First midterm FYS4480
Quantum mechanics for many-particle systems

August Femtehjell & Oskar Idland

October 2024

Introduction

In this midterm we will develop two simple models for studying the helium atom (with two electrons) and the beryllium atom with four electrons.

After having introduced the Born-Oppenheimer approximation which effectively freezes out the nucleonic degrees of freedom, the Hamiltonian for N electrons takes the following form

$$\hat{H} = \sum_{i=1}^{N} t(x_i) - \sum_{i=1}^{N} k\frac{Ze^2}{r_i} + \sum_{i<j}^{N} \frac{ke^2}{r_{ij}},$$

with $k = 1.44$ eVnm. Throughout this work we will use atomic units, this means that $\hbar = c = e = m_e = 1$. The constant k becomes also equal 1. The resulting energies have to be multiplied by 2×13.6 eV in order to obtain energies in eletronvolts.

We can rewrite our Hamiltonians as

$$\hat{H} = \hat{H}_0 + \hat{H}_I = \sum_{i=1}^{N} \hat{h}_0(x_i) + \sum_{i<j}^{N} \frac{1}{r_{ij}}, \tag{1}$$

where we have defined $r_{ij} = |\boldsymbol{r}_i - \boldsymbol{r}_j|$ and $\hat{h}_0(x_i) = \hat{t}(x_i) - \frac{Z}{r_i}$.

The variable x contains both the spatial coordinates and the spin values. The first term of Eq. (1), H_0, is the sum of the N *one-body* Hamiltonians $\hat{h}_0$. Each individual Hamiltonian $\hat{h}_0$ contains the kinetic energy operator of an electron and its potential energy due to the attraction of the nucleus. The second term, H_I, is the sum of the $N(N-1)/2$ two-body interactions between each pair of electrons. Note that the double sum carries a restriction $i < j$.

As basis functions for our calculations we will use hydrogen-like single-particle functions. This means the onebody operator is diagonal in this basis for states i, j with quantum numbers n, l, m_l, s, m_s with energies

$$\langle i|\hat{h}_0|j\rangle = -\frac{Z^2}{2n^2}\delta_{ij}. \tag{2}$$

The quantum number n refers to the number of nodes of the wave function. Observe that this expectation value is independent of spin.

We will in all calculations here restrict ourselves to only so-called s-waves, that is the orbital momentum l is zero. We will also limit the quantum number n to $n \leq 3$. It means that every ns state can accommodate two electrons due to the spin degeneracy.

In the calculations you will need the Coulomb interaction with matrix elements involving single-particle wave functions with $l = 0$ only, the so-called s-waves. We need only the radial part since the spherical harmonics for the s-waves are rather simple. We omit single-particle states with $l > 0$. The actual integrals we need, are tabulated at the end. Our radial wave functions are

$$R_{n0}(r) = \left(\frac{2Z}{n}\right)^{3/2} \sqrt{\frac{(n-1)!}{2n \times n!}} L^1_{n-1}\left(\frac{2Zr}{n}\right) \exp\left(-\frac{Zr}{n}\right),$$

where $L^1_{n-1}(r)$ are the so-called Laguerre polynomials. These wave functions can then be used to compute the direct part of the Coulomb interaction

$$\langle \alpha\beta|V|\gamma\delta\rangle = \int r_1^2 dr_1 \int r_2^2 dr_2 R^*_{n_\alpha 0}(r_1) R^*_{n_\beta 0}(r_2) \frac{1}{r_{12}} R_{n_\gamma 0}(r_1) R_{n_\delta 0}(r_2).$$

Observe that this is only the radial integral and that the labels $\alpha, \beta, \gamma, \delta$ refer only to the quantum numbers n, l, m_l, with m_l the projection of the orbital momentum l. A similar expression can be found for the exchange part. Since we have restricted ourselves to only s-waves, these integrals are straightforward but tedious to calculate. As an addendum to this midterm we list all closed-form expressions for the relevant matrix elements. Note well that these matrix elements do not include spin. When setting up the final antisymmetrized matrix elements you need to consider the spin degrees of freedom as well. Please pay in particular attention to the exchange part and the pertinent spin values of the single-particle states.

