Question

Rotational Energy Levels: For large quantum numbers, the frequency of radiation for a hydrogen atom that drops from an initial state of quantum number n to a final state of quantum number $n-1$ is equal to the classical frequency of revolution of an electron in the n^{th} Bohr orbit. This is an example of Bohr's correspondence principle. Show that a similar correspondence holds for a diatomic molecule rotating about its centre of mass.

Solution

The moment of inertia I of a diatomic molecule is $m'R^2$ where m' is the reduced mass and R the distance between the nuclei. This is equivalent to a mass m' rotating about a point a distance R away with, say, velocity v.

De Broglie wavelength

$$\lambda = \frac{h}{m'v}$$

Bohr condition for stability

$$n\lambda = 2\pi R \qquad n = 1,\, 2,\, 3\,...$$

Hence

$$\begin{aligned} \frac{nh}{m'v_n} &= 2\pi R \\ v_n &= \frac{n\hbar}{m'R} \end{aligned}$$

$$\begin{aligned} E_n &= \tfrac{1}{2}m'v_n^2 \\ &= \frac{n^2\hbar^2}{2m'R^2} \\ &= \frac{n^2\hbar^2}{2I} \end{aligned}$$

$$\begin{aligned} E_n - E_{n-1} &= \frac{\hbar^2}{2I}\left(n^2 - (n-1)^2\right) \\ \Delta E &\approx \frac{n\hbar^2}{I} \qquad \text{for large } n \\ \nu_{n\to n-1} &= \frac{\Delta E}{h} \\ &= \frac{\hbar}{2\pi I}\, n \end{aligned}$$

Equivalent to the quantum formula for rotational spectra $\quad \nu_{J\to J+1} = \dfrac{\hbar}{2\pi I}(J+1) \qquad J = 0,\, 1,\, 2\,...$

The Bohr correspondence principle also holds for a diatomic molecule rotating about its centre of mass.