Computing Energy Levels of the Confined Hydrogen Atom

Literature Study in Preparation for the Master Thesis

by

Karl Kästner
Delft University of Technology

Supervisors

Dr. Ir. Martin van Gijzen (TU Delft)
Dr. Domenico Giordano (ESA-ESTEC)

March 26, 2012

Contents

Nomenclature

FDM   finite difference method

FEM   finite element method

GPU   graphics processing unit

PDE   partial differential equation

SMP   symmetric multiprocessing

TDSE   time dependent Schrödinger equation

TISE   time invariant Schrödinger equation

Introduction

The hydrogen atom is the most simplistic atom. Its typical isotope consists just of a single proton nucleus and a single electron shell. Hydrogen is not only the most abundant element in the universe, but all other elements are literally generated by nuclear fusion processes starting with hydrogen. Many other elements have therefore similar electronic properties and hydrogenic atom models can be used to describe them. Those models find amongst others applications in chemistry, solid state physics and plasma physics.

Each element has a distinct set of energy levels which determine its behaviour in chemical reactions. The energy levels also correspond to emission lines in the spectrum of an element. The spectrum of hydrogen is partially visible and can be probed by making the gas glow in a discharge lamp and splitting the emitted light with a prism into its spectral components. This is depicted in figure 1.

The energy levels of hydrogen are given by the eigenvalues of the Schrödinger equation. For the unconfined hydrogen atom those eigenvalues can be computed analytically. A general formula to compute those eigenvalues was even found in the advent of quantum mechanics. However, for the arbitrarily confined atom, if at all, only analytic approximations exist.

This literature study is about the numerical approximation of the eigenvalues of a cubically confined hydrogen atom. It consists of three parts. In part one a short introduction into the physical background is given. Part two describes numerical methods used for discretising the differential equation and for computing its eigenvalues. The last part is an evaluation of the aforementioned methods with regard to their applicability to the confined hydrogen atom. Research questions are stated and a road map for the forthcoming master project is laid out.

This work was commissioned by the Space Research and Technology Centre of the European Space Agency (ESA-ESTEC) [esa12] and was facilitated by the Commission of the European Union under the Erasmus Mundus COSSE programme [ec-12], [cos12].
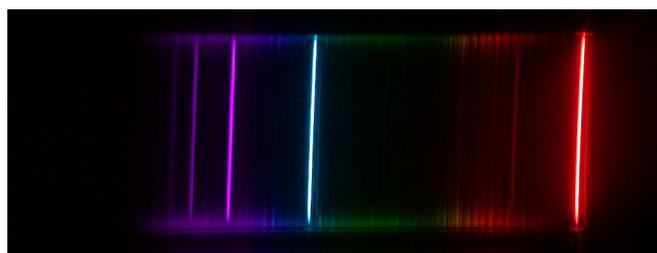
Figure 1: Visible Spectrum of the Hydrogen Atom

Literature Overview

In the history of quantum physics the confined hydrogen atom was the topic of many publications. The first publications were by Michels and de Boer in 1937 [MdBB37] and Sommerfeld and Welker in 1938 [SW38] and focused on the determination of the ground state. Higher states and the splitting of degenerated energy levels was then described by Groot and Seldam in 1946 [dGtSCA46]. In 1976 Ley-Koy and Runbinstein first considered the hydrogen atom confined in penetrable boundaries [LKR79]. These works considered only the cylindrical confined hydrogen atom. It followed solutions in other coordinate systems and domains, parabolic by Krähmer in 1998 [KSY98], cylindrical by Yurenyey in 2008 [Yur08] and spheroidal by Cruz in 2009 [Cru09]. A cubic cavity with the atom located at off-centred positions was first discussed by Kretov in 2009, [KVI09]. Most authors used analytic methods based on perturbation theory and basis functions.

The Hydrogen atom was also topic of numerical computations after Schroeder's original analytic solution. Application of finite difference methods reach furthest back, see Bolton 1956 [Bol56] and Kimball 1934 [KS34]. The finite element method was used by Levin and Shertzer in 1985 [Lev85]. A very important development due to their high accuracy are the Lagrangian-mesh methods introduced by Baye and Heenen in 1986 [BH86]. Less common techniques like shooting methods were also applied (Killingbeck 1987 [Kil77]). The most recent development is the use of Sparse Grid methods, (Garcke 2000 [Gar98]). Excluding the sparse grid methods, most methods were only applied to the the radial Schrödinger equation.

So, although there are many publications about the hydrogenic Schrödinger equation, few actually tangent the numerical solution in Cartesian coordinates. Note that many time dependent solutions were also published, which are, however, not reviewed here as it is of no importance for this thesis.

Chapter 1

Physical Background

The purpose of this thesis is to compute energy levels of the confined hydrogen atom. The energy levels are required for further computations in plasma physics, as described in section 1.2. The hydrogen atom is modelled by the Schrödinger equation with Coulomb potential, the hydrogenic Schrödinger equation. The numerical approximation of the solutions of the hydrogenic Schrödinger equation is the central part of this thesis.

The hydrogenic Schrödinger equation itself is stated in section 1.3. The relation between computed values and physical quantities is derived in section 1.4 . The model error of the hydrogenic Schrödinger equation is discussed in 1.6.

1.1   Overview of Quantities Referred to throughout the Thesis

If not otherwise stated the symbols used in this thesis have the meaning as given in table 1.1. For simplicity vectors are not highlighted in bold face or indicated by arrows. The symbols given in table 1.1 and used throughout this chapter are to be interpreted as quantities commonly used in physics, e.g. h is Planck's constant, λ a wave length and E an energy levels. In later chapters symbols are to be interpreted as quantities commonly used in mathematics, e.g. λ refers to an eigenvalue and h to the step width.

1.2   Motivation: The Divergence of the Partition Function for the Unconfined Hydrogen Atom

Most of everyday scientific phenomena and engineering problems can be accurately described and solved using classical physics. However, some particular fields of physics cannot be thoroughly understood solely with classical methods, but require frequently the consideration of quantum mechanics. Such fields are thermodynamics and solid state physics.

The partition function is used to describe essential properties of gases and plasmas such as free energy, entropy and enthalpy (equation (1.1)). It forms a connection between quantum mechanics and its macroscopic effects,

$$Z = \sum g_i e^{-\beta E_i}, i = 1, 2, 3, ... \tag{1.1}$$

The value Z of the partition function is determined by the value of the quantum states, e.g. energy levels E, the Boltzmann factor β, and the degeneration factor g.

As the eigenvalues are raised to their exponential the partition function either converges with very few terms to a finite value or approaches infinity.

So does the value of the partition function not converge to a finite value in case of the unconfined hydrogen atom. As a finite value is essential to utilise the partition function in further calculations, the hydrogen model has to be adapted.

Quantity	Symbol	Dimension	
Elementary Quantities			
mass	m	kilogramme, kg	scalar
time	t	second, s	scalar
length	x	meter, m	vector
Current	I	Ampere, A	scalar
Voltage	U	Volt, V	scalar
frequency	f	Hertz, one per second, $1/s$	scalar
Derived Quantities			
Energy	E	$kg \cdot m^2/s^2$	scalar
momentum	$p = mv$	m^2/s	scalar
wave length	$\lambda = c/f$	$1/m$	scalar
velocity	$\dot{x} = \frac{\partial x}{\partial t} = v$	m/s	vector
wave number	k	$1/m$	scalar
angular frequency	$\omega = 2\pi/f$	$1/s$	scalar
radius	$r = \sqrt{\sum_{i=1}^{3} x_i}$	m	scalar
Operators			
spatial derivative in one dimension	$\phi' = \frac{d\phi}{dx}$		
Laplacian operator	$\Delta = \sum_{i=1}^{3} \frac{\partial^2}{\partial^2 x_i}$		
Euclidean vector norm	$\|x\|_2 = \sqrt{x^T x}$		
Constants			
elementary charge	e	$1.602 \cdot 10^{-19} As$	scalar
Planck's constant	h	$6.602 \cdot 10^{-31} As/V$	scalar
reduced Planck's constant	$\hbar = h/2\pi$	$1/2\pi \cdot [h]$	scalar
Pi	π	3.142	scalar
velocity of light in vacuum	c	$2.999 \cdot 10^8 m/s$	scalar
imaginary unit	$i = \sqrt{-1}$	1	scalar
nanometre	nm	$1nm = 10^{-9}m$	scalar
picometre	pm	$1pm = 10^{-12}m$	scalar
Others			
computational domain	Ω		
boundary of the computational domain	Γ		

Table 1.1: Overview of Physical Quantities and Constants up to four digits of accuracy

A possible solution is to assume that the hydrogen atom is confined, e.g. that the empty space around the atom is limited by other atoms in a finite distance.

1.3 Formulation of the Boundary Value Problem

The boundary value problem (1.2) is referred to as the hydrogenic Schrödinger equation. It corresponds to the time independent non-dimensional Schrödinger equation (1.29), if one ignores the reduced mass correction (1.19). The eigenvalue $\mathcal{E}$ and eigenfunction $\psi(\chi)$ are its solutions. Both are real valued. The eigenfunctions are furthermore square integrable. The solutions are restricted to the computational domain Ω and depend on location of the nucleus χ_0 within it,

$$\mathcal{E}\psi(\chi) = -\left(\frac{1}{2}\Delta + \frac{1}{\rho(\chi)}\right)\psi(\chi) \tag{1.2}$$

$$\rho = \|\chi - \chi_0\| \tag{1.3}$$

$$\chi \in \Omega. \tag{1.4}$$

$$\mathcal{E} = \mathbb{R} \tag{1.5}$$

$$\psi(\chi) \in \mathcal{L}^2. \tag{1.6}$$

In case of no confinement the domain Ω are the complete three natural space dimensions $\Omega = \mathbb{R}^3$ and in case of confinement it is an connected subspace of it. In particular the confinement to cuboids $\Omega \subset \mathbb{R}^3$, rectangles $\Omega \subset \mathbb{R}^2$ and closed lines $\Omega \subset \mathbb{R}^1$ is considered.

As the boundary Γ of the domain is assumed to consist of walls of infinite potential height, such that the electron cannot penetrate it. Therefore the eigenfunction $\psi(\chi)$ vanishes at the boundary. This corresponds to homogeneous Dirichlet boundary conditions (equation (1.7)),

$$\psi(\chi) = 0 \text{ on } \Gamma. \tag{1.7}$$

The eigenfunctions of $\psi(\chi)$ are square integrable and remain bounded at the location of the nucleus χ_0. Therefore no additional boundary condition is required for the point χ_0.

Note that some authors define different scaling constants and come up with the equation $-(\Delta + \frac{2}{\rho})\psi(\chi) = \tilde{\mathcal{E}}\psi(\chi)$ as hydrogenic Schrödinger equation. The eigenvalues $\tilde{\mathcal{E}} = 2\mathcal{E}$ yield of course the same energy levels E upon back-transformation into physical quantities.

1.4 Derivation of the Boundary Value Problem

The hydrogen atom can be modelled by the Schrödinger equation with a Coulomb potential. The energy levels are found as the eigenvalues of this equation. The general Schrödinger equation is time dependent (TDSE), but as the energy levels do not change as time elapses, it is beneficial to bring the equation into a time independent form. This form is known as the time independent Schrödinger equation (TISE), a second order elliptic partial differential equation which is derived in this section.

The behaviour of the hydrogen atom is described by the time dependent Schrödinger equation (1.8) [Sch26],

$$i\hbar \frac{\partial}{\partial t}\Psi(t, x) = \hat{H}\Psi(t, x). \tag{1.8}$$

Where the wave function $\Psi(x, t)$ determines the probability distribution of the electron's current location and the Hamiltonian operator $\hat{H}$ denotes the total energy of the system, e.g. the sum of the potential and the kinetic energy,

$$\hat{H} = E_{kin} + E_{pot}. \tag{1.9}$$

As the Schrödinger equation is not relativistic, space and and time can be separated from each other,

$$\Psi(t, x) = \phi(t)\psi(x) \tag{1.10}$$

$$ih\frac{1}{\phi(t)}\frac{\partial\phi(t)}{\partial t} = \frac{1}{\psi(x)}\hat{H}\psi(x). \tag{1.11}$$

