

Assignment 2

Electronic Structures of the Helium atom and Hydrogen Molecule

Due: 2022/02/11

1 Directions

The goal in this assignment is to calculate the electronic structure of the helium atom and the hydrogen molecule (two separate systems). The distance between the two hydrogen atoms (the bond length) is 0.74 Å. In this assignment, do not perform geometry optimization, and instead use that fixed bond length in order to calculate the molecular orbitals (both energies and wave functions). Also, note that the problem is in full 3-dimensional space. The goal is to solve the Hartree-Fock equation for these two systems.

Note that you are solving an iterative problem. The Fock operator depends on the orbitals, which you do not have. So, start by making a guess for the orbital shapes, form the Fock operator, solve for the orbitals, and keep iterating until convergence. Use the convergence of the total energy of the system as your convergence criterion.

In this assignment, the calculations must be done directly on a real-space grid, over which the orbitals (wave functions) are defined. So, do not use the Roothaan equations (which we will see soon).

- (a) (7 points) Directly discretize the Fock operator to put it into matrix form. Describe your approach and show the steps of your derivation all the way to obtaining the matrix equation.
- (b) (5 points) Write a computer code to implement what you built in part (a).
- (c) (4 points) Plot several molecular orbitals and give their associated energies for the helium atom. Also calculate the total energy of the system (not including the nucleus-nucleus interaction). Discuss your results.
- (d) (4 points) Plot several molecular orbitals and give their associated energies for the hydrogen molecule. Also calculate the total energy of the system (not including the nucleus-nucleus interaction). Discuss your results.

2 Derivation of Solution

2.1 Hartree-Fock Matrix Equation Derivation

Since both subjects for this assignment have an even number of electrons that close shells, we can use the restricted Hartree-Fock equation for closed shell systems to numerically calculate the resulting orbitals. The equation is as follows:

$$\hat{F}(\vec{r})\psi_n(\vec{r}) = \epsilon_n\psi_n(\vec{r})$$

Where $\hat{F}(\vec{r})$ is the Fock operator which is defined as follows:

$$\hat{F}(\vec{r}) = \hat{H}_{core}(\vec{r}) + \sum_{n=1}^{N/2} [2J_n(\vec{r}) - K_n(\vec{r})]$$

The Fock operator is composed of the core Hamiltonian operator $\hat{H}(\vec{r})$, the Coulomb operator $\hat{J}(\vec{r})$, and the exchange operator $\hat{K}(\vec{r})$. P_2 is a transposition operator which switches the indices of the electron indices, something required by the exchange operator.

$$\begin{aligned}\hat{H}_{core}(\vec{r}) &= -\frac{1}{2}\nabla_1^2 - \sum_A \frac{Z_A}{\|\vec{r}_{1A}\|} \\ \hat{J}_j(\vec{r}_1)\psi_i(\vec{r}_1) &= \psi_i(\vec{r}_1) \int_{-\infty}^{\infty} |\psi_i(\vec{r}_2)|^2 \frac{1}{\|\vec{r}_{12}\|} d\vec{r}_2 \\ \hat{K}_j(\vec{r}_1)\psi_i(\vec{r}_1) &= \psi_j(\vec{r}_1) \int_{-\infty}^{\infty} \frac{\psi_j^*(\vec{r}_2)\psi_i(\vec{r}_2)}{\|\vec{r}_{12}\|} d\vec{r}_2\end{aligned}$$

Expanded, the Fock operator takes the following form:

$$\hat{F}(\vec{r}) = -\frac{1}{2}\nabla_1^2 - \sum_A \frac{Z_A}{\|\vec{r}_{1A}\|} + \sum_{n=1}^{N/2} \left[2 \int_{-\infty}^{\infty} |\psi_n(\vec{r}_2)|^2 \frac{1}{\|\vec{r}_{12}\|} d\vec{r}_2 - \int_{-\infty}^{\infty} \frac{\psi_n^*(\vec{r}_2)P_2\psi_n(\vec{r}_2)}{\|\vec{r}_{12}\|} d\vec{r}_2 \right]$$

For the Helium atom, the Fock operator takes the following form:

$$\hat{F}(\vec{r}) = -\frac{1}{2}\nabla_1^2 - \frac{2}{\|\vec{r}_{1A}\|} + \int_{-\infty}^{\infty} |\psi_1(\vec{r}_2)|^2 \frac{1}{\|\vec{r}_{12}\|} d\vec{r}_2$$

and for the Hydrogen molecule, the Fock operator takes the following form:

$$\hat{F}(\vec{r}) = -\frac{1}{2}\nabla_1^2 - \frac{1}{\|\vec{r}_{1A}\|} - \frac{1}{\|\vec{r}_{1B}\|} + \int_{-\infty}^{\infty} |\psi_1(\vec{r}_2)|^2 \frac{1}{\|\vec{r}_{12}\|} d\vec{r}_2$$

For the ground state, we only consider one orbital to fill, which simplifies the exchange operator's index-switch operator in both Fock operators. This also has the effect of making the Coulomb and exchange integrals identical, greatly simplifying the equation. Note that: $\psi_n^*(\vec{r}_2)\psi_n(\vec{r}_2) = |\psi_1(\vec{r}_2)|^2$. For the Helium atom, our value for Z_A is 2 as there are two protons in the nucleus and for the Hydrogen molecule, we

consider both Hydrogen nuclei containing one proton each, so $Z_A = Z_B = 1$. The nuclei are separated by 0.74 Å. Since we are solving this problem using Hartree atomic units, we must convert this value accordingly when considering the coordinates of the hydrogen nuclei. In Hartree atomic units, the atomic unit of length converts the Bohr radius a_0 to 1. Therefore, the distance between the two Hydrogen nuclei is $\frac{0.74 \times 0.1 \times 10^{-9}}{5.29177210903 \times 10^{-11}} = 1.39839733222307$ atomic units of length.

In order to discretize these equations, the second order differentiation and the finite integration must be numerically performed, in the three spatial dimensions x , y , and z . For the second order differentiation, it will discretize in the following manner:

$$\begin{aligned}\nabla^2 f(x, y, z) \approx & \frac{f(x + \Delta x, y, z) - 2f(x, y, z) + f(x - \Delta x, y, z)}{\Delta x^2} \\ & + \frac{f(x, y + \Delta y, z) - 2f(x, y, z) + f(x, y - \Delta y, z)}{\Delta y^2} \\ & + \frac{f(x, y, z + \Delta z) - 2f(x, y, z) + f(x, y, z - \Delta z)}{\Delta z^2}\end{aligned}$$

If we choose the same discretization size, such that $\Delta x = \Delta y = \Delta z = h$, the discretization takes the following simplification:

$$\nabla^2 f(x, y, z) \approx \frac{f(x + h, y, z) + f(x, y + h, z) + f(x, y, z + h) - 6f(x, y, z) + f(x - h, y, z) + f(x, y - h, z) + f(x, y, z - h)}{h^2}$$

As seen in the previous assignment, by forming a column vector in the following form:

$$|\psi\rangle = [\psi(0, 0, 0), \dots, \psi(N, 0, 0), \psi(0, 1, 0), \dots, \psi(N, 1, 0), \dots, \psi(0, N, 0), \dots, \psi(N, N, N)]^T$$

The indices found in this vector will depend on the limits chosen for the solution in all directions, as well as the number of partitions N . With three dimensions and N discretization points, the total number of equations to solve will be N^3 . The sparse matrix S_{∇^2} for the Laplacian differential operator on three variables for $N = 3$ and $h = 1$ is shown below. Three rows have been highlighted to demonstrate how they correspond to an equation in the total solution.

