Chemistry 3P51 – Fall 2013
Quantum Chemistry

Lecture No. 15
Oct 11th, 2013

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Objectives

- To introduce the classical angular momentum vector.
- To state the physical significance of the angular momentum vector.
- To introduce the quantum-mechanical angular momentum vector operator.
- To present the commutation relations involving the angular momentum operator components.
- To remind the student the spherical polar coordiantes.
- To show the angular momentum operator components and square in spherical coordinates.

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Angular momentum

In classical mechanics, the angular momentum of a particle is a vector quantity defined by

$$\mathbf{L} = \mathbf{r} \times \mathbf{p}$$

vector product

$\mathbf{r} = (x, y, z)$ is the particle's position vector;
$\mathbf{p} = (p_x, p_y, p_z)$ is the particle's linear momentum vector

The Cartesian components of $\mathbf{L} = (L_x, L_y, L_z)$ are given by

$$L_x = yp_z - zp_y$$
$$L_y = zp_x - xp_z$$
$$L_z = xp_y - yp_x$$

Cartesian unit vectors

Remark: One can formally write the vector $\mathbf{L}$ as a 3 × 3 determinant:

$$\mathbf{L} = \begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$

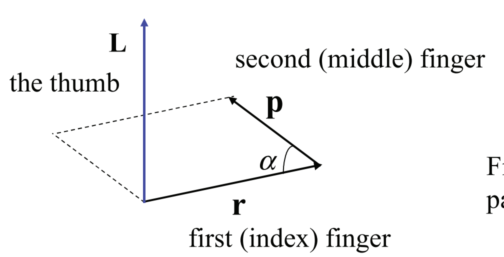
Magnitude and direction of the angular momentum

The magnitude of the $\mathbf{L}$-vector is

$$L \equiv |\mathbf{L}| = \sqrt{L^2} = \sqrt{\mathbf{L}\cdot\mathbf{L}} = \sqrt{L_x^2 + L_y^2 + L_z^2}$$

$\mathbf{L}$ is always perpendicular to the plane defined by the vectors $\mathbf{r}$ and $\mathbf{p}$. The direction of $\mathbf{L}$ is determined by the right-hand rule (see Fig. 1).

Geometric interpretation:



$$L \equiv |\mathbf{L}| = |\mathbf{r}||\mathbf{p}|\sin\alpha$$

Fig. 1: $|\mathbf{L}|$ equals the area of the parallelogram defined by $\mathbf{r}$ and $\mathbf{p}$

The angular momentum of a particle is proportional to the particle's velocity and its distance $r=|\mathbf{r}|$ from the origin.

Physical significance of the angular momentum

For an isolated particle (or a system of particles), the total angular momentum is a conserved quantity (just like the total energy) that can be used to characterize the state of the system.

The angular momentum of a particle of mass m is related to the **kinetic energy** by a simple formula, provided that the particle moves in such a manner that its distance r from the origin remain fixed:

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

The above formula applies when the particle is in **orbital motion**, specifically, when it moves:

(a) in a circle of radius r centered at the origin, or
(b) on the surface of a sphere of radius r

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Quantum-mechanical operators of angular momentum

Angular momentum is a three-component (vector) quantity represented by linear Hermitian operators.

In Cartesian coordinates, these operators are:

$$\hat{L}_x = y\hat{p}_z - z\hat{p}_y = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$

$$\hat{L}_y = z\hat{p}_x - x\hat{p}_z = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$

$$\hat{L}_z = x\hat{p}_y - y\hat{p}_x = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

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No two components of the angular momentum vector operator can be determined simultaneously

Using the definitions of the operators for the x-, y-, z-components of the angular momentum one can show that no two of them commute:

$$[\hat{L}_x, \hat{L}_y] = i\hbar\, \hat{L}_z \qquad [\hat{L}_y, \hat{L}_z] = i\hbar\, \hat{L}_x \qquad [\hat{L}_z, \hat{L}_x] = i\hbar\, \hat{L}_y$$

Each of the three components, however, commutes individually with the square of the total angular momentum:

$$[\hat{L}_x, \hat{L}^2] = 0, \qquad [\hat{L}_y, \hat{L}^2] = 0, \qquad [\hat{L}_z, \hat{L}^2] = 0$$

This means that one can observe simultaneously definite values of the total angular momentum and **only one** of its x-, y-, z-components.

By convention, the "definite" component is always chosen to be L_z.

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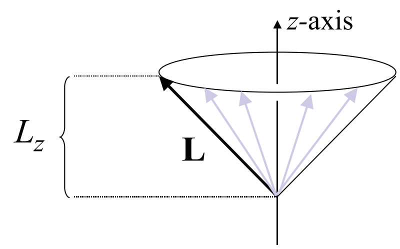
Physical interpretation of the commutation relations for the angular momentum

A particle can have simultaneously definite values of L and L_z, but then the other two components (L_x and L_y) will not have definite values.

In other words, only the component L_z of the total angular momentum can be known precisely alongside with L^2.



Note that by specifying $L = |\mathbf{L}|$ and L_z we are not specifying the vector $\mathbf{L}$, only its magnitude and the projection on the z-axis.

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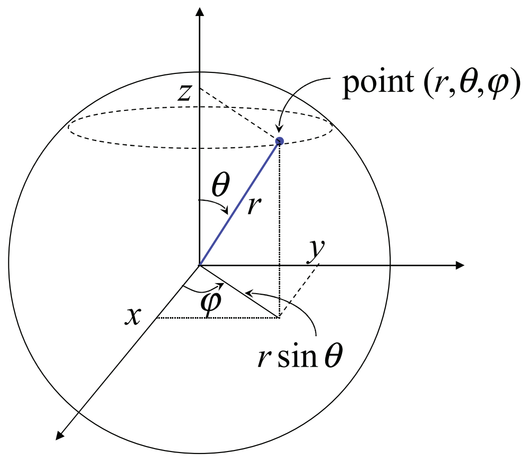
Spherical polar coordinates

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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