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

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

μ 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

$$\begin{aligned} \epsilon &\equiv \frac{2\mu E a^2}{\hbar^2}, \\ \kappa^2 &\equiv \frac{2\mu D a^2}{\hbar^2}, \\ r &\equiv \sqrt{\kappa}\mathrm{e}^{-x/2a}. \end{aligned}$$

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

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}r^2} + \frac{1}{r}\frac{\mathrm{d}\psi}{\mathrm{d}r} + \frac{r^2}{2}\psi + \frac{4\epsilon}{r^2}\psi = 2\kappa\psi.$$

(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 $D \leq D_\mathrm{c}$, there are no bound states to the Morse potential. Find the value of D_c.

(f) On the other hand, if $D \gg D_\mathrm{c}$, 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, ω_eff, in terms of $\hbar$, a, D and μ. What is the physical reason why this approximation is valid?