N = 3	S =	
-6 1	1	f(0,0,0)
1-6 1	1	f(1,0,0)
1 6	1	f(2,0,0)
1 -6 1	1	f(0,1,0)
1 1-6 1	1	f(1,1,0)
1 1 6	1	f(2,1,0)
1 1 -6 1	1	f(0,2,0)
1 1 1-6 1	1	f(1,2,0)
1 1 1 6	1	f(2,2,0)
1 1 -6 1	1	f(0,0,1)
1 1 1-6 1	1	f(1,0,1)
1 1 1 6	1	f(2,0,1)
1 1 1 -6 1	1	f(0,1,1) (+)
1 1 1 1-6 1	1	f(1,1,1) (*)
1 1 1 1 6	1	f(2,1,1) (&)
1 1 1 1 -6 1	1	f(0,2,1)
1 1 1 1 1-6 1	1	f(1,2,1)
1 1 1 1 1 6	1	f(2,2,1)
1 1 1 1 1 -6 1	1	f(0,0,2)
1 1 1 1 1 1-6 1	1	f(1,0,2)
1 1 1 1 1 1 6	1	f(2,0,2)
1 1 1 1 1 1 -6 1	1	f(0,1,2)
1 1 1 1 1 1 1-6 1	1	f(1,1,2)
1 1 1 1 1 1 1 6	1	f(2,1,2)
1 1 1 1 1 1 1 -6 1	1	f(0,2,2)
1 1 1 1 1 1 1 1-6 1	1	f(1,2,2)
1 1 1 1 1 1 1 1 6	1	f(2,2,2)
(+) f(1,1,1) + f(0,2,1) + f(0,1,2) -6f(0,1,1) +	+ f(0,0,1) + f(0,1,0)	
(*) f(2,1,1) + f(1,2,1) + f(1,1,2) -6f(1,1,1) + f(0,1,1) + f(1,0,1) + f(1,1,0)		
(&) + f(2,2,1) + f(2,1,2) -6f(2,1,1) + f(1,1,1) + f(2,0,1) + f(2,1,0)		

The next operator to be considered for discretization is the integration that is performed on the Coulomb and exchange terms. For this integration, we can extend the one dimensional numerical integration into three dimensions. First we consider the expanded form of the spatial integral:

$$\int_{-\infty}^{\infty} f(\vec{r}) d\vec{r} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(x, y, z) dx dy dz$$

We then split the three spatial dimensions into N partitions in all cardinal directions to quantize the problem into discretized volumes of the solution, Δx , Δy , and Δz as we did in the differential discretization. Once again, if we choose the same discretization size, such that $\Delta x = \Delta y = \Delta z = h$, we evenly divide the solution space into partitions. By evaluating the function at each coordinate, multiplying the result by our discretization size h , and summing over the solution space, we obtain a Riemann sum, which is a trivial implementation of numerical integration. The sums approximate the integral as follows:

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(x, y, z) dx dy dz \approx \sum_{k_z=0}^N \sum_{k_y=0}^N \sum_{k_x=0}^N \left[w^{[k_x, k_y, k_z]} f(k_x, k_y, k_z) \right]$$

$$w_{k_x} = w_{k_y} = w_{k_z} = \{0, h, h, \dots, h\}$$

One limitation of this approximated integration is that the infinite limit definite integral required by the original equation is now confined within the limits we choose for the problem and the N partitions we make out of the space in all directions. Choosing the limits and N must be done carefully as the matrices generated for the solution will easily balloon into very difficult diagonalization problems.

Both the Helium atom and the Hydrogen molecule share the following integral term:

$$\int_{-\infty}^{\infty} |\psi_1(\vec{r}_2)|^2 \frac{1}{\|\vec{r}_{12}\|} d\vec{r}_2$$

For every iteration of the Hartree-Fock algorithm, a solution set will be generated for $\psi_1(\vec{r}_1)$ when the Fock matrix \mathbf{F} is diagonalized. This solution is then re-used in the upcoming iteration as the solution for $\psi_1(\vec{r}_2)$ for use in the integrals. For the first iteration, a version of $\psi_1(\vec{r}_2)$ will be used where every entry is 0. If that fails to converge, then a noisy solution will be attempted. Another thing to take into account is the fact that there will be multiple solutions in the eigenvectors. For every energy to be plotted, that energy's resulting wavefunction will need to be used in each iteration step. Using the sums above, $\psi_1(x_2, y_2, z_2)$ will be evaluated and a value will be obtained. Depending on which energy is being calculated, that energy's eigenvector will be chosen to calculate the integral. This integral also possesses a distance calculation between the current and other electron. This calculation relies on the position of the current step as seen below:

$$\frac{1}{\|\vec{r}_{12}\|} = \frac{1}{\sqrt{(x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2}}$$

This integral will be evaluated for every partition in the problem; therefore, the values for x_1 , y_1 , and z_1 will correspond to those found in the column vector $|\psi\rangle$ as defined above. This integration operator can be summarized as follows:

$$I(x_1, y_1, z_1) = \int_{-\infty}^{\infty} |\psi_1(\vec{r}_2)|^2 \frac{1}{\|\vec{r}_{12}\|} d\vec{r}_2$$

This equation will form a diagonal in a matrix J of size $N \times N \times N$ as follows:

$$J = \begin{bmatrix} I(x_1, y_1, z_1) & 0 & \dots & 0 \\ 0 & I(x_1, y_1, z_1) & \dots & 0 \\ \vdots & \vdots & \ddots & 0 \\ 0 & 0 & 0 & I(x_1, y_1, z_1) \end{bmatrix}$$

The final term of the Fock equation that needs to be considered is the nuclear attraction operator. For the Helium atom case, we have a single term, and for the Hydrogen molecule we have two terms. For the Helium atom, the expanded nuclear attraction term is as follows:

$$A_{He}(x_1, y_1, z_1) = - \sum_A \frac{Z_A}{\|\vec{r}_{1A}\|} = - \frac{2}{\sqrt{(x_1^2 + y_1^2 + z_1^2)}}$$

With the Helium nucleus placed at the origin of the problem, the distance between the electron and the nucleus becomes the distance of the electron from the origin. Also, the atomic number for Helium is 2, which puts that number in the denominator.

The Hydrogen molecule on the other hand takes a slightly different form. A hydrogen molecule has two nuclei in its system and they are separated by 1.39839733222307 atomic units of length as calculated above. For this problem, the Hydrogen nuclei will be placed $\frac{1.39839733222307}{2}$ in the positive and negative x directions from the origin. With an atomic number of 1 for the Hydrogen element, the nuclear attraction terms will take the following form:

$$A_{H_2}(x_1, y_1, z_1) = - \sum_A \frac{Z_A}{\|\vec{r}_{1A}\|} = - \frac{1}{\sqrt{\left(\frac{-1.39839733222307}{2} - x_1\right)^2 + y_1^2 + z_1^2}} - \frac{1}{\sqrt{\left(\frac{1.39839733222307}{2} - x_1\right)^2 + y_1^2 + z_1^2}}$$

The nuclear attraction operator will form a diagonal in a matrix A of size $N \times N \times N$ as follows:

$$\mathbf{A} = \begin{bmatrix} A(x_1, y_1, z_1) & 0 & \dots & 0 \\ 0 & A(x_1, y_1, z_1) & \dots & 0 \\ \vdots & \vdots & \ddots & 0 \\ 0 & 0 & 0 & A(x_1, y_1, z_1) \end{bmatrix}$$

Now we have all of the components necessary to implement a solution. To summarize, for the Helium atom, the following matrix system will be solved:

$$\begin{aligned} \mathbf{F}_{He} |\psi\rangle &= \epsilon |\psi\rangle \\ \mathbf{F}_{He} &= -\frac{1}{2h^2} \mathbf{S}_{\nabla^2} + \mathbf{A}_{He} + \mathbf{J} \end{aligned}$$

and for the Hydrogen molecule, the following matrix system will be solved:

$$\begin{aligned} \mathbf{F}_{H_2} |\psi\rangle &= \epsilon |\psi\rangle \\ \mathbf{F}_{H_2} &= -\frac{1}{2h^2} \mathbf{S}_{\nabla^2} + \mathbf{A}_{H_2} + \mathbf{J} \end{aligned}$$

3 Program Implementation

The program for this assignment was written in Python and the source can be viewed in Section 6.1. It relies heavily on the SciPy package to perform the matrix algebra required to obtain the results. The program constructs the sparse matrices outlined in the previous section, obtains solutions based on convergence criteria, and outputs the plots and data for further analysis.

