

# Computational Quantum Mechanics

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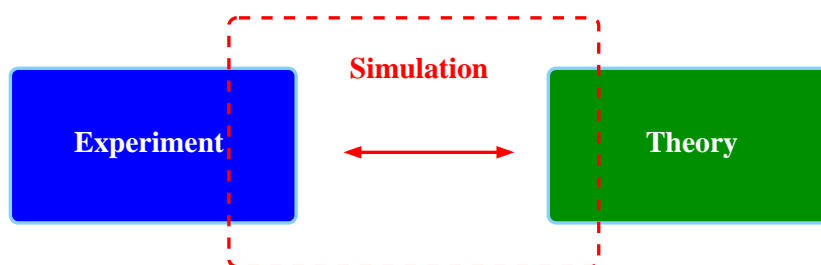
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# 1 Introduction

## Aim of this lecture course

This course focuses on the atomistic modeling of properties through the numerical solution of the many-electron Schrödinger equation. There are a number of important cases for which the stationary SE can be solved analytically, e.g., the harmonic oscillator (in any number of dimensions) and the hydrogen atom. However, in most cases of practical interest (in, i.e., atomic, molecular, and solid state physics) exact or approximate numerical methods must be employed. The students will be introduced to computational methods used in electronic structure calculations to reduce the complexity of the Schrödinger equation at various levels of sophistication/approximation. Specific topics include: numerical solution of the Schrödinger equation, variational method, the many-body problem, Hartree-Fock (HF) and Density Functional Theories (DFT), band structure methods (tight binding, pseudopotentials, full potential). The applicability of the various computational tools to diverse problems will be discussed (also through computational experiments involving the implementation of model HF and DFT programs). This course requires some basic knowledge of quantum mechanics, solid states physics and computer programming.

Computer experiments: solving physical problems by means of computers:



General Procedure:

1. Specify the physical phenomenon to study
2. Develop a theory and a mathematical model to describe the phenomenon
3. Discretize the mathematical model in computer language
4. Implement the simulation program (numerical algorithms)
5. Perform the computational simulation and compare with experiment

**Continuum methods:** Assume that matter is continuous and treat the properties of the system as field quantities (phenomenological equations). + any size, any timescale;  
- experimental inputs required, no detailed on the electronic structure.

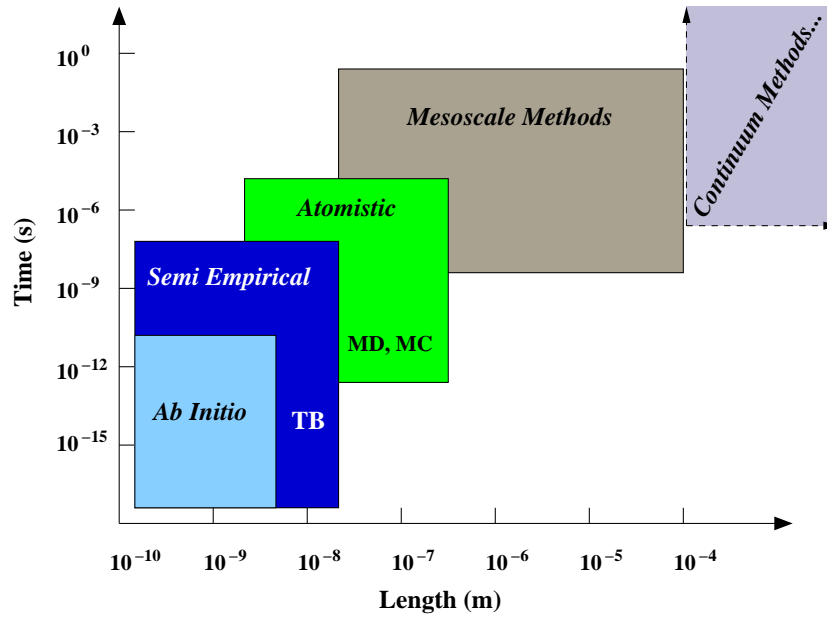


Figure 1: Simulation scale: from micro to MACRO

**Mesoscale methods:** Introduce simplifications to atomistic methods (effective potentials) + many atoms ( $10^8$ – $10^9$ ), time scale of 1s; - only qualitative description.

**Atomistic Methods:** Use empirical/*ab initio* parameters to determine thermodynamic (MC,MD) and transport (MD) properties. +  $10^4$ – $10^5$  atoms,  $O(1)$   $\mu$ s; - inputs dependent

**Semi-empirical methods:** simplified version of *ab initio* methods throughout adjustable parameters. + more atoms and longer timescale as compared to *ab initio* ; - The quality of the results depends on the inputs.

**Ab Initio:** Materials properties from first principles solving the *quantum-mechanical Schrödinger equation* numerically. + In principle able to obtain "exact" solutions at the electrons level. - small system, very fast process, very time-consuming (numerically expensive).

