

PHYS 304 Final Project Hartree Fock Theory

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The Hartree Fock theory is a powerful approximation method for describing a many-electron system. In this project, we reported the best orbital for lithium ions using the Hartree Fock method. The self-consistent field is simulated ten times, guaranteeing a convergent fixed point. The input takes two arrays, one for each orbital, and a plot was formed to find the lowest energy state. By using differential equations and numpy functions, we got two sets of orbitals, and they share similar values with $\zeta_1 = 4.6$ and $\zeta_2 = 2.4$. The result is in agreement with the IBM laboratory.

1. INTRODUCTION

From quantum physics, we learned that it is hard to solve the Schrodinger equation exactly, and it is only feasible for a limited number of physical systems such as single-electron or hydrogen-like atoms. However, most atoms or molecules have many electrons, which complicates the system. To understand the electronic structure, We need an approximation method. Hartree Fock theory is an approximation method using a single Slater determinant (which will be explained later) to find the best electronic state by minimizing the energy. The equations and methods illustrated in this report follow the derivation in the textbook, *Introduction to Computational Physical Chemistry*, by Professor Joshua Schrier [1].

1.1. Hartree Fock Energy

When analyzing a physical system, Hamiltonian is always of physicists' interest, which is an operator calculating the total energy of the system. When considering a many-electron system, the Hamiltonian can be written as,

$$E_{HF} = \sum_i^{\text{electrons}} \langle i | \hat{h} | i \rangle + \sum_{i>j} J_{ij}, \quad (1)$$

where the first term involving \hat{h} is the kinetic and the potential energy of attraction to the nuclei, which is in the form,

$$\hat{h}_i = -\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i}, \quad (2)$$

where Z is the number of protons in the nucleus of the atom, ∇_i calculates the kinetic energy, and $\frac{Z}{r_i}$ gives the potential energy.

The second term in equation 1 is the Coulomb repulsion between electrons. An assumption used in Hartree Fock's theory is that the nuclei are fixed while the electrons are moving around since the nuclei are much heavier than electrons based on the Born-Oppenheimer approximation [2].

The Hartree Fock theory depicts the many-electron system's wavefunction as a single Slater determinant, as defined in equation 4. Suppose a helium atom with two electron. The wave function is shown below,

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \chi_a(1) & \chi_b(1) \\ \chi_a(2) & \chi_b(2) \end{vmatrix} \quad (3)$$

$$= \frac{1}{\sqrt{2}} (\chi_a(1)\chi_b(2) - \chi_a(2)\chi_b(1)) \quad (4)$$

$\chi_a(1)$ is the spatial and spin dependence of the orbital containing electron 1. The numbers 1 and 2 are the indices of electrons. The letters a and b are the orbitals. To write the spatial and spin dependence separately, we split the orbital function into,

$$\begin{aligned} \chi_a(1) &= \psi(\mathbf{r}_1)\alpha(1) \\ \chi_b(1) &= \psi(\mathbf{r}_1)\beta(1), \end{aligned} \quad (5)$$

where ψ represents the spatial orbital, and α for spinning upward and β for spinning downward, which are orthonormal to each other. Due to the orthonormality of spin functions, the electron orbitals are also orthonormal,

$$\begin{aligned} \langle \chi_a(1) | \chi_a(1) \rangle &= 1 \\ \langle \chi_b(1) | \chi_b(1) \rangle &= 1 \\ \langle \chi_a(1) | \chi_b(1) \rangle &= 0 \end{aligned} \quad (6)$$

Given these relations, the energy of a helium atom can be written as,

$$E_{HF} = \langle \Psi | \hat{h}_1 | \Psi \rangle + \langle \Psi | \hat{h}_2 | \Psi \rangle + \langle \Psi | \frac{1}{r_{12}} | \Psi \rangle \quad (7)$$

The expectation values of h_1 and h_2 can be written and simplified as,

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$$h_1 = \langle \psi_1 | \hat{h}_1 | \psi_1 \rangle \quad (8)$$

$$h_2 = \langle \psi_2 | \hat{h}_2 | \psi_2 \rangle \quad (9)$$

For the third term in equation 7, the expectation value can be calculated in a similar way as h_1 and h_2 . A simplified way to denote this term by indexing the spin orbitals is,

$$[ii|jj] = \int dx_1 \int dx_2 \chi_i^*(x_1) \chi_i(x_1) \frac{1}{r_{12}} \chi_j^*(x_2) \chi_j(x_2) \quad (10)$$

By examining this integral, we observe that the term $\chi_i^*(x_1) \chi_i(x_1)$ is the probability of electrons 1 in orbital 1 located at x_1 , while $\chi_j^*(x_2) \chi_j(x_2)$ is the probability of electrons 2 in orbital j located at x_2 , and the $\frac{1}{r_{ij}}$ is the Coulomb repulsion [3]. Each pair of electrons in the atom has a Coulomb integral. Overall, this term gives the Coulomb repulsion between electron 1 in orbital i and electron 2 in orbital j .

