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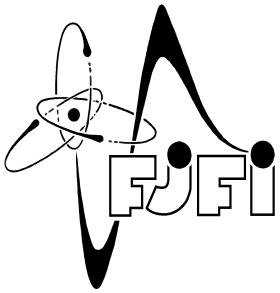

RESEARCH WORK

Discrete variable representation of quantum problems

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September 6, 2010

Acknowledgements

I thank doc. Ing. Pavel Soldán, Dr. for many illuminating discussions, his kind support and for his careful reading of this manuscript.

Abstract

Discrete Variable Representation (DVR) method is a numerical method for solving the bound-state problem of the Schrödinger equation. Derivation of the method is provided, and its advantages and disadvantages are discussed. Computer implementation of the DVR method is applied to model one-dimensional and two-dimensional problems.

Contents

Introduction

Numerical procedures for solution of the bound-state problem of the Sturm-Liouville potential-based equations describing certain physical system have been the subject of great interest, the aim being to achieve a fast and reliable method that generates an approximate numerical solution. Discrete Variable Representation (DVR) technique has been widely used with success to solve quantum problems that occurs in chemical physics, especially in molecular vibrations and rotations calculations.

The DVR is a grid-point representation and it solves the problem of integral evaluation by using basis set together with the quadrature approximation for the matrix elements. Its great advantage over other methods is that in DVR, any local operator, such as the potential energy, is diagonal. These properties facilitate linear algebra operations and reduce memory limitations.

Let us do the brief overview of the contents of this research work. In Chapter 1 we shall show how to use variational procedures to investigate eigenvalues of the certain model problems in quantum mechanics. We shall consider the use of the Rayleigh-Ritz variational method to find approximate values for these eigenvalues. The purpose of Chapter 2 is to derive and treat all basic concepts of DVR using a one-dimensional terminology. The benefit of using this approach will be demonstrated by considering one-dimensional numerical examples based on the anharmonic oscillator and the Morse potential to solve the bound-state problem. The computer-based implementation of the DVR technique compared with a variational approach and with additional published results is also included in this chapter. The Chapter 3 is devoted by the application of the methodology for a two-dimensional problem and the calculation of energy levels of "double-well" potentials. All computations are carried out in the programming language FORTRAN 95. The auxiliary formulas required to do our calculation are enclosed in Appendix.

Chapter 1

Variational theory of the Sturm-Liouville problem arising from quantum physical phenomena

1.1 Background of the Sturm-Liouville problem

In this section we give a variational description of certain Sturm-Liouville boundary value problem. Many eigenvalue problems in quantum mechanics as well as classical physics fit into the class of second order linear ordinary differential equations called Sturm-Liouville (from now on referred to as SL) equations. We consider self-adjoint operators generated by the following form of SL problem [18]:

Definition 1. Let $J = (a, b)$, $-\infty \leq a < b \leq +\infty$, and consider the equation

$$\frac{1}{\rho(x)}\left[-\frac{\mathrm{d}}{\mathrm{d}x}\left(p(x)\frac{\mathrm{d}\psi}{\mathrm{d}x}\right) + q(x)\psi\right] = \lambda\psi \qquad \text{for } x \in (a, b). \tag{1.1}$$

with conditions:

p, q, ρ are real-valued measurable functions on J,
$p(x), \rho(x) > 0$ *a.e.*, in J,
$1/p, q, \rho \in L_{loc}(J, \mathbb{R})$.

We say that equation (1.2) is regular at a, if $a > -\infty$ and the above assumptions hold in $\langle a, b)$ instead of (a, b), otherwise it is called singular. Similarly, one defines regularity at the endpoint b. Equation (1.2) is called regular if it is regular at a and at b. Equation (1.2) is said to be singular at a (resp. b) if it is not regular at a (resp. b); it is said to be singular if it is singular at a or at b.

A number of the SL differential equations arising from quantum mechanical problems is singular, *e.g.*, the equations for linear harmonic oscillator, the hydrogen

atom, the Morse oscillator and all molecular potentials. In [3] singular SL problems have been solved by means of approximation of singular problems by regular problems [4, 18]. Iterations of finite subintervals was performed until requested accuracy has been achieved. In this research work we use a different approach with regard to applications in chemical physics. Boundary conditions are fulfilled by appropriate choice of basis [13].

1.2 Rayleigh-Ritz method

In this section we illustrate the Rayleigh-Ritz variational method on a regular SL problem. The Rayleigh-Ritz method (for details, see *e.g.*[17]) provides an approximation of the lowest eigenvalue of the original regular Sturm-Liouville problem for the following general equation

$$-\frac{\mathrm{d}}{\mathrm{d}x}\left[p(x)\frac{\mathrm{d}\psi}{\mathrm{d}x}\right]+q(x)\psi=\lambda\rho(x)\psi \qquad \text{for } x\in(x_0,x_1), \tag{1.2}$$

subject to the Dirichlet boundary conditions $\psi(x_0)=0$ and $\psi(x_1)=0$. We assume that the given function ρ and q are continuous while p is continuously differentiable and $p>0, \rho>0$ a.e. on (x_0,x_1). In particular case which arises as time-independent one-dimensional Schrödinger equation, the function $p=p(x)$ and $\rho=\rho(x)$ are known as positive constants

$$p(x)\equiv\frac{\hbar^2}{2\mu},\ \rho(x)\equiv 1\,,$$

and $q(x)\equiv V(x)$ is a potential describing a certain physical system of a non-relativistic single quantum-mechanical particle of mass M. The eigenvalue parameter λ is proportional to the system energy E. Then the Sturm-Liouville problem reads

$$-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}+V(x)\psi=E\psi \qquad \text{for } x\in(x_0,x_1)\,, \tag{1.3}$$

with

$$\psi(x_0)=0 \quad \text{and} \quad \psi(x_1)=0\,. \tag{1.4}$$

In can be shown [21] that the spectrum of a regular Sturm-Liouville eigenvalue problem consists of an infinite but countable number of real and simple eigenvalues which are bounded from below and can be arranged in an increasing sequence

$$\lambda_1<\lambda_2<\lambda_3<\cdots$$

such that $\lambda_n\to\infty$ as $n\to\infty$.

The Rayleigh method is based on the principle that the lowest eigenvalue $\lambda^* = \lambda_1$ is equal to the minimum value of the quotient $R = D/H$, called Rayleigh quotient after the English mathematical physicist John William Strutt (3rd Baron Rayleigh);

$$R(\psi) = \frac{D(\psi)}{H(\psi)}\,,$$

where[1]

$$D(\psi) = \int_{x_0}^{x_1} \left(\frac{\hbar^2}{2\mu} \psi'(x)^2 + V(x)\psi(x)^2 \right) \mathrm{d}x = \langle \psi | \, \hat{H} \, | \psi \rangle$$

and

$$H(\psi) = \int_{x_0}^{x_1} \psi(x)^2 \mathrm{d}x = \langle \psi | \psi \rangle$$

for any nonzero vector ψ in the vector space $C^1\langle x_0, x_1 \rangle$, which consist of all continuously differentiable functions on the interval $\langle x_0, x_1 \rangle$. We require in addition such functions to vanish at the end points. Let us denote such domain by x. A fundamental necessary condition states that a minimum vector[2] ψ_1 vanishes the Gâteaux differential of the functional $R = R(\psi)$, *i.e.*,

$$\delta R(\psi_1, \triangle\psi) = 0$$

for all vectors $\triangle\psi$ in x. Since

$$\delta R(\psi, \triangle\psi) = \frac{1}{H(\psi)} \left(\delta D(\psi, \triangle\psi) - R(\psi) \delta H(\psi, \triangle\psi) \right) ,$$

then ψ_1 must satisfy

$$\delta D(\psi_1, \triangle\psi) = R(\psi_1) \delta H(\psi_1, \triangle\psi) \qquad \forall\, \triangle\psi \in x\,. \tag{1.5}$$

From definitions of D and H and applying integration by parts we get

$$\begin{aligned}
\delta D(\psi, \triangle\psi) &= 2 \int_{x_0}^{x_1} \left(\frac{\hbar^2}{2\mu} \psi'(x)\, \triangle\psi'(x) + V(x)\psi(x)\, \triangle\psi(x) \right) \mathrm{d}x \\
&= 2 \int_{x_0}^{x_1} \left(-\frac{\hbar^2}{2\mu} \psi''(x) + V(x)\psi(x) \right) \triangle\psi(x) \mathrm{d}x\,, \\
\delta H(\psi, \triangle\psi) &= 2 \int_{x_0}^{x_1} \psi(x)\, \triangle\psi(x) \mathrm{d}x
\end{aligned}$$

