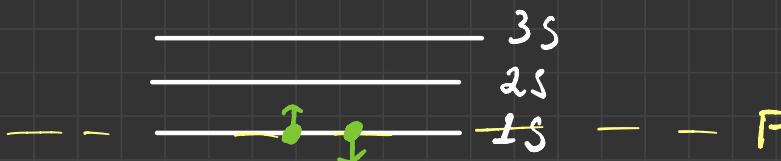


a) He with s.p orbits $1s$ $2s$ $3s$ and spin

1. Ansatz for ground state $|c\rangle = |\Phi_0\rangle$

Each single particle state can have up to 2 particles due to spin



$$\text{with } \sigma = \{\pm\}$$

Also, let $1s \equiv 1$, $2s \equiv 2$ and $3s \equiv 3$

The ground state can be written

$$|\bar{\Phi}_0\rangle = a_{1+}^+ a_{1-}^+ |0\rangle$$

And the possible single particle states:

$$a_{1+}^+ |0\rangle, a_{1-}^+ |0\rangle, a_{2+}^+ |0\rangle, a_{2-}^+ |0\rangle$$

$$a_{3+}^+ |0\rangle, a_{3-}^+ |0\rangle$$

we define the Fermi Level as $F=1s$

Then Hole States are vacancies of the $1s$ state, and particle states

Are excitations above 1S.

Therefore, the $|\bar{\Phi}_i^a\rangle$ excitations:

$$|\bar{\Phi}_{1+}^{2+}\rangle = a_{2+}^+ a_{1+} | \bar{\Phi}_0 \rangle \quad |\bar{\Phi}_{1-}^{2-}\rangle = a_{2-}^+ a_{1-} | \bar{\Phi}_0 \rangle$$

$$|\bar{\Phi}_{1+}^{3+}\rangle = a_{3+}^+ a_{1+} | \bar{\Phi}_0 \rangle \quad |\bar{\Phi}_{1-}^{3-}\rangle = a_{3-}^+ a_{1-} | \bar{\Phi}_0 \rangle$$

And $|\bar{\Phi}_{ij}^{ab}\rangle$ excitations:

$$|\bar{\Phi}_{1+1-}^{2+2-}\rangle = a_{2+}^+ a_{2-}^+ a_{1+} a_{1-} | \bar{\Phi}_0 \rangle$$

$$|\bar{\Phi}_{1+1-}^{3+3-}\rangle = a_{3+}^+ a_{3-}^+ a_{1+} a_{1-} | \bar{\Phi}_0 \rangle$$

B) Writing \hat{H} in normal ordered form

write $\hat{H} = \hat{H}_0 + \hat{H}_I$ with

$$\hat{H}_0 = \boxed{\sum_{pq} \langle p | \hat{h}_0 | q \rangle a_p^\dagger a_q} + \sum_i \langle i | \hat{h}_0 | i \rangle$$

$$\hat{H}_I = \boxed{\frac{1}{4} \sum_{pqst} \langle pq | \hat{V} | st \rangle_{AS} a_p^\dagger a_q^\dagger a_t a_s}^B$$

$$+ \boxed{\sum_{pq_i} \langle pi | \hat{V} | q_i \rangle_{AS} a_p^\dagger a_q}^C$$

$$+ \frac{1}{2} \sum_{ij} \langle ij | \hat{V} | ij \rangle_{AS}$$

we see that all chains of creation
annihilation operators are normal-ordered

$$\text{so } \langle \Phi_0 | \textcircled{A} | \Phi_0 \rangle = \langle \Phi_0 | \textcircled{B} | \Phi_0 \rangle = \langle \Phi_0 | \textcircled{C} | \Phi_0 \rangle = 0$$

therefore

$$\langle \Phi_0 | \hat{H} | \Phi_0 \rangle = \sum_i \langle i | \hat{h}_0 | i \rangle + \frac{1}{2} \sum_{ij} \langle ij | \hat{V} | ij \rangle \quad \text{AS}$$

