

Subject	Chemistry
Paper No and Title	2 and Physical Chemistry-I
Module No and Title	18 and Addition of Angular Momenta I
Module Tag	CHE_P2_M18

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SUBJECT
PAPER No. : 2, Physical Chemistry I
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SUBJECT

PAPER No. : 2, Physical Chemistry I

MODULE : 18, Addition of Angular Momenta I

1. Learning Outcomes

After studying this module, you shall be able to:

- Understand the addition of angular momenta for a multi-electron system
- Know the commutation relations of total (or coupled) angular momentum
- Learn about Dirac notation in quantum mechanics

2. Angular Momentum in Quantum Mechanics

Angular momentum is an observable for which there exists an operator in quantum mechanics. We have already seen in the previous modules that it is possible to measure angular momentum of a particle in a given quantum state (characterized by a set of quantum numbers).

The classical definition of angular momentum ($\vec{L} = \vec{r} \times \vec{p}$) is carried over to quantum mechanics by replacing the coordinates and momenta in the classical equation by their corresponding operators. The Cartesian components of angular momentum operator are

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

$$\hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z = -i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \quad \dots(18.1)$$

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

Using the fundamental commutation property, it is known that the components of the angular momentum operator obey the following set of commutation relations:

$$[\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z \quad \dots(18.2)$$

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

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

Although the components of angular momentum operator do not commute with each other, however, each of them is known to commute with the \widehat{L}^2 operator.

$$\widehat{L}^2 = \widehat{L}_x^2 + \widehat{L}_y^2 + \widehat{L}_z^2 \quad \dots(18.3)$$

$$[\widehat{L}^2, \widehat{L}_x] = 0 \quad \dots(18.4)$$

$$[\widehat{L}^2, \widehat{L}_y] = 0$$

$$[\widehat{L}^2, \widehat{L}_z] = 0$$

From this we conclude that the components of angular momentum have no common eigen functions. Only, the total angular momentum \widehat{L}^2 and any one component of angular momentum can share simultaneous eigen states (simultaneously measurable).

Using the above commutation relations, the eigen values constructed for the angular momentum \widehat{L}^2 and component \widehat{L}_z are

$$\widehat{L}_z Y = m_j \hbar Y \quad m_j = -j, \dots, +j \quad \dots(18.5)$$

$$\widehat{L}^2 Y = j(j+1)\hbar^2 Y \quad j = 0, 1/2, 1, 3/2, 2, \dots \quad \dots(18.6)$$

The range of eigen values of \widehat{L}_z is limited by j and $-j$, which means a total of $2j+1$ eigen states are possible for angular momentum component \widehat{L}_z .

Further, it has been found that the partial differential equations obtained using Cartesian coordinates are not separable which suggests the spherical polar coordinates as the natural coordinates for this problem. The angular momentum operator in spherical harmonics is obtained as

$$\widehat{L}_x = i\hbar \left[\sin \phi \frac{\partial}{\partial \theta} + \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right]$$

$$\widehat{L}_y = i\hbar \left[\cos \phi \frac{\partial}{\partial \theta} - \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right]$$

$$\widehat{L}_z = -i\hbar \frac{\partial}{\partial \phi}$$

$$\hat{L}^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \cdot \frac{\partial^2}{\partial \phi^2} \right]$$

The eigen functions of \hat{L}_z component are dependent on only one coordinate of the physical system, ϕ and are given by (derived in earlier module)

$$f(\phi) = \frac{1}{\sqrt{2\pi}} e^{im_j\phi}, \quad m_j = 0, \pm 1, \pm 2, \dots$$

The eigen functions of \hat{L}^2 are depend on two coordinates of the physical system and are given by (derived in earlier module)

$$Y(\theta, \phi) = P(\theta) \cdot f(\phi)$$

$$Y_{j,m}(\theta, \phi) = (-1)^m \left[\frac{(2j+1)(j-|m_j|)!}{4\pi(j+|m_j|)!} \right]^{1/2} e^{im_j\phi} P_j^{m_j}(\cos\theta)$$

In quantum mechanics we encounter two types of angular momenta viz., (a) Orbital Angular Momentum (L) due to circular motion of a particle through space and is analog of classical angular momentum and (b) Spin Angular Momentum (S) which is an intrinsic property of a particle unrelated to any sort of motion or with any classical mechanical significance.

