Part I

One-dimensional problems

1 Variational solution of the Schrödinger equation

In this chapter we solve the eigenvalue problem for the quantum mechanical Hamiltonian

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x) \tag{1.1}$$

using the variational method. We are interested in finding the discrete eigenvalues E_i and eigenfunctions Φ_i that satisfy

$$H\Phi_i(x) = E_i\Phi_i(x), \tag{1.2}$$

which is the time-independent Schrödinger equation (TISE).

For now, we restrict ourselves to bound state problems. The bound state wave function is confined to a finite region and is zero on the region's boundary. Scattering problems are presented in later chapters.

Here we will describe variational solutions using analytical basis functions. Numerical grid approaches for the solution of the Schrödinger equation will be presented in the next chapter.

1.1 Variational principle

The variational method is one of the most powerful approaches for solving quantum mechanical problems. The basic idea is to guess a "trial" wave function for the problem, which consists of some adjustable parameters called variational parameters. These parameters are adjusted until the energy of the trial wave function is minimized. The resulting wave function and its corresponding energy are then the variational-method approximations to the exact wave function and energy.

The variational approach is based on the following theorems [307]:

THEOREM 1.1 *Ritz theorem: For an arbitrary function Ψ, the expectation value of H is given by*

$$E = \frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle} \geq E_1, \tag{1.3}$$

where the equality holds if and only if Ψ is the exact ground state wave function of H with eigenvalue E_1.

This theorem gives us an upper bound for the ground state energy. The theorem can be generalized to excited states:

THEOREM 1.2 *Generalized Ritz theorem: The expectation value of the Hamiltonian is stationary in the neighborhood of its discrete eigenvalues.*

The proofs of these theorems can be found in many quantum mechanics textbooks (see e.g. [218]).

Minimizing the energy corresponding to the trial wave function gives an approximation to the true ground state energy, as long as the ground state wave function can be represented by the trial wave function. To use this method for the first excited state we need to choose a trial wave function that is orthogonal to the ground state. For the second excited state we use a trial wave function orthogonal to both the ground state and first excited state wave functions and repeat the minimization. This can be continued for higher states. A procedure such as the Gram–Schmidt algorithm [105] can be used to generate orthogonal wave functions.

To use the variational principle one has to choose a suitable trial function. In most cases a linear combination of independent "basis" functions is used. The trial wave function Φ is expanded into a set of N basis functions as

$$\Phi(x) = \sum_{i=1}^{N} c_i \phi_i(x) \tag{1.4}$$

where the ϕ_i are basis functions and the c_i are linear-combination coefficients. According to the Ritz variational principle, the correct expectation value E of the Hamiltonian with this trial function is stationary against infinitesimal changes of the linear combination coefficients c_i. This condition leads to the generalized eigenvalue problem

$$HC_k = \epsilon_k O C_k, \tag{1.5}$$

which in detailed form reads as

$$\sum_{i=1}^{N} H_{ij} c_{ki} = \epsilon_k \sum_{i=1}^{N} O_{ij} c_{ki} \qquad (j = 1, \ldots, N) \tag{1.6}$$

where

$$H_{ij} = \langle \phi_i | H | \phi_j \rangle \tag{1.7}$$

are the matrix elements of the Hamiltonian,

$$O_{ij} = \langle \phi_i | \phi_j \rangle \tag{1.8}$$

are the overlap matrix elements of the basis functions, and C_k is a vector of linear combination coefficients for the kth eigenvector:

$$C_k = \begin{pmatrix} c_{k1} \\ \vdots \\ c_{kN} \end{pmatrix}. \tag{1.9}$$

Solving the eigenproblem Eq. (1.5) gives the variational approximation to the true eigensolutions.

The mini-max theorem [307] relates the (exact) eigenvalues E_i of the Hamiltonian and the (approximate) eigenvalues ϵ_i of Eq. (1.5):

THEOREM 1.3 *Mini-max theorem: Let H be a Hermitian Hamiltonian with discrete eigenvalues $E_1 \le E_2 \le E_3 \le \cdots$ and let $\epsilon_1 \le \epsilon_2 \le \epsilon_3 \le \cdots \le \epsilon_N$ be the eigenvalues of Eq.* (1.5)*, then*

$$E_1 \le \epsilon_1, \quad E_2 \le \epsilon_2, \quad \cdots \quad E_N \le \epsilon_N. \tag{1.10}$$

The variational principle gives an upper bound to the true eigenenergy. To improve this approximation one has to decrease the upper bound and this can be done by increasing the number of basis functions in the expansion in Eq. (1.4), as shown by the following theorem [307]:

THEOREM 1.4 *Let $\epsilon_1 \le \epsilon_2 \le \epsilon_3 \le \cdots \le \epsilon_N$ be the solution of Eq.* (1.5) *using the basis functions $\phi_i(x)_{i=1}^N$ and let $\epsilon'_1 \le \epsilon'_2 \le \epsilon'_3 \le \cdots \le \epsilon'_{N+1}$ be the solution of Eq.* (1.5) *using the basis functions $\phi_i(x)_{i=1}^N$ and also $\phi_{N+1}(x)$. Then*

$$\epsilon'_1 \le \epsilon_1 \le \epsilon'_2 \le \epsilon_2 \le \cdots \le \epsilon'_N \le \epsilon_N \le \epsilon'_{N+1}. \tag{1.11}$$

Using these theorems one can calculate the approximate eigenvalues and eigenvectors of the Hamiltonian operator using a suitable set of basis functions.

1.2 Variational calculations with Gaussian basis functions

In a variational calculation many different basis functions can be used, but, depending on the nature of the problem, certain basis functions might be more appropriate than others. In this section we will use Gaussian basis functions as an example. The main reason for this choice is that these basis functions are simple and so their matrix elements can be calculated analytically in one, two, and three dimensions. The Gaussian basis functions are defined as

$$\phi_i(x) = \left(\frac{\nu_i}{\pi}\right)^{1/2} \mathrm{e}^{-\nu_i (x - s_i)^2}. \tag{1.12}$$

This function has two variational parameters: ν_i, the width of the Gaussian, and s_i, the center of the Gaussian. For simplicity we vary only one of these parameters at a time and so perform calculations with either fixed widths or fixed centers. The nonorthogonality of these basis functions is another reason to avoid varying

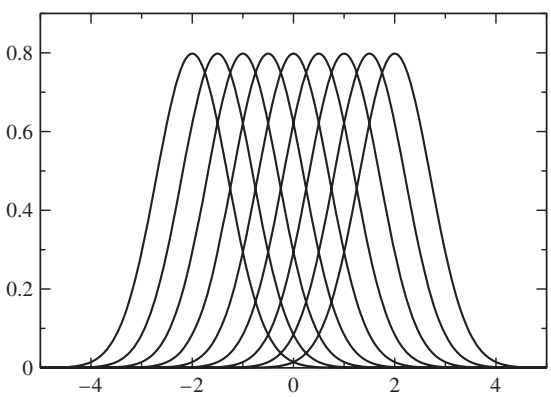

Figure 1.1 Shifted Gaussian basis functions.

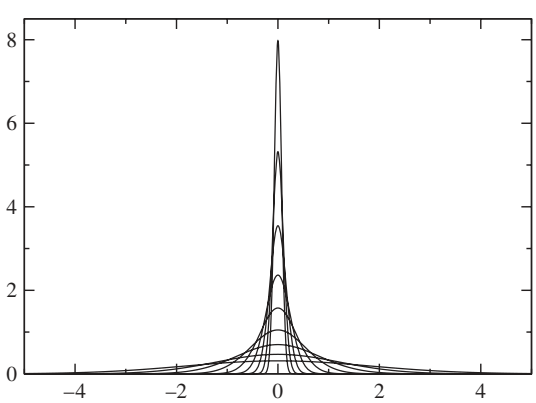

Figure 1.2 Gaussian basis functions with widths chosen as a geometric progression.

both parameters at the same time: the basis functions overlap and their overlap depends on both the relative positions and the widths of the Gaussians. A large overlap between the basis functions can cause linear dependencies in the basis states, leading to spurious solutions of the eigenvalue problem. By varying only one parameter at a time these linear dependencies can be easily avoided.

With the first choice (i.e., keeping the width fixed) we can place the Gaussians so that they are centered at different locations within a uniformly spaced grid of points in space. An example of these "shifted Gaussians" is shown in Fig. 1.1. The free parameters are the locations of the curve centers and the common width $\nu_i = \nu$.

The second possibility is to keep the center fixed, e.g. at the origin, and vary the width of the Gaussians (see Fig. 1.2). A popular choice is to use a geometric progression $a_0 b_0^{i-1}$ to define the widths as

$$\nu_i = \frac{1}{\left(a_0 b_0^{i-1}\right)^2}, \tag{1.13}$$

where a_0 is the starting value of the geometric progression and $b_0 \neq 0$ is the progression's common ratio. This results in three free parameters: the location of the common center and the values of a_0 and b_0.