1.2. Hartree Fock equation

The main idea of Hartree Fock theory is to minimize the energy with respect to the orbitals. We define a F operator as,

$$\hat{F}(x_1) = h(x_1) + \sum_j J_j(x_1) \quad (11)$$

Because this calculates the total energy of electron 1, the equation should equal to some constant ϵ_1 . If we have the \hat{F} operator act on orbital $\chi_i(x_1)$, it should give the energy ϵ_i , which can be expressed as,

$$\hat{F}(x_1) \chi_i(x_1) = \epsilon_i \chi_i(x_1), \quad (12)$$

which is simplified into an eigenvalue question. This means the best orbitals which give the lowest energy for the Slater determinant should satisfy the eigenvalue equation.

However, this is a complicated integral equation involving the second order differentiation. A physicist, Clemens Roothaan, introduces a method using a basis set to represent the χ equations, $\chi_i = \sum_{v=1} c_{vi} \tilde{\chi}_v$. Through a rigorous proof, we end up with a linear algebra equation,

$$\sum_v F_{\mu v} c_{vi} = \epsilon_i \sum_v S_{\mu v} c_{vi}, \quad (13)$$

where the $S_{\mu v}$ is an overlap matrix. It calculates how much the basis function μ overlaps with basis function v . $F_{\mu v}$ is the matrix element using \hat{F} operator acting on basis function μ and basis function v . The equation 13 is a

linear algebra function that can be analyzed numerically by the computer. Since every element has two index, we can write equation 13 into the matrix form while extending ϵ term as a diagonal matrix,

$$\mathbf{FC} = \mathbf{SC}\epsilon \quad (14)$$

However, the problem is that to solve \mathbf{C} , we need the \mathbf{F} matrix; forming \mathbf{F} matrix, we need information of \mathbf{C} since the Coulomb term J is a summation of all χ_i s which need \mathbf{C} . Here, we introduce the self-consistent field.

2. METHOD

Self-consistent calculation is the procedure used to solve the Hartree Fock equations. Suppose the spatial orbitals, $\psi_i(\mathbf{r})$, can be described as a linear combination of basis functions,

$$\psi_i(\mathbf{r}) = \sum_r^{N_{basis}} c_{ir} \phi_r(\mathbf{r}), \quad (15)$$

However, to solve the wavefunction $\psi_i(\mathbf{r})$, c_{ir} is calculated by diagonalizing the Hamiltonian matrix, which contains the two-electron integrals. The two-electron integrals require the knowledge of the wave function, which results in an unsolvable loop. The basic idea of the Self-consistent theory is that we solve a single-particle Fock operator, \hat{F} , involving \hat{h} and $1/r_{1j}$ interactions with other particles. While maintaining other electrons fixed, we take a guess of the coefficient c_{ir} , and the eigenfunctions of \hat{F} describe ψ_j . With the new set of coefficients c_{ri} and the wave functions, we update the Fock operator and repeat this process. The final ψ_j should converge to a fixed point, which is a self-consistent field. The specific procedures are split into the following sections.

2.1. Form the Hamiltonian matrix

The Hamiltonian matrix consists of two elements, which are two single-electron operators, \hat{h}_1 and \hat{h}_2 . We need the expectation value of the two operators, which is in the form of,

$$h_i = \langle \psi_{\mathbf{r}_i} | \hat{h}_i | \mathbf{r}_i \rangle \quad (16)$$

Recalling the intro chemistry class, with the spherical harmonic wave function, the Hamiltonian matrix element is,

$$h_{rs} = 4(\zeta_r^3 \zeta_s^3)^{1/2} (\zeta_r \zeta_s - Z(\zeta_r + \zeta_s)) / (\zeta_r + \zeta_s)^3 \quad (17)$$

2.2. Define the two-electron matrix

Following the steps in the textbook, the two-electron matrix is four 2×2 matrices inside a 2×2 matrix, with each element equal to,

$$(\psi_1\psi_1|\psi_1\psi_1)_{rs} = \sum_{t=1}^{N_{basis}} \sum_{u=1}^{N_{basis}} c_{1t}^* c_{1u}^* (rs|tu), \quad (18)$$

where the integral is,

$$(rs|tu) = \int \int \frac{\phi_r^*(\mathbf{r}_1)\phi_s(\mathbf{r}_1)\phi_t^*(\mathbf{r}_2)\phi_u(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 \quad (19)$$

The physical interpretation of the two electron term is the electrostatic energy of two electron interaction, while one in orbital ϕ_r and the other in orbital ϕ_s . t and u serve as indices of the coefficient for the basis functions. Based on this, the two electron matrix is symmetrical.

