Spectral Estimates for Schrödinger Operators

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Abstract

Spectral Estimates for Schrödinger Operators.

Alexandra Lemus Rodríguez.

In quantum mechanics, one of the most studied problems is that of solving the Schrödinger equation to find its discrete spectrum. This problem cannot always be solved in an exact form, and so comes the need of approximations. This thesis is based on the theory of the Schrödinger operators and Sturm-Liouville problems. We use the Rayleigh-Ritz variational method (mix-max theory) to find eigenvalues for these operators.

The variational analysis we present in this thesis relies on the sine-basis, which we obtain from the solutions of the particle-in-a-box problem. Using this basis we approximate the eigenvalues of a variety of potentials using computational implementations. The potentials studied here include problems such as the harmonic oscillator in d dimensions, the quartic anharmonic oscillator, the hydrogen atom, a confined hydrogenic system, and a highly singular potential. When possible the results are compared either with those obtained in exact form or results from the literature.

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To my mother and father,

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Introduction

In non-relativistic quantum mechanics, Schrödinger's equation governs the time evolution of a particle's wave function, and is given by

$$i\hbar\frac{\partial}{\partial t}\Psi(x,t) = -\frac{\hbar^2}{2m}\Delta_x\Psi(x,t) + V(x)\Psi(x,t). \tag{1}$$

In this equation, $\hbar \approx 6.6255 \times 10^{-27}$ erg sec is known as Planck's constant, $V(\mathbf{x})$ is a potential independent of time, and the operator Δ_x is the Laplacian corresponding to the kinetic energy.

One of the main problems in Quantum Mechanics is to determine the solutions of this equation, in particular, finding the energy levels of a particle. There are many different approaches to solve it, one is to find exact solutions and the other is to use methods that will give estimates of the solutions that cannot be found in an exact manner. The examples in physics that have an exact solution are very few compared to the ones that do not. This motivates an approach that allows us to approximate solutions. In this thesis we describe an approach using variational analysis.

In Chapter 1 we review the theory concerning Schrödinger operators. In particular, its relation with functional analysis, and we present the variational characterization of the discrete spectrum of a Schrödinger operator, related to the min-max principle.

In Chapter 2 we review the theory of Sturm-Liouville problems. This is of importance because we can transform a number of problems in the Schrödinger normal form.

In Chapter 3 we describe the variational analysis of quantum mechanical problems and introduce a special variational basis related to the solutions of the particle-in-a-box problem.

In Chapter 4 we describe the implementation of a program to approximate the eigenvalues and the eigenfunctions of a problem. This chapter is also devoted to the results obtained in the application of the variational method to a variety of explicit problems.

Chapter 1

Schrödinger Operators

1.1 Introduction

For the problem of finding the solutions to the Schrödinger equation given in (1), we can rescale the equation, and given the assumption that $\Psi(x,t) = \psi(x)\Theta(t)$, derive a time independent Schrödinger equation which is represented as follows

$$-\Delta\psi(x) + V(x)\psi(x) = E\psi(x). \tag{1.1}$$

In this chapter we will relate this equation to the famous Schrödinger operator. The results from this part are mainly studied by Griffiths [9], Gustafson and Sigal [10], Hall *et al.* [13], Hannabus [14], Kryezig [16], and Reed and Simon [19].

1.2 Operator theory

The theory of Schrödinger operators relies on functional analysis. In the following section, we describe various results that are very helpful for the purposes of this work.

Let $\mathcal{H}$ be a Hilbert space, in particular the space of all quantum mechanical states of a given system. The main example used in quantum mechanics, and in this thesis is the L^2-space defined as follows

$$L^2(\mathbb{R}^d) = \left\{ \psi : \mathbb{R}^d \to \mathbb{C} \mid \int_{\mathbb{R}^d} |\psi|^2 < \infty \right\}.$$

$\mathcal{H}$ is endowed with the inner product given by

$$(\psi, \phi) = \int_{\mathbb{R}^d} \overline{\psi}\phi \, dx, \text{ with } x \in \mathbb{R}^d, \tag{1.2}$$

where $\overline{\psi}$ represents the complex conjugate of ψ. The above inner product defines the **norm**

$$||\psi|| = (\psi, \psi)^{\frac{1}{2}}.$$

We recall that an operator A in a Hilbert space $\mathcal{H}$ is a mapping of its domain $D(A) \subset \mathcal{H}$ into $\mathcal{H}$.

Definition 1.1. A **linear operator** A in a Hilbert space $\mathcal{H}$ is an operator such that

1. the domain $D(A)$ and the range $R(A)$ of A are subsets of $\mathcal{H}$,
2. for all $\psi, \phi \in D(A)$ and scalars $\alpha, \beta \in \mathbb{C}$,

$$A(\alpha\psi + \beta\phi) = \alpha A\psi + \beta A\phi.$$

Definition 1.2. An operator A on $D(A) \subset \mathcal{H}$ is **bounded** if

$$||A|| = \sup_{\{\psi \in D(A)\}} \frac{||A\psi||}{||\psi||} = \sup_{\{\psi \in D(A) \mid ||\psi||=1\}} ||A\psi|| < \infty.$$

Lemma 1.1. [10] *If an operator A satisfies $||A\psi|| \leq C||\psi||$ (with C independent of ψ) for ψ in a dense domain $D(A) \subset \mathcal{H}$, then it extends to a bounded operator, also denoted A on all $\mathcal{H}$, satisfying the same bound: $||A\psi|| \leq C||\psi||$ for $\psi \in \mathcal{H}$.*

This result is important because the domain in which an operator is defined can be a very complicated set, with this lemma we can find operators that are extended to bounded operators and not worry about the domain itself.

Definition 1.3. Given an operator A on $\mathcal{H}$, an operator B is called the **inverse** of A if $D(B) = Ran(A)$, $D(A) = Ran(B)$, and

$$BA = 1|_{Ran(A)}, \ AB = 1|_{Ran(B)},$$

where $Ran(A) = \{A\psi \mid \psi \in D(A)\}$. The inverse of A is denoted by A^{-1}.

We note that finding the inverse of an operator is equivalent to solving the equation $A\psi = f$ for all $f \in Ran(A)$.

Definition 1.4. The operator A is said to be **invertible** if A has a bounded inverse.

An operator A is not invertible if it is not bounded below, that is, if there is no $c > 0$ such that $||A\psi|| \geq c||\psi||$ for all $\psi \in \mathcal{H}$.

We assume that all operators A are defined on a dense domain $D(A) \subset \mathcal{H}$.

Definition 1.5. The **adjoint** of an operator A on a Hilbert space $\mathcal{H}$ is the operator A^* satisfying

$$(A^*\psi, \phi) = (\psi, A\phi)$$

for all $\phi \in D(A)$, for $\psi \in D(A^*)$, where

$$D(A^*) = \{\psi \in \mathcal{H} \mid |(\psi, A\phi)| \leq C_\psi ||\phi||, \ \forall \ \phi \in D(A)\}.$$

Note that the constant C_ψ is independent of ϕ.

Definition 1.6. An operator A is **symmetric** if

$$(A\psi, \phi) = (\psi, A\phi)$$

for all $\psi, \phi \in D(A)$.

Theorem 1.1. **(Hellinger-Toeplitz Theorem)** [16] *Let T be a symmetric linear operator on all of a complex Hilbert space $\mathcal{H}$, then T is bounded.*

Definition 1.7. An operator A is **self-adjoint** if $A = A^*$.

It follows immediately from this definition that a self-adjoint operator is also symmetric, but the opposite is not always true, we have then the following lemma.

Lemma 1.2. [10] *If A is bounded and symmetric, then it is self-adjoint.*

Theorem (1.1) and the above lemma (1.2) suggest that the class of operators that we can use is sufficiently wide.

Definition 1.8. A self-adjoint operator A is called **positive**, denoted $A > 0$ if

$$(\psi, A\psi) > 0$$

for all $\psi \in D(A)$, $\psi \neq 0$. Similarly we may define non-negative, negative and non-positive operators.

Theorem 1.2. [10] *If A is a self-adjoint operator, then for any $z \in \mathbb{C}$ with $Im(z) \neq 0$, the operator $A - zI$ has a bounded inverse, and this inverse satisfies*

$$||(A - zI)^{-1}\phi|| \leq |Im(z)|^{-1}||\phi||.$$

The above theorems are important concerning the domains of linear operators.

1.2.1 Variational characterization of the spectrum of an operator

Definition 1.9. The **spectrum** of an operator A on $\mathcal{H}$ is the subset of $\mathbb{C}$ given by

$$\sigma(A) = \{\lambda \in \mathbb{C} \mid A - \lambda \text{ is not invertible}\}.$$

Definition 1.10. The complement of the spectrum of an operator A in $\mathbb{C}$ is called the **resolvent set** of A, denoted by

$$\rho(A) = \mathbb{C} \setminus \sigma(A)$$

We note that for $\lambda \in \rho(A)$, the operator $(A - \lambda)^{-1}$, called the **resolvent** of A, is well-defined.

Definition 1.11. A number $\lambda \in \mathbb{C}$ is called an **eigenvalue** of the operator A, if the equation $(A - \lambda)\psi = 0$ has a non-zero solution $\psi \in D(A)$.

Definition 1.12. The **discrete spectrum** of an operator A is

$$\sigma_{disc}(A) = \{\lambda \in \mathbb{C} \mid \lambda \text{ is an isolated eigenvalue of } A \text{ with finite multiplicity}\},$$

isolated meaning that some neighborhood of λ is disjoint from the rest of $\sigma(A)$.

Definition 1.13. The **essential spectrum** of an operator is

$$\sigma_{ess}(A) = \sigma(A) \setminus \sigma_{disc}(A).$$

Theorem 1.3. [10] *If* $A = A^*$ *then* $\sigma(A) \subset \mathbb{R}$.

Definition 1.14. The ratio

$$\frac{(\psi, A\psi)}{(\psi, \psi)}, \tag{1.3}$$

where $\psi \in D(A)$ is called the **Rayleigh quotient**.

Let us note that if $||\psi|| = 1$, the Rayleigh quotient becomes $(\psi, A\psi)$.

Let T be a self-adjoint operator on $\mathcal{H}$ as previously defined. We can apply variational techniques to derive a characterization of the spectrum of T, that is, to find its eigenvalues.

Theorem 1.4. [10] *Given T as above with spectrum $\sigma(T) \subset [a, \infty)$, then*

$$\frac{(\psi, T\psi)}{(\psi, \psi)} \geq a$$

for all $\psi \in D(T)$.

The above theorem states that the Rayleigh quotient is bounded below.

Theorem 1.5. [10] *Let $S(\psi) = (\psi, T\psi)$ for $\psi \in D(T)$ with $||\psi|| = 1$. Then $\inf \sigma(T) = \inf S$. Moreover, $\lambda = \inf \sigma(T)$ is an eigenvalue of T if and only if there is a minimizer $\psi \in D(T)$ for $S(\psi)$ such that $||\psi|| = 1$.*

The above result leads to the Ritz variational principle, given that for any $\psi \in D(T)$,

$$(\psi, T\psi) \geq \lambda = \inf \sigma(T)$$

and equality holds if and only if $T\psi = \lambda\psi$, this particular ψ is the corresponding eigenfunction, for all other $\psi \in \mathcal{H}$, all values of $(\psi, T\psi)$ are upper bounds to the operator's eigenvalues.

Theorem 1.6. (Min-max principle) [10] *The operator T has at least n eigenvalues (counting multiplicities) less than $\inf \sigma_{ess}(T)$, if and only if $\lambda_n < \inf \sigma_{ess}(T)$ where*

$$\lambda_n = \inf_{\{D_n \in D(T) \ | \ dim(D_n) = n\}} \max_{\{\psi \in X \ | \ ||\psi|| = 1\}} (\psi, T\psi).$$

In this case, the n-th eigenvalue is exactly λ_n.

