Exact 1-D Morse wavefunctions for heavy molecules

H. Ambalampitiya
Department of Physics and Astronomy, University of Nebraska, Lincoln, Nebraska 68588-0111, USA
(Dated: December 23, 2018)

The analytic solutions for the Schrödinger equation in the Morse potential are available in closed form [1]. Here we shall give a brief description on the solutions of the following Schrödinger equation.

$$V(x) = A[e^{-\alpha x} - 1]^2$$

$$-\frac{1}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x)$$

By substituting $y = ke^{-\alpha x}$ where $k = 2\sqrt{2mA}/\alpha$, we have the following differential equation.

$$y^2\frac{d^2\psi}{dy^2} + y\frac{d\psi}{dy} + \big[\frac{ky}{2} - \frac{y^2}{4} - \beta^2\big]\psi = 0, \quad \beta^2 = \frac{2m(A-E)}{\alpha^2} \tag{1}$$

Let us assume the following un-normalized solution form,

$$\psi = e^{-by}y^cF(y)$$

where $F(y)$ is a polynomial of y and the parameters b and c are to be determined. After substituting into Eq. 1, we will get

$$y\frac{d^2F}{dy^2} + [2c - 2by + 1]\frac{dF}{dy} + \big[y(b^2 - 1/4) + (c^2 - \beta^2)/y + k/2 - 2bc - b\big]F = 0.$$

For the non-trivial choice of $c = \beta$ and $b = 1/2$, the above differential equation reduces to the *standard* form,

$$y\frac{d^2F}{dy^2} + [2\beta + 1 - y]\frac{dF}{dy} + [k/2 - \beta - 1/2]F = 0, \tag{2}$$

of which the solutions are generalized Laguerre polynomials, $L_n^{2\beta}(y)$ provided that,

$$k/2 - \beta - 1/2 = n. \;\; n = 0, 1, 2, .. \tag{3}$$

Equation 3 readily gives the relation for the eigen-energies of the bound states

$$E_n = (n + 1/2)\big[1 - \frac{1}{k}(n + 1/2)\big]\omega. \quad \omega = \sqrt{2A\alpha^2/m} \tag{4}$$

Therefore, the bound state wavefunctions of 1D Morse potential can be expressed as,

$$\psi_n(y) = N(n,k)e^{-y/2}y^{k/2-n-1/2}L_n^{k-2n-1}(y), \tag{5}$$

The generalized Laguerre polynomials can be expressed via the confluent hypergeomtric functions (Kummer's functions)$M(a, b; x)$ [2] as

$$L_n^{k-2n-1}(y) = \frac{\Gamma(k-n)}{n!\Gamma(k-2n)}M(-n, k-2n; y), \tag{6}$$

where

$$M(-n, k-2n; y) = 1 - \frac{n}{k-2n}y + \frac{n(n-1)}{(k-2n)(k-2n+1)}\frac{y^2}{2!} - ..., \quad n \le k/2 - 1 \tag{7}$$

