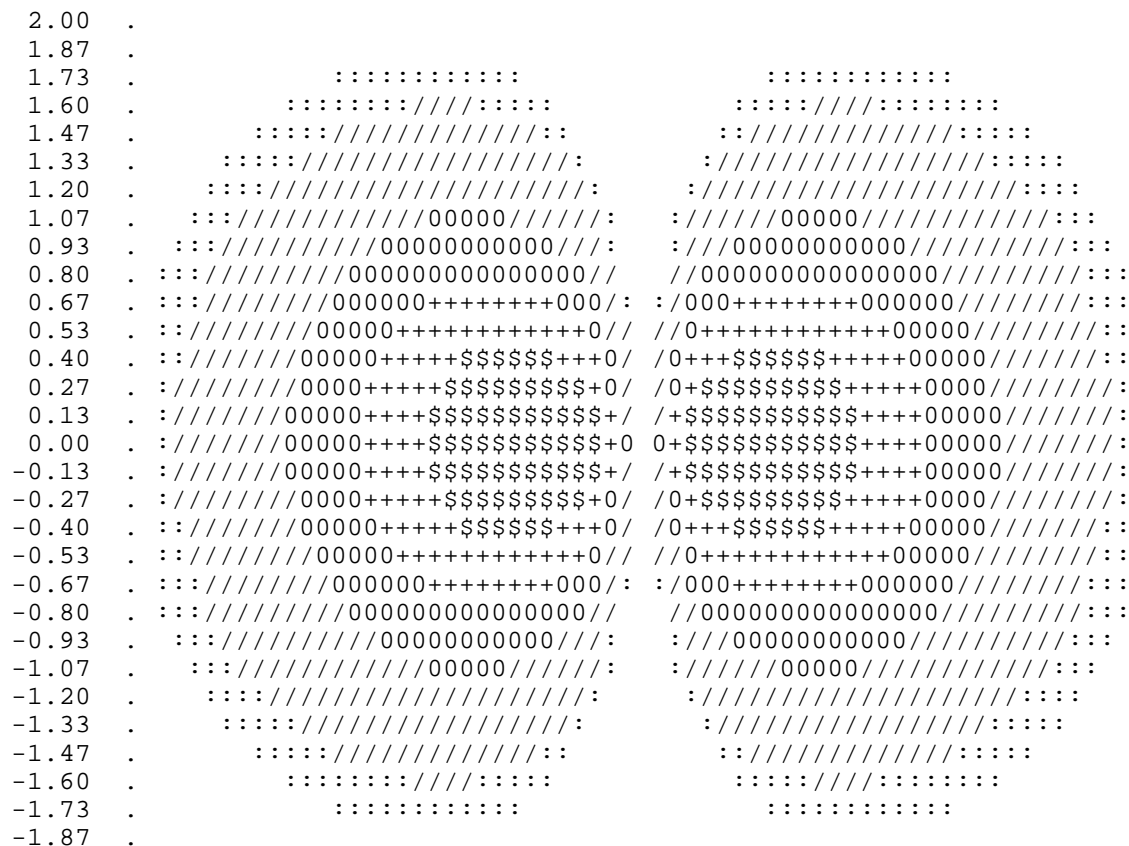


Note: The number of nodes in addition to the node at the nucleus = n - l - 1.

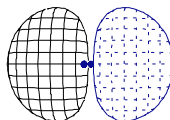
2) 2p_x AO for Hydrogen (n = 2, l = 1, m_l = 1)

$$\Psi_{2p_x} = \left[\left(\frac{1}{32\pi(a_0)^3} \right)^{\frac{1}{2}} \left(\frac{r}{a_0} \right) \exp\left(\frac{-r}{2a_0} \right) \right] \cos\theta \sin\phi$$

