ISLAMIC UNIVERSITY OF TECHNOLOGY

Computer Science and Engineering (CSE)

Chem 4241: Chemistry

Atomic Structure

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Postulates of Dalton's Atomic Theory (1805)

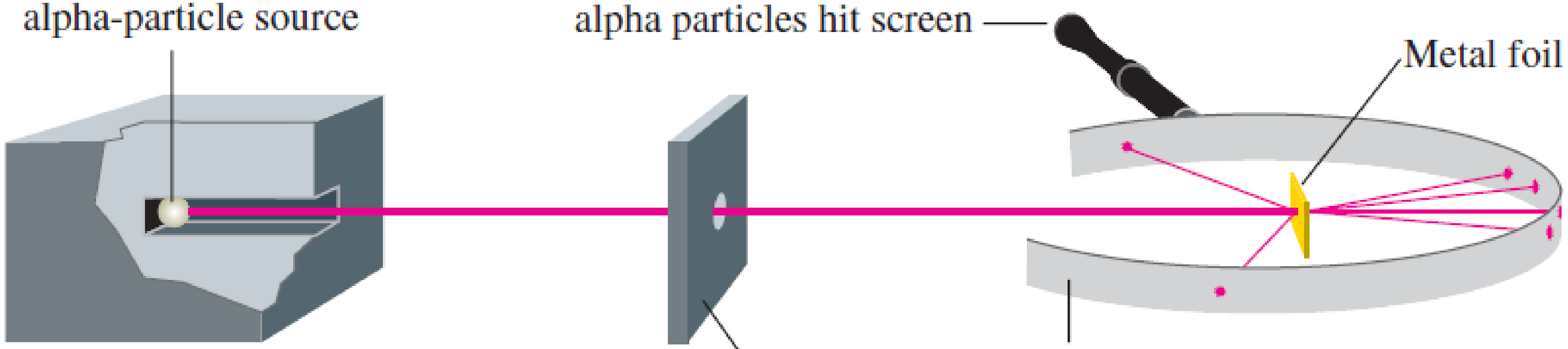
- Matter is composed of extremely small indivisible particles called atoms.
- All the atoms of a particular element have identical properties such as mass, density, chemical properties etc.
- All atoms of an element are identical, and different from those of other elements.
- Atom is the smallest particle that takes part in chemical reactions.
- Atoms can neither be created nor destroyed during chemical reactions.
- Atoms of different elements may combine in a simple whole number ratio to form compound atoms or molecules.

Limitations

- An atom can be further subdivided into protons, neutrons and electrons.
- Atoms of same element vary in their masses (Isotopes). For example, chlorine has two isotopes with mass numbers 35 and 37.
- Different atoms can have same atomic masses (Isobars). Argon and calcium atoms each have an atomic mass of 40 amu.
- The theory fails to explain the existence of allotropes. It does not account for differences in properties of charcoal, graphite, diamond.

