Chapter 1

One-dimensional Schrödinger equation

In this chapter we start from the harmonic oscillator to introduce a general numerical methodology to solve the one-dimensional, time-independent Schrödinger equation. The analytical solution of the harmonic oscillator will be first derived and described. A specific integration algorithm (Numerov) will be used. The extension of the numerical methodology to other, more general types of potentials does not present any special difficulty.

For a particle of mass m under a potential $V(x)$, the one-dimensional, time-independent Schrödinger equation is given by:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi(x) = E\psi(x), \tag{1.1}$$

where $\psi(x)$ is the wave function, that can be chosen to be real, and $\hbar$ is the Planck constant h divided by 2π. In the following we are focusing on the *discrete spectrum*: the set of isolated energy values for which Eq.(1.1) has normalizable solutions, localized in space.

1.1 The harmonic oscillator

The harmonic oscillator is a fundamental problem in classical dynamics as well as in quantum mechanics. It represents the simplest model system in which attractive forces are present and is an important paradigm for all kinds of vibrational phenomena. For instance, the vibrations around equilibrium positions of a system of interacting particles may be described, via an appropriate coordinate transformation, as a set of independent harmonic oscillators known as *normal vibrational modes*. The same holds in quantum mechanics. The study of the quantum oscillator allows a deeper understanding of quantization and of its effects and of wave functions of bound states.

In this chapter we first remind the main results of the theory of the harmonic oscillator, then we show how to set up a computer code that allows to numerically solve the Schrödinger equation for the harmonic oscillator. The resulting code can be easily modified and adapted to a different, not simply

quadratic, interaction potential. This allows to study problems that, unlike the harmonic oscillator, do not have a simple analytical solution.

1.1.1 Units

The Schrödinger equation for a one-dimensional harmonic oscillator is, in usual notations:

$$\frac{d^2\psi}{dx^2} = -\frac{2m}{\hbar^2}\left(E - \frac{1}{2}Kx^2\right)\psi(x) \tag{1.2}$$

where K is the force constant. The force on the mass is $F = -Kx$, proportional to the displacement x and directed towards the origin. Classically such an oscillator has a frequency (angular frequency)

$$\omega = \sqrt{\frac{K}{m}}. \tag{1.3}$$

It is convenient to work with adimensional units, the same that are used by the codes presented at the end of this chapter. Let us introduce an adimensional variable ξ and a length λ such that $x = \lambda\xi$. By substituting into Eq.(1.2), one finds

$$\frac{d^2\psi}{d\xi^2} = \left(-\frac{2mE\lambda^2}{\hbar^2} + \frac{mK\lambda^4}{\hbar^2}\xi^2\right)\psi. \tag{1.4}$$

The natural choice is to set $mK\lambda^4/\hbar^2 = 1$, leading to $\lambda = (\hbar^2/mK)^{1/4}$ and, using Eq.(1.3), to

$$\xi = \left(\frac{m\omega}{\hbar}\right)^{1/2} x \tag{1.5}$$

By further introducing an adimensional "energy" ε such that

$$\varepsilon = \frac{E}{\hbar\omega}, \tag{1.6}$$

one finally rewrites Eq.(1.2) in adimensional units:

$$\frac{d^2\psi}{d\xi^2} = -2\left(\varepsilon - \frac{\xi^2}{2}\right)\psi(\xi). \tag{1.7}$$

1.1.2 Exact solution

One can easily verify that for large ξ (such that ε can be neglected) the solutions of Eq.(1.7) must have an asymptotic behavior like

$$\psi(\xi) \sim \xi^n e^{\pm\xi^2/2} \tag{1.8}$$

where n is any finite value. The $+$ sign in the exponent must however be discarded: it would give raise to diverging, non-physical solutions (in which the particle would tend to leave the $\xi = 0$ point, instead of being attracted towards it by the elastic force). It is thus convenient to extract the asymptotic behavior and assume

$$\psi(\xi) = H(\xi)e^{-\xi^2/2} \tag{1.9}$$

where $H(\xi)$ is a well-behaved function for large ξ (i.e. the asymptotic behavior is determined by the second factor $e^{-\xi^2/2}$). In particular, $H(\xi)$ must not grow like e^{ξ^2}, or else we fall back into a undesirable non-physical solution.

