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.,

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

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

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

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 the Hamiltonian $\hat{H} = \hat{H}_0 + \hat{H}_I$, where $\hat{H}_0$ is the one-body part and $\hat{H}_I$ is the two-body part, given by

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

In second quantization, we rewrite the one-body part as

$$\hat{H}_0 = \sum_{\alpha\beta} \langle\alpha|\hat{h}_0|\beta\rangle a_\alpha^\dagger a_\beta. \tag{5}$$

With the new annihilation and creation operators b_α and $b_\alpha^\dagger$ with respect to the new vacuum state $|\Phi_0\rangle$, we can rewrite this as

$$\begin{aligned}\hat{H}_0 = &\sum_{ab}\langle a|\hat{h}_0|b\rangle b_a^\dagger b_b + \sum_{ai}\left[\langle a|\hat{h}_0|i\rangle b_a^\dagger b_i^\dagger + \langle i|\hat{h}_0|a\rangle b_i b_a\right] \\ &+ \sum_i \langle i|\hat{h}_0|i\rangle - \sum_{ij}\langle j|\hat{h}_0|i\rangle b_i^\dagger b_j.\end{aligned} \tag{6}$$

Recalling that

$$\langle\alpha|\hat{h}_0|\beta\rangle = -\frac{Z^2}{2n^2}\delta_{\alpha\beta},$$

we can simplify the expression to

$$\hat{H}_0 = \sum_a \langle a|\hat{h}_0|a\rangle b_a^\dagger b_a + \sum_i \langle i|\hat{h}_0|i\rangle - \sum_i \langle i|\hat{h}_0|i\rangle b_i^\dagger b_i.$$

The first and last terms vanish, as both $b_b|\Phi_0\rangle = 0$ and $b_j|\Phi_0\rangle = 0$, leaving us with

$$\hat{H}_0 = \sum_i \langle i|\hat{h}_0|i\rangle. \tag{7}$$

The two-body part is rewritten in second quantization as

$$\hat{H}_I = \frac{1}{2}\sum_{\alpha\beta\gamma\delta}\langle\alpha\beta|V|\gamma\delta\rangle a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma. \tag{8}$$

With the new annihilation and creation operators, we can rewrite this as

$$\hat{H}_I = \hat{H}_I^{(1)} + \hat{H}_I^{(2)} + \hat{H}_I^{(3)} + \hat{H}_I^{(4)} + \hat{H}_I^{(5)},$$

where utilizing antisymmetrized matrix elements for the sake of brevity, we have

$$\begin{aligned}
\hat{H}_I^{(1)} &= \frac{1}{4}\sum_{abcd}\langle ab|V|cd\rangle b_a^\dagger b_b^\dagger b_d b_c, \\
\hat{H}_I^{(2)} &= \frac{1}{4}\sum_{abci}\langle ab|V|ci\rangle b_a^\dagger b_b^\dagger b_i^\dagger b_c + \langle ai|V|cb\rangle b_a^\dagger b_i b_b b_c \\
\hat{H}_I^{(3)} &= \frac{1}{4}\sum_{abij}\Big[\langle ab|V|ij\rangle b_a^\dagger b_b^\dagger b_j^\dagger b_i^\dagger + \langle ij|V|ab\rangle b_a b_b b_j b_i\Big] \\
&\quad + \frac{1}{2}\sum_{abij}\langle ai|V|bj\rangle b_a^\dagger b_j^\dagger b_b b_i + \frac{1}{2}\sum_{abi}\langle ai|V|bi\rangle b_a^\dagger b_b \\
\hat{H}_I^{(4)} &= \frac{1}{4}\sum_{aijk}\Big[\langle ai|V|jk\rangle b_a^\dagger b_k^\dagger b_j^\dagger b_i + \langle ji|V|ak\rangle b_k^\dagger b_j b_i b_a\Big] \\
&\quad + \frac{1}{2}\sum_{aij}\Big[\langle ai|V|ji\rangle b_a^\dagger b_j^\dagger + \langle ji|V|ai\rangle b_j b_a - \langle ji|V|ia\rangle b_j b_a\Big] \\
\hat{H}_I^{(5)} &= \frac{1}{4}\sum_{ijkl}\langle kl|V|ij\rangle b_i^\dagger b_j^\dagger b_l b_k + \frac{1}{2}\sum_{ijk}\langle ij|V|kj\rangle b_k^\dagger b_i + \frac{1}{2}\sum_{ij}\langle ij|V|ij\rangle.
\end{aligned}$$

In order to simplify the computations later, we briefly summarize the qualitative properties of each of the terms above.