The program features command line arguments for the user to set various runtime variables and features the ability to load and save the data in a specially formatted file. These files will also contain the configuration values for the simulation run as well as metrics to gauge how quickly each solution was able to converge to a final solution. The user can specify the number of partitions N to use for the problem, resulting in an $N \times N \times N$ sized sparse matrix to calculate eigenvectors and eigenvalues from. Increasing the partition size has a severe impact on performance, so the user must be careful to pick a reasonable size.

In order to optimize the calculations, sparse matrices provided by the SciPy package are used to reduce the memory footprint as well as enable more effective linear algebra operations. All of the sparse matrices are combined together into the Hermitian representing the Fock matrix, and the SciPy `scipy.sparse.linalg.eigsh` function is used to calculate the associated eigenvalues and eigenvectors. This eigenvalue solver does not fully utilize the capabilities of the computer, using very little CPU time.

Only the lowest six eigenvalues and eigenvectors are calculated for from the Fock matrix. These six eigenvalues are used for the convergence criteria. Their absolute value is summed up, and their percent change is compared from iteration to iteration. If the percent change between two iterations is less than what was specified, the simulation finishes.

The matplotlib Python package is used to generate 4D plots of the resulting orbitals. A 3D scatter plot is used with a heatmap and a mask. The mask allows the plot to selectively ignore points which fall out of a certain range, which allows the plots to effectively illustrate the calculated orbitals. The orbitals are plotted from their lowest energy to the highest energy. Since the resulting waveform will have both negative and positive values, the eigenvector is squared so that the resulting waveform only has positive values. This corresponds to the probability density of the waveform.

A Windows batch file was created to more easily construct simulation runs for execution and data retrieval. The batch file executes concurrent scripts which run in the background.

4 Results

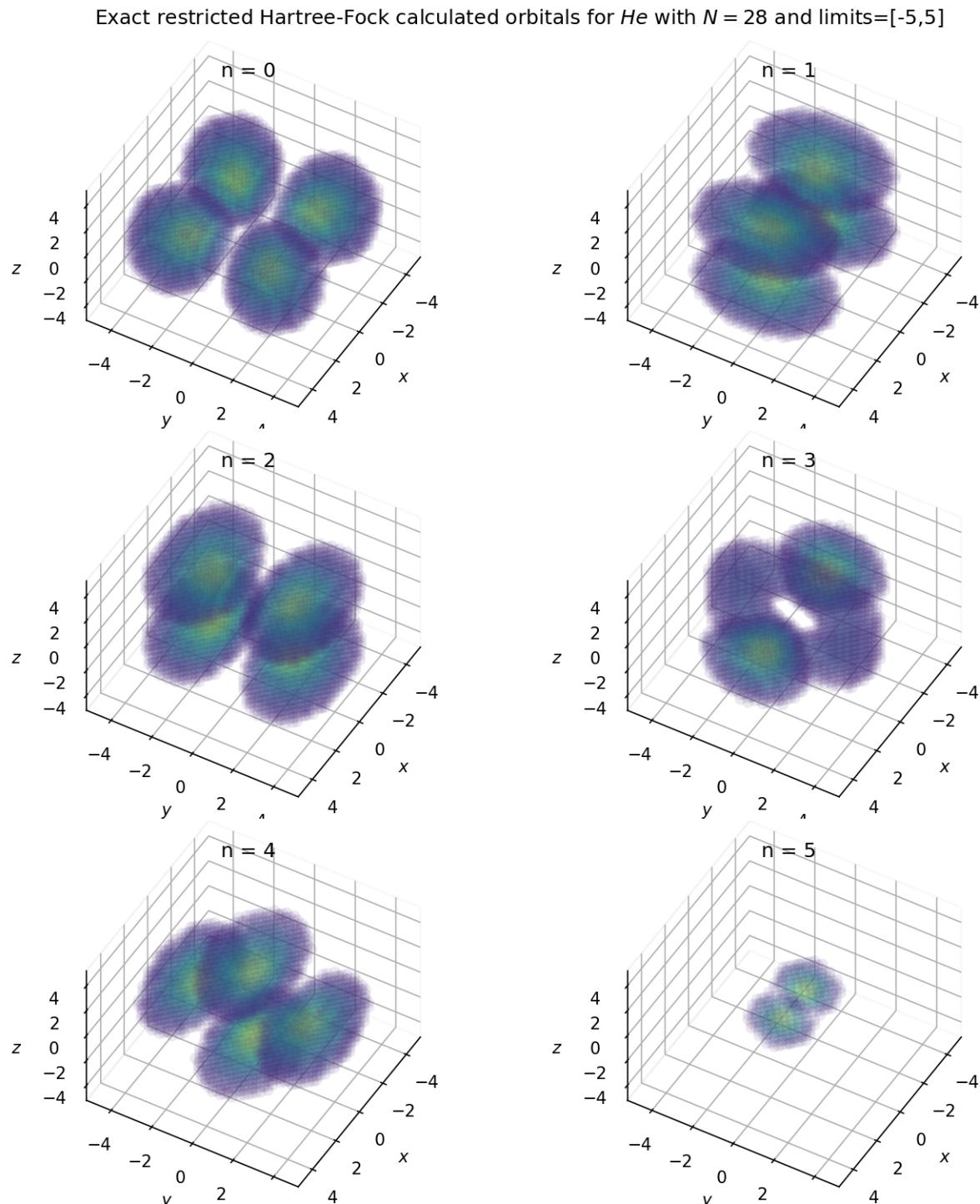


Figure 1: Calculated orbitals for He atom using limits of [-5,5]

