FYS4480 - Quantum Mechanics for Many-Particle Systems

Project 1

Even M. Nordhagen

October 26, 2018

- Github repository containing programs and results:

  https://github.com/evenmn/FYS4480

Abstract

The aim of this project is to study the performance of linear regression in order to fit a two dimensional polynomial to terrain data. Both Ordinary Least Square (OLS), Ridge and Lasso regression methods were implemented, and for minimizing Lasso's cost function Gradient Descent (GD) was used. A fourth method was to minimize the cost function of Ridge using GD. The fitted polynomial was visualized and compared with the data, the Mean Square Error (MSE) and R^2-score were analyzed, and finally the polynomial coefficients were studied applying visualization tools and Confidence Intervals (CI). To benchmark the results, we used Scikit Learn.

We found the self-implemented OLS and Ridge regression functions to reproduce the benchmarks, and Lasso was close to reproducing the benchmark as well. However, the difference between results produced by standard Ridge regression and when minimizing its cost function is large. The OLS regression method is considered as the most successful due to its small MSE and high R^2-score.

Contents

1 Introduction

In the childhood of quantum mechanics, immense efforts were placed on Helium computations, because leading physicists found it crucial to provide calculations in agreement with experiments in order to prove the theory. The Norwegian physicist Egil Hylleraas calculated the ground state energy of the Helium atom with impressive accuracy already in 1929, which confirmed the validity of quantum mechanics. After that, physicists and chemists have managed to study systems of ever higher complexities, thanks to better methods and stronger computers.

In this project, we estimate the energy levels of the Helium and Beryllium atom, with focus on the ground state energy. For doing that, we first apply the Configuration Interaction Singles (CIS), and thereafter turn to Hartree-Fock.

2 Theory

To calculate the energies, we need to solve the Schrödinger equation

$$\hat{H} \left| \Psi_p \right\rangle = \varepsilon_p \left| \Psi_p \right\rangle \tag{1}$$

where we expect to find the exact ground state energy, ε_0, when the correct ground state wave function (GSWF) has been used. In this project we will stick to the Born-Oppenheimer approximation, which gives the Hamiltonian when the nucleus is stationary (is not affected by the electrons),

$$\hat{H} = \sum_{i=1}^{N} t(x_i) - \sum_{i=1}^{N} k \frac{Ze^2}{r_i} + \sum_{i<j}^{N} \frac{ke^2}{r_{ij}}. \tag{2}$$

The first term gives the kinetic energy, the second gives the energy from the external potential (nucleus) and the last term gives the interaction energy. Z is the atomic number, defining the number of protons in the nucleus, k is the constant from Coulomb's law and e is the elementary change.

We now introduce the atomic units, setting $\hbar = c = e = m_e = k = 1$. The energies can be converted between atomic units and electronvolts using the relation

$$1 \text{ a.u.} = 2 \cdot 13.6 \text{ eV}. \tag{3}$$

The Hamiltonian now reads

$$\hat{H} = \hat{H}_0 + \hat{H}_I = \sum_{i=1}^{N} \hat{h}_0(x_i) + \sum_{i<j}^{N} \frac{1}{r_{ij}} \tag{4}$$

with $r_{ij} \equiv \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}$ and $\hat{h}_0$ as the one-body operator for each electron. The single particle functions (SPF) are assumed to be hydrogen-like, where the one-body energies are known from the Bohr model, stating

$$E_n = -\frac{Z^2}{2n^2} \tag{5}$$

where n is the number of nodes in the wave function. In order to calculate the two-body energies, we need to solve the integrals

$$\int r_1^2 dr_1 \int r_2^2 dr_2 \Phi_\alpha^*(r_1) \Phi_\beta^*(r_2) \frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \Phi_\gamma(r_1) \Phi_\delta(r_2) \equiv \langle \alpha\beta | \hat{v} | \gamma\delta \rangle \tag{6}$$

where the Dirac notation is used for shorthand notation. Note carefully that the Φ's are the total wave functions, where both the radial and spin parts are included. The spin part is known to not affect the energies, and it can therefore be factorized out,

