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SCHRÖDINGERS WAVE EQUATION:

Let consider that electron behaves like a stationary wave, so its motion can be described by the wave function ψ . ψ alone have no significance, ψ^2 denotes probability of finding an electron within small volume element $(dx dy dz) d\tau$ around the point (x,y,z) within space.

From Heisenbergs uncertainty principle we know that we can not find exact position and momentum of an electron, so we can find only the probability of finding it around a point (x,y,z) .

The wave motion of a vibrating string can be described by the equation:

$$\psi = A \sin 2\pi x/\lambda \quad \text{-----(1)}$$

On differentiation with respect to x we have:

$$d\psi/dx = A \cos 2\pi x/\lambda (2\pi/\lambda) \quad \text{-----(2)}$$

differentiating again with respect to x:

$$d^2\psi/dx^2 = -4\pi^2/\lambda^2 A \sin 2\pi x/\lambda$$

$d^2\psi/dx^2 = -4\pi^2 \psi / \lambda^2 \quad \text{-----(3)}$

This equation is called classical wave equation , which describes the wave motion of any wave vibrating along x-axis.

From de-Broglies Equation we have:

$$\lambda^2 = h^2 / m^2 c^2$$

or
$$d^2\psi/dx^2 = -4\pi^2 m^2 c^2 \psi / h^2$$

or
$$d^2\psi/dx^2 = -8\pi^2 m E_K \psi / h^2$$

or
$$d^2\psi/dx^2 = -8\pi^2 m(E - E_p) \psi / h^2 \quad \text{-----(4)}$$

If the motion is described by three space coordinates x,y,z, then the above becomes

$$(d^2\psi/dx^2 + d^2\psi/dy^2 + d^2\psi/dz^2) = -8\pi^2 m(E - E_p) \psi(x,y,z) / h^2$$

or,

$\nabla^2 \psi = -8\pi^2 m(E - E_p) \psi(x,y,z) / h^2 \quad \text{-----(5)}$
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∇^2 is called LAPLACIAN OPERATOR

Equation (6) is called as SCHRÖDINGERS WAVE EQUATION. This can also be written as follows:

$$[-h^2/8\pi^2 m(d^2\psi/dx^2 + d^2\psi/dy^2 + d^2\psi/dz^2) + E_p]\psi = E \psi$$

------(7)

or

$$H\Psi = E\Psi$$

H = Hamiltonian operator.

In Polar coordinate,

$$x = r \sin\theta \cos \phi$$

$$y = r \sin\theta \sin \phi$$

$$z = r \cos \theta$$

$$\frac{1}{r^2} \left[\frac{d}{dr}(r^2 \frac{d\psi}{dr}) + \frac{1}{\sin\theta} \frac{d}{d\theta}(\sin\theta \frac{d\psi}{d\theta}) + \frac{1}{\sin^2\theta} \frac{d^2\psi}{d\phi^2} \right] + \frac{8\pi^2 m}{h^2} (E - E_p)\psi = 0$$

$$\text{For H atom } E_p = -e^2/r$$

$$\Psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$$

The classical and quantum mechanical wave equation are of a special class of equations called Eigen value equation. Eigen value equation have the format

$$op.f = constant.f$$

op = operator; C = Constant; f = function

The Eigen value equation have the property that operating on a function , regenerates the same function times a constant. The function that satisfied the above equation called the Eigenfunction of the operator. The constant C is called the EIGENVALUE associated with the Eigenfunction f.

CONDITIONS ON Ψ

Eigen Function must have following properties.

- (i) FINITE
- (ii) SINGLE VALUED
- (iii) CONTINUOUS
- (iv) NORMALISED
- (v) ORTHOGONAL

Arnold Sommerfelds' Theory

In 1915 Sommerfeld suggested that the moving electron might describe, in addition to the circular orbits, elliptical orbits as well with the nucleus situated at one of the foci. According to Sommerfeld the two quantum numbers are (i)

Radial quantum number, n_r and

(ii) Azimuthal quantum number, n_ϕ

and these are related as $n = n_r + n_\phi$

[n = total quantum number]

n and n_ϕ are related to the geometry of ellipse as

n/n_ϕ = length of major axis/ length of minor axis

$n_\phi < n$ then elliptical orbit.

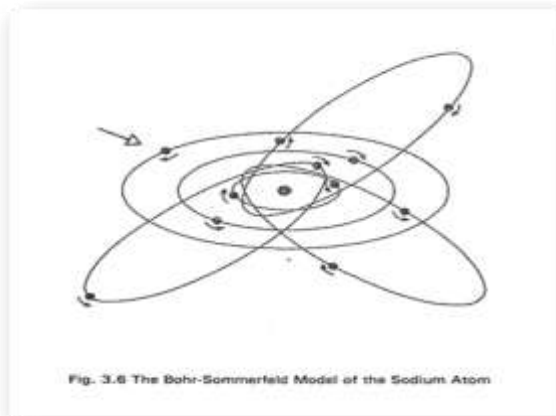
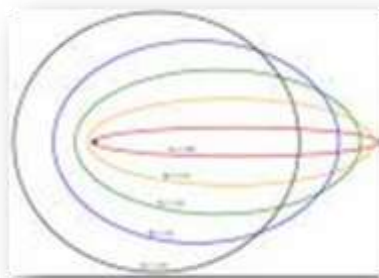
When, $n_\phi = n$ then circular orbit.