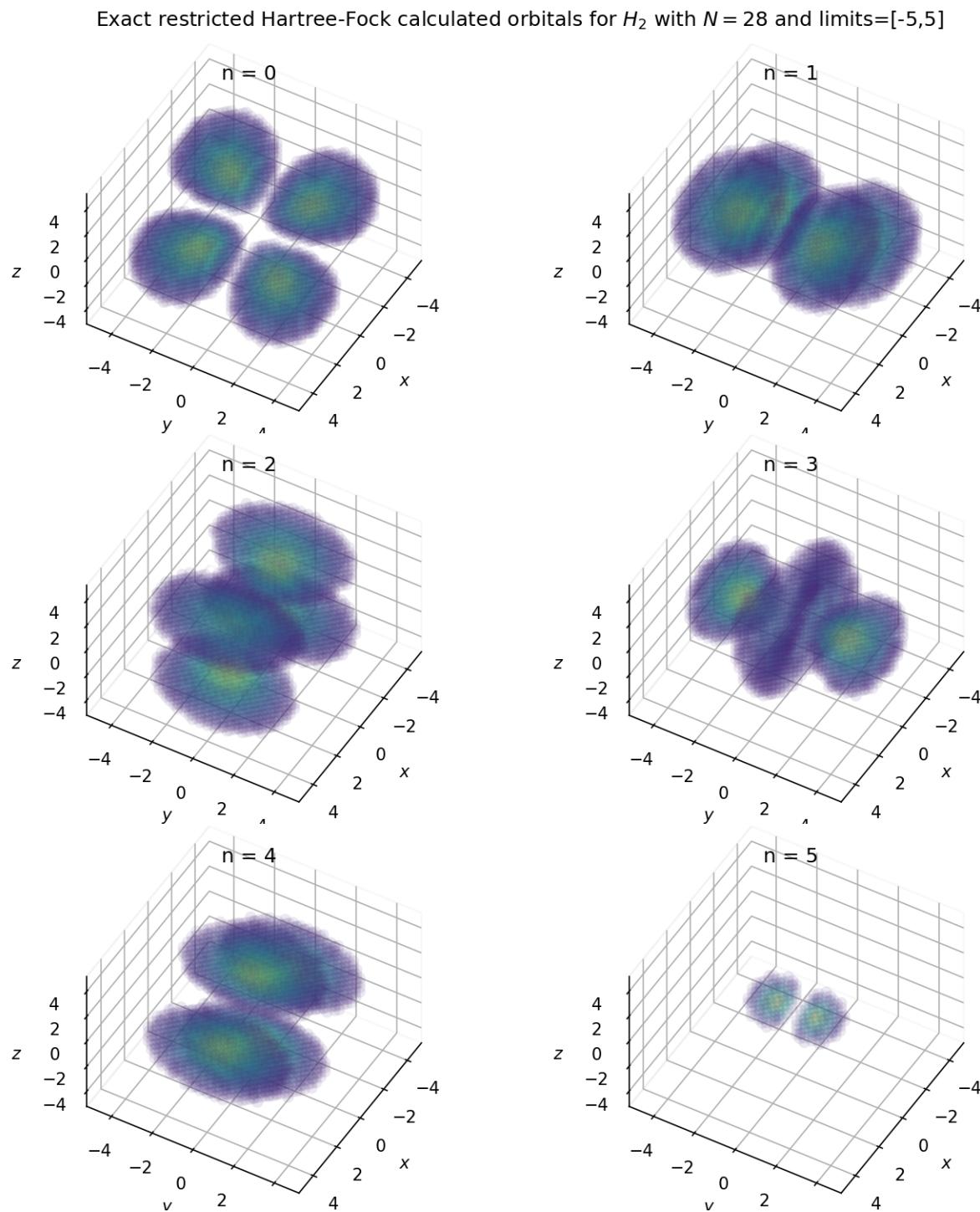


Figure 2: Calculated orbitals for H_2 molecule using limits of [-5,5]

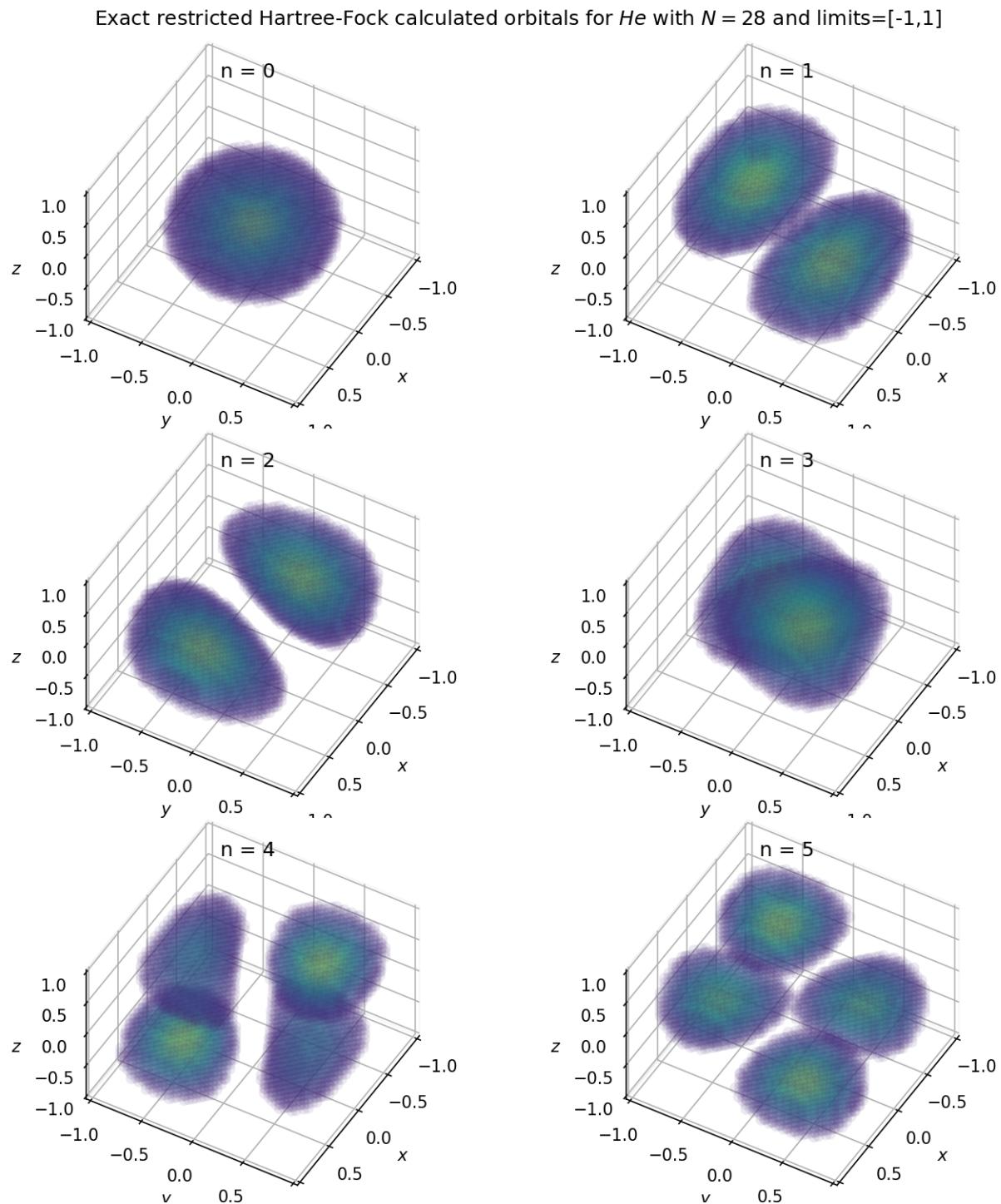


Figure 3: Calculated orbitals for He atom using limits of [-1,1]

