First midterm FYS4480
Quantum mechanics for many-particle systems

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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

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

where $L_{n-1}^1(r)$ 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

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

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

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

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

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 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

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

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 $\{a_p^\dagger a_q\} = a_p^\dagger a_q$, $\{a_p a_q^\dagger\} = -a_q^\dagger a_p$, where the sign is dependent on the number of permutations required to bring the operators to normal order. We are interested in this, as

$$\langle c|\{AB\cdots\}|c\rangle = 0$$

if $\{AB\cdots\}$ is not empty, where $A, B, \ldots$ are annihilation or creation operators.

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

$$\overparen{AB} = AB - \{AB\}.$$

Relative to our reference state, we have that

$$\overparen{a_i^\dagger a_j} = \delta_{ij} \qquad \text{and} \qquad \overparen{a_a a_b^\dagger} = \delta_{ab}$$

are the only non-zero contractions.

For the one-body term, we then have

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

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

$$\overparen{a_j a_i a_p^\dagger a_q^\dagger a_s a_r a_i^\dagger a_j^\dagger} = \delta_{jq}\delta_{ip}\delta_{sj}\delta_{ri} \rightarrow \langle ij|V|ij\rangle_{AS},$$

$$\overparen{a_j a_i a_p^\dagger a_q^\dagger a_s a_r a_i^\dagger a_j^\dagger} = -\delta_{jq}\delta_{ip}\delta_{si}\delta_{rj} \rightarrow -\langle ij|V|ji\rangle_{AS},$$

$$\overparen{a_j a_i a_p^\dagger a_q^\dagger a_s a_r a_i^\dagger a_j^\dagger} = -\delta_{jp}\delta_{iq}\delta_{sj}\delta_{ri} \rightarrow -\langle ji|V|ij\rangle_{AS},$$

$$\overparen{a_j a_i a_p^\dagger a_q^\dagger a_s a_r a_i^\dagger a_j^\dagger} = \delta_{jp}\delta_{iq}\delta_{si}\delta_{rj} \rightarrow \langle ji|V|ji\rangle_{AS}.$$

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

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

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

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

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 $n = 1$,

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

The exchange term vanishes as 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

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

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

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

which as a function of Z is shown in Figure 1. For $Z = 2$, we find that

$$E[\Phi_0] = -2.75 = -74.8 \text{ eV}. \qquad (10)$$

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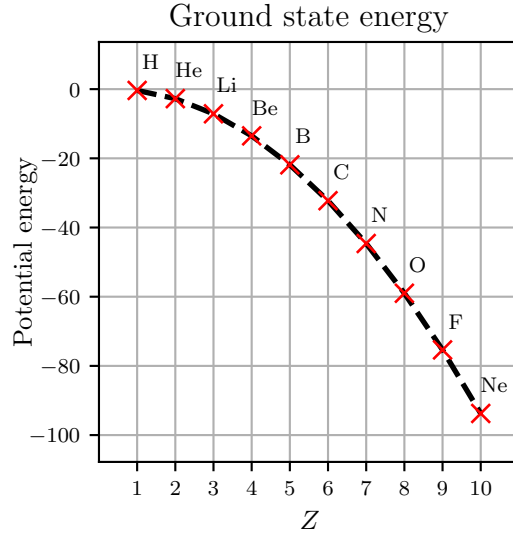
$$\langle c|\hat{H}|\Phi_i^a\rangle,$$

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

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

$$\hat{H} = \underbrace{\mathcal{E}_0^{\text{Ref}}}_{\langle c | \hat{H} | c \rangle} + \hat{F}_N + \hat{V}_N, \tag{11}$$

where

$$\hat{F}_N = \sum_{pq} \langle p|f|q\rangle \{a_p^\dagger a_q\}, \qquad \langle p|f|q\rangle = \langle p|\hat{h}_0|q\rangle + \sum_i \langle pi|V|qi\rangle_{AS},$$

$$\hat{V}_N = \frac{1}{4} \sum_{pqrs} \langle pq|V|rs\rangle_{AS} \{a_p^\dagger a_q^\dagger a_s a_r\}.$$

