First Midterm

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Contents

This midterm contains parts a) through g), in addition to two appendices, A and B, which contain some Kronecker Delta contractions and diagrams respectively. Everything requested in the midterm should be answered unless I missed something, except the second quantization of the Hartree-Fock operator, which I could not find.
Repository with all code is at https://github.com/simloken/FYS4480

Part a

First, some formalism:
As we're dealing with hydrogen-like single-particle states, dealing with $n = 1, 2, 3$, we have that $m_l = 0$ with $l = 0$. Given that we're dealing with fermions, we know also that these states must have $s = \frac{1}{2}$. As such, we will represent the spins with the common representation $m_s = \pm\frac{1}{2} = \uparrow\downarrow$.
As $l = 0$ and $m_l = 0$, we may represent the single particle states by only the quantum numbers n, m_s, and we get the generic form:

$$|nm_s\rangle = a^\dagger_{nm_s}|0\rangle \tag{1}$$

or more specifically, the six single particle states as:

$$\begin{aligned}
|1\uparrow\rangle &= a^\dagger_{1\uparrow}|0\rangle \\
|1\downarrow\rangle &= a^\dagger_{1\downarrow}|0\rangle \\
|2\uparrow\rangle &= a^\dagger_{2\uparrow}|0\rangle \\
|2\downarrow\rangle &= a^\dagger_{1\downarrow}|0\rangle \\
|3\uparrow\rangle &= a^\dagger_{3\uparrow}|0\rangle \\
|3\downarrow\rangle &= a^\dagger_{1\downarrow}|0\rangle
\end{aligned}$$

We may now move onto the ansatz for the ground state $|c\rangle = |\Phi_0\rangle$, which is deceptively simple.
We select our ansatz for the ground state as the lowest energy state of our chosen basis, which becomes:

$$|\Phi_0\rangle = |1\uparrow 1\downarrow\rangle = a^\dagger_{1\uparrow}a^\dagger_{1\downarrow}|0\rangle \tag{2}$$

To better deal with the excitations of $|0\rangle$, we set $|\Phi_0\rangle$ to be the Fermi level, which makes for less tedious work when constructing excited states as opposed to using $|0\rangle$. We now (as suggested in the

midterm) need to use particles and holes, of the form $|\Phi_i^\alpha\rangle$. Here, i are the levels below the Fermi level (as defined above), and α are the particle states. When we say particles and holes, what we really mean is a filled state or a non-filled state, above or below the Fermi level respectively.
We can then define the generic form of $|\Phi_i^\alpha\rangle$ as:

$$|\Phi_i^\alpha\rangle = a_\alpha^\dagger a_i |\Phi_0\rangle \tag{3}$$

Or more specifically the four states:

$$\begin{aligned}
|\Phi_{1\uparrow}^{2\uparrow}\rangle &= a_{2\uparrow}^\dagger a_{1\uparrow}|\Phi_0\rangle \\
|\Phi_{1\downarrow}^{2\downarrow}\rangle &= a_{2\downarrow}^\dagger a_{1\downarrow}|\Phi_0\rangle \\
|\Phi_{1\uparrow}^{3\uparrow}\rangle &= a_{3\uparrow}^\dagger a_{1\uparrow}|\Phi_0\rangle \\
|\Phi_{1\downarrow}^{3\downarrow}\rangle &= a_{3\downarrow}^\dagger a_{1\downarrow}|\Phi_0\rangle
\end{aligned}$$

which are the one-particle-one-hole excitations. Similarly, we may construct the two-particle-two-hole excitations by the generic form:

$$|\Phi_{ij}^{ab} = a_a^\dagger a_b^\dagger a_i a_j |\Phi_0\rangle \tag{4}$$

Or again, more specifically:

$$\begin{aligned}
|\Phi_{1\uparrow 1\downarrow}^{2\uparrow 2\downarrow}\rangle &= a_{2\uparrow}^\dagger a_{2\downarrow}^\dagger a_{1\uparrow} a_{1\downarrow}|\Phi_0\rangle \\
|\Phi_{1\uparrow 1\downarrow}^{3\uparrow 2\downarrow}\rangle &= a_{3\uparrow}^\dagger a_{2\downarrow}^\dagger a_{1\uparrow} a_{1\downarrow}|\Phi_0\rangle \\
|\Phi_{1\uparrow 1\downarrow}^{2\uparrow 3\downarrow}\rangle &= a_{2\uparrow}^\dagger a_{3\downarrow}^\dagger a_{1\uparrow} a_{1\downarrow}|\Phi_0\rangle \\
|\Phi_{1\uparrow 1\downarrow}^{3\uparrow 3\downarrow}\rangle &= a_{3\uparrow}^\dagger a_{3\downarrow}^\dagger a_{1\uparrow} a_{1\downarrow}|\Phi_0\rangle
\end{aligned}$$

