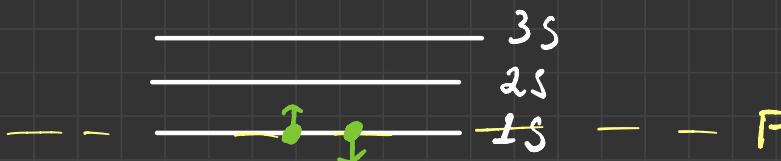


a) He with s.p orbits  $1s$   $2s$   $3s$  and spin

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 :

$$\begin{aligned} E(\Phi_0) &= \langle 1+ | h_0 | 1+ \rangle + \langle 1- | h_0 | 1- \rangle + \\ &\frac{1}{2} \left( \langle 1+ 1- | V | 1+ 1- \rangle - \cancel{\langle 1+ 1- | V | 1- 1+ \rangle^0} \right. \\ &\quad \left. + \langle 1- 1+ | V | 1- 1+ \rangle - \cancel{\langle 1- 1+ | V | 1+ 1- \rangle^0} \right) \\ &= -2^2 + \langle 11 | V | 11 \rangle \\ &= -2^2 + 5 \cdot \frac{e}{8} = -2.75 \text{ atomic units} \end{aligned}$$


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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

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

$\boxed{\neq}$

$$\text{So } \langle \Phi_0 | \hat{H} | \Phi_i^a \rangle = \langle i | h_0 | a \rangle + \sum_j \langle ij | V | aj \rangle_{\text{AS}}$$

$$\text{but } \langle i | h_0 | j \rangle = -e^2 / 2m^2 \delta_{ij}, \text{ so } \langle i | h_0 | a \rangle = 0$$

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

$$\langle c | \hat{H} | \Phi_{1+}^{2+} \rangle = \sum_j \langle 1+j | v | 2+j \rangle_{AS}$$

$$= \langle 1+1- | v | 2+1- \rangle_{AS} + \langle 1+1+ | v | 2+1+ \rangle_{AS}$$

Similarly

$$\langle c | \hat{H} | \Phi_{1-}^{2-} \rangle = \sum_j \langle 1-j | v | 2-j \rangle_{AS} \quad \langle c | \hat{H} | \Phi_{1+}^{3+} \rangle = \sum_j \langle 1+j | v | 3+j \rangle_{AS}$$

$$\langle c | \hat{H} | \Phi_{1-}^{3-} \rangle = \sum_j \langle 1-j | v | 3-j \rangle_{AS}$$

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

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

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

because

$$\left. \begin{aligned} E_0 \langle \Phi_0 | a_i^+ a_a a_b a_j^+ | \Phi_0 \rangle \\ \boxed{\underbrace{a_i^+ a_a}_{\delta_{ip}} \underbrace{a_b a_j^+}_{\delta_{pj}}} = 0 \end{aligned} \right\}$$

One body part  
will always  
have a 0  
contraction

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

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

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

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

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

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:

$$\begin{aligned} \langle \Phi_i^a | \hat{H} | \Phi_i^a \rangle &= \langle a | \hat{f} | a \rangle - \langle i | \hat{f} | i \rangle + E_0^{\text{Ref}} \\ &= \langle a | h_0 | a \rangle + \sum_j \langle a j | V | a j \rangle_{AS} \\ &\quad - \left( \langle i | h_0 | i \rangle + \sum_j \langle i j | V | i j \rangle_{AS} \right) + E_0^{\text{Ref}} \end{aligned}$$

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

$$\langle \Phi_{1+}^{2+} | \hat{H} | \Phi_{1+}^{2+} \rangle = \langle 2+ | h_0 | 2+ \rangle + \sum_j \langle 2+j | V | 2+j \rangle_{AS}$$

$$- \langle 2+ | h_0 | 1+ \rangle - \sum_j \langle 1+j | V | 1+j \rangle_{AS} + E_0^{\text{Ref}}$$

$$\langle \Phi_{1-}^{2-} | \hat{H} | \Phi_{1-}^{2-} \rangle = \langle 2- | h_0 | 2- \rangle + \sum_j \langle 2-j | V | 2-j \rangle_{AS}$$

$$- \langle 2- | h_0 | 1- \rangle - \sum_j \langle 1-j | V | 1-j \rangle_{AS} + E_0^{\text{Ref}}$$

$$\langle \Phi_{1-}^{3-} | \hat{H} | \Phi_{1-}^{3-} \rangle = \langle 3- | h_0 | 3- \rangle + \sum_j \langle 3-j | V | 3-j \rangle_{AS}$$

$$- \langle 3- | h_0 | 1- \rangle - \sum_j \langle 1-j | V | 1-j \rangle_{AS} + E_0^{\text{Ref}}$$

$$\langle \Phi_{1+}^{3+} | \hat{H} | \Phi_{1+}^{3+} \rangle = \langle 3+ | h_0 | 3+ \rangle + \sum_j \langle 3+j | V | 3+j \rangle_{AS}$$

$$- \langle 3+ | h_0 | 1+ \rangle - \sum_j \langle 1+j | V | 1+j \rangle_{AS} + E_0^{\text{Ref}}$$