Ernest Rutherford Alpha particle experiment

$${}_{2}^{4}He \rightarrow {}_{2}^{4}\boldsymbol{He}^{2+} + 2e^{-}$$

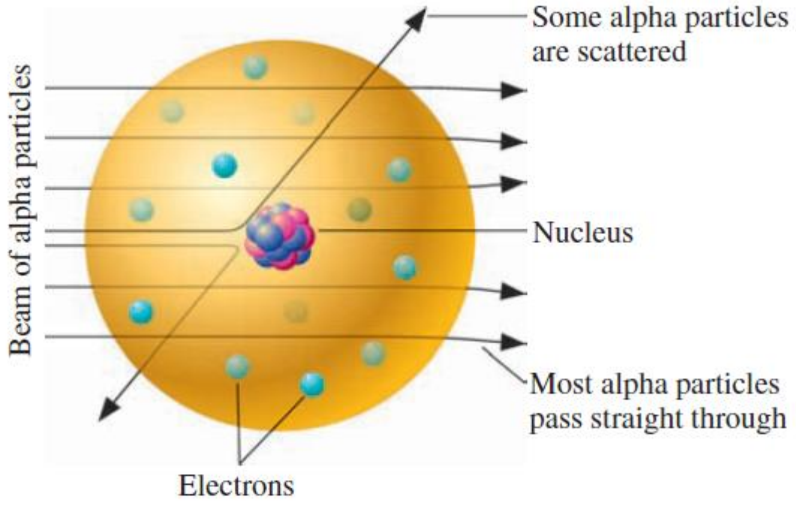


Ernest Rutherford Alpha particle experiment

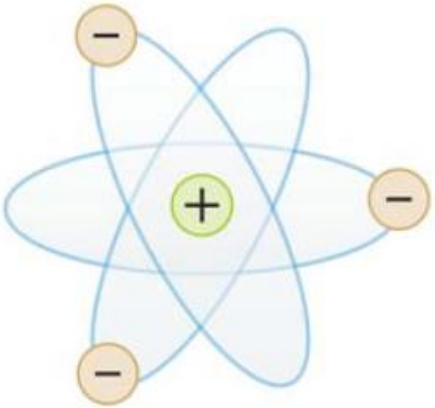
Observations

- Most of the alpha particles passed through the metal foil as though nothing were there

- A few (about 1 in 8000) were scattered at large angles and sometimes almost backward



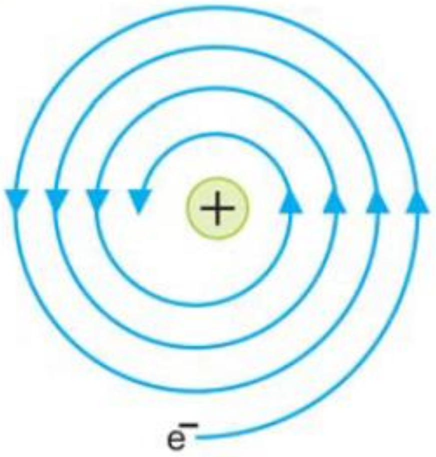
Nuclear Model of Atom (1911)



- Atom has a tiny dense central core or the nucleus which contains practically the entire mass (99.95%) of the atom, leaving the rest of the atom almost empty. The diameter of the nucleus is about 10^{-15} m as compared to that of the atom 10^{-10} m.
- The entire positive charge of the atom is located on the nucleus, while electrons were distributed in vacant space around it.
- The electrons were moving in orbits or closed circular paths around the nucleus like planets around the sun.

Limitations

According to the classical electromagnetic theory if a charged particle accelerates around an oppositely charged particle, the former will radiate energy. If an electron radiates energy, its speed will decrease and it will go into spiral motion, finally falling into the nucleus. This does not happen actually as then the atom would be unstable which it is not.



Electrons, Protons and Neutrons

An **electron** is a very light, negatively charged particle that exists in the region around the atom's positively charged nucleus.

A **proton** is a nuclear particle having a positive charge equal to that of the electron and a mass more than 1800 times that of the electron.

The **neutron** is a nuclear particle having a mass almost identical to that of the proton but no electric charge.

TABLE 2.1 Properties of the Electron, Proton, and Neutron

Particle	Mass (kg)	Charge (C)	Mass (amu)*	Charge (e)
Electron	9.10939×10^{-31}	-1.60218×10^{-19}	0.00055	-1
Proton	1.67262×10^{-27}	$+1.60218 \times 10^{-19}$	1.00728	$+1$
Neutron	1.67493×10^{-27}	0	1.00866	0

A **nuclide** is an atom characterized by a definite atomic number and mass number.

The **atomic number** (Z) is the number of protons in the nucleus of an atom.

The **mass number** (A) is the total number of protons and neutrons in a nucleus.

$${}^{A}_{Z}X$$

Isotopes, Isobars and Isotones

Isotopes: The atoms having same atomic number but different atomic mass number are called Isotopes.

$${}^{16}_{8}O,\ {}^{17}_{8}O \text{ and } {}^{18}_{8}O$$

Isobars: Nuclides having the same mass number but having the different Proton/Atomic number are called Isobar.

$${}^{76}_{32}Ce \text{ and } {}^{76}_{34}Se \qquad {}^{58}_{26}Fe \text{ and } {}^{58}_{27}Ni$$

Isotones: Atoms of different elements having different mass number and different atomic number but same neutron number are called Isotones.