Under the assumption of Eq.(1.9), Eq.(1.7) becomes an equation for $H(\xi)$:

$$\frac{d^2 H}{d\xi^2}(\xi) - 2\xi \frac{dH}{d\xi}(\xi) + (2\varepsilon - 1)H(\xi) = 0. \tag{1.10}$$

It is immediate to notice that $\varepsilon_0 = 1/2$, $H_0(\xi) = 1$ is the simplest solution. This is the *ground state*, i.e. the lowest-energy solution, as will soon be clear.

In order to find all solutions, we expand $H(\xi)$ into a series, in principle with infinite terms:

$$H(\xi) = \sum_{n=0}^{\infty} A_n \xi^n, \tag{1.11}$$

we derive the series to find $dH/d\xi$ and $d^2H/d\xi^2$, plug the results into Eq.(1.10) and regroup terms with the same power of ξ. We find an equation

$$\sum_{n=0}^{\infty} \left[(n+2)(n+1)A_{n+2} + (2\varepsilon - 2n - 1)A_n \right] \xi^n = 0 \tag{1.12}$$

that can be satisfied for any value of ξ only if the coefficients of all the orders are zero:

$$(n+2)(n+1)A_{n+2} + (2\varepsilon - 2n - 1)A_n = 0. \tag{1.13}$$

Thus, once A_0 and A_1 are given, Eq.(1.13) allows to determine by recursion the solution under the form of a power series.

For large n, the coefficient of the series behave like $A_{n+2} \sim 2A_n/n$, that is:

$$A_{n+2} \sim \frac{1}{(n/2)!}. \tag{1.14}$$

This asymptotic behavior is the same as for the series expansion $\exp(\xi^2) = \sum_n \xi^{2n}/n!$, indicating that the recursion relation Eq.(1.13) produces a function $H(\xi)$ that grows like $\exp(\xi^2)$ and yields a diverging nonphysical solution.

The only way to prevent this from happening is to have in Eq.(1.13) all coefficients beyond a given n vanish, so that the infinite series reduces to a finite-degree polynomial. This happens if and only if

$$\varepsilon = n + \frac{1}{2} \tag{1.15}$$

where n is a non-negative integer.

Allowed energies for the harmonic oscillator are thus *quantized*:

$$E_n = \left(n + \frac{1}{2} \right) \hbar\omega \quad n = 0, 1, 2, \ldots \tag{1.16}$$

The corresponding polynomials $H_n(\xi)$ are known as *Hermite polynomials*. $H_n(\xi)$ is of degree n in ξ, has n nodes, is even $[H_n(-\xi) = H_n(\xi)]$ for even n, odd
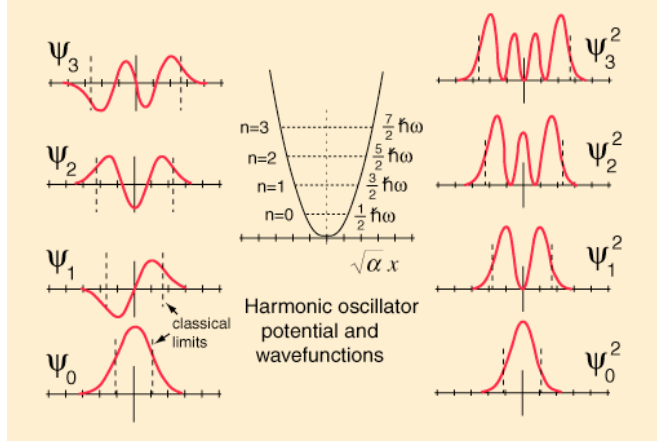
Figure 1.1: Wave functions and probability density for the harmonic oscillator.

$[H_n(-\xi) = -H_n(\xi)]$ for odd n. Since $\mathrm{e}^{-\xi^2/2}$ is node-less and even, the complete wave function corresponding to the energy E_n:

$$\psi_n(\xi) = H_n(\xi)\mathrm{e}^{-\xi^2/2} \tag{1.17}$$

has n nodes and the same parity as n. The fact that all solutions of the Schrödinger equation are either odd or even functions is a consequence of the symmetry of the potential: $V(-x) = V(x)$.