The above mentioned relations holds true for both the spin and orbital angular momentum respectively.

In this module, we will learn to calculate the angular momentum of multi-electron chemical systems.

3. Addition of Angular Momenta

From our earlier discussions, we know that angular momentum commutes with the Hamiltonian. For a multi-electron system, the individual angular momentum operators of the electrons do not commute with the Hamiltonian, but it's the sum of individual angular momentum operators that commute with the Hamiltonian.

Suppose we consider a system of two electrons associated with angular momentum \widehat{L}_1 and \widehat{L}_2 respectively.

Note: Over here, we have considered Orbital Angular Momentum (**L**) associated with both the electrons. They might be the Spin Angular-Momentum (**S**) of two electrons, or one might be the spin and the other the orbital angular momentum of a single electron.

- (a) Two Orbital angular momenta $\widehat{L} = \widehat{L}_1 + \widehat{L}_2$
 (b) Two Spin angular momenta $\widehat{S} = \widehat{S}_1 + \widehat{S}_2$
 (c) Orbital angular momentum and Spin $\widehat{J} = \widehat{L}_1 + \widehat{S}_2$

The eigen-values associated with the magnitude and z component of \widehat{L}_1 and \widehat{L}_2 respectively are as follows:

$$\widehat{L}_{1z}Y = m_{j_1} \hbar Y \quad m_{j_1} = -j_1, \dots, +j_1$$

$$\widehat{L}_1^2 Y = j_1(j_1 + 1)\hbar^2 Y \quad j_1 = 0, 1/2, 1, 3/2, 2, \dots$$

$$\widehat{L}_{2z}Y = m_{j_2} \hbar Y \quad m_{j_2} = -j_2, \dots, +j_2$$

$$\widehat{L}_2^2 Y = j_2(j_2 + 1)\hbar^2 Y \quad j_2 = 0, 1/2, 1, 3/2, 2, \dots$$

The components of \widehat{L}_1 and \widehat{L}_2 obey the usual angular momentum commutation relations as stated above.

$$[\widehat{L}_{1x}, \widehat{L}_{1y}] = i\hbar \widehat{L}_{1z}$$

$$[\widehat{L}_{1y}, \widehat{L}_{1z}] = i\hbar \widehat{L}_{1x}$$

$$[\widehat{L}_{1z}, \widehat{L}_{1x}] = i\hbar \widehat{L}_{1y}$$

$$[\hat{L}_{2x}, \hat{L}_{2y}] = i\hbar\hat{L}_{2z}$$

$$[\hat{L}_{2y}, \hat{L}_{2z}] = i\hbar\hat{L}_{2x}$$

$$[\hat{L}_{2z}, \hat{L}_{2x}] = i\hbar\hat{L}_{2y}$$

The total angular momentum for the two electron system is taken as sum of angular momentum associated with the two electrons respectively.

$$\hat{L} = \hat{L}_1 + \hat{L}_2 \text{ where the three Cartesian components of } \hat{L} \text{ are} \quad \dots(18.7)$$

$$\hat{L}_x = \hat{L}_{1x} + \hat{L}_{2x}$$

$$\hat{L}_y = \hat{L}_{1y} + \hat{L}_{2y}$$

$$\hat{L}_z = \hat{L}_{1z} + \hat{L}_{2z}$$

And the magnitude of total angular momentum is defined in the usual manner as done earlier.