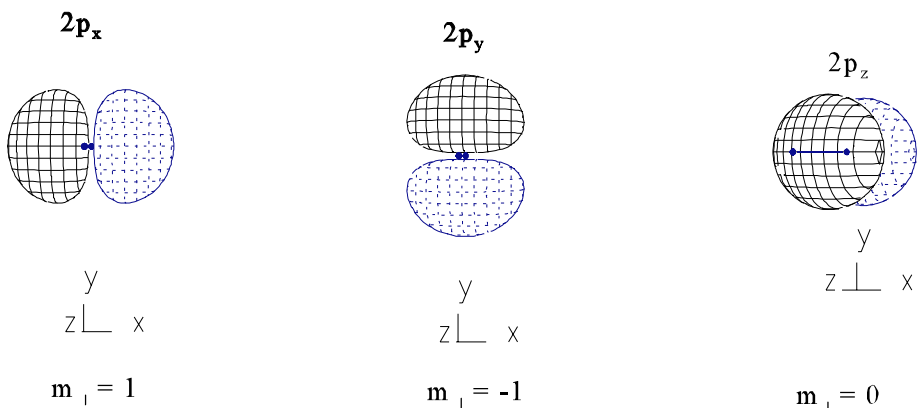
Contour Plot for 2p_x Atomic Orbital



Boundary surface of the electron density cloud for the $2p_x$ atomic orbital.

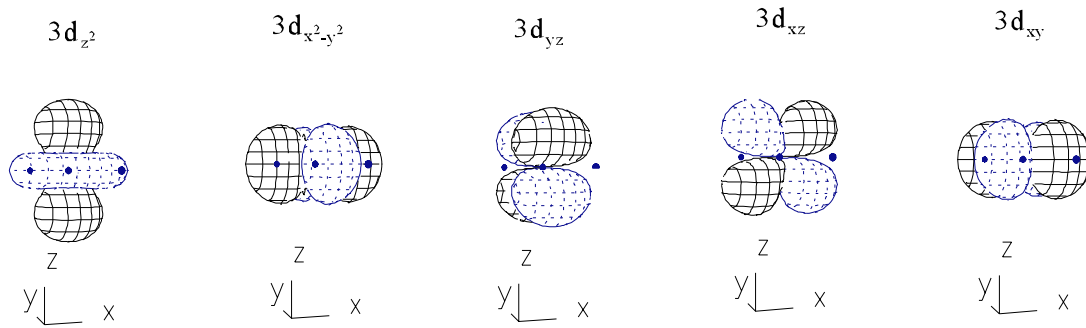


- 3) When $l = 1$, then $m_l = 1, 0, -1$. Thus there are three AOs with the same n and l values but different m_l values. The electron density clouds for these AOs have the same size and shape but different spatial orientation.



The change from solid cross-hatching to dashed cross-hatching on the boundary surfaces indicates an algebraic sign change in the wave function, ψ_{n, l, m_l} , i.e. positive to negative algebraic sign change.

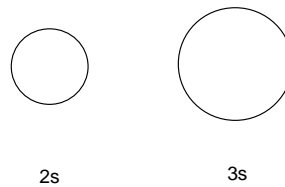
- 4) When $l = 2$, then $m_l = 2, 1, 0, -1, -2$. Thus there are five AOs with the same n and l values but different m_l values. The electron density clouds for these AOs have the same size and shape but different spatial orientation.



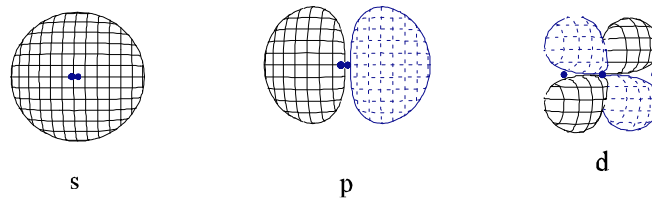
Summary: The size, shape, and spatial orientation of the electron density $(\psi_{n, l, m})^2$ cloud are related to the quantum numbers n , l , and m_l that define the atomic orbital $(\psi_{n, l, m})$.