where $i, j \in F$, meaning that

$i, j \in \{1+, 1-\}$ So that :

$$\begin{aligned} E(\Phi_0) &= \langle 1+ | \hat{h}_0 | 1+ \rangle + \langle 1- | \hat{h}_0 | 1- \rangle + \\ &\frac{1}{2} \left(\langle 1+ 1- | \hat{V} | 1+ 1- \rangle - \cancel{\langle 1+ 1- | \hat{V}^0 | 1- 1+ \rangle} \right. \\ &\quad \left. + \langle 1- 1+ | \hat{V} | 1- 1+ \rangle - \cancel{\langle 1- 1+ | \hat{V}^0 | 1+ 1- \rangle} \right) \\ &= -2^2 + \langle 11 | \hat{V} | 11 \rangle \\ &= -2^2 + 5 \cdot \frac{e}{8} = -2.75 \text{ atomic units} \end{aligned}$$

c) The possible 1 particle 1 hole excitations are:

$$|\Phi_{1+}^{2+}\rangle = a_{2+}^+ a_{1+} | \Phi_0 \rangle \quad | \Phi_{1-}^{2-}\rangle = a_{2-}^+ a_{1-} | \Phi_0 \rangle$$

$$|\Phi_{1+}^{3+}\rangle = a_{3+}^+ a_{1+} | \Phi_0 \rangle \quad | \Phi_{1-}^{3-}\rangle = a_{3-}^+ a_{1-} | \Phi_0 \rangle$$

Let us write $\hat{H} = E_0^{\text{Ref}} + \hat{F} + \hat{V}$ with

$$\hat{F} = \sum_{pq} \langle p | \hat{f} | q \rangle \{ a_p^+ a_q \}$$

$$\hat{V} = \frac{1}{4} \sum_{pqrs} \langle pq | \hat{V} | rs \rangle_{\text{AS}} \{ a_p^+ a_q^+ a_s a_r \}$$

But notice:

$$\langle c | \hat{H} | \Phi_i^a \rangle = E_0^{\text{Ref}} \langle c | \underbrace{a_a^+ a_i}_= | c \rangle$$

only contribution

$$\left\{ + \sum_{pq} \langle p | \hat{f} | q \rangle \langle c | a_p^+ a_q^+ a_a^+ a_i | c \rangle \right.$$

$\boxed{\delta_{qa}}$ $\boxed{\delta_{pi}}$

Always has a contraction

$$\left\{ + \frac{1}{4} \sum_{pqrs} \langle pq | \hat{V} | rs \rangle \langle c | \underbrace{a_p^+ a_q^+ a_s a_r}_{=0} \underbrace{a_a^+ a_i}_= | c \rangle \right.$$

$$\text{So } \langle \Phi_0 | \hat{H} | \Phi_i^a \rangle = \langle i | \hat{h}_0 | a \rangle + \sum_j \langle ij | \hat{V} | aj \rangle_{\text{AS}}$$

but $\langle i | \hat{h}_0 | j \rangle = -e^2 / 2m^2 \delta_{ij}$, so $\langle i | \hat{h}_0 | a \rangle = 0$

So, for our $1p1h$ excitations of He,

$$\begin{aligned}\langle c | \hat{H} | \Phi_{1+}^{2+} \rangle &= \sum_j \langle 1+j | \hat{V} | 2+j \rangle_{AS} \\ &= \langle 1+1- | \hat{V} | 2+1- \rangle_{AS} + \langle 1+1+ | \hat{V} | 2+1+ \rangle_{AS}\end{aligned}$$

Similarly

$$\begin{aligned}\langle c | \hat{H} | \Phi_{1-}^{2-} \rangle &= \sum_j \langle 1-j | \hat{V} | 2-j \rangle_{AS} & \langle c | \hat{H} | \Phi_{1+}^{3+} \rangle &= \sum_j \langle 1+j | \hat{V} | 3+j \rangle_{AS} \\ \langle c | \hat{H} | \Phi_{1-}^{3-} \rangle &= \sum_j \langle 1-j | \hat{V} | 3-j \rangle_{AS}\end{aligned}$$

where $j \in \{1-, 1+\}$.