## Literature

*Computational Physics*

J.M. Thijssen (Cambridge University Press)

*Electronic Structure: Basic Theory and Practical Methods*

R. Martin (Cambridge University Press, 2004)

*Band Theory and Electronic Properties of Solids*

J. Singleton (Oxford University Press, 2001)

*FORTRAN 90/95 Explained*

M. Metcalf und J.K. Reid (Oxford University Press)

*Numerical Recipes*

W.H. Press, S.A. Teukolsky, W.T. Vetterling, B.P. Flannery (Cambridge University Press)

## Online Resources

Anders Sandvik: *Computational Physics*

<http://physics.bu.edu/py502/>

Paolo Giannozzi: *Numerical Methods in Quantum Mechanics*

<http://www.fisica.uniud.it/~giannozz/Corsi/MQ/mq.html>

## 2 Basic Principles of Quantum Mechanics

### 2.1 Classical vs. quantum mechanics

**Classical mechanics:** A point-particle is described by its position  $\mathbf{r}(t)$  and velocity  $\mathbf{v}(t)$ , and its evolution in time is described by the Newton's equation of motion.

The position and the velocity of any classical particle are exactly determined at any given time. Its energy is a continuous function of the particle velocity

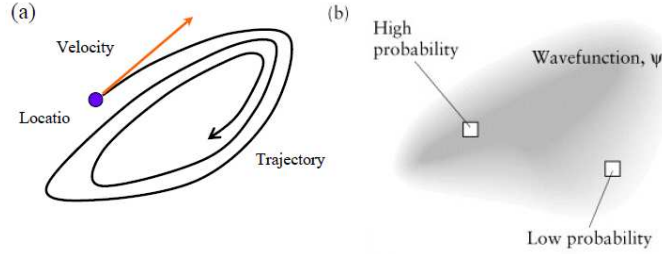


Figure 2: (a) Trajectory of a classical particle, and (b) probability distribution of a quantum particle

**Quantum mechanics:**

1.  $\mathbf{x}$  and  $\mathbf{v}$  cannot be precisely known simultaneously (the Heisenberg uncertainty principle). In QM a particle is described by a wave function  $\Psi(\mathbf{r}, t)$  (the probability amplitude for different configurations of the system). For a quantum particle, we can only say that the particle is at a given position with a certain probability:

$$P(\mathbf{r}, t) d\mathbf{r} \propto |\Psi(\mathbf{r}, t)|^2 d\mathbf{r}$$

2. Every observable  $\mathcal{A}$  in classical mechanics can be described by a corresponding operator  $\hat{O}_{\mathcal{A}}$  in quantum mechanics that acts on the wavefunction to produce the value of the observable  $\mathcal{A}$  multiplied by the wavefunction:

$$\hat{O}_{\mathcal{A}} \Psi = \mathcal{A} \Psi \quad (\text{eigenvalue equation})$$

Some examples:

Observable	Classical Mechanics	Quantum Mechanics
Position	$\mathbf{r} = (x, y, z)$	$\hat{\mathbf{r}} = (x, y, z)$
Momentum	$\mathbf{p} = m\mathbf{v}$	$\hat{\mathbf{p}} = -i\hbar\nabla = -i\hbar\left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)$
Kinetic Energy	$T(E_{kin}) = \frac{p^2}{2m}$	$\hat{T} = -\frac{\hbar^2}{2m}\nabla^2 = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial^2 x} + \frac{\partial^2}{\partial^2 y} + \frac{\partial^2}{\partial^2 z}\right)$

3. The expectation value of  $\mathcal{A}$  (the probability-weighted sum of the possible values) in the state  $\Psi$  is defined as:

$$\langle \Psi | \hat{O}_{\mathcal{A}} | \Psi \rangle = \int_{-\infty}^{\infty} \Psi^*(\mathbf{r}) \mathcal{A} \Psi(\mathbf{r}) d\mathbf{r}. \quad (2.1)$$

4. All properties of a quantum system can be determined once its wavefunction  $\Psi(\mathbf{r}, t)$  is known. The equation that determines the wavefunction and its time evolution is the time-dependent Schrödinger equation:

$$\hat{H}\Psi(\mathbf{r}, t) = i\hbar \frac{\partial \Psi(\mathbf{r}, t)}{\partial t} \quad (2.2)$$

Where  $\hat{H}$  is the Hamiltonian operator, which is the quantum operator for the total energy of the system. For a single particle in 3D the SE reads:

$$i\hbar \frac{\partial \Psi(\mathbf{r}, t)}{\partial t} = \hat{T}\Psi(\mathbf{r}, t) + \hat{V}(\mathbf{r})\Psi(\mathbf{r}, t) = -\frac{\hbar^2}{2m} \nabla^2 \Psi(\mathbf{r}, t) + V(\mathbf{r})\Psi(\mathbf{r}, t) \quad (2.3)$$

For stationary states (i.e. non-time dependent systems) one can use the time independent Schrödinger equation, obtained by setting  $\Psi_n(\mathbf{r}, t) = \Psi_n(\mathbf{r})e^{iE_n t/\hbar}$ :

$$\hat{H}\Psi_n = E_n \Psi_n \quad (2.4)$$

This is the equation for the standing waves, the eigenvalue equation for  $\hat{H}$ .

## 2.2 Units

In this context we will adopt atomic units (a.u.), a system of units convenient for atomic physics, electromagnetism, and quantum electrodynamics, especially when the focus is on the properties of electrons. There are two different kinds of atomic units, which one might name Hartree atomic units and Rydberg atomic units. Fundamental physical constants in a.u.:

	Rydberg units	Hartree units
$\hbar$	1	1
$e^2$	2	1
$m_e$	1/2 a.u.	1 a.u.