- n is related to size

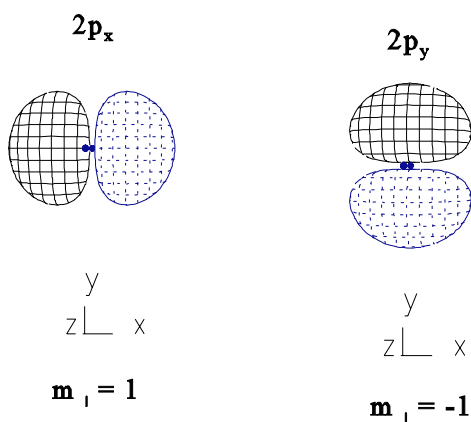
For the hydrogen atom the size of the electron density cloud increases as n increases.



- l is related to the shape.

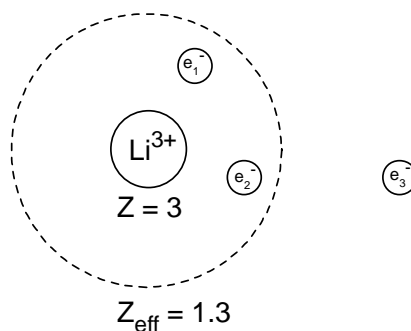


- m_l is related to the spatial orientation.



5) Polyelectronic Atoms

Exact solutions to the Schrödinger wave equation for atoms with two or more electrons are not possible and we must settle for approximate solutions. The *independent particle model* is often utilized to obtain approximate solutions. In this model each electron in the atom is treated independently of the other electrons. Each electron is treated as if it were the only electron in an atom that has a nucleus with a charge Z_{eff} . For example consider the lithium atom



To calculate the energy of Electron #3, we solve the Schrödinger wave equation for a hydrogenlike atom (one-electron atom) with a nuclear charge of $Z_{\text{eff}} = 1.3$. To calculate the energy of Electron #2, we solve the Schrödinger wave equation for a hydrogenlike atom with a nuclear charge of $Z_{\text{eff}} = 2.7$. Thus solutions to the three-electron problem are approximated by the solutions to three one-electron problems.

$$\text{Effective Nuclear Charge: } Z_{\text{eff}} = \underbrace{Z}_{\substack{\text{Actual Charge} \\ \text{on Nucleus}}} - \underbrace{S}_{\substack{\text{Screening Constant: the part of the} \\ \text{nuclear charge, } Z, \text{ "screened" from} \\ \text{the "outer" electrons by the "inner"} \\ \text{electrons}}}$$

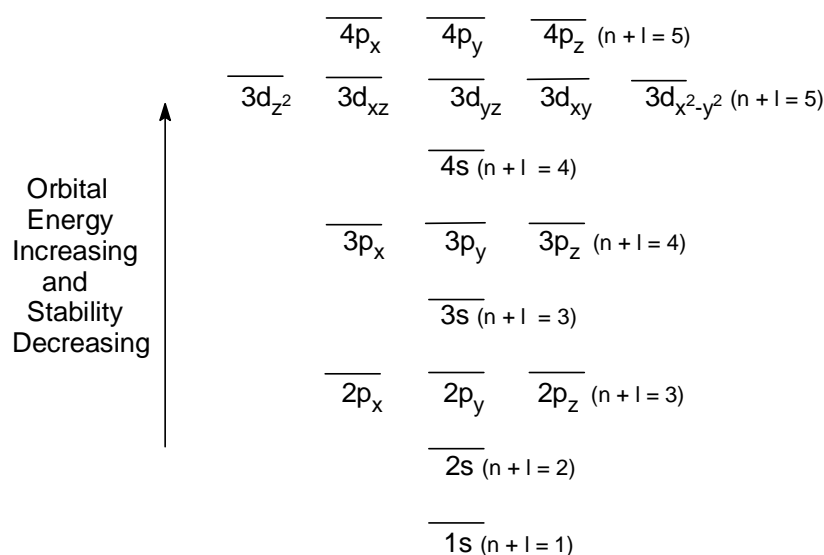
With this model the electronic structure of a polyelectronic atom may be described in terms of atomic orbitals, $\psi_{n, l, m}$, that are *hydrogenlike* and are defined by the quantum numbers n , l , and m_l . The shape and spatial orientation of the electron density clouds for these AOs are identical to shape and spatial orientation of the clouds for the hydrogen AOs. However, *the size of the cloud will increase as n increases and Z_{eff} decreases.*