We will also, for both helium and beryllium assume that the many-particle states we construct have always the same total spin projection $M_S = 0$. This means that if we excite one or two particles from the ground state, the spins of the various single-particle states should always sum up to zero.

Part a) Setting up the basis

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 degeneracies.

Set up the ansatz for the ground state $|c\rangle = |\Phi_0\rangle$ in second quantization. Define the second quantization and define a table of single-particle states. Construct thereafter all possible one-particle-one-hole excitations $|\Phi_i^a\rangle$ where i refer to levels below the Fermi level (define this level) and a refers to particle states. Define particles and holes. The Slater determinants have to be written in terms

of the respective creation and annihilation operators. The states you construct should all have total spin projection $M_S = 0$. Construct also all possible two-particle-two-hole states $\left|\Phi_{ij}^{ab}\right\rangle$ in a second quantization representation.

Solution

We define the Fermi level as $1s$, such that the ground state is given by

$$|\Phi_0\rangle = |c\rangle = a_{1\sigma_+}^\dagger a_{1\sigma_-}^\dagger |0\rangle, \tag{3}$$

where we define $\sigma_+ = \uparrow = +1/2$ and $\sigma_- = \downarrow = -1/2$. Here, we define particles as electrons above the Fermi level, and holes as the lack of electrons in slots below the Fermi level.

In order to have a one-particle-one-hole excitation, the spin in the hole and particle states must match. All possible one-particle-one-hole (1p1h) excitations are then

$$\left|\Phi_{1\sigma_+}^{2\sigma_+}\right\rangle = a_{2\sigma_+}^\dagger a_{1\sigma_+}|\Phi_0\rangle, \qquad \left|\Phi_{1\sigma_+}^{3\sigma_+}\right\rangle = a_{3\sigma_+}^\dagger a_{1\sigma_+}|\Phi_0\rangle,$$
$$\left|\Phi_{1\sigma_-}^{2\sigma_-}\right\rangle = a_{2\sigma_-}^\dagger a_{1\sigma_-}|\Phi_0\rangle, \qquad \left|\Phi_{1\sigma_-}^{3\sigma_-}\right\rangle = a_{3\sigma_-}^\dagger a_{1\sigma_-}|\Phi_0\rangle,$$

where we always excite a particle from the $1s$ state, to the higher states, with the same spin such that $M_S = 0$.

For the possible two-particle-two-hole (2p2h) excitations $\left|\Phi_{ij}^{ab}\right\rangle$, we have that both electrons below the Fermi level excite, and that the particles above the Fermi level have opposite spins. We then have that the possible configurations are

$$\left|\Phi_{1\sigma_+,1\sigma_-}^{2\sigma_+,2\sigma_-}\right\rangle = a_{2\sigma_+}^\dagger a_{2\sigma_-}^\dagger a_{1\sigma_-} a_{1\sigma_+}|\Phi_0\rangle, \quad \left|\Phi_{1\sigma_+,1\sigma_-}^{2\sigma_+,3\sigma_-}\right\rangle = a_{2\sigma_+}^\dagger a_{3\sigma_-}^\dagger a_{1\sigma_-} a_{1\sigma_+}|\Phi_0\rangle,$$
$$\left|\Phi_{1\sigma_+,1\sigma_-}^{3\sigma_+,2\sigma_-}\right\rangle = a_{3\sigma_+}^\dagger a_{2\sigma_-}^\dagger a_{1\sigma_-} a_{1\sigma_+}|\Phi_0\rangle, \quad \left|\Phi_{1\sigma_+,1\sigma_-}^{3\sigma_+,3\sigma_-}\right\rangle = a_{3\sigma_+}^\dagger a_{3\sigma_-}^\dagger a_{1\sigma_-} a_{1\sigma_+}|\Phi_0\rangle.$$

We now redefine the annihlation and creation operators with respect to the new vaccuum state $|\Phi_0\rangle$, i.e.,

$$b_\alpha^\dagger = \begin{cases} a_\alpha^\dagger & \text{if } \alpha > F, \\ a_\alpha & \text{if } \alpha \leq F, \end{cases} \quad \text{and} \quad b_\alpha = \begin{cases} a_\alpha & \text{if } \alpha > F, \\ a_\alpha^\dagger & \text{if } \alpha \leq F. \end{cases}$$