The lowest-order Hermite polynomials are

$$H_0(\xi) = 1, \quad H_1(\xi) = 2\xi, \quad H_2(\xi) = 4\xi^2 - 2, \quad H_3(\xi) = 8\xi^3 - 12\xi. \tag{1.18}$$

1.1.3 Comparison with classical probability density

The probability density for wave function $\psi_n(x)$ of the harmonic oscillator has in general $n+1$ peaks, whose height increases while approaching the corresponding classical inversion points (i.e. points where $V(x) = E$).

These probability density can be compared to that of the classical harmonic oscillator, in which the mass moves according to $x(t) = x_0 \sin(\omega t)$. The probability $\rho(x)dx$ to find the mass between x and $x + dx$ is proportional to the time needed to cross such a region, i.e. it is inversely proportional to the speed as a function of x:

$$\rho(x)dx \propto \frac{dx}{v(x)}. \tag{1.19}$$

Since $v(t) = x_0\omega \cos(\omega t) = \omega\sqrt{x_0^2 - x_0^2 \sin^2(\omega t)}$, we have

$$\rho(x) \propto \frac{1}{\sqrt{x_0^2 - x^2}}. \tag{1.20}$$

This probability density has a minimum for $x = 0$, diverges at inversion points, is zero beyond inversion points.

The quantum probability density for the ground state is completely different: has a maximum for $x = 0$, decreases for increasing x. At the classical inversion point its value is still $\sim 60\%$ of the maximum value: the particle has a high probability to be in the classically forbidden region (for which $V(x) > E$).

In the limit of large quantum numbers, i.e., large n values, the quantum density tends however to look similar to the quantum one, but it still displays the oscillatory behavior in the allowed region, typical for quantum systems.

1.2 Quantum mechanics and numerical codes

1.2.1 Quantization

A first aspect to be considered in the numerical solution of quantum problems is the presence of *quantization* of energy levels for bound states, such as for instance Eq.(1.16) for the harmonic oscillator. The acceptable energy values E_n are not known *a priori*. Thus in the Schrödinger equation (1.1) the unknown is not just $\psi(x)$ but also E. For each allowed energy level, or *eigenvalue*, E_n, there will be a corresponding wave function, or *eigenfunction*, $\psi_n(x)$.

What happens if we try to solve the Schrödinger equation for an energy E that does not correspond to an eigenvalue? In fact, a "solution" exists for *any* value of E, but not a physical one. The quantization of the energy originates from boundary conditions, requiring no nonphysical divergence of the wave function in the forbidden regions. Thus, if E is not an eigenvalue, we will observe a divergence of $\psi(x)$. Numerical codes searching for allowed energies must be able to recognize when the energy is not correct and search for a better energy, until it coincides – within numerical or predetermined accuracy – with an eigenvalue. The first code presented at the end of this chapter implements such a strategy.

1.2.2 A pitfall: pathological asymptotic behavior

An important aspect of quantum mechanics is the existence of "negative" kinetic energies: i.e., the wave function can be non zero (and thus the probability to find a particle can be finite) in regions for which $V(x) > E$, forbidden according to classical mechanics. Based on (1.1) and assuming the simple case in which V is (or can be considered) constant, this means

$$\frac{d^2\psi}{dx^2} = k^2 \psi(x) \tag{1.21}$$

where k^2 is a positive quantity. This in turns implies an exponential behavior, with both $\psi(x) \simeq \exp(kx)$ and $\psi(x) \simeq \exp(-kx)$ satisfying (1.21). As a rule only one of these two possibilities has a physical meaning: the one that gives raise to a wave function that *decreases* exponentially at large $|x|$.

It is very easy to distinguish between the "good" and the "bad" solution for a human, much less so for a numerical code that produces whatever comes out from the equations. If even a tiny amount of the "bad" solution, for instance due to numerical noise, is present, the integration algorithm will inexorably

make it grow in the classically forbidden region. As the integration goes on, the "bad" solution will dominate the "good" one and eventually produce crazy numbers (or crazy NaN's: Not a Number). Thus a nice-looking wave function in the classically allowed region, smoothly decaying in the classically forbidden region, may suddenly start to diverge at some point, unless a wise strategy is employed to prevent it. The second code presented at the end of this chapter implements such a strategy.