I) $n + l$ Rule and Electron Configuration

1) $n + l$ Rule

In the absence of a magnetic field, the energy of an AO for a polyelectronic atom is determined by the quantum numbers n and l . In a neutral, isolated atom the smaller the sum of the values of n and l ($n + l$), the more stable (lower energy) the AO described by n and l . If two AOs have the **same** $n + l$ value, the AO with the smaller n value will be the more stable AO.

Relative Orbital Energy Level Diagram



The set of AOs with the same n value is called a *shell*.

Example: $2s$, $2p_x$, $2p_y$, and $2p_z$

The set of AOs with the same n value and the same l value is called a *subshell*.

Example: $2p_x$, $2p_y$, and $2p_z$

Note: The AOs in a subshell have the same energy and are said to be *degenerate*.

2) Pauli Exclusion Principle

No two electrons in an atom can have the same values for all four quantum numbers.

Example: He Atom

Electron #	n	l	m_l	m_s
1	1	0	0	$1/2$
2	1	0	0	$-1/2$

Since both electrons have the same values for the quantum numbers n, l, and m_l , then the two electrons must have different values for the m_s quantum number in order to satisfy the Pauli principle.

Implication: Since there are only two possible values for m_s ($1/2$, $-1/2$), then only two electrons may have the same values for the quantum numbers n, l, and m_l . Hence, only two electrons can “occupy” the same AO, $\psi_{n,l,m}$, and these electrons must have different m_s values.

3) Electron Configuration, Ground State

A representation of the “occupied” AOs in an atom

Symbols:

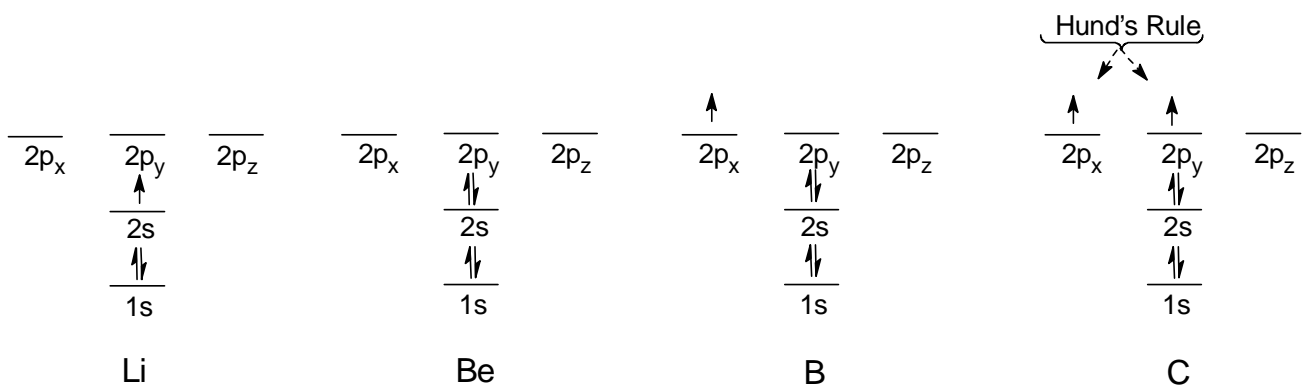
—	represents the relative energy of the AO.
↑	represents an electron with $m_s = 1/2$.
↓	represents an electron with $m_s = -1/2$.

