FYS4480 - Quantum Mechanics for Many-Particle Systems

Project 1

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- Github repository containing programs and results:

  `https://github.com/evenmn/FYS4480`

Abstract

This project aims studying the ground state (GS) energy of neural atoms with total spin zero. More precisely we look at Helium and Beryllium, and we limit ourselves to the single-particle orbits 1s, 2s and 3s. Both Configuration interaction (CI) and Hartree-Fock (HF) was used to estimate the energy levels, and as benchmarks recently experimental energy values were used.

For Helium, we found the Configuration Interaction singles (CIS) to give the lowest energy with a relative error of 2.24%, compared to 2.50% by using HF. For Beryllium, the situation was different, with 1.08% relative error when using HF and 2.08% relative error when using CIS.

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1 Introduction

In the childhood of quantum mechanics, immense efforts were placed on Helium computations, because leading physicists found it crucial to provide calculations in agreement with experiments in order to prove the theory. The Norwegian physicist Egil Hylleraas calculated the ground state energy of the Helium atom with impressive accuracy already in 1929, which in some ways confirmed the validity of quantum mechanics. After that, physicists and chemists have managed to study systems of ever higher complexities, thanks to better methods and stronger computers.

In this project, we estimate the energy levels of the Helium and Beryllium atoms, with focus on the ground state energy. For doing that, we first apply the Configuration Interaction Singles (CIS), and thereafter turn to Hartree-Fock (HF). Can we compete with Hylleraas?

The background theory and notation is presented in section (2), *theory*, and the methods we used, in particular CIS and HF, are presented in section (3) *methods*. The results are in section (4) with the same name, and the discussion and conclusion are given in section (5) and (6) respectively. Finally, calculations of the matrix elements used in CIS are moved to Appendix A.

2 Theory

To calculate the energies, we need to solve the Schrödinger equation

$$\hat{H}\left|\Psi_p\right\rangle = \varepsilon_p \left|\Psi_p\right\rangle \tag{1}$$

where we expect to find the exact ground state energy, ε_0, when the correct ground state wave function (GSWF) has been used. In this project we will stick to the Born-Oppenheimer approximation, which gives the Hamiltonian when the nucleus is stationary (is not affected by the electrons),

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

The first term gives the kinetic energy, the second gives the energy from the external potential (nucleus) and the last term gives the interaction energy. Z is the atomic number, defining the number of protons in the nucleus, k is the constant from Coulomb's law and e is the elementary change.

We now introduce the atomic units, setting $\hbar = c = e = m_e = k = 1$. The energies can be converted between atomic units and electronvolts using the relation

$$1 \text{ a.u.} = 2 \cdot 13.6 \text{ eV}. \tag{3}$$

The Hamiltonian thus reads

$$\hat{H} = \hat{H}_0 + \hat{H}_I = \sum_{i=1}^{N} \hat{h}_0(x_i) + \sum_{i<j}^{N} \frac{1}{r_{ij}} \tag{4}$$

with $r_{ij} \equiv \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}$ and $\hat{h}_0$ as the one-body operator for each electron. The single particle functions (SPF) are assumed to be hydrogen-like, where the one-body energies are known from the Bohr model, stating

$$E_n = -\frac{Z^2}{2n^2} \tag{5}$$

where n is the number of nodes in the wave function. In order to calculate the two-body energies, we need to solve the integrals

$$\int r_1^2 dr_1 \int r_2^2 dr_2 \Phi_\alpha^*(r_1) \Phi_\beta^*(r_2) \frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \Phi_\gamma(r_1) \Phi_\delta(r_2) \equiv \langle \alpha\beta | \hat{v} | \gamma\delta \rangle \tag{6}$$

where the Dirac notation is used for shorthand notation. Note carefully that the Φ's are the total wave functions, where both the radial and spin parts are included. The spin part is known to not affect the energies, and it can therefore be factorized out,

$$
\begin{aligned}
\langle \alpha\beta | \hat{v} | \gamma\delta \rangle &= (\alpha\beta | \hat{v} | \gamma\delta) \langle \chi_\alpha \chi_\beta | \chi_\gamma \chi_\delta \rangle \\
&= (\alpha\beta | \hat{v} | \gamma\delta) \langle \chi_\alpha | \chi_\gamma \rangle \langle \chi_\beta | \chi_\delta \rangle \\
&= (\alpha\beta | \hat{v} | \gamma\delta) \delta_{\sigma_\alpha \sigma_\gamma} \delta_{\sigma_\beta \sigma_\delta}.
\end{aligned} \tag{7}
$$

We observe that the integral is non-zero if and only if α and γ got the same spin, and β and δ got the same spin.

2.1 Second Quantization

For quick and compact calculations, we use second quantization as our formalism. The idea is to introduce creation and annihilation operators, which working on a Slater Determinant (SD) can create or annihilate a particle. A creation operator acting on a SD containing zero particles (called a vacuum state), will result in a SD containing one particle, and an annihilation operator acting on a SD containing zero particles will just give zero,

$$a_p^\dagger |0\rangle = |p\rangle \tag{8}$$

$$a_p |0\rangle = 0. \tag{9}$$

where $a_p^\dagger$ is the creation operator and a_p is the annihilation operator. Note that we again use Dirac notation for the Slater Determinant. This simplifies things a lot, since we can rewrite

$$\begin{vmatrix} \phi_1(x_1) & \phi_1(x_2) & \dots & \phi_1(x_N) \\ \phi_2(x_1) & \phi_2(x_2) & \dots & \phi_2(x_N) \\ \vdots & \vdots & \ddots & \\ \phi_N(x_1) & \phi_N(x_2) & \dots & \phi_N(x_N) \end{vmatrix} \equiv |1, 2, \dots, N\rangle \tag{10}$$

