❖ Radial Distribution Function

The radial distribution function is the behavior of $R_{n,l}^2 . 4\pi r^2 dr$ as a function of distance r from the center of the nucleus. These plots solve the problem posed by the simple "probability distribution curves" which suggested that the probability of finding the electron must be highest at the center of the nucleus in the ground electronic state. In the radial distribution plots, we assume that the probability of finding the particle at a distance r from the nucleus depends not only upon the density of electron wave but also varies with the magnitude of the volume of the spherical shell of dr thickness at the same distance. This is quite rational because the r can be in any direction around the nucleus.

Consider that the space around the nucleus is divided into an infinite number of concentric shells of thickness dr. Now though the electron density will show a decrease with increasing r, the volume of the concentric shells will increase. More volume at distance r means more the chances of finding the electron at same. The two effects will try to counter each other, and therefore, the resultant probability at distance r must be the multiplication of the two effects i.e.

$$Radial\ probability = \psi_{n,l,m}^2 \times dV_{shell} \tag{433}$$

Nevertheless, since it is only the radial part ($R_{n,l}$) that varies with the distance from the nucleus, the above expression for simplicity can be reduced to

$$Radial\ probability = R_{n,l}^2 \times dV_{shell} \tag{434}$$

Now as we have already derived the mathematical expression of radial wavefunction hydrogen atom already in this previously, the only thing we need is the mathematical expression of the volume element also.

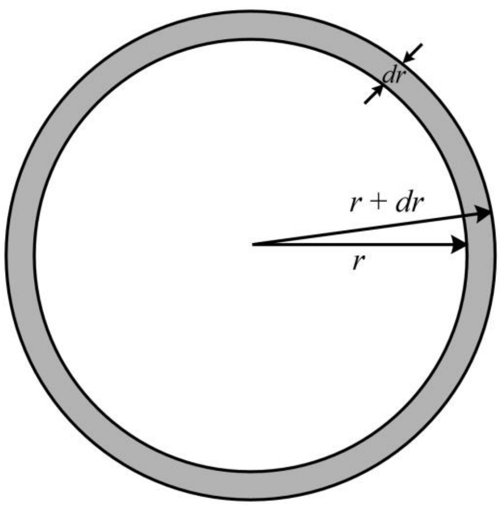

Figure 23. The depiction of a concentric shell of thickness *dr* around the nucleus of a hydrogen atom at a distance *r*.

The volume of the shaded portion (spherical shell of thickness *dr*) can be obtained subtracting the volume of the inner sphere from the outer sphere i.e.

$$dV = \frac{4}{3}\pi(r + dr)^3 - \frac{4}{3}\pi r^3 \tag{435}$$

$$= \frac{4}{3}\pi(r^3 + dr^3 + 3r^2 dr + 3r\,dr^2) - \frac{4}{3}\pi r^3 \tag{436}$$

$$= \frac{4}{3}\pi r^3 + \frac{4}{3}\pi dr^3 + 4\pi r^2 dr + 4\pi r\,dr^2 - \frac{4}{3}\pi r^3 \tag{437}$$

$$dV = \frac{4}{3}\pi dr^3 + 4\pi r^2 dr + 4\pi r\,dr^2 \tag{438}$$

Since *dr* is very small, the terms involving square and cube of *dr* can be neglected for simplicity. All this leaves us with only one term i.e. $dV = 4\pi r^2 dr$. After using the value of *dV* in equation (434), we get

$$Radial\ probability = R_{n,l}^2 \times 4\pi r^2 dr \tag{439}$$

To understand this more precisely, consider the plot for the ground quantum mechanical state of an electron in a hydrogen atom i.e. 1*s* orbital.

