

# FYS4480 - Quantum Mechanics for Many-Particle Systems

## Project 1

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- Github repository containing programs and results:

<https://github.com/evenmn/FYS4480>

### **Abstract**

This project aims studying the ground state (GS) energy of neutral atoms with total spin zero. More precisely we look at Helium and Beryllium, and we limit ourselves to the single-particle orbits 1s, 2s and 3s. Both Configuration interaction (CI) and Hartree-Fock (HF) was used to estimate the energy levels, and as benchmarks recently experimental energy values were used.

For Helium, we found the Configuration Interaction singles (CIS) to give the lowest energy with a relative error of 2.24%, compared to 2.50% by using HF. For Beryllium, the situation was different, with 1.08% relative error when using HF and 2.08% relative error when using CIS.

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# 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 in some ways 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 atoms, with focus on the ground state energy. For doing that, we first apply the Configuration Interaction Singles (CIS), and thereafter turn to Hartree-Fock (HF). Can we compete with Hylleraas?

The background theory and notation is presented in section (2), *theory*, and the methods we used, in particular CIS and HF, are presented in section (3) *methods*. The results are in section (4) with the same name, and the discussion and conclusion are given in section (5) and (6) respectively. Finally, calculations of the matrix elements used in CIS are moved to Appendix A.

## 2 Theory

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

$$\hat{H} |\Psi_p\rangle = \varepsilon_p |\Psi_p\rangle \quad (1)$$

where we expect to find the exact ground state energy,  $\varepsilon_0$ , 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),

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

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 charge.

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

$$1 \text{ a.u.} = 2 \cdot 13.6 \text{ eV}. \quad (3)$$

The Hamiltonian thus reads

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

with  $r_{ij} \equiv \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$  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

$$E_n = -\frac{Z^2}{2n^2} \quad (5)$$

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

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

where the Dirac notation is used for shorthand notation. Note carefully that the  $\Phi$ '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,

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

We observe that the integral is non-zero if and only if  $\alpha$  and  $\gamma$  got the same spin, and  $\beta$  and  $\delta$  got the same spin.

## 2.1 Second Quantization

For quick and compact calculations, we use second quantization as our formalism. The idea is to introduce creation and annihilation operators, which working on a Slater Determinant (SD) can create or annihilate a particle. A creation operator acting on a SD containing zero particles (called a vacuum state), will result in a SD containing one particle, and an annihilation operator acting on a SD containing zero particles will just give zero,

$$a_p^\dagger |0\rangle = |p\rangle \quad (8)$$

$$a_p |0\rangle = 0. \quad (9)$$

where  $a_p^\dagger$  is the creation operator and  $a_p$  is the annihilation operator. Note that we again use Dirac notation for the Slater Determinant. This simplifies things a lot, since we can rewrite

$$\begin{vmatrix} \phi_1(x_1) & \phi_1(x_2) & \dots & \phi_1(x_N) \\ \phi_2(x_1) & \phi_2(x_2) & \dots & \phi_2(x_N) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_N(x_1) & \phi_N(x_2) & \dots & \phi_N(x_N) \end{vmatrix} \equiv |1, 2, \dots, N\rangle \quad (10)$$

Further, the Slater Determinant can only contain one particle in the same state at the same time (ref. Pauli principle), such that adding a particle that already exists in the SD should automatically give zero. In the same manner, removing a particle that does not exist should also give zero. The operations that contribute are when adding a particle that does not exist and removing a particle that exists:

$$a_a^\dagger |abc \dots xyz\rangle = 0 \quad (11)$$

$$a_a |bc \dots xyz\rangle = 0 \quad (12)$$

$$a_a^\dagger |bc \dots xyz\rangle = |abc \dots xyz\rangle \quad (13)$$

$$a_a |abc \dots xyz\rangle = |bc \dots xyz\rangle. \quad (14)$$

If we now look at a sequence of creation and annihilation operators, shuffling two operators of the same kind will just give a negative sign. On the other hand, when shuffling a creation operator with an annihilation operator, we get a Kronecker delta minus the new ordering,

$$\{a_p^\dagger, a_q^\dagger\} \equiv a_p^\dagger a_q^\dagger - a_q^\dagger a_p^\dagger = 0 \quad (15)$$

$$\{a_p, a_q\} \equiv a_p a_q - a_q a_p = 0 \quad (16)$$

$$\{a_p^\dagger, a_q\} \equiv a_p^\dagger a_q + a_q a_p^\dagger = \delta_{pq}. \quad (17)$$

With a sequence of operators acting on a vacuum state, we can use this to determine expectation values by moving annihilation operators against the vacuum. However, this is really tedious when we have many operators, and fortunately we have Wick's theorem to simplify these operations. More about that in section (2.1.2).