$$\begin{aligned}
\langle \alpha\beta | \hat{v} | \gamma\delta \rangle &= (\alpha\beta | \hat{v} | \gamma\delta) \langle \chi_\alpha \chi_\beta | \chi_\gamma \chi_\delta \rangle \\
&= (\alpha\beta | \hat{v} | \gamma\delta) \langle \chi_\alpha | \chi_\gamma \rangle \langle \chi_\beta | \chi_\delta \rangle \\
&= (\alpha\beta | \hat{v} | \gamma\delta) \delta_{\sigma_\alpha \sigma_\gamma} \delta_{\sigma_\beta \sigma_\delta}.
\end{aligned} \tag{7}$$

We observe that the integral is non-zero if and only if α and γ got the same spin, and β and δ got the same spin.

2.1 Second Quantization and particle-hole-formalism

First write some general second quantization statements, when define the Hamiltonian in second quantization

2.1.1 Wick's theorem

State Wick's theorem

2.1.2 Energy formulas

For calculating the ground state energy of an atom with atomic number Z, we need to calculate

$$\varepsilon_0 = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle = \sum_i \langle i | \hat{h}_0 | i \rangle + \frac{1}{2} \sum_{ij} \langle ij | \hat{v} | ij \rangle_{\text{AS}} \tag{8}$$

where the subscript AS... See appendix A. Should also add cHia and iaHja, and mention that they are gonna be used in CIS.

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2.2 The Helium atom

A neutral Helium atom consists of a nucleus of two protons with two electrons orbiting, and is one of the most simple many-body systems one can study. The difficulty of dealing with many-body systems lies in the interaction, where the elements $\langle \alpha\beta|\hat{v}|\gamma\delta\rangle$ can be really tricky to handle. Hard to find exact wave function.

There exist various methods for solving this problem, where one of the most successful is to define a wave function which is varied such that the energy is minimized. This method was used by E. Hylleraas already in 1929, when he minimized the energy with a wave function of 10 variational parameters, using a mechanical desk calculator. [https://www.encyclopedia.com/science/dictionaries-thesauruses-pictures-and-press-releases/hylleraas-egil-andersen] He found the energy to be -2.90363 eV, which is close to recent experimental values. [http://www.umich.edu/ chem46

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2.2.1 Ground state

Helium is in its ground state when both electrons occupy the 1s orbital, thus they have opposite spins and $M_s = 0$. In this project, we will study systems of $M_s = 0$ only, such that an electron can only be excited to a state with the same spin.

Taking the Pauli principle into account, the two-body wavefunction needs to be nulled out if two particles are in the same state, and it should also be antisymmetric under exchange of two particles. We are therefore in need of a Slater Determinant (SD), given by

$$\Psi(x_1, x_2, \sigma_1, \sigma_2) = A\begin{vmatrix}\psi_{\sigma_1}(x_1) & \psi_{\sigma_1}(x_2)\\ \psi_{\sigma_2}(x_1) & \psi_{\sigma_2}(x_2)\end{vmatrix} \tag{9}$$

$$= A\Big[\psi_{\sigma_1}(x_1)\psi_{\sigma_2}(x_2) - \psi_{\sigma_2}(x_1)\psi_{\sigma_1}(x_2)\Big] \tag{10}$$

where ψ_{σ_1} is the SPF with spin $m_s = \sigma_1$ and A is a normalization constant. If we assume that the SPFs are normalized, our ansatz can be written as

$$|\Phi_0\rangle = \frac{1}{\sqrt{2}}(|1\rangle\,|\bar{1}\rangle - |\bar{1}\rangle\,|1\rangle) \tag{11}$$

with $|\bar{1}\rangle$ describing a particle with principle quantum number 1 and spin σ_2, which we will illustrate with spin down. In second quantization, we can construct the ground state from the true vacuum,

$$|\Phi_0\rangle = a_1^\dagger a_{\bar{1}}^\dagger\,|0\rangle, \tag{12}$$

which is understand to take the anti-symmetry property. The ground state is illustrated in figure (1).
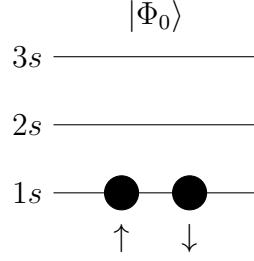
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Figure 1: Ground state of Helium.

