Physics 221B: Solution to Midterm, Problem # 6

3) The Morse Potential

The Morse potential mimics the inter-atomic potential in a diatomic molecule but has the advantage of having a known exact solution. In this problem we go through this solution, which at least in my view is quite original. The potential is

$$V(r) = V_0(e^{-2(r-r_0)/b} - 2e^{-(r-r_0)/b}) \tag{1}$$

Here we will use $b = 0.92a_0$, $r_0 = 1.64254a_0$ and $V_0 = 0.116e^2/a_0$.

a)

See Mathematica notebook.

b)

The radial Schrödinger equation (SE) is

$$\left(-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + V(r)\right)\psi(r) = E\psi(r). \tag{2}$$

Defining $\xi = K_0 b e^{-(r-r_0)/b}$ with $K_0 = \frac{\sqrt{2\mu V_0}}{\hbar}$ and $\kappa = \frac{\sqrt{2\mu E}}{\hbar}$ we would like to rewrite the SE with ξ as the variable.

We must be careful when changing variables in the second derivative, since the result is not simply the second derivative with respect to ξ.

$$\begin{aligned}
\frac{d\psi}{dr} &= \frac{d\xi}{dr}\frac{d\psi}{d\xi} = \left(-K_0 e^{-(r-r_0)/b}\right)\frac{d\psi}{d\xi} = -\frac{1}{b}\xi\frac{d\psi}{d\xi} \\
\frac{d^2\psi}{dr^2} &= \frac{d}{dr}\left(\frac{d\psi}{dr}\right) = -\frac{1}{b}\xi\frac{d}{d\xi}\left(-\frac{1}{b}\xi\frac{d\psi}{d\xi}\right) = \frac{1}{b^2}\left(\xi^2\frac{d^2\psi}{d\xi^2} + \xi\frac{d\psi}{d\xi}\right) \qquad (3)
\end{aligned}$$

After expressing the potential in terms of the new variable and parameters the SE becomes (after multiplying by b^2/ξ^2)

$$\psi'' + \frac{1}{\xi}\psi' + \left(\frac{2K_0 b}{\xi} - 1\right)\psi = \frac{\kappa^2 b^2}{\xi^2}\psi \tag{4}$$

where primes stand for derivatives with respect to ξ.

c)

Taking ξ large, we drop terms suppressed by ξ^{-1} or ξ^{-2}. Equation (4) becomes

$$\psi'' - \psi = 0 \tag{5}$$

which has solutions $\psi \propto e^{\pm\xi}$. Since $\xi \to \infty$ corresponds to $r \to 0$ we demand ψ be finite for $\xi \to \infty$ leaving only $\psi \propto e^{-\xi}$ and $c = 1$.

d)

Inspired by this we define $\psi(\xi) = w(\xi)e^{-\xi}$. Working out the derivatives of ψ

$$\begin{aligned} \psi' &= (w' - w)e^{-\xi} \\ \psi'' &= (w'' - 2w' + w)e^{-\xi}. \end{aligned} \tag{6}$$

Substituting into Eq. (4) we can divide by $e^{-\xi}$

$$\begin{aligned} & w'' - 2w' + w + \xi^{-1}(w' - w) + (2K_0 b\xi^{-1} - 1 - \kappa^2 b^2 \xi^{-2}) = 0 \\ \implies \quad & w'' + (\xi^{-1} - 2)w' + \left[(2K_0 b - 1)\xi^{-1} - \kappa^2 b^2 \xi^{-2}\right] = 0. \end{aligned} \tag{7}$$

e)

Introducing yet another definition we write w as a power series

$$w(\xi) = \xi^\alpha(1 + c_1\xi + c_2\xi^2 + \ldots) = \sum_{n=0}^{\infty} c_n \xi^{\alpha+n} \tag{8}$$

with $c_0 = 1$. Once again we rewrite the first and second derivatives of w

$$\begin{aligned} w' &= \sum_{n=0}^{\infty} c_n(\alpha + n)\xi^{\alpha+n-1} \\ w'' &= \sum_{n=0}^{\infty} c_n(\alpha + n)(\alpha + n - 1)\xi^{\alpha+n-2}. \end{aligned} \tag{9}$$

