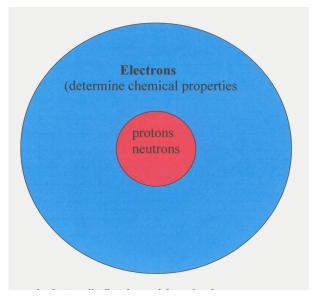
QUANTUM THEORY OF THE ATOM

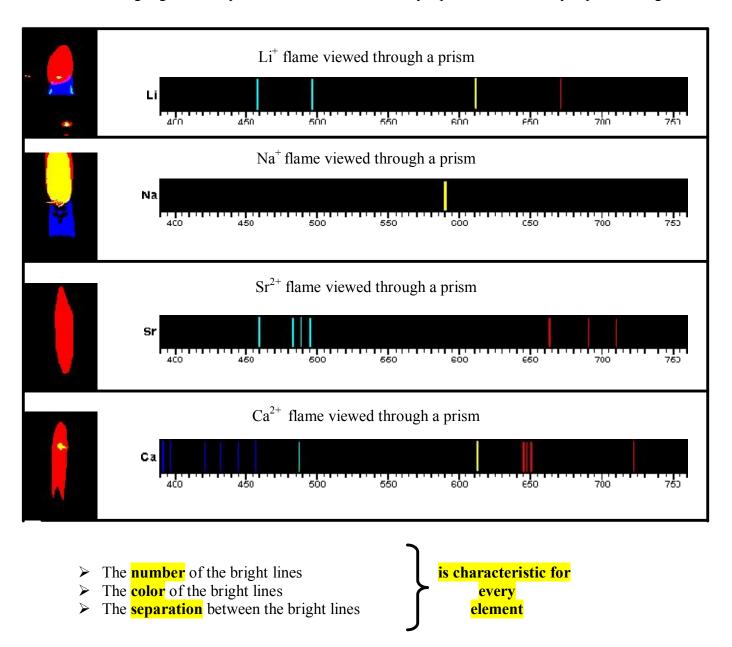
- According to Rutherford's Atomic Model, an atom consists of:
 - 1. a very small and dense **NUCLEUS** (center)
 - 2. **ELECTRONS**, which surround the nucleus.



- How are the electrons distributed around the nucleus?
- Present knowledge of ELECTRONIC STRUCTURE (arrangement of electrons around the nucleus) is based on the study of colored flames of different metals.

ATOMIC SPECTRA

- When metal compounds burn in a flame:
 - > the flame changes to a color characteristic for the element.
 - > the light given off by the flame can be resolved by a prism into distinctly separated bright lines.



• To understand the nature and origin of the light emitted by the flame tests, the nature and properties of light will be investigated.

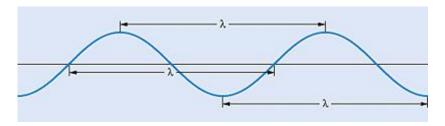
THE WAVE NATURE OF LIGHT

LIGHT:

- is a form of energy
- > is considered sometimes to travel as waves
- \triangleright consists of oscillations in electric and magnetic fields that can travel through space at a speed of 3.00 x 10⁸ m/s (in vacuum)
- is referred to as a form of ELECTROMAGNETIC RADIATION

NOTE: Visible light, X rays, gamma rays, radio waves are all forms of electromagnetic radiation.

PROPERTIES OF WAVES



λ (lambda) = Wavelength

- is the distance between any two adjacent identical points of a wave
- > is measured in units of length (m, cm, nm, Angstroms)

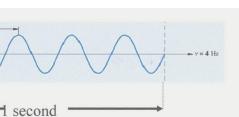
v (nu, new) = Frequency

- is the number of waves that pass through a point in one unit of time (1 s)
- > is measured in waves/second, or simply 1/second

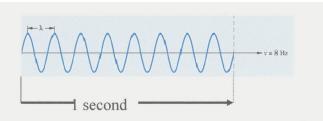
$$\frac{1}{s} = s^{-1} = 1 \text{ Hertz} = 1 \text{ Hz}$$

Relationship between Wavelength (λ), Frequency (ν), and Energy (E)

WAVE 1



WAVE 2



 λ_1 , ν_1 , E_1 speed of light (c)

 λ_2 , ν_2 , E_2 speed of light (c)

Long wavelength

$$(\lambda_1 = 2 \lambda_2)$$

Low frequency

$$(v_1 = 4 \text{ Hz})$$

Same speed

(c)

Short wavelength $(\lambda_2 = \frac{1}{2} \lambda_1)$

High frequency

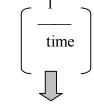
 $(v_2 = 8 \text{ Hz})$

Same speed (c)

