Angular Momentum

$$\vec{L} = \vec{r} \times \vec{p} = \frac{\hbar}{i}\,\vec{r} \times \vec{\nabla}$$

$$\vec{\nabla} = \hat{r}\frac{\partial}{\partial r} + \hat{\theta}\frac{1}{r}\frac{\partial}{\partial \theta} + \hat{\phi}\frac{1}{r\sin\theta}\frac{\partial}{\partial \phi}$$

$$\begin{aligned}
\hat{\theta} &= \cos\theta\cos\phi\,\hat{x} + \cos\theta\sin\phi\,\hat{y} - \sin\theta\,\hat{z} \\
\hat{\phi} &= -\sin\phi\,\hat{x} + \cos\phi\,\hat{y}
\end{aligned}$$

$$\begin{aligned}
\vec{L} &= \frac{\hbar}{i}\left[\vec{r} \times \hat{r}\frac{\partial}{\partial r} + \vec{r} \times \hat{\theta}\frac{1}{r}\frac{\partial}{\partial \theta} + \vec{r} \times \hat{\phi}\frac{1}{r\sin\theta}\frac{\partial}{\partial \phi}\right] \\
&= \frac{\hbar}{i}\left[\hat{\phi}\frac{\partial}{\partial \theta} - \hat{\theta}\frac{1}{\sin\theta}\frac{\partial}{\partial \phi}\right] \\
&= \frac{\hbar}{i}\Big[(-\sin\phi\,\hat{x} + \cos\phi\,\hat{y})\frac{\partial}{\partial \theta} \\
&\qquad - (\cos\theta\cos\phi\,\hat{x} + \cos\theta\sin\phi\,\hat{y} - \sin\theta\,\hat{z})\frac{1}{\sin\theta}\frac{\partial}{\partial \phi}\Big]
\end{aligned}$$

$$\begin{aligned}
L_x &= \frac{\hbar}{i}\left(-\sin\phi\frac{\partial}{\partial \theta} - \frac{\cos\theta}{\sin\theta}\cos\phi\frac{\partial}{\partial \phi}\right) \\
L_y &= \frac{\hbar}{i}\left(\cos\phi\frac{\partial}{\partial \theta} - \frac{\cos\theta}{\sin\theta}\sin\phi\frac{\partial}{\partial \phi}\right) \\
L_z &= \frac{\hbar}{i}\frac{\partial}{\partial \phi}
\end{aligned}$$

Angular Momentum

$$\begin{aligned}
L_\pm &= L_x \pm i\, L_y \\
&= \frac{\hbar}{i}\left[(-\sin\phi \pm i\,\cos\phi)\,\frac{\partial}{\partial\theta} - (\cos\phi \pm i\,\sin\phi)\cot\theta\,\frac{\partial}{\partial\phi}\right] \\
&= \pm\,\hbar\, e^{\pm i\phi}\left[\frac{\partial}{\partial\theta} \pm i\,\cot\theta\,\frac{\partial}{\partial\phi}\right]
\end{aligned}$$

$$\begin{aligned}
L_+ L_- &= \hbar^2\, e^{i\phi}\left[\frac{\partial}{\partial\theta} + i\,\cot\theta\,\frac{\partial}{\partial\phi}\right]\left(-e^{-i\phi}\right)\left[\frac{\partial}{\partial\theta} - i\,\cot\theta\,\frac{\partial}{\partial\phi}\right] \\
&= -\hbar^2\, e^{i\phi}\Bigg[e^{-i\phi}\left(\frac{\partial^2}{\partial\theta^2} - i\,\frac{-1}{\sin^2\theta}\,\frac{\partial}{\partial\phi} - i\,\cot\theta\,\frac{\partial^2}{\partial\theta\partial\phi}\right) \\
&\qquad i\cot\theta\,(-i)\;e^{-i\phi}\left(\frac{\partial}{\partial\theta} - i\,\cot\theta\,\frac{\partial}{\partial\phi}\right) \\
&\qquad i\cot\theta\;\; e^{-i\phi}\left(\frac{\partial^2}{\partial\theta\partial\phi} - i\,\cot\theta\,\frac{\partial^2}{\partial\phi^2}\right)\Bigg] \\
&= -\hbar^2\left[\frac{\partial^2}{\partial\theta^2} + \cot\theta\,\frac{\partial}{\partial\theta} + \cot^2\theta\,\frac{\partial^2}{\partial\phi^2} + i\,\frac{\partial}{\partial\phi}\right]
\end{aligned}$$

$$\begin{aligned}
L^2 &= L_+L_- - i[L_y, L_x] + L_z^2 = L_+L_- + L_z^2 - \hbar L_z \\
&= -\hbar^2\left[\frac{\partial^2}{\partial\theta^2} + \cot\theta\,\frac{\partial}{\partial\theta} + \cot^2\theta\,\frac{\partial^2}{\partial\phi^2} + i\,\frac{\partial}{\partial\phi} + \frac{\partial^2}{\partial\phi^2} + \frac{1}{i}\,\frac{\partial}{\partial\phi}\right] \\
&= -\hbar^2\left[\frac{1}{\sin\theta}\,\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\,\frac{\partial^2}{\partial\phi^2}\right]
\end{aligned}$$

Angular Momentum

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

eigenfunctions $Y_\ell^m(\theta,\phi)$

no Y_ℓ^m for half-integer ℓ

$$\left[\frac{1}{2\mu r^2}\left(-\hbar^2\frac{d}{dr}\left(r^2\frac{d}{dr}\right) + L^2\right) + V(r)\right]\psi = E\,\psi$$

$$K_{rad} = \frac{p^2}{2\mu}, \qquad K_{rot} = \frac{L^2}{2I}, \qquad I = \mu r^2$$

Diatomic Molecule

$$m_1\, r_1 = m_2\, r_2$$

$$(m_1 + m_2)\, r_1 = m_2\, (r_1 + r_2), \quad (m_1 + m_2)\, r_2 = m_1\, (r_1 + r_2)$$

$$\begin{aligned} I &= m_1 r_1^2 + m_2 r_2^2 = m_1 \tfrac{m_2^2 (r_1+r_2)^2}{(m_1+m_2)^2} + m_2 \tfrac{m_1^2 (r_1+r_2)^2}{(m_1+m_2)^2} \\ &= \tfrac{m_1 m_2 (r_1+r_2)^2}{m_1+m_2} = \mu r^2 \end{aligned}$$

$$H\psi = \tfrac{L^2}{2I}\psi = E\psi$$

$$\psi = Y_\ell^m(\theta, \phi)$$

$$E = \tfrac{\hbar^2\, \ell(\ell+1)}{2I}$$

O_2 Diatomic Molecule

$$E_{rot} = \frac{\hbar^2\, 2}{M_O r^2} = \frac{2\hbar^2\, c^2}{16 M_p c^2 r^2} \approx \frac{(6.58\times10^{-16} eV\, s)^2\, (3\times10^8 m/s)^2}{8\times938\times10^6 eV\, (10^{-10} m)^2}$$

$$\approx \frac{40\times10^{-16} eV^2}{8\times10^8 eV\, 10^{-20}}$$

$$\approx 5\times10^{-3}\, eV$$

$$f_{vib} = 5\times10^{13} Hz$$

$$E_{vib} = hf_{vib} = 2\pi\, 6.58\times10^{-16} eV\, s \times 5\times10^{13}\, 1/s$$

$$= 0.2\, eV$$

$$E_{vib} \gg E_{rot}$$

Diatomic Molecule