

3.4: Rotation and Vibration of Diatomic Molecules

For a diatomic species, the vibration-rotation $\left(\frac{V}{R}\right)$ kinetic energy operator can be expressed as follows in terms of the bond length R and the angles θ and ϕ that describe the orientation of the bond axis relative to a laboratory-fixed coordinate system:

$$T_{V/R} = \frac{-\hbar^2}{2\mu} \left[\frac{1}{R^2} \frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R} \right) - \left(\frac{L}{R\hbar} \right)^2 \right],$$

where the square of the rotational angular momentum of the diatomic species is

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

Because the potential $E_j(R)$ depends on R but not on θ or ϕ , the $\frac{V}{R}$ function $X_{j,n}^0$ can be written as a product of an angular part and an R -dependent part; moreover, because L^2 contains the full angle-dependence of $T_{V/R}$, $X_{j,n}^0$ can be written as

$$\Xi_{j,n}^0 = Y_{J,M}(\theta, \phi) F_{j,J,v}(R).$$

The general subscript n , which had represented the state in the full set of 3M-3 R -space coordinates, is replaced by the three quantum numbers J, M , and v (i.e., once one focuses on the three specific coordinates R, θ , and ϕ , a total of three quantum numbers arise in place of the symbol n).

Substituting this product form for $\Xi_{j,n}^0$ into the $\frac{V}{R}$ equation gives:

$$\frac{-\hbar^2}{2\mu} \left[\frac{1}{R^2} \frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R} \right) - \frac{J(J+1)}{R^2\hbar^2} \right] F_{j,J,v}(R) + E_j(R) F_{j,J,v}(R) = E_{j,J,v}^0 F_{j,J,v}$$

as the equation for the vibrational (i.e., R -dependent) wavefunction within electronic state j and with the species rotating with $J(J+1)\hbar^2$ as the square of the total angular momentum and a projection along the laboratory-fixed Z -axis of $M\hbar$. The fact that the $F_{j,J,v}$ functions do not depend on the M quantum number derives from the fact that the $T_{V/R}$ kinetic energy operator does not explicitly contain J_Z ; only J^2 appears in $T_{V/R}$.

The solutions for which $J=0$ correspond to vibrational states in which the species has no rotational energy; they obey

$$\frac{-\hbar^2}{2\mu} \left[\frac{1}{R^2} \frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R} \right) \right] F_{j,0,v}(R) + E_j(R) F_{j,0,v}(R) = E_{j,0,v}^0 F_{j,0,v}.$$

The differential-operator parts of this equation can be simplified somewhat by substituting $F = \frac{\chi}{R}$ and thus obtaining the following equation for the new function χ :

$$\frac{-\hbar^2}{2\mu} \frac{\partial}{\partial R} \frac{\partial}{\partial R} \chi_{j,0,v}(R) + E_j(R) \chi_{j,0,v}(R) = E_{j,0,v}^0 \chi_{j,0,v}.$$

Solutions for which $J \neq 0$ require the vibrational wavefunction and energy to respond to the presence of the 'centrifugal potential' given by $\frac{\hbar^2 J(J+1)}{2\mu R^2}$; these solutions obey the full coupled V/R equations given above.

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