We then get

$$\left|\Phi_{1\sigma_+}^{2\sigma_+}\right\rangle = b_{2\sigma_+}^\dagger b_{1\sigma_+}^\dagger |\Phi_0\rangle, \qquad \left|\Phi_{1\sigma_+}^{3\sigma_+}\right\rangle = b_{3\sigma_+}^\dagger b_{1\sigma_+}^\dagger |\Phi_0\rangle,$$
$$\left|\Phi_{1\sigma_-}^{2\sigma_-}\right\rangle = b_{2\sigma_-}^\dagger b_{1\sigma_-}^\dagger |\Phi_0\rangle, \qquad \left|\Phi_{1\sigma_-}^{3\sigma_-}\right\rangle = b_{3\sigma_-}^\dagger b_{1\sigma_-}^\dagger |\Phi_0\rangle,$$

and

$$\left|\Phi_{1\sigma_+,1\sigma_-}^{2\sigma_+,2\sigma_-}\right\rangle = b_{2\sigma_+}^\dagger b_{2\sigma_-}^\dagger b_{1\sigma_-}^\dagger b_{1\sigma_+}^\dagger |\Phi_0\rangle, \quad \left|\Phi_{1\sigma_+,1\sigma_-}^{2\sigma_+,3\sigma_-}\right\rangle = b_{2\sigma_+}^\dagger b_{3\sigma_-}^\dagger b_{1\sigma_-}^\dagger b_{1\sigma_+}^\dagger |\Phi_0\rangle,$$
$$\left|\Phi_{1\sigma_+,1\sigma_-}^{3\sigma_+,2\sigma_-}\right\rangle = b_{3\sigma_+}^\dagger b_{2\sigma_-}^\dagger b_{1\sigma_-}^\dagger b_{1\sigma_+}^\dagger |\Phi_0\rangle, \quad \left|\Phi_{1\sigma_+,1\sigma_-}^{3\sigma_+,3\sigma_-}\right\rangle = b_{3\sigma_+}^\dagger b_{3\sigma_-}^\dagger b_{1\sigma_-}^\dagger b_{1\sigma_+}^\dagger |\Phi_0\rangle.$$

Part b) Second quantized Hamiltonian

Define the Hamiltonian in a second-quantized form and use this to compute the expectation value of the ground state (defining the so-called reference energy and later our Hartree-Fock functional) of the helium atom. Show that it is given by

$$E[\Phi_0] = \langle c|\hat{H}|c\rangle = \sum_i \langle i|\hat{h}_0|i\rangle + \frac{1}{2}\sum_{ij}\left[\left\langle ij\left|\frac{1}{r_{ij}}\right|ij\right\rangle - \left\langle ij\left|\frac{1}{r_{ij}}\right|ji\right\rangle\right]. \quad (4)$$

Define properly the sums keeping in mind that the states ij refer to all quantum numbers n, l, m_l, s, m_s. Use the values for the various matrix elements listed at the end of the midterm to find the value of E as function of Z and compute E as function of Z.

Solution

We consider a Hamiltonian $\hat{H} = \hat{H}_0 + \hat{H}_I$, where $\hat{H}_0$ and $\hat{H}_I$ are one-electron and two-electron parts respectively, defined by

$$\hat{H}_0 = \sum_{pq}\langle p|\hat{h}_0|q\rangle a_p^\dagger a_q, \qquad \hat{H}_I = \frac{1}{4}\sum_{pqrs}\langle pq|\hat{v}|rs\rangle_{AS} a_p^\dagger a_q^\dagger a_s a_r. \quad (5)$$

We have the normal-ordered form of annihilation and creation operators, relative to the reference state, where all creation operators are to the left of all annihilation operators. For example, we have $N[a_p^\dagger a_q] = a_p^\dagger a_q$, $N[a_p a_q^\dagger] = -a_q^\dagger a_p$, where the sign is dependent on the number of permutations required to bring the operators to normal order. We are interested in this, as

$$\langle c|N[AB\cdots]|c\rangle = 0$$

if $N[AB\cdots]$ is not empty, where $A, B, \ldots$ are annihilation or creation operators.

