

Computational Quantum Physics

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Chapter 1

Introduction

1.1 General

For **physics students** the computational quantum physics courses is a recommended prerequisite for any computationally oriented semester thesis, proseminar, master thesis or doctoral thesis.

For **computational science and engineering (RW) students** the computational quantum physics courses is part of the “Vertiefung” in theoretical physics.

1.1.1 Exercises

Programming Languages

Except when a specific programming language or tool is explicitly requested you are free to choose any programming language you like. Solutions will often be given either as C++ programs or Mathematica Notebooks.

Computer Access

The lecture rooms offer both Linux workstations, for which accounts can be requested with the computer support group of the physics department in the HPR building, as well as connections for your notebook computers.

1.1.2 Prerequisites

As a prerequisite for this course we expect knowledge of the following topics. Please contact us if you have any doubts or questions.

Computing

- Basic knowledge of UNIX
- At least one procedural programming language such as C, C++, Pascal, Java or FORTRAN. C++ knowledge is preferred.
- Knowledge of a symbolic mathematics program such as Mathematica or Maple.
- Ability to produce graphical plots.

Numerical Analysis

- Numerical integration and differentiation
- Linear solvers and eigensolvers
- Root solvers and optimization
- Statistical analysis

Quantum Mechanics

Basic knowledge of quantum mechanics, at the level of the quantum mechanics taught to computational scientists, should be sufficient to follow the course. If you feel lost at any point, please ask the lecturer to explain whatever you do not understand. We want you to be able to follow this course without taking an advanced quantum mechanics class.

1.1.3 References

1. J.M. Thijssen, *Computational Physics*, Cambridge University Press (1999) ISBN 0521575885
2. Nicholas J. Giordano, *Computational Physics*, Pearson Education (1996) ISBN 0133677230.
3. Harvey Gould and Jan Tobochnik, *An Introduction to Computer Simulation Methods*, 2nd edition, Addison Wesley (1996), ISBN 00201506041
4. Tao Pang, *An Introduction to Computational Physics*, Cambridge University Press (1997) ISBN 0521485924

1.2 Overview

In this class we will learn how to simulate quantum systems, starting from the simple one-dimensional Schrödinger equation to simulations of interacting quantum many body problems in condensed matter physics and in quantum field theories. In particular we will study

- The one-body Schrödinger equation and its numerical solution
- The many-body Schrödinger equation and second quantization
- Approximate solutions to the many body Schrödinger equation
- Path integrals and quantum Monte Carlo simulations
- Numerically exact solutions to (some) many body quantum problems
- Some simple quantum field theories

Chapter 2

Quantum mechanics in one hour

2.1 Introduction

The purpose of this chapter is to refresh your knowledge of quantum mechanics and to establish notation. Depending on your background you might not be familiar with all the material presented here. If that is the case, please ask the lecturers and we will expand the introduction. Those students who are familiar with advanced quantum mechanics are asked to glance over some omissions.

2.2 Basis of quantum mechanics

2.2.1 Wave functions and Hilbert spaces

Quantum mechanics is nothing but simple linear algebra, albeit in huge Hilbert spaces, which makes the problem hard. The foundations are pretty simple though.

A pure state of a quantum system is described by a “wave function” $|\Psi\rangle$, which is an element of a Hilbert space \mathcal{H} :

$$|\Psi\rangle \in \mathcal{H} \tag{2.1}$$

Usually the wave functions are normalized:

$$\| |\Psi\rangle \| = \sqrt{\langle\Psi|\Psi\rangle} = 1. \tag{2.2}$$

Here the “bra-ket” notation

$$\langle\Phi|\Psi\rangle \tag{2.3}$$

denotes the scalar product of the two wave functions $|\Phi\rangle$ and $|\Psi\rangle$.

The simplest example is the spin-1/2 system, describing e.g. the two spin states of an electron. Classically the spin \vec{S} of the electron (which can be visualized as an internal angular momentum), can point in any direction. In quantum mechanics it is described by a two-dimensional complex Hilbert space $\mathcal{H} = \mathbb{C}^2$. A common choice of

basis vectors are the “up” and “down” spin states

$$|\uparrow\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad (2.4)$$

$$|\downarrow\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad (2.5)$$

This is similar to the classical Ising model, but in contrast to a classical Ising spin that can point only either up or down, the quantum spin can exist in any complex superposition

$$|\Psi\rangle = \alpha|\uparrow\rangle + \beta|\downarrow\rangle \quad (2.6)$$

of the basis states, where the normalization condition (2.2) requires that $|\alpha|^2 + |\beta|^2 = 1$.

For example, as we will see below the state

$$|\rightarrow\rangle = \frac{1}{\sqrt{2}}(|\uparrow\rangle + |\downarrow\rangle) \quad (2.7)$$

is a superposition that describes the spin pointing in the positive x -direction.

