18PCB101J
Engineering Physics, Chemistry and Biology

Chemistry - UNIT- III

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Quantum Mechanical Model of an Atom

Historical Background

- **Rishi Kanad** (6th – 4th century BCE): *paramanu* (atom) is an indestructible particle of matter.

- **John Dalton** (1766 – 1844)

1. Elements are made of extremely small particles called atoms.

2. Atoms of a given element are identical in size, mass and other properties; atoms of different elements differ in size, mass and other properties.

(Wrong! Note: Isotopes, Isobar etc)

3. Atoms cannot be subdivided, created or destroyed.

4. Atoms can be combined, separated or rearranged.

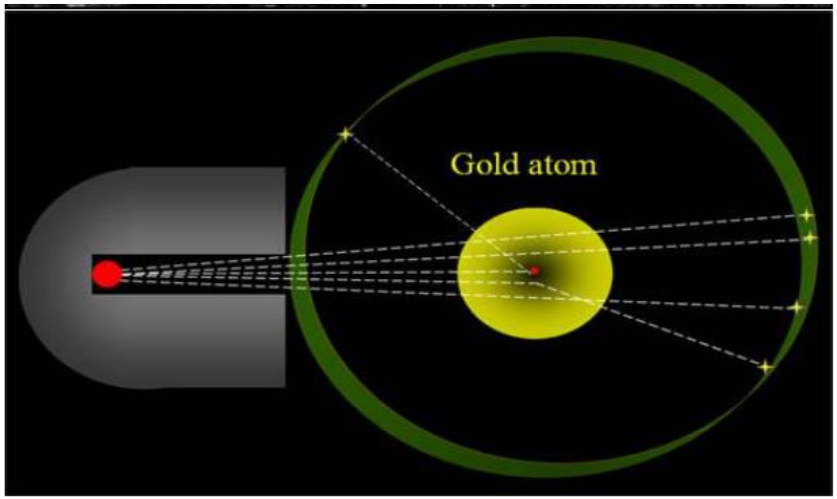
Atoms can be subdivided further – Electron, Proton, and Neutron!

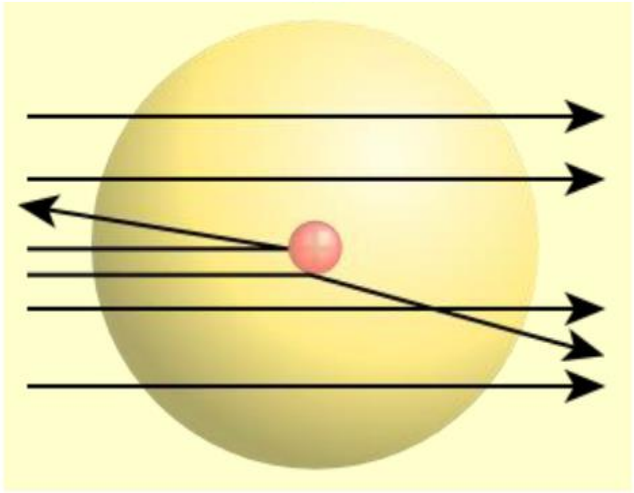
Many other scientists contributed…….

Rutherford's Gold-Foil Experiments

- Rutherford's conducted an experiment by bombarding a thin sheet of gold with α-particles and then studied the trajectory of these particles after their interaction with the gold foil.

❑ Rutherford (1911): Explained the gold foil experiment. Very high central positive charge concentrated into a very small volume in comparison to the rest of the atom and with this central volume also containing the bulk of the atomic mass. This region would be known as the nucleus of the atom.





Conclusion

- A major fraction of the α-particles bombarded towards the gold sheet passed through it without any deflection, and hence **most of the space in an atom is empty**.
- Some of the α-particles were deflected by the gold sheet by very small angles, and hence the **positive charge** in an atom **is not uniformly distributed**. **The positive charge** in an atom **is concentrated in a very small volume**.

- Very few of the α-particles were deflected back, that is only a few α-particles had nearly 180° angle of deflection. So the **volume occupied by the positively charged particles in an atom is very small as compared to the total volume of an atom**.

Size of Nucleus compared to the Atom is as a Ball compared to a Football Field.

Size of atom
$\sim 10^{-8}$m

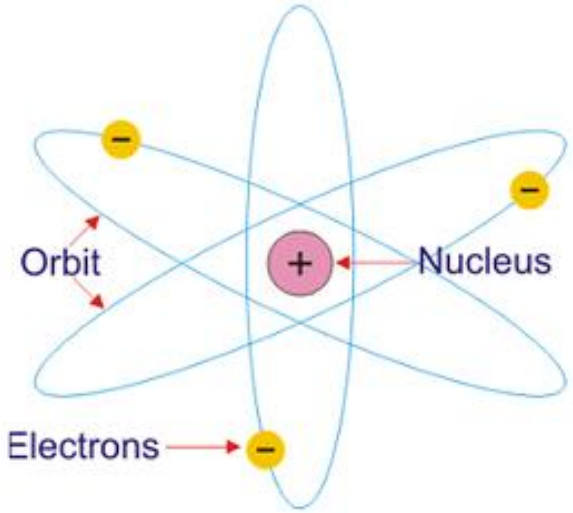
Size of nucleus
$\sim 10^{-15}$m

Rutherford's Model of Atomic Structure

- The positively charged particles and most of the mass of an atom was concentrated in an extremely small volume. He called this region of the atom as a **nucleus**.

- The model proposed that the negatively charged electrons surround the nucleus of an atom, and revolve around it with very high speed in circular paths. He named these circular paths as **orbits**. (Ref: Kepler's planetary motion)

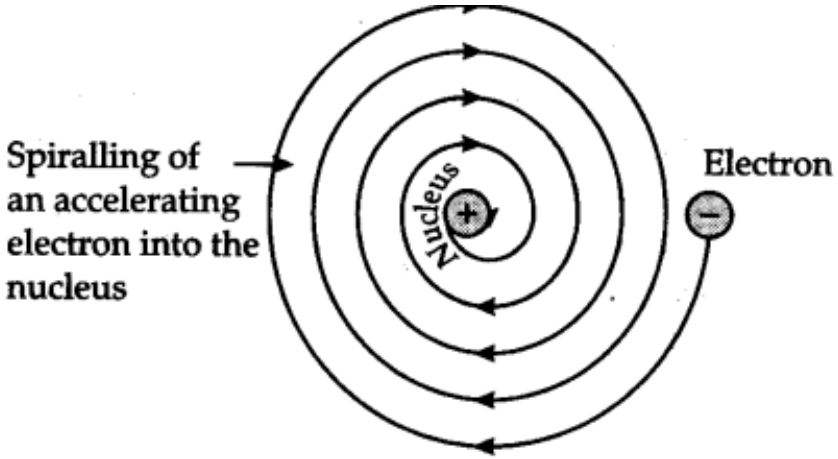
- Electrons being negatively charged and nucleus being a densely concentrated mass of positively charged particles are held together by a strong electrostatic force of attraction.



Drawbacks

• According to Maxwell (theory or electromagnetic waves), accelerated charged particles emit electromagnetic radiations and hence an electron revolving around the nucleus should emit electromagnetic radiation. This radiation would carry energy from the motion of the electron which would come at the cost of shrinking of orbits. Ultimately the electrons would collapse in to the nucleus. So Rutherford model was **not in accordance with Maxwell's theory and could not explain the stability of an atom**.