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

$$\hat{L}^2 = \hat{L} \cdot \hat{L} = (\hat{L}_1 + \hat{L}_2) \cdot (\hat{L}_1 + \hat{L}_2) = \hat{L}_1^2 + \hat{L}_2^2 + \hat{L}_1 \cdot \hat{L}_2 + \hat{L}_2 \cdot \hat{L}_1 \quad \dots(18.8)$$

If \hat{L}_1 and \hat{L}_2 refer to different electrons they will commute with each other, since each will affect only functions of the coordinates of one electron and not the other (Non-interacting system).

$$[\hat{L}_1, \hat{L}_2] = 0$$

$$[\hat{L}_1, \hat{L}_2] = \hat{L}_1\hat{L}_2 - \hat{L}_2\hat{L}_1 = 0 \Rightarrow \hat{L}_1\hat{L}_2 = \hat{L}_2\hat{L}_1 \quad \dots(18.9)$$

Even if we consider orbital \hat{L}_1 and spin angular momenta \hat{S}_1 of the same electron, they will commute as one will affect only functions of the spatial coordinates while the other will affect functions of the spin coordinates.

$$[\hat{L}_1, \hat{S}_1] = 0$$

$$[\hat{L}_2, \hat{S}_2] = 0$$

Using equation (18.9) modifies equation (18.8) to

$$\widehat{L}^2 = \widehat{L} \cdot \widehat{L} = (\widehat{L}_1 + \widehat{L}_2) \cdot (\widehat{L}_1 + \widehat{L}_2) = \widehat{L}_1^2 + \widehat{L}_2^2 + 2\widehat{L}_1 \cdot \widehat{L}_2$$

Substituting the components of \widehat{L}_1 and \widehat{L}_2 (L_x, L_y and L_z) in the above equation gives,

$$\widehat{L}^2 = \widehat{L} \cdot \widehat{L} = (\widehat{L}_1 + \widehat{L}_2) \cdot (\widehat{L}_1 + \widehat{L}_2) = \widehat{L}_1^2 + \widehat{L}_2^2 + 2(\widehat{L}_{1x} \cdot \widehat{L}_{2x} + \widehat{L}_{1y} \cdot \widehat{L}_{2y} + \widehat{L}_{1z} \cdot \widehat{L}_{2z}) \quad \dots(18.10)$$

To simplify the above equation, we now show that the components of the total angular momentum obey the usual angular-momentum commutation relations.

$$[\widehat{L}_x, \widehat{L}_y] = [\widehat{L}_{1x} + \widehat{L}_{2x}, \widehat{L}_{1y} + \widehat{L}_{2y}] = [\widehat{L}_{1x}, \widehat{L}_{1y} + \widehat{L}_{2y}] + [\widehat{L}_{2x}, \widehat{L}_{1y} + \widehat{L}_{2y}]$$

$$[\widehat{L}_x, \widehat{L}_y] = [\widehat{L}_{1x}, \widehat{L}_{1y}] + [\widehat{L}_{1x}, \widehat{L}_{2y}] + [\widehat{L}_{2x}, \widehat{L}_{1y}] + [\widehat{L}_{2x}, \widehat{L}_{2y}]$$

Using equation (18.9) modifies the above equation as

$$[\widehat{L}_x, \widehat{L}_y] = [\widehat{L}_{1x}, \widehat{L}_{1y}] + [\widehat{L}_{2x}, \widehat{L}_{2y}] = i\hbar\widehat{L}_{1z} + i\hbar\widehat{L}_{2z} = i\hbar\widehat{L}_z \quad \dots(18.11)$$

Cyclic permutation of $x, y,$ and z gives,

$$[\widehat{L}_y, \widehat{L}_z] = i\hbar\widehat{L}_x \quad \dots(18.12)$$

$$[\widehat{L}_z, \widehat{L}_x] = i\hbar\widehat{L}_y \quad \dots(18.13)$$

The same commutator algebra proves the following as well for the two electron system,

$$[\widehat{L}^2, \widehat{L}_x] = 0$$

$$[\widehat{L}^2, \widehat{L}_y] = 0$$

$$[\widehat{L}^2, \widehat{L}_z] = 0$$

After concluding that the total angular momentum operator for a multi-electron system obeys the usual commutation relations of the angular momentum, we will now find how the total angular-momentum quantum numbers J and M_J are related to the quantum numbers j_1, j_2, m_{j_1} and m_{j_2} of the two angular momenta we are adding in (18.7).

$$\widehat{L}_z Y = M_J \hbar Y \quad M_J = -J, \dots, \dots, \dots, +J \quad \dots(18.14)$$

$$\widehat{L}^2 Y = J(J + 1) \hbar^2 Y \quad J = 0, 1/2, 1, 3/2, 2, \dots \quad \dots(18.15)$$

We further want the eigen-functions of total angular momentum of two electron system \widehat{L}^2 and its \widehat{L}_z component. These eigen-functions are characterized by the quantum numbers J and M_J .