Assuming furthermore conservation of energy, e.g. that the Hamiltonian does not change over time, both sides of the equation remain constant. This constant is the energy level E,

$$E = \frac{1}{\psi(x)}\hat{H}\psi(x). \tag{1.12}$$

For the potential energy the notation $E_{pot} = V(r)$ with radius $r = ||x||$ is further on used,

$$E\psi(x) = (E_{kin} + V(r))\psi(x). \tag{1.13}$$

For an external observer both the proton and the electron encircle the centre of mass and hence contribute together to the energy contained in the system. Therefore the kinetic energy is given by formula (1.20),

$$E_{kin} = \frac{1}{2}m_p\dot{x}_p^2 + \frac{1}{2}m_e\dot{x}_e^2. \tag{1.14}$$

To determine the kinetic energy it is sufficient to consider only the distance x between the electron and proton instead of the absolute positions x_p and x_e,

$$x = x_p - x_e \tag{1.15}$$

$$\tag{1.16}$$

If one also chooses the centre of mass x_c as origin of the coordinate system,

$$x_c(m_p + m_e) = m_p x_p + m_e x_e \tag{1.17}$$

$$0 = m_p x_p + m_e x_e, \tag{1.18}$$

then the expression of the kinetic energy simplifies to one term

$$E_{kin} = \frac{1}{2} m_p \left(\frac{m_e \dot{x}}{m_p + m_e} \right)^2 + \frac{1}{2} m_e \left(\frac{m_p \dot{x}}{m_p + m_e} \right)^2$$

$$= \frac{1}{2} \frac{m_p m_e}{m_p + m_e} \dot{x}^2.$$

Where the constant m_r is called the reduced mass,

$$m_r = \frac{m_p m_e}{m_p + m_e}, \tag{1.19}$$

a common quantity in the solution of two body systems. Note that $m_r \approx m_e$ as the mass of the electron is much smaller as the mass of the proton,

$$E_{kin} = \frac{1}{2} m_r \dot{x}^2 = \frac{1}{2} m_r v^2. \tag{1.20}$$

Substitution of equation (1.20) into equation (1.13) yields

$$E\psi(x) = \left(\frac{m_r v^2}{2} + V(r) \right) \psi(x)$$

$$= \left(\frac{p^2}{2m_r} + V(r) \right) \psi(x). \tag{1.21}$$

In quantum physics the momentum p can be interpreted as an operator acting on the wave-function [vN31],

$$p = -i\hbar\nabla. \tag{1.22}$$

The squared momentum can subsequently be replaced by the scaled Laplacian operator $\Delta = \sum \partial^2/\partial x_i^2$,

$$E\psi(x) = \left(\frac{(-i\hbar\nabla)^2}{2m_r} + V(r) \right) \psi(x) \tag{1.23}$$

$$= \left(\frac{-\hbar^2}{2m_r} \Delta + V(r) \right) \psi(x). \tag{1.24}$$

The potential energy $E_{pot} = V$ is given by the Coulomb potential,

$$i\hbar \frac{\partial}{\partial t} \psi(x) = \left(\frac{-\hbar^2}{2m_r} \Delta + \frac{-e^2}{r4\pi\epsilon_0} \right) \psi(x). \tag{1.25}$$

To ease further computations the equation is transformed into a non-dimensional form. The Hartree energy E_H and the Bohr radius a_0 are introduced. And the variables of energy and space are then replace by their respective non-dimensional forms $E = \mathcal{E}E_H$, $x = a_0\chi$, $r = a_0\rho$, $\Delta_x = \frac{1}{a_0^2}\Delta_\chi$,

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} \tag{1.26}$$

$$E_H = \frac{m_e e^4}{(4\pi\epsilon_0\hbar)^2} = \frac{1}{a_0^2} \frac{h^2}{m_e^2} \tag{1.27}$$

$$\mathcal{E}E_H\psi(\chi) = \left(\frac{1}{a_0^2} \frac{-\hbar^2}{2m_r} - \frac{e^2}{\rho a_0 4\pi\epsilon_0} \right) \psi(\chi) \tag{1.28}$$

$$\mathcal{E} \frac{1}{a_0^2} h^2 m_e \psi(\chi) = \left(-\frac{1}{2} \frac{m_e}{m_r} \frac{1}{a_0^2} \frac{\hbar^2}{m_e} - \frac{\hbar^2}{\rho a_0^2 m_e} \right) \psi(\chi)$$

$$-\mathcal{E}\psi(\chi) = \left(\frac{1}{2} \frac{m_e}{m_r} \Delta + \frac{1}{\rho} \right) \psi(\chi). \tag{1.29}$$

This represents the boundary value problem as introduced in section 1.3.

1.5   Singular Potentials

Depending on the author the term *singular potential* is more or less strictly interpreted and used for functions which are singular at one point and finite elsewhere. Following three different definitions exist [And76].

1. The first class includes potentials who's integral remains finite,

$$\lim_{\epsilon \to 0} \int_{\epsilon}^{a} V(x)dx < \infty. \tag{1.30}$$

2. The second class contains potentials which do not satisfy the requirements for class one, but who's singularity tends slower to infinity than x tends to zero. This applies to the Coulomb potential and hence to the hydrogenic Schrödinger equation. The solutions to the Schrödinger equation with such a potential are still bound,

$$\lim_{\epsilon \to 0} \int_{\epsilon}^{a} xV(x)dx < \infty. \tag{1.31}$$

3. The third class of potentials are these who's singularities tend faster to infinity than x tends to zero. Some authors only regard these potentials as singular, as here the solutions to the Schrödinger equation themselves are unbound,

$$\lim_{\epsilon \to 0} \int_{\epsilon}^{a} xV(x)dx = \infty. \tag{1.32}$$

1.6   Physical Limitations of the Mathematical Model

The Schrödinger equation is a simplified model of the real hydrogen atom and neglects several physical effects. The true energy levels differ therefore slightly from those computed with the Schrödinger equation. However, for the unconfined hydrogen atom this error is lower than 0.01%. Hence even if the eigenvalues are found exactly or are approximated with arbitrary precision, their physical significance does not exceed a few digits. The deviation of the energy levels are referred to as fine structure and is mainly due to

- the relativistic corrections to the kinetic energy,

- the spin-orbit interaction,

- the Darwin term

- and the Lamb shift.

Relativistic effects can be accounted for by using the Dirac equation instead of the Schrödinger equation. For a more detailed explanation of relativistic quantum mechanics, see [Dom11].

1.7   General Solution Properties

The Schrödinger equation consists of a symmetric Hamiltonian. Therefore the eigenvalues are real. However, the eigenvalues are not necessarily unique depending on the symmetry of the system. The eigenvalues of the hydrogen atom correspond to the energy levels and are interpreted as follows. When a hydrogen ion catches and binds an electron a photon is emitted. The electron is bound to one of the energy levels and the wavelength of the photon, e.g. the amount of released energy is determined by the energy level.

The squared eigenfunctions correspond to the probability P to find an electron at a given point inside the domain. Therefore the eigenfunction is normed such that the area beneath the probability function is one,

$$\int_{\Omega} \Psi^*(x)\Psi(x)dx = 1. \tag{1.33}$$

For illustration the probability function of the unconfined hydrogen atom is usually integrated over the sphere,

$$P(r) = 4\pi \left(rR(r)\right)^* \left(rR(r)\right). \tag{1.34}$$

1.8 Solution of the Unconfined Hydrogen Atom

The Schrödinger atom of the unconfined hydrogen atom has an analytic solution. As the Coulomb potential is spherically symmetric, a transformation to spherical coordinates allows a separation of variables. The Schrödinger equation in spherical coordinates is given by equation (1.35),

$$\frac{1}{2}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\Psi\right) + \frac{1}{r^2\sin\phi}\frac{\partial}{\partial\phi}\left(\sin\phi\frac{\partial}{\partial\phi}\Psi\right) + \frac{1}{r^2\sin^2\phi}\left(\frac{\partial^2}{\partial\theta^2}\Psi\right)\right) + \frac{1}{r}\Psi = -\mathcal{E}\Psi. \tag{1.35}$$

The separation of variables leads to one radial and two angular equations. It is sufficient to consider only the radial equation (1.37) for determining the energy levels,

$$\Psi = R(r)\Phi(\phi)\Theta(\theta) \tag{1.36}$$

$$\frac{1}{2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}R\right) + rR = -\mathcal{E}r^2R. \tag{1.37}$$

To simplify the radial equation further, one does a substitution and solves for the radial probability instead for the radial wave-function,

$$y = rR \tag{1.38}$$

$$\frac{1}{2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\left(\frac{1}{r}y\right)\right) + y = -\mathcal{E}ry \tag{1.39}$$

$$\frac{1}{2}\frac{\partial}{\partial r}\left(-y + ry'\right) + y = -\mathcal{E}ry \tag{1.40}$$

$$\frac{1}{2}ry'' + y = -\mathcal{E}ry \tag{1.41}$$

$$\frac{1}{2}y'' + \frac{1}{r}y = -\mathcal{E}y. \tag{1.42}$$

With the boundary conditions as stated below. The additional boundary condition at zero is deduced from the assumed square integrability of the solution,

$$y(0) = 0 \tag{1.43}$$

$$\lim_{r\to\infty} y(r) = 0. \tag{1.44}$$

Equation (1.42) determines the eigenvalues of the unconfined hydrogen atom. It is an ordinary differential equation, but has the same structure of the unseparated Schrödinger equation (1.29). Its analytic solutions come in the form of Laguerre polynomials and spherical harmonics. The radial equation can easily be solved by the finite difference method, as the singularity is on the boundary and the derivatives are defined everywhere inside the domain.

For the ground state, the radial wave function is given by

$$R_1(r) = \frac{1}{\sqrt{\pi a_0^3}}e^{-r/a_0}. \tag{1.45}$$

It is also depicted in figure 1.1. The wave function of higher energy levels reach further, but asymptotically all energy levels decay exponentially towards infinity. As in case of the ground state, wave functions of higher energy levels may not be differentiable at the nucleus, depending on the corresponding spherical harmonic.

1.9 Influence of the Confinement on the Solution

The cubically confined hydrogen atom is best understood if one considers it as the transition between two separate problems, namely that of the particle in the box and that of the unconfined hydrogen atom.

Unconfined Hydrogen Atom The unconfined hydrogen atom is the limit case of the confined hydrogen atom, if one considers the box of the confinement to be infinitely large. The energy levels of the free
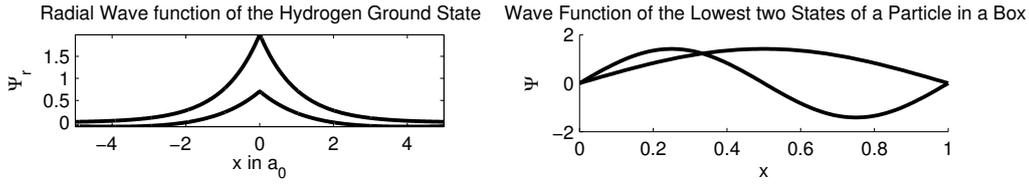
Figure 1.1: Wave functions of the unconfined hydrogen atom and of a particle in a box
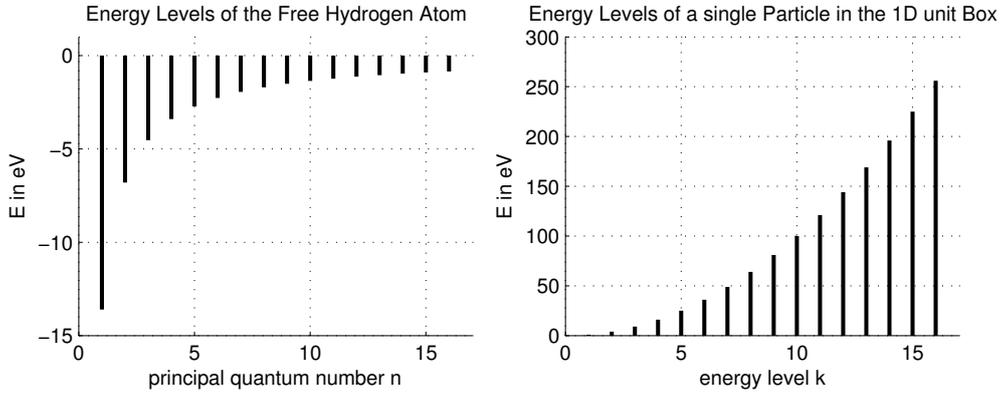
Figure 1.2: Energy levels of the unconfined hydrogen atom and of a particle in a box

hydrogen atom follow a rational series given by equation (1.46) and are depicted in figure 1.2. Here Ry is the Rydberg constant and equals the energy of the hydrogen ground state,

$$E = -Ry\frac{1}{n^2}, n = 1, 2, 3, \ldots \tag{1.46}$$

$$Ry = hc\frac{m_e e^4}{8\epsilon_0^2 h^3 c} \approx 13.605 eV.$$

The wave function takes the form of general Laguerre polynomials for the radial and spherical harmonics for the angular component. It decays exponentially with increasing distance from the nucleus (figure 1.1). A plot of the wave-function shows that the derivative at the location of the nucleus does not exist. This implies numerical complications discussed later.

Particle in a Box Here one considers only the electron confined in a box without a proton and the Schrödinger equation does not contain a potential. In this case the energy levels follow the series (1.47) which is also depicted in figure 1.2. The wave functions take the form of elementary sines,

$$E = \frac{n^2}{L^2}\frac{h^2}{8m_e}. \tag{1.47}$$

Implications for the Confined Hydrogen Atom The solution of the unconfined hydrogen atom and the particle in the box problem are obviously antagonistic. The energy levels of the unconfined hydrogen atom are negative and bound, as they converge to zero. The energy levels of the particle in the box are positive and approach infinity. The eigenvalue spectrum of a confined hydrogen atom is indefinite and resemble a combination of both spectra, with a limited number of negative eigenvalues being similar to those of the unconfined hydrogen atom and an infinite number of eigenvalues approaching asymptotically those of the particle in the box.

1.9.1 Position of the Nucleus Inside the Confining Box

The spherical confined hydrogen atom with centred nucleus can also be solved by separation of variables. However, the energy levels given as roots of the confluent hypergeometric function are not rational numbers anymore [SW38, p. 57], [SPM, p. 127]. If the nucleus is shifted off-centre, its distance to the boundary

varies depending on the direction. Thus the radial part cannot be separated from the angular parts. In this case it is simpler to consider the problem in Cartesian coordinates, which, however, do not allow a separation of variables.

1.9.2 Shape of the Confining Box

The behaviour of an confined hydrogen atom does not depend solely on the size of the box, but also on its form. For various reasons different shapes have been considered, spherically and parabolic shapes as the hydrogenic Schrödinger equation is separable in the respective coordinate systems, or cylindrical, triangular or rectangular shapes, as they best represent manufactured quantum structures.