• The model did not say anything about the arrangement of electrons in an atom.



- The future models are collective efforts by many scientists in the field of Quantum Mechanics…

Status of Atomic Structures before 1913

- Atom is stable.
- Atom is electrically neutral.
- Atom has a positively charged nucleus and negatively charged electrons.
- Electrons have to rotate around the nucleus so that the centrifugal force can balance coulombic attraction.

The concept of Quantum – The origin of Quantum Physics

Quantum = how much (Latin)

- **Planck's Postulate:** the electromagnetic energy could be emitted only in **quantized** form (**discrete or packets of energy**), in other words, the energy could only be a multiple of an elementary unit:

$$E = nhv$$

where n is an integer (1, 2, 3.....) and h = Planck constant

($h = 6.62 \times 10^{-34}\ J.s$)

Max Planck, Nobel prize in Physics, 1918

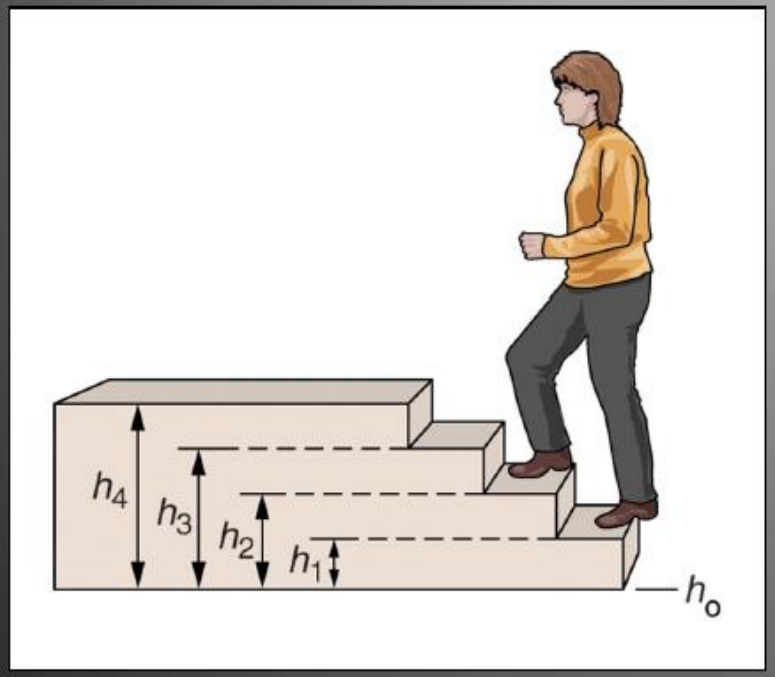
- Note: Einstein's Photoelectric effect is also based on the concept of quantization of energy (photon).

- Dual Nature of light (both particle and wave) – photon (particle)

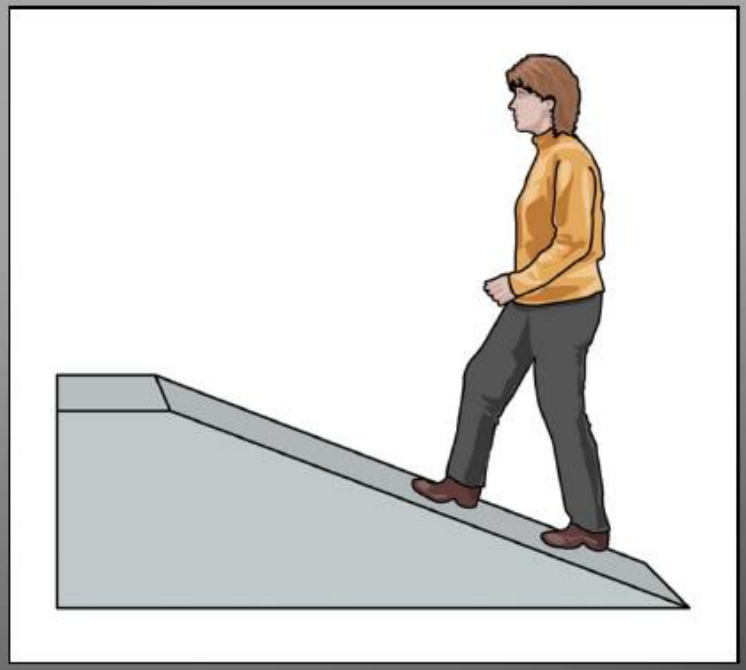
Concept of Quantized Energy

four specific potential energy values

Quantized Energy



Continuous Energy



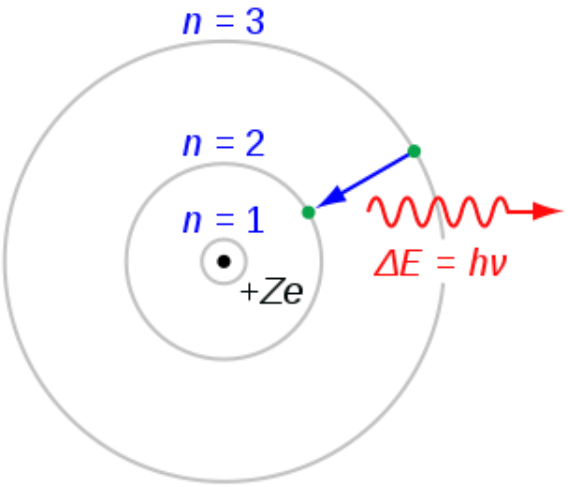
Bohr Model or Bohr-Rutherford Model

Bohr utilized the concept of Planck's Quantum theory

1. The electron is able to revolve in certain stable orbits around the nucleus without radiating any energy. These stable orbits are called stationary orbits, and are attained at certain discrete distances from the nucleus. The electron cannot have any other orbit in between the discrete ones.

2. The stationary orbits are attained at distances for which the angular momentum of the revolving electron is an integer multiple of the reduced Planck constant: $m_e vr = n\hbar$ where n = 1, 2, 3, ... is called the principal quantum number, and $\hbar = h/2\pi$. The lowest value of n is 1; this gives the smallest possible orbital radius of 0.0529 nm known as the Bohr radius. Once an electron is in this lowest orbit, it can get no closer to the proton.

3. Electrons can only gain and lose energy by jumping from one allowed orbit to another, absorbing or emitting electromagnetic radiation with a frequency ν determined by the energy difference of the levels according to the Planck relation: $\Delta E = E_2 - E_1 = h\nu$, where h is Planck's constant.