Wavelength (λ) and Frequency (ν) are inversely proportional **NOTE:**

distance Speed = -

Speed

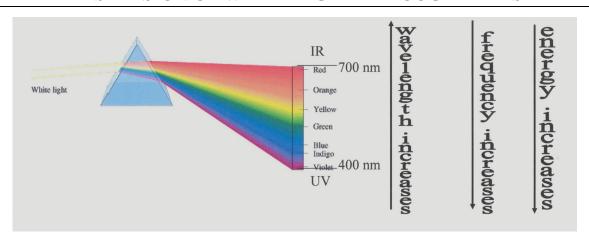


For Light Waves:

Speed of Light = Wavelength x

Frequency

DISPERSION OF WHITE LIGHT THROUGH A PRISM



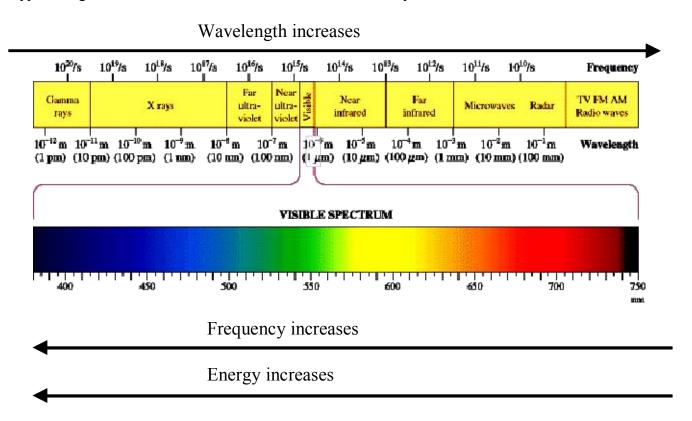
- The range of different color lights (different wavelengths) is referred to as a **SPECTRUM**
- THE SPECTRUM OF WHITE LIGHT IS A CONTINUOUS SPECTRUM

Meaning: - the colors fuse together

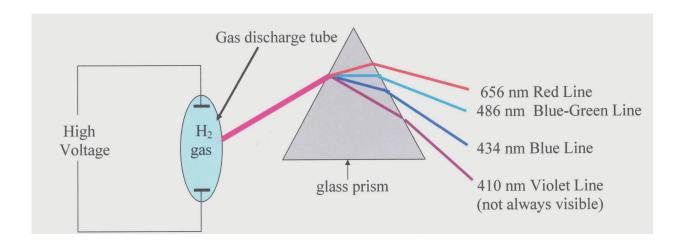
- there is **gradual transition** from

long wavelength light
 low frequency light
 low energy light
 to short wavelength light
 high frequency light
 high energy light

• Visible Light is only a very narrow portion of the Electromagnetic Spectrum which also contains other types of light radiations which are not visible to the human eye.



DISPERSION OF LIGHT EMITTED BY HYDROGEN BULB THROUGH A PRISM



The Emission Spectrum of Hydrogen



NOTE: The Emission Spectrum of Hydrogen is a BRIGHT LINE SPECTRUM

The spectrum of H contains only light of specific wavelengths, frequencies and

energies

Meaning: - the light must have been emitted by H atoms that have been energized

- the H atoms can only emit specific amounts of light energy

- it follows that the H atoms can only absorb specific amounts of energy

THE RYDBERG EQUATION

- The source of lines in the emission spectrum of Hydrogen baffled scientists for many years.
- In 1885 Rydberg (a mathematician) and Balmer (a physicist) **empirically** discovered an equation which related mathematically the wavelengths of the 4 bright lines observed in the emission spectrum of Hydrogen.
- This equation is known as **RYDBERG'S EQUATION**:

$$\frac{1}{\lambda} = 1.097 \text{ x} 10^7 \left(\frac{1}{2^2} - \frac{1}{n^2} \right) \text{ m}^{-1}$$

$$\frac{1}{2^2} = 0.25$$

n = an integer greater than 2

• Later Rydberg generalized his equation to include the wavelengths of those spectral lines whose wavelengths are not in the range of visible light.

GENERALIZED RYDBERG EQUATION:

$$\frac{1}{\lambda} = 1.097 \times 10^7 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{ m}^{-1}$$
 where: n_1 and n_2 are integers $n_2 > n_1$

Rydberg did not provide an actual explanation of the line spectra

PLANCK'S QUANTIZATION OF ENERGY

• Planck's theory is based on experimental observations.