Further, the Slater Determinant can only contain one particle in the same state at the same time (ref. Pauli principle), such that adding a particle that already exists in the SD should automatically give zero. In the same manner, removing a particle that does not exist should also give zero. The operations that contribute are when adding a particle that does not exist and removing a particle that exists:

$$a_a^\dagger |abc \dots xyz\rangle = 0 \tag{11}$$

$$a_a |bc \dots xyz\rangle = 0 \tag{12}$$

$$a_a^\dagger |bc \dots xyz\rangle = |abc \dots xyz\rangle \tag{13}$$

$$a_a |abc \dots xyz\rangle = |bc \dots xyz\rangle. \tag{14}$$

If we now look at a sequence of creation and annihilation operators, shuffling two operators of the same kind will just give a negative sign. On the other hand, when shuffling a creation operator with an annihilation operator, we get a Kroenecker delta minus the new ordering,

$$\{a_p^\dagger, a_q^\dagger\} \equiv a_p^\dagger a_q^\dagger - a_p^\dagger a_q^\dagger = 0 \tag{15}$$

$$\{a_p, a_q\} \equiv a_p a_q - a_p a_q = 0 \tag{16}$$

$$\{a_p^\dagger, a_q\} \equiv a_p^\dagger a_q + a_p a_q^\dagger = \delta_{pq}. \tag{17}$$

With a sequence of operators acting on a vacuum state, we can use this to determine expectation values by moving annihilation operators against the vacuum. However, this is really tedious when we have many operators, and fortunately we have Wick's theorem to simplify these operations. More about that in section (2.1.2).

The one-body Hamiltonian is in second quantization given by

$$H_0 = \frac{1}{2} \sum_{\alpha\beta} \langle \alpha | \hat{h}_0 | \beta \rangle \, a_\alpha^\dagger a_\beta \tag{18}$$

while the interaction part is given by

$$H_I = \frac{1}{4} \sum_{\alpha\beta\gamma\delta} \langle \alpha\beta | \hat{v} | \gamma\delta \rangle_{\text{AS}} \, a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma. \tag{19}$$

2.1.1 Particle-hole formalism

For large system, it is not very tempting to write out the entire Slater Determinant as operators acting on the vacuum state. If we assume that the Slater is orthonormal onto itself, $\langle SD|SD \rangle = 1$, we can redefine our vacuum containing all states in the $|SD\rangle$. This is often called the Fermi vacuum. When annihilating a particle below the Fermi level (one of the particles in the Fermi vacuum), we say that we create a hole. When replacing the hole with a particle, we say that we annihilate the hole. Similarly above the Fermi level, we can create and annihilate particles. The annihilation operator therefore now works as before above the Fermi level, but below the Fermi level the creation operator works as the annihilation operator before, and vice versa. In that manner, we specify whether the quasiparticle is a hole or a particle by giving holes indices $i, j, k, l, \ldots$ and particles indices $a, b, c, d, \ldots$. $p, q, r, s, \ldots$ are without restrictions. This leads to

$$\{a_a^\dagger, a_b\} = \delta_{ab} \tag{20}$$

$$\{a_i, a_j^\dagger\} = \delta_{ij} \tag{21}$$

which we again can use to calculate expectation values, or just to simplify.

2.1.2 Wick's theorem

Wick's theorem is extremely useful when calculating expectation values in second quantization. It states that a sequence of operators can be written as the normal ordering of the operators plus the sum over all normal orderings after one contraction plus the sum over all normal orderings after two contractions and so on and so forth. Mathematically, we can write it as

$$ABC\ldots XYZ = \{ABC\ldots XYZ\} \tag{22}$$

$$+ \sum_{\text{Single cont.}} \{AB\overline{C\ldots X}YZ\} \tag{23}$$

$$+ \sum_{\text{Double cont.}} \{A\overline{B}\overline{C\ldots X}\overline{Y}Z\} \tag{24}$$

$$+ \ldots \tag{25}$$

Immediately, it does not seem to simplify the sequence, the clue lies in the normalizing. When calculating expectation values, we will always have an equal number of creation and annihilation operators between the vacuum states (otherwise the expectation value is zero). This means that a normal ordering will always contain an annihilation operator, which is located to the right, acts on the vacuum state and everything goes to zero. In other words, the only terms that contribute

in an expectation value calculation are the fully contracted terms, which gives a major simplification.

The theorem can also be generalized, taking operators of multiple creation and annihilation operators into account. If those operators are normal ordered, Wick's theorem states that only external contractions will contribute, i.e, no contractions inward the operators. [https://manybodyphysics.github.io/FYS4480/doc/pub/secondquant/html/s bs.html]

2.1.3 Energy formulas

We are now ready to calculate some expectation values based on the theory above. We will later do Configuration Interaction Singles (CIS) only, so it is sufficient to calculate $\langle\Phi_0|\hat{H}|\Phi_0\rangle$, $\langle\Phi_0|\hat{H}|\Phi_i^a\rangle$ and $\langle\Phi_i^a|\hat{H}|\Phi_j^b\rangle$. The calculations are moved to Appendix A in order to maintain some sort of neatness. We obtain that the reference energy as a function of Z is

$$\varepsilon_0 = \langle\Phi_0|\hat{H}|\Phi_0\rangle = \sum_i \langle i|\hat{h}_0|i\rangle + \frac{1}{2}\sum_{ij} \langle ij|\hat{v}|ij\rangle_{\mathrm{AS}} \tag{26}$$

where the subscript AS indicates an antisymmetric elements,

$$\langle ij|\hat{v}|ij\rangle_{\mathrm{AS}} = \langle ij|\hat{v}|ij\rangle - \langle ij|\hat{v}|ji\rangle. \tag{27}$$

Further, we obtained

$$\langle\Phi_0|\hat{H}|\Phi_i^a\rangle = \langle i|\hat{h}_0|a\rangle + \sum_j \langle aj|\hat{v}|ij\rangle_{\mathrm{AS}} \tag{28}$$

and

$$\begin{aligned}
\langle\Phi_i^a|\hat{H}|\Phi_j^b\rangle = {} & \langle aj|\hat{v}|ib\rangle_{\mathrm{AS}} - \delta_{ab}\Big[\langle i|\hat{h}_0|j\rangle + \sum_k \langle ik|\hat{v}|jk\rangle_{\mathrm{AS}}\Big] \\
& + \delta_{ij}\Big[\langle a|\hat{h}_0|b\rangle + \sum_k \langle ak|\hat{v}|bk\rangle_{\mathrm{AS}}\Big] \\
& + \delta_{ab}\delta_{ij}\Big[\sum_k \langle k|\hat{h}_0|k\rangle + \frac{1}{2}\sum_{kl} \langle kl|\hat{v}|kl\rangle_{\mathrm{AS}}\Big]
\end{aligned} \tag{29}$$

where the two latter are functions of Z as well. They are then general.

