

Problem Set 4
Physics 480 / Fall 1999
Professor Klaus Schulten

Problem 1: Wave Functions of One-Dim. Harmonic Oscillator

In this problem we consider three different numerical evaluations of the stationary states $\phi_n(x)$ of the one-dimensional harmonic oscillator described by the Schrödinger equation

$$\left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} m \omega^2 x^2 \right) \phi_n(x) = E_n \phi_n(x), \quad E_n = \hbar\omega \left(n + \frac{1}{2} \right) \quad (1)$$

Employ in the following the variable $y = \sqrt{m\omega/\hbar} x$ and assume the normalization $\int_{-\infty}^{\infty} dy |\phi_n(y)|^2 = 1$.

(a) Starting from the ground state $\phi_0(y)$ construct the five stationary states lowest in energy by application of the differential operator \hat{a}^\dagger according to

$$\phi_n(y) = \frac{\hat{a}^\dagger}{\sqrt{n}} \phi_{n-1}(y). \quad (2)$$

Obtain explicit expressions using the differential operation available in **Mathematica**. Plot the results.

(b) Employing the expression of $\phi_n(y)$ in terms of Hermite polynomials, determine the Hermite polynomials using the recursion relationship

$$H_{n+1}(y) - 2y H_n(y) + 2n H_{n-1}(y) = 0, \quad n = 1, 2, \dots \quad (3)$$

starting from

$$H_0(y) = 1, \quad H_1(y) = 2y \quad (4)$$

Use for this purpose again **Mathematica** to obtain explicit expressions for $\phi_n(y)$. Compare with the expressions determined in (a).

(c) Evaluate the stationary states $\phi_n(x)$, $n = 1, 2, 3, 4, 5$ employing the explicit expression for the Hermite polynomials

$$H_n(y) = \sum_{k=0}^{\lfloor n/2 \rfloor} \frac{(-1)^k n!}{k! (n-2k)!} (2y)^{n-2k}. \quad (5)$$

Compare the result with (a) and (b).

Problem 2: Displaced Harmonic Oscillator

We consider the time evolution of the quantum state of a harmonic oscillator which experiences an external force

$$F(\tau) = \begin{cases} 0 & \text{for } \tau < 0 \\ F_0 & \text{for } \tau > 0. \end{cases} \quad (6)$$

and for $\tau < 0$ is in its initial ground state

$$\Psi_0(x, \tau) = \left[\frac{m\omega}{\pi\hbar} \right]^{\frac{1}{4}} \exp\left(-\frac{m\omega}{2\hbar}x^2\right) \exp\left(-i\frac{\omega\tau}{2}\right), \quad (7)$$

Since for $t > 0$ the force is time-independent one can describe the system through stationary states of a harmonic oscillator corresponding to a potential $V(x) = \frac{1}{2}m\omega^2x^2 - F_0x$ and introduce for such description the stationary states characterized by discrete energy values E_n^F , ($n = 0, 1, \dots$) and wave functions

$$\Psi_n^F(x, t) = \psi_n^F(x) \exp\left(-i\frac{E_n^F}{\hbar}t\right). \quad (8)$$

In the following employ time and length units

$$T = \frac{2\pi}{\omega}, \quad (9)$$

and, respectively,

$$L = \sqrt{\frac{\hbar}{m\omega}}. \quad (10)$$

(a) Show that the stationary states $\psi_n^F(x)$, for $t > 0$, can be expressed in terms of the Hermite polynomials $H_n(x)$ as follows

$$\psi_n^F(x) = \frac{1}{\sqrt{2^n n! \sqrt{\pi}}} \exp\left[-\frac{(x-a)^2}{2}\right] H_n(x-a). \quad (11)$$

(b) Prove that the probability to find the considered system, for $t > 0$, in state $\psi_n^F(x)$ is

$$P_n = \left| \int_{-\infty}^{\infty} dx [\Psi_n^F(x)]^* \Psi(x) \right|^2 = \frac{(a^2/2)^n}{n!} e^{-(a^2/2)}, \quad n = 0, 1, 2, \dots, \quad (12)$$

and check that $\sum_{n=0}^{\infty} P_n = 1$ holds.