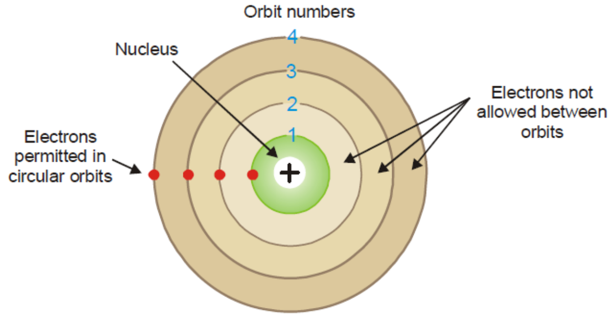
$${}^{14}_{6}C,\ {}^{15}_{7}N \text{ and } {}^{16}_{8}O$$

Select the isotopes, isobars, and isotones from the following list of atoms:

$${}^{131}_{54}Xe,\ {}^{130}_{53}I,\ {}^{132}_{55}Cs \text{ and } {}^{131}_{53}I$$

Postulates of Bohr's Theory (1913)

- **Electrons travel around the nucleus in specific permitted circular orbits and in no others**.
  Electrons in each orbit have a definite energy and are at a fixed distance from the nucleus. The orbits are given the letter designation n and each is numbered 1, 2, 3, etc. (or K, L, M, etc.) as the distance from the nucleus increases.



- **While in these specific orbits, an electron does not radiate (or lose) energy.**

- **An electron can move from one energy level to another by quantum or photon jumps only.**
  The quantum or photon of energy absorbed or emitted is the difference between the lower and higher energy levels of the atom

$$\Delta E = E_1 - E_2 = h\nu$$

  where h is Planck's constant and ν the frequency of a photon emitted or absorbed energy.

- **The angular momentum (mvr) of an electron orbiting around the nucleus is an integral multiple of Planck's constant divided by 2π.**

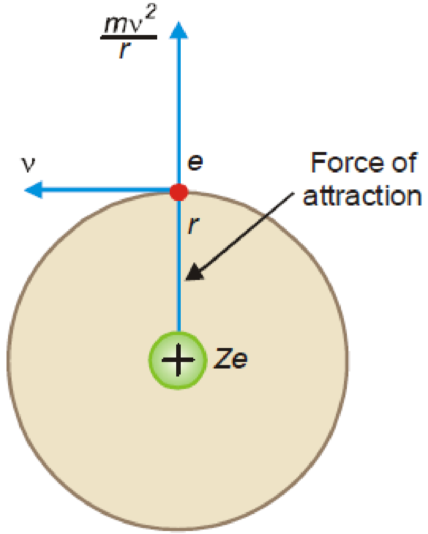
$$Angular\ momentum = mvr = \frac{nh}{2\pi}$$

  where m = mass of electron, v = velocity of the electron, r = radius of the orbit ; n = 1, 2, 3…… and h = Planck's constant.

Limitations of Bohr's Theory

- Bohr model assumed that electrons have both a known radius and orbit. But according to Heisenberg "The position and momentum of a particle cannot be simultaneously measured with arbitrarily high precision".
- Bohr model useful for predicting the behavior of electrons in hydrogen atoms but it fails to explain the spectra of larger atoms and atoms have multiple electrons. The model also didn't work with neutral helium atoms.
- The Bohr model also could not account for the Zeeman effect, where spectral lines are split into two or more in the presence of an external, static magnetic field.

Radius of Orbits



Consider an electron of charge *e* revolving around a nucleus of charge *Ze*, where *Z* is the atomic number and *e* the charge on a proton. Let *m* be the mass of the electron, *r* the radius of the orbit and *v* the tangential velocity of the revolving electron.

The electrostatic force of attraction between the nucleus and the electron (Coulomb's law),

$$= \frac{1}{4\pi\epsilon_0} \cdot \frac{Ze \times e}{r^2}$$

The centrifugal force acting on the electron

$$= \frac{mv^2}{r}$$

Bohr assumed that these two opposing forces must be balancing each other exactly to keep the electron in orbit. Thus,

$$\frac{1}{4\pi\epsilon_0} \cdot \frac{Ze \times e}{r^2} = \frac{mv^2}{r}$$

For hydrogen $Z = 1$, therefore,

$$\frac{1}{4\pi\epsilon_0} \cdot \frac{e^2}{r^2} = \frac{mv^2}{r} \implies \frac{e^2}{4\pi\epsilon_0 r} = mv^2 \quad \text{......................................(1)}$$

Radius of Orbits

According to one of the postulates of Bohr's theory, angular momentum of the revolving electron is given by the expression

$$mvr = \frac{nh}{2\pi}$$

$$v = \frac{nh}{2\pi\, mr}$$

Substituting the value of v in equation (1),

$$\frac{e^2}{4\pi\epsilon_0 r} = m\left(\frac{nh}{2\pi\, mr}\right)^2$$

Solving for r,

$$r = \frac{n^2\epsilon_0 h^2}{\pi m e^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(2)$$

Substituting the values of h, m, ϵ_0 and e in equation (2),

$$r = n^2 \times 0.529 \times 10^{-10}\ \text{m}$$

where n is the principal quantum number and hence the number of the orbit.