Dirac Notation

This notation also referred to as **bra-ket** notation is very useful in quantum mechanics.

- A general quantum state (or **wave-function**) is represented as $|\psi\rangle$ called a **ket** vector.
- Associated with every state $|\psi\rangle$, there is dual $\langle\psi|$ called **bra** vector.
- The inner product of two states is given as $\langle\varphi|\psi\rangle$ and is scalar (Probability amplitude)

$$\langle\varphi|\psi\rangle = \int_{-\infty}^{\infty} dx \varphi^*(x)\psi(x) = \langle\varphi|\psi\rangle^*$$

- Action of some operator A is represented by $A|\psi\rangle$.
- Suppose, $|\varphi\rangle = A|\psi\rangle$, then $\langle\varphi| = \langle\psi|A^\dagger$ (adjoint)
- The expectation value for a normalized operator A is given by the equation

$$\langle A \rangle = \langle\psi|A|\psi\rangle$$
- The **eigen ket** of operator \widehat{A} associated with eigen value a is denoted by $|a\rangle$ with $A|a\rangle = a|a\rangle$

Using Dirac notation, we can denote the eigen-functions of total angular momentum operator by $|JM_J\rangle$. Similarly, let $|j_1m_{j_1}\rangle$ denote the eigen-functions of \widehat{L}_1^2 and its \widehat{L}_{1z} and $|j_2m_{j_2}\rangle$ denote the eigen-functions of \widehat{L}_2^2 and its \widehat{L}_{2z} .

We already know from equation (18.4) that,

$$[\widehat{L}_1^2, \widehat{L}_{1x}] = 0$$

$$[\widehat{L}_1^2, \widehat{L}_{1y}] = 0$$

$$[\widehat{L}_1^2, \widehat{L}_{1z}] = 0$$

$$[\widehat{L}_2^2, \widehat{L}_{2x}] = 0$$

$$[\widehat{L}_2^2, \widehat{L}_{2y}] = 0$$

$$[\widehat{L}_2^2, \widehat{L}_{2z}] = 0$$

Hence one can have simultaneous eigen-functions of all four operators $\widehat{L}_1^2, \widehat{L}_2^2, \widehat{L}^2 (\widehat{L} = \widehat{L}_1 + \widehat{L}_2), \widehat{L}_z (\widehat{L}_z = \widehat{L}_{1z} + \widehat{L}_{2z})$ and the eigen-functions $|JM_J\rangle$ can be more fully written as $|j_1j_2JM_J\rangle$. However, it is important to note over here that $\widehat{L}^2 (L = L_1 + L_2)$ does not commute with \widehat{L}_{1z} and \widehat{L}_{2z} , so the eigen-functions $|j_1j_2JM_J\rangle$ are not necessarily eigen-functions of \widehat{L}_{1z} and \widehat{L}_{2z} ($[\widehat{L}^2, \widehat{L}_{1z}] \neq 0$ and $[\widehat{L}^2, \widehat{L}_{2z}] \neq 0$).

If we consider the complete set of functions $|j_1m_{j_1}\rangle$ for electron (or entity under consideration) 1 and the complete set of functions $|j_2m_{j_2}\rangle$ for electron 2 and form all possible products of the form $|j_1m_{j_1}\rangle |j_2m_{j_2}\rangle$, then we obtain a complete set of functions for the two electron system. Each unknown eigen-function $|j_1j_2JM_J\rangle$ can then be expanded using the complete set of functions:

$$|j_1j_2JM_J\rangle = \sum C(j_1j_2JM_J; m_{j_1}m_{j_2}) |j_1m_{j_1}\rangle |j_2m_{j_2}\rangle \quad \dots(18.16)$$

where the expansion coefficients are $C(j_1j_2JM_J; m_{j_1}m_{j_2})$. The functions $|j_1j_2JM_J\rangle$ are eigen-functions of the commuting operators $\widehat{L}_1^2, \widehat{L}_2^2, \widehat{L}^2 (L = L_1 + L_2), \widehat{L}_z (L_z = \widehat{L}_{1z} + \widehat{L}_{2z})$ with the following eigen-values