2.2.2 Excited states

When entering excited states, we can risk having angular quantum numbers unlike zero, because $l \in [0, n-1]$. This makes the computations more difficult, but in this project we will ignore that challenge setting $l = 0$, and thus limit us to the s-waves.

Consider now a system consisting of the orbitals 1s, 2s and 3s only. For that case, the possible energy states of the Helium atom are listed in figure (2).
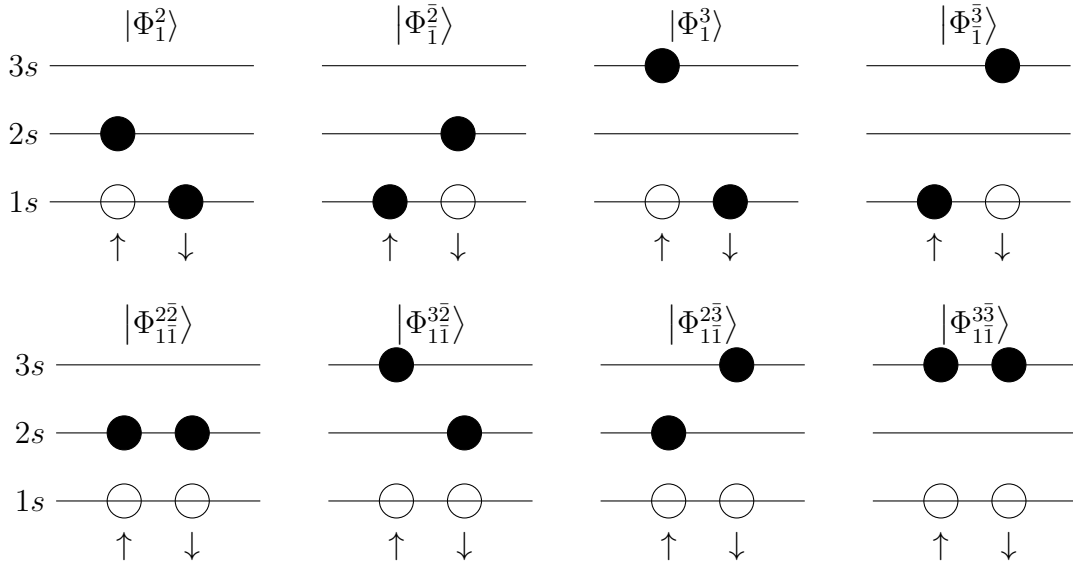

Figure 2: Possible states in the 1s, 2s and 3s orbitals of Helium. In the first row, all single excited states are listed, while in the second row all double excited states are listed.

2.3   The Beryllium atom

2.3.1   Ground state

Helium is in its ground state when both electrons occupy the 1s orbital, thus they have opposite spins and $M_s = 0$. In this project, we will study systems of $M_s = 0$ only, such that an electron can only be excited to a state with the same spin.

Taking the Pauli principle into account, the two-body wavefunction needs to be nulled out if two particles are in the same state, and it should also be antisymmetric under exchange of two particles. We are therefore in need of a Slater Determinant (SD), given by

$$\Psi(x_1, x_2, \sigma_1, \sigma_2) = A \begin{vmatrix} \psi_{\sigma_1}(x_1) & \psi_{\sigma_1}(x_2) \\ \psi_{\sigma_2}(x_1) & \psi_{\sigma_2}(x_2) \end{vmatrix} \tag{13}$$

$$= A \Big[\psi_{\sigma_1}(x_1)\psi_{\sigma_2}(x_2) - \psi_{\sigma_2}(x_1)\psi_{\sigma_1}(x_2) \Big] \tag{14}$$

where ψ_{σ_1} is the SPF with spin $m_s = \sigma_1$ and A is a normalization constant. If we assume that the SPFs are normalized, our ansatz can be written as

$$|\Phi_0\rangle = \frac{1}{\sqrt{2}}(|1\rangle\,|\bar{1}\rangle - |\bar{1}\rangle\,|1\rangle) \tag{15}$$

