

# FYS4480 - Project 1

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## Abstract

In this study we wanted to approximate the ground state energy of the Helium and Beryllium atom using Configuration interaction (CI) theory and the Hartree-Fock (HF) method. We used a truncated single-particle basis consisting of six Hydrogen-like states and our (truncated) Slater determinant basis did not exceed single particle excitations. We then wanted to see how the ground state energy depended on the strength of the Coloumb interaction between electron and proton for a two- and four-electron system utilizing the above methods. For the Helium atom, CI provided the best ground state energy approximation with  $E_{CI} = -2.8386[a.u]$ , while HF gave  $E_{HF} = -2.8311[a.u]$  (table 9). For the Beryllium atom however, HF gave the best approximation with  $E_{HF} = -14.5083$  while CI yielded  $E_{CI} = -14.3621[a.u]$  (table 13). We argued that HF surpassing CI was a result of not expanding the truncated Slater determinant basis when moving from a two to a four-electron system. When studying the dependence of the ground state energy on the strength of the Coloumb interaction, we found that CI and HF yielded unbound ground states ( $E > 0$ ) for both the four and two-electron system (figure 4 and figure 3 respectively). The four-electron system had this for stronger electron-proton interactions than the two-electron system and we concluded that this may be a result of a decrease of the effective nuclear charge on electrons in the outer shells due to electron-electron repulsion[3].

## 1 Introduction

Unfortunately there exists only a limited amount of quantum-mechanical problems that can be solved exactly. This makes good approximation methods immensely important and it is why it didn't take long after the discovery of the Schrödinger equation before attempts at finding such methods were made. The Hartree-Fock (HF) approximation has played an important role in this field and many of the more accurate approximation method are built upon this one[7]. It is a variational method based on the variational principle, which states that the expectation value of our Hamiltonian with respect to a trial wave function can never fall short of the actual ground state energy. Configuration Interaction (CI) theory is an example of another method. In theory it can yield the exact solution to a many-particle problem within the Born-Oppenheimer approximation. It is built upon the fact that the soluton to the Schrödinger equation can be written as a linear combination of orthogonal Slater determinants built from a basis of single particle functions. In practice however, we will have to truncate the single particle basis because of computational limitations.

In this report, we will study the Helium and Beryllium atom. The Helium atom consists of two electrons bound by the electromagnetic force to a nucleus containing two protons and neutrons. It is the simplest atom in the periodic table for which Quantum theory does not provide an exact solution. The Beryllium atom consists of four electrons bound to a nucleus containing four protons

and five neutrons and is a relatively rare element. Our aim in this study is to use CI and HF to approximate the ground state energy of these atoms and compare the approximation to the exact energy (within the given digits). In order to do this we need to calculate a range of expectation values of our Hamiltonian, which can be a tedious task. We will simplify our calculations with the use of Second quantization and Particle-hole formalism. Six Hydrogen-like single particle functions are used to form our truncated basis and our CI method will not include Slater determinants with more than single particle excitations. Finally we will study the dependence of the ground state energy on the strength of the Coloumb interaction between electron and proton for a two- and four-electron system utilizing these methods.

Section 2 contains the theory and methods applied in this project: Section 2.1 gives a quick overview of Second Quantization, Particle-Hole formalism and Wicks theorem, while section 2.2 presents our Hamiltonian, basis states and Slater determinants. Section 2.3 and 2.4 explains Configuration Interaction theory and Hartree-Fock approximation, respectively. In section 2.5 we construct our Slater determinant basis for the Helium atom and we do the same for the Beryllium atom in section 2.6. Section 3 contains our results and we discuss these in section 4. Finally we conclude our discussion in section 5 and present the python code used to produce the results and more detailed derivations of the CI matrix elements in section 6.

## 2 Theory

### 2.1 Second Quantization, Particle-Hole formalism and Wicks Theorem

In order to ease the calculations of our expectation values, we will use Second quantization formalism. This is a quick overview of the properties that were used during this study. For a more thorough review of the Second Quantization and Particle-Hole formalism see for example Morten Hjort Jensen's notes on the subject [2]. The Second quantization formalism presents the operators  $a_\alpha^\dagger$  and  $a_\alpha$  which creates and annihilates a particle in a single particle state  $|\alpha\rangle$ . For fermionic systems the creation operator  $a_{\alpha_i}^\dagger$  will act the following way on an N particle state

$$a_{\alpha_i}^\dagger |\alpha_1 \alpha_2 \cdots \alpha_N\rangle = \begin{cases} 0, & \text{if } i \in \{1, 2, \dots, N\} \\ |\alpha_i \alpha_1 \alpha_2 \cdots \alpha_N\rangle, & \text{otherwise} \end{cases}$$

where  $|\alpha_1 \alpha_2 \cdots \alpha_N\rangle$  is an N-particle Slater determinant. The creation operators hermitian conjugate, the annihilation operator  $a_{\alpha_i}$ , acts the following way:

$$a_{\alpha_i} |\alpha_1 \alpha_2 \cdots \alpha_N\rangle = \begin{cases} 0, & \text{if } i \notin \{1, 2, \dots, N\} \\ (-1)^{i-1} |\alpha_1 \alpha_2 \cdots \cancel{\alpha_i} \cdots \alpha_N\rangle, & \text{otherwise} \end{cases}$$

where  $\cancel{\alpha_i}$  indicates that the single particle state  $\alpha_i$  is removed from the N particle state.  $(-1)^{i-1}$  ensures that the Pauli exclusion principle is satisfied. By defining a vacuum  $|0\rangle$  by a state which does not contain any particles, the operators act the following way

$$a_\alpha^\dagger |0\rangle = |\alpha\rangle \quad a_\alpha |0\rangle = 0 \quad (1)$$

We can write a hamiltonian in second quantization form as a sum of one body operators  $\hat{h}$  and two body operators  $\hat{v}$ :

$$\hat{H} = \hat{H}_0 + \hat{H}_1 = \sum_{\alpha\beta} \langle \alpha | \hat{h} | \beta \rangle a_\alpha^\dagger a_\beta + \frac{1}{4} \sum_{\alpha\beta\gamma\delta} \langle \alpha\beta | \hat{v} | \gamma\delta \rangle_{AS} a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma \quad (2)$$

where  $\alpha, \beta, \gamma$  and  $\delta$  runs through all single particle states and  $\langle \alpha\beta | \hat{v} | \gamma\delta \rangle_{AS} = \langle \alpha\beta | \hat{v} | \gamma\delta \rangle - \langle \alpha\beta | \hat{v} | \delta\gamma \rangle$ . The usefulness of Second Quantization really shines when introducing the Particle Hole-formalism. With this formalism, we introduce a new reference/vacuum state

$$|c\rangle = |\alpha_1\alpha_2\cdots\alpha_N\rangle$$

where the particles occupy the combination of single particle states which yields the lowest energies, keeping in mind that our fermionic system can only have two particles in the same spatial state. We refer to all single particle states  $\alpha_i$  with  $i \leq N$  as being below the Fermi level and  $i > N$  as being above Fermi level. Its important to note that equation 1 does not hold for our new reference state. We will relabel our annihilation and creation operators with the labels  $i, j, k, l$  referring to states below this Fermi level and the labels  $a, b, c, d$  referring to states above this Fermi level.

The operators will act the following way on our reference state

$$a_i^\dagger |c\rangle = 0 \quad a_a |c\rangle = 0 \quad (3)$$

which we will now call our annihilation operators and

$$a_i |c\rangle = (-1)^{i-1} |\alpha_1\alpha_2\cdots\cancel{\alpha_i}\cdots\alpha_N\rangle \quad a_a^\dagger |c\rangle = |\alpha_a\alpha_1\alpha_2\cdots\alpha_N\rangle \quad (4)$$

which we will now call our creation operators. We refer to states where we have removed a particle below Fermi level from our reference state as hole-states and states where we have added a particle above the Fermi level to our reference state as particle-states. We use the shorthand notation

$$|\Phi_i^a\rangle = a_a^\dagger a_i |c\rangle \quad (5)$$

for one-particle-one-hole states and

$$|\Phi_{ij}^{ab}\rangle = a_a^\dagger a_b^\dagger a_j a_i |c\rangle \quad (6)$$

for two-particle-two-hole states.

How this eases our calculation of the expectation values of our hamiltonian can be seen by introducing Wick's theorem. It states that a product with an equal number of fermionic creation and annihilation operators can be expressed as[8]

$$\begin{aligned} ABCDEF\cdots &= : ABCDEF\cdots : + \\ &\sum_{singles} : \overline{AB} CDEF\cdots : + \\ &\sum_{doubles} : \overline{AB} \overline{CD} EF\cdots : + \\ &\vdots + \\ &\sum_{\frac{N}{2}} : \overline{AB} \overline{CD} \overline{EF} \cdots : \end{aligned} \quad (7)$$

where  $: ABCDEF\cdots :$  is the normal order of our operators, which puts the all operators that annihilates our reference state to the right of the operators that creates holes or particles.  $\overline{AB}$  is called a contraction and can be defined as

$$\overline{AB} = \langle c | AB | c \rangle$$

One needs to ensure that contracted terms are adjacent in the string, introducing a minus sign every time two operators are swapped. This theorem is useful because the only part of equation 7 that will contribute to our calculation of the expectation values are the sum over  $\frac{N}{2}$  contractions. This is because all the other terms will end up with annihilation operators on the far right and will act on our reference state according to equation 3 and yield zero. If we have an unequal number of creation and annihilation operators, there is no need to apply Wicks theorem as the expectation value will always be zero. Consider calculating the sum

$$\langle c | \hat{H}_1 | c \rangle = \frac{1}{4} \sum_{\alpha\beta\gamma\delta} \langle \alpha\beta | \hat{v} | \gamma\delta \rangle_{AS} \langle c | a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma | c \rangle$$

where  $\hat{H}_1$  is as in equation 2. We can apply Wicks theorem and consider the possible contractions

$$\overbrace{a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma} = \langle c | a_\alpha^\dagger a_\gamma | c \rangle \langle c | a_\beta^\dagger a_\delta | c \rangle = \delta_{\alpha\gamma < F} \delta_{\beta\delta < F}$$

$$\overbrace{a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma} = -\langle c | a_\alpha^\dagger a_\delta | c \rangle \langle c | a_\beta^\dagger a_\gamma | c \rangle = -\delta_{\alpha\delta < F} \delta_{\beta\gamma < F}$$

which thankfully reduces the sum considerably.