Procedure:

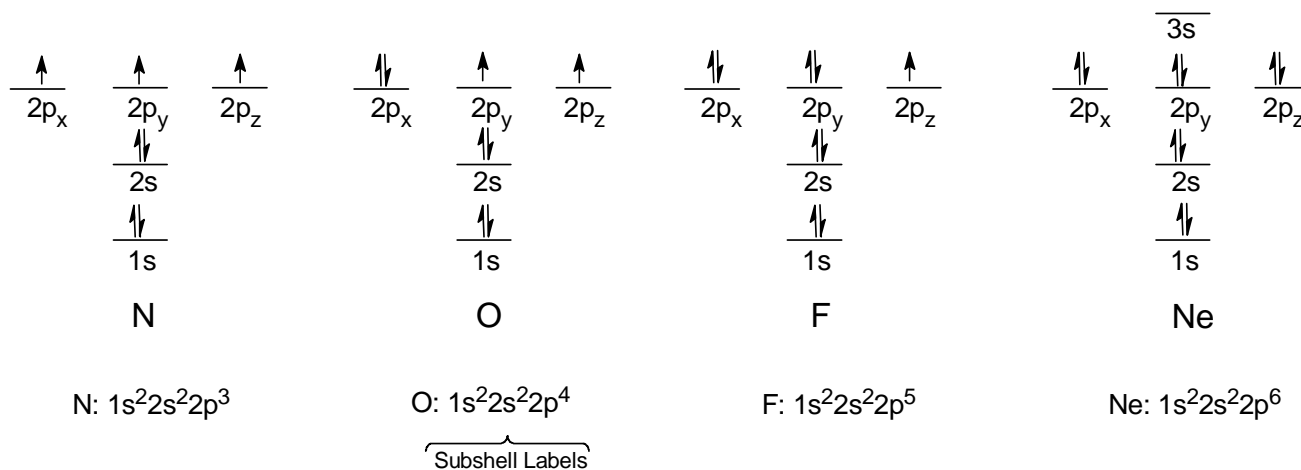
Determine the total number of electrons and distribute the electrons as follows.

- Fill the most stable AO (the AO with the smallest $n + l$ value) according to the Pauli principle.
- Fill the next most stable AO according to the Pauli principle.
- Continue in this fashion until all the electrons have been distributed.

Example: Write the ground state electron configurations for Li through Ne.



Hund's rule states that the most stable configuration is the one in which the *electrons are in different orbitals with the SAME energy*.



Anomalies are found for Cr, Cu, and members of their groups (6 and 11).

Example: Ground State Electron Configuration for Cr

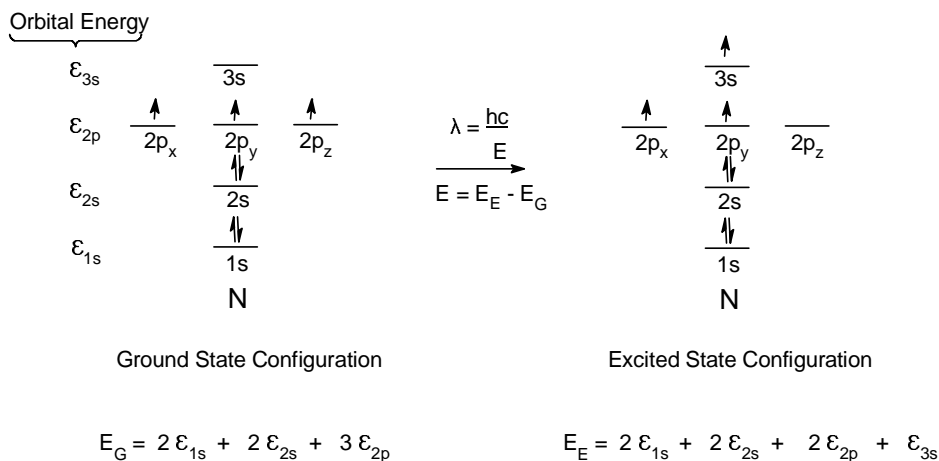
Predicted: Cr: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^4$

Found: Cr: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$

Reason: *Half-filled and filled subshells are more stable (lower energy) than partially filled subshells.* Note: The 4s and 3d subshells of Cr are half-filled.