With this, we have the contractions of operators, defined as

$$\overbrace{AB} = AB - N[AB].$$

Relative to our reference state, we have that

$$\overbrace{a_i^\dagger a_j} = \delta_{ij}, \qquad \overbrace{a_a a_b^\dagger} = \delta_{ab}$$

are the only non-zero contractions.

For the one-body term, we then have

$$\langle c|\hat{H}_0|c\rangle = \sum_{pq}\langle p|\hat{h}_0|q\rangle\langle c|a_p^\dagger a_q|c\rangle = \sum_{ij}\langle i|\hat{h}_0|j\rangle\delta_{ij} = \sum_i \langle i|\hat{h}_0|i\rangle. \quad (6)$$

For the two-body term, writing $|c\rangle = |ij\rangle$ we first need to examine the possible contractions of $ijp^\dagger q^\dagger srj^\dagger i^\dagger$ and the resulting matrix element $\langle pq|V|rs\rangle_{AS}$. We have

$$\begin{aligned}
\overbrace{jip^\dagger}\overbrace{q^\dagger sri^\dagger}j^\dagger &= \delta_{jq}\delta_{ip}\delta_{sj}\delta_{ri} \to \langle ij|V|ij\rangle_{AS}, \\
\overbrace{jip^\dagger}\overbrace{q^\dagger sri^\dagger}j^\dagger &= -\delta_{jq}\delta_{ip}\delta_{si}\delta_{rj} \to -\langle ij|V|ji\rangle_{AS}, \\
\overbrace{jip^\dagger}\overbrace{q^\dagger sri^\dagger}j^\dagger &= \delta_{jp}\delta_{iq}\delta_{si}\delta_{rj} \to \langle ji|V|ji\rangle_{AS}, \\
\overbrace{jip^\dagger}\overbrace{q^\dagger sri^\dagger}j^\dagger &= -\delta_{jp}\delta_{iq}\delta_{sj}\delta_{ri} \to -\langle ji|V|ij\rangle_{AS}.
\end{aligned}$$

As $\langle \alpha\beta|V|\gamma\delta\rangle_{AS} = -\langle \alpha\alpha|V|\delta\gamma\rangle_{AS}$ we gather these terms, and inserting for V, leaving us with

$$\langle c|\hat{H}_I|c\rangle = \frac{1}{2}\sum_{ij}\langle ij|\frac{1}{r_{ij}}|ij\rangle_{AS} = \frac{1}{2}\sum_{ij}\langle ij|\frac{1}{r_{ij}}|ij\rangle - \langle ij|\frac{1}{r_{ij}}|ji\rangle. \tag{7}$$

Combining this with the one-body term, we have the total reference energy

$$E[\Phi_0] = \langle c|\hat{H}|c\rangle = \sum_i \langle i|\hat{h}_0|i\rangle + \frac{1}{2}\sum_{ij}\langle ij|\frac{1}{r_{ij}}|ij\rangle - \langle ij|\frac{1}{r_{ij}}|ji\rangle, \tag{8}$$

as we wanted to show.

In the case of the electrons in the helium atom, we only have $n = 1$, $l = 0$, differing only in the spin quantum number $m_s = \pm 1/2$. The expectation value of the one-body part is then

$$\langle \Phi_0|\hat{H}_0|\Phi_0\rangle = \sum_{\sigma\in\{\pm 1/2\}} \langle 1\sigma|\hat{h}_0|1\sigma\rangle = -Z^2,$$

and the expectation value of the two-body part is, writing just σ_+ and σ_- for the spins with $n = 1$,

$$\langle \Phi_0|\hat{H}_I|\Phi_0\rangle = \frac{1}{2}\sum_{\substack{\sigma_+\sigma_- \\ \sigma_+\neq\sigma_-}} \underbrace{\left\langle \sigma_+\sigma_- \middle| \frac{1}{r_{\sigma_+\sigma_-}} \middle| \sigma_+\sigma_- \right\rangle}_{\text{Direct term}} - \underbrace{\left\langle \sigma_+\sigma_- \middle| \frac{1}{r_{\sigma_+\sigma_-}} \middle| \sigma_-\sigma_+ \right\rangle}_{\text{Exchange term}}.$$