(1). Contributes for $\geq$two-particle states

(2). Creates or removes a three-particle-one-hole state, while conserving the number of particles

(3). Term by term,

   (a) Creates a two-particle-two-hole state by either removing two particles and creating two holes, or by removing two holes and creating two particles.

   (b) Creates two one-particle-one-hole pairs.

   (c) Contributions between particle pairs, and the hole states.

(4). Term by term,

   (a) Creation of a one-particle-one-hole pair, interacting with a hole.

(b) One-particle-one-hole pair interacting with a hole.

(5). Term by term,

(a) Interactions between pairs of two hole states.

(b) Interactions between a hole and the other holes.

(c) Energy from the ground state.

We can now quickly see that $\langle c|\hat{H}_I|c\rangle$ only gets a contribution from the last $H_I^{(5)}$ term, as the other terms vanish due to either an annihilation operator acting on the vacuum state, or orthogonality of the states created. We are then just left with

$$\langle \Phi_0|\hat{H}_I|\Phi_0\rangle = \frac{1}{2}\sum_{ij}\langle ij|V|ij\rangle_{AS} = \frac{1}{2}\sum_{ij}\langle ij|V|ij\rangle - \langle ij|V|ji\rangle. \tag{9}$$

Finally, combining this with the expectation value of the one-body part, we get that the complete expectation value of the ground state is

$$E[\Phi_0] = \langle c|\hat{H}|c\rangle = \sum_i \langle i|\hat{h}_0|i\rangle + \frac{1}{2}\sum_{\substack{ij\\ i\neq j}}\left[\left\langle ij\left|\frac{1}{r_{ij}}\right|ij\right\rangle - \left\langle ij\left|\frac{1}{r_{ij}}\right|ji\right\rangle\right], \tag{10}$$

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

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

and the expectation value of the two-body part is, writing just σ_+ and σ_- for the spins,

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

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

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

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

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

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

$$E[\Phi_0] = -Z^2 + \tfrac{5}{8}Z, \tag{11}$$

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

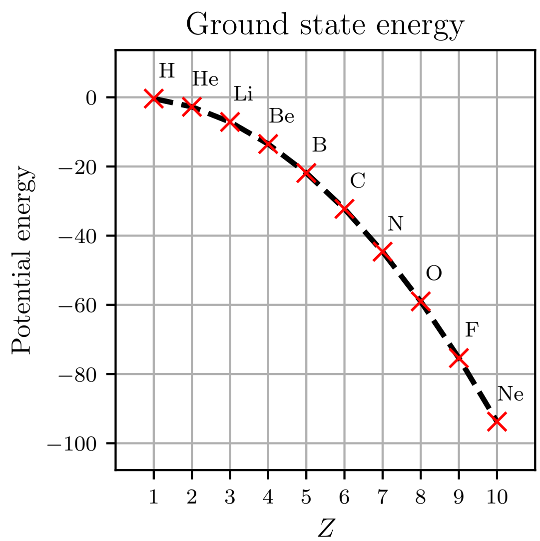

Figure 1: The expectation value of the ground states of an atom with two electrons as a function of the nuclear charge Z.

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

We start by finding the expectation value of the Hamiltonian between the ground state $|c\rangle$ and a one-particle-one-hole excitation $|\Phi_i^a\rangle$. 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. (6) that the one-body part of the Hamiltonian is

$$
\langle c|\hat{H}_0|\Phi_i^a\rangle = \langle a|\hat{h}_0|a\rangle - \langle i|\hat{h}_0|i\rangle - \mathcal{E}_0^{\mathrm{Ref}},
$$

where $\mathcal{E}_0^{\mathrm{Ref}} = \langle c|\hat{H}_0|c\rangle$ is the reference energy of the ground state.