Theorem 1.7. **(The Rayleigh-Ritz theorem)** [19] *Let T be a semibounded self-adjoint operator. let $D_n \subset D(T)$ be an n-dimensional subspace, and let P be the orthogonal projection onto D_n. Let $T_{D_n} = PTP$. Let $\widehat{\lambda}_1,\ \widehat{\lambda}_2, \ldots, \widehat{\lambda}_n$ be the eigenvalues of $T_{D_n} \restriction D_n$, ordered by $\widehat{\lambda}_1 \leq \widehat{\lambda}_2 \leq \ldots \leq \widehat{\lambda}_n$. Then*

$$\lambda_i(T) \leq \widehat{\lambda}_i,\ i = 1, \ldots, n.$$

In particular, if T has eigenvalues (counting multiplicity) $\lambda_1, \ldots, \lambda_k$ at the bottom of its spectrum with $\lambda_1 \leq \ldots \leq \lambda_k$, then

$$\lambda_i \leq \widehat{\lambda}_i,\ i = 1, \ldots, \min(k, n).$$

It is important to point out that the min-max principle can be used to find upper estimates for the eigenvalues of operators, thus having both quantitative and qualitative consequences.

In practice, we simply analyze T in an N-dimensional linear space $D_N = span\{\phi_1, \ldots, \phi_N\}$, where $\{\phi_i\}_i^N$ is an orthonormal basis for D_N. The eigenvalues of the $N \times N$ matrix $[(\phi_i, T\phi_j)]$ then provide upper bounds to the first N eigenvalues of T. Very often, as N is increased, these upper approximations steadily improve. We shall use this technique in later chapters.

1.3 Schrödinger operators

Let $\mathcal{H} = L^2(\mathbb{R}^d)$ with inner product (ψ, ϕ) as defined in (1.2), at the beginning of this chapter. We can write equation (1.1) as a linear operator.

Definition 1.15. The linear operator $H : D(H) \subset \mathcal{H} \to \mathcal{H}$ defined by

$$H = -\Delta + V \tag{1.4}$$

is called a Schrödinger operator; where $-\Delta$ is the Laplacian in d dimensions, and $V : \mathbb{R}^d \to \mathbb{R}$ a given potential corresponding to a quantum mechanical problem.

It is important to know for which potentials V, the Schrödinger operator is self-adjoint. The main purpose is also to characterize the spectrum $\sigma(H)$ of the operator H, because that gives information about the nature of the solutions of the main Schrödinger equation.

In the following section we write a series of important results related to this operator.

Theorem 1.8. [10] *Let $V(x)$ be a continuous function on $\mathbb{R}^d$ satisfying $V(x) \geq 0$ and $V(x) \to \infty$ as $|x| \to \infty$, then*

1. *H defined as in (1.4) is self-adjoint on $\mathcal{H}$.*
2. *$\sigma(H)$ consists of isolated eigenvalues $\{\lambda_i\}_{i=1}^{\infty}$ with $\lambda_i \to \infty$ as $n \to \infty$.*

Theorem 1.9. [10] *Let $V(x)$ be a continuous function on $\mathbb{R}^d$ satisfying $V(x) \to 0$ as $|x| \to \infty$, then*

1. *H defined as in (1.4) is self-adjoint on $\mathcal{H}$.*
2. *$\sigma_{ess}(H) = [0, \infty)$, which means that H can have only negative isolated eigenvalues, possibly accumulating at 0.*

Theorem 1.10. [10] *Let Λ be a cube in $\mathbb{R}^d$, and V a continuous function on Λ. Then the Schrödinger operator $H = -\Delta + V$, acting on the space $L^2(\Lambda)$ with Dirichlet boundary conditions has purely discrete spectrum, accumulating at ∞.*

The Dirichlet boundary conditions are given by $\psi|_{\partial\Lambda} = 0$, which means that $\psi = 0$ outside Λ. We shall refer to such a Sturm-Liouville problem by the term "particle-in-a-box".

The previous results give us very valuable information in the study of the solutions of different problems of quantum mechanics corresponding to various potentials. The eigenvectors associated with the discrete spectrum of H are called bound states, while the points in the discrete spectrum are called bound state energies, or energy levels.

We can use the variational characterization of the spectrum described in the previous section to analyze a series of problems.

1.3.1 The dimension d

The most common quantum mechanical problems are usually posed in dimension $d = 1, 2, 3$.

If the dimension is $d = 1$ the two parts of the Schrödinger operator become $\Delta = \frac{\partial^2}{\partial x^2}$, and $V : \mathbb{R} \to \mathbb{R}$.

When $d > 1$ the structure of the Laplacian becomes more complicated. In order to work in higher dimensions, we transform the problem from cartesian coordinates into a more appropriate system. Let $x \in \mathbb{R}^d$ be $x = (x_1, \dots, x_d)$, we can transform this vector into another vector $\rho = (r, \theta_1, \dots, \theta_{d-1})$, where $r = ||x||$. Then the we assume that the wave function is now given by

$$\Psi_\ell(\rho) = \psi(r) Y_\ell(\theta_1, \dots, \theta_{d-1}), \tag{1.5}$$

with $\psi(r)$ being the spherically symmetric factor, and Y_ℓ the spherical harmonic factor, where $\ell = 0, 1, 2, \dots$. The derivation of this change of variables can be found in Sommerfeld [22].

The above analysis is particularly suitable for central potentials given as functions of $r = ||x||$ rather than as functions of the individual components of $x \in \mathbb{R}^d$. In these cases we denote the potential function as $V(r)$.

Given a spherically symmetric potential $V(r)$ in a d-dimensional space, if we change the system of coordinates described above, and remove the spherical harmonic factor, as shown in Hall, *et al.* [13], we get the following radial Schrödinger equation

$$-\frac{d^2\psi}{dr^2} - \frac{d-1}{r}\frac{d\psi}{dr} + \frac{\ell(\ell+d-2)}{r^2}\psi + V(r)\psi = E\psi. \tag{1.6}$$

A correspondence can now be made with a problem on the half line in one dimension, we define the radial wave function

$$R(r) = r^{(d-1)/2}\psi(r), \quad R(0) = 0.$$

We can then rewrite equation (1.6) as

$$-\frac{d^2R}{dr^2} + UR = ER, \tag{1.7}$$

with effective potential

$$U(r) = V(r) + \frac{(2\ell+d-1)(2\ell+d-3)}{4r^2}. \tag{1.8}$$

Given the above analysis is now clear how one can work with central potentials in dimensions $d > 1$. We also note that the above equation (1.7) is in the form of a Sturm-Liouville problem, but on the semi-infinite interval $[0, \infty)$. We shall return to this in chapter 2.

1.3.2 Examples

Clearly, the family of potentials which have exact analytical solutions is very small compared to the family of those that do not. We now exhibit a series of examples that have exact solutions. These examples are of utmost importance because they provide us with exactly soluble test problems for our variational methods: if the method gives good results for these, we can apply it to others with some degree of confidence.

Harmonic oscillator. The harmonic oscillator is a problem in quantum mechanics that is linked to the classical spring, as it can be thought of as a particle having the oscillating behaviour of a spring-mass system.

The one-dimensional harmonic oscillator is defined by the potential $V(\chi) = \omega\chi^2$. As mentioned before, using a scaling argument we can reduce this problem to a family of problems related by a factor to the potential $V(x) = x^2$. We simply use the transformation $\chi = sx$, and substitute it in equation

$$-\frac{d^2}{d\chi^2}\psi + (\omega\chi)^2\psi = E_\chi\psi,$$

obtaining the new equation

$$\frac{1}{s^2}\left(-\frac{d^2}{dx^2}\psi + \omega s^4 x^2\psi\right) = E_\chi\psi,$$

if we then find s such that $\omega s^4 = 1$, we will get the relation

$$\omega^{\frac{1}{4}} E_x\psi = E_\chi\psi$$

Therefore we need only to solve the following differential equation defined by the Schrödinger operator

$$-\frac{d^2}{dx^2}\psi + x^2\psi = E\psi \tag{1.9}$$

with solutions

$$\psi_n(x) = H_n(x)e^{-\frac{x^2}{2}}, \tag{1.10}$$

where H_n is the Hermite polynomial of order n. The energy levels are given by

$$E_n = 2n + 1,\ n = 0, 1, 2, \dots \tag{1.11}$$

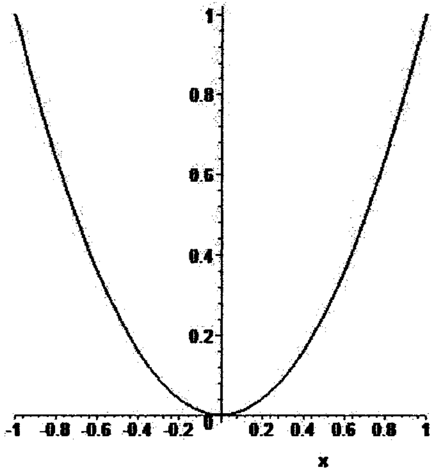

Figure 1.1: Harmonic oscillator

We can also find the solutions for this problem in dimension $d = 3$, studied in Griffiths [9] and Greiner [8], where the symmetric potential is $V(r) = r^2$, and the equation needed to solve is the following

$$-\frac{d^2R}{dr^2} + UR = ER, \tag{1.12}$$

with effective potential

$$U(r) = r^2 + \frac{\ell(\ell+1)}{r^2}. \tag{1.13}$$

and energy levels

$$E_{n\ell} = 4n + 2\ell - 1, \tag{1.14}$$

where $\ell = 0, 1, 2, \ldots$, and $n = 1, 2, 3, \ldots$.

Using algebra we can extend to the problem for dimensions $d \geq 2$. This is done comparing the effective potentials, the one for dimension $d = 3$ given by (1.13) and

$$U(r) = r^2 + \frac{(2\ell' + d - 1)(2\ell' + d - 3)}{4r^2}. \tag{1.15}$$

for dimension d.

We set the equation

$$\ell(\ell+1) = \left(\ell' + \frac{d-1}{2}\right)\left(\ell' + \frac{d-3}{2}\right)$$

in order to solve for ℓ, obtaining

$$\ell = \ell' + \frac{d}{2} - \frac{3}{2},$$

and substituting back into the values of the energy (1.14), thus obtaining

$$E_{n\ell d} = 4n + 2\ell' + d - 4, \tag{1.16}$$

where $\ell' = 0, 1, 2, \ldots$ denotes de angular momentum of the d-dimensional problem.

Hydrogen-like atoms. The electron in the hydrogen atom is bound by the Coulumb potential. The hydrogen atom is modeled as an infinitely heavy and fixed proton with an electron revolving around it. The potential that defines this problem is given by $V(x) = -\frac{e^2}{|r|}$ with $r = ||x||$ for $x \in \mathbb{R}^d$.

If $d = 1$ the problem of the hydrogen atom is as interesting as it is troublesome, given its nature, the singularity splits the space in two pieces acting as a barrier. The solutions to this problem are not trivial and require a thorough analysis of the geometry of the problem as studied by [2].

Thus, the hydrogen atom is usually studied in 3 dimensions, [9], [8]. The discrete spectrum of this problem in $d = 3$ is given by the energy levels

$$E_{n\ell} = -\frac{e^2}{4(n+\ell)^2}, \tag{1.17}$$

where $\ell = 0, 1, 2, \ldots$, and $n = 1, 2, 3, \ldots$.

We can also scale and extend this problem to the d-dimensional case using the

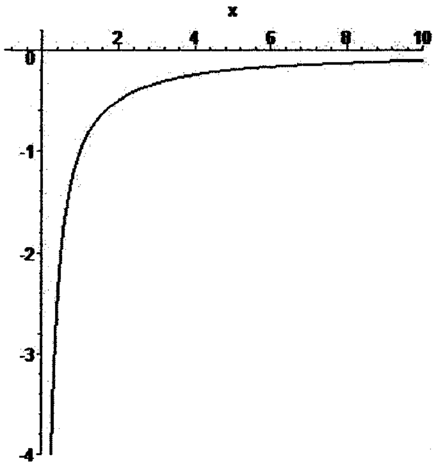

Figure 1.2: Hydrogen atom

arguments and algebraic analysis as in the above example. In this case we get the following energy levels

$$E_{n\ell d} = -\frac{e^2}{4\left(n+\ell+\frac{d}{2}-\frac{3}{2}\right)^2}, \tag{1.18}$$

again with $\ell = 0, 1, 2, \ldots$, and $n = 1, 2, 3, \ldots$.