➢ ***Radial Probability Distribution Curve for Ground State of Hydrogen Atom***

The valid values of *n*, *l* and *m* that can be put in the general form of the hydrogenic wavefunction to obtain ground state are 1, 0 and 0, respectively. Therefore, we can start by writing the mathematical expression for the same i.e.

$$R_{1,0} = 2\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0} \tag{440}$$

The probability distribution function can be obtained by squaring equation (440) i.e.

$$R_{1,0}^2 = \frac{4}{a_0^3} e^{-2r/a_0} \tag{441}$$

After multiplying the "probability distribution function" with "volume element", the expression for the "radial distribution function" can be formulated. Mathematically, we can say that

$$P(r) = \frac{4}{a_0^3} e^{-2r/a_0} \times 4\pi r^2 dr \tag{442}$$

It is obvious from the equation (442) that probability will become zero if we put *r* = 0 ($4\pi r^2 dr = 0$). Now, if we increase the *r*, the radial probability will first increase due to increasing volume element, attaining maxima; and then it will start declining due to the dominance of $R_{1,0}^2$ part. In other words, the density of electron-wave decreases exponentially but the volume of the concentric shell increases continuously.

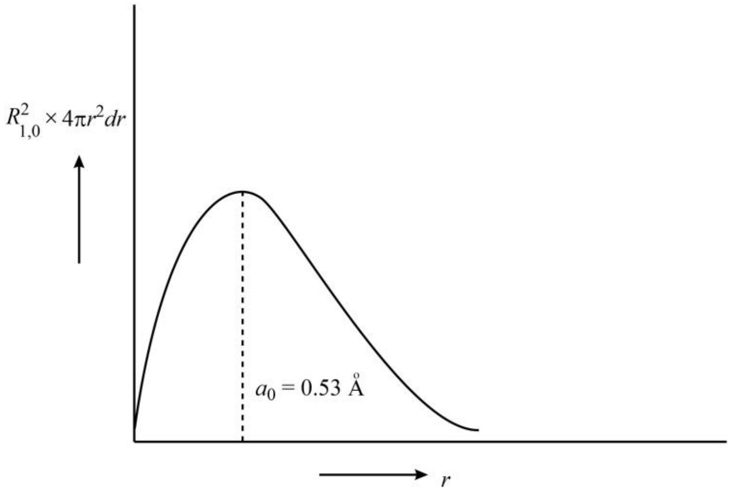

Figure 24. The variation of radial probability as a function of r (1s orbital).

In order to find the radius of maximum probability, we need to put dP/dr equal to zero. It has been found that the radius of maximum probability will come out to be 0.53×10^{-10} m, which is exactly equal to the radius of the first Bohr orbit (a_0).

➢ ***Radial Probability Distribution Curves for Other Hydrogenic Wavefunctions***

The other valid sets of n, l can be put in the general form of radial part of the wavefunction, to obtain $R^2_{n,l}$, and hence the corresponding "radial distribution functions".

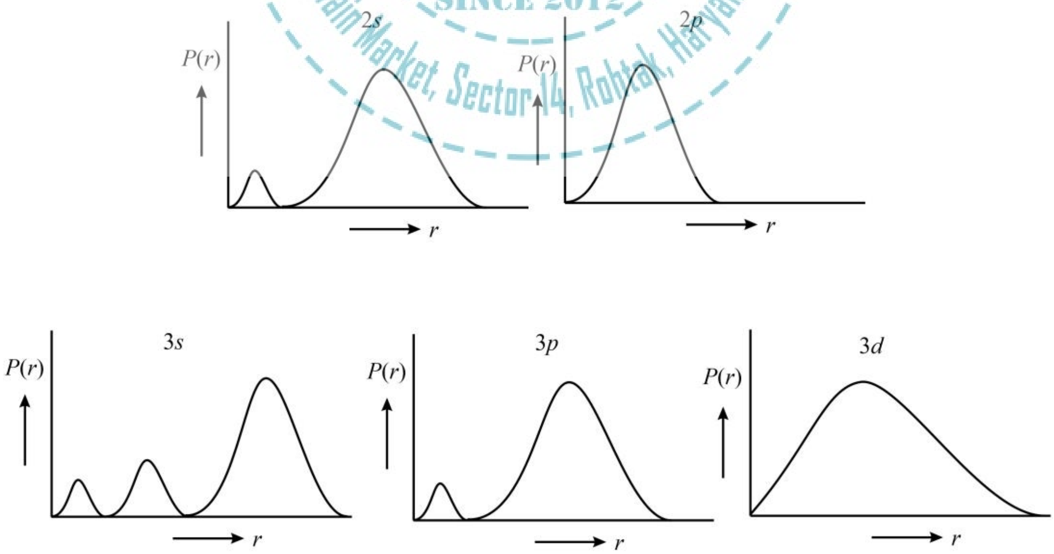

Figure 25. The variation of radial probability as a function of distance from the center of the nucleus.