\widehat{L}_1^2	\widehat{L}_2^2	\widehat{L}^2	\widehat{L}_z
$j_1(j_1 + 1)\hbar^2$	$j_2(j_2 + 1)\hbar^2$	$J(J + 1)\hbar^2$	$M_J\hbar$

The functions $|j_1m_{j_1}\rangle |j_2m_{j_2}\rangle$ are eigen-functions of the commuting operators with the following eigen-values:

\widehat{L}_1^2	\widehat{L}_{1z}	\widehat{L}_2^2	\widehat{L}_{2z}
$j_1(j_1 + 1)\hbar^2$	$m_{j_1}\hbar$	$j_2(j_2 + 1)\hbar^2$	$m_{j_2}\hbar$

The expanded expression for the function $|j_1 j_2 J M_J\rangle$ in equation (18.16) is an eigenfunction of \widehat{L}_1^2 with eigen-value $j_1(j_1 + 1)\hbar^2$ (considering only those terms that have the same value of j_1 as in the function $|j_1 j_2 J M_J\rangle$) and so is the case with other operator \widehat{L}_2^2 . Only terms with the same j_2 value as in $|j_1 j_2 J M_J\rangle$ are included in the sum. Hence the sum goes over only the m_{j_1} and m_{j_2} values (as m_{j_1} and m_{j_2} can respectively have $(2j_1 + 1)$ and $(2j_2 + 1)$ values).

As a consequence of $\widehat{L} = \widehat{L}_1 + \widehat{L}_2$, we have $\widehat{L}_z = \widehat{L}_{1z} + \widehat{L}_{2z}$ and therefore, their eigenvalues satisfy the relation

$$M_J = m_{j_1} + m_{j_2} \quad \dots(18.17)$$

To find the total-angular-momentum eigen-functions, one must evaluate the coefficients in (18.16). These $(C(j_1 j_2 J M_J; m_{j_1} m_{j_2}))$ are called **Clebsch-Gordan or Wigner or vector addition coefficients**.

Thus, each total angular momentum eigen-function $|j_1 j_2 J M_J\rangle$ is a linear combination of those product functions $|j_1 m_{j_1}\rangle |j_2 m_{j_2}\rangle$ whose m values satisfy equation (18.17).

$$\widehat{L}_z Y = M_J \hbar Y \quad M_J = -J, \dots, +J$$

$$\widehat{L}_{1z} Y = m_{j_1} \hbar Y \quad m_{j_1} = -j_1, \dots, +j_1$$

$$\widehat{L}_{2z} Y = m_{j_2} \hbar Y \quad m_{j_2} = -j_2, \dots, +j_2$$

$$M_J = m_{j_1} + m_{j_2}$$

4. Summary

1. The total angular momentum for the two electron system is taken as sum of angular momentum associated with the two electrons respectively.

- Possibilities of combination can be
 - I. Two Orbital angular momenta $\hat{L} = \hat{L}_1 + \hat{L}_2$
 - II. Two Spin angular momenta $\hat{S} = \hat{S}_1 + \hat{S}_2$
 - III. Orbital and Spin angular momentum $\hat{J} = \hat{L}_1 + \hat{S}_2$
- The total angular momentum for the two electron system is taken as sum of angular momentum associated with the two electrons respectively.

$$\hat{L} = \hat{L}_1 + \hat{L}_2$$

- **Commutation Relations**

$$[\hat{L}_1, \hat{L}_2] = 0 \quad [\hat{L}^2, \hat{L}_x] = 0 \quad [\hat{L}^2, \hat{L}_y] = 0 \quad [\hat{L}^2, \hat{L}_z] = 0$$

2. Eigen-value equation for the total angular momentum for the two electron system

$$\hat{L}_z Y = M_J \hbar Y \quad M_J = -J, \dots, +J$$

$$\hat{L}^2 Y = J(J+1)\hbar^2 Y \quad J = 0, 1/2, 1, 3/2, 2, \dots$$

- $M_J = m_{j_1} + m_{j_2}$