Part b

We define $\hat{H}$ as a function of the creation and annihilation operators:

$$\hat{H} = \sum_{ab}\langle a|\hat{h}_0|b\rangle a_a^\dagger a_b + \frac{1}{4}\sum_{abcd}\left(\langle ab|\hat{v}|cd\rangle - \langle ab|\hat{v}|dc\rangle\right) a_a^\dagger a_b^\dagger a_c a_d$$

which we will now use as a means of computing the expectation value of the ground state. To do this, we will employ a few tricks, namely from exercise 2 in week 38, that allowed us to rewrite respectively the definitions of $\hat{H}_0, \hat{H}_1$ in normal ordered form.
We have then:

$$\hat{H}_0 = \sum_{ab}\langle a|\hat{h}_0|b\rangle a_a^\dagger a_b$$

$$\hat{H}_1 = \frac{1}{4}\sum_{abcd}\left(\langle ab|\hat{v}|cd\rangle - \langle ab|\hat{v}|dc\rangle\right) a_a^\dagger a_b^\dagger a_c a_d$$

which we rewrite respectively as:

$$\hat{H}_0 = \sum_{ab}\langle a|\hat{h}_0|b\rangle\{a_a^\dagger a_b\} + \sum_i \langle i|\hat{h}_0|i\rangle \tag{5}$$

$$\hat{H}_1 = \frac{1}{4}\sum_{abcd}\langle ab|\hat{v}|cd\rangle\{a_a^\dagger a_b^\dagger a_c a_d\} + \sum_{abi}\langle ai|\hat{v}|bi\rangle\{a_a^\dagger a_b\} + \frac{1}{2}\sum_{ij}\langle ij|\hat{v}|ij\rangle \tag{6}$$

As it is now normal ordered, we can employ our second trick: Wick's Generalized Theorem. Given that $\hat{H}$ is normal ordered, we then have that the squigly-bracketed terms (that is $\{a_a^\dagger a_b\}$ and $\{a_a^\dagger a_b^\dagger a_c a_d\}$) become zero, giving:

$$E\left[\Phi_0\right] = \langle\Phi_0|\hat{H}|\Phi_0\rangle$$

where we find the expectation values of $\hat{H}_0$ and $\hat{H}_1$ to be:

$$\langle\Phi_0|\hat{H}_0|\Phi_0\rangle = \sum_i \langle i|\hat{h}_0|i\rangle$$

$$\langle\Phi_0|\hat{H}_1|\Phi_0\rangle = \frac{1}{2}\sum_{ij}\langle ij|\hat{v}|ij\rangle - \langle ij|\hat{v}|ji\rangle$$

Giving finally the requested expression for the ground state:

$$E\left[\Phi_0\right] = \sum_i \langle i|\hat{h}_0|i\rangle + \frac{1}{2}\sum_{ij}\langle ij|\hat{v}|ij\rangle - \langle ij|\hat{v}|ji\rangle \tag{7}$$

the only difference being we have exchanged $1/r$ for $\hat{v}$ for readability.
We now wish to evaluate this expression as a function of Z.
We start at:

$$E\left[\Phi_0\right] = \sum_i \langle i|\hat{h}_0|i\rangle + \frac{1}{2}\sum_{ij}\langle ij|\hat{v}|ij\rangle - \langle ij|\hat{v}|ji\rangle$$

from which we get:

$$E\left[\Phi_0\right] = \langle 1\uparrow|\hat{h}_0|1\uparrow\rangle + \langle 1\downarrow|\hat{h}_0|1\downarrow\rangle + \frac{1}{2}(\langle 1\uparrow 1\downarrow|\hat{v}|1\uparrow 1\downarrow\rangle - \langle 1\uparrow 1\downarrow|\hat{v}|1\downarrow 1\uparrow\rangle$$
$$+\langle 1\downarrow 1\uparrow 1\hat{v}|1\downarrow 1\uparrow\rangle - \langle 1\downarrow 1\uparrow|\hat{v}|1\uparrow 1\downarrow\rangle)$$

Here, the last term on both lines of the equation becomes 0, and thus we get:

$$E\left[\Phi_0\right] = 2\langle 1|\hat{h}_0|1\rangle + \langle 11|\hat{v}|11\rangle \tag{8}$$

We look at the table given in the exercise and find that $\langle 11|\hat{v}|11\rangle = \frac{5Z}{8}$, giving us:

$$E\left[\Phi_0\right] = -Z^2 + \frac{5Z}{8} \xrightarrow{Z=2} E\left[\Phi_0\right] = -\frac{11}{4}\ a.u. \tag{9}$$

Part c

The natural place to start is to find a term for $\langle\Phi_0|\hat{H}|\Phi_i^\alpha\rangle$. If we rewrite the term as:

$$\langle\Phi_0|\hat{H}|\Phi_i^\alpha\rangle = \langle\Phi_0|\hat{H}a_a^\dagger a_i|\Phi_0\rangle$$