2.2 The Helium atom

A neutral Helium atom consists of a nucleus of two protons with two electrons orbiting, and is the simplest many-body atom one can study (atoms with more

than 1 electron). The difficulty of dealing with many-body systems lies in the interaction, where the elements $\langle \alpha\beta|\hat{v}|\gamma\delta\rangle$ can be really tricky to handle. The interaction term makes the exact wave function almost impossible to find.

There exist various methods for solving this problem, where one of the most successful is to define a wave function which is varied such that the energy is minimized. This method was used by E. Hylleraas already in 1929, when he minimized the energy with a wave function of 10 variational parameters, using a mechanical desk calculator. [https://www.encyclopedia.com/science/dictionaries-thesauruses-pictures-and-press-releases/hylleraas-egil-andersen] He found the energy to be -2.90363 eV, which is close to recent experimental values, and which we will compare our energies to. [http://www.umich.edu/ chem461/QMChap8.pdf][https://journals.aps

2.2.1 Ground state

Helium is in its ground state when both electrons occupy the 1s orbital, thus they have opposite spins and $M_s = 0$. In this project, we will study systems of $M_s = 0$ only, such that an electron can only be excited to a state with the same spin.

Taking the Pauli principle into account, the two-body wavefunction needs to be nulled out if two particles are in the same state, and it should also be antisymmetric under exchange of two particles. We are therefore in need of a Slater Determinant, given by

$$\Psi(x_1, x_2, \sigma_1, \sigma_2) = A \begin{vmatrix} \psi_{\sigma_1}(x_1) & \psi_{\sigma_1}(x_2) \\ \psi_{\sigma_2}(x_1) & \psi_{\sigma_2}(x_2) \end{vmatrix} \tag{30}$$

$$= A\Big[\psi_{\sigma_1}(x_1)\psi_{\sigma_2}(x_2) - \psi_{\sigma_2}(x_1)\psi_{\sigma_1}(x_2)\Big] \tag{31}$$

where ψ_{σ_1} is the SPF with spin $m_s = \sigma_1$ and A is a normalization constant. If we assume that the SPFs are normalized, our ansatz can be written as

$$|\Phi_0\rangle = \frac{1}{\sqrt{2}}(|1\rangle\,|\bar{1}\rangle - |\bar{1}\rangle\,|1\rangle) \tag{32}$$

with $|\bar{1}\rangle$ describing a particle with principle quantum number 1 and spin σ_2, which we will illustrate with spin down. In second quantization, we can construct the ground state from the true vacuum,

$$|\Phi_0\rangle = a_1^\dagger a_{\bar{1}}^\dagger |0\rangle, \tag{33}$$

which is understand to take the anti-symmetry property. The ground state is illustrated in figure (1).
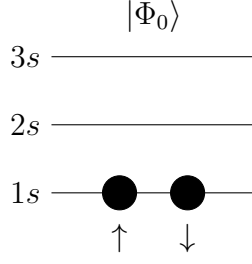
Figure 1: Ground state of Helium.

2.2.2 Excited states

When entering excited states, we can risk having angular quantum numbers unlike zero, because $l \in [0, n-1]$. This makes the computations more difficult, but in this project we will ignore that challenge setting $l = 0$, and thus limit us to the s-waves.

Consider now a system consisting of the orbitals 1s, 2s and 3s only. For that case, the possible energy states of the Helium atom are listed in figure (2).
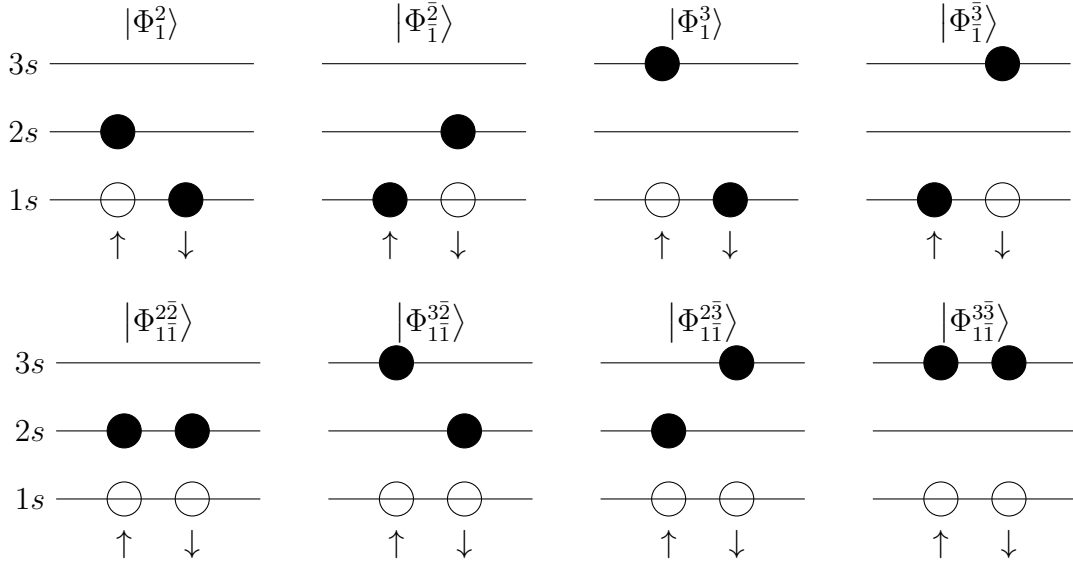

Figure 2: Possible states in the 1s, 2s and 3s orbitals of Helium. In the first row, all singly excited states are listed, while in the second row all doubly excited states are listed.

2.3   The Beryllium atom

Beryllium has atomic number $Z = 4$, so a neutral Beryllium atom has four protons in its nucleus and four electrons swarming around. To study atoms with even atomic numbers is easier than odd atomic number, since the Fermi level is well defined.

2.3.1   Ground state

Beryllium is in its ground state when the electrons occupy the 1s and 2s orbitals (we again set $l = 0$). In second quantization, the ground state can then be expressed as

$$|\Phi_0\rangle = a_1^\dagger a_{\bar{1}}^\dagger a_2^\dagger a_{\bar{2}}^\dagger |0\rangle \,, \tag{34}$$

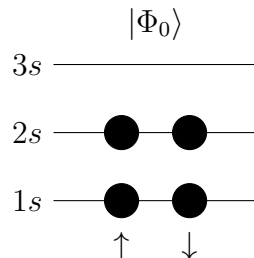and is illustrated in figure (3).