Here are the expectation values we will need in our study. A thorough calculation of them are found in "Finding matrix elements using Second Quantization" under the Appendix section:

$$\langle c | \hat{H} | c \rangle = \sum_i \langle i | \hat{h} | i \rangle + \frac{1}{2} \sum_{ij} [\langle ij | \hat{v} | ij \rangle - \langle ij | \hat{v} | ji \rangle] \quad (8)$$

$$\langle c | \hat{H} | \Phi_i^a \rangle = \langle i | \hat{h} | a \rangle + \sum_j [\langle ij | \hat{v} | aj \rangle - \langle ij | \hat{v} | ja \rangle] \quad (9)$$

$$\begin{aligned} \langle \Phi_i^a | \hat{H} | \Phi_j^b \rangle &= \langle ja | \hat{v} | bi \rangle_{AS} + \delta_{ij} [\langle a | \hat{h} | b \rangle + \sum_k \langle ak | \hat{v} | bk \rangle_{AS}] \\ &\quad + \delta_{ab} [\sum_k \langle jk | \hat{v} | ki \rangle_{AS} - \langle j | \hat{h} | i \rangle] \\ &\quad + \delta_{ij} \delta_{ab} [\sum_k \langle k | \hat{h} | k \rangle + \frac{1}{2} \sum_{kl} \langle kl | \hat{v} | kl \rangle_{AS}] \end{aligned} \quad (10)$$

The end of the project description (see reference [4]) provides the two body expectation values needed. Keep in mind that these only run over the quantum number  $n$  while equation 2 runs over the secondary spin quantum number as well.

## 2.2 Hamiltonian, basis and Slater determinants.

With the Hamiltonian we will work with we have introduced the Born-Oppenheimer approximation which effectively freezes our the nucleonic degrees of freedom. For  $N$  electrons it has the following form:

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

where  $k = 1.44eVnm$  and  $r_{ij} = |r_i - r_j|$ . We will introduce atomic units, which means that  $c = e = m_e = \hbar = 1$ . This makes the constant  $k = 1$ . The energies represented can be multiplied with  $2 \times 13.6eV$  to obtain energies in electron volts. The Hamiltonian can then be rewritten as

$$\hat{H} = \hat{H}_0 + \hat{H}_1 = \sum_{i=1}^N \hat{h}(x_i) + \sum_{i<j}^N \frac{1}{r_{ij}} \quad (11)$$

where  $\hat{h} = \hat{t} - \frac{Z}{r_i}$ . Thus the Hamiltonian can be represented by a sum over  $N$  one body Hamiltonians  $\hat{h}(x_i)$  and a sum over  $N(N-1)/2$  two body interactions  $\frac{1}{r_{ij}}$ . We will use hydrogen-like single particle functions for our calculations which makes the one body operator  $\hat{h}$  diagonal in our basis. The one body expectation values are given by

$$\langle i | \hat{h} | j \rangle = -\frac{Z^2}{2n^2} \delta_{ij} \quad (12)$$

where the quantum number  $n$  refers to the number of nodes of the wave function. We will restrict ourselves to s-waves, which means that the orbital momentum  $l = 0$ . We will also assume that the total spin projection  $M_S = 0$ . [4] In addition, we need to be careful when calculating the expectation values since our wave function is a product of spatial and spin functions. Our Hamiltonian consists of operators that are not dependent on spin, which means that we can integrate over the spin variable separately.

For our one-electron integrals, this means that

$$\langle \psi_i | \hat{h} | \psi_j \rangle = \langle i | \hat{h} | j \rangle \langle \sigma_i | \sigma_j \rangle = \langle i | \hat{h} | j \rangle \delta_{\sigma_i \sigma_j} \quad (13)$$

where  $|\psi_i\rangle$  represents the spin orbitals,  $|i\rangle$  represents the spatial part and  $|\sigma_i\rangle$  represents the spin part.

For two-electron integrals, we get

$$\langle \psi_i \psi_j | \hat{v} | \psi_k \psi_l \rangle = \langle ij | \hat{h} | kl \rangle \langle \sigma_i | \sigma_k \rangle \langle \sigma_j | \sigma_l \rangle = \langle ij | \hat{h} | kl \rangle \delta_{\sigma_i \sigma_l} \delta_{\sigma_j \sigma_k} \quad (14)$$

The most convenient many-particle wave functions to work with are given by the simple product

$$\Psi(x_1, x_2, \dots, x_N) = \psi_1(x_1) \psi_2(x_2) \dots \psi_N(x_N)$$

For fermionic systems however, the Pauli exclusion principle requires wave functions to be anti-symmetric under the exchange of two particles. This requirement is satisfied by  $\Psi$  being represented by a Slater determinant

$$\Psi(x_1 x_2 \dots x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(x_1) & \psi_1(x_2) & \psi_1(x_3) & \dots & \psi_1(x_N) \\ \psi_2(x_1) & \psi_2(x_2) & \psi_2(x_3) & \dots & \psi_2(x_N) \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \psi_N(x_1) & \psi_N(x_2) & \psi_N(x_3) & \dots & \psi_N(x_N) \end{vmatrix} \quad (15)$$

An important property is that if the set  $\{\psi_i\}$  is complete, an arbitrary antisymmetric N-electron wave function can be written as a linear combination of all possible N-electron Slater determinants:

$$|\Phi\rangle = c_0 |\Psi_0\rangle + \sum_{ia} c_i^a |\Psi_i^a\rangle + \sum_{i<j, a<b} c_{ij}^{ab} |\Psi_{ij}^{ab}\rangle + \dots \quad (16)$$

Where  $|\Psi_i^a\rangle$  and  $|\Psi_{ij}^{ab}\rangle$  are given by equation 5 and equation 6 respectively. The number of  $N$ -electron Slater determinants that can be formed from  $2K$  spin orbitals is

$$\text{Number of Slater Determinants} = \binom{2K}{N} \quad (17)$$

Given that we are working with the s-waves 1s-3s and electrons, we will have six basis states to work with. We omit the labels  $s, l$  and  $m_l$ , and write our single-particle states as  $\psi_{n,m_s}$  with  $n$  being the number of nodes of the wave function and  $m_s \in \{\uparrow, \downarrow\}$  refers to the secondary spin quantum number. To simplify our notation further, we label our basis states as in table 1 below

Table 1: Basis States

$$\begin{aligned} |1\rangle &= |\psi_{1,\uparrow}\rangle & |2\rangle &= |\psi_{1,\downarrow}\rangle \\ |3\rangle &= |\psi_{2,\uparrow}\rangle & |4\rangle &= |\psi_{2,\downarrow}\rangle \\ |5\rangle &= |\psi_{3,\uparrow}\rangle & |6\rangle &= |\psi_{3,\downarrow}\rangle \end{aligned}$$

## 2.3 CI

We want to solve the time-independent Schrödinger Equation

$$\hat{H} |\Phi_k\rangle = (\hat{H}_0 + \hat{H}_1) |\Phi_k\rangle = \epsilon_k |\Phi_k\rangle \quad (18)$$

Where the hamiltonian is given as in equation 11. The problem is that we do not know the solution when the electron-electron interaction is present. We do know from equation 16 however, that an arbitrary antisymmetric  $N$ -particle wave function can be written as a linear combination of Slater determinants. If we choose the  $2K$  eigenfunctions  $\psi_k$  of  $\hat{H}_0$  as our basis, the solutions to equation 18 are then given by

$$|\Phi_k\rangle = c_0^{(k)} |\Psi_0\rangle + \sum_{ia} c_i^{a(k)} |\Psi_i^a\rangle + \sum_{i<j, a<b} c_{ij}^{ab(k)} |\Psi_{ij}^{ab}\rangle + \dots \quad (19)$$

We can write the Hamiltonian in the  $|\Psi_i\rangle$  basis by utilizing the fact that  $\sum_i |\Psi_i\rangle \langle \Psi_i| = I$ :

$$\hat{H} = \sum_{ij} |\Psi_i\rangle \langle \Psi_i| \hat{H} |\Psi_j\rangle \langle \Psi_j| \quad (20)$$

By multiplying both sides with  $\langle \Psi_l|$  and using equation 18 and 19, we see that

$$\langle \Psi_l | \hat{H} | \Phi_k \rangle = \sum_j \langle \Psi_l | \hat{H} | \Psi_j \rangle c_j = \epsilon_k c_l \quad (21)$$

