Quantum Mechanics: Vibration and Rotation of Molecules

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I. Classical Orbital Angular Momentum and Extension to Q. M. Operators

Before considering the eigenvalue equations describing the energetics and eigenfunctions for describing orbital angular momentum in a q.m. sense, we will first consider the operators that are pertinent to measurements of angular momentum on such systems (remembering that operators are associated with measureables/observables in a q.m. sense). We also note that we will consider angular momentum in general, though the formulation in the following is based on classical analogues, which are based on analogy to orbital motion). We have considered, so far, the translational (particle-in-a-box) and vibrational (harmonic-oscillator) models to describe translational and vibrational dynamical modes as we understand in classical mechanics. With a discussion of angular momentum, we focus on the rotational model of such dynamics to arrive at a complete set of eigenfunctions that we can apply towards describing actual systems, such as atoms and molecules.

Consider a particle described by the Cartesian coordinates $(x, y, z) \equiv \mathbf{r}$ and their conjugate momenta $(p_x, p_y, p_z) \equiv \mathbf{p}$

The classical definition of the orbital angular momentum of such a particle about the origin is $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ giving,

$$L_x = y\,p_z - z\,p_y, \tag{1}$$

$$L_y = z\,p_x - x\,p_z, \tag{2}$$

$$L_z = x\,p_y - y\,p_x. \tag{3}$$

Let us assume that the operators $(\hat{L}_x, \hat{L}_y, \hat{L}_z) \equiv \hat{\mathbf{L}}$ represent the components of orbital angular momentum in quantum mechanics can be defined in an analogous manner to the corresponding components of classical angular momentum. In other words, we are going to assume that the above equations specify the angular momentum operators in terms of the position and linear momentum operators. Note that $\hat{L}_x$, $\hat{L}_y$, $\hat{L}_z$ are Hermitian (have real eigenvalues), so they represent things which can, in principle, be measured. Note, also, that there is no ambiguity regarding the order in which operators appear in products on the right-hand sides of , since all of the products consist of operators which commute. The fundamental commutation relations satisfied by the position and linear momentum operators are

$$[x_i, x_j] = 0, \tag{4}$$

$$[p_i, p_j] = 0, \tag{5}$$

$$[x_i, p_j] = \mathrm{i}\,\hbar\,\delta_{ij}, \tag{6}$$

where i and j stand for either x, y, or z.

Consider the commutator of the operators $\hat{L}_x$ and $\hat{L}_y$

$$\begin{aligned} [\hat{L}_x, \hat{L}_y] &= [(y\,p_z - z\,p_y), (z\,p_x - x\,p_z)] = y\,[p_z, z]\,p_x + x\,p_y\,[z, p_z] \\ &= \mathrm{i}\,\hbar\,(-y\,p_x + x\,p_y) = \mathrm{i}\,\hbar\,\hat{L}_z. \end{aligned} \tag{7}$$

The cyclic permutations of the above result yield the fundamental commutation relations satisfied by the components of an angular momentum:

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

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

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

These can be summed up more succinctly by writing

$$\mathbf{L} \times \mathbf{L} = \mathrm{i}\,\hbar\,\mathbf{L}. \tag{8}$$

The three commutation relations are the foundation for the whole theory of angular momentum in quantum mechanics. Whenever we encounter three operators having these commutation relations, we know that the dynamical variables which they represent have identical properties to those of the components of an angular momentum (which we are about to derive). In fact, we shall assume that any three operators which satisfy the commutation relations represent the components of an angular momentum.

Suppose that there are N particles in the sysetm, with angular momentum vectors

$\mathbf{L}_i$ (where i runs from 1 to N. Each of these vectors satisfies Eq., so that

$$\mathbf{L}_i \times \mathbf{L}_i = \mathrm{i}\,\hbar\,\mathbf{L}_i. \tag{9}$$

However, we expect the angular momentum operators belonging to different particles to commute, since they represent different degrees of freedom of the system. **by analogy to the classical Poisson Bracket, q. m. operators for different degrees of freedom commute; those for the same degree of freedom do not commute**. So, we can write

$$\mathbf{L}_i \times \mathbf{L}_j + \mathbf{L}_j \times \mathbf{L}_i = 0, \tag{10}$$

$i \neq j$. Consider the total angular momentum of the system,
$\mathbf{L} = \sum_{i=1}^{N} \mathbf{L}_i$
$\mathbf{L} = \sum_{i=1}^{N} \mathbf{L}_i$. It is clear from Eqs. and that

$$\begin{aligned} \mathbf{L} \times \mathbf{L} &= \sum_{i=1}^{N} \mathbf{L}_i \times \sum_{j=1}^{N} \mathbf{L}_j = \sum_{i=1}^{N} \mathbf{L}_i \times \mathbf{L}_i + \frac{1}{2} \sum_{i,j=1}^{N} (\mathbf{L}_i \times \mathbf{L}_j + \mathbf{L}_j \times \mathbf{L}_i) \\ &= \mathrm{i}\,\hbar \sum_{i=1}^{N} \mathbf{L}_i = \mathrm{i}\,\hbar\,\mathbf{L}. \end{aligned} \tag{11}$$

Thus, the sum of two or more angular momentum vectors satisfies the same commutation relation as a primitive angular momentum vector. In particular, the total angular momentum of the system satisfies the commutation relation .

The immediate conclusion which can be drawn from the commutation relations is that the three components of an angular momentum vector cannot be specified (or measured) simultaneously. In fact, once we have specified one component, the values of other two components become uncertain. It is conventional to specify the z-component, $\hat{L}_z$.

Consider the magnitude squared of the angular momentum vector, $L^2 \equiv {L_x}^2 + {L_y}^2 + {L_z}^2$ **The commutator of L^2 and L_z is written**

$$[L^2, L_z] = [{L_x}^2, L_z] + [{L_y}^2, L_z] + [{L_z}^2, L_z]. \tag{12}$$

It is easily demonstrated that

$$\boxed{[{\mathbf{L}_x}^2, L_z] = -\mathrm{i}\,\hbar\,(L_x\,L_y + L_y\,L_x),}$$

$$\boxed{[{\mathbf{L}_y}^2, L_z] = +\mathrm{i}\,\hbar\,(L_x\,L_y + L_y\,L_x),}$$

$$\boxed{[{\mathbf{L}_z}^2, L_z] = 0,}$$

so

$$\boxed{[\mathbf{L}^2, L_z] = 0.}$$

Since there is nothing special about the z-axis, we conclude that L^2 also commutes with L_x and L_y. It is clear from Eqs and that the best we can do in quantum mechanics is to specify the magnitude of an angular momentum vector along with one of its components (by convention, the z-component).

Raising and Lowering Operators / Shift Operators

It is convenient to define the shift operators L^+ and L^-:

$$
\begin{aligned}
L^+ &= L_x + \mathrm{i}\, L_y, && (13)\\
L^- &= L_x - \mathrm{i}\, L_y. && (14)
\end{aligned}
$$

Note that

$$
\begin{aligned}
[L^+, L_z] &= -\hbar\, L^+, && (15)\\
[L^-, L_z] &= +\hbar\, L^-, && (16)\\
[L^+, L^-] &= 2\,\hbar\, L_z. && (17)
\end{aligned}
$$

Note, also, that both shift operators commute with L^2.