UiO : Department of Chemistry
University of Oslo

FYS4480: Quantum mechanics for many-particle systems

Midterm

Quantum mechanical models of the electronic structures of the Helium and Beryllium atoms

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1. System and Model

We develop two models; one for the Helium atom (two electrons), another for the Beryllium atom (four electrons). The models will be similar, only the number of electrons will change.

Our model is based on the Born-Oppenheimer approximation; the nucleus will have no degrees of freedom. The Coulomb potential of the nucleus is given as

$$V(\mathbf{r}, \mathbf{R}) = k\frac{Ze}{\|\mathbf{r} - \mathbf{R}\|_2}, \tag{1.1}$$

where $\mathbf{r}$ is the position in space, $\mathbf{R}$ is the position of the nucleus, Z is the charge of the nucleus and $k = 1.44eV$ is the Couloumb's constant. We assume that three- or more-body interactions can be neglected, and we place the origo of our coordinate system at the position of the nucleus ($\mathbf{R} = \mathbf{0}$). In order to make the Hamiltonian reflect our specific system, we need the Hamiltonian to take into account the magnetic spin quantum number of the electrons. If we define the spin-position vector

$$x_i \coloneqq \mathbf{r}_i\alpha_i,$$

where α_i (up or down) is the spin coordinate of electron i, then the Hamiltonian of a system of N electrons takes the form

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

where $r_i = \|\mathbf{r}_i - \mathbf{R}\|_2$, $r_{ij} = \|\mathbf{r}_i - \mathbf{r}_j\|$, $\hat{t}$ is the kinetic energy operator, and the notation $\sum_{i<j}^{N}$ means that we sum over all unique pairs of electrons. Furthermore, we apply natural units to this system, making $\hbar = c = e = k = 1$, and we rewrite the Hamiltonian as one- and two-body operators, $\hat{H} = \hat{H}_0 + \hat{H}_I$, where

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

where $\hat{u}(x_i)$ represents the potential energy of the electron i induced by the electric field from the nuclei, and $\hat{v}(x_i, x_j)$ reflects the Coulomb interactions between electron i and electron j. We will use the hydrogen-like single-particle functions as basis for our calculations. This makes the one-body operator $\hat{H}_0$ diagonal in this basis for states i, j with the quantum numbers nlm_lsm_s with energies

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

with δ_{ij} as the Dirac delta function.
The radial parts of the general single-particle basis function with quantum numbers nlm_lsm_s is given as

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

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

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

Notice that the Coulomb interaction only operates on the spatial part of the wave function, and we also need to integrate over spin when we calculate our expectation values. We already have the values of these integrals tabulated, and therefore we do not need to calculate these integrals.
We restrict our basis to only cover the first three s-orbitals of the hydrogen atom. These single-particle states have quantum numbers displayed in Table 1.1.

Single-particle state	n	l	m_l	s	m_s
$1s\alpha_1$	1	0	0	$\frac{1}{2}$	$+\frac{1}{2}$
$1s\alpha_2$	1	0	0	$\frac{1}{2}$	$-\frac{1}{2}$
$2s\alpha_1$	2	0	0	$\frac{1}{2}$	$+\frac{1}{2}$
$2s\alpha_2$	2	0	0	$\frac{1}{2}$	$-\frac{1}{2}$
$3s\alpha_1$	3	0	0	$\frac{1}{2}$	$+\frac{1}{2}$
$3s\alpha_2$	3	0	0	$\frac{1}{2}$	$-\frac{1}{2}$

Table 1.1: *All states in our single-particle basis, where α_1 means spin up and α_2 means spin down.*

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.

