FYS4480 - Project 2

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Abstract

The aim of this project is to perform a Coupled Cluster Doubles (CCD) implementation from scratch and apply it on ground state energy estimations of Helium and Beryllium. We limit ourselves to the s-waves and let the single-particle orbitals 1s, 2s and 3s form the basis. The obtained energies were compared to energies found using configuration interaction (CI), Hartree-Fock (HF) and second order many-body perturbation theory (MBPT), and we also use the HF-basis as input to CCD.

The results provided by CCD turned out to be poor using the original basis for both atoms, and it was outperformed by all other methods but MBPT. In fact, the energies were just slightly lower than the reference energies. When moving to HF-basis, the results improved dramatically giving relative errors of 2.22% and 1.05% for Helium and Beryllium respectively, compared to the experimental values. With a ground state energy approximation of $-2.839144[a.u.]$ for Helium and $-14.5129[a.u.]$ for Beryllium, this approach provided the best results yet.

1   Introduction

Over the past century, plenty of methods have been developed in order to solve the time-independent Schrödinger equation,

$$\hat{H}\Psi_n(\boldsymbol{r}) = \epsilon_n\Psi_n(\boldsymbol{r}),$$

which is the equation to solve to find the energy of a stationary quantum mechanical system. One of those clever methods is the Coupled Cluster method (CC), which approximates the wave function with an exponential expansion. Actually, this approach is in principle capable of giving the exact results if not limited by computational capacity [3]. The method was invented by Fritz Coester and Herman Kümmel during the 1950's, but it was not given that the method would be a success. In his biography, Kümmel writes the following about his thoughts on the situation of coupled cluster in the late fifties [1]:

> "I myself at the time had almost given up the CC method as not tractable..."

As a paradox, the method is today the *de facto* standard wave function-based method for electronic-structure calculations. [2]

In this project, we will use Coupled Cluster Doubles (CCD) to estimate the ground state energy of Helium and Beryllium, with and without a Hartree-Fock basis. We will then compare the obtained energies with the experimental values and our previously obtained results for the Configuration Interaction Singles (CIS) and Hartree-Fock (HF) method [7]. In section 2, we will introduce the theory and methods used to obtain our results, starting with a representation of our Hamiltonian and basis states in section 2.1. We then give a derivation of the CCD energy and amplitude equations, as well as a comparison between this method and CIS in section 2.2 - 2.3. When we move over to the

results section, we represent our results for the Helium and Beryllium atom in section 3.1 and 3.2, respectively. In section 4 we will discuss these results and finally conclude them in section 5.

We recommend reading the theory section of our previous projects [7][5] as it contains details about CIS, HF and second quantization that are not provided here.

2 Theory

2.1 Many Body Quantum Theory

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

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

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

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

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 $M_S = 0$. 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 intergrals, this means that

$$\langle \psi_i | \hat{h} | \psi_j \rangle = \langle i | \hat{h} | j \rangle \langle \sigma_i | \sigma_j \rangle = \langle i | \hat{h} | j \rangle \delta_{\sigma_i \sigma_j} \tag{3}$$

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

$$\langle \psi_i \psi_j | \hat{v} | \psi_k \psi_l \rangle = \langle ij | \hat{h} | kl \rangle \langle \sigma_i | \sigma_k \rangle \langle \sigma_j | \sigma_l \rangle = \langle ij | \hat{h} | kl \rangle \delta_{\sigma_i \sigma_k} \delta_{\sigma_j \sigma_l} \tag{4}$$

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

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

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 Ψ being represented by a Slater determinant (SD),

$$\Psi(x_1 x_2 \cdots x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(x_1) & \psi_1(x_2) & \psi_1(x_3) & \ldots & \psi_1(x_N) \\ \psi_2(x_1) & \psi_2(x_2) & \psi_2(x_3 & \ldots & \psi_2(x_N) \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \psi_N(x_1) & \psi_N(x_2) & \psi_N(x_3) & \ldots & \psi_N(x_N) \end{vmatrix}. \tag{5}$$

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:

$$|\Phi\rangle = c_0 |\Psi_0\rangle + \sum_{ia} c_i^a |\Psi_i^a\rangle + \sum_{i<j,a<b} c_{ij}^{ab} \left| \Psi_{ij}^{ab} \right\rangle + \cdots \tag{6}$$

The number of N-electron Slater determinants that can be formed from $2K$ spin orbitals are

$$\textit{Number of Slater Determinants} = \binom{2K}{N} \tag{7}$$

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 ψ_{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

$$|1\rangle = |\psi_{1,\uparrow}\rangle \quad |2\rangle = |\psi_{1,\downarrow}\rangle$$

$$|3\rangle = |\psi_{2,\uparrow}\rangle \quad |4\rangle = |\psi_{2,\downarrow}\rangle$$

$$|5\rangle = |\psi_{3,\uparrow}\rangle \quad |6\rangle = |\psi_{3,\downarrow}\rangle$$

Whenever we use ket notation for a many-particle state in our report, we are referring to a SD. For example, the ket $|c\rangle$ refers to the reference vacuum SD.

2.1.1 Helium

When approximating the ground state of the Helium atom, we will use

$$|c\rangle \equiv \frac{1}{2}\Big[|12\rangle - |21\rangle\Big] \equiv |12\rangle_{\text{AS}}$$

as our reference vacuum, which schematically is represented in figure 1, where the hole labels are defined as $ijk... \in \{1, 2\}$ and particle labels as $abc... \in \{3, 4, 5, 6\}$. The attribute AS will henceforth be skipped.

$$|c\rangle$$

$3s$ ——————

$2s$ ——————
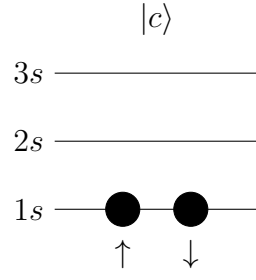
$1s$ ——●——●——
   　　↑　　↓

Figure 1: Ground state of Helium.