For $2p\cdot2h$, it follows, if $a \neq b$ and $i \neq j$

$$\langle \Phi_i^a | \hat{H} | \Phi_j^b \rangle = \langle a_j | \hat{V} | i_b \rangle_{AS}$$

because

$$\left. \begin{aligned} E_0 \langle \Phi_0 | a_i^+ a_a a_b a_j^+ | \Phi_0 \rangle \\ \quad \boxed{\begin{array}{c} a_i^+ a_a \\ a_b \\ a_j^+ \end{array}} = 0 \\ \quad \boxed{\begin{array}{c} a_i^+ a_a \\ a_p \\ a_q \\ a_s \\ a_r \\ a_b \\ a_j^+ \end{array}} = 0 \end{aligned} \right\}$$

One body part
will always
have a 0
contraction

$$\langle \Phi_0 | a_i^+ a_a a_p a_q a_s a_r a_b a_j^+ | \Phi_0 \rangle = -\delta_{is} \delta_{ap} \delta_{qj} \delta_{rb}$$

$$\langle \Phi_0 | a_i^+ a_a a_p a_q a_s a_r a_b a_j^+ | \Phi_0 \rangle = -\delta_{is} \delta_{aq} \delta_{pr} \delta_{sb}$$

$$\langle \Phi_0 | a_i^+ a_a a_p a_q a_s a_r a_b a_j^+ | \Phi_0 \rangle = \delta_{ss} \delta_{ap} \delta_{ir} \delta_{qj}$$

$$\langle \Phi_0 | a_i^+ a_a a_p a_q a_s a_r a_b a_j^+ | \Phi_0 \rangle = \delta_{ir} \delta_{aq} \delta_{pr} \delta_{sb}$$

$$= \langle a_j | \hat{V} | i_b \rangle - \langle a_j | \hat{V} | b_i \rangle = \langle a_j | \hat{V} | i_b \rangle_{AS}$$

Such that

$$\langle \Phi_{1-}^{2-} | \hat{H} | \Phi_{1+}^{3+} \rangle = \langle 2-1+1V|1-3+ \rangle_{AS}$$

$$\langle \Phi_{1-}^{2-} | \hat{H} | \Phi_{1-}^{3-} \rangle = \langle 2-1-1V|1-3- \rangle_{AS}$$

$$\langle \Phi_{1+}^{2+} | \hat{H} | \Phi_{1-}^{2-} \rangle = \langle 2+1-1V|1+2- \rangle_{AS}$$

$$\langle \Phi_{1+}^{2+} | \hat{H} | \Phi_{1+}^{3+} \rangle = \langle 2+1+1V|1+3+ \rangle_{AS}$$

$$\langle \Phi_{1-}^{3-} | \hat{H} | \Phi_{1+}^{3+} \rangle = \langle 3-1+1V|1-3+ \rangle_{AS}$$

$$\langle \Phi_{1+}^{2+} | \hat{H} | \Phi_{1-}^{3-} \rangle = \langle 2+1-1V|1+3- \rangle_{AS}$$

Similarly, for the diagonal case:

$$\begin{aligned} \langle \Phi_i^a | \hat{H} | \Phi_i^a \rangle &= \langle a | \hat{f} | a \rangle - \langle i | \hat{f} | i \rangle + E_0^{\text{Ref}} \\ &= \langle a | \hat{h}_0 | a \rangle + \sum_j \langle a j | \hat{v} | a j \rangle_{AS} \\ &\quad - \left(\langle i | \hat{h}_0 | i \rangle + \sum_j \langle i j | \hat{v} | i j \rangle_{AS} \right) + E_0^{\text{Ref}} \end{aligned}$$