2.2.2 Mixed states and density matrices

Unless specifically prepared in a pure state in an experiment, quantum systems in Nature rarely exist as pure states but instead as probabilistic superpositions. The most general state of a quantum system is then described as a density matrix ρ , with unit trace

$$\text{Tr}\rho = 1. \quad (2.8)$$

The density matrix of a pure state is just the projector onto that state

$$\rho_{\text{pure}} = |\Psi\rangle\langle\Psi|. \quad (2.9)$$

For example, the density matrix of a spin pointing in the positive x -direction is

$$\rho_{\rightarrow} = |\rightarrow\rangle\langle\rightarrow| = \begin{pmatrix} 1/2 & 1/2 \\ 1/2 & 1/2 \end{pmatrix}. \quad (2.10)$$

Instead of being in a coherent superposition of up and down, the system could also be in a probabilistic mixed state, with a 50% probability of pointing up and a 50% probability of pointing down, which would be described by the density matrix

$$\rho_{\text{mixed}} = \begin{pmatrix} 1/2 & 0 \\ 0 & 1/2 \end{pmatrix}. \quad (2.11)$$

2.2.3 Observables

Any physical observable is represented by a self-adjoint linear operator acting on the Hilbert space, which in a finite dimensional Hilbert space can be represented by a Hermitian matrix. For our spin-1/2 system, using the basis introduced above, the components

S^x , S^y and S^z of the spin in the x -, y -, and z -directions are represented by the Pauli matrices

$$S^x = \frac{\hbar}{2}\sigma_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad (2.12)$$

$$S^y = \frac{\hbar}{2}\sigma_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad (2.13)$$

$$S^z = \frac{\hbar}{2}\sigma_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (2.14)$$

The spin component along an arbitrary unit vector \hat{e} is the linear superposition of the components, i.e.

$$\hat{e} \cdot \vec{S} = e^x S^x + e^y S^y + e^z S^z = \frac{\hbar}{2} \begin{pmatrix} e^z & e^x - ie^y \\ e^x + ie^y & -e^z \end{pmatrix} \quad (2.15)$$

The fact that these observables do not commute but instead satisfy the non-trivial commutation relations

$$[S^x, S^y] = S^x S^y - S^y S^x = i\hbar S^z, \quad (2.16)$$

$$[S^y, S^z] = i\hbar S^x, \quad (2.17)$$

$$[S^z, S^x] = i\hbar S^y, \quad (2.18)$$

is the root of the differences between classical and quantum mechanics .

2.2.4 The measurement process

The outcome of a measurement in a quantum system is usually intrusive and not deterministic. After measuring an observable A , the new wave function of the system will be an eigenvector of A and the outcome of the measurement the corresponding eigenvalue. The state of the system is thus changed by the measurement process!

For example, if we start with a spin pointing up with wave function

$$|\Psi\rangle = |\uparrow\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad (2.19)$$

or alternatively density matrix

$$\rho_{\uparrow} = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \quad (2.20)$$

and we measure the x -component of the spin S^x , the resulting measurement will be either $+\hbar/2$ or $-\hbar/2$, depending on whether the spin after the measurement points in the $+$ or $-$ x -direction, and the wave function after the measurement will be either of

$$|\rightarrow\rangle = \frac{1}{\sqrt{2}}(|\uparrow\rangle + |\downarrow\rangle) = \begin{pmatrix} 1/\sqrt{2} \\ 1/\sqrt{2} \end{pmatrix} \quad (2.21)$$

$$|\leftarrow\rangle = \frac{1}{\sqrt{2}}(|\uparrow\rangle - |\downarrow\rangle) = \begin{pmatrix} 1/\sqrt{2} \\ -1/\sqrt{2} \end{pmatrix} \quad (2.22)$$

Either of these states will be picked with a probability given by the overlap of the initial wave function by the individual eigenstates:

$$p_{\rightarrow} = |\langle \rightarrow | \Psi \rangle|^2 = 1/2 \quad (2.23)$$

$$p_{\leftarrow} = |\langle \leftarrow | \Psi \rangle|^2 = 1/2 \quad (2.24)$$

The final state is a probabilistic superposition of these two outcomes, described by the density matrix

$$\rho = p_{\rightarrow} |\rightarrow\rangle\langle\rightarrow| + p_{\leftarrow} |\leftarrow\rangle\langle\leftarrow| = \begin{pmatrix} 1/2 & 0 \\ 0 & 1/2 \end{pmatrix}. \quad (2.25)$$

which differs from the initial density matrix ρ_{\uparrow} .

If we are not interested in the result of a particular outcome, but just in the average, the expectation value of the measurement can easily be calculated from a wave function $|\Psi\rangle$ as

$$\langle A \rangle = \langle \Psi | A | \Psi \rangle \quad (2.26)$$

or from a density matrix ρ as

$$\langle A \rangle = \text{Tr}(\rho A). \quad (2.27)$$

For pure states with density matrix $\rho_{\Psi} = |\Psi\rangle\langle\Psi|$ the two formulations are identical:

$$\text{Tr}(\rho_0 A) = \text{Tr}(|\Psi\rangle\langle\Psi| A) = \langle \Psi | A | \Psi \rangle. \quad (2.28)$$

2.2.5 The uncertainty relation

If two observables A and B do not commute $[A, B] \neq 0$, they cannot be measured simultaneously. If A is measured first, the wave function is changed to an eigenstate of A , which changes the result of a subsequent measurement of B . As a consequence the values of A and B in a state Ψ cannot be simultaneously known, which is quantified by the famous Heisenberg uncertainty relation which states that if two observables A and B do not commute but satisfy

$$[A, B] = i\hbar \quad (2.29)$$

then the product of the root-mean-square deviations ΔA and ΔB of simultaneous measurements of A and B has to be larger than

$$\Delta A \Delta B \geq \hbar/2 \quad (2.30)$$

For more details about the uncertainty relation, the measurement process or the interpretation of quantum mechanics we refer interested students to an advanced quantum mechanics class or text book.

2.2.6 The Schrödinger equation

The time-dependent Schrödinger equation

After so much introduction the Schrödinger equation is very easy to present. The wave function $|\Psi\rangle$ of a quantum system evolves according to

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = H |\Psi(t)\rangle, \quad (2.31)$$

where H is the Hamilton operator. This is just a first order linear differential equation.

