- **Variational Method**

The expectation value of the Hamiltonian operator is calculated for a stationary state ψ as

$$E = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle}. \tag{1}$$

Let us take an orthonormal set of basis vectors, $|\chi_p\rangle, p = 1, ..., N$, i.e., $\langle\chi_p|\chi_q\rangle = \delta_{pq}$. Here δ_{pq} is the Kronecker delta-function which is 0 unless $p = q$, and in that case it is 1. Expanding ψ in terms of these basis sets,

$$|\psi\rangle = \sum_P C_P \ |\chi_p\rangle, \tag{2}$$

the energy is obtained as

$$E = \frac{\sum_{p,q=1}^{N} C_p^* C_q H_{pq}}{\sum_{p,q=1}^{N} C_p^* C_q \delta_{pq}}, \tag{3}$$

with

$$H_{pq} = \langle\chi_p|H|\chi_q\rangle. \tag{4}$$

For stationary state, the condition will be that the derivative of this functional vanishes with respect to C_P and this leads to

$$\sum_{pq}^{N} (H_{pq} - E\delta_{pq})\, C_q = 0. \tag{5}$$

Eq. 5 is an eigenvalue problem which can be writeen in matrix notation as

$$\mathbf{HC} = E\mathbf{C}. \tag{6}$$

This is the time-independent Schrödinger's equation written in a matrix format for a finite orthonormal basis.

In case of a non-orthonormal basis, the above eigenvalue equation looks as follows

$$\mathbf{HC} = E\mathbf{SC}. \tag{7}$$

Here, S is the overlap matrix which was 1 in the case of orthonormal basis set. This is called a *generalised eigenvalue equation*.

- Solution of the *generalised eigenvalue equation*

  In practice, the solution is a two-step process, i.e. two simple eigenvalue problems need to be solved.

  - Solve the S-matrix part first: We solve the following auxiliary problem first

    $$S\mathbf{d} = \sigma\mathbf{d}.$$

    This is a simple eigenvalue problem. The S-matrix can be diagonalized to produce $\mathbf{d}$(whose elements are denoted as D_{ij} and σ.

– We define a second transformation matrix

$$\begin{aligned} A_{ij} &= \frac{D_{ij}}{\sigma_j} \\ \sum_i A^*_{ik} \sum_j S_{ij} A_{jn} &= \delta_{kn} \\ \implies A^\dagger S A &= I \\ \text{If } \mathbf{c} &= A\mathbf{v} \\ \implies H\ A\ \mathbf{v} &= \epsilon\ S\ A\ \mathbf{v} \\ A^\dagger H\ A\ \mathbf{v} &= \epsilon\ A^\dagger\ S\ A\ \mathbf{v} = \epsilon \mathbf{v} \end{aligned}$$

$\implies$ Diagonalize $A^\dagger H\ A$ to get the eigenvalues. The eigenvectors can be obtained by applying A to $\mathbf{v}$.

- **Problem 1**

The potential well with infinite barriers is given by:

$$V(x) = \begin{cases} \infty, & |x| > |a| \\ 0, & |x| \leq |a|. \end{cases} \tag{8}$$

This forces the wave function to vanish at the boundaries of the well. The problem can be solved analytically and you already know those. In the present example, we will use a variational approach to solve the problem We will use the atomic units and mass as 1 unit so that $\hbar^2/2m$=1. Let us take a=1.

As basis function, let us take the following polynomials

$$\psi_n(x) = x^n(x-1)(x+1), n = 0, 1, 2, ... \tag{9}$$

For this basis, the relevant matrix elements can be calculated analytically. The overlap matrix will look as and those are

$$S_{mn} = \int_{-1}^{1} \psi_n(x)\psi_m(x)dx = \frac{2}{n+m+5} - \frac{4}{n+m+3} + \frac{2}{n+m+1} \tag{10}$$

for $n+m$ even; otherwise it is 0. The Hamiltonian matrix elements are given as

$$H_{mn} = \langle\psi_n|p^2|\psi_m\rangle = \int_{-1}^{1} \psi_n(x)\left(\frac{-d^2}{dx^2}\right)\psi_m(x)dx \tag{11}$$

$$= -8\left[\frac{1-m-n-2mn}{(m+n+3)(m+n+1)(m+n-1)}\right], \tag{12}$$

for $m+n$ even, otherwise H_{mn}=0.

Problem 1: Construct a Fortra90 program to compute the overlap and Hamiltonian matrix for the above problem. Use the DSYEV routine to solve the problem. The "DSYEV" routine will be called twice as explained. The boundaries of the box are at (-1,1) which makes the length of the box to be 2. Take 121 equidistant points between -1 and 1 for plotting the wavefunction.

Make a table, for N=5,8, and 12, comparing the exact numerical eigenvalues to the exact ones. The first three exact results for N=5 are 2.4674, 9.8754, 22.2934. The resultant eigenvectors will give the eigenfunction of the system as $|\psi\rangle = \sum_{p=1}^{N} C_P\ |\chi_p\rangle$. Remember that the "eigenvectors C " are the output of the generalised eigenvalue problem. Make a plot of the numerically calculated eigenfunction with the exact one for the ground state.

- **Problem 2** The potential for a finite well is given by

$$V(x) = \begin{cases} 0, & |x| > |a| \\ -V0, & |x| \leq |a|. \end{cases} \tag{13}$$

Let us take the plane waves as the basis functions in the interval (-L,+L) as

$$\psi_n(x) = \frac{1}{\sqrt{2L}} e^{ik_n x}, \ k_n = \pm \frac{n\pi}{L}, \ n = 0, 1, ... \tag{14}$$

The relevant matrix elements are as follows:

$$\begin{aligned} S_{mn} &= \delta_{mn} && (15) \\ \langle \psi_n | p^2 | \psi_m \rangle &= -k_n^2 \delta_{mn} && (16) \\ \langle \psi_n | V | \psi_m \rangle &= -\frac{V0}{L} \frac{sin(k_m - k_n)a}{k_m - k_n}, \ for \ n \ \neq m, && (17) \\ \langle \psi_n | V | \psi_m \rangle &= -\frac{V0}{L} a && (18) \end{aligned}$$

Write a program to determine the eigenvalues for $V0$=1 and a=1.