with $|\bar{1}\rangle$ describing a particle with principle quantum number 1 and spin σ_2, which we will illustrate with spin down. In second quantization, we can construct the ground state from the true vacuum,

$$|\Phi_0\rangle = a_1^\dagger a_{\bar{1}}^\dagger |0\rangle\,, \tag{16}$$

which is understand to take the anti-symmetry property. The ground state is illustrated in figure (1).
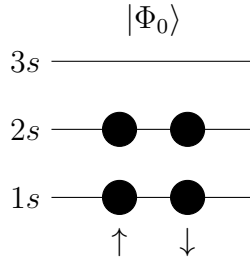

Figure 3: Ground state of Beryllium.

2.3.2 Excited states

When entering excited states, we can risk having angular quantum numbers unlike zero, because $l \in [0, n-1]$. This makes the computations more difficult, but in this project we will ignore that challenge setting $l = 0$, and thus limit us to the s-waves.

Consider now a system consisting of the orbitals 1s, 2s and 3s only. For that case, the possible energy states of the Helium atom are listed in figure (2).
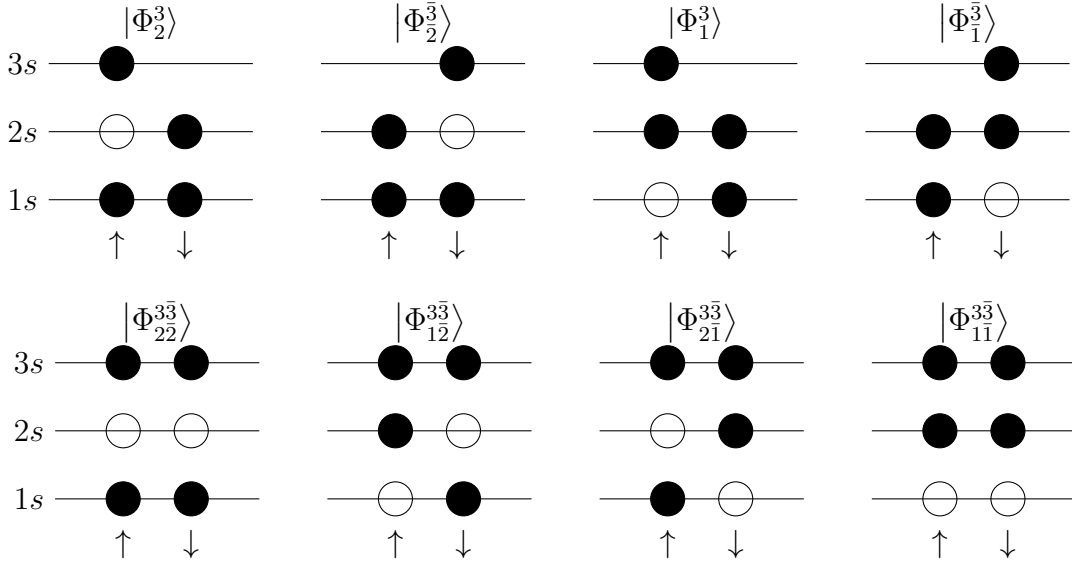

Figure 4: Possible states in the 1s, 2s and 3s orbitals of Beryllium. In the first row, all single excited states are listed, while in the second row all double excited states are listed.

3 Methods

To find the energies, we apply two popular methods: *Configuration Interaction* and *Hartree-Fock*.

3.1 Configuration Interaction (CI)

Often, we start with SDs, $|\Phi_p\rangle$, which are the true wavefunctions in the external potential, but are off when interaction is added

$$\hat{H}_0 |\Phi_i\rangle = \varepsilon_i |\Phi_i\rangle , \qquad (\hat{H}_0 + \hat{H}_I) |\Phi_i\rangle \neq \varepsilon_i |\Phi_i\rangle . \tag{17}$$