(In your derivation you may find useful the following two formulae

$$\int_{-\infty}^{\infty} dx e^{-x^2} H_n(x) H_m(x) = 2^n n! \sqrt{\pi} \delta_{n,m},$$

and

$$e^{2tx-t^2} = \sum_{n=0}^{\infty} \frac{H_n(x)}{n!} t^n.$$

(c) Using *Mathematica* plot P_n as function of n for $a \in [0, 5]$ and $n \leq 5$ and discuss the result.

(d) For which value(s) of the external force F_0 will the chance to find the oscillator, for $t > 0$, in its second excited state be larger than the probability to find the oscillator in any other state?

Problem 3: Two-Dimensional Harmonic Oscillator

Determine the stationary states of the two-dimensional isotropic harmonic oscillator described by the time-independent Schrödinger equation

$$\left[-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} \right) + \frac{1}{2} m \omega^2 (x_1^2 + x_2^2) \right] \phi_E(x_1, x_2) = E \phi_E(x_1, x_2) \quad (13)$$

employing the method of separation of variables applied previously for particles in a three-dimensional box (see notes), i.e., seeking solutions of the form $\phi_E(x_1, x_2) = \phi_{E_1}(x_1) \phi_{E_2}(x_2)$, $E = E_1 + E_2$.

(a) Show that the factors in $\phi_{E_1}(x_1) \phi_{E_2}(x_2)$ obey the time-independent Schrödinger equation of the one-dimensional harmonic oscillator.

(b) Plot the probability density of all stationary states with energy $E \leq 4 \cdot \hbar\omega$. Use for this purpose the routine `Plot3D[...]` of `Mathematica` and the wave functions as determined in Problem Set 3.

(c) Plot for the stationary states in (b) the points in the x_1, x_2 -plane where the wave functions vanish, the so-called node lines.

Problem 4: Vibrations of Linear Triatomic Molecule

We want to describe the stretching vibrations of a linear, symmetric triatomic molecule $Y=X=Y$. The atomic masses are m_X , m_Y . We consider only consider the vibrations along the long axis of the molecule, the so-called stretching vibrations.

These vibrations are described by the potential energy function

$$V = \frac{1}{2} k_0 [(x_2 - x_1)^2 + (x_3 - x_2)^2] + k_1 (x_2 - x_1)(x_3 - x_2) \quad (14)$$

where the coordinates x_1 , x_2 and x_3 are defined in the figure below. k_0 and k_1 are two constants (see below). The first term on the r.h.s. of (14) describes the vibrational energy of each bond separately, and the second term describes the interaction between two bond vibrations.

(a) Express the Hamiltonian of the system in term of the center of mass coordinate y_1 , and in terms of displacements of bond lengths y_2 and y_3 defined through

$$\begin{aligned} y_1 &= \frac{m_Y (x_1 + x_3) + m_X x_2}{m_X + 2m_Y} \\ y_2 &= x_2 - x_1 \\ y_3 &= x_3 - x_2 \end{aligned} \quad (15)$$

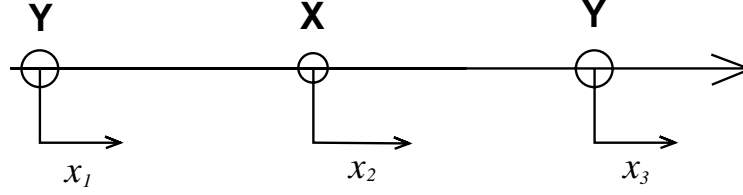


Figure 1: The three small sphere represent the X-ray structure of molecule $Y=X=Y$. x_2 is the displacement of X atom away from its equilibrium position. So do x_1 and x_3 .

and show that the resulting Hamiltonian can be written as

$$\hat{H} = -\frac{\hbar^2}{2(m_X + 2m_Y)} \frac{\partial^2}{\partial y_1^2} + \hat{H}_1(y_2, y_3) \quad (16)$$

where

$$\begin{aligned} \hat{H}_1(y_2, y_3) = & -\frac{\hbar^2}{2} \left(\frac{1}{m_X} + \frac{1}{m_Y} \right) \left(\frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial y_3^2} \right) \\ & + \frac{\hbar^2}{m_X} \frac{\partial}{\partial y_2} \frac{\partial}{\partial y_3} + \frac{1}{2} k_0 (y_2^2 + y_3^2) + k_1 y_2 y_3 \end{aligned} \quad (17)$$