The exchange term vanishes since the states are orthogonal, and we are left with the direct term. We are then just left with

$$\langle \Phi_0|\hat{H}_I|\Phi_0\rangle = \frac{1}{2}\left[\left\langle \sigma_+\sigma_- \middle| \frac{1}{r_{\sigma_+\sigma_-}} \middle| \sigma_+\sigma_- \right\rangle + \left\langle \sigma_-\sigma_+ \middle| \frac{1}{r_{\sigma_+\sigma_-}} \middle| \sigma_-\sigma_+ \right\rangle\right].$$

As $\hat{H}_I$ is invariant under the change of label σ, we can simplify this to

$$\langle \Phi_0|\hat{H}_I|\Phi_0\rangle = \left\langle \sigma_+\sigma_- \middle| \frac{1}{r_{\sigma_+\sigma_-}} \middle| \sigma_+\sigma_- \right\rangle = \frac{5}{8}Z.$$

Combining this, we find that the expectation value of the ground state is

$$E[\Phi_0] = -Z^2 + \tfrac{5}{8}Z, \tag{9}$$

which as a function of Z is shown in Figure 1.

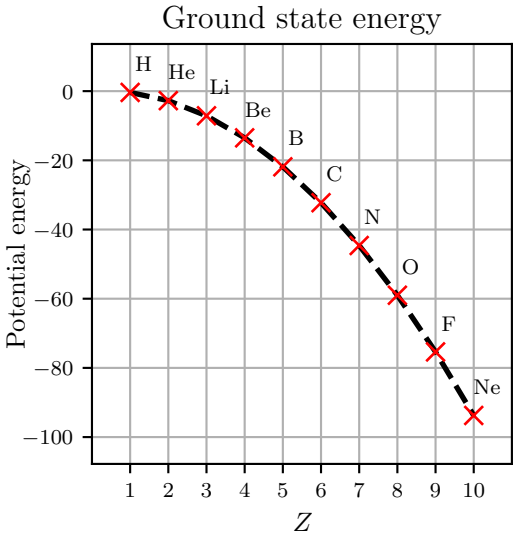

Figure 1: The expectation value of the ground states of an atom with two electrons as a function of the nuclear charge Z.

Part c) Limiting ourselves to one-particle-one excitations

Hereafter we will limit ourselves to a system which now contains only one-particle-one-hole excitations beyond the chosen state $|c\rangle$. Using the possible Slater determinants from exercise a) for the helium atom, find the expressions (without inserting the explicit values for the matrix elements first) for

$$\langle c|\hat{H}|\Phi_i^a\rangle,$$

and

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

Represent these expressions in a diagrammatic form, both for the onebody part and the two-body part of the Hamiltonian.

Insert then the explicit values for the various matrix elements and set up the final Hamiltonian matrix and diagonalize it using for example Python as programming language. Compare your results from those of exercise b) and comment your results.

The exact energy with our Hamiltonian is -2.9037 atomic units for helium. This value is also close to the experimental energy.

Solution

In order to be able to handle the more complicated systems, we partition the Hamiltonian into

$$\hat{H} = \underbrace{\mathcal{E}_0^{\text{ref}}}_{\langle c|\hat{H}_0|c\rangle} + \hat{F}_N + \hat{V}_N, \tag{10}$$

where

$$\hat{F}_N = \sum_{pq} \langle p|\hat{f}|q\rangle \{a_p^\dagger a_q\}, \qquad \langle p|f|q\rangle = \langle p|\hat{h}_0|q\rangle + \sum_i \langle pi|\hat{V}|qi\rangle_{AS},$$
$$\hat{V}_N = \frac{1}{4}\sum_{pqrs} \langle pq|\hat{V}|rs\rangle_{AS} \{a_p^\dagger a_q^\dagger a_s a_r\}.$$

