

1.8: Rotational Motion for a Rigid Diatomic Molecule

A diatomic molecule with fixed bond length R rotating in the absence of any external potential is described by the following Schrödinger equation:

$$\frac{\hbar^2}{2\mu} \left[\frac{1}{R^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{R^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \psi = E\psi$$

or

$$\frac{L^2 \psi}{2\mu R^2} = E\psi.$$

The angles θ and ϕ describe the orientation of the diatomic molecule's axis relative to a laboratory-fixed coordinate system, and μ is the reduced mass of the diatomic molecule

$$\mu = \frac{m_1 m_2}{m_1 + m_2}.$$

The differential operators can be seen to be exactly the same as those that arose in the hydrogen-like-atom case, and, as discussed above, these θ and ϕ differential operators are identical to the L^2 angular momentum operator whose general properties are analyzed in **Appendix G**. Therefore, the same spherical harmonics that served as the angular parts of the wavefunction in the earlier case now serve as the entire wavefunction for the so-called rigid rotor: $\psi = Y_{J,M}(\theta, \phi)$. As detailed later in this text, the eigenvalues corresponding to each such eigenfunction are given as:

$$E_J = \hbar^2 \frac{J(J+1)}{(2\mu R^2)} = BJ(J+1)$$

and are independent of M . Thus each energy level is labeled by J and is $2J+1$ -fold degenerate (because M ranges from $-J$ to J). The so-called rotational constant B (defined as $\frac{\hbar^2}{2\mu R^2}$) depends on the molecule's bond length and reduced mass. Spacings between successive rotational levels (which are of spectroscopic relevance because angular momentum selection rules often restrict ΔJ to 1, 0, and -1) are given by

$$\Delta E = B(J+1)(J+2) - BJ(J+1) = 2B(J+1).$$

These energy spacings are of relevance to microwave spectroscopy which probes the rotational energy levels of molecules.

This Schrödinger equation relates to the rotation of diatomic and linear polyatomic molecules. It also arises when treating the angular motions of electrons in any spherically symmetric potential.

Summary

The rigid rotor provides the most commonly employed approximation to the rotational energies and wavefunctions of linear molecules. As presented above, the model restricts the bond length to be fixed. Vibrational motion of the molecule gives rise to changes in R which are then reflected in changes in the rotational energy levels. The coupling between rotational and vibrational motion gives rise to rotational B constants that depend on vibrational state as well as dynamical couplings, called centrifugal distortions, that cause the total ro-vibrational energy of the molecule to depend on rotational and vibrational quantum numbers in a non-separable manner

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