FYS4480 - Quantum Mechanics for Many-Particle Systems

Project 1

Even M. Nordhagen

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- 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 **2**

2 Theory **3**
2.1 The Helium atom 4
2.1.1 Ground state 4
2.1.2 Excited states 5
2.2 The Beryllium atom 5

3 Methods **5**
3.1 Configuration Interaction (CI) 5
3.2 Hartree-Fock 5

4 Code **7**
4.1 Code structure 7

5 Results **7**

6 Discussion **8**

7 Conclusion **8**

A Appendix A **8**

B References **9**

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 proved the quantum theory to be correct. 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 wave 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.

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

$$\varepsilon_0 = \langle\Phi_0|\hat{H}|\Phi_0\rangle = \sum_i \langle i|\hat{h}_0|i\rangle + \frac{1}{2}\sum_{ij}\Big[\langle ij|\hat{v}|ij\rangle - \langle ij|\hat{v}|ji\rangle\Big] \tag{7}$$

$$= E_0(Z) + \ldots \tag{8}$$

See appendix A.

Should also write about spins, Pauli principle, quantum numbers and so on.

2.1 The Helium atom

A neutral Helium atom consists of a nucleus of two protons with two electrons swarming around it, 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

Lide 1992 Handbook of Chem. and Phys. lide 1992

2.1.1 Ground state

Spin up/spin down - Pauli principle

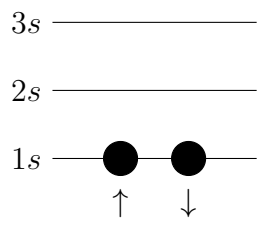

Figure 1

2.1.2 Excited states

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).

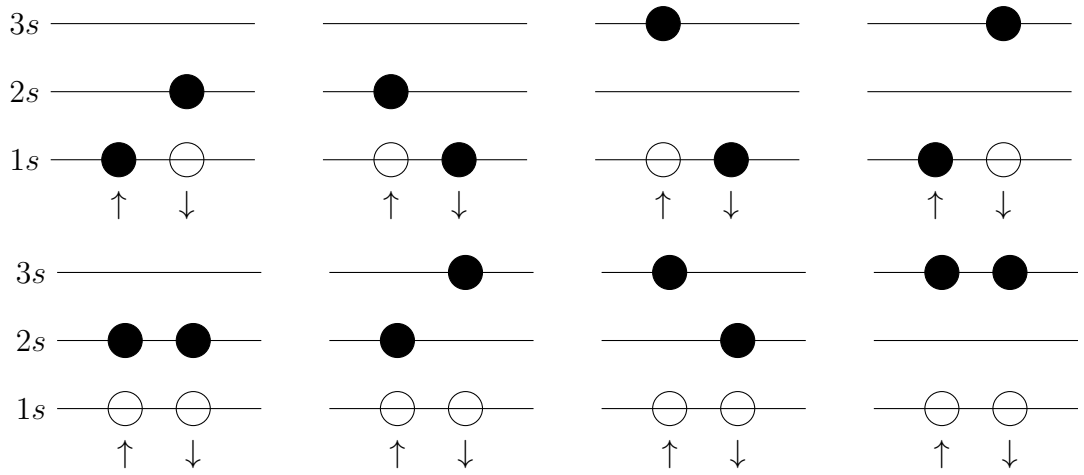

Figure 2

2.2 The Beryllium atom

3 Methods

3.1 Configuration Interaction (CI)

3.2 Hartree-Fock

The implementation could look something like this

```
def bootstrap(data, K=1000):
  dataVec = np.zeros(K)
  for k in range(K):
    dataVec[k] = np.average(np.random.choice(data, len(data)))
  Avg = np.average(dataVec)
  Var = np.var(dataVec)
  Std = np.std(dataVec)

  return Avg, Var, Std
```

