

Chemistry 3P51 – Fall 2013

Quantum Chemistry

Lecture No. 17
Oct 22nd, 2013

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Objectives

- To derive the eigenfunctions and eigenvalues of the particle-in-a-ring system.
- To present the energy level diagram for the particle-in-a-ring system.
- To show a simple chemical application of the particle-in-ring system
- To introduce the particle-on-the-surface-of-a-sphere system in order to motivate the eigenvalues and eigenfunctions of the angular momentum operator.
- To introduce the spherical harmonics as eigenfunctions of the angular momentum operator.
- To present the energy level diagram for a particle on the surface of a sphere.

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Particle in a ring

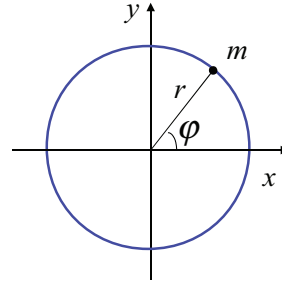
Consider a particle of mass m constrained to move in a ring of radius r and assume that the potential energy $V(\varphi)$ of the particle is zero.

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

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

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

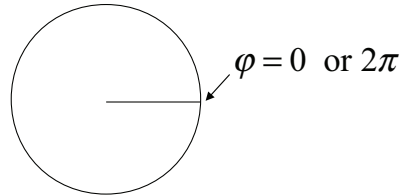
$$\psi(\varphi) = e^{in\varphi},$$

where n is any real number, positive or negative.

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Periodic boundary conditions for a particle in a ring

For continuity, the wave function must have the same value at φ as at $\varphi + 2\pi$



Therefore, we demand that

$$\psi(\varphi) = \psi(\varphi + 2\pi), \quad \text{i.e.,} \quad e^{in(\varphi+2\pi)} = e^{in\varphi} e^{2\pi in}$$

This requires $e^{2\pi in} = 1$, which is equivalent to

$$\cos(2\pi n) + i \sin(2\pi n) = 1,$$

The last condition is satisfied only if n is an integer: $n = 0, \pm 1, \pm 2, \pm 3, \dots$

Periodic boundary conditions for a particle in a ring

Thus, the normalized wave functions of a particle in a ring are

$$\psi_n(\varphi) = \frac{1}{\sqrt{2\pi}} e^{in\varphi}, \quad n = 0, \pm 1, \pm 2, \pm 3 \dots$$

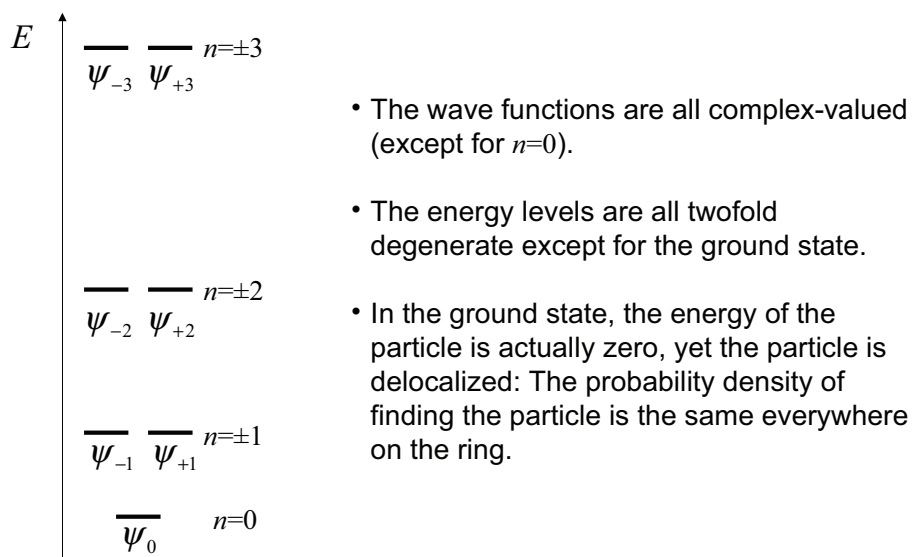
The allowed energy are:

$$E_n = \frac{n^2 \hbar^2}{2mr^2} = \frac{n^2 h^2}{8\pi^2 mr^2}, \quad n = 0, \pm 1, \pm 2, \pm 3 \dots$$

Note that all levels except $n = 0$ are twofold degenerate.