We also have the excited 1p-1h and 2p-2h states listed in figure 2. These states together form our truncated SD basis.

$$|\Phi_1^3\rangle \qquad |\Phi_2^4\rangle \qquad |\Phi_1^5\rangle \qquad |\Phi_2^6\rangle$$

$$|\Phi_{12}^{34}\rangle \qquad |\Phi_{12}^{54}\rangle \qquad |\Phi_{12}^{36}\rangle \qquad |\Phi_{12}^{56}\rangle$$
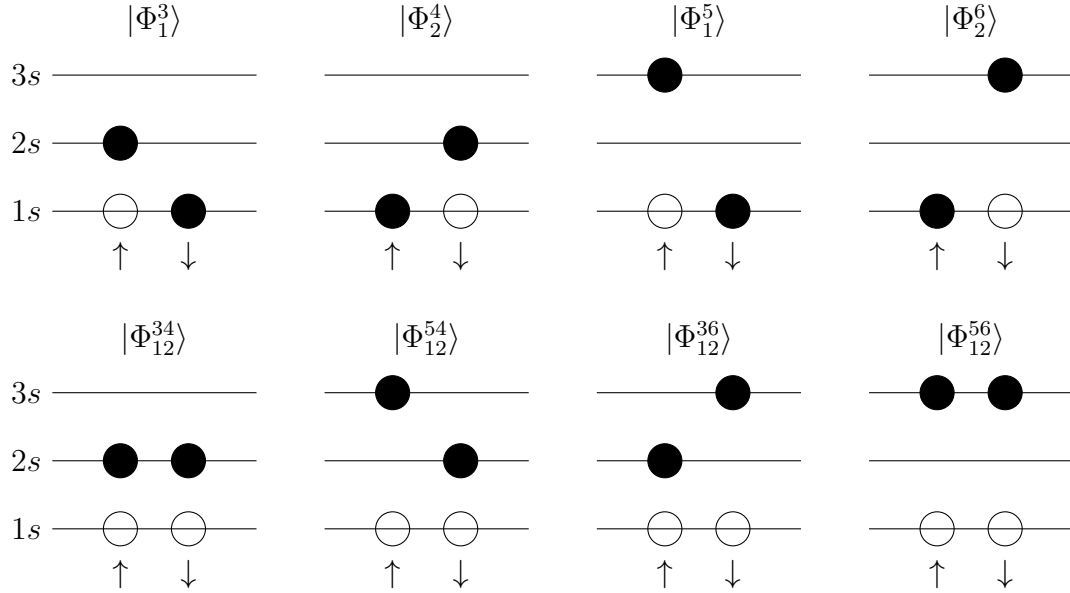
Figure 2: Possible states in the 1s, 2s and 3s orbitals of Helium. In the first row, all singly excited states are listed, while in the second row all doubly excited states are listed.

2.1.2 Beryllium

For the Beryllium atom, we will use the following state as our reference vacuum SD
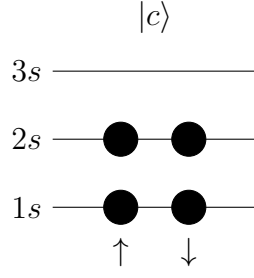
$$|c\rangle$$

$$3s \underline{\hspace{3cm}}$$

Figure 3: Ground state of Beryllium.

which defines our hole labels $ijk... \in \{1, 2, 3, 4\}$ and particle labels $abc... \in \{5, 6\}$. The possible 1p-1h and 2p-2h states in our basis are
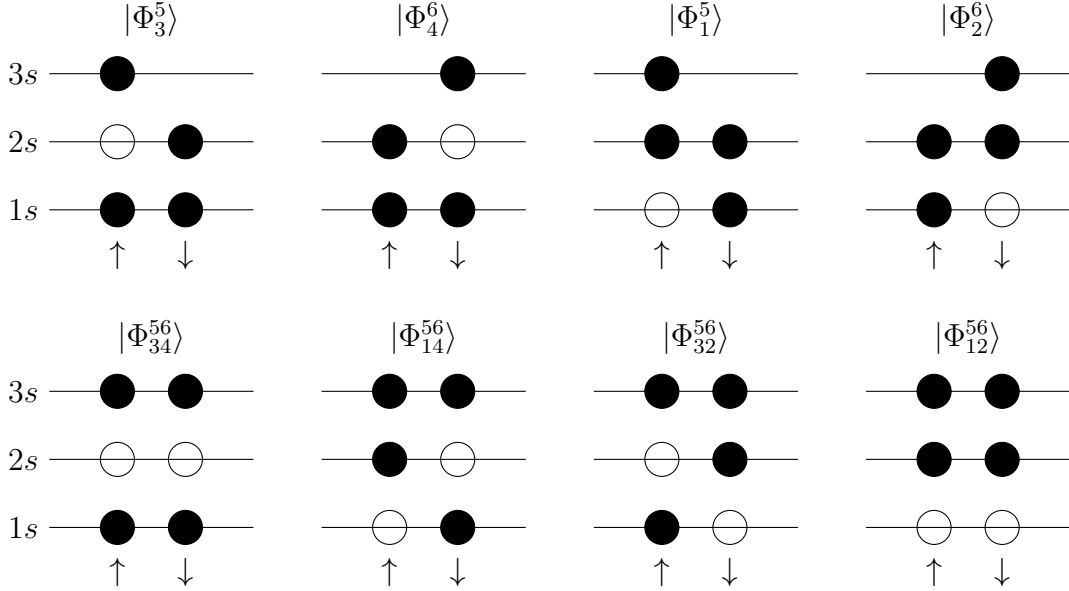

Figure 4: Possible states in the 1s, 2s and 3s orbitals of Beryllium. In the first row, all singly excited states are listed, while in the second row all doubly excited states are listed.

Which completes our truncated SD basis.

2.2   Coupled Cluster Method

In coupled cluster theory, we start out with an ansatz for the ground state

$$|\Psi_{CC}\rangle = e^{\hat{T}} |c\rangle \tag{8}$$

where $|c\rangle$ is our reference vacuum and $\hat{T}$ is the cluster operator

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \cdots$$

$$\hat{T}_n = \left(\frac{1}{n!}\right)^2 \sum_{abc...} \sum_{ijk...} t_{ijk...}^{abc...} a_a^\dagger a_b^\dagger a_c^\dagger \cdots a_k a_j a_i$$

In our project, we will limit ourselves to Coupled Cluster Doubles (CCD), which makes our cluster operator

$$\hat{T} = \hat{T}_2 = \frac{1}{4} \sum_{ab} \sum_{ij} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i \tag{9}$$

The Schrödinger equation becomes

$$\hat{H} \left| \Psi_{CC} \right\rangle = E_{CC} \left| \Psi_{CC} \right\rangle \qquad \hat{H} e^{\hat{T}} \left| c \right\rangle = E_{CC} e^{\hat{T}} \left| c \right\rangle \tag{10}$$

If we left multiply this equation with $\langle c | e^{-\hat{T}}$, we get

$$\langle c | e^{-\hat{T}} \hat{H} e^{\hat{T}} | c \rangle = E_{CC} \langle c | e^{-\hat{T}} e^{\hat{T}} | c \rangle = E_{CC}$$

