Solutions to Problem Set 4/Problem 5
Physics 480 / Fall 1999
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Problem 5: Algebraic Solutions for Stationary States of Morse Potential [L. Infeld and T. E. Hull, **The Factorization Method**, *Rev. Mod. Phys.* **23**, 21–68 (1951)]

The following problem will demonstrate that the method of creation and annihilation operators $A^{\pm}$, introduced for the linear harmonic oscillator, can be generalized to other potentials. For this purpose we consider the one-dimensional time-independent Schrödinger equation

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dy^2} + U(y) \right] \phi(y) = E\,\phi(y) \tag{1}$$

for the so-called *Morse* potential often employed to model the interaction between atoms and molecules ($D > 0$)

$$U(y) = D\,[\,e^{-2ay} - 2\,e^{-ay}\,]\,. \tag{2}$$

We seek to determine the eigenvalues and wave functions of the bound states of the Morse potential.

(a) Show

1. For the bound states holds $E < 0$. [Hint: Plot the potential (2).]
2. The lowest eigenvalue should be

$$E_o = -D + a\hbar\sqrt{\frac{D}{2m}} - \epsilon,\ \epsilon > 0\,. \tag{3}$$

   [Hint: Compare the plot of the potential (2) with a plot of its quadratic expansion at its minimum.]

3. Provide an estimate for the number of stationary bound states of the Morse potential. Evaluate for this purpose the classical action integral $\int dy\,p(y)$ for motion at $E = 0$.

(b) Show that the stationary Schrödinger equation for the Morse potential through the transformation of variables

$$x = -ay + \ln\left(\frac{\sqrt{8mD}}{a\hbar}\right)\,, \tag{4}$$

$$s + \frac{1}{2} \;=\; \frac{\sqrt{2mD}}{a\hbar}\;, \tag{5}$$

$$t^2 \;=\; -\frac{2mE}{a^2\hbar^2} \;>\; 0 \tag{6}$$

yields

$$\mathcal{H}_s\,\phi_t(x) \;=\; \left[-\frac{d^2}{dx^2} \;+\; \frac{1}{4}\,e^{2x} \;-\; \left(s + \frac{1}{2}\right)\,e^x \right]\,\phi_t(x) \;=\; -t^2\phi_t(x) \tag{7}$$

where

$$\mathcal{H}_s \;=\; \frac{2m}{a^2\hbar^2}\,H\;, \qquad s \text{ defined through (5).} \tag{8}$$

Consider in the follwing s as a *variable* and t as a *constant*. Show that (7) is equivalent to

$$A^-_{s+1}A^+_{s+1}\,\phi_t^{(s)}(x) \;=\; [(s+1)^2 - t^2]\,\phi_t^{(s)}(x) \tag{9}$$

as well as to

$$A^+_s A^-_s\,\phi_t^{(s)}(x) \;=\; [\,s^2 \;-\; t^2\,]\,\phi_t^{(s)}(x) \tag{10}$$

where

$$A^\pm_s \;=\; \mp\frac{d}{dx} \;+\; \frac{e^x}{2} \;-\; s\;. \tag{11}$$

(c) Show that for fixed t the operators A^+_s, A^-_s generate new solutions to Eq. (7) according to the rule

$$A^+_{s+1}\,\phi_t^{(s)}(x) \;=\; c_s\,\phi_t^{(s+1)}(x)\;, \tag{12}$$

$$A^-_s\,\phi_t^{(s)}(x) \;=\; d_s\,\phi_t^{(s-1)}(x)\;. \tag{13}$$

For the normalization factor d_s holds (as long as the functions $\phi_t^{(s)}(x)$ and $\phi_t^{(s-1)}(x)$ are normalizable)

$$d_s^2 \;=\; s^2 \;-\; t^2\;. \tag{14}$$

Why should hold $s \;>\; t$?

