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 $e = D$:

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

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

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

(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:

$$E'_n = \frac{2}{\alpha}\left(n + \tfrac{1}{2}\right) - \frac{1}{\alpha^2}\left(n + \tfrac{1}{2}\right)^2 \tag{8}$$

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

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:

$$\psi = \exp(-qx^2) \tag{10}$$

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 estimate 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:

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

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: $-\dfrac{\hbar\omega}{2a}x^3$

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:

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

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.