Then we may again use Wick's Generalized Theorem, and we find that:

$$\langle\Phi_0|\hat{H}|\Phi_i^\alpha\rangle = \sum_{ab}\langle a|\hat{h}_0|b\rangle\langle\Phi_0|\{a_a^\dagger a_b\}|\Phi_i^\alpha\rangle + \sum_{abj}(\langle pj|\hat{v}|qj\rangle - \langle pj|\hat{v}|jq\rangle)\langle\Phi_0|\{a_a^\dagger a_b\}|\Phi_i^\alpha\rangle$$

Notice the term $\langle\Phi_0|\{a_a^\dagger a_b\}|\Phi_i^\alpha\rangle$, which is present in both terms. We may rewrite this as:

$$\langle\Phi_0|\{a_a^\dagger a_b\}|\Phi_i^\alpha\rangle = \delta_{ai}\delta_{b\alpha}$$

from which we get the much neater form:

$$\langle\Phi_0|\hat{H}|\Phi_i^\alpha\rangle = \langle i|\hat{h}_0|\alpha\rangle + \sum_j \langle ij|\hat{v}|\alpha j\rangle - \langle ij|\hat{v}|j\alpha\rangle \tag{10}$$

We wish now to find the expression for all one-particle-one-hole states, which we may write as:

$$\langle\Phi_i^\alpha|\hat{H}|\Phi_j^\beta\rangle = \langle\Phi_0|a_i^\dagger a_\alpha \hat{H} a_b^\dagger a_j|\Phi_0\rangle$$

which becomes for H_0 and H_1 respectively:

$$\begin{aligned}\langle\Phi_i^\alpha|\hat{H}_0|\Phi_j^\beta\rangle = &\sum_{ab}\langle a|\hat{h}_0|b\rangle\left(\{a_i^\dagger a_\alpha\}\{a_a^\dagger a_b\}\{a_\beta^\dagger a_j\}\right)\\ &+\sum_k\langle k|\hat{h}_0|k\rangle\left(\{a_i^\dagger a_\alpha\}\{a_\beta^\dagger a_j\}\right)\end{aligned}$$

$$\begin{aligned}\langle\Phi_i^\alpha|\hat{H}_1|\Phi_j^\beta\rangle = &\frac{1}{4}\sum_{abcd}\left(\langle ab|\hat{v}|cd\rangle - \langle ab|\hat{v}|dc\rangle\right)\left(\{a_i^\dagger a_\alpha\}\{a_a^\dagger a_b^\dagger a_d a_c\}\{a_\beta^\dagger a_j\}\right)\\ &+\sum_{abk}\left(\langle ak|\hat{v}|bk\rangle - \langle ak|\hat{v}|kb\rangle\right)\left(\{a_i^\dagger a_\alpha\}\{a_a^\dagger a_b\}\{a_\beta^\dagger a_j\}\right)\\ &+\sum_{kl}\left(\langle kl|\hat{v}|kl\rangle - \langle kl|\hat{v}|lk\rangle\right)\left(\{a_i^\dagger a_\alpha\}\{a_\beta^\dagger a_j\}\right)\end{aligned}$$

Again, we may contract these terms, giving a much neater (see Appendix A for a more robust derivation of the term below):

$$\langle\Phi_i^\alpha|\hat{H}_0|\Phi_j^\beta\rangle = \langle\alpha|\hat{h}_0|\beta\rangle\delta_{ij} - \langle j|\hat{h}_0|i\rangle\delta_{\alpha\beta} + \sum_k\langle k|\hat{h}_0|k\rangle\delta_{ij}\delta_{\alpha\beta} \tag{11}$$

$$\begin{aligned}\langle\Phi_i^\alpha|\hat{H}_1|\Phi_j^\beta\rangle = &\langle\alpha j|\hat{v}|i\beta\rangle - \langle\alpha j|\hat{v}|\beta i\rangle\\ &+\sum_k\left(\left(\langle\alpha k|\hat{v}|\beta k\rangle - \langle\alpha k|\hat{v}|k\beta\rangle\right)\delta_{ij} - \left(\langle jk|\hat{v}|ik\rangle - \langle jk|\hat{v}|ki\rangle\right)\delta_{\alpha\beta}\right)\\ &+\frac{1}{2}\sum_{kl}\left(\langle kl|\hat{v}|kl\rangle - \langle kl|\hat{v}|lk\rangle\right)\delta_{ij}\delta_{\alpha\beta}\end{aligned} \tag{12}$$