Considering then $\langle c|\hat{H}|\Phi_i^a\rangle$, we firstly have $\langle c|\mathcal{E}_0^{\text{Ref}}|\Phi_i^a\rangle = 0$, as $\langle c|\Phi_i^a\rangle = 0$. For the next term, we have

$$\begin{aligned}
\langle c|\hat{F}_N|\Phi_i^a\rangle &= \sum_{pq}\langle p|\hat{f}|q\rangle\langle c|a_p^\dagger a_q|\Phi_i^a\rangle = \sum_{pq}\langle p|\hat{f}|q\rangle\langle c|\overbrace{a_p^\dagger a_q a_a^\dagger}a_i|c\rangle \\
&= \sum_{pq}\langle p|\hat{f}|q\rangle\delta_{pi}\delta_{qa} = \langle i|\hat{f}|a\rangle \\
&= \langle i|\hat{h}_0|a\rangle + \sum_j \langle ij|\hat{V}|aj\rangle_{AS}.
\end{aligned}$$

For the last term, we get

$$\begin{aligned}
\langle c|\hat{V}_N|\Phi_i^a\rangle &= \frac{1}{4}\sum_{pqrs}\langle pq|\hat{V}|rs\rangle_{AS}\langle c|a_p^\dagger a_q^\dagger a_s a_r|\Phi_i^a\rangle \\
&= \frac{1}{4}\sum_{pqrs}\langle pq|\hat{V}|rs\rangle_{AS}\langle c|\overbrace{a_p^\dagger \overbrace{a_q^\dagger a_s}a_r}a_a^\dagger a_i|c\rangle \\
&= 0,
\end{aligned}$$

as we cannot make the $\overbrace{a_a^\dagger a_i}$ contraction.

Solution

We start by finding the value of the expression $\langle c|\hat{H}|\Phi_i^a\rangle$. Writing out the terms, we have

$$\begin{aligned}
\langle c|\hat{H}|\Phi_i^a\rangle &= \langle c|\hat{H}_0 + \hat{H}_I|\Phi_i^a\rangle \\
&= \langle c|\hat{H}_0|\Phi_i^a\rangle + \langle c|\hat{H}_I|\Phi_i^a\rangle.
\end{aligned}$$

We can now read from Eq. (**??**) that the one-body part of the expression vanishes, either through an unmatched $b_\alpha^\dagger$ or simply $\langle c|\Phi_i^a\rangle = 0$. This gives us

$$\langle c|\hat{H}_0|\Phi_i^a\rangle = 0. \tag{11}$$

In order to make sure the number of annihilation and creation terms are correct, the contributing terms from H_I are those with two more annihilation operators than creation operators, while also matching the number of holes and particles created. We can then quickly reduce the possible contributing candidates to

$$\frac{1}{4}\sum_{aijk}\langle ji|V|ak\rangle b_k^\dagger b_j b_i b_a, \qquad \frac{1}{2}\sum_{aij}\langle ji|V|ai\rangle b_j b_a, \qquad \text{and} \qquad \mathcal{E}_I^{\text{Ref}}.$$

On closer inspection, we see that the first term vanishes, as $b_k^\dagger$ is unmatched, while the last term vanished due to $\langle c|\Phi_i^a\rangle = 0$.

We then just need to evaluate the contractions of the second term, changing the labels of the sum $(a,i,j) \mapsto (b,j,k)$ to avoid confusion with $|\Phi_i^a\rangle$, which simply is

$$\langle c|\overbrace{b_k b_b b_a^\dagger b_i^\dagger}|c\rangle = \delta_{ik}\delta_{ab}.$$

We then get

$$\left\langle c\middle|\hat{H}_I\middle|\Phi_i^a\right\rangle = \frac{1}{2}\sum_j \langle ij|V|aj\rangle_{AS}, \tag{12}$$

taking into account that the matrix element in the sum is antisymmetrized. Now, considering spin, the exchange term vanishes, leaving us with two times the direct term. This gives us the final expression

$$\langle c|\hat{H}|\Phi_i^a\rangle = \sum_{ij}\langle ij|V|aj\rangle. \tag{13}$$