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

$$\langle c|\hat{F}_N|\Phi_i^a\rangle = \sum_{pq} \langle p|f|q\rangle \langle c|\{a_p^\dagger a_q\}|\Phi_i^a\rangle = \sum_{pq} \langle p|f|q\rangle \langle c|\{\overset{\frown}{a_p^\dagger a_q}\}\{\overset{\frown}{a_a^\dagger a_i}\}|c\rangle$$

$$= \sum_{pq} \langle p|f|q\rangle \delta_{pi}\delta_{qa} = \langle i|f|a\rangle$$

$$= \langle i|\hat{h}_0|a\rangle + \sum_j \langle ij|V|aj\rangle_{AS}.$$

For the last term, we get

$$\langle c|\hat{V}_N|\Phi_i^a\rangle = \frac{1}{4} \sum_{pqrs} \langle pq|V|rs\rangle_{AS} \langle c|\{a_p^\dagger a_q^\dagger a_s a_r\}|\Phi_i^a\rangle$$

$$= \frac{1}{4} \sum_{pqrs} \langle pq|V|rs\rangle_{AS} \langle c|\{a_p^\dagger a_q^\dagger a_s a_r\}\{a_a^\dagger a_i\}|c\rangle$$

$$= 0,$$

which vanishes as this would require a contraction within the normal ordered operator $\{a_p^\dagger a_q^\dagger a_s a_r\}$.

Considering next $\langle \Phi_i^a|\hat{H}|\Phi_j^b\rangle$, we have

$$\langle \Phi_i^a|\mathcal{E}_0^{\text{Ref}}|\Phi_j^b\rangle = \mathcal{E}_0^{\text{Ref}}\langle c|\{\overset{\frown}{a_i^\dagger a_a}\}\{\overset{\frown}{a_b^\dagger a_j}\}|c\rangle = \delta_{ij}\delta_{ab}\mathcal{E}_0^{\text{Ref}}.$$

Next, we have

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

$$= \sum_{pq} \langle p|f|q\rangle \langle c|\{a_i^\dagger a_a\}\{a_p^\dagger a_q\}\{a_b^\dagger a_j\}|c\rangle.$$

Considering the contractions seperately, we have the two possible contractions

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

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

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leaving us with

$$\langle \Phi_i^a | \hat{F}_N | \Phi_j^b \rangle = \langle a | f | b \rangle \delta_{ij} - \langle j | f | i \rangle \delta_{ab}.$$

Finally, considering the last term, we have

$$\langle \Phi_i^a | \hat{V}_N | \Phi_j^b \rangle = \frac{1}{4} \sum_{pqrs} \langle pq | V | rs \rangle_{AS} \langle \Phi_i^a | \{ a_p^\dagger a_q^\dagger a_s a_r \} | \Phi_j^b \rangle$$

$$= \frac{1}{4} \sum_{pqrs} \langle pq | V | rs \rangle_{AS} \langle c | \{ a_i^\dagger a_a \} \{ a_p^\dagger a_q^\dagger a_s a_r \} \{ a_b^\dagger a_j \} | c \rangle.$$

Considering the contractions seperately, we have the four possible contractions

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

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

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

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

Any contraction between $\{ a_i^\dagger a_a \}$ and $\{ a_b^\dagger a_j \}$ will vanish, as this would require a contraction within central normal ordered operator. This leaves us with

$$\langle \Phi_i^a | \hat{V}_N | \Phi_j^b \rangle = \frac{1}{4} \sum_{pqrs} \langle pq | V | rs \rangle_{AS}$$

$$\times \left[-\delta_{is} \delta_{ap} \delta_{jq} \delta_{br} + \delta_{is} \delta_{aq} \delta_{jp} \delta_{br} + \delta_{ir} \delta_{ap} \delta_{jq} \delta_{bs} - \delta_{ir} \delta_{aq} \delta_{jp} \delta_{bs} \right],$$

which when inserted gives

$$\langle \Phi_i^a | \hat{V}_N | \Phi_j^b \rangle = \frac{1}{4} \left[-\langle aj | V | bi \rangle_{AS} + \langle ja | V | bi \rangle_{AS} + \langle aj | V | ib \rangle_{AS} - \langle ja | V | ib \rangle_{AS} \right]$$

$$= \frac{1}{4} \left[\langle aj | V | ib \rangle_{AS} + \langle ja | V | bi \rangle_{AS} + \langle aj | V | ib \rangle_{AS} + \langle ja | V | bi \rangle_{AS} \right]$$

$$= \langle aj | V | ib \rangle_{AS}.$$

We have thus shown that

$$\langle c | \hat{H} | \Phi_i^a \rangle = \langle i | \hat{h}_0 | a \rangle + \sum_j \langle ij | V | aj \rangle_{AS},$$