[1] in Dirac's bra-ket formalism

[2] We do not distinguish between eigenvector and space spanned by an eigenvector, as the wave function is determined up to an arbitrary multiplicative constant. So the states are represented by one-dimensional subspace of vectors in the Hilbert space.

for any $\triangle\psi$ in x. Introducing the above expressions into the equation (1.5) for ψ_1 we obtain

$$\int_{x_0}^{x_1} \left(-\frac{\hbar^2}{2\mu}\psi_1''(x) + V(x)\psi_1(x) - R(\psi_1)\psi_1(x) \right) \triangle\psi(x)\mathrm{d}x = 0 \qquad \forall\, \triangle\psi \in x\ .$$

By a fundamental lemma of the variational calculus (sometimes known as Du Bois-Reymond lemma [17]) we derive the Euler-Lagrange equation for the given extremum problem in the form

$$-\frac{\hbar^2}{2\mu}\psi_1''(x) + V(x)\psi_1 = R(\psi_1)\psi_1 \qquad \text{for } x \in (x_0, x_1)\,.$$

Hence $\lambda^* \equiv R(\psi_1)$ is an eigenvalue for the original SL problem, moreover λ^* equals to the smallest eigenvalue λ_1, because the corresponding eigenfunction ψ_1 minimizes the functional $R = R(\psi)$.

The Rayleigh-Ritz method considers the problem of minimizing the Rayleigh quotient over some subspace $\mathcal{Y} = \mathrm{span}\{\varphi_1, \varphi_2, \ldots, \varphi_n\}$ of the space x, where $\varphi_1, \varphi_2, \ldots, \varphi_n$ is a given collection of fixed real function from x. Thus any function ψ from $\mathcal{Y}$ may be written in the form

$$\psi = c_1\varphi_1 + c_2\varphi_2 + \cdots + c_n\varphi_n$$

for an arbitrary real nonzero n-tuple of constants $(c_1, c_2, \ldots, c_n) = \vec{c}$.

Let us define two real functions d and h on $\mathbb{R}^n$ by

$$d(\vec{c}) = D\left(\sum_{i=1}^{n} c_i\varphi_i \right)$$

and

$$h(\vec{c}) = H\left(\sum_{i=1}^{n} c_i\varphi_i \right).$$

Equivalently, they can be expressed as

$$d(\vec{c}) = \sum_{i=1}^{n} a_{i,j}c_ic_j\,,$$

$$h(\vec{c}) = \sum_{i=1}^{n} b_{i,j}c_ic_j\,,$$

where

$$a_{i,j} = \int_{x_0}^{x_1} \left(\frac{\hbar^2}{2\mu} \varphi_i'(x)\varphi_j'(x) + V(x)\varphi_i(x)\varphi_j(x) \right) \mathrm{d}x = \langle \varphi_i | \, \hat{H} \, | \varphi_j \rangle \tag{1.6}$$

and

$$b_{i,j} = \int_{x_0}^{x_1} \varphi_i(x)\varphi_j(x)\mathrm{d}x = \langle \varphi_i | \varphi_j \rangle \,, \qquad i,j = 1,\ldots,n \,. \tag{1.7}$$

It is obvious from the above given form that the matrices $\mathbf{A} = (a_{i,j})$ and $\mathbf{B} = (b_{i,j})$ are symmetric.

The problem of minimizing the Rayleigh quotient $D(\psi)/H(\psi)$ over the subspace $\mathcal{Y}$ is equivalent to the problem of minimizing the ratio $d(\vec{c})/h(\vec{c})$ over $\mathbb{R}^n$. If $\vec{c}^* = (c_1^*, c_2^*, \ldots, c_n^*) \in \mathbb{R}^n$ is a minimum vector of the function d/h then necessarily it must hold

$$\left. \frac{\partial}{\partial c_k} \frac{d(\vec{c})}{h(\vec{c})} \right|_{\vec{c}=\vec{c}^*} = 0 \,, \qquad k = 1,\ldots,n \,,$$

i.e.,

$$\left. \frac{\partial d(\vec{c})}{\partial c_k} \right|_{\vec{c}=\vec{c}^*} = \frac{d(\vec{c}^*)}{h(\vec{c}^*)} \left. \frac{\partial h(\vec{c})}{\partial c_k} \right|_{\vec{c}=\vec{c}^*} , \qquad k = 1,\ldots,n \,. \tag{1.8}$$

Use of the symmetry properties of matrices $\mathbf{A}$ and $\mathbf{B}$ enables us to calculate the partial derivatives of d and h with respect to c_k, $k = 1,\ldots,n$ and after introducing these results into (1.8), we get the following system of equations

$$\sum_{j=1}^{n} a_{k,j} c_j^* = r \sum_{j=1}^{n} b_{k,j} c_j^* \,, \qquad k = 1,\ldots,n \,; \tag{1.9}$$

in the vector-matrix formulation as

$$\mathbf{A}\vec{c}^* = r\mathbf{B}\vec{c}^*, \tag{1.10}$$

where we have set

$$r = \frac{d(\vec{c}^*)}{h(\vec{c}^*)} \,.$$

The latter identity can be verified by multiplying (1.9) by c_k^* and summing over k. The matrix equation (1.10) has a nonzero solution $\vec{c}^*$ called an eigenvector if and only if

$$\det(\mathbf{A} - r\mathbf{B}) = 0 \,. \tag{1.11}$$

This generalized characteristic equation represents a polynomial equation of degree n with respect to the variable r which has generally n solutions. Due to symmetric

properties of given matrices $\mathbf{A}$ and $\mathbf{B}$ all solutions r are real. From the construction of the Rayleigh quotient $R(\psi) = d(\vec{c})/h(\vec{c})$ it follows that each solution r of (1.11) is an eigenvalue for the generalized matrix eigenvalue problem (1.10).

According to the Rayleigh's principle the smallest such eigenvalue $r = r_1$ gives an upper bound for the lowest eigenvalue λ_1 of the original SL problem, *i.e.*, $\lambda_1 \leq r_1$. It is clear that the Rayleigh-Ritz approximation r_1 is dependent on $n \in \mathbb{N}$, the number of given function $\varphi_1, \varphi_2, \ldots, \varphi_n$ in a way that $r_1(n) \leq r_1(m)$ if $n > m$. This result, which actually puts better accuracy of the desired eigenvalue approximation for larger n, can be proved by induction [16].

1.3 Variational principle for excited states

Our task is now to calculate approximate values for higher eigenvalues $\lambda_2, \lambda_3, \ldots$ so-called excited states. Finding the second eigenvalue λ_2 constitutes a variational problem on domain $x' = \ker(\hat{H} - \lambda_1 \mathbb{1})^{\perp}$. Applying the previous procedure on x' represents a searching for the minimum value of the Rayleigh quotient $R(\psi)$ over x subject to the added constraint

$$\int_{x_0}^{x_1} \psi_1(x)\psi(x)\mathrm{d}x = 0 \tag{1.12}$$

where ψ_1 is the eigenfunction of the SL problem corresponding to λ_1.

By the Euler-Lagrange multiplier theorem, we find that for a solution ψ_2 of the given extremum problem it holds

$$\delta D(\psi_2, \triangle\psi) - R(\psi_2)\delta H(\psi_2, \triangle\psi) - \alpha \int_{x_0}^{x_1} \psi_1(x)\, \triangle\psi(x)\mathrm{d}x = 0 \qquad \forall\, \triangle\psi \in x$$

for some suitable constant regarded as Euler-Lagrange multiplier. Using the formulas for the variations of D and H we receive

$$\int_{x_0}^{x_1} \left(-\frac{\hbar^2}{2\mu}\psi_2''(x) + V(x)\psi_2(x) - R(\psi_2)\psi_2(x) - \alpha\psi_1(x) \right) \triangle\psi(x)\mathrm{d}x = 0 \qquad \forall\, \triangle\psi \in x\,.$$

Fundamental lemma of the variational calculus provides a differential equation, which we afterwards multiply by function ψ_1 and integrate over (x_0, x_1). We find that

$$\int_{x_0}^{x_1} \left(-\frac{\hbar^2}{2\mu}\psi_2''(x) + V(x)\psi_2(x) - \lambda^*\psi_2(x) \right) \psi_1(x)\mathrm{d}x = \alpha \int_{x_0}^{x_1} \psi_1^2(x)\mathrm{d}x$$

where we set $\lambda^* = R(\psi_2)$. Applying constraint (1.12) for $\psi = \psi_2$ and two integrations by parts reduce the previous equation into

$$\begin{aligned}\alpha \int_{x_0}^{x_1} \psi_1^2(x)\mathrm{d}x &= \int_{x_0}^{x_1} \left(-\frac{\hbar^2}{2\mu}\psi_1''(x) + V(x)\psi_1(x)\right)\psi_2(x)\mathrm{d}x \\ &= \lambda_1 \int_{x_0}^{x_1} \psi_1(x)\psi_2(x)\mathrm{d}x\,.\end{aligned}$$

Since the last integral is equal to zero, it follows that

$$\alpha \int_{x_0}^{x_1} \psi_1^2(x)\mathrm{d}x = 0\,.$$

At the same time ψ_1 is a nonzero vector, hence $\alpha = 0$. Thus ψ_2 satisfies

$$-\frac{\hbar^2}{2\mu}\psi_2'' + V(x)\psi_2 = \lambda^*\psi_2 \qquad \text{for } x \in (x_0, x_1)\,.$$

Hence it is clear that $\lambda^* = R(\psi_2)$ is an eigenvalue for the SL problem. Since ψ_2 is a minimum vector in x for the Rayleigh quotient $R = R(\psi)$ subject to the orthogonality constraint (1.12), we can conclude that λ^* equals to the second eigenvalue λ_2.