Figure 3: Ground state of Beryllium.

2.3.2   Excited states

We again limit us to the 1s, 2s and 3s orbits. When the electrons have only two free slots to be excited to. Anyway, since we have four particles that can be excited, there are still as many possible excited states as for Helium, see figure (4).
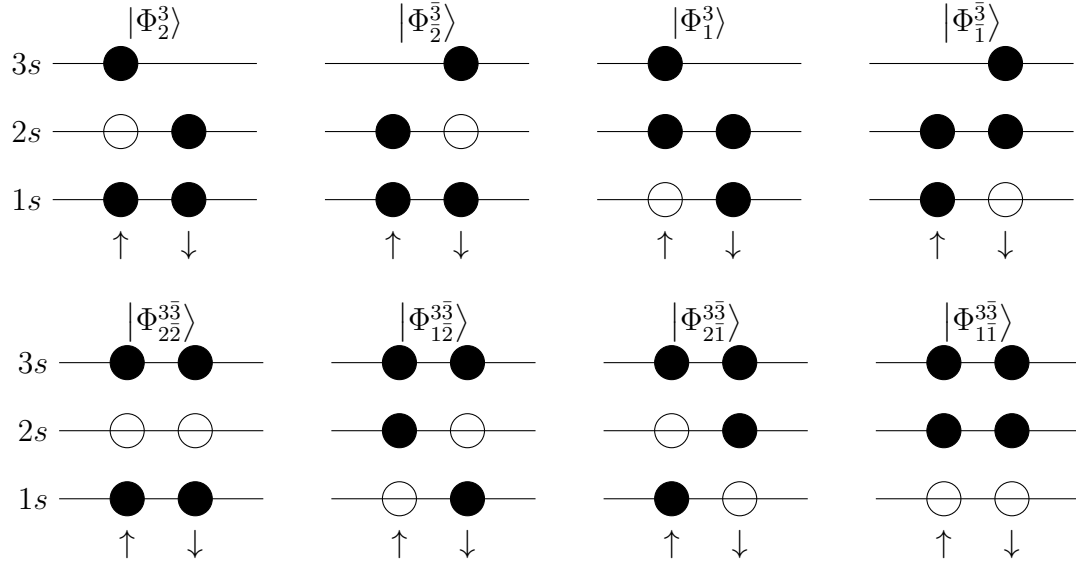
Figure 4: Possible states in the 1s, 2s and 3s orbitals of Beryllium. In the first row, all singly excited states are listed, while in the second row all doubly excited states are listed.

3 Methods

There exist many methods for solving the Schrödinger equation. Some of them are exact, but always heavy to deal with. Other are approximation, but hopefully not that expensive. We are going to look at *Configuration Interaction* (CI), which in principle gives the exact energy (then called *Full Configuration Interaction* (FCI)) and *Hartree-Fock*, which is a mean field theory and will not give exact results.

3.1 Configuration Interaction (CI)

Often, we know the true wavefunctions $|\Phi_i\rangle$ in the external potential, but are off when interaction is added

$$\hat{H}_0 |\Phi_i\rangle = \varepsilon_i |\Phi_i\rangle, \qquad (\hat{H}_0 + \hat{H}_I) |\Phi_i\rangle \neq \varepsilon_i |\Phi_i\rangle. \tag{35}$$

However, the SDs form a ket basis, meaning we can write out eigenstates of $\hat{H}_I$ as a linear combination of the SDs

$$\begin{aligned}
|\Psi_0\rangle &= C_0^{(0)} |\Phi_0\rangle + C_1^{(0)} |\Phi_1\rangle + \ldots + C_{N-1}^{(0)} |\Phi_{N-1}\rangle \\
|\Psi_1\rangle &= C_0^{(1)} |\Phi_0\rangle + C_1^{(1)} |\Phi_1\rangle + \ldots + C_{N-1}^{(1)} |\Phi_{N-1}\rangle \\
|\Psi_2\rangle &= C_0^{(2)} |\Phi_0\rangle + C_1^{(2)} |\Phi_1\rangle + \ldots + C_{N-1}^{(2)} |\Phi_{N-1}\rangle \\
&\quad\vdots \qquad \vdots \qquad \vdots \\
|\Psi_{N-1}\rangle &= C_0^{(N-1)} |\Phi_0\rangle + C_1^{(N-1)} |\Phi_1\rangle + \ldots + C_N^{(N-1)} |\Phi_{N-1}\rangle.
\end{aligned} \tag{36}$$

such that

$$\hat{H} |\Psi_p\rangle = \varepsilon_p |\Psi_p\rangle. \tag{37}$$

The Hamiltonian can be rewritten as a double sum over all states using the so-called *completeness relation*,

$$\hat{H} = \sum_{ij} |\Phi_i\rangle \langle\Phi_i|\hat{H}|\Phi_j\rangle \langle\Phi_j| \tag{38}$$

such that the Schrödinger equation can be rewritten as

$$\begin{pmatrix}
\langle\Phi_0|\hat{H}|\Phi_0\rangle & \langle\Phi_0|\hat{H}|\Phi_1\rangle & \ldots & \langle\Phi_0|\hat{H}|\Phi_{N-1}\rangle \\
\langle\Phi_1|\hat{H}|\Phi_0\rangle & \langle\Phi_1|\hat{H}|\Phi_1\rangle & \ldots & \langle\Phi_1|\hat{H}|\Phi_{N-1}\rangle \\
\vdots & \vdots & \ddots & \vdots \\
\langle\Phi_{N-1}|\hat{H}|\Phi_0\rangle & \langle\Phi_{N-1}|\hat{H}|\Phi_1\rangle & \ldots & \langle\Phi_{N-1}|\hat{H}|\Phi_{N-1}\rangle
\end{pmatrix}
\begin{pmatrix}
c_0^{(p)} \\
c_1^{(p)} \\
\vdots \\
c_{N-1}^{(p)}
\end{pmatrix}
= \varepsilon_p
\begin{pmatrix}
c_0^{(p)} \\
c_1^{(p)} \\
\vdots \\
c_{N-1}^{(p)}
\end{pmatrix} \tag{39}$$