In this thesis a rectangular domain is considered and further shapes are not investigated. Note that the qualitative results with different domains are expected to be similar.

1.9.3 Size of the Confining Box

The wave functions of the hydrogen atom decay exponentially. So does the radial wave function of the ground state R_1 (equation (1.45)) already falls below 10^{-15} parts of its maximum at a distance of about 35 Bohr radii. Therefore a box with a side length of only 70 Bohr radii becomes quasi infinitely large. The wave functions of the n-th energy level require moderately larger boxes, as they range in relation to the ground state n-times further.

Reversely one expects a completely different behaviour of the confined hydrogen atom compared to the unconfined atom once the box radius drops below one Bohr radius. For comparison: One Bohr radius (53pm) is the mean distance between the electron and the proton of the unconfined hydrogen atom and the the bond length of the hydrogen molecule is about two Bohr radii.

1.10 Confinement to Lower Dimensions

The spectrum of an confined hydrogen atom differs from that of an unconfined atom. So limits a confinement in all three dimensions the number of negative energy levels and makes the partition function converge. Of particular interest are the limit cases where the atom is confined some axes to an infinitesimal region whilst it remains unconfined in the remaining axes, viz. an atom constraint to a lower dimensional space. Such systems are described by hydrogen atoms constrained in their movement by strong magnetic or laser fields. Quasi lower dimensional solid state devices have also been manufactured. However, the behaviour of those devices is influenced by other adverse physical effects such as permeability of the material or penetrable boundaries. In these cases one usually does not consider atoms but electron-hole pairs, which are referred to as *excitons*.

1.10.1 Two Dimensions

If an atom resides in a quantum well, e.g. if its wave functions are constrained to two dimensions, its ground state energy is four times as large as that of the unconfined atom [Bry84]. Some authors replace the Coulomb potential by a logarithmic potential in the two dimensional Schrödinger equation. However, this is not considered here, as only the movement of the degrees of freedom of the atom, but not the forces are constrained to two dimensions.

1.10.2 One Dimension

The one dimensional hydrogen atom was extensively discussed by theorists with contradicting views. Loudon published the first comprehensive paper about this topic and claimed the existence of an infinite ground state and a double degeneracy of the remaining states, both conclusions are disputed until today [Lou59], [GC97]. In general the authors consent that the Balmer series of the three dimensional hydrogen atom is part of the spectrum of the one dimensional hydrogen atom as well.

One must keep in mind that truly one dimensional systems do not exist, but resemble limit cases where the atom is constrained to a long thin cylinder. Physical systems with this properties are quantum wires, nano-tubes or hydrogen atoms in strong laser field. Such systems indeed appear to have a ground state which is even much more amplified than that of the two dimensional system [Spa04].

No final conclusion about the one dimensional hydrogen atom shall be drawn here, as it only a side issue in this thesis and would require a much more extensive study of literature or even research to be resolved. However, the dissent about the findings of Loudon are of importance for this thesis as the findings are based on a weakened potential.

It should further be noted that the one proton nucleus itself is not infinitesimal small, but has a finite radius, called the *charge radius*. Albeit this radius is much smaller than the perturbation to achieve numerical stability it shows that any prediction about the wave function very close to the nucleus based on the Schrödinger equation are futile, as they are beyond the physical capability of the model, see also section 1.6.

1.10.3 Quasi Zero-Dimensions

A particle tightly constrained in all dimensions becomes a quantum dot. Here the ground state energy becomes also more and more amplified the smaller the confining box becomes. The high binding energy of an electron confined to a region close to the nucleus can be illustrated with an analogy to celestial mechanics, where by Kepler's third law, the velocity of planets orbiting close to the central star is larger compared to those orbiting further away.

Chapter 2

Discretisation of the Schrödinger Equation

As the the hydrogenic Schrödinger equation is not separable in Cartesian coordinates, only analytic approximations exist. A numerical approximation is therefore preferable. The numerical method should be chosen such that it is convergent and the result physically plausible.

The properties of the Hamiltonian resembling the hydrogenic Schrödinger equation are carried over to the discretised system. Hence the matrices will be real and symmetric, its eigenvalues and eigenvectors real and orthogonal. Finite difference and finite element discretisations furthermore yield sparse and usually banded discretisation methods. This gives rise to eigensolver for large symmetric systems as discussed in chapter 5.

2.1   Notation used throughout the Numerical Analysis Parts

If not otherwise declared the symbols used in the numerical analysis parts have the meaning explained in table 2.1

Symbol	Meaning
a capital letter, e.g. A	a matrix
a_i	the ith-column of a matrix A
a_{ij}	the jth-element of the ith-column of the matrix A
a minor Latin letter, e.g. x	a vector
x_i	the ith-element of the vector x
minor Greek letter α	a scalar
λ	exact eigenvalue
v	exact eigenvector
θ	eigenvalue of the projected system, approximated eigenvalue (Ritz value)
s	eigenvector of the projected system
z	approximated eigenvector (Ritz vector)
Q	an orthogonal matrix
T	a tridiagonal matrix
D	a diagonal matrix
$\lvert\alpha\rvert = \{\alpha \text{ if } \alpha \leq 0, -\alpha \text{ if } \alpha < 0\}$	absolute value
$\kappa(A) = \frac{max_{i=1..n}\lvert\lambda_i\rvert}{min_{j=1..n}\lvert\lambda_j\rvert}$	matrix condition number
$A^T : a_{ij} \leftarrow a_{ji}$	transpose, exchanges columns with rows
$A^* : a_{ij} \leftarrow a_{ji}^*$	conjugate transpose, changes columns with rows and negates imaginary parts

Table 2.1: Meaning of symbols frequently used in the numerical analysis parts

2.2 Finite Difference Discretisation

In this section the finite difference discretisation of the Schrödinger equation will be developed. The finite difference method (FDM) is a numerical method to approximate the solution of differential equations. The approximation is computed for a set of points inside the domain which are usually arranged in form of a structured grid. In case of convergence, the accuracy of the approximation increases with the number of grid points. At each grid point the differential equation is discretised and approximated by a finite difference equation of the point itself and its imminent neighbours. The set of equations is usually represented in matrix form.

2.2.1 Basic Concepts of Finite Difference Approximations

To discretise a PDE with the finite difference method a set of points inside the computational domain is chosen ($\Omega_h \subset \Omega$). The derivatives at each of those grid points are approximated by the a difference scheme, like equation (2.11). An approximation with n points leads to n-independent equations which are combined into a matrix. The second derivative (Laplacian operator) with constant step width can be approximated in one dimension by the matrix

$$L = \frac{1}{h^2} \begin{bmatrix} 2 & -1 & & \\ -1 & 2 & ... & \\ & ... & ... & -1 \\ & & -1 & 2 \end{bmatrix}. \tag{2.1}$$

The Schrödigner equation (1.2) discretisation consists of a matrix which is the sum of the Laplacian operator L and a diagonal matrix specifying the potential V,

$$A = \frac{1}{2}L + V. \tag{2.2}$$

The eigenvalues of this discretisation matrix are the approximated energy levels,

$$A\psi = \lambda\psi. \tag{2.3}$$

The matrix A is sparse, eq. it has only few non-zero entries. This allows to find even the eigenvalues of very large matrices with the algorithms introduced in chapter 5.

2.2.2 Definition of the Derivative

In general the derivative $f'(x) = \frac{d}{dx}f(x)$ of a function $f(x)$ is given by equation (2.4) if the limits exists and are equal. The conditions for the derivative to exist are usually satisfied if the function is sufficiently smooth, e.g. if there are no peaks or high frequency oscillations,

$$f'(x)_+ = \lim_{h \to 0, h > 0} \frac{f(x+h) - f(x)}{h} \tag{2.4}$$

$$f'(x)_- = \lim_{h \to 0, h > 0} \frac{f(x) - f(x-h)}{h} \tag{2.5}$$

$$f'(x)_- = f'(x)_+. \tag{2.6}$$

The nth-derivative of the function can be determined by recursively forming the derivative,

$$\frac{d^n}{dx^n}f = \frac{d^{n-1}}{dx^{n-1}}\left(\frac{d}{dx}f\right). \tag{2.7}$$

2.2.3 Taylor's Theorem

Let the function f be at least k-times continuously differentiable in the neighbourhood of x_0, then f has a series expansion in the neighbourhood of x_0 in the form of equation (2.8),

$$f(x) = \lim_{x \to x_0} \sum_{i=0}^{k} \frac{1}{i!}(x - x_0)\left(\frac{d^k}{dx^k}f(x_0)\right). \tag{2.8}$$

2.2.4 Derivation of Finite Difference Schemes

A finite difference approximation of the nth-derivative are derived by using the first n terms of the Taylor series expansion (2.9). Note that according to the Taylor theorem this requires the first n derivatives of the function to exist,

$$f(x_0 + h) \approx \sum_{i=0}^{n} \frac{h^i}{i!} f^i(x_0). \tag{2.9}$$

The Taylor series expansion gives rise to a system of equations. For second order accurate approximation the system becomes (2.10) and the resulting convolution kernel of the second derivative is (2.11),

$$\begin{bmatrix} -1 & 1/2 \\ 1 & 1/2 \end{bmatrix} \begin{bmatrix} f'(x)/h \\ f''(x)/h^2 \end{bmatrix} = \begin{bmatrix} 1 & -1 & 0 \\ 0 & -1 & 1 \end{bmatrix} \underbrace{\begin{bmatrix} f(x-h) \\ f(x) \\ f(x+h) \end{bmatrix}}_{F} \tag{2.10}$$

$$f_2''(x) \approx \frac{1}{h^2} \begin{bmatrix} 1 & -2 & 1 \end{bmatrix} F. \tag{2.11}$$

If more points are incorporated into the expansion and higher derivatives exist, then the order of accuracy increases. The system of a fourth order accurate approximation is given by (2.12) and the resulting convolution kernel of the second derivative is (2.13),

$$\begin{bmatrix} -2 & 4/2 & -8/6 & 16/24 \\ -1 & 1/2 & -1/6 & 1/24 \\ 1 & 1/2 & 1/6 & 1/24 \\ 2 & 4/2 & 8/6 & 16/24 \end{bmatrix} \begin{bmatrix} f'(x)/h \\ f''(x)/h^2 \\ f'''(x)/h^3 \\ f^{iv}(x)/h^4 \end{bmatrix} = \begin{bmatrix} 1 & 0 & -1 & 0 & 0 \\ 0 & 1 & -1 & 0 & 0 \\ 0 & 0 & -1 & 1 & 0 \\ 0 & 0 & -1 & 0 & 1 \end{bmatrix} \underbrace{\begin{bmatrix} f(x-2h) \\ f(x-h) \\ f(x) \\ f(x+h) \\ f(x+2h) \end{bmatrix}}_{F} \tag{2.12}$$

$$f_4''(x) = \frac{1}{12 h^2} \begin{bmatrix} -1 & 16 & -30 & 16 & -1 \end{bmatrix} F \tag{2.13}$$

$$f_4^{iv}(x) = \frac{1}{12 h^4} \begin{bmatrix} -1 & -4 & 6 & -4 & 1 \end{bmatrix} F. \tag{2.14}$$

The residual of the finite difference solution to the analytic solution f_*^n can be estimated by comparing approximations consisting of differently many terms from the Taylor expansion,

$$f_2''(x) - f_*''(x) \approx f_2''(x) - f_4''(x) = \frac{1}{12h^2} \begin{bmatrix} -1 & -4 & 6 & -4 & 1 \end{bmatrix} \tag{2.15}$$

$$= 12h^2 f_4^{iv}(x). \tag{2.16}$$

So the approximation f_2'' is second order accurate, as the residual is proportional to h^2, abbreviated with the short hand notation $O(h^2)$. This implies that the accuracy of the approximation f_2'' increases four times if one uses twice as many grid points.

2.2.5 Boundary Conditions

As the hydrogen atom is confined, Dirichlet boundary condition conditions are assumed where the wave function is zero at the boundary of the domain. This requires no changes of the matrix.

2.2.6 Richardson Extrapolation

The special behaviour of the finite difference approximation to be proportional to higher order derivatives allows to extrapolate solutions with a higher order of accuracy from two solutions on differently spaced grids [Ric11]. Assume that the error of the finite difference approximation is of the form

$$f_*(x) = f_h(x) + a(x)h^2 + b(x)h^4 + O(h^6). \tag{2.17}$$

Then, by doing another approximation with a different step-width of ch again an equation system can be set up. If one eliminates the highest residual term $a(x)$ this yields an approximation to the analytic solution $f_*(x)$ with an higher order of accuracy,

$$\begin{bmatrix} 1 & -h^2 \\ 1 & -c^2h^2 \end{bmatrix} \begin{bmatrix} f_*(x) \\ b(x) \end{bmatrix} = \begin{bmatrix} 1 & 0 & h^4 \\ 0 & 1 & c^4h^4 \end{bmatrix} \begin{bmatrix} f_h(x) \\ f_{ch}(x) \\ a(x) \end{bmatrix} \tag{2.18}$$

$$f_*(x) = \frac{f_{ch}(x) - c^2 f_h(x)}{1 - c^2} - h^4 b(x) \frac{c^2 - c^4}{1 - c^2} \tag{2.19}$$

$$f_*(x) = \frac{4 f_{ch}(x) - f_h(x)}{3} - \frac{1}{4} h^4 b(x), c = 1/2. \tag{2.20}$$

This can be recursively continued to eliminate yet more higher order terms from the residual. The coefficients of up to 10th order accuracy are given in table 2.2.6

```
f_h        f_h/2    f_h/4    f_h/8        f_h/16            Residual
    -1/3,      4/3,       0,         0,              0,       -1/4 h^4
    1/45,     -4/9,   64/45,         0,              0,       1/64 h^6
 -1/2835,    4/135, -64/135,  4096/2835,             0,   -1/4096 h^8
1/722925, -4/8505, 64/2025, -4096/8505, 1048576/722925, 1/1048576 h^10
```

Table 2.2: Coefficients of extrapolation and largest remaining residual term of the Richardson extrapolation.