Inductively, we can now continue the construction of higher eigenvalues. The n-th eigenvalue λ_n will be equal to the minimum value of the Rayleigh quotient $R(\psi)$ subject to the $n-1$ simultaneous orthogonality conditions

$$\int_{x_0}^{x_1} \psi_i(x)\psi(x)\mathrm{d}x = 0 \qquad \text{for } i = 1, \ldots, n-1\,.$$

In the following, let us show that for any distinct eigenvalues $\lambda^* \neq \lambda^{**}$ of the SL problem (1.3) with (1.4), the corresponding eigenfunction ψ^*, ψ^{**} must satisfy the orthogonality condition

$$\int_{x_0}^{x_1} \psi^*(x)\psi^{**}(x)\mathrm{d}x = 0\,.$$

Multiplying the Schrödinger equation (1.3) which is to be fulfilled for ψ^* by ψ^{**} and integrating over (x_0, x_1), and similarly multiplying (1.3) which is to be hold for ψ^{**} by ψ^* and integrating the resulting equation over (x_0, x_1) we find

$$\int_{x_0}^{x_1} -\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2\psi^*}{\mathrm{d}x^2}(x)\psi^{**}(x) + V(x)\psi^*(x)\psi^{**}(x)\mathrm{d}x = \lambda^* \int_{x_0}^{x_1} \psi^*(x)\psi^{**}(x)\mathrm{d}x$$

and

$$\int_{x_0}^{x_1} -\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2\psi^{**}}{\mathrm{d}x^2}(x)\psi^*(x) + V(x)\psi^{**}(x)\psi^*(x)\mathrm{d}x = \lambda^{**} \int_{x_0}^{x_1} \psi^{**}(x)\psi^*(x)\mathrm{d}x.$$

Now two integration by parts applied to one of these two equations are required to demonstrate the equality of left sides of both equations. From this result we obtain

$$(\lambda^* - \lambda^{**}) \int_{x_0}^{x_1} \psi^*(x)\psi^{**}(x)\mathrm{d}x = 0\,.$$

The desired result should arise for any distinct eigenvalues λ^*, λ^{**}.

♠

In the previous we have seen that the Rayleigh-Ritz method can be used to find approximate values for the minimum value of the Rayleigh quotient over some subspace $\mathcal{Y}$ spanned by finite set of function $\varphi_1, \varphi_2, \ldots, \varphi_n$. Let $r_1, r_2, \ldots, r_n$ be the eigenvalues of the matrix equation (1.10) obtained from the Rayleigh-Ritz procedure described in section 1.2. The numbers $r_1, r_2, \ldots, r_n$ are the solutions of generalized characteristic equation (1.11) and we index them in increasing order such that $r_1 \leq r_2 \leq \cdots \leq r_n$. Let $\vec{c}^{(1)}, \vec{c}^{(2)}, \ldots, \vec{c}^{(n)}$ be the corresponding eigenvectors in $\mathbb{R}^n$ for a generalized eigenvalue problem $\mathbf{A}\vec{c}^{(i)} = r_i\mathbf{B}\vec{c}^{(i)}$ for $i = 1, \ldots, n$, where $\vec{c}^{(i)} = (c_1^{(i)}, c_2^{(i)}, \ldots, c_n^{(i)})$. We let $\phi_i = \sum_{j=1}^n c_j^{(i)}\varphi_j$ denote the corresponding function for related problem in $\mathcal{Y}$. We shall prove that the second eigenvalue r_2 is equal to the minimum of $R = R(\psi)$ over $\mathcal{Y}$ subject to the constraint

$$\int_{x_0}^{x_1} \phi_1(x)\psi(x)\mathrm{d}x = 0\,. \tag{1.13}$$

If ϕ_2 is a minimum vector in $\mathcal{Y}$ for the functional R, then the Euler-Lagrange multiplier theorem implies that

$$\int_{x_0}^{x_1} \left(-\frac{\hbar^2}{2\mu}\phi_2''(x) + V(x)\phi_2(x) - R(\phi_2)\phi_2(x) - \alpha\phi_1(x)\right)\Delta\psi(x)\mathrm{d}x = 0 \qquad \forall\ \Delta\psi \in x$$

for some suitable multiplier α. We set $r^* \equiv R(\phi_2)$. It follows now from this last result and from a fundamental lemma of the variational calculus that $\phi_2 = \sum_{j=1}^n c_j^{(2)}\varphi_j$ must satisfy the following differential equation:

$$\sum_{j=1}^n c_j^{(2)} \left(-\frac{\hbar^2}{2\mu}\varphi_j''(x) + V(x)\varphi_j(x) - r^*\varphi_j(x)\right) = \alpha\sum_{j=1}^n c_j^{(1)}\varphi_j(x)$$

for $x \in (x_0, x_1)$. If we now multiply the latter equation on both sides by the function $\phi_1 = \sum_{k=1}^n c_k^{(1)}\varphi_k$ and integrate both sides over (x_0, x_1), then two integrations by parts are required to demonstrate the validity of the following equality.

$$\int_{x_0}^{x_1} \sum_{j,k=1}^n c_j^{(2)}c_k^{(1)} \left(\frac{\hbar^2}{2\mu}\varphi_j'(x)\varphi_k'(x) + V(x)\varphi_j(x)\varphi_k(x) - r^*\varphi_j(x)\varphi_k(x)\right)\mathrm{d}x =$$

$$= \alpha\int_{x_0}^{x_1} \sum_{j,k=1}^n c_j^{(1)}c_k^{(1)}\varphi_j(x)\varphi_k(x)\mathrm{d}x\,.$$

In order to simplify the notation we introduce matrix elements formulation (1.6) and (1.7). Thus we read

$$\sum_{j=1}^{n} c_j^{(2)} \left(\sum_{k=1}^{n} a_{j,k} c_k^{(1)} - r^* b_{j,k} c_k^{(1)} \right) = \alpha \sum_{j=1}^{n} c_j^{(1)} \left(\sum_{k=1}^{n} b_{j,k} c_k^{(1)} \right) .$$

The constraint (1.13) imposed on $\psi = \phi_2$ serves to eliminate $\sum_{j,k=1}^{n} b_{j,k} c_j^{(2)} c_k^{(1)}$, and the fact that $\vec{c}^{(1)}$ is a nonzero solution vector for the eigenvalue problem (1.9) with r_1 gives

$$r_1 \sum_{j,k=1}^{n} b_{j,k} c_j^{(2)} c_k^{(1)} = \alpha \sum_{j,k=1}^{n} b_{j,k} c_j^{(1)} c_k^{(1)} .$$

Again, due to the fulfilment of the constraint (1.13), we have

$$\alpha \sum_{j,k=1}^{n} b_{j,k} c_j^{(1)} c_k^{(1)} = 0 ,$$

whence $\alpha = 0$, and finally we can conclude that r^* must be equal to the second eigenvalue r_2.