Which we write in terms of the similarity transformed Hamiltonian $\bar{H} = e^{-\hat{T}} \hat{H} e^{\hat{T}}$:

$$\langle c | \bar{H} | c \rangle = E_{CC} \tag{11}$$

In the same manner, we can left multiply the Schrödinger equation with $e^{-\hat{T}} \left| \Phi_{ij\ldots}^{ab\ldots} \right\rangle$ to obtain

$$\left\langle \Phi_{ij\ldots}^{ab\ldots} \left| \bar{H} \right| c \right\rangle = 0 \tag{12}$$

Equation 12 can be used to find the unknowns $t_{ijk\ldots}^{abc\ldots}$. To do this, we can expand our Coupled Cluster Hamiltonian using the Baker-Campbell-Hausdorff expansion

$$
\begin{aligned}
\overline{H} = \hat{H} &+ [\hat{H}, \hat{T}] \\
&+ \frac{1}{2}[[\hat{H}, \hat{T}], \hat{T}] \\
&+ \frac{1}{6}[[[\hat{H}, \hat{T}], \hat{T}], \hat{T}] \\
&+ \frac{1}{24}[[[[\hat{H}, \hat{T}], \hat{T}], \hat{T}], \hat{T}] \\
&+ \cdots
\end{aligned}
\tag{13}
$$

where our Hamiltonian $\hat{H}$ is given by

$$
\begin{aligned}
\hat{H} &= E_{\text{ref}} + \hat{F} + \hat{H}_I \\
&= E_{\text{ref}} + \sum_{pq} \langle p | \hat{f} | q \rangle \{ a_p^\dagger a_q \} + \frac{1}{4} \sum_{pqrs} \langle pq | \hat{v} | rs \rangle \{ a_p^\dagger a_q^\dagger a_s a_r \}
\end{aligned}
\tag{14}
$$

2.2.1 Energy equations

To calculate the coupled cluster energy, we need to solve

$$E = \langle c | \bar{H} | c \rangle \tag{15}$$

where $\bar{H}$ is the similarity transformed Hamiltonian described above. Inserting Baker-Campbell-Hausdorff expansion (eq. 13), we get

$$E = \langle c | \hat{H} | c \rangle + \langle c | [\hat{H}, \hat{T}_2] | c \rangle + \frac{1}{2} \langle c | [[\hat{H}, \hat{T}_2], \hat{T}_2] | c \rangle + \text{higher order terms} \tag{16}$$

where the Hamiltonian is given by eq. 14. From Wick's generalized theorem, we immediately see that the first term is the reference energy,

$$\langle c|\hat{H}|c\rangle = E_{\text{ref}}. \tag{17}$$

Further, the second term can be split up into four terms

$$\langle c|[\hat{H}, \hat{T}_2]|c\rangle = \langle c|\hat{F}\hat{T}_2|c\rangle - \langle c|\hat{T}_2\hat{F}|c\rangle + \langle c|\hat{H}_I\hat{T}_2|c\rangle - \langle c|\hat{T}_2\hat{H}_I|c\rangle \tag{18}$$

where the two former terms obviously do not contribute due to lack of full contractions. The third term can be calculated using Wicks's theorem:

$$\langle c|\hat{H}_I\hat{T}_2|c\rangle = \frac{1}{16}\sum_{pqrs}\sum_{abij} t_{ij}^{ab} \langle pq|\hat{v}|rs\rangle \langle c|\{a_p^\dagger a_q^\dagger a_s a_r\}\{a_a^\dagger a_b^\dagger a_j a_i\}|c\rangle \tag{19}$$

$$= \frac{1}{16}\sum_{pqrs}\sum_{abij} t_{ij}^{ab} \langle pq|\hat{v}|rs\rangle \left(\delta_{pi}\delta_{qj}\delta_{sb}\delta_{ra} - \delta_{pi}\delta_{qj}\delta_{sa}\delta_{rb} + \delta_{pj}\delta_{qi}\delta_{sa}\delta_{rb} - \delta_{pj}\delta_{qi}\delta_{sb}\delta_{ra}\right) \tag{20}$$

$$= \frac{1}{4}\sum_{abij} t_{ij}^{ab} \langle ij|\hat{v}|ab\rangle . \tag{21}$$

Finally, the last term becomes zero because it has a creation operator acting on the bra, which means that

$$\langle c|[\hat{H}, \hat{T}_2]|c\rangle = \frac{1}{4}\sum_{abij} t_{ij}^{ab} \langle ij|\hat{v}|ab\rangle . \tag{22}$$

The last term in the energy expression can be simplified

$$\begin{aligned} \langle c|[[\hat{H}, \hat{T}_2], \hat{T}_2]|c\rangle &= \langle c|[(\hat{H}\hat{T}_2 - \hat{T}_2\hat{H}), \hat{T}_2]|c\rangle \\ &= \langle c|(\hat{H}\hat{T}_2^2 - \hat{T}_2\hat{H}\hat{T}_2 + \hat{T}_2\hat{H}\hat{T}_2 - \hat{T}_2^2\hat{H})|c\rangle \\ &= \langle c|(\hat{H}\hat{T}_2^2 - \hat{T}_2^2\hat{H})|c\rangle . \end{aligned} \tag{23}$$

This is zero since our Slater determinants (SD) are orthogonal and $\hat{T}_2^2$ creates 4p-4h states, while the Hamiltonian is only able to create 2p-2h states. The fully CCD energy then reads

$$E_{\text{CCD}} = E_{\text{ref}} + \frac{1}{4}\sum_{abij} t_{ij}^{ab} \langle ij|\hat{v}|ab\rangle \tag{24}$$

2.2.2 Amplitude equations

We now need to solve for t_{ij}^{ab} in order to find the CCD energy given above. This can be done by first finding an algebraic expression for the amplitude equation (eq. 12). By using eq. 13, we get

$$\begin{aligned} \left\langle \Phi_{ij}^{ab} \middle| \bar{H} \middle| c \right\rangle &= \left\langle \Phi_{ij}^{ab} \middle| \hat{H} \middle| c \right\rangle \\ &+ \left\langle \Phi_{ij}^{ab} \middle| [\hat{H}, \hat{T}_2] \middle| c \right\rangle \\ &+ \frac{1}{2} \left\langle \Phi_{ij}^{ab} \middle| [[\hat{H}, \hat{T}_2], \hat{T}_2] \middle| c \right\rangle \\ &+ \frac{1}{6} \left\langle \Phi_{ij}^{ab} \middle| [[[\hat{H}, \hat{T}_2], \hat{T}_2], \hat{T}_2] \middle| c \right\rangle \\ &+ \cdots \end{aligned} \tag{25}$$

