# 9.12: Numerical Solutions for Morse Oscillator

Schrödinger's equation is integrated numerically for the first three energy states for the Morse oscillator. The integration algorithm is taken from J. C. Hansen, ***J. Chem. Educ. Software,*** **8C2**, 1996.

Set parameters:

n = 300

xmin = -2

xmax = 12

$$\Delta = \frac{xmax - xmin}{n - 1}$$

$\mu$ = 1

D = 2

$\beta$ = 2

$x_e$ = 0

Calculate position vector, the potential energy matrix, and the kinetic energy matrix. Then combine them into a total energy matrix.

i = 1 .. n j = 1 .. n $x_i$ = xmin + (i - 1) $\Delta$

$$V_{i,\,j} = if\left[i = j,\ D[1 - exp[\beta(x_i - x_e)]]^2,\ 0\right]$$

$$T_{i,\,j} = if\left[i = j,\ \frac{\pi^2}{6\mu\Delta^2},\ \frac{(-1)^{i-j}}{(i-j)^2\mu\Delta^2}\right]$$

Hamiltonian matrix: H = T + V

Find eigenvalues: E = sort(eigenvals(H))

Display three eigenvalues: m = 1 .. 3

$E_m$ =

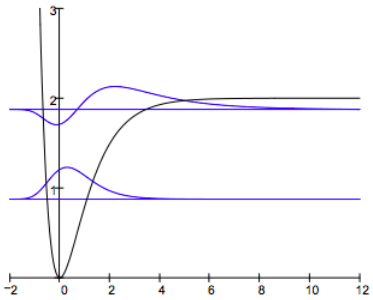
| |
|---|
| 0.8750 |
| 1.8750 |
| 2.0596 |

Calculate associated eigenfunctions:

k = 1 .. 3

$$\psi(k) = eigenvec(H, E_k)$$

Plot the potential energy and selected eigenfunctions:




For $V = ax^n$ , the virial theorem requires the following relationship between the expectation values for kinetic and potential energy:

$$< T >= 0.5n < V >.$$

The calculations below show that virial theorem is not satisfied for the Morse oscillator. The reason is revealed in the following series expansion in $x$. The expansion contains cubic, quartic and higher order terms in $x$, so the virial theorem **does not** apply to the quartic oscillator.

$$D(1 - exp(-\beta x))^2 \text{ converts to the series } D\beta^2 x^2 + (-D)\beta^3 x^3 + \tfrac{7}{12} D\beta^4 x^4 + O(x^5)$$

$$\begin{pmatrix} \text{" } Kinetic\ Energy \text{"} & \text{" } Potential\ Energy \text{"} & \text{" } Total\ Energy \text{"} \\ \psi(1)^T T \psi(1) & \psi(1)^T V \psi(1) & E_1 \\ \psi(2)^T T \psi(2) & \psi(2)^T V \psi(2) & E_2 \end{pmatrix}$$

$$= \begin{pmatrix} \text{" } Kinetic\ Energy \text{"} & \text{" } Potential\ Energy \text{"} & \text{" } Total\ Energy \text{"} \\ 0.3750 & 0.5000 & 0.8750 \\ 0.3754 & 1.4996 & 1.8750 \end{pmatrix}$$

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