The time-independent Schrödinger equation

For a stationary time-independent problem the Schrödinger equation can be simplified. Using the ansatz

$$|\Psi(t)\rangle = \exp(-iEt/\hbar)|\Psi\rangle, \quad (2.32)$$

where E is the energy of the system, the Schrödinger equation simplifies to a linear eigenvalue problem

$$H|\Psi\rangle = E|\Psi\rangle. \quad (2.33)$$

The rest of the semester will be spent solving just this simple eigenvalue problem!

The Schrödinger equation for the density matrix

The time evolution of a density matrix $\rho(t)$ can be derived from the time evolution of pure states, and can be written as

$$i\hbar \frac{\partial}{\partial t} \rho(t) = [H, \rho(t)] \quad (2.34)$$

The proof is left as a simple exercise.

2.2.7 The thermal density matrix

Finally we want to describe a physical system not in the ground state but in thermal equilibrium at a given inverse temperature $\beta = 1/k_B T$. In a classical system each microstate i of energy E_i is occupied with a probability given by the Boltzmann distribution

$$p_i = \frac{1}{Z} \exp(-\beta E_i), \quad (2.35)$$

where the partition function

$$Z = \sum_i \exp(-\beta E_i) \quad (2.36)$$

normalizes the probabilities.

In a quantum system, if we use a basis of eigenstates $|i\rangle$ with energy E_i , the density matrix can be written analogously as

$$\rho_\beta = \frac{1}{Z} \sum_i \exp(-\beta E_i) |i\rangle\langle i| \quad (2.37)$$

For a general basis, which is not necessarily an eigenbasis of the Hamiltonian H , the density matrix can be obtained by diagonalizing the Hamiltonian, using above equation, and transforming back to the original basis. The resulting density matrix is

$$\rho_\beta = \frac{1}{Z} \exp(-\beta H) \quad (2.38)$$

where the partition function now is

$$Z = \text{Tr} \exp(-\beta H) \quad (2.39)$$

Calculating the thermal average of an observable A in a quantum system is hence formally very easy:

$$\langle A \rangle = \text{Tr}(A\rho_\beta) = \frac{\text{Tr} A \exp(-\beta H)}{\text{Tr} \exp(-\beta H)}, \quad (2.40)$$

but actually evaluating this expression is a hard problem.

2.3 The spin- S problem

Before discussing solutions of the Schrödinger equation we will review two very simple systems: a localized particle with general spin S and a free quantum particle.

In section 2.2.1 we have already seen the Hilbert space and the spin operators for the most common case of a spin-1/2 particle. The algebra of the spin operators given by the commutation relations (2.12)-(2.12) allows not only the two-dimensional representation shown there, but a series of $2S + 1$ -dimensional representations in the Hilbert space \mathbb{C}^{2S+1} for all integer and half-integer values $S = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \dots$. The basis states $\{|s\rangle\}$ are usually chosen as eigenstates of the S^z operator

$$S^z |s\rangle = \hbar s |s\rangle, \quad (2.41)$$

where s can take any value in the range $-S, -S + 1, -S + 2, \dots, S - 1, S$. In this basis the S_z operator is diagonal, and the S^x and S^y operators can be constructed from the “ladder operators”

$$S^+ |s\rangle = \sqrt{S(S+1) - s(s+1)} |s+1\rangle \quad (2.42)$$

$$S^- |s\rangle = \sqrt{S(S+1) - s(s-1)} |s-1\rangle \quad (2.43)$$

which increment or decrement the S^z value by 1 through

$$S^x = \frac{1}{2} (S^+ + S^-) \quad (2.44)$$

$$S^y = \frac{1}{2i} (S^+ - S^-). \quad (2.45)$$

The Hamiltonian of the spin coupled to a magnetic field \vec{h} is

$$H = -g\mu_B \vec{h} \cdot \vec{S}, \quad (2.46)$$

which introduces nontrivial dynamics since the components of \vec{S} do not commute. As a consequence the spin precesses around the magnetic field direction.

Exercise: Derive the differential equation governing the rotation of a spin starting along the $+x$ -direction rotating under a field in the $+z$ -direction

2.4 A quantum particle in free space

Our second example is a single quantum particle in an n -dimensional free space. Its Hilbert space is given by all twice-continuously differentiable complex functions over

the real space \mathbb{R}^n . The wave functions $|\Psi\rangle$ are complex-valued functions $\Psi(\vec{x})$ in n -dimensional space. In this representation the operator \hat{x} , measuring the position of the particle is simple and diagonal

$$\hat{x} = \vec{x}, \quad (2.47)$$

while the momentum operator \hat{p} becomes a differential operator

$$\hat{p} = -i\hbar\nabla. \quad (2.48)$$

These two operators do not commute but their commutator is

$$[\hat{x}, \hat{p}] = i\hbar. \quad (2.49)$$

The Schrödinger equation of a quantum particle in an external potential $V(\vec{x})$ can be obtained from the classical Hamilton function by replacing the momentum and position variables by the operators above. Instead of the classical Hamilton function

$$H(\vec{x}, \vec{p}) = \frac{\vec{p}^2}{2m} + V(\vec{x}) \quad (2.50)$$

we use the quantum mechanical Hamiltonian operator

$$H = \frac{\hat{p}^2}{2m} + V(\hat{x}) = -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{x}), \quad (2.51)$$

which gives the famous form

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi + V(\vec{x})\psi \quad (2.52)$$

of the one-body Schrödinger equation.

