Midterm 1

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1 Quantum mechanics for many-particle systems

Note: Link to codes and the diagrams are placed at the end of the document.

a)

We start with the helium atom and define our single particle Hilbert space to consist of the single-particle orbits $1s$, $2s$ and $3s$, with their corresponding spin degenracies.
Ansatz for the ground state $|c\rangle = |\Phi_0\rangle$ in second quantization:

$$|c\rangle = a^\dagger_{1s,\uparrow} a^\dagger_{1s,\downarrow} |0\rangle$$

n	m_s	
1	$+\frac{1}{2}$	$\uparrow$
1	$-\frac{1}{2}$	$\downarrow$
2	$+\frac{1}{2}$	$\uparrow$
2	$-\frac{1}{2}$	$\downarrow$
3	$+\frac{1}{2}$	$\uparrow$
3	$-\frac{1}{2}$	$\downarrow$

Now we need to contruct all possible one-particle-one-hole excitations from the ground state, $|\Phi^a_i\rangle$. i are levels below the Fermi level and a refers to particle states.

$$\left|\Phi^{2s\sigma}_{1s\sigma}\right\rangle = a^\dagger_{2s\sigma} a_{1s\sigma} |\Phi_0\rangle$$
$$\left|\Phi^{3s\sigma}_{1s\sigma}\right\rangle = a^\dagger_{3s\sigma} a_{1s\sigma} |\Phi_0\rangle$$

Where σ refers to the spin of the electron $\sigma \in \{\uparrow, \downarrow\} = \{+\frac{1}{2}, -\frac{1}{2}\}$.
And for the two-particle-two-hole excitations, $\left|\Phi^{ab}_{ij}\right\rangle$:

$$\left|\Phi^{2s\sigma 2s-\sigma}_{1s\sigma 1s-\sigma}\right\rangle = a^\dagger_{2s\sigma} a^\dagger_{2s-\sigma} a_{1s\sigma} a_{1s-\sigma} |\Phi_0\rangle$$
$$\left|\Phi^{3s\sigma 3s-\sigma}_{1s\sigma 1s-\sigma}\right\rangle = a^\dagger_{3s\sigma} a^\dagger_{3s-\sigma} a_{1s\sigma} a_{1s-\sigma} |\Phi_0\rangle$$

With the same values for σ as above, and keeping the Pauli principle in mind.

b)

The general form of the second-quantized Hamiltonian for a system with two-body interactions is:

$$\hat{H} = \sum_{\alpha\beta} \langle\alpha|\, \hat{h}_0 \,|\beta\rangle\, a^\dagger_\alpha a_\beta + \frac{1}{4} \sum_{\alpha\beta\gamma\delta} \langle\alpha\beta|\, \frac{1}{r} \,|\gamma\delta\rangle_{AS}\, a^\dagger_\alpha a^\dagger_q a_\gamma a_\delta$$

Applying the Hamiltonian to the ground state $|\Phi_0\rangle$:

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

$$E[\Phi_0] = \sum_{\alpha\beta} \langle\alpha|\, \hat{h}_0 \,|\beta\rangle\, \langle\Phi_0|\, a^\dagger_\alpha a_\beta \,|\Phi_0\rangle + \frac{1}{4} \sum_{\alpha\beta\gamma\delta} \langle\alpha\beta|\, \frac{1}{r} \,|\gamma\delta\rangle_{AS}\, \langle\Phi_0|\, a^\dagger_\alpha a^\dagger_\beta a_\gamma a_\delta \,|\Phi_0\rangle$$

We can take the one body term first:

$$\sum_{\alpha\beta} \langle\alpha|\, \hat{h}_0 \,|\beta\rangle\, \langle\Phi_0|\, a^\dagger_\alpha a_\beta \,|\Phi_0\rangle = \sum_{\alpha\beta} \langle\alpha|\, \hat{h}_0 \,|\beta\rangle\, \langle c|\, a^\dagger_\alpha a_\beta \,|0\rangle$$

$$= \sum_{ij} \langle i|\, \hat{h}_0 \,|j\rangle\, \delta_{ij} = \sum_i \langle i|\, \hat{h}_0 \,|i\rangle$$