The above examples are discussed as they will serve as test problems in the following chapters. For more insight on the solutions for this problems see literature from Greiner [8], Griffiths [9], Gustafson and Sigal [10], and Hannabus [14].

Chapter 2

Sturm-Liouville Problems

2.1 Introduction

Sturm-Liouville systems arise in a large number of physical problems. They are one-dimensional models of oscillating systems, and therefore we can also relate the notion of energy to these particular problems.

The general form of a classical Sturm-Liouville problem is a second-order real differential equation given by

$$-\frac{d}{dx}\left(p(x)\frac{du}{dx}\right)+q(x)u=\lambda w(x)u \tag{2.1}$$

defined on a finite or infinite interval $a < x < b$ with boundary conditions.

It is obvious that the functions p, q and w are relevant in the analysis of this differential equation. For example, if we assume that p and w are constant, without any loss of generality we can use a scaling argument and remove them from equation. This is, if we divide (2.1) by p and let $t = \gamma x$ be the new independent variable, where $\gamma = (w/p)^{\frac{1}{2}}$, then we obtain

$$-\frac{d^2u}{dt^2}+Q(t)u=\lambda u, \tag{2.2}$$

where $Q(t) = q(x)/w$. In fact, equation (2.2) is known as the Liouville or Schrödinger normal form. Even more, by means of the Liouville transformation that we will describe in the section 2.3, the general Sturm-Liouville problem (2.1) can be transformed into this normal form.

From now on we will refer to these kind of problems as Sturm-Liouville problems or SLP.

Definition 2.1. We say that the SLP (2.1) is **regular** if

1. a and b are finite.
2. p, q and w are defined on the closed interval $[a, b]$ and are continuous (maybe except for a finite number of discontinuities), with p and w strictly positive.
3. The regular boundary conditions

$$\begin{aligned} a_1 u(a) &= a_2 p(a) u'(a) \\ b_1 u(b) &= b_2 p(b) u'(b) \end{aligned} \tag{2.3}$$

   are imposed at the end points of the interval, where a_1, a_2, b_1 and b_2 are real numbers different from zero.

Our interest in regular Sturm-Liouville problems will be justified by the application we shall use in the following chapters.

Given equation (2.1), for the rest of this chapter we will assume that the functions $p, q, w : \mathbb{R} \to \mathbb{R}$ defined on the interval $[a, b]$ are piecewise continuous, and that p and w are strictly positive. If we take p, q and w to be complex function, then these problems will no longer in the Sturm-Liouville form. The results from this chapter are mainly studied by Braun [3], Coddington *et al.* [5], Pryce [18], and Sagan [20].

2.2 Sturm-Liouville theory

We can rewrite the Sturm-Liouville equation as the homogeneous equation

$$-\left(p(x)u'\right)' + \left(q(x) - \lambda w(x)\right)u = 0. \tag{2.4}$$

This is a second-order linear differential equation; it is not always self-evident that the solution to this kind of equations is unique or if it even exists. We resort to a familiar result from the theory of differential equations.

Theorem 2.1. [3]

Given the equation

$$\frac{d^2y}{dt^2} + g(t)\frac{dy}{dt} + h(t)y = 0 \tag{2.5}$$

with initial conditions

$$y(t_0) = y_0,\ y^{'}(t_0) = y_0'. \tag{2.6}$$

Let the functions $g(t)$ and $h(t)$ be continuous functions in the open interval $\alpha < t < \beta$. Then, there exists one and only one function $y(t)$ satisfying the differential equation (2.5) and the prescribed initial conditions (2.6) on the entire interval $\alpha < t < \beta$. In particular, any solution $y = y(t)$ of (2.5) which satisfies $y(t_0) = 0$ and $y'(t_0) = 0$ at the time $t = t_0$ must be identically zero.

Although this theorem refers to the homogeneous case only, it can be extended to the non-homogeneous case, [3] and [5].

From the above theorem if we let p, q and w be as we defined in the previous section on the interval $[a, b]$, the Sturm-Liouville equation (2.4) has unique solutions satisfying the initial conditions

$$u(c) = u_c, (pu'(c)) = v_c,$$

for $c \in [a, b]$.

In the case of the Sturm-Liouville problems local solutions will not suffice: we need global solutions that satisfy boundary conditions, not only initial solutions. This is not a trivial problem, and further analysis is required as the solutions are related to the eigenvalues and the eigenfunctions.

2.2.1 Operator form of SLP

We can relate the Sturm-Liouville theory to the operator theory from chapter 1. Because (2.1) is a linear equation, we can define the differential operator

$$L = \frac{1}{w(x)} \left\{ -\frac{d}{dx} \left(p(x) \frac{d}{dx} \right) + q(x) \right\} \tag{2.7}$$

on the interval $a < x < b$. The domain of this operator is contained in the set of admissible solutions for the Sturm-Liouville problems, which are the square integrable functions with respect to the weight function w

$$L^2([a, b]) = \left\{ u : [a, b] \to \mathbb{C} \mid \int_a^b |u(x)|^2 w(x) dx < \infty \right\}.$$

The above space has the weighted inner product defined as

$$(u, v) = \int_a^b u \bar{v} w dx, \tag{2.8}$$

$\bar{v}$, again, representing the complex conjugate of v.

One of the properties of L is that it is a linear operator, following directly from its differential and multiplicative form, and it satisfies

$$L(\alpha u + \beta v) = \alpha L u + \beta L v.$$

Another fundamental property of this operator is that it is self-adjoint and symmetric with respect to the weight function $w(x)$, implying that with the given inner product (2.8) the following equality holds true

$$(Lu, v) = (u, Lv).$$

Lemma 2.1. (Green's Identity) [18] *Let $u, v \in D(L)$ be twice differentiable functions defined on $[a, b]$, then*

$$\int_a^b (Lu\overline{v} - uL\overline{v})\, w dx = [pu\overline{v}' - pu'\overline{v}]_a^b.$$

The above lemma is useful to solve this boundary condition problems. In particular, Green's identity relies on the fact that L is self-adjoint, and if u and v satisfy the boundary conditions in (2.3), we have that $[pu\overline{v}' - pu'\overline{v}]_a^b = 0$.

There exists a different and equivalent approach to the operator theory of the Sturm-Liouville problems using the operator form

$$\mathcal{L} = -\frac{d}{dx}\left(p(x)\frac{d}{dx}\right) + q(x), \tag{2.9}$$

and the inner product defined in (1.2), studied by Sagan [20].

2.2.2 Eigenvalues and Eigenfunctions of the SLP

We can now pose equation (2.1) as the eigenvalue problem

$$Lu = \lambda u \tag{2.10}$$

where $u \in D(L)$ and it satisfies the conditions (2.3).

We have the following important results.

Property 2.1. [18]

Let u be as above and the functions p, q and w that define the operator L in (2.7) be piecewise continuous on $[a,b]$, with p, $w > 0$, then:

1. *The eigenvalues of the Sturm-Liouville problem (2.10) are real.*
2. *The eigenfunctions belonging to distinct eigenvalues are orthogonal with respect to the inner product (2.8).*

Theorem 2.2. [5], [18], [20]

For a regular SLP the following statements hold true:

1. *The eigenvalues λ_k are simple, this is, there do not exist two linearly independent eigenfunctions with the same value.*
2. *The eigenvalues can be ordered in an increasing sequence $\lambda_0 < \lambda_1 < \lambda_2 < \ldots$, and with this labeling the eigenfunction u_k corresponding to the eigenvalue λ_k has exactly k zeros on the open interval (a,b).*
3. *The set of eigenfunctions $\{u_k\}$ form a complete orthogonal set of functions over (a,b) with respect to the inner product (2.8). That is, any function $f \in L^2([a,b])$ can be represented on (a,b) by its Fourier series with respect to the eigenfunctions*

$$f(x) \sim \sum_{k=0}^{\infty} c_k u_k(x),$$

where $c_k = \frac{(f,u_k)}{(u_k,u_k)}$.

2.3 Schrödinger normal form

If we take $p = w = 1$ all the above theory is equivalent to the theory for the Schrödinger operator in dimension $d = 1$. We note that the normal Liouville form

(2.2) is equivalent to the one-dimensional Schrödinger equation that we studied in chapter 1.

For dimension $d = 1$ we can rewrite equation (1.1) as

$$-\frac{d^2}{dx^2}\psi + V(x)\psi = E\psi \tag{2.11}$$

where ψ, $V(x)$ and E represent the wave function, potential, and level of energy of the system respectively.

As mentioned before, there are a number general Sturm-Liouville problems that can be transformed into the Liouville normal form; we demonstrate this in the following subsection.

2.3.1 The Liouville transformation

We can apply several transformations to equation (2.1), with the functions p, q, w satisfying the conditions above [18].

Independent variable transformation.

Let $x = x(t)$, this makes (2.1) transform into a new Sturm-Liouville differential equation that is of the form

$$-\frac{d}{dt}\left(\frac{p(x(t))}{x'}\frac{du}{dt}\right) + q(x(t))x'u = \lambda w(x(t))x'u, \tag{2.12}$$

where we assume that the mapping $x(t) : (\alpha, \beta) \to (a, b)$ is onto and that x' has the same sign over the interval $\alpha < t < \beta$.

Dependent variable transformation.

Let $u = m(x)v$, where $m(x)$ is a given function. If we substitute u in (2.1) we get

$$-\frac{d}{dx}\left(p\frac{d}{dx}mv\right) + qmv = \lambda wmv,$$

which is not in self-adjoint form, though we can multiply by m both sides of the above expression to obtain

$$\left(pm^2v'\right)' + \left(-\left(pm'\right)'m + qm^2\right)v = \lambda wm^2v, \tag{2.13}$$

which is now a self adjoint problem.

Liouville's transformation.

Using both transformations above we get the transformed equation,

$$-\frac{d}{dt}\left(P\frac{dv}{dt}\right) + Qv = \lambda Wv, \tag{2.14}$$

with

$$\begin{aligned} P &= \frac{pm^2}{x'}, \\ Q &= (-(pm')' + qm)mx', \\ W &= wm^2x'. \end{aligned}$$

The boundary conditions are also transformed to

$$\begin{aligned} A_1v(\alpha) &= A_2(Pv')(\alpha), \\ B_1v(\beta) &= B_2(Pv')(\beta). \end{aligned} \tag{2.15}$$

where

$$A_1 = (a_1 m^2 - a_2 p m' m)|_{x=a},\ A_2 = a_2,$$

$$B_1 = (b_1 m^2 - b_2 p m' m)|_{x=b},\ B_2 = b_2.$$

Furthermore, if p, q and w are such that w/p and q/w are defined, then the general SLP in (2.1) is finally converted to the Liouville normal form or Schrödinger form

$$-\frac{d^2v}{dt^2} + Iv = \lambda v, \tag{2.16}$$

using Liouville's transformation given by

$$\begin{aligned} t &= \int \sqrt{\frac{w}{p}} dx, \\ m &= (pw)^{-\frac{1}{4}}. \end{aligned} \tag{2.17}$$

This is an important result: thanks to this transformation it is possible to solve the general SLP by first transforming to the Liouville normal form (2.16).

2.3.2 A numerical approach to solving the SLP

For some symmetric problems that can be transformed to the Sturm-Liouville form, it is possible to develop what is called a shooting method to calculate its eigenvalues and eigenfunctions.

Given the problem (2.16) we can solve it numerically defining it as an initial value problem satisfying the left hand boundary conditions over a specific range, depending on the nature of the problem. The differential equation is then solved for a sequence of trial values of the eigenvalue λ. The eigenvalue is adjusted until the required number of zeros is obtained and the right hand boundary conditions are met. We refer to Theorem (2.2).

Though the process is quite straightforward it is not always easy to implement such a numerical program. But it opens the door to have another option to approximate the eigenvalues which we can later compare to the original method studied in this work, that is the variational technique. For an example see Appendix B.