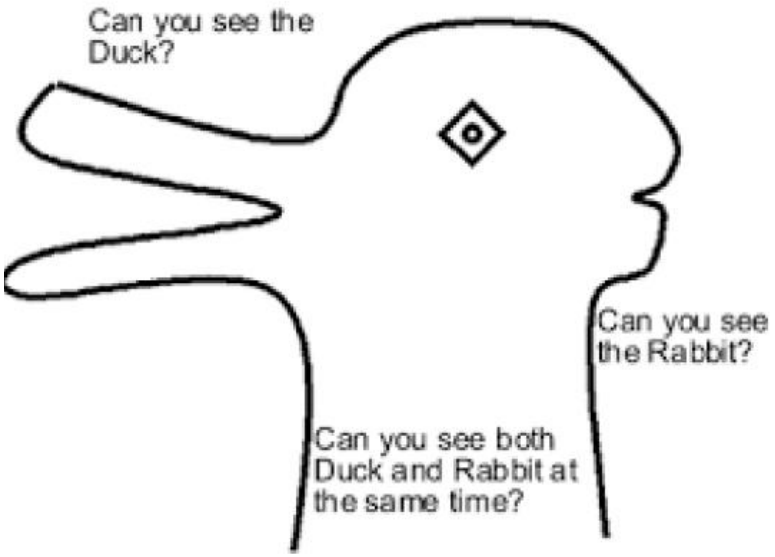


de Broglie's Hypothesis : Wave-particle duality

- **Wave nature of electron**

- Louis de Broglie suggested that similar to dual nature of light **every moving matter has an associated wave**. The wave associated with the moving particle is known as ***matter wave*** or ***de-Broglie wave.***

- de Borglie wavelength of matter waves



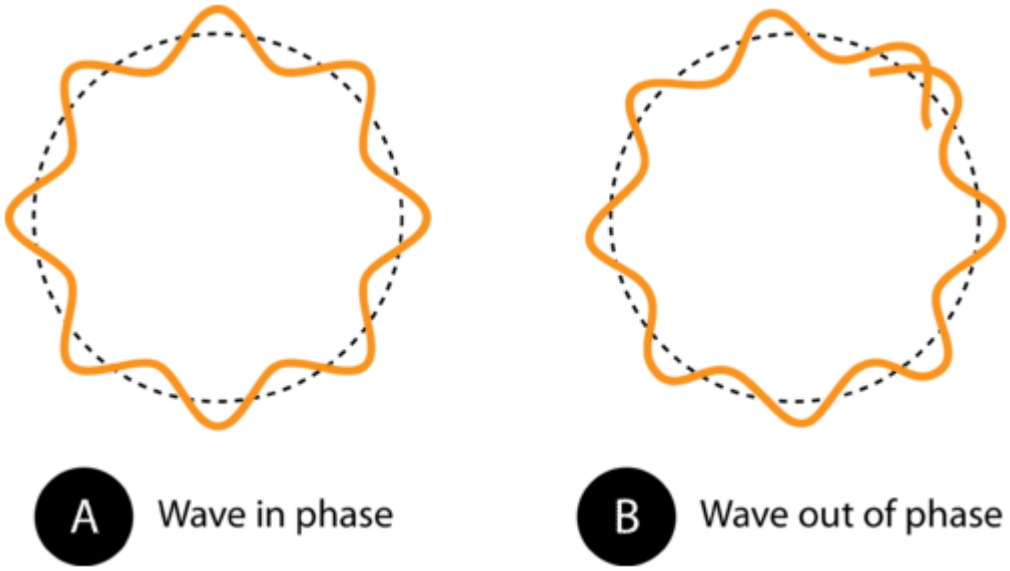
Nobel Prize in Physics in 1929

de Broglie's Quantization Rule and Bohr Theory

Even if one considers electron as a particle it has to satisfy Bohr's theory.

de Broglie's quantization rule →

To have a stationary orbit there must fit integral number of waves within the circumference of the orbit.



Heisenberg's Uncertainty Principle

- It is impossible to know both the position and velocity of an electron simultaneously.

If uncertainty in position and momentum are Δx and Δp respectively, then:

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi} \quad \text{or} \quad \Delta x \Delta p \geq \frac{\hbar}{2}$$

$$\hbar = \frac{h}{2\pi}$$

h-bar or *h*-cross = reduced Planck's Constant

Nobel Prize in Physics in 1932

- The more accurately you know the position (i.e., the smaller Δx is), the less accurately you know the momentum (i.e., the larger Δp is); and vice versa

- Only we can know the probability of finding an object at a particular position

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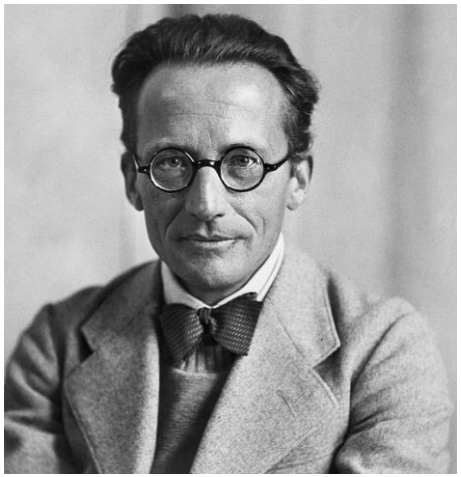
Schrödinger Equation

- Predicts the probable location of an electron around the nucleus

Erwin Schrödinger refined the wave-particle theory proposed by de Broglie. He developed an equation that treated an electron like a wave and predicted the probable location of an electron around the nucleus called the atomic orbital.



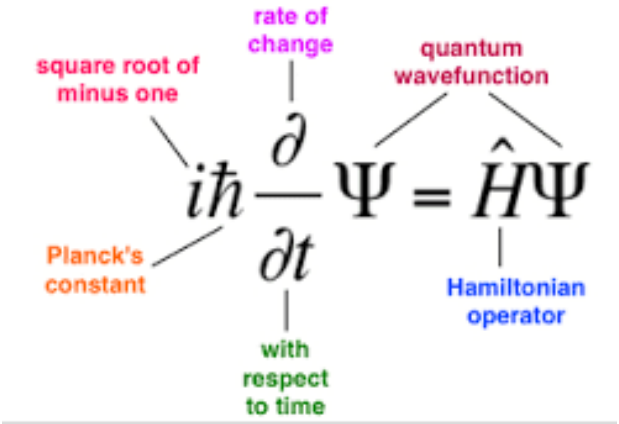
Nobel Prize in Physics in 1933

Wave function (Ψ) : Mathematically describes the wave characteristics of a particle. This is a complex valued entity. The square of the wave function, Ψ^2, however, does have physical significance. The probability of finding the particle described by a specific wave function Ψ at a given point and time is proportional to the value of Ψ^2.

Schrödinger Equation

- **Time dependent Equation for Progressive wave:**

$$H(t)|\psi(t)\rangle = i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle$$



- **Time independent Equation for standing wave:**

$$\hat{H}\,\Psi = E\,\Psi$$

Hamiltonian Operator (Energy operator)