(d) Equation (7) above can only have bound states, i.e., normalizable solutions, for $s \;>\; t$. This implies that the sequence $\ldots A^-_{s-2}A^-_{s-1}A^-_s\,\phi_t^{(s)}(x)$ for $s - n \;<\; 0$ leads to a solution which is not admissable as a bound state. Hence, the sequence must break up for some s_o, i.e., there must exist an s_o for which holds

$$A^-_{s_o}\,\phi_t^{(s_o)}(x) \;=\; 0\;. \tag{15}$$

Show that this property implies $s_o \;=\; t$ and $s \;=\; t,\, t+1,\, t+2\,\ldots$

(e) Argue under which condition the derivation in (d) yields the allowed negative eigenvalues for the Morse potential

$$
\begin{aligned}
E_n &= -D + a\hbar\sqrt{\frac{2D}{m}}\left(n+\frac{1}{2}\right) - \frac{a^2\hbar^2}{2m}\left(n+\frac{1}{2}\right)^2 , \\
n &= 0,1,2,\ldots \leq \frac{\sqrt{2mD}}{a\hbar} - \frac{1}{2} . \qquad (16)
\end{aligned}
$$

Rationalize the upper bound for n in view of the derivations in (c), (d).

(f) Assume in the following $D = a = 1$ and $\sqrt{2m}/\hbar = 3$. Determine and plot the wave function for $n = 0$. To normalize the wave function use

$$
\Gamma(z) = \int_0^\infty dt\, t^{z-1}\, e^{-t} \qquad (17)
$$

where $\Gamma(z)$ is the Gamma function.

(g) How can one obtain also the stationary states corresponding to the energies (16) for $n > 0$. Determine and plot the wave functions of these states using `Mathematica`.

Solution

(a) The potential depicted in Figure 1 has a shape which yields classical bounded motion only for $E < 0$. In fact, for $E \geq 0$ there are two classical turning points, one at $y < 0$ and one at $y \to \infty$.

To obtain an estimate for the lowest energy of the stationary states of the system we expand the potential around its minimum

$$
U(y) \approx U_o(y) = U(y_{min}) + \frac{1}{2}\left.\frac{d^2U}{dy^2}\right|_{y_{min}} (y - y_{min})^2 . \qquad (18)
$$

y_{min} can be determined from $dU(y_{min})/dy = 0$ from which follows

$$
-2\,D\,a\left(e^{-2ay_{min}} - e^{-ay_{min}}\right) = 0 \qquad (19)
$$

, i.e., $\exp(-ay_{min}) = 1$, or

$$
y_{min} = 0 . \qquad (20)
$$

Using

$$
U(y_{min}) = -D , \quad \left.\frac{d^2U}{dy^2}\right|_{y_{min}} = 2\,D\,a^2 \qquad (21)
$$

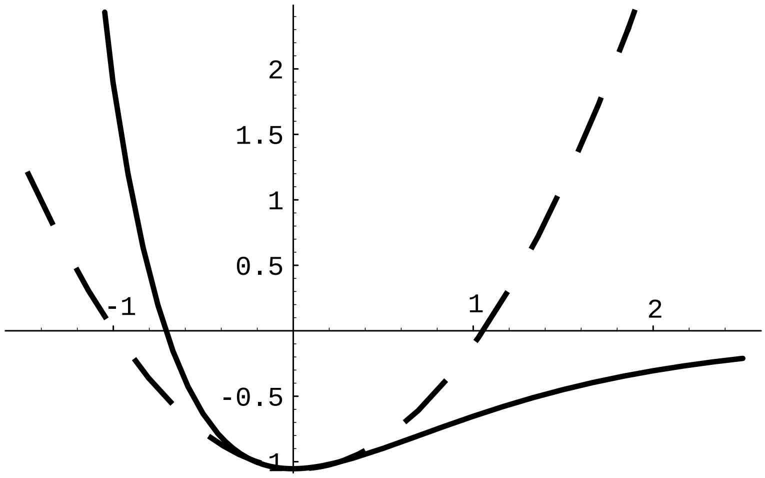

Figure 1: Comparision of Morse potential $U(y)$ (2) and its quadratic approximation $U_o(y)$ (22) for $D = a = 1$.