The one-body Hamiltonian is in second quantization given by

$$H_0 = \sum_{\alpha\beta} \langle \alpha | \hat{h}_0 | \beta \rangle a_\alpha^\dagger a_\beta \quad (18)$$

while the interaction part is given by

$$H_I = \frac{1}{4} \sum_{\alpha\beta\gamma\delta} \langle \alpha\beta | \hat{v} | \gamma\delta \rangle_{\text{AS}} a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma. \quad (19)$$

### 2.1.1 Particle-hole formalism

For large system, it is not very tempting to write out the entire Slater Determinant as operators acting on the vacuum state. If we assume that the Slater is orthonormal onto itself,  $\langle SD|SD \rangle = 1$ , we can redefine our vacuum containing all states in the  $|SD\rangle$ . This is often called the Fermi vacuum. When annihilating a particle below the Fermi level (one of the particles in the Fermi vacuum), we say that we create a hole. When replacing the hole with a particle, we say that we annihilate the hole. Similarly above the Fermi level, we can create and annihilate particles. The annihilation operator therefore now works as before above the Fermi level, but below the Fermi level the creation operator works as the annihilation operator before, and vice versa. In that manner, we specify whether the quasiparticle is a hole or a particle by giving holes indices  $i, j, k, l, \dots$  and particles indices  $a, b, c, d, \dots$ .  $p, q, r, s, \dots$  are without restrictions. This leads to

$$\{a_a^\dagger, a_b\} = \delta_{ab} \quad (20)$$

$$\{a_i, a_j^\dagger\} = \delta_{ij} \quad (21)$$

which we again can use to calculate expectation values, or just to simplify.

### 2.1.2 Wick's theorem

Wick's theorem is extremely useful when calculating expectation values in second quantization. It states that a sequence of operators can be written as the normal ordering of the operators plus the sum over all normal orderings after one contraction plus the sum over all normal orderings after two contractions and so on and so forth. Mathematically, we can write it as

$$ABC \dots XYZ = \{ABC \dots XYZ\} \quad (22)$$

$$+ \sum_{\text{Single cont.}} \{ABC \dots \overline{XYZ}\} \quad (23)$$

$$+ \sum_{\text{Double cont.}} \{ABC \dots \overline{\overline{XYZ}}\} \quad (24)$$

$$+ \dots \quad (25)$$

Immediately, it does not seem to simplify the sequence, the clue lies in the normalizing. When calculating expectation values, we will always have an equal number of creation and annihilation operators between the vacuum states (otherwise the expectation value is zero). This means that a normal ordering will always contain an annihilation operator, which is located to the right, acts on the vacuum state and everything goes to zero. In other words, the only terms that contribute

in an expectation value calculation are the fully contracted terms, which gives a major simplification.

The theorem can also be generalized, taking operators of multiple creation and annihilation operators into account. If those operators are normal ordered, Wick's theorem states that only external contractions will contribute, i.e, no contractions inward the operators. [<https://manybodyphysics.github.io/FYS4480/doc/pub/secondquant/html/sbs.html>]

### 2.1.3 Energy formulas

We are now ready to calculate some expectation values based on the theory above. We will later do Configuration Interaction Singles (CIS) only, so it is sufficient to calculate  $\langle \Phi_0 | \hat{H} | \Phi_0 \rangle$ ,  $\langle \Phi_0 | \hat{H} | \Phi_i^a \rangle$  and  $\langle \Phi_i^a | \hat{H} | \Phi_j^b \rangle$ . The calculations are moved to Appendix A in order to maintain some sort of neatness. We obtain that the reference energy as a function of  $Z$  is

$$\varepsilon_0 = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle = \sum_i \langle i | \hat{h}_0 | i \rangle + \frac{1}{2} \sum_{ij} \langle ij | \hat{v} | ij \rangle_{\text{AS}} \quad (26)$$

where the subscript AS indicates an antisymmetric elements,

$$\langle ij | \hat{v} | ij \rangle_{\text{AS}} = \langle ij | \hat{v} | ij \rangle - \langle ij | \hat{v} | ji \rangle. \quad (27)$$