Hence, for our problem, and $j \in \{1-, 1+\}$

$$\begin{aligned} \langle \Phi_{1+}^{2+} | \hat{H} | \Phi_{1+}^{2+} \rangle &= \langle 2+1h_0|2+ \rangle + \sum_j \langle 2+j | \hat{v} | 2+j \rangle_{AS} \\ &\quad - \langle 1+ | \hat{h}_0 | 1+ \rangle - \sum_j \langle 1+j | \hat{v} | 1+j \rangle_{AS} + E_0^{\text{Ref}} \end{aligned}$$

$$\begin{aligned} \langle \Phi_{1-}^{2-} | \hat{H} | \Phi_{1-}^{2-} \rangle &= \langle 2-1h_0|2- \rangle + \sum_j \langle 2-j | \hat{v} | 2-j \rangle_{AS} \\ &\quad - \langle 1- | \hat{h}_0 | 1- \rangle - \sum_j \langle 1-j | \hat{v} | 1-j \rangle_{AS} + E_0^{\text{Ref}} \end{aligned}$$

$$\begin{aligned} \langle \Phi_{1-}^{3-} | \hat{H} | \Phi_{1-}^{3-} \rangle &= \langle 3-1h_0|3- \rangle + \sum_j \langle 3-j | \hat{v} | 3-j \rangle_{AS} \\ &\quad - \langle 1- | \hat{h}_0 | 1- \rangle - \sum_j \langle 1-j | \hat{v} | 1-j \rangle_{AS} + E_0^{\text{Ref}} \end{aligned}$$

$$\begin{aligned} \langle \Phi_{1+}^{3+} | \hat{H} | \Phi_{1+}^{3+} \rangle &= \langle 3+1h_0|3+ \rangle + \sum_j \langle 3+j | \hat{v} | 3+j \rangle_{AS} \\ &\quad - \langle 1+ | \hat{h}_0 | 1+ \rangle - \sum_j \langle 1+j | \hat{v} | 1+j \rangle_{AS} + E_0^{\text{Ref}} \end{aligned}$$

In diagrammatic form:

$$\langle \bar{\Phi}_0 | \hat{H} | \bar{\Phi}_i^a \rangle = \langle \dot{c} | \hat{f} | a \rangle = \langle \dot{c} | \hat{h}_0 | a \rangle + \sum_j \langle \dot{c}_j | \hat{V} | a_j \rangle$$

$$\langle \dot{c} | \hat{h}_0 | a \rangle = \text{Diagram with } i \text{ and } a \text{ connected by a dashed line, } h_0 \text{ above it} +$$

$$\sum_j \langle \dot{c}_j | \hat{V} | a_j \rangle = \text{Diagram with } i \text{ and } j \text{ connected by a dashed line, } a \text{ below it} +$$

$$-\sum_j \langle \dot{c}_j | \hat{V} | j_a \rangle = \text{Diagram with } i \text{ and } j \text{ connected by a dashed line, } a \text{ below it}$$

$$\langle \bar{\Phi}_i^a | \hat{H} | \bar{\Phi}_j^b \rangle = \langle a | \hat{f} | a \rangle - \langle \dot{c} | \hat{f} | i \rangle + E_0^{\text{ref}}$$

$$\text{where } E_0^{\text{ref}} = \sum_i \langle \dot{c}_i | \hat{h}_0 | i \rangle + \frac{1}{2} \sum_{ij} \langle \dot{c}_j | \hat{V} | i_j \rangle - \langle \dot{c}_j | \hat{V} | j_i \rangle$$

$$\text{So } E_0^{\text{ref}}: \text{Diagram with } i \text{ and } j \text{ connected by a dashed line, } h_0 \text{ above it}$$

$$\sum_{ij} \langle \dot{c}_j | \hat{V} | i_j \rangle = \text{Diagram with } i \text{ and } j \text{ connected by a dashed line, } i \text{ above it}$$

