Morse Oscillator

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Schrodinger'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. There are only two bound states for the Morse parameters used in this calculation.

Set parameters:

$n := 300 \quad xmin := -2 \quad xmax := 12 \quad \Delta := \frac{xmax - xmin}{n-1}$

$\mu := 1 \quad D := 2 \quad \beta := 1 \quad x_e := 0$

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

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

$$V_{i,j} := \mathrm{if}\left[i = j, D\cdot\left[1 - \exp\left[-\beta\cdot\left(x_i - x_e\right)\right]\right]^2, 0\right] \qquad T_{i,j} := \mathrm{if}\left[i = j, \frac{\pi^2}{6\cdot\mu\cdot\Delta^2}, \frac{(-1)^{i-j}}{(i-j)^2\cdot\mu\cdot\Delta^2}\right]$$

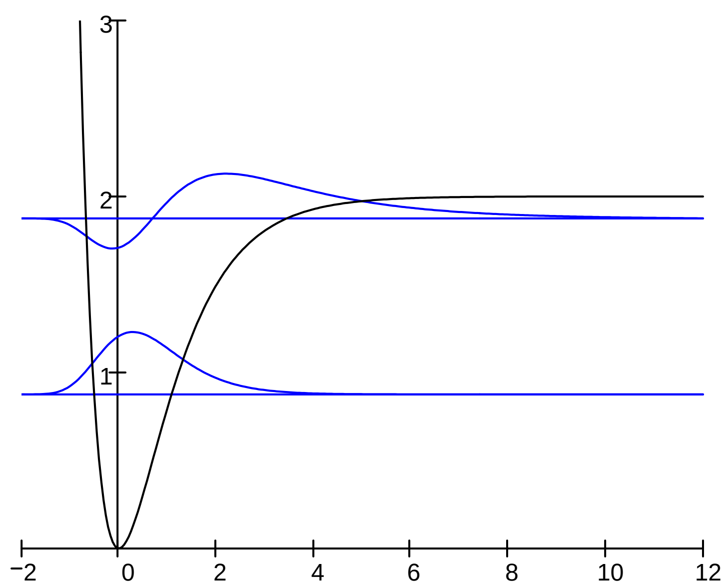
Form Hamiltonian energy matrix: $H := T + V$

Find eigenvalues: $E := \mathrm{sort}(\mathrm{eigenvals}(H))$ Display three eigenvalues: $m := 1..3$ $E_m =$

0.8750
1.8750
2.0596

Calculate associated eigenfunctions: $k := 1..3$ $\Psi(k) := \mathrm{eigenvec}\left(H, E_k\right)$

Plot the potential energy and bound state 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.

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

$$\begin{pmatrix} \text{"Kinetic Energy"} & \text{"Potential Energy"} & \text{"Total Energy"} \\ \Psi(1)^T \cdot T \cdot \Psi(1) & \Psi(1)^T \cdot V \cdot \Psi(1) & E_1 \\ \Psi(2)^T \cdot T \cdot \Psi(2) & \Psi(2)^T \cdot V \cdot \Psi(2) & E_2 \end{pmatrix} = \begin{pmatrix} \text{"Kinetic Energy"} & \text{"Potential Energy"} & \text{"Total Energy"} \\ 0.3750 & 0.5000 & 0.8750 \\ 0.3754 & 1.4996 & 1.8750 \end{pmatrix}$$