Background:

• THE LIGHT GIVEN OFF BY A HOT SOLID VARIES WITH TEMPERATURE

At lower temperatures (750 °C) - red light is emitted

(a heated solid glows red)

At higher temperatures (1200 °C) - yellow and blue light is also emitted and mixes with the

red light (the heated solid glows white)

Planck's Explanation:

- 1. The atoms of the solid vibrate with a specific frequency which depends on the:
 - type of solid, and
 - temperature of the solid
- 2. An atom could have only certain energies of vibration: E = nhv

where: E = energy

n = an integer, called quantum number (can be 1, 2, 3...)

v = frequency of vibration

 $h = Planck's constant = 6.63 \times 10^{-34} J.s$

3. The only energies a vibrating atom can have are: hv, 2hv, 3hv, 4hv...)

PLANCK'S CONCLUSION:

• THE VIBRATIONAL ENERGIES OF THE ATOMS ARE QUANTIZED (the possible energies of atoms are limited to certain values)

THE DUAL NATURE OF LIGHT

• Traditionally: Light was considered to be made of waves

Einstein rationalized that:

- If a vibrating atom changed energy (say from 3hv to 2hv):
 - > the energy of the atom would decrease by hv,
 - > a quantum of light energy equal to hy would be emitted,
 - (called this quantum of energy a photon)

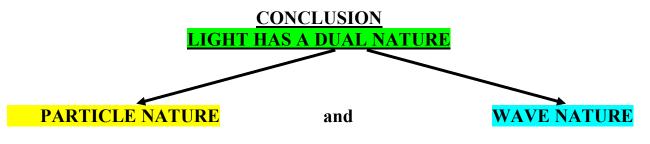
Einstein postulated that:

• Light consists of quanta of energy, called photons, which are particles of electromagnetic energy (particles of light)

E = hv where E = energy of photon (light particle) h = Planck's constant $(6.63 \times 10^{-34} \text{ J. s})$

v = frequency of light

E = h v



This is illustrated by the formula:

E = energy of a **light particle**(a photon)

v = the frequency of the associated light wave

Chapter 7 Chemistry 101

Examples:

1. What is the energy of a photon corresponding to radio waves of frequency $1.255 \times 10^6 \,\mathrm{s}^{-1}$?

$$\upsilon = 1.255 \times 10^{6} \text{ s}^{-1}$$
 $E = h \upsilon$ $E = 6.63 \times 10^{-34} \text{ J. s} (1.255 \times 10^{6} \text{ s}^{-1})$ $E = ?$ $E = 8.32 \times 10^{-28} \text{ J}$

2. Light with a wavelength of 465 nm lies in the blue region of the visible spectrum. Calculate the frequency of this light.

$$\lambda = 465 \text{ nm}$$

$$c = \lambda \times \upsilon$$

$$\upsilon = \frac{c}{\lambda}$$

$$\upsilon = \frac{3.00 \times 10^8 \frac{m}{s}}{465 \text{ nm} \times \frac{1 \text{ m}}{10^9 \text{ nm}}} = 6.45 \times 10^{14} \text{ s}^{-1}$$
at is the wavelength of microwave radiation whose frequency is $1.145 \times 10^{10} \text{ s}^{-1}$?

3. What is the wavelength of microwave radiation whose frequency is $1.145 \times 10^{10} \text{ s}^{-1}$?

$$v = 1.145 \times 10^{10} \text{ s}^{-1}$$

$$c = \lambda \times v$$

$$\lambda = \frac{c}{v}$$

$$\lambda = \frac{3.00 \times 10^8 \text{ m}}{\frac{s}{s}} = 2.62 \times 10^{-2} \text{ m}$$

$$\lambda = ?$$

4. The green line in the atomic spectrum of thallium has a wavelength of 535 nm. Calculate the energy of a photon of this light.

$$\lambda = 535 \text{ nm} \text{ x } \frac{1 \text{ m}}{10^9 \text{ nm}} = 5.35 \text{ x } 10^{-7} \text{ m}$$

$$c = 3.00 \text{ x } 10^8 \text{ m/s}$$

$$h = 6.63 \text{ x } 10^{-34} \text{ J. s}$$

$$E = h \text{ x } v \qquad c = \lambda \text{ x } v$$

$$v = \frac{c}{\lambda}$$

$$E = h \text{ x } \frac{c}{\lambda}$$

$$E = h \text{ x } \frac{c}{\lambda}$$

$$E = \frac{(6.634 \text{x } 10^{-34} \text{ J s})(3.00 \text{x } 10^8 \text{ m}/\text{s})}{5.35 \text{x } 10^{-7} \text{ m}}$$

$$E = 3.72 \text{ x } 10^{-19} \text{ J}$$

BOHR'S POSTULATES

- Bohr tried to account for two phenomena that were unaccounted for in his time:
 - 1. The electron in the H atom does not spiral into the nucleus (the electron would continuously give off energy as it spirals into the nucleus)
 - 2. The line spectrum of the H atom.