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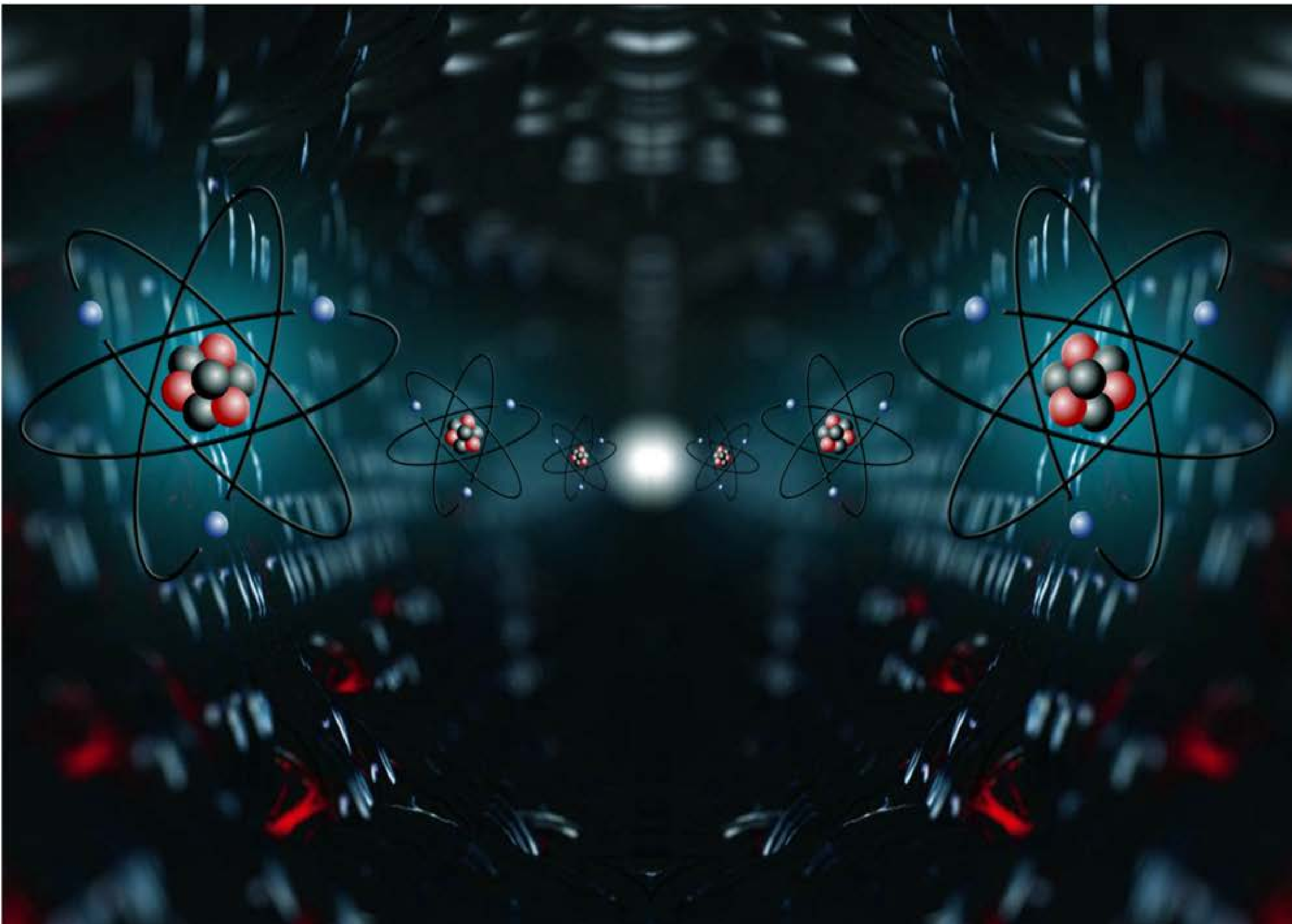

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