Some derived units:

length	1 a.u. = 0.52918 Å
energy	1 a.u. = 1 Rydberg (Ry) = 13.60578 eV
mass	1 a.u. = 2 $m_e$ = 2 9.109 10 <sup>-31</sup>
velocity	1 a.u. = 4.19 Å/fs
time	1 a.u. = 0.126 fs

Within this system of units the stationary SE can be written as:

$$\left[-\nabla^2 + \hat{V}\right] \Psi_n(\mathbf{r}) = E_n \Psi_n(\mathbf{r}) \quad (2.5)$$

Since the SE is a partial linear differential equation, the solution  $\Psi_n$  are orthogonal and form a complete set:

$$\langle \Psi_n | \Psi_m \rangle = \delta_{mn} \quad \text{and} \quad \sum_{n=1}^{\infty} \langle \Psi_n | \Psi_n \rangle = 1 \quad (2.6)$$

The energetically more favourable solution represents the electronic groundstate, whereas excited states are described by the solution with higher energy.



### 3 Stationary Schrödinger Equation: Numerov's method

The most basic problem in quantum mechanics is to solve the stationary Schrödinger equation,

$$-\frac{\hbar^2}{2m}\nabla^2\Psi_n(\mathbf{r}) + V(\mathbf{r})\Psi_n(\mathbf{r}) = E_n\Psi_n(\mathbf{r}) \quad (3.1)$$

Here,  $\hbar$  is Planck's constant,  $m$  is the mass of the particle,  $V$  is the potential energy,  $E_n$  is the energy of the particle (energy eigenvalues),  $\Psi_n(\mathbf{r})$  is the wavefunction (energy eigenfunctions, stationary states), and  $n$  is the quantum number for the discrete energy spectrum.

There are a number of important cases for which the stationary SE can be solved analitically, e.g., the harmonic oscillator (in any number of dimensions) and the hydrogen atom. However, in most cases of practical interest (atomic, molecular and solid-state physics) exact or approximate numerical methods must be employed (we must rely on computer simulations!). In the most general case,  $\Psi_n(\mathbf{r})$  is a complex function of the position (in many cases, included our numerical works,  $\Psi_n(\mathbf{r})$  reduced to a real function upon a suitably chosen phase), and when properly normalized,  $\Psi_n(\mathbf{r})^*\Psi_n(\mathbf{r})$  is the probability per unit volume that the particle will be found at  $\mathbf{r}$ .

This is a partial differential equation, in which the also the energy  $E$  and not only the wavefunction  $\Psi$  is an unknown. A complete solution involves *determining both  $\Psi$  and the corresponding energy*. This are also known as the *eigenfunction and eigenvalue* of the equation. An important property of the eigenvalue problems is that in many cases solution exist only for certain special values of the eigenvalues, in this case  $E$ . Mathematically, this is the origin of the discrete energy levels of quantum theory.

#### 3.1 1D Schrödinger Equation

For a single particle moving in one dimension, the stationary SE reduces to an ordinary differential equation (see Eq.3.2) solvable with techniques similar to those used in solving Newton's equation, namely simple discretization and standard integration algorithms such as the Euler's method, the Runge-Kutta method and the Verlet algorithm. In higher dimensions (2D or 3D) or for many particle systems the SE is expressed in terms of a partial differential equation, and other techniques as well as approximations must be used. In one dimension, the time independent Schrödinger equation reduces to:

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi(x)}{dx^2} + V(x)\Psi(x) = E\Psi(x) \quad (3.2)$$

The solution of the SE in one dimension is a problem almost identical to solving the radial wave function for spherically symmetric potentials in two or three dimensions. For a spherically symmetric potential, the solution of the SE can be factorized into a radial and spherical part:

$$\Psi(\mathbf{x}) = \sum_{l=0}^{\infty} \sum_{m=-l}^l A_{lm} \frac{u_l(r)}{r} Y_l^m(\theta, \varphi) \quad (3.3)$$

where  $Y_l^m(\theta, \varphi)$  are the spherical harmonics and the  $u_l$  are the radial functions which satisfies the radial SE:

$$\left( -\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + \frac{\hbar^2 l(l+1)}{2mr^2} + V(r) \right) u_l(r) = E u_l(r) \quad (3.4)$$

This is of the same form of Eq.3.2, apart from the fact that  $-\infty < x < \infty$  but  $r \geq 0$ . We will study the radial solution in more details later on.

Let us consider a particle moving in a 1D region in which the potential is constant. Since we are free to shift the origin of the potential energy scale, we will take  $V = 0$  everywhere. The SE reduces to:

$$-\frac{\hbar^2}{2m} \frac{d^2 \Psi(x)}{dx^2} = E \Psi(x) \quad (3.5)$$

which has the general solution

$$\Psi(x) = A e^{ikx} \quad (3.6)$$

where  $i \equiv \sqrt{-1}$  and  $e^{ikx} = \cos kx + i \sin kx$ . That this is indeed a solution to Eq. 3.5 can be verified by substitution, which yields

$$E = \frac{\hbar^2 k^2}{2m} \quad (3.7)$$

The wavefunction  $\Psi(x) = A e^{ikx}$  has the form of a plane wave with wave vector  $k = 2\pi/\lambda$ , where  $\lambda$  is the wavelength of the particle.  $k$  is also related to the particle's momentum,  $p$ , with  $p = \hbar k$ . In this particular problem there is a solution to the SE for any value of  $k$ , and thus all nonnegative values of  $E$  are allowed: *we do not have quantized energy levels*. Our solutions satisfies the SE for any value of the constant  $A$ , which determines the overall magnitude of the wave function. The constant  $A$  is indeed determined by the physical interpretation of  $\Psi$  and its relation to the probability density. Since we are considering the behavior of a single particle this probability must satisfy the normalized condition:

$$\int \Psi^* \Psi dx = 1 \quad \rightarrow \quad 1 = \int \Psi^* \Psi dx = A^2 \int dx \quad (3.8)$$

If our particle is allowed to roam freely over an infinitely large region, we must make  $A$  infinitely small in order to preserve normalization.