2.4 The particle-in-a-box

The infinite square well potential, also known as the one-dimensional particle-in-a-box problem, is an important in quantum mechanics. The potential that defines the Schrödinger operator is the following:

$$V(x) = \begin{cases} 0, & \text{if } 0 \leq x \leq b; \\ \infty, & \text{otherwise.} \end{cases}$$

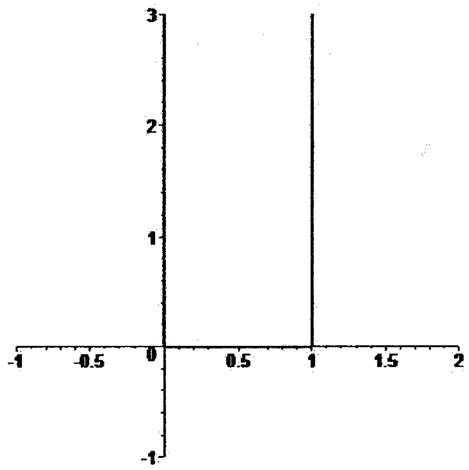

Figure 2.1: Infinite square well potential

The Schrödinger operator H defines the following equation which is also a regular Sturm-Liouville problem, with ψ defined on the interval $0 \leq x \leq b$ and boundary conditions $\psi(0) = \psi(b) = 0$, and with

$$-\frac{d^2}{dx^2}\psi = E\psi. \tag{2.18}$$

Solving this equation we find that for $n = 1, 2, \ldots$ we have the following energy levels or eigenvalues

$$E_n = \left(\frac{n\pi}{b}\right)^2, \tag{2.19}$$

with corresponding wave functions or eigenfunctions

$$\psi_n(x) = \sqrt{\frac{2}{b}} \sin\left(\frac{n\pi x}{b}\right). \tag{2.20}$$

We can verify the importance of theorem (2.2) with this example. The energy levels form an increasing sequence, and as these levels go up, each successive wave function or state has one more node. The eigenfunctions form a complete orthonormal set: from Fourier analysis we know that each $\psi \in L^2([0,b])$ can be written $\psi = \sum_{n=1}^{\infty} c_n \psi_n$. We also note that $L^2([0,b]) \subset L^2(\mathbb{R})$, this basis might be useful later on in the analysis of problems in a wider space.

Chapter 3

Variational Analysis for Schrödinger Operators

3.1 Introduction

When facing a quantum mechanical problem, in order to approximate the values of the ground state energy, we can apply the variational principle which characterizes the discrete spectrum. There are a number of variational approaches that have been widely used since the nineteenth century to solve physical problems, in particular, the work of Lord Rayleigh and Walther Ritz opened up the doors to the use of these techniques.

The simplest variational analysis consist in the following: given a particular problem with potential $V(x)$, we define the Schrödinger operator H as in (1.1). By the theory studied in chapter 1, the domain of this operator is $D(H) \subset L^2(\mathbb{R}^d)$, and H is self-adjoint. We then choose a normalized trial function $\psi \in D(H)$, which may be different from ψ_0, the ground state. Then we know that

$$E_0 \leq (\psi, H\psi),$$

where E_0 is the ground-state energy. This means that by finding a suitable trial function we can obtain an upper bound of the ground state energy [9].

Even more, if we choose ψ as a function of x and other parameters, we can manipulate these parameters in order to obtain a better approximation, that is to say, a lower upper bound. If we know the exact solution of a particular problem we can compare results and study the accuracy of the variational estimate.

3.2 Variational method

Based on the Rayleigh-Ritz principle and theorem (1.6), we can develop a variational method to approximate the energy levels of a problem.

Given a specific problem with a potential $V(x)$, where the corresponding Schrödinger operator $H = -\Delta + V$ is self-adjoint and bounded below, and its domain $D(H) \subset \mathcal{H} = L^2(\mathbb{R}^d)$, we consider of the following steps leading to approximate energy levels.

1. Basis. We choose an orthonormal variational basis $B = \{\phi_1, \phi_2, \ldots\} \subset \mathcal{H}$. The functions belonging to the basis are dependent on one or more parameters. The basis we use in this thesis is related to the solutions of the particle-in-a-box problem, though the use of the basis and the number of free parameters depend on the dimension d of the problem, this will be explained in the following sections.

The variational basis spans a Hilbert space $\mathcal{B}$ contained in $\mathcal{H}$ and may be finite dimensional, say of dimension N. A general element $\psi \in \mathcal{B}$ may be written

$$\psi = \sum_{i=1}^{N} c_i \phi_i \tag{3.1}$$

where $c_i = (\psi, \phi_i)$ with $i = 1, 2, \ldots$ are the Fourier coefficients of the series expansion of ψ. If the variational basis is infinite we can substitute ∞ for N.

2. Optimization. We suppose that ψ is the trial wave function solution to the problem posed by H, we can then write ψ as a series of the variational basis B as in (3.1).

The variational problem now becomes that of minimizing the energies or eigenvalues of H with respect to the free parameter or parameters of the above functions. This is equivalent to calculating the eigenvalues of the Hamiltonian matrix $\mathbb{H}$ and minimizing them over the same parameter set. The Hamiltonian matrix is defined as

$$\mathbb{H} = \begin{bmatrix} (\phi_1, H\phi_1) & (\phi_1, H\phi_2) & \dots & (\phi_1, H\phi_N) \\ (\phi_2, H\phi_1) & (\phi_2, H\phi_2) & \dots & (\phi_2, H\phi_N) \\ \vdots & \vdots & \ddots & \vdots \\ (\phi_N, H\phi_1) & (\phi_N, H\phi_2) & \dots & (\phi_N, H\phi_N) \end{bmatrix}, \tag{3.2}$$

and, as a consequence of the linearity of H, we can separate this matrix into the sum of two parts, corresponding to the kinetic and potential energies. Thus

$$\mathbb{H} = \mathbb{K} + \mathbb{P}, \tag{3.3}$$

with

$$\begin{aligned} \mathbb{K} &= \begin{bmatrix} (\phi_1, -\Delta\phi_1) & (\phi_1, -\Delta\phi_2) & \dots & (\phi_1, -\Delta\phi_N) \\ (\phi_2, -\Delta\phi_1) & (\phi_2, -\Delta\phi_2) & \dots & (\phi_2, -\Delta\phi_N) \\ \vdots & \vdots & \ddots & \vdots \\ (\phi_N, -\Delta\phi_1) & (\phi_N, -\Delta\phi_2) & \dots & (\phi_N, -\Delta\phi_N) \end{bmatrix}, \\ \mathbb{P} &= \begin{bmatrix} (\phi_1, V\phi_1) & (\phi_1, V\phi_2) & \dots & (\phi_1, V\phi_N) \\ (\phi_2, V\phi_1) & (\phi_2, V\phi_2) & \dots & (\phi_2, V\phi_N) \\ \vdots & \vdots & \ddots & \vdots \\ (\phi_N, V\phi_1) & (\phi_N, V\phi_2) & \dots & (\phi_N, V\phi_N) \end{bmatrix}. \end{aligned} \tag{3.4}$$

We note that the kinetic component of the matrix $\mathbb{H}$ is the same regardless of the potential for any given problem, this is helpful in a numerical application of the method.

By the variational principle, we know that the eigenvalues of $\mathbb{H}$ will be upper bounds to the eigenvalues of the operator H. That is, if the eigenvalues of $\mathbb{H}$ are given by $\varepsilon_1 \leq \varepsilon_2 \leq \ldots$, and the energy levels or eigenvalues of H are given by $E_1 \leq E_2 \leq \ldots$, then the following hold true

$$\begin{gathered} E_1 \leq \varepsilon_1, \\ E_2 \leq \varepsilon_2, \\ \vdots \end{gathered}$$

Furthermore, if we are able to find the eigenvectors of $\mathbb{H}$, these will be related to the eigenfunctions or wave functions that are solutions to H in the sense that if $\nu_k = \left(c_1^k, c_2^k, \ldots\right)$ is the eigenvector corresponding to the k-th eigenvalue of $\mathbb{H}$, with $k = 1, 2, \ldots$, then the k-th approximate eigenfunction ψ_k can be written as

$$\psi_k = \sum_{i=1}^{N} c_i^k \phi_i. \tag{3.5}$$

This means that the components of the eigenvector are the Fourier coefficients of the series expansion, [11], [15].

3. Computational implementation. We face several obstacles in trying to implement a computational algorithm to calculate the above eigenvalues and eigenfunctions numerically.

First, in order to implement a numerical approach to the above variational method, we need to work in a subspace of $\mathcal{H}$, implying that we can only get an approximation of the results, not the exact solution, as we cannot work with a suitable infinite basis. Then the dimension of the matrix $\mathbb{H}$ is truncated and denoted by the letter N. The numerical accuracy of the method depends greatly on how large this value is. Secondly, we depend on a computer program to solve the eigenvalue problem for $\mathbb{H}$. And last, the optimization over the parameters can be very complicated as well.

The implementation of this method will be discussed in chapter 4 through an example.

3.3 The basis for the analysis in dimension $d = 1$

As stated before, the problems in dimension $d = 1$ can be defined by any potential such that $x \in \mathbb{R}$. The basis we will use for the variational analysis is the set of solutions that are obtained from the particle-in-a-box problem. By applying a simple transformation, we shift the box from the interval $[0, b]$ to a new interval $[-L, L]$, where $L > 0$ is introduced as our variational parameter.

From the particle-in-a-box problem in chapter 2, let $b = 1$ without loss of generality. We have that the wave functions given by (2.20) can be written as

$$\psi_n(\chi) = \sqrt{2}\sin\left(n\pi\chi\right),$$

if we apply the transformation $\chi = x/2L + 1/2$, we obtain the shifted functions

$$\psi_n(x) = \sqrt{2}\sin\left(n\pi\left(\frac{x}{2L} + \frac{1}{2}\right)\right), \tag{3.6}$$

where $\chi \in [0, 1]$ and $x \in [-L, L]$.

Even though we know that the function ψ_n was normalized, after applying the transformation it loses this property, so we have to normalize it once more in order for our base to be orthonormal.

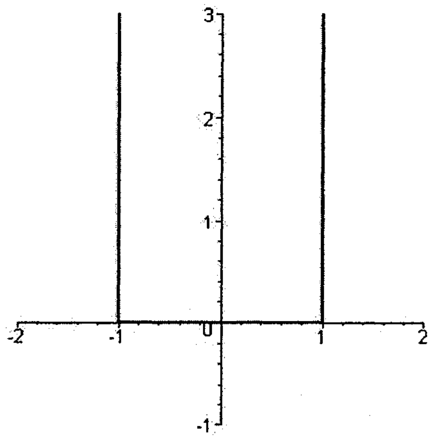

Figure 3.1: Shifted particle-in-a-box

Let

$$\phi_n(x) = \frac{1}{\sqrt{L}} \sin\left((n+1)\pi\left(\frac{x}{2L}+\frac{1}{2}\right)\right) \tag{3.7}$$

be the functions that define the variational basis $B = \{\phi_1, \phi_2, \ldots\}$. This basis has the following properties that we require:

1. B is a complete set, in the sense that a function in the same Hilbert space $L^2([-L, L]) \subset L^2(\mathbb{R}^d)$ can be expressed as a linear combination of B.

2. The members of B are orthonormal, this is

$$(\phi_n, \phi_m) = \begin{cases} 1, & \text{if } n = m; \\ 0, & \text{otherwise.} \end{cases}$$

3. The functions are even or odd with respect to the origin depending the index. ϕ_i is even if $i = 0, 2, \ldots$, or it is odd if $i = 1, 3, \ldots$.

Then, with the above basis we can implement a program to calculate the eigenvalues of the matrix $\mathbb{H}$ as in (3.2). In this case, the calculation of the matrices $\mathbb{H}$, $\mathbb{K}$, and $\mathbb{P}$ depends on the members of B.

The implementation of such a program, however, can be simpler if we analyze the properties of $V(x)$ first. We can have three different choices to build up the matrix

$\mathbb{H}$ thanks to the above basis, for any suitable potential, for even potentials, and for polynomial potentials. The cases where the potentials are either even functions or polynomials present interesting opportunities when it comes to the implementation of a computer algorithm to attack the problem.