Until now, we have not made any assumptions, such that the equation above will give exact results when all SPFs are included. The problem is that the matrix scales so badly, the number of Slater Determinant that we need to include goes as

$$N_{\text{FCI}} = \binom{N_{\text{single orbitals}}}{N_{\text{electrons}}} \tag{40}$$

which is exploding. This is quite annoying since we in principle know how to solve the problems exact. However, in this project we restrict ourselves to three orbitals and single excitations only, which makes the problem more manageable. [https://github.com/ManyBodyPhysics/FYS4480/blob/master/doc/Exercises/Answers/FirstsetAn matrices are given in results, and a program calculating solutions to equation (26-30) is outlined below

```python
class CIS:
  '''Configuration Interction Singles class for atomic structure'''

  def __init__(self, Z, basis):

    self.elem = Integrals(Z,basis)  # Matrix elements/integrals
    self.n = Z                       # Assume neutral atom


  def c_H_c(self):
    '''Reference energy'''

    OBT = 0
    for i in range(self.n):
      OBT += self.elem.OBME(i,i)
    TBT = 0
    for i in range(self.n):
      for j in range(self.n):
        TBT += 0.5*self.elem.AS(i,j,i,j)
    return OBT + TBT


  def c_H_ia(self, i,a):
    '''Singly excited ket'''

    OBT = self.elem.OBME(i,a)
    TBT = 0
    for j in range(self.n):
      TBT += self.elem.AS(a,j,i,j)
    return OBT + TBT


  def ia_H_jb(self, i,a,j,b):
    '''Singly excited bra and ket'''

    Result = self.elem.AS(a,j,i,b)
    if a==b:
    Result -= self.elem.OBME(i,j)
    for k in range(self.n):
      Result -= self.elem.AS(i,k,j,k)
      if i==j:
        for l in range(self.n):
          Result += self.elem.OBME(l,l)
```

```
        for m in range(self.n):
            Result += 0.5*self.elem.AS(l,m,l,m)
    if i==j:
        Result += self.elem.OBME(a,b)
        for k in range(self.n):
            Result += self.elem.AS(a,k,b,k)
    return Result
```

3.2 Hartree-Fock

When we calculated the reference energy above, our basis contained only one Slater determinant, more specifically the ground state. In Hartree-Fock, we still have a single Slater determinant basis, but we now construct new SPFs with the constraint of minimizing the energy.

In general, one can change from one single-particle basis to another by a unitary transform,

$$|p\rangle = \sum_{\alpha} c_{p\alpha} |\alpha\rangle , \tag{41}$$

where we use greek letters for the old basis and roman letters for the new one. If we then insert into (26), we get a find energy formula with coefficients, $C_{p\lambda}$, that we can vary

$$E = \sum_{p}^{N} \sum_{\alpha\beta} C_{p\alpha}^* C_{p\beta} \langle\alpha|\hat{h}_0|\beta\rangle + \frac{1}{2} \sum_{pq}^{N} \sum_{\alpha\beta\gamma\delta} C_{p\alpha}^* C_{q\beta}^* C_{p\gamma} C_{q\delta} \langle\alpha\beta|\hat{v}|\gamma\delta\rangle_{\mathrm{AS}} . \tag{42}$$

Further, we assume that also our new basis is orthonormal, i.e,

$$\langle p|q\rangle = \sum_{\alpha} c_{p\alpha}^* c_{q\alpha} \langle\alpha|\alpha\rangle = \sum_{\alpha} c_{p\alpha}^* c_{q\alpha} = \delta_{pq} \tag{43}$$

$$\Rightarrow \sum_{\alpha} c_{p\alpha}^* c_{q\alpha} - \delta_{pq} = 0 \tag{44}$$

We now have a function, E, that we want to minimize with respect to a constraint given in equation (44). This is a typical situation where Lagrange Multipliers is convenient to use, which in this case can be written as

$$\mathcal{L}(\{C_{p\alpha}\}) = E(\{C_{p\alpha}\}) - \sum_{a} \varepsilon_a \Big(\sum_{\alpha} c_{p\alpha}^* c_{q\alpha} - \delta_{pq} \Big). \tag{45}$$

The variation in reference energy is then find to be

$$\delta E = \sum_{k\alpha} \frac{\partial E}{\partial C_{k\alpha}^*} \delta C_{k\alpha}^* + \sum_{k\alpha} \frac{\partial E}{\partial C_{k\alpha}} \delta C_{k\alpha} - \sum_{k\alpha} \varepsilon_k (C_{k\alpha}\delta C_{k\alpha}^* + C_{k\alpha}^* \delta C_{k\alpha}) \tag{46}$$

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which is zero when E is minimized. Each coefficient $C_{k\alpha}$ and $C_{k\alpha}^*$ is independent, so they can be varied independently. Thus

$$\left(\frac{\partial E}{\partial C_{k\alpha}^*} - \varepsilon_k C_{k\alpha}\right)\delta C_{k\alpha}^* = 0, \tag{47}$$

which is satisfied if and only if

$$\frac{\partial E}{\partial C_{k\alpha}^*} - \varepsilon_k C_{k\alpha} = 0 \qquad \forall\ k, \alpha \tag{48}$$

The first term can be derived from (46), and reads

$$\frac{\partial E}{\partial C_{k\alpha}^*} = \sum_\beta C_{k\beta} \langle\alpha|\hat{h}_0|\beta\rangle + \sum_p^N \sum_{\beta\gamma\delta} C_{p\beta}^* C_{k\gamma} C_{p\delta} \langle\alpha\beta|\hat{v}|\gamma\delta\rangle_{\mathrm{AS}}. \tag{49}$$

This results in the equation

$$\sum_\gamma \hat{h}_{\alpha\gamma}^{\mathrm{HF}} C_{k\gamma} = \varepsilon_k C_{k\gamma} \tag{50}$$

where we have defined

$$\hat{h}_{\alpha\gamma}^{\mathrm{HF}} \equiv \langle\alpha|\hat{h}_0|\gamma\rangle + \sum_p^N \sum_{\beta\delta} C_{p\beta}^* C_{p\delta} \langle\alpha\beta|\hat{v}|\gamma\delta\rangle_{\mathrm{AS}}. \tag{51}$$

We recognize that (50) can be written as a matrix-vector product

$$\hat{h}^{\mathrm{HF}} C_k = \varepsilon_k^{\mathrm{HF}} C_k \tag{52}$$

where C_k are columns in our coefficient matrix and $\varepsilon_k^{\mathrm{HF}}$ are just the eigenvalues of $\hat{h}^{\mathrm{HF}}$, they have no physical significance. We will use this equation to find the optimal SPFs (optimal C_k's) and then find the energy from equation (46).

$$\hat{h}^{\mathrm{HF}}(C_k^{i+1})C_k^i = \varepsilon_k^{\mathrm{HF}} C_k^i \tag{53}$$

Usually one initialize this with $\hat{C} = \hat{\mathcal{I}}$, the identity matrix.