Bohr's Postulates:

1. ENERGY-LEVEL POSTULATE

An electron can have only specific energy values in atom, called energy levels

Consequence:

- The atom can have only specific energy values.
- Bohr derived a formula which can be used to calculate the energy values for the electron in the H atom

$$E = -\frac{R_H}{n^2}$$

where:

 $R_H = constant = 2.179 \times 10^{-18} J$

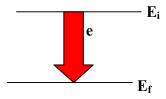
n = an integer, which can have the follow values: 1, 2, 3, 4, 5....∞ (also called the principal quantum number)

2. TRANSITIONS BETWEEN ENERGY LEVELS

An electron in an atom can change energy only by going from one energy level to another level. The electron undergoes a transition.

a) **Emission of Light Energy**

• An electron in a higher energy level (**initial** energy level, E_i) undergoes a transition to a lower energy level (**final** energy level, E_f)



In this process, the electron loses energy, which is emitted by the atom as a photon

Result: A bright line appears in the line spectrum

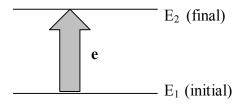
Energy of the emitted photon = $E_i - E_f = hv$

b) Absorbtion of Heat or Electrical Energy

- Normally, the electron in the H atom exists in its lowest energy level (n = 1)
- To get into a higher energy level, the electron must gain energy or get excited.

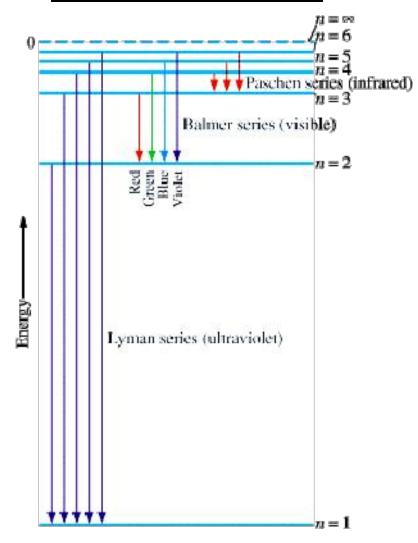
When Hydrogen gas is heated, its molecules move much faster.

High energy collision between molecules will make one atom gain energy from another, by moving the electron from the lowest energy level (E_1) to a higher level (for example E_2)



Energy absorbed = $E_f - E_i = E_2 - E_1 = hv$

Transition of the electron in the H atom



Using the concept of electron transitions, Bohr was able to reproduce Rydberg's (Balmer's) equation:

Energy of initial energy level = E_i

$$\mathbf{E_i} = -\frac{\mathbf{R_H}}{\mathbf{n_i}^2}$$

 n_i = principal quantum number for the initial energy level

Energy of final energy level = E_f

$$\mathbf{E_f} = -\frac{\mathbf{R_H}}{\mathbf{n_f}^2}$$

 $n_f = principal quantum number$ for the final energy level

Energy of the emitted photon = $\mathbf{h}v = \mathbf{E}_i - \mathbf{E}_f = (-\frac{\mathbf{R}_H}{\mathbf{n}^2}) - (-\frac{\mathbf{R}_H}{\mathbf{n}^2})$

$$hv = \frac{R_H}{n_f^2} - \frac{R_H}{n_i^2} = R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

Recall: $c = \upsilon \lambda$ and therefore $\upsilon = \frac{c}{\lambda}$

$$\mathbf{v} = \frac{\mathbf{c}}{\lambda}$$

$$h \frac{c}{\lambda} = R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

$$h \frac{c}{\lambda} = R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad \text{By rearrangement:} \quad \boxed{\frac{1}{\lambda} = \frac{R_H}{hc} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)}$$

By substituting:

 $R_H = 2.179 \times 10^{-18} \text{ J}$ $h = 6.63 \times 10^{-34} \text{ J.s}$ $c = 3.00 \times 10^8 \text{ m/s}$

$$\frac{1}{\lambda} = 1.097 \times 10^7 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) m^{-1}$$

RYDBERG'S GENERALIZED EQUATION IS OBTAINED.

