

1.7: Harmonic Vibrational Motion

The radial motion of a diatomic molecule in its lowest ($J=0$) rotational level can be described by the following Schrödinger equation:

$$\frac{-\hbar^2}{2\mu r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) \psi + V(r)\psi = E\psi,$$

where m is the reduced mass

$$\mu = \frac{m_1 m_2}{(m_1 + m_2)}$$

of the two atoms. By substituting $\psi = \frac{F(r)}{r}$ into this equation, one obtains an equation for $F(r)$ in which the differential operators appear to be less complicated:

$$\frac{-\hbar^2}{2\mu} \frac{d^2 F}{dr^2} + V(r)F = EF.$$

This equation is exactly the same as the equation seen above for the radial motion of the electron in the hydrogen-like atoms except that the reduced mass μ replaces the electron mass m and the potential $V(r)$ is **not** the Coulomb potential.

If the potential is approximated as a quadratic function of the bond displacement $x = r - r_e$ expanded about the point at which V is minimum:

$$V = \frac{1}{2}k(r - r_e)^2,$$

the resulting harmonic-oscillator equation can be solved exactly. Because the potential V grows without bound as x approaches ∞ or $-\infty$, only bound-state solutions exist for this model problem; that is, the motion is confined by the nature of the potential, so no continuum states exist.

This Schrödinger equation forms the basis for our thinking about bond stretching and angle bending vibrations as well as collective phonon motions in solids

In solving the radial differential equation for this potential (see Chapter 5 of McQuarrie), the large- r behavior is first examined. For large- r , the equation reads:

$$\frac{d^2 F}{dx^2} = \frac{1}{2}kx^2 \left(\frac{2\mu}{\hbar^2} \right) F,$$

where $x = r - r_e$ is the bond displacement away from equilibrium. Defining $\xi = \sqrt{\frac{\mu k}{\hbar^2}} x$ as a new scaled radial coordinate allows the solution of the large- r equation to be written as:

$$F_{\text{larger-}r} = e^{-\frac{x^2}{2}}$$

The general solution to the radial equation is then taken to be of the form:

$$F = e^{-\frac{\xi^2}{2}} \sum_{n=0}^{\infty} \xi^n C_n,$$

where the C_n are coefficients to be determined. Substituting this expression into the full radial equation generates a set of recursion equations for the C_n amplitudes. As in the solution of the hydrogen-like radial equation, the series described by these coefficients is divergent unless the energy E happens to equal specific values. It is this requirement that the wavefunction not diverge so it can be normalized that yields energy quantization. The energies of the states that arise are given by:

$$E_n = \hbar \sqrt{\frac{k}{\mu}} \left(n + \frac{1}{2} \right)$$

and the eigenfunctions are given in terms of the so-called **Hermite polynomials** $H_n(y)$ as follows:

$$\psi_n(x) = \frac{1}{\sqrt{n!2^n}} \sqrt{\frac{\alpha}{\pi}} \left(e^{-\frac{\alpha x^2}{2}} \right) H_n(\sqrt{\alpha}x),$$

where $\alpha = \left(\sqrt{\frac{k\mu}{\hbar^2}} \right)$. Within this harmonic approximation to the potential, the vibrational energy levels are evenly spaced:

$$\Delta E = E_{n+1} - E_n = \hbar \left(\frac{k}{\mu} \right).$$

In experimental data such evenly spaced energy level patterns are seldom seen; most commonly, one finds spacings $E_{n+1} - E_n$ that decrease as the quantum number n increases. In such cases, one says that the progression of vibrational levels displays anharmonicity.

Because the H_n are odd or even functions of x (depending on whether n is odd or even), the wavefunctions $\psi_n(x)$ are odd or even. This splitting of the solutions into two distinct classes is an example of the effect of symmetry; in this case, the symmetry is caused by the symmetry of the harmonic potential with respect to reflection through the origin along the x -axis. Throughout this text, many symmetries will arise; in each case, symmetry properties of the potential will cause the solutions of the Schrödinger equation to be decomposed into various symmetry groupings. Such symmetry decompositions are of great use because they provide additional quantum numbers (i.e., symmetry labels) by which the wavefunctions and energies can be labeled.

The harmonic oscillator energies and wavefunctions comprise the simplest reasonable model for vibrational motion. Vibrations of a polyatomic molecule are often characterized in terms of individual bond-stretching and angle-bending motions each of which is, in turn, approximated harmonically. This results in a total vibrational wavefunction that is written as a product of functions one for each of the vibrational coordinates.

Two of the most severe limitations of the harmonic oscillator model, the lack of anharmonicity (i.e., non-uniform energy level spacings) and lack of bond dissociation, result from the quadratic nature of its potential. By introducing model potentials that allow for proper bond dissociation (i.e., that do not increase without bound as $x \rightarrow \infty$), the major shortcomings of the harmonic oscillator picture can be overcome. The so-called Morse potential (see the figure below)

$$V(r) = D_e \left(1 - e^{-a(r-r_e)} \right)^2,$$

is often used in this regard.

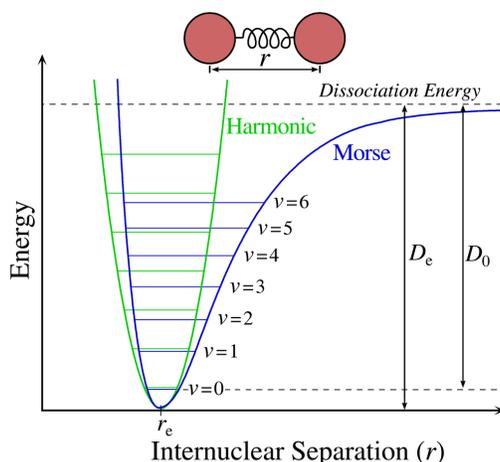


Figure 1.7.1: The Morse potential (blue) and harmonic oscillator potential (green). Unlike the energy levels of the harmonic oscillator potential, which are evenly spaced by $\hbar\omega$, the Morse potential level spacing decreases as the energy approaches the dissociation energy. The dissociation energy D_e is larger than the true energy required for dissociation D_0 due to the zero point energy of the lowest ($v = 0$) vibrational level. (CC-SA-BY-3.0; Somoza).

Here, D_e is the bond dissociation energy, r_e is the equilibrium bond length, and a is a constant that characterizes the 'steepness' of the potential and determines the vibrational frequencies. The advantage of using the Morse potential to improve upon harmonic

oscillator-level predictions is that its energy levels and wavefunctions are also known exactly. The energies are given in terms of the parameters of the potential as follows:

$$E_n = \hbar \sqrt{\frac{k}{\mu}} \left[\left(n + \frac{1}{2} \right) - \left(n + \frac{1}{2} \right)^2 \frac{\hbar}{4} \sqrt{\frac{k}{\mu}} D_e \right]$$

where the force constant k is $k = 2D_e a^2$. The Morse potential supports both bound states (those lying below the dissociation threshold for which vibration is confined by an outer turning point) and continuum states lying above the dissociation threshold. Its degree of anharmonicity is governed by the ratio of the harmonic energy $\hbar \sqrt{\frac{k}{\mu}}$ to the dissociation energy D_e .

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