2.4.1 The harmonic oscillator

As a special exactly solvable case let us consider the one-dimensional quantum harmonic oscillator with mass m and potential $\frac{K}{2}x^2$. Defining momentum \hat{p} and position operators \hat{q} in units where $m = \hbar = K = 1$, the time-independent Schrödinger equation is given by

$$H|n\rangle = \frac{1}{2}(\hat{p}^2 + \hat{q}^2)|n\rangle = E_n|n\rangle \quad (2.53)$$

Inserting the definition of \hat{p} we obtain an eigenvalue problem of an ordinary differential equation

$$-\frac{1}{2}\phi_n''(q) + \frac{1}{2}q^2\phi_n(q) = E_n\phi_n(q) \quad (2.54)$$

whose eigenvalues $E_n = (n + 1/2)$ and eigenfunctions

$$\phi_n(q) = \frac{1}{\sqrt{2^n n! \sqrt{\pi}}} \exp\left(-\frac{1}{2}q^2\right) H_n(q), \quad (2.55)$$

are known analytically. Here the H_n are the Hermite polynomials and $n = 0, 1, \dots$

Using these eigenstates as a basis sets we need to find the representation of \hat{q} and \hat{p} . Performing the integrals

$$\langle m|\hat{q}|n\rangle \quad \text{and} \quad \langle m|\hat{p}|n\rangle \quad (2.56)$$

it turns out that they are nonzero only for $m = n \pm 1$ and they can be written in terms of “ladder operators” a and a^\dagger :

$$\hat{q} = \frac{1}{\sqrt{2}}(a^\dagger + a) \quad (2.57)$$

$$\hat{p} = \frac{1}{i\sqrt{2}}(a^\dagger - a) \quad (2.58)$$

$$(2.59)$$

where the raising and lowering operators a^\dagger and a only have the following nonzero matrix elements:

$$\langle n+1|a^\dagger|n\rangle = \langle n|a|n+1\rangle = \sqrt{n+1}. \quad (2.60)$$

and commutation relations

$$[a, a] = [a^\dagger, a^\dagger] = 0 \quad (2.61)$$

$$[a, a^\dagger] = 1. \quad (2.62)$$

It will also be useful to introduce the number operator $\hat{n} = a^\dagger a$ which is diagonal with eigenvalue n : elements

$$\hat{n}|n\rangle = a^\dagger a|n\rangle = \sqrt{n}a^\dagger|n-1\rangle = n|n\rangle. \quad (2.63)$$

To check this representation let us plug the definitions back into the Hamiltonian to obtain

$$\begin{aligned} H &= \frac{1}{2}(\hat{p}^2 + \hat{q}^2) \\ &= \frac{1}{4}[-(a^\dagger - a)^2 + (a^\dagger + a)^2] \\ &= \frac{1}{2}(a^\dagger a + a a^\dagger) \\ &= \frac{1}{2}(2a^\dagger a + 1) = \hat{n} + \frac{1}{2}, \end{aligned} \quad (2.64)$$

which has the correct spectrum. In deriving the last lines we have used the commutation relation (2.62).

Chapter 3

The quantum one-body problem

3.1 The time-independent 1D Schrödinger equation

We start the numerical solution of quantum problems with the time-indepent one-dimensional Schrödinger equation for a particle with mass m in a Potential $V(x)$. In one dimension the Schrödinger equation is just an ordinary differential equation

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V(x)\psi(x) = E\psi(x). \quad (3.1)$$

We start with simple finite-difference schemes and discretize space into intervals of length Δx and denote the space points by

$$x_n = n\Delta x \quad (3.2)$$

and the wave function at these points by

$$\psi_n = \psi(x_n). \quad (3.3)$$

3.1.1 The Numerov algorithm

After rewriting the second order differential equation to a coupled system of two first order differential equations, any ODE solver such as the Runge-Kutta method could be applied, but there exist better methods. For the special form

$$\psi''(x) + k(x)\psi(x) = 0, \quad (3.4)$$

of the Schrödinger equation, with $k(x) = 2m(E - V(x))/\hbar^2$ we can derive the Numerov algorithm by starting from the Taylor expansion of ψ_n :

$$\psi_{n\pm 1} = \psi_n \pm \Delta x \psi'_n + \frac{\Delta x^2}{2} \psi''_n \pm \frac{\Delta x^3}{6} \psi_n^{(3)} + \frac{\Delta x^4}{24} \psi_n^{(4)} \pm \frac{\Delta x^5}{120} \psi_n^{(5)} + O(\Delta x^6) \quad (3.5)$$

Adding ψ_{n+1} and ψ_{n-1} we obtain

$$\psi_{n+1} + \psi_{n-1} = 2\psi_n + (\Delta x)^2 \psi''_n + \frac{(\Delta x)^4}{12} \psi_n^{(4)}. \quad (3.6)$$

Replacing the fourth derivatives by a finite difference second derivative of the second derivatives

$$\psi_n^{(4)} = \frac{\psi_{n+1}'' + \psi_{n-1}'' - 2\psi_n''}{\Delta x^2} \quad (3.7)$$

and substituting $-k(x)\psi(x)$ for $\psi''(x)$ we obtain the Numerov algorithm

$$\begin{aligned} \left(1 + \frac{(\Delta x)^2}{12}k_{n+1}\right)\psi_{n+1} = & 2\left(1 - \frac{5(\Delta x)^2}{12}k_n\right)\psi_n \\ & - \left(1 + \frac{(\Delta x)^2}{12}k_{n-1}\right)\psi_{n-1} + O(\Delta x^6), \end{aligned} \quad (3.8)$$

which is locally of sixth order!

Initial values

To start the Numerov algorithm we need the wave function not just at one but at two initial values and will now present several ways to obtain these.