The implementation could look something like this

```python
class HF:
  '''Hartree-Fock class for atomic structure'''

  def __init__(self, Z, basis):

    self.elem = Integrals(Z,basis)   # Matrix elements/integrals
    self.n = Z                        # Number of electrons, assuming neutral atom
    self.N = len(basis)               # Number of states
```

```python
def HF_elements(self,i,j,C):
    '''HF matrix elements (i,j)'''

    Result = self.elem.OBME(i, j)
    for p in range(self.n):
        for c in range(self.N):
            for d in range(self.N):
                Result += C[p,c]*C[p,d]*self.elem.AS(i,c,j,d)
    return Result


def HF_matrix(self,C):
    '''HF-matrix'''

    HF_mat = np.empty((self.N,self.N))
    for i in range(self.N):
        for j in range(self.N):
            HF_mat[i,j] = HF.HF_elements(self,i,j,C)
    return HF_mat


def HF_iter(self,tol=1e-8,max_iter=50):
    '''Solving HF with an iterative scheme'''

    C = np.eye(self.N)
    eps = np.ones(self.N)
    for i in range(max_iter):
        HF_mat = HF.HF_matrix(self,C)
        eps_new, C = np.linalg.eigh(HF_mat)
        C = C.T

        if abs(eps[0]-eps_new[0]) < tol:
            break
        eps = eps_new
    return HF.calc_E(self,C), i


def calc_E(self,C):
    '''Calculate energy'''

    E = 0
    for p in range(self.n):
        for a in range(self.N):
            for b in range(self.N):
                E += C[p,a]*C[p,b]*self.elem.OBME(a,b)
                for q in range(self.n):
                    for c in range(self.N):
                        for d in range(self.N):
                            E += 0.5*C[p,a]*C[q,b]*C[p,c]*C[q,d]*self.elem.AS(a,b,c,d)
    return E
```

4 Results

In this project, the results are mainly er energies, where we will present the obtained reference energy, the CIS energy, HF energy after 1 iteration and HF energy

after it has converged. We will compare with recent experimental energies, and for Helium we will also compare to what Hylleraas obtained in 1929.

Furthermore, we will show how the matrices look like, which can be useful to know in some contexts.

4.1 The Helium atom

Let's start with the Helium atom. The ground state energies are presented in the first subsection, and after that we present the HF matrices and the CIS matrix respectively.

4.1.1 Ground state energies

The obtained ground state energies are given in table (1).

Table 1: Ground state energies of the Helium atom and the relative error with respect to the experimental value. The experimental value is taken from [Bergerson, 1998], and Hylleraas' energy is taken from [http://www.umich.edu/ chem461/QMChap8.pdf]. Further the reference value is obtained from equation (26), the CIS calculation is based on equation (39) and the two last energies are obtained from equation (53) with the identity matrix as initial $\hat{C}$, and the energy converged after 10 iterations with a maximum change of 1e-8.

Method	Energy [a.u.]	Relative error
Experimental	-2.903694	0.00%
Hylleraas	-2.90363	0.0022%
Reference	-2.750000	5.29%
CIS	-2.838648	2.24%
$\text{HF}_{1 \text{ iteration}}$	-2.829193	2.56%
$\text{HF}_{\text{converge}}$	-2.831096	2.50%

4.1.2 CIS

The CIS matrix reads

$$\hat{H}_{\text{CIS}} = \begin{pmatrix} -2.750 & 0.179 & 0.179 & 0.088 & 0.088 \\ 0.179 & -2.080 & 0.044 & 0.101 & 0.022 \\ 0.179 & 0.044 & -2.080 & 0.022 & 0.101 \\ 0.088 & 0.101 & 0.022 & -2.023 & 0.012 \\ 0.088 & 0.022 & 0.101 & 0.012 & -2.023 \end{pmatrix} \tag{54}$$

where the SPF order of choice is $|\Phi_0\rangle, |\Phi_1^2\rangle, |\Phi_1^{\bar{2}}\rangle, |\Phi_1^3\rangle, |\Phi_1^{\bar{3}}\rangle$.

4.1.3 HF

Below you can find the HF matrices. The first matrix is the one obtained after an iteration, while the last is after the energy has converged. We have initialized with the identity matrix in both cases.

$$
\hat{h}_{1\,\mathrm{iter}}^{\mathrm{HF}} =
\begin{pmatrix}
-0.750 & 0.000 & 0.179 & 0.000 & 0.088 & 0.000 \\
0.000 & -0.750 & 0.000 & 0.179 & 0.000 & 0.088 \\
0.179 & 0.000 & 0.296 & 0.000 & 0.180 & 0.000 \\
0.000 & 0.179 & 0.000 & 0.296 & 0.000 & 0.180 \\
0.088 & 0.000 & 0.180 & 0.000 & 0.164 & 0.000 \\
0.000 & 0.088 & 0.000 & 0.180 & 0.000 & 0.164
\end{pmatrix}
\tag{55}
$$

$$
\hat{h}_{\mathrm{converge}}^{\mathrm{HF}} =
\begin{pmatrix}
-0.840 & 0.000 & 0.226 & 0.000 & 0.102 & 0.000 \\
0.000 & -0.840 & 0.000 & 0.226 & 0.000 & 0.102 \\
0.226 & 0.000 & 0.271 & 0.000 & 0.169 & 0.000 \\
0.000 & 0.226 & 0.000 & 0.271 & 0.000 & 0.169 \\
0.102 & 0.000 & 0.169 & 0.000 & 0.159 & 0.000 \\
0.000 & 0.102 & 0.000 & 0.169 & 0.000 & 0.159
\end{pmatrix}
\tag{56}
$$

Observe that they are not very different. Unlike the zeros in matrix (55), the zeros in (56) are not exactly zero, but smaller than 1e-17.