where $\hat{H}$ is still given by eq. 14. The first expression to the right of the equal sign can be broken into three parts. The first:

$$\left\langle \Phi_{ij}^{ab} \middle| E_{\text{ref}} \middle| c \right\rangle = 0$$

because of the orthogonality of our SDs. Next up is

$$\left\langle \Phi_{ij}^{ab} \middle| \hat{F} \middle| c \right\rangle = 0$$

for the same reason ($\hat{F}$ is only able to create 1p-1h on the reference vacuum). This is known as the Slater-Condon rule. The final can be simplified using Wicks generalized theorem:

$$\left\langle \Phi_{ij}^{ab} \middle| \hat{H}_I \middle| c \right\rangle = \frac{1}{4} \sum_{pqrs} \langle pq|\hat{v}|rs\rangle \langle c| a_i^\dagger a_j^\dagger a_b a_a \{a_p^\dagger a_q^\dagger a_s a_r\} |c\rangle$$

$$= \frac{1}{4} \sum_{pqrs} \langle pq|\hat{v}|rs\rangle \left(\delta_{ir}\delta_{js}\delta_{ap}\delta_{bq} - \delta_{si}\delta_{jr}\delta_{bq}\delta_{ap} + \right.$$

$$\left. \delta_{si}\delta_{jr}\delta_{bp}\delta_{aq} - \delta_{ir}\delta_{js}\delta_{bp}\delta_{aq} \right)$$

$$= \langle ab|\hat{v}|ij\rangle$$

The second term in eq. 25 can be split into six parts,

$$\left\langle \Phi_{ij}^{ab} \middle| [\hat{H}, \hat{T}_2] \middle| c \right\rangle = \left\langle \Phi_{ij}^{ab} \middle| E_{\text{ref}} \hat{T}_2 \middle| c \right\rangle - \left\langle \Phi_{ij}^{ab} \middle| \hat{T}_2 E_{\text{ref}} \middle| c \right\rangle$$

$$+ \left\langle \Phi_{ij}^{ab} \middle| \hat{F} \hat{T}_2 \middle| c \right\rangle - \left\langle \Phi_{ij}^{ab} \middle| \hat{T}_2 \hat{F} \middle| c \right\rangle$$

$$+ \left\langle \Phi_{ij}^{ab} \middle| \hat{H}_I \hat{T}_2 \middle| c \right\rangle - \left\langle \Phi_{ij}^{ab} \middle| \hat{T}_2 \hat{H}_I \middle| c \right\rangle$$

The first two terms obviously cancel out. The third term can again be calculated using Wick's generalized theorem. The result is

$$\left\langle \Phi_{ij}^{ab} \middle| \hat{F} \hat{T}_2 \middle| c \right\rangle = \sum_k f_i^k t_{jk}^{ab} \hat{P}(ij) - \sum_c f_c^a t_{ij}^{bc} \hat{P}(ab), \tag{26}$$

which is shown in Appendix A. The operator $\hat{P}(pq)$ gives the current term minus a similar term with indices p and q switched,

$$\hat{P}(pq) = 1 - \hat{P}_{pq} \tag{27}$$

where $\hat{P}_{pq}$ permutes the indices p and q.

Now to the second and last term

$$\left\langle \Phi_{ij}^{ab} \middle| \hat{H}_I \hat{T}_2 \middle| c \right\rangle = \frac{1}{16} \sum_{cd} \sum_{kl} t_{kl}^{cd} \sum_{pqrs} \langle c| a_i^\dagger a_j^\dagger a_b a_a \{a_p^\dagger a_q^\dagger a_s a_r\} a_c^\dagger a_d^\dagger a_l a_k |c\rangle \tag{28}$$

By using Wicks generalized theorem we see that this can be written as

$$\left\langle \Phi_{ij}^{ab} \middle| \hat{H}_I \hat{T}_2 \middle| c \right\rangle = \frac{1}{2} \sum_{cd} t_{ij}^{cd} \langle ab|\hat{v}|cd\rangle + \frac{1}{2} \sum_{kl} t_{kl}^{ab} \langle kl|\hat{v}|ij\rangle + \hat{P}(ab)\hat{P}(ij) \sum_{kc} t_{jk}^{bc} \langle ak|\hat{v}|ic\rangle \tag{29}$$

because of the anti-symmetry of $t_{kl\ldots}^{cd\ldots}$ and the anti-symmetry of the matrix elements. The derivation is given in appendix A. The final term of eq. 25 will be zero since we have the normal ordered terms of the Hamiltonian next to the reference vacuum ket.

For the third term in eq. 25 we proceed in the same manner. First we have

$$\left\langle \Phi_{ij}^{ab} \middle| [[E_{\text{ref}}, \hat{T}_2], \hat{T}_2] \middle| c \right\rangle = 0$$

since E_{ref} is a constant. Next we have

$$\left\langle \Phi_{ij}^{ab} \middle| [[\hat{F}, \hat{T}_2], \hat{T}_2] \middle| c \right\rangle = \left\langle \Phi_{ij}^{ab} \middle| (\hat{F}\hat{T}_2^2 - \hat{T}_2^2 \hat{F}) \middle| c \right\rangle = 0$$

since $\hat{T}_2^2$ creates 4p-4h while $\hat{F}$ is a one-body operator. Finally we have

$$\left\langle \Phi_{ij}^{ab} \middle| [[\hat{H}_I, \hat{T}_2], \hat{T}_2] \middle| c \right\rangle = \left\langle \Phi_{ij}^{ab} \middle| \hat{H}_I \hat{T}_2^2 \middle| c \right\rangle - \left\langle \Phi_{ij}^{ab} \middle| \hat{T}_2^2 \hat{H}_I \middle| c \right\rangle$$

where the final term becomes zero since $\hat{H}_I$ is normal ordered. We are then left with

$$
\begin{aligned}
\frac{1}{2} \left\langle \Phi_{ij}^{ab} \middle| [[\hat{H}_I, \hat{T}_2], \hat{T}_2] \middle| c \right\rangle = \frac{1}{2} \left\langle \Phi_{ij}^{ab} \middle| \hat{H}_I \hat{T}_2^2 \middle| c \right\rangle = {} & \frac{1}{4} \sum_{klcd} \langle kl|\hat{v}|cd\rangle \, t_{kl}^{ab} t_{ij}^{cd} \\
& - \frac{1}{2} \hat{P}(ij) \sum_{klcd} \langle kl|\hat{v}|cd\rangle \, t_{il}^{ab} t_{kj}^{cd} \\
& - \hat{P}(ab) \sum_{klcd} \langle kl|\hat{v}|cd\rangle \, t_{ik}^{ac} t_{lj}^{bd} \\
& - \frac{1}{2} \hat{P}(ab) \sum_{klcd} \langle kl|\hat{v}|cd\rangle \, t_{ij}^{ac} t_{kl}^{bd}
\end{aligned}
$$

The derivation is given in appendix A. All the subsequent terms of eq. 25 will be zero. This can be explained by the fact that the n'th term will contain $\hat{T}_2^{n-1}$, which for $n \geq 4$ will result in zero due to the Slater-Condon rules.