1.a. Setting up the basis

We define our single-particle Hilbert space , which we will call $\mathscr{H}_{3\mathrm{n}0}$ to consist of the single-particle states tabulated in Table 1.1. We will define the wave function for a particle with spin-position coordinates x, $\phi_{n,m_s}(x)$ to be a product state of a radial part $R_n(\mathbf{r})$ and a spin part $\alpha(m_s)$,

$$\phi_{n,\mathrm{m_s}}(x) = R_n(\mathbf{r})\alpha(\mathrm{m_s}),$$

where the radial part of our single-particle states will only depend on the principal quantum number n, and we have to integrate over position and spin coordinates to calculate our expectation values. The radial part of the eigenbasis is orthonormal, and this will true also for the spin part of the constructed basis, as in

$$\left\langle \alpha(m_s) \middle| \alpha\left(m_s'\right) \right\rangle = \delta_{m_s m_s'}.$$

We define the creation operator, $\hat{a}^\dagger_{n,m_s}$, to be the creation operator for an electron to be placed in the single-particle state with quantum numbers n and m_s, that is

$$\hat{a}^\dagger_{n,m_s}\,|0\rangle \coloneqq |\psi_{n,m_s}\rangle\,, \tag{1.2}$$

where $|0\rangle$ is the vacuum state. The corresponding annihiliation operator, $\hat{a}_{n,m_s}$, to be $\hat{a}_{n,m_s} \coloneqq \left(\hat{a}^\dagger_{n,m_s}\right)^\dagger$, which will annihilate a particle in the single-particle state with quantum

Quantum numbers	$m_s = +\frac{1}{2}$	$m_s = -\frac{1}{2}$
$n = 1$	$R_1(\mathbf{r})\alpha(+\frac{1}{2})$	$R_1(\mathbf{r})\alpha(-\frac{1}{2})$
$n = 2$	$R_2(\mathbf{r})\alpha(+\frac{1}{2})$	$R_2(\mathbf{r})\alpha(-\frac{1}{2})$
$n = 3$	$R_3(\mathbf{r})\alpha(+\frac{1}{2})$	$R_3(\mathbf{r})\alpha(-\frac{1}{2})$

Table 1.2: *Single-particle wave functions as product states.*

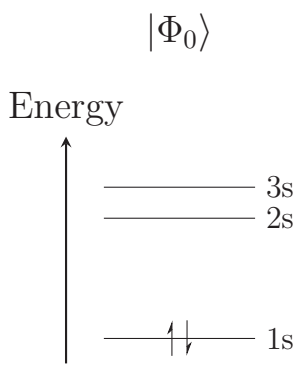

Figure 1.1: *Schematic drawing of our anzats for the ground state of Helium in $\mathscr{H}_{3n0}$, if there were no interactions between the electrons.*

numbers n and m_s.
Our ansatz for the ground state will simply be the state with lowest energy in our chosen basis. We can write our ansatz of the ground state for the helium atom as

$$|\Phi_0\rangle = \left|\psi_{1,+1/2}\psi_{1,-1/2}\right\rangle = \hat{a}^\dagger_{1,+1/2}\,\hat{a}^\dagger_{1,-1/2}\,|0\rangle\,, \tag{1.3}$$

and a schematic drawing of it is given in Figure 1.1. Due to the Pauli antisymmetric principle we need the wave function to be antisymmetric under exchange of particles, and we apply the Slater determinant convention to achieve this. Therefore,

$$\begin{aligned}|\Phi_0\rangle = \hat{a}^\dagger_{1,+1/2}\,\hat{a}^\dagger_{1,-1/2}\,|0\rangle &= \sqrt{\frac{1}{2!}}\begin{vmatrix}\phi_{1,+\frac{1}{2}}(x_1) & \phi_{1,-\frac{1}{2}}(x_1)\\ \phi_{1,+\frac{1}{2}}(x_2) & \phi_{1,-\frac{1}{2}}(x_2)\end{vmatrix}\\ &= \sqrt{\frac{1}{2!}}\Big[\phi_{1,+\frac{1}{2}}(x_1)\phi_{1,-\frac{1}{2}}(x_2) - \phi_{1,-\frac{1}{2}}(x_2)\phi_{1,+\frac{1}{2}}(x_1)\Big],\end{aligned}$$

will be the function for the ground state of the helium atom, and the creation and annihilation operators will create states that are antisymmetric under exchange of particles.
In Table 1.2 the single-particle states are listed as functions.