4) Excited States

To a *very crude* approximation, the total electronic energy of the atom is equal to the sum of the energies of the electrons.



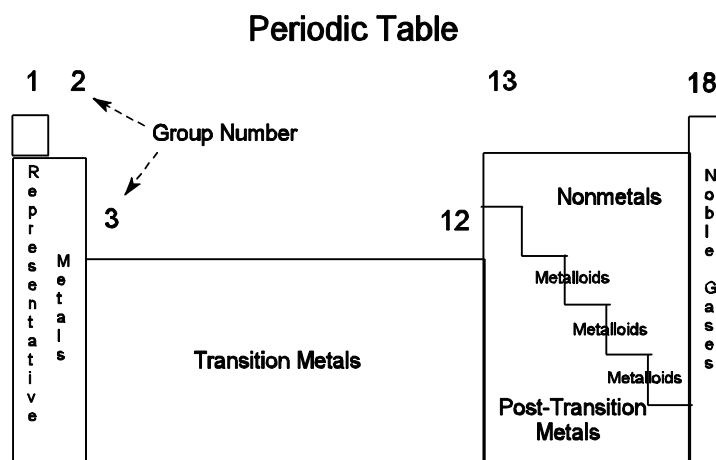
When a nitrogen atom in its ground electronic state absorbs monochromatic light of wavelength λ , it is promoted to an excited electronic state.

The *ground state* is the lowest energy state of an atom, ion, or molecule.

An *excited state* is any energy state other than the ground state.

J) Periodic Table

The properties of the elements are a periodic function of their atomic numbers.

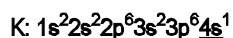
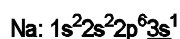
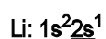


The horizontal divisions of the periodic table are called *periods* and the vertical divisions are called *groups*.

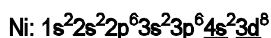
The least-stable, “occupied” shell in the electron configuration of the atom is called the **valence shell**.

Example: Valence shell is underlined.

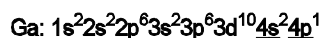
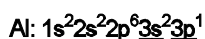
Group: 1



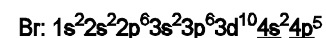
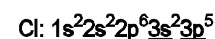
10



13



17



Valence
Shell
Configuration }

 ns¹

 ns²(n-1)d⁸

 ns²np¹

 ns²np⁵

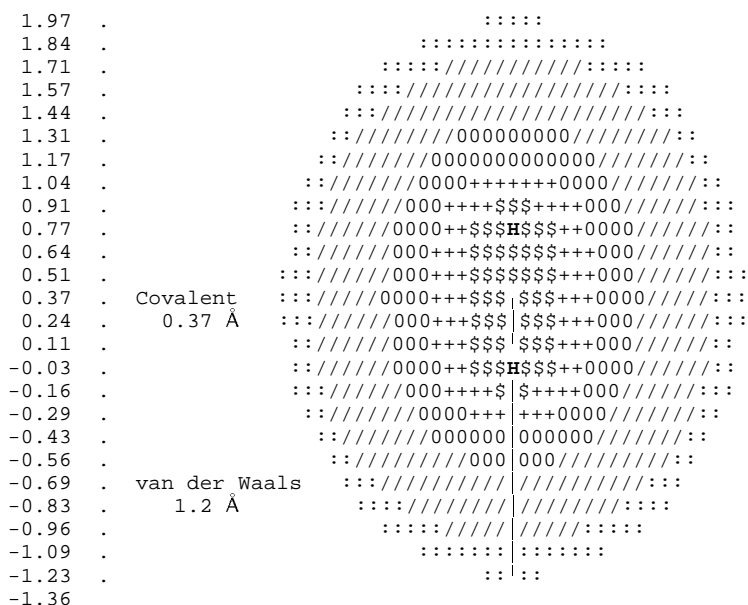
Note: Elements in the same group of the periodic table have the same type of valence shell configuration.