Further, we obtained

$$\langle \Phi_0 | \hat{H} | \Phi_i^a \rangle = \langle i | \hat{h}_0 | a \rangle + \sum_j \langle aj | \hat{v} | ij \rangle_{\text{AS}} \quad (28)$$

and

$$\begin{aligned} \langle \Phi_i^a | \hat{H} | \Phi_j^b \rangle &= \langle aj | \hat{v} | ib \rangle_{\text{AS}} - \delta_{ab} \left[ \langle i | \hat{h}_0 | j \rangle + \sum_k \langle ik | \hat{v} | jk \rangle_{\text{AS}} \right] \\ &\quad + \delta_{ij} \left[ \langle a | \hat{h}_0 | b \rangle + \sum_k \langle ak | \hat{v} | bk \rangle_{\text{AS}} \right] \\ &\quad + \delta_{ab} \delta_{ij} \left[ \sum_k \langle k | \hat{h}_0 | k \rangle + \frac{1}{2} \sum_{kl} \langle kl | \hat{v} | kl \rangle_{\text{AS}} \right] \end{aligned} \quad (29)$$

where the two latter are functions of  $Z$  as well. They are then general.

## 2.2 The Helium atom

A neutral Helium atom consists of a nucleus of two protons with two electrons orbiting, and is the simplest many-body atom one can study (atoms with more

than 1 electron). 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. The interaction term makes the exact wave function almost impossible to find.

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, and which we will compare our energies to. [<http://www.umich.edu/chem461/QMChap8.pdf>][<https://journals.aps.org/prl/abstract/10.1103/PhysRevLett.22.589>]

### 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, given by

$$\Psi(x_1, x_2, \sigma_1, \sigma_2) = A \begin{vmatrix} \psi_{\sigma_1}(x_1) & \psi_{\sigma_1}(x_2) \\ \psi_{\sigma_2}(x_1) & \psi_{\sigma_2}(x_2) \end{vmatrix} \quad (30)$$

$$= A [\psi_{\sigma_1}(x_1)\psi_{\sigma_2}(x_2) - \psi_{\sigma_2}(x_1)\psi_{\sigma_1}(x_2)] \quad (31)$$

where  $\psi_{\sigma_1}$  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

$$|\Phi_0\rangle = \frac{1}{\sqrt{2}}(|1\rangle |\bar{1}\rangle - |\bar{1}\rangle |1\rangle) \quad (32)$$

with  $|\bar{1}\rangle$  describing a particle with principle quantum number 1 and spin  $\sigma_2$ , which we will illustrate with spin down. In second quantization, we can construct the ground state from the true vacuum,

$$|\Phi_0\rangle = a_1^\dagger a_{\bar{1}}^\dagger |0\rangle, \quad (33)$$

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



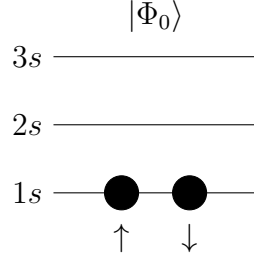


Figure 1: Ground state of Helium.