In diagrammatic form:

$$\langle \bar{\Phi}_0 | H | \bar{\Phi}_i^a \rangle = \langle \dot{c} | \hat{f} | a \rangle = \langle \dot{c} | h_0 | a \rangle + \sum_j \langle \dot{c}_j | \hat{V} | a_j \rangle$$

$$\langle \dot{c} | h_0 | a \rangle = \text{Diagram showing } \dot{c} \text{ and } a \text{ connected by a dashed line with a dot at } h_0 \text{, followed by a plus sign}$$

$$\sum_j \langle \dot{c}_j | \hat{V} | a_j \rangle = \text{Diagram showing } \dot{c} \text{ and } a \text{ connected by a dashed line with a dot at } V \text{, followed by a plus sign}$$

$$-\sum_j \langle \dot{c}_j | \hat{V} | j_a \rangle = \text{Diagram showing } \dot{c}_i \text{ and } a \text{ connected by a dashed line with a dot at } V \text{, with a curved arrow from } j \text{ to } i \text{ above the line, followed by a plus sign}$$

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

$$\text{where } E_0^{\text{ref}} = \sum_i \langle \dot{c}_i | h_0 | i \rangle + \frac{1}{2} \sum_{ij} \langle \dot{c}_i | V | \dot{c}_j \rangle - \langle \dot{c}_i | V | i \rangle$$

$$\text{So } E_0^{\text{ref}}: \text{Diagram showing } \dot{c} \text{ and } a \text{ connected by a dashed line with a dot at } h_0$$

$$\sum_{ij} \langle \dot{c}_j | V | \dot{c}_i \rangle = \text{Diagram showing } \dot{c}_i \text{ and } \dot{c}_j \text{ connected by a dashed line with a dot at } V$$

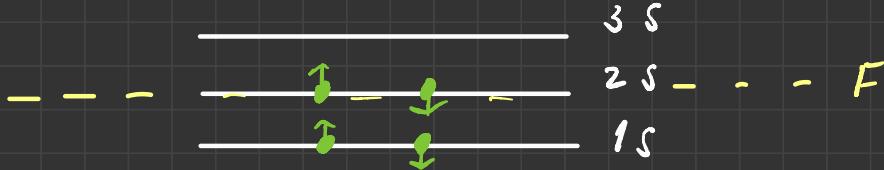
$$-\sum_{ij} \langle \dot{c}_j | V | j_i \rangle = \text{Diagram showing } i \text{ and } j \text{ connected by a dashed line with a dot at } V$$

the explicit Hamiltonian was constructed in code, but it is a  $5 \times 5$  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  $E_0^{HF}$

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

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

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

$$F(\Psi_0) = E_0^{HF} - \sum_{i=1}^N \epsilon_i \sum_{\alpha}^* c_{i\alpha}^* c_{i\alpha}$$

where the double sum with  $\beta$  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  $c_{i\alpha}^*$ :

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

$$= \sum_{\beta} c_{i\beta} \langle \alpha | h_0 | \beta \rangle + \sum_{\substack{j \in F \\ j \neq i}} \sum_{\substack{\beta \\ \delta, \delta}} c_{j\beta}^* c_{i\delta} c_{j\delta} \langle \alpha \beta | v | \gamma \delta \rangle_{AS}$$

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

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

$$\sum_{\gamma} c_{p\gamma} \langle \alpha | h_0 | \gamma \rangle + \sum_{\substack{p \in F \\ p \neq i}} \sum_{\substack{\beta \\ \delta, \delta}} c_{p\beta}^* c_{p\delta} c_{p\delta} \langle \alpha \beta | v | \gamma \delta \rangle_{AS} = \epsilon_p c_{p\alpha}$$

So:

$$\sum_{\gamma} c_{p\gamma} \left[ \langle \alpha | h_0 | \gamma \rangle + \sum_{\substack{p \in F \\ p \neq i}} \sum_{\substack{\beta \\ \delta, \delta}} c_{p\beta}^* c_{p\delta} \langle \alpha \beta | v | \gamma \delta \rangle_{AS} \right] = \epsilon_p c_{p\alpha}$$

then if

$$h_{\alpha\gamma} = \langle \alpha | h | \gamma \rangle + \sum_{\substack{p \in F \\ p \neq i}} \sum_{\substack{\beta \\ \delta, \delta}} c_{p\beta}^* c_{p\delta} \langle \alpha \beta | v | \gamma \delta \rangle_{AS}$$

$$\sum_{\gamma} h_{\alpha\gamma} c_{p\gamma} = \epsilon_p c_{p\alpha}$$


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• 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,  $\epsilon_p^H$  are the eigenvalues of such matrix.

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

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

$$\hat{h}^{HF} = \sum_{\alpha\beta} \left( \langle \alpha | \hat{h} | \beta \rangle a_{\alpha}^{\dagger} a_{\beta} + \sum_{\rho\sigma} \sum_{\rho\sigma} c_{\rho\rho}^* c_{\sigma\sigma} \langle \alpha\beta | \hat{v} | \gamma\delta \rangle_{\rho\sigma} a_{\alpha}^{\dagger} a_{\beta} a_{\gamma}^{\dagger} a_{\delta} \right)$$

I know this is wrong but don't really know how to fix it.

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

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

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

and we have a single particle basis such  
that

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

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

$\sim -2.83$  atomic units, and for  
Beryllium,  $\sim -14.50$ .

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.

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