Chemistry 3P51 – Fall 2013
Quantum Chemistry

Lecture No. 18
Oct 23rd, 2013

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Objectives

- To remind the students the main ideas about the particle-on-the-surface-of-a-sphere system.
- To remind the students that spherical harmonics are eigenfunctions of the angular momentum operator.
- To present the energy level diagram for a particle on the surface of a sphere.
- To show angular momentum diagrams.
- To visualize combinations of spherical harmonics as orbitals in chemistry.

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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

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

This means that the allowed magnitudes of the angular momentum are

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

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:

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

normalization factor

Specifically,

$$Y_0^0 = \frac{1}{(4\pi)^{1/2}} \qquad\qquad Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2}(3\cos^2\theta - 1)$$

$$Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2}\cos\theta \qquad\qquad Y_2^{\pm 1} = \left(\frac{15}{8\pi}\right)^{1/2}\sin\theta\cos\theta e^{\pm i\varphi}$$

$$Y_1^{\pm 1} = \left(\frac{3}{8\pi}\right)^{1/2}\sin\theta e^{\pm i\varphi} \qquad\qquad Y_2^{\pm 2} = \left(\frac{15}{32\pi}\right)^{1/2}\sin^2\theta e^{\pm 2i\varphi}$$

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

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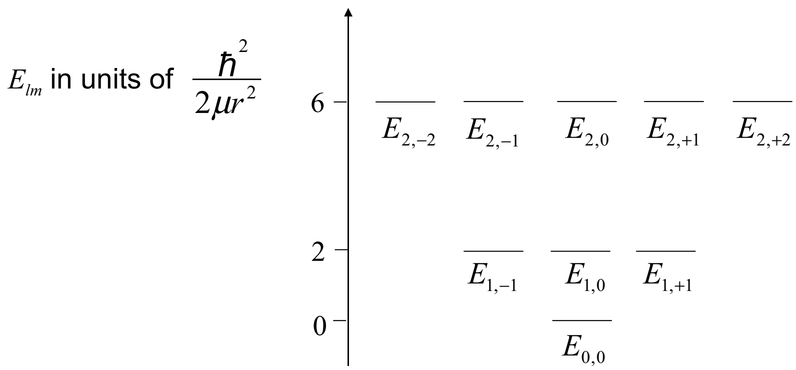
Energy levels for a particle on a sphere

The energy levels of a particle on a sphere of radius r are given by

$$E_{lm} = \frac{\hbar^2}{2\mu r^2} l(l+1) \qquad \begin{array}{l} l = 0, 1, 2, \dots \\ m = 0, \pm 1, \pm 2, \dots, \pm l \end{array}$$

Each level E_{lm} is $(2l+1)$-fold degenerate, as shown on the diagram:



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

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

$$= -i\hbar\,(im) Y_l^m(\theta,\varphi) = m\hbar\, Y_l^m(\theta,\varphi)$$

Therefore, the eigenvalues of the z-component operator are

$$\boxed{L_z = m\hbar, \qquad m = 0, \pm 1, \pm 2, \dots, \pm l}$$

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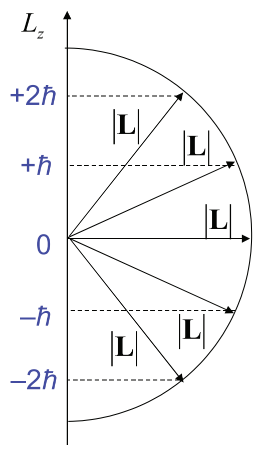
Angular momentum diagrams

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

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

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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).

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

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

$$\left|Y_1^{\pm1}(\theta,\varphi)\right|^2 = \left|\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta\, e^{\pm i\varphi}\right|^2 = \frac{3}{8\pi}\sin^2\theta$$

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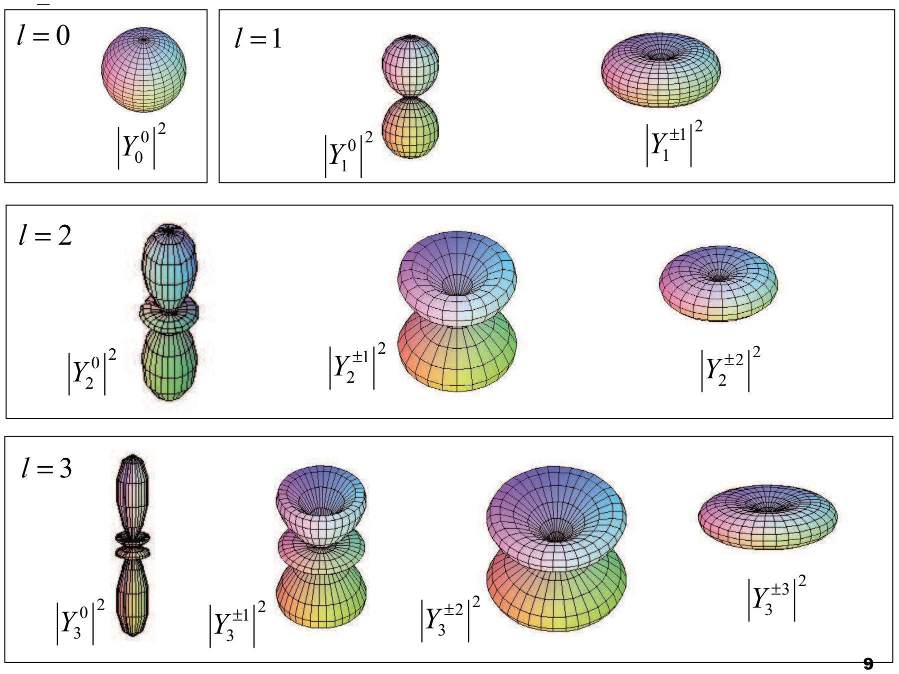

