The rigid rotor

The motion of rigid diatomic molecule serves as an application of the quantum-mechanical treatment of angular momentum to a chemical system.

Suppose we have a system of two particles of mass m_1 and m_2, which can rotate about their center of mass while the distance between the two particles is kept fixed. Let us denote this fixed distance R.

The time τ for a classical particle to make a complete revolution on its circular path is equal to the distance traveled divided by its linear velocity

$$\tau = \frac{2\pi r_i}{v_i}.$$

v_i can be expressed as $v_i = \frac{2\pi r_i}{\tau} = \omega r_i$

The angular momentum $\vec{L}_i$ of the particle i is

$$\vec{L}_i = \vec{r}_i \times \vec{p}_i = m_i(\vec{r}_i \times \vec{v}_i)$$

Since we deal with a rigid rotor, $\vec{v}_i$ is perpendicular to to $\vec{r}_i$.

$$|\vec{L}_i| = m_i r_i v_i = \omega m_i r_i^2$$

The potential energy can be treated as zero (because the distance betwen particles, R, cannot change.

The classical Hamiltonian function is given by

$$H = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} = \frac{m_1 v_1^2}{2} + \frac{m_2 v_2^2}{2} = \frac{1}{2}\omega^2(m_1 r_1^2 + m_2 r_2^2)$$

$$= \frac{1}{2} I\omega^2 \quad \text{where } I = m_1 r_1^2 + m_1 r_2^2$$

Let us now determine the the moment of inertia relative to the axis of rotation:

$$r_1 + r_2 = R \qquad m_1 r_1 = m_2 r_2$$

$$r_1 = \frac{m_2}{m_1+m_2} R \qquad r_2 = \frac{m_1}{m_1+m_2} R$$

No if we plug these into the formula for I we obtain

$$I = \mu R^2 \quad \text{where} \quad \mu = \frac{m_1 m_2}{m_1+m_2}$$

The total angular momentum L for the two particle system is given by

$$L = L_1 + L_2 = \omega(m_1 r_1^2 + m_2 r_2^2) = I\omega$$

A comparison between $L_i = \omega m_i r_i^2$ and $L = I\omega$ shows that

$$H = \frac{L^2}{2I}$$

Accordingly, the quantum-mechanical Hamiltonian for this system is

$$\hat{H} = \frac{1}{2I}\hat{L}^2$$

The eigenvalues of $\hat{H}$ are obtained by noting that

$$\hat{H}\, Y_J^m(\theta,\varphi) = \frac{1}{2I}\hat{L}^2 Y_J^m(\theta,\varphi) = \frac{J(J+1)\hbar^2}{2I} Y_J^m(\theta,\varphi)$$

The energy levels E_J for the rigid rotor are given by

$$E_J = J(J+1)\frac{\hbar^2}{2I} = J(J+1)B \qquad J = 0, 1, 2 \ldots$$

where $B = \frac{\hbar^2}{2I}$ is the rotational constant