

FYS4480 First Midterm

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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 ($a_{nm_s}^\dagger, a_{nm_s}$) from the second quantization formalism, we can construct all six SPS as excitations of the vacuum state $|0\rangle$:

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

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:

$$|\Phi_0\rangle = a_{1\uparrow}^\dagger a_{1\downarrow}^\dagger |0\rangle$$

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, \dots and particle states using letters a, b, c, \dots 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 $|\Phi_i^a\rangle$. 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:

$$|\Phi_i^a\rangle = a_a^\dagger a_i |\Phi_0\rangle$$

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:

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

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

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

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:

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

Part b), Second quantized Hamiltonian.

We now define the Hamiltonian in a second quantized form. As seen in both the lectures and lecture notes, the one body part (\hat{H}_0) and two body part (\hat{H}_I) can be written using creation and annihilation operators as:

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

With \hat{h}_0 containing both the electrons kinetic term and electromagnetic interaction with the stationary nucleus (modeled as an external potential). Here, the interaction potential $\hat{v} = 1/r$ is the electron-electron interaction. The AS subscript on the two body matrix element is defined as $\langle pq | \hat{v} | rs \rangle_{\text{AS}} = \langle pq | \hat{v} | rs \rangle - \langle pq | \hat{v} | sr \rangle$. The indices p, q, r, s, \dots are used to note both particle and hole states (above and below the Fermi level). In the exercise from week 39, we rewrote this in *normal ordered* form w.r.t. to the Fermi level (NOTE TO SELF: Do I need to show this?). The result is:

$$\hat{H}_0 = \sum_{pq} \langle p | \hat{h}_0 | q \rangle \{ a_p^\dagger a_q \} + \sum_i \langle i | \hat{h}_0 | i \rangle \quad (1)$$

$$\hat{H}_I = \frac{1}{4} \sum_{pqrs} \langle pq | \hat{v} | rs \rangle_{\text{AS}} \{ a_p^\dagger a_q^\dagger a_s a_r \} + \sum_{pqi} \langle pi | \hat{v} | qi \rangle_{\text{AS}} \{ a_p^\dagger a_q \} + \frac{1}{2} \sum_{ij} \langle ij | \hat{v} | ij \rangle_{\text{AS}} \quad (2)$$

This allows us the use Wick's generalized theorem, such that only operators between different normal ordered strings need to be contracted. Using this, we want to calculate the energy expectation value of the ground state $|\Phi_0\rangle$. Since we have \hat{H} expressed in a normal ordered formed, the terms with $\{ a_p^\dagger a_q \}$ and the term with $\{ a_p^\dagger a_q^\dagger a_s a_r \}$ becomes 0 when applied to an inner product of $|\Phi_0\rangle$. Thus, the calculation becomes rather simple.

$$\begin{aligned} E[\Phi_0] &= \langle \Phi_0 | \hat{H} | \Phi_0 \rangle = \langle \Phi_0 | \hat{H}_0 + \hat{H}_I | \Phi_0 \rangle \\ \langle \Phi_0 | \hat{H}_0 | \Phi_0 \rangle &= 0 + \sum_i \langle i | \hat{h}_0 | i \rangle \langle \Phi_0 | \Phi_0 \rangle = \sum_i \langle i | \hat{h}_0 | i \rangle \\ \langle \Phi_0 | \hat{H}_I | \Phi_0 \rangle &= 0 + 0 + \frac{1}{2} \sum_{ij} \langle ij | \hat{v} | ij \rangle_{\text{AS}} \langle \Phi_0 | \Phi_0 \rangle = \frac{1}{2} \sum_{ij} \langle ij | \hat{v} | ij \rangle_{\text{AS}} \\ \Rightarrow E[\Phi_0] &= \sum_i \langle i | \hat{h}_0 | i \rangle + \frac{1}{2} \sum_{ij} \langle ij | \hat{v} | ij \rangle_{\text{AS}} \quad (3) \end{aligned}$$

The sum indices i and j are over all energy levels n and spin states $m_s \in \{ \uparrow, \downarrow \}$ which are below the Fermi level. Explicitly, this can be written as:

$$\begin{aligned} \sum_i \langle i | \hat{h}_0 | i \rangle &= \sum_{n \leq F} \sum_{m_s} \langle nm_s | \hat{h}_0 | nm_s \rangle \\ \frac{1}{2} \sum_{ij} \langle ij | \hat{v} | ij \rangle_{\text{AS}} &= \sum_{n \leq F} \sum_{n' \leq F} \sum_{m_s} \sum_{m'_s} \langle nm_s, n'm'_s | \hat{v} | nm_s, n'm'_s \rangle_{\text{AS}} \end{aligned}$$