2.2.7 Higher Order Finite Differences

Higher order difference methods can also be constructed by matrix exponentials, which is simpler as the construction based on the solution of linear systems as described in the previous section. The second order accurate finite difference approximations of the 2-nth derivative are given by

$$D_2^{2n} = \left(D_2^2 \right)^n. \tag{2.21}$$

Where $D_2^2 = L$ is the second order accurate Laplacian operator (see equation (2.1)).

A higher order accurate approximation to the second derivative is then obtained by combining the several second order accurate approximations of higher derivatives,

$$D_{2k}^2 = \sum_{k=1}^{K} \frac{1}{c_{2k}} (-1h^2)^{k-1} D_2^{2k} \tag{2.22}$$

$$= \sum_{k=1}^{K} \frac{1}{c_{2k}} (-1h^2)^{k-1} (D_2^2)^k \tag{2.23}$$

Where the coefficients are given by the error terms of the finite difference method (cf. (2.16)),

$$c_{2k} = \binom{2n+1}{n} (n+1)^2 \tag{2.24}$$

$$= 1, 12, 90, 560, 3150, ... \tag{2.25}$$

The kernels of higher order difference matrices can be found as convolutions of the second order kernel instead of computing the matrix powers explicitly,

$$K_{2k+2} = (K_{2k} * K_2)[i] = \sum_{j=0}^{2k+1} K_2[i] * K_{2k}[j - i + 1], i = 1, 2, ..., 2k + 2, \tag{2.26}$$

if one considers the kernels to be padded with zeros at the ends. For a correct approximation of the homogeneous Dirichlet boundary the first terms of the sum have to be dropped. Note that the homogeneous Dirichlet boundary conditions are implicitly retained in the matrix powers.

Matrix powers can also be used to set up difference matrices of higher derivatives on non-uniform grids. However, the error of the finite difference approximation on a non-uniform grid is not anymore the multiple of higher order derivatives and higher order accurate differences on non-uniform grids can therefore not be set up in this way.

2.2.8 Finite Differences in Higher Dimensions

Total derivatives in higher dimensions are formed as the sum of partial derivatives of each dimension. So are the derivative matrices in higher dimension the sum of partial derivative matrices (equation (2.27)),

$$\Delta = \sum_{i=0}^{n} \frac{\partial^2}{\partial \rho_i^2}. \tag{2.27}$$

A partial derivative matrix is the Kronecker product of a one dimensional derivative matrix and further identity matrices. The Laplacian can be set up as described in algorithm 2.1.

Algorithm 2.1 Matrix Combination in Higher dimensions

```
1          A = A_x
2          I = I_x
3          for  i = y, z
4                  A = kron(A, I_i) + kron(I, A_i)
5                  I = kron(I, I_i)
```

The potential term does not contain any derivative and hence yields a diagonal matrix in real space. However, the potential contains a distance term which in Cartesian coordinates equals $\rho = ||x_c - x||$ for a nucleus located at x_c. The potential matrix is set up in three steps by first computing the distances in each dimension V_x^2, V_y^2, V_z^2 followed by the combining the matrices as in algorithm 2.1 into V^2 and completed by taking the square root of the elements.

If the nucleus is located such that the domain is symmetric then the energy levels degenerate. This means that some eigenvalues occur multiple times. For the hydrogen atom in free space the energy levels are n^2 degenerated. Non-unique eigenvalues may complicate the eigenvalue computation. One can avoid duplicate eigenvalues by slightly perturbing the location of the nucleus. This is justified, as long as the perturbation is smaller than the model error.

2.2.9 Influence of Smoothness on the Accuracy of Finite Difference Approximations

A function which is not sufficiently smooth cannot be accurately approximated by finite differences. This applies to highly oscillating functions and to functions with discontinuous derivatives where equation (2.6) does not hold. A quantitative criteria to determine whether a function is sufficiently smooth is found by investigating the basic oscillatory function

$$f(x) = e^{ikx}. \tag{2.28}$$

Where the first two analytic derivatives f'_* and f''_* are given by

$$f'_*(x) = ik e^{ikx} \tag{2.29}$$

$$f''_*(x) = -k^2 e^{ikx}. \tag{2.30}$$

The finite difference approximations f'_h and f''_h of the derivative differ from the analytic solution,

$$f'_h(x) = \frac{e^{ik(x+h)} - e^{ik(x-h)}}{2h} \tag{2.31}$$

$$= \frac{1}{h} \sinh(ikh) e^{ikx} \tag{2.32}$$

$$= \frac{i}{h} \sin(kh) e^{ikx} \tag{2.33}$$

$$f''_h(x) = \frac{e^{ik(x-h)} - 2e^{ikx} + e^{-ik(x+h)}}{h^2} \tag{2.34}$$

$$= \frac{2}{h^2}(1 - \cosh(ikh)) e^{ikx} \tag{2.35}$$

$$= \frac{2}{h^2}(1 - \cos(kh)) e^{ikx} \tag{2.36}$$

The relations (2.33) and (2.36) show that the approximations are more exact for small step widths h and low frequency components k. The approximation is furthermore only valid as long as the argument of the trigonometric functions hk is smaller than π. This is also known as Nyquist-Shannon sampling theorem [Sha49].

Ergo, a second order finite difference approximation of the first derivative of a function with highest frequency component $k = 2\omega$ is only valid iff the step width h satisfies:

$$h < \frac{\pi}{k} = \frac{1}{2\omega}. \tag{2.37}$$

The second order finite difference approximation of the second derivative requires a step width of

$$h < \frac{\pi}{2k} = \frac{1}{\omega}. \tag{2.38}$$

The quality of approximation with respect to frequency and step width is depicted in figure 2.2.9.

This analysis can be repeated for higher order accurate approximations. Higher order accurate approximations require in general a smaller step width for the same frequency.
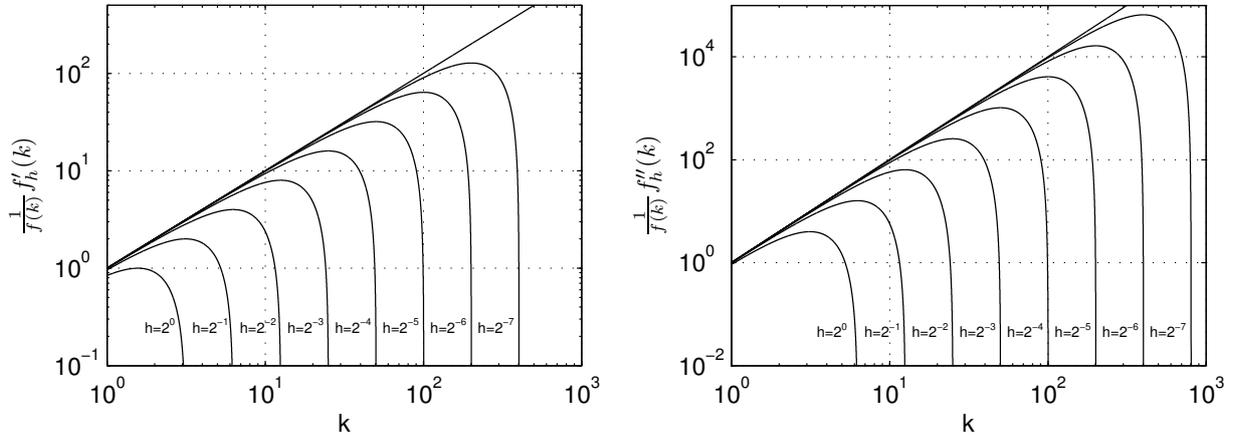
Figure 2.1: Quality of the second order accurate finite difference approximation to the function e^{ikx} for different step widths h and frequencies k, left: first derivative, right: second derivative.

2.2.10 Smoothness of the Eigenfunctions of the Schrödinger Equation

The frequency components of the Schrödinger Equation are obtained transforming its solution into Fourier space. For the ground state (1.45) along the x-axis this yields with $\chi = a_0 x$

$$\hat{\psi}(k) = \int_{-\infty}^{\infty} \frac{1}{\sqrt{\pi a_0^3}} e^{-|\chi|} e^{-2\pi ikx} d\chi \tag{2.39}$$

$$= \frac{1}{\sqrt{\pi a_0^3}} \left(\int_{-\infty}^{0} e^{-\chi(2\pi ik-1)} d\chi + \int_{0}^{\infty} e^{-\chi(2\pi ik+1)} d\chi \right) \tag{2.40}$$

$$= \frac{1}{\sqrt{\pi a_0^3}} \left(\frac{-1}{2\pi ik - 1} + \frac{1}{2\pi ik + 1} \right) \tag{2.41}$$

$$= \frac{1}{\sqrt{\pi a_0^3}} \frac{2}{4\pi^2 k^2 + 1} + 0\, i. \tag{2.42}$$

The Fourier coefficients (2.42) decay slowly compared to the coefficients of analytic functions, which decay exponentially. The solution contains therefore high frequency components and according to equation (2.36) this implies that a small step width is required before convergence of the finite difference method sets in.

Based on the Fourier transform of the ground state one can also reason that the solutions of the Schrödinger

equation become smoother with increasing dimensions, as the Fourier coefficients decay faster due to the relation

$$e^{-\sqrt{x^2+y^2+z^2}} \le e^{-\sqrt{x^2+y^2}} \le e^{-\sqrt{x^2}}. \tag{2.43}$$

This implies that conversion sets in earlier in higher dimensions.

The solutions to the Schrödinger equation are not only none smooth, but the derivative of the wave-function are undefined at the location of the nucleus. Therefore the grid has to be set up in a distinctive way to assure convergence. In two and higher dimensions the grid should be set up such that

- the nucleus is not located directly on a grid point,

- the grid spaces are fine close to the location of the nucleus.

In one dimension this approach breaks down as one would still differentiate over the location of the nucleus, even if it is not directly located on a grid point. An exception is the radial equation, where the discontinuity is located at the boundary and not inside the computational domain.

2.2.11   Non-Uniform Grids

A common layout of a finite difference quotient has constant spaces in-between the grid points. For homogeneous Dirichlet boundary conditions in one dimension there are n grid points inside the domain and two boundary points, where the eigenfunctions are zero. There are therefore $n+1$ steps inside the domain Ω and hence the step width is calculated as in equation (2.45),

$$\Omega = [-L, L] \tag{2.44}$$

$$h = \frac{2L}{n+1}. \tag{2.45}$$

Sometimes a grid with a step size varying inside the domain may be desirable, to resolve parts of the domain with higher accuracy while keeping the overall number of grid points small.

This is the case for the hydrogenic Schrödinger equation. Recall that wave functions and their derivatives of the unconfined hydrogen atom are large close to the nucleus and decay exponentially towards infinity (equation (1.45)). Therefore the discretisation error is large close to the nucleus as well (equation (2.16)) and a grid with many grid points close to the nucleus reduces the discretisation error.

Predetermined Setup of a Variable Grid   A relocation scheme for the grid points can be set up by realising that, for a constant step size h the error varies proportional to the fourth derivative of the solution:

$$err(r_i) = c_1 h^2 \psi^{vi}(r_i) = c_1 h^2 e^{-r_i} \tag{2.46}$$

Which implies that the error remains constant if the step width h is chosen to be proportional to the inverse of the fourth derivative of the solution,

$$h(r_i) = c_2 e^{r_i/2}. \tag{2.47}$$

As the location of a grid point is equal to the sum of grid spaces between the origin and the grid point, this leads to a relocation scheme for the grid points of a constant grid

$$r_v(r) = \alpha_1 \left(e^{\alpha_2 r} - 1 \right). \tag{2.48}$$

A varying grid in higher dimension can be set up by relocating the grid points according to equation (2.48) for each coordinate axis by choosing the distance to the nucleus as parameter r.

Adaptive Grid   For a confined atom the solution differs from those of the unconfined atom and a predetermined grid based on the unconfined wave functions is therefore not anymore optimal. In this case it is preferable to refine the mesh locally according to algorithm 2.2.

Algorithm 2.2 Adaptive FDM Refinement

1. compute fourth derivative of the solution as $\psi^{iv}(x) = L^2\psi(x)$

2. estimate local error as $err_{loc} = \frac{1}{12}h^2\psi(x)$

3. interpolate error into element centres

4. find maximum absolute error err_{max}

5. mark elements with large error contribution $|err_{loc}| > \frac{1}{4}|err_{max}|$

6. add the midpoints of the marked elements to the grid

Difference Scheme The matrix kernel for a variable grid can also be recovered by setting up a system of equations, (2.2.11),

$$\begin{bmatrix} (x_{i+1} - x_i) & 1/2(x_{i+1} - x_i)^2 \\ (x_{i-1} - x_i) & 1/2(x_{i-1} - x_i)^2 \end{bmatrix} \begin{bmatrix} f'(x_i) \\ f''(x_i) \end{bmatrix} = \begin{bmatrix} 0 & -1 & 1 \\ 1 & -1 & 0 \end{bmatrix} \begin{bmatrix} f(x_{i-1}) \\ f(x_i) \\ f(x_{i+1}) \end{bmatrix}. \tag{2.49}$$

$$f_2''(x_i) = \left[\frac{2}{(x_i - x_{i-1})(x_{i+1} - x_{i-1})}, \frac{2}{(x_i - x_{i+1})(x_i - x_{i-1})}, \frac{2}{(x_{i+1} - x_i)(x_{i+1} - x_{i-1})}\right] F. \tag{2.50}$$

As the coefficients of the difference matrices are not any more integers divided by a constant factor, it is especially important to avoid cancellation errors while setting up the difference matrices on a variable grid.