In the case of the helium atom, the only possible value for j when $i = 1_{\sigma_1}$ is $j = 1_{\sigma_2}$. Inserting for the explicit excitations, we get

$$\begin{aligned}
j = 1_- : \quad & \left\langle c\middle|\hat{H}\middle|\Phi_{1_+}^{2_+}\right\rangle = \langle 1_-1_+|V|2_+1_-\rangle \\
j = 1_- : \quad & \left\langle c\middle|\hat{H}\middle|\Phi_{1_+}^{3_+}\right\rangle = \langle 1_-1_+|V|3_+1_-\rangle \\
j = 1_+ : \quad & \left\langle c\middle|\hat{H}\middle|\Phi_{1_-}^{2_-}\right\rangle = \langle 1_+1_-|V|2_-1_+\rangle \\
j = 1_+ : \quad & \left\langle c\middle|\hat{H}\middle|\Phi_{1_-}^{3_-}\right\rangle = \langle 1_+1_-|V|3_-1_+\rangle
\end{aligned} \tag{14}$$

Next, we find a simplified expression for $\langle\Phi_i^a|\hat{H}|\Phi_j^b\rangle$, noting that

$$\langle\Phi_i^a|\hat{H}|\Phi_j^b\rangle = \langle c|b_i b_a \hat{H} b_b^\dagger b_j^\dagger|c\rangle.$$

Beginning again with the one-body part of the Hamiltonian, we have can read from Eq. (**??**) that if $(i,a) \neq (j,b)$, the expression vanishes. If however the pair is equal, we get a contribution, giving us

$$\langle\Phi_i^a|\hat{H}_0|\Phi_j^b\rangle = \delta_{ij}\delta_{ab}\left[\langle a|\hat{h}_0|a\rangle - \langle i|\hat{h}_0|i\rangle + \mathcal{E}_0^{\text{Ref}}\right]$$

For the two-body part, we have that the possible contributing terms must then have an equal number of annihilation and creation operators in order to not vanish, reducing the candidates to

1. $\frac{1}{4}\sum_{abcd}\langle ab|V|cd\rangle b_a^\dagger b_b^\dagger b_d b_c$
2. $\frac{1}{2}\sum_{abij}\langle ai|V|bj\rangle b_a^\dagger b_j^\dagger b_b b_i$
3. $\frac{1}{2}\sum_{abi}\langle ai|V|bi\rangle b_a^\dagger b_b$
4. $\frac{1}{4}\sum_{ijkl}\langle kl|V|ij\rangle b_i^\dagger b_j^\dagger b_l b_k$
5. $\frac{1}{2}\sum_{ijk}\langle ij|V|kj\rangle b_k^\dagger b_i$
6. $\mathcal{E}_I^{\text{Ref}}$.

For the terms here, recall that $\langle c|\overbrace{b_\alpha^\dagger b_\beta}|c\rangle = \delta_{\alpha\beta}$, while $\langle c|\overbrace{b_\alpha b_\beta^\dagger}|c\rangle = 0$. The first term vanishes as $b_d b_c|\Phi_j^b\rangle = \underbrace{b_d b_c b_b^\dagger b_j^\dagger}_{0}|c\rangle = 0$, due to over-annihilation of particles. For the second term, relabeling $(a,b,i,j)\mapsto(c,d,k,l)$ we get

$$\begin{aligned}\langle c|\overbrace{b_i b_a b_c^\dagger b_l^\dagger}\,\overbrace{b_d b_k b_b^\dagger b_j^\dagger}|c\rangle = -\delta_{il}\delta_{ac}\delta_{db}\delta_{kj} \implies &-\frac{1}{2}\langle aj|V|bi\rangle \\ &= \frac{1}{2}\langle aj|V|ib\rangle.\end{aligned}$$

For the third term, relabeling $(a,b,i)\mapsto(c,d,k)$, we have

$$\langle c|\overbrace{b_i b_a b_c^\dagger b_d b_b^\dagger}\,b_j^\dagger|c\rangle = \delta_{ij}\delta_{ab}\delta_{cd} \implies \frac{1}{2}\delta_{ij}\sum_k\langle ak|V|bk\rangle.$$

The fourth term vanishes as the number of hole annihilation operator to the left of the creation operators does not match. The fifth term, relabeling $(i,j,k)\mapsto(k,l,m)$, gives

$$\begin{aligned}\langle c|\overbrace{b_i b_a b_m^\dagger\,\overbrace{b_k b_b^\dagger}\,b_j^\dagger}|c\rangle = \delta_{im}\delta_{ab}\delta_{kj} \implies &\frac{1}{2}\delta_{ab}\sum_l\langle jl|V|il\rangle, \\ &= \frac{1}{2}\delta_{ab}\sum_k\langle jk|V|ik\rangle.\end{aligned}$$

The last term simply gives us $\delta_{ab}\delta_{ij}\mathcal{E}_I^{\text{Ref}}$.