Energy eigenvalue

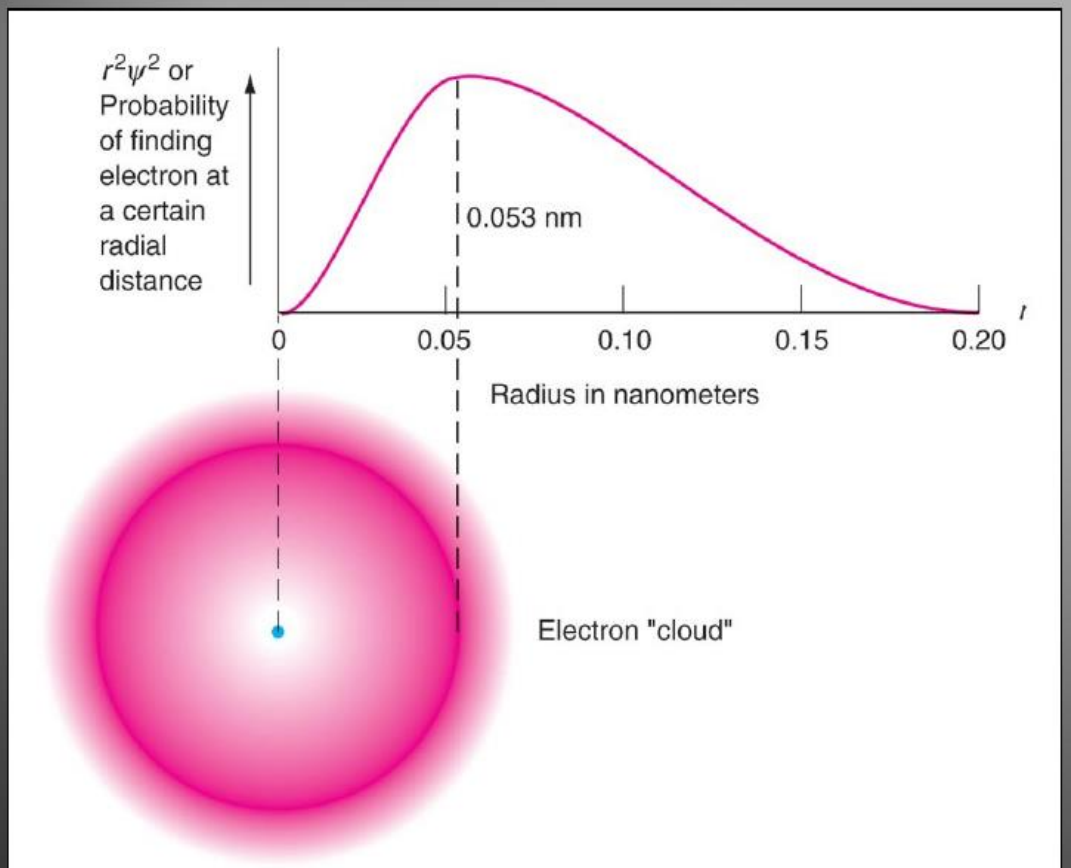
- It is used in physics and most of chemistry to deal with problems about the atomic structure of matter. It is an extremely powerful mathematical tool and the whole basis of wave mechanics.

- Shapes of orbitals are the outcome of Schrödinger equation.

Guidelines for Quantum Mechanics

1. Define the Potential Energy (V), Kinetic energy
2. So, define the Energy Operator
3. Solve the Schrödinger Equation
4. Solve for the wavefunctions
5. Solve for the allowed energies

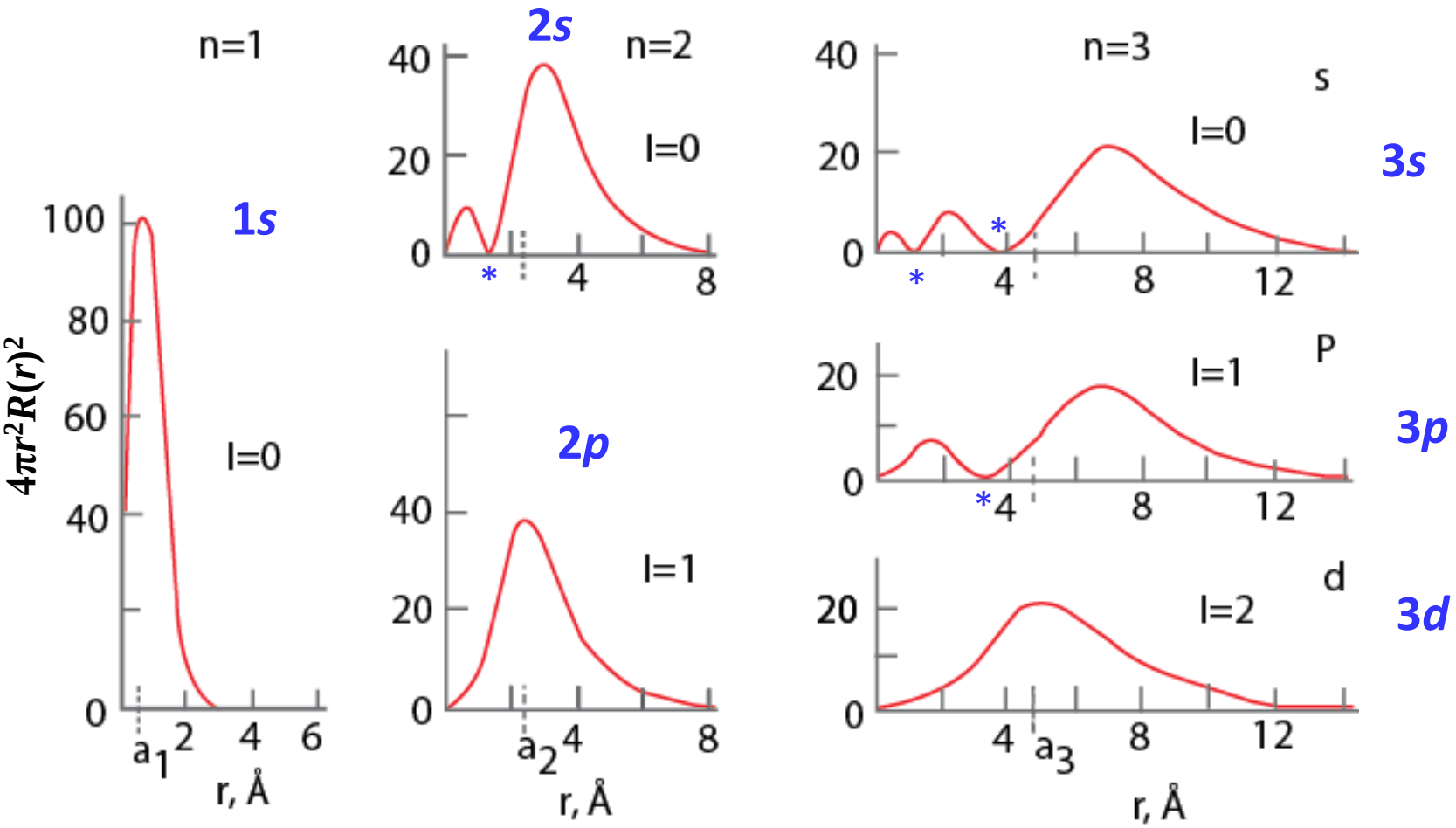
$r^2 \Psi^2$ (Probability) versus r (Radius)



- A plot of $r^2\Psi^2$ versus r for the hydrogen electron shows that the most probable radius for the hydrogen electron is r = 0.053 nm
- Same value as Bohr predicted in 1913!

