FYS4480 First Midterm

Håkon Kvernmoen

October 2022

Part a), setting up the basis.

Since we use hydrogen-like single particle states, we consider the quantum numbers nlm_lsm_s. We constrain ourselves to only look at $n = 1, 2, 3$, with $l = 0$ implying $m_l = 0$ In addition, since electrons are fermions, all single particle states (SPS) must have $s = 1/2$, giving two possible spin projections $m_s = 1/2, -1/2$, which we will write as $\uparrow, \downarrow$ respectively. Due to these restrictions, the only relevant quantum numbers are nm_s. Using the creation and annihilation operators $(a^\dagger_{nm_s}, a_{nm_s})$ from the second quantization formalism, we can construct all six SPS as excitations of the vacuum state $|0\rangle$:

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

We now wish to set up an ansatz (educated guess) for the helium ground state $|\Phi_0\rangle$. The one body energy $\langle i|\hat{h}_0|i\rangle$ is increasing with n, thus it makes sense that the lowest energy multi particle state (MPS) should prioritize the $n = 1$ SPS. No two fermions can be in the same state, thus setting both electrons in $n = 1$ requires antiparallel spin. This gives:

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

Working with $|0\rangle$ becomes cumbersome when we wish to look at excitations of $|\Phi_0\rangle$, especially if $|\Phi_0\rangle$ contains many electrons. Therefor we "redefine the vacuum", that is set $|\Phi_0\rangle$ as the Fermi level. This means that we will add and remove particles from $|\Phi_0\rangle$ to represent excited states, instead of constructing these from $|0\rangle$. This introduces the language of *particles* and *holes*. A particle state is a filled state above the Fermi level, that is adding a $n = 2$ or 3 state to $|\Phi_0\rangle$. On the contrary a hole state is a non-filled state below the Fermi level, that is removing one of the $n = 1$ electrons from $|\Phi_0\rangle$. We will refer to hole states using letters $i, j, k, ...$ and particle states using letters $a, b, c, ...$ with each of these indices referring to the relevant quantum numbers nm_s.

We will now construct one-particle-one-hole excitations of our ground state $|\Phi_0\rangle$, which we will write $|\Phi^a_i\rangle$. To simplify the number of excitations we will only consider states with a total spin projection $M_s = 0$. Since we have two electrons, this implies that they must have opposite spins. In terms of creation and annihilation operators, the one-particle-one-hole states can be expressed as:

$$|\Phi^a_i\rangle = a^\dagger_a a_i|\Phi_0\rangle$$

The annihilation operator must have the same quantum numbers as one of the electrons in $|\Phi_0\rangle$, giving $i \in \{\,(1\uparrow), (1\downarrow)\,\}$. In addition, to keep the $M_s = 0$ constraint the creation operator must have the same spin projection as the annihilation operator giving $a \in \{\,(2\uparrow), (3\uparrow)\,\}$ for $i = (1\uparrow)$ and $\{\,(2\downarrow), (3\downarrow)\,\}$ for $i = (1\downarrow)$, giving a total of four one-particle-one-hole states:

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

Using the same methodology, we construct all possible two-particle-two-hole states in the second quantization representation:

$$|\Phi^{ab}_{ij}\rangle = a^\dagger_a a^\dagger_b a_i a_j|\Phi_0\rangle$$

The annihilation operators must again have the same quantum numbers as one the electrons in $|\Phi_0\rangle$. Since we have two on them, they are now locked to $i = (1\uparrow), j = (1\downarrow)$. This leaves us with the vacuum again, where we can fill the states

$n = 2, 3$ and $m_s = \uparrow, \downarrow$ giving $4 * 2 = 8$ states. However, the $M_s = 0$ restriction reduces this to 4 states since we must have antiparallel spins:

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

Part b), Second quantized Hamiltonian.

$$
\begin{aligned}
\hat{H} &= \hat{H}_0 + \hat{H}_I \\
\hat{H}_0 &= \sum_{pq} \langle p|\hat{h}_0|q\rangle \, a^\dagger_p a_q \\
\hat{H}_I &= \frac{1}{4} \sum_{pqrs} \langle pq|\hat{v}|rs\rangle_{\mathrm{AS}} \, a^\dagger_p a^\dagger_q a_s a_r
\end{aligned}
$$

$$
\begin{aligned}
\hat{H}_0 &= \sum_{pq} \langle p|\hat{h}_0|q\rangle \left\{ a^\dagger_p a_q \right\} + \sum_i \langle i|\hat{h}_0|i\rangle \\
\hat{H}_I &= \frac{1}{4} \sum_{pqrs} \langle pq|\hat{v}|rs\rangle_{\mathrm{AS}} \left\{ a^\dagger_p a^\dagger_q a_s a_r \right\} + \sum_{pqi} \langle pi|\hat{v}|qi\rangle_{\mathrm{AS}} \left\{ a^\dagger_p a^\dagger_q \right\} + \frac{1}{2} \sum_{ij} \langle ij|\hat{v}|ij\rangle_{\mathrm{AS}}
\end{aligned}
$$

Part c), Limiting ourselves to one-particle-one-hole excitations.

Part d), Moving to the Beryllium atom.

Part e), Hartree-Fock.

Part f), The Hartree-Fock matrices.

Part g), Writing a Hartree-Fock code.

A Appendix entry

some appendix things [1]

References

[1] John P. Perdew et al. "Understanding band gaps of solids in generalized Kohn–Sham theory". In: *Proceedings of the National Academy of Sciences* 114.11 (2017), 2801–2806. ISSN: 1091-6490. DOI: 10.1073/pnas.1621352114. URL: http://dx.doi.org/10.1073/pnas.1621352114.