### 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).

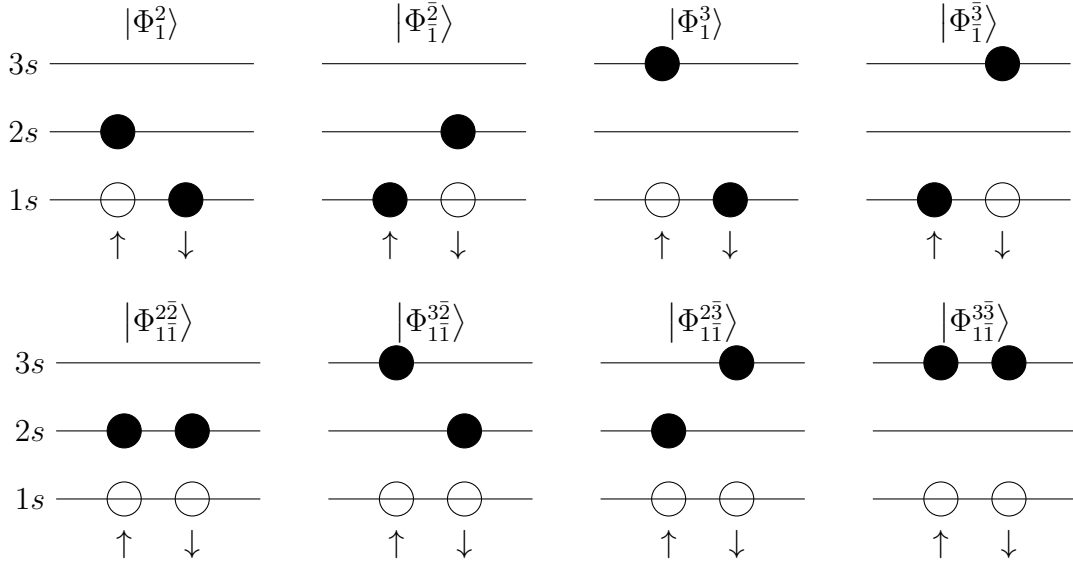


Figure 2: Possible states in the 1s, 2s and 3s orbitals of Helium. In the first row, all singly excited states are listed, while in the second row all doubly excited states are listed.

## 2.3 The Beryllium atom

Beryllium has atomic number  $Z = 4$ , so a neutral Beryllium atom has four protons in its nucleus and four electrons swarming around. To study atoms with even atomic numbers is easier than odd atomic number, since the Fermi level is well defined.

### 2.3.1 Ground state

Beryllium is in its ground state when the electrons occupy the 1s and 2s orbitals (we again set  $l = 0$ ). In second quantization, the ground state can then be expressed as

$$|\Phi_0\rangle = a_1^\dagger a_1^\dagger a_2^\dagger a_2^\dagger |0\rangle, \quad (34)$$

and is illustrated in figure (3).

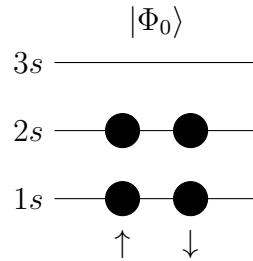


Figure 3: Ground state of Beryllium.

### 2.3.2 Excited states

We again limit us to the 1s, 2s and 3s orbits. When the electrons have only two free slots to be excited to. Anyway, since we have four particles that can be excited, there are still as many possible excited states as for Helium, see figure (4).

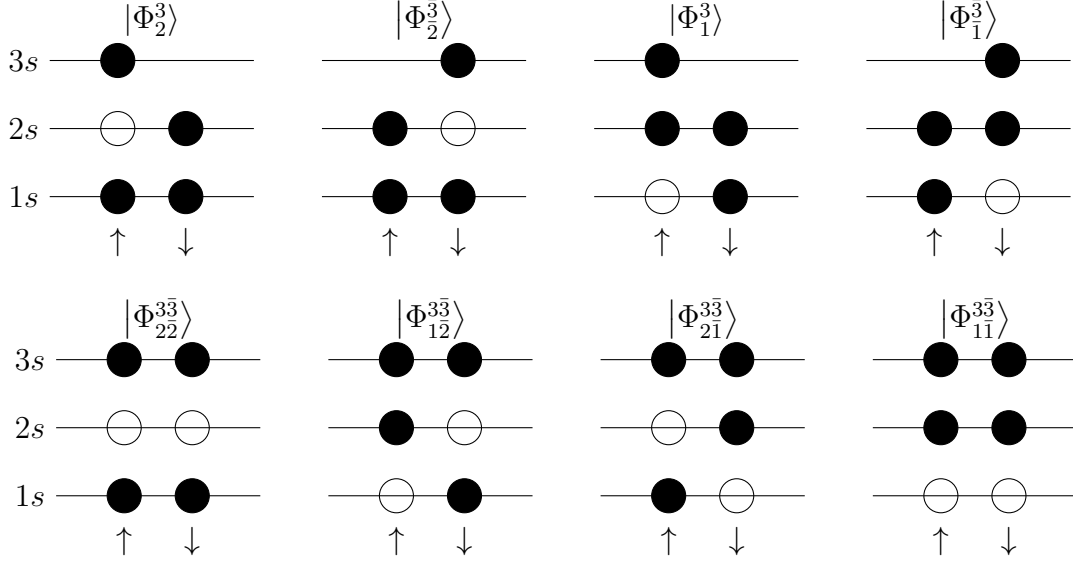


Figure 4: Possible states in the 1s, 2s and 3s orbitals of Beryllium. In the first row, all singly excited states are listed, while in the second row all doubly excited states are listed.