This can be written in matrix notation as

$$\begin{bmatrix} \langle \Psi_0 | \hat{H} | \Psi_0 \rangle & \langle \Psi_0 | \hat{H} | \Psi_1 \rangle & \dots & \langle \Psi_0 | \hat{H} | \Psi_{\binom{2K}{N}} \rangle \\ \langle \Psi_1 | \hat{H} | \Psi_0 \rangle & \langle \Psi_1 | \hat{H} | \Psi_1 \rangle & \dots & \langle \Psi_1 | \hat{H} | \Psi_{\binom{2K}{N}} \rangle \\ \vdots & \vdots & \ddots & \vdots \\ \langle \Psi_{\binom{2K}{N}} | \hat{H} | \Psi_0 \rangle & \langle \Psi_{\binom{2K}{N}} | \hat{H} | \Psi_1 \rangle & \dots & \langle \Psi_{\binom{2K}{N}} | \hat{H} | \Psi_{\binom{2K}{N}} \rangle \end{bmatrix} \begin{bmatrix} c_0 \\ c_1 \\ \vdots \\ c_{\binom{2K}{N}} \end{bmatrix} = \epsilon_k \begin{bmatrix} c_0 \\ c_1 \\ \vdots \\ c_{\binom{2K}{N}} \end{bmatrix} \quad (22)$$

Thus we can in principle solve equation 18 exactly by finding the eigenfunctions and eigenvalues of the above matrix. In practice however, we require an infinite number of single-particle wave functions to form a complete set, which means that the  $\binom{2K}{N}$  Slater determinants will not form a basis for our N-particle functions. Nevertheless, the solutions will be exact within the N-particle subspace spanned by our Slater determinants [1]. A more detailed walk-through of Configuration Interaction theory can be found in Morten Hjort-Jensens lecture notes on the subject [5].

## 2.4 Hartree-Fock Method

Another way to approximate our wave-functions and energies is the Hartree-Fock Method. Rather than finding an appropriate linear combination of already known Slater Determinants, like with CI, we now aim to find a set  $\{\psi_i\}$  of spin orbitals such that the Slater determinant

$$|\Phi_0\rangle = |\psi_1\psi_2\cdots\psi_N\rangle$$

gives the best approximation to the ground state energy given our Hamiltonian.

The method is built upon the variational principle, which states that the ground state energy of our Hamiltonian is always less or equal to the expected value of our Hamiltonian with respect to a trial wave function  $|\psi_{Trial}\rangle$ :

$$E_0 \leq \langle \psi_{Trial} | \hat{H} | \psi_{Trial} \rangle \quad (23)$$

This means that we can approximate the ground state and energy by varying  $|\psi_{Trial}\rangle$  until this expectation value is minimized.

To do this, we write our trial function as a unitary transformation of an orthonormal basis:

$$|i\rangle = \sum_{\alpha} C_{i\alpha} |\alpha\rangle \quad (24)$$

An important property of a unitary transformation  $|i\rangle = C |a\rangle$  is that if  $|\alpha\rangle$  is orthonormal

$$\langle i | j \rangle = \langle \alpha | C^\dagger C | \beta \rangle = \langle \alpha | \beta \rangle = \delta_{\alpha\beta} = \delta_{ij} \quad (25)$$

so is  $|i\rangle$ . The expectation value of our Hamiltonian with respect to our trial function is

$$E_{Trial} = \sum_i \langle i | \hat{H} | i \rangle + \frac{1}{2} \sum_{ij} \langle ij | \hat{v} | ij \rangle_{AS}$$

Written in terms of our old basis (using equation 24):

$$E_{Trial} = \sum_i \sum_{\alpha\beta} C_{i\alpha}^* C_{i\beta} \langle \alpha | \hat{H} | \beta \rangle + \frac{1}{2} \sum_{ij} \sum_{\alpha\beta\gamma\delta} C_{i\alpha}^* C_{j\beta}^* C_{i\gamma} C_{j\delta} \langle \alpha\beta | \hat{v} | \gamma\delta \rangle_{AS} \quad (26)$$

We wish to minimize this with respect to the unitary transformation coefficients such that the trial function remain normalized, i.e

$$\begin{aligned} \langle i | i \rangle &= \sum_{\alpha} C_{i\alpha}^* C_{i\alpha} \langle \alpha | \alpha \rangle = \sum_{\alpha} C_{i\alpha}^* C_{i\alpha} = 1 \\ \implies \sum_{\alpha} C_{i\alpha}^* C_{i\alpha} - 1 &= 0 \end{aligned}$$

This can be done with Lagranges method of undetermined multipliers:

$$\mathcal{L} = E_{Trial} - \sum_i \epsilon_i \left( \sum_{\alpha} C_{i\alpha}^* C_{i\alpha} - 1 \right)$$

We now minimize this with respect to  $C_{i\alpha}^*$  since  $C_{i\alpha}$  and  $C_{i\alpha}^*$  can be viewed as independent variables:

$$\begin{aligned}\frac{d\mathcal{L}}{dC_{i\alpha}^*} &= \sum_i \sum_{\alpha\beta} C_{i\beta} \langle \alpha | \hat{h} | \beta \rangle + \sum_{ij} \sum_{\alpha\beta\gamma\delta} C_{j\beta}^* C_{i\gamma} C_{j\delta} \langle \alpha\beta | \hat{v} | \gamma\delta \rangle_{AS} - \sum_{i\alpha} \epsilon_i C_{i\alpha} \\ &= \sum_{i\alpha} \left[ \sum_{\beta} C_{i\beta} \langle \alpha | \hat{h} | \beta \rangle + \sum_j \sum_{\beta\gamma\delta} C_{j\beta}^* C_{i\gamma} C_{j\delta} \langle \alpha\beta | \hat{v} | \gamma\delta \rangle_{AS} - \epsilon_i C_{i\alpha} \right] = 0\end{aligned}$$

Since  $C_{i\alpha}$  is arbitrary, the term within the square bracket must be zero. By factoring out the sum over  $\beta$  and exchanging dummy variables ( $\beta \leftrightarrow \gamma$ ) we get

$$\begin{aligned}\sum_{\beta} \left[ \langle \alpha | \hat{h} | \beta \rangle + \sum_j \sum_{\gamma\delta} C_{j\gamma}^* C_{j\delta} \langle \alpha\gamma | \hat{v} | \beta\delta \rangle_{AS} \right] C_{i\beta} &= \epsilon_i C_{i\alpha} \\ \sum_{\beta} h_{\alpha\beta}^{HF} C_{i\beta} &= \epsilon_i C_{i\alpha}\end{aligned}\tag{27}$$

We can write this in a more compact form:

$$H^{HF} \hat{C} = \epsilon^{HF} \hat{C}\tag{28}$$

We can solve this eigenvalue problem by an iterative process. If our original single particle basis are eigenfunctions of  $\hat{h}$ , then  $h_{\alpha\beta}^{HF}$  simplifies to

$$h_{\alpha\beta}^{HF} = \epsilon_{\alpha} \delta_{\alpha\beta} + \sum_j \sum_{\gamma\delta} C_{j\gamma}^* C_{j\delta} \langle \alpha\gamma | \hat{v} | \beta\delta \rangle_{AS}$$

By making an initial guess on  $C_{i\alpha}^0 = \delta_{i\alpha}$ , we can calculate

$$h_{\alpha\beta}^{HF} = \epsilon_{\alpha} \delta_{\alpha\beta} + \sum_j \sum_{\gamma\delta} C_{j\gamma}^{(0)*} C_{j\delta}^{(0)} \langle \alpha\gamma | \hat{v} | \beta\delta \rangle_{AS}$$

Solving the eigenproblem then yields new eigenvectors  $C_{i\alpha}^{(1)}$  and eigenvalues  $\epsilon_i^{HF(1)}$ . We then calculate

$$h_{\alpha\beta}^{HF} = \epsilon_{\alpha} \delta_{\alpha\beta} + \sum_j \sum_{\gamma\delta} C_{j\gamma}^{(1)*} C_{j\delta}^{(1)} \langle \alpha\gamma | \hat{v} | \beta\delta \rangle_{AS}$$

and continue this process until

$$\frac{\sum_i |\epsilon_i^{HF(n)} - \epsilon_i^{HF(n-1)}|}{m} \leq \lambda\tag{29}$$

where  $\lambda$  is normally set to  $10^{-8}$  or smaller and  $m$  is the number of single particle states.[6]

## 2.5 Helium

The Helium atom consists of two electrons which are bound to a nucleus with charge  $Z = 2$ . The two electrons can only be in the same spatial state if the spins are opposite. We also require the total spin projection  $M_S = 0$ , which means that opposite spins are a general requirement. In order to approximate our ground state with CI we need to specify our Slater determinants. In Second quantization form our reference state can be written as

$$|\Phi_0\rangle = |c\rangle = a_1^\dagger a_2^\dagger |0\rangle = |12\rangle$$



where the label  $i$  in  $a_i^\dagger$  refers to state  $|i\rangle$  in table 1. Hence single particle states  $|i\rangle$  with  $i > 2$  are above Fermi level. The possible one-particle-one-hole states are

Table 2: Helium: One-particle-one-hole states

$$|\Phi_1^3\rangle = a_3^\dagger a_1 |c\rangle = |32\rangle \quad |\Phi_2^4\rangle = a_4^\dagger a_2 |c\rangle = |14\rangle$$

$$|\Phi_1^5\rangle = a_5^\dagger a_1 |c\rangle = |52\rangle \quad |\Phi_2^6\rangle = a_6^\dagger a_2 |c\rangle = |16\rangle$$

We also have the following two-particle-two-hole states

Table 3: Helium: Two-particle-two-hole states.

$$|\Phi_{12}^{34}\rangle = a_3^\dagger a_4^\dagger a_2 a_1 |c\rangle = |34\rangle \quad |\Phi_{12}^{56}\rangle = a_5^\dagger a_6^\dagger a_2 a_1 |c\rangle = |56\rangle$$

$$|\Phi_{12}^{36}\rangle = a_3^\dagger a_6^\dagger a_2 a_1 |c\rangle = |36\rangle \quad |\Phi_{12}^{54}\rangle = a_5^\dagger a_4^\dagger a_2 a_1 |c\rangle = |54\rangle$$

All the above states are illustrated in the diagrams below.