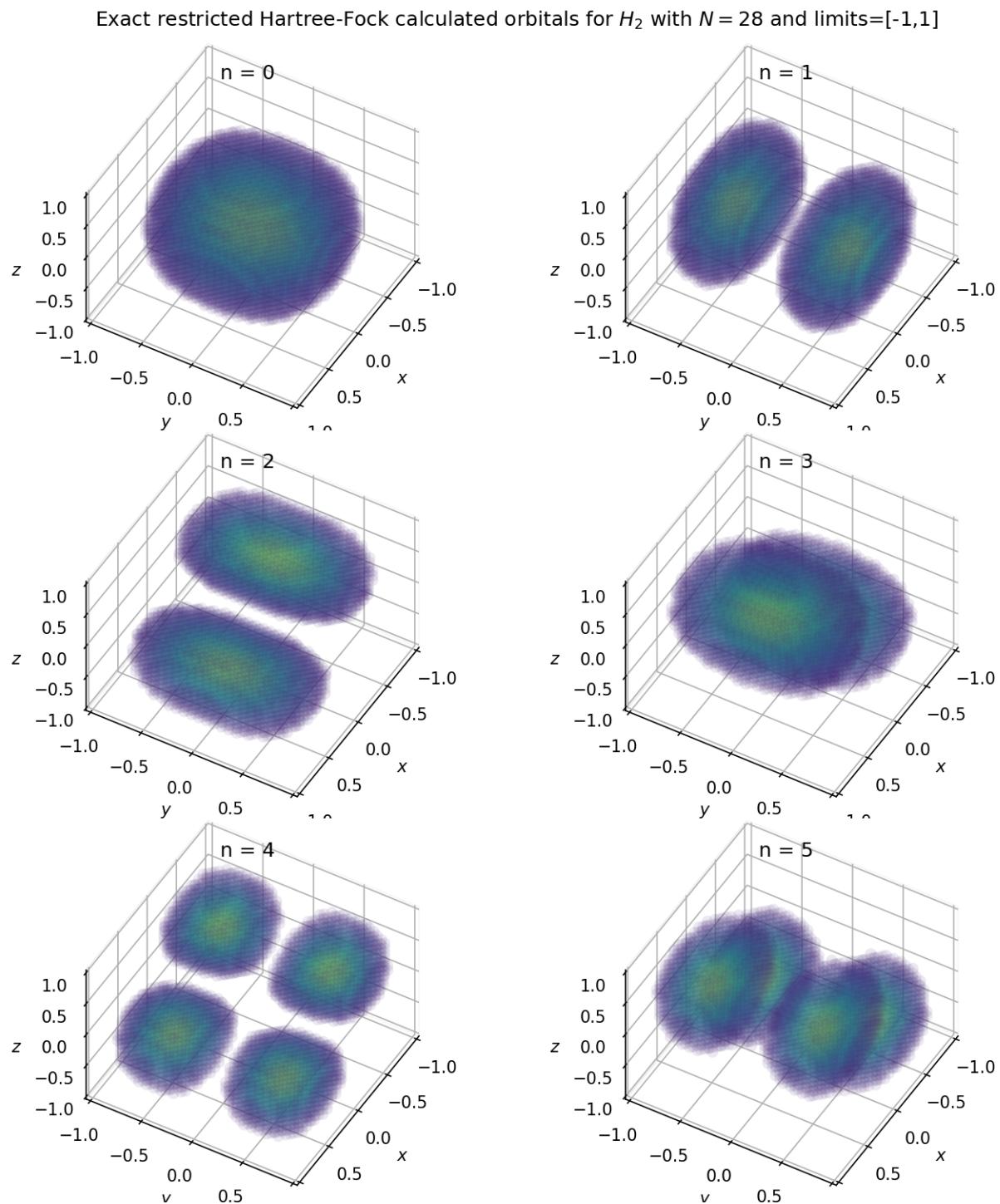


Figure 4: Calculated orbitals for H_2 molecule using limits of [-1,1]

n	1	2	3	4	5	6
E_n	-0.049968	-0.049878	-0.041970	0.011558	-0.007816	0.065703

Table 1: The first six orbital energy levels obtained from applying HF to the Helium atom using limits of [-5,5]

n	1	2	3	4	5	6
E_n	-0.054140	-0.044237	-0.040912	-0.019278	0.000325	0.036600

Table 2: The first six orbital energy levels obtained from applying HF to the Hydrogen molecule using limits of [-5,5]

n	1	2	3	4	5	6
E_n	0.007629	3.942602	3.942602	3.942602	7.489690	7.489690

Table 3: The first six orbital energy levels obtained from applying HF to the Helium atom using limits of [-1,1]

n	1	2	3	4	5	6
E_n	1.005352	4.004340	4.510553	4.510553	7.648020	7.648020

Table 4: The first six orbital energy levels obtained from applying HF to the Hydrogen molecule using limits of [-1,1]

5 Discussion

- Obtaining these final results took several hours, with each run taking approximately 1h15m to converge on a result. With a partition size of $N = 28$, the sparse matrices were $N \times N \times N = 21,952$ in row and column length, for a total of 481,890,304 entries. The solver took very long to chug through these numbers. Many more hours were spent in the development phase trying to tweak and debug the program. This was an incredible challenge.
- Vastly different solutions were obtained when using smaller limits for the problem. This is likely tied to the problem being constrained into a virtual box of sorts where the electrons weren't free to orbit further. It is assumed that the more correct orbital results are those for when the limits are set to larger values.
- There were repeated eigenvalues (of approximately the same value) with very similar shapes. This is likely the solver finding identical or similar orbitals in different orientations. It was reassuring to see some familiar shapes in the orbitals that were previously spotted as illustrations in textbooks.
- As mentioned in the program implementation, the eigenvalue solver used in this program does not fully utilize the capabilities of the computer. Future improvements on this solver would likely involve a re-write in a compiled language like C and make use of matrix algebra packages that are optimized to run on multiple cores and make use of large memory pools. This would help decrease the iteration speed and increase the possible resolution of the simulator.
- The current implementation does not treat the solution space as an infinite space and is more similar to a closed box. Either the limits need to be made large enough for the system or the implementation needs to simulate a larger space. The numerical integration, for example, may be able to extend its range, to allow the "other" electron to smear further.
- The solutions are extremely sensitive to partition size and the limits of the problem. Since the solver only reports the first six lowest eigenvalues, it's likely that similar solutions get moved in and out of these six slots as the parameters change.
- Unfortunately, the theory behind the total energy and orbital energy was not understood in time to include in the report. This is why the eigenvalues representing the orbital energies are left as they are without any units. This is also why they are used as-is as the convergence criteria for the algorithm instead of the total energy of the system. The orbital energies do not sum the Hartree-Fock energy. Koopman's theorem states that in restricted Hartree-Fock, the energies associated with occupied orbitals approximate the ionization energy of that orbital, and the energies associated with unoccupied orbitals approximate the energy required to place an electron into that orbital. The total energy of the system must be calculated using the following equation which accounts for the double contribution of electrons in the double electron integrals (hence the $\frac{1}{2}$):

$$E_o = \sum_i^N \langle i | \hat{h} | i \rangle + \frac{1}{2} \sum_i^N \sum_j^N \langle ij | | ij \rangle$$

