❖ Debye-Huckel Reciprocal Length

The concept of Debye-Huckel length can be understood in a better way only after knowing how much charge actually surrounds the reference ion. For this, assume that the total space around the reference ion is divided into the infinite number of hollow spherical shells of thickness *dr* with the inner and outer radii as *r* and *r*+*dr*, respectively. The volume of each such shell will be $4\pi r^2 dr$, and the total excess charge (*dq*) in the same can be obtained by multiplying this volume element with the excess charge density, i.e.,

$$dq = \rho_r 4\pi r^2 dr \tag{68}$$

Now, as we know that the excess charge density at distance *r* from the reference ion is

$$\rho_r = -\frac{Z_i e_0 \kappa^2}{4\pi r} e^{-\kappa r} \tag{69}$$

Putting the value of equation (69) in equation (68), we get

$$dq = \left(-\frac{Z_i e_0 \kappa^2}{4\pi r} e^{-\kappa r}\right) 4\pi r^2 dr \tag{70}$$

or

$$dq = -Z_i e_0 e^{-\kappa r} \kappa^2 r dr \tag{71}$$

Since the exponential part becomes zero only at $r = \infty$, the total charge around the reference ion can be obtained by integrating the equation (71) from $r = 0$ to $r = \infty$.

$$q_{cloud} = \int_{r=0}^{r=\infty} dq = \int_{r=0}^{r=\infty} -Z_i e_0 e^{-\kappa r} \kappa^2 r dr \tag{72}$$

or

$$q_{cloud} = -Z_i e_0 \tag{73}$$

This is an important result which proves that a reference ion, with the charge $+Z_i e_0$, is surrounded by an exactly equal but oppositely charged cloud i.e. $-Z_i e_0$.

Now, since the exponential part decreases with increasing r while the non-exponential part shows a continuous increase as we move away from the reference ion, there should be a distance of maximum charge.

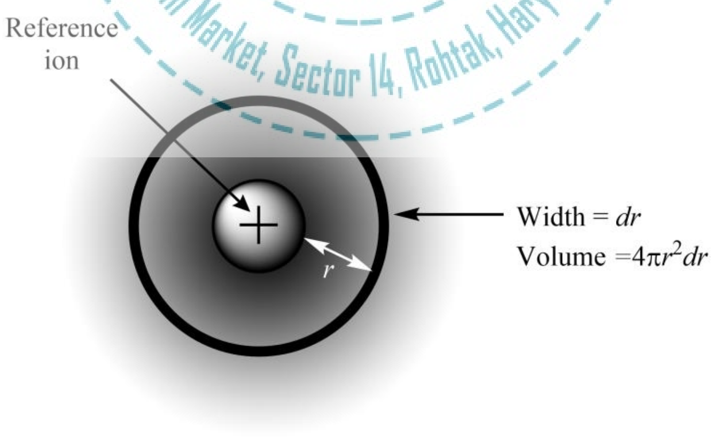

Figure 9. The depiction of excess charge density in a volume element of thickness 'dr' as a function of the distance r from the reference ion.

In order to find the distance of maximum "excess charge", we need to differentiate the equation (71) with respect to r, and then derivative needs to be put equal to zero i.e.

$$\frac{dq}{dr} = -Z_i e_0 \kappa^2 (e^{-\kappa r} - \kappa r e^{-\kappa r}) = 0 \tag{74}$$

Since $-Z_i e_0 \kappa^2$ is non zero for sure, the above equation holds true only if

$$e^{-\kappa r} - \kappa r e^{-\kappa r} = 0 \tag{75}$$

Which implies

$$r = \kappa^{-1} \tag{76}$$

Also as we know that

$$\kappa = \left(\frac{4\pi}{\varepsilon kT} \sum_i n_i^0 Z_i^2 e_0^2\right)^{1/2} \tag{77}$$

Hence, the radius of maximum excess charge from the center of the reference ion can be obtained by putting the value of κ from equation (77) in equation (76), we get r_{max} or the "Debye-Huckel length" as

$$r_{max} = \left(\frac{\varepsilon kT}{4\pi} \frac{1}{\sum_i n_i^0 Z_i^2 e_0^2}\right)^{1/2} \tag{78}$$

It is also worthy to note that the cloud will tend to fade out ever more with the decreasing concentration.