### 3.1.1 Particle in a Box

It is convenient to deal with the infinitely small  $A$  situation by assuming that the particle is confined to a box that extends from  $x = -L$  to  $x = +L$ . The plane wave must then fit in this box. Inside we have  $V = 0$  and outside  $V_0$ . If we assume  $V = \infty$  then  $\Psi = 0$  outside the box. Physically this result is not surprising. A particle with a finite energy will have no chance of being found in a region where  $V = \infty$ , so the probability amplitude of  $\Psi$  must vanish.

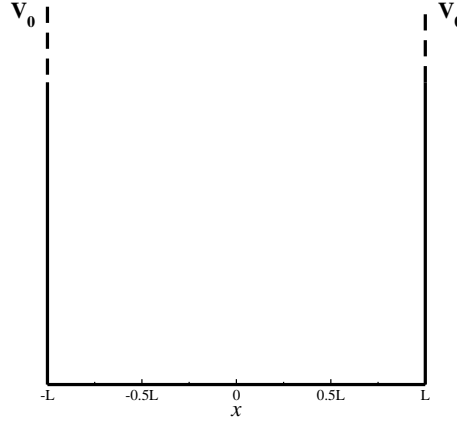


Figure 3: Potential energy for a particle in a box. The potential is  $V = 0$  inside the box ( $-L \leq x \leq +L$ ) and  $V_0$  outside.

To complete our solution we make use of one more constrain on  $\Psi$ ; it must be a continuous function of  $x$ : the solution for  $\Psi$  inside the box must vanish at  $x \pm L$ . To satisfy this solution we take into account that the SE is a linear equation, and therefore the sum of two solutions is also a solution:

$$\begin{aligned}\Psi_+ &= \frac{A}{2}[e^{ik_+x} + e^{-ik_+x}] = A \cos(k_+x) & \text{even} \\ \Psi_- &= \frac{A}{2}[e^{ik_-x} - e^{-ik_-x}] = A \sin(k_-x) & \text{odd}\end{aligned}$$

These are just standing waves. The condition  $\Psi(x = \pm L) = 0$  requires that

$$\begin{aligned}k_+ &= \frac{\pi}{2L}, \frac{3\pi}{2L}, \dots = \frac{(2n-1)\pi}{2L} \\ k_- &= \frac{\pi}{L}, \frac{2\pi}{2L}, \dots = \frac{n\pi}{L}\end{aligned}$$

This constrain on  $k$  means that we now have discrete energy levels. Only special values of the wave vector are allowed. These values are those yielding standing waves

that satisfy the boundary conditions (see Fig. 4). Quantization of  $k$  also implies quantization of the energy since

$$E = \frac{\hbar^2 k^2}{2m} \rightarrow E_n = \frac{\hbar^2 k_n^2}{2m} \quad (3.9)$$

The ground state energy is obtained from the  $n = 1$  even solution.

It is interesting to notice that the wave functions  $\Psi_+$  and  $\Psi_-$  have a well defined parity; they are either *even*  $\Psi(+x) = \Psi(-x)$ , or *odd*  $\Psi(+x) = -\Psi(-x)$ , with respect to  $x$ . The normalization condition can be used to determine the value of  $A$ , yielding  $A = L^{-1/2}$ . Finally, these wave functions form a complete set of orthogonal functions inside the box. The term orthogonal means that

$$\int \Psi_1^* \Psi_2 dx = 0 \quad (3.10)$$

and *complete set* means that any function in this interval that vanishes at  $x = \pm L$  can be written as a sum of these wave functions with suitably chosen coefficients.

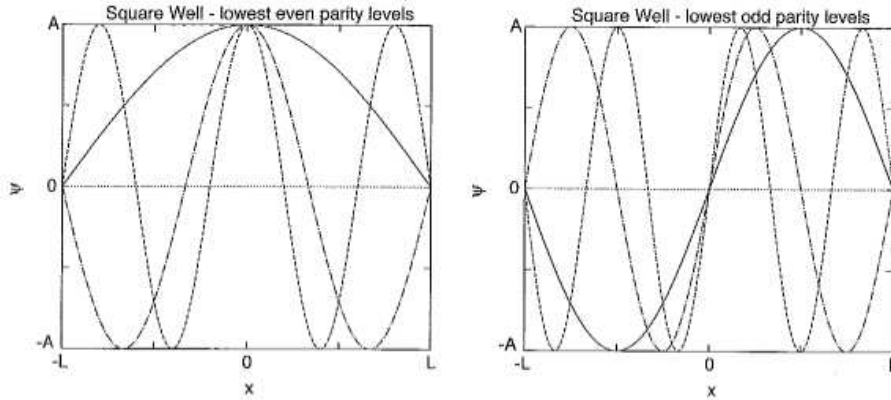


Figure 4: Wave functions for the lowest six eigenstates for a particle in a box. Left: cosine-like even-parity solution; right: sine-like odd parity solutions.