### 3 Methods

There exist many methods for solving the Schrödinger equation. Some of them are exact, but always heavy to deal with. Other are approximation, but hopefully not that expensive. We are going to look at *Configuration Interaction* (CI), which in principle gives the exact energy (then called *Full Configuration Interaction* (FCI)) and *Hartree-Fock*, which is a mean field theory and will not give exact results.

#### 3.1 Configuration Interaction (CI)

Often, we know the true wavefunctions  $|\Phi_i\rangle$  in the external potential, but are off when interaction is added

$$\hat{H}_0 |\Phi_i\rangle = \varepsilon_i |\Phi_i\rangle, \quad (\hat{H}_0 + \hat{H}_I) |\Phi_i\rangle \neq \varepsilon_i |\Phi_i\rangle. \quad (35)$$

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

$$\begin{aligned}
|\Psi_0\rangle &= C_0^{(0)} |\Phi_0\rangle + C_1^{(0)} |\Phi_1\rangle + \dots + C_{N-1}^{(0)} |\Phi_{N-1}\rangle \\
|\Psi_1\rangle &= C_0^{(1)} |\Phi_0\rangle + C_1^{(1)} |\Phi_1\rangle + \dots + C_{N-1}^{(1)} |\Phi_{N-1}\rangle \\
|\Psi_2\rangle &= C_0^{(2)} |\Phi_0\rangle + C_1^{(2)} |\Phi_1\rangle + \dots + C_{N-1}^{(2)} |\Phi_{N-1}\rangle \\
&\vdots \quad \vdots \quad \vdots \\
|\Psi_{N-1}\rangle &= C_0^{(N-1)} |\Phi_0\rangle + C_1^{(N-1)} |\Phi_1\rangle + \dots + C_{N-1}^{(N-1)} |\Phi_{N-1}\rangle.
\end{aligned} \tag{36}$$

such that

$$\hat{H} |\Psi_p\rangle = \varepsilon_p |\Psi_p\rangle. \tag{37}$$

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

$$\hat{H} = \sum_{ij} |\Phi_i\rangle \langle \Phi_i| \hat{H} |\Phi_j\rangle \langle \Phi_j| \tag{38}$$

such that the Schrödinger equation can be rewritten as

$$\begin{pmatrix}
\langle \Phi_0 | \hat{H} | \Phi_0 \rangle & \langle \Phi_0 | \hat{H} | \Phi_1 \rangle & \dots & \langle \Phi_0 | \hat{H} | \Phi_{N-1} \rangle \\
\langle \Phi_1 | \hat{H} | \Phi_0 \rangle & \langle \Phi_1 | \hat{H} | \Phi_1 \rangle & \dots & \langle \Phi_1 | \hat{H} | \Phi_{N-1} \rangle \\
\vdots & \vdots & \ddots & \vdots \\
\langle \Phi_{N-1} | \hat{H} | \Phi_0 \rangle & \langle \Phi_{N-1} | \hat{H} | \Phi_1 \rangle & \dots & \langle \Phi_{N-1} | \hat{H} | \Phi_{N-1} \rangle
\end{pmatrix}
\begin{pmatrix}
c_0^{(p)} \\
c_1^{(p)} \\
\vdots \\
c_{N-1}^{(p)}
\end{pmatrix}
= \varepsilon_p
\begin{pmatrix}
c_0^{(p)} \\
c_1^{(p)} \\
\vdots \\
c_{N-1}^{(p)}
\end{pmatrix}$$

Until now, we have not made any assumptions, such that the equation above will give exact results when all SPFs are included. The problem is that the matrix scales so badly, the number of Slater Determinant that we need to include goes as

$$N_{\text{FCI}} = \binom{N_{\text{single orbitals}}}{N_{\text{electrons}}} \tag{39}$$

which is exploding. This is quite annoying since we in principle know how to solve the problems exact. However, in this project we restrict ourselves to three orbitals and single excitations only, which makes the problem more manageable.