6 Code Listings and Data

6.1 Python Code Listing

The following is the code written in Python to generate the solutions and plots used in this report.

```
"""
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AUTHORS OR COPYRIGHT HOLDERS BE LIABLE FOR ANY CLAIM, DAMAGES OR OTHER
LIABILITY, WHETHER IN AN ACTION OF CONTRACT, TORT OR OTHERWISE, ARISING FROM,
OUT OF OR IN CONNECTION WITH THE SOFTWARE OR THE USE OR OTHER DEALINGS IN THE
SOFTWARE.

"""

import argparse
import matplotlib
import matplotlib.pyplot as plt
import numpy
import scipy
import scipy.sparse
import scipy.sparse.linalg
import math
import functools
import time
import pickle
import datetime

numpy.set_printoptions(edgeitems=30, linewidth=100000,
    formatter=dict(float=lambda x: '%.3g' % x))

# Matplotlib export settings
if False:
    matplotlib.use('pgf')
    matplotlib.rcParams.update({
        'pgf.texsystem': 'pdflatex',
        'font.size': 10 ,
        'font.family': 'serif', # use serif/main font for text elements
        'text.usetex': True, # use inline math for ticks
        'pgf.rcfonts': False # don't setup fonts from rc parameters
    })

# program constants
H2_BOND_LENGTH_ATOMIC_UNITS = 1.39839733222307
IDX_X = 0
IDX_Y = 1
IDX_Z = 2
IDX_START = 0
IDX_END = 1
DATETIME_STR_FORMAT = '[%Y/%m/%d-%H:%M:%S]',
```

```
#  
# This object encapsulates the results for pickling/unpickling  
#  
class Results:  
  
    def __init__(self, eigenvectors=None, eigenvalues=None, args=None):  
  
        self.eigenvectors = eigenvectors  
        self.eigenvalues = eigenvalues  
        self.args = args  
        self.iteration_times = []  
        self.total_time = None  
  
    def load(self, input_file):  
        with open(input_file, 'rb') as file:  
            tmp_dict = pickle.load(file)  
  
        self.__dict__.update(tmp_dict)  
  
    def save(self, output_file):  
        with open(output_file, 'wb') as file:  
            pickle.dump(self.__dict__, file, 2)  
  
    def display_data(self):  
        for key in self.__dict__:  
            print(key)  
            print(self.__dict__[key])  
  
#  
# This function generates the plots  
#  
def make_plots(results):  
  
    # with help from this SO answer (4D scatter plots in matplotlib)  
    # https://stackoverflow.com/a/66939879  
  
    # number of partitions in the solution  
    N = results.args.num_partitions  
    # limits of sim  
    limits = (-1*results.args.limit, results.args.limit)  
    # generate coordinates  
    coords = generate_coordinates(limits[IDX_START], limits[IDX_END], N)  
  
    # eigenvectors  
    eigenvectors = results.eigenvectors  
  
    # total energy levels  
    total_energy_levels = len(results.eigenvalues)  
  
    # create figure object  
    fig = plt.figure(figsize=(9,10), dpi=150, constrained_layout=True)  
  
    # modify subject formatting  
    if results.args.target_subject == 'he':  
        title_subject = 'He'  
    elif results.args.target_subject == 'h2':  
        title_subject = 'H_2'  
  
    fig.suptitle('Exact_restricted_Hartree-Fock_calculated_orbitals_for %s with N=%d and  
    limits=[%d,%d]' % (title_subject, N, limits[IDX_START], limits[IDX_END]))  
    axes = []  
  
    # create results table  
    for current_energy_level in range(total_energy_levels):  
  
        # reshape eigenvectors for specified  
        data = numpy.square(eigenvectors[:,current_energy_level]).reshape((N,N,N)).transpose()  
()
```

```
# three rows, two columns, index
axes.append(fig.add_subplot(3, 2, current_energy_level + 1, projection='3d',
                           proj_type='ortho'))

# change viewing angles
axes[-1].view_init(45, 30)

axes[-1].xaxis.pane.fill = False
axes[-1].yaxis.pane.fill = False
axes[-1].zaxis.pane.fill = False

# set limits
axes[-1].set_xlim3d(limits[IDX_START], limits[IDX_END])
axes[-1].set_ylim3d(limits[IDX_START], limits[IDX_END])
axes[-1].set_zlim3d(limits[IDX_START], limits[IDX_END])

axes[-1].set_xlabel('$x$')
axes[-1].set_ylabel('$y$')
axes[-1].set_zlabel('$z$')

# set title
axes[-1].set_title('n=%d' % current_energy_level, y=0.95)

# create a mask for the data to make the visualization clearer
mask = data > (data.max() * 0.1)
idx = numpy.arange(int(numpy.prod(data.shape)))
x, y, z = numpy.unravel_index(idx, data.shape)
x, y, z = numpy.meshgrid(coords[IDX_X], coords[IDX_Y], coords[IDX_Z])
axes[-1].scatter(x, y, z, c=data.flatten(), s=50.0 * mask, edgecolor='face', alpha
                  =0.1, marker='o', cmap='viridis', linewidth=0)

plot_file_name = results.args.output_file.replace('.xyzp', '') + ('.png')
fig.savefig(plot_file_name)
# plt.show()

#
# This is the main function
#
def main(cmd_args):

    print('\n**Exact Hartree-Fock simulator**\n')

    # results object
    results = Results()

    ## extract arguments

    print('**Arguments:**')

    # input file to process
    input_file = cmd_args.input_file

    # if we have an input file, it will have data and args, load them
    if input_file:
        print('Input %s supplied, reading its data and arguments...' % input_file)
        results.load(input_file)
        args = results.args
        args.input_file = input_file
    else:
        args = cmd_args

    # print args
    for arg in vars(args):
        print('\t' + arg, getattr(args, arg))

    # output file to save results to
    output_file = args.output_file
```

```
# energy level to converge on
# always use value provided by command line
energy_level = cmd_args.energy_level

# target subject to run sim on
target_subject = args.target_subject

# convergence condition percentage
convergence_percentage = args.convergence_percentage

# number of eigenvalues to calculate
total_energy_levels = 6

# number of partitions in the solution
N = args.num_partitions

# limits of sim
limits = (-1*args.limit, args.limit)

# generate coordinates
coords = generate_coordinates(limits[IDX_START], limits[IDX_END], N)

# calculate partition size
h = coords[IDX_X][1]-coords[IDX_X][0]

## start program

print('\n** Program start!\n')

print('\tPartition size: %f' % h)

# check if we're simulating something new (no input file specified)
if not input_file:

    # generate attraction matrix for hydrogen molecule
    attraction_matrix_hydrogen = attraction_matrix_gen(attraction_func_hydrogen, N,
                                                          coords)

    # generate attraction matrix for helium molecule
    attraction_matrix_helium = attraction_matrix_gen(attraction_func_helium, N, coords)

    # generate laplacian matrix
    laplacian_matrix = second_order_laplacian_3d_sparse_matrix_gen(N)

    # generate kinetic matrix
    kinetic_energy_matrix = (-1.0/(2.0*h**2))*laplacian_matrix

    # create base solution
    eigenvectors = scipy.sparse.csr_matrix((N**3, total_energy_levels))

    # last eigenvalues
    last_total_energy = 0

    # first iteration
    first_iteration = True

    # iteration counter
    iteration_count = 1

    # total time
    total_time_start = time.time()

    datetime_now = datetime.datetime.now()
    print('\n** Simulation start! %s\n' % datetime_now.strftime(DATETIME_STR_FORMAT))

    # main loop
    while True:
```

```
# iteration time
iteration_time_start = time.time()

if first_iteration:
    print('**\uFirst\uiteration,\uzeros\uused\uas\ufirst\uguess')
    first_iteration = False
else:

    print('**\uIteration:\u%d' % iteration_count)

# create integration matrix
integration_matrix = integration_matrix_gen(eigenvectors, energy_level, N,
                                              coords)

# create Fock matrix
if target_subject == 'h2':
    fock_matrix = kinetic_energy_matrix + attraction_matrix_hydrogen +
                  integration_matrix
elif target_subject == 'he':
    fock_matrix = kinetic_energy_matrix + attraction_matrix_helium +
                  integration_matrix
else:
    print('Fatal\uerror,\uexiting.')
    return

# get (total_energy_levels) eigenvectors and eigenvalues and order them from
# smallest to largest
eigenvalues, eigenvectors = scipy.sparse.linalg.eigsh(fock_matrix, k=
    total_energy_levels, which='SM')

# check percentage difference between previous and current eigenvalues
total_energy = numpy.sum(numpy.absolute(eigenvalues))

# calculate total energy
total_energy_percent_diff = abs(total_energy - last_total_energy)/((total_energy +
    last_total_energy) / 2)

print('Total\uorbital\uenergy\u%%\udiff:\u%.3f%%' % (total_energy_percent_diff *
    100.0))

# update last value
last_total_energy = total_energy

# update iteration count
iteration_count = iteration_count + 1

# append iteration time
iteration_time = time.time() - iteration_time_start
results.iteration_times.append(iteration_time)

datetime_now = datetime.datetime.now()
print('\n**\uIteration\uend!\u%s\n' % datetime_now.strftime(DATETIME_STR_FORMAT))
print('**\uIteration\uTime:\u%.3f\useconds**' % iteration_time)
print('\n**\uEigenvalues:\n')
print(eigenvalues)

# check if we meet convergence condition
if total_energy_percent_diff < (convergence_percentage/100.0):
    break

# append total time
total_time_end = time.time()
total_time = total_time_end - total_time_start
results.total_time = total_time
datetime_now = datetime.datetime.now()
print('\n**\uSimulation\uend!\u%s\n' % datetime_now.strftime(DATETIME_STR_FORMAT))
print('**\uTotal\uTime:\u%.3f\useconds**' % results.total_time)
```

```

# construct file name
if not output_file:
    output_file = target_subject + '_N%d_l%d.xyzp' % (N, limits[IDX_END])
args.output_file = output_file

print('** Saving results to ' + output_file)
results.eigenvectors = eigenvectors
results.eigenvalues = eigenvalues
results.args = args
results.save(output_file)

print('\n** Solution summary:\n')

print('** Solution took %d iterations to converge with a convergence criteria of %.1f%% in %.3f seconds' % (len(results.iteration_times), results.args.convergence_percentage, results.total_time))
for iteration, iteration_time in enumerate(results.iteration_times):
    print('\tIteration %i took %.3f seconds' % (iteration, iteration_time))

# solution results display

print('\n** Coordinates:\n')
print(coords)
print('\n** Eigenvalues:\n')
print(results.eigenvalues)
print('\n** Orbital energies:\n')
for n in range(len(results.eigenvalues)):
    print('\tn=%d orbital energy: %f' % (n, results.eigenvalues[n]))
    eigenvector = results.eigenvectors[:, n]
    squared_eigenvector = numpy.square(eigenvector)
    expectation = integrate(squared_eigenvector, coords)
    print('\t\tPsi_%d expectation value: %f' % (n, expectation))

# plot data
print('\n** Plotting data...\n')
make_plots(results)

#
# This functions returns whether or not the matrix is symmetric
#
def is_symmetric(A, tol=1e-8):
    return scipy.sparse.linalg.norm(A-A.T, scipy.inf) < tol;

#
# This functions returns whether or not the matrix is hermitian
#
def is_hermitian(A, tol=1e-8):
    return scipy.sparse.linalg.norm(A-A.H, scipy.inf) < tol;

#
# This function takes in a matrix index (row or column) and returns the
# associated coordinate indices as a tuple.
#
def matrix_index_to_coordinate_indices(matrix_index, N):

    # Z is kind of like the MSB, as it changes less often, so we'll treat this
    # as base conversion of sorts where to new base is N

    base_10_num = matrix_index
    digits = []

    # while we have a base 10 number to work with
    for i in range(3):
        # do modulus to extract the digits of the new number
        digits = digits + [base_10_num % N]
        # go to the next digit
        base_10_num = base_10_num // N