However, the SDs form a ket basis, meaning we can write out eigenstates of $\hat{H}_I$ as a linear combination of the SDs

$$
\begin{aligned}
|\Psi_0\rangle &= C_0^{(0)}|\Phi_0\rangle + C_1^{(0)}|\Phi_1\rangle + \ldots + C_{N-1}^{(0)}|\Phi_{N-1}\rangle \\
|\Psi_1\rangle &= C_0^{(1)}|\Phi_0\rangle + C_1^{(1)}|\Phi_1\rangle + \ldots + C_{N-1}^{(1)}|\Phi_{N-1}\rangle \\
|\Psi_2\rangle &= C_0^{(2)}|\Phi_0\rangle + C_1^{(2)}|\Phi_1\rangle + \ldots + C_{N-1}^{(2)}|\Phi_{N-1}\rangle \\
&\quad \vdots \qquad \vdots \qquad \vdots \\
|\Psi_{N-1}\rangle &= C_0^{(N-1)}|\Phi_0\rangle + C_1^{(N-1)}|\Phi_1\rangle + \ldots + C_N^{(N-1)}|\Phi_{N-1}\rangle .
\end{aligned}
\tag{18}
$$

such that

$$
\hat{H}|\Psi_p\rangle = \varepsilon_p|\Psi_p\rangle .
\tag{19}
$$

The Hamiltonian can be rewritten as a double sum over all states using the so-called *completeness relation*,

$$
\hat{H} = \sum_{ij}|\Phi_i\rangle\,\langle\Phi_i|\hat{H}|\Phi_j\rangle\,\langle\Phi_j|
\tag{20}
$$

such that

Here we need to show how to go from Schrodinger to the Hamilton matrix. Show some general implementations.

Add implementation

3.2   Hartree-Fock

When we calculated the reference energy above, our basis contained only one Slater determinant, more specifically the ground state. In Hartree-Fock, we still have a single Slater determinant basis, but we now construct new SPFs with the constraint of minimizing the energy.

In general, one can change from one single-particle basis to another by a unitary transform,

$$
|p\rangle = \sum_{\alpha} c_{p\alpha}|\alpha\rangle ,
\tag{21}
$$

where we use greek letters for the old basis and roman letters for the new one. If we then insert into (8), we get a find energy formula with coefficients, $C_{p\lambda}$, that we can vary

$$
E = \sum_p^N \sum_{\alpha\beta} C_{p\alpha}^* C_{p\beta} \langle\alpha|\hat{h}_0|\beta\rangle + \frac{1}{2}\sum_{pq}^N \sum_{\alpha\beta\gamma\delta} C_{p\alpha}^* C_{q\beta}^* C_{p\gamma} C_{q\delta} \langle\alpha\beta|\hat{v}|\gamma\delta\rangle_{\text{AS}} .
\tag{22}
$$

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Further, we assume that also our new basis is orthonormal, i.e,

$$\langle p|q \rangle = \sum_\alpha c_{p\alpha}^* c_{q\alpha} \langle \alpha | \alpha \rangle = \sum_\alpha c_{p\alpha}^* c_{q\alpha} = \delta_{pq} \tag{23}$$

$$\Rightarrow \sum_\alpha c_{p\alpha}^* c_{q\alpha} - \delta_{pq} = 0 \tag{24}$$

We now have a function, E, that we want to minimize with respect to a constraint given in equation (24). This is a typical situation where Lagrange Multipliers is convenient to use, which in this case can be written as

$$\mathcal{L}(\{C_{p\alpha}\}) = E(\{C_{p\alpha}\}) - \sum_a \varepsilon_a \left(\sum_\alpha c_{p\alpha}^* c_{q\alpha} - \delta_{pq} \right). \tag{25}$$

The variation in reference energy is then find to be

$$\delta E = \sum_{k\alpha} \frac{\partial E}{\partial C_{k\alpha}^*} \delta C_{k\alpha}^* + \sum_{k\alpha} \frac{\partial E}{\partial C_{k\alpha}} \delta C_{k\alpha} - \sum_{k\alpha} \varepsilon_k (C_{k\alpha} \delta C_{k\alpha}^* + C_{k\alpha}^* \delta C_{k\alpha}) \tag{26}$$

which is zero when E is minimized. Each coefficient $C_{k\alpha}$ and $C_{k\alpha}^*$ is independent, so they can be varied independently. Thus

$$\left(\frac{\partial E}{\partial C_{k\alpha}^*} - \varepsilon_k C_{k\alpha} \right) \delta C_{k\alpha}^* = 0, \tag{27}$$

which is satisfied if and only if

$$\frac{\partial E}{\partial C_{k\alpha}^*} - \varepsilon_k C_{k\alpha} = 0 \qquad \forall \ k, \alpha \tag{28}$$