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 holes and particles created. Those are

$$
\begin{gathered}
\frac{1}{4}\sum_{aijk}\langle ji|V|ak\rangle b_k^\dagger b_j b_i b_a, \\
\frac{1}{2}\sum_{aij}\langle ji|V|ai\rangle b_j b_a - \langle ji|V|ia\rangle b_j b_a.
\end{gathered}
$$

Computing the contractions, we find for the first term

$$
\begin{gathered}
\langle c|b_k^\dagger b_j b_i b_a b_b^\dagger b_l^\dagger|c\rangle \\
\langle c|b_k^\dagger b_j b_i b_a b_b^\dagger b_l^\dagger|c\rangle
\end{gathered}
$$

For the two-body part, writing V for the two-particle operator, we have

$$\begin{aligned}\langle c|\hat{H}_I|\Phi_i^a\rangle &= \frac{1}{2}\sum_{\alpha\beta\gamma\delta}\langle\alpha\beta|V|\gamma\delta\rangle\langle c|a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma|\Phi_i^a\rangle \\ &= \frac{1}{2}\sum_{\alpha\beta\gamma\delta}\langle\alpha\beta|V|\gamma\delta\rangle\langle c|a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma a_a^\dagger a_i|c\rangle.\end{aligned}$$

The possible contractions are then

$$\begin{aligned}\langle\alpha\beta|V|\gamma\delta\rangle\langle c|a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma a_a^\dagger a_i|c\rangle &= \delta_{\alpha\gamma}\delta_{\beta i}\delta_{\delta a}\langle\alpha\beta|V|\gamma\delta\rangle = \langle\alpha i|V|\alpha a\rangle, \\ \langle\alpha\beta|V|\gamma\delta\rangle\langle c|a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma a_a^\dagger a_i|c\rangle &= -\delta_{\alpha\delta}\delta_{\beta i}\delta_{\gamma a}\langle\alpha\beta|V|\gamma\delta\rangle = -\langle\alpha i|V|a\alpha\rangle, \\ \langle\alpha\beta|V|\gamma\delta\rangle\langle c|a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma a_a^\dagger a_i|c\rangle &= -\delta_{\alpha i}\delta_{\beta\gamma}\delta_{a\delta}\langle\alpha\beta|V|\gamma\delta\rangle = -\langle i\beta|V|\beta a\rangle, \\ \langle\alpha\beta|V|\gamma\delta\rangle\langle c|a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma a_a^\dagger a_i|c\rangle &= \delta_{\alpha i}\delta_{\beta\delta}\delta_{\gamma a}\langle\alpha\beta|V|\gamma\delta\rangle = \langle i\beta|V|a\beta\rangle.\end{aligned}$$

Using the general fact that $\langle\alpha\beta|V|\gamma\delta\rangle = \langle\beta\alpha|V|\delta\gamma\rangle$, we can gather these terms into a single term

$$\langle c|\hat{H}_I|\Phi_i^a\rangle = \sum_\alpha\langle\alpha i|V|\alpha a\rangle - \langle\alpha i|V|a\alpha\rangle.$$

The final expression for the expectation value of the Hamiltonian between the ground state and a one-particle-one-hole excitation is then

$$\langle c|\hat{H}|\Phi_i^a\rangle = \langle c|\hat{H}_0|\Phi_i^a\rangle + \langle c|\hat{H}_I|\Phi_i^a\rangle = 0 + \sum_\alpha\langle\alpha i|V|\alpha a\rangle - \langle\alpha i|V|a\alpha\rangle. \tag{12}$$

Finally, the values we get for the one-particle-one-hole excitations are listed in Eq. (13), with the only possible value for α in each case of Eq. (12) listed to the far left. For brevity, we write $\beta\sigma_\pm$ as just $\beta_\pm$ here.