If the potential is even, in order to construct the $\mathbb{H}$ matrix, we can split it up in two different matrices, the even part and the odd part, this is thanks to the property of the functions in the basis B of being alternately even and odd: when we multiply by the potential the functions in the basis will retain their even or odd property.

If the potential is a polynomial function, we have a very interesting result.

Property 3.1. *Let* $\mathbb{P}_x$ *and* $\mathbb{P}_{x^2}$ *be the matrices corresponding to the potentials* $V_1(x) = x$ *and* $V_2(x) = x^2$ *as defined in (3.4) respectively, then*

$$\mathbb{P}_{x^2} = \mathbb{P}_x^2. \tag{3.8}$$

Proof. Given that

$$\mathbb{P}_x = \begin{bmatrix} (\phi_1, x\phi_1) & (\phi_1, x\phi_2) & \dots \\ (\phi_2, x\phi_1) & (\phi_2, x\phi_2) & \dots \\ \vdots & \vdots & \ddots \end{bmatrix},$$

and that

$$\mathbb{P}_{x^2} = \begin{bmatrix} (\phi_1, x^2\phi_1) & (\phi_1, x^2\phi_2) & \dots \\ (\phi_2, x^2\phi_1) & (\phi_2, x^2\phi_2) & \dots \\ \vdots & \vdots & \ddots \end{bmatrix},$$

we know that $(\mathbb{P}_x^2)_{ij} = \sum_{r=1}^{\infty} (\phi_i, x\phi_r)(\phi_r, x\phi_j)$, and that $(\mathbb{P}_{x^2})_{ij} = (\phi_i, x^2\phi_j)$

Then we need to prove that $(\phi_i, x^2\phi_j) = \sum_{r=1}^{\infty} (\phi_i, x\phi_r)(\phi_r, x\phi_j)$.

As B is a complete basis for $L^2([-L, L])$ we can write the function $x\phi_j$ as the following series

$$x\phi_j = \sum_{r=1}^{\infty} \phi_r \left(\phi_r, x\phi_j\right) \tag{3.9}$$

for $j = 1, 2, \ldots$.

If we multiply (3.9) by x we obtain

$$\begin{aligned} x^2\phi_j = x(x\phi_j) &= x\left(\sum_{r=1}^{\infty} \phi_r \left(\phi_r, x\phi_j\right)\right) \\ &= \sum_{r=1}^{\infty} x\phi_r \left(\phi_r, x\phi_j\right). \end{aligned}$$

Then, the inner product

$$\left(\phi_i, x^2\phi_j\right) = \left(\phi_i, \sum_{r=1}^{\infty} x\phi_r \left(\phi_r, x\phi_j\right)\right),$$

by the linearity of the inner product we get that

$$\begin{aligned} \left(\phi_i, x^2\phi_j\right) &= \sum_{r=1}^{\infty} \left(\phi_i, x\phi_r \left(\phi_r, x\phi_j\right)\right) \\ &= \sum_{r=1}^{\infty} \left(\phi_i, x\phi_r\right)\left(\phi_r, x\phi_j\right). \end{aligned}$$

Thus $\left(\mathbb{P}_{x^2}\right)_{ij} = \left(\mathbb{P}_x^2\right)_{ij}$.

$\square$.

It is straightforward to extend the above property to the power n by using an induction argument. Thus, in an infinite basis, $\mathbb{P}_{x^n} = \mathbb{P}_x^n$.

The above result states that these matrices are equal for the infinite case, but if we are working in a N-dimensional subspace, then the equality is not true, we can only say that in a numerical analysis $\mathbb{P}_x^n$ is only an approximation for $\mathbb{P}_{x^n}$.

3.4 The basis for the analysis in dimension $d \geq 2$

We can use a similar analysis from the previous section in the case of higher dimensions, as we explained in chapter 1, in $d \geq 2$, the introduction of a set of $d-1$ coordinate angles, and the used of a suitable radial transformation, allows us to recast the residual problem in 1 dimension, namely (1.7) is this one-dimensional problem for which we shall use the basis functions that are described below.

For $d \geq 2$, we shall consider central potentials, and for the analysis of this problem, we need to work with the effective potential given by (1.8). In fact, the matrix $\mathbb{H}$ has one more component which corresponds to the effective potential.

Let $Q(\ell, d) = \frac{1}{4}(2\ell + d - 2)(2\ell + d - 3)$, and the matrix $\mathbb{U}$ defined as follows:

$$\mathbb{U} = \begin{bmatrix} (\phi_1, \frac{1}{r^2}\phi_1) & (\phi_1, \frac{1}{r^2}\phi_2) & \cdots \\ (\phi_2, \frac{1}{r^2}\phi_1) & (\phi_2, \frac{1}{r^2}\phi_2) & \cdots \\ \vdots & \vdots & \ddots \end{bmatrix}$$

Then

$$\mathbb{H} = \mathbb{K} + \mathbb{P} + Q(\ell, d)\mathbb{U}. \tag{3.10}$$

Another challenge is added to any implementation of the variational method because we now have a potential with singular behaviour which needs to be take into account. Not only this, as we are working with spherically symmetric potentials, these too can be singular. The singularity of this potential becomes a problem when we need to calculate $\mathbb{H}$ as the inner product (1.2) might not be defined for certain potentials and a given set of variational parameters.

Non-singular and weakly singular potentials. Examples of these potentials were given in section 1.3.2, the harmonic oscillator and the hydrogen atom in dimensions $d \geq 2$. For this kind of problem we choose the functions in our variational basis

B to be exactly the set of solutions from the particle-in-a-box given by

$$\phi_n(r) = \sqrt{\frac{2}{b}} \sin\left(\frac{n\pi r}{b}\right), \tag{3.11}$$

with $r \in [0, b]$, and $n = 1, 2, \ldots$. That is to say, we use variational trial functions in $L^2([0, b]) \subset L^2([0, \infty))$.

This basis satisfies again the properties mentioned before such as orthonormality and completeness for $L^2([0, b])$. Here the box size b is a variational parameter.

Highly singular potentials. These potentials are functions that have at least one term of the form $1/r^s$ with $s > 2$. In these cases we cannot use the above basis because the inner product $(\phi_i, H\phi_j)$ is not defined on $[0, b]$, therefore we will use, in addition to b, a parameter $a > 0$ so that the variational basis is in $L^2([a, b])$.

As in the case of dimension $d = 1$ we apply a transformation that shifts the interval $[0, b]$ to a new interval $[a, b]$ where $a, b > 0$ are the variational parameters.

The transformation is given by $\chi = \frac{r-a}{b-a}$, and we obtain the shifted functions

$$\psi_n(r) = \sqrt{2} \sin\left(n\pi \left(\frac{r-a}{b-a}\right)\right), \tag{3.12}$$

where $\chi \in [0, 1]$ and $r \in [a, b]$.

Normalizing (3.12) we obtain the functions

$$\psi_n(r) = \sqrt{\frac{2}{b-a}} \sin\left(n\pi \left(\frac{r-a}{b-a}\right)\right), \tag{3.13}$$

with $n = 1, 2, \ldots$.

Chapter 4

Results

4.1 Implementation of the method

In order to use the variational method to approximate the discrete spectrum of the Schrödinger operators studied in chapter 3, we implemented the following analysis, using the mathematical software Maple 11.

We will explain the main idea of the implementation by using the example of the harmonic oscillator in dimension $d = 1$. The implementation for other problems is very similar to this, and we shall discuss it at the end of this section.

Given the basis $B = \{\phi_n\}_n$, with ϕ_n defined as in (3.7), we need to calculate the matrices $\mathbb{K}$ and $\mathbb{P}$, corresponding to the problem of the harmonic oscillator with the potential $V(x) = x^2$. The components of the matrices are given analytically by the expressions:

$$\mathbb{K}_{ij} = \left(\phi_i, -\frac{d^2}{dx^2}\phi_j\right) = \begin{cases} \frac{i^2\pi^2}{4L^2}, & \text{if } i = j; \\ 0, & \text{otherwise,} \end{cases}$$

and

$$\mathbb{P}_{ij} = (\phi_i, V(x)\phi_j) = \begin{cases} \frac{L^2\left(i^2\pi^2-6\right)}{3i^2\pi^2}, & \text{if } i = j; \\ \frac{4L^2\left(4(-1)^{i+j}ij+4ij\right)}{\pi^2(i^2-j^2)^2}, & \text{otherwise.} \end{cases}$$

The Hamiltonian matrix is then given by the sum of the above two matrices, as in (3.3).

For a numerical analysis the above matrices need to be finite, so the first thing to do is to choose the dimension N, and then $i, j = 1, 2, \ldots, N$. This means that we can build numerical matrices of dimension N which depend on a fixed box size L, which becomes a variational parameter. For each value of L we can obtain the eigenvalues using the built in functions of the mathematical software, in our case Maple 11. The problem then arises when we need to find which is the specific L that will give us an acceptable approximation of the energy levels, in the sense that each eigenvalue we obtain from the variational analysis is the lowest upper bound to the exact solutions. In the case of the harmonic oscillator we can compare the results we obtain from this numerical program with the exact solutions given by (1.11).

For the optimization process over L, we take a simple approach, justified by the very flat region of a graph of the energy levels against the values of the variational parameter L, near the minimum, namely, we calculate the eigenvalues of $\mathbb{H}$ for a sequence of values of L. We chose an initial value of $L = L_0$ and a step size s, the next value of L would be equal to $L_0 + s$, and so on, for a certain number of iterations. The matrix would depend on the parameter $L_k = L_0 + ks$ for $k = 0, 1, 2, \ldots, M$, where M is the final number of iterations. We can make an educated guess to choose a suitable L_0 depending on each problem, or choose a large value of s first, to get a rough idea of an L that would be close to the minimum.

As we already know the exact solutions of the harmonic oscillator, we know that its wave functions decay swiftly to 0 as x grows. Thus, we assume that the value of an optimal L will not be too large, but this might not be the case for other problems. The value of L might also differ from one state to another, that is, the value needed to optimize the energy of the ground state might be different from the following state, and so on.

When we find an acceptable value of L, the one that minimizes the given eigenvalue, we can also obtain the corresponding eigenvectors of the matrix, and use this to graph the approximate eigenfunction as a linear combination of the basis, as stated in (3.5).

The implementation details for different problems depend on the potential and on the dimension. For an example concerning potentials, the harmonic oscillator potential is a simple function, and moreover, an even function: in this case the inner product $(\phi_i, V(x)\phi_j)$ has an analytical expression that can be exactly calculated by a program like Maple 11. If the potential is such that we need to use numerical integration to calculate the inner product, the calculation of the matrix $\mathbb{P}$ becomes slower and possibly less accurate.

On the other hand, we do have the approximation given in (3.8) by the relation $\mathbb{P}_{x^n} \approx \mathbb{P}_x^n$, which allows us to calculate the Hamiltonian matrix of a polynomial potential such as $V(x) = \sum_{k=0}^{m} a_k x^k$ by the computation of only two matrices, $\mathbb{K}$ and $\mathbb{P}_x$. Thus we have

$$\mathbb{H} = \mathbb{K} + \sum_{k=0}^{m} a_k \mathbb{P}_x^k. \tag{4.1}$$

We shall refer to this approach as the "polynomial approach" in future.

When $d \geq 2$, we also have to be concerned about the angular momentum, and use the effective potential which now contains a singular term, for this we use the bases defined in section 3.4, depending whether the potentials are non-singular, weakly-singular or highly-singular.

4.2 Dimension $d = 1$

4.2.1 The harmonic oscillator

We calculated the eigenvalues of the harmonic oscillator in dimension $d = 1$ described in section 1.3.2. using the implementation described in the previous section. Since the harmonic oscillator falls into the category of being a polynomial potential, we also used the polynomial approach to analyse this problem. We then compared the results obtained from both of these calculations to the exact solutions.

Table (4.1) shows the results obtained in the optimization process for approaches using a matrix of dimension $N = 50$, and a step size $s = 0.1$. In this table n represents the state, where $n = 0$ is the ground state. E is the exact solution for the energy given by (1.11). E_V represents the approximation to the eigenvalue using the direct approach described in the previous section, L_V represents the optimal variational parameter, E_P is the approximation using the polynomial approach, with corresponding optimized variational parameter L_P.