Note

$$\frac{\partial}{\partial x_1} = \frac{\partial y_1}{\partial x_1} \frac{\partial}{\partial y_1} + \frac{\partial y_2}{\partial x_1} \frac{\partial}{\partial y_2} + \frac{\partial y_3}{\partial x_1} \frac{\partial}{\partial y_3} \quad (18)$$

(b) Determine a linear coordinate transformation

$$\begin{aligned} z_2 &= y_2 + c_2 y_3 \\ z_3 &= y_2 + c_3 y_3 \end{aligned} \quad (19)$$

which brings $\hat{H}_1(y_2, y_3)$ to the form

$$\hat{H}_1 = -\frac{\hbar^2}{2m_2} \frac{\partial^2}{\partial z_2^2} + \frac{1}{2} k_2' z_2^2 - \frac{\hbar^2}{2m_3} \frac{\partial^2}{\partial z_3^2} + \frac{1}{2} k_3' z_3^2. \quad (20)$$

(c) Determine the stationary states by means of separation of variables, i.e., assuming a wave function of the form

$$\Psi(y_1, z_2, z_3, t) = e^{-\frac{i}{\hbar} E t} \phi_1(y_1) \phi_2(z_2) \phi_3(z_3). \quad (21)$$

Express an arbitrary wave function in terms of the coordinates y_1 , y_2 and y_3 .

(d) Apply your result to the molecule CO_2 . In this case holds: $m_X = 12 \text{ u}$; $m_Y = 16 \text{ u}$, where $1 \text{ u} = 1.66 \times 10^{-27} \text{ kg}$. Determine the corresponding vibrational energies first for potential energy coefficients $k_0 =$

1160 Kcal/molÅ² and $k_1 = 0$. The observed normal mode frequencies are 1337 cm⁻¹ and 2349 cm⁻¹. Evaluate the percentage errors. Note that 1 rad/sec = 5.341×10^{-12} cm⁻¹.

(e) If infrared light linearly polarized along the long axis of the molecule irradiates CO₂, which of the two normal modes can be possibly excited? Keep in mind that linearly polarized electromagnetic radiation is described by an electric field vector oscillating along the direction of polarization, and that C, O atoms are partially charged with opposite charges.

(f) The density plots in Fig. 2 are the stationary wave functions $\phi_1(z_2) \phi_1(z_3)$ as defined in (21) generated by Mathematica. **The axes in these plots correspond to the y_2 and y_3 coordinates.** State the vibrational quantum numbers corresponding to the wave numbers, each state being associated with two quantum numbers n_2 for the z_2 and n_3 for the z_3 coordinate. Specify the quantum numbers like $n_2 = 2, n_3 = 6$.

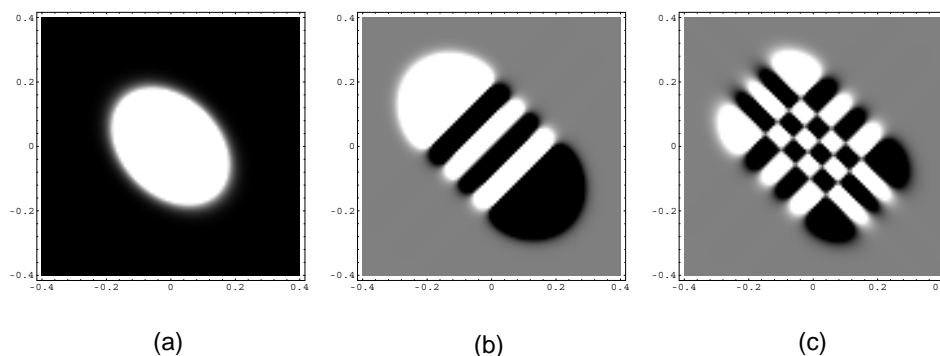


Figure 2: The density plots generated by Mathematica represent the stationary wave functions $\phi_1(z_2) \phi_1(z_3)$ with z_2 and z_3 expressed as functions of y_2 and y_3 (in Å). The horizontal axis in these plots corresponds to the y_2 and the vertical one corresponds to the y_3 coordinates. White codes values of the density above average, and black values below average.