[<https://github.com/ManyBodyPhysics/FYS4480/blob/master/doc/Exercises/Answers/FirstsetAnswers.md>]  
 matrices are given in results, and a program calculating solutions to equation (26-30) is outlined below

```

class CIS:
    '''Configuration Interction Singles class for atomic structure'''

    def __init__(self, Z, basis):

```

```

self.elem = Integrals(Z, basis) # Matrix elements/integrals
self.n = Z                      # Assume neutral atom

def c_H_c(self):
    '''Reference energy'''

    OBT = 0
    for i in range(self.n):
        OBT += self.elem.OBME(i, i)

    TBT = 0
    for i in range(self.n):
        for j in range(self.n):
            TBT += 0.5*self.elem.AS(i, j, i, j)

    return OBT + TBT

def c_H_ia(self, i, a):
    '''Singly excited ket'''

    OBT = self.elem.OBME(i, a)

    TBT = 0
    for j in range(self.n):
        TBT += self.elem.AS(a, j, i, j)

    return OBT + TBT

def ia_H_jb(self, i, a, j, b):
    '''Singly excited bra and ket'''

    Result = self.elem.AS(a, j, i, b)

    if a==b:
        Result -= self.elem.OBME(i, j)
    for k in range(self.n):
        Result -= self.elem.AS(i, k, j, k)

    if i==j:
        for l in range(self.n):
            Result += self.elem.OBME(l, l)
        for m in range(self.n):
            Result += 0.5*self.elem.AS(l, m, l, m)

    if i==j:
        Result += self.elem.OBME(a, b)
    for k in range(self.n):
        Result += self.elem.AS(a, k, b, k)

    return Result

```

### 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,

$$|p\rangle = \sum_{\alpha} c_{p\alpha} |\alpha\rangle, \quad (40)$$

where we use greek letters for the old basis and roman letters for the new one. If we then insert into (26), we get a find energy formula with coefficients,  $C_{p\lambda}$ , that we can vary

$$E = \sum_p^N \sum_{\alpha\beta} C_{p\alpha}^* C_{p\beta} \langle \alpha | \hat{h}_0 | \beta \rangle + \frac{1}{2} \sum_{pq}^N \sum_{\alpha\beta\gamma\delta} C_{p\alpha}^* C_{q\beta}^* C_{p\gamma} C_{q\delta} \langle \alpha\beta | \hat{v} | \gamma\delta \rangle_{\text{AS}}. \quad (41)$$

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

$$\langle p | q \rangle = \sum_{\alpha} c_{p\alpha}^* c_{q\alpha} \langle \alpha | \alpha \rangle = \sum_{\alpha} c_{p\alpha}^* c_{q\alpha} = \delta_{pq} \quad (42)$$

$$\Rightarrow \sum_{\alpha} c_{p\alpha}^* c_{q\alpha} - \delta_{pq} = 0 \quad (43)$$

We now have a function,  $E$ , that we want to minimize with respect to a constraint given in equation (43). This is a typical situation where Lagrange Multipliers is convenient to use, which in this case can be written as

$$\mathcal{L}(\{C_{p\alpha}\}) = E(\{C_{p\alpha}\}) - \sum_a \varepsilon_a \left( \sum_{\alpha} c_{p\alpha}^* c_{q\alpha} - \delta_{pq} \right). \quad (44)$$

The variation in reference energy is then find to be

$$\delta E = \sum_{k\alpha} \frac{\partial E}{\partial C_{k\alpha}^*} \delta C_{k\alpha}^* + \sum_{k\alpha} \frac{\partial E}{\partial C_{k\alpha}} \delta C_{k\alpha} - \sum_{k\alpha} \varepsilon_k (C_{k\alpha} \delta C_{k\alpha}^* + C_{k\alpha}^* \delta C_{k\alpha}) \quad (45)$$

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

$$\left( \frac{\partial E}{\partial C_{k\alpha}^*} - \varepsilon_k C_{k\alpha} \right) \delta C_{k\alpha}^* = 0, \quad (46)$$

which is satisfied if and only if

$$\frac{\partial E}{\partial C_{k\alpha}^*} - \varepsilon_k C_{k\alpha} = 0 \quad \forall k, \alpha \quad (47)$$