For potentials $V(x)$ with reflection symmetry $V(x) = V(-x)$ the wave functions need to be either even $\psi(x) = \psi(-x)$ or odd $\psi(x) = -\psi(-x)$ under reflection, which can be used to find initial values:

- For the even solution we use a half-integer mesh with mesh points $x_{n+1/2} = (n + 1/2)\Delta x$ and pick initial values $\psi(x_{-1/2}) = \psi(x_{1/2}) = 1$.
- For the odd solution we know that $\psi(0) = -\psi(0)$ and hence $\psi(0) = 0$, specifying the first starting value. Using an integer mesh with mesh points $x_n = n\Delta x$ we pick $\psi(x_1) = 1$ as the second starting value.

In general potentials we need to use other approaches. If the potentials vanishes for large distances: $V(x) = 0$ for $|x| \geq a$ we can use the exact solution of the Schrödinger equation at large distances to define starting points, e.g.

$$\psi(-a) = 1 \quad (3.9)$$

$$\psi(-a - \Delta x) = \exp(-\Delta x \sqrt{2mE/\hbar}). \quad (3.10)$$

Finally, if the potential never vanishes we need to begin with a single starting value $\psi(x_0)$ and obtain the second starting value $\psi(x_1)$ by performing an integration over the first time step $\Delta\tau$ with an Euler or Runge-Kutta algorithm.

3.1.2 The one-dimensional scattering problem

The scattering problem is the numerically easiest quantum problem since solutions exist for all energies $E > 0$, if the potential vanishes at large distances ($V(x) \rightarrow 0$ for $|x| \rightarrow \infty$). The solution becomes particularly simple if the potential is nonzero only on a finite interval $[0, a]$. For a particle approaching the potential barrier from the left ($x < 0$) we can make the following ansatz for the free propagation when $x < 0$:

$$\psi_L(x) = A \exp(-iqx) + B \exp(iqx) \quad (3.11)$$

where A is the amplitude of the incoming wave and B the amplitude of the reflected wave. On the right hand side, once the particle has left the region of finite potential ($x > a$), we can again make a free propagation ansatz,

$$\psi_R(x) = C \exp(-iqx) \quad (3.12)$$

The coefficients A , B and C have to be determined self-consistently by matching to a numerical solution of the Schrödinger equation in the interval $[0, a]$. This is best done in the following way:

- Set $C = 1$ and use the two points a and $a + \Delta x$ as starting points for a Numerov integration.
- Integrate the Schrödinger equation numerically – backwards in space, from a to 0 – using the Numerov algorithm.
- Match the numerical solution of the Schrödinger equation for $x < 0$ to the free propagation ansatz (3.11) to determine A and B .

Once A and B have been determined the reflection and transmission probabilities R and T are given by

$$R = |B|^2/|A|^2 \quad (3.13)$$

$$T = 1/|A|^2 \quad (3.14)$$

3.1.3 Bound states and solution of the eigenvalue problem

While there exist scattering states for all energies $E > 0$, bound states solutions of the Schrödinger equation with $E < 0$ exist only for discrete energy eigenvalues. Integrating the Schrödinger equation from $-\infty$ to $+\infty$ the solution will diverge to $\pm\infty$ as $x \rightarrow \infty$ for almost all values. These functions cannot be normalized and thus do not constitute solutions to the Schrödinger equation. Only for some special eigenvalues E , will the solution go to zero as $x \rightarrow \infty$.

A simple eigensolver can be implemented using the following shooting method, where we again will assume that the potential is zero outside an interval $[0, a]$:

- Start with an initial guess E
- Integrate the Schrödinger equation for $\psi_E(x)$ from $x = 0$ to $x_f \gg a$ and determine the value $\psi_E(x_f)$
- use a root solver, such as a bisection method (see appendix A.1), to look for an energy E with $\psi_E(x_f) \approx 0$

This algorithm is not ideal since the divergence of the wave function for $x \pm \infty$ will cause roundoff error to proliferate.

A better solution is to integrate the Schrödinger equation from both sides towards the center:

- We pick a starting point b and choose as energy $E = V(b)$

- Starting from $x = 0$ we integrate the left hand side solution $\psi_L(x)$ to a chosen point b and obtain $\psi_L(b)$ and a numerical estimate for $\psi'_L(b) = (\psi_L(b) - \psi_L(b - \Delta x)) / \Delta x$.
- Starting from $x = a$ we integrate the right hand solution $\psi_R(x)$ down to the same point b and obtain $\psi_R(b)$ and a numerical estimate for $\psi'_R(b) = (\psi_R(b + \Delta x) - \psi_R(b)) / \Delta x$.
- At the point b the wave functions and their first two derivatives have to match, since solutions to the Schrödinger equation have to be twice continuously differentiable. Keeping in mind that we can multiply the wave functions by an arbitrary factor we obtain the conditions

$$\psi_L(b) = \alpha \psi_R(b) \quad (3.15)$$

$$\psi'_L(b) = \alpha \psi'_R(b) \quad (3.16)$$

$$\psi''_L(b) = \alpha \psi''_R(b) \quad (3.17)$$

The last condition is automatically fulfilled since by the choice $V(b) = E$ the Schrödinger equation at b reduces to $\psi''(b) = 0$. The first two conditions can be combined to the condition that the logarithmic derivatives vanish:

$$\frac{d \log \psi_L}{dx} \Big|_{x=b} = \frac{\psi'_L(b)}{\psi_L(b)} = \frac{\psi'_R(b)}{\psi_R(b)} = \frac{d \log \psi_R}{dx} \Big|_{x=b} \quad (3.18)$$

- This last equation has to be solved for in a shooting method, e.g. using a bisection algorithm

Finally, at the end of the calculation, normalize the wave function.