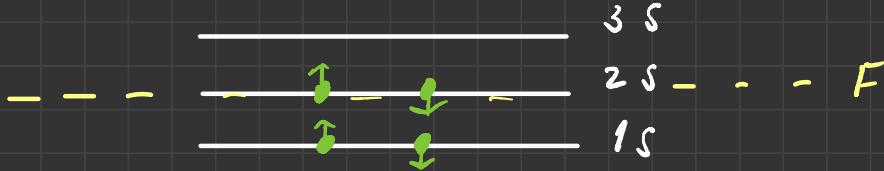
$$-\sum_{ij} \langle \dot{c}_j | \hat{V} | j_i \rangle = \text{Diagram with } i \text{ and } j \text{ connected by a dashed line, } j \text{ above it}$$

the explicit Hamiltonian was constructed in code, but it is a 5×5 matrix of the form

$$\begin{bmatrix} \langle \Psi_0 | \hat{H} | \Psi_0 \rangle & \langle \Psi_0 | \hat{H} | \Psi_{2+}^{2+} \rangle & \langle \Psi_0 | \hat{H} | \Psi_{1-}^{2-} \rangle & \langle \Psi_0 | \hat{H} | \Psi_{2+}^{3+} \rangle & \langle \Psi_0 | \hat{H} | \Psi_{1-}^{3-} \rangle \\ \langle \Psi_{2+}^{2+} | \hat{H} | \Psi_0 \rangle & \langle \Psi_{2+}^{2+} | \hat{H} | \Psi_{2+}^{2+} \rangle & \langle \Psi_{2+}^{2+} | \hat{H} | \Psi_{1-}^{2-} \rangle & \langle \Psi_{2+}^{2+} | \hat{H} | \Psi_{2+}^{3+} \rangle & \langle \Psi_{2+}^{2+} | \hat{H} | \Psi_{1-}^{3-} \rangle \\ \langle \Psi_{1-}^{2-} | \hat{H} | \Psi_0 \rangle & \langle \Psi_{1-}^{2-} | \hat{H} | \Psi_{2+}^{2+} \rangle & \langle \Psi_{1-}^{2-} | \hat{H} | \Psi_{1-}^{2-} \rangle & \langle \Psi_{1-}^{2-} | \hat{H} | \Psi_{2+}^{3+} \rangle & \langle \Psi_{1-}^{2-} | \hat{H} | \Psi_{1-}^{3-} \rangle \\ \langle \Psi_{2+}^{3+} | \hat{H} | \Psi_0 \rangle & \langle \Psi_{2+}^{3+} | \hat{H} | \Psi_{2+}^{2+} \rangle & \langle \Psi_{2+}^{3+} | \hat{H} | \Psi_{1-}^{2-} \rangle & \langle \Psi_{2+}^{3+} | \hat{H} | \Psi_{2+}^{3+} \rangle & \langle \Psi_{2+}^{3+} | \hat{H} | \Psi_{1-}^{3-} \rangle \\ \langle \Psi_{1-}^{3-} | \hat{H} | \Psi_0 \rangle & \langle \Psi_{1-}^{3-} | \hat{H} | \Psi_{2+}^{2+} \rangle & \langle \Psi_{1-}^{3-} | \hat{H} | \Psi_{1-}^{2-} \rangle & \langle \Psi_{1-}^{3-} | \hat{H} | \Psi_{2+}^{3+} \rangle & \langle \Psi_{1-}^{3-} | \hat{H} | \Psi_{1-}^{3-} \rangle \end{bmatrix}$$

After diagonalizing the matrix, the smallest eigenvalue was -2.824 which is relatively close to -2.904 considering we are only dealing with 1 particle hole excitations and several approximations

c) for Berillium, we have Schematically



So, given the Fermi level to be 2s, we have

$$|C\rangle = a_{1+}^+ a_{1-}^+ a_{2+}^+ a_{2-}^+ |0\rangle$$

The single particle states are the same as for He.