Chemistry 101

Examples:

1. An electron in a hydrogen atom in the level n = 5 undergoes a transition to level n = 3. What is the **frequency** of the emitted radiation?

$$n_{i} = 5$$

$$n_{f=3}$$

$$\lambda = ???$$

$$v = ???$$

$$\frac{1}{\lambda} = 1.097 \times 10^{7} \left(\frac{1}{n_{f}^{2}} - \frac{1}{n_{i}^{2}}\right) m^{-1}$$

$$\lambda = \frac{1}{\lambda} = 1.097 \times 10^{7} \left(\frac{1}{3^{2}} - \frac{1}{5^{2}}\right) m^{-1}$$

$$\lambda = \frac{c}{\lambda}$$

2. What is the difference in energy between the two levels responsible for the violet emission line of the calcium atom at 422.7 nm?

$$\lambda = 422.7 \text{ nm x} - \text{m}$$

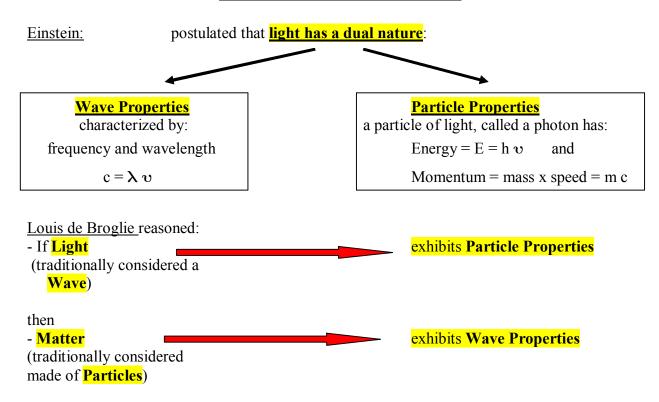
$$\mathbf{v} = \frac{\mathbf{c}}{\lambda} =$$

$$\mathbf{E} = \mathbf{h} \mathbf{v} =$$

QUANTUM MECHANICS

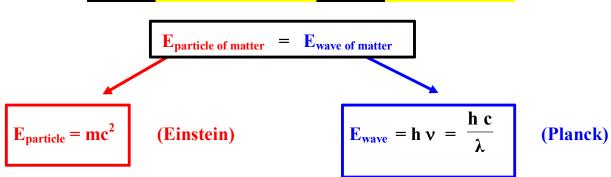
• Quantum mechanics is a theory that applies to extremely small particles, such as electrons.

DUAL NATURE OF MATTER



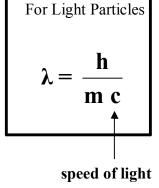
• This implies, that for a particle of matter:

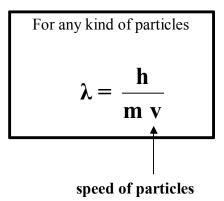
ENERGY of Particle of Matter = ENERGY of Wave of Matter



• It follows:

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





NOTE:

- 1. Wave properties of common forms of matter are not observed because their relatively large mass results in a very short wavelengths, which cannot be detected. (in the range of 10^{-34} m)
- 2. Electrons, with a very small mass produce longer wavelengths which can be detected (in the range of 10^{-9})

CONCLUSION: THE ELECTRON HAS DUAL NATURE:

• The electron has both particle and wave properties

WAVE FUNCTIONS

Erwin Schrodinger (1926)

- Based on de Broglie's work devised a theory that could be used to find the wave properties of electrons
- Established the basis of **quantum mechanics** (the branch of physics that mathematically describes the wave properties of submicroscopic particles)
- Motion is viewed differently by Classical Mechanics and by Quantum Mechanics;

Motion in Classical Mechanics

(for example: the path of a thrown ball)

- The path of the ball is given by its position and velocity at various times
- We think of the ball as moving along a continuous path

Motion in Quantum Mechanics:

For example: the motion of an electron in an atom

- The electron is moving so fast and it has such a small mass, that its **path cannot be predicted.**
- **Heisenberg's Uncertainty Principle** states that for particles of very small mass and moving at high speeds, it is impossible to predict:
 - > the exact location of the particle at any particular time,
 - > the direction in which the particle is moving
- In Bohr's theory, the electron was thought of as orbiting around the nucleus, in the way the earth orbits the sun.
- Quantum Mechanics completely invalidates this view of the motion of the electron

MOTION OF THE ELECTRON AS VIEWED BY QUANTUM MECHANICS

- 1. We cannot describe the electron in an atom as moving in a definite orbit.
- 2. We can obtain the probability of finding the electron at a certain point in a H atom; we can say that the electron is likely (or not likely) to be at this position.
- 3. Information about the probability of finding the electron at a certain point is given by a mathematical expression called a wave function.
- 4. The wave function indicates that the probability of finding the electron at a certain position is high at some distance away from the nucleus
- 5. A wave function for an electron in an atom is called an atomic orbital.