Since only $n = 1$ is included in and below the Fermi level for the Helium atom, the sum here is only over spin projections $m_s \in \{\uparrow, \downarrow\}$. This removes the sums over radial quantum numbers with $n = n' = 1$ substituted in. We now insert the matrix elements to get the energy expectation value as a function of Z :

$$\begin{aligned}
\sum_i \langle i | \hat{h}_0 | i \rangle &= \langle 1\uparrow | \hat{h}_0 | 1\uparrow \rangle + \langle 1\downarrow | \hat{h}_0 | 1\downarrow \rangle = -\frac{Z^2}{2} - \frac{Z^2}{2} = -Z^2 \\
\sum_{ij} \langle ij | \hat{v} | ij \rangle_{\text{AS}} &= \langle 1\uparrow 1\downarrow | \hat{v} | 1\uparrow 1\downarrow \rangle_{\text{AS}} + \langle 1\downarrow 1\uparrow | \hat{v} | 1\downarrow 1\uparrow \rangle_{\text{AS}} \\
&= (\langle 1\uparrow 1\downarrow | \hat{v} | 1\uparrow 1\downarrow \rangle - \langle 1\uparrow 1\downarrow | \hat{v} | 1\downarrow 1\uparrow \rangle) \\
&\quad + (\langle 1\downarrow 1\uparrow | \hat{v} | 1\downarrow 1\uparrow \rangle - \langle 1\downarrow 1\uparrow | \hat{v} | 1\uparrow 1\downarrow \rangle) \\
&= \langle 11 | \hat{v} | 11 \rangle + \langle 11 | \hat{v} | 11 \rangle = \frac{5Z}{4} \\
E[\Phi_0] &= -Z^2 + \frac{5Z}{8}
\end{aligned}$$

Where we have used that the antisymmetric terms with $m_s = m'_s$ evaluates to 0 and the fact that the interaction \hat{v} only acts on the spatial part of the state, with our spin projection states being orthonormal:

$$\langle \alpha\sigma\beta\tau | v | \beta\mu\gamma\nu \rangle = \langle \alpha\beta | \hat{v} | \gamma\delta \rangle \delta_{\sigma\mu} \delta_{\tau\nu}$$

With $\alpha, \beta, \gamma, \delta$ referring to the n (spatial) quantum number and σ, τ, μ, ν referring to the spin projection m_s .
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Part c), Limiting ourselves to one-particle-one-hole excitations.

We will now calculate the matrix elements involving the one-particle-one-hole states. Firstly, we compute the elements including a single excited state $\langle \Phi_0 | \hat{H} | \Phi_i^a \rangle$. This is done by using the expressions for the Hamiltonian $\hat{H} = \hat{H}_0 + \hat{H}_I$ from eq. 1, 2 in addition to Wick's generalized theorem. The excited state is also in normal order. We see that the terms without any operators simply give a term $\langle \Phi_0 | \Phi_i^a \rangle$ which yields zero. In addition, the term including four normal ordered operators leaves us with two uncontracted normal ordered operators, which gives zero when applied inside an inner product between $|\Phi_0\rangle$'s. Thus, only the terms with two normal ordered operators $\{a_p^\dagger a_q\}$ will contribute. There are two such terms and we therefor calculate these contractions before applying the sums.

$$\begin{aligned}
\langle \Phi_0 | \{a_p^\dagger a_q\} | \Phi_i^a \rangle &= \langle \Phi_0 | \{a_p^\dagger a_q\} \{a_a^\dagger a_i\} | \Phi_0 \rangle = \langle \Phi_0 | \overline{a_p^\dagger a_q a_a^\dagger a_i} | \Phi_0 \rangle = \delta_{pi} \delta_{qa} \\
\langle \Phi_0 | \hat{H} | \Phi_i^a \rangle &= \sum_{pq} \langle p | \hat{h}_0 | q \rangle \delta_{pi} \delta_{qa} + 0 + 0 + \sum_{pqj} \langle pj | \hat{v} | qj \rangle_{\text{AS}} \delta_{pi} \delta_{qa} + 0 \\
&= \langle i | \hat{h}_0 | a \rangle + \sum_j \langle ij | \hat{v} | aj \rangle_{\text{AS}}
\end{aligned} \tag{4}$$

We now move on to the elements including two one-particle-one-hole states, $\langle \Phi_i^a | \hat{H} | \Phi_j^b \rangle$. For the terms in the Hamiltonian not having any normal ordered operators, we need be careful since we can have the same states on both sides in the case $i = j$ and $a = b$. In addition, both the term with two and four normal ordered operators can now contribute. For less clutter, we first calculate the contractions giving the relevant Kronecker delta's before inserting them into their respective sums.

