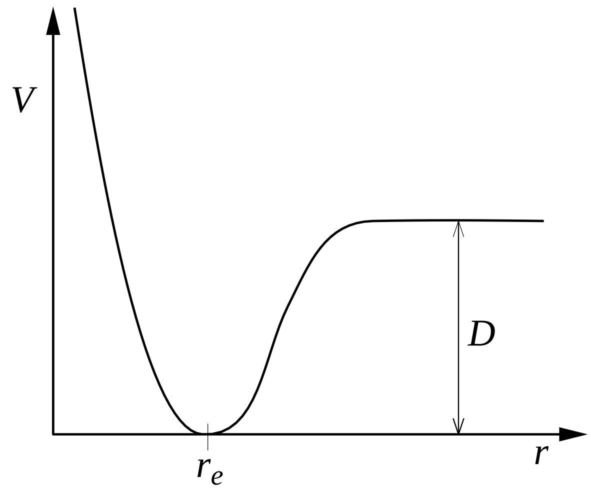

The Morse potential

$$V(x) = D\left(1 - e^{-(r-r_e)/a}\right)^2 \tag{1}$$

is exactly solvable and so provides a test case for various approximation methods. This potential approximates that felt in a diatomic molecule as the nuclei vibrate. Note that the potential resembles a half-infinite square well in that as $r \to \infty$ the potential approaches a constant, whereas as $r \to -\infty$ the potential grows exponentially. There are only a finite number of bound states ($0 < E < D$) in addition to the continuum of free ($E > D$) states. The potential is approximately simple harmonic, as

$$D\left(1 - e^{-x/a}\right)^2 \approx \frac{D}{a^2}\, x^2 \left[1 - \left(\frac{x}{a}\right) + \frac{7}{12}\, \left(\frac{x}{a}\right)^2 + \cdots\right] \tag{2}$$

where we have defined $x = r - r_e$ (the displacement from equilibrium). Note that if we approximate the potential as simple harmonic (i.e., neglect the higher order terms in square brackets above),

$$\frac{D}{a^2} \equiv \frac{1}{2}\, m\omega^2 \tag{3}$$

Deviations from a simple harmonic potential are a result of the fact that the force required to push the nuclei together is more than that required to stretch them apart an equivalent distance. An energy D is required to disassociate (separate) the two nuclei (i.e., $H_2 \to H + H$). First as usual go to dimensionless coordinates with unit length $l = a$ and unit energy $e = D$:

$$\frac{-\hbar^2}{2m}\,\frac{\partial^2}{\partial r^2}\,\psi + D\left(1 - e^{-(r-r_e)/a}\right)^2\,\psi \;=\; E\psi \tag{4}$$

$$\frac{-\hbar^2}{2ma^2D}\,\frac{\partial^2}{\partial x'^2}\,\psi + \left(1 - e^{-x/a}\right)^2\,\psi \;=\; \frac{E}{D}\,\psi \tag{5}$$

$$\frac{-1}{\alpha^2}\,\frac{\partial^2}{\partial x'^2}\,\psi + \left(1 - e^{-x'}\right)^2\,\psi \;=\; E'\psi \tag{6}$$

(As usual we now simplify by not writing the primes.) The WKB form of this equation is:

$$\psi'' = -\alpha^2\left[E - \left(1 - e^{-x}\right)^2\right]\psi \tag{7}$$

The exact bound state eigenenergies are given by:

$$E_n' = \frac{2}{\alpha}\,(n+\tfrac{1}{2}) - \frac{1}{\alpha^2}\,(n+\tfrac{1}{2})^2 \qquad (8)$$

$$E_n = \hbar\omega(n+\tfrac{1}{2}) - \frac{\hbar^2}{2ma^2}\,(n+\tfrac{1}{2})^2 \qquad (9)$$

for $n = 0, 1, 2\ldots$ up to the maximum value of E (which will of course be less than D).

1. Use the Rayleigh-Ritz (variational) method to estimate the eigenenergy of the ground state for $\alpha = 10$. Use the trial wavefunction:

   $$\psi = \exp(-qx^2) \qquad (10)$$

   You will need to use *Mathematica* to do the integrals. Note: the potential is not reflection symmetric so for the potential energy at least, you must integrate over the range $[-\infty, \infty]$. Use the *Mathematica* function `FindMinimum` to do the minimization: `FindMinimum[e,{q,`*your guess here*`}]`

   Note that you must give *Mathematica* a starting guess for q. I'd plot E vs. q to find a good guess for the minimum.

   Compare your estimates to the exact eigenenergy given above.

2. Use the Rayleigh-Ritz (variational) method to estimate the eigenenergy of the ground state for $\alpha = 10$. Use the trial wavefunction:

   $$\psi = \begin{cases} 0 & |x| > a \\ a^2 - x^2 & |x| < a \end{cases} \qquad (11)$$

3. Since the potential looks quadratic for $x \sim 0$, we should be able to approximate using SHO. Use first order perturbation theory to determine the energy correction for a state $|n\rangle$ of all the terms in the above series expansion Eq. 2. Hint: remember your raising and lower operators!

4. Calculate the second order correction to energy for a state $|n\rangle$ due to the term: $-\frac{\hbar\omega}{2a}\,x^3$

5. Find the WKB approximation for these eigenenergies. Hint: change variables in the WKB integral to $u = 1 - e^{-x}$, note closely the range of integration in u and use the fact:

   $$\int_{-A}^{A} \frac{\sqrt{A^2 - u^2}}{1 - u}\,du = \pi\left(1 - \sqrt{1 - A^2}\right) \qquad (12)$$

   for $A < 1$. (Again: *Mathematica* does not seem to know this result!)

   P.S. For folks knowing contour integration: Prove the above integral for extra credit.