```

```

        return tuple(digits)

#
# This function converts coordinate indices to a matrix index
#
def coordinate_indices_to_matrix_index(coord_indices, N):

    return coord_indices[IDX_X] + coord_indices[IDX_Y]*N + coord_indices[IDX_Z]*N*N
#
# This function takes in coordinate indices and returns the coordinates
# associated with them.
#
def coordinate_index_to_coordinates(coord_indices, coords):

    return (coords[IDX_X][coord_indices[IDX_X]], coords[IDX_Y][coord_indices[IDX_Y]], coords
[IDX_Z][coord_indices[IDX_Z]])

#
# Generate the coordinates for the solution space, with the assumption that it
# is cubic.
#
def generate_coordinates(minimum, maximum, N):

    x = numpy.linspace(minimum, maximum, N)
    y = numpy.linspace(minimum, maximum, N)
    z = numpy.linspace(minimum, maximum, N)

    return (x, y, z)

#
# This function returns the nuclear attraction for an electron in the Helium
# element simulation. A small number tiny_number is provided to prevent divide
# by zero scenarios.
#
def attraction_func_helium(coords, h):

    x = coords[IDX_X]
    y = coords[IDX_Y]
    z = coords[IDX_Z]

    tiny_number = 0.1

    denominator = math.sqrt(x**2 + y**2 + z**2)

    return -((2.0/(tiny_number + denominator)))

#
# This function returns the nuclear attraction for an electron in the Hydrogen
# molecule simulation. A small number tiny_number is provided to prevent divide
# by zero scenarios.
#
def attraction_func_hydrogen(coords, h):

    x = coords[IDX_X]
    y = coords[IDX_Y]
    z = coords[IDX_Z]

    tiny_number = 0.1

    denominator_1 = math.sqrt(((H2_BOND_LENGTH_ATOMIC_UNITS/2) - x)**2 + y**2 + z**2)
    denominator_2 = math.sqrt(((H2_BOND_LENGTH_ATOMIC_UNITS/2) - x)**2 + y**2 + z**2)

    return -((1.0/(tiny_number + denominator_1)) + (1.0/(tiny_number + denominator_2)))

#
# This functions calculates the repulsion between two electrons. A small number
# TINY_NUMBER is provided to prevent divide by zero scenarios.

```

```

#
@functools.lru_cache
def repulsion_func(coords_1, coords_2, h):

    x1 = coords_1[IDX_X]
    y1 = coords_1[IDX_Y]
    z1 = coords_1[IDX_Z]

    x2 = coords_2[IDX_X]
    y2 = coords_2[IDX_Y]
    z2 = coords_2[IDX_Z]

    TINY_NUMBER = 0.1

    denominator = math.sqrt((x2 - x1)**2 + (y2 - y1)**2 + (z2 - z1)**2)

    return ((1.0/(TINY_NUMBER + denominator)))

#
# This function generates an attraction matrix with the specified attraction
# function and coordinates
#
def attraction_matrix_gen(attraction_func, N, coords):

    # extract h
    h = coords[IDX_X][1] - coords[IDX_X][0]

    # use scipy sparse matrix generation
    # create the diagonal
    diagonal = [attraction_func(coordinate_index_to_coordinates(
        matrix_index_to_coordinate_indices(i, N), coords), h) for i in range(N**3)]

    # now generate the matrix with the desired diagonal
    matrix = scipy.sparse.spdiags(data=diagonal, diags=0, m=N**3, n=N**3)

    return matrix.tocoo()

#
# This function generates the second order laplacian matrix for 3D space for N
# partitions.
#
# e.g. N = 3
#
+-----+-----+-----+-----+-----+-----+
# | -6 1 |   1 |       |   1 |       |       |
# | 1-6 1 |   1 |       |   1 |       |       |
# |   1-6 |   1 |       |   1 |       |       |
# +-----+-----+-----+-----+-----+-----+
# |   1 | -6 1 |   1 |       |   1 |       |
# |   1 | 1-6 1 |   1 |       |   1 |       |
# |   1 |   1-6 |   1 |       |   1 |       |
# +-----+-----+-----+-----+-----+-----+
# |       |   1 | -6 1 |       |       |   1 |
# |       |   1 | 1-6 1 |       |       |   1 |
# |       |   1 |   1-6 |       |       |   1 |
# +-----+-----+-----+-----+-----+-----+
# |   1 |       |   1 | -6 1 |   1 |       |
# |   1 |       |   1 | 1-6 1 |   1 |       |
# |   1 |       |   1 |   1-6 |   1 |       |
# +-----+-----+-----+-----+-----+-----+
# |       |   1 |       |   1 | -6 1 |   1 |
# |       |   1 |       |   1 | 1-6 1 |   1 |
# |       |   1 |       |   1 |   1-6 |   1 |
# +-----+-----+-----+-----+-----+-----+
# |       |       |   1 |       |   1 | -6 1 |
# |       |       |   1 |       |   1 | 1-6 1 |
# |       |       |   1 |       |   1 |   1-6 |
# +-----+-----+-----+-----+-----+-----+

