

Linear Variational Method-Solutions

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1 Computational Exercise 1: Linear Variational Principle

We will apply the Linear Variational Method to the particle in a box of length 10 atomic units with a delta function potential centered at $x = 5$ atomic units. In particular, we will optimize the trial wavefunction given by

$$\Phi(x) = \sum_{i=1}^N c_i \psi_i(x) \quad (1)$$

where the coefficients c_i are real numbers and $\psi_i(x)$ are the energy eigenfunctions of the particle in a box with no potential:

$$\psi_n(x) = \sqrt{\frac{2}{10}} \sin\left(\frac{n\pi x}{10}\right). \quad (2)$$

We will seek to minimize the energy functional through the expansion coefficients, where the energy functional can be written as

$$E[\Phi(x)] = \frac{\int_0^\infty \Phi^*(x) \hat{H} \Phi(x) dx}{\int_0^\infty \Phi^*(x) \Phi(x) dx}. \quad (3)$$

The Hamiltonian operator in the box is given by

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \delta(x - 5); \quad (4)$$

in natural units, \hbar and m are equal to 1.

As we saw in class, $E[\Phi(x)]$ can be expanded as

$$E[\Phi(x)] \sum_{i=1}^N \sum_{j=1}^N c_i c_j S_{ij} = \sum_{i=1}^N \sum_{j=1}^N c_i c_j H_{ij} \quad (5)$$

where

$$S_{ij} = \int_0^L \psi_i(x) \psi_j(x) dx = \delta_{ij} \quad (6)$$

and

$$H_{ij} = \int_0^L \psi_i(x) \hat{H} \psi_j(x) dx. \quad (7)$$

1.0.1 Questions Part 1:

1. Work out a general expression for the integrals H_{ij}

$$H_{ij} = \frac{\hbar^2 \pi^2 j^2}{2mL^2} \delta_{ij} + \frac{2}{L} \sin\left(\frac{i\pi}{2}\right) \sin\left(\frac{j\pi}{2}\right) \quad (8)$$

2. Write a python function that takes the indices i and j and returns the value of the integral H_{ij} .

```
In [2]: import numpy as np
        ### Function to return integrals involving Hamiltonian and basis functions
        def H_ij(i, j):
            i = i+1
            j = j+1
            if i==j:
                ham_int = np.pi**2 * j**2/(2 * 10**2) + (2/10) * np.sin(i*np.pi/2) * np.sin(j*np.pi/2)
            else:
                ham_int = (2/10) * np.sin(i*np.pi/2) * np.sin(j*np.pi/2)

            return ham_int
```

3. Show that differentiating the energy functional with respect to all coefficients and setting the derivative to zero results in the following set of equations:

$$\sum_i^N H_{ik} c_i = E[\Phi(x)] c_k. \quad (9)$$

First differentiate both sides of the energy functional expression:

$$\frac{\partial}{\partial c_k} E[\Phi(x)] \sum_{i=1}^N \sum_{j=1}^N c_i c_j S_{ij} = \frac{\partial}{\partial c_k} \sum_{i=1}^N \sum_{j=1}^N c_i c_j H_{ij}. \quad (10)$$

Apply the product rule to both sides. Looking at the left-hand-side first.

$$\frac{\partial E[\Phi(x)]}{\partial c_k} \sum_{i=1}^N \sum_{j=1}^N c_i c_j S_{ij} + E[\Phi(x)] \sum_{i=1}^N \sum_{j=1}^N S_{ij} \left(\frac{\partial c_i}{\partial c_k} c_j + \frac{\partial c_j}{\partial c_k} c_i \right), \quad (11)$$

which can be simplified by noting that $S_{ij} = \delta_{ij}$ so the only terms that survive the sum are those where $i = j$ (meaning we only sum over one index), and also by noting that $\frac{\partial c_i}{\partial c_k} = \delta_{ik}$,

$$\frac{\partial E[\Phi(x)]}{\partial c_k} \sum_{i=1}^N c_i^2 + E[\Phi(x)] \sum_{i=1}^N (\delta_{ik} c_i + \delta_{ik} c_i) = \frac{\partial E[\Phi(x)]}{\partial c_k} \sum_{i=1}^N c_i^2 + 2E[\Phi(x)] c_k. \quad (12)$$