The Hamiltonian Matrix is now:

$$\hat{H}_{mat} = \begin{bmatrix}\langle\Phi_0|\hat{H}|\Phi_0\rangle & \langle\Phi_0|\hat{H}|\Phi_{1\uparrow}^{2\downarrow}\rangle & \langle\Phi_0|\hat{H}|\Phi_{1\downarrow}^{2\downarrow}\rangle & \langle\Phi_0|\hat{H}|\Phi_{1\uparrow}^{3\uparrow}\rangle & \langle\Phi_0|\hat{H}|\Phi_{1\downarrow}^{3\downarrow}\rangle\\ \langle\Phi_{1\uparrow}^{2\uparrow}|\hat{H}|\Phi_0\rangle & \langle\Phi_{1\uparrow}^{2\uparrow}|\hat{H}|\Phi_{1\uparrow}^{2\downarrow}\rangle & \langle\Phi_{1\uparrow}^{2\uparrow}|\hat{H}|\Phi_{1\downarrow}^{2\downarrow}\rangle & \langle\Phi_{1\uparrow}^{2\uparrow}|\hat{H}|\Phi_{1\uparrow}^{3\uparrow}\rangle & \langle\Phi_{1\uparrow}^{2\uparrow}|\hat{H}|\Phi_{1\downarrow}^{3\downarrow}\rangle\\ \langle\Phi_{1\downarrow}^{2\downarrow}|\hat{H}|\Phi_0\rangle & \langle\Phi_{1\downarrow}^{2\downarrow}|\hat{H}|\Phi_{1\uparrow}^{2\downarrow}\rangle & \langle\Phi_{1\downarrow}^{2\downarrow}|\hat{H}|\Phi_{1\downarrow}^{2\downarrow}\rangle & \langle\Phi_{1\downarrow}^{2\downarrow}|\hat{H}|\Phi_{1\uparrow}^{3\uparrow}\rangle & \langle\Phi_{1\downarrow}^{2\downarrow}|\hat{H}|\Phi_{1\downarrow}^{3\downarrow}\rangle\\ \langle\Phi_{1\uparrow}^{3\uparrow}|\hat{H}|\Phi_0\rangle & \langle\Phi_{1\uparrow}^{3\uparrow}|\hat{H}|\Phi_{1\uparrow}^{2\downarrow}\rangle & \langle\Phi_{1\uparrow}^{3\uparrow}|\hat{H}|\Phi_{1\downarrow}^{2\downarrow}\rangle & \langle\Phi_{1\uparrow}^{3\uparrow}|\hat{H}|\Phi_{1\uparrow}^{3\uparrow}\rangle & \langle\Phi_{1\uparrow}^{3\uparrow}|\hat{H}|\Phi_{1\downarrow}^{3\downarrow}\rangle\\ \langle\Phi_{1\downarrow}^{3\downarrow}|\hat{H}|\Phi_0\rangle & \langle\Phi_{1\downarrow}^{3\downarrow}|\hat{H}|\Phi_{1\uparrow}^{2\downarrow}\rangle & \langle\Phi_{1\downarrow}^{3\downarrow}|\hat{H}|\Phi_{1\downarrow}^{2\downarrow}\rangle & \langle\Phi_{1\downarrow}^{3\downarrow}|\hat{H}|\Phi_{1\uparrow}^{3\uparrow}\rangle & \langle\Phi_{1\downarrow}^{3\downarrow}|\hat{H}|\Phi_{1\downarrow}^{3\downarrow}\rangle\end{bmatrix} \tag{13}$$

Performing now the calculation with the python script, we find that such an approach yields the energy $E_{Mat}^{He} = -2.77\ a.u.$ which is a relatively good measurement.

Part d

We use the same approach as we did for Helium, and the same basis, except that we're now dealing with $Z = 4$. Thus we get the ansatz:

$$|\Phi_0\rangle = a^\dagger_{1\uparrow} a^\dagger_{1\downarrow} a_{2\uparrow} a_{2\downarrow} |0\rangle \tag{14}$$

And we again get the same generic form from Eq. [3] and the specific states:

$$\begin{aligned}
|\Phi^{3\uparrow}_{1\uparrow}\rangle &= a^\dagger_{3\uparrow} a_{1\uparrow} |\Phi_0\rangle \\
|\Phi^{3\downarrow}_{1\downarrow}\rangle &= a^\dagger_{3\downarrow} a_{1\downarrow} |\Phi_0\rangle \\
|\Phi^{3\uparrow}_{2\uparrow}\rangle &= a^\dagger_{3\uparrow} a_{2\uparrow} |\Phi_0\rangle \\
|\Phi^{3\downarrow}_{2\downarrow}\rangle &= a^\dagger_{3\uparrow} a_{2\downarrow} |\Phi_0\rangle
\end{aligned}$$

and we end up with:

$$E[\Phi_0] = \sum_i \langle i|\hat{h}_0|i\rangle + \langle 11|V|11\rangle + \langle 22|V|22\rangle + 2\left(\langle 12|V|12\rangle + \langle 21|V|21\rangle\right) - \left(\langle 12|V|21\rangle + \langle 21|V|12\rangle\right)$$

$$E[\Phi_0] = -\frac{5Z^2}{4} + \frac{586373}{373248} Z \xrightarrow{Z=4} E\left[\Phi_0\right] = -13.716\ a.u. \tag{15}$$

We perform now again the same calculation as in c), except that we now move the Fermi level up 1. We find then the energy $E^{Be}_{Mat} = -13.75 a.u.$, which is a small improvement from the rudimentary value we found just above.

