Quantum Mechanics: Vibration and Rotation of Molecules

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I. Q. M. Orbital Angular Momentum: Eigenvalues and Eigenfunctions of Rigid Rotor

Having determined the *orbital angular momentum* operators for q.m. rotation, we will now consider rotation in 3-dimensions (i.e, in a plane). The systems is a rigid two-body rotor with fixed distance between the two masses at each end of the rotor. Using the commutativity of the total angular momentum and one of its components, we will arrive at the eigenfunctions and eigenvalues of the angular momentum operators.

Consider Figure 1. The momentum vector is along the z-direction, so let's determine the eigenvalues and eigenfunctions for the operator corresponding to the z-component of orbital angular momentum.

The z-component angular momentum operator, $\hat{l}_z$, in Cartesian coordinates is:

$$l_z = x\,p_y - y\,p_x. \quad (classical)$$

$$\hat{l}_z = -i\hbar \left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x} \right)$$

The equivalent expressions for the $x-$ and $y-$ components are:

$$\hat{l}_x = -i\hbar \left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y} \right)$$

$$\hat{l}_y = -i\hbar \left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z} \right)$$

We also have:

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

More succinctly:

$$\hat{l} = -i\hbar \mathbf{r} \times \nabla$$

$$\hat{l}^2 = -\hbar^2 \left(\mathbf{r} \times \nabla \right) \bullet \left(\mathbf{r} \times \nabla \right)$$

Also recall the commutation relations:
Since the total angular momentum, $\hat{l}^2$, and the z-component, $\hat{l}_z$, commute, they must share the same eigenstates. Thus:

$$\hat{l}^2 \Psi_{km} = k\hbar^2 \Psi_{km}$$

$$\hat{l}_z \Psi_{km} = m\hbar \Psi_{km}$$

Since $\hbar$ has units of momentum, the eigenvalues are just a simple scalar value multiplying the unit of momentum.

In spherical polar coordinates:

$$x = r sin\theta cos\phi$$

$$y = r sin\theta sin\phi$$

$$x = r cos\phi$$

For the 3-dimensional rotor case, switching to polar coordinates (r, θ, ϕ).

The separation vector, $\mathbf{r}$, is taken to be fixed, and so we can take the wavefunction to be $\Psi(\theta, \phi)$. The operators in spherical polar coordinates are thus:

$$\hat{l}_x = -i\hbar \left(sin\phi \, \frac{\partial}{\partial \theta} + cot\theta \, cos\phi \, \frac{\partial}{\partial \phi} \right)$$

$$\hat{l}_y = -i\hbar \left(cos\phi \, \frac{\partial}{\partial \theta} - cot\theta \, sin\phi \, \frac{\partial}{\partial \phi} \right)$$

$$\hat{l}_z = -i\hbar \frac{\partial}{\partial \phi}$$

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

If we compare the Hamiltonian operator for the 3-d rigid rotor (considered previously), we see that:

$$\hat{H} = \hat{K} = \frac{\hat{l}^2}{2I}$$

The Hamiltonian and Angular momentum operators commute, **sharing eigenstates**. Thus, the spherical harmonics are eigenfunctions of $\hat{l}^2$ with eigenvalues, $l^2 = \hbar^2 l(l + 1)$.

$$\hat{l}^2 Y_l^m = l^2 Y_l^m = \hbar^2 l(l+1) Y_l^m \qquad l = 0, 1, 2, 3, ...$$

The length of the momentum vector is quantized in units of $\hbar$; l is the angular momentum quantum number.

The z-component of angular momentume, l_z, is the eigenvalue of the operator, $\hat{l}_z$:

$$\hat{l}_z Y_l^m = -i\hbar \frac{\partial}{\partial\phi} Y_l^m = \hbar m Y_l^m$$

Thus, the eigenvalues of the z-component are $\hbar m$. The spherical harmonics are also eigenfunctions (eigenstates) of the $\hat{l}_z$ operator. Thus, $\hat{H}, \hat{l}_2$, and $\hat{l}_z$ commute.

Up to now, we again have introduced l and l_z and m, etc. However, we have not shown what the relation is between, most importantly, m and l. It can be shown that the operators $\hat{l}^2$ and $\hat{l}_z$ commute; thus, we can know/measure the observables associated with these operators simultaneously.

$$\boxed{[l^2, l_z] = 0.}$$

These observables are the total angular momentum and the z-component of the total angular momentum. Since the z-component of the total can only be less than or equal to the total, we have the following:

Since, $|l_z| \leq |l| \quad \rightarrow \quad |m| \leq \sqrt{l(l+1)} \quad \rightarrow \quad |m| \leq l$

Thus, $m = 0, \pm1, \pm2, \pm3, ..., \pm l$. For each value of l, there are $2l+1$ possible m values. Since the energy does not depend m, each state is then (2l+1)-fold degenerate!

Table .

l	m	Y_l^m	Degeneracy (2l+1)
0	0	Y_0^0	1
1	-1, 0, 1	$Y_1^{-1},\ \ Y_1^0,\ \ Y_1^1$	3
2	-2, -1, 0, 1, 2	$Y_2^{-2},\ \ Y_2^{-1},\ \ Y_2^0,\ \ Y_2^1,\ \ Y_2^2$	5
3	-3, -2, -1, 0, 1, 2, 3	$Y_3^{-3},\ \ Y_3^{-2},\ \ Y_3^{-1},\ \ Y_3^0,\ \ Y_3^1,\ \ Y_3^2,\ \ Y_3^3$	7