Finally, by using the fact that when the energy is minimized with respect to all variational coefficients (all c_k), then $\frac{\partial E[\Phi(x)]}{\partial c_k} = 0$ by definition, so the left hand side can be simplified to

$$2E[\Phi(x)] c_k. \quad (13)$$

Let's now consider the right hand side, using several of the same tricks as before:

$$\frac{\partial}{\partial c_k} \sum_{i=1}^N \sum_{j=1}^N c_i c_j H_{ij} = \sum_{i=1}^N \sum_{j=1}^N H_{ij} \left(\frac{\partial c_i}{\partial c_k} c_j + \frac{\partial c_j}{\partial c_k} c_i \right) = \sum_{i=1}^N \sum_{j=1}^N H_{ij} (\delta_{ik} c_j + \delta_{jk} c_i) = \sum_{j=1}^N H_{kj} c_j + \sum_{i=1}^N H_{ik} c_i. \quad (14)$$

Using the fact that the Hamiltonian matrix is Hermitian (in this case, symmetric because the basis functions are real, so $H_{ij} = H_{ji}$) and realizing the dummy indices can be made the same (i.e. sum over i is the same as sum over j), we can simplify the right hand side to $2 \sum_{i=1}^N H_{ik} c_i$. Then, the equation (l.h.s. and r.h.s.) becomes

$$E[\Phi(x)]c_k = \sum_{i=1}^N H_{ik} c_i, \quad (15)$$

which is exactly what we wanted to show. This can be written as an eigenvalue equation

$$\mathbf{H}\mathbf{c} = E\mathbf{c}, \quad (16)$$

where \mathbf{H} is the matrix whose elements are given by H_{ij} and \mathbf{c} is the vector of coefficients.

Create an array called H_{mat} that can be used to store the Hamiltonian matrix elements. We can start by considering a trial wavefunction that is an expansion of the first 3 PIB energy eigenfunctions, so our Hamiltonian in this case should be a 3x3 matrix.

```
In [16]: H_mat = np.zeros((6,6))
```

You can use two nested *for* loops along with your H_{ij} function to fill out the values of this matrix.

```
In [17]: ### loop over indices of the basis you are expanding in
### and compute and store the corresponding Hamiltonian matrix elements
for i in range(0,6):
    for j in range(0,6):
        H_mat[i][j] = H_ij(i, j)

### Print the resulting Hamiltonian matrix
print(H_mat)
```

```
[[ 2.49348022e-01  2.44929360e-17 -2.00000000e-01 -4.89858720e-17
  2.00000000e-01  7.34788079e-17]
 [ 2.44929360e-17  1.97392088e-01 -2.44929360e-17 -5.99903913e-33
  2.44929360e-17  8.99855870e-33]
 [-2.00000000e-01 -2.44929360e-17  6.44132198e-01  4.89858720e-17
 -2.00000000e-01 -7.34788079e-17]
 [-4.89858720e-17 -5.99903913e-33  4.89858720e-17  7.89568352e-01
 -4.89858720e-17 -1.79971174e-32]
 [ 2.00000000e-01  2.44929360e-17 -2.00000000e-01 -4.89858720e-17
  1.43370055e+00  7.34788079e-17]
 [ 7.34788079e-17  8.99855870e-33 -7.34788079e-17 -1.79971174e-32
  7.34788079e-17  1.77652879e+00]]
```