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Real combinations of spherical harmonics

When two degenerate spherical harmonics with the factors $e^{+im\varphi}$ and $e^{-im\varphi}$ are added (subtracted), one can obtain a purely real function.

For example, for $l = 1$ and $m = \pm 1$,

$$Y_1^1 + Y_1^{-1} = \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{i\varphi} + \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{-i\varphi} = 2\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta\cos\varphi$$

$$\frac{Y_1^1 - Y_1^{-1}}{i} = \frac{1}{i}\left[\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{i\varphi} - \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{-i\varphi}\right] = 2\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta\sin\varphi$$

Verify this using the Euler formula: $e^{\pm im\varphi} = \cos(m\varphi) \pm i\sin(m\varphi)$

The spherical harmonics also turn up in the wavefunctions of the electron in a hydrogen atom. Manipulations such as above give rise to p_x, p_y, d_{xy}, d_{xz}, d_{yz}, etc. orbitals.

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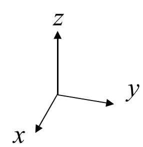
Real combinations of spherical harmonics

When all spherical harmonics are processed in this way and normalized, we obtain:

$l = 0$

$$Y_0^0 = \left(\frac{1}{4\pi}\right)^{1/2}$$



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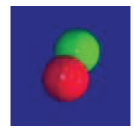
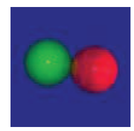
$l = 1$

$$\frac{1}{\sqrt{2}}(Y_1^1 + Y_1^{-1}) = \left(\frac{3}{4\pi}\right)^{1/2} \underbrace{\sin\theta\cos\varphi}_{\sim x}$$



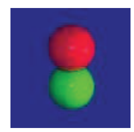
p_x

$$\frac{1}{i\sqrt{2}}(Y_1^1 - Y_1^{-1}) = \left(\frac{3}{4\pi}\right)^{1/2} \underbrace{\sin\theta\sin\varphi}_{\sim y}$$



p_y

$$Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2} \underbrace{\cos\theta}_{\sim z}$$



p_z

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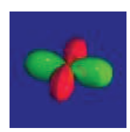
Real combinations of spherical harmonics

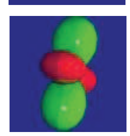
$l = 2$

$$\frac{1}{\sqrt{2}}(Y_2^2 + Y_2^{-2}) = \left(\frac{15}{16\pi}\right)^{1/2} \underbrace{\sin^2\theta\cos 2\varphi}_{\sim x^2 - y^2}$$

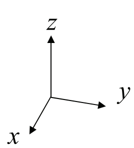


$d_{x^2-y^2}$

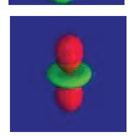
$$\frac{1}{\sqrt{2}}(Y_2^1 + Y_2^{-1}) = \left(\frac{15}{4\pi}\right)^{1/2} \underbrace{\sin\theta\cos\theta\cos\varphi}_{\sim xz}$$



d_{xz}

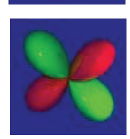


$$Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2} \underbrace{(3\cos^2\theta - 1)}_{\sim z^2}$$



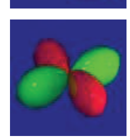
d_{z^2}

$$\frac{1}{i\sqrt{2}}(Y_2^1 - Y_2^{-1}) = \left(\frac{15}{4\pi}\right)^{1/2} \underbrace{\sin\theta\cos\theta\sin\varphi}_{\sim yz}$$



d_{yz}

$$\frac{1}{i\sqrt{2}}(Y_2^2 - Y_2^{-2}) = \left(\frac{15}{16\pi}\right)^{1/2} \underbrace{\sin^2\theta\sin 2\varphi}_{\sim xy}$$



d_{xy}

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Suggested exercise: Real combinations of spherical harmonics

It is strongly suggested that the math involved in the previous three slides is reproduced by the student in order to gain confidence when manipulating spherical harmonics.