

The Rotational Hamiltonian *

I. THE SINGLE PARTICLE ROTATING ABOUT THE ORIGIN

The kinetic energy of rotation was

$$\frac{1}{2}I \left(\dot{\vartheta}^2 + \sin^2 \vartheta \dot{\varphi}_H^2 \right)$$

which means that a single pseudo-particle rotating about the origin, with mass μ , is mathematically equivalent to the two particle (diatomic molecule) motion which is under study here.

The Cartesian coördinate representation of this kinetic energy would be

$$\frac{1}{2}\mu (\dot{x}^2 + \dot{y}^2 + \dot{z}^2)$$

which is

$$\frac{1}{2\mu} (p_x^2 + p_y^2 + p_z^2)$$

with the *proviso* that the radius is unchanging. This is not the best coördinate system for this purpose, but it is the one in which the prescription for transforming to operator form is known, i.e.,

$$x \rightarrow x$$

and

$$p_x = -i\hbar \frac{\partial}{\partial x}$$

with equivalent expressions for y and z. We then have that the Hamiltonian operator in this case would be

$$H_{op} = -\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) = -\frac{\hbar^2}{2\mu} \nabla^2$$

This means that we can use other readings in this series to convert from the Cartesian to the Spherical Polar form of the ∇^2 operator, the Laplacian, leading to

$$-\frac{\hbar^2}{2\mu} \frac{1}{r^2} \left(\frac{\partial r^2}{\partial r} \frac{\partial}{\partial r} + \frac{1}{\sin^2 \vartheta} \left(\sin \vartheta \frac{\partial \sin \vartheta}{\partial \vartheta} \frac{\partial}{\partial \vartheta} + \frac{\partial^2}{\partial \varphi^2} \right) \right)$$

But $r=R$ is fixed, so the first term disappears and we have

$$H_{op} = -\frac{\hbar^2}{2\mu} \left(\frac{1}{R^2 \sin^2 \vartheta} \left(\sin \vartheta \frac{\partial \sin \vartheta}{\partial \vartheta} \frac{\partial}{\partial \vartheta} + \frac{\partial^2}{\partial \varphi^2} \right) \right)$$

which is

$$H_{op} = -\frac{\hbar^2}{2I} \left(\frac{1}{\sin^2 \vartheta} \left(\sin \vartheta \frac{\partial \sin \vartheta}{\partial \vartheta} \frac{\partial}{\partial \vartheta} + \frac{\partial^2}{\partial \varphi^2} \right) \right)$$

The Schrödinger Equation now becomes

$$H_{op}\psi = -\frac{\hbar^2}{2I} \left(\frac{1}{\sin^2 \vartheta} \left(\sin \vartheta \frac{\partial \sin \vartheta}{\partial \vartheta} \frac{\partial \psi}{\partial \vartheta} + \frac{\partial^2 \psi}{\partial \varphi^2} \right) \right) = E\psi$$

*12h2:rot5

where $E = E_{rot}$. Remember, as long as we use μ (or I), we are assured that we are dealing with a diatomic molecule properly. Also, remember that in the hierarchy of energy terms, we have so far

$$E = E_{trans} + E_{vib} + E_{rot}$$

where we are excluding coupling between vibration and rotation (for the time being).