The first term can be derived from (26), and reads

$$\frac{\partial E}{\partial C_{k\alpha}^*} = \sum_\beta C_{k\beta} \langle \alpha | \hat{h}_0 | \beta \rangle + \sum_p^N \sum_{\beta\gamma\delta} C_{p\beta}^* C_{k\gamma} C_{p\delta} \langle \alpha\beta | \hat{v} | \gamma\delta \rangle_{\text{AS}}. \tag{29}$$

This results in the equation

$$\sum_\gamma \hat{h}_{\alpha\gamma}^{\text{HF}} C_{k\gamma} = \varepsilon_k C_{k\gamma} \tag{30}$$

where we have defined

$$\hat{h}_{\alpha\gamma}^{\text{HF}} \equiv \langle \alpha | \hat{h}_0 | \gamma \rangle + \sum_p^N \sum_{\beta\delta} C_{p\beta}^* C_{p\delta} \langle \alpha\beta | \hat{v} | \gamma\delta \rangle_{\text{AS}}. \tag{31}$$

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We recognize that (30) can be written as a matrix-vector product

$$\hat{h}^{\text{HF}} C_k = \varepsilon_k^{\text{HF}} C_k \tag{32}$$

where C_k are columns in our coefficient matrix and $\varepsilon_k^{\text{HF}}$ are just the eigenvalues of $\hat{h}^{\text{HF}}$, they have no physical significance. We will use this equation to find the optimal SPFs (optimal C_k's) and then find the energy from equation (26).

$$\hat{h}^{\text{HF}}(C_k^{i+1}) C_k^i = \varepsilon_k^{\text{HF}} C_k^i \tag{33}$$

The implementation could look something like this

```python
class HF:
    '''Hartree-Fock class for atomic structure'''

    def __init__(self, Z, basis):
        '''
        Arguments:
        ----------
        Z:      Int.
        Atomic number (proton number)
        '''

        self.elem = Integrals(Z, basis)   # Matrix elements/integrals
        self.n = Z                        # Number of electrons, assuming neutral atom
        self.N = len(basis)               # Number of states


    def HF_elements(self, i, j, C):
        '''HF matrix elements (i,j)'''

        Result = self.elem.OBME(i, j)

        for p in range(self.n):
        for c in range(self.N):
        for d in range(self.N):
        Result += C[p,c]*C[p,d]*self.elem.AS(i,c,j,d)

        return Result


    def HF_matrix(self, C):
        '''HF-matrix'''

        HF_mat = np.empty((self.N, self.N))

        for i in range(self.N):
        for j in range(self.N):
        HF_mat[i,j] = HF.HF_elements(self, i, j, C)

        return HF_mat


    def HF_iter(self, tol=1e-8, max_iter=50):
        '''Solving HF with an iterative scheme'''

        C = np.eye(self.N)
        eps = np.ones(self.N)
```
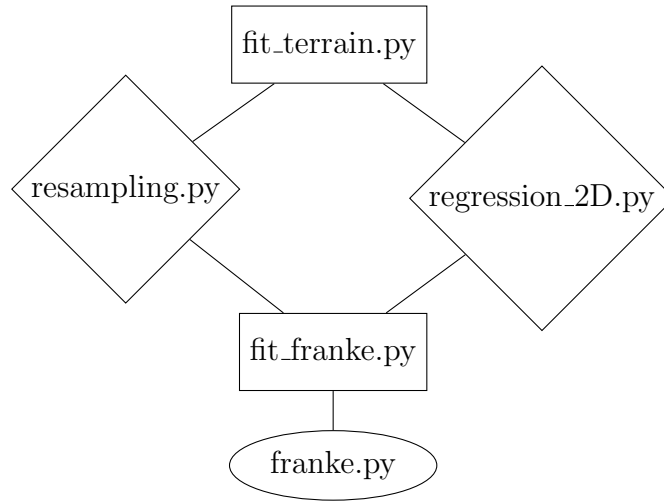
Figure 5: Code structure

```python
for i in range(max_iter):
    HF_mat = HF.HF_matrix(self,C)
    eps_new, C = np.linalg.eigh(HF_mat)
    C = C.T

    if abs(eps[0]-eps_new[0]) < tol:
        break
    eps = eps_new

    return HF.calc_E(self,C), i


def calc_E(self,C):
    '''Calculate energy'''

    E = 0
    for p in range(self.n):
        for a in range(self.N):
            for b in range(self.N):
                E += C[p,a]*C[p,b]*self.elem.OBME(a,b)
                for q in range(self.n):
                    for c in range(self.N):
                        for d in range(self.N):
                            E += 0.5*C[p,a]*C[q,b]*C[p,c]*C[q,d]*self.elem.AS(a,b,c,d)

    return E
```