1.3 Numerov's method

In order to solve numerically the time-independent Schrödinger equation in one dimension, one has to *discretize* it on a suitable finite grid of points and to *integrate* (solve) it, the solution being also given on the grid of points.

There are many big thick books on this subject, describing old and new methods, from the very simple to the very sophisticated, for all kinds of differential equations and all kinds of discretization and integration algorithms. In the following, we will consider *Numerov's method*, named after Russian astronomer Boris Vasilyevich Numerov, as an example of a simple yet powerful and accurate algorithm.

Numerov's method is useful to integrate second-order differential equations of the general form

$$\frac{d^2y}{dx^2} = -g(x)y(x) + s(x) \tag{1.22}$$

where $g(x)$ and $s(x)$ are known functions. The Schrödinger equation, Eq.(1.1), has this form, with $g(x) = (2m/\hbar^2)[E - V(x)]$ and $s(x) = 0$. We will see in the next chapter that also the radial Schrödinger equations for three-dimensional systems having spherical symmetry belongs to such class. Another important equation falling into this category is Poisson's equation of electromagnetism,

$$\frac{d^2\phi}{dx^2} = -4\pi\rho(x) \tag{1.23}$$

where $\rho(x)$ is the charge density. In this case $g(x) = 0$ and $s(x) = -4\pi\rho(x)$.

Let us consider a finite box containing the system: for instance, $-x_{\max} \leq x \leq x_{\max}$, with $x_{\max}$ large enough for our solutions to decay to negligibly small values. Let us divide our finite box into N small intervals of equal size, Δx wide. We call x_i the points of the grid so obtained, $y_i = y(x_i)$ the values of the unknown function $y(x)$ on grid points. In the same way we indicate by g_i and s_i the values of the (known) functions $g(x)$ and $s(x)$ in the same grid points. In order to obtain a discretized version of the differential equation (i.e. to obtain an equation involving finite differences), we expand $y(x)$ into a Taylor series around a point x_n, up to fifth order:

$$
\begin{aligned}
y_{n-1} =\ & y_n - y'_n\Delta x + \tfrac{1}{2}y''_n(\Delta x)^2 - \tfrac{1}{6}y'''_n(\Delta x)^3 + \tfrac{1}{24}y''''_n(\Delta x)^4 - \tfrac{1}{120}y'''''_n(\Delta x)^5 \\
& + O[(\Delta x)^6] \\
y_{n+1} =\ & y_n + y'_n\Delta x + \tfrac{1}{2}y''_n(\Delta x)^2 + \tfrac{1}{6}y'''_n(\Delta x)^3 + \tfrac{1}{24}y''''_n(\Delta x)^4 + \tfrac{1}{120}y'''''_n(\Delta x)^5 \\
& + O[(\Delta x)^6].
\end{aligned}
\tag{1.24}
$$

We have switched to notation $y'(x) = dy/dx$ etc. for compactness. If we sum the two equations, we obtain:

$$y_{n+1} + y_{n-1} = 2y_n + y_n''(\Delta x)^2 + \frac{1}{12}y_n''''(\Delta x)^4 + O[(\Delta x)^6]. \qquad (1.25)$$

Eq.(1.22) tells us that

$$y_n'' = -g_n y_n + s_n \equiv z_n. \qquad (1.26)$$

The quantity z_n above is introduced to simplify the notations. The following relation holds:

$$z_{n+1} + z_{n-1} = 2z_n + z_n''(\Delta x)^2 + O[(\Delta x)^4]. \qquad (1.27)$$

This is the simple formula for the discretized second derivative, that can be obtained in a straightforward way by Taylor expansion up to third order. Thus:

$$y_n'''' \equiv z_n'' = \frac{z_{n+1} + z_{n-1} - 2z_n}{(\Delta x)^2} + O[(\Delta x)^2]. \qquad (1.28)$$