### 3.2 Numerical solution: Numerov's method

Eqs. 3.2 and 3.4 can both be written in form:

$$\ddot{\Psi}(x) = \Psi^{(2)}(x) = f(x)\Psi(x) \quad (3.11)$$

This kind of equation can be solved using the Numerov's method. Numerov's method is a numerical fifth-order scheme to solve ordinary differential equations of second order.

To solve this type of equation numerically, we discretize the space coordinate  $x$  using a uniform grid:  $x_k = k\Delta_x$ . The Numerov's method is derived by adding the Taylor expansion for  $\Psi(x_{k\pm 1}) = \Psi(x_k \pm \Delta_x)$ :

$$\Psi(x_{k+1}) = \Psi(x_k) + \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \Delta_x^n \Psi^{(n)}(x_k) \quad (3.12)$$

$$\Psi(x_{k-1}) = \Psi(x_k) + \sum_{n=1}^{\infty} \frac{(1)^n}{n!} \Delta_x^n \Psi^{(n)}(x_k) \quad (3.13)$$

If we sum the two equations, we obtain:

$$\Psi(x_{k+1}) + \Psi(x_{k-1}) = 2\Psi(x_k) + \Delta_x^2 \Psi^{(2)}(x_k) + \frac{1}{12} \Delta_x^4 \Psi^{(4)}(x_k) + O(\Delta_x^6) \quad (3.14)$$

The next problem is to deal with the fourth derivative. It can be tackled by defining the central difference operator, acting on an arbitrary function  $f(x)$ :

$$\delta f(x) = f(x + \frac{1}{2}\Delta_x) - f(x - \frac{1}{2}\Delta_x) \quad (3.15)$$

$$\delta^2 f(x) = \delta[\delta f(x)] = f(x + \Delta_x) - 2f(x) + f(x - \Delta_x) \quad (3.16)$$

By applying the central difference operator Eq.3.14 can be written as:

$$\Psi(x_{k+1}) + \Psi(x_{k-1}) - 2\Psi(x_k) = \delta^2 \Psi(x) = \Delta_x^2 \Psi^{(2)}(x_k) + \frac{1}{12} \Delta_x^4 \Psi^{(4)}(x_k) + O(\Delta_x^6) \quad (3.17)$$

Similarly, we can now write the fourth derivative as a central difference of the second derivative using the above equation with the fourth-order term neglected (we can evaluate the fourth derivative as the discrete second derivative of the second derivative):

$$\Delta_x^2 \Psi^4(x_k) = \Delta_x^2 [\Psi^{(2)}(x_k)]^{(2)} = \delta^2 \Psi^{(2)}(x_k) + O(\Delta_x^4) \quad (3.18)$$

And finally Eq. 3.17 become:

$$\delta^2 \Psi(x_k) = \Delta_x^2 \Psi^{(2)}(x_k) + \frac{1}{12} \Delta_x^2 \delta^2 \Psi^{(2)}(x_k) + O(\Delta_x^6) \quad (3.19)$$

Coming back to the the Schrödinger-like equation  $\ddot{\Psi}(x) = \Psi^{(2)}(x) = f(x)\Psi(x)$ , and replacing  $\Psi^{(2)}(x_k)$  by  $f(x_k)\Psi(x_k)$  we obtain:

$$\delta^2 \Psi(x_k) = \Delta_x^2 f(x_k) \Psi(x_k) + \frac{1}{12} \Delta_x^2 \delta^2 [f(x_k) \Psi(x_k)] + O(\Delta_x^6) \quad (3.20)$$

Or, in a more compact notation ( $f(x_k) = f_k$ ):

$$\Psi_{k+1} - 2\Psi_k + \Psi_{k-1} = \Delta_x^2 f_k \Psi_k + \frac{1}{12} \Delta_x^2 [f_{k+1} \Psi_{k+1} - 2f_k \Psi_k + f_{k-1} \Psi_{k-1}] + O(\Delta_x^6) \quad (3.21)$$

Introducing the new function:

$$\phi_k = \Psi_k (1 - \Delta_x^2 f_k / 12) \quad (3.22)$$

a simpler form of Eq. 3.21 is obtained:

$$\boxed{\phi_{k+1} = 2\phi_k - \phi_{k-1} + \Delta_x^2 f_k \Psi_k + O(\Delta_x^6)}$$

for  $k = 0$  (i.e. at  $x_0 = 0$ )

$$\phi_1 = 2\phi_0 - \phi_{-1} + \Delta_x^2 f_0 \Psi_0 + O(\Delta_x^6) \quad (3.23)$$

The Numerov's formula allows to obtain the  $\phi_{k+1}$  starting from  $\phi_k$  and  $\phi_{k-1}$ , and recursively the function in the entire box, as long as the value of the function is known in the first two points (note the difference with "traditional" initial conditions, in which the value at one point and the derivative in the same point is 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.

### One more note on boundary conditions

In general the eigenfunctions  $\Psi_n(x)$  are defined for all  $-\infty < x < \infty$ , but numerically we have to restrict the integration to within a finite range, as already underlined. Appropriate boundary conditions have to be imposed at the end points. For  $\Psi_n(x \rightarrow \pm\infty)$  one can often obtain an asymptotic form that can be used for boundary condition at  $x = \pm x_{max}$ , or there may be "hard walls" beyond which the potential is considered infinite and the wave function vanishes (as an example, with hard walls at  $x = x_0$  one can start with  $\Psi(x_0) = 0$  and  $\Psi(x_0 + \Delta_x) = 1$ ). Note that the starting values do not have to correspond to a normalized wave function (can be carried out after the integration).