```

```

#      |      |      |      | 1      |      |      | -6 1      | 1      |      |
#      |      |      |      | 1      |      |      | 1-6 1      | 1      |      |
#      |      |      |      | 1      |      |      | 1-6 |      | 1      |      |
# +-----+-----+-----+-----+-----+-----+-----+-----+-----+
#      |      |      |      |      | 1      |      | 1      | -6 1      | 1      |
#      |      |      |      |      | 1      |      | 1      | 1-6 1      | 1      |
#      |      |      |      |      | 1      |      | 1      | 1-6 |      | 1      |
# +-----+-----+-----+-----+-----+-----+-----+-----+-----+
#      |      |      |      |      |      | 1      |      | 1      | -6 1      |
#      |      |      |      |      |      | 1      |      | 1      | 1-6 1      |
#      |      |      |      |      |      | 1      |      | 1      | 1-6 |      |
# +-----+-----+-----+-----+-----+-----+-----+-----+-----+
#      |      |      |      |      |      |      | 1      |      | -6 1      |
#      |      |      |      |      |      |      | 1      |      | 1-6 1      |
#      |      |      |      |      |      |      | 1      |      | 1-6 |      |
# +-----+-----+-----+-----+-----+-----+-----+-----+-----+
def second_order_laplacian_3d_sparse_matrix_gen(N):

    # create block matrices
    # sub main block diagonals (containing -6 surrounded by 1s) found within N*N blocks
    # e.g N=3
    # +-----+
    # | -6 1      |
    # | 1-6 1      |
    # | 1       1-6 |
    # +-----+
    sub_main_block_diag = [-6.0 for i in range(N)]
    sub_main_block_outer_diags = [1.0 for i in range(N)]
    sub_main_block = scipy.sparse.spdiags(data=[sub_main_block_outer_diags,
                                                sub_main_block_diag, sub_main_block_outer_diags], diags=[-1,0,1], m=N, n=N)

    # create mini identity blocks found within N*N blocks
    # e.g N=3
    # +-----+
    # | 1      |
    # | 1      |
    # | 1      |
    # +-----+
    mini_ident_block = scipy.sparse.identity(N)

    # create a list of blocks to be used in the sparse.bmat function to generate
    # main block along the diagonal
    # e.g. N=3
    # +-----+-----+-----+
    # | -6 1      | 1      |      |
    # | 1-6 1      | 1      |      |
    # | 1       1-6 | 1      |      |
    # +-----+-----+-----+
    # | 1      | -6 1      | 1      |
    # | 1      | 1-6 1      | 1      |
    # | 1      | 1       1-6 | 1      |
    # +-----+-----+-----+
    # | 1      | 1      | -6 1      |
    # | 1      | 1      | 1-6 1      |
    # | 1      | 1      | 1       1-6 |
    # +-----+-----+-----+
    block_lists = [[None for i in range(N)] for j in range(N)]
    for i in range(N):
        for j in range(N):
            # add main blocks
            if j == i:
                block_lists[i][j] = sub_main_block
            # add diagonal blocks
            if (j == (i + 1)) and ((i + 1) != N):
                block_lists[i][j] = mini_ident_block
            if (j == (i - 1)) and ((i - 1) != -1):
                block_lists[i][j] = mini_ident_block
    main_block = scipy.sparse.bmat(block_lists)

    # create large identity blocks of size N*N
    # e.g. N=3
    # +-----+-----+-----+

```

```

# | 1 | | | |
# |   1 | | | |
# |     1 | | | |
# +-----+-----+-----+
# |       1 | | | |
# |         1 | | | |
# |           1 | | | |
# +-----+-----+-----+
# |       | | 1 | |
# |       | | 1 | |
# |       | | 1 | |
# +-----+-----+-----+
large_ident_block = scipy.sparse.identity(N*N)

# create a list of blocks to be used in the sparse.bmat function to generate
# the final laplacian_matrix
block_lists = [[None for i in range(N)] for j in range(N)]
for i in range(N):
    for j in range(N):
        # add main blocks
        if j == i:
            block_lists[i][j] = main_block
        # add diagonal blocks
        if (j == (i + 1)) and ((i + 1) != N):
            block_lists[i][j] = large_ident_block
        if (j == (i - 1)) and ((i - 1) != -1):
            block_lists[i][j] = large_ident_block

return scipy.sparse.bmat(block_lists)

#
# This is a generic numerical integration over the cubic 3D space covered by the
# solution space
#
def integrate(function_values_3d, coords):

    # get partition size
    h = coords[IDX_X][1] - coords[IDX_X][0]
    # get number of partitions
    N = len(coords[IDX_X])

    # running sum
    sum = 0

    # calculate the integration over the solution space
    for xi, x in enumerate(coords[IDX_X]):
        for yi, y in enumerate(coords[IDX_Y]):
            for zi, z in enumerate(coords[IDX_Z]):
                # first integration weight is 0
                if xi == 0 or yi == 0 or zi == 0:
                    w = 0
                else:
                    w = h
                row_index = xi + yi*N + zi*N*N
                sum = sum + w*function_values_3d[row_index]

    # return result
    return sum

#
# This function evaluates the integration function used by both the Helium
# element and the Hydrogen molecule.
#
def integration_term_func(eigenvectors, eigenvector_index, N, coords_1, all_coords, h):

    # running sum
    sum = 0

```

```

# calculate the integration over the solution space of the specified psi squared
for xi, x in enumerate(all_coords[IDX_X]):
    for yi, y in enumerate(all_coords[IDX_Y]):
        for zi, z in enumerate(all_coords[IDX_Z]):
            # first integration weight is 0
            if xi == 0 or yi == 0 or zi == 0:
                w = 0
            else:
                w = h
            matrix_index = xi + yi*N + zi*N*N
            coords_2 = (x, y, z)
            sum = sum + w*(eigenvectors[:,eigenvector_index][matrix_index])**2*
                  repulsion_func(coords_1, coords_2, h)

return sum

#
# This function generates the the integration matrix
#
def integration_matrix_gen(eigenvectors, eigenvector_index, N, coords):

    # extract h from coordinates
    h = coords[IDX_X][1] - coords[IDX_X][0]

    # turn eigenvectors into a normal array if necessary
    if type(eigenvectors) != numpy.ndarray:
        eigenvectors = eigenvectors.toarray()

    # use scipy sparse matrix generation
    # create the diagonal
    diagonal = [integration_term_func(eigenvectors, eigenvector_index, N,
                                       coordinate_index_to_coordinates(matrix_index_to_coordinate_indices(i, N), coords),
                                       h) for i in range(N**3)]

    # now generate the matrix with the desired diagonal
    matrix = scipy.sparse.spdiags(data=diagonal, diags=0, m=N**3, n=N**3)

    return matrix.tocoo()

if __name__ == '__main__':
    # the following sets up the argument parser for the program
    parser = argparse.ArgumentParser(description='Exact Hartree-Fock simulator')

    # arguments for the program
    parser.add_argument('-i', type=str, dest='input_file', action='store',
                        help='input file (*.xyzp) to plot')

    parser.add_argument('-o', type=str, dest='output_file', action='store',
                        help='path and name of the file containing the results of the current run')

    parser.add_argument('-e', type=int, default=0, dest='energy_level', action='store',
                        choices=[0, 1, 2, 3, 4, 5],
                        help='energy level to generate and/or plot')

    parser.add_argument('-t', type=str, default='h2', dest='target_subject', action='store',
                        choices=['h2', 'he'],
                        help='target subject to run exact HF simulation')

    parser.add_argument('-p', type=int, default=12, dest='num_partitions', action='store',
                        help='number of partitions to discretize the simulation')

    parser.add_argument('-l', type=float, default=1, dest='limit', action='store',
                        help='the x,y,z max limit, forming a cubic solution space')

    parser.add_argument('-c', type=float, default=1.0, dest='convergence_percentage', action='store',
                        help='percent change threshold for convergence')

```

```
args = parser.parse_args()  
main(args)
```

7 References

These aren't citing anything, but they were useful in helping me figure out this assignment.

- https://www.12000.org/my_notes/mma_matlab_control/KERNEL/KEse83.htm
- <https://www.value-at-risk.net/numerical-integration-multiple-dimensions/>
- [https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Book%3A_Quantum_States_of_Atoms_and_Molecules_\(Zielinski_et_al\)/09%3A_The_Electronic_States_of_the_Multielectron_Atoms/9.07%3A_The_Self-Consistent_Field_Approximation_\(Hartree-Fock_Method\)](https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Book%3A_Quantum_States_of_Atoms_and_Molecules_(Zielinski_et_al)/09%3A_The_Electronic_States_of_the_Multielectron_Atoms/9.07%3A_The_Self-Consistent_Field_Approximation_(Hartree-Fock_Method))
- <http://vergil.chemistry.gatech.edu/notes/hf-intro/hf-intro.html>
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