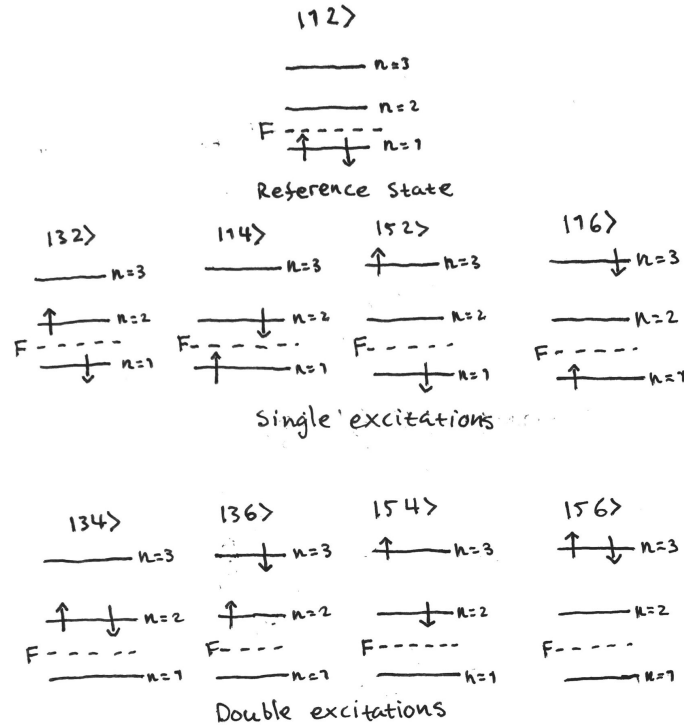


Figure 1: Slater determinants for Helium.

We can also calculate the so called reference energies of the Helium atom. This is the expectation value of the hamiltonian with respect to our reference state and can be calculated with the use of equation 32:

$$\begin{aligned}
\langle c | \hat{H} | c \rangle &= \sum_{i=1}^2 \langle i | \hat{h} | i \rangle + \frac{1}{2} \sum_{i,j=1}^2 [\langle ij | \hat{v} | ij \rangle - \langle ij | \hat{v} | ji \rangle] \\
&= \langle 1 | \hat{h} | 1 \rangle + \langle 2 | \hat{h} | 2 \rangle + \frac{1}{2} [\langle 11 | \hat{v} | 11 \rangle_{AS} + \langle 12 | \hat{v} | 12 \rangle_{AS} + \langle 21 | \hat{v} | 21 \rangle_{AS} + \langle 22 | \hat{v} | 22 \rangle]
\end{aligned}$$

The first and last term within the square brackets will be zero since we have two electrons in the same spin orbital state. We are left with

$$\langle 1 | \hat{h} | 1 \rangle + \langle 2 | \hat{h} | 2 \rangle + \frac{1}{2} [\langle 12 | \hat{v} | 12 \rangle - \langle 12 | \hat{v} | 21 \rangle + \langle 21 | \hat{v} | 21 \rangle - \langle 21 | \hat{v} | 12 \rangle]$$

The second and last term within the square bracket will be zero because of the spin requirement from equation 14. We then have

$$\begin{aligned}
&\langle 1 | \hat{h} | 1 \rangle + \langle 2 | \hat{h} | 2 \rangle + \frac{1}{2} [\langle 12 | \hat{v} | 12 \rangle + \langle 21 | \hat{v} | 21 \rangle] \\
&= -\frac{Z^2}{2} - \frac{Z^2}{2} + \frac{1}{2} [5\frac{Z}{8} + 5\frac{Z}{8}]
\end{aligned}$$

so

$$\langle c | \hat{H} | c \rangle = (\frac{5}{8} - Z)Z \quad (30)$$

## 2.6 Beryllium Atom

The Beryllium Atom consists of four electrons bound to a nucleus of charge  $Z = 4$ . In the same manner as with the Helium atom, we need to construct a (truncated) Slater determinant basis in order to use CI to approximate the ground state energy.

For the Beryllium atom, our reference state will now be

$$|\Phi_0\rangle = |c\rangle = a_1^\dagger a_2^\dagger a_3^\dagger a_4^\dagger |0\rangle = |1234\rangle$$

Hence the single particle state  $|i\rangle$  for  $i > 4$  will be above Fermi level. The possible one-particle-one-hole states are

Table 4: Beryllium: One-particle-one-hole states

$$|\Phi_3^5\rangle = a_5^\dagger a_3 |c\rangle = |1254\rangle \quad |\Phi_4^6\rangle = a_6^\dagger a_4 |c\rangle = |1236\rangle$$

$$|\Phi_1^5\rangle = a_5^\dagger a_1 |c\rangle = |5234\rangle \quad |\Phi_2^6\rangle = a_6^\dagger a_2 |c\rangle = |1634\rangle$$

and the possible two-particle-two-hole states are

Table 5: Beryllium: Two-particle-two-hole states.

$$|\Phi_{23}^{56}\rangle = a_6^\dagger a_3 a_5^\dagger a_2 |c\rangle = |1256\rangle \quad |\Phi_{14}^{56}\rangle = a_6^\dagger a_4 a_5^\dagger a_1 |c\rangle = |5236\rangle$$

$$|\Phi_{23}^{65}\rangle = a_5^\dagger a_3 a_6^\dagger a_2 |c\rangle = |1654\rangle \quad |\Phi_{12}^{56}\rangle = a_6^\dagger a_2 a_5^\dagger a_1 |c\rangle = |5634\rangle$$

All the above states are illustrated below.

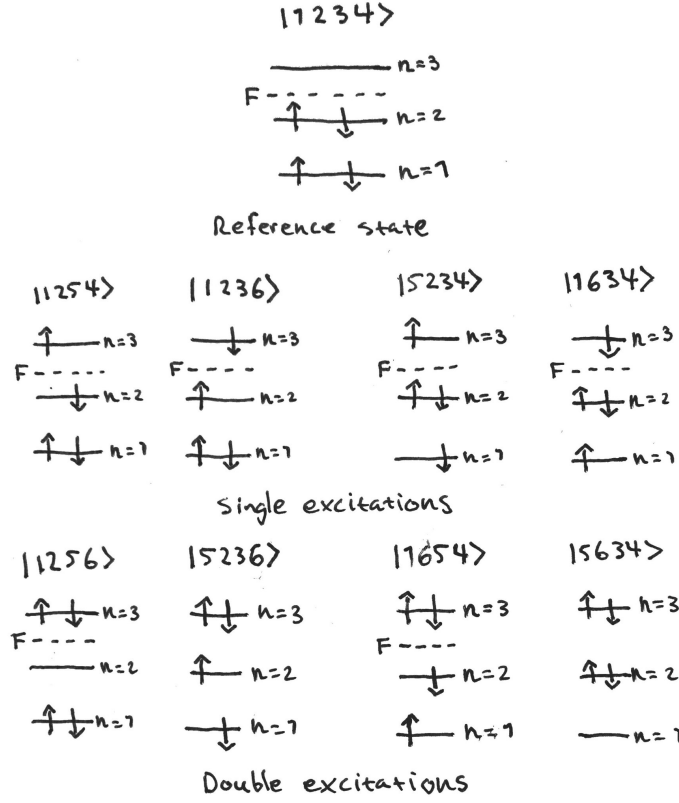


Figure 2: Slater determinants for Beryllium.

The reference energy of the hamiltonian is here

$$\langle c | \hat{H} | c \rangle = \sum_{i=1}^4 \langle i | \hat{h} | i \rangle + \frac{1}{2} \sum_{i,j=1}^4 [\langle ij | \hat{v} | ij \rangle - \langle ij | \hat{v} | ji \rangle]$$

which by following the same procedure as with Helium we get

$$\langle c | \hat{H} | c \rangle = \left( \frac{586373}{373248} - \frac{5}{4} Z \right) Z \quad (31)$$

## 3 Results

### 3.1 Helium

We first calculated the CI matrix by following the procedure explained in section 2.3 with a truncated Slater determinant basis. We used the determinants shown in figure 1, but excluded the double excitations. The elements in equation 22 of the Helium CI matrix were given by labeling

$$\begin{aligned} |\Psi_0\rangle &= |c\rangle \\ |\Psi_1\rangle &= |\Phi_1^3\rangle \quad |\Psi_2\rangle = |\Phi_1^4\rangle \quad |\Psi_3\rangle = |\Phi_1^5\rangle \quad |\Psi_4\rangle = |\Phi_1^6\rangle \\ |\Psi_5\rangle &= |\Phi_2^3\rangle \quad |\Psi_6\rangle = |\Phi_2^4\rangle \quad |\Psi_7\rangle = |\Phi_2^5\rangle \quad |\Psi_8\rangle = |\Phi_2^6\rangle \end{aligned}$$