Similarly, the k-th eigenvalue r_k is equal to the minimum value of the Rayleigh quotient $R(\psi)$ over $\mathcal{Y}$ subject to the $k-1$ simultaneous constraints

$$\int_{x_0}^{x_1} \phi_i(x) \psi(x) \mathrm{d}x = 0 \qquad \text{for } i = 1, \ldots, k-1 .$$

♠

Finally, we shall point out that in the case of finite basis approximation of the Hilbert space, it is not ensured that the function ϕ_1 lies in $\ker(\hat{H} - \lambda_1 \mathbb{1})$, because ϕ_1 is only an approximation of ψ_1. Thereafter, the use of the Rayleigh-Ritz procedure for finding eigenvalue r_n is subject to the choice of the trial function ψ from $(\ker(\hat{H} - r_1 \mathbb{1}) \oplus \cdots \oplus \ker(\hat{H} - r_{n-1} \mathbb{1}))^{\perp}$ but it is not guaranteed that ψ is from $(\ker(\hat{H} - \lambda_1 \mathbb{1}) \oplus \cdots \oplus \ker(\hat{H} - \lambda_{n-1} \mathbb{1}))^{\perp}$.

Chapter 2

Discrete variable approximation

2.1 Basic principles

In this section we present a method using the techniques of transformation theory for the Hamiltonian matrix evaluation (our conventions and notation in this section are consisted with Ref. [12]).

We consider a system whose Hamiltonian $\hat{H} = \hat{H}_0 + \triangle V$ is a Hamiltonian of a perturbed one-dimensional harmonic oscillator. The aim is to obtain an approximate energy levels by setting up the Hamiltonian in some convenient representation. Let $\{\varphi_i\}_{i=1}^{\infty}$ be a basis of $L^2(\mathbb{R}, dx)$ composed of eigenfunctions of $\hat{H}_0$. We have the usual completeness and orthogonality relations

$$\langle\varphi_i|\varphi_j\rangle \equiv \int \varphi_i^*(x)\varphi_j(x)\mathrm{d}x = \delta_{ij}$$

$$\sum_{i=1}^{\infty} |\varphi_i\rangle\langle\varphi_i| \equiv \sum_{i=1}^{\infty} \varphi_i^*(x)\varphi_i(x') = \delta(x - x')\,, \qquad i, j = 1, 2, \ldots$$

with $x \in (0, \infty)$ or $(-\infty, +\infty)$. Systems having infinite basis set can be handled approximately by a truncated basis $\{\varphi_i\}_{i=1}^{n}$. For simplicity we consider a real basis. The matrix representation of an operator $\hat{H}$ in a truncated bases is called the variational basis representation (VBR). The matrix elements are defined by

$$\mathbf{H}_{ij}^{\mathrm{VBR}} = \int \varphi_i(x) H \varphi_j(x)\mathrm{d}x\,, \qquad i, j = 1, 2, \ldots, n\,. \tag{2.1}$$

According the variational principle, as described in the previous chapter, an n function representation of $\hat{H}$ yields eigenvalues depending on n — the size of the basis set — which decrease monotonically to the true eigenvalues of $\hat{H}$. The basis sets $\{\varphi_i(x)\}_{i=1}^{n}$ are usually chosen with the physics of the problem in mind. Often orthogonal polynomials [1] times the square root of their appropriate weight functions are used.

Introducing a grid consisting of n coordinate points $\{x_\alpha\}_{\alpha=1}^n$ together with basis functions $\{\varphi_i\}_{i=1}^n$ define a finite quadrature called finite basis representation (FBR), which replaces the normal definition of the inner product in the Hilbert space of square integrable functions. Discrete variable representation (DVR) is isomorphic with the FBR, *i.e.*, approximate VBR on the set of n grid points. In section 2.2 we show that the isomorphism is ensured by an orthogonal transformation.

The Hamiltonian $\hat{H}_0$ can be essentially exactly evaluated in the VBR

$$\hat{H}_0\,\varphi_i = E_0\,\varphi_i\,,$$

thus in the FBR the matrix elements of $\hat{H}_0$ have the form

$$\mathbf{H}_0^{\mathrm{FBR}} = E_0\,.$$

Apparently

$$\mathbf{H}^{\mathrm{FBR}} = E_0 + \triangle\mathbf{V}^{\mathrm{FBR}}\,,$$

which is our task to obtain using numerical quadrature for a given basis.

2.2 DVR-FBR transformation

The matrix transformation method proposed by Harris *et al.* [8], and by Dickinson *et al.* [7], provides a facilitation of the matrix elements computation of a one-dimensional potential function. Suppose the function may be expressed as a convergent power series in the variable (coordinate operator X). Let $\mathbf{X}^{\mathrm{DVR}}$ be diagonal equivalent to $\mathbf{X}^{\mathrm{FBR}}$ given by a similarity transformation

$$\mathbf{X}^{\mathrm{DVR}} = P^T\mathbf{X}^{\mathrm{FBR}}P = \mathrm{diag}(x_1,\ldots,x_n)\,.$$

A potential matrix in the DVR is diagonal and it is generated by

$$\triangle\mathbf{V}^{\mathrm{DVR}} = \mathrm{diag}\left(\triangle V(x_1),\ldots,\triangle V(x_n)\right)\,.$$

Transforming back to the original representation we gain

$$\triangle\mathbf{V}^{\mathrm{FBR}} = P\,\triangle\mathbf{V}^{\mathrm{DVR}}P^T\,.$$

The transformation is defined [12] as

$$P_{i\alpha} = \varphi_i(x_\alpha)\,,$$

which corresponds to the fact that in the FBR the matrix elements are determined by numerical quadrature rather than by continuous integration (2.1), *i.e.*,

$$\triangle\mathbf{V}_{ij}^{\mathrm{FBR}} = \sum_{\alpha=1}^{n}\varphi_i(x_\alpha)\,\triangle V(x_\alpha)\varphi_j(x_\alpha)\,.$$

The grid points are chosen as the abscissas of Gauss-Hermite quadrature. The discrete orthogonality and completeness relation are given by[1]

$$\langle\varphi_i|\varphi_j\rangle = \sum_{\alpha=1}^{n} \varphi_i(x_\alpha)\varphi_j(x_\alpha) = (PP^T)_{ij} = \delta_{ij}\,,$$

$$\sum_{i=1}^{n} |\varphi_i\rangle\langle\varphi_i| \equiv \sum_{i=1}^{n} \varphi_i(x_\alpha)\varphi_i(x_\beta) = (P^TP)_{\alpha\beta} = \delta_{\alpha\beta}\,.$$

We are going to use the Hermite polynomials as the basis functions. This choice is corroborated by the later application to the harmonic oscillator representation. In the next section we summarize all necessary formulas concerning the Gauss-Hermite integration.

2.3 Gauss-Hermite quadrature

The sequence of functions $\mathrm{H}_n : \mathbb{R} \to \mathbb{R}$ for each $n = 0, 1, \ldots$ defined by the Rodrigues formula

$$\mathrm{H}_n(x) = (-1)^n e^{x^2} \frac{d^n}{\mathrm{d}x^n} e^{-x^2} \tag{2.2}$$

are known as Hermite polynomials. In the following we briefly summarize properties for the set $\{\mathrm{H}_n\}_{n=0}^{\infty}$. Their proof is not presented as it is technical and it can be found in almost all textbooks concerned with orthogonal polynomials (*e.g.* [2, 11]).

Using the formula (2.2) we find out that H_n is indeed a real polynomial of degree n.

The Hermite polynomials can be also generated from the following recurrence relation

$$\mathrm{H}_{n+1}(x) = 2x\mathrm{H}_n(x) - 2n\mathrm{H}_{n-1}(x)$$

with $\mathrm{H}_0(x) = 1$ and $\mathrm{H}_1(x) = 2x$.

Furthermore, they are orthogonal over $(-\infty, +\infty)$ with respect to the weight factor e^{-x^2}

$$\int_{-\infty}^{+\infty} e^{-x^2}\mathrm{H}_n(x)\mathrm{H}_m(x)\mathrm{d}x = \sqrt{\pi}2^n n!\delta_{n,m} \tag{2.3}$$

and they form an orthogonal basis for $L^2(\mathbb{R}, w(x)\mathrm{d}x)$ [5].