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Energy level diagram for a particle in a ring

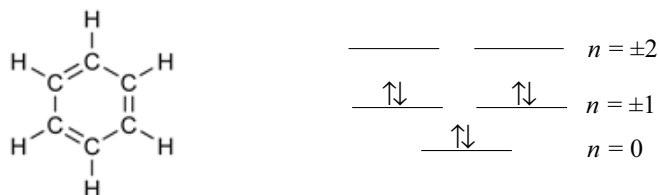


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Particle-on-a-circle model for a cyclic conjugated system

The “electron in a ring” model can be used to estimate the lowest-energy excitation of cyclic π -conjugated molecules.

Consider the benzene molecule. We can think of its six π -electrons as being confined to a ring.



The radius r of the ring can be approximated by the CC distance in benzene:

$$r \approx r_{\text{CC}} = 1.40 \text{ \AA}$$

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Particle-on-a-circle model for cyclic conjugated system

The lowest-energy excitation is $|n| = 1 \rightarrow 2$. Its energy is:

$$\Delta E = E_2 - E_1 = \frac{\hbar^2}{2mr^2}(2^2 - 1^2) = \frac{3\hbar^2}{8\pi^2 mr^2}$$

This should be equal to

$$\Delta E = h\nu = \frac{hc}{\lambda}$$

Equating the right-hand sides we obtain

$$\lambda = \frac{8\pi^2 cmr^2}{3h} = 213 \text{ nm}$$

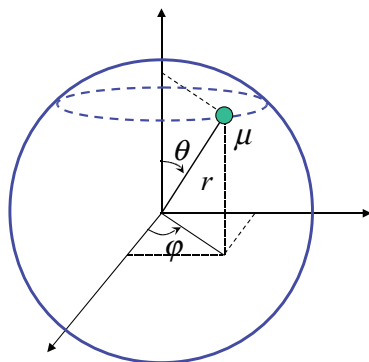
Experimentally, the lowest-energy band in the UV absorption spectrum of benzene occurs near

$$\lambda_{\text{exp}} = 260 \text{ nm}$$

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Particle on the surface of a sphere

Consider a particle of mass μ (we reserve m for something else) which is constrained to remain on the surface of a sphere of radius r :



Let us assume that the potential energy of the particle is zero: $V=0$. Then the Hamiltonian becomes

$$\hat{H} = \hat{T} = \frac{\hat{L}^2}{2I} = \frac{\hat{L}^2}{2\mu r^2}$$

Because the radial coordinate r of the particle is fixed, the wave function will be a function of the angles θ and φ only.

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The Schrödinger equation for a particle on a sphere

The Schrödinger equation for a particle on a sphere may be written as:

$$\frac{\hat{L}^2}{2\mu r^2} \psi(\theta, \varphi) = E \psi(\theta, \varphi)$$

This form suggests that the wavefunctions of the particle are the same as the eigenfunctions of the operator

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

and that the eigenvalues E are the eigenvalues of \hat{L}^2 divided by $2\mu r^2$:

$$E = \frac{\text{const}}{2\mu r^2}$$

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Eigenvalues and eigenfunctions of the angular momentum operator

Let us now consider the eigenvalue problem

$$\hat{L}^2 \psi(\theta, \varphi) = \text{const} \times \psi(\theta, \varphi)$$

Solving this equation is not easy. But it turns out that the eigenvalues of the operator \hat{L}^2 are

$$L^2 = \hbar^2 l(l+1), \quad \text{where } l = 0, 1, 2, \dots$$

This means that the allowed magnitudes of the angular momentum are

$$L = \hbar \sqrt{l(l+1)} \quad l = 0, 1, 2, \dots$$

The eigenfunctions of \hat{L}^2 are denoted $Y_l^m(\theta, \varphi)$ and, for historical reasons, called **spherical harmonics**

$$\hat{L}^2 Y_l^m(\theta, \varphi) = \hbar^2 l(l+1) Y_l^m(\theta, \varphi)$$

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Expressions for the first spherical harmonics