Next we will look at the different excited states. Remembering that the total spin, $M_s = m_{s'} + m_s$, of the atom cannot be changed unless it is interacting with a photon, we get these

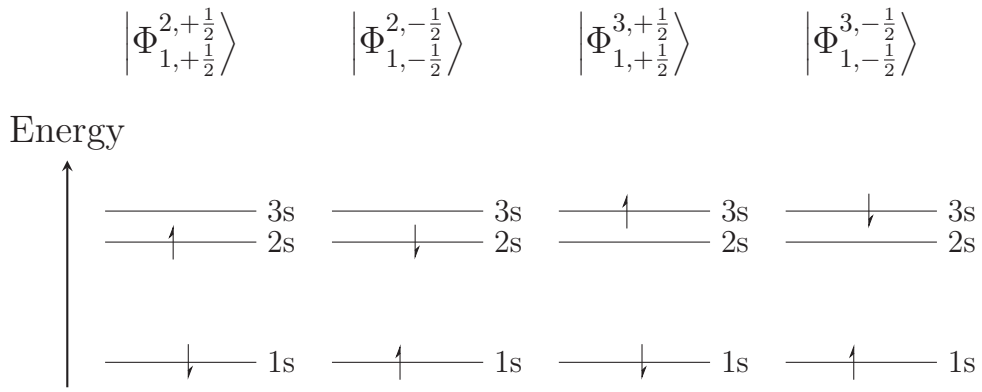

Figure 1.2: *Schematic drawing of all possible singly-excited states, $|\Phi_i^a\rangle$ for the Helium atom in the hydrogen-like single-particle basis.*

singly excited states

$$\begin{aligned}
\left|\Phi^{2,+\frac{1}{2}}_{1,+\frac{1}{2}}\right\rangle &= \hat{a}^\dagger_{2,+\frac{1}{2}}\,\hat{a}_{1,+\frac{1}{2}}\,|\Phi_0\rangle\,,\\
\left|\Phi^{2,-\frac{1}{2}}_{1,-\frac{1}{2}}\right\rangle &= \hat{a}^\dagger_{2,-\frac{1}{2}}\,\hat{a}_{1,-\frac{1}{2}}\,|\Phi_0\rangle\,,\\
\left|\Phi^{3,+\frac{1}{2}}_{1,+\frac{1}{2}}\right\rangle &= \hat{a}^\dagger_{3,+\frac{1}{2}}\,\hat{a}_{1,+\frac{1}{2}}\,|\Phi_0\rangle\,,\\
\left|\Phi^{3,-\frac{1}{2}}_{1,-\frac{1}{2}}\right\rangle &= \hat{a}^\dagger_{3,-\frac{1}{2}}\,\hat{a}_{1,-\frac{1}{2}}\,|\Phi_0\rangle\,,
\end{aligned}$$

which are schematically drawn in Figure 1.2. For the doubly-excited states, $\left|\Phi^{ab}_{ij}\right\rangle$ we have four possibilities, given as

$$\begin{aligned}
\left|\Phi^{2,+\frac{1}{2}2,-\frac{1}{2}}_{1,+\frac{1}{2}1,-\frac{1}{2}}\right\rangle &= \hat{a}^\dagger_{2,+\frac{1}{2}}\,\hat{a}^\dagger_{2,-\frac{1}{2}}\,\hat{a}_{1,+\frac{1}{2}}\,\hat{a}_{1,-\frac{1}{2}}\,|\Phi_0\rangle\,,\\
\left|\Phi^{2,+\frac{1}{2}3,-\frac{1}{2}}_{1,+\frac{1}{2}1,-\frac{1}{2}}\right\rangle &= \hat{a}^\dagger_{2,+\frac{1}{2}}\,\hat{a}^\dagger_{3,-\frac{1}{2}}\,\hat{a}_{1,+\frac{1}{2}}\,\hat{a}_{1,-\frac{1}{2}}\,|\Phi_0\rangle\,,\\
\left|\Phi^{3,+\frac{1}{2}2,-\frac{1}{2}}_{1,+\frac{1}{2}1,-\frac{1}{2}}\right\rangle &= \hat{a}^\dagger_{3,+\frac{1}{2}}\,\hat{a}^\dagger_{2,-\frac{1}{2}}\,\hat{a}_{1,+\frac{1}{2}}\,\hat{a}_{1,-\frac{1}{2}}\,|\Phi_0\rangle\,,\\
\left|\Phi^{3,+\frac{1}{2}3,-\frac{1}{2}}_{1,+\frac{1}{2}1,-\frac{1}{2}}\right\rangle &= \hat{a}^\dagger_{3,+\frac{1}{2}}\,\hat{a}^\dagger_{3,-\frac{1}{2}}\,\hat{a}_{1,+\frac{1}{2}}\,\hat{a}_{1,-\frac{1}{2}}\,|\Phi_0\rangle\,,
\end{aligned}$$