$$\begin{aligned}
\{a_i^\dagger a_a\} \{a_b^\dagger a_j\} &= \overline{a_i^\dagger a_a a_b^\dagger a_j} = \delta_{ij} \delta_{ab} \\
\{a_i^\dagger a_a\} \{a_p^\dagger a_q\} \{a_b^\dagger a_j\} &= \overline{a_i^\dagger a_a a_p^\dagger a_q a_b^\dagger a_j} + \overline{a_i^\dagger a_a a_p^\dagger a_q a_b^\dagger a_j} = \delta_{ij} \delta_{ap} \delta_{qb} - \delta_{iq} \delta_{ab} \delta_{pj} \\
\{a_i^\dagger a_a\} \{a_p^\dagger a_q^\dagger a_s a_r\} \{a_b^\dagger a_j\} &= \overline{a_i^\dagger a_a a_p^\dagger a_q^\dagger a_s a_r a_b^\dagger a_j} + \overline{a_i^\dagger a_a a_p^\dagger a_q^\dagger a_s a_r a_b^\dagger a_j} + \overline{a_i^\dagger a_a a_p^\dagger a_q^\dagger a_s a_r a_b^\dagger a_j} + \overline{a_i^\dagger a_a a_p^\dagger a_q^\dagger a_s a_r a_b^\dagger a_j} \\
&= \delta_{ir} \delta_{ap} \delta_{qj} \delta_{sb} - \delta_{ir} \delta_{aq} \delta_{pj} \delta_{sb} + \delta_{is} \delta_{aq} \delta_{pj} \delta_{rb} - \delta_{is} \delta_{ap} \delta_{qj} \delta_{rb}
\end{aligned}$$

Inserting this into the sum then yields the following expression for the matrix elements:

$$\begin{aligned}\langle \Phi_i^a | \hat{H}_0 | \Phi_j^b \rangle &= \sum_{pq} \langle p | \hat{h}_0 | q \rangle (\delta_{ij} \delta_{ap} \delta_{qb} - \delta_{iq} \delta_{ab} \delta_{pj}) + \sum_k \langle k | \hat{h}_0 | k \rangle \delta_{ij} \delta_{ab} \\ &= \langle a | \hat{h}_0 | b \rangle \delta_{ij} - \langle j | \hat{h}_0 | i \rangle \delta_{ab} + \sum_k \langle k | \hat{h}_0 | k \rangle \delta_{ij} \delta_{ab}\end{aligned}\quad (5)$$

$$\begin{aligned}\langle \Phi_i^a | \hat{H}_I | \Phi_j^b \rangle &= \frac{1}{4} \sum_{pqrs} \langle pq | \hat{v} | rs \rangle_{\text{AS}} (\delta_{ir} \delta_{ap} \delta_{qj} \delta_{sb} - \delta_{ir} \delta_{aq} \delta_{pj} \delta_{sb} + \delta_{is} \delta_{aq} \delta_{pj} \delta_{rb} - \delta_{is} \delta_{ap} \delta_{qj} \delta_{rb}) \\ &\quad + \sum_{pqk} \langle pk | \hat{v} | qk \rangle_{\text{AS}} (\delta_{ij} \delta_{ap} \delta_{qb} - \delta_{iq} \delta_{ab} \delta_{pj}) \\ &\quad + \frac{1}{2} \sum_{kl} \langle kl | \hat{v} | kl \rangle_{\text{AS}} \delta_{ij} \delta_{ab} \\ &= \langle aj | \hat{v} | ib \rangle_{\text{AS}} + \sum_k (\langle ak | \hat{v} | bk \rangle_{\text{AS}} \delta_{ij} - \langle jk | \hat{v} | ik \rangle_{\text{AS}} \delta_{ab}) + \frac{1}{2} \sum_{kl} \langle kl | \hat{v} | kl \rangle_{\text{AS}} \delta_{ij} \delta_{ab}\end{aligned}\quad (6)$$

DIAGRAMS

Now we have everything we need to construct the Hamiltonian matrix containing all single particle excitations. This must include the ground state, as well as the 4 possible single particle excitations, giving a 5×5 matrix. The ordering chosen here is first the ground state, thereafter excitations with increasing n with alternating spin, starting with up. Explicitly $|\Phi_0\rangle, |\Phi_{1\uparrow}^{\uparrow}\rangle, |\Phi_{1\downarrow}^{2\downarrow}\rangle, |\Phi_{1\uparrow}^{3\uparrow}\rangle, |\Phi_{1\downarrow}^{3\downarrow}\rangle$

Part d), Moving to the Beryllium atom.

We now wish to look at the $Z = 4$ Beryllium atom. Instead of having 2 electrons, we now have 4. Using the logic as for the Helium atom, an ansatz for the ground state can now be written as:

$$|\Phi_0\rangle = a_{2\uparrow}^\dagger a_{2\downarrow}^\dagger a_{1\uparrow}^\dagger a_{1\downarrow}^\dagger |0\rangle$$

The one-particle-one-hole excitations can be found through the same procedure:

$$|\Phi_i^a\rangle = a_a^\dagger a_i |\Phi_0\rangle$$

Now we can remove any of the four electrons $i \in \{(1\uparrow), (1\downarrow), (2\uparrow), (2\downarrow)\}$. However, we can only place it $n = 3$, and due to the $M_s = 0$ constraint, it must have the same spin as the removed electron. This again leaves us with four one-particle-one-hole states:

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

Previously we set the Fermi level at $n = 1$. Since we want to use the matrix elements derived for the Helium atom, we now simply move this to $n = 2$, such that the Beryllium $|\Phi_0\rangle$ becomes our zero-particle-zero-hole state.

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](https://doi.org/10.1073/pnas.1621352114). URL: <http://dx.doi.org/10.1073/pnas.1621352114>.