By inserting back these results into Eq.(1.25) one finds

$$
\begin{aligned}
y_{n+1} &= 2y_n - y_{n-1} + (-g_n y_n + s_n)(\Delta x)^2 \\
&+ \tfrac{1}{12}(-g_{n+1}y_{n+1} + s_{n+1} - g_{n-1}y_{n-1} + s_{n-1} + 2g_n y_n - 2s_n)(\Delta x)^2 \\
&+ O[(\Delta x)^6]
\end{aligned}
\qquad (1.29)
$$

and finally the *Numerov's formula*

$$
\begin{aligned}
y_{n+1}\left[1 + g_{n+1}\tfrac{(\Delta x)^2}{12}\right] &= 2y_n\left[1 - 5g_n\tfrac{(\Delta x)^2}{12}\right] - y_{n-1}\left[1 + g_{n-1}\tfrac{(\Delta x)^2}{12}\right] \\
&+ (s_{n+1} + 10s_n + s_{n-1})\tfrac{(\Delta x)^2}{12} + O[(\Delta x)^6]
\end{aligned}
\qquad (1.30)
$$

that allows to obtain y_{n+1} starting from y_n and y_{n-1}, and recursively the function in the entire box.

The value of the function in the first two points are needed in order to start the recurrence. We remark that such initial conditions differ from the more traditional ones for second-order differential equations:

$$y(x_0) = y_0, \quad y'(x_0) = y_0', \qquad (1.31)$$

in which the value at one point and the derivative in the same point are specified.

It is of course possible to integrate both in the direction of positive x and in the direction of negative x. In the presence of inversion symmetry, it will be sufficient to integrate in just one direction.

In our case—Schrödinger equation—the s_n terms are absent. It is convenient to introduce an auxiliary array f_n, defined as

$$f_n \equiv 1 + g_n\frac{(\Delta x)^2}{12}, \qquad \text{where} \qquad g_n = \frac{2m}{\hbar^2}[E - V(x_n)], \qquad (1.32)$$

and to rewrite Numerov's formula as

$$y_{n+1} = \frac{(12 - 10f_n)y_n - f_{n-1}y_{n-1}}{f_{n+1}}. \qquad (1.33)$$

The value of the energy is now hidden into g_n and f_n.

1.3.1 Code: harmonic0

Code `harmonic0.f90`[1] (or `harmonic0.c`[2]) solves the Schrödinger equation for the quantum harmonic oscillator, Eq.(1.7) in adimensional units. using the Numerov's algorithm above described for integration, and searching eigenvalues with a pre-determined number n of nodes using the "shooting method".

The shooting method is quite similar to the bisection procedure for the search of the zero of a function. We define an initial energy range $[E_{min}, E_{max}]$ that must contain the eigenvalue E_n. We start with an energy E equal to the mid-point of the energy range, $E = (E_{max} + E_{min})/2$. The wave function is integrated starting from $x = 0$ in the direction of positive x; at the same time, the number of nodes (i.e. of changes of sign of the function) is counted. If the number of nodes is larger than n, E is too high; if the number of nodes is smaller than n, E is too low. We then choose the lower half-interval $[E_{min}, E_{max} = E]$, or the upper half-interval $[E_{min} = E, E_{max}]$, respectively, select a new trial eigenvalue E in the mid-point of the new interval, iterate the procedure. When the energy interval is smaller than a pre-determined threshold, we assume that convergence has been reached.

For negative x the function is constructed using symmetry, since $\psi_n(-x) = (-1)^n \psi_n(x)$. This is of course possible only because $V(-x) = V(x)$, otherwise integration would have to be performed on the entire interval. The parity of the wave function determines the choice of the starting points for the recursion. For n odd, the two first points can be chosen as $y_0 = 0$ and an arbitrary finite value for y_1. For n even, y_0 is arbitrary and finite, y_1 is determined by Numerov's formula, Eq.(1.33), with $f_1 = f_{-1}$ and $y_1 = y_{-1}$:

$$y_1 = \frac{(12 - 10f_0)y_0}{2f_1}. \tag{1.34}$$

The code prompts for some input data:

- the limit x_{max} for integration (typical values: $5 \div 10$);

- the number N of grid points (typical values range from hundreds to a few thousand); note that the grid point index actually runs from 0 to N, so that $\Delta x = x_{max}/N$;

- the name of the file where output data is written;

- the required number n of nodes (the code will stop if n is negative).