The 1ph excitations are

$$|\Phi_{1+}^{3+}\rangle = a_{3+}^+ a_{1+}^- |\Phi_0\rangle \quad |\Phi_{1-}^{3-}\rangle = a_{3-}^+ a_{1-}^- |\Phi_0\rangle$$

$$|\Phi_{2+}^{3+}\rangle = a_{3+}^+ a_{2+}^- |\Phi_0\rangle \quad |\Phi_{2-}^{3-}\rangle = a_{3-}^+ a_{2-}^- |\Phi_0\rangle$$

while the 2p2h excitations are

$$|\Phi_{2+2-}^{3+3-}\rangle = a_{3+}^+ a_{3-}^+ a_{2+}^- a_{2-}^- |\Phi_0\rangle$$

$$|\Phi_{1+1-}^{3+3-}\rangle = a_{3+}^+ a_{3-}^+ a_{1+}^- a_{1-}^- |\Phi_0\rangle$$

$$|\Phi_{1+2-}^{3+3-}\rangle = a_{3+}^+ a_{3-}^+ a_{1+}^- a_{2-}^- |\Phi_0\rangle$$

$$|\Phi_{2+1-}^{3+3-}\rangle = a_{3+}^+ a_{3-}^+ a_{2+}^- a_{1-}^- |\Phi_0\rangle$$

Since the number of 1p1h excitations is still 4, the hamiltonian matrix will still be 5x5.

We can still use the same expression for the expectation of the ground state

$$\langle \Phi_0 | \hat{H} | \Phi_0 \rangle = \sum_i \langle i | \hat{h}_0 | i \rangle + \frac{1}{2} \sum_{ij} \langle ij | \hat{V} | ij \rangle \quad \text{as}$$

But the states $i, j \in F$ are now $i, j \in \{1+, 1-, 2+, 2-\}$
so we will not open up the sums.

Again, the diagonalization can be found in the code, and the hamiltonian matrix will have the form

$$\begin{bmatrix} \langle \Phi_0 | \hat{H} | \Phi_0 \rangle & \langle \Phi_0 | \hat{H} | \Phi_{2+}^{3+} \rangle & \langle \Phi_0 | \hat{H} | \Phi_{2+}^{3-} \rangle & \langle \Phi_0 | \hat{H} | \Phi_{1-}^{3-} \rangle & \langle \Phi_0 | \hat{H} | \Phi_{2-}^{3-} \rangle \\ \langle \Phi_{2+}^{3+} | \hat{H} | \Phi_0 \rangle & \langle \Phi_{2+}^{3+} | \hat{H} | \Phi_{2+}^{3+} \rangle & \langle \Phi_{2+}^{3+} | \hat{H} | \Phi_{2+}^{3-} \rangle & \langle \Phi_{2+}^{3+} | \hat{H} | \Phi_{1-}^{3-} \rangle & \langle \Phi_{2+}^{3+} | \hat{H} | \Phi_{2-}^{3-} \rangle \\ \langle \Phi_{2+}^{3-} | \hat{H} | \Phi_0 \rangle & \langle \Phi_{2+}^{3-} | \hat{H} | \Phi_{2+}^{3+} \rangle & \langle \Phi_{2+}^{3-} | \hat{H} | \Phi_{2+}^{3-} \rangle & \langle \Phi_{2+}^{3-} | \hat{H} | \Phi_{1-}^{3-} \rangle & \langle \Phi_{2+}^{3-} | \hat{H} | \Phi_{2-}^{3-} \rangle \\ \langle \Phi_{1-}^{3-} | \hat{H} | \Phi_0 \rangle & \langle \Phi_{1-}^{3-} | \hat{H} | \Phi_{2+}^{3+} \rangle & \langle \Phi_{1-}^{3-} | \hat{H} | \Phi_{2+}^{3-} \rangle & \langle \Phi_{1-}^{3-} | \hat{H} | \Phi_{1-}^{3-} \rangle & \langle \Phi_{1-}^{3-} | \hat{H} | \Phi_{2-}^{3-} \rangle \\ \langle \Phi_{2-}^{3-} | \hat{H} | \Phi_0 \rangle & \langle \Phi_{2-}^{3-} | \hat{H} | \Phi_{2+}^{3+} \rangle & \langle \Phi_{2-}^{3-} | \hat{H} | \Phi_{2+}^{3-} \rangle & \langle \Phi_{2-}^{3-} | \hat{H} | \Phi_{1-}^{3-} \rangle & \langle \Phi_{2-}^{3-} | \hat{H} | \Phi_{2-}^{3-} \rangle \end{bmatrix}$$