3.2 The time-independent Schrödinger equation in higher dimensions

The time independent Schrödinger equation in more than one dimension is a partial differential equation and cannot, in general, be solved by a simple ODE solver such as the Numerov algorithm. Before employing a PDE solver we should thus always first try to reduce the problem to a one-dimensional problem. This can be done if the problem factorizes.

3.2.1 Factorization along coordinate axis

A first example is a three-dimensional Schrödinger equation in a cubic box with potential $V(\vec{r}) = V(x)V(y)V(z)$ with $\vec{r} = (x, y, z)$. Using the product ansatz

$$\psi(\vec{r}) = \psi_x(x)\psi_y(y)\psi_z(z) \quad (3.19)$$

the PDE factorizes into three ODEs which can be solved as above.

3.2.2 Potential with spherical symmetry

Another famous trick is possible for spherically symmetric potentials with $V(\vec{r}) = V(|\vec{r}|)$ where an ansatz using spherical harmonics

$$\psi_{l,m}(\vec{r}) = \psi_{l,m}(r, \theta, \phi) = \frac{u(r)}{r} Y_{lm}(\theta, \phi) \quad (3.20)$$

can be used to reduce the three-dimensional Schrödinger equation to a one-dimensional one for the radial wave function $u(r)$:

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + \frac{\hbar^2 l(l+1)}{2mr^2} + V(r) \right] u(r) = Eu(r) \quad (3.21)$$

in the interval $[0, \infty[$. Given the singular character of the potential for $r \rightarrow 0$, a numerical integration should start at large distances r and integrate towards $r = 0$, so that the largest errors are accumulated only at the last steps of the integration.

In the exercises we will solve a three-dimensional scattering problem and calculate the scattering length for two atoms.

3.2.3 Finite difference methods

The simplest solvers for partial differential equations, the finite difference solvers can also be used for the Schrödinger equation. Replacing differentials by differences we convert the Schrödinger equation to a system of coupled linear equations. Starting from the three-dimensional Schrödinger equation (we set $\hbar = 1$ from now on)

$$\nabla^2 \psi(\vec{x}) + 2m(V - E(\vec{x}))\psi(\vec{x}) = 0, \quad (3.22)$$

we discretize space and obtain the system of linear equations

$$\begin{aligned} & \frac{1}{\Delta x^2} [\psi(x_{n+1}, y_n, z_n) + \psi(x_{n-1}, y_n, z_n) \\ & \quad + \psi(x_n, y_{n+1}, z_n) + \psi(x_n, y_{n-1}, z_n) \\ & \quad + \psi(x_n, y_n, z_{n+1}) + \psi(x_n, y_n, z_{n-1})] \\ & + \left[2m(V(\vec{x}) - E) - \frac{6}{\Delta x^2} \right] \psi(x_n, y_n, z_n) = 0. \end{aligned} \quad (3.23)$$

For the scattering problem a linear equation solver can now be used to solve the system of equations. For small linear problems Mathematica can be used, or the `dsysv` function of the LAPACK library. For larger problems it is essential to realize that the matrices produced by the discretization of the Schrödinger equation are usually very sparse, meaning that only $O(N)$ of the N^2 matrix elements are nonzero. For these sparse systems of equations, optimized iterative numerical algorithms exist¹ and are implemented in numerical libraries such as in the ITL library.²

¹R. Barret, M. Berry, T.F. Chan, J. Demmel, J. Donato, J. Dongarra, V. Eijkhout, R. Pozo, C. Romine, and H. van der Vorst, *Templates for the Solution of Linear Systems: Building Blocks for Iterative Methods* (SIAM, 1993)

²J.G. Siek, A. Lumsdaine and Lie-Quan Lee, *Generic Programming for High Performance Numerical Linear Algebra in Proceedings of the SIAM Workshop on Object Oriented Methods for Inter-operable Scientific and Engineering Computing (OO'98)* (SIAM, 1998); the library is available on the web at: <http://www.osl.iu.edu/research/itl/>

To calculate bound states, an eigenvalue problem has to be solved. For small problems, where the full matrix can be stored in memory, Mathematica or the `dsyev` eigensolver in the LAPACK library can be used. For bigger systems, sparse solvers such as the Lanczos algorithm (see appendix A.2) are best. Again there exist efficient implementations³ of iterative algorithms for sparse matrices.⁴

3.2.4 Variational solutions using a finite basis set

In the case of general potentials, or for more than two particles, it will not be possible to reduce the Schrödinger equation to a one-dimensional problem and we need to employ a PDE solver. One approach will again be to discretize the Schrödinger equation on a discrete mesh using a finite difference approximation. A better solution is to expand the wave functions in terms of a finite set of basis functions

$$|\phi\rangle = \sum_{i=1}^N a_i |u_i\rangle. \quad (3.24)$$

To estimate the ground state energy we want to minimize the energy of the variational wave function

$$E^* = \frac{\langle \phi | H | \phi \rangle}{\langle \phi | \phi \rangle}. \quad (3.25)$$

Keep in mind that, since we only chose a finite basis set $\{|u_i\rangle\}$ the variational estimate E^* will always be larger than the true ground state energy E_0 , but will converge towards E_0 as the size of the basis set is increased, e.g. by reducing the mesh size in a finite element basis.