When $n = 1$,

$$r = 0.529 \times 10^{-10}\ \text{m} = \alpha_0$$

α_0 is called the first Bohr radius or radius of hydrogen atom in the ground state.

Radius of an orbit is directly proportional to the principal quantum number

Energy of an electron in orbits

For hydrogen atom, the energy of the revolving electron, E is the sum of its kinetic energy $\left(\frac{1}{2}mv^2\right)$ and potential energy $\left(-\frac{e^2}{4\pi\epsilon_0 r}\right)$

$$E = \frac{1}{2}mv^2 - \frac{e^2}{4\pi\epsilon_0 r} \quad \text{.........................(3)}$$

From equation (1),

$$mv^2 = \frac{e^2}{4\pi\epsilon_0 r}$$

Substituting the value of mv^2 in (3),

$$E = \frac{1}{2}\frac{e^2}{4\pi\epsilon_0 r} - \frac{e^2}{4\pi\epsilon_0 r} = -\frac{e^2}{8\pi\epsilon_0 r} \quad \text{.........................(4)}$$

Substituting the value of r from equation (2) in (4)

$$E = -\frac{e^2}{8\pi\epsilon_0} \times \frac{m\pi e^2}{\epsilon_0 n^2 h^2} = -\frac{me^4}{8\epsilon_0{}^2 n^2 h^2} \quad \text{.........................(5)}$$

Substituting the values h, m, ϵ_0 and e in equation (5),

$$E = -\frac{2.179 \times 10^{-18}}{n^2} j = -\frac{1311.8}{n^2} \; Kj \; mol^{-1}$$

Energy of an electron is inversely proportional to the principal quantum number

Explanation of Hydrogen Spectrum

According to Bohr model, the energy of the electrons in orbit n_1 and n_2 are

$$E_1 = -\frac{me^4}{8\epsilon_0{}^2 n_1{}^2 h^2} \text{ and } E_2 = -\frac{me^4}{8\epsilon_0{}^2 n_2{}^2 h^2}$$

The difference of energy between the levels n_1 and n_2 is

$$\Delta E = E_2 - E_1 = \frac{me^4}{8\epsilon_0{}^2 h^2}\left[\frac{1}{n_1{}^2} - \frac{1}{n_2{}^2}\right] \text{ .... (1)}$$

According to Planck's equation,

$$\Delta E = h\nu = \frac{hc}{\lambda} \text{.............. (2)}$$

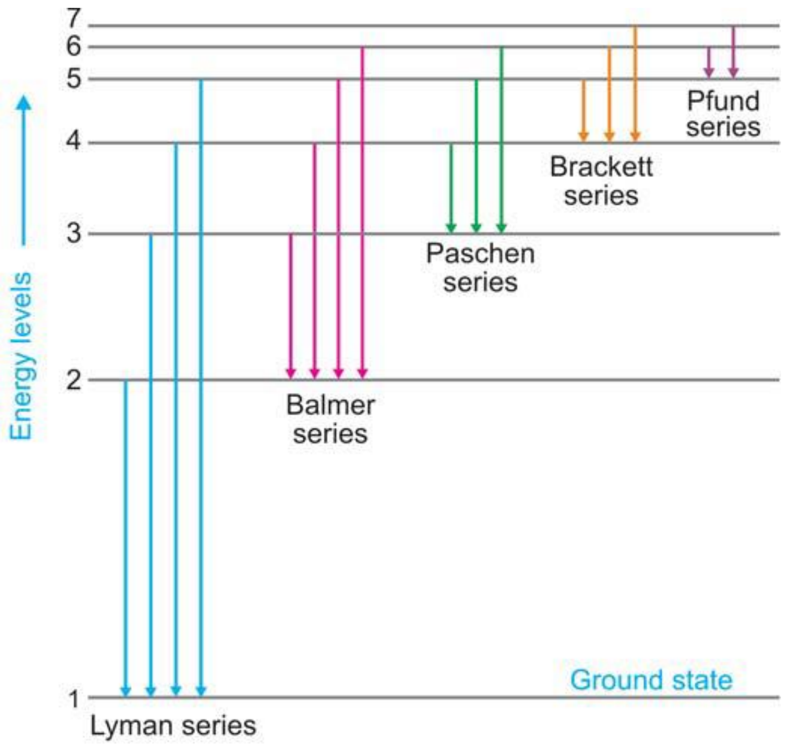
where λ is wavelength of photon and c is velocity of light.