All spherical harmonics have the following form:

$$Y_l^m(\theta, \varphi) = N(\text{a function of } \theta) \times e^{im\varphi}, \quad \begin{array}{l} \text{where } l = 0, 1, 2, \dots \\ m = 0, \pm 1, \pm 2, \dots, \pm l \end{array}$$

\nwarrow
 normalization factor

Specifically,

$$\begin{aligned} Y_0^0 &= \frac{1}{(4\pi)^{1/2}} & Y_2^0 &= \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1) \\ Y_1^0 &= \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta & Y_2^{\pm 1} &= \left(\frac{15}{8\pi}\right)^{1/2} \sin\theta \cos\theta e^{\pm i\varphi} \\ Y_1^{\pm 1} &= \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{\pm i\varphi} & Y_2^{\pm 2} &= \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta e^{\pm 2i\varphi} \end{aligned}$$

Spherical harmonics with $m = 0$ are real. All others are complex-valued.

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Spherical harmonics are simultaneous eigenfunctions of the \hat{L}_z and \hat{L}^2 operators

The fact that $[\hat{L}_z, \hat{L}^2] = 0$ means that the functions $Y_l^m(\theta, \varphi)$ are simultaneous eigenfunctions of the operators \hat{L}_z and \hat{L}^2

We already know the eigenvalues of \hat{L}^2 . To determine the eigenvalues of \hat{L}_z let us directly apply this operator to the spherical harmonics:

$$\begin{aligned} \hat{L}_z Y_l^m(\theta, \varphi) &= -i\hbar \frac{\partial}{\partial \varphi} Y_l^m(\theta, \varphi) = -i\hbar \frac{\partial}{\partial \varphi} [(\text{a function of } \theta) e^{im\varphi}] \\ &= -i\hbar (im) Y_l^m(\theta, \varphi) = m\hbar Y_l^m(\theta, \varphi) \end{aligned}$$

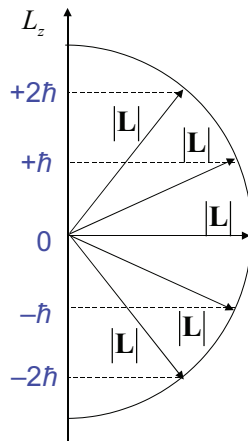
Therefore, the eigenvalues of the z -component operator are

$$L_z = m\hbar, \quad m = 0, \pm 1, \pm 2, \dots, \pm l$$

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Angular momentum diagrams

The magnitude and z -component of the angular momentum vector are quantized and can have simultaneously definite values. This is conveniently illustrated by **angular momentum diagrams**.



The quantum number m defines the orientation of the angular momentum vector (spatial quantization).

Example: Consider a state with the angular momentum quantum number $l = 2$

$$|\mathbf{L}| = \hbar \sqrt{l(l+1)} = \hbar \sqrt{2(2+1)} = \hbar \sqrt{6}$$

There are $2l+1 = 5$ allowed orientations of \mathbf{L} with z -components $L_z = m\hbar$, where

$$\begin{aligned} m &= -l, -(l-1), \dots, l-1, l \\ &= -2, -1, 0, +1, +2 \end{aligned}$$

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Visualizing spherical harmonics

One way to represent a wave function $Y_l^m(\theta, \varphi)$ is to plot the probability density $|Y_l^m(\theta, \varphi)|^2$ as a function of the angles θ and φ .

For each pair of the angles θ and φ we draw a line from the origin. The direction of the line is (θ, φ) and the length is $|Y_l^m(\theta, \varphi)|^2$. The end points of all such lines form a surface which represents the probability density for finding a particle on the surface of a sphere near the position (θ, φ) .

$$\text{For } l = 0: \quad |Y_0^0(\theta, \varphi)|^2 = \left| \frac{1}{(4\pi)^{1/2}} \right|^2 = \frac{1}{4\pi}$$

$$\text{For } l = 1: \quad |Y_1^0(\theta, \varphi)|^2 = \left| \left(\frac{3}{4\pi} \right)^{1/2} \cos \theta \right|^2 = \frac{3}{4\pi} \cos^2 \theta$$

$$|Y_1^{\pm 1}(\theta, \varphi)|^2 = \left| \left(\frac{3}{8\pi} \right)^{1/2} \sin \theta e^{\pm i\varphi} \right|^2 = \frac{3}{8\pi} \sin^2 \theta$$

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