which are schematically drawn in Figure 1.3.

Particles and Holes

First we define the Fermi level, which is a single-particle energy level above or equal to the highest occupied single-particle energy level for the ground state ansatz in our single-particle basis. This means that the Fermi level for the helium atom will be above or equal to the 1s state,

$$\epsilon_i \leq \epsilon_F,$$

for all states $|i\rangle$ which are below the Fermi level. We can then define a hole state as the annihilation of a particle (creating a hole in the ansatz for the ground state) below the Fermi

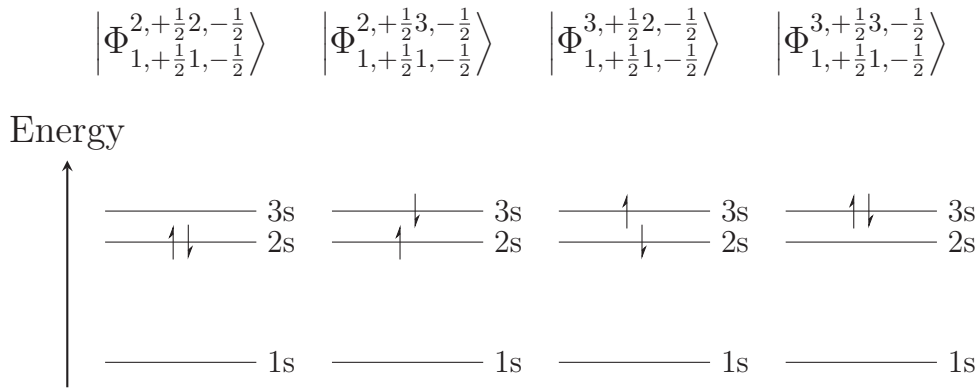

Figure 1.3: *Schematic drawing of all possible doubly-excited states,* $\left|\Phi^{ab}_{ij}\right\rangle$ *for the Helium atom in the hydrogen-like single-particle basis.*

level,

$$|\Phi_i\rangle = \hat{a}_i |\Phi_0\rangle ,$$

and we will denote the hole states with the letters $i, j, k, \ldots$, and they have the property that $\hat{h}_0 |i\rangle = \epsilon_i |i\rangle$ with $\epsilon_i, \epsilon_j, \cdots \leq \epsilon_F$.
Next we can define a particle state as the creation of a particle above the Fermi level,

$$|\Phi^a\rangle = \hat{a}^\dagger_a |\Phi_0\rangle ,$$

and we denote the particle states with the letters $a, b, c, \ldots$ and they have the property that $\hat{h}_0 |a\rangle = \epsilon_a |a\rangle$ with $\epsilon_a, \epsilon_b, \cdots \geq \epsilon_F$.

