QUANTUM CHEMISTRY

Dr. A. DAYALAN, *Former Professor & Head*, Dept. of Chemistry,

LOYOLA COLLEGE (*Autonomous*), Chennai – 34

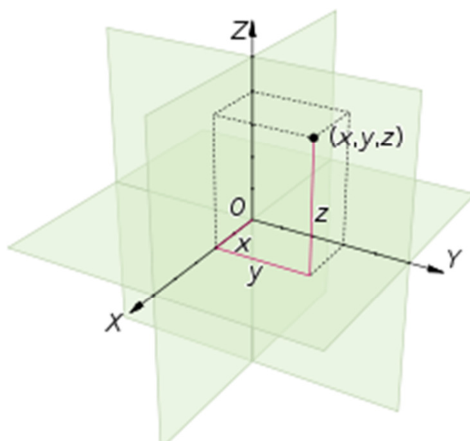
QC-1.1-COORDINATE SYSTEMS

1) CARTESIAN COORDINATES

Cartesian coordinates in two dimensions(x, y)

A two dimensional plane with *x* and *y*-axes defined is referred to as the Cartesian plane or *xy* (horizontal) plane. The ***x***-coordinate is called **ABSCISSA** and the ***y***-coordinate is called **ORDINATE**.

Cartesian coordinates in three dimensions(x, y, z)



The Cartesian coordinate (x,y,z) represents the perpendicular distances along x, y & z axis

$- \infty < x < + \infty$; $- \infty < y < + \infty$; $- \infty < z < + \infty$

Distance between two points (x_1,y_1,z_1) & (x_2,y_2,z_2) , $d = [(x_2-x_1)^2+(y_2-y_1)^2+(z_2-z_1)^2]^{½}$

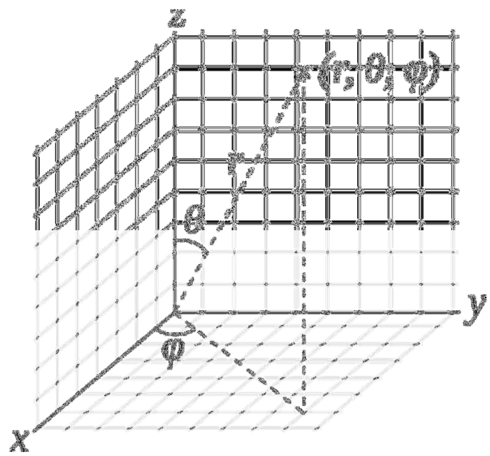
Distance from the origin to the point (x,y,z), $r^2 = x^2+y^2+z^2$

Horizontal plane σ_{xy}

Vertical plane is the one which contains the z-axis (σ_{zx}, σ_{zy})

Applications of Cartesian coordinate system: This coordinate system is used for the study quantum systems like Particle in a box (1D & 2D); Harmonic oscillator; Analysis of vibration & Normal modes of vibration.

2) SPHERICAL POLAR COORDINAES(r, θ, φ)



Spherical coordinates (r, θ, φ):Radialdistance r, polar angle θ and azimuthal angle φ.

$r > 0$; $0 \leq \theta \leq \pi$; $0 \leq \varphi < 2\pi$

SPHERICALPOLAR coordinates (r, θ, φ) from CARTESIAN coordinates

$$r = \sqrt{x^2 + y^2 + z^2}$$

$$\varphi = \tan^{-1}(y/x)$$

$$\theta = \cos^{-1}(z/r)$$

CARTESIAN coordinates from SPHERICAL polar coordinates

Conversely, the Cartesian coordinates may be retrieved from the spherical coordinates as follows :

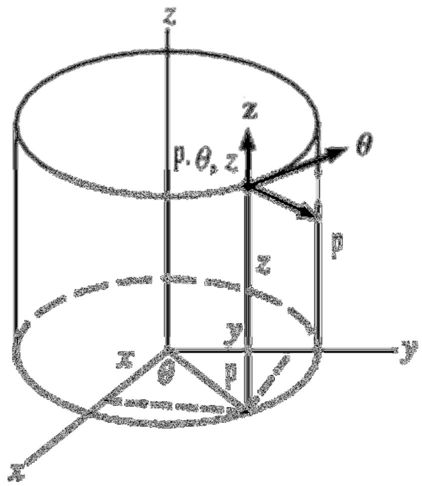
$$x = r \sin\theta \cos\phi$$

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

$$z = r \cos\theta$$

Applications of spherical polar coordinate system: Rigidrotor; Hydrogen atom

3) CYLINDRICAL COORDINATES (p, θ, z)



Cylindrical coordinates are three dimensional representation involving height (z) along z-axis ,pknown as radial coordinate and θas azimuthal coordinate.

Where, $0 \leq p \leq \infty$; $0 \leq \theta \leq 2\pi$; $-\infty \leq z \leq +\infty$.

CYLINDRICAL to **CARTESIAN** coordinates

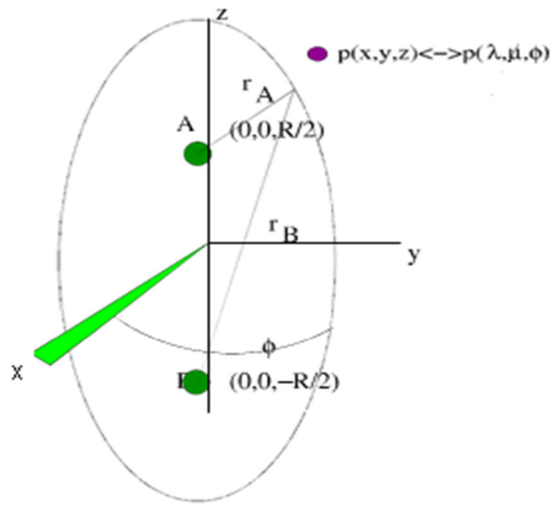
$p = (x^2 + y^2)^{1/2}$; $\theta = \tan^{-1}(y/x)$; $z = z$

CARTESIAN to **CYLINDRICAL** coordinates

$x = p\cos\theta$; $y = p \sin \theta$; $z = z$

Applications of cylindrical coordinate system: Acetylene& olefin π-electron systems.

4) ELLIPTICAL COORDINATES (λ, μ, φ)



Where the elliptical coordinate is defined as follows (A.K.Chandra p-165)

$$\lambda = \frac{r_A + r_B}{R} \qquad 1 \le \lambda \le \infty$$

$$\mu = \frac{r_A - r_B}{R} \qquad -1 \le \mu \le +1$$

$\phi = \phi$ $\quad 0 \le \phi \le 2\pi$ *(Same as the coordinate used in spherical polar coordinate)*

CARTESIAN COORDINATES are related to **ELLIPTICAL** coordinates as follows

$$x = \frac{R}{2}\cos\phi\sqrt{(\lambda^2-1)(1-\mu^2)}$$

$$y = \frac{R}{2}\sin\phi\sqrt{(\lambda^2-1)(1-\mu^2)}$$

$z = ½(R\lambda\mu)$

$r^2 = x^2 + y^2 + z^2 = (R/2)^2(\lambda^2+\mu^2-1)$

Applications of elliptical coordinate system: Hydrogen molecular ion & related systems.