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

(12)

Inserting for the explicit matrix elements, we get that the energy with our Hamiltonian is -2.8386 atomic units, or -77.2112 eV for the helium atom. We see that we have a higher value than the exact energy, which is expected as the true energy serves as a lower bound to the truncated Hamiltonian. We also see an improvement from our previous results, which stem from the fact that we are truncating at a higher level of excitations. The energy is computed with the code in `get_energy.py`.

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Part d)   Moving to the Beryllium atom

We repeat parts b) and c) but now for the beryllium atom.

Define the ansatz for $|c\rangle$ and limit yourself again to one-particle-one-hole excitations. Compute the reference energy $\langle c|\hat{H}|c\rangle$ as a function of Z. Thereafter you will need to set up the appropriate Hamiltonian matrix which involves also one-particle-one-hole excitations. Diagonalize this matrix and compare your eigenvalues with $\langle c|\hat{H}|c\rangle$ as function of Z and comment your results. The exact energy with our Hamiltonian is -14.6674 atomic units for beryllium. This value is again close to the experimental energy.

Solution

We define the ansatz for the ground state as

$$|c\rangle = a^{\dagger}_{1\sigma_+} a^{\dagger}_{1\sigma_-} a^{\dagger}_{2\sigma_+} a^{\dagger}_{2\sigma_-} |0\rangle, \tag{13}$$

where we now define the Fermi level as the $2s$ state, $F = 2$. As we are working with the same Hamiltonian, the only difference from the expressions found previously are the new one-particle-one-hole excitations, as well as the specific value of Z.

As our code can handle these variations, we again utilize the code in `get_energy.py` and find the reference energy to be

$$\langle c|\hat{H}|c\rangle = -\frac{5}{4}Z^2 + \frac{586373}{373248}Z \approx -1.25 \cdot Z^2 + 1.5710 \cdot Z. \tag{14}$$

For beryllium, we have $Z = 4$, and the reference energy is then -13.7159 atomic units or -373.0751 eV.

Setting up and diagonalizing the Hamiltonian truncated to one-particle-one-hole contributions, we find a new estimate for the energy to be -14.3621 atomic units or -390.6493 eV. Here, we see the estimate improve drastically, lying much closer to the exact energy.

Part e)   Hartree-Fock

Preamble

With a given energy functional, we can perform at least two types of variational strategies. These are:

1. Vary the Slater determinant by changing the spatial part of the single-particle wave functions themselves, or

2. Expand the single-particle functions in a known basis and vary the coefficients, that is, the new function single-particle wave function $|p\rangle$ is written

as a linear expansion in terms of a fixed basis ϕ (harmonic oscillator, Laguerre polynomials etc)

$$\psi_p = \sum_\lambda C_{p\lambda}\phi_\lambda$$

Both cases lead to a new Slater determinant which is related to the previous via a unitary transformation. Below we will set up the Hartree-Fock equations using the second option. We assume that our basis is still formed by the hydrogen-like wave functions. We consider a Slater determinant built up of single-particle orbitals ϕ_λ where the indices λ refer to specific single-particle states. As an example, you could think of the ground state ansatz for the beryllium atom.

The unitary transformation

$$\psi_p = \sum_\lambda C_{p\lambda}\phi_\lambda,$$

brings us into the new basis ψ. The new basis is orthonormal and C is a unitary matrix.