K) Size of the Atom

1) Atomic Radii

- van der Waals radius* - distance from the center of the atom to a point where the electron density is effectively zero
- Covalent radius* - one half the distance between the centers of two bonded atoms

Contour Plot for Bonding Molecular Orbital in H₂



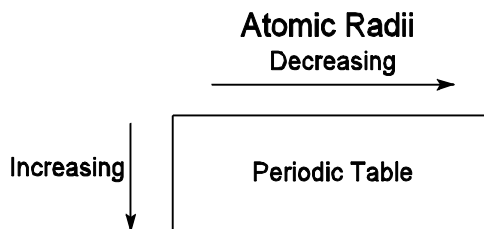
2) Periodic Trends in Atomic Radii

- The atomic radii decrease with an increase in atomic number across a period.

Explanation: Z_{eff} increases while n remains constant across a period.

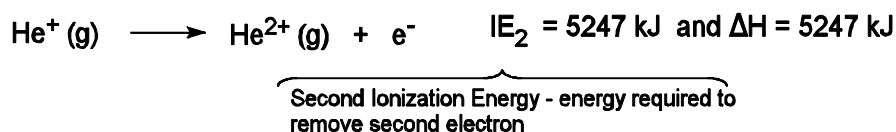
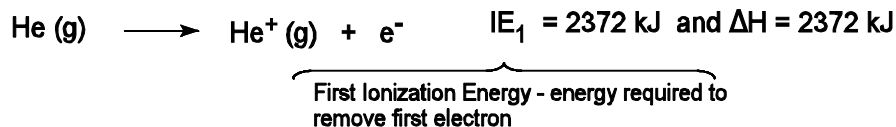
- The atomic radii increase with an increase in atomic number down a group.

Explanation: n increases while Z_{eff} increases only slightly down a group.

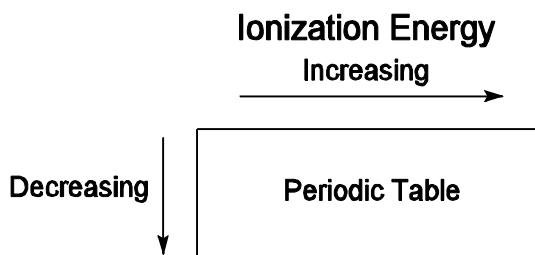


L) Ionization Energy

The minimum energy *required to remove* an electron from a *gaseous* atom or ion in its *ground state*.

Example: He Atom

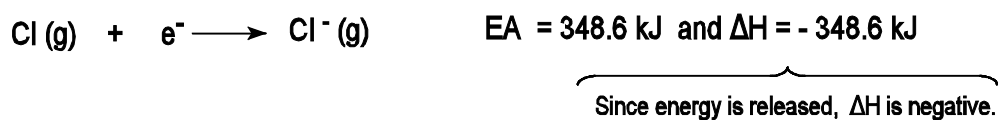
Periodic Trends in Ionization Energies



Note: The periodic trends for ionization energies are the opposite of the trends for atomic radii. As Z_{eff} increases across a period, more energy is required to remove the electron. As n increases while Z_{eff} increases only slightly down a group, less energy is needed to remove the electron.

M) Electron Affinity

The energy *released* when a *gaseous* atom or ion in its *ground state* *adds* an electron.



Periodic Trends in Electron Affinities