From equation (1) and (2),

$$\frac{hc}{\lambda} = \frac{me^4}{8\epsilon_0{}^2 h^2}\left[\frac{1}{n_1{}^2} - \frac{1}{n_2{}^2}\right]$$

$$\frac{1}{\lambda} = \frac{me^4}{8c\epsilon_0{}^2 h^3}\left[\frac{1}{n_1{}^2} - \frac{1}{n_2{}^2}\right]$$

$$\frac{1}{\lambda} = R_H\left[\frac{1}{n_1{}^2} - \frac{1}{n_2{}^2}\right]$$ Where, $R_H = \frac{me^4}{8c\epsilon_0{}^2 h^3}$ = Rydberg constant = 1.097×10^7 m^{-1}



Problems

What is the wavelength (nm) of light emitted when the electron in a hydrogen atom undergoes a transition from energy level n =4 to level n = 2? Rydberg constant = 1.097×10^7 m^{-1}

$$\frac{1}{\lambda} = R_H\left[\frac{1}{n_1{}^2} - \frac{1}{n_2{}^2}\right]$$

$n_1 = 2$

$n_2 = 4$

486 nm

Find the wavelength in Å of the line in Balmer series that is associated with drop of the electron from the third orbit. Rydberg constant = 1.097×10^7 m^{-1}

A line at 434 nm in Balmer series of spectrum corresponds to a transition of an electron from the nth to 2nd Bohr orbit. What is the value of n?

Of the following possible transitions of an electron in a hydrogen atom, which emits light of the highest energy?

a. Transition from the n = 1 to the n = 3 level

b. Transition from the n = 1 to the n = 2 level

c. Transition from the n = 3 to the n = 1 level

d. Transition from the n = 2 to the n = 1 level

e. Transition from the n = 5 to the n = 4 level

Quantum Numbers

According to quantum mechanics, each electron in an atom is described by four different quantum numbers:

1. Principal Quantum Number (n)
2. Azimuthal Quantum Number/ Angular Momentum Quantum Number (l)
3. Magnetic Quantum Number (m_l)
4. Spin Quantum Number (m_s)

Principal Quantum Number (*n*) *This quantum number is the one on which the energy of an electron in an atom principally depends; it can have any positive value: 1, 2, 3, and so on*. The energy of an electron in an atom depends *principally* on *n*. The smaller *n* is, the lower the energy. The *size* of an orbital also depends on *n*. The larger the value of *n* is, the larger the orbital. Orbitals of the same quantum state *n* are said to belong to the same *shell*. Shells are sometimes designated by the following letters:

Letter	*K*	*L*	*M*	*N* . . .
n	1	2	3	4 . . .

Quantum Numbers

Angular Momentum Quantum Number (*l*) *This quantum number distinguishes orbitals of given n having different shapes; it can have any integer value from 0 to n-1*. Within each shell of quantum number *n*, there are *n* different kinds of orbitals, each with a distinctive shape denoted by an *l* quantum number.

Although the energy of an orbital is principally determined by the *n* quantum number, the energy also depends somewhat on the *l* quantum number (except for the H atom). For a given *n*, the energy of an orbital increases with *l*.

Orbitals of the same *n* but different *l* are said to belong to different *subshells* of a given shell. The different subshells are usually denoted by letters as follows:

Letter	*s*	*p*	*d*	*f*	*g* . . .
l	0	1	2	3	4 . . .

Quantum Numbers

Magnetic Quantum Number (m_l) *This quantum number distinguishes orbitals of given n and l that is, of given energy and shape but having a different orientation in space; the allowed values are the integers from -l to l.* For $l = 0$ (*s* subshell), the allowed l quantum number is 0 only; there is only one orbital in the *s* subshell. For $l = 1$ (*p* subshell), $l = -1, 0$, and 1; there are three different orbitals in the *p* subshell. The orbitals have the same shape but different orientations in space. there are $2l + 1$ orbitals in each subshell of quantum number l.

Spin Quantum Number (m_s) *This quantum number refers to the two possible orientations of the spin axis of an electron; possible values are* -1/2 *and* +1/2. An electron acts as though it were spinning. Such an electron spin would give rise to a circulating electric charge that would generate a magnetic field. In this way, an electron behaves like a small bar magnet.