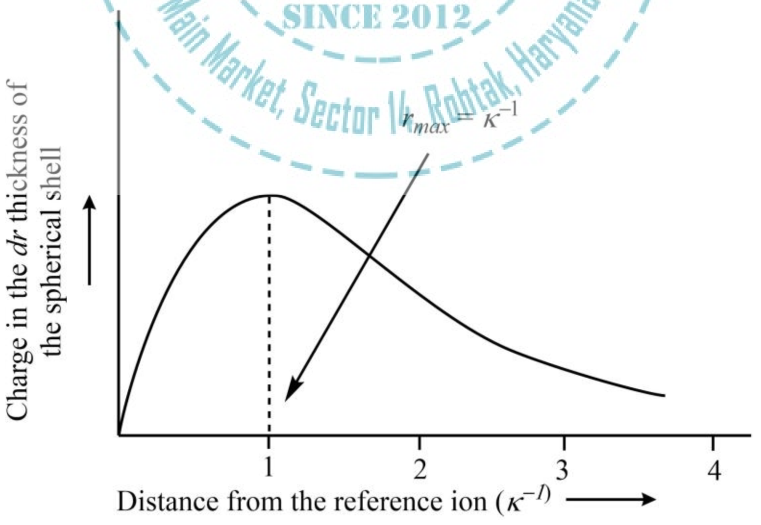

Figure 10. The variation of total charge enclosed in the *dr* thickness of the spherical shell as a function of the distance *r* from the reference ion.

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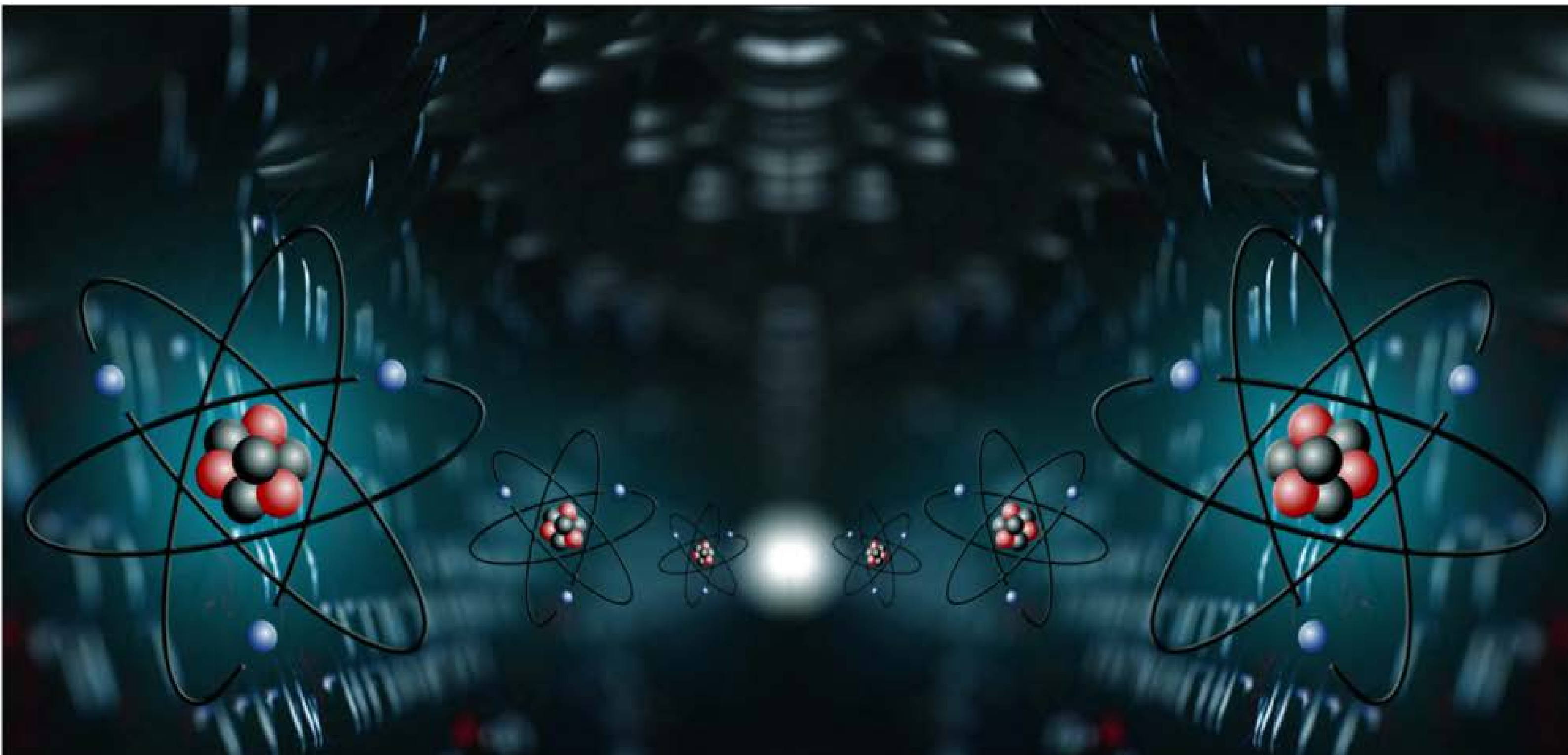

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