The Morse Potential*
(Dated: February 13, 2003)

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After studying the harmonic oscillator as a representation of molecule vibration, one notices that a diatomic molecule which was actually bound using a harmonic potential would never dissociate. The Morse potential realistically leads to dissociation, making it more useful than the Harmonic potential. The Morse potential is the simplest representative of the potential between two nuclei in which dissociation is possible.
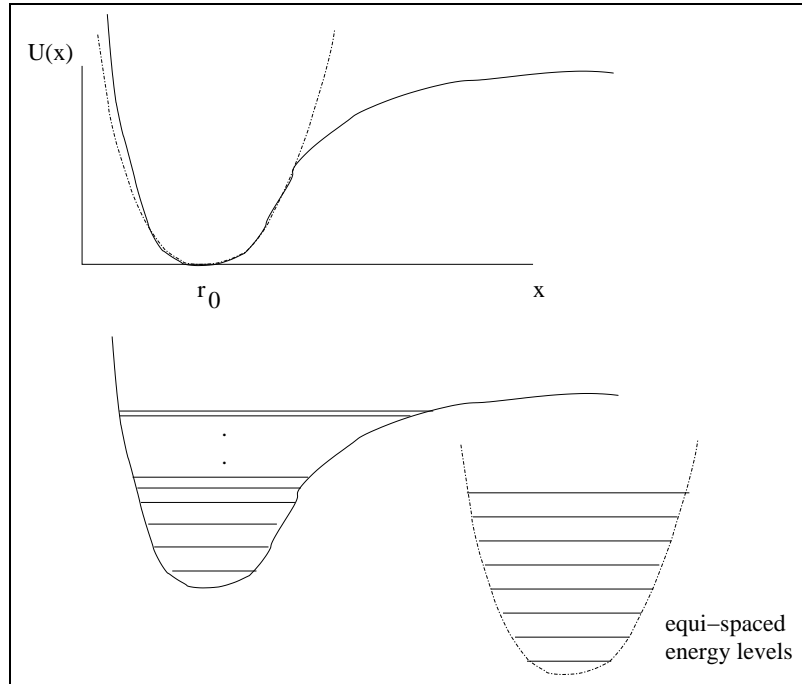

FIG. 1: Contrasting A Harmonic Oscillator Potential and the Morse (or "Real") Potential and the Associated Energy Levels

The form of the Morse potential, in terms of the internuclear distance, is

$$D \left(1 - e^{-\alpha \frac{r - r_0}{r_0}}\right)^2$$

where r_0 is the equilibrium internuclear distance.

Notice in Figure 1 that the energy levels of the harmonic oscillator decrease as the "box" expands to the size of the Morse (or "real") potential.

It is common to define a variable x, $x = \frac{r - r_0}{r_0}$, which allows us to rewrite the potential as

$$D \left(1 - e^{-\alpha x}\right)^2$$

than the Simple Harmonic Oscillator's $\frac{k}{2}x^2$, for studying diatomic molecular vibrations, and the Morse potential is

$$V(x) = D \left(1 - e^{-\alpha x}\right)^2 \tag{1}$$

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*morse.tex

It's use leads to a Schrödinger Equation of the form

$$-\frac{\hbar^2}{2\mu}\frac{d^2\psi}{dx^2} + D\left(1 - e^{-\alpha x}\right)^2 \psi = E\psi$$

Notice that the Taylor expansion of the potential energy operator yields a quadratic leading term.

Before attempting a solution, we follow standard practice and attempt to clean up this equation by changing variables. Thus, we define $y = \alpha x$, so that

$$\frac{d}{dx} = \frac{dy}{dx}\frac{d}{dy} = \alpha\frac{d}{dy}$$

which transforms the Schrödinger Equation into

$$-\frac{\hbar^2\alpha^2}{2\mu}\frac{d^2\psi}{dy^2} + D\left(1 - e^{-y}\right)^2 \psi = E\psi$$

which becomes upon cross multiplying

$$\frac{d^2\psi}{dy^2} - \frac{2\mu}{\hbar^2\alpha^2}D\left(1 - e^{-y}\right)^2 \psi = -\frac{2\mu}{\hbar^2\alpha^2}E\psi$$

or

$$\frac{d^2\psi}{dy^2} - \frac{2\mu}{\hbar^2\alpha^2}\left(E - D\left(1 - e^{-y}\right)^2\right)\psi = 0$$

$$\frac{d^2\psi}{dy^2} - \frac{2\mu D}{\hbar^2\alpha^2}\left(\frac{E}{D} - \left(1 - e^{-y}\right)^2\right)\psi = 0$$

i.e., defining λ

$$\lambda = \frac{\sqrt{2\mu D}}{\alpha\hbar}$$

and ϵ

$$\epsilon = \frac{E}{D}$$

we have

$$\frac{d^2\psi}{dy^2} - \lambda^2\left(\epsilon - \left(1 - e^{-y}\right)^2\right)\psi = 0$$

a nice, clean form.

Now, we have the equation with simplified constants; we have reduced the notation to a bare minimum (getting rid of the exponential in the potential energy operator). Next, we change variables to make the equation even more tractable. Define $\zeta = \lambda e^{-y}$ i.e., $e^{-y} = \frac{\zeta}{\lambda}$. Then

$$d\zeta = -\lambda e^{-y}dy$$

so

$$\frac{d}{dy} = \frac{d\zeta}{dy}\frac{d}{d\zeta} = -\lambda e^{-y}\frac{d}{d\zeta} = -\zeta\frac{d}{d\zeta}$$

The new Schrödinger Equation is

$$-\zeta\frac{d\left(-\zeta\frac{d\psi}{d\zeta}\right)}{d\zeta} - \lambda^2\left(\epsilon - \left(1 - \frac{\zeta}{\lambda}\right)^2\right)\psi = 0$$

$$+\zeta\frac{d\left(\zeta\frac{d\psi}{d\zeta}\right)}{d\zeta} - \lambda^2\left(\epsilon - \left(\frac{\lambda-\zeta}{\lambda}\right)^2\right)\psi = 0$$

so, expanding the square,

$$+\zeta\frac{d\left(\zeta\frac{d\psi}{d\zeta}\right)}{d\zeta} - \lambda^2\left(\epsilon - \left(\frac{\lambda^2 - 2\lambda\zeta + \zeta^2}{\lambda^2}\right)\right)\psi = 0$$

$$+\zeta\frac{d\left(\zeta\frac{d\psi}{d\zeta}\right)}{d\zeta} - \left(\lambda^2\epsilon - \left(\lambda^2 - 2\lambda\zeta + \zeta^2\right)\right)\psi = 0$$

$$+\zeta\frac{d\left(\zeta\frac{d\psi}{d\zeta}\right)}{d\zeta} - \left(\lambda^2(\epsilon - 1) + 2\lambda\zeta - \zeta^2\right)\psi = 0$$

i.e., bringing to textbook form,

$$\zeta^2\frac{d^2\psi}{d\zeta^2} + \zeta\frac{d\psi}{d\zeta} - \left(a + b\zeta - \zeta^2\right))\psi = 0 \tag{2}$$

where

$$a = \lambda^2(\epsilon - 1)$$

and

$$b = 2\lambda$$

and $b = 4\lambda$.

One sees immediately that there is going to be a problem here. The ordinary quantum chemistry problems contain terms arranged in such a way as to guarantee a two term recurrence, but the term $b\lambda\zeta$ in Equation 2 guarantees that this will be a three term recurrence.

Three term recurrence relations lead to a continued fraction solution in a natural way.