This gave the following Hamiltonian matrix

Table 6: CI matrix for Helium Atom

$$H^{CI} = \begin{bmatrix} -2.750 & 0.179 & 0.000 & 0.088 & 0.000 & 0.000 & 0.179 & 0.000 & 0.088 \\ 0.179 & -2.080 & 0.000 & 0.101 & 0.000 & 0.000 & 0.044 & 0.000 & 0.022 \\ 0.000 & 0.000 & -2.124 & 0.000 & 0.079 & 0.000 & 0.000 & 0.000 & 0.000 \\ 0.088 & 0.101 & 0.000 & -2.023 & 0.000 & 0.000 & 0.022 & 0.000 & 0.012 \\ 0.000 & 0.000 & 0.079 & 0.000 & -2.035 & 0.000 & 0.000 & 0.000 & 0.000 \\ 0.000 & 0.000 & 0.000 & 0.000 & 0.000 & -2.124 & 0.000 & 0.079 & 0.000 \\ 0.179 & 0.044 & 0.000 & 0.022 & 0.000 & 0.000 & -2.080 & 0.000 & 0.101 \\ 0.000 & 0.000 & 0.000 & 0.000 & 0.000 & 0.079 & 0.000 & -2.035 & 0.000 \\ 0.088 & 0.022 & 0.000 & 0.012 & 0.000 & 0.000 & 0.101 & 0.000 & -2.023 \end{bmatrix}$$

which we can see is a symmetric matrix as we wanted. The lowest eigenvalue of this matrix corresponds to our approximation for the ground state energy. We got

$$E^{CI} = -2.8386 \quad [a.u]$$

Next up we followed the HF procedure explained in section 2.4. Our single particle basis consists of the 6 basis states in table 1. After one iteration of the HF algorithm we got the following Hartree-Fock matrix:

Table 7: HF matrix for Helium atom after one iteration

$$H^{HF} = \begin{bmatrix} -0.750 & 0.000 & 0.179 & 0.000 & 0.088 & 0.000 \\ 0.000 & -0.750 & 0.000 & 0.179 & 0.000 & 0.088 \\ 0.179 & 0.000 & 0.296 & 0.000 & 0.180 & 0.000 \\ 0.000 & 0.179 & 0.000 & 0.296 & 0.000 & 0.180 \\ 0.088 & 0.000 & 0.180 & 0.000 & 0.164 & 0.000 \\ 0.000 & 0.088 & 0.000 & 0.180 & 0.000 & 0.164 \end{bmatrix}$$

The resulting C matrix with equation 26 gave us the energy

$$E_{OneIteration}^{HF} = -2.8291 \quad [a.u]$$

When allowing our algorithm to converge, with  $\lambda = 10^{-8}$  in equation 29, we got the following Hartree-Fock matrix

Table 8: HF matrix for Helium atom

$$H^{HF} = \begin{bmatrix} -0.840 & 0.000 & 0.226 & 0.000 & 0.102 & 0.000 \\ 0.000 & -0.840 & 0.000 & 0.226 & 0.000 & 0.102 \\ 0.226 & 0.000 & 0.271 & 0.000 & 0.169 & 0.000 \\ 0.000 & 0.226 & 0.000 & 0.271 & 0.000 & 0.169 \\ 0.102 & 0.000 & 0.169 & 0.000 & 0.159 & 0.000 \\ 0.000 & 0.102 & 0.000 & 0.169 & 0.000 & 0.159 \end{bmatrix}$$

with the resulting energy

$$E^{HF} = -2.8311 \quad [a.u]$$

The table below shows us the energy approximations together with the exact energy. The reference state energy is the expectation value  $\langle c | \hat{H} | c \rangle$  (equation 30):

Table 9: Calculated and exact energy for Helium atom ground state:

	Energy [a.u]
Reference State	-2.7500
CI	-2.8386
HF - One iteration	-2.8291
HF	-2.8311
Exact	-2.9037

We see that the best approximation was with CI. Below is a plot of our approximation of the ground state energy against the atomic number  $Z$  for an atom with two electrons. The reference energy again refers to  $\langle c | \hat{H} | c \rangle$ . The black dashed line is the exact ground state energy of the Helium atom:

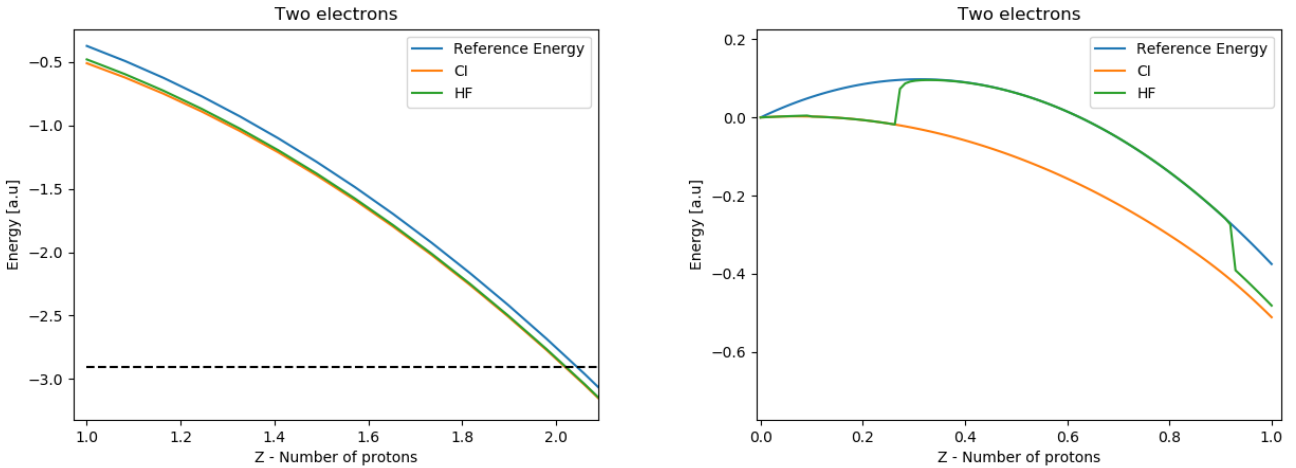


Figure 3: Energy against  $Z$  for a two electron system.

Notice from the right figure that for small  $Z$ , we have positive energies for the ground state approximations. The Hartree-fock algorithm did not converge for  $Z \in [0.3, 0.9]$ , which is seen by the sudden bounce of the energy. Also pay attention to that the reference energy expectation value  $\langle c | \hat{H} | c \rangle$  is always higher than our CI approximation of  $E_0$ . The same can be said for  $HF$  when the algorithm converged.

## 3.2 Beryllium

We followed the same procedure as with the Helium atom, but with our truncated Slater determinant basis consisting of the determinants in figure 2. Again we excluded double excitations and used the following labels for getting the matrix elements in equation 22:

$$\begin{aligned}
|\Psi_0\rangle &= |c\rangle \\
|\Psi_1\rangle &= |\Phi_1^5\rangle \quad |\Psi_2\rangle = |\Phi_1^6\rangle \quad |\Psi_3\rangle = |\Phi_2^5\rangle \quad |\Psi_4\rangle = |\Phi_2^6\rangle \\
|\Psi_5\rangle &= |\Phi_3^5\rangle \quad |\Psi_6\rangle = |\Phi_3^6\rangle \quad |\Psi_7\rangle = |\Phi_4^5\rangle \quad |\Psi_8\rangle = |\Phi_4^6\rangle
\end{aligned}$$

We got the following CI Matrix:

Table 10: CI matrix for Beryllium atom

$$H^{CI} = \begin{bmatrix} -13.716 & 0.189 & 0.000 & 0.000 & 0.189 & 0.445 & 0.000 & 0.000 & 0.445 \\ 0.189 & -9.655 & 0.000 & 0.000 & 0.023 & -0.393 & 0.000 & 0.000 & 0.008 \\ 0.000 & 0.000 & -9.678 & 0.000 & 0.000 & 0.000 & -0.401 & 0.000 & 0.000 \\ 0.000 & 0.000 & 0.000 & -9.678 & 0.000 & 0.000 & 0.000 & -0.401 & 0.000 \\ 0.189 & 0.023 & 0.000 & 0.000 & -9.655 & 0.008 & 0.000 & 0.000 & -0.393 \\ 0.445 & -0.393 & 0.000 & 0.000 & 0.008 & -13.688 & 0.000 & 0.000 & 0.030 \\ 0.000 & 0.000 & -0.401 & 0.000 & 0.000 & 0.000 & -13.718 & 0.000 & 0.000 \\ 0.000 & 0.000 & 0.000 & -0.401 & 0.000 & 0.000 & 0.000 & -13.718 & 0.000 \\ 0.445 & 0.008 & 0.000 & 0.000 & -0.393 & 0.030 & 0.000 & 0.000 & -13.688 \end{bmatrix}$$

It is its own conjugate transpose as expected from a Hamiltonian matrix. Its lowest eigenvalue corresponds to our approximation for the ground state energy. We got

$$E^{CI} = -14.3621$$

We then followed the HF procedure explained in section 2.4. Our single particle basis again consists of the 6 basis states in table 1. After one iteration of the HF algorithm we got the following Hartree-Fock matrix:

Table 11: HF Matrix for Beryllium atom after one iteration

$$H^{HF} = \begin{bmatrix} -3.909 & 0.000 & 0.392 & 0.000 & 0.189 & 0.000 \\ 0.000 & -3.909 & 0.000 & 0.392 & 0.000 & 0.189 \\ 0.392 & 0.000 & 0.193 & 0.000 & 0.445 & 0.000 \\ 0.000 & 0.392 & 0.000 & 0.193 & 0.000 & 0.445 \\ 0.189 & 0.000 & 0.445 & 0.000 & 0.527 & 0.000 \\ 0.000 & 0.189 & 0.000 & 0.445 & 0.000 & 0.527 \end{bmatrix}$$