To perform the minimization we denote by

$$H_{ij} = \langle u_i | H | u_j \rangle = \int d\vec{r} u_i(\vec{r})^* \left(-\frac{\hbar^2}{2m} \nabla^2 + V \right) u_j(\vec{r}) \quad (3.26)$$

the matrix elements of the Hamilton operator H and by

$$S_{ij} = \langle u_i | u_j \rangle = \int d\vec{r} u_i(\vec{r})^* u_j(\vec{r}) \quad (3.27)$$

the overlap matrix. Note that for an orthogonal basis set, S_{ij} is the identity matrix δ_{ij} . Minimizing equation (3.25) we obtain a generalized eigenvalue problem

$$\sum_j H_{ij} a_j = E \sum_k S_{ik} a_k. \quad (3.28)$$

or in a compact notation with $\vec{a} = (a_1, \dots, a_N)$

$$H\vec{a} = ES\vec{a}. \quad (3.29)$$

³<http://www.comp-phys.org/software/ietl/>

⁴Z. Bai, J. Demmel and J. Dongarra (Eds.), *Templates for the Solution of Algebraic Eigenvalue Problems: A Practical Guide* (SIAM, 2000).

If the basis set is orthogonal this reduces to an ordinary eigenvalue problem and we can use the Lanczos algorithm.

In the general case we have to find orthogonal matrices U such that $U^T S U$ is the identity matrix. Introducing a new vector $\vec{b} = U^{-1} \vec{a}$. we can then rearrange the problem into

$$\begin{aligned} H\vec{a} &= ES\vec{a} \\ HU\vec{b} &= ESU\vec{b} \\ U^T HU\vec{b} &= EU^T S U\vec{b} = E\vec{b} \end{aligned} \quad (3.30)$$

and we end up with a standard eigenvalue problem for $U^T H U$. Mathematica and LAPACK both contain eigensolvers for such generalized eigenvalue problems.

Example: the anharmonic oscillator

The final issue is the choice of basis functions. It is advantageous to make use of known solutions to a similar problem as we will illustrate in the case of an anharmonic oscillator with Hamilton operator

$$\begin{aligned} H &= H_0 + \lambda q^4 \\ H_0 &= \frac{1}{2}(p^2 + q^2), \end{aligned} \quad (3.31)$$

where the harmonic oscillator H_0 was already discussed in section 2.4.1. It makes sense to use the N lowest harmonic oscillator eigenvectors $|n\rangle$ as basis states of a finite basis and write the Hamiltonian as

$$H = \frac{1}{2} + \hat{n} + \lambda \hat{q}^4 = \frac{1}{2} + \hat{n} + \frac{\lambda}{4}(a^\dagger + a)^4 \quad (3.32)$$

Since the operators a and a^\dagger are nonzero only in the first sub or superdiagonal, the resulting matrix is a banded matrix of bandwidth 9. A sparse eigensolver such as the Lanczos algorithm can again be used to calculate the spectrum. Note that since we use the orthonormal eigenstates of H_0 as basis elements, the overlap matrix S here is the identity matrix and we have to deal only with a standard eigenvalue problem.

The finite element method

In cases where we have irregular geometries or want higher precision than the lowest order finite difference method, and do not know a suitable set of basis function, the finite element method (FEM) should be chosen over the finite difference method. Since explaining the FEM can take a full semester in itself, we refer interested students to classes on solving partial differential equations.

3.3 The time-dependent Schrödinger equation

Finally we will reintroduce the time dependence to study dynamics in non-stationary quantum systems.

3.3.1 Spectral methods

By introducing a basis and solving for the complete spectrum of energy eigenstates we can directly solve the time-dependent problem in the case of a stationary Hamiltonian. This is a consequence of the linearity of the Schrödinger equation.

To calculate the time evolution of a state $|\psi(t_0)\rangle$ from time t_0 to t we first solve the stationary eigenvalue problem $H|\phi\rangle = E|\phi\rangle$ and calculate the eigenvectors $|\phi_n\rangle$ and eigenvalues ϵ_n . Next we represent the initial wave function $|\psi\rangle$ by a spectral decomposition

$$|\psi(t_0)\rangle = \sum_n c_n |\phi_n\rangle. \quad (3.33)$$

Since each of the $|\phi_n\rangle$ is an eigenvector of H , the time evolution $e^{-i\hbar H(t-t_0)}$ is trivial and we obtain at time t :

$$|\psi(t)\rangle = \sum_n c_n e^{-i\hbar\epsilon_n(t-t_0)} |\phi_n\rangle. \quad (3.34)$$

3.3.2 Direct numerical integration

If the number of basis states is too large to perform a complete diagonalization of the Hamiltonian, or if the Hamiltonian changes over time we need to perform a direct integration of the Schrödinger equation. Like other initial value problems of partial differential equations the Schrödinger equation can be solved by the method of lines. After choosing a set of basis functions or discretizing the spatial derivatives we obtain a set of coupled ordinary differential equations which can be evolved for each point along the time line (hence the name) by standard ODE solvers.

In the remainder of this chapter we use the symbol H to refer the representation of the Hamiltonian in the chosen finite basis set. A forward Euler scheme

$$|\psi(t_{n+1})\rangle = |\psi(t_n)\rangle - i\hbar\Delta_t H |\psi(t_n)\rangle \quad (3.35)$$

is not only numerically unstable. It also violates the conservation of the norm of the wave function $\langle\psi|\psi\rangle = 1$. Since the exact quantum evolution

$$\psi(x, t + \Delta_t) = e^{-i\hbar H\Delta_t} \psi(x, t). \quad (3.36)$$

is unitary and thus conserves the norm, we want to look for a unitary approximant as integrator. Instead of using the forward Euler method (3.35) which is just a first order Taylor expansion of the exact time evolution

$$e^{-i\hbar H\Delta_t} = 1 - i\hbar H\Delta_t + \mathcal{O}(\Delta_t^2), \quad (3.37)$$

we reformulate the time evolution operator as

$$e^{-i\hbar H\Delta_t} = (e^{i\hbar H\Delta_t/2})^{-1} e^{-i\hbar H\Delta_t/2} = \left(1 + i\hbar H \frac{\Delta_t}{2}\right)^{-1} \left(1 - i\hbar H \frac{\Delta_t}{2}\right) + \mathcal{O}(\Delta_t^3), \quad (3.38)$$

which is unitary!