1.b. Second quantized Hamiltonian

We defined the Hamiltonian, $\hat{H}$ of the system in Section 1 to be a sum of a one-body operator, $\hat{H}_0$, and a two-body operator, $\hat{H}_I$,

$$\hat{H} = \hat{H}_0 + \hat{H}_I = \sum_{p=1}^{N} \hat{h}_0(x_p) + \sum_{p<q}^{N} \hat{v}(x_p, x_q),$$

where $\sum_{i<j}^{N}$ means a sum over all unique pairs of particles. We will rewrite this double sum as

$$\sum_{p<q}^{N} \hat{v}(x_p, x_q) = \frac{1}{2} \sum_{p}^{N} \sum_{q}^{N} \hat{v}(x_p, x_q) \coloneqq \frac{1}{2} \sum_{pq}^{N} \hat{v}(x_p, x_q),$$

which will be correct because $\hat{v}(x_r, x_r) = 0$, which means no self-interaction for any particles. For any one-body operator, $\hat{F}$, we can write its expectation value as

$$\hat{F} = \sum_{pq}^{N} \langle p| \hat{f} |q\rangle \, \hat{a}^\dagger_p \hat{a}_q.$$

We write the general two-body operator, $\hat{G}$, as

$$\hat{G} = \sum_{pqrs}^{N} \langle pq| \hat{g} |rs\rangle \, \hat{a}^\dagger_p \hat{a}^\dagger_q \hat{a}_s \hat{a}_r.$$

In our particle-hole formalism, we have that the creation and annihilation operators act differently, depending on whether it is acting on a particle or a hole. To be able to apply

Wick's generalized theorem, we want to write the one- and two-body operators in normal order. We therefore normal order the operators, starting with the one-body operator, which becomes

$$\begin{aligned}\hat{a}_p^\dagger \hat{a}_q &= \left\{\hat{a}_p^\dagger \hat{a}_q\right\} + \hat{a}_p^\dagger \hat{a}_q \\ &= \left\{\hat{a}_p^\dagger \hat{a}_q\right\} + \delta_{pq\leq F},\end{aligned}$$

which leads to one-body operator, $\hat{F}$, taking the form

$$\hat{F} = \sum_{pq}^{N} \langle p|\, \hat{f}\, |q\rangle \left\{\hat{a}_p^\dagger \hat{a}_q\right\} + \sum_{i<F}^{N} \langle i|\, \hat{f}\, |i\rangle .$$

We normal order the creation and annihilation operators in the general two-body operator, $\hat{G}$, and get

$$\begin{aligned}\hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r =& \left\{\hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r\right\} - \hat{a}_p^\dagger \hat{a}_s \left\{\hat{a}_q^\dagger \hat{a}_r\right\} + \hat{a}_p^\dagger \hat{a}_r \left\{\hat{a}_q^\dagger \hat{a}_s\right\} \\ &+ \hat{a}_q^\dagger \hat{a}_s \left\{\hat{a}_p^\dagger \hat{a}_r\right\} - \hat{a}_q^\dagger \hat{a}_r \left\{\hat{a}_p^\dagger \hat{a}_s\right\} \\ &+ \hat{a}_p^\dagger \hat{a}_r \hat{a}_q^\dagger \hat{a}_s - \hat{a}_p^\dagger \hat{a}_s \hat{a}_q^\dagger \hat{a}_r \\ =& \left\{\hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r\right\} - \delta_{ps\leq F}\left\{\hat{a}_q^\dagger \hat{a}_r\right\} + \delta_{pr\leq F}\left\{\hat{a}_q^\dagger \hat{a}_s\right\} + \delta_{qs\leq F}\left\{\hat{a}_p^\dagger \hat{a}_r\right\} \\ &- \delta_{qr\leq F}\left\{\hat{a}_p^\dagger \hat{a}_s\right\} + \delta_{pr\leq F}\delta_{qs\leq F} - \delta_{ps\leq F}\delta_{qr\leq F},\end{aligned}$$