one obtains for the quadratic approximation (18)

$$U_o(y) \; = \; -D \; + \; D\, a^2 y^2 \; . \tag{22}$$

Stationary states exist for $U_o(y)$ for the energies

$$E_n^{(o)} \; = \; -D \; + \; \hbar\, a \sqrt{\frac{2D}{m}}\, (n \; + \; \frac{1}{2}) \; , \quad n \; = \; 0, 1, \ldots \infty \tag{23}$$

In Figure 1 we compare the Morse potential (2) with its quadratic approximation (18). Since the Morse potential $U(y)$ is flatter than the harmonic potential $U_o(y)$ one expects that the energy values of the stationary states of $U(y)$ are lower than those of $U_o(y)$. In particular, (3) should hold for the lowest energy bound state.

Furthermore, one expects that $U(y)$ has only a finite number of stationary bound states. The number of bound states can be estimated using the classical action integral

$$S(E) \; = \; \frac{2}{\hbar} \int_{y_\ell(E)}^{y_r(E)} dy \, \sqrt{2m\,[E \; - \; U(y)]} \tag{24}$$

where $y_{\ell,r}(E)$ are the left/right classical turning points at energy E. One expects that the quantity s defined through

$$S(0) \; = \; (\, s \; + \; \frac{1}{2}\,)\, 2\pi \tag{25}$$

provides an upper bound for the number of bound states. One obtains in the present case for the left turning point $y_\ell(0) = -\frac{1}{a}\ln 2$ and $y_r(0) \to \infty$ and, hence,

$$S(0) \;=\; \int_{-\frac{1}{a}\ln 2}^{\infty} dy \, \sqrt{\frac{8mD}{\hbar^2}(2e^{-ay} \,-\, e^{-2ay})} \;. \tag{26}$$

The change of variables $y' = 2\exp(ay)$ yields

$$S(0) \;=\; \sqrt{\frac{32mD}{\hbar^2 a^2}} \int_1^{\infty} dy' \, \frac{\sqrt{y' - 1}}{y'} \;. \tag{27}$$

The integral on the r.h.s. has the value $\pi/2$ and, hence,

$$S(0) \;=\; \frac{2\pi}{\hbar a} \sqrt{2mD} \tag{28}$$

Comparision with (25) yields

$$s + \frac{1}{2} \;=\; \sqrt{\frac{2mD}{\hbar^2 a^2}} \;. \tag{29}$$

The related integer $[s]$ ($n = [s]$ is defined to be the largest integer with the property $n \le s$.) provides then a semiclassical estimate for the number of bound states of the Morse potential.

(b) The suggested change of variables (4) is to be applied to the time-independent Schrödinger equation (1). One obtains

$$\left(-\frac{d^2}{dx^2} \,+\, \frac{1}{4}\, e^{2x} \,-\, \sqrt{\frac{2mD}{\hbar^2 a^2}}\, e^{x} \right) \phi_E(x) \;=\; \frac{2mE}{\hbar^2 a^2}\, \phi_E(x) \tag{30}$$

Employing (5,6) – note that according to (29) the quantity s introduced here is an upper bound for the number of bound states of the potential – the time-independent Schrödinger equation is

$$\left(-\frac{d^2}{dx^2} \,+\, \frac{1}{4}\, e^{2x} \,-\, (s + \frac{1}{2})\, e^{x} \right) \phi_t(x) \;=\; -t^2\, \phi_t(x) \;. \tag{31}$$

The label 't' denotes the energy of the respective states.

To demonstrate that (9) is equivalent to (31) we insert the definition (11) into (9) and obtain

$$\begin{aligned} & A^-_{s+1} A^+_{s+1}\, \phi_t^{(s)}(x) \\ = \;& \left(\frac{d}{dx} \,+\, \frac{1}{2}e^{x} \,-\, (s+1) \right) \left(-\frac{d}{dx} \,+\, \frac{1}{2}e^{x} \,-\, (s+1) \right) \phi_t^{(s)}(x) \\ = \;& \left(-\frac{d^2}{dx^2} \,+\, \frac{1}{4}\, e^{2x} \,-\, (s + \frac{1}{2})\, e^{x} \,+\, (s+1)^2 \right) \phi_t^{(s)}(x) \end{aligned} \tag{32}$$

which is equivalent to (9). Hence, (9) states the time-dependent Schrödinger equation for the bound states of a Morse potential characterized through its s–value [see (5, 29)].

