MORSE OSCILLATOR

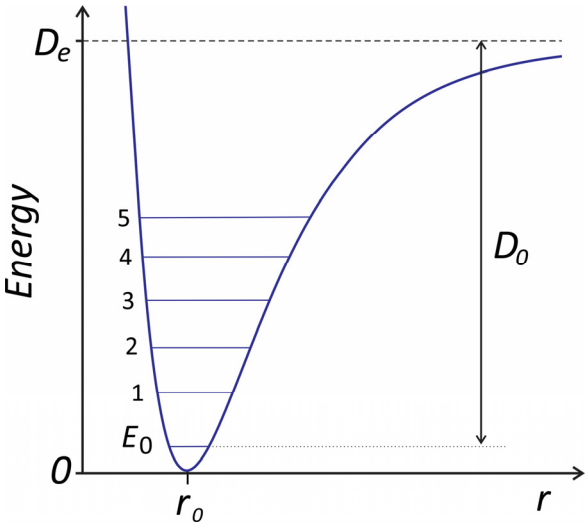
The Morse oscillator is a model for a particle in a one-dimensional anharmonic potential energy surface with a dissociative limit at infinite displacement.[1] It is commonly used for describing the spectroscopy of diatomic molecules and anharmonic vibrational dynamics, and most of its properties can be expressed through analytical expressions.[2] The Morse potential is

$$V(x) = D_e\left[1 - e^{-\alpha x}\right]^2 \tag{1}$$

where $x = (r - r_0)$. D_e sets the depth of the energy minimum at $r = r_0$ relative to the dissociation limit as $r \to \infty$, and α sets the curvature of the potential. If we expand V in powers of x about x=0,

$$V(x) \approx \tfrac{1}{2}\kappa x^2 + \tfrac{1}{6} g x^3 + \tfrac{1}{24} h x^4 + \cdots$$

we find that the harmonic, cubic, and quartic expansion coefficients are $\kappa = 2D_e\alpha^2$, $g = -6D_e\alpha^3$, and $h = 14D_e\alpha^4$.



The Morse oscillator Hamiltonian for a diatomic molecule of reduced mass m_R bound by this potential is

$$H = \frac{p^2}{2m_R} + V(x)$$

and has the eigenvalues

$$E_n = \hbar\omega_0\left[\left(n + \tfrac{1}{2}\right) - x_e\left(n + \tfrac{1}{2}\right)^2\right] \qquad n = 0,1,2,3... \tag{2}$$

Here $\omega_0 = \sqrt{2D_e\alpha^2/m_R}$ is the fundamental frequency and $x_e = \hbar\omega_0 / 4D_e$ is the anharmonic constant. The frequency ω_0 is equivalent to equating the harmonic force constant $\kappa = (\partial^2 V / \partial x^2)_{x=0}$ with $m_R\omega_0^2$. The anharmonic constant x_e is commonly seen in the spectroscopy expression for the anharmonic vibrational energy levels

$$G(v) = \omega_e(v + \tfrac{1}{2}) - \omega_e x_e(v + \tfrac{1}{2})^2 + \omega_e y_e(v + \tfrac{1}{2})^3 + \cdots \tag{3}$$

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[1] Morse, P. M., Diatomic Molecules According to the Wave Mechanics. II. Vibrational Levels. *Physical Review* **1929,** *34* (1), 57-64.

[2] Lefebvre-Brion, H. l. n.; Field, R. W., *The spectra and dynamics of diatomic molecules*. 2nd ed.; Academic Press: Boston, 2004.

From eq. (1.1) the ground state (or zero-point) energy is

$$E_0 = \tfrac{1}{2}\hbar\omega_0\left(1-\tfrac{1}{2}x_e\right) \tag{4}$$

So the dissociation energy for the Morse potential is given by $D_0 = D_e - E_0$. The transition energies are

$$E_n - E_m = \hbar\omega_0\left(n-m\right)\left[1-x_e\left(n+m+\tfrac{1}{2}\right)\right] \tag{5}$$

The proper harmonic expressions are obtained from the above for the Morse oscillator by setting $D_e \to \infty$ or $x_e \to 0$.

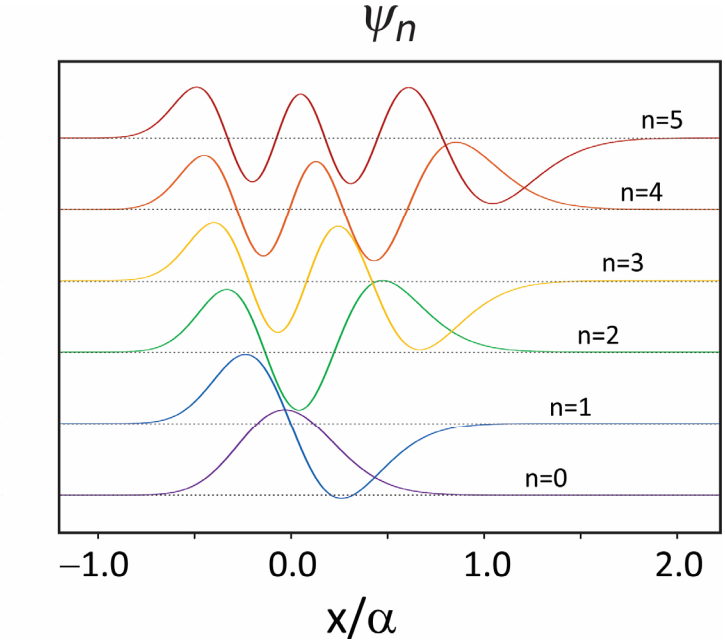
The wavefunctions for the Morse oscillator can also be expressed analytically in terms of associated Laguerre polynomials $\mathcal{L}_n^b(z)$:[3]

$$\psi_n = N_n e^{-z/2} z^{b/2} \mathcal{L}_n^b(z) \tag{6}$$

where

$$N_n = [\alpha \cdot b \cdot n! / \Gamma(k-n)]^{1/2}$$
$$z = k\exp[-\alpha q]$$
$$b = k - 2n - 1$$
$$k = 4D_e / \hbar\omega_0$$

These expressions and those for matrix elements in q, q^2, $e^{-\alpha q}$, and $qe^{-\alpha q}$ have been given by Vasan and Cross.[4]



[3] Gallas, J. A. C., Some matrix elements for Morse oscillators. *Physical Review A* **1980,** *21* (6), 1829-1834.
[4] Vasan, V. S.; Cross, R. J., Matrix elements for Morse oscillators. *The Journal of Chemical Physics* **1983,** *78* (6), 3869-3871.