CONCLUSION

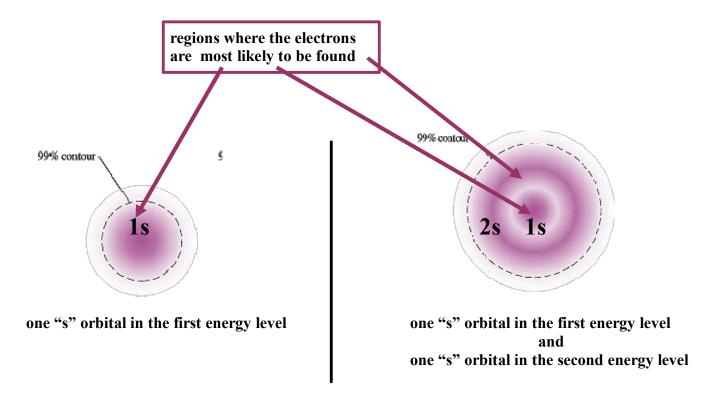
• AN ATOMIC ORBITAL IS A REGION IN SPACE WHERE THE PROBABILITY OF FINDING THE ELECTRON IS HIGH. (A region in space where the electron is most likely to be found)

ATOMIC ORBITALS

- Atomic orbitals are regions in space where the electron is most likely to be found.
- Atomic Orbitals are of 4 types that differ in:
 - > their shape
 - > the number of orbitals that group together
 - > their energy

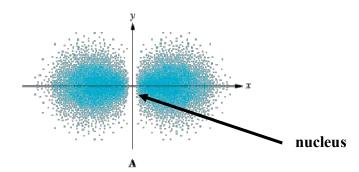
I. "s" Orbitals are the simplest orbitals

- The shape of an "s" orbital is spherical.
- An "s" orbital occurs alone (there is only one "s" orbital in any particular energy level)

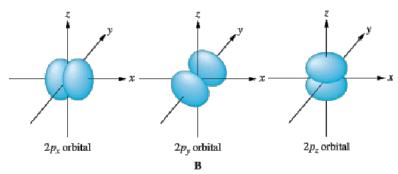


II. "p" orbitals

The shape of a "p" orbital is like a dumbbell (two lobes arranged along a straight line with the nucleus between the lobes)

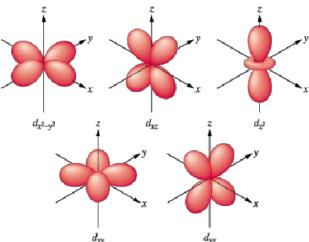


"p" orbitals occur in group of three set at right angles to each other (there are three "p" orbitals in any particular energy level)



III. "d" orbitals

- These orbtals have complex shapes
- ➤ They occur in group of five (there are **five "d" orbitals** in any particular energy level)

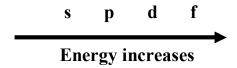


IV. "f" orbitals

- > These orbitals have complex shapes
- ➤ They occur in group of seven (there are seven "f" orbitals in any particular energy level)

IMPORTANT POINTS TO REMEMBER ABOUT ORBITALS:

1. The energy of the different types of orbitals increases in the following order



• Remember the type of orbitals in increasing energy order:

"Some People Don't Forget" s p d f

2. Orbitals occur in a specific number in a group:

ORBITALS	OCCUR IN GROUP OF
s	1 (alone)
p	3
d	5
f	7

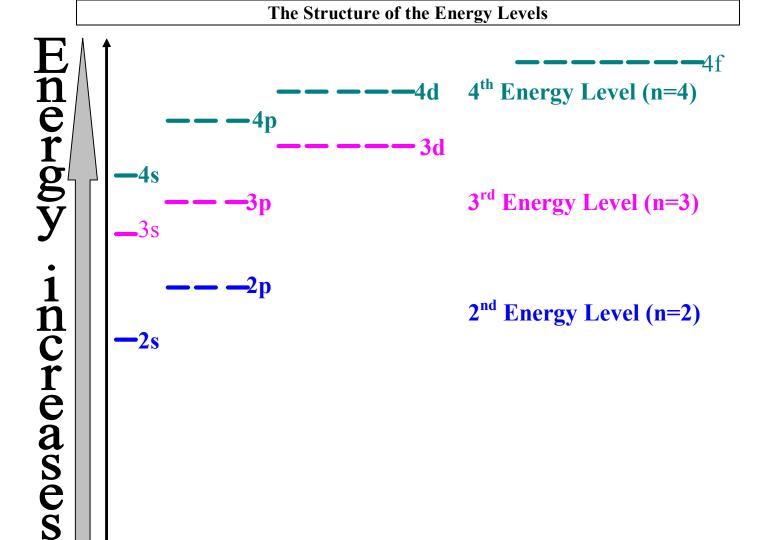
3. Several orbitals of the same type form (constitute) an Energy Sublevel (sometimes called a Subshell)