This gives the simplest stable and unitary integrator algorithm

$$\psi(x, t + \Delta_t) = \left(1 + i\hbar H \frac{\Delta_t}{2}\right)^{-1} \left(1 - i\hbar H \frac{\Delta_t}{2}\right) \psi(x, t) \quad (3.39)$$

or equivalently

$$\left(1 + i\hbar H \frac{\Delta_t}{2}\right) \psi(x, t + \Delta_t) = \left(1 - i\hbar H \frac{\Delta_t}{2}\right) \psi(x, t). \quad (3.40)$$

Unfortunately this is an implicit integrator. At each time step, after evaluating the right hand side a linear system of equations needs to be solved. For one-dimensional problems the matrix representation of H is often tridiagonal and a tridiagonal solver can be used. In higher dimensions the matrix H will no longer be simply tridiagonal but still very sparse and we can use iterative algorithms, similar to the Lanczos algorithm for the eigenvalue problem. For details about these algorithms we refer to the nice summary at <http://mathworld.wolfram.com/topics/Templates.html> and especially the biconjugate gradient (BiCG) algorithm. Implementations of this algorithm are available, e.g. in the Iterative Template Library (ITL).

3.3.3 The split operator method

A simpler and explicit method is possible for a quantum particle in the real space picture with the “standard” Schrödinger equation (2.52). Writing the Hamilton operator as

$$H = \hat{T} + \hat{V} \quad (3.41)$$

with

$$\hat{T} = \frac{1}{2m} \hat{p}^2 \quad (3.42)$$

$$\hat{V} = V(\vec{x}) \quad (3.43)$$

it is easy to see that \hat{V} is diagonal in position space while \hat{T} is diagonal in momentum space. If we split the time evolution as

$$e^{-i\hbar\Delta_t H} = e^{-i\hbar\Delta_t \hat{V}/2} e^{-i\hbar\Delta_t \hat{T}} e^{-i\hbar\Delta_t \hat{V}/2} + \mathcal{O}(\Delta_t^3) \quad (3.44)$$

we can perform the individual time evolutions $e^{-i\hbar\Delta_t \hat{V}/2}$ and $e^{-i\hbar\Delta_t \hat{T}}$ exactly:

$$\left[e^{-i\hbar\Delta_t \hat{V}/2} |\psi\rangle \right] (\vec{x}) = e^{-i\hbar\Delta_t V(\vec{x})/2} \psi(\vec{x}) \quad (3.45)$$

$$\left[e^{-i\hbar\Delta_t \hat{T}/2} |\psi\rangle \right] (\vec{k}) = e^{-i\hbar\Delta_t \|\vec{k}\|^2/2m} \psi(\vec{k}) \quad (3.46)$$

in real space for the first term and momentum space for the second term. This requires a basis change from real to momentum space, which is efficiently performed using a Fast Fourier Transform (FFT) algorithm. Propagating for a time $t = N\Delta_t$, two consecutive

applications of $e^{-i\hbar\Delta_t\hat{V}/2}$ can easily be combined into a propagation by a full time step $e^{-i\hbar\Delta_t\hat{V}}$, resulting in the propagation:

$$\begin{aligned} e^{-i\hbar\Delta_t H} &= \left(e^{-i\hbar\Delta_t\hat{V}/2} e^{-i\hbar\Delta_t\hat{T}} e^{-i\hbar\Delta_t\hat{V}/2} \right)^N + \mathcal{O}(\Delta_t^2) \\ &= e^{-i\hbar\Delta_t\hat{V}/2} \left[e^{-i\hbar\Delta_t\hat{T}} e^{-i\hbar\Delta_t\hat{V}} \right]^{N-1} e^{-i\hbar\Delta_t\hat{T}} e^{-i\hbar\Delta_t\hat{V}/2} \end{aligned} \quad (3.47)$$

and the discretized algorithm starts as

$$\psi_1(\vec{x}) = e^{-i\hbar\Delta_t V(\vec{x})/2} \psi_0(\vec{x}) \quad (3.48)$$

$$\psi_1(\vec{k}) = \mathcal{F}\psi_1(\vec{x}) \quad (3.49)$$

where \mathcal{F} denotes the Fourier transform and \mathcal{F}^{-1} will denote the inverse Fourier transform. Next we propagate in time using full time steps:

$$\psi_{2n}(\vec{k}) = e^{-i\hbar\Delta_t \|\vec{k}\|^2/2m} \psi_{2n-1}(\vec{k}) \quad (3.50)$$

$$\psi_{2n}(\vec{x}) = \mathcal{F}^{-1}\psi_{2n}(\vec{k}) \quad (3.51)$$

$$\psi_{2n+1}(\vec{x}) = e^{-i\hbar\Delta_t V(\vec{x})} \psi_{2n}(\vec{x}) \quad (3.52)$$

$$\psi_{2n+1}(\vec{k}) = \mathcal{F}\psi_{2n+1}(\vec{x}) \quad (3.53)$$

except that in the last step we finish with another half time step in real space:

$$\psi_{2N+1}(\vec{x}) = e^{-i\hbar\Delta_t V(\vec{x})/2} \psi_{2N}(\vec{x}) \quad (3.54)$$

This is a fast and unitary integrator for the Schrödinger equation in real space. It could be improved by replacing the locally third order splitting (3.44) by a fifth-order version involving five instead of three terms.