Similarly, one can demonstrate that (10) is equivalent to (31). Inserting (11) into (10) one obtains

$$\begin{aligned} A_s^+ A_s^- \, \phi_t^{(s)}(x) &= \left(-\frac{d}{dx} + \frac{1}{2} e^x - s \right) \left(\frac{d}{dx} + \frac{1}{2} e^x - s \right) \phi_t^{(s)}(x) \\ &= \left(-\frac{d^2}{dx^2} + \frac{1}{4} e^{2x} - (s + \frac{1}{2}) \, e^x + s^2 \right) \phi_t^{(s)}(x) \, . \end{aligned} \tag{33}$$

(c) In order to prove property (12) we demonstrate that $A_{s+1}^+ \, \phi_t^{(s)}(x)$ is a solution of the time-dependent Schrödinger equation for a Morse potential characterized through $s+1$. For this purpose we show that $A_{s+1}^+ \, \phi_t^{(s)}(x)$ satisfies (10) for $s \to s+1$, i.e., we prove

$$A_{s+1}^+ \, A_{s+1}^- \, A_{s+1}^+ \, \phi_t^{(s)}(x) \;=\; [\, (s+1)^2 \,-\, t^2 \,] \, A_{s+1}^+ \, \phi_t^{(s)}(x) \, . \tag{34}$$

In fact, using (9) one can rewrite the l.h.s. of (34)

$$A_{s+1}^+ \, A_{s+1}^- \, A_{s+1}^+ \, \phi_t^{(s)}(x) \;=\; A_{s+1}^+ \, [\, (s+1)^2 \,-\, t^2 \,] \, \phi_t^{(s)}(x) \, . \tag{35}$$

Similarly, to prove (12) we demonstrate that $A_s^- \, \phi_t^{(s)}(x)$ is a solution of the time-dependent Schrödinger equation for a Morse potential characterized through $s-1$. For this purpose we show that $A_s^- \, \phi_t^{(s)}(x)$ satisfies (9) for $s \to s-1$, i.e., we prove

$$A_s^- \, A_s^+ \, A_s^- \, \phi_t^{(s)}(x) \;=\; [\, s^2 \,-\, t^2 \,] \, A_s^- \, \phi_t^{(s)}(x) \, . \tag{36}$$

This follows again readily noting that (10) allows one to rewrite the l.h.s. of (36)

$$A_s^- \, A_s^+ \, A_s^- \, \phi_t^{(s)}(x) \;=\; A_s^- \, [\, s^2 \,-\, t^2 \,] \, \phi_t^{(s)}(x) \, . \tag{37}$$

We want to determine now the normalization constant d_s defined through (13). We assume that the states $\phi_t^{(s)}(x)$ are normalized, i.e.,

$$\int_{-\infty}^{+\infty} dx \, |\phi_t^{(s)}(x)|^2 \;=\; \int_{-\infty}^{+\infty} dx \, |\phi_t^{(s-1)}(x)|^2 \, . \tag{38}$$

We will exploit in our derivation that the operators A_s^+ and A_s^- are adjoint to each other, i.e., it holds,

$$\int_{-\infty}^{+\infty} dx \, f(x) \, A_s^+ \, g(x) \;=\; \int_{-\infty}^{+\infty} dx \, g(x) \, A_s^- \, f(x) \, . \tag{39}$$

This property follows readily from the definition (11), integration by parts and using that, for bounds states, $f(x)$, $g(x)$ must vanish at $x \to \pm\infty$. It follows then

$$|d_s|^2 \;=\; \int_{-\infty}^{+\infty} dx\, A_s^- \,\overline{\phi_t^{(s)}(x)}\, A_s^- \,\phi_t^{(s)}(x) \;=\; \int_{-\infty}^{+\infty} dx\, \overline{\phi_t^{(s)}(x)}\, A_s^+ \,A_s^- \,\phi_t^{(s)}(x)\;. \tag{40}$$

Using (10) yields

$$|d_s|^2 \;=\; s^2 \;-\; t^2\;. \tag{41}$$

Obviously, $s > t$ must hold for the latter equation to be true.