Which we got from contracting the creation and annihilation operators.
For the two body term:

$$\langle\Phi_0|\, \hat{H}_I \,|\Phi_0\rangle = \frac{1}{4} \sum_{ij} \langle\alpha\beta|\, V \,|\gamma\delta\rangle_{AS}\, \langle c|\, a^\dagger_\alpha a^\dagger_\beta a_\gamma a_\delta \,|c\rangle$$

$$= \frac{1}{4} \sum_{ij} \langle\alpha\beta|\, V \,|\gamma\delta\rangle_{AS}\, \langle 0|\, a_j a_i a^\dagger_\alpha a^\dagger_\beta a_\gamma a_\delta a^\dagger_i a^\dagger_j \,|0\rangle$$

Now we can take a look at the contractions:

$$\langle 0|\, \overbrace{a_j a_i a^\dagger_\alpha}\, a^\dagger_\beta \overbrace{a_\gamma a_\delta a^\dagger_i}\, a^\dagger_j \,|0\rangle = \delta_{j\beta}\delta_{i\alpha}\delta_{\gamma j}\delta_{\delta i}$$

$$\langle 0|\, \overbrace{a_j a_i a^\dagger_\alpha}\, a^\dagger_\beta \overbrace{a_\gamma a_\delta a^\dagger_i}\, a^\dagger_j \,|0\rangle = -\delta_{j\beta}\delta_{i\alpha}\delta_{\gamma i}\delta_{\delta j}$$

$$\langle 0|\, \overbrace{a_j a_i a^\dagger_\alpha}\, a^\dagger_\beta \overbrace{a_\gamma a_\delta a^\dagger_i}\, a^\dagger_j \,|0\rangle = \delta_{j\alpha}\delta_{i\beta}\delta_{\gamma i}\delta_{\delta j}$$

$$\langle 0|\, \overbrace{a_j a_i a^\dagger_\alpha}\, a^\dagger_\beta \overbrace{a_\gamma a_\delta a^\dagger_i}\, a^\dagger_j \,|0\rangle = -\delta_{j\alpha}\delta_{i\beta}\delta_{\gamma i}\delta_{\delta j}$$

In chronological order, we get the terms:

$$\langle ij|\, \hat{V} \,|ij\rangle_{AS}\,, -\langle ij|\, \hat{V} \,|ji\rangle_{AS}\,, \langle ji|\, \hat{V} \,|ji\rangle_{AS}\,, -\langle ji|\, \hat{V} \,|ij\rangle_{AS}$$

And since $\langle ij|\, \hat{V} \,|ij\rangle = -\langle ji|\, \hat{V} \,|ji\rangle$, we can simplify the expression to:

$$\langle c|\, \hat{H}_I \,|c\rangle = \frac{1}{2} \sum_{ij} \langle ij|\, V \,|ij\rangle_{AS} = \frac{1}{2} \sum_{ij} \langle ij|\, \frac{1}{r_{ij}} \,|ij\rangle - \langle ij|\, \frac{1}{r_{ij}} \,|ji\rangle$$

And so the full energy of the system is:

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

The energy of from the one-body term is:

$$\langle\Phi_0|\,\hat{H}_0\,|\Phi_0\rangle = \sum_i \langle i|\,\hat{h}_0\,|i\rangle = 2\left(-\frac{Z^2}{2}\right) = -Z^2$$

The energy from the two-body term is:

$$\langle\Phi_0|\,\hat{H}_I\,|\Phi_0\rangle = \frac{1}{2}\sum_{ij}\left[\langle ij|\,V\,|ij\rangle - \langle ij|\,V\,|ji\rangle\right] = 2 * \frac{1}{2} * \frac{5Z}{8} = \frac{5Z}{8}$$

The helium atom has $Z = 2$, and so the total energy of the system is:

$$E[\Phi_0] = -4 + \frac{5}{4} = -\frac{11}{4} = 74.8eV$$

c)