Notice the ordering is slightly different because we are ordering via the particle state and "3+" < "3-" in the code

After diagonalizing the matrix, the smallest eigenvalue was -14.198 which is relatively close to -14.667 considering we are only dealing with 1 particle hole excitations and several approximations.

e) Given $\Psi_p = \sum_{\alpha} c_{p\alpha} \phi_{\alpha}$ we can write E_o^{HF}

$$\langle \Psi_0 | \hat{H} | \Psi_0 \rangle = \sum_{i \in F} \sum_{\alpha, \beta}^* c_{i\alpha}^* c_{i\beta} \langle \alpha | h_0 | \beta \rangle$$

$$+ \frac{1}{2} \sum_{i \notin F} \sum_{\alpha, \beta}^* c_{i\alpha}^* c_{j\beta}^* c_{i\gamma} c_{j\delta} \langle \alpha \beta | \hat{v} | \gamma \delta \rangle_{AS}$$

which we want to minimize. For that we introduce the following functional $F(\Psi_0)$ with Lagrangian multipliers ϵ_i :

$$F(\Psi_0) = E_o^{HF} - \sum_{i=1}^N \epsilon_i \sum_{\alpha}^* c_{i\alpha}^* c_{i\alpha}$$

where the double sum with β is gone since $\langle \alpha | \beta \rangle = \delta_{\alpha\beta}$
Now we can derive remembering $c_{i\alpha}$ and $c_{i\beta}$ are independent and fixing a specific $c_{i\alpha}^*$:

$$\frac{d}{dc_{i\alpha}} \left[F(x_0) \right] = \frac{d}{dc_{i\alpha}} \left(E_0 - \sum_{i=1}^{HF} \epsilon_i \sum_{\alpha} c_{i\alpha} c_{i\alpha} \right) = 0$$

$$= \sum_{\beta} c_{i\beta} \langle \alpha | \hat{h}_0 | \beta \rangle + \sum_{\substack{\rho, \delta \\ \rho \in F}} \sum_{\substack{\beta \\ \delta, \delta}} c_{j\rho}^* c_{i\rho} c_{j\delta} \langle \alpha \beta | \hat{V} | \gamma \delta \rangle_{AS}$$

$$- \epsilon_i c_{i\alpha} = 0$$

now we can just change the dummy variables
 $\rho \leftrightarrow \gamma$ for the first summand $j \leftrightarrow \rho$ for the second
and $i \leftrightarrow \rho$ in general

$$\sum_{\gamma} c_{\rho\gamma} \langle \alpha | \hat{h}_0 | \gamma \rangle + \sum_{\substack{\rho, \delta \\ \rho \in F}} \sum_{\substack{\beta \\ \delta, \delta}} c_{\rho\beta}^* c_{\rho\delta} c_{\rho\delta} \langle \alpha \beta | \hat{V} | \gamma \delta \rangle_{AS} = \epsilon_{\rho} c_{\rho\alpha}$$