Radial Distribution Function (RDF)

- **The complete wavefunction represents an orbital, in which the radial part gives its SIZE and the angular part gives its SHAPE.**
- **RDF = $4\pi r^2 R(r)^2$ = describes how density varies as a function of distance.**

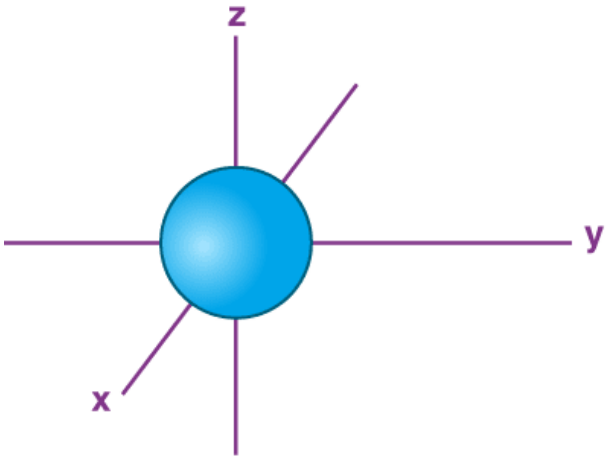


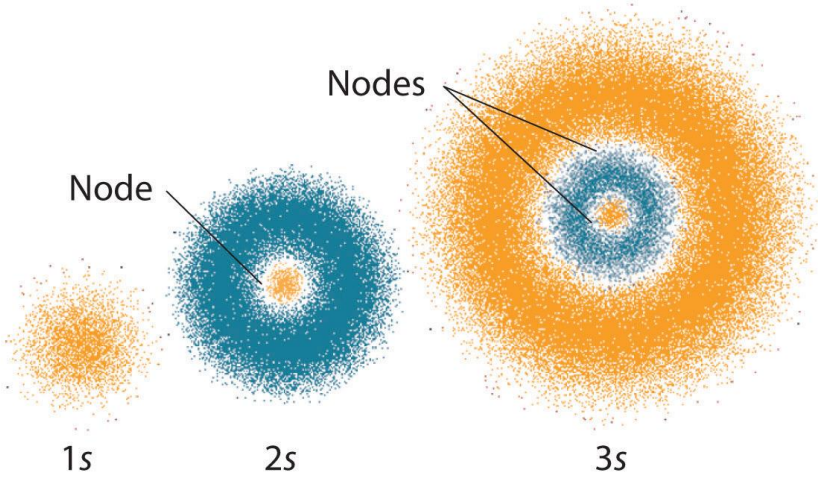
* = nodes = where probability density is zero.

Number of radial nodes = *n*-*l*-1

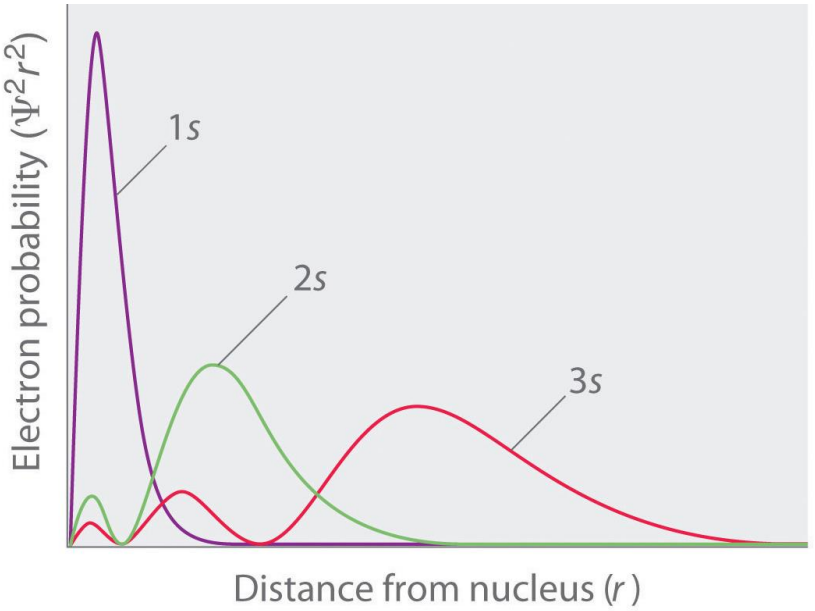
s orbitals

- The s-orbitals are spherical - the probability of finding the electron at a given distance equal in all the directions.
- The size of the s orbital is also found to increase with the increase in the value of the principal quantum number (n), thus, **4s > 3s> 2s > 1s**.





(a) Electron probability

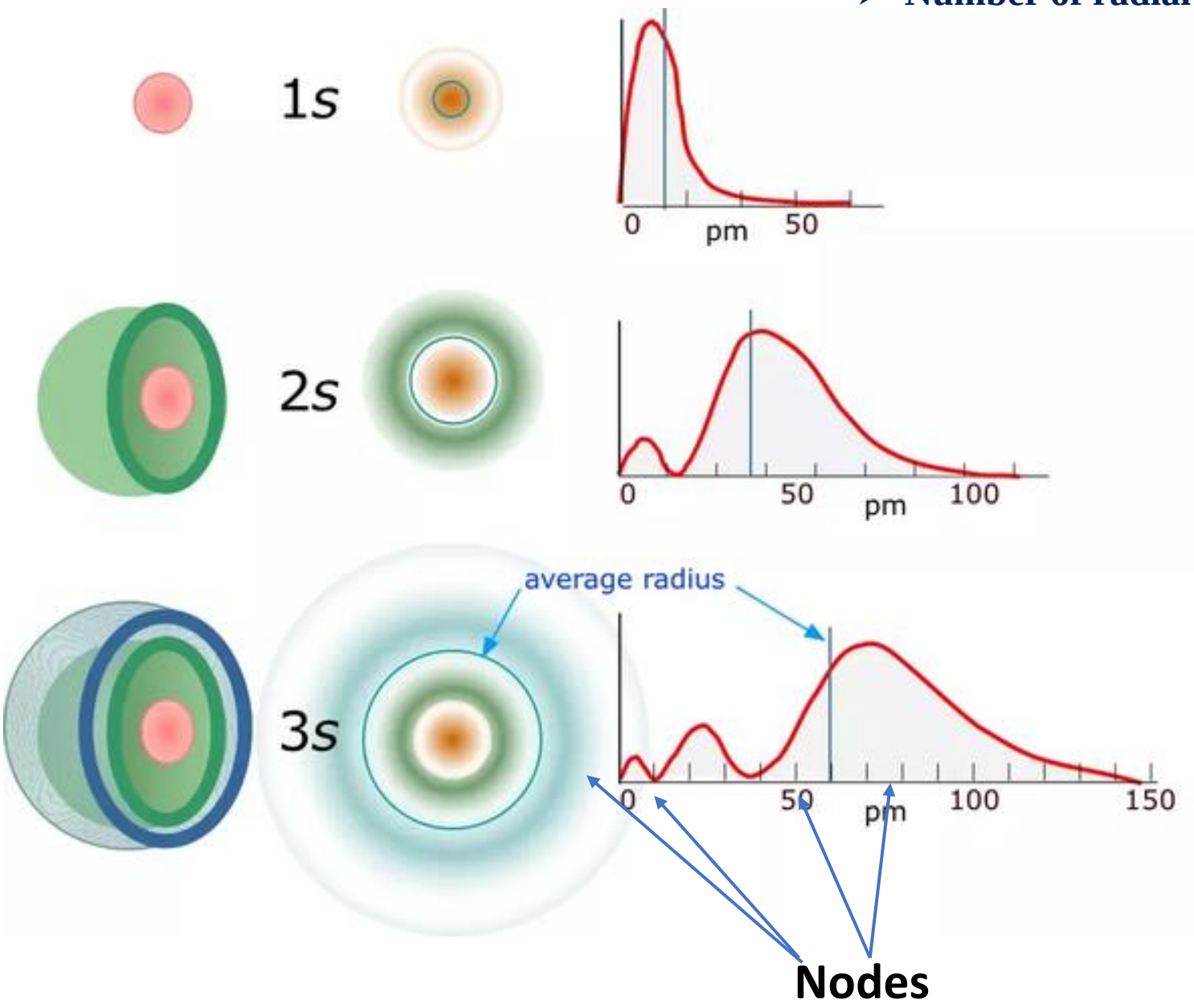


(c) Radial probability

- A radial node will occur where the radial wavefunction, **R(r)**, equals zero.
- At a node the probability of finding an electron is zero; which means that we will **never** find an electron at a node.