The resulting C matrix with equation 26 gave us the energy

$$E_{OneIteration}^{HF} = -14.4998 \quad [a.u.]$$

When allowing the algorithm to converge, using  $\lambda = 10^{-8}$  in equation 29, we got

Table 12: HF matrix for Beryllium atom

$$H^{HF} = \begin{bmatrix} -4.650 & 0.000 & 0.392 & 0.000 & 0.199 & 0.000 \\ 0.000 & -4.650 & 0.000 & 0.392 & 0.000 & 0.199 \\ 0.392 & 0.000 & 0.116 & 0.000 & 0.534 & 0.000 \\ 0.000 & 0.392 & 0.000 & 0.116 & 0.000 & 0.534 \\ 0.199 & 0.000 & 0.534 & 0.000 & 0.353 & 0.000 \\ 0.000 & 0.199 & 0.000 & 0.534 & 0.000 & 0.353 \end{bmatrix}$$

This time the C matrix gave us the following energy

$$E^{HF} = -14.5083$$

Below we have a table of the energy approximations as well as the exact ground state energy of the Beryllium atom:

Table 13: Calculated and exact energy for Beryllium atom ground state:

	Energy [a.u]
Reference State	-13.7160
CI	-14.3621
HF - One iteration	-14.4998
HF	-14.5083
Exact	-14.6674

We see that the Hartree-fock solution is the best approximation to the ground state energy. Below is a figure of the energy approximations against the atomic number  $Z$  for a four electron system:

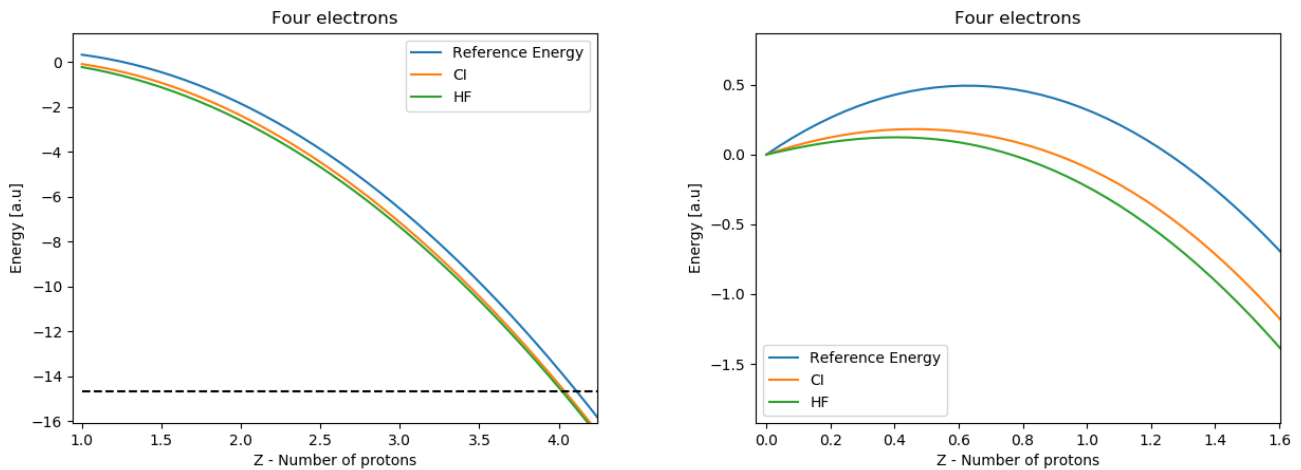


Figure 4: Energy against  $Z$  for a four electron system.

We notice again from that the HF and CI approximation suggest that there are unbound ( $E > 0$ ) ground states, but this time for a wider range of  $Z$ 's. The HF algorithm converged for all  $Z$  tested and we see that the CI and HF approximation of  $E_0$  is always lower than  $\langle c | \hat{H} | c \rangle$ .

## 4 Discussion

In our results we see that the obtained CI matrices (table 6 and 10) are indeed symmetric as is required for a Hamiltonian matrix. They also contain several elements which are zero and this comes as a result of spin degrees of freedom, which is seen by comparing equation 14 with equation 33. In table 9 we see the ground state energy approximations for CF and HF together with the exact energy for the Helium atom. CI gives the best approximation with an absolute error of  $|E_{CI} - E_{exact}| = 0.0651 \text{ [a.u.]}$ . The Hartree-Fock algorithm provided a better estimate for the ground state energy when allowing the algorithm to converge than after one iteration, which is an expected result with a working HF algorithm. In figure 3 we see the approximations of the ground state energies together with the expectation values  $\langle c | \hat{H} | c \rangle$  (called reference energy) for different  $Z$  for a two-electron system. The right side of the figure suggests that the ground states when  $Z$  is approximately in the range  $0 < Z < 0.2$  are unbound as we got positive energies for this range. The right hand side also shows that the HF solution was not continuous - it did not converge for all  $Z$ . The HF solutions can represent a local rather than a global minimum and this could explain the behavior. For the Beryllium atom, we got the energy approximations in table 13. For this atom, HF gave a better approximation to the ground state energy with an absolute error of  $|E_{HF} - E_{exact}| = 0.1591 \text{ [a.u.]}$ , which can be seen from table 13. The reason that HF did better than CI this time could be that we still use five linearly independent Slater determinants to approximate the ground state with CI, but now we aim to do so for a four particle space rather than a two particle space. Like with the two-electron system, we see from figure 4 that our approximations suggest unbound ground states for a range of  $Z$ 's for the four-electron system, but the range is wider (approximately  $0 < Z < 1$ ). The explanation for the wider range could be a reduction of the effective nuclear charge on electrons in the outer shells due to electron-electron repulsion. This is sometimes called the Shielding effect[3]. We also see from the figures of  $E$  against  $Z$  that CI (and HF when it converged) provides a lower approximation to the ground state energy than the expectation value  $\langle c | \hat{h} | c \rangle$ . This speaks in our favor as the opposite would question the validity of the variational principle (equation 23).

## 5 Conclusion

For the Helium atom, which we know the exact ground state energy within the given digits to be  $E_{exact} = -2.9037 \text{ [a.u.]}$ , configuration interaction gave the best approximation when not exceeding single excitations for our truncated Slater determinant basis. This method gave the approximate  $E_{CI} = -2.8386 \text{ [a.u.]}$  while the HF algorithm resulted in  $E_{HF} = -2.8311 \text{ [a.u.]}$ . These results are outlined in table 9. When studying the dependence of the ground state energy on the atomic number  $Z$  for a two electron system (figure 3), we saw that the approximations suggest unbound ground states as CI gave positive energies for  $0 < Z < 0.2$ . For the Beryllium atom, with an exact ground state energy within the given digits of  $E_{exact} = -14.6674 \text{ [a.u.]}$ , HF yielded the best approximation  $E_{HF} = -14.5083 \text{ [a.u.]}$ . CI gave  $E_{CI} = -14.3621 \text{ [a.u.]}$  and we concluded that it was not as successful for the Beryllium atom because we didn't expand the Slater determinant basis. These results can be seen in table 13. When studying the dependence of the ground state energy on the atomic number  $Z$ , but this time for a four electron system (figure 4), our methods again suggested that there exists unbound ground states. The range of  $Z$  for which the ground states were unbound was wider ( $0 < Z < 1$ ) than for the two electron system and we concluded that this could be a result of a decrease of the effective nuclear charge on electrons in the outer shells due to electron-electron repulsion[3].



## 6 Appendix

The figures and python scripts can be found on the github page <https://github.com/stiandb/ManyBodyFys4480>.

### 6.1 Python Class

Here is the Python class used to produce the results. The main program can be found in the Script folder on the github page.