4 Code

4.1 Code structure

5 Results

5.1 The Helium atom

I will start presenting my main results: the ground state energies, and then

5.1.1 Ground state energies

Table 1

Method	Energy [a.u.]	Relative error
Experimental	-2.903694[1]	0.00%
Hylleraas	-2.90363	0.0022%
Reference	-2.750000	5.29%
CIS	-2.838648	2.24%
$HF_{1\text{ iteration}}$	-2.829193	2.56%
HF_{converge}	-2.831096	2.50%

5.1.2 CIS

Set up matrix and eigenvectors

$$\hat{H}_{\text{CIS}} = \begin{pmatrix} -2.750 & 0.179 & 0.179 & 0.088 & 0.088 \\ 0.179 & -2.080 & 0.044 & 0.101 & 0.022 \\ 0.179 & 0.044 & -2.080 & 0.022 & 0.101 \\ 0.088 & 0.101 & 0.022 & -2.023 & 0.012 \\ 0.088 & 0.022 & 0.101 & 0.012 & -2.023 \end{pmatrix} \tag{34}$$

5.1.3 HF

Set up matrix and eigenvectors after first iteration (basically when inserting C=I). Hartree-Fock matrix after one iteration (basically after inserting the identity ma-

trix as the coefficients)

$$
\hat{h}^{\mathrm{HF}} = \begin{pmatrix}
-0.750 & 0.000 & 0.179 & 0.000 & 0.088 & 0.000 \\
0.000 & -0.750 & 0.000 & 0.179 & 0.000 & 0.088 \\
0.179 & 0.000 & 0.296 & 0.000 & 0.180 & 0.000 \\
0.000 & 0.179 & 0.000 & 0.296 & 0.000 & 0.180 \\
0.088 & 0.000 & 0.180 & 0.000 & 0.164 & 0.000 \\
0.000 & 0.088 & 0.000 & 0.180 & 0.000 & 0.164
\end{pmatrix}
\tag{35}
$$

After the energy has converged, we find this matrix:

$$
\hat{h}^{\mathrm{HF}} = \begin{pmatrix}
-0.840 & 0.000 & 0.226 & 0.000 & 0.102 & 0.000 \\
0.000 & -0.840 & 0.000 & 0.226 & 0.000 & 0.102 \\
0.226 & 0.000 & 0.271 & 0.000 & 0.169 & 0.000 \\
0.000 & 0.226 & 0.000 & 0.271 & 0.000 & 0.169 \\
0.102 & 0.000 & 0.169 & 0.000 & 0.159 & 0.000 \\
0.000 & 0.102 & 0.000 & 0.169 & 0.000 & 0.159
\end{pmatrix}
\tag{36}
$$

Observe that they are not very different. Unlike the zeros in matrix (35), the zeros in (36) are not exactly zero, but smaller than 1e-17.

5.2 The Beryllium atom

Table 2

Method	Energy [a.u.]	Relative error
Experimental	-14.6674[2]	0.00%
Reference	-13.7160	6.49%
CIS	-14.3621	2.08%
HF	-14.5083	1.08%

6 Discussion

7 Conclusion

A Appendix A

Expression for energy of ground state.

B References

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