## 3.3 Fortran implementation: Numerov + Shooting method

For the stationary SE (Eq. 3.2), setting  $\hbar = m = 1$  we have:

$$\frac{d^2\Psi(x)}{dx^2} = 2[V(x) - E]\Psi(x) \quad [\dots\text{same form as } \Psi^{(2)}(x) = f(x)\Psi(x)\dots] \quad (3.24)$$

For a particle in a square well potential with infinite repulsion [ $V(x) = 0$  for  $|x| \leq 1$ ] the solutions (with boundary condition:  $\Psi(\pm 1) = 0$ ) are:

$$\Psi(x) = \cos(n\pi x/2L) \quad (n \text{ odd}) \quad (3.25)$$

$$\Psi(x) = \sin(n\pi x/2L) \quad (n \text{ even}) \quad (3.26)$$

with

$$E_n = \frac{\pi^2 n^2}{8} \quad (E_0 = \frac{\pi^2}{8} = 1.23370055) \quad (3.27)$$

Now, we show how to solve computationally this problem using the Numerov's method.

### (A) Choose valid boundary conditions:

We use boundary conditions to generate  $\Psi_0$  ( $\Psi_0 = 0$ ) and  $\Psi_1$  ( $\Psi_0 = 1$ ) and then calculated  $\phi_0$  and  $\phi_1$  according to Eq.3.22. This initial procedure can be done by the following subroutine:

```

!----- square-well with infinite walls
psi0=0.d0
psi1=1.d0

p1=psi1
f1=2.d0*(potential(-xmax)-ee)
q0=psi0*(1.d0-h12*f1)
f1=2.d0*(potential(-xmax+h)-ee)
q1=psi1*(1.d0-h12*f1)

```

where

$$\begin{array}{ll}
h12 & = \Delta_x^2/12 \\
q0 & = \phi_0 \\
q1 & = \phi_1 \\
psi0 & = \Psi_0 \\
psi1 & = \Psi_1 \\
potential(x) & = \text{potential energy} \\
ee & = \text{initial guess for energy}
\end{array}$$

Where the potential is given by the function `potential(x)`, for  $x$  in the range  $(-x_{\max}, x_{\max})$ :

```
potential=0.d0
```

### (B) Apply Numerov's algorithm:

We have seen that Eq. 3.24 can be solved using the Numerov's algorithm and reduced to:

$$\phi_{k+1} = 2\phi_k - \phi_{k-1} + \Delta_x^2 f_k \Psi_k + O(\Delta_x^6)$$

A Fortran code segment for integrating a total `nx` steps can look like this:

```

DO ix = 2,nx
  q2 = h2*f1*psi(ix-1)+2.d0*q1-q0
  q0 = q1
  q1 = q2
  f1 = 2.d0*(potential(x0+h*dbble(ix))-energy)
  psi(ix) = q1/(1.d0-h2*f1)
END DO

```

where

$$\begin{array}{ll}
h2 & = \Delta_x^2 \\
q0 & = \phi_{k-1} \\
q1 & = \phi_k \\
q2 & = \phi_{k+1} \\
psi(n) & = \Psi_n \\
potential(x) & = \text{potential energy} \\
energy & = \text{current guess for the energy}
\end{array}$$

The loop has to be repeated several times in order to adjust the energy and obtain the correct  $\Psi$  [The wavefunction must satisfy the appropriate boundary conditions ( $\Psi(x_{\max}) = 0$ ) and the number of nodes must be correct].

### (C) Energy finding strategy:

1. Make a guess for  $E$ . If we use a particular  $E$ , and start the integration from  $-x_{\max}$  to  $x_{\max}$  (using Numerov's method), we will arrive to a normalized solution ( $\int \Psi(x)dx = 1$ ) which does not satisfy the boundary condition at  $x_{\max}$  ( $\Psi(x_{\max}) \neq 0$ ). It is instructive to consider the behaviour of  $\Psi_n$  obtained by using

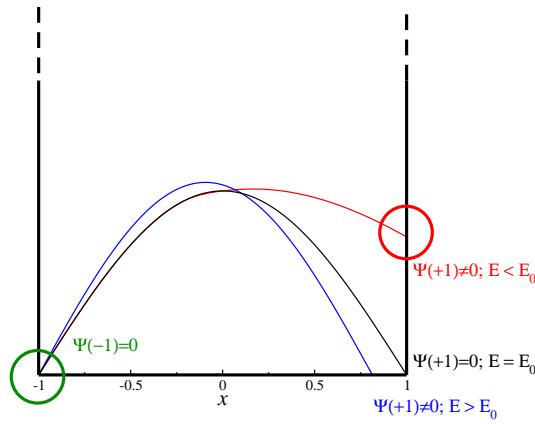


Figure 5: Schematic results for  $\Psi$  calculated using the Numerov's method for several values of  $E$ .

different values of  $E$ , which are not eigenvalues of the SE. The results are shown in Fig. 5. While all these functions are solution of the SE, only the one for which the boundary condition  $\Psi(1) = 0$  is an allowed wavefunction for our particle, and can be normalized to give a physically acceptable probability density. In our code, if the boundary condition is not satisfied (or, for excited states, the number of nodes is incorrect) one has to adjust  $E$ , and integrate again. This method is analogous to trying to throw a baseball or shoot a cannon shell so as to hit a specific target. Only for certain conditions (that is, will the ball land at the desired spot). In the present case the boundary conditions are such that the WF must vanish at the two extrema  $x = \pm L$ . The situation is a bit different when we have soft walls, rather than hard walls. In this case the wave function will not be zero at the soft wall positions  $x = \pm L$ , because the potential is not infinite and therefore there must be a certain (quantum) probability to find the particle in the *forbidden* region. We will study this case later on.