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

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dy^2} + U(y) \right] \phi(y) = E \phi(y) \quad (22)$$

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

$$U(y) = D[e^{-2ay} - 2e^{-ay}]. \quad (23)$$

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

(a)

1. Show that for the bound states holds $E < 0$. [Hint: Plot the potential (23).]
2. Show that the lowest eigenvalue should be

$$E_o = -D + a\hbar\sqrt{\frac{D}{2m}} - \epsilon, \quad \epsilon > 0. \quad (24)$$

[Hint: Compare the plot of the potential (23) 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 $I = \int dy p(y)$ for motion at $E = 0$. It holds then (this result will be proven later in the course)

$$\text{number of bound states} \leq I/\hbar \quad (25)$$

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

$$x = -ay + \ln\left(\frac{\sqrt{8mD}}{a\hbar}\right), \quad (26)$$

$$s + \frac{1}{2} = \frac{\sqrt{2mD}}{a\hbar}, \quad (27)$$

$$t^2 = -\frac{2mE}{a^2\hbar^2} > 0 \quad (28)$$

yields

$$\mathcal{H}_s \phi_t(x) = \left[-\frac{d^2}{dx^2} + \frac{1}{4}e^{2x} - \left(s + \frac{1}{2}\right)e^x \right] \phi_t(x) = -t^2 \phi_t(x) \quad (29)$$

where

$$\mathcal{H}_s = \frac{2m}{a^2\hbar^2} H, \quad s \text{ defined through (27)}. \quad (30)$$

Consider in the following s as a *variable* and t as a *constant*. Show that (29) is equivalent to

$$A_{s+1}^- A_{s+1}^+ \phi_t^{(s)}(x) = [(s+1)^2 - t^2] \phi_t^{(s)}(x) \quad (31)$$

as well as to

$$A_s^+ A_s^- \phi_t^{(s)}(x) = [s^2 - t^2] \phi_t^{(s)}(x) \quad (32)$$

where

$$A_s^\pm = \mp \frac{d}{dx} + \frac{e^x}{2} - s. \quad (33)$$

(c) Show that for fixed t the operators A_s^+ , A_s^- generate new solutions to Eq. (29) according to the rule

$$A_{s+1}^+ \phi_t^{(s)}(x) = c_s \phi_t^{(s+1)}(x), \quad (34)$$

$$A_s^- \phi_t^{(s)}(x) = d_s \phi_t^{(s-1)}(x). \quad (35)$$

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

$$d_s^2 = s^2 - t^2. \quad (36)$$

Why should hold $s > t$?

(d) Equation (29) above can only have bound states, i.e., normalizable solutions, for $s > t$. This implies that the sequence $\dots A_{s-2}^- A_{s-1}^- A_s^- \phi_t^{(s)}(x)$ for $s - n < 0$ leads to a solution which is not admissible 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

$$A_{s_o}^- \phi_t^{(s_o)}(x) = 0. \quad (37)$$

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

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

$$\begin{aligned} E_n &= -D + a\hbar \sqrt{\frac{2D}{m}} \left(n + \frac{1}{2} \right) - \frac{a^2 \hbar^2}{2m} \left(n + \frac{1}{2} \right)^2, \\ n &= 0, 1, 2, \dots \leq \frac{\sqrt{2mD}}{a\hbar} - \frac{1}{2}. \end{aligned} \quad (38)$$

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

$$\Gamma(z) = \int_0^{\infty} dt t^{z-1} e^{-t} \quad (39)$$

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

(g) How can one obtain also the stationary states corresponding to the energies (38) for $n > 0$. Determine and plot the wave functions of these states using *Mathematica*.

The problem set needs to be handed in by Tuesday, October 19.
The web page of Physics 480 is at
<http://www.ks.uiuc.edu/Services/Class/PHYS480/>