Problem definition

Minimizing with respect to $C_{p\alpha}^*$, remembering that $C_{p\alpha}^*$ and $C_{p\alpha}$ (and that the indices contain all single-particle quantum numbers including spin) are independent and defining

$$h_{\alpha\gamma}^{\mathrm{HF}} = \langle\alpha|h|\gamma\rangle + \sum_p \sum_{\beta\delta} C_{p\beta}^* C_{p\delta} \langle\alpha\beta|V|\gamma\delta\rangle_{AS},$$

show that you can write the Hartree-Fock equations as

$$\sum_\gamma h_{\alpha\gamma}^{\mathrm{HF}} C_{p\gamma} = \epsilon_p^{\mathrm{HF}} C_{p\alpha}.$$

Explain the meaning of the different terms and define the Hartree-Fock operator in second quantization. Write down its diagrammatic representation as well. The greek letters refer to the wave functions in the original basis (in our case the hydrogen-like wave functions) while roman letters refer to the new basis.

Solution

We previously defined the energy functional as, using greek indices for the original basis,

$$E[\Phi] = \langle\Phi|\hat{H}|\Phi\rangle = \sum_\alpha \langle\alpha|\hat{h}_0|\alpha\rangle + \frac{1}{2}\sum_{\alpha\beta}\langle\alpha\beta|V|\alpha\beta\rangle_{AS}.$$

In the new basis, we have

$$E[\Phi^{\mathrm{HF}}] = \sum_i \langle i|\hat{h}_0|i\rangle + \frac{1}{2}\sum_{ij}\langle ij|V|ij\rangle_{AS}.$$

As $|i\rangle = \sum_\alpha C_{i\alpha}|\alpha\rangle$, we also have

$$\langle i| = |i\rangle^\dagger = \left[\sum_\alpha C_{i\alpha}|\alpha\rangle\right]^\dagger = \sum_\alpha C_{i\alpha}^*\langle\alpha|.$$

This means that we can rewrite the one-body as

$$\sum_i \langle i|\hat{h}_0|i\rangle = \sum_i\sum_{\alpha\beta}\langle\alpha|C_{i\alpha}^*\hat{h}_0 C_{i\beta}|\beta\rangle = \sum_i\sum_{\alpha\beta}C_{i\alpha}^*C_{i\beta}\langle\alpha|\hat{h}_0|\beta\rangle.$$

Similarly, we get the two-body part as

$$\frac{1}{2}\sum_{ij}\langle ij|V|ij\rangle_{AS} = \frac{1}{2}\sum_{ij}\sum_{\alpha\beta\gamma\delta}C_{i\alpha}^*C_{j\beta}^*C_{i\gamma}C_{j\delta}\langle\alpha\beta|V|\gamma\delta\rangle_{AS}.$$

Defining this as a functional of the coefficients C, we have

$$E_0[C] = \sum_i\sum_{\alpha\beta}C_{i\alpha}^*C_{i\beta}\langle\alpha|\hat{h}_0|\beta\rangle + \frac{1}{2}\sum_{ij}\sum_{\alpha\beta\gamma\delta}C_{i\alpha}^*C_{j\beta}^*C_{i\gamma}C_{j\delta}\langle\alpha\beta|V|\gamma\delta\rangle_{AS}. \quad (15)$$

As we are working with orthonormal basis functions, we have

$$\langle i|j\rangle = \delta_{ij} = \sum_{\alpha\beta}C_{i\alpha}^*C_{i\beta}\langle\alpha|\beta\rangle = \sum_\alpha C_{i\alpha}^*C_{i\alpha}.$$

With this, we define a functional $F[C]$ as

$$F[C] = E_0[C] - \sum_i\lambda_i\sum_\alpha C_{i\alpha}^*C_{i\alpha},$$

where λ_i are the Lagrange multipliers enforcing the orthonormality of the basis functions.