Part e

We must now rewrite our expression for the ground state estimation, we have that:

$$E[\Phi^{\mathcal{HF}}_0] = \sum_i \langle i|\hat{h}_0|i\rangle + \frac{1}{2}\sum_{ij} \langle ij|\hat{v}|ij\rangle - \langle ij|\hat{v}|ji\rangle$$

Note that we here have swapped basis. We denote our old basis by greek letters $\alpha\beta$ etc.. Our new basis uses roman letters i, j and so forth. We may then rewrite in terms of our old basis:

$$E[\Phi^{\mathcal{HF}}_0] = \sum_i \sum_{\alpha\beta} C^*_{i\alpha} C^*_{i\beta} \langle \alpha|\hat{h}_0|\beta\rangle + \frac{1}{2}\sum_{ij}\sum_{\alpha\beta\gamma\delta} C^*_{i\alpha} C^*_{j\beta} C_{i\gamma} C_{j\delta} \left(\langle \alpha\beta|\hat{v}|\gamma\delta\langle - \langle \alpha\beta|\hat{v}|\delta\gamma\rangle\right)$$

We know that our new single particle basis is orthonormal, that is:

$$\langle a|b\rangle = \delta_{ab} = \sum_{\alpha\beta} C^*_{a\alpha} C_{a\beta} \langle \alpha|\beta\rangle = \sum_\alpha C^*_{a\alpha} C_{a\alpha}$$

and thus we write our functional to minimize:

$$\mathcal{F}[\Phi^{\mathcal{HF}}_0] = E[\Phi^{\mathcal{HF}}_0] - \sum_i \epsilon_i \sum_\alpha C^*_{i\alpha} C_{i\alpha} \tag{16}$$

where ϵ_i are our Lagrange multipliers.
We can now minimize $\mathcal{F}$ with respect to $C^*_{i\alpha}$, and thus we must solve:

$$\frac{\partial}{\partial C^*_{i\alpha}}\mathcal{F}[\Phi_0^{\mathcal{HF}}] = \frac{\partial}{\partial C^*_{i\alpha}}\left(E[\Phi_0^{\mathcal{HF}}] - \sum_j \epsilon_j \sum_a C^*_{j\alpha}C_{j\alpha}\right) = 0$$

This can look quite intimidating, but if we take it one term at a time, it's not *that* bad. Let us start at the beginning with $E[\Phi_0^{\mathcal{HF}}]$, which is made up of two terms, the one-body and two-body contribution respectively. The one-body is simple, giving:

$$\frac{\partial}{\partial C^*_{i\alpha}}\sum_i\sum_{\alpha\beta} C^*_{i\alpha}C^*_{i\beta}\langle\alpha|\hat{h}_0|\beta\rangle = \sum_\beta C_{i\beta}\langle\alpha|\hat{h}_0|\beta\rangle$$

and the two-body is a step up, giving:

$$\frac{\partial}{\partial C^*_{i\alpha}}\frac{1}{2}\sum_{ij}\sum_{\alpha\beta\gamma\delta} C^*_{i\alpha}C^*_{j\beta}C_{i\gamma}C_{j\delta}\left(\langle\alpha\beta|\hat{v}|\gamma\delta\langle - \langle\alpha\beta|\hat{v}|\delta\gamma\rangle\right) = \sum_j\sum_{\beta\gamma\delta} C^*_{j\beta}C_{i\gamma}C_j\delta\left(\langle\alpha\beta|\hat{v}|\gamma\delta\rangle - \langle\alpha\beta|\hat{v}|\delta\gamma\rangle\right)$$

We are now finally left with only the Lagrange multiplier term of $\mathcal{F}$, which is:

$$\frac{\partial}{\partial C_{[i\alpha]^*}}\sum_i \epsilon_i \sum_\alpha C^*_{i\alpha}C_{i\alpha} = \epsilon_i C_{i\alpha}$$

Although selecting ϵ as our Lagrange multiplier (as opposed to the more normal λ) may have been "cheating" in the sense that it makes the connection easier to see, it is now trivial to see with these three terms where this is going. Namely we have:

$$\frac{\partial}{\partial C^*_{i\alpha}}\mathcal{F}[\Phi_0^{\mathcal{HF}}] = \sum_\beta C_{i\beta}\langle\alpha|\hat{h}_0|\beta\rangle + \sum_j\sum_{\beta\gamma\delta} C^*_{j\beta}C_{i\gamma}C_j\delta\left(\langle\alpha\beta|\hat{v}|\gamma\delta\rangle - \langle\alpha\beta|\hat{v}|\delta\gamma\rangle\right) - \epsilon_i C_{i\alpha} = 0 \quad (17)$$