Quantum Numbers

State whether each of the following sets of quantum numbers is permissible for an electron in an atom. If a set is not permissible, explain why.

a. $n = 1, l = 1, m_l = 0, m_s = +1/2$
b. $n = 3, l = 1, m_l = -2, m_s = -1/2$
c. $n = 2, l = 1, m_l = 0, m_s = +1/2$
d. $n = 2, l = 0, m_l = 0, m_s = 1$

What is the notation for the subshell in which n = 4 and l = 3? How many orbitals are in this subshell?

What is the number of different orbitals in each of the following subshells?

a. *3d* b. *4f* c. *4p* d. *5s*

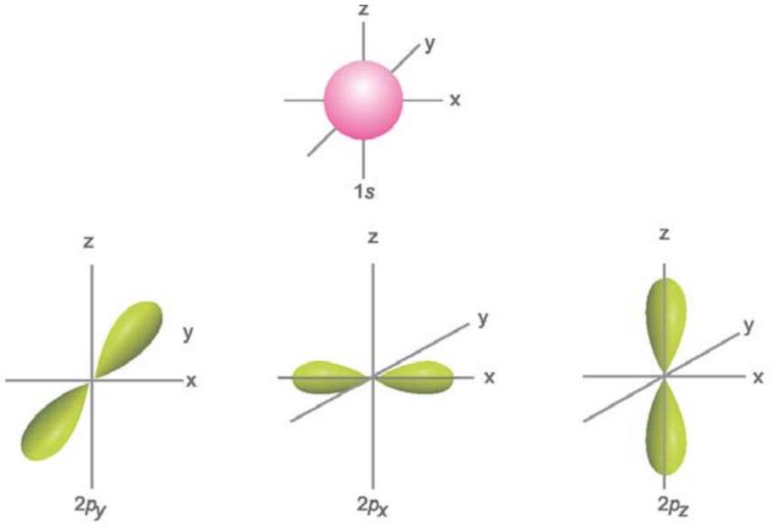
The n quantum number of an atomic orbital is 6. What are the possible values of l? What are the possible values of ml if the l quantum number is 5?

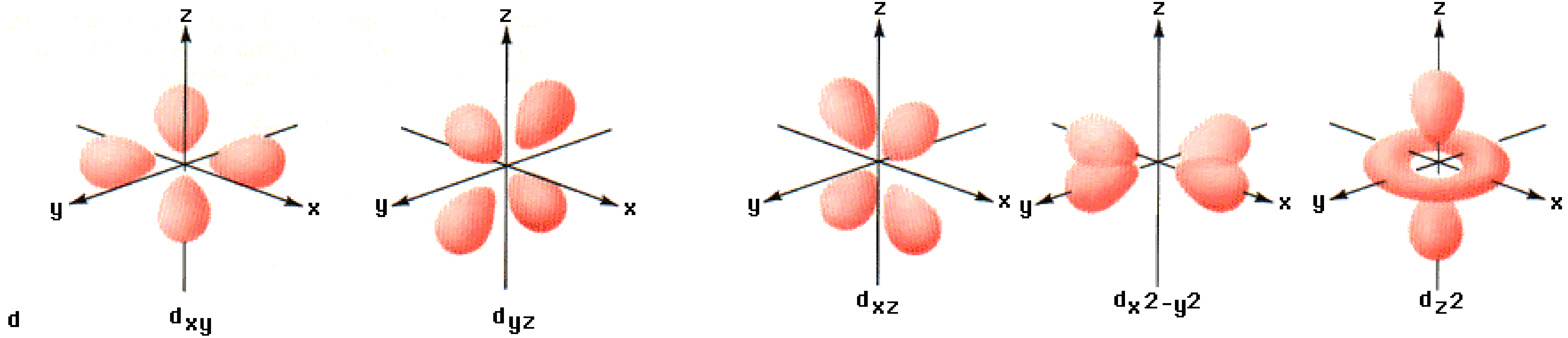
How many subshells are there in the M shell? How many orbitals are there in the f subshell?

Shape of Orbitals

Orbit: According to Bohr theory electron are revolved around the nucleus in definite circular path with certain energy. This circular path of electron is called orbit.

Orbital: According to the quantum mechanical theory, the three dimensional space around the nucleus of an atom in which probability of finding the electrons are maximum is called orbital.





Heisenberg's Uncertainty Principle (1927)

Heisenberg's uncertainty principle states that it is impossible to know precisely and accurately both the position and momentum of a particles simultaneously. It is also stated that the product of the uncertainty in position and the uncertainty in momentum of a particle can be no smaller than Planck's constant divided by 4π . Thus, letting Δ x be the uncertainty in the x coordinate of the particle and letting Δp_x be the uncertainty in the momentum in the x direction, we have

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

Here, $\Delta p_x = m\Delta v_x$

$$(\Delta x)(\Delta v_x) \geq \frac{h}{4\pi m}$$

Calculate the uncertainty in position of an electron if the uncertainty in velocity is 5.7×10^5 m sec^{-1}.