s orbitals

- **Number of radial nodes = *n*-*l*-1**



first shell (n=1) number of nodes= n-1=0 so there aren't any nodes

second shell (n=2) number of nodes=n-1=1 total nodes

for 2s orbital l=0 so there are 0 angular nodes and 1 radial node

for 2p orbital l=1 so there is 1 angular node and 0 radial nodes

third shell (n=3) number of nodes=n-1=2 total nodes

for 3s orbital l=0 so there are 0 angular nodes and 2 radial nodes

for 3p orbital l=1 so there is 1 angular node and 1 radial node

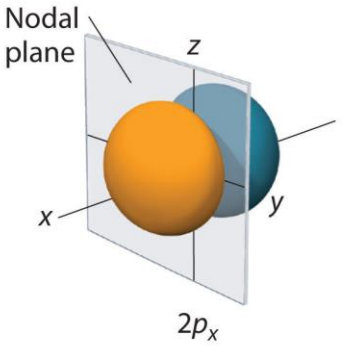
for 3d orbital l=2 so there are 2 angular nodes and 0 radial nodes

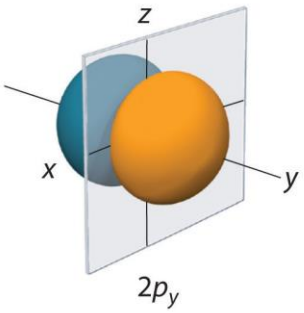
Exercise 1

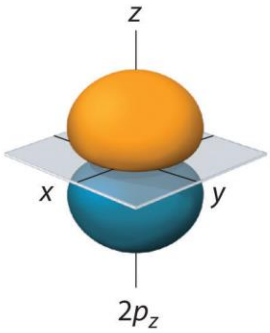
Find the radial nodes in a 3p orbital.

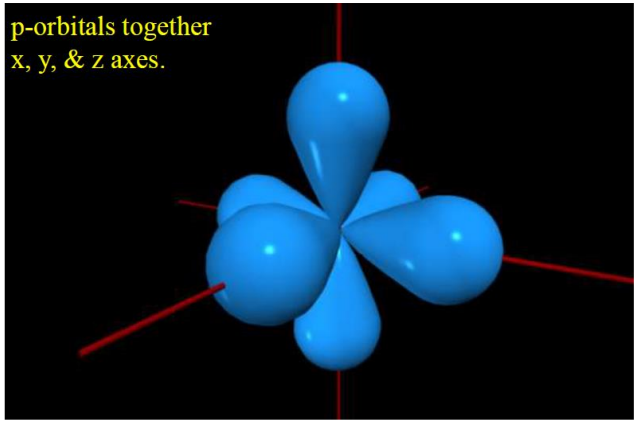
p orbitals

- Each p orbital consists of two sections, better known as lobes – dumbbell shaped
- As the lobes lie along one of the x, y or z-axis, these three orbitals are given the designations p_x, p_y, and p_z. Thus, the three p orbitals are mutually perpendicular.
- Similar to s orbitals, size, and energy of p orbitals increases with an increase in the principal quantum number (4p > 3p > 2p).