For this exercise, we are going to explore the one-particle-one-hole excitations $\langle c|\,\hat{H}\,|\Phi_i^a\rangle$ and $\langle\Phi_i^a|\,\hat{H}\,|\Phi_j^b\rangle$.
For the more complicated systems, we can split the Hamiltionan:

$$\hat{H} = \mathcal{E}_0^{ref} + \hat{F}_N + \hat{V}_N$$

Where $\mathcal{E}_0^{ref}$ is the reference energy, or the ground state energy of the system, $\hat{F}_N$ is the normal-ordered one-body part of the Hamiltonian and $\hat{V}_N$ is the normal-ordered two-body part of the Hamiltonian.

$$\hat{F}_N = \sum_{pq}\langle p|\,\hat{f}\,|q\rangle\, a_p^\dagger a_q, \quad \langle p|\,\hat{f}\,|q\rangle = \langle p|\,\hat{h}_0\,|q\rangle \sum_i \langle pi|\,\hat{V}\,|qi\rangle_{AS}$$

$$\hat{V}_N = \frac{1}{4}\sum_{pqrs}\langle pq|\,\hat{v}\,|rs\rangle\, a_p^\dagger a_q^\dagger a_s a_r$$

Now we can start with $\langle c|\,\hat{H}\,|\Phi_i^a\rangle$:

$$\langle c|\,\mathcal{E}_0^{ref}\,|\Phi_i^a\rangle = 0$$

$$\langle c|\,\hat{F}_N\,|\Phi_i^a\rangle = \sum_{pq}\langle p|\,\hat{f}\,|q\rangle\,\langle c|\,a_p^\dagger a_q\,|\Phi_i^a\rangle$$

Here we can take a look at the contractions:

$$\langle c|\,a_p^\dagger a_q a_a^\dagger a_i\,|c\rangle$$

$$\langle 0|\,\overbrace{a_p a_q a_a^\dagger}\, a_i^\dagger\,|0\rangle = \delta_{pi}\delta_{qa}$$

Then we get:

$$\langle c|\,\hat{F}_N\,|\Phi_i^a\rangle = \langle i|\,\hat{f}\,|a\rangle = \langle i|\,\hat{h}_0\,|a\rangle + \sum_j \langle ij|\,\hat{V}\,|aj\rangle$$

For the two-body term:

$$\langle c|\,\hat{V}_N\,|\Phi_i^a\rangle = \frac{1}{4}\sum_{pqrs}\langle pq|\,\hat{v}\,|rs\rangle\,\langle c|\,a_p^\dagger a_q^\dagger a_s a_r\,|\Phi_i^a\rangle = 0$$

This is because to perform contractions, we would have to contract whithin the normal ordered operator, which would result in zero.
Therefor, the total expression for $\langle c|\,\hat{H}\,|\Phi_i^a\rangle$ is:

$$\langle c|\,\hat{H}\,|\Phi_i^a\rangle = \langle i|\,\hat{h}_0\,|a\rangle + \sum_j \langle ij|\,\hat{V}\,|aj\rangle$$

Now we can move on to $\langle\Phi_i^a|\,\hat{H}\,|\Phi_j^b\rangle$:

$$\langle\Phi_i^a|\,\mathcal{E}_0^{ref}\,|\Phi_j^b\rangle = \mathcal{E}_0^{ref}\delta_{ij}\delta_{ab}$$

$$\langle\Phi_i^a|\,\hat{F}_N\,|\Phi_j^b\rangle = \sum_{pq}\langle p|\,\hat{f}\,|q\rangle\,\langle\Phi_i^a|\,a_p^\dagger a_q\,|\Phi_j^b\rangle$$

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

$$\langle c|\,\overbrace{a_i^\dagger a_a a_p^\dagger a_q a_b^\dagger a_j}\,|c\rangle = \delta_{ij}\delta_{ap}\delta_{qb} nvergedin15iterationsFinalsingle{-}particleenergies : [-0.888475{-}0.8$$

$$\langle c|\,\overbrace{a_i^\dagger a_a a_p^\dagger a_q a_b^\dagger a_j}\,|c\rangle = -\delta_{iq}\delta_{ab}\delta_{qj}$$

Then we get:

$$\langle\Phi_i^a|\,\hat{F}_N\,|\Phi_j^b\rangle = \langle a|\,\hat{f}\,|b\rangle\,\delta_{ij} - \langle j|\,\hat{f}\,|i\rangle\,\delta_{ab}$$