The normalization constant $N(n,k)$ of Eq. 5 can be obtained by requiring

$$\int_0^\infty \frac{1}{\alpha y}\psi_n(y)^*\psi_n(y)dy = 1$$

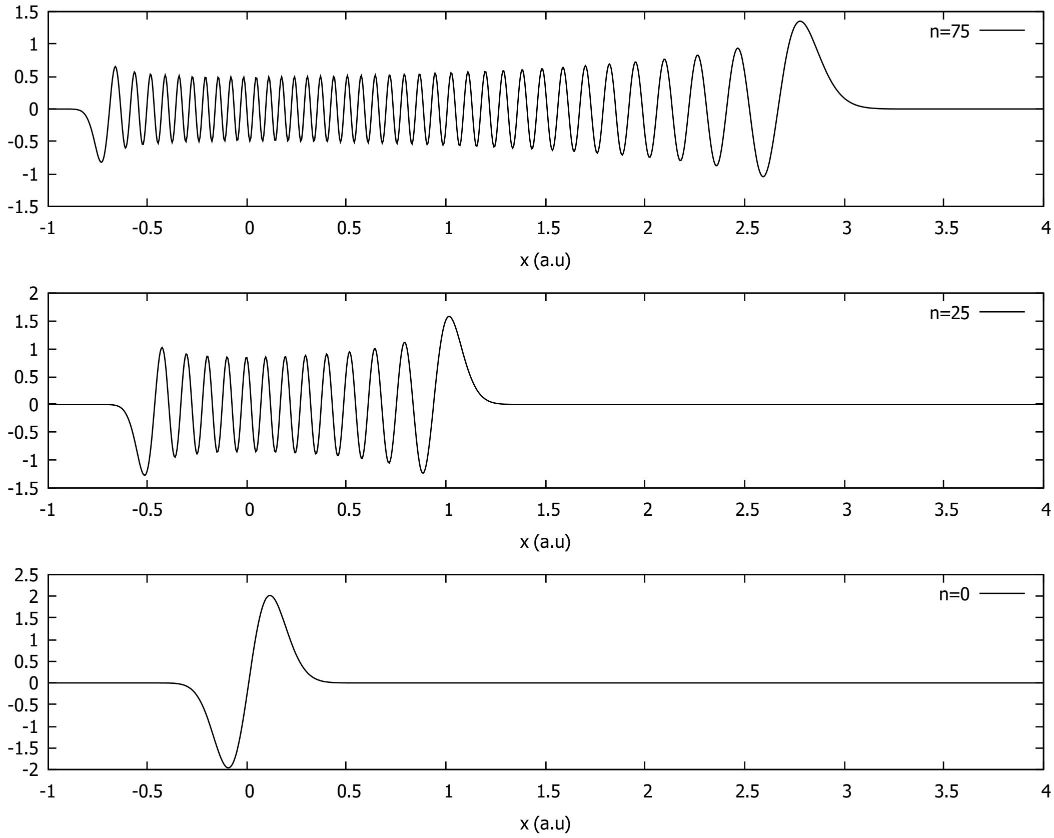

FIG. 1: few vibrational wavefunctions for a molecule of reduced mass 42000 (a.u) in a 1D Morse potential, $A = 0.1382, \alpha = 0.8507$

i.e.,

$$\frac{1}{\alpha} N^2 \int_0^\infty e^{-y} y^{k-2n-2} [L_n^{k-2n-1}(y)]^2 dy = 1$$

The above integration will give[1]

$$N(n, k) = \left[\frac{\alpha(k - 2n - 1)n!}{\Gamma(k - n)} \right]^{1/2} \tag{8}$$

Numerical evaluation of Eq. 5 as it stands is highly inefficient due to the large numbers involved ($k >> 1$). When $k \sim 10^2$, typical for heavy molecules, we will use the asymptotic series exapnsion for the Gamma functions[2] . For the computation of generlaized Laguerre polynomials, we will use the following recurrence relation [2, 3],

$$nL_n^\lambda(z) = (\lambda + 2n - 1 - z)L_{n-1}^\lambda - (\lambda + n - 1)L_{n-2}^\lambda(z) \tag{9}$$

Figure 1 shows a sample calculation of three vibrational wavefunctions belonging to $n = 0, n = 25$ and $n = 75$ levels.

---

[1] We have used the identity [3]:

$$\int_0^\infty t^{\alpha-1} e^{-t} [L_n^\lambda(t)]^2 dt = \frac{\Gamma(\alpha)\Gamma(n+1)\Gamma(n+\lambda+1)}{n!n!\Gamma(\lambda+1)}$$

[2] Asymptotic $\Gamma(z)$ for $z >> 1$ [2]

$$\Gamma(z) = \sqrt(2\pi) z^{z-1/2} e^{-z} \left[1 + \frac{1}{12z} + \frac{1}{288z^2} - \frac{139}{51840z^3} - \frac{571}{2488320z^4} + ... \right]$$

[1] P. M. Morse, Phys. Rev. **34**, 57 (1929)
[2] M. Abramowitz and I. A. Stegun *Handbook of mathematical functions* Online version
[3] More details on the generalized Laguerre polynomials can be found here: *Wolfram*