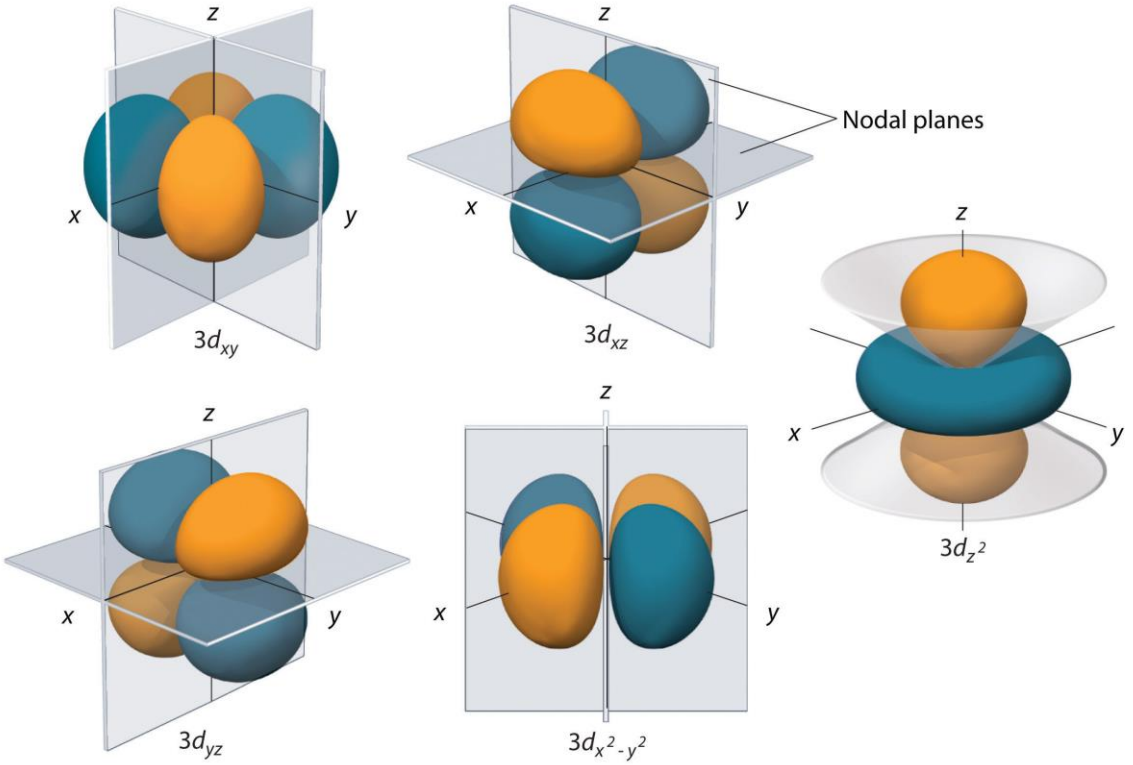




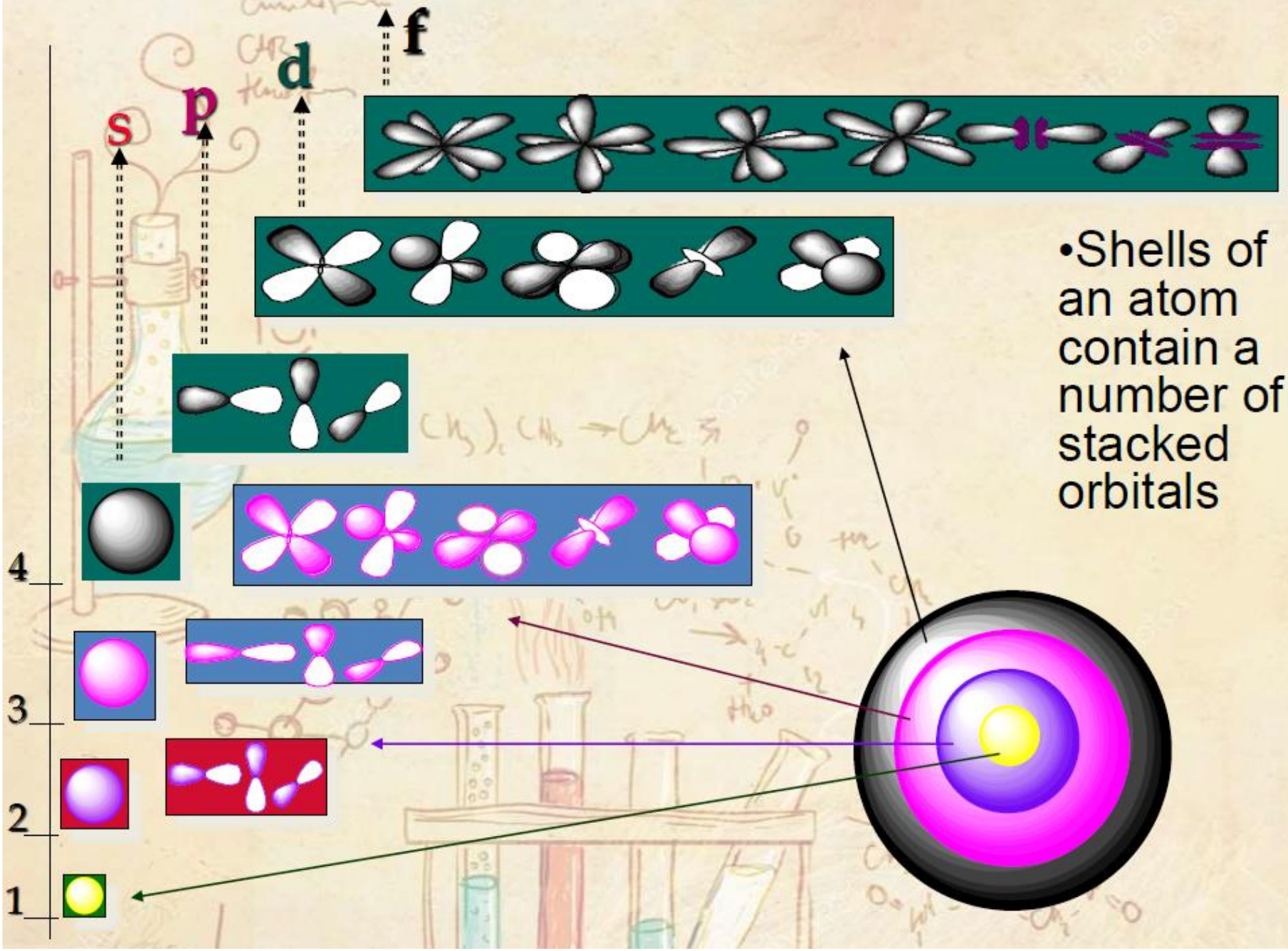


d Orbitals

- The magnetic orbital quantum number for d orbitals is given as (-2, -1, 0, 1, 2). There are five d-orbitals.
- These orbitals are designated as d_{xy}, d_{yz}, d_{xz}, $d_{x^2-y^2}$ and d_{z^2}.
- Out of these five d orbitals, shapes of the first four d-orbitals are similar to each other, which is different from the d_{z^2} orbital, whereas the energy of all five d orbitals is the same.



Shells and Orbitals and Atomic Structure

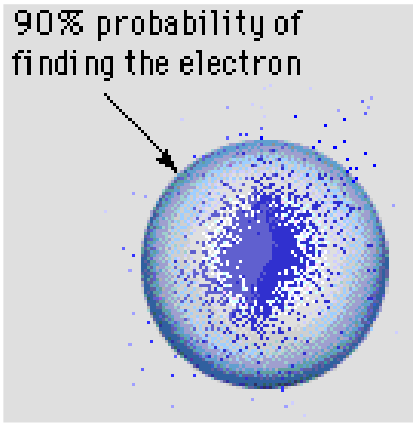


- Shells of an atom contain a number of stacked orbitals

Quantum Mechanical Model of Atom States That:

- Electrons are NOT in circular orbits around nucleus.
- Electrons are in a 3-D region around the nucleus called atomic orbitals.
- The atomic orbital describes the probable location of the electron.
- The probability of finding an electron within a certain volume of space surrounding the nucleus can be represented as a fuzzy cloud.
- The cloud is more dense where the probability of finding the electron is high.

Atomic orbitals: An atomic orbital is often thought of as a region of space in which there is a high probability (> 90 %) of finding an electron.



Quantum Numbers

- **The principal quantum number (*n*)** represents the "shell number" in which an electron "resides." n = 1 (K), 2 (L), 3 (M), 4 (N)…

- **The angular momentum (azimuthal) quantum number (*l*)** distinguishes "sub shells" within a given shell that have different shapes

- Each main "shell" is subdivided into "sub shells." Within each shell of quantum number n, there are n sub shells, each with a distinctive shape.

l can have any integer value from 0 to (n - 1)

– The different subshells are denoted by letters.

– Letter s p d f g …

– *l* 0 1 2 3 4 ….

- **The magnetic quantum number (m_l)** distinguishes orbitals within a given sub-shell that have different shapes and orientations in space. Each sub shell is subdivided into "orbitals," each capable of holding a pair of electrons. m_l can have any integer value from $-l$ to $+l$. Each orbital within a given sub shell has the same energy.

- **The spin quantum number (m_s)** refers to the two possible spin orientations of the electrons residing within a given orbital. Each orbital can hold only two electrons whose spins must oppose one another. The possible values of m_s are + ½ and - ½ .

Analogy:

- principal quantum number (n) = different floors
- angular momentum quantum number (l) = different flats on the same floor
- magnetic quantum number (m_l) = different rooms in a flat

Permissible Values of Quantum Numbers for Atomic Orbitals

Integers 0 to (n - 1)

Integers $-l$ to $+l$

n	l	m_l*	Subshell Notation	Number of Orbitals in the Subshell
1	0	0	1*s*	1
2	0	0	2*s*	1
2	1	−1, 0, +1	2*p*	3
3	0	0	3*s*	1
3	1	−1, 0, +1	3*p*	3
3	2	−2, −1, 0, +1, +2	3*d*	5
4	0	0	4*s*	1
4	1	−1, 0, +1	4*p*	3
4	2	−2, −1, 0, +1, +2	4*d*	5
4	3	−3, −2, −1, 0, +1, +2, +3	4*f*	7

*Any one of the m_l quantum numbers may be associated with the n and l quantum numbers on the same line.