Minimizing F with respect to $C_{i\alpha}^*$, we wish to solve

$$\frac{\mathrm{d}F}{\mathrm{d}C_{i\alpha}^*}[C] = \frac{\mathrm{d}}{\mathrm{d}C_{i\alpha}^*}\left[E_0[C] - \sum_j\lambda_j\sum_\alpha C_{j\alpha}^*C_{j\alpha}\right] = 0.$$

Considering the one-body part of E_0, we have

$$\frac{\mathrm{d}}{\mathrm{d}C_{i\alpha}^*}\sum_i\sum_{\alpha\beta}C_{i\alpha}^*C_{i\beta}\langle\alpha|\hat{h}_0|\beta\rangle = \sum_\beta C_{i\beta}\langle\alpha|\hat{h}_0|\beta\rangle.$$

For the two-body part, we firstly note that $C_{i\alpha}^*$ and $C_{j\beta}^*$ of Eq. (15) are dummy indices, meaning the factor of $1/2$ gets canceled out. This gives us

$$\frac{\mathrm{d}}{\mathrm{d}C_{i\alpha}^*} \frac{1}{2} \sum_{ij} \sum_{\alpha\beta\gamma\delta} C_{i\alpha}^* C_{j\beta}^* C_{i\gamma} C_{j\delta} \langle\alpha\beta|V|\gamma\delta\rangle_{AS} = \sum_{j} \sum_{\beta\gamma\delta} C_{j\beta}^* C_{i\gamma} C_{j\delta} \langle\alpha\beta|V|\gamma\delta\rangle_{AS}.$$

For the term enforcing orthonormality, we have simply

$$\frac{\mathrm{d}}{\mathrm{d}C_{i\alpha}^*} \sum_{i} \lambda_i \sum_{\alpha} C_{i\alpha}^* C_{i\alpha} = \lambda_i C_{i\alpha}.$$

Combining these terms, we have

$$\sum_{\beta} C_{i\beta} \langle\alpha|\hat{h}_0|\beta\rangle + \sum_{j} \sum_{\beta\gamma\delta} C_{j\beta}^* C_{i\gamma} C_{j\delta} \langle\alpha\beta|V|\gamma\delta\rangle_{AS} - \lambda_i C_{i\alpha} = 0.$$

Recognizing λ_i as the eigenvalues $\varepsilon_i^{\mathrm{HF}}$, we can rewrite this as

$$\sum_{\beta} C_{i\beta} \langle\alpha|\hat{h}_0|\beta\rangle + \sum_{j} \sum_{\beta\gamma\delta} C_{j\beta}^* C_{i\gamma} C_{j\delta} \langle\alpha\beta|V|\gamma\delta\rangle_{AS} = \varepsilon_i^{\mathrm{HF}} C_{i\alpha}.$$

Changing the label of the dummy variables $\beta \mapsto \gamma$ in the one-body term and $i \mapsto p$ everywhere, we can write this as

$$\sum_{\gamma} C_{p\gamma} \langle\alpha|\hat{h}_0|\gamma\rangle + \sum_{j} \sum_{\beta\gamma\delta} C_{j\beta}^* C_{p\gamma} C_{j\delta} \langle\alpha\beta|V|\gamma\delta\rangle_{AS} = \varepsilon_p^{\mathrm{HF}} C_{p\alpha}$$

$$\sum_{\gamma} C_{p\gamma} \left[\langle\alpha|\hat{h}_0|\gamma\rangle + \sum_{j} \sum_{\beta\delta} C_{j\beta}^* C_{j\delta} \langle\alpha\beta|V|\gamma\delta\rangle_{AS} \right] = \varepsilon_p^{\mathrm{HF}} C_{p\alpha}$$

$$\sum_{\gamma} h_{\alpha\gamma}^{\mathrm{HF}} C_{p\gamma} = \varepsilon_p^{\mathrm{HF}} C_{p\alpha},$$

as we wanted to show, where $\varepsilon_p^{\mathrm{HF}}$ are the new single-particle energies we solve for.

Using the density matrix, defined by

$$\rho_{\beta\delta} = \sum_{i} \langle\beta|i\rangle\langle i|\delta\rangle = \sum_{i} C_{i\beta} C_{i\delta}^*,$$

we can write $h_{\alpha\gamma}^{\mathrm{HF}}$ as

$$h_{\alpha\gamma}^{\mathrm{HF}} = \langle\alpha|\hat{h}_0|\gamma\rangle + \sum_{\beta\delta} \rho_{\beta\delta} \langle\alpha\beta|V|\gamma\delta\rangle_{AS}.$$

