The Morse Potential

The Morse potential is used to model the vibrational excitations of a chemical bond. If the length of the chemical bond is \( x \), with conjugate momentum \( p \), then the Hamiltonian of the system is given by

\[
H = \frac{p^2}{2\mu} + D \left( e^{-2x/a} - 2e^{-x/a} \right).
\]

\( \mu \) roughly corresponds to the “mass” of the two atoms in the bond in the center of mass frame, \( D \) is a measure of the strength of the chemical bond, and \( a \) is a measure of the possibility of variations about equilibrium.

(a) Plot or sketch the Morse potential (the potential energy part of the Hamiltonian) as a function of \( x \). Verify that the statements made about \( D \) and \( a \) are reasonable.

It is tricky to find the eigenvalues \( E \) of a Hamiltonian like this, in general. However, here we can do it with a trick. Begin by defining the dimensionless variables

\[
\epsilon \equiv \frac{2\mu E a^2}{\hbar^2},
\]

\[
\kappa^2 \equiv \frac{2\mu D a^2}{\hbar^2},
\]

\[
r \equiv \sqrt{\kappa} e^{-x/2a}.
\]

(b) Write Schrödinger’s equation in position space, make the substitutions above, and show that it becomes

\[
\frac{d^2 \psi}{dr^2} + \frac{1}{r} \frac{d \psi}{dr} + \frac{r^2}{2} \psi + \frac{4\epsilon}{r^2} \psi = 2\kappa \psi.
\]

(c) Make an analogy to the 2D harmonic oscillator, and conclude that the eigenvalues \( E_n \) of \( H \) (now in dimensionful units) are given by

\[
E_n = -D \left( 1 - \frac{\hbar}{a\sqrt{2\mu D}} \left( n + \frac{1}{2} \right) \right)^2.
\]

(d) Show that at some point, \( E_n \geq E_{n+1} \). Argue that only the eigenvalues \( E_0, E_1, \ldots E_n \) correspond to actual bound states for \( H \).

(e) There is a critical value of \( D \), \( D_c \), such that if \( D \leq D_c \), there are no bound states to the Morse potential. Find the value of \( D_c \).

(f) On the other hand, if \( D \gg D_c \), then we can approximate that the first few excited states will approximately look like a harmonic oscillator spectrum (in 1D). Express the effective frequency of this oscillator, \( \omega_{\text{eff}} \), in terms of \( \hbar, a, D \) and \( \mu \). What is the physical reason why this approximation is valid?