Which is:

$$\sum_\beta C_{i\beta}\langle\alpha|\hat{h}_0|\beta\rangle + \sum_j\sum_{\beta\gamma\delta} C^*_{j\beta}C_{i\gamma}C_j\delta\left(\langle\alpha\beta|\hat{v}|\gamma\delta\rangle - \langle\alpha\beta|\hat{v}|\delta\gamma\rangle\right) = \epsilon_i C_{i\alpha}$$

We're now only missing one step, inserting the expression for $h^{\mathcal{HF}}$ given. It is quite trivial to see that if:

$$h^{\mathcal{HF}}_{\alpha\beta} = \left[\langle\alpha|\hat{h}_0|\beta\rangle + \sum_j\sum_{\gamma\delta} C^*_{j\gamma}C_{j\delta}\left(\langle\alpha\gamma|\hat{v}|\beta\delta\rangle - \langle\alpha\gamma|\hat{v}|\delta\beta\rangle\right)\right]$$

we can then pull out the summation over β, giving:

$$\sum_\beta\left[\langle\alpha|\hat{h}_0|\beta\rangle + \sum_j\sum_{\gamma\delta} C^*_{j\gamma}C_{j\delta}\left(\langle\alpha\gamma|\hat{v}|\beta\delta\rangle - \langle\alpha\gamma|\hat{v}|\delta\beta\rangle\right)\right] = \epsilon_i C_{i\alpha}$$

Finally giving us:

$$\sum_\beta h^{\mathcal{HF}}_{\alpha\beta} = \epsilon_i C_{i\alpha} \quad (18)$$

as requested.
No idea how to find the second quantization.

Part f

We use the single particle orbits in our Hartree-Fock code to find the diagonalization:

$$\epsilon_1^{He} = -0.783$$
$$\epsilon_2^{He} = -0.783$$
$$\epsilon_3^{He} = 0.040$$
$$\epsilon_4^{He} = 0.040$$
$$\epsilon_5^{He} = 0.453$$
$$\epsilon_6^{He} = 0.453$$

and

$$\epsilon_1^{Be} = -3.951$$
$$\epsilon_2^{Be} = -3.951$$
$$\epsilon_3^{Be} = -0.104$$
$$\epsilon_4^{Be} = -0.104$$
$$\epsilon_5^{Be} = 0.866$$
$$\epsilon_6^{Be} = 0.866$$

Additionally, after one iteration of our Hartree-Fock code we find that $E_0^{He} = -2.83$ $a.u.$ and $E_0^{Be} = -14.50$ $a.u.$

Part g

We extend our approach from above to be an iterative one. The most sensible way to do this is to continually measure the slope of our convergence, and whenever it is lower than some tolerance we end the calculation.
To do this, we take the norm of the density matrix eigenvalues ϵ, as:

$$\delta_{tol} > \frac{|\epsilon_{new} - \epsilon_{old}|}{N}$$

where ϵ_{new} are our current eigenvalues, and ϵ_{old} are our old values. Other alternatives could be looking at the ground state energy or using a rolling average, although a rolling average is better served for volatile systems/problems, which this is not.
When we let our system iterate with a tolerance of 1×10^{-15}, we find that our system converges after 19 and 20 iterations respectively. We find the energies to be almost the exact same as the non-iterative version of the Hartree-Fock code, at $E_0^{He} = -2.83\ a.u.$ and $E_0^{Be} = -14.51\ a.u.$ respectively.

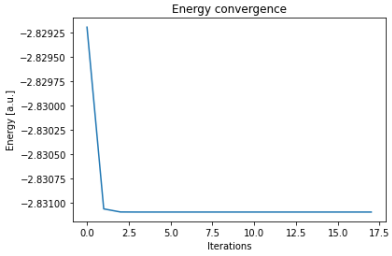

Figure 1: The convergence of our Hartree-Fock Algorithm for Helium

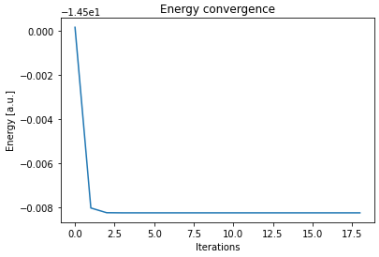

Figure 2: The convergence of our Hartree-Fock Algorithm for Beryllium

Lastly, let us review all our results and discuss them for a little bit, we found the following:

Table 1: Energy Values for Helium and Beryllium for each method

Method	Helium (He) [a.u.]	Beryllium (Be) [a.u.]
E	-2.91	-14.67
E_{gs}	-2.75	-13.72
E_{Mat}	-2.77	-13.75
E_{HF1}	-2.83	-14.50
E_{HF}	-2.83	-14.51

We find, perhaps somewhat unsurprisingly, that there is an upwards trend in our results as we either improve or further increase the 'complexity' of our models. This is as expected. It should however be noted that there might be something wrong with the Hartree-Fock method, as I believe we should be seeing more improvement that the very miniscule percent we're seeing after 20 or so iterations.