H_n are such polynomials p_n of degree n which vanish the integral

$$\int_{-\infty}^{+\infty} x^k p_n(x) e^{-x^2}\mathrm{d}x \qquad \text{for } k = 0, \ldots, n-1\,.$$

[1] we adopt the bra-ket notation

Considering the computer programming, factorials that occur in the normalization formula (2.3) can cause numerical overflow for large n. To avoid this, a constructive procedure is finding the orthonormal set of Hermite polynomials, denoted as $\tilde{\mathrm{H}}_j$, from the recurrence relation

$$\tilde{\mathrm{H}}_{-1} = 0,\, \tilde{\mathrm{H}}_0 = \frac{1}{\pi^{1/4}},\, \tilde{\mathrm{H}}_{j+1} = x\sqrt{\frac{2}{j+1}}\tilde{\mathrm{H}}_j - \sqrt{\frac{j}{j+1}}\tilde{\mathrm{H}}_{j-1}\,.$$

We shall be concerned with the numerical quadrature over infinite intervals appearing the weighting function $w(x) = e^{-x^2}$. The Gauss integration formula takes the form

$$\int_{-\infty}^{+\infty} w(x)f(x)\mathrm{d}x = \sum_{j=1}^{n} w_j f(a_j) + E_{rr}$$

and is known to be exact if $f(x)$ is a polynomial whose order is not greater than $2n-1$. For an approximation of the order n and Hermite polynomials the grid points a_j, $j = 1, \ldots, n$ will be identical with the Gauss-Hermite abscissas, which are given as the zeros of the Hermite polynomial H_n of degree n. The weights w_j, $j = 1, \ldots, n$ are obtained by solving a set of $2n$ non-linear equations

$$\sum_{j=1}^{n} w_j a_j^k = \int_{-\infty}^{+\infty} w(x)x^k\mathrm{d}x\,, \qquad k = 0, \ldots, 2n-1$$

for $2n$ constant. The Gauss-Hermite weights have the form [15]

$$w_j = -\frac{2^{n+1}n!\sqrt{\pi}}{\mathrm{H}_n'(a_j)\mathrm{H}_{n+1}(a_j)}$$

and the error term becomes [15]

$$E_{rr} = \frac{n!\sqrt{\pi}}{2^n(2n)!}f^{(2n)}(\eta)$$

for η lying in $(-\infty, +\infty)$.

2.4 Numerical examples

In this section we present numerical results to illustrate the DVR-FBR formulation which verify the utility of the formal approach. We apply the DVR method which has been discussed above to bound-state calculations in one-dimensional model problems.

2.4.1 Anharmonic oscillator

The very simple example is an anharmonic oscillator with a quartic anharmonicity in its Hamiltonian.

$$\hat{H} = -\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \frac{1}{2}x^2 + \lambda x^4 \,. \tag{2.4}$$

We can use this system to illustrate the approximation DVR to VBR. The DVR technique lead to the lowest nine energy levels for the Hamiltonian (2.4) using truncated basis of 75 harmonic oscillator wave functions. The energy eigenvalues are quoted in Table 2.1. The energies obtained in the DVR yield good agreement of the variational eigenvalues and of results obtained by other method [9]. In order to obtain Hamiltonial (2.4) in the standard harmonic oscillator representation, we calculated the formula (4.1) enclosed in Appendix. For matrix diagonalization the subroutine `jacobi` [14] was used.

It is noteworthy that the error of the matrix elements may be eliminated by increasing the size of the basis set. An example of this convergence is provided in Table 2.2 for the ground state E_0, over a wide range of values of perturbation parameter.

Table 2.1: Comparison of eigenvalues of single quartic anharmonic oscillator: First line – data taken from ref. [9]. Second line – values obtained in the VBR. Third line – values obtained in the DVR.

λ	E_0	E_1	E_2	E_3	E_4
0.1	0.559146	1.76950	3.13862	4.62888	6.22030
	0.55914632718351957	1.76950264394905425	3.13862430849812044	4.62888280888814174	6.22030090000652188
	0.55914632718351964	1.76950264394905465	3.13862430849812002	4.62888280888814307	6.22030090000652347
0.2	0.602405	1.95054	3.53630	5.29127	7.18446
	0.60240516368624971	1.95054352563477926	3.53629936323546239	5.29126854258952996	7.18445629300991506
	0.60240516368624974	1.95054352563478006	3.53629936323546312	5.29126854258953294	7.18445629300991406
0.3	0.637992	2.09464	3.84478	5.79657	7.91175
	0.63799178317127853	2.09464198569305194	3.84478264749769176	5.79657363271648246	7.91175272980421213
	0.63799178317127858	2.09464198569305182	3.84478264749769361	5.79657363271648229	7.91175272980421784
0.4	0.668773	2.21693	4.10284	6.21559	8.51141
	0.66877260407408747	2.21692576979442643	4.10283869576092831	6.21559131970722670	8.51141353884573374
	0.66877260407408767	2.21692576979442757	4.10283869576092819	6.21559131970723211	8.51141353884569796
0.5	0.696176	2.32441	4.32752	6.57840	9.02878
	0.69617582076514593	2.32440635210603879	4.32752497887965693	6.57840194902495179	9.02877871815169633
	0.69617582076514595	2.32440635210604007	4.32752497887965681	6.57840194902495679	9.02877871815190858
0.6	0.721039	2.42102	4.52812	6.90105	9.48773
	0.72103891120418120	2.42101793469132793	4.52812188268907896	6.90105165739502403	9.48772738101590676
	0.72103891120418107	2.42101793469132698	4.52812188268905924	6.90105165739489124	9.48772738101470559
0.7	0.743904	2.50923	4.71033	7.19327	9.90261
	0.74390349531419521	2.50922810209887901	4.71032809821740301	7.19326528107694360	9.90261069822691289
	0.74390349531419553	2.50922810209887936	4.71032809821737519	7.19326528107613594	9.90261069821267093
0.8	0.765144	2.59070	4.87793	7.46145	10.2828
	0.76514387828334895	2.59070354398019141	4.87793258015952203	7.46144743962700733	10.28282325190509432
	0.76514387828334895	2.59070354398019731	4.87793258015964515	7.46144743962543089	10.28282325186833646
0.9	0.785032	2.66663	5.03360	7.71007	10.6349
	0.78503151653427469	2.66663148191317781	5.03360132263310591	7.71007182330099569	10.63489714198502120
	0.78503151653427150	2.66663148191317534	5.03360132263333249	7.71007182330050966	10.63489714196150260
1	0.803771	2.73789	5.17929	7.94240	10.9636
	0.80377065123428077	2.73789226800845548	5.17929168764087678	7.94240398440376487	10.96358309416107544
	0.80377065123426839	2.73789226800838703	5.17929168763997083	7.94240398440649109	10.96358309424070754
10	1.50497	5.32161	10.3471	16.0901	22.4088
	1.50497242892918107	5.32160869140996983	10.34706508449636792	16.09016539100116304	22.40908801505264604
	1.50497238680653034	5.32160764313518975	10.34705025403443734	16.09015140492408236	22.40914896709792714

Table 2.1 – continued from previous page

λ	E_5	E_6	E_7	E_8
0.1	7.89977	9.65784	11.4873	13.3790
	7.8997672278714262	9.6578399921601460	11.4873155794442057	13.3824748074457703
	7.8997672278714282	9.6578399921601523	11.4873155794442088	13.3824748074457727
0.2	9.19634	11.3132	13.5249	15.8222
	9.1963395070359248	11.3132385264636586	13.5249070268748856	15.8233190304556312
	9.1963395070359297	11.3132385264636604	13.5249070268749012	15.8233190304556732
0.3	10.1665	12.5443	15.0328	17.6224
	10.1664888874193629	12.5442586590131458	15.0327712465112421	17.6224482070739071
	10.1664888874193693	12.5442586590132184	15.0327712465104053	17.6224482070577437
0.4	10.9631	13.5520	16.2642	19.0889
	10.9631374762192589	13.5520345491231725	16.2642253396762832	19.0889230985864354
	10.9631374762189555	13.5520345491199077	16.2642253396799212	19.0889230986928062
0.5	11.6487	14.4177	17.3204	20.3452
	11.6487207256133387	14.4176692297676385	17.3204241605784050	20.3451930424110085
	11.6487207256122254	14.4176692297343685	17.3204241603858549	20.3451930413026503
0.6	12.2557	15.1832	18.2535	21.4542
	12.2558276535138908	15.1832136255226953	18.2535435621961727	21.4541547637678592
	12.2558276535171924	15.1832136255823276	18.2535435611720800	21.4541547485485289
0.7	12.8039	15.8737	19.0945	22.4530
	12.8039297077360315	15.8736836230350341	19.0945182824262445	22.4529987085608745
	12.8039297077149712	15.8736836232272953	19.0945182815824950	22.4529986786402631
0.8	13.3057	16.5053	19.8634	23.3658
	13.3057199176887599	16.5053359236445088	19.8634030353324201	23.3657886099105909
	13.3057199174693928	16.5053359219619154	19.8634030374443711	23.3657886332191360
0.9	13.7700	17.0894	20.5740	24.2091
	13.7699956825781401	17.0894112853921606	20.5740393843532310	24.2091087806493759
	13.7699956818428575	17.0894112762460892	20.5740393819314065	24.2091089255967020
1	14.2031	17.6340	21.2364	24.9950
	14.2031391054388894	17.6340491274851290	21.2364355035083524	24.9949368128145636
	14.2031391040178452	17.6340491049835819	21.2364354562788940	24.9949368624830406
10	29.2115	36.4369	44.0401	51.9865
	29.2148501463718370	36.4480047551850968	44.0561474239281953	52.2605519223092867
	29.2121423978726043	36.4237990904842732	44.0032063666431199	52.2894683315904132

Table 2.2: Convergence of the ground state energy with the increase in dimension. Values are obtained in the DVR. Data from ref. [10] are shown in the last column.