Table 4.1: Approximation of the energy levels of the harmonic oscillator in dimension $d = 1$.

n	E	E_V	L_V	E_P	L_P
0	1	1.000000001	6.1	0.999999998	7.3
1	3	3.000000001	5.6	2.999999998	6.5
2	5	5.000000001	5.8	4.999999997	6.6
3	7	7.000000002	5.9	6.999999996	6.6
4	9	9.000000003	6.3	6.999999996	6.6
5	11	11.00000000	6.3	10.99999999	8.3
22	45	45.00000006	8.9	45.00000005	8.9
23	47	47.00000010	9.0	46.32075646	11.7
24	49	49.00000120	8.9	49.00000117	8.9
25	51	51.00000185	9.0	50.32353151	11.2
26	53	53.00001881	8.9	53.00001868	8.9
32	65	65.01513530	8.9	62.32028554	10.1
34	69	69.07941805	8.9	69.07905146	8.9
37	75	75.36273369	9.0	74.35832785	9.3
42	85	89.861473970	8.9	98.14418440	8.9

For this case we have also plotted the energy levels E versus the parameter L, as shown in figure (4.1): we observe that the energy levels as a function of L are U-shaped and flat near the minima. Also, the values of L we get as minimizers for each of the states are not that different from each other. From the graph we can think of choosing only one value of L to obtain a "good" approximation for all the eigenvalues considered. If N is large enough, say, bigger than 20, any value of L in the range $[6, 10]$ gives good approximations to the energy levels.

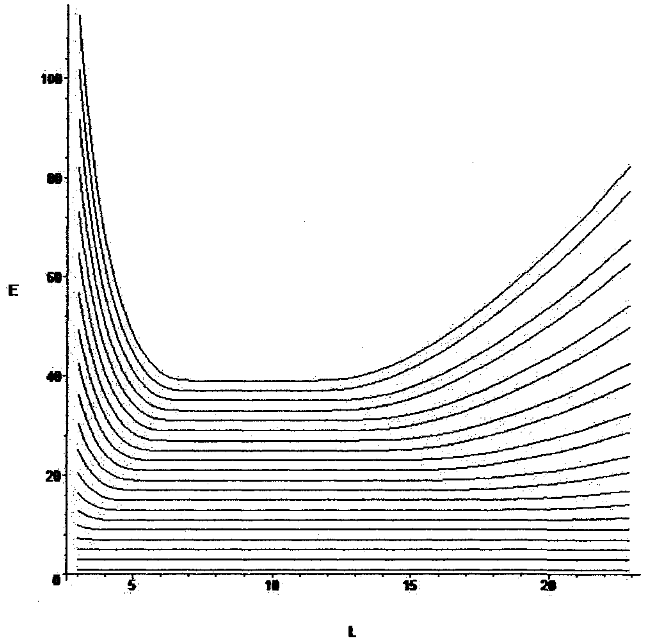

Figure 4.1: Energy vs. Parameter L for the harmonic oscillator in dimension $d = 1$.

Once the optimal L is determined, the eigenvectors of the first 3 states also obtained and graphed with their corresponding eigenfunctions as defined in (3.5). Figures (4.2), (4.3), and (4.4), represent the trial wave functions obtained, each one calculated with the values of L stated in table (4.1).

We note that the approximations obtained by both methods are good. After experimenting with different values of N we can confirm that the larger this value is the better the approximations become, that is to say, closer to the exact solution. Also, by this same observations we can say that up to $N/2$ states are good approximations

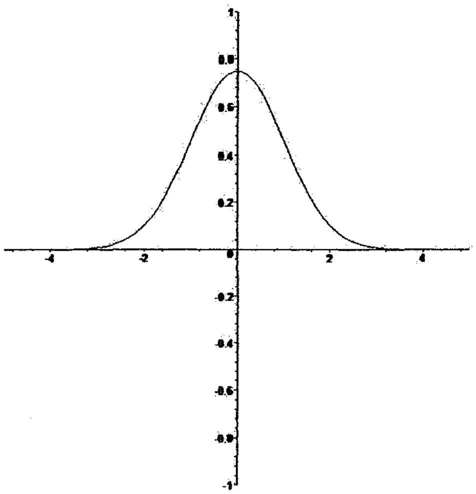

Figure 4.2: Trial wave function for the ground state ψ_0 of the harmonic oscillator in dimension $d = 1$ with minimizer $L = 6.1$.

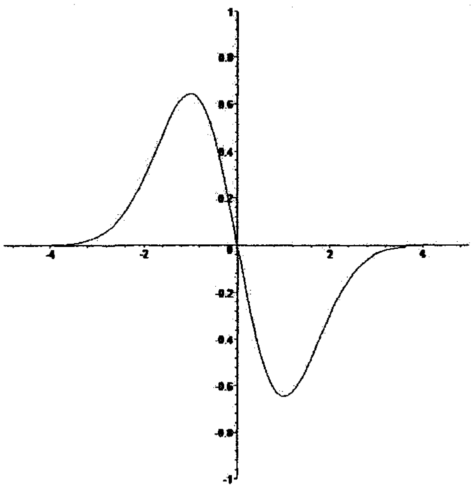

Figure 4.3: Trial wave function for the first excited state ψ_1 of the harmonic oscillator in dimension $d = 1$ with minimizer $L = 5.6$.

in both approaches, the direct and the polynomial one. However, it is interesting to note that the polynomial approach, as it involves yet another approximation, from proposition (3.8), does not always give upper bounds. This is clear for some of the results showed in table (4.1), for example states $n = 25, 32, 37$. In contrast we observe that the variational approach always gives upper bounds even though N is not very large. To overcome the problem of inaccuracy of the polynomial approach we need only to increase the value of N to be greater than 100, this will give better results.

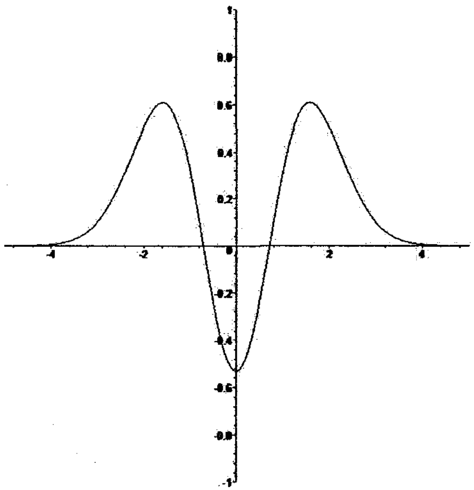

Figure 4.4: Trial wave function for the second excited state ψ_2 of the harmonic oscillator in dimension $d = 1$ with minimizer $L = 5.8$.

4.2.2 The potential $V(x) = |x|$

The function $V(x) = |x|$ is symmetric and non-differentiable at the origin. This is a linear potential that represents the attraction of a small particle to a large plate with a hole in it under Newtonian gravity. The exact analytical solutions to this problem are given in terms of the zeros of Airy functions and its first derivatives, studied in Flügge [7] and shown in Abramowitz *et al.* [1].

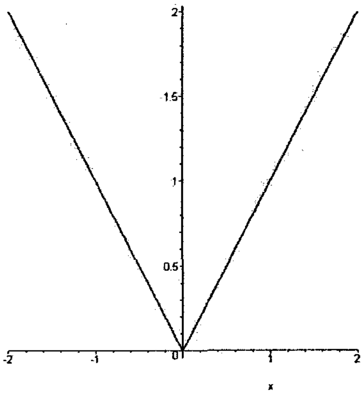

Figure 4.5: The potential $V(x) = |x|$

It can be thought of as a non-harmonic oscillator for it represents an oscillating behaviour, with the difference that the force has a sudden change of direction at $x = 0$.

In table (4.2) we show the results for this problem found by applying the variational method with a matrix of dimension $N = 50$, and a step size $s = 0.25$ for the optimization process. Again, n represents the state. As there exist suitable expressions for the exact solutions to this problem, we compare the results obtained in the variational method to these. We can also use a shooting method which is known to give good approximations for the energy levels. E and E_S denote the exact energy levels and those obtained by this shooting method respectively, while E_V represents the approximation to the eigenvalue using an implementation of the variational method, and L is the minimum value of the variational parameter.

Table 4.2: Approximation of the energy levels of the potential $V(x) = |x|$.

n	E	E_S	E_V	L
0	1.01879297	1.01879305	1.01879344	6.25
1	2.33810741	2.33810752	2.33810745	8.00
2	3.24819758	3.24819770	3.24819827	8.25
3	4.08794944	4.08794959	4.08794960	9.25
4	4.82009921	4.82009938	4.82010046	9.75
5	5.52055983	5.52056000	5.52056026	10.50
6	6.16330736	6.16330750	6.16330960	10.75
7	6.78670809	6.78670828	6.78670915	11.50
8	7.37217726	7.37277509	7.37218128	12.00
9	7.94413359	7.94413380	7.94413594	12.50
10	8.48848673	8.48848690	8.48849407	12.75
11	9.02265085	9.02265108	9.02265603	13.50
12	9.53544905	9.53544923	9.53546280	13.75

Following the theory from chapter 3, and the observations made in the harmonic oscillator the energy levels obtained by the variational methods are optimized upper bounds to the energy levels. In this case, when we optimize over the variational parameter L, we obtained lower upper bounds, in fact, the goal was to obtain the lowest upper bound. Here we show the best lower bound calculated using the optimization process.

For the shooting method, as described in Appendix B, we need to solve an ordinary differential equation numerically, which depends strongly on the software we are using where we cannot control the accuracy of the results, therefore, the eigenvalues we obtained by the shooting process are just approximations. We cannot claim how accurate they are, but this is a matter for further numerical analysis which is not the main point in this thesis. Though the approximations obtained by the shooting method are very close to the exact solutions, if we face a problem that has no exact solutions we can only use this approximations to get an idea about the eigenvalues, not as a point of comparison to determine how accurate the results obtained from the variational method are.

4.2.3 Polynomial potential: $V(x) = x^4$

We considered the potential $V(x) = x^4$ to test the accuracy of the method using the polynomial approach, and compared it to the direct approach of the variational method and the results obtained from the shooting method as well.

We used a matrix of dimension $N = 50$, and a step size of $s = 0.5$. Again the subindexes S, V, and P represent the results obtained with the shooting, the variational, and the polynomial methods respectively.

Table 4.3: Approximation of the energy levels of the potential $V(x) = x^4$.

n	E_S	E_V	L_V	E_P	L_P
0	1.060361945	1.060362090	3.5	1.060362089	7.5
1	3.799673304	3.799673024	4.0	3.799673027	6.5
2	7.455698365	7.455697938	4.0	7.455697934	4.5
3	11.64474628	11.64474551	4.0	11.64474550	5.0
4	16.26182677	16.26182602	4.0	16.26182601	4.0
5	21.23837423	21.23837292	4.0	21.23837290	7.5
6	26.52847225	26.52847118	4.5	26.52847117	4.0
7	32.09859965	32.09859772	4.0	32.09859769	6.5
8	37.92300243	37.92300103	4.0	37.92300029	7.5
9	43.98116073	43.98115811	4.0	43.98114584	7.5

From this results we note that in some cases, the eigenvalues obtained from the variational method are smaller than the ones obtained from the shooting method.

This reinforces the notion that the approximations obtained by the shooting method cannot be compared to the ones obtained by the variational one.

We do observe that for the first states, the approximations obtained from the variational and polynomial approaches are close. The polynomial approach has the advantage that it is fast for an optimization process compared to the variational method, therefore if we choose a large N we can get good approximations using it.

4.2.4 Polynomial potential: $V(x) = x^2 + x^4$

The potential $V(x) = x^2 + x^4$ is a special case of the quartic anharmonic oscillator. There interest in this problem has a long history. Simon has written an extensive review [21]. We consider the case of dimension $d = 1$, though this problem can also be studied in higher dimensions as presented, for example, by Hall [12].