4.2 The Beryllium atom

We now turn to the Beryllium atom. The ground state energies are presented in the first subsection, and after that we present the HF matrices and the CIS matrix respectively.

4.2.1 Ground state energy

Table 2: Ground state energies of the Beryllium atom and the relative error with respect to the experimental value. The experimental value is taken from [Kramida, Martin, 1997] and the reference value is obtained from equation (26), the CIS calculation is based on equation (39) and the two last energies are obtained from equation (53) with the identity matrix as initial $\hat{C}$, and the energy converged after 11 iterations with a maximum change of 1e-8.

Method	Energy [a.u.]	Relative error
Experimental	-14.6674	0.00%
Reference	-13.7160	6.49%
CIS	-14.3621	2.08%
$\text{HF}_{1 \text{ iteration}}$	-14.4998	1.14%
$\text{HF}_{\text{converge}}$	-14.5083	1.08%

4.2.2 CIS

The CIS matrix reads

$$\hat{H}_{\text{CIS}} = \begin{pmatrix} -2.372 & 0.189 & 0.189 & 0.445 & 0.445 \\ 0.189 & -9.655 & 2.307 & -0.390 & 0.001 \\ 0.189 & 0.023 & -9.655 & 0.001 & -0.393 \\ 0.445 & -0.393 & 0.001 & -13.688 & 0.030 \\ 0.445 & 0.001 & -0.393 & 0.030 & -13.688 \end{pmatrix} \tag{57}$$

where the SPF order of choice is $|\Phi_0\rangle, |\Phi_1^3\rangle, |\Phi_1^{\bar{3}}\rangle, |\Phi_2^3\rangle, |\Phi_2^{\bar{3}}\rangle$.

4.2.3 HF

Below you can find the HF matrices. The first matrix is the one obtained after an iteration, while the last is after the energy has converged. We have initialized with the identity matrix in both cases.

$$\hat{h}_{1\ \text{iter}}^{\text{HF}} = \begin{pmatrix} -3.909 & 0.000 & 0.392 & 0.000 & 0.189 & 0.000 \\ 0.000 & -3.909 & 0.000 & 0.392 & 0.000 & 0.189 \\ 0.392 & 0.000 & 0.193 & 0.000 & 0.445 & 0.000 \\ 0.000 & 0.392 & 0.000 & 0.193 & 0.000 & 0.445 \\ 0.189 & 0.000 & 0.445 & 0.000 & 0.527 & 0.000 \\ 0.000 & 0.189 & 0.000 & 0.445 & 0.000 & 0.527 \end{pmatrix} \tag{58}$$

$$\hat{h}_{\text{converge}}^{\text{HF}} = \begin{pmatrix} -4.650 & 0.000 & 0.392 & 0.000 & 0.199 & 0.000 \\ 0.000 & -4.650 & 0.000 & 0.392 & 0.000 & 0.199 \\ 0.392 & 0.000 & 0.116 & 0.000 & 0.534 & 0.000 \\ 0.000 & 0.392 & 0.000 & 0.116 & 0.000 & 0.534 \\ 0.199 & 0.000 & 0.534 & 0.000 & 0.353 & 0.000 \\ 0.000 & 0.199 & 0.000 & 0.534 & 0.000 & 0.353 \end{pmatrix} \tag{59}$$

Observe that they are not very different. Unlike the zeros in matrix (58), the zeros in (59) are not exactly zero, but smaller than 1e-17.

5   Discussion

The first thing that we can observe from table (1), is how accurate Hylleraas' computation was. Creds to him! CIS turned out to be our best method, as expected since we used a basis of 5 SPFs. What is more surprising is that the HF energy was close, even though we only had one Slater Determinant. We also observe that CIS, $\text{HF}_{1\ \text{iteration}}$ and $\text{HF}_{\text{converge}}$ all lie in between the reference energy and the experimental, which indicates that our calculations are correct.

Switching to the CIS matrix for Helium, we see that it is symmetric as expected, and the diagonal elements are dominating.

For the HF matrices, we observe that every second element is zero, which are the elements where the excited particle in the ket got opposite spin of the excited particle in the bra. We could find a row equivalent matrices to the HF matrices with four block sections where two contained zeros only. We can also see that the two matrices are not very different, something that is reflected in the two HF energies.

For Beryllium, the HF energies are actually lower than the CIS energy, which is surprising. The reason could be that we only allow the electrons to be excited to one energy level above the Fermi level, with a more complex CIS matrix the energy would be lower for sure. The CIS and HF energies again lie in between the reference energy and the experimental energy, which is good.

6   Conclusion

Based on the results we have obtained, we can conclude that our implementations are successful. What we have seen, is that for the Helium atom, CIS gives the best result, while for the Beryllium atom HF gives best result. This might be caused by the fact that Beryllium has more electrons, so they have not so many states to be excited to.

By including the doubles as well (performing a CISD), we would probably got a way lower energy.

A   Appendix A - Calculate matrix elements

Recall that the Hamiltonian in second quantization is

$$\hat{H} = \hat{H}_0 + \hat{H}_I$$
$$= \frac{1}{2} \sum_{\alpha\beta} \langle \alpha | \hat{h}_0 | \beta \rangle \, a_\alpha^\dagger a_\beta + \frac{1}{4} \sum_{\alpha\beta\gamma\delta} \langle \alpha\beta | \hat{v} | \gamma\delta \rangle_{\mathrm{AS}} \, a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma. \tag{60}$$

A.1   Calculating $\langle \Phi_0 | \hat{H} | \Phi_0 \rangle$

Inserting the Hamiltonian from (60), we find

$$E[\Phi_0] = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle$$
$$= \frac{1}{2} \sum_{\alpha\beta} \langle \alpha | \hat{h}_0 | \beta \rangle \, \langle c | a_\alpha^\dagger a_\beta | c \rangle \tag{61}$$
$$+ \frac{1}{4} \sum_{\alpha\beta\gamma\delta} \langle \alpha\beta | \hat{v} | \gamma\delta \rangle \, \langle c | a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma | c \rangle$$

