

4.3: Strengths and Weaknesses

Keeping in mind that the harmonic oscillator model is an approximate model, it should not come as a surprise that there are a number of shortcomings to it.

The harmonic oscillator does not place any constraints on bond length. At the short bond length side of the potential, there is nothing in the model to prevent the bond length from becoming zero or even negative (implying that it is possible for one atom to pass through the other in a molecule). Additionally, the harmonic oscillator does not allow for molecular dissociation as the potential energy just keeps increasing with increasing bond length. None the less, the harmonic oscillator model works quite well for small displacements from the equilibrium bond length.

The Morse Potential

One improved form of a potential energy function was provided by Phillip Morse (Morse, 1929). The Morse potential is given by the following function

$$U(r) = D_e \left(1 - e^{-\beta(r-r_e)} \right)^2$$

where D_e is the dissociation energy of the molecule. While this function still allows for negative bond lengths, it does allow for molecular dissociation at long bond lengths.

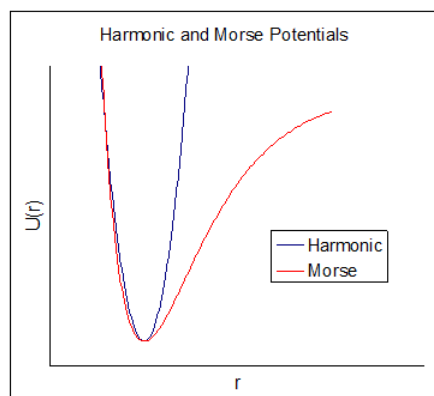


Figure 4.3.1

The force constant for the Morse potential is determined by evaluating the second derivative of the potential energy function at the potential minimum.

$$k = \left. \frac{d^2}{dr^2} U(r) \right|_{r=r_e}$$

Based on the expression given above for the Morse potential, the following result is obtained.

$$k = 2D_e\beta^2$$

Anharmonicity

A solution to the Schrödinger equation using the Morse potential produces an additional constant in the energy expression for vibrational energy.

$$G_v = \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2$$

The new constant, $\omega_e x_e$, is called an **anharmonicity constant**, as it accounts for deviation from the harmonic potential. For a more general potential energy function, the expression for the vibrational term value can be expressed as a longer power series in $(v + 1/2)$.

$$G_v = \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2 + \omega_e y_e(v + 1/2)^3 + \dots$$

For well-behaved molecules, the magnitude of the anharmonicity constants decreases with increasing order in $(v + 1/2)$. Thus, the series can be truncated at some point and will provide an adequate model for the purposes of fitting experimental data.

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