So:

$$\sum_{\gamma} c_{\rho\gamma} \left[\langle \alpha | \hat{h}_0 | \gamma \rangle + \sum_{\substack{\rho, \delta \\ \rho \in F}} \sum_{\substack{\beta \\ \delta, \delta}} c_{\rho\beta}^* c_{\rho\delta} \langle \alpha \beta | \hat{V} | \gamma \delta \rangle_{AS} \right] = \epsilon_{\rho} c_{\rho\alpha}$$

then if

$$h_{\alpha\gamma}^{HF} = \langle \alpha | \hat{h} | \gamma \rangle + \sum_{\substack{\rho, \delta \\ \rho \in F}} \sum_{\substack{\beta \\ \delta, \delta}} c_{\rho\beta}^* c_{\rho\delta} \langle \alpha \beta | \hat{V} | \gamma \delta \rangle_{AS}$$

$$\sum_{\gamma} h_{\alpha\gamma}^{HF} c_{\rho\gamma} = \epsilon_{\rho} c_{\rho\alpha}$$

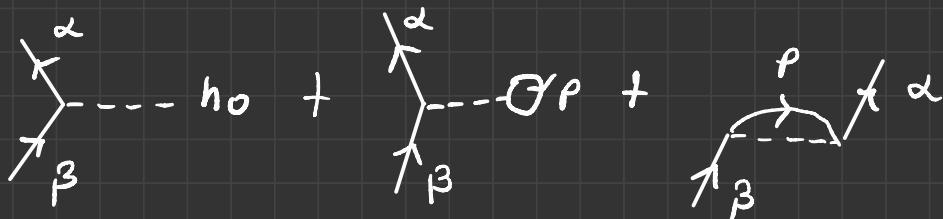
• the coefficients c_p are then the eigenvectors of the diagonalization of this newly defined Hartree-Fock hamiltonian which has elements $\hat{h}_{\alpha\gamma}^H$. Consequently, ϵ_p^H are the eigenvalues of such matrix.

We then write \hat{h}^{HF} in second quantization

$$\hat{h}^{HF} \cdot \mathcal{C} = \lambda \mathcal{C}$$

Disclaimer: I do not know if the following makes sense

$$\hat{h}^{HF} = \sum_{\alpha\beta} \left(\langle \alpha | \hat{h}_0 | \beta \rangle + \sum_{P \leq F} \langle \alpha \rho | \hat{V} | \beta \rho \rangle_A S \right) \{ a_\alpha^\dagger a_\beta \}$$



f) Considering then for a 0-th iteration
that $\langle \rho \beta = \delta_{\rho \beta}$, we have

$$h_{\alpha \gamma}^{\text{HF}} = \langle \alpha | h_0 | \gamma \rangle + \sum_{\rho \in F} \langle \alpha \rho | v | \gamma \rho \rangle_{AS}$$

where $\alpha, \gamma \in \{1+, 1-, 2+, 2-, 3+, 3-\}$

and we have a single particle basis such
that

$$\langle \alpha | h_0 | \gamma \rangle = -e^2 / 2m^2 \delta_{\alpha \gamma}$$

for He we will have $\rho \in \{1+, 1-\}$, while

for Beryllium, $\rho \in \{1+, 1-, 2+, 2-\}$

The diagonalizations for the 0-th
iteration were done in the code.

Writing the density matrix

$$\rho_{\alpha \gamma} = \sum_{i \in F} c_i \alpha c_i^* \gamma$$

we can return the

Ground state expectation energy

$$\langle \psi_0 | H | \psi_0 \rangle = \sum_{\alpha \beta} \rho_{\alpha \beta} \langle \alpha | h_0 | \beta \rangle + \frac{1}{2} \sum_{\alpha \beta \gamma \delta} \rho_{\alpha \gamma} \rho_{\delta \beta} \langle \alpha \beta | v | \gamma \delta \rangle_{AS}$$

For He, after the first diagonalization,

the given ground state energy was

~ -2.83 atomic units, and for
Beryllium, ~ -14.50 .

Both values are, in fact, closer to the exact energies than what was obtained with the $1p1h$ configuration.

It is relevant to notice that while both values got more accurate, this effect was more significant for the Beryllium.

Given its larger numbers of electrons,
the $1p1h$ approximation is too inaccurate.