---

```
import numpy as np
```

```
class Quantum:
```

```
    def __init__(self, n_fermi, TBME):
```

```
        """
```

```
        n_fermi – Number of electrons (number of states below fermi level)
```

```
        TBME – function which returns the two–body matrix elements of the Hamiltonian.
```

```
        """
```

```
        self.n_fermi = n_fermi
```

```
        self.TBME = TBME
```

```
    def set_Z(self, Z):
```

```
        """
```

```
        Z – Atomic number / coulomb interaction
```

```
        """
```

```
        self.Z = Z
```

```
        self.u = self.TBME(Z)
```

```
    def set_states(self, states):
```

```
        """
```

```
        states – list containing lists [n,m_s] (basis states), where n refers to quantum number  
                  n of the state
```

```
                  and m_s is the secondary spin number of the state.
```

```
        """
```

```
        self.n_basis = len(states)
```

```
        self.states = states
```

```
    def ihj(self, i, j):
```

```
        if self.states[i,1] == self.states[j,1] and self.states[i,0] == self.states[j,0]:
```

```
            return(-self.Z**2/(2*self.states[i,0]**2))
```

```
        else:
```

```
            return(0)
```

```
    def ijvkl(self, i, j, k, l):
```

```
        if self.states[i,1] == self.states[k,1] and self.states[j,1] == self.states[l,1]:
```

```
            if self.states[i,0] == self.states[j,0] and self.states[i,1] == self.states[j,1]:
```

```
                return(0)
```

```
            elif self.states[k,0] == self.states[l,0] and self.states[k,1] == self.states[l,1]:
```

```
                return(0)
```

```
            else:
```

```
                return(self.u[self.states[i,0]-1, self.states[j,0]-1, \  
                             self.states[k,0]-1, self.states[l,0]-1])
```

```
        else:
```

```
            return(0)
```

```
    def cHc(self):
```

```

expval = 0
for i in range(self.n_fermi):
    expval += self.ihj(i,i)
    for j in range(self.n_fermi):
        expval += 0.5*(self.ijvkl(i,j,i,j) - self.ijvkl(i,j,j,i))
    return(expval)
def cHia(self,i,a):
    expval = self.ihj(i,a)
    for j in range(self.n_fermi):
        expval += self.ijvkl(i,j,a,j) - self.ijvkl(i,j,j,a)
    return(expval)
def iaHjb(self,i,a,j,b):
    expval = self.ijvkl(j,a,b,i) - self.ijvkl(j,a,i,b)
    if i == j:
        expval += self.ihj(a,b)
        for k in range(self.n_fermi):
            expval += self.ijvkl(a,k,b,k) - self.ijvkl(a,k,k,b)
        if a == b:
            for k in range(self.n_fermi):
                expval += self.ihj(k,k)
                for l in range(self.n_fermi):
                    expval += 0.5*(self.ijvkl(k,l,k,l) - self.ijvkl(k,l,l,k))
    if a == b:
        expval -= self.ihj(j,i)
        for k in range(self.n_fermi):
            expval += self.ijvkl(j,k,k,i) - self.ijvkl(j,k,i,k)
    return(expval)

class CI(Quantum):
    """
    Find CI (singles) approximation of eigenstates of the Hamiltonian
    """
    def solve(self):
        n_fermi = self.n_fermi
        n_basis = self.n_basis
        n = n_fermi*(n_basis - n_fermi) + 1
        H = np.zeros((n,n))
        H[0,0] = self.cHc()
        for i in range(n_fermi):
            for j in range(n_fermi,n_basis):
                cHa = self.cHia(i,j)
                H[0,1+i*(n_basis-n_fermi)+j-n_fermi] = cHa
                H[1+i*(n_basis-n_fermi)+j-n_fermi,0] = cHa
            for k in range(n_fermi):
                for l in range(n_fermi,n_basis):
                    H[j+1-n_fermi+i*(n_basis-n_fermi),k*(n_basis-n_fermi)+l+1-n_fermi] = self.iaHjb(i,j,k,l)
        self.H_CI = H
        self.e_CI, self.u_CI = np.linalg.eigh(H)
        return(self.e_CI,self.u_CI,self.H_CI)

```

```

class HF(Quantum):
    """
    Find the Hartree–Fock approximation of the ground state energy
    """
    def iter(self):
        n_basis = self.n_basis
        self.H_hf = np.zeros((n_basis,n_basis))
        for alpha in range(n_basis):
            for beta in range(n_basis):
                self.H_hf[alpha,beta] += self.ihj(alpha,beta)
            for j in range(self.n_fermi):
                for gamma in range(n_basis):
                    for delta in range(n_basis):
                        self.H_hf[alpha,beta] += self.C[j,gamma]*self.C[j,delta]*\
                            (self.ijvkl(alpha,gamma,beta,delta) - self.ijvkl(alpha,
                                gamma,delta,beta))

        self.e_1,C = np.linalg.eigh(self.H_hf)
        self.C = C.T
    def calculate_energies(self):
        n_basis = self.n_basis
        n_fermi = self.n_fermi
        e = 0
        for i in range(n_fermi):
            for alpha in range(n_basis):
                for beta in range(n_basis):
                    e += self.C[i,alpha]*self.C[i,beta]*self.ihj(alpha,beta)
                for j in range(n_fermi):
                    for gamma in range(n_basis):
                        for delta in range(n_basis):
                            e += 0.5*self.C[i,alpha]*self.C[j,beta]*self.C[i,gamma]*self.C[j,delta]\
                                *(self.ijvkl(alpha,beta,gamma,delta) - self.ijvkl(alpha,beta,delta,
                                    gamma))

        return(e)

    def solve(self, tol = 1e-8,max_iter=1000):
        n_basis = self.n_basis
        n_fermi = self.n_fermi
        self.C = np.identity(n_basis)
        e_0 = np.zeros(n_basis)
        err=1
        converge=False
        for i in range(max_iter):
            self.iter()
            err=np.sum(np.abs(self.e_1 - e_0))/n_basis
            e_0 = self.e_1
            if err < tol:
                converge = True
                break
        if converge != True:

```

```

print('HF did not converge')
E = self.calculate_energies()
return(self.e_1, self.C, self.H_hf, E)

```

---

## 6.2 Finding matrix elements using Second Quantization

We can write our hamiltonian in second quantization form as a sum of one body and two body operators (equation 2):

$$H = H_0 + H_1 = \sum_{\alpha\beta} \langle \alpha | \hat{h} | \beta \rangle a_{\alpha}^{\dagger} a_{\beta} + \frac{1}{4} \sum_{\alpha\beta\gamma\delta} \langle \alpha\beta | \hat{v} | \gamma\delta \rangle_{AS} a_{\alpha}^{\dagger} a_{\beta}^{\dagger} a_{\delta} a_{\gamma}$$

We can now find the expectation values that makes up the matrix elements of our hamiltonian. Since  $\langle \alpha | \hat{H} | \beta \rangle = \langle \alpha | \hat{H}_0 | \beta \rangle + \langle \alpha | \hat{H}_1 | \beta \rangle$  we start with the one-body part of the ground state expectation value:

$$\langle c | H | c \rangle = \sum_{\alpha\beta} \langle \alpha | \hat{h} | \beta \rangle \langle c | a_{\alpha}^{\dagger} a_{\beta} | c \rangle$$

By applying Wick's theorem (equation 7) we only need to consider the possible contractions of our operators. The only contraction here is

$$\overline{a_{\alpha}^{\dagger} a_{\beta}} = \delta_{\alpha\beta < F}$$

which yields the following result

$$\langle c | H_0 | c \rangle = \sum_i \langle i | \hat{h} | i \rangle$$

The two-body part is

$$\langle c | H_1 | c \rangle = \frac{1}{4} \sum_{\alpha\beta\gamma\delta} \langle \alpha\beta | \hat{v} | \gamma\delta \rangle_{AS} \langle c | a_{\alpha}^{\dagger} a_{\beta}^{\dagger} a_{\delta} a_{\gamma} | c \rangle$$

There are only two possible contractions here

$$\overline{a_{\alpha}^{\dagger} a_{\beta}^{\dagger} a_{\delta} a_{\gamma}} = \delta_{\alpha\gamma < F} \delta_{\beta\delta < F}$$

$$\overline{a_{\alpha}^{\dagger} a_{\beta}^{\dagger} a_{\delta} a_{\gamma}} = -\delta_{\alpha\delta < F} \delta_{\beta\gamma < F}$$

This gives the result

$$\begin{aligned} \langle c | H_1 | c \rangle &= \frac{1}{4} [\sum_{ij} \langle ij | \hat{v} | ij \rangle_{AS} - \langle ij | \hat{v} | ji \rangle_{AS}] \\ &= \frac{1}{4} [\sum_{ij} \langle ij | \hat{v} | ij \rangle - \langle ij | \hat{v} | ji \rangle - \langle ij | \hat{v} | ji \rangle + \langle ij | \hat{v} | ij \rangle] \\ &= \frac{1}{2} \sum_{ij} [\langle ij | \hat{v} | ij \rangle - \langle ij | \hat{v} | ji \rangle] \end{aligned}$$

So we have

$$\langle c | H | c \rangle = \sum_i \langle i | \hat{h} | i \rangle + \frac{1}{2} \sum_{ij} [\langle ij | \hat{v} | ij \rangle - \langle ij | \hat{v} | ji \rangle]$$

The next expectation values we want to find are

$$\langle c | H | \Phi_i^a \rangle = \langle c | H a_a^\dagger a_i | c \rangle$$

The one-body part of this is

$$\langle c | \hat{h} a_a^\dagger a_i | c \rangle = \sum_{\alpha\beta} \langle \alpha | \hat{h} | \beta \rangle \langle c | a_\alpha^\dagger a_\beta a_a^\dagger a_i | c \rangle$$

We again use Wicks theorem and notice that the only contribution contraction is

$$\overline{a_\alpha^\dagger a_\beta a_a^\dagger a_i} = \delta_{\alpha i} \delta_{\beta a}$$

which gives

$$\langle c | H_0 | \Phi_i^a \rangle = \langle i | \hat{h} | a \rangle$$

The two-body part gives:

$$\langle c | H_1 | \Phi_i^a \rangle = \frac{1}{4} \sum_{\alpha\beta\gamma\delta} \langle \alpha\beta | \hat{v} | \gamma\delta \rangle \langle c | a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma a_a^\dagger a_i | c \rangle$$

The possible contractions are

$$\overline{a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma a_a^\dagger a_i} = \delta_{\alpha i} \delta_{\beta\delta} \delta_{\gamma a}$$

$$\overline{a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma a_a^\dagger a_i} = -\delta_{\alpha i} \delta_{\beta\gamma} \delta_{\delta a}$$

$$\overline{a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma a_a^\dagger a_i} = -\delta_{\alpha\delta} \delta_{\beta i} \delta_{\gamma a}$$

$$\overline{a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma a_a^\dagger a_i} = \delta_{\alpha\gamma} \delta_{\beta i} \delta_{\delta a}$$