Preserving Symmetry A discretisation matrix based on a grid with varying step-size is asymmetric. However, the asymmetric eigenvalue problem can be transformed into a symmetric generalised eigenvalue problem by a similarity transform (equation (2.51) and section 3.12),

$$DTD^{-1} = \tilde{T} \tag{2.51}$$
$$Tx = \lambda x \tag{2.52}$$
$$Dx = y \tag{2.53}$$
$$DTD^{-1}y = DD^{-1}y \tag{2.54}$$
$$\tilde{T}y = \lambda y. \tag{2.55}$$

2.2.12 Finite Difference Solution of the Radial Schrödinger Equation

In the radial Schrödinger equation (1.37) the the Coulomb singularity is located on the boundary of the computational domain. Therefore a solution by the finite difference method is possible. Figure 2.2.12 shows the convergence of the finite difference approximation to the radial Schrödinger equation for the unconfined atom. As the solution is not smooth enough close to the Coulomb singularity, it cannot be sufficiently sampled by a uniform grid with few grid points. Therefore convergence for a uniform grid does not set in until the grid becomes very fine. However, if one uses a variable grid, such that the region close to the Coulomb singularity is sufficiently sampled even with few grid points, then convergence sets in immediately and the discretisation error is much lower.
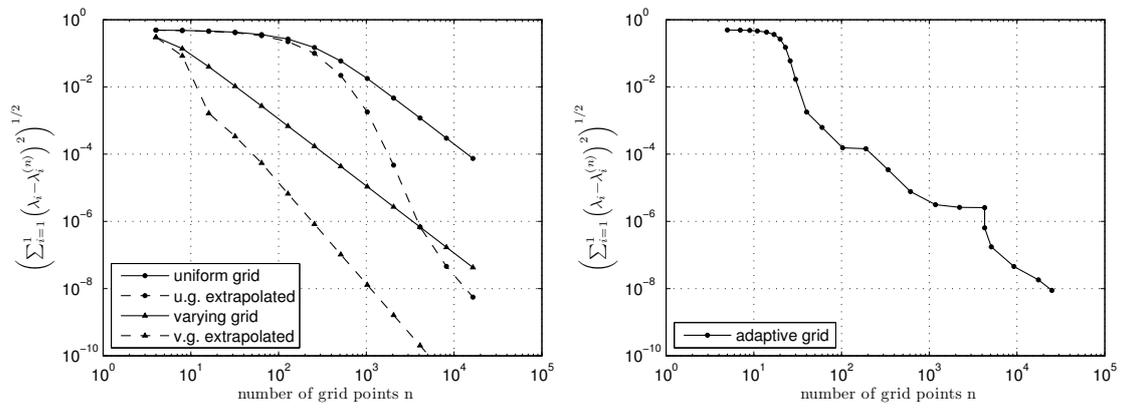
Figure 2.2: Finite difference approximation to the radial Schrödinger equation for the domain $\Omega = [0, 400]\, a_0$, the graphs show the discretisation error of the first eigenvalue compared to the analytic solution. Left: predetermined uniform and varying grid, right: adaptive grid.

Chapter 3

Revision of Matrix Properties and Decompositions

Some fundamental matrix properties and decomposition are repeated first before some of the Hermitian eigenvalue methods are applied to the given physical problem. The interested reader may refer to a classic compendium such as [Gol96] for a more extensive coverage of this topic.

3.1 Symmetry

A matrix A is called Hermitian if it is equal to its conjugate transpose. If A is real, the conjugate transpose is simply the transpose and the matrix is called symmetric. Hermitian matrices expose certain favourable properties in regard to their decompositions,

$$A = A^*, A \in \mathbb{C} \tag{3.1}$$
$$A = A^T, A \in \mathbb{R}. \tag{3.2}$$

3.2 Orthogonality

A matrix U is called unitary, if its conjugate transpose is equal to its inverse. If real unitary matrix Q is more commonly referred to as orthogonal or orthonormal,

$$U^*U = I, U^* = U^{-1}, U \in \mathbb{C} \tag{3.3}$$
$$Q^TQ = I, Q^T = Q^{-1}, Q \in \mathbb{R}. \tag{3.4}$$

3.3 Similarity

The matrices A and B are similar, if there exists an invertible matrix of same rank P, such that

$$AP = PB. \tag{3.5}$$

Similar matrices have the same eigenvalues. If A and B are Hermitian, then P is unitary.

3.4 Projectors

Any projector P is an idempotent matrix:

$$P^2 = P. \tag{3.6}$$

The complementary projector is given by

$$P_c = I - P. \tag{3.7}$$

A projector which is also a symmetric matrix is an orthogonal projector, but it is usually not an orthogonal matrix,

$$P^T = P. \tag{3.8}$$

For each vector x there exists a projector P, such that

$$Px = x \tag{3.9}$$
$$P_c x = 0. \tag{3.10}$$

This projector is given by the outer product of x:

$$P = xx^T \tag{3.11}$$
$$P_c = I - xx^T. \tag{3.12}$$

3.5   Orthogonal Transformation

An orthogonal transformation is a transformation with an linear operator T, which preserves angles between vectors and lengths of vectors (equation (3.13). The most common orthogonal transformations are rotations and mirroring,

$$v^T w = (Tv)^T (Tw). \tag{3.13}$$

3.6   Cholesky Decomposition

The Cholesky decomposition is a factorisation of a matrix A into the product of an upper tridiagonal L matrix and its conjugate transpose. It is one of the two possible interpretations of a matrix square root. The Cholesky factorisation only exists if the matrix A is positive definite,

$$L^T L = A. \tag{3.14}$$

3.7   Eigenvalue Decomposition

Each matrix A acts on a distinct set of vectors, its eigenvectors v, as if it were a scalar. The corresponding scalars are referred to as the eigenvalues λ and a pair of an eigenvector and its eigenvalue is referred to as an eigenpair. An eigenvector is not unique as it is only unanimously defined up to an arbitrary coefficient,

$$Av = \lambda v. \tag{3.15}$$

The eigenvalue decomposition of A is defined as

$$A = V\Lambda V^{-1}. \tag{3.16}$$

Where Λ is a diagonal matrix consisting of the eigenvalues λ of A and V is the matrix consisting of the eigenvectors corresponding to the eigenvalues in Λ.

If A is Hermitian, then V is orthogonal and Λ is real.

3.8   Generalised Eigenvalue Decomposition

A generalised eigenproblem is of the form

$$Ax = \lambda Bx. \tag{3.17}$$

Such problems arise in many physical applications such as mass spring systems which discretisation yields a mass and a stiffness matrix. The finite element discretisation of the Schrödinger equation also yields a generalised Hermitian eigenvalue problem.

Note that equation (3.17) can usually be transformed into a standard eigenvalue problem by inverting B,

$$B^{-1}Ax = \lambda x. \tag{3.18}$$

However if A and B are Hermitian, the symmetry is usually lost and $B^{-1}A$ is not Hermitian. If B is positive definite a Cholesky decomposition is preferable instead which keeps the eigenvalue problem Hermitian,

$$L^T L = B \tag{3.19}$$
$$L^{-1}ALy = \lambda y \tag{3.20}$$
$$x = Ly. \tag{3.21}$$

However, the Cholesky factor L is dense, as long as the matrix B is not close to being diagonal. Therefore specialised solvers for generalised eigenvalue problems exists which exploit symmetry as well as sparsity of the matrices A and B.

3.9 Determinant

The determinant is defined as the product of the eigenvalues λ of the matrix A,

$$det(A) = \prod_{i=1}^{n} \lambda_i. \tag{3.22}$$

3.10 Hessenberg Decomposition

The Hessenberg decomposition is defined as

$$AQ = QH. \tag{3.23}$$

Where the matrix H is upper triangular with one additional non-zero sub-diagonal and the matrix Q is orthogonal. Note that A and H are similar and hence have the same eigenvalues.

If A is Hermitian then H is tridiagonal symmetric and real,

$$AQ = QT, A = A^*. \tag{3.24}$$

3.11 QR-Decomposition

The QR-decomposition is defined as

$$A = QR. \tag{3.25}$$

Where the matrix Q is orthogonal and the matrix R upper triangular.

If A is tridiagonal so is R.

3.12 Similarity Transform into a Symmetric Matrix

Factors of asymmetric tridiagonal matrices are in general not tridiagonal anymore. This increases the computational effort and the round off error in some algorithms which build on repeated matrix factorisations. However, under certain circumstances it is possible to transform an asymmetric tridiagonal matrix T into a symmetric tridiagonal matrix $\tilde{T}$ with help of a diagonal matrix D.

For example, finite difference discretisations on a variable grid yield asymmetric matrices which can be transformed to become symmetric. In this case it is also possible to derive the matrices D and $\tilde{T}$ directly without actually performing the factorisation. See [TSCH90],

$$DTD^{-1} = \tilde{T} \tag{3.26}$$
$$d_1 = 1 \tag{3.27}$$
$$d_{i+1} = d_i \sqrt{b_{i+1}/c_{i+1}} \tag{3.28}$$
$$b_i/c_i > 0 \tag{3.29}$$

$$\begin{bmatrix} d_1 & \\ & d_2 \end{bmatrix} \begin{bmatrix} a_1 & b_2 \\ c_2 & a_2 \end{bmatrix} \begin{bmatrix} d_1 & \\ & d_2 \end{bmatrix}^{-1} = \begin{bmatrix} a_1 & \tilde{b}_2 \\ \tilde{b}_2 & a_2 \end{bmatrix}. \tag{3.30}$$

3.13   Orthogonalising a Set of Vectors - The Modified Gram-Schmidt Process

The Gram-Schmidt algorithm orthogonalises a vector x with respect to an existing set of orthonormal basis vectors Q. Orthogonalisation can be achieved by an orthogonal projection (equation (3.31)),

$$x = (I - QQ^T)x. \tag{3.31}$$

An improved version which reduces round off errors is listed in algorithm 3.1.

Algorithm 3.1 Modified Gram-Schmidt Algorithm

```
1          for idx=1:n
2                x = x − (Q_{:,idx}^T x)Q_{:,idx};
3          end % for idx
4          repeat if ||x|| << 1
5          x = x/||x||;
```

$$1 \qquad \text{for idx=1:n}$$
$$2 \qquad\qquad x = x - (Q_{:,idx}^T x)Q_{:,idx};$$
$$3 \qquad \text{end \% for idx}$$
$$4 \qquad \text{repeat if } ||x|| \ll 1$$
$$5 \qquad x = x/||x||;$$

Chapter 4

Basic Eigenvalue Algorithms

The eigenvalue problem can be formulated as finding the zeros of an n-degree polynomial, where n is the rank of the matrix A,

$$(A - \lambda I)x = 0. \tag{4.1}$$

The Abel-Ruffini theorem states that there exists no closed form solution in the general case if the polynomial is of order five or larger. Hence it is in general impossible to find the exact eigenvalues of a matrix in a finite number of steps and it is necessary to apply an iterative method to approximate the eigenvalues.

4.1 Power Iteration

The power iterations is the most basic method for computing eigenvalues. It is slowly convergent and only yields the largest eigenvalue. It is stated here as most advanced eigenvalue algorithms can be retraced to a form of power iteration.

Assume that the matrix A a has a unique real eigenvalue whose absolute value is larger than the absolute values of the other eigenvalues,

$$|\lambda_1| > |\lambda_2| \geq |\lambda_3| \geq \ldots \geq |\lambda_n|. \tag{4.2}$$

For simplicity, but not necessity, consider the matrix A also to be symmetric. Then one realises that the powers of the matrix A converge of the powers of the eigenpair of λ_1,

$$A^k x_0 = V \Lambda^k V^T x_0 = \lambda_1^k v_1 v_1^T x_0 + \lambda_2^k v_2 v_2^T x_0 + \ldots + \lambda_n^k v_n v_n^T x_0. \tag{4.3}$$

The idea of the power method, given by algorithm 4.1 is to indirectly compute the matrix powers by iteratively forming a matrix vector product.

Algorithm 4.1 Power Iteration

```
1   x_0 = random vector
2   for k=0,1,2,...
3          x_{k+1} = Ax_k
4          λ_{k+1} = ||x_{k+1}||_2
5          x_{k+1} = (1/λ_{k+1}) x_{k+1}
```

4.2 Inverse Iteration

The inverse iteration is a variant of the power method, which allows to find eigenvalues and eigenvectors close to a value called shift μ. This method can be used to find eigenvectors for known eigenvalues and converges quicker than the power method at the cost of the solution of a linear system at each iteration, see algorithm 4.2. The shift μ can be updated during the iteration with the vector norm σ for faster convergence.

