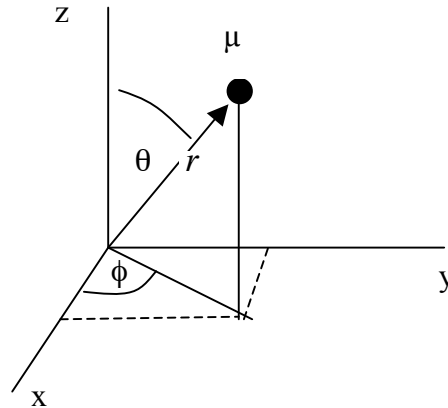


So now we look at this model for the internal (vibrational and rotational) motion of a diatomic using r as the bond length and μ as the reduced mass of the system. We can see that we could write the vector \vec{r} in two ways using Cartesian components (x,y,z) or spherical polar coordinates (r,θ,ϕ)



$$E = \frac{1}{2} \mu \dot{r}^2 + V(r)$$

We will consider two types of motion:

- 1) Elongation and contraction of the vector distance r about an equilibrium bond distance $r_e = d$. This is the vibration of the diatomic molecule and for this we isolate the energy terms that depend on the distance r

$$\text{alone: } E = \frac{1}{2} \mu \dot{r}^2 + V(r) = \frac{1}{2\mu} p^2 + V(r)$$

The corresponding Hamiltonian operator is

$$\hat{H} = \frac{-\hbar^2}{2\mu} \frac{\partial^2}{\partial x^2} + \frac{1}{2} kx^2 \text{ where } x = (r - r_e). \text{ Clearly this is just the harmonic oscillator}$$

we have already considered.

- 2) Angular motion in the θ and ϕ “directions. It turns out that we can write the kinetic energy operator terms that depend on θ and ϕ as follows:

$$\hat{H}_{rot} = -\frac{\hbar^2}{2\mu} \left[\frac{1}{d^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{d^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]$$

It turns out that the operator for the angular momentum squared is simply :

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

so we can write the Hamiltonian for the rotational motion as

$$\hat{H}_{rot} = \frac{\hat{L}^2}{2\mu d^2} = \frac{\hat{L}^2}{2I} \text{ where the moment of inertia of a diatomic is } I = \mu d^2$$

Note the similarity between translational kinetic energy $\frac{p^2}{2m}$ and rotational kinetic energy.

Solving the Schrödinger equation for the rotation we get the following result :

$$\hat{H}_{rot} Y_{JM}(\theta, \phi) = \frac{J(J+1)\hbar^2}{2I} Y_{JM}(\theta, \phi), J = 0, 1, 2, 3, \dots$$

where the wavefunctions $Y_{JM}(\theta, \phi)$ are called the spherical harmonics.