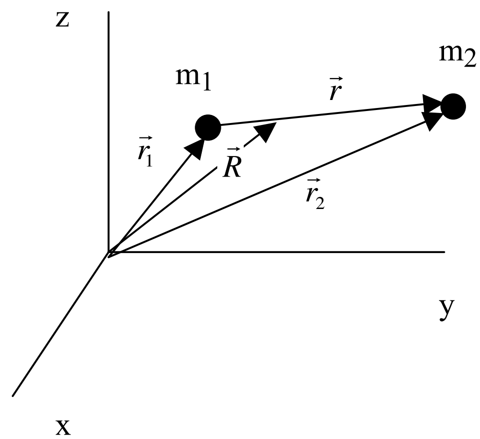
Given below is the classical energy expression for two atoms interacting with each other via a potential V(r) where r is the distance between the two particles. The following diagram illustrates what is going on.



$$E = \frac{1}{2}m_1[\mathrm{v}_{x,1}^2 + \mathrm{v}_{y,1}^2 + \mathrm{v}_{z,1}^2] + \frac{1}{2}m_2[\mathrm{v}_{x,2}^2 + \mathrm{v}_{y,2}^2 + \mathrm{v}_{z,2}^2] + V(r)$$

but in vector notation we might write:

$$E = \frac{1}{2}m_1\vec{\mathrm{v}}_1^2 + \frac{1}{2}m_2\vec{\mathrm{v}}_2^2 + V(r)$$

We'll now define the center-of-mass coordinate vector and the interparticle vector:

$$\vec{R} = \frac{m_1\vec{r}_1 + m_2\vec{r}_2}{M} \text{ where } M = m_1 + m_2$$

$$\vec{r} = \vec{r}_{12} = \vec{r}_2 - \vec{r}_1 \quad ; \quad r = |\vec{r}| = |\vec{r}_{12}|.$$

Let's now solve for $\vec{r}_1$ and $\vec{r}_2$ in terms of $\vec{R}$ and $\vec{\mathrm{r}}$. Treating the above two equations as two equations with two unknowns we get

$$\vec{r}_1 = \vec{R} - \frac{m_2}{M}\vec{r} \text{ and } \vec{r}_2 = \vec{R} + \frac{m_1}{M}\vec{r}$$

Now recall that

$$\vec{\mathrm{v}}_1 = \frac{d\vec{r}_1}{dt} = \dot{\vec{r}}_1 = \dot{\vec{R}} - \frac{m_2}{M}\dot{\vec{r}} = \text{and } \vec{\mathrm{v}}_2 = \frac{d\vec{r}_2}{dt} = \dot{\vec{r}}_2 = \dot{\vec{R}} + \frac{m_1}{M}\dot{\vec{r}}$$

If we now plug these expressions into the energy formula above, we get:

$$E = \frac{1}{2}m_1\left[\dot{\vec{R}} - \frac{m_2}{M}\dot{\vec{r}}\right]\cdot\left[\dot{\vec{R}} - \frac{m_2}{M}\dot{\vec{r}}\right] + \frac{1}{2}m_2\left[\dot{\vec{R}} + \frac{m_1}{M}\dot{\vec{r}}\right]\cdot\left[\dot{\vec{R}} + \frac{m_1}{M}\dot{\vec{r}}\right] + V(r)$$

$$= \frac{1}{2}m_1\left[\dot{\vec{R}}^2 - 2\frac{m_2}{M}\dot{\vec{R}}\cdot\dot{\vec{r}} + \frac{m_2^2}{M^2}\dot{\vec{r}}^2\right] + \frac{1}{2}m_2\left[\dot{\vec{R}}^2 + 2\frac{m_1}{M}\dot{\vec{R}}\cdot\dot{\vec{r}} + \frac{m_1^2}{M^2}\dot{\vec{r}}^2\right]\cdot + V(r)$$

We now see that the $\dot{\vec{R}}\cdot\dot{\vec{r}}$ terms cancel and we can collect the terms in $\dot{\vec{R}}^2$ and $\dot{\vec{r}}^2$

$$E = \frac{1}{2}m_1\dot{\vec{R}}^2 + \frac{1}{2}m_2\dot{\vec{R}}^2 + \frac{1}{2}m_1\frac{m_2^2}{M^2}\dot{\vec{r}}^2 + \frac{1}{2}m_2\frac{m_1^2}{M^2}\dot{\vec{r}}^2 + V(r)$$

$$= \frac{1}{2}M\dot{\vec{R}}^2 + \frac{1}{2}\frac{m_1m_2}{M}\left[\frac{m_2}{M} + \frac{m_1}{M}\right]\dot{\vec{r}}^2 + V(r) \qquad \text{I}$$

$$E = \frac{1}{2}M\dot{\vec{R}}^2 + \frac{1}{2}\mu\dot{\vec{r}}^2 + V(r) \text{ where we define } \mu = \frac{m_1m_2}{M} = \frac{m_1m_2}{m_1 + m_2} \text{ to be the reduced mass.}$$

It is this E that we can convert to a Hamiltonian operator. We consider the translational motion of the center of mass to be irrelevant to the internal workings of a molecule and focus on the internal vector coordinate, $\vec{r}$.