which leads to the general one-body operator, $\hat{G}$, taking the form

$$\begin{aligned}\hat{G} =& \frac{1}{2}\sum_{pqrs}^{N} \langle pq|\, \hat{g}\, |rs\rangle \left\{\hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r\right\} \\ &+ \frac{1}{2}\sum_{i,pq>F}^{N} \left[\langle pi|\, \hat{g}\, |ri\rangle \left\{\hat{a}_p^\dagger \hat{a}_r\right\} - \langle pi|\, \hat{g}\, |is\rangle \left\{\hat{a}_p^\dagger \hat{a}_s\right\} - \langle iq|\, \hat{g}\, |ri\rangle \left\{\hat{a}_q^\dagger \hat{a}_s\right\} + \langle iq|\, \hat{g}\, |is\rangle \left\{\hat{a}_q^\dagger \hat{a}_s\right\}\right] \\ &+ \frac{1}{2}\sum_{ij\leq F}^{N} \left[\langle ij|\, \hat{g}\, |ij\rangle - \langle ij|\, \hat{g}\, |ji\rangle\right] \\ =& \frac{1}{4}\sum_{pqrs}^{N} \langle pq|\, \hat{g}\, |rs\rangle_{AS} \left\{\hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r\right\} + \sum_{i,pq>F}^{N} \langle pi|\, \hat{g}\, |qi\rangle_{AS} \left\{\hat{a}_p^\dagger \hat{a}_q\right\} + \frac{1}{2}\sum_{ij\leq F}^{N} \langle ij|\, \hat{g}\, |ij\rangle_{AS} .\end{aligned}$$

Our normal-ordered Hamiltonian then becomes

$$\begin{aligned}\hat{H} =& \hat{H}_0 + \hat{H}_I \\ =& \sum_{pq}^{N} \langle p|\, \hat{h}_0\, |q\rangle \left\{\hat{a}_p^\dagger \hat{a}_q\right\} + \sum_{i\leq F}^{N} \langle i|\, \hat{h}_0\, |i\rangle \\ &+ \frac{1}{4}\sum_{pqrs}^{N} \langle pq|\, \frac{1}{r}\, |rs\rangle_{AS} \left\{\hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r\right\} + \sum_{i\leq F,pq}^{N} \langle pi|\, \frac{1}{r}\, |qi\rangle_{AS} \left\{\hat{a}_p^\dagger \hat{a}_q\right\} + \frac{1}{2}\sum_{ij\leq F}^{N} \langle ij|\, \frac{1}{r}\, |ij\rangle_{AS} ,\end{aligned}$$

and we will use this expression to calculate the expected value of the Hamiltonian on the ground state, $|\Phi_0\rangle$, (which can also be referred to as the energy functional, because it is the expected value of the energy with respect to the wave function)

$$\mathrm{E}[\Phi] = \langle \Phi|\, \hat{H}\, |\Phi\rangle = \int \Phi^* \hat{H} \Phi \mathrm{d}\tau,$$

where $\mathrm{d}\tau$, means all the degrees of freedom we have to integrate over.

Calculating the reference energy of helium

The reference energy, which we'll denote E_0^{Ref}, is given by the expected energy of our ansatz for the ground state of helium, $|\Phi_0\rangle = \hat{a}^\dagger_{1,+\frac{1}{2}} \hat{a}^\dagger_{1,-\frac{1}{2}} |0\rangle$. The expected energy of our ground state is given by

$$\begin{aligned}\langle\Phi_0|\hat{H}|\Phi_0\rangle = &\langle\Phi_0| \left[\sum_{pq}^{N} \langle p|\hat{h}_0|q\rangle \left\{\hat{a}^\dagger_p \hat{a}_q\right\} + \sum_{i\leq F}^{N} \langle i|\hat{h}_0|i\rangle\right] |\Phi_0\rangle \\ &+ \langle\Phi_0| \left[\frac{1}{4}\sum_{pqrs}^{N} \langle pq|\frac{1}{r}|rs\rangle_{AS} \left\{\hat{a}^\dagger_p \hat{a}^\dagger_q \hat{a}_s \hat{a}_r\right\}\right] |\Phi_0\rangle \\ &+ \langle\Phi_0| \left[\sum_{i\leq F,pq}^{N} \langle pi|\frac{1}{r}|qi\rangle_{AS} \left\{\hat{a}^\dagger_p \hat{a}_q