Since we are investigating the L_i^+ , which only has two electrons, the L_i^+ system is similar to helium system with a different value Z . For the two electron integrals, we use the values from the textbook.

2.3. Forming S matrix and X matrix

However, the basis wave functions, ϕ_r , are usually nonorthogonal, which requires a overlap matrix \mathbf{S} to calculate the overlap between the orbitals. In this way, the basis is orthogonalized and the molecular orbitals are linearly independent. The element of \mathbf{S} matrix is defined as,

$$S_{rs} = \langle r|s \rangle = \int \phi_r^*(\mathbf{r}_1)\phi_s(\mathbf{r}_1)d^3\mathbf{r}_1 \quad (20)$$

After the overlap matrix is created, a transformation matrix is needed to diagonalize it. In this way, the orbital is defined orthonormal, which is easier to calculate. The transformation matrix is defined as,

$$\mathbf{X}^* \mathbf{S} \mathbf{X} = \mathbf{1} \quad (21)$$

2.4. Energy calculation with varying ζ

After all matrices are defined, we are ready to perform the Hartree Fock calculation. The function we are solving for eigenvalues is,

$$\mathbf{F} \mathbf{c}_i = \epsilon_i \mathbf{S} \mathbf{c}_i \quad (22)$$

We start with an initial guess and construct the Fock matrix. Then, we transform the Fock matrix using the transformation matrix \mathbf{X} . After this, we diagonalize the

transformed Fock matrix. Then, each vector is transformed back to the original basis. The coefficients within the original basis are used to construct a new Fock matrix. This process is repeated until we have a convergent result. Once the result is convergent, we are ready to calculate the energy.

Below is the pseudo-code of the main part: First of all, we set up a loop to make sure the self consistent field is obtained. Inside the loop, we need to update the F matrix and the new coefficient.

Set up a counter and a while loop

count = 0

while count < 10:

count += 1

for r in range(2):

for s in range(2):

$F_{matrix}[r][s] = h_{matrix}(\zeta_1, \zeta_2)[r][s]$

for i in range(2):

for j in range(2):

Update F_{matrix}

Following the updated F_{matrix} , the transformation matrix \mathbf{X} should be updated. This will give a new transformed F_{matrix} . One thing noticeable is that Python has a different way of dealing with matrix multiplication. The function used to do matrix multiplication is "np.matmul".

Update every matrix for the next run

Xnew = np.conjugate(np.transpose(Xmatr(ζ_1, ζ_2)))

Fnew = np.matmul(np.matmul(Xmatr(ζ_1, ζ_2), F_{matrix}), Xnew)

x,c = np.linalg.eigh(Fnew)

for k in range(2):

c[k] = np.matmul(Xmatr(ζ_1, ζ_2), c[k])

End of the while loop

In the pseudo-code above, $Xmatr$ is the function that define to generate the transformation matrix. We use the "np.linalg.eigh" to solve the eigensystem. The last line calculating $c[k]$ is the end of the while loop, and a self-consistent field is formed by iterating for 10 times. Then, we are ready to calculate the energy. The energy is defined as,

$$E = h_1 + h_2 + (\psi\psi|\psi\psi) \quad (23)$$

The pseudo-code is shown below,

Set up two empty number h_{sum} and ψ_{sum} for each of the term in the energy equation above

$h_{sum} = 0$

for r in range(2):

for s in range(2):

$h_{sum} += []$

$\psi_{sum} = 0$

for r in range(2):

for s in range(2):

for i in range(2):

for j in range(2):

$\psi_{sum} += []$

$E = 2 \times h_{sum} + \psi_{sum}$

return E

3. RESULT

To determine which set of ζ gives the lowest energy, we generate two arrays for each electron. The choice of number is based on the hint given in the textbook. For Li^+ atom, there are three protons, so $Z = 3$. To calculate the energy, we create a two dimensional array. One thing noticeable is that we need two loops, one in the other so that all combinations of ζ_1 and ζ_2 are taken into account,

```
ζ1=np.linspace()
ζ2=np.linspace()
E=np.zeros((len(ζ1),len(ζ2)))
for i in range(len(ζ1)):
    for j in range(len(ζ2)):
        energy_point=energy(ζ1[i],ζ2[j])
        E[i][j] = energy_point
```

Then we make a plot in 3 dimensions, with one axis for ζ_1 and the other axis for ζ_2 . The height of the plot is the energy. The result is shown in figure 1. As expected, there is an energy valley, indicating the best value of ζ_1 and ζ_2 . To get the specific value for ζ_1 and ζ_2 where the energy is minimized, "np.where" is used to locate the minimum. We get $\zeta_1 = 4.57$ and $\zeta_2 = 2.44$.