The uncertainty in the position and velocity of a particle are 10^{-10} m and 5.27×10^{-24} m sec^{-1} respectively. Calculate the mass of the particle.

de Broglie Relation (1923)

Louis **de Broglie** reasoned that if light (considered as a wave) exhibits particle aspects, then perhaps particles of matter show characteristics of waves under the proper circumstances. He therefore postulated that a particle of matter of mass *m* and speed *v* has an associated wavelength, by analogy with light:

$$\lambda = \frac{h}{mv}$$

Derivation of de Broglie equation

According to Planck, The photon energy E is given by

$E = h\nu$ --------------------------------(1)

Where h is the Planck's constant, ν (neu) is the frequency of radiation.

According to Einstein's mass-energy relationship, the energy associated with photon of mass '*m*' and velocity c is given as

$E = mc^2$--------------------------------(2)

From equation (1) and (2), we get

$mc^2 = h\nu = h\frac{c}{\lambda} \quad \left[\because \nu = \frac{c}{\lambda}\right]$

Or, $mc = \frac{h}{\lambda}$

de Broglie Relation (1923)

Or, $\lambda = \frac{h}{mc}$

Or, $\lambda = \frac{h}{p}$ Where p = mc = Momentum

Wavelength $= \frac{h}{\text{Momentum}}$

Or, Wavelength $\propto \frac{1}{\text{Momentum}}$ -----------------------------(3)

The de Broglie's equation is not true for all particles, but it is only with very small particles, such as electrons, that the wave-like aspect is of any significance. Large particles in motion though possess wavelength, but it is not measurable or observable.

(*a*) For a large mass

Let us consider a stone of mass 100 *g* moving with a velocity of 1000 cm/sec. The de Broglie's wavelength λ will be given as follows :

$$\lambda = \frac{h}{mv} = \frac{6.6256 \times 10^{-27}}{100 \times 1000} = 6.6256 \times 10^{-32} \text{ cm}$$

This is too small to be measurable by any instrument and hence no significance.

de Broglie Relation (1923)

(*b*) For a small mass

Let us now consider an electron in a hydrogen atom. It has a mass = 9.1091 × 10^{-28} g and moves with a velocity 2.188 × 10^{-8} cm/sec. The de Broglie's wavelength λ is given as

$$\lambda = \frac{h}{mv} = \frac{6.6256 \times 10^{-27}}{9.1091 \times 10^{-28} \times 2.188 \times 10^{-8}} = 3.32 \times 10^{-8} \text{ cm}$$

This value is quite comparable to the wavelength of X-rays and hence detectable. It is, therefore, reasonable to expect from the above discussion that **everything in nature possesses both the properties of particles (or discrete units) and also the properties of waves (or continuity).**

a. Calculate the wavelength (in meters) of the wave associated with a 1.00-kg mass moving at 1.00 km/hr.
b. What is the wavelength (in picometers) associated with an electron, whose mass is 9.11 × 10^{-31} kg, traveling at a speed of 4.19 × 10^{6} m/s?

2.38 × 10^{-33} m and 174 pm

Calculate the wavelength of an α particle having mass 6.6 × 10^{-27} kg moving with a speed of 10^{5} cm sec^{-1}

1 × 10^{-10} m

Schrödinger's Wave Equation

The equation for the standing wave comparable with that of a stretched string is

$\Psi = A \sin 2\pi \frac{x}{\lambda}$ ……………………………(1)

where Ψ is a mathematical function representing the amplitude of wave, *x* is the displacement in a given direction, and λ is the wavelength and *A* is a constant. Differentiating equation (1) twice with respect to x we have

$\frac{d\Psi}{dx} = A \frac{2\pi}{\lambda} \cos 2\pi \frac{x}{\lambda}$ ………………………(2) and

$\frac{d^2\Psi}{dx^2} = - A \frac{4\pi^2}{\lambda^2} \text{Sin } 2\pi \frac{x}{\lambda} = - \frac{4\pi^2}{\lambda^2} \Psi$……….(3)

The K.E. of the particle of mass *m* and velocity v is given by the relation

$K.E = \frac{mv^2}{2} = \frac{m^2v^2}{2m}$ …………………………(4)

