Midterm 1

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1 Quantum mechanics for many-particle systems

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, $|\Phi_i^a\rangle$. 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:

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

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

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

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

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:

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

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:

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

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:

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

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

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 $\langle\Phi_i^a|\,\hat{H}\,|\Phi_j^b\rangle$:

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

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

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

$$\langle c|\,a_i^\dagger a_a a_p^\dagger a_q a_b^\dagger a_j\,|c\rangle = \delta_{ij}\delta_{ap}\delta_{qb}$$

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

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:

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

$$\langle c|\,a_i^\dagger a_a a_p^\dagger a_q^\dagger a_s a_r a_b^\dagger a_j\,|c\rangle = \delta_{ap}\delta_{ir}\delta_{qj}\delta_{bs}$$

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

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

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:

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

d)

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

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

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:

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

And the Hartree Fock equation:

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

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

$$\hat{F} = \sum_{\alpha\gamma} h^{HF}_{\alpha\gamma} a^\dagger_\alpha a_\gamma$$

f)

g)