A common method used to find the extreme of a function with multiple parameters is using a partial differential equation, which we have talked about during class. Since the plot shown in figure 1 exhibits a quadratic trend, a polynomial function is used to fit the data (which we have also covered during class). For ζ_1 , we fixed the value of ζ_2 . The energy we use is $E[:, \zeta_2]$, and the value of ζ_2 is the point finding from the 3 dimensional plot. After we get the polynomial function, "np.polyder" function is used to find the derivative. To find the minimum, set the derivative equal to zero, and the roots of the function indicate the extreme.

The polynomial we fit for ζ_1 is $-0.000542x^3 + 0.01021x^2 - 0.05936x - 7.127$, and the derivative is $-0.001626x^2 + 0.02042x - 0.05936$. The derivative is a second order function, i.e., there are two roots. To find the right one, we use a loop to set the range to get the correct root,

```
allroot = np.roots(derivative.coefficients)
root = []
for i in allroot:
    if ζ1[0] <= i <= ζ1[-1]:
        root.append(i)
```

The fitting function, the original data, the ζ_1 found using the Hartree Fock calculation, and the ζ_1 found using the polynomial fit is plotted in figure 2. Similarly, we did the same calculation for ζ_2 , and the result is shown in figure 3. One trivial note is that since we are only interested in the values, all the constants we imported are unitless.

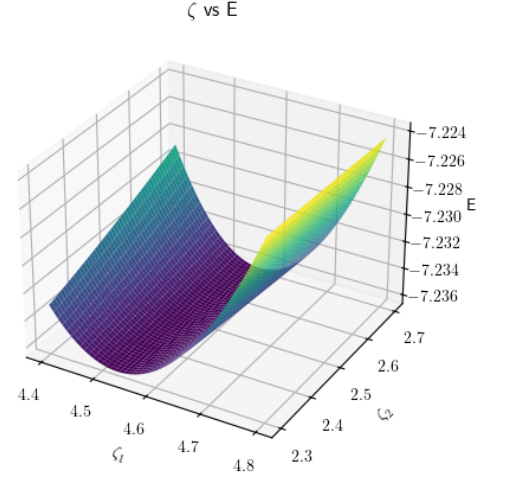


FIG. 1: [Energy vs ζ in 3 dimensional plot]

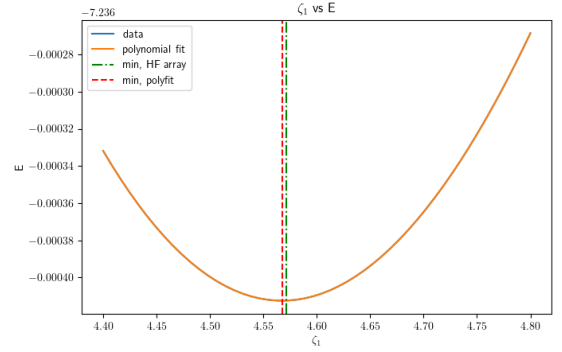


FIG. 2: [Polynomial fit of ζ_1 when maintaining ζ_2 constant]

4. DISCUSSION

Compare the two results we get from Hartree Fock (HF) theory and the polynomial fit respectively. For ζ_1 , the HF gives 4.571 while the polynomial fit is 4.569. For ζ_2 , the HF gives 2.446 while the polynomial fit is 2.446. According to the IBM research lab [4], the $1s$ orbital exponents are 4.617 and 2.462 for lithium atoms, respectively. The discrepancy for both ζ is within 0.8%, which states that our calculation is accurate enough.

5. CONCLUSION

We have constructed a Hartree Fock calculation for the lithium ions, which share a similar electron system as helium but with a different proton number. Using the numpy function and differentiation, we obtain two sets of ζ values. Compared with the results from the IBM laboratory, they agree.

6. COLLABORATION

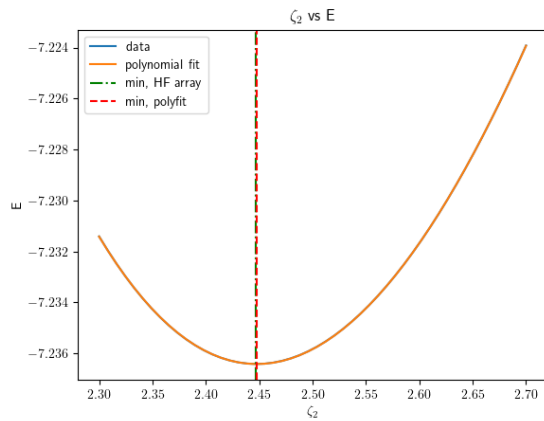


FIG. 3: [Polynomial fit of ζ_2 when maintaining ζ_1 constant]

In this project, I collaborate with Xingyun Yang and Aditya Advani. We contribute equally to the coding part, and I appreciate their work in this collaboration. There is one ".py" file for this project named "PHYS304_Final_Project_HartreeFock_Xiyue_Shen."

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