Which means that we can write the two body contribution as

$$\begin{aligned} \langle c | H_1 | \Phi_i^a \rangle &= \frac{1}{4} \sum_j [\langle ij | \hat{v} | aj \rangle_{AS} - \langle ij | \hat{v} | ja \rangle_{AS} - \langle ji | \hat{v} | aj \rangle_{AS} + \langle ji | \hat{v} | ja \rangle_{AS}] \\ &= \sum_j [\langle ij | \hat{v} | aj \rangle_{AS} - \langle ij | \hat{v} | ja \rangle_{AS}] \end{aligned}$$

This results in

$$\langle c | H | \Phi_i^a \rangle = \langle i | \hat{h} | a \rangle + \sum_j [\langle ij | \hat{v} | aj \rangle - \langle ij | \hat{v} | ja \rangle]$$

The final expression we want to find is

$$\langle \Phi_i^a | H | \Phi_j^b \rangle = \langle c | a_i^\dagger a_a H a_b^\dagger a_j | c \rangle$$

The one-body contribution is

$$\langle \Phi_i^a | H_0 | \Phi_j^b \rangle = \sum_{\alpha\beta} \langle \alpha | \hat{h} | \beta \rangle \langle c | a_i^\dagger a_a a_\alpha^\dagger a_\beta a_b^\dagger a_j | c \rangle$$

The contractions that contribute to the sum are

$$\begin{aligned} \overbrace{a_i^\dagger a_a a_\alpha^\dagger a_\beta a_b^\dagger a_j} &= \delta_{ij} \delta_{a\alpha} \delta_{\beta b} & \overbrace{a_i^\dagger a_a a_\alpha^\dagger a_\beta a_b^\dagger a_j} &= \delta_{ij} \delta_{ab} \delta_{\alpha\beta < F} & \overbrace{a_i^\dagger a_a a_\alpha^\dagger a_\beta a_b^\dagger a_j} &= -\delta_{i\beta} \delta_{ab} \delta_{\alpha j} \end{aligned}$$

This gives

$$\langle \Phi_i^a | H_0 | \Phi_j^b \rangle = \delta_{ij} [\langle a | \hat{h} | b \rangle + \delta_{ab} \sum_k \langle k | \hat{h} | k \rangle] - \delta_{ab} \langle j | \hat{h} | i \rangle$$

The two-body contribution:

$$\langle \Phi_i^a | H_1 | \Phi_j^b \rangle = \frac{1}{4} \sum_{\alpha\beta\gamma\delta} \langle \alpha\beta | \hat{v} | \gamma\delta \rangle_{AS} \langle c | a_i^\dagger a_a a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma a_b^\dagger a_j | c \rangle$$

The following contractions contribute to this sum

$$\begin{aligned} \overbrace{a_i^\dagger a_a a_\alpha^\dagger a_\beta a_\delta a_\gamma a_b^\dagger a_j} &= \delta_{ij} \delta_{\alpha a} \delta_{\beta \delta < F} \delta_{\gamma b} & \overbrace{a_i^\dagger a_a a_\alpha^\dagger a_\beta a_\delta a_\gamma a_b^\dagger a_j} &= -\delta_{ij} \delta_{\alpha a} \delta_{\beta \gamma < F} \delta_{\delta b} \\ \overbrace{a_i^\dagger a_a a_\alpha^\dagger a_\beta a_\delta a_\gamma a_b^\dagger a_j} &= \delta_{ij} \delta_{\beta a} \delta_{\alpha \gamma < F} \delta_{\delta b} & \overbrace{a_i^\dagger a_a a_\alpha^\dagger a_\beta a_\delta a_\gamma a_b^\dagger a_j} &= -\delta_{ij} \delta_{\beta a} \delta_{\alpha \delta < F} \delta_{\gamma b} \\ \overbrace{a_i^\dagger a_a a_\alpha^\dagger a_\beta a_\delta a_\gamma a_b^\dagger a_j} &= \delta_{ij} \delta_{ab} \delta_{\alpha \gamma < F} \delta_{\beta \delta < F} & \overbrace{a_i^\dagger a_a a_\alpha^\dagger a_\beta a_\delta a_\gamma a_b^\dagger a_j} &= -\delta_{ij} \delta_{ab} \delta_{\alpha \delta < F} \delta_{\beta \gamma < F} \\ \overbrace{a_i^\dagger a_a a_\alpha^\dagger a_\beta a_\delta a_\gamma a_b^\dagger a_j} &= \delta_{\delta i} \delta_{\beta a} \delta_{\alpha j} \delta_{\gamma b} & \overbrace{a_i^\dagger a_a a_\alpha^\dagger a_\beta a_\delta a_\gamma a_b^\dagger a_j} &= -\delta_{\delta i} \delta_{\alpha a} \delta_{\beta j} \delta_{\gamma b} \\ \overbrace{a_i^\dagger a_a a_\alpha^\dagger a_\beta a_\delta a_\gamma a_b^\dagger a_j} &= \delta_{\delta i} \delta_{ab} \delta_{\alpha j} \delta_{\beta \gamma < F} & \overbrace{a_i^\dagger a_a a_\alpha^\dagger a_\beta a_\delta a_\gamma a_b^\dagger a_j} &= -\delta_{\delta i} \delta_{ab} \delta_{\alpha \gamma < F} \delta_{\beta j} \\ \overbrace{a_i^\dagger a_a a_\alpha^\dagger a_\beta a_\delta a_\gamma a_b^\dagger a_j} &= \delta_{\gamma i} \delta_{ab} \delta_{\alpha \delta < F} \delta_{\beta j} & \overbrace{a_i^\dagger a_a a_\alpha^\dagger a_\beta a_\delta a_\gamma a_b^\dagger a_j} &= -\delta_{\gamma i} \delta_{ab} \delta_{\alpha j} \delta_{\beta \delta < F} \\ \overbrace{a_i^\dagger a_a a_\alpha^\dagger a_\beta a_\delta a_\gamma a_b^\dagger a_j} &= \delta_{\gamma i} \delta_{\alpha a} \delta_{\beta j} \delta_{\delta b} & \overbrace{a_i^\dagger a_a a_\alpha^\dagger a_\beta a_\delta a_\gamma a_b^\dagger a_j} &= -\delta_{\gamma i} \delta_{\beta a} \delta_{\alpha j} \delta_{\delta b} \end{aligned}$$

This gives, using the anti-symmetry of these terms and that  $\langle ab | \hat{v} | cd \rangle = -\langle ab | \hat{v} | dc \rangle$ :

$$\begin{aligned} \langle \Phi_i^a | H_1 | \Phi_j^b \rangle &= \delta_{ij} \sum_k \langle ak | \hat{v} | bk \rangle_{AS} + \delta_{ij} \delta_{ab} \frac{1}{2} \sum_{kl} \langle kl | \hat{v} | kl \rangle_{AS} \\ &\quad + \delta_{ab} \sum_k \langle jk | \hat{v} | ki \rangle_{AS} + \langle ja | \hat{v} | bi \rangle_{AS} \end{aligned}$$

To summarize, the matrix elements of our Hamiltonian are:

$$\langle c | \hat{H} | c \rangle = \sum_i \langle i | \hat{h} | i \rangle + \frac{1}{2} \sum_{ij} [\langle ij | \hat{v} | ij \rangle - \langle ij | \hat{v} | ji \rangle] \quad (32)$$

$$\langle c | \hat{H} | \Phi_i^a \rangle = \langle i | \hat{h} | a \rangle + \sum_j [\langle ij | \hat{v} | aj \rangle - \langle ij | \hat{v} | ja \rangle] \quad (33)$$

$$\begin{aligned} \langle \Phi_i^a | \hat{H} | \Phi_j^b \rangle &= \langle ja | \hat{v} | bi \rangle_{AS} + \delta_{ij} [\langle a | \hat{h} | b \rangle + \sum_k \langle ak | \hat{v} | bk \rangle_{AS}] \\ &\quad + \delta_{ab} [\sum_k \langle jk | \hat{v} | ki \rangle_{AS} - \langle j | \hat{h} | i \rangle] \\ &\quad + \delta_{ij} \delta_{ab} [\sum_k \langle k | \hat{h} | k \rangle + \frac{1}{2} \sum_{kl} \langle kl | \hat{v} | kl \rangle_{AS}] \end{aligned} \quad (34)$$

## 7 References

- [1]. Modern Quantum Chemistry, Chapter 2.2 - Attila Szabo and Neil S. Ostlund
- [2]. Second Quantization - Morten Hjort-Jensen - <https://github.com/ManyBodyPhysics/FYS4480/tree/master/doc/pub/secondquant/pdf>
- [3]. Boundless Chemistry - <https://courses.lumenlearning.com/introchem/chapter/the-shielding-effect->
- [4]. FYS4480 Project - Morten Hjort-Jensen, UiO - <https://github.com/ManyBodyPhysics/FYS4480/tree/master/doc/Projects/2018/Project1/pdf>
- [5]. FCI - Morten Hjort-Jensen - <https://github.com/ManyBodyPhysics/FYS4480/blob/master/doc/pub/fci/pdf/fci-minted.pdf>
- [6]. Hartree-Fock - Morten Hjort-Jensen - <https://github.com/ManyBodyPhysics/FYS4480/blob/master/doc/pub/hf/hf-minted.pdf>
- [7]. Modern Quantum Chemistry, Chapter 3 - Attila Szabo and Neil S. Ostlund
- [8]. Notes Wick's Theorem - Tim Evans - <https://www.imperial.ac.uk/media/imperial-college/research-centres-and-groups/theoretical-physics/msc/current/qft/handouts/qftwickstheorem.pdf>