

18.5: Solutions to Schroedinger Equations for Harmonic Oscillators and Rigid Rotors

We can approximate the wavefunction for a molecule by partitioning it into wavefunctions for individual translational, rotational, vibrational, and electronic modes. The wavefunctions for each of these modes can be approximated by solutions to a Schrödinger equation that approximates that mode. Our objective in this chapter is to introduce the quantized energy levels that are found.

Translational modes are approximated by the particle in a box model that we discuss above.

Vibrational modes are approximated by the solutions of the Schrödinger equation for coupled harmonic oscillators. The vibrational motion of a diatomic molecule is approximated by the solutions of the Schrödinger equation for the vibration of two masses linked by a spring. Let the distance between the masses be r and the equilibrium distance be r_0 . Let the reduced mass of the molecule be μ , and let the force constant for the spring be λ . From classical mechanics, the potential energy of the system is

$$V(r) = \frac{\lambda(r - r_0)^2}{2}$$

and the vibrational frequency of the classical oscillator is

$$\nu = \frac{1}{2\pi} \sqrt{\frac{\lambda}{\mu}}$$

The Schrödinger equation is

$$-\left(\frac{h^2}{8\pi^2\mu}\right) \frac{d^2\psi}{dr^2} + \frac{\lambda(r - r_0)^2}{2} \psi = E\psi$$

The solutions to this equation are wavefunctions and energy levels that constitute the quantum mechanical description of the classical harmonic oscillator. The energy levels are given by

$$E_n = h\nu \left(n + \frac{1}{2}\right)$$

where the quantum numbers, n , can have any of the values $n = 0, 1, 2, 3, \dots$. The lowest energy level, that for which $n = 0$, has a non-zero energy; that is,

$$E_0 = h\nu/2$$

The quantum mechanical oscillator can have infinitely many energies, each of which is a half-integral multiple of the classical frequency, ν . Each quantum mechanical energy corresponds to a quantum mechanical frequency:

$$\nu_n = \nu \left(n + \frac{1}{2}\right)$$

A classical rigid rotor consists of two masses that are connected by a weightless rigid rod. The rigid rotor is a dumbbell. The masses rotate about their center of mass. Each **two-dimensional rotational motion of a diatomic molecule** is approximated by the solutions of the Schrödinger equation for the motion of a rigid rotor in a plane. The simplest model assumes that the potential term is zero for all angles of rotation. Letting I be the molecule's moment of inertia and φ be the rotation angle, the Schrödinger equation is

$$-\left(\frac{h^2}{8\pi^2 I}\right) \frac{d^2\psi}{d\varphi^2} = E\psi$$

The energy levels are given by

$$E_m = \frac{m^2 h^2}{8\pi^2 I}$$

where the quantum numbers, m , can have any of the values $m = 1, 2, 3, \dots$, (but not zero). Each of these energy levels is two-fold degenerate. That is, two quantum mechanical states of the molecule have the energy E_m .

The **three-dimensional rotational motion of a diatomic molecule** is approximated by the solutions of the Schrödinger equation for the motion of a rigid rotor in three dimensions. Again, the simplest model assumes that the potential term is zero for all angles of rotation. Letting θ and φ be the two rotation angles required to describe the orientation in three dimensions, the Schrödinger equation is

$$-\frac{h^2}{8\pi^2 I} \left(\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial\psi}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{d^2\psi}{d\varphi^2} \right) = E\psi$$

The energy levels are given by

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1)$$

where the quantum numbers, J , can have any of the values $J = 0, 1, 2, 3, \dots$. E_J is $(2J+1)$ -fold degenerate. That is, there are $2J+1$ quantum mechanical states of the molecule all of which have the same energy, E_J .

Equations for the rotational energy levels of larger molecules are more complex.

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