Algorithm 4.2 Inverse Iteration

```
1               x_0 = random vector
2               for k = 0,1,2,...
3                   (A − μI)x_{k+1} = x_k
4                   σ_{k+1} = ||x_{k+1}||
5                   x_{k+1} = (1/σ_{k+1}) x_{k+1}
```

4.3 QR-Algorithm

The QR-Algorithm is such an iterative method to compute the eigenvalue decomposition of the matrix A [Fra61]. The inner loop of the QR-algorithm with shift μ is given by algorithm 4.3.

Algorithm 4.3 QR-Algorithm

```
1   while  a_{n,n−1} > ε
2           QR = (A_k − μI)
3           A_{k+1} = RQ + μI
4           Q̃_k = Q̃_k Q_k  (optional)
5   end
```

If A is Hermitian then the off diagonal entries in A_k converge always to zero and A_k approaches the diagonal matrix of eigenvalues Λ [1]. $\tilde{Q}_k$ converges simultaneously to the matrix of eigenvectors V. However, it is not required to compute this matrix explicitly,

$$A_{k+1} = Q_k^T A_k Q_k \tag{4.4}$$

$$= Q_k^T ... Q_1^T A_1 Q_1 ... Q_k \tag{4.5}$$

$$= \tilde{Q}_k^T A_1 \tilde{Q}_k \tag{4.6}$$

$$V \Lambda V^T \approx \tilde{Q}^T A_1 \tilde{Q}. \tag{4.7}$$

The lowest right element of A_k converges most rapidly. This permits to deflate the matrix by its last row and column each time an eigenvalue has converged. The iteration is then continued with the deflated matrix $\tilde{A}_k$. If the the lowest right element of the matrix A_k is chosen as shift, then this element converges cubically to an eigenvalue of A if A is Hermitian,

$$A_k = \begin{pmatrix} \tilde{A}_k & 0 \\ 0 & \lambda \end{pmatrix}. \tag{4.8}$$

A QR-decomposition can be computed using the modified Gram-Schmidt algorithm in $O(n^3)$ steps. However in the QR-algorithm the explicit computation of Q can be avoided and if A is tridiagonal, then a single QR-iteration step can be computed in $O(n)$ steps.

The QR-Algorithm is numerically stable, in a sense that round off errors do not considerably accumulate during the iterations and compromise the computed eigenvalues.

4.3.1 Relation with the Power Iteration and Inverse Iteration

The QR-algorithm can be interpreted as a combination of the power iteration and inverse iteration [Par73]. If no shift is applied then the iteration (equation (4.6)) may be rewritten as follows:

$$\tilde{Q}_{k−1} A_k = A_1 \tilde{Q}_{k−1} \tag{4.9}$$

$$\tilde{Q}_{k−1} Q_k R_k = A_1 \tilde{Q}_{k−1} \tag{4.10}$$

$$\tilde{Q}_k R_k = A_1 \tilde{Q}_{k−1}. \tag{4.11}$$

---

[1]For asymmetric matrices the matrix A_k converges to the Schur-factor of A, if A does not have multiple or complex eigenvalues.

By multiplying equation (4.11) with the first unit vector and considering that the R matrix is upper triangular one realises that the left part of (4.12) is just the power iteration,

$$\tilde{Q}_k = A_1 \tilde{Q}_{k-1} R_k^{-1} \tag{4.12}$$

$$\tilde{Q}_k e_1 = A_1 \tilde{Q}_{k-1} R_k^{-1} e_1 \tag{4.13}$$

$$\tilde{q}_1^{(k)} = \frac{1}{r_{1,1}^{(k)}} A_1 \tilde{q}_1^{(k-1)}. \tag{4.14}$$

If equation (4.11) is inverted and transposed before the multiplication with the first unit vector e_1, the inverse power method becomes apparent if the matrix A is symmetric,

$$R_k^{-1} \tilde{Q}_k^{-1} = \tilde{Q}_{k-1}^{-1} A_1^{-1} \tag{4.15}$$

$$\tilde{Q}_k R_k^{-T} = \tilde{A}_1^{-T} \tilde{Q}_{k-1} \tag{4.16}$$

$$A_1^T \tilde{Q}_k R_k^{-T} e_1 = \tilde{A}_1^{-T} \tilde{Q}_{k-1} e_1 \tag{4.17}$$

$$\frac{1}{r_{1,1}^{(k)}} A^T \tilde{q}_1^{(k)} = \tilde{q}_1^{(k-1)}. \tag{4.18}$$

Hence the topmost element a_{11} of A_k converges to the dominant eigenvalue λ_1 and the first column $\tilde{q}_1$ of $(\tilde{Q})$ converges to the corresponding eigenvector v_1 of λ_1 if the convergence criteria of the power method are met,

$$\lim_{k \to \infty} \tilde{Q}_k^T A \tilde{Q}_k e_1 = \lim_{k \to \infty} \tilde{q}_1^{T(k)} r_{1,1}^{(k)} e_1 \, \tilde{q}_1^{(k)} \tag{4.19}$$

$$= v_1^T \lambda_1 v_1 e_1 = \lambda_1 e_1. \tag{4.20}$$

During the QR iteration all the elements on the main diagonal of the R matrix converge simultaneously. It resembles de facto a nested power iteration. Note that above only the convergence of the first element of the R matrix was shown. However, in practise the last element of the R matrix converges first and the the deflation is carried out as shown in equation (4.8).

4.4 Eigenvalues by Bisection

If only few eigenvalues are required the bisection algorithm offers an alternative to the QR-algorithm. The bisection algorithm finds a single eigenvalue in an selected interval in $n \log(\epsilon)$ time. Recall that the determinant of a matrix is equal to the product of its eigenvalues (equation (4.21)) and that the eigenvalues of a matrix can be shifted by subtracting a multiple of the identity matrix (equation (4.22)),

$$det(A) = \prod \lambda \tag{4.21}$$

$$(A - \mu I)x = \lambda - \mu. \tag{4.22}$$

The upper principal minors of the matrix A form furthermore a Sturm sequence. This means that the number of sign changes of the determinants of the principal minors is equal to the number of negative eigenvalues. As determining the determinant of a tridiagonal matrix requires only $O(n)$ steps, one can find eigenvalues by shifting the spectrum in an interval which is successively halved in each step. A start interval can be determined by Gershgorin's circle theorem.

Algorithm 4.4 Bisection Algorithm

```
1       while ( abs(λ_l − λ_u) > tol*(abs(λ_l) + abs(λ_u)) && abs(λ_l) + abs(λ_u) > tol)
2           % interval midpoint
3           λ_c = 1/2 (λ_l + λ_u);
4           n_s = 0;
5           p_2 = 0;
6           p_1 = 1;
7           % count sign changes in upper determinant
8           for idx=1:n
9                   p = (A_ii − λ_c)p_1 − (A_{ii+1})^2 p_2
10                   if (p·_1 ≤ 0)
11                           n_s = n_s + 1
12                   end
13                   p_2 = p_1
14                   p_1 = p
15           end
16           % select half with sign change
17           if (n_s > n−k)
18               λ_u = λ_c
19           else
20               λ_l = λ_c
21           end
22       end
```

Chapter 5

Eigenvalue Algorithms for Large Sparse Matrices

Even if a matrix where sparse the QR-algorithm becomes inapplicable once the matrix is to large. Exceptions are matrices with very small bandwidths. Two general methods are analysed in the following section which allow the computation of eigenvalues for large sparse matrices. The first approach uses the Lanczos algorithm to factorise the matrix into tridiagonal form before computing the eigenvalues. The second approach uses a correction method in form of the Jacobi-Davidson algorithm which directly finds the eigenpairs. Especially the well established Lanczos method is extensively covered in the literature [Saa11], [Par87], [CW02], [Gol96] and [BDJ^{+}00], [Vor].

5.1 Projection Methods

Projection methods approximate a matrix by its projection onto an orthogonal subspace. Orthogonal projection methods find wide application in the solution of linear systems and eigenvalue computation. The projection is chosen such that the original problem is much easier to solve with the projected matrix and that the solution approximated with the projected matrix is close to the proper solution of the original problem.

The eigenvalues of a matrix A are computed by constructing the projection matrix Q at first, then by finding the eigenvalues of the projected matrix $Q^T AQ$ and finally by projecting the eigenvalues s of the projected system back to get approximate eigenvalues z,

$$Ax = \lambda x \tag{5.1}$$
$$Q^T AQs = \lambda s \tag{5.2}$$
$$z = Qs. \tag{5.3}$$

An intriguing property of the orthogonal projection methods is that the residual of the approximated solution r is orthogonal to the projection space,

$$r = AQs - \lambda Qs \tag{5.4}$$
$$Q^T r = 0. \tag{5.5}$$

The eigenvalues and eigenvectors of the projected system are referred to as Ritz values and Ritz vectors respectively.

5.2 Lanczos Iteration

The Lanczos iteration is a method to compute the Hessenberg decomposition of a Hermitian matrix [Lan50]. Such a decomposition precedes the QR-algorithm, as the iterations on the tridiagonal Hessian are much less costly, as shown in the previous chapter. Furthermore an incomplete decomposition can be computed such that the rank of T is much lower than the rank of A. A complete Lanczos factorisation takes $O(n^2)$

operations, if A is a banded sparse matrix with few nonzero diagonals. The computed Hessenberg matrix T computed by algorithm 5.1 takes the form given in equation (5.6),

$$T = \begin{bmatrix} a_1 & b_2 & & & \\ b_2 & a_2 & b_3 & & \\ & b_3 & ... & ... & \\ & & ... & a_{m-1} & b_m \\ & & & b_m & a_m \end{bmatrix}. \tag{5.6}$$

Algorithm 5.1 Lanczos-Algorithm

```
1   q_0 = 0̄
2   q_1 = arbitrary nonzero vector (1)
3   q_1 = q_1/||q_1||
4   b_1 = 0
5
6   for  i = 1..m
7              q_{i+1} = Aq_i - b_i q_{i-1}
8              a_i     = q_{i+1}^T q_i
9              q_{i+1} = q_{i+1} - a_i q_i
10             b_{i+1} = ||q_{i+1}||
11             q_{i+1} = q_{i+1}/b
12  end
13             % compute approximate eigenvalues by bisection
14             % sort out spurious eigenvalues
15             % approximated eigenvectors by inverse iteration
```

5.2.1   The Lanczos-Iteration as Eigenvalue Method

The eigenvalues θ of T equal the eigenvalues λ of A upon complete factorisation with exact arithmetic as both matrices are similar. The same holds for the Ritz vectors z and eigenvectors v. If the factorisation is computed with finite precision or incomplete , i.e. only performed until step k, then the factorisation has an residual $r^{(k)}$ (equation (5.8)),

$$AQ_k - Q_k T_k = r^{(k)} e_k^T \tag{5.7}$$
$$= \beta_{k+1} q_{k+1} e_k^T \tag{5.8}$$
$$T_k = S_k \Theta_k S_k^T \tag{5.9}$$
$$Z_k = Q_k S_k. \tag{5.10}$$

Implementations of the Lanczos algorithm vary depending on when the eigenvalues are calculated. Parlett [Par87] recommends to calculate the eigenvalues after each iteration. However, this becomes expensive if many iterations are required to achieve convergence. Hence Cullum [CW02] recommends almost a complete factorisation before the eigenvalues are calculated.

5.2.2   Convergence Estimation

The residual $r^{(k)}$ of the factorisation also leads to an residual $r_i^{(k)}$ of the approximate eigenvectors $z_i^{(k)}$ (equation (5.14)),

$$AQ_k = Q_k T_k + r^{(k)} e_k^T \tag{5.11}$$
$$AQ_k = Q_k S_k \Theta_k S_k^T + r^{(k)} e_k^T \tag{5.12}$$
$$(A - \theta_i^{(k)} I) Q_k s_i^{(k)} = \beta_{k+1} q_{k+1} e_k^T s_i^{(k)} \tag{5.13}$$
$$(A - \theta_i^{(k)}) z_i^{(k)} = r_i^{(k)}. \tag{5.14}$$

The residual norm of the Ritz vectors $||r_i^{(k)}||$ is therefore determined only by the last coefficient β_{k+1} and the last element of the respective eigenvector $s_i^{(k)}$ of the matrix T_k (equation (5.15)). The error of the

approximate eigenvalue can be estimated by the residual norm and the distance γ_i to the closest eigenvalue (equation (5.16)). Hence only the eigenvalues of the tridiagonal system, but not the Ritz-vectors themselves are required to estimate the convergence,

$$||r_i^{(k)}|| = \beta_{k+1} s_{i,k} \tag{5.15}$$

$$|\theta_i^{(k)} - \lambda_i| \approx (\beta_{k+1} s_{i,k})^2 / \gamma_i \tag{5.16}$$

$$\gamma_i = min_{i \neq j} |\theta_i^{(k)} - \theta_j^{(k)}|. \tag{5.17}$$

The Lanczos method usually requires many iterations m before the eigenvalues converge. Sometimes the number of iterations exceeds the matrix rank n, [CW81]. The eigenvalues in the required range are found by bisection, due to the large size of the projected system. The respective eigenvectors can be computed by inverse iteration afterwards.

5.2.3 Invariant Subspaces

If the matrix A contains at least one eigenvalues multiple times, i.e. if its spectrum is degenerated, then after some iterations the Lanczos has explored a complete invariant subspace. As a consequence the eigenvalues of the subspace are not only approximations but the exact eigenvalues of A as their residual βs_{ij} is zero up to rounding errors. However, the iteration cannot continue and some modifications are required to find the remaining eigenvalues. There are three possibilities:

- Restarting the Lanczos iteration with a start vector orthogonal to the converged eigenvectors. However, this requires the storage of the complete subspace.