For a given n value,

$n_\phi = 1, 2, 3, \dots, (n)$.

Actual azimuthal quantum number,

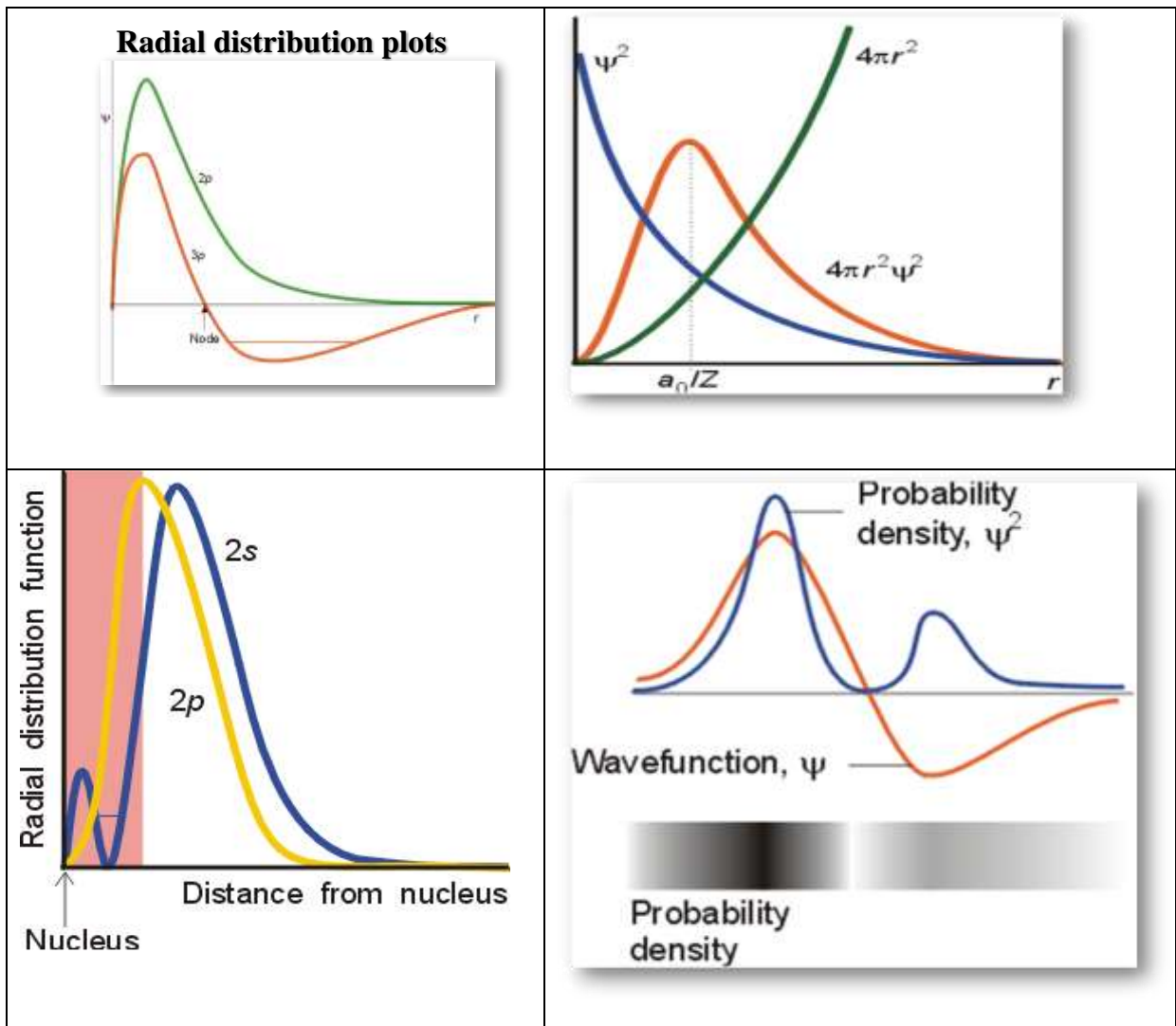
$l = n_\phi - 1$



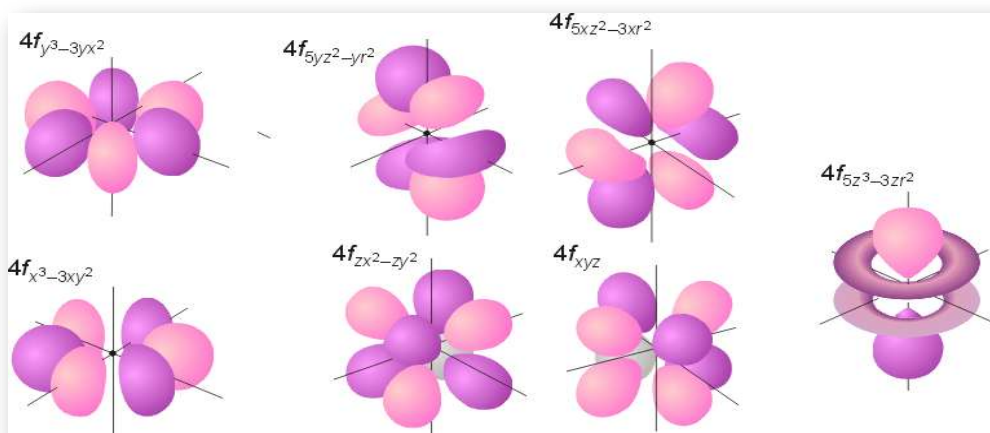
Sommerfeld introduced a relativistic correction in the mass of the electron because of its varying velocity in the orbit. The velocity of the electron is greater in perihelion position in the ellipse (close to nucleus) than the aphelion position (farthest from the nucleus).

$$\text{So, } m = m_0 [1 - (v^2/c^2)]^{-1/2}$$