The matrix elements of the Gaussian basis functions can be easily calculated. The overlap of two basis functions is

$$\langle \phi_i | \phi_j \rangle = \left(\frac{2\sqrt{\nu_i \nu_j}}{\nu_i + \nu_j} \right)^{1/2} \exp\left(-\frac{\nu_i \nu_j}{\nu_i + \nu_j} (s_i - s_j)^2 \right). \tag{1.14}$$

The kinetic energy matrix elements are given by

$$\left\langle \phi_i \left| -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \right| \phi_j \right\rangle = \frac{\hbar^2}{2m} \frac{2\nu_i \nu_j}{\nu_i + \nu_j} \left(1 - \frac{2\nu_i \nu_j}{\nu_i + \nu_j} (s_i - s_j)^2 \right) \langle \phi_i | \phi_j \rangle. \tag{1.15}$$

For some potentials, e.g. for a harmonic oscillator, with potential

$$V(x) = \tfrac{1}{2} m\omega^2 x^2 \tag{1.16}$$

where m is the particle's mass and ω is the frequency of the oscillator, or for a Gaussian potential

$$V(x) = V_0 \mathrm{e}^{-\mu x^2} \tag{1.17}$$

where V_0 and μ are the parameters of the potential, the matrix elements can be calculated analytically. In other cases one has to use numerical integration, or one can expand the potential as a sum of Gaussian potentials. The matrix elements for a harmonic oscillator potential are

$$\left\langle \phi_i \left| \tfrac{1}{2} m\omega^2 x^2 \right| \phi_j \right\rangle = \tfrac{1}{2} m\omega^2 \left(\frac{1}{\nu_i + \nu_j} + \left(\frac{\nu_i s_i + \nu_j s_j}{\nu_i + \nu_j} \right)^2 \right) \langle \phi_i | \phi_j \rangle,$$

and the matrix elements for a Gaussian potential are

$$\left\langle \phi_i \left| \mathrm{e}^{-\mu x^2} \right| \phi_j \right\rangle = \left(\frac{2\sqrt{\nu_i \nu_j}}{\nu_i + \nu_j + \mu} \right)^{1/2} \exp\left(-\frac{\nu_i \nu_j (s_i - s_j)^2 + \mu \nu_i s_i^2 + \mu \nu_j s_j^2}{\nu_i + \nu_j + \mu} \right).$$

Two simple programs will now be presented to solve the TISE for a one-dimensional (1D) harmonic oscillator potential using the two types of Gaussian basis discussed above. For shifted Gaussians the matrix elements are simplified ($\nu_i = \nu$) and can be calculated using the simple code **gauss_1d_c.f90** (see Listing 1.1). After diagonalization the eigensolutions are obtained as listed in Table 1.1. The eigenenergies are very accurate not only for the ground state but for the excited states as well.

For Gaussians centered at the origin $s_i = 0$ but having varying width, a similar code, **gauss_1d_w.f90** (see Listing 1.2) can be used. Again the results are shown in Table 1.1. This basis function is even and so we get only the even eigensolutions of the TISE. The accuracy is somewhat less than in the previous case but more careful optimization may improve the results.

Table 1.1 The eigenenergies of the harmonic oscillator potential obtained by using shifted or variable-width Gaussian bases

Exact	Shifted	Variable-width
0.5	0.500 000 000 000	0.500 000 000 000
1.5	1.500 000 000 000	
2.5	2.500 000 000 000	2.499 999 999 954
3.5	3.500 000 000 009	
4.5	4.500 000 000 059	4.499 999 998 287
5.5	5.500 000 001 890	
6.5	6.500 000 005 356	6.499 999 967 019
7.5	7.500 000 161 985	
8.5	8.500 000 213 739	8.499 997 966 523
9.5	9.500 007 221 469	

Listing 1.1 Solution of the Schrödinger equation for a 1D harmonic oscillator potential with a shifted Gaussian basis

```
PROGRAM gauss_1d_c
  ! Basis of 1D Gaussians, with varying centers,
  !   all with same width
  implicit none
  integer,parameter :: n=101
  real*8,parameter  :: nu=1.d0,h2m=0.5d0
  integer           :: i,j
  real*8            :: h(n,n),o(n,n),s(n),eigenvalues(n),
      eigenvectors(n,n)
  real*8            :: t,p,ss

  ! Calculate the centers for the Gaussians
  do i=1,n
    s(i)=-25.d0+(i-1)*0.5d0
  end do

  ! Setup the Hamiltonian
  do i=1,n
    do j=1,n
      ss=(s(i)-s(j))**2
      o(i,j)=exp(-0.5d0*nu*ss)
      t=exp(-0.5d0*nu*ss)*nu*h2m*(1.d0-nu*ss)
      p=0.5d0*exp(-0.5d0*nu*ss)*0.25d0*(1.d0/nu+(s(i)+s(j))
          **2)
      h(i,j)=t+p
    end do
  end do

  ! Diagonalize
  call diag1(h,o,n,eigenvalues,eigenvectors)
END PROGRAM gauss_1d_c
```