Collecting all the terms finally gives

$$
\begin{aligned}
\left\langle \Phi_{ij}^{ab} \middle| \overline{H} \middle| c \right\rangle = {} & \langle ab|\hat{v}|ij\rangle + \hat{P}(ij) \sum_k f_i^k t_{jk}^{ab} - \hat{P}(ab) \sum_c f_c^a t_{ij}^{bc} \\
& + \frac{1}{2} \sum_{kl} \langle kl|\hat{v}|ij\rangle \, t_{kl}^{ab} + \hat{P}(ab)\hat{P}(ij) \sum_{kc} \langle ak|\hat{v}|ic\rangle \, t_{jk}^{bc} \\
& + \frac{1}{2} \sum_{cd} \langle ab|\hat{v}|cd\rangle \, t_{ij}^{cd} + \frac{1}{4} \sum_{klcd} \langle kl|\hat{v}|cd\rangle \, t_{kl}^{ab} t_{ij}^{cd} - \frac{1}{2}\hat{P}(ij) \sum_{klcd} \langle kl|\hat{v}|cd\rangle \, t_{il}^{ab} t_{kj}^{cd} \\
& - \hat{P}(ab) \sum_{klcd} \langle kl|\hat{v}|cd\rangle \, t_{ik}^{ac} t_{lj}^{bd} - \frac{1}{2}\hat{P}(ab) \sum_{klcd} \langle kl|\hat{v}|cd\rangle \, t_{ij}^{ac} t_{kl}^{bd} = 0
\end{aligned}
$$

By observing that

$$\hat{P}(ij) \sum_k f_i^k t_{jk}^{ab} = \hat{P}(ij) f_i^i t_{ji}^{ab} + \hat{P}(ij) \sum_{k \neq i} f_i^k t_{jk}^{ab} = -f_i^i t_{ij}^{ab} - f_j^j t_{ij}^{ab} + \hat{P}(ij) \sum_{k \neq i} f_i^k t_{jk}^{ab}$$

and that

$$\hat{P}(ab) \sum_c f_c^a t_{ij}^{bc} = \hat{P}(ab) f_a^a t_{ij}^{ba} + \hat{P}(ab) \sum_{c \neq a} f_c^a t_{ij}^{bc} = -f_a^a t_{ij}^{ab} - f_b^b t_{ij}^{ab} + \hat{P}(ab) \sum_{c \neq a} f_c^a t_{ij}^{bc}$$

we can rewrite the above equation as

$$
\begin{aligned}
t_{ij}^{ab} D_{ab}^{ij} = {} & \langle ab|\hat{v}|ij\rangle + \hat{P}(ij) \sum_{k \neq i} f_i^k t_{jk}^{ab} - \hat{P}(ab) \sum_{c \neq a} f_c^a t_{ij}^{bc} \\
& + \frac{1}{2} \sum_{kl} \langle kl|\hat{v}|ij\rangle \, t_{kl}^{ab} + \hat{P}(ab)\hat{P}(ij) \sum_{kc} \langle ak|\hat{v}|ic\rangle \, t_{jk}^{bc} \\
& + \frac{1}{2} \sum_{cd} \langle ab|\hat{v}|cd\rangle \, t_{ij}^{cd} + \frac{1}{4} \sum_{klcd} \langle kl|\hat{v}|cd\rangle \, t_{kl}^{ab} t_{ij}^{cd} - \frac{1}{2}\hat{P}(ij) \sum_{klcd} \langle kl|\hat{v}|cd\rangle \, t_{il}^{ab} t_{kj}^{cd} \qquad (30) \\
& - \hat{P}(ab) \sum_{klcd} \langle kl|\hat{v}|cd\rangle \, t_{ik}^{ac} t_{lj}^{bd} - \frac{1}{2}\hat{P}(ab) \sum_{klcd} \langle kl|\hat{v}|cd\rangle \, t_{ij}^{ac} t_{kl}^{bd}
\end{aligned}
$$

with $D_{ab}^{ij} = f_i^i + f_j^j - f_a^a - f_b^b$. Dividing the above equation by this factor, we can find t_{ij}^{ab} with an iterative scheme. Defining the initial guess as

$$t_{ij}^{ab(0)} = \frac{\langle ab|\hat{v}|ij\rangle}{D_{ab}^{ij}} \tag{31}$$

we see by inserting this into the CCD energy equation 24 that we get the second-order perturbation theory energy expression

$$E_{\text{CCD}} = E_{\text{ref}} + \frac{1}{4} \sum_{abij} \frac{\langle ab|\hat{v}|ij\rangle \, \langle ij|\hat{v}|ab\rangle}{D_{ab}^{ij}} \tag{32}$$

Furthermore, if the single particle functions are given by the Hartree-Fock solution

$$|i\rangle = \sum_{\alpha} C_{i\alpha} |\alpha\rangle$$

where $|\alpha\rangle$ is our orthonormal single particle basis, we see that

$$\hat{P}(ij) \sum_{k \neq i} f_i^k t_{jk}^{ab} - \hat{P}(ab) \sum_{c \neq a} f_c^a t_{ij}^{bc} = 0$$

since the Hartree Fock basis functions are the eigenfunctions of the Fock matrix and f_p^q will hence be diagonal in this basis.

The python class used to estimate the ground state energy with CCD is called 'Quantum.py' and can be found in our github [8].

2.3   Configuration Interaction vs. Coupled Cluster

For Configuration interaction theory, we use a linear excitation operator for our wave function ansatz

$$\Psi^{CI} = (1 + \hat{C}) |c\rangle = (1 + \hat{C}_1 + \hat{C}_2 + \cdots) |c\rangle$$

where $\hat{C}_1$ is a single excitation operator, $\hat{C}_2$ is a double excitation operator, etc. In our task, we will restrict ourselves to the CIS approximation, which means that the ansatz for the ground state energy will be

$$\Psi^{CIS} = (1 + \hat{C}_1) |c\rangle$$

For Coupled Cluster theory however, we instead use the expression

$$\Psi^{CC} = (1 + \hat{T}_1 + \frac{1}{2!}\hat{T}_1^2 + \frac{1}{3!}\hat{T}_1^3 + \hat{T}_2 + \frac{1}{2!}\hat{T}_2^2 + \cdots) |c\rangle$$

where just like with CI, $\hat{T}_1$ is a single excitation operator, $\hat{T}_2$ is a double excitation operator, etc. The above expression matches that of a power series expansion of an exponential function, which is the reason for the expression in eq. 8. We will also limit ourselves to the CCD approximation, and we will therefore in this case end up with the following ansatz for the ground state

$$\Psi^{CCD} = (1 + \hat{T}_2 + \frac{1}{2}\hat{T}_2^2) |c\rangle$$

The above expression implicitly includes higher excitation levels than doubles as we are dealing with the inclusion of $\hat{T}_2^2$ [3].