Throwing Eqns. (8) and (9) into Eq. (7) gives

$$\begin{aligned}
&\sum_{n=0}^{\infty} c_n(\alpha+n)(\alpha+n-1)\xi^{\alpha+n-2} + \sum_{n=0}^{\infty} c_n(\alpha+n)\xi^{\alpha+n-2} \\
&-2\sum_{n=0}^{\infty} c_n(\alpha+n)\xi^{\alpha+n-1} + (2K_0 b - 1)\sum_{n=0}^{\infty} c_n\xi^{\alpha+n-1} \\
&-\kappa^2 b^2 \sum_{n=0}^{\infty} c_n \xi^{\alpha+n-2} = 0 \qquad (10)
\end{aligned}$$

The huge polynomial on the left hand side of Eq. (10) must be identically zero for all ξ. This can only happen if the coefficient preceding every power of ξ vanishes separately. Lets start with the lowest power of ξ, $\alpha - 2$, that appears only in the first two terms and the last term of (10):

$$c_0\alpha(\alpha-1) + c_0\alpha - c_0\kappa^2 b^2 = 0 \qquad (11)$$

Since we know $c_0 \neq 0$ (recall $c_0 = 1$ by definition) we get an equation for α alone

$$\begin{aligned}
&\alpha(\alpha-1) + \alpha - \kappa^2 b^2 = 0 \\
&\Longrightarrow \alpha = \pm\kappa b. \qquad (12)
\end{aligned}$$

The sign of α will not change the result for the energy. However, note that demanding $w \to 0$ ($\psi \to 0$) for $\xi \to 0$ (which means $r \to \infty$) suggests $\alpha > 0$.

To get a recursion relation between c_n and c_{n-1} lets look at the coefficient of $\xi^{\alpha+n-2}$ that will appear in all the terms on the l.h.s of Eq. (10).

$$c_n(\alpha+n)(\alpha+n-1)+c_n(\alpha+n)-2c_{n-1}(\alpha+n-1)+(2K_0b-1)c_{n-1}-\kappa^2b^2c_n = 0 \qquad (13)$$

Rearranging, we get a simple equation relating c_n to c_{n-1}

$$c_n = \frac{2\alpha + 2n - 2K_0 + 1}{(\alpha+n)^2 - \kappa^2 b^2} c_{n-1}. \qquad (14)$$

f)

Finally we are about to find the energy levels. Demanding a normalizable wavefunction enforces that the power series Eq. (8) stops at some n. this will happen if for that n the coefficient of c_{n-1} in Eq. (14) will vanish. Demanding the numerator vanish for some n will suffice

$$2\alpha + 2n - 2K_0 + 1 = 0. \qquad (15)$$

Inserting $\alpha = \kappa b$ and substituting the definitions of κ and K_0 gives a quantization condition for the energy

$$E_n = -\frac{\hbar^2}{2\mu b^2}\left(K_0 b - n + \frac{1}{2}\right)^2, \qquad n = 1, 2, 3, \ldots \tag{16}$$

Note that when I wrote $n = 1, 2, \ldots$ above I was cheating. This is because beyond some $n_{max} \sim K_0 b$ equation (15) cannot be satisfied with a real energy. In other words, since the Morse potential is not an infinite potential well there is only a finite number of bound states.

g)

Taking $n \ll K_0 b$, we can expand Eq. (16) to leading order in $n/K_0 b$

$$E_n = -\frac{\hbar^2}{2\mu b^2} K_0^2 b^2 \left(1 - \frac{n + \frac{1}{2}}{K_0 b}\right)^2 \sim -\frac{\hbar^2}{2\mu b^2} K_0^2 b^2 \left(1 - 2\frac{n + \frac{1}{2}}{K_0 b}\right) \tag{17}$$

Indeed, we get evenly spaced energy levels as in a harmonic oscillator. Extracting only the $\hbar\omega n$ part we see

$$\omega = \frac{\hbar K_0}{\mu b} = \sqrt{\frac{2V_0}{\mu b^2}} \tag{18}$$

h)

The lowest vibrational excitations will be of order ω calculated above. Estimating this (recall that $V_0 = 0.116 e^2/a_0,\ \mu = M_{proton}/2$ and $b \sim a_0$) we get $E_{vib} \sim 0.5$ eV. This is much smaller than the typical electronic excitation of

$$E_{elec} \sim \frac{e^2}{2a_0}(1 - \frac{1}{4}) \sim 10\text{eV}.$$

On the other hand it is much bigger than the typical rotational excitation (using a rigid rotator for an estimate)

$$E_{rot} \sim \frac{\hbar^2 l(l+1)}{M_{proton} r_0^2} \sim 0.01\text{eV}.$$

This can be seen as justification for the Born-Oppenheimer approximation.