- Using a block-version of the Lanczos algorithm starting with a set of orthogonal vectors. However, this produces a banded matrix with more than three diagonals and requires to deflate the block once a residual becomes zero.

- Discretising the PDE, such that it is not degenerated and hence does not contain multiple eigenvalues.

Even if the matrix does not contain invariant subspaces, a similar behaviour is observed once the eigenvalues of T start to converge.

5.2.4 Loss of Orthogonality and Spurious Eigenvalues

As the Lanczos algorithm is only based on a three term recurrence, orthogonality of the basis vectors Q is soon lost in finite precision arithmetic,

$$Err = Q^T Q - I. \tag{5.18}$$

As a consequence the matrices A and T are not anymore similar and have a different set of eigenvalues. However, the eigenvalues sets are not completely different, but

- The matrix T contains spurious eigenvalues. A spurious eigenvalue is an eigenvalue of the tridiagonal matrix T which is not an eigenvalue of the original matrix A. Spurious eigenvalues usually occur directly after one of the eigenvalues of T has converged to an eigenvalue of A. Thereafter the spurious eigenvalue converges to a copy of one of the already converged eigenvalues.

- The eigenvalues of A are still eigenvalues of the matrix T. To obtain all eigenvalues of A it is necessary to continue the iterations, such that the rank of T exceeds the rank of A.

Several methods have been developed to overcome the shortcomings of the Lanczos method and to compute the correct eigenvalues. There are basically two ideas, the first idea is to restore the orthogonality [PS79] and the second idea is to identify and remove spurious eigenvalues from the result, see [Pai80].

5.2.5 Partial Reorthogonalisation

A possible remedy is to keep track of the loss of orthogonality by a recurrence formula and to reorthogonalise the last two basis vectors against the complete basis [Sim84],

$$\max_{ij}(Q^T Q - I) > \sqrt{\epsilon}\kappa(A). \tag{5.19}$$

Although the partial reorthogonalisation is less expensive than a complete reorthogonalisation, it may become infeasible for large subspaces. It can be shown that the eigenvalues of the partially reorthogonalised matrix are as accurate as if they were computed with full orthognonalisation, as long as equation (5.19) is satisfied.

5.2.6 Filtering Spurious Eigenvalues

Paige [Pai80] showed that all the eigenvalues of A will eventually be contained in T, if the iteration is continued long enough. Note that this could yield a matrix T which is larger than A.

Spurious and truly multiple eigenvalues could be distinguished by testing the orthogonality of the approximate eigenvectors. The true multiplicity of the eigenvalue is equal to the number of approximate eigenvectors who's inner product is close to zero,

$$v_i^T v_j = (Qs_j)^T Qs_i, i \neq j. \tag{5.20}$$

However, this method can not be applied in practise as it requires to store the complete basis Q.

Cullum [CW81] described how one may sort out the spurious eigenvalues by comparing the eigenvalues of T to the eigenvalues of the matrix T without first row and column T_2.

- Keep a single copy of θ_i as converged eigenvalue, if is multiple eigenvalue of T.
- Keep θ_i as approximation if it is a single eigenvalue of T and not an eigenvalue of T_2.
- Discard θ_i as spurious if it is single eigenvalue of T and also eigenvalue of T_2.

5.2.7 Lanczos Iteration for Generalised Eigenvalue Problems

The Lanczos method is adapted for generalised eigenproblems by forming the basis Q such that it is orthogonal with respect to its generalised inner product with B,

$$Ax = \lambda Bx \tag{5.21}$$
$$AQ = BQT \tag{5.22}$$
$$Q^T BQ = I. \tag{5.23}$$

Algorithm 5.2 is the Lanczos iteration adapted for the generalised eigenvalue problem. The most obvious difference is the solution of a linear system at every iteration step. This can of course be formed with with an iterative solver such as the conjugate gradient or minimum residual method [PS75]. Note that in the actual implementation the matrix vector products of BQ are not explicitly formed but kept in an auxiliary matrix.

Algorithm 5.2 Generalised Lanczos Algorithm

```
1   for  i = 1..m
2               q_{i+1}  = Av_i;
3               Bq_{i+1}  = q_{i+1};
4               q_{i+1}  = q_{i+1} - b_i q_{i-1}
5               a_i      = q_{i+1}^T Bq_i
6               q_{i+1}  = q_{i+1} - a_i q_i
7               b_{i+1}  = sqrt(q_{i+1}^T Bq_{i+1})
8   %           if (b < eps) stop
9               q_{i+1}  = q_{i+1}/b
10              % compute approximated eigenvalues
11  %           T = SΘS
12              % test for convergence
13  %           r = |βs_{i,j}|/||Qs_i||
14  %           if ( ||r|| < tol )
15  %                   break
16  %           end
17  end
```

5.2.8 Approximate the Solution of Linear Systems

Some of the algorithms for large sparse matrices introduced in this chapter require the solution of a symmetric linear system at each iteration (equation (5.24)),

$$Ax = b. \tag{5.24}$$

It is reasonable to approximate the solution instead to solve them directly. The most elementary solver for symmetric linear system is the conjugate gradient (CG) method. However it is not applicable to indefinite systems. An equation solver applicable for indefinite systems is the minimum residual method (MINRES). The key of this method is the factorisation of the matrix A into a tridiagonal matrix T and an orthogonal basis Q (equation (5.26)). This can be achieved by the Lanczos method. The factorised system is easily solved as T is tridiagonal (equation (5.28)),

$$AQ_k = Q_k T_k + \beta_{k+1} q_{k+1} \tag{5.25}$$

$$= Q_{k+1} \tilde{T}_k \tag{5.26}$$

$$Q_k^T A Q_k y = b \tag{5.27}$$

$$\tilde{T}_k = b. \tag{5.28}$$

The residual norm can be estimated with the help of an orthogonal transformation by the matrix $D_{k+1} Q_{k+1}^T$ (equation (5.33)). Where D is the diagonal matrix of the residuals. Note that by choice $y^{(1)} = 0$ and hence $\beta_1 = ||b||, q_1 = 1/\beta_1 b$,

$$D_{k+1} = diag(||\beta_1||, ..., ||\beta_{k+1}||) \tag{5.29}$$

$$r_k = ||A_k Q_k y - b|| \tag{5.30}$$

$$= ||Q_{k+1} \tilde{T}_k - b|| \tag{5.31}$$

$$= ||D_{k+1} Q_{k+1}^T Q_{k+1} \tilde{T}_k - D Q_{k+1}^T b|| \tag{5.32}$$

$$= ||D_{k+1} \tilde{T}_k - \beta_1 e_1||. \tag{5.33}$$

5.2.9 Numerical Experiment

The convergence of eigenvalues approximated by the Lanczos method depend strongly on the distribution of the eigenvalues, see figure 5.1. For the two dimensional Laplacian convergence sets in almost immediately and a new eigenvalue is found on average at every other iteration. However, in case of the one dimensional Laplacian none of the eigenvalues converges until the matrix is completely factorised, see figure 5.1.

The Lanczos routine is tested on a Laplacian operator for the one dimensional domain 1x250 and the two dimensional domain 10x25. The eigenvalues are compared to the analytic solutions and are accepted as converged if the error $|\lambda_i - \theta_i|$ is less than the square root of the machine precision ϵ. The start vector consists of random elements.
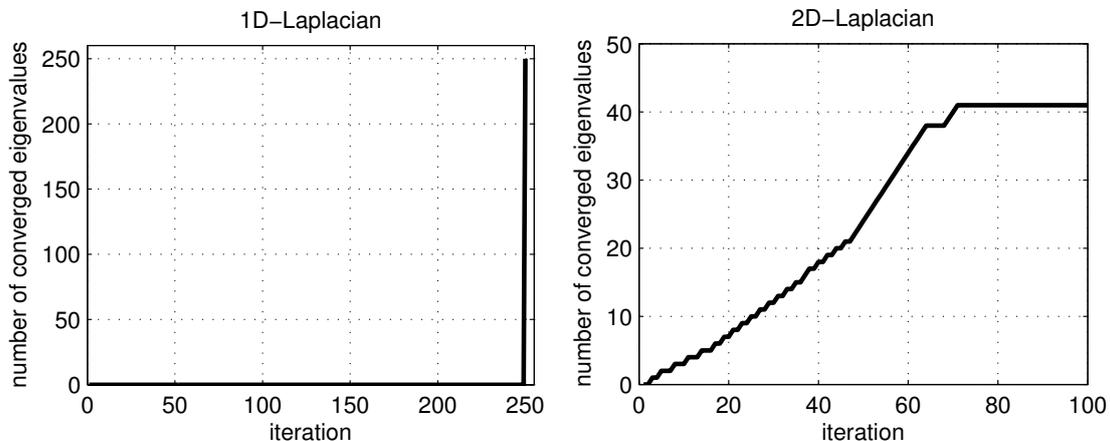

Figure 5.1: Convergence of eigenvalues approximated with the Lanczos method. Acceptance tolerance $\sqrt{\epsilon} \approx 10^{-7}$, see equation (5.16).

5.3 The Jacobi-Davidson Method

The Jacobi-Davidson method is best understood if one considers the Davidson method first.

5.3.1 The Davidson Method

Other than the Lanczos-Iteration, the Davidson method computes approximate eigenvectors v and eigenvalues θ directly without factorising the matrix A [Dav75]. It does so by constructing an orthogonal basis constituting of successive corrections to an initial vector (equation (5.35)). The correction step is a simplified inverse iteration step where the matrix A is approximated by its diagonal D. Therefore the computational costs per iteration are just of order $O(n)$. However, the algorithm converges only for matrices with dominant diagonal and usually requires a restart after some iteration to keep the basis at a tractable size. The core algorithm consists of three steps: calculating the residual (equation (5.34)), correcting the current approximation (equation (5.35)) and orthogonalising the new search vector against the existing search space (equation (5.36)). The complete algorithm is listed as algorithm 5.3,

$$r^{(k)} = (A - \theta_k I)v_k \tag{5.34}$$

$$(D - \theta_k I)v_{k+1} = -r^{(k)} \tag{5.35}$$

$$v_{k+1} = (I - V_k V_k^T)v_{k+1}. \tag{5.36}$$

Algorithm 5.3 Davidson Algorithm

```
1            % guess initial search space
2            V_{:,1} = rand();
3            V = V/||V||;
4            k = 1;
5            while (1)
6                    % expand projected system
7                    AV_{:,k} = AV_{:,k}
8                    H_{1:k,k} = V_{:,k}^T AV
9                    H_{k,1:k} = H_{1:k,k}^T
10                   % BV and G are only updated in case of GHEP
11                   BV_{:,k} = BV_{:,k}
12                   G_{1:k,k} = V_{:,k}BV
13                   G_{k,1:k} = G_{1:k,k}
14                   % find approximate eigenvalue
15                   [y  θ] = eigs(H_{1:k,1:k}, G_{1:k,1:k}, 1,'LA');
16                   % approximated eigenvector
17                   x = Vy;
18                   % residual (r = Ax - θBx)
19                   r = AVy - θBVy
20                   % check for convergence
21                   if (||r|| < abstol)
22                           return;
23                   end
24                   % expand search space
25                   V_{:,k+1} = minres(D - \theta I, r);
26                   % orthogonalise by modified Gram–Schmidt
27                   V_{:,k+1} = mgs(V_{:,1:k}, V_{:,k+1}, k);
28                   k = k+1;
29        end % while 1
```

5.3.2 Jacobi-Davidson Algorithm

The Jacobi-Davidson [SV00] method combines the Davidson method with an idea from Jacobi, which is to search for corrections only in an space orthogonal to the current vector,

$$A(x + \delta x) = \lambda(x + \delta x) \tag{5.37}$$

$$x^T \delta x = 0. \tag{5.38}$$

This space is determined by the projector,

$$P = I - x_k x_k^T. \tag{5.39}$$

Thus the Jacobi-Davidson algorithm is identical to the Davidson method beside the correction step, which solves

$$(I - x^T x)(Ax - \theta I)(I - x^T x)x_{k+1} = -r \tag{5.40}$$

$$x_{k+1} = XX^T x_{k+1}. \tag{5.41}$$

The correction equation is singular and has to be solved approximately. If the correction equation is solved exactly, the method converges cubically.

5.3.3 The Jacobi-Davidson Method for the Generalised Eigenvalue Problem

The extension of the Jacobi-Davidson method to generalised Hermitian eigenvalue problem requires three major changes. Firstly, the basis V is orthogonalised with respect to the generalised inner product with B,

$$V^T B V = I. \tag{5.42}$$

The matrix B is furthermore incorporated into the calculation of the residual,

$$r = Au - \theta B u. \tag{5.43}$$

And thirdly the correction equation changes as follows:

$$-r = (I - Q^T Z)(A - \theta B)(I - Z^T Q)t \tag{5.44}$$

$$Q = Au = AVs_1 \tag{5.45}$$

$$Z = Bu = BVs_1. \tag{5.46}$$

Again the matrix-matrix products AV and BV are stored in auxiliary memory to avoid unnecessary recalculation.

Chapter 6

Available Software

As finding eigenvalues and eigenvectors is a standard task with many applications a variety of implementations exist.