Using that only fully contracted terms contribute (statement from Wick's theorem), we get

$$\langle c | a_\alpha^\dagger a_\beta | c \rangle = \delta_{\alpha\beta} \tag{62}$$

and

$$\langle c | a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma | c \rangle = \delta_{\alpha\gamma} \delta_{\beta\delta} - \delta_{\alpha\delta} \delta_{\beta\gamma}. \tag{63}$$

Since the operator to the right is going to remove a particle from the Slater Determinant $|c\rangle$, all the indices need to be $i, j, k, l, \ldots$. We obtain

$$E[\Phi_0] = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle = \sum_i \langle i | \hat{h}_0 | i \rangle + \frac{1}{2} \sum_{ij} \Big[\langle ij | \hat{v} | ij \rangle - \langle ij | \hat{v} | ji \rangle \Big]. \tag{64}$$

A.2   Calculating $\langle \Phi_0 | \hat{H} | \Phi_i^a \rangle$

$$\langle \Phi_0 | \hat{H} | \Phi_i^a \rangle = \frac{1}{2} \sum_{\alpha\beta} \langle \alpha | \hat{h}_0 | \beta \rangle \, \langle c | a_\alpha^\dagger a_\beta a_a^\dagger a_i | c \rangle \tag{65}$$
$$+ \frac{1}{4} \sum_{\alpha\beta\gamma\delta} \langle \alpha\beta | \hat{v} | \gamma\delta \rangle \, \langle c | a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma a_a^\dagger a_i | c \rangle$$

$$\langle c|a_\alpha^\dagger a_\beta a_a^\dagger a_i|c\rangle = \delta_{\alpha i}\delta_{\beta a} \tag{66}$$

$$\langle c|a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma a_a^\dagger a_i|c\rangle = \delta_{\alpha i}\delta_{\beta\delta}\delta_{\gamma a} - \delta_{\alpha\delta}\delta_{\beta i}\delta_{\gamma a} \tag{67}$$

$$+ \delta_{\alpha\gamma}\delta_{\beta i}\delta_{\delta a} - \delta_{\alpha i}\delta_{\beta\gamma}\delta_{\delta a} \tag{68}$$

Using the fact the the matrix elements are symmetric, i.e, $\langle aj|\hat{v}|ij\rangle = \langle ja|\hat{v}|ji\rangle$.

$$\langle\Phi_0|\hat{H}|\Phi_i^a\rangle = \langle i|\hat{h}_0|a\rangle + \sum_j \Big[\langle aj|\hat{v}|ij\rangle - \langle aj|\hat{v}|ji\rangle \Big] \tag{69}$$

A.3 Calculating $\langle\Phi_i^a|\hat{H}|\Phi_j^b\rangle$

$$\langle\Phi_i^a|\hat{H}|\Phi_j^b\rangle = \frac{1}{2}\sum_{\alpha\beta} \langle\alpha|\hat{h}_0|\beta\rangle \, \langle c|a_j^\dagger a_b a_\alpha^\dagger a_\beta a_a^\dagger a_i|c\rangle \tag{70}$$

$$+ \frac{1}{4}\sum_{\alpha\beta\gamma\delta} \langle\alpha\beta|\hat{v}|\gamma\delta\rangle \, \langle c|a_j^\dagger a_b a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma a_a^\dagger a_i|c\rangle$$

$$\langle c|a_j^\dagger a_b a_\alpha^\dagger a_\beta a_a^\dagger a_i|c\rangle = \delta_{ij}\delta_{ab}\delta_{\alpha\beta} + \delta_{ij}\delta_{a\alpha}\delta_{\beta b} - \delta_{i\beta}\delta_{ab}\delta_{\alpha j} \tag{71}$$

$$\langle c|a_j^\dagger a_b a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma a_a^\dagger a_i|c\rangle = \delta_{i\delta}\delta_{a\beta}\delta_{\alpha j}\delta_{\gamma b} - \delta_{i\delta}\delta_{a\alpha}\delta_{\beta j}\delta_{\gamma b}$$

$$+ \delta_{i\delta}\delta_{ab}\delta_{\alpha j}\delta_{\beta\gamma} - \delta_{i\delta}\delta_{ab}\delta_{\alpha j}\delta_{\beta\gamma}$$

$$+ \delta_{i\gamma}\delta_{a\alpha}\delta_{\beta j}\delta_{\delta b} - \delta_{i\gamma}\delta_{a\beta}\delta_{\alpha j}\delta_{\delta b}$$

$$+ \delta_{i\gamma}\delta_{ab}\delta_{\alpha\delta}\delta_{\beta j} - \delta_{i\gamma}\delta_{ab}\delta_{\alpha j}\delta_{\beta\delta} \tag{72}$$

$$+ \delta_{ij}\delta_{a\alpha}\delta_{\beta\delta}\delta_{\gamma b} - \delta_{ij}\delta_{a\alpha}\delta_{\beta\gamma}\delta_{\delta b}$$

$$+ \delta_{ij}\delta_{a\beta}\delta_{\alpha\gamma}\delta_{\delta b} - \delta_{ij}\delta_{a\beta}\delta_{\alpha\delta}\delta_{\gamma b}$$

$$+ \delta_{ij}\delta_{ab}\delta_{\alpha\gamma}\delta_{\beta\delta} - \delta_{ij}\delta_{ab}\delta_{\alpha\delta}\delta_{\beta\gamma}$$

We observe that all two-body terms are antisymmetric. When using that the matrix elements are symmetric, we obtain

$$\langle\Phi_i^a|\hat{H}|\Phi_j^b\rangle = \langle aj|\hat{v}|ib\rangle_{\text{AS}} - \delta_{ab}\Big[\langle i|\hat{h}_0|j\rangle + \sum_k \langle ik|\hat{v}|jk\rangle_{\text{AS}} \Big]$$

$$+ \delta_{ij}\Big[\langle a|\hat{h}_0|b\rangle + \sum_k \langle ak|\hat{v}|bk\rangle_{\text{AS}} \Big] \tag{73}$$

$$+ \delta_{ab}\delta_{ij}\Big[\sum_k \langle k|\hat{h}_0|k\rangle + \frac{1}{2}\sum_{kl} \langle kl|\hat{v}|kl\rangle_{\text{AS}} \Big]$$

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