[m_0 = rest mass of e^-]



f Orbitals



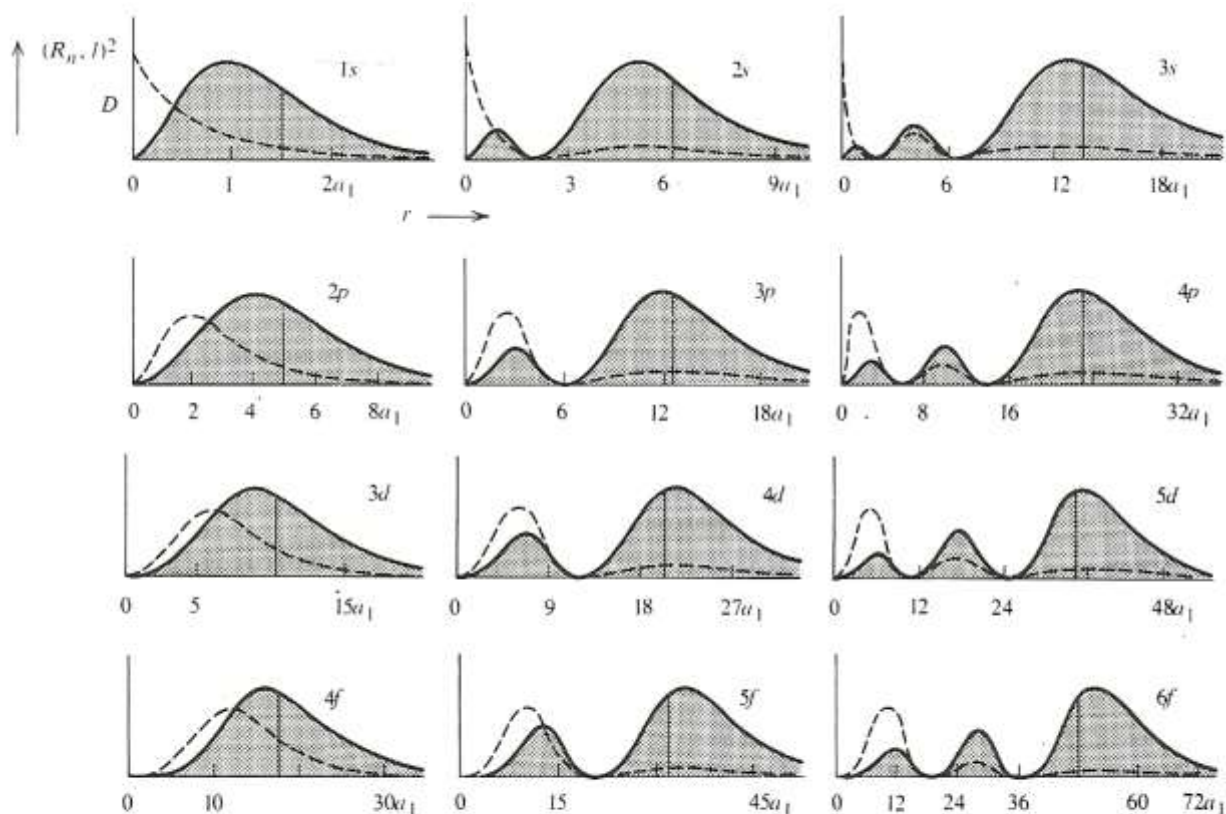


Figure 1.5 The probability-density factor $(R_{n,l})^2$ plotted as a function of the electron-nuclear distance r (r is given in units $a_0 = 53$ pm, the radius of the first Bohr circular orbit). The density distribution curves, $D = 4\pi r^2(R_{n,l})^2$, are the shaded areas. Vertical lines represent average distance over time for $(R_{n,l})^2$. (From H. E. White, *Introduction to Atomic Spectra*, McGraw-Hill, New York, 1934, p. 68.)