Appendix A - Contractions: Kronecker-Deltas

The contractions made in part c) may feel a little too hand-wavy, so here are the complete derivation of the Kronecker-Deltas:

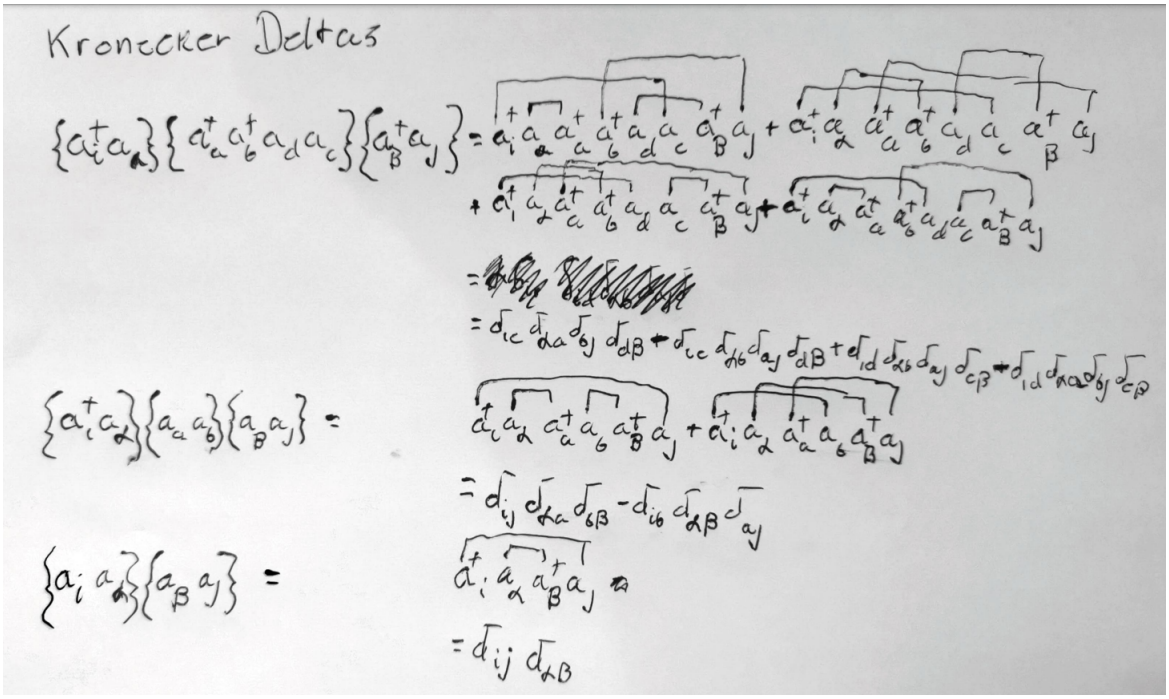

Figure 3: Kronecker Deltas for c)

Appendix B - Diagrams

The diagrams can be found here:

$\langle\theta_0|\hat{H}|\theta_i^\alpha\rangle$ Diagram

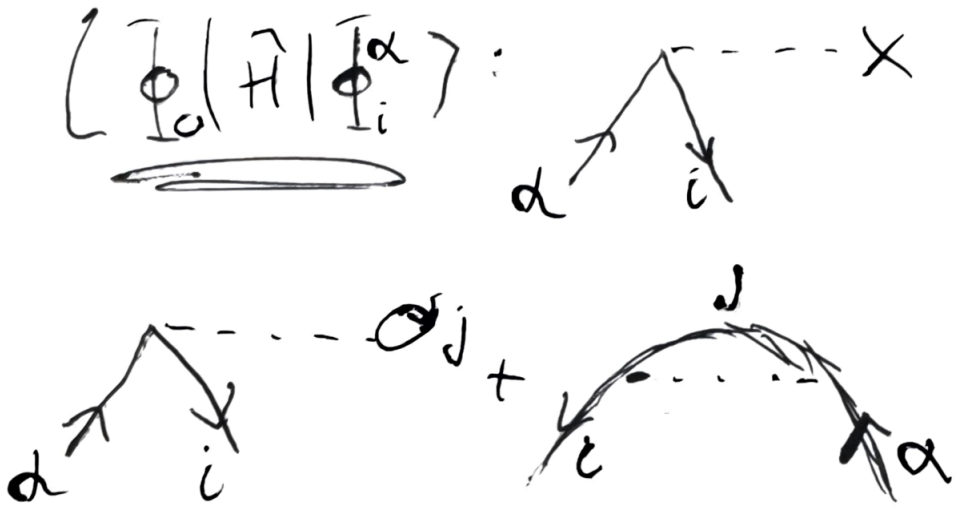

Figure 4: Diagrams for $\langle\Phi_0|\hat{H}|\Phi_i^\alpha\rangle$

$\langle\theta_i^\alpha|\hat{H}|\theta_i^\beta\rangle$ **Diagram**

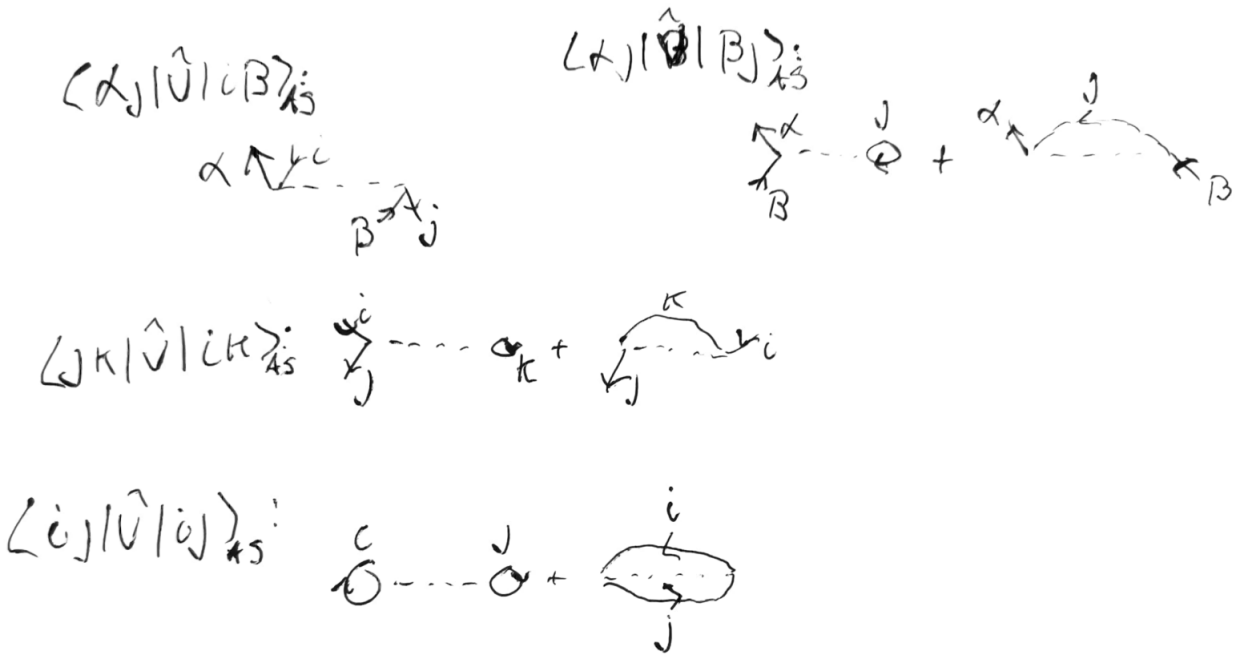

Figure 5: Diagrams for $\langle\Phi_i^\alpha|\hat{H}|\Phi_j^\beta\rangle$

$h_{\alpha\beta}^{\mathcal{HF}}$ Diagram

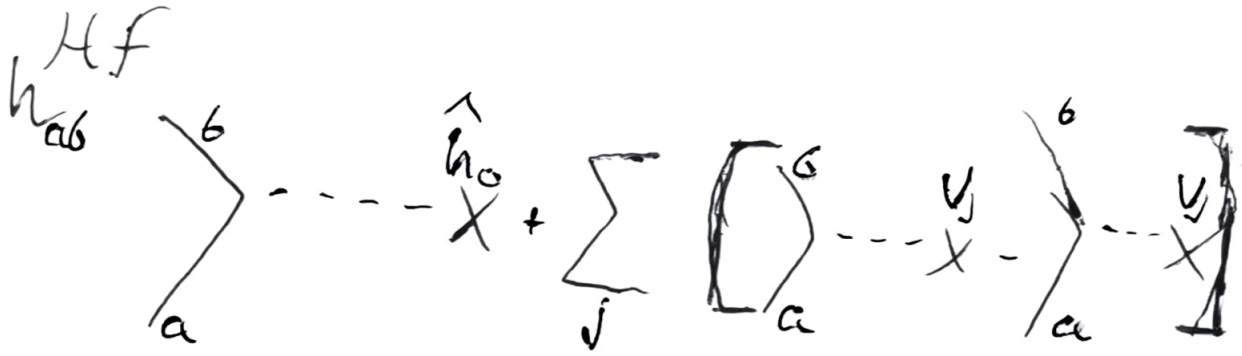

Figure 6: Diagram for Hartree Fock