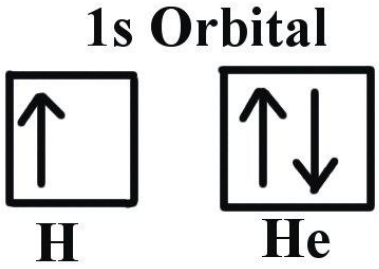
Pauli Exclusion Principle

- No two electrons in an atom can exists in the same quantum state. Accordingly, the same set of values of all four quantum numbers cannot be assigned to more than one electron in an atom.
- Two unique sets of four quantum numbers of two electrons in the 1s orbital should be:

  1, 0, 0, +½ and 1, 0, 0, -½

- Thus, s orbital can accommodate only two electrons of opposite spins.

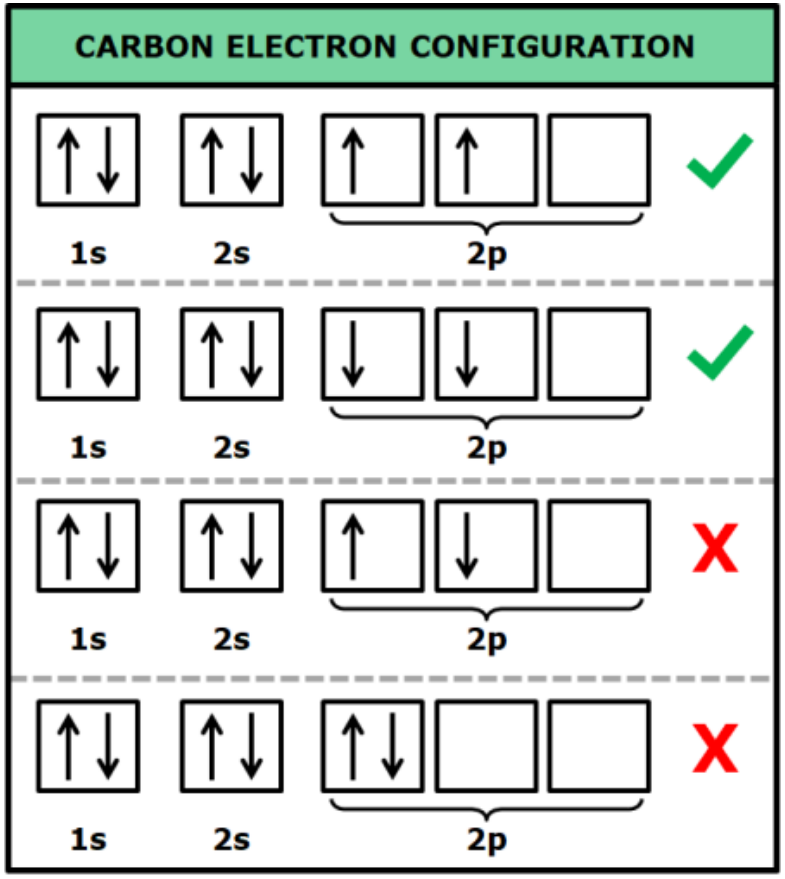
- Similarly, three *p*-orbitals can accommodate a maximum of 6 electrons.



For helium two different sets of quantum numbers for two electrons in the 1s orbitals are
1, 0, 0, +½ and 1, 0, 0, -½

Hund's Rule of maximum multiplicity

- Every orbital in a subshell is singly occupied with one electron before any one orbital is doubly occupied, and all electrons in singly occupied orbitals have the same spin.



Electron Configuration – Afbau Principle

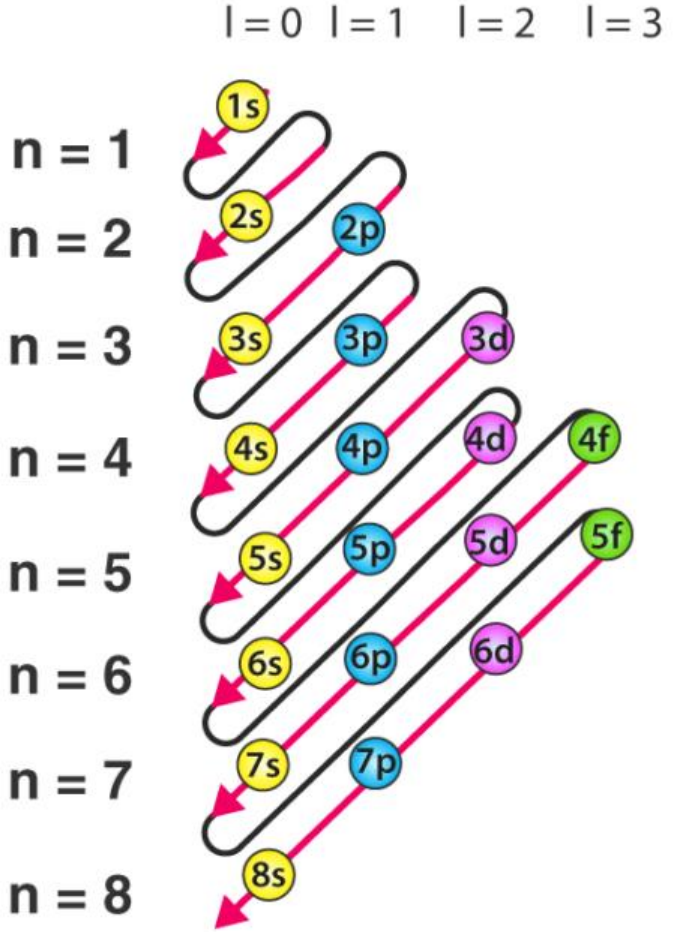
- The electron configuration of an element describes how electrons are distributed in its atomic orbitals.

- For example, the electron configuration for lithium is : $1s^2\ 2s^1$

- For phosphorus (Z = 15) it is as follows: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$.

- Afbau = building up

- The Aufbau principle dictates the manner in which electrons are filled in the atomic orbitals of an atom in its ground state. It states that electrons are filled into atomic orbitals in the increasing order of orbital energy level.



Take Home Messages

- Dual nature of electron
- Its not the exact position and energy – only the probabilities.
- Electron cloud
- Quantum numbers are like our addresses or coordinates of a place.
- The quantum mechanical model of atomic structure was developed by the collective efforts by many Scientists.

Questions

1. What are the drawbacks of Rutherford's model of atom?
2. Describe the observations of Rutherford's gold foil experiment?
3. Describe de Broglie's hypothesis. Why is the de Broglie wavelength for subatomic particle (e.g. electron) significant and why not for macro-objects (e.g. bullet)?
4. Describe Heisenberg's uncertainty principle with equation and its significances.

5. What is wave function (Ψ)? What is the significance of Ψ^2? Write the time independent Schrödinger equation and explain the parameters involved.

6. What is the significance of quantum numbers? How many quantum numbers for an electron in an atom possible?
7. What are the permissible values for angular momentum quantum number (l) for a given principal quantum number n?

8. If n = 3, l = 2, then which orbital is it?
9. What are the shapes of s-, p-, and d-orbitals? Draw these orbitals with axes labelling.
10. How many maximum electrons can be accommodated in 3d and 4f orbitals?
11. **Draw probability density plots for 1s, 2s, 2p, 3s, 3p, 3d orbitals.**
12. What is Hund's rule of maximum multiplicity and its significance?
13. Write the electron configuration for Na, N, O, F, Cl, P, Ca^{2+}, Cl^-, O^{2-}.

Thank you