3 Results

In Project 1 we estimated the ground state energy of Helium and Beryllium using Configuration Interaction (CI) and Hartree-Fock (HF), and in this project we have added Coupled Cluster Doubles with and without Hartree-Fock basis to our toolbox. For comparison, the results from Project 1 are included with reference to [7] and [5], and we also add the energy from second order perturbation theory (MBPT), which is our initial guess (eq. 32).

3.1 The Helium atom

Table 2: *Ground state energy of the Helium atom calculated using Configuration Interaction Singles (CIS), Hartree-Fock (HF), second order Many-body Perturbation theory (MBPT) and Coupled Cluster Doubles (CCD). The latter was calculated with and without HF-basis.*

Method	Energy [a.u.]	Relative error
Experimental	-2.903694	0.00%
Reference	-2.750000	5.29%
CIS	-2.838648	2.24%
$\text{HF}_{1 \text{ iteration}}$	-2.829193	2.56%
$\text{HF}_{\text{converge}}$	-2.831096	2.50%
$\text{MBPT}_{2\text{nd order}}$	-2.751508	5.24%
E_{CCD}	-2.751408	5.24%
$\text{E}_{\text{CCD, HF-basis}}$	-2.839144	2.22%

3.2 The Beryllium atom

Table 3: *Ground state energy of the Beryllium atom calculated using Configuration Interaction Singles (CIS), Hartree-Fock (HF), second order Many-body Perturbation theory (MBPT) and Coupled Cluster Doubles (CCD). The latter was calculated with and without HF-basis.*

Method	Energy [a.u.]	Relative error
Experimental	-14.6674	0.00%
Reference	-13.7160	6.49%
CIS	-14.3621	2.08%
$\text{HF}_{1 \text{ iteration}}$	-14.4998	1.14%
$\text{HF}_{\text{converge}}$	-14.5083	1.08%
$\text{MBPT}_{2\text{nd order}}$	-13.7174	6.47%
E_{CCD}	-13.7211	6.45%
$\text{E}_{\text{CCD, HF-basis}}$	-14.5129	1.05%

4 Discussion

As we can see from both the results for Helium and for Beryllium, table 2 and table 3 respectively, the CCD method with our single particle basis did not provide better results than our previous calculations. The relative error of 5.24% for Helium with respect to the experimental value is only

a slight improvement over the reference vacuum expectation value, which provided a relative error of 5.29%. It is also worth noting that our initial guess, which corresponds to second order MBPT, provided an estimate closer to the experimental results than when letting the CCD algorithm converge. For the Beryllium atom, we got a relative error of 6.45% which is still not great when compared to the other results and compared to the relative error of 6.49% for the reference vacuum expectation value. However, letting the algorithm converge did provide a slightly better estimate than for MBPT, which had a relative error of 6.47%. Subsection 2.3 states an important fact that could explain the underwhelming results of CCD. We would expect this method to perform well since it implicitly contains higher order excitations than doubles. However, since our basis (see table 1) only contains six states, we will not be able to make use of this property as Helium only has two electrons to excite and Beryllium only has two available particle states to excite to. The results of CIS for both Helium and Beryllium being more accurate, with a relative error of 2.24% and 2.08% respectively, seems to therefore suggest that the single excitations are more important in these cases than the double excitations. We would expect CCSD to perform better and it would be interesting to implement this method in later studies.

When instead using CCD with the Hartree-Fock basis, we achieved a much better result. For the Helium atom we beat the current champion, the CIS method, and got an energy estimate of $E_{HF}^{CCD} = -2.839144[a.u]$. This is a slight improvement over CIS, which gave the approximation $E^{CIS} = -2.838648[a.u]$, but it is an improvement none the less. For the Beryllium atom we also beat the previous best, the Hartree-Fock method, and got the energy $E_{HF}^{CCD} = -14.5129[a.u]$. This is also a slight improvement as Hartree-Fock gave $E_{HF} = -14.4998[a.u]$. This is the expected behavious when introducing the HF basis as we replace the reference energy in eq. 24 by the Hartree-Fock energy, $HF_{converge}$, which is already a significantly better approximation. We also expected the correction term to give an even better result, which is exactly what happened.

5 Conclusion

When compared to our obtained energies for HF and CIS, we did not see an improvement with the CCD method using our single particle basis for either of the atoms. The results were in fact just a minor enhancement when compared to the reference vacuum expectation value. We argued that the underwhelming results were due to the fact that our basis only included six states, and the implicit inclusion of higher excitation levels than doubles in the CCD method would therefore not be exploited.

However, when switching over to the HF basis we obtained a drastic improvement. For both Helium and Beryllium, the CCD method with the HF basis gave the best results yet with an energy of -2.839144 [a.u.] and -14.5129 [a.u.], respectively. This was in agreement with our expectations as the reference energy in equation 24 is replaced by the HF energy, which is already a significantly better approximation.

A   Calculations of amplitude equations

Because derivation of the amplitude equation is quite long, we decided to move it to an appendix to keep the text neat and clean.