Before systematically identifying the optimal coefficients, it is instructive to try a few "trial" wavefunctions "by hand". A few suggestions include:

$$\mathbf{c} = (1, 0, 0) \quad \mathbf{c} = (0, 1, 0) \quad \mathbf{c} = (0, 0, 1) \quad (17)$$

$$\mathbf{c} = \left(\sqrt{1/2}, \sqrt{1/2}, 0 \right) \quad \mathbf{c} = \left(0, \sqrt{1/2}, \sqrt{1/2} \right) \quad \mathbf{c} = \left(\sqrt{1/2}, 0, \sqrt{1/2} \right) \quad (18)$$

In Matrix form, the energy functional can be computed as follows:

$$E = \mathbf{c}^t \mathbf{H} \mathbf{c} \quad (19)$$

where \mathbf{c}^t is just the transpose of \mathbf{c} . Using numpy, this can be done with the Hamiltonian matrix defined above and a vector $\mathbf{c} = (1, 0, 0)$ as follows:

```
In [5]: ### create an empty numpy array for the c vector
        c = np.zeros(3)
        ### assign c vector to be (1, 0, 0)
        c[2] = 1

        ### compute H_mat * c and store it to a new array called Hc
        Hc = np.dot(H_mat, c)

        ### compute c^t * Hc and store it to a variable E
        E = np.dot(np.transpose(c), Hc)

        ### print the result
        print(E)

0.6441321980490211
```

Continue evaluating the energy of different trial wavefunctions by changing the values of the \mathbf{c} vector and repeating the calculation above. Does increasing the contribution of excited states impact the energy as you expect? Explain.

Finally, to get the optimal values of the \mathbf{c} vector, we can find the set of vectors (there will be 3) that satisfy the eigenvalue equation we wrote before. We can use the *eig* function of numpy to do this in one line:

```
In [18]: ### compute eigenvalues and eigenvectors of H_mat
        ### store eigenvalues to E_opt and eigenvectors to c_opt
        E_opt, c_opt = np.linalg.eig(H_mat)

        ### print lowest eigenvalues corresponding to the
        ### variational estimate of the ground state energy
        print("Ground state energy with potential is approximately ", E_opt)
        print("Ground state energy of PIB is ", np.pi**2/(200))

        ### print coefficients that define the trial wavefunction with the lowest eigenvalue
        ### which corresponds to the variational estimate of the ground state wavefunction
        print(c_opt[0])
```

Ground state energy with potential is approximately [1.52775227 0.15577979 0.64364871 1.7765287
 Ground state energy of PIB is 0.04934802200544679
 [-1.88514391e-01 -9.34136379e-01 3.03070206e-01 1.16345328e-16
 6.62763018e-16 1.10085006e-16]

1.0.2 Questions Part 2:

1. Is the energy you calculated above higher or lower than the ground state energy of the ordinary particle in a box system (without the delta function potential)? Answer: The energy calculated to approximate the ground state energy of the PIB + Potential using the linear variational method is higher than the true PIB ground state energy (0.165 atomic units for the PIB + Potential compared to 0.0493 atomic units for the ordinary PIB). The addition of the potential should increase the ground state energy because it is repulsive.
2. Why do you think mixing in functions that correspond to excited states in the ordinary particle in a box system actually helped to improve (i.e. lower) your energy in the system with the delta function potential? Answer: Certain excited states (all states with even n) go to zero at the center of the box, and the repulsive potential is localized to the center of the box. Therefore, all excited states with even n will move electron density away from the repulsive potential, which can potentially lower the energy.
3. Increase the number of basis functions to 6 (so that \mathbf{H} is a 6x6 matrix and \mathbf{c} is a vector with 6 entries) and repeat your calculation of the variational estimate of the ground state energy. Does the energy improve (lower) compared to what it was when 3 basis functions were used? Answer: Yes, the energy improves. With 3 basis functions, the ground state energy is approximated to be 0.165 atomic units and with 6 basis functions, the ground state energy is approximated to be 0.155 atomic units. The added flexibility of these additional basis functions (specifically more basis functions with n even) allows greater flexibility in optimizing a wavefunction that describes an electron effectively avoiding the repulsive potential in the center of the box.