Fortran code to integrate and normalize the wavefunction:

!-----!



```

subroutine integrate(xmax,nx,e1,psi)
implicit none

real(8) :: q0,q1,p1,f1,ee,h2,h12
common/block1/q0,q1,p1,f1,ee,h2,h12

integer :: i,n,nx
real(8) :: psi(-nx:nx),xmax,x,h,de,e1

ee=e1
h=xmax/dbble(nx)
h2=h**2
h12=h2/12.d0
call setinitcond(xmax,h,psi(-nx),psi(-nx+1))
do i=-nx+2,nx
    x=dbble(i)*h
    call numerovstep(x)
    psi(i)=p1
end do
call normalize(psi,nx,h)

end subroutine integrate
!-----!

!-----!
!Integrates the wave function one step, using Numerov's method.  !
!On entry, the wave-function at the previous step is p1, on exit !
!it is the wave-function after the integration step. The modified!
!wave function, Psi(x)*[1-(h**2)*f1], at the two previous steps !
!are q0,q1 on entry, and f1=2.d0*(potential(x1)-energy).      !
!-----!

subroutine numerovstep(x)
implicit none

real(8) :: q0,q1,p1,f1,ee,h2,h12
common/block1/q0,q1,p1,f1,ee,h2,h12

real(8) :: x,q2,potential

q2=h2*f1*p1+2.d0*q1-q0
q0=q1; q1=q2
f1=2.d0*(potential(x)-ee)
p1=q1/(1.d0-h12*f1)

```

```

end subroutine numerovstep
!-----!

!-----!
subroutine normalize(psi,nx,h)
implicit none

integer :: i,nx
real(8) :: psi(-nx:nx),norm,h

norm=psi(-nx)**2+psi(nx)**2
do i=-nx+1,nx-3,2
    norm=norm+4.d0*psi(i)**2+2.d0*psi(i+1)**2
end do
norm=norm+4.d0*psi(nx-1)**2
norm=1.d0/sqrt(norm*h/3.d0)
do i=-nx,nx
    psi(i)=psi(i)*norm
end do

end subroutine normalize
!-----!

```

2. Adjust the energy and repeat the previous step until the desired solution is reached. An efficient way to systematically adjust the energy towards a solution is to use bisection (an other, less efficient method is the Newton-Raphson algorithm).

*Solving an equation using bisection (general)*

We wish to find the zero of some function:

$$f(E) = 0 \tag{3.28}$$

First find  $E_1$  and  $E_2$  for which:

$$f(E_1) < 0, \quad f(E_2) > 0 \tag{3.29}$$

Then we know that the function  $f$  must have a node between  $E_1$  and  $E_2$ . We can simply evaluate the function at the midpoint of the interval and check whether the function has the same sign at this point as at  $E_1$  or  $E_2$ :

$$E_3 = \frac{1}{2}(E_1 + E_2) \tag{3.30}$$

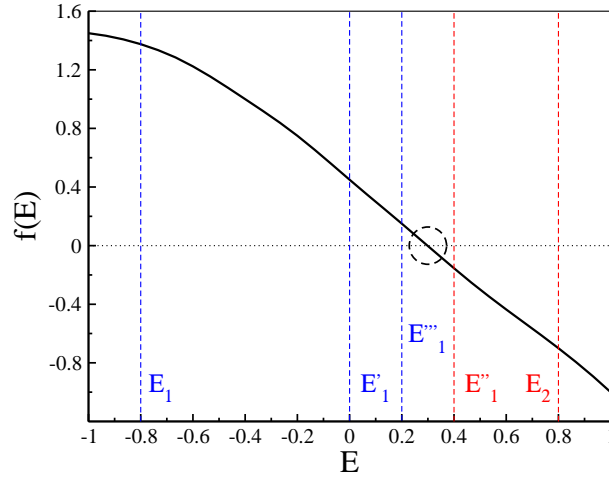


Figure 6: Graphical interpretation of the bisection method

Choose new bracketing values:

$$\text{if } f(E_3) < 0, \text{ then } E'_1 = E_3, E'_2 = E_2 \quad (3.31)$$

$$\text{if } f(E_3) > 0, \text{ then } E'_1 = E_1, E'_2 = E_3 \quad (3.32)$$

Repeat the procedure with the new bracketing values until  $f(E_3)$  is sufficiently small ( $f(E_3) < \epsilon$ , see Fig.6). This technique for gradually refining the solution is often called "shooting method".

How does this method works for the present case?