The final expression for $\langle\Phi_i^a|\hat{H}|\Phi_j^b\rangle$ is then

$$\begin{aligned}\langle\Phi_i^a|\hat{H}|\Phi_j^b\rangle = \delta_{ij}\delta_{ab}\Big[\langle a|\hat{h}_0|a\rangle - \langle i|\hat{h}_0|i\rangle + \mathcal{E}_0^{\text{Ref}} + \mathcal{E}_I^{\text{Ref}}\Big] \\ \frac{1}{2}\langle aj|V|ib\rangle + \frac{1}{2}\sum_k\delta_{ij}\langle ak|V|bk\rangle + \delta_{ab}\langle jk|V|ik\rangle.\end{aligned} \tag{15}$$

We split the expression into the different cases. Firstly, when $i\neq j$ and $a\neq b$, we have

$$\langle\Phi_i^a|\hat{H}|\Phi_j^b\rangle = -\frac{1}{2}\langle aj|V|bi\rangle_{AS} = \frac{1}{2}\left[\langle aj|V|ib\rangle - \langle aj|V|bi\rangle\right].$$

Considering just the spin part, and placing disregarding the energy levels for now, we have

$$\frac{1}{2}\left[\langle\sigma_1\sigma_2|V|\sigma_1\sigma_2\rangle - \langle\sigma_1\sigma_2|V|\sigma_2\sigma_1\rangle\right],$$

where we can now see that the second state vanishes due to the orthogonality of the spin. This leaves us with

$$\langle\Phi_i^a|\hat{H}|\Phi_j^b\rangle = \frac{1}{2}\langle aj|V|ib\rangle.$$

Next, we consider the case when $i = j$ and $a \neq b$. The expression then becomes

$$\begin{aligned}\langle\Phi_i^a|\hat{H}|\Phi_i^b\rangle &= -\frac{1}{2}\langle ai|V|bi\rangle_{AS} + \frac{1}{2}\sum_k \langle ak|V|bk\rangle_{AS} \\ &= \frac{1}{2}\Big[-\langle ai|V|bi\rangle_{AS} + \langle ai|V|bi\rangle_{AS} + \langle aj|V|bj\rangle_{AS}\Big] \\ &= \frac{1}{2}\langle aj|V|bj\rangle_{AS}.\end{aligned}$$

Again, considering the spin, we have

$$\frac{1}{2}\left[\langle\sigma_1\sigma_2|V|\sigma_1\sigma_2\rangle - \langle\sigma_1\sigma_2|V|\sigma_2\sigma_1\rangle\right],$$

where the second term again vanishes, leaving us with

$$\langle\Phi_i^a|\hat{H}|\Phi_i^b\rangle = \frac{1}{2}\langle aj|V|bj\rangle.$$

In the case where $i \neq j$ and $a = b$, the entire expression vanishes, as this would imply that we would have a state where $M_S \neq 0$.

Finally, the expectation value of the Hamiltonian with the one-particle-one-hole excitation is

$$\langle\Phi_i^a|\hat{H}|\Phi_i^a\rangle = \langle a|\hat{h}_0|a\rangle - \langle i|\hat{h}_0|i\rangle + \mathcal{E}_0^{\text{Ref}} + \mathcal{E}_I^{\text{Ref}} - . \tag{16}$$

A summary of the cases is listed in Table 1

Table 1: The different cases for $\langle\Phi_i^a|\hat{H}|\Phi_j^b\rangle$.

$i \neq j$	$a \neq b$	$\frac{1}{2}\langle aj|V|ib\rangle$
$i = j$	$a \neq b$	$\frac{1}{2}\langle aj|V|bj\rangle$
$i \neq j$	$a = b$	0
$i = j$	$a = b$	$\langle a|\hat{h}_0|a\rangle - \langle i|\hat{h}_0|i\rangle + \mathcal{E}^{\text{Ref}}$

Now, getting the explicit values for the matrix elements, so that we can set up the Hamiltonian matrix and diagonalize it using Python.