$$\begin{aligned}\alpha = 1_-: &\quad \left\langle c\middle|\hat{H}\middle|\Phi_{1_+}^{2+}\right\rangle = \langle 1_-1_+|V|1_-2_+\rangle - \langle 1_-1_+|V|2_+1_-\rangle \\ \alpha = 1_-: &\quad \left\langle c\middle|\hat{H}\middle|\Phi_{1_+}^{2+}\right\rangle = \langle 1_-1_+|V|1_-3_+\rangle - \langle 1_-1_+|V|3_+1_-\rangle \\ \alpha = 1_+: &\quad \left\langle c\middle|\hat{H}\middle|\Phi_{1_-}^{2-}\right\rangle = \langle 1_+1_-|V|1_+2_-\rangle - \langle 1_+1_-|V|2_-1_+\rangle \\ \alpha = 1_+: &\quad \left\langle c\middle|\hat{H}\middle|\Phi_{1_-}^{3-}\right\rangle = \langle 1_+1_-|V|1_+3_-\rangle - \langle 1_+1_-|V|3_-1_+\rangle\end{aligned} \tag{13}$$

Next, we find the expectation value of the Hamiltonian between two one-particle-one-hole excitations. Considering the one-body part, we have

$$\begin{aligned}\langle\Phi_i^a|\hat{H}_0|\Phi_j^b\rangle &= \sum_{\alpha\beta}\langle\alpha|\hat{h}_0|\beta\rangle\langle\Phi_i^a|a_\alpha^\dagger a_\beta|\Phi_j^b\rangle \\ &= \sum_{\alpha\beta}\langle\alpha|\hat{h}_0|\beta\rangle\langle c|a_i^\dagger a_a a_\alpha^\dagger a_\beta a_b^\dagger a_j|c\rangle.\end{aligned}$$

Note that if $\alpha > F$ or $\beta > F$, the expectation value vanishes.

The contractions are then

$$\begin{aligned}
\langle\alpha|\hat{h}_0|\beta\rangle\langle c|a_i^\dagger a_a a_\alpha^\dagger a_\beta a_b^\dagger a_j|c\rangle &= \delta_{ij}\delta_{a\alpha}\delta_{b\beta}\langle\alpha|\hat{h}_0|\beta\rangle = \delta_{ij}\langle a|\hat{h}_0|b\rangle \\
\langle\alpha|\hat{h}_0|\beta\rangle\langle c|a_i^\dagger a_a a_\alpha^\dagger a_\beta a_b^\dagger a_j|c\rangle &= -\delta_{i\beta}\delta_{ab}\delta_{\alpha j}\langle\alpha|\hat{h}_0|\beta\rangle = -\delta_{ab}\langle j|\hat{h}_0|i\rangle \\
\langle\alpha|\hat{h}_0|\beta\rangle\langle c|a_i^\dagger a_a a_\alpha^\dagger a_\beta a_b^\dagger a_j|c\rangle &= \delta_{ij}\delta_{ab}\delta_{\alpha\beta}\langle\alpha|\hat{h}_0|\beta\rangle = \delta_{ij}\delta_{ab}\langle\alpha|\hat{h}_0|\alpha\rangle
\end{aligned}$$

meaning that the expectation value of the one-body part is

$$\langle\Phi_i^a|\hat{H}_0|\Phi_j^b\rangle = \delta_{ij}\langle a|\hat{h}_0|b\rangle - \delta_{ab}\langle j|\hat{h}_0|i\rangle + \delta_{ij}\delta_{ab}\sum_{\alpha\leq F}\langle\alpha|\hat{h}_0|\alpha\rangle,$$

where we recognize the right-most term as the expectation value of the one-body operator in the ground state, known as the reference energy $\mathcal{E}_0^{\mathrm{Ref}}$. The term then vanishes whenever $i \neq j$ or $a \neq b$.

For the two-body part, we have

$$\begin{aligned}
\langle\Phi_i^a|\hat{H}_I|\Phi_j^b\rangle &= \frac{1}{2}\sum_{\alpha\beta\gamma\delta}\langle\alpha\beta|V|\gamma\delta\rangle\langle\Phi_i^a|a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma|\Phi_j^b\rangle \\
&= \frac{1}{2}\sum_{\alpha\beta\gamma\delta}\langle\alpha\beta|V|\gamma\delta\rangle\langle c|a_i^\dagger a_a a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma a_b^\dagger a_j|c\rangle.
\end{aligned}$$

The possible contractions are then