According to Broglie's equation

$\lambda = \frac{h}{mv}$ or $\lambda^2 = \frac{h^2}{m^2v^2}$ or $m^2v^2 = \frac{h^2}{\lambda^2}$ ………....(5)

Putting the values of m^2v^2 in equation (4), we get

$K.E = \frac{1}{2} \times \frac{h^2}{m\lambda^2} = - \frac{1}{2m} \times \frac{h^2}{4\pi^2\Psi} \cdot \frac{d^2\Psi}{dx^2}$ (From equation 3, putting the values of λ^2)

Schrödinger's Wave Equation

$$K.E = -\frac{h^2}{8\pi^2 m\Psi} \cdot \frac{d^2\Psi}{dx^2} \ldots\ldots\ldots(6)$$

Total energy is the sum of kinetic energy and potential energy

$$E = K.E + P.E$$

Or $K.E = E - P.E = -\frac{h^2}{8\pi^2 m\Psi} \cdot \frac{d^2\Psi}{dx^2}$

Or, $\frac{d^2\Psi}{dx^2} = -\frac{8\pi^2 m}{h^2}(E - P.E)\Psi$

Or, $\frac{d^2\Psi}{dx^2} + \frac{8\pi^2 m}{h^2}(E - P.E)\Psi = 0 \ldots\ldots\ldots (7)$

This is Schrödinger's equation in one dimension. It need be generalized for a particle whose motion is described by three space coordinates x, y and z. Thus,

$$\frac{d^2\Psi}{dx^2} + \frac{d^2\Psi}{dy^2} + \frac{d^2\Psi}{dz^2} + \frac{8\pi^2 m}{h^2}(E - P.E)\Psi = 0 \ldots\ldots\ldots(8)$$

This equation is called the **Schrödinger's Wave Equation.** The first three terms on the left-hand side are represented by $\Delta^2\psi$.

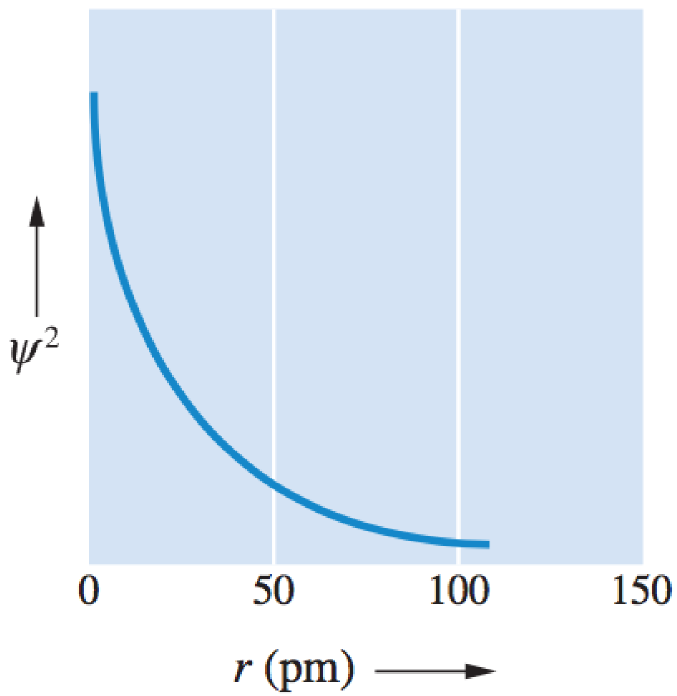
$$\Delta^2\Psi + \frac{8\pi^2 m}{h^2}(E - P.E)\Psi = 0 \ldots\ldots\ldots(9)$$

Where, $\Delta^2 = \frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}$ is called **Laplacian Operator.**

Significance of ψ and ψ^2

Information about a particle in a given energy level is contained in a mathematical expression called a *wave function,* ψ. Its square, ψ^2, gives the probability of finding the particle within a region of space.

The wave function and its square, ψ^2, have values for all locations about a nucleus. Figure shows values of ψ^2 for the electron in the lowest energy level of the hydrogen atom along a line starting from the nucleus. Note that ψ^2 is large near the nucleus ($r = 0$), indicating that the electron is most likely to be found in this region. The value of ψ^2 decreases rapidly as the distance from the nucleus increases, but ψ^2 never goes to exactly zero, although the probability does become extremely small at large distances from the nucleus. This means that an atom does not have a definite boundary, unlike in the Bohr model of the atom.



The square of the wave function (ψ^2) is plotted versus distance, r, from the nucleus.