Denote  $\delta(E)$  the deviation of the wavefunction  $\Psi_N$  (normalized) at the end of the integration range from the boundary condition  $\Psi_N = \Psi_N^b$  to be satisfied there where the energy used in the integration is  $E$ . We first search for two energies  $E_1$  and  $E_2$  leading to different signs of  $\delta$  (i.e.  $\delta(E_1)\delta(E_2) \leq 0$ ). These energies must bracket an eigenvalue  $E_n$ . Such a bracketing pair can simply be searched for by carrying out the integration using energies  $E = E_0 + k\Delta_E$ , with  $k = 0, 1, \dots$  until the sign of  $\delta$  changes (assuming that there is an eigenvalue with energy  $< E_0$ , and that the increment  $\Delta_E$  is small enough for there not to be two eigenvalues within one step). When such a pair  $E_1$  and  $E_2$  has been found, an integration is carried out using  $E = (E_1 + E_2)/2$ , and depending on whether  $\delta(E_3)\delta(E_1)$  is positive or negative the pair  $(E_1, E_3)$  or  $(E_2, E_3)$  is used as the bracketing pair in a repetition of the above procedure. This bisection is continued until either the difference between the bracketing energies or the deviation  $|\delta|$  is smaller than some  $\epsilon$  corresponding to a sufficiently accurate solution.

The fortran implementation of the bisection method look like this:

```
write(*,*)'Starting bisection'
```

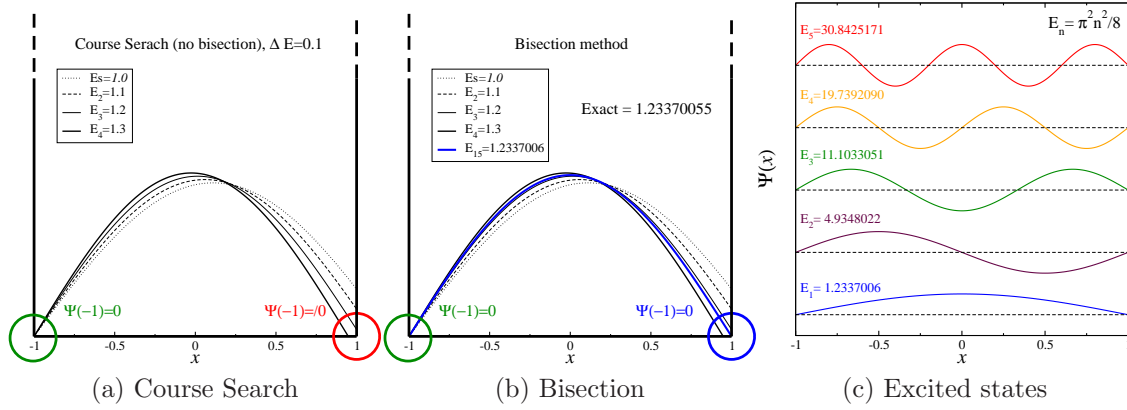


Figure 7: Wavefunction for the potential well with infinitely repulsive walls using the shooting method (a) without and (b-c) with bisection method. In (c) some excited states are also displayed.

```

ni=0
do
  ni=ni+1
  e0=(e1+e2)/2.0d0
  call integrate(xmax,nx,e0,psi)
  b0=psi(nx)-psi(-nx)

  if (abs(b0) <= eps) exit
  if (b0*b1 <= 0.0d0) then
    e2=e0
    b2=b0
  else
    e1=e0
    b1=b0
  end if
end do

```

3. Results: Fig. 7 illustrates the wavefunction for the square well potential with infinite repulsion for  $|x| > 1$  and  $V(x) = 0$  for  $|x| \leq 1$  with boundary condition for the integration given by  $\Psi(-1) = 0$  and  $\Psi(-1 + \Delta_x) = 1$  and with  $\Delta_x=0.002$  (1000 divisions).

Though the shooting method is usually used to solve the SE in one dimension (or for spherical symmetric potentials) it is generally slow because the SE must be solved many times for different energies. Alternative ways to solve the SE relies on iterative scheme and will be discussed in the next sections.

### 3.4 Soft walls

Let us briefly consider the case in which we have a soft walls potential barrier in the center of box. The above program can be used to attack this problem. It is only necessary to redefine the potential in the function `potential(x)` subroutine:

```
!----- square well with hard walls internal and box
if (x > -0.1d0 .and. x < 0.1d0) then
  potential=100.d0
else
  potential=0.d0
end if
```

From the results sketched in Fig. 8, we can draw the following conclusions:

1. There is indeed a finite probability to find the particle inside the potential barrier
2. From the actual calculation it is seen that many iterations are required to achieve a satisfactory convergence as compared to the hard walls case. As we will see in the next section this kind of problem are more efficiently treated within a variation approach rather than a Numerov-based scheme.

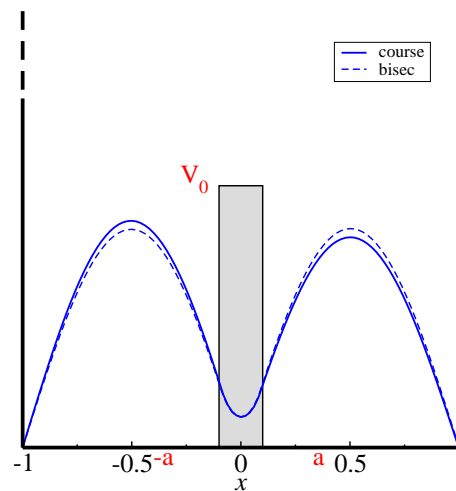


Figure 8: Wave function for a particle in a box with an internal soft barrier