λ	5	10	20	50	190	ref.[10]
0.002	0.50148962	0.50148966	0.50148966	0.50148966	0.50148966	0.50148966
0.006	0.50440879	0.50440971	0.50440971	0.50440971	0.50440971	0.50440971
0.01	0.50725239	0.50725620	0.50725620	0.50725620	0.50725620	0.50725620
0.05	0.53245436	0.53264279	0.53264279	0.53264275	0.53264275	0.53264275
0.1	0.55859395	0.55914355	0.55914633	0.55914633	0.55914633	0.55914633
0.3	0.63970413	0.63795822	0.63799174	0.63799178	0.63799178	0.63799178
0.5	0.70629058	0.69636689	0.69617656	0.69617582	0.69617582	0.69617582
0.7	0.76583722	0.74462484	0.74390600	0.74390350	0.74390350	0.74390350
1	0.84589443	0.80546194	0.80376942	0.80377065	0.80377065	0.80377065
2	1.05480932	0.95305322	0.95144484	0.95156848	0.95156847	0.95156847
50	1.77793502	2.06351493	2.37658429	2.49915094	2.49970877	2.49970877
200	1.81932006	4.16758055	3.27105383	3.94731130	3.93093119	3.93093134
1000	1.83052250	15.23625601	6.29066011	6.19159111	6.69418023	6.69422085

2.4.2 Morse oscillator

It is instructive to take the Morse oscillator for which analytic eigenvalues are known and for which accurate variational solutions are difficult to obtain. The Morse potential (Figure 2.1) is given by the expression

$$V(r) = D(1 - e^{-a(r-r_e)})^2 - D\,,$$

which is a function of the interatomic distance. Here D represents the bond dissociation energy, r is the distance between the bonded atoms and r_e is the equilibrium bond length.

The allowed vibrational energy levels E_n are described by,

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right) - \hbar\omega x_e\left(n + \frac{1}{2}\right)^2 - D\,, \tag{2.5}$$

where n is the vibrational quantum number, ω is the harmonic vibrational frequency and is related to a and D by

$$a = \omega\sqrt{\frac{\mu}{2D}}\,.$$

The analytic formula (2.5) expresses the experimental values quite accurately. The parameter x_e is called the anharmonicity constant,

$$x_e = \frac{\hbar\omega}{4D}\,.$$

In our numerical study we consider a particular Morse oscillator with the parameters $r_e = 1.9975\,\mathrm{a}_0$, $a = 0.711248\,\mathrm{a}_0^{-1}$, $D = 188.4355\ 2\mu\,\mathrm{a.u.}$ [6]. These were obtained by fitting the Morse potential to a computed potential energy curve for H_2^+. Energy is given in units of 2μ atomic units, where μ is the reduced mass of the nuclei.

The nine lowest calculated bound-states are listed in Table 2.3. As a test of the numerical accuracy we presented additional data for comparison. The results obtained from numerical integration using Numerov's method based on polynomial approximation (column $[e]$) and exponentially fitted method of Raptis and Allison (column $[f]$) as well as analytic eigenvalues (column $[a]$) are considered. We carried out the DVR calculations in the search space of dimension 19. In defining the DVR basis functions the truncated basis of 19 standard harmonic oscillator basis functions $\{\varphi_i\}$ were used along with Gauss-Hermite quadrature points $\{x_i\}$ and weights $\{w_i\}$. In columns $[b]$ and $[c]$ we compare the DVR with standard quadrature points ($r_e = 1.9975\,\mathrm{a}_0$) vs shifted quadrature points ($r_e + \triangle = 2.76763\,\mathrm{a}_0$).

Table 2.3: Comparison of computed eigenvalues with various approximation for Morse potential: $[a]$ analytical from the formula (2.5), $[b]$ with 19 Gauss-Hermite DVR points ($r_e = 1.9975\,\mathrm{a_0}$), $[c]$ with 19 shifted Gauss-Hermite DVR points ($r_e + \triangle = 2.76763\,\mathrm{a_0}$), $[d]$ with 25 shifted Gauss-Hermite DVR points ($r_e + \triangle = 2.8479\,\mathrm{a_0}$), $[e]$ by the method of Numerov from ref. [3], $[f]$ by the exponentially fitted method of Raptis and Allison from ref. [3].

n	$[a]$	$[b]$	$[c]$	$[d]$	$[e]$	$[f]$
0	-178.79853835	-178.79853968	-178.79853854	-178.79853969	-178.79853968	-178.79853968
1	-160.28342563	-160.28342736	-160.28342639	-160.28342733	-160.28342738	-160.28342739
2	-142.78006034	-142.78006337	-142.78019917	-142.78006079	-142.78006246	-142.78006248
3	-126.28844249	-126.28845054	-126.28921194	-126.28843705	-126.28844493	-126.28844496
4	-110.80857207	-110.80847905	-110.80923038	-110.80857691	-110.80857478	-110.80857481
5	-96.34044909	-96.33554770	-96.33456450	-96.34057955	-96.34045201	-96.34045205
6	-82.88407355	-82.78357935	-82.86222111	-82.88455205	-82.88407662	-82.88407666
7	-70.43944543	-69.54156948	-70.41075747	-70.44024758	-70.43944861	-70.43944865
8	-59.00656476	-55.19856438	-59.00656772	-59.00656474	-59.00656798	-59.00656802

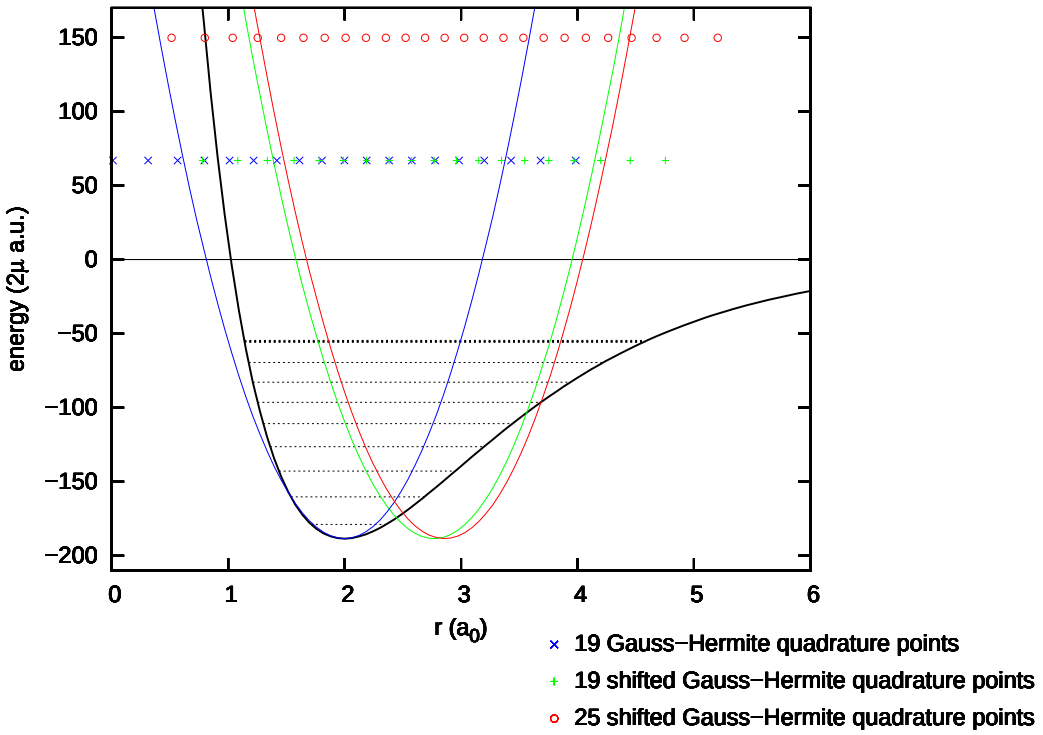

Figure 2.1: *Plot of the Morse potential with its nine bound states of interest, and linear harmonic oscillator potentials with 19 non-shifted quadrature points (blue line), 19 shifted quadrature points (green line), and 25 shifted quadrature points (red line).*

From the listed results, we observed that the accuracy produced by the DVR technique is in good agreement with other numerical integration method. For higher energy levels the numerical accuracy decreases. In order to achieve desired accuracy the method would get numerically more expensive. For the high excited states calculation it is preferable to use methods discussed in [3].