6.1 LAPACK

The Linear Algebra PACKage, short LAPACK is a well established software suite. It provides basic eigenvalue routines such as the QR algorithm. However, it does not include specialist solvers for large sparse eigenproblems. LAPACK is released under the BSD license and is accessible in several ways

- original documentation and software from netlib [UoTUoCL], the latest stable release as of November 2011 is 3.4.0

- in most Linux distributions as precompiled package optimised for current processors, for example in Debian 6.0.4 (Squeeze) the package groups liblapack* and libatlas*

- in Matlab/Octave integrated and accessible via the command *eig*

There exist furthermore offshoots which offer support for SMP, GPU or quad precision computing.

6.2 ARPACK

The ARnoldi PACKage, short ARPACK provides solvers for large sparse eigensystems. It implements the restarted Arnoldi and Lanczos methods. It does not perform any matrix operations directly, but requires respective routines to be provided elsewise. ARPACK was originally released by the Rice University [LDC97], but is not maintained anymore. An up to date version named Arpack New Generation (arpack-ng) is provided by an open source initiative [Led11]. arpack is like LAPACK a standard package in most Linux distributions and is integrated in Matlab/Octave integrated as the command *eigs*.

6.3 Lanczos Algorithms for Large Symmetric Eigenvalue Computations

The book by Cullum covering extensively Eigenvalue computations with the Lanczos method [CW02] is accompanied by a second volume consisting of source code listings. The second volume and the source can also be downloaded at netlib [CW].

6.4 Jacobi-Davidson Implementation

Gerard L.G. Sleijpen provides a Matlab implementation of the Jacobi-Davidson method for the standard [Slea] and generalised eigenvalue problem [Sleb].

Chapter 7

Conclusion

7.1 Research Questions and Objectives

Following topics are planned to become part of the final thesis.

- Discretisation

  - Can the PDE be consistently discretised with the finite element method?
  - Comparing the results obtained with the consistent finite element method and the finite difference method with fixed singularity

- Numerical Analysis

  - Investigating and comparing the capability of both the Lanczos and Jacobi-Davidson method and selecting the more suitable algorithm
  - Determining the number of required grid points for computing the eigenvalues with sufficient accuracy

- Implementation

  - Implementing the final algorithm on an SMP or GPU system
  - Optional: Implementing on both systems and comparing the performance

- Physics

  - Using the application to compute the eigenvalues of the cubically confined hydrogen atom at least in two dimension, with respect to the
    * size of the cavity,
    * aspect ratio of the cavity, including the limit case towards one dimension,
    * location of the hydrogen atom inside the cavity.
  - Comparing of the results to the unconfined and spherically confined hydrogen atom
  - Optional: Computing the hydrogen atom in three dimensions and comparing to the energy levels in two dimension
  - How does value of the partition function change depending on the well size and the location of the atom inside the well?

7.2 Conclusion and Prospect

In this study numerical methods for the hydrogenic Schrödinger equation were analysed. It was shown that the separation of variables in spherical coordinates is possible for the equation of the unconfined atom. This allows the analytical or the numerical computation of the energy levels. However, if the atom is confined and shifted to an arbitrary position inside the cavity, a separation of variables becomes impossible. In this case a Cartesian coordinate system is preferred.

There exists no analytic solution to the unseparated equation and therefore an approximation is required. The solutions have furthermore a discontinuous derivative at the location of the nucleus due to the singular potential. If the variables are not separated then this point is located inside the domain. In two and higher dimensions a convergent finite difference scheme can be set up by using a variable grid. At the moment the variable grid is not optimal as it is set up heuristically. This could be improved by implementing adaptive grid refinement by using a posteriori information of computed solutions.

A finite element discretisation is proposed, as it offers a higher versatility for adaptive grids, and its convergence requirements respective smoothness of the solution are weaker than those of the finite difference method. Higher order approximations are not favoured, as the solutions are not smooth enough close to the nucleus.

Numerical methods for large sparse eigensystems are well developed. Both the Lanczos and Jacobi-Davidson method are suitable algorithms. Several established implementations of these algorithms are freely available. The algorithms and their existing implementations have to be closer analysed in the oncoming study to determine whether existing software should be used or yet another implementation on a recent GPU/SMP architecture is favourable.

Chapter 8

Appendix

List of Algorithms

List of Figures

List of Tables

Bibliography

[And76]   Andrews. Singular Potentials in one Dimension. *American Journal of Physics*, 44:1064–1066, 1976.

[BDJ⁺00]   Z. Bai, J. Demmel, Dongarra J., A. Ruhe, and H. van der Vorst. *Templates for the solution of Algebraic Eigenvalue Problems: A Practical Guide*. SIAM, Philadelphia, 2000.

[BH86]   D Baye and P-H Heenen. Generalised meshes for quantum mechanical problems. *J. Phys. A: Math. Gen.*, 19:2041–2059, 1986.

[Bol56]   Bolton, H.C. and Scoinsa, H.I. and Rushbrooke, G.S. Eigenvalues of differential equations by finite-difference methods. *Mathematical Proceedings of the Cambridge Philosophical Society*, 52:215–229, 1956.

[Bry84]   Garnett W. Bryant. Hydrogenic impurity states in quantum-well wires. *Phys. Rev. B*, 29:6632–6639, 1984.

[cos12]   COSSE - Computer Simulations for Science and Engineering. `http://www.kth.se/en/studies/programmes/master/em/cosse`, 2012.

[Cru09]   Cruz, Salvador A., Colín-Rodríguez, Ricardo. Spheroidal Confinement of a Single Electron and of the Hydrogen Atom, the H_2^+ and HeH^{++} Molecular Ions With Arbitrary Nuclear Positions Along the Major Axis. *International Journal of Quantum Chemistry*, 109(13):3041–3054, 2009.

[CW]   Jane K. Cullum and Ralf A. Willoughby. Lanczos algorithms for large symmetric eigenvalue computations, volume 2 - programs. `http://www.netlib.org/lanczos/`.

[CW81]   Jane K. Cullum and Ralph. A. Willoughby. Computing eigenvalues of very large symmetric matrices-An implementation of a Lanczos algorithm with no reorthogonalization. *Journal of Computational Physics*, 44((2)):329–358, 1981.

[CW02]   Jane K. Cullum and Ralph A. Wiloughby. *Lanczos Algorithms for Large Symmetric Eigenvalue Computations Volume 1: Theory (Classics in Applied Mathematics)*. SIAM: Society for Industrial and Applied Mathematics, 1st edition, 2002.

[Dav75]   E.R. Davidson. The iterative calculation of a few of the lowest eigenvalues and corresponding eigenvectors of large real-symmetric matrices. *Journal of Computational Physics*, 17, 1975.

[dGtSCA46] S. R. de Groot and ten Seldam C. A. On the Energy Levels of a Model of the Compressed Hydrogen Atom. *Physica*, XII(9-10):669–682, 1946.

[Dom11]   Dommelen, Leon van. Quantum Mechanics for Engineers, 2011.

[ec-12]   Erasmus mundus. `http://ec.europa.eu/education/external-relation-programmes/doc72_en.htm`, 2012.

[esa12]   European Space Agency - European Space Research and Technology Centre (ESA-ESTEC). `http://www.esa.int/esaMI/ESTEC/index.html`, 2012.

[Fra61]   J. G. F. Francis. The QR Transformation - A Unitary Analogue to the LR Transformation. *The Computer Journal*, 4(3):265–271, 1961.

[Gar98]   Garcke. Berechnung von Eigenwerten der Stationären Schrödingergleichung mit der Kombinationstechnik, 1998.

[GC97]   A N Gordeyevy and S C Chhajlanyz. One-dimensional hydrogen atom: a singular potential in quantum mechanics. *J. Phys. A: Math. Gen.*, 30:6893–6909, 1997.

[Gol96]   Golub, Gene H. and van Loan, Charles F. *Matrix Computations*. The John Hopkins University Press, Stanford, Cornell, 3rd edition, 1996.

[Kil77]   John Killingbeck. A pocket calculator determination of energy eigenvalues. *J. Phys. A: Math. Gen.*, 10(6):L99–L103, 1977.

[KS34]   G. E. Kimball and G. H. Shortley. The Numerical Solution of Schrödinger's Equation. *Phys. Rev.*, 45:815–820, Jun 1934.

[KSY98]   D S Krähmer, W P Schleich, and V P Yakovlev. Confined quantum systems: The parabolically confined hydrogen atom. *J. Phys. A: Math. Gen.*, 31:4493–4520, 1998.

[KVI09]   M K Kretov, Scherbinin A V, and Pupyshev V I. States of a hydrogen atom in an impenetrable cubic cavity. *Phys. Scr.*, 80, 2009.

[Lan50]   Cornelius Lanczos. An iteration method for the solution of the eigenvalue problem of linear differential and integral operators. *J. Res. Nat. Bureau Standards*, 45(4):255–282, 1950.

[LDC97]   R.B. Lehoucq, Sorensen D.C., and Yang C. Arpack. `http://www.caam.rice.edu/software/ARPACK/`, 1997.

[Led11]   S. Ledru. arpack-ng. `http://forge.scilab.org/index.php/p/arpack-ng/`, 2011.

[Lev85]   Levin, F.S. and Shertzer, J. Finite-element solution of the Schrodinger equation for the helium ground state. *Physical Review A*, 32(6), 1985.

[LKR79]   E. Ley-Koo and Sergio Rubinstein. The hydrogen atom within spherical boxes with penetrable walls. *J. Chem. Phys.*, 71:351–357, 1979.

[Lou59]   Rodney Loudon. One-Dimensional Hydrogen Atom. *American Journal of Physics*, pages 649–655, 1959.

[MdBB37]   Michels, de Boer, and Bijl. Remarks Concerning Molecular Interaction and their Influence on the Polarisation. *Phyisca*, VI:981–994, 1937.

[Pai80]   C. C. Paige. Accuracy and Effectiveness of the Lanczos Algorithm for the Symmetric Eigenproblem. *Linear Algebra & Its Applications*, 34:235–258, 1980.

[Par73]   Parlett, B. N. and Poole, W. G. A Geometric Theory for the QR, LU and Power Iterations. *Journal on Numerical Analysis*, 10(2):389, 1973.

[Par87]   Beresford N. Parlett. *The Symmetric Eigenvalue Problem (Classics in Applied Mathematics)*. Society for Industrial Mathematics, 1987.

[PS75]   C. C. Paige and M. A. Saunders. Solution of sparse indefinite systems of linear equations. *SIAM J. Numer. Anal.*, 12(4):617–629, 1975.

[PS79]   B.N. Parlett and D.S Scott. Lanczos Algorithm with Selective Orthogonalization. *Mathematics of computation*, 33(145):217–238, 1979.

[Ric11]   Richardson, L.F. The Approximate Arithmetical Solution by Finite Differences of Physical Problems Involving Differential Equations, with an Application to the Stresses in a Masonry Dam. *Transactions of the Royal Society of London. Series A*, 210:307, 1911.

[Saa11]   Youcef Saad. *Numerical Methods for Large Eigenvalue Problems (Algorithms and Architecture for Advanced Scientific Computing)*. Halsted Pr, 2nd edition, 2011.

[Sch26]   Erwin Schrödinger. Quantisierung als Eigenwertproblem (Erste Mitteilung). *Annalen der Physik*, 79:361–376, 1926.

[Sha49]   C.E. Shannon. Communication in the Presence of Noise. *Proceedings of the IRE*, 37(1):10 – 21, jan. 1949.

[Sim84]   HD Simon. Analysis of the symmetric Lanczos algorithm with reorthogonalization methods. *Linear Algebra and Its Applications*, 61((C)):101–131, 1984.

[Slea]   Gerard L.G. Sleijpen.   jdqr.   `http://www.staff.science.uu.nl/~sleij101/JD%5Fsoftware/JDQR.html`.

[Sleb]   Gerard L.G. Sleijpen.   jdqz.   `http://www.staff.science.uu.nl/~sleij101/JD%5Fsoftware/JDQZ.html`.

[Spa04]   et. al. Spataru. Excitonic Effects and Optical Spectra of Single-Walled Carbon Nanotubes. *Phys. Rev. Lett.*, 92(7), 2004.

[SPM]   K.D. Sen, V.I. Pupyshev, and H.E. Jr. Montgomery. Exact Relations for Confined One-Electron Systems. *Advances in Quantum Chemistry*, 57:25.

[SV00]   Gerard L. G. Sleijpen and Henk A. Van Der Vorst. A Jacobi-Davidson Iteration Method for Linear Eigenvalue Problems. *SIAM J. Matrix Anal. Appl*, 17:401–425, 2000.

[SW38]   Arno Sommerfeld and H Welker. Künstliche Grenzbedingungen beim Keplerproblem. *Annalen der Physik*, 5. Folge 32:56–65, 1938.

[TSCH90]   I-H. Tan, G. L. Snider, L. D. Chang, and E. L. Hu. A Self-Consistent Solution of Schrödinger-Poisson Equations Using a nonuniform Mesh. *Journal of Applied Physics*, 68:4071–4076, 1990.

[UoTUoCL]   Berkeley; Univ. of Colorado Denver; Univ. of Tennessee; Univ. of California and NAG Ltd. LAPACK (Linear Algebra PACKage). `http://www.netlib.org/lapack/`.

[vN31]   J. von Neumann. Die Eindeutigkeit der Schrödingerschen Operatoren. *Mathematische Annalen*, 104(1):570–578, 1931.

[Vor]   Henk A. van der Vorst. Computational Methods for Large Eigenvalue Problems.

[Yur08]   Yurenev, P. V. and Scherbinin, A.V. and Pupyshev, V.I. Shifts of the Hydrogen Atom in a Cylindrical Cavity. *International Journal of Quantum Chemistry*, 108(14):2666–2667, 2008.