And lastly for the two-body term:

$$\langle\Phi_i^a|\,\hat{V}_N\,|\Phi_j^b\rangle = \frac{1}{4}\sum_{pqrs}\langle pq|\,\hat{v}\,|rs\rangle\,\langle\Phi_i^a|\,a_p^\dagger a_q^\dagger a_s a_r\,|\Phi_j^b\rangle$$

$$\langle\Phi_i^a|\,a_p^\dagger a_q^\dagger a_s a_r\,|\Phi_j^b\rangle = \langle c|\,a_i^\dagger a_a a_p^\dagger a_q^\dagger a_s a_r a_b^\dagger a_j\,|c\rangle$$

Now we can take a look at the contractions again:

$$\langle c|\,\overbrace{a_i^\dagger a_a a_p^\dagger a_q^\dagger a_s a_r a_b^\dagger a_j}\,|c\rangle = -\delta_{ap}\delta_{is}\delta_{qj}\delta_{br}$$

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$$\langle c|\,\overbrace{a_i^\dagger a_a a_p^\dagger a_q^\dagger a_s a_r a_b^\dagger a_j}\,|c\rangle = \delta_{is}\delta_{aq}\delta_{pj}\delta_{br}$$

$$\langle c|\,\overbrace{a_i^\dagger a_a a_p^\dagger a_q^\dagger a_s a_r a_b^\dagger a_j}\,|c\rangle = -\delta_{ir}\delta_{aq}\delta_{pj}\delta_{bs}$$

From this we get:

$$\langle\Phi_i^a|\,\hat{V}_N\,|\Phi_j^b\rangle = \frac{1}{4}\sum_{pqrs}\langle pq|\,\hat{v}\,|rs\rangle\,\left[-\delta_{ap}\delta_{is}\delta_{qj}\delta_{br} + \delta_{ap}\delta_{ir}\delta_{qj}\delta_{bs} + \delta_{is}\delta_{aq}\delta_{pj}\delta_{br} - \delta_{ir}\delta_{aq}\delta_{pj}\delta_{bs}\right]$$

$$= \langle aj|\,\hat{V}\,|ib\rangle_{AS}$$

And so the total expression for $\langle\Phi_i^a|\,\hat{H}\,|\Phi_j^b\rangle$ is:

$$\langle\Phi_i^a|\,\hat{H}\,|\Phi_j^b\rangle = \mathcal{E}_0^{ref}\delta_{ij}\delta_{ab} + \langle a|\,\hat{f}\,|b\rangle\,\delta_{ij} - \langle j|\,\hat{f}\,|i\rangle\,\delta_{ab} + \langle aj|\,\hat{V}\,|ib\rangle_{AS}$$

Computing the values numerically we get the following energy: -2.141 in atomic units, or -58.2 eV. Which is slighlty off the real value, but I cant find the error in the code. I was hoping for a higher accuracy here.

d)

The ansatz for the ground state for the beryllium atom is:

$$|c\rangle = a^\dagger_{1s,\uparrow} a^\dagger_{1s,\downarrow} a^\dagger_{2s,\uparrow} a^\dagger_{2s,\downarrow} |0\rangle$$

The energy i calculated numerically came down to: -13.716 in atomic units, or -373.23 eV. Which is more accurate than what i got for the helium atom.

e)

We aim to minimize the totalen ergy of the system with respect t the coefficients $C_{p\alpha}$, while ensuring that the Hartree Fock orbitals remain orthonormal.
The energy functional is:

$$E[C_{p\alpha}] = \sum_{\alpha\beta} C^*_{p\alpha} \langle\alpha| h |\beta\rangle C_{p\beta} + \frac{1}{2} \sum_{\alpha\beta\gamma\delta} C^*_{p\alpha} C^*_{q\beta} \langle\alpha\beta| V |\gamma\delta\rangle_{AS} C_{q\gamma} C_{p\delta}$$