The Morse potential and energy levels and the linear harmonic potential are shown in Fig. 2.1. Also 19 non-shifted and shifted Gaussian quadrature points are plotted. As one can see in Fig. 2.1 the use of shifted Gauss-Hermite quadrature points appears to be deliberately chosen for a region of potential well which is reflected in the convergence for higher eigenvalues. Figure 2.2 contains a graph of the normalized wave function corresponding to $n = 9$ state and Gaussian points.

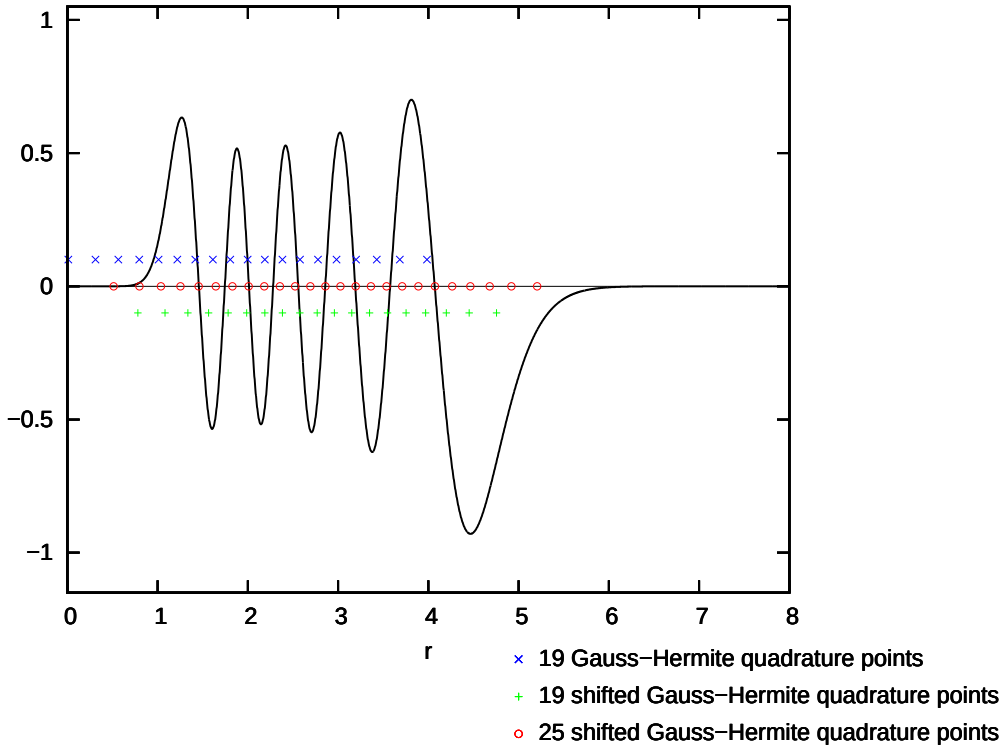

Figure 2.2: *Plot of the normalized wave function obtained for the $n = 9$ state.*

Chapter 3

Extension to two dimensions

3.1 Theoretical background

Let $\hat{H}$ be a quantum Hamiltonial with two degrees of freedom. We consider the potential

$$V(x,y) = V_x \otimes \mathbb{1}_y + \mathbb{1}_x \otimes V_y + W(x,y)$$

containing a coupling term $W(x,y)$. The present chapter describes eigenvalue calculations for the Hamiltonian operator

$$\hat{H}(x,y) = \hat{H}_x \otimes \mathbb{1}_y + \mathbb{1}_x \otimes \hat{H}_y + W(x,y)\,. \tag{3.1}$$

Let the one-dimensional operators $\hat{H}_x$ and $\hat{H}_y$ have known energy levels and eigenstates forming orthonormal bases in $\mathscr{H}_x$ and $\mathscr{H}_y$, arising from the time-independent Schrödinger equations:

$$\hat{H}_x \varphi_n(x) = E_n^x \varphi_n(x)\,, \tag{3.2}$$

$$\hat{H}_y \chi_m(y) = E_m^y \chi_m(y)\,. \tag{3.3}$$

The most obvious way to build a two-dimensional basis for solving a coupled Schrödinger equation is to make a direct product of one-dimensional basis sets

$$\{\varphi_n(x) \otimes \chi_m(y)\}_{\substack{n\geq 1 \\ m \geq 1}}\,. \tag{3.4}$$

The eigenstates of $\hat{H}$ are not, in general, direct product function in x and y.

An arbitrary diagonal matrix element of the Hamiltonian (3.1) in the matrix representation is given by conventional action on $\mathscr{H} = \mathscr{H}_x \otimes \mathscr{H}_y$ by

$$\langle \varphi_n \otimes \chi_m | \, \hat{H}(x,y) \, | \varphi_n \otimes \chi_m \rangle = E_n^x + E_m^y + W_{n,n;m,m}\,,$$

where $W_{n,n;m,m} = \langle \varphi_n \otimes \chi_m | \, W(x,y) \, | \varphi_n \otimes \chi_m \rangle$. Note that if $W(x,y) = 0$ then the direct product functions (3.4) form eigenfunctions corresponding to the eigenvalues $E_n^x + E_m^y$. In this basis two-dimensional Hamiltonian with a non-zero coupling term has off-diagonal matrix elements. In a special case $W(x,y) = W_x \otimes W_y$ we have

$$\begin{aligned} \langle \varphi_n \otimes \chi_m | \, \hat{H}(x,y) \, | \varphi_{n'} \otimes \chi_{m'} \rangle = & E_n^x \, \delta_{n,n'} \delta_{m,m'} \; + \; E_m^y \, \delta_{n,n'} \delta_{m,m'} + \\ & + \langle \varphi_n | \, W_x \, | \varphi_{n'} \rangle \langle \chi_m | \, W_y \, | \chi_{m'} \rangle \, . \end{aligned}$$

In this case the extension of the DVR method into two-dimensional systems is straightforward.

3.2 Numerical illustration

The DVR method is applied to a pair of coupled oscillators with quartic coupling. These systems are characterized by the Hamiltonian:

$$\hat{H}(x,y) = -\frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial y^2} + x^2 + y^2 + W(x,y).$$

We have chosen units in which $\hbar = 1$. For this problem we take "double-well" potentials given by the expression

$$V(Z^2, \lambda; x, y) = -Z^2(x^2 + y^2) + \lambda(x^4 + 2x^2y^2 + y^4).$$

The depth of the double-well is controlled by the parameters Z^2 and λ (Figure 3.1).

The Hamiltonian is evaluated in the standard two-dimensional harmonic oscillator basis representation:

$$\psi_{n,m}(x,y) \propto \mathrm{H}_n(x) \mathrm{H}_m(y) e^{-\frac{x^2}{2} - \frac{y^2}{2}} \, .$$

The energy eigenvalues of two-dimensional oscillators have been calculated for several state numbers and over a wide range of the perturbation parameters Z^2 and λ. The used DVR technique requires handling of matrix direct product. The convention of matrix multiplication used is enclosed in Appendix. We are dealing with matrices of dimensions 30×30.

Table 3.1: Eigenvalues of a double-well potential $V(Z^2, \lambda; x, y)$ for several sets of perturbation parameters computed with various approximation for three eigenstates: First line – power series method, data from ref. [19]. Second line – inner product technique, data from ref. [20]. Third line – DVR method.