Listing 1.2 Solution of the Schrödinger equation of the 1D harmonic oscillator potential with a variable-width Gaussian basis

```
PROGRAM gauss_1d_w
 ! Basis of 1D Gaussians, with varying widths,
 !   all centered at origin
 implicit none
 integer,parameter :: n=101
 real*8,parameter  :: h2m=0.5d0
 integer :: i,j
 real*8  :: h(n,n),o(n,n),nu(n)
 real*8  :: eigenvalues(n),eigenvectors(n,n)
 real*8  :: t,p,ss,x0,a0,w

 ! Calculate the widths for the Gaussians
 x0=1.14d0
 a0=0.01d0
 do i=1,n
   nu(i)=1.d0/(a0*x0**(i-1))**2
 end do

 ! Set up the Hamiltonian
 do i=1,n
   do j=1,n
     o(i,j)=sqrt(2.d0*sqrt(nu(i)*nu(j))/(nu(i)+nu(j)))
     w=nu(i)*nu(j)/(nu(i)+nu(j))
     t=h2m*2.d0*w*o(i,j)
     p=0.5d0/(2.d0*(nu(i)+nu(j)))*o(i,j)
     h(i,j)=t+p
   end do
 end do

 ! Diagonalize
 call diag1(h,o,n,eigenvalues,eigenvectors)
END PROGRAM gauss_1d_w
```

2 Solution of bound state problems using a grid

In the previous chapter we showed that the one-dimensional time-independent Schrödinger equation (TISE)

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} + V(x)\Psi(x) = E\Psi(x) \tag{2.1}$$

can be solved using the variational method with a suitable set of basis functions. In this chapter we will use simple basis functions based on a numerical grid. The advantage of this family of approaches is that one does not have to calculate matrix elements and it is easy to extend the approach to two and three dimensions. The simplest version of the grid-type approaches is called the finite difference method and it can be considered a limiting case of the Gaussian basis, where an infinitesimally small width is used for the Gaussians. Another grid-based family of basis functions is the Lagrange function basis. These functions keep the simplicity of the finite difference approach while enhancing the accuracy of the solution.

2.1 Discretization in space

While a mathematical function may be defined at an infinite number of points, a computer can only store a finite number of these values. To perform numerical computations we must therefore find a way to approximate a function, to some desired accuracy, by a finite set of values.

A grid consists of a finite set of locations in space and/or time and is the discrete analog of a continuous coordinate system. The various quantities that we will be working with will be defined only at these points. In this way the grid provides a method to obtain a discrete sampling of continuous quantities. Grids can be used for problems with any number of dimensions, but here we introduce concepts using the simple case of one dimension; the extension to more dimensions is straightforward and will be demonstrated later, in Part II.

To set up a one-dimensional grid, we need to know the start coordinate a, the ending coordinate b, and the "step size" (i.e., the distance between points) h. Given these values, the total number of grid points N is

$$N = 1 + \frac{b-a}{h} \tag{2.2}$$

Notice that $(b-a)/h$ gives the number of intervals of size h that will fit into the space between a and b. The grid points are defined at the borders of these intervals, and so the number of grid points is one more than the number of these intervals. For example, in the simple case of a single interval there are two grid points (the two ends of the interval).

The location of the ith grid point is

$$x_i = a + (i-1)h \tag{2.3}$$

where i runs from 1 to N. For some applications it is more convenient to specify the total number of grid points N rather than the step size. In this case, one obtains h as

$$h = \frac{b-a}{N-1}. \tag{2.4}$$

Now that we have defined a grid, we can use it to represent various quantities. Potentials are simply sampled at the grid locations, but it is less clear how to handle the derivative in the kinetic energy term in Eq. (2.1). In the next section we show how to represent derivatives on a grid using finite differences.

2.2 Finite differences

The finite difference method replaces the derivatives in a differential equation by approximations. These approximations are made up of weighted sums of function values. This results in a large system of equations to be solved in place of the differential equation.

Suppose that we want to calculate the first derivative of some function $\varphi(x)$. The obvious choice, using the definition of the first derivative, is

$$\varphi'(x) = \frac{\varphi(x+h) - \varphi(x)}{h} \tag{2.5}$$

for some suitably small h. For a given expression, smaller values of h lead to more accurate approximations. This is a "one-sided" and "forward" approximation because $\varphi'(x)$ is calculated only at values that are larger than or equal to x. Another one-sided possibility is the "backward" difference

$$\varphi'(x) = \frac{\varphi(x) - \varphi(x-h)}{h}. \tag{2.6}$$

Each of these finite difference formulas gives an approximation to $\varphi'(x)$ that is accurate to first order, meaning that the size of the error is roughly proportional to h itself.

Another possibility is to use a centered approximation, for which

$$\varphi'(x) = \frac{\varphi(x+h) - \varphi(x-h)}{2h}. \tag{2.7}$$