There are several types of sublevels, depending on the types of orbitals they contain:

"s sublevel" contains: one s orbital an "p sublevel" three p orbitals contains: a "d sublevel" five d orbitals contains: a "f sublevel" seven f orbital contains: an

4. <u>Several sublevels with close values of energy form (constitute) an Energy Level (sometimes called an Electron Shell)</u>

```
1<sup>st</sup> Energy Level contains: one sublevel: 1s
2<sup>nd</sup> Energy Level contains: two sublevels: 2s 2p
3<sup>rd</sup> Energy Level contains: three sublevels: 3s 3p 3d
4<sup>th</sup> Energy Level contains: four sublevels: 4s 4p 4d 4f
5<sup>th</sup> Energy Level contains; five sublevels: 5s 5p 5d 5f, 5g
```



Note: - Energy values increase with increasing values of "n".

As "n" increases:

- > the spacing between successive levels decreases
- the structure of the energy levels becomes more complex

Result: From the "3rd Energy Level", the sublevels start to overlap:

4s is lower than 3d
5s is lower than 4d
7s is lower than 5f
6s is lower than 5d

1st Energy Level (n=1)

QUANTUM NUMBERS AND ATOMIC ORBITALS

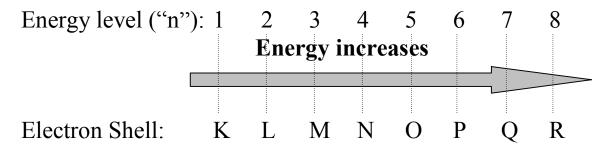
Each orbital is described by 3 quantum numbers:

1. PRINCIPAL QUANTUM NUMBER ("n")

- Identifies the **Energy Level** in which the orbital is found
- n can have only positive values; $n = 1, 2, 3, 4, 5, 6, 7, 8, \dots$
 - o the smaller "n" is, the lower the energy
- n also determines the **Size of the Orbital**:

For example:

- An orbital in a 3rd energy level ("n=3") is larger than an orbital in the 2nd energy level ("n=2")
- An orbital in the second energy level is larger than an orbital in the first energy level (n=1)
- **Energy Levels** are sometimes also referred to as **"Electron Shells"** and designated by letters (starting from K, in alphabetical order)



- The First Energy Level (n=1) is also referred to as the K shell
- The Second Energy Level (n=2) is also referred to as the L shell, and so on.

2. SECONDARY QUANTUM NUMBER ("I")

- Also called Angular momentum Quantum Number or Azimuthal Quantum Number
- "I" distinguishes orbitals of different shapes
- "I" identifies different sublevels (also referred to as "subshells)
- For a given "n" (a specific energy level): "l" can have the following values: 0, 1, 2, 3,(n-1)

For example:

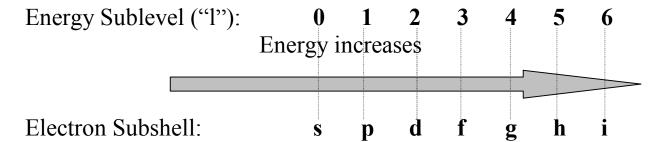
- For $\underline{\mathbf{n} = \mathbf{1}}$ (1st energy level)
 - l = 0 (only one type of orbital shape exists which is spherical) (identifies the 1s sublevel)

(identifies the 1s sublevel) For n = 2 (2^{nd} energy level)

- <u>l = 0</u>: one spherical orbital is identified (2s sublevel)
- l = 1: three dumbbell orbital are identified (2p sublevel)

Note: "1" cannot be 2, since its largest value is (n-1), which is 1

• Sublevels (subshells) are commonly designated by Letters:



It follows:

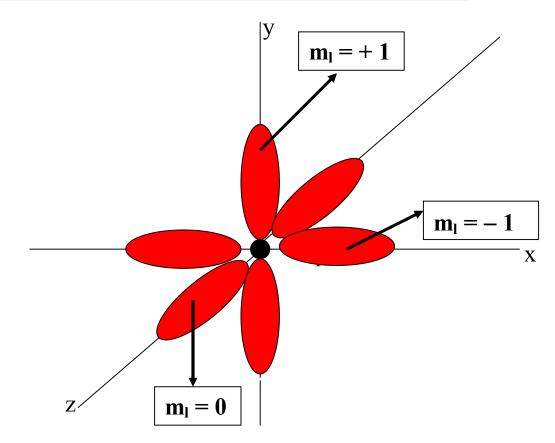
1st Energy Level	(n = 1) l = 0	An"1s" sublevel	1 sublevel
2 nd Energy Level	(n = 2) l = 0 l = 1	A "2s" sublevel A "2p" sublevel	2 sublevels
3 rd Energy Level	(n = 3) l = 0 l = 1 l = 2	A "3s" sublevel A "3p" sublevel A "3d" sublevel	3 sublevels
4 th Energy Level	(n = 4) l = 0 l = 1 l = 2 l = 3	A "4s" sublevel A "4p" sublevel A "4d" sublevel A "4f" sublevel	4 sublevels
5 th Energy Level	(n = 5) l = 0 l = 1 l = 2 l = 3 l = 4	A "5s" sublevel A "5p" sublevel A "5d" sublevel A "5f" sublevel A "5g" sublevel	5 sublevels

3. MAGNETIC QUANTUM NUMBER ("m₁")

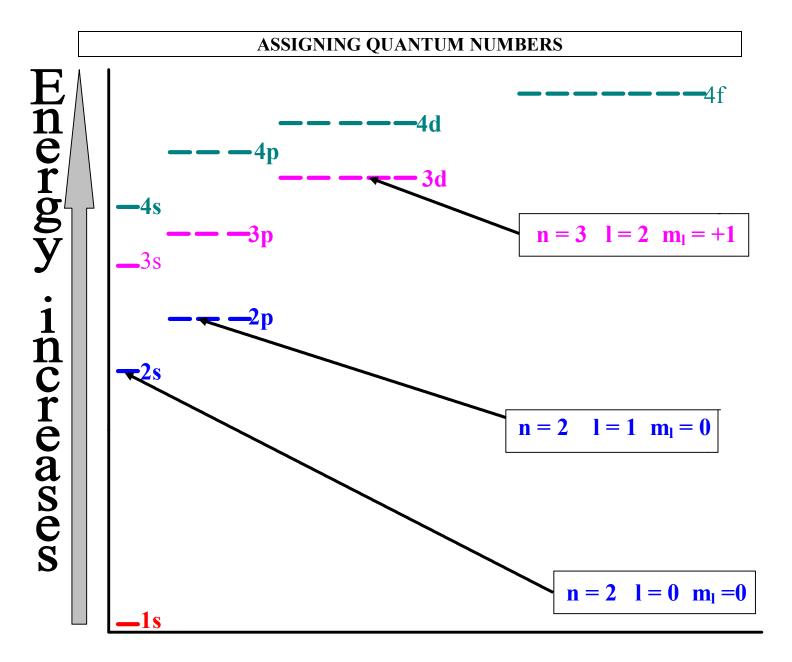
- Indicates the orientation in space of different orbitals that belong
 - > to the same energy sublevel (same "l"), and
 - > to the same energy level (same "n")
- The allowed values for "m₁" are integers ranging from "-l" to "+l"

For example:

For $l=0$ ("s" subshell) $m_l=0$ There is only one orbital in the "s" subshell				
For 1=1	("p" subshell)	$m_l = -1$ $m_l = 0$		
$m_l = +1 \label{eq:ml}$ There are three orbitals in the "p" subshell				



n Principal Quantum #	l Secondary Quantum #	m _l Magnetic Quantum #	Subshell Notation	# of Orbitals in Sublevel	# of Orbitals in Energy Level
1	0	0	1s	1	1
	0	0	2s	1	4
2	1	-1 0 +1	2p	3	
	0	0	3s	1	
3	1	-1 0 +1	3 p	4	9
	2	-2 -1 0 +1 +2	3d	5	
	0	0	4s	1	16
4	1	-1 0 +1	4 p	3	
	2	-2 -1 0 +1 +2	4d	5	
	3	-3 -2 -1 0 +1 +2 +3	4f	7	
n	n subshells				n² orbitals



Examples:

- 1. If the "n" quantum number of an atomic orbital is 4, what are the possible values of "l"?
- 2. Give the notation (using letter designations for "l") for the subshells denoted by the following quantum numbers:

$$n = 6 \quad l = 2$$

$$n = 4 \quad l = 3$$

$$n = 6 \quad l = 1$$