(d) According to (14) the l.h.s. of (15) is proportional to $s_o^2 - t^2$. This factor vanishes for $s_o = t$. The solution of (15) is then the function $\phi_{s_o}^{(s_o)}(x)$. The action of the operator $A_{s_o+1}^+$ according to (12) yields the state $\phi_{s_o}^{(s_o+1)}(x)$, the operator $A_{s_o+2}^+$ yields the function $\phi_{s_o}^{(s_o+2)}(x)$.

(e) We are actually interested in the eigenfunctions of a fixed Morse potential, i.e., for fixed s. According to our construction we can state that the bound state wave functions of the type

$$\phi_s^{(s)}(x),\, \phi_{s-1}^{(s)}(x),\, \phi_{s-2}^{(s)}(x),\, \ldots,\, \phi_{s-[s]}^{(s)}(x) \tag{42}$$

exist. The energies of these states according to (5, 6, 7) are

$$E_n \;=\; -\frac{\hbar^2 a^2}{2m}\;(\,s\;-n\,)^2\;,\quad n\;=\;0,1,\ldots\,[s]\;,\quad s\;=\;\frac{\sqrt{2mD}}{\hbar\, a}\;-\;\frac{1}{2}\;. \tag{43}$$

Note that in case $s < 0$ the Morse potential does not have any bound state. One can express E_n as given in (43)

$$E_n \;=\; -D \;+\; \hbar\, a\sqrt{\frac{2D}{m}}\left(n\;+\;\frac{1}{2}\right) \;-\; \frac{\hbar^2 a^2}{2m}\left(n\;+\;\frac{1}{2}\right)^2\;. \tag{44}$$

which is identical to (16). The first two terms agree with the eigenvalues (23) of the quadratic approximation (18, 22) of the Morse potential. The third term is the non-harmonic correction.

(f) The wave function corresponding to E_0, i.e., to $n = 0$ in (16, 43), is defined through

$$A_s^-\,\phi_s^{(s)}(x) \;=\; 0\;. \tag{45}$$

According to (11) this corresponds to the differential equation

$$\frac{d}{dx}\phi_s^{(s)}(x) \;=\; \left(-\frac{1}{2}\,e^x\;+\;s\right)\phi_s^{(s)}(x) \tag{46}$$

or

$$\frac{d}{dx} \ln \phi_s^{(s)}(x) \;=\; \left(-\frac{1}{2}\, e^x \;+\; s \right) \;. \tag{47}$$

The solution of this equation is

$$\phi_s^{(s)}(x) \;=\; C' \exp \left(-\frac{1}{2} e^x \;+\; s\, x \right) \;. \tag{48}$$

Using $x \;=\; -a\, y \,+\, \ln(2s+1)$, which follows from (4, 5), the function expressed in terms of the original coordinate y is

$$\phi_s^{(s)}(x) \;=\; C_s \exp \left(-(s + \frac{1}{2}) e^{-ay} \;-\; s\, a\, y \right) \;. \tag{49}$$

The normalization factor is determined through the condition

$$|C_s|^2 \int_{-\infty}^{+\infty} dy \exp\big(-(2s+1) e^{-ay} \;-\; 2\, s\, a\, y \big) \;=\; 1 \;. \tag{50}$$

This condition can be written

$$\begin{aligned} |C_s|^2 a^{-1} \quad & \Bigg[\int_0^\infty dy \exp\big(-(2s+1) e^y \;+ 2\, s\, y \big) \\ & + \int_0^\infty dy \exp\big(-(2s+1) e^{-y} \;-\; 2\, s\, y \big) \Bigg] \;=\; 1 \;. \end{aligned} \tag{51}$$

