# 5.2: Potential Energy and the Hamiltonian

Since there is no energy barrier to rotation, there is no potential energy involved in the rotation of a molecule. All of the energy is kinetic energy. This simplifies the writing of the Hamiltonian.

In Cartesian coordinates, the Hamiltonian can be written

$$\begin{aligned}\hat{H} &= -\frac{\hbar^2}{2\mu}\nabla^2 \\ &= -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\end{aligned}$$

In spherical polar coordinates, the Hamiltonian can be written

$$\begin{aligned}\hat{H} &= -\frac{\hbar^2}{2\mu}\nabla^2 \\ &= -\frac{\hbar^2}{2\mu}\left(\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\end{aligned}$$

For the rigid rotor problem, $\mathrm{r}$ is taken to be a constant, simplifying the operator.

$$\hat{H} = -\frac{\hbar^2}{2\mu r^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)$$

The expression $\mu\mathrm{r}^2$ is the **moment of inertia** for the molecule. This value shows up often in problems involving the rotation of a molecule.

$$I = \mu r^2$$

While the expression for the Hamiltonian in spherical polar coordinates looks considerably more cumbersome than the Hamiltonian expressed in Cartesian coordinates, it will still be simpler to solve the problem describing the rotation of a molecule.