The first amplitude term, $\left\langle \Phi_{ij}^{ab} \middle| \hat{F}\hat{T}_2 \middle| c \right\rangle$, will be carefully calculated using Wick's generalized theorem and symmetry arguments. Thereafter we will turn to the other terms and skip the contraction lines.

$$\left\langle \Phi_{ij}^{ab} \middle| \hat{F}\hat{T}_2 \middle| c \right\rangle = \frac{1}{4} \sum_{pq} \sum_{cdkl} f_q^p t_{kl}^{cd} \left\langle c | \{a_i^\dagger a_j^\dagger a_b a_a\}\{a_p^\dagger a_q\}\{a_c^\dagger a_d^\dagger a_l a_k\} | c \right\rangle \tag{33}$$

$$= \frac{1}{4} \sum_{pq} \sum_{cdkl} f_q^p t_{kl}^{cd} \hat{P}(ij)\hat{P}(ab)\hat{P}(cd) \left\langle c | a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q a_c^\dagger a_d^\dagger a_l a_k | c \right\rangle$$

$$+ \frac{1}{4} \sum_{pq} \sum_{cdkl} f_q^p t_{kl}^{cd} \hat{P}(ij)\hat{P}(ab)\hat{P}(lk) \left\langle c | a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q a_c^\dagger a_d^\dagger a_l a_k | c \right\rangle \tag{34}$$

$$= \frac{1}{4} \sum_{pq} \sum_{cdkl} f_q^p t_{kl}^{cd} \hat{P}(ij)\hat{P}(ab) \Big[\delta_{ik}\delta_{jl}\delta_{bd}\delta_{ap}\delta_{qc} - \delta_{ik}\delta_{jl}\delta_{bc}\delta_{ap}\delta_{qd}$$

$$- \delta_{ik}\delta_{jq}\delta_{bd}\delta_{ac}\delta_{pl} + \delta_{il}\delta_{jq}\delta_{bd}\delta_{ac}\delta_{pk} \Big] \tag{35}$$

$$= \frac{1}{4} \sum_c f_c^a t_{ij}^{cb} \hat{P}(ij)\hat{P}(ab) - \frac{1}{4} \sum_d f_d^a t_{ij}^{bd} \hat{P}(ij)\hat{P}(ab)$$

$$- \frac{1}{4} \sum_l f_j^l t_{il}^{ab} \hat{P}(ij)\hat{P}(ab) + \frac{1}{4} \sum_k f_j^k t_{ki}^{ab} \hat{P}(ij)\hat{P}(ab) \tag{36}$$

$$= \frac{1}{2} \sum_c f_c^a t_{ij}^{cb} \hat{P}(ij)\hat{P}(ab) - \frac{1}{2} \sum_k f_j^k t_{ik}^{ab} \hat{P}(ij)\hat{P}(ab) \tag{37}$$

$$= \sum_k f_i^k t_{jk}^{ab} \hat{P}(ij) - \sum_c f_c^a t_{ij}^{bc} \hat{P}(ab) \tag{38}$$

The second term is calculated similarly,

$$\left\langle \Phi_{ij}^{ab}\middle|\hat{H}_I\hat{T}_2\middle|c\right\rangle = \frac{1}{16}\sum_{pqrs}\sum_{cdkl} t_{kl}^{cd}\left\langle pq|\hat{v}|rs\right\rangle \left\langle c|\{a_i^\dagger a_j^\dagger a_b a_a\}\{a_p^\dagger a_q^\dagger a_s a_r\}\{a_c^\dagger a_d^\dagger a_l a_k\}|c\right\rangle \tag{39}$$

$$= \frac{1}{16}\sum_{pqrs}\sum_{cdkl} t_{kl}^{cd}\left\langle pq|\hat{v}|rs\right\rangle \Big[\hat{P}(ij)\hat{P}(ab)\hat{P}(pq)\delta_{ir}\delta_{js}\delta_{bd}\delta_{ac}\delta_{pk}\delta_{ql}$$

$$+\hat{P}(ij)\hat{P}(ab)\hat{P}(rs)\delta_{ik}\delta_{jl}\delta_{bq}\delta_{ap}\delta_{sd}\delta_{rc}$$

$$-\hat{P}(ij)\hat{P}(ab)\hat{P}(pq)\hat{P}(sr)\hat{P}(cd)\hat{P}(lk)\delta_{ik}\delta_{js}\delta_{bd}\delta_{ap}\delta_{ql}\delta_{rc}\Big] \tag{40}$$

$$= \frac{1}{16}\hat{P}(ij)\hat{P}(ab)\Big[\sum_{cd} t_{ij}^{cd}\big(\left\langle ab|\hat{v}|cd\right\rangle - \left\langle ab|\hat{v}|dc\right\rangle\big)\Big]$$

$$+\frac{1}{16}\hat{P}(ij)\hat{P}(ab)\Big[\sum_{kl} t_{kl}^{ab}\big(\left\langle kl|\hat{v}|ij\right\rangle - \left\langle lk|\hat{v}|ij\right\rangle\big)\Big]$$

$$-\frac{1}{16}\hat{P}(ij)\hat{P}(ab)\Big[\sum_{lc} t_{il}^{cb}\left\langle al|\hat{v}|cj\right\rangle - \sum_{kc} t_{ki}^{cb}\left\langle ak|\hat{v}|cj\right\rangle$$

$$-\sum_{ld} t_{il}^{bd}\left\langle al|\hat{v}|dj\right\rangle + \sum_{kd} t_{ki}^{bd}\left\langle ak|\hat{v}|dj\right\rangle$$

$$-\sum_{lc} t_{il}^{cb}\left\langle al|\hat{v}|jc\right\rangle + \sum_{kc} t_{ki}^{cb}\left\langle ak|\hat{v}|jc\right\rangle$$

$$+\sum_{ld} t_{il}^{bd}\left\langle al|\hat{v}|jd\right\rangle - \sum_{kd} t_{ki}^{bd}\left\langle ak|\hat{v}|jd\right\rangle$$

$$+\sum_{lc} t_{il}^{cb}\left\langle la|\hat{v}|jc\right\rangle - \sum_{kc} t_{ki}^{cb}\left\langle ka|\hat{v}|jc\right\rangle$$

$$-\sum_{ld} t_{il}^{bd}\left\langle la|\hat{v}|jd\right\rangle + \sum_{kd} t_{ki}^{bd}\left\langle ka|\hat{v}|jd\right\rangle$$

$$-\sum_{lc} t_{il}^{cb}\left\langle la|\hat{v}|cj\right\rangle + \sum_{kc} t_{ki}^{cb}\left\langle ka|\hat{v}|cj\right\rangle$$

$$+\sum_{ld} t_{il}^{bd}\left\langle la|\hat{v}|dj\right\rangle - \sum_{kd} t_{ki}^{bd}\left\langle ka|\hat{v}|dj\right\rangle\Big] \tag{41}$$

$$= \frac{1}{2}\sum_{cd}\left\langle ab|\hat{v}|cd\right\rangle t_{ij}^{cd} + \frac{1}{2}\sum_{kl}\left\langle kl|\hat{v}|ij\right\rangle t_{kl}^{ab} + \hat{P}(ab)\hat{P}(ij)\sum_{kc}\left\langle ak|\hat{v}|ic\right\rangle t_{jk}^{bc}. \tag{42}$$