Z^2	λ	$E_{0,0}$	$E_{1,0} = E_{0,1}$	$E_{2,0} = E_{0,2}$
1/6	1/6	1.0843151777768309192	2.61649090835940491	4.439089607962285029
		1.084315	2.61649	4.43908
		1.08431518	2.61649091	4.43908961
1	1	1.6374879527236908208	4.19968538748636154	7.328144388065296548
		1.63748	4.19968	7.32814
		1.63748794	4.1996852	7.3281444
2	2	1.8044830442464193546	4.86881781300593481	8.676133945433321839
		1.8044	4.8688	8.67613
		1.8044833	4.86882	8.676132
$\sqrt{5}$	$\sqrt{5}$	1.8220774473995417074	4.971144762873404234 39	8.897084051577699173 76
		1.8221	4.9711	8.89708
		1.8220773	4.97115	8.89707
3	3	1.8488321914370639803	5.22422325263170673	9.474465483207472146
		1.8488	5.2242	9.4744
		1.84882	5.22421	9.47443
5	5	1.7968689041605638879	5.56732946175554058	10.418323520678918695
		1.796	5.567	10.418
		1.79684	5.5671	10.41839
6	6	1.73462465018626441306	5.64268198028411299	10.717618348733334183
		1.734	5.642	10.717
		1.734625	5.642466	10.7179
10	10	1.3709684666267474547	5.63641781301499726	11.355415550499845011
		1.371	5.636	11.355
		1.371	5.637	11.357

Table 3.1 – continued from previous page

Z^2	λ	$E_{0,0}$	$E_{1,0} = E_{0,1}$	$E_{2,0} = E_{0,2}$
1/4	1	2.1787811759361418227	5.10862071412588021162	8.54203369483475573005
		2.178781	5.108621	8.542033
		2.17878119	5.10862074	8.5420338
1	1/4	0.16516532922363154 86	1.29666328921032645832	2.87513314732153278819
		0.16516	1.29666	2.87513
		0.16516533	1.29666329	2.87513315
1	4	3.2988377079349240454	7.83701536032146873650	13.19306206246391090591
		3.298837	7.837015	13.193062
		3.29884	7.837014	13.1931
4	1	-1.6746781702247934097	-0.56212069832440285085	1.36847851852892882643
		-1.674	-0.5621	1.36847
		-1.6746788	-0.5621205	1.368479
$\sqrt{2}$	$4\sqrt{2}$	3.6425216866654988021	8.69439952226333190438	14.671297085025425 26061
		3.64252	8.694399	14.671297
		3.64255	8.6946	14.6713
$4\sqrt{2}$	$\sqrt{2}$	-2.8174073854179428693	-1.77619140084241815847	0.19646195361830885756
		-2.817	-1.776	0.19646
		-2.817402	-1.77618	0.196462
2	8	4.0119688764113039501	9.62939034169658128114	16.29400223524496885588
		4.0119	9.62939	16.294002
		4.011967	9.6299	16.294
8	2	-4.5221383627768976017	-3.57193644204140065221	-1.58417228650699250109
		-4.522	-3.572	-1.584
		-4.52212	-3.57190	-1.58419
$\sqrt{7}$	$4\sqrt{7}$	4.3281447185753846384	10.44233030057788965314	17.71490107592092 72767
		4.3281	10.44233	17.714901
		4.328	10.4426	17.712
$4\sqrt{7}$	$\sqrt{7}$	-6.4901059947471383543	-5.61858663113509389619	-3.63865699600365 90324
		-6.490	-5.618	-3.638
		-6.49013	-5.618583	-3.6387

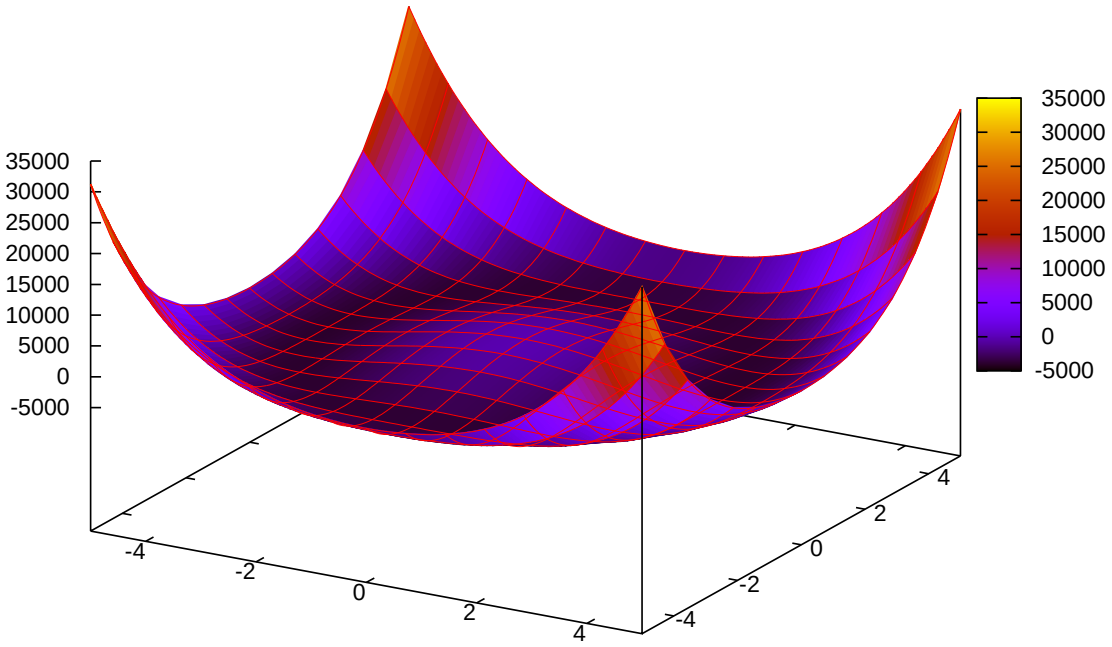

Figure 3.1: *Illustration of the "double-well" potential* $V(Z^2 = 625, \lambda = 25; x, y)$.

Our results are compared in Table 3.1 with results produced by power series [19] and inner product perturbative techniques [20], the agreement among them being good. We can observe in Table 3.1 that for larger values of Z^2/λ, the well is deep and wide, the magnitude of the difference between the calculated ground state level and excited states decreases.

Chapter 4

Conclusion

In this research project a method for constructing discrete variable representation of quantum mechanical Hamiltonian has been introduced and its properties have been explored by means of mathematical analysis and numerical calculations. Numerical examples, the solution of the single anharmonic oscillator and Morse oscillator eigenvalue problems using the DVR method based on the standard harmonic oscillator basis set, and the solution of the eigenvalue problem of a two-dimensional coupled Hamiltonian in a direct product basis, have revealed remarkable accuracy of the method. Numerical and theoretical results show that the efficiency of quantum mechanical numerical calculations rely in great part on the right choice of basis functions.

Appendix

Convention of matrix direct product

We may define the direct product of matrices as follows. Let $\mathbf{B} = (B_{ij})$, $\mathbf{C} = (C_{kl})$ be matrices, where $\mathbf{B}$ is of size $(m \times m)$, and $\mathbf{C}$ of size $(n \times n)$, then the matrix $\mathbf{A} = \mathbf{B} \otimes \mathbf{C}$ with indices (α, β) is their direct product. The following convenient ordering convention is used:

$$\mathbf{A} = \begin{pmatrix} B_{11}\,\mathbf{C} & B_{12}\,\mathbf{C} & \dots & B_{1m}\,\mathbf{C} \\ B_{21}\,\mathbf{C} & B_{22}\,\mathbf{C} & \dots & B_{2m}\,\mathbf{C} \\ \vdots & \vdots & \ddots & \vdots \\ B_{m1}\,\mathbf{C} & B_{m2}\,\mathbf{C} & \dots & B_{mm}\,\mathbf{C} \end{pmatrix}$$

We may represent this by index notation.

$$A_{\alpha\beta} = B_{ij} C_{kl}\,,$$

where

$$\alpha = n(i-1) + k\,,$$
$$\beta = n(j-1) + l\,.$$

We note that the size of $\mathbf{B} \otimes \mathbf{C}$ is $(mn \times mn)$.

Useful integrals

$$\int_{-\infty}^{+\infty} \mathrm{H}_n(x)\mathrm{H}_m(x)x^2e^{-x^2}\mathrm{d}x = \frac{1}{2}\sqrt{\pi}2^n n!\delta_{n,m} + \\ + \sqrt{\pi}\sum_{i=0}^{2}\binom{2}{i}\binom{n}{i}2^{n-i}i!(n+2(1-i))!\delta_{n+2(1-i),m}\,.$$

$$\int_{-\infty}^{+\infty} \mathrm{H}_n(x)\mathrm{H}_m(x)x^4e^{-x^2}\mathrm{d}x = \frac{3}{4}\sqrt{\pi}2^n n!\delta_{n,m} + \\ + 3\sqrt{\pi}\sum_{i=0}^{2}\binom{2}{i}\binom{n}{i}2^{n-i}i!(n+2(1-i))!\delta_{n+2(1-i),m} + \\ + \sqrt{\pi}\sum_{i=0}^{4}\binom{4}{i}\binom{n}{i}2^{n-i}i!(n+2(2-i))!\delta_{n+2(2-i),m}\,. \tag{4.1}$$

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