Introducing the variable $t \;=\; e^y$ in the first integral, $t \;=\; e^{-y}$ in the second integral and combining the resulting expressions yields

$$\begin{aligned} & |C_s|^2 a^{-1} \int_0^\infty dt\, t^{2s-1} \exp[-(2s+1)t] \\ & \quad = \; |C_s|^2 \frac{1}{(2s+1)^{2s} a} \int_0^\infty dt\, t^{2s-1} \exp[-t] \;=\; 1 \;. \end{aligned} \tag{52}$$

Employing the definition (17) of the gamma function yields

$$C_s \;=\; \sqrt{\frac{(2s+1)^{2s} a}{\Gamma(2s)}} \;. \tag{53}$$

The ground state wave function is then

$$\phi_s^{(s)}(y) \;=\; \sqrt{\frac{(2s+1)^{2s} a}{\Gamma(2s)}} \exp \left[-(s + \frac{1}{2})\, e^{-ay} \;-\; s\, a\, y \right] \;. \tag{54}$$

Figure 2 shows a plot of the wave function for $s \;=\; 3$.

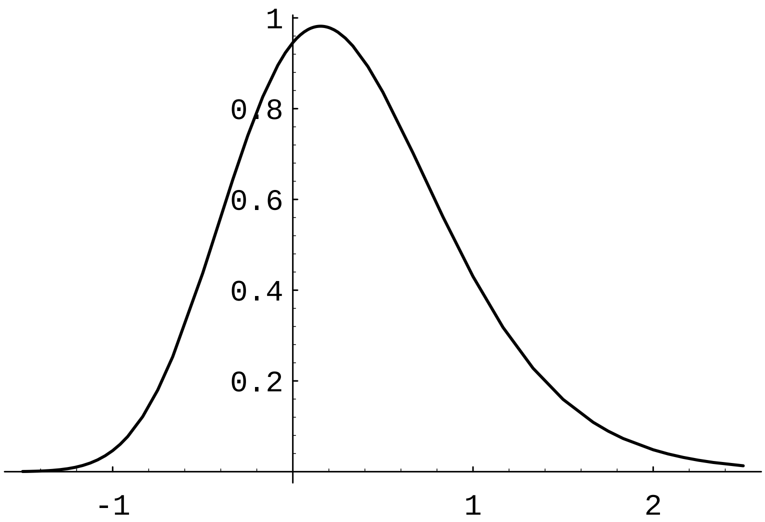

Figure 2: Ground state wave function $\phi_s^{(s)}(y)$, i.e., (54), for Morse potential with $D = a = 1$ and $s = 3$.

(g) For $s = 3$ the Morse potential has three bound states, i.e., beside the state (54), also the states $\phi_{s-1}^{(s)}$ and $\phi_{s-2}^{(s)}$. These states can be determined from the states $\phi_{s-1}^{(s-1)}$ and $\phi_{s-2}^{(s-2)}$, respectively. One applies for this purpose (12). The constants c_s, which appear in (12), are $c_s = \sqrt{(s+1)^2 - t^2}$, an expression which can be derived in an analogous way to expression (41). Hence,

$$\phi_{s-1}^{(s)}(y) = \frac{A_s^+}{\sqrt{s^2 - (s-1)^2}}\, \phi_{s-1}^{(s-1)}(y) \tag{55}$$

$$\phi_{s-2}^{(s)}(y) = \frac{A_s^+ \, A_{s-1}^+}{\sqrt{[s^2 - (s-2)^2]\,[(s-1)^2 - (s-2)^2]}}\, \phi_{s-2}^{(s-2)}(y) \tag{56}$$

where

$$A_s^+ = -\frac{d}{dy} + s\, e^{-ay} - s\,. \tag{57}$$

It is of interest to compare these wave functions graphically to the corresponding wave functions of the potential $U_o(y)$, i.e., to the harmonic oscillator wqve functions for $n = 1, 2$.