The first term can be derived from (45), and reads

$$\frac{\partial E}{\partial C_{k\alpha}^*} = \sum_{\beta} C_{k\beta} \langle \alpha | \hat{h}_0 | \beta \rangle + \sum_p^N \sum_{\beta\gamma\delta} C_{p\beta}^* C_{k\gamma} C_{p\delta} \langle \alpha\beta | \hat{v} | \gamma\delta \rangle_{\text{AS}}. \quad (48)$$

This results in the equation

$$\sum_{\gamma} \hat{h}_{\alpha\gamma}^{\text{HF}} C_{k\gamma} = \varepsilon_k C_{k\gamma} \quad (49)$$

where we have defined

$$\hat{h}_{\alpha\gamma}^{\text{HF}} \equiv \langle \alpha | \hat{h}_0 | \gamma \rangle + \sum_p^N \sum_{\beta\delta} C_{p\beta}^* C_{p\delta} \langle \alpha\beta | \hat{v} | \gamma\delta \rangle_{\text{AS}}. \quad (50)$$

We recognize that (49) can be written as a matrix-vector product

$$\hat{h}^{\text{HF}} C_k = \varepsilon_k^{\text{HF}} C_k \quad (51)$$

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 (45).

$$\hat{h}^{\text{HF}}(C_k^{i+1}) C_k^i = \varepsilon_k^{\text{HF}} C_k^i \quad (52)$$

The implementation could look something like this

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

    def __init__(self, Z, basis):

        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)
    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 Results

### 4.1 The Helium atom

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



### 4.1.1 Ground state energies

Table 1

Method	Energy [a.u.]	Relative error
Experimental	-2.903694 <sup>1</sup>	0.00%
Hylleraas	-2.90363	0.0022%
Reference	-2.750000	5.29%
CIS	-2.838648	2.24%
HF <sub>1 iteration</sub>	-2.829193	2.56%
HF <sub>converge</sub>	-2.831096	2.50%

### 4.1.2 CIS

Set up matrix and eigenvectors

$$\hat{H}_{\text{CIS}} = \begin{pmatrix} -2.750 & 0.179 & 0.179 & 0.088 & 0.088 \\ 0.179 & -2.080 & 0.044 & 0.101 & 0.022 \\ 0.179 & 0.044 & -2.080 & 0.022 & 0.101 \\ 0.088 & 0.101 & 0.022 & -2.023 & 0.012 \\ 0.088 & 0.022 & 0.101 & 0.012 & -2.023 \end{pmatrix} \quad (53)$$

### 4.1.3 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 matrix as the coefficients)

$$\hat{h}^{\text{HF}} = \begin{pmatrix} -0.750 & 0.000 & 0.179 & 0.000 & 0.088 & 0.000 \\ 0.000 & -0.750 & 0.000 & 0.179 & 0.000 & 0.088 \\ 0.179 & 0.000 & 0.296 & 0.000 & 0.180 & 0.000 \\ 0.000 & 0.179 & 0.000 & 0.296 & 0.000 & 0.180 \\ 0.088 & 0.000 & 0.180 & 0.000 & 0.164 & 0.000 \\ 0.000 & 0.088 & 0.000 & 0.180 & 0.000 & 0.164 \end{pmatrix} \quad (54)$$

After the energy has converged, we find this matrix:

$$\hat{h}^{\text{HF}} = \begin{pmatrix} -0.840 & 0.000 & 0.226 & 0.000 & 0.102 & 0.000 \\ 0.000 & -0.840 & 0.000 & 0.226 & 0.000 & 0.102 \\ 0.226 & 0.000 & 0.271 & 0.000 & 0.169 & 0.000 \\ 0.000 & 0.226 & 0.000 & 0.271 & 0.000 & 0.169 \\ 0.102 & 0.000 & 0.169 & 0.000 & 0.159 & 0.000 \\ 0.000 & 0.102 & 0.000 & 0.169 & 0.000 & 0.159 \end{pmatrix} \quad (55)$$

Observe that they are not very different. Unlike the zeros in matrix (54), the zeros in (55) are not exactly zero, but smaller than  $1e-17$ .

## 4.2 The Beryllium atom

Table 2

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

## 5 Discussion

## 6 Conclusion

## A Appendix A

Expression for energy of ground state.

## B References

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