Finally the code prompts for a trial energy. You should answer 0 in order to search for an eigenvalue with n nodes. The code will start iterating on the energy, printing on standard output (i.e. at the terminal): iteration number, number of nodes found (on the positive x axis only), the current energy eigenvalue estimate. It is however possible to specify an energy, not necessarily an eigenvalue, to force the code to perform an integration at fixed energy and see

---

[1]http://www.fisica.uniud.it/%7Egiannozz/Didattica/MQ/Software/F90/harmonic0.f90
[2]http://www.fisica.uniud.it/%7Egiannozz/Didattica/MQ/Software/C/harmonic0.c

the resulting wave function. It is useful for testing purposes and to better understand how the eigenvalue search works (or doesn't work). Note that in this case the required number of nodes will not be honored; however the integration will be different for odd or even number of nodes, because the parity of n determines how the first two grid points are chosen.

The output file contains five columns: respectively, x, $\psi(x)$, $|\psi(x)|^2$, $\rho_{cl}(x)$ and $V(x)$. $\rho_{cl}(x)$ is the classical probability density (normalized to 1) of the harmonic oscillator, given in Eq.(1.20). All these quantities can be plotted as a function of x using any plotting program, such as `gnuplot`, shortly described in the introduction. Note that the code will prompt for a new value of the number of nodes after each calculation of the wave function: answer -1 to stop the code. If you perform more than one calculation, the output file will contain the result for all of them in sequence. Also note that the wave function are written for the entire box, from $-x_{max}$ to x_{max}.

It will become quickly evident that the code "sort of" works: the results look good in the region where the wave function is not vanishingly small, but invariably, the pathological behavior described in Sec.(1.2.2) sets up and wave functions diverge at large $|x|$. As a consequence, it is impossible to normalize the $\psi(x)$. The code definitely needs to be improved. The proper way to deal with such difficulty is to find an inherently stable algorithm.

1.3.2 Code: harmonic1

Code `harmonic1.f90`[3] (or `harmonic1.c`[4]) is the improved version of `harmonic0` that does not suffer from the problem of divergence at large x.

Two integrations are performed: a forward recursion, starting from $x = 0$, and a backward one, starting from x_{max}. The eigenvalue is fixed by the condition that the two parts of the function match with continuous first derivative (as required for a physical wave function, if the potential is finite). The matching point is chosen in correspondence of the classical inversion point, x_{cl}, i.e. where $V(x_{cl}) = E$. Such point depends upon the trial energy E. For a function defined on a finite grid, the matching point is defined with an accuracy that is limited by the interval between grid points. In practice, one finds the index `icl` of the first grid point $x_c = \text{icl}\Delta x$ such that $V(x_c) > E$; the classical inversion point will be located somewhere between $x_c - \Delta x$ and x_c.

The outward integration is performed until grid point `icl`, yielding a function $\psi_L(x)$ defined in $[0, x_c]$; the number n of changes of sign is counted in the same way as in `harmonic0`. If n is not correct the energy is adjusted (lowered if n too high, raised if n too low) as in `harmonic0`. We note that it is not needed to look for changes of sign beyond x_c: in fact we know *a priori* that in the classically forbidden region there cannot be any nodes (no oscillations, just decaying solutions).

If the number of nodes is the expected one, the code starts to integrate inward from the rightmost points. Note the statement `y(mesh) = dx`: its only goal is to force solutions to be positive, since the solution at the left of the

---

[3]http://www.fisica.uniud.it/%7Egiannozz/Didattica/MQ/Software/F90/harmonic1.f90
[4]http://www.fisica.uniud.it/%7Egiannozz/Didattica/MQ/Software/C/harmonic1.c

matching point is also positive. The value `dx` is arbitrary: the solution is anyway rescaled in order to be continuous at the matching point. The code stops the same index `icl` corresponding to x_c. We thus get a function $\psi_R(x)$ defined in $[x_c, x_{\max}]$.

In general, the two parts of the wave function have different values in x_c: $\psi_L(x_c)$ and $\psi_R(x_c)$. We first of all re-scale $\psi_R(x)$ by a factor $\psi_L(x_c)/\psi_R(x_c)$, so that the two functions match continuously in x_c. Then, the whole function $\psi(x)$ is renormalized in such a way that $\int |\psi(x)|^2 dx = 1$.