The last term we need to calculate, is the following

$$\left\langle \Phi_{ij}^{ab}\middle|\hat{H}_I\hat{T}_2^2\middle|c\right\rangle = \frac{1}{64}\sum_{pqrs}\sum_{cdkl}\sum_{efmn} t_{kl}^{cd}t_{mn}^{ef}\left\langle pq|\hat{v}|rs\right\rangle \left\langle c|\{a_i^\dagger a_j^\dagger a_b a_a\}\{a_p^\dagger a_q^\dagger a_s a_r\}\{a_c^\dagger a_d^\dagger a_l a_k\}\{a_e^\dagger a_f^\dagger a_n a_m\}|c\right\rangle \tag{43}$$

which can be calculated in the same way as the previous terms. However, it is a tedious affair since there are hundreds of ways we can draw the contraction lines. Even though the permutation operators give some simplifications, it is not a tempting exercise to do. Instead, we turn to diagrammatic representation which is known to be more efficient. First, let us recall the operators

$$\hat{T}_2 = \frac{1}{4}\sum_{abij} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i$$

$$\hat{H}_I = \frac{1}{4}\sum_{pqrs}\left\langle pq|\hat{v}|rs\right\rangle \{a_p^\dagger a_q^\dagger a_s a_r\}.$$

As we can see, $\hat{T}_2$ creates two particles and annihilates two holes, and can by a diagram be represented as
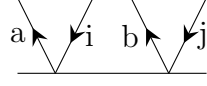
with the convention that particles point upwards and holes point downwards. Further, $\hat{H}_I$ is initially not restricted, i.e, the operators can either be particles or holes.

Nevertheless, the only term that do contribute, is when the operator annihilates two particles and creates two holes, corresponding to two particles lines into the vertex and two hole lines out from the vertex:
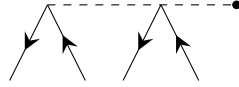
We will henceforth skip labeling of lines. The diagrams that represent the operator $\hat{H}_I\hat{T}_2\hat{T}_2$ is simply all unique connections between the operators with hole lines on hole lines and particle lines on particle lines. It turns out to be five unique connections,

$$\frac{1}{2}\left\langle\Phi_{ij}^{ab}\big|\hat{H}_I\hat{T}_2^2\big|c\right\rangle =$$

which can be represented diagrammatically by

$$\frac{1}{2}\left\langle\Phi_{ij}^{ab}\middle|\hat{H}_I\hat{T}_2^2\middle|c\right\rangle =$$

To convert the diagrams to ordinary equations, we need to introduce some diagrammatic rules. We will focus on the rules that we use for those specific diagrams, the reader should be aware that there exist more rules (for instance, we ignore all one-body rules).

1. The sign is found from the rule $(-1)^{h-l}$ where h is the total number of hole lines, and l is the total number of loops (internal and external). External loops are loops that are made with a line going from $ijk\ldots$ to $abc\ldots$.

2. For each pair of lines which connect the two same vertices in the same direction, one needs to add a factor $1/2$.

3. For each pair of equivalent $\hat{T}_m$ vertices, one needs to add a factor $1/2$. Equivalent $\hat{T}_m$ vertices are vertices with the same number of line pairs that are connected to the interaction vertex in the same way.

4. Any two-particle interaction vertex line is associated with an antisymmetric two-electron integral on the form $\langle$left-out, right-out$||$left-in, right-in$\rangle$

5. One should sum over all distinct permutations $\hat{P}$, i.e, permutations that give unique terms.

6. Disconnected terms (terms with operators that are neither directly nor indirectly connected) do always cancel with other terms, and can be ignored.

For the first diagram, we have $h = 4$ and $l = 2$ due to two external lines, such that the term is positive. We have a pair of lines connecting the right-hand-side $\hat{T}_2$-vertex to the interaction vertex, and a pair connecting the left-hand-side $\hat{T}_2$-vertex to the interaction line. Since we do not have any equivalent $\hat{T}_m$ vertices nor distinct permutations, we end up with a prefactor $1/4$.

 $= \frac{1}{4}\sum_{klcd} t_{kl}^{ab} t_{ij}^{cd} \langle kl|\hat{v}|cd\rangle$

The second diagram has $h = 4$ and $l = 4$, such that the sign again is positive. This diagram has two equivalent $\hat{T}_m$ vertices (due to the symmetry), such that we get a factor $1/2$. We need to permute $\hat{P}(ab)$ and $\hat{P}(ij)$, but it turns out that they give the same terms such that we can choose which one to use and remove the factor in front. Using the same permutation operator as in the project description, the result is

$$= \hat{P}(ab) \sum_{klcd} t_{ik}^{ac} t_{lj}^{db} \langle kl|\hat{v}|cd \rangle$$

Going further to the third term, we see that this term has one internal loop and two external, giving a negative sign. We have a pair of lines connecting the right-hand-side $\hat{T}_2$-vertex to the interaction vertex in the same direction, giving a factor $1/2$. In addition we need to permute a, b since they point from two different vertices, and we obtain

$$= -\frac{1}{2}\hat{P}(ab) \sum_{klcd} t_{kl}^{ca} t_{ij}^{cb} \langle kl|\hat{v}|cd \rangle$$

The understanding of the fourth diagram is similar to the third one, but now all the particle lines are replaced by hole lines and vice versa. We have one internal line and two external lines, giving a negative sign. The factor is again $1/2$, due to two lines going between the left-hand-side $\hat{T}_2$-vertex and the interaction vertex in the same direction. Now i and j are connected to different vertices, such that we need to permute them.

$$= -\frac{1}{2}\hat{P}(ij) \sum_{klcd} t_{ki}^{cd} t_{lj}^{ab} \langle kl|\hat{v}|cd \rangle$$

The final diagram is affected by the final rule, and cancel since it is both disconnected and unlinked. In fact, it cancel out the energy in the amplitude equations. [4]

Thus, we end up with the total expression

$$
\begin{aligned}
\frac{1}{2} \left\langle \Phi_{ij}^{ab} \middle| \hat{H}_I \hat{T}_2^2 \middle| c \right\rangle =& \frac{1}{4} \sum_{klcd} \langle kl|\hat{v}|cd \rangle \, t_{kl}^{ab} t_{ij}^{cd} \\
&- \frac{1}{2}\hat{P}(ij) \sum_{klcd} \langle kl|\hat{v}|cd \rangle \, t_{il}^{ab} t_{kj}^{cd} \\
&- \hat{P}(ab) \sum_{klcd} \langle kl|\hat{v}|cd \rangle \, t_{ik}^{ac} t_{lj}^{bd} \\
&- \frac{1}{2}\hat{P}(ab) \sum_{klcd} \langle kl|\hat{v}|cd \rangle \, t_{ij}^{ac} t_{kl}^{bd}
\end{aligned}
$$

where we have made use of the antisymmetric property of the amplitudes.

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