Chemistry 3P51 – Fall 2013
Quantum Chemistry

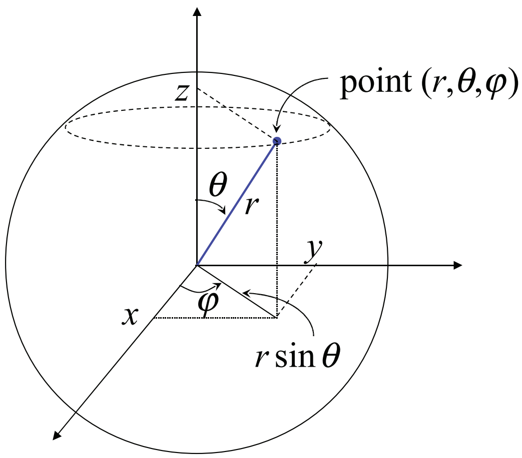
Lecture No. 16
Oct 21th, 2013

Objectives

- To remind the student the spherical polar coordinates.
- To show the angular momentum operator components and square in spherical coordinates.
- To show the relationship between the kinetic energy operator and the angular momentum operator in rotational motion.
- To derive the Schrödinger equation for a particle in a ring.

Spherical polar coordinates

Cartesian coordinates are not ideal for describing orbital motion. Spherical coordinates are better suited for this purpose.



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

$$y = r\sin\theta\sin\varphi$$

$$z = r\cos\theta$$

$$r^2 = x^2 + y^2 + z^2 \qquad (1)$$

$$\cos\theta = \frac{z}{r} \qquad (2)$$

$$\tan\varphi = \frac{y}{x} \qquad (3)$$

$$0 \le r < \infty, \quad 0 \le \theta \le \pi, \quad 0 \le \varphi \le 2\pi$$

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Angular momentum in spherical coordinates

When expressed in spherical coordinates, the **components of the angular momentum operator** and **its square** take the following form

$$\hat{L}_x = -i\hbar\left(-\sin\varphi\frac{\partial}{\partial\theta} - \frac{\cos\theta}{\sin\theta}\cos\varphi\frac{\partial}{\partial\varphi}\right)$$

$$\hat{L}_y = -i\,\hbar\left(\cos\varphi\frac{\partial}{\partial\theta} - \frac{\cos\theta}{\sin\theta}\sin\varphi\frac{\partial}{\partial\varphi}\right)$$

$$\hat{L}_z = -i\,\hbar\frac{\partial}{\partial\varphi}$$

$$\hat{L}^2 = -\,\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \frac{\cos\theta}{\sin\theta}\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right)$$

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Angular momentum and kinetic energy operators

The angular momentum operator is very useful because is closely related to the **rotational motion** kinetic energy operator; that is, motion about a **fixed point** where the distance is *r*

$$\hat{T} = \frac{\hat{L}^2}{2mr^2} \qquad \text{provided } \; r = \text{const}$$

The quantity

$$I = mr^2$$

is called the **moment of inertia**.

Thus, the Schrödinger equation for a free $(V = 0)$ particle in a ring *or* on the surface of a sphere of radius r can be written as

$$\frac{\hat{L}^2}{2I}\psi = E\psi$$

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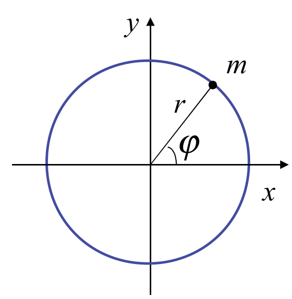
Particle in a ring

Consider a particle of mass m constrained to move in a ring of radius r and assume that the potential energy $V(\varphi)$ of the particle is zero.

The Schrödinger equation for this system is



$$\hat{H}\psi = E\psi$$

where

$$\hat{H} = \frac{\hat{L}^2}{2I} = \frac{\hat{L}^2}{2mr^2}$$

Since the particle is constrained to remain in the z=0 plane,

$$\hat{L}_x = \hat{L}_y = 0, \quad \text{so} \quad \hat{L}^2 = \hat{L}_z^2$$

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Particle in a ring

Recall that

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \varphi} \qquad \hat{L}_z^2 = -\hbar^2 \frac{\partial^2}{\partial \varphi^2}$$

The Schrödinger equation for this particular problem is one-dimensional:

$$-\frac{\hbar^2}{2mr^2}\frac{\partial^2}{\partial \varphi^2}\psi(\varphi) = E\psi(\varphi)$$

Let us define

$$n^2 = \frac{2mr^2 E}{\hbar^2}$$

Therefore, we can rewrite the equation as $\frac{d^2\psi}{d\varphi^2} = -n^2\psi(\varphi)$

The solution is

$$\psi(\varphi) = e^{in\varphi},$$

where n is any real number, positive or negative.

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