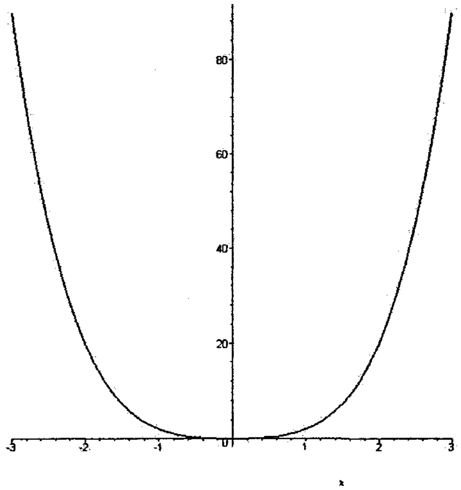

Figure 4.6: Quartic anharmonic potential

Table (4.4) reflects the results after applying the method to a matrix of dimension $N = 50$, and using a step size $s = 1$ for the optimization process. Again, n represents the state, and because this kind of potentials do not have exact solutions, yet again we need to make use of a shooting method to approximate the solutions given by E_S, E_V, as usual, represents the approximation to the eigenvalue using the direct approach, with the respect value L_V of the optimized variational parameter, and E_P represents the approximation using the polynomial approach, with corresponding optimized variational parameter L_P.

Table 4.4: Approximation of the energy levels of the potential $V(x) = x^2 + x^4$.

n	E_S	E_V	L_V	E_P	L_P
0	1.392351594	1.392351474	6.0	1.392351640	5.0
1	4.648813066	4.648812622	5.0	4.648812702	4.0
2	8.655050433	8.655049869	6.0	8.655049951	9.0
3	13.15680476	13.15680388	4.0	13.15680051	10.0
4	18.05755824	18.05755739	5.0	18.05751328	10.0
5	23.29744288	23.29744128	6.0	23.29743858	9.0
6	28.83533959	28.83533840	6.0	28.83525815	9.0
7	34.64085039	34.64084825	5.0	34.63779703	10.0
8	40.69038755	40.69038606	5.0	40.62769619	10.0
9	46.96501230	46.96500945	6.0	46.96212176	9.0

The results in this table confirm what we mentioned for the problem in the previous section, regarding the accuracy of the three methods used. However, calculating these energies using the variational approach is computationally expensive, because in order to construct the matrix $\mathbb{H}$ of dimension N we need to integrate numerically for each component of $\mathbb{P}$ for each value of L. This makes us think that the polynomial approach might be more useful, as it is faster, we need only to calculate the matrix $\mathbb{P}_x$ which has an analytical form depending on L, and multiply it by itself according to the relation (4.1).

One of the problems is that after experimenting with L using this approach, sometimes we get values for the higher excited states that are lower than the energy levels of the problem, we show in figure (4.7) the behaviour of the eigenvalues in function of L.

We can see from this that after $L = 10$, using the polynomial approach, the numerical results might be not so reliable, this can be the explanation that this approach has sometimes good results, but some other times goes even lower than the shooting or exact results, as seen in previous examples. We also observe that

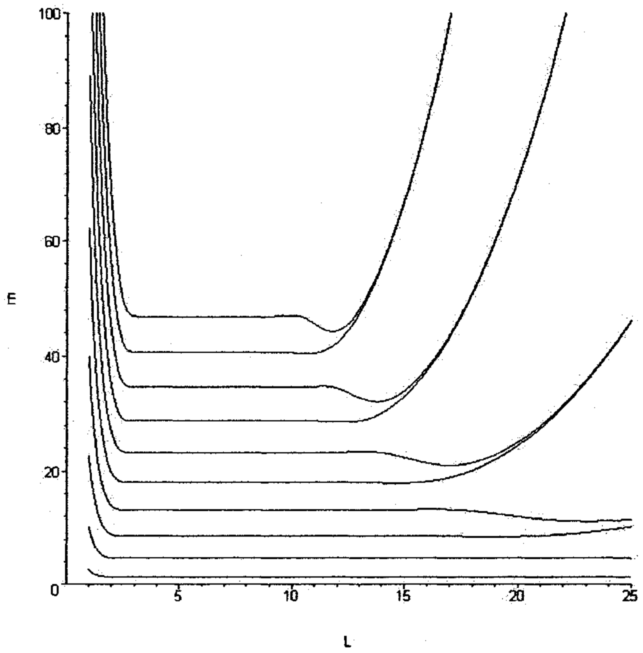

Figure 4.7: Energy vs. L of the quartic anharmonic oscillator in dimension $d = 1$.

before this specific value of the variational parameter, the eigenvalues have a smooth behaviour, if we choose an L before this critical value and take a large value of N, we then again obtain good results.

4.3 Higher dimensions

The analysis of dimensions $d \geq 2$ is different from the one in dimension $d = 1$ in the sense that we do not use the shifted solutions for the particle in a box. We now consider radial wave functions, which means we need to do the analysis in the interval $[0, b]$ or $[a, b]$, depending on how singular the problem is.

4.3.1 The harmonic oscillator

The energy values for the harmonic oscillator in dimensions $d = 2, 3, 4, 5$ and quantum number $\ell = 0, 1, 2, 3$ are calculated. We used a matrix of dimension $N = 40$ and a step size of $s = 0.25$. This problem has known exact solutions (1.16), which can be used for comparisons. Since the expression of each element of the matrices corresponding to the kinetic and potential energies is given by an exact analytical function of L, the calculations of these eigenvalues are quite fast.

We present two different tables of results. For all of them ℓ represents the quantum number related to the angular momentum, n is the state (1 plus the number of nodes in the radial function for a given ℓ), E is the exact value of the energy levels, and E_V the variational approximation with minimal parameter b.

Table 4.5: Approximation of the energy levels of the harmonic oscillator in dimension $d = 2$.

ℓ	n	E	E_V	b
0	1	2	2.28622395	4.00
	2	6	6.30816202	4.00
	3	10	10.32728254	4.50
	4	14	14.34185985	5.25
1	1	4	4.00073469	4.25
	2	8	8.00185191	4.75
	3	12	12.00337390	5.25
	4	16	16.00524280	5.50
2	1	6	6.00000262	5.00
	2	10	10.00001068	5.50
	3	14	14.00002888	6.00
	4	18	18.00005965	6.25

Table (4.5) shows case of dimension $d = 2$. It is clear that when $\ell = 0$ we obtain results that are not quite accurate. This is due to the behaviour of the effective potential, which for this case is given from (1.15) by

$$U(r) = r^2 - \frac{1}{4r^2},$$

and we can see in Figure (4.8). For this case the singular term makes the potential tend to $-\infty$ when r is close to 0. This shows that the original oscillating behaviour might be lost and the matrix we get from the variational analysis is not as quite accurate. This is a hint that we might have problems with singular problems, even when they are weakly-singular. Here the difficulty is removed for $\ell > 0$ (or $d > 2$)

since the effective potential $U(r)$, generally given by (1.8), has a positive pole at $r = 0$ and the particle is confined in effectively a "soft box" between this pole and the rising potential at large r. This point will be discussed further in the conclusion.

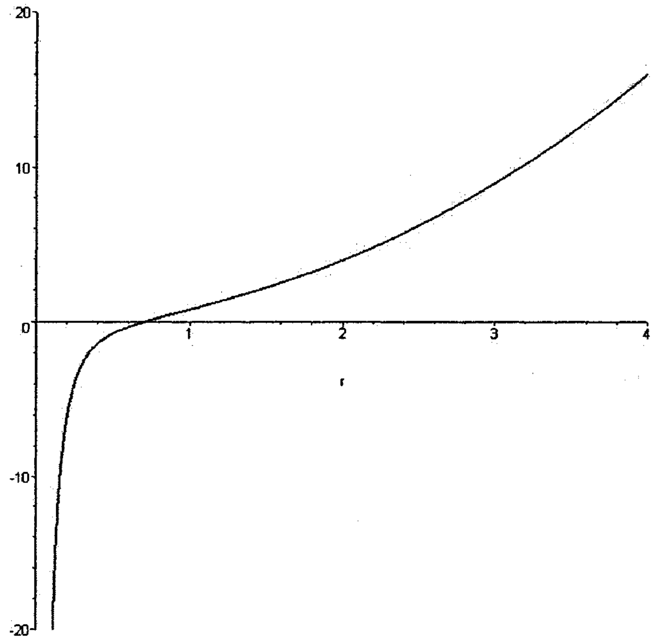

Figure 4.8: Harmonic oscillator in dimension $d = 2$, and $\ell = 0$.

Table (4.6) shows a small sample of the results for dimensions $d = 3, 4, 5$ and quantum numbers $\ell = 0, 1, 2, 4$. Most of the results are very accurate, except for some values of ℓ.

Table 4.6: Approximation of the energy levels of the harmonic oscillator in dimension $d = 3, 4, 5$.

d	ℓ	n	E	E_V	b
3	0	1	3	3.00000000	6.00
		5	19	19.00000001	7.00
		10	39	39.00000001	8.75
	1	1	5	5.00007348	4.50
		5	21	21.00167944	6.25
		10	41	41.00907276	7.75
	2	1	7	7.00000000	6.00
		5	23	23.00000001	7.75
		10	43	43.00000001	9.25
	3	1	9	9.00000001	6.00
		5	25	25.00000076	7.25
		10	45	45.00002070	8.50
4	0	1	4	4.00073469	4.25
		5	20	20.00745550	6.00
		10	40	40.02454449	7.50
	1	1	6	6.00000262	5.00
		5	22	22.00011370	6.50
		10	42	42.00094014	8.00
	2	1	8	8.00000002	6.00
		5	24	24.00000248	7.25
		10	44	44.00004592	8.50
	3	1	10	10.00000000	6.00
		5	26	26.00000008	7.50
		10	46	46.00000274	8.75
5	0	1	5	5.00007348	4.50
		5	21	21.00167944	6.25
		10	41	41.00907276	7.75
	1	1	7	7.00000000	6.00
		5	23	23.00000001	7.75
		10	43	43.00000001	9.25
	2	1	9	9.00000001	6.00
		5	25	25.00000076	7.25
		10	45	45.00002070	8.50
	3	1	11	11.00000001	6.00
		5	27	27.00000000	8.00
		10	47	47.00000001	10.00

4.3.2 The hydrogen atom

The hydrogen atom is studied in section 1.3.2. We now show results obtained with our method. Here the size of the matrix is $N = 25$, and the step size used in the optimization process is $s = 1$, the step size is chosen so large because this weakly bound system is all together large. The variational method is slow in this case, given the singular nature of the problem and because for the matrix $\mathbb{P}$ (corresponding to the potential energy) we need to integrate numerically for each term.

Table 4.7: Approximation of the energy levels of the hydrogen atom in dimension $d = 3$.

ℓ	n	E	E_V	b
0	1	-0.2500000000	-0.2494292776	13
	2	-0.06250000000	-0.06173021569	32
	3	-0.02777777778	-0.02682855454	57
	4	-0.01562500000	-0.01457726183	90
1	1	-0.06250000000	-0.06231120892	33
	2	-0.02777777778	-0.02747649731	60
	3	-0.01562500000	-0.01526320869	94
	4	-0.01000000000	-0.009656788911	143
2	1	-0.02777777778	-0.02777640178	75
	2	-0.01562500000	-0.01561644406	108
	3	-0.01000000000	-0.009970374676	146
	4	-0.006944444444	-0.006872824074	189

The results we get are not as accurate as the ones obtained for the harmonic oscillator. The hydrogen atom is a complicated problem; its energy levels are all negative and they they get closer and closer to each other as n grows. The most serious difficulty is posed by the weak binding leading to a spread-out wave function, quite unlike a particle in a box. We can see that in the values of the variational parameter, each following state needs a larger b, and similarly with each next quantum number ℓ.

4.3.3 Confined hydrogenic atoms

With our variational approach we can think that we are confining the potential we want to study to a box of specific size, and we want to find the optimal size that will give us the best approximations to the energy levels. In the case of the hydrogen atom mentioned in the previous section, we find that we need bigger boxers for each following state, this is because, as already mentioned, the problem is spread out. But this opens up the possibility to study the behaviour of a system that is already confined.