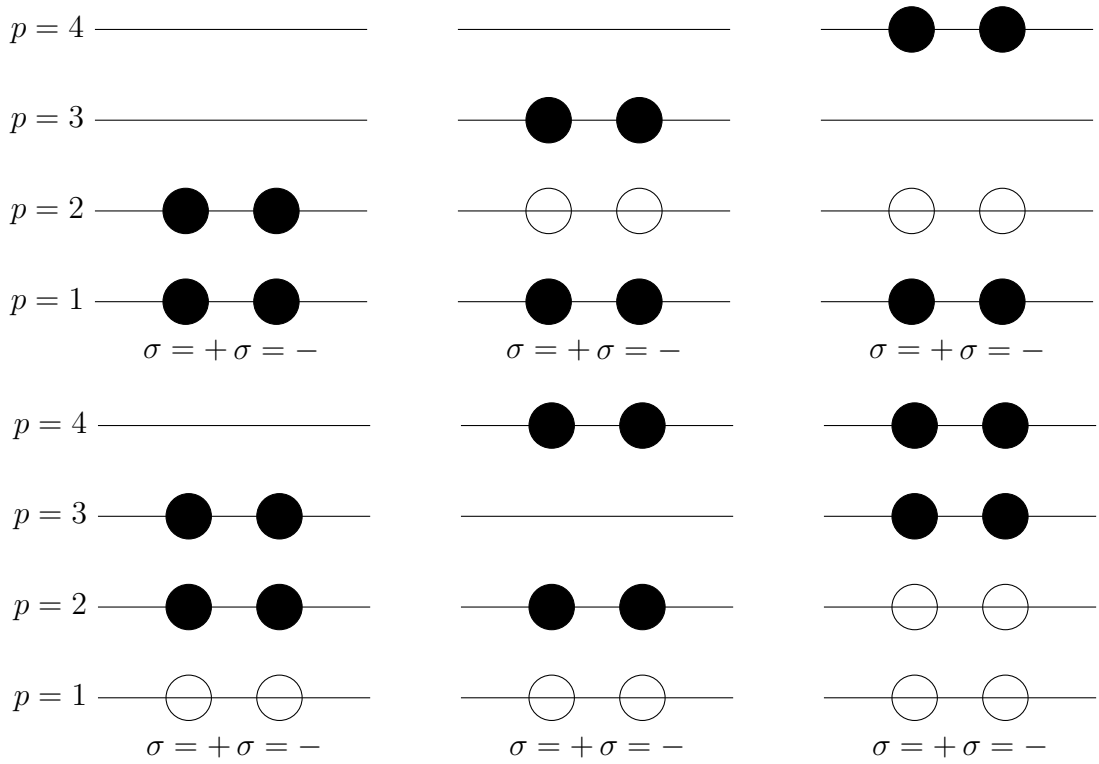

Figure 3: Above all basis states of our pair interaction system are presented schematically with $P = 2$ as the number of pairs and $S_z = 0$ are the total spin. The solid dots indicate occupied states, while the empty dots indicate unoccupied states (holes). The reference state $|\Phi\rangle$ is represented in the upper left corner. This is all possible states since the excusion principle does not allow two particles with same spin to stay at the same level. For further description, see the text.

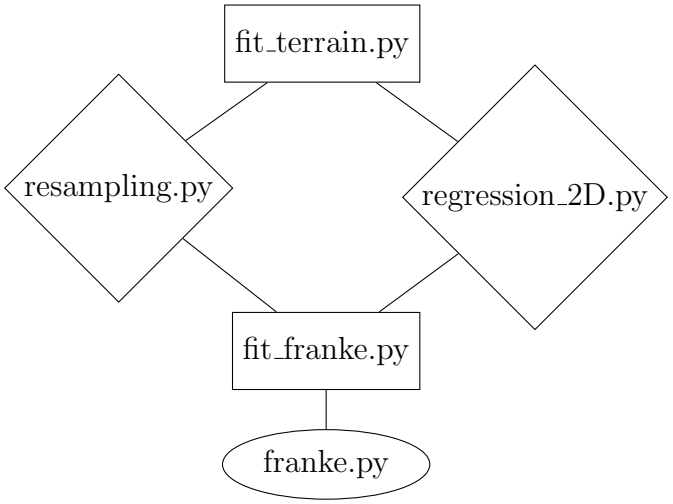

Figure 4: Code structure

4 Code

4.1 Code structure

5 Results

Table 1: Mean Square Error and R^2-score presented for OLS, Ridge, Lasso and Ridge + gradient descent (RidgeGD), where noise was added to the data. The parameters used were $\lambda = 1e-5$ (penalty), $\eta = 1e-4$ (learning rate), niter $= 1e5$ (number of iterations) and $\mathcal{N}(0, \sigma^2 = 0.1)$ (noise). See text for more information.

	MSE			**R2**		
	Self	K-fold	Scikit	Self	K-fold	Scikit
OLS	0.008494	0.009119	0.008494	0.9048	0.8956	0.9048
Ridge	0.009128	0.009651	0.009128	0.8977	0.8895	0.8977
Lasso	0.01439	0.01489	0.01555	0.8387	0.8296	0.8257
RidgeGD	0.01451	0.01504	0.009128	0.8373	0.8280	0.8977

6 Discussion

7 Conclusion

A Appendix A

Expression for energy of ground state.

B References

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