Where $\langle\alpha| h |\beta\rangle$ represents the one-body Hamiltionan matrix elements and $\langle\alpha\beta| V |\gamma\delta\rangle_{AS}$ represents the two-body interaction matrix elements.
We will proceed by minimizing $E[C_{p\alpha}]$ with respect to the coefficients $C_{p\alpha}$, while keeping the orbitals orthonormal.

$$\frac{\partial}{\partial C^*_{p\alpha}} \left(E - \sum_p \epsilon_p \left(\sum_\alpha C^*_{p\alpha} C_{p\alpha} - 1 \right) \right) = 0$$

The term $\sum_p \epsilon_p \left(\sum_\alpha C^*_{p\alpha} C_{p\alpha} - 1 \right)$ is the constraint that the orbitals are orthonormal, where ϵ_p is the Lagrange multiplier.
We can now take the derivative and start with the one-body term:

$$\frac{\partial}{\partial C^*_{p\alpha}} \sum_{\alpha\gamma} C^*_{p\alpha} h_{\alpha\gamma} C_{p\gamma} = h_{\alpha\gamma} C_{p\gamma}$$

For the two-body term:

$$\frac{\partial}{\partial C^*_{p\alpha}} \left(\frac{1}{2} \sum_{\alpha\beta\gamma\delta} \sum_{pq} C^*_{p\alpha} C^*_{q\beta} \langle\alpha\beta| V |\gamma\delta\rangle_{AS} C_{q\gamma} C_{p\delta} \right)$$

$$= \sum_{\alpha\beta\gamma\delta} \sum_q C^*_{q\beta} \langle\alpha\beta| V |\gamma\delta\rangle_{AS} C_{q\gamma} C_{p\delta}$$

The orthonormality constraint:

$$\frac{\partial}{\partial C^*_{p\alpha}} \sum_p \epsilon_p \left(\sum_\alpha C^*_{p\alpha} C_{p\alpha} - 1 \right) = \epsilon_p C_{p\alpha}$$

Combining the three terms:

$$\sum_\gamma h_{\alpha\gamma} C_{p\gamma} + \sum_q \sum_{\beta\gamma\delta} C^*_{q\beta} \langle\alpha\beta| V |\gamma\delta\rangle_{AS} C_{q\gamma} C_{p\delta} = \epsilon_p C_{p\alpha}$$

We can now define the Hartree Fock matrix elements:

$$h_{\alpha\gamma}^{HF} = \langle\alpha|\, h\, |\gamma\rangle + \sum_{q}\sum_{\beta\delta} C_{q\beta}^{*} C_{q\delta}\, \langle\alpha\beta|\, V\, |\gamma\delta\rangle_{AS}$$

And the Hartree Fock equation:

$$h_{\alpha\gamma}^{HF} C_{p\gamma} = \epsilon_p C_{p\alpha}$$

And lastly, in the second quiantized form, we can define the Hartree Fock operator $\hat{F}$:

$$\hat{F} = \sum_{\alpha\gamma} h_{\alpha\gamma}^{HF} a_{\alpha}^{\dagger} a_{\gamma}$$

f)

Atom	Single particle energy	New energy
helium	-0.7832	-2.8991
beryllium	-3.9506	-14.4998

Table 1: Hartree Fock energies for the beryllium atom

For the helium atom, the new energy was slightly impro using the hartree fck method, with -2.8991 slighlty more accurate than the previous -2.75 atomic units.
For beryllium, the new energy -14.4998 is also more accurate than the previous -13.716 atomic units.

g)

The diagonalization with the new Hartree-Fock potential yields new eigenvectors and eigenvalues. This process is continued till for example

$$\frac{\sum_p \epsilon_i - \epsilon_{i+n}}{m} < \lambda$$

Where λ is some number smaller than a given tolerance (1e-8).
For helium:
After 15 iterations I obtained -2.831 in atomic units
For beryllium:
After 16 iterations I obtained -14.508 in atomic units
These results were obtained with a tolerance of 1e-12.
For the helium atom we found the best results when diagonalising the hamiltonian directly, but when moving on to just slightly heavier atoms (beryllium) we saw that the iterative scheme payed off.

Diagrams and github link)

`https://github.com/hishemok/FYS4480/tree/main/Documents/GitHub/Fys4480/Midterm1`