Now comes the crucial point: the two parts of the function will have in general a discontinuity at the matching point $\psi'_R(x_c) - \psi'_L(x_c)$. This difference should be zero for a good solution, but it will not in practice, unless we are really close to the good energy $E = E_n$. The sign of the difference allows us to understand whether E is too high or too low, and thus to apply again the bisection method to improve the estimate of the energy.

In order to calculate the discontinuity with good accuracy, we write the Taylor expansions:

$$y_{i-1}^L = y_i^L - y_i'^L \Delta x + \frac{1}{2} y_i''^L (\Delta x)^2 + O[(\Delta x)^3]$$
$$y_{i+1}^R = y_i^R + y_i'^R \Delta x + \frac{1}{2} y_i''^R (\Delta x)^2 + O[(\Delta x)^3] \tag{1.35}$$

For clarity, in the above equation i indicates the index `icl`. We sum the two Taylor expansions and obtain, noting that $y_i^L = y_i^R = y_i$, and that $y_i''^L = y_i''^R = y_i'' = -g_i y_i$ as guaranteed by Numerov's method:

$$y_{i-1}^L + y_{i+1}^R = 2y_i + (y_i'^R - y_i'^L)\Delta x - g_i y_i (\Delta x)^2 + O[(\Delta x)^3] \tag{1.36}$$

that is

$$y_i'^R - y_i'^L = \frac{y_{i-1}^L + y_{i+1}^R - [2 - g_i(\Delta x)^2]y_i}{\Delta x} + O[(\Delta x)^2] \tag{1.37}$$

or else, by using the notations as in Eq.(1.32),

$$y_i'^R - y_i'^L = \frac{y_{i-1}^L + y_{i+1}^R - (14 - 12 f_i)y_i}{\Delta x} + O[(\Delta x)^2] \tag{1.38}$$

In this way the code calculated the discontinuity of the first derivative. If the sign of $y_i'^R - y_i'^L$ is positive, the energy is too high (can you give an argument for this?) and thus we move to the lower half-interval; if negative, the energy is too low and we move to the upper half interval. As usual, convergence is declared when the size of the energy range has been reduced, by successive bisection, to less than a pre-determined tolerance threshold.

During the procedure, the code prints on standard output a line for each iteration, containing: the iteration number; the number of nodes found (on the positive x axis only); if the number of nodes is the correct one, the discontinuity of the derivative $y_i'^R - y_i'^L$ (zero if number of nodes not yet correct); the current estimate for the energy eigenvalue. At the end, the code writes the final wave function (this time, correctly normalized to 1!) to the output file.

1.3.3 Laboratory

Here are a few hints for "numerical experiments" to be performed in the computer lab (or afterward), using both codes:

- Calculate and plot eigenfunctions for various values of n. It may be useful to plot, together with eigenfunctions or eigenfunctions squared, the classical probability density, contained in the fourth column of the output file. It will clearly show the classical inversion points. With `gnuplot`, e.g.:

  `plot "`*filename*`" u 1:3 w l, "`*filename*`" u 1:4 w l`

  (`u` = using, `1:3` = plot column3 vs column 1, `w l` = with lines; the second "*filename*" can be replaced by "").

- Look at the wave functions obtained by specifying an energy value not corresponding to an eigenvalue. Notice the difference between the results of `harmonic0` and `harmonic1` in this case.

- Look at what happens when the energy is close to but not exactly an eigenvalue. Again, compare the behavior of the two codes.

- Examine the effects of the parameters `xmax`, `mesh`. For a given Δx, how large can be the number of nodes?

- Verify how close you go to the exact results (remember that there is a convergence threshold on the energy hardwired in the code). What are the factors that affect the accuracy of the results?

Possible code modifications and extensions:

- Modify the potential, keeping inversion symmetry. This will require very little changes to be done. You might for instance consider a "double-well" potential described by the form:

$$V(x) = \epsilon \left[\left(\frac{x}{\delta}\right)^4 - 2\left(\frac{x}{\delta}\right)^2 + 1 \right], \qquad \epsilon, \delta > 0. \qquad (1.39)$$

- Modify the potential, breaking inversion symmetry. You might consider for instance the *Morse potential*:

$$V(x) = D \left[e^{-2ax} - 2e^{-ax} + 1 \right], \qquad (1.40)$$

  widely used to model the potential energy of a diatomic molecule. Which changes are needed in order to adapt the algorithm to cover this case?