In second quantization, the Hartree-Fock operator is then defined as

$$\hat{h}^{\mathrm{HF}} = \sum_{\alpha\gamma} h_{\alpha\gamma}^{\mathrm{HF}} a_\alpha^\dagger a_\gamma.$$

TODO: LEGG TIL DIAGRAM OG FORKLAR TERMENE

Part f)   The Hartree-Fock matrices

The Hartree-Fock equations with a variation of the coefficients $C_{p\alpha}$ lead to an eigenvalue problem whose eigenvectors are the coefficients $C_{p\alpha}$ and eigenvalues are the new single-particle energies. Use the single-particle orbits $1s-3s$ and set up the Hartree-Fock matrix for both the helium atom and the beryllium atom. Find after the first diagonalization the new single-particle energies and the new ground state energy. Compare these results with those you obtained under the minimization of the ground states as functions of Z and the full diagonalization. When setting up the Hartree-Fock matrix in the first iteration, our guess for the coefficients $C_{p\beta}$ etc. is $C_{p\beta} = 1$ for $p = \beta$ and zero else.

Solution

We set up the Hartree-Fock matrices with the code in `hartree_fock.py`, for both the helium and beryllium atoms. After the first diagonalization, we find the new single-particle energies and the new ground state energy, listed in Table 1. The untruncated values can be found in `hartree_fock.txt`.

Table 1: Single-particle energies and new ground state energies for Helium and Beryllium atoms, after one Hartree-Fock iteration.

Atom	Single-Particle Energies				New Energy
Helium		$\begin{bmatrix} -0.7832 & -0.7832 \end{bmatrix}$			-2.8291
Beryllium	$\begin{bmatrix} -3.9506 & -3.9506 & -0.1040 & -0.1040 \end{bmatrix}$				-14.4998

For the helium atom, we find that the new ground state energy is -2.8291 atomic units, which is an improvement from the value -2.75 atomic units we found when minimizing with respect to Z, but slightly worse than the result -2.8386 atomic units we found when fully diagonalizing the Hamiltonian.

For the beryllium atom, the new ground state energy of -14.4998 atomic units is a large improvement from the estimate of -13.7159 we got when minimizing with respect to Z, and is still better than the fully diagonalized result of -14.3621 atomic units.

Part g)   Writing a Hartree-Fock code

The final stage is to set up an iterative scheme where you use the new wave functions determined via the coefficients $C_{p\alpha}$ to solve iteratively the Hartree-Fock equations till a given self-consistency is reached. A typical way of doing this is to compare the single-particle energies from the previous iteration with those obtained from the new diagonalization. If the total difference is smaller than a prefixed value, the iterative process is stopped. Feel free to use the code presented in the lecture notes of week 40. Compare these results with the those

you obtained under the minimization of the ground states as functions of Z and the full diagonalization. Discuss your results.

Solution

Setting up the iterative scheme now simply amounts to repeating the diagonalization process implemented previously, until convergence is reached. We measure converge by checking the condition

$$\frac{|\varepsilon^{(n)} - \varepsilon^{(n-1)}|}{m} \leq \lambda,$$

where $\varepsilon^{(n)}$ is the new ground state energy, $\varepsilon^{(n-1)}$ is the previous ground state energy, m is the number of single-particle states, λ is a predefined tolerance, and $|\cdot|$ denotes the 1-norm. We set $\lambda = 10^{-14}$.

The code for this can again be found in `hartree_fock.py`, and the results are listed in Table 2. The untruncated values can be found in `hartree_fock.txt`. Here, we see only marginal improvements as opposed to the results from the first iteration.

Table 2: Single-particle energies and new ground state energies for Helium and Beryllium atoms, after one Hartree-Fock iteration.

Atom	Iterations	Final Energy
Helium	17	-2.8310
Beryllium	18	-14.5082

For the helium atom we found the best results when diagonalizing the Hamiltonian directly. This is unsurprising, given the simpler nature of the problem. This approach does not however scale well to larger systems, where the iterative scheme is more efficient. We see tendencies of this already in the beryllium atom, where the iterative scheme gives the best results. When setting up the Hamiltonian for the beryllium atom, we truncated the excitations at one level above the Fermi level, as opposed to two levels as with the helium atom.