The example of an hydrogen atom confined to a spherical box has been studied by Varshni [23] and by Ciftci, Hall, and Saad [4]. For this sort of problem the Schrödinger equation is given by:

$$-\frac{d^2}{dr^2}\psi(r) + \left(\frac{\ell(\ell+1)}{r^2} - \frac{A}{r}\right)\psi(r) = E\psi(r), \tag{4.2}$$

with boundary conditions $\psi(0) = \psi(b) = 0$, and $A > 0$. In the latter study [4], exact solutions are given for specific radii. We then applied the variational method to this problem using the radii suggested by the exact solutions and obtained the following results for $A = 1$.

Table 4.8: Approximation of the energy levels of a confined hydrogenic atom in dimension $d = 3$.

ℓ	n	b	E	E_V	N
0	1	4	-0.06250000000	-0.06249993558	200
1	1	12	-0.02777777778	-0.02777772347	150
2	1	24	-0.01562500000	-0.01562500004	150
3	1	40	-0.01000000000	-0.01000000002	100
0	1	3.803847576	-0.02777777778	-0.02777730093	100
	2	14.19615242	-0.02777777778	-0.02777473502	100
1	1	11.05572809	-0.01562500000	-0.01562458222	100
	2	28.94427191	-0.01562500000	-0.01562321913	100
2	1	21.77124344	-0.01000000000	-0.009999999956	150
	2	48.22875656	-0.01000000000	-0.009999999937	150
3	1	36	-0.006944444444	-0.006944444423	150
	2	72	-0.006944444444	-0.006944444436	150

Here ℓ is the quantum number, n is 1 plus the number of nodes of the wave function, E the exact solution for the energy, and E_V the variational approximation using a matrix of dimension N. In contrast to what happened with the hydrogen atom, we find that for the confined atom the approximations are comparable. We also show the graphs for the approximations of the confined wave functions for radii

$b = 4$ and $b = 72$ in figures (4.9) and (4.10) respectively.

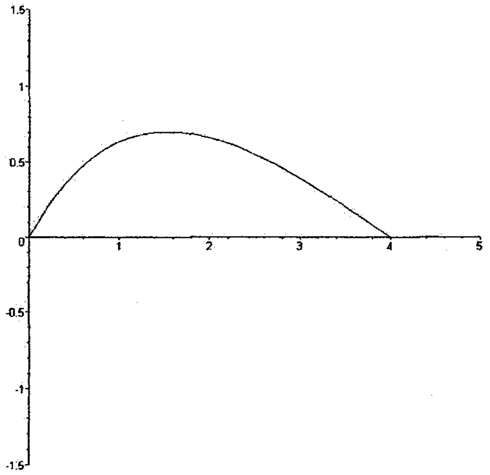

Figure 4.9: Hydrogenic atom in $d = 3$ confined to a box of size $b = 4$.

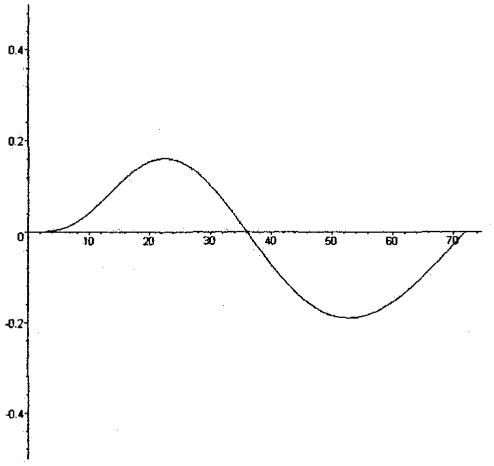

Figure 4.10: Hydrogenic atom in $d = 3$ confined to a box of size $b = 72$.

4.3.4 Highly-singular potentials

Highly-singular potentials are problems that have been widely studied as it is difficult to find exact solutions. There are a special kind of potentials that are called quasi exactly solvable, this means that we can find a part of the energy spectrum exactly when the potential parameters satisfy specific conditions. For example, Dong *et al.*

[6] studied the potential

$$V(r) = ar^2 + br^{-4} + cr^{-6}$$

by assuming that the radial equations for the ground state and first excited state were given by:

$$R_\ell(r) = r^\kappa \left(\alpha + \beta r^2 + \gamma r^{-2}\right) \exp - \left(\sqrt{a}r^2 + \sqrt{c}r^{-2}\right)/2, \tag{4.3}$$

with $\beta = \gamma = 0$, and $\kappa = \kappa_0$ for the ground state. Although there are more studies on this matter, where different wave functions are used to calculate the exact solutions, and the parameters a, b, and c have to satisfy certain constraints.

We find the the exact solutions for the ground state energy in the cases where $a = b = c = 1$ and $a = 1$, $b = c = 9$ mentioned in Hall *et al.* [13].

For $a = b = c = 1$ we have the potential

$$V(r) = r^2 + r^{-4} + r^{-6}$$

the ground state energy is given by $E_0 = 5$. Using different implementations of the variational approach, with both bases described in Section 3.4, the best result we obtained was the approximation $E_V = 5.000008414$, for a matrix of size $N = 50$, and optimal parameters $a = 0.01$ and $b = 5$.

For the case where $a = 1$ and $b = c = 9$ we now have the potential

$$V(r) = r^2 + 9r^{-4} + 9r^{-6}$$

the ground state energy is given by $E_0 = 7$. And our approximation is $E_V = 7.000019409$, where N, a, and b are the same as above.

Conclusions

Throughout the history of physics, scientists have studied how to find solutions to all sort of mathematical problems posed by physical theories. In this way the explicit implications of these theories can be revealed, and verification and falsification of the theories become possible. In this thesis we have studied a small portion of this wide world of physical problems, namely that related to Schrödinger operators and their discrete spectra.

The variational method we have adopted relies strongly in the use of the sine-basis obtained from the solutions of the particle-in-a-box problem, which we have presented in section 2.4. One of the questions we wanted to answer was, can this basis be applied effectively to construct a variational analysis for unconfined problems?

From the results shown in chapter 4. we conclude that this basis is appropriate for the study of problems that have some similar characteristics to the particle-in-a-box problem. That is why a potential such as the harmonic oscillator, whose wave functions vanish very quickly with $|x|$, as though the particle were already in a box, leads to good results. This points out that in theory, even if we are working with potentials that are highly singular but strongly U-shaped, then the problem would be suitable for a variational analysis in the sine-basis.

Other kinds of singularities that do not sufficiently confine the particle might represent a problem, such as the harmonic oscillator in dimension $d = 2$ and with quantum number $\ell = 0$. An effective use of the sine-basis for this case is still an open issue.

We also conclude that the sine-basis does not work too well with loosely-bound systems such as the hydrogen atom in dimension $d = 3$. The explanation for this is that such problems are not effectively confined, and require large boxes to approximate their energy levels; and the resulting computations proved to be slow.

However, as we found for the hydrogen atom, if the quantum system studied is already confined in a box, the approximations for the eigenvalues are highly accurate. The study of confined systems has been of great interest in recent years, since the early work of Michels [17]. These physical systems are important because of the necessity of finding information about atoms or molecules trapped in microscopic cavities, or places in high pressure environments. It appears that this sine-basis gives excellent results when applied to estimate the spectra of this class of physical problem.

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Appendix A

Maple Code for the Variational Analysis of the Harmonic Oscillator

```
>restart:with(LinearAlgebra): with(plots): with(Statistics):
```

The basis functions are defined by :

```
> Psin:= (x, n, L) -> (1/sqrt(L))*sin(n*Pi*(x/(2*L) + 1/2));
```

The kinetic energy matrix.

```
> Ki:= proc (L, n)
> local i, j, p;
> p := Matrix(n,n);
> for i to n do
>       p[i,i] := evalf(i^2*Pi^2/(4*L^2));
> end do;
> p;
> end proc;
```

The potential energy matrix.

```
> Po:= proc (L, n)
> local i, j, k, m, p;
> p := Matrix(n,n);
> for i to n do
>     p[i,i]:= evalf(L^2*(i^2*Pi^2-6)/i^2/(3*Pi^2));
>     for j from i+1 to n do
>         p[i,j] := evalf(4*L^2/Pi^2/(i^4-2*i^2*j^2+j^4)*
          (4*(-1)^(i+j)*i*j+4*i*j));
>         p[j,i] := p[i,j];
>     end do
> end do;
> p;
> end proc;
```

The Hamiltonian matrix.

```
> HM:= proc (L, n)
> local HM;
> HM := Ki(L,n)+Po(L,n);
> end proc;
```

This is the optimization process.

n : = dimension of the Hamiltonian matrix.

L : = initial value of the variational parameter

s : = stepsize so the next variational parameter used in the process will be L+s

it : = number of iterations

dig : = number of digits in the approximation

flag : = 1 or 2

If flag : = 1 OPT will give a matrix with the first row being that containing the values of the parameters L, and the next rows will be the corresponding eigenvalues of the Hamiltonian matrix.

If flag : = 2 OPT will give a matrix which in the first column will obtain the ordered eigenvalues of the Hamiltonian matrix, and in the second column we will have their corresponding values of the optimum parameter.

```
> OPT:= proc (n, L, s, it,dig,flag)
> local M, P, T, i, j, l,E;
> Digits:=dig;
> l := L;
> #for i from 1 to n+1 do;
> #   T[i,1]:=i-2;
> #end do;
> for j to it do
>     T[1,j]:=l;
>     M := HM(l,n);
>     P := evalf(simplify(LinearAlgebra:-Eigenvalues(M)));
>     for i to n do
>         P[i] := Re(P[i])
>     end do;
>     P := sort(P);
>     for i to n do
>         T[i+1,j] := P[i];
>    # print(j,l,T[i,j],i-1)
>     end do;
>     l := l+s;
```

```
> end do;
> T:=convert(T,array);
> for i from 2 to n+1 do
>   E[i-1,1]:=10^10;
>   for j from 1 to it do
>     if T[i,j] < E[i-1,1] then
>      E[i-1,1]:=T[i,j];
>      E[i-1,2]:=T[1,j];
>     end if;
>   end do;
> end do;
> E:=convert(E,array);
> if flag=1 then
>   T;
> else
>   E;
> end if;
> end proc;
```

Appendix B

Shooting Method

Given a Sturm-Liouville problem in the normal form, we can develop a numerical shooting method to calculate its eigenvalues and eigenfunctions [18].

Roughly speaking, the shooting method consists of choosing a sequence of eigenvalues and adjusting them to the conditions given by theorem (2.2), that is, for each state $n = 0, 1, 2, \ldots$, the function has $k = 0, 1, 2, \ldots$ nodes or zeros respectively. Then solving for each trial eigenvalue the equation (2.16) and choosing the eigenvalue that gives the best approximation.

As we want to focus this method to find solutions for quantum mechanical problems, we know that the solutions have to belong to $L^2(\mathbb{R}^d)$, that is, they need to vanish at infinity. For the numerical analysis we have to choose a suitable range for which the function will start vanishing quickly, for some problems it might be bigger than expected.

Another thing to take into account is the initial conditions of each problem; this is of utmost importance while solving a differential equation numerically.

Algorithm. The algorithm we use is a simple refining algorithm, and it is described as follows:

For each state $n = 0, 1, 2, \ldots$ we set up the node goal, that is, the number of zeros that the function corresponding to the particular state to be ng. We then choose upper and lower values λ_u and $\lambda_{\mathfrak{l}}$ respectively,

1. Let λ be the average $(\lambda_u + \lambda_{\mathfrak{l}})/2$. This value will be our trial eigenvalue.
2. Solve the equation

$$-\frac{d^2u}{dx^2} + Q(x)u = \lambda u, \tag{B.1}$$

satisfying the initial conditions imposed by the original problem.

3. Given the numerical solution of the above equation we count its number of roots or nodes. If this number is lesser or equal than node goal ng, then the eigenvalue λ is too small, and we need to update the lower value $\lambda_{\mathfrak{l}} = \lambda$. Else, the number of roots is greater than node goal ng, which means that the eigenvalue λ is too big, then we update the upper value $\lambda_u = \lambda$.
4. And we return to step 1 unless the stop criteria is met.

Though the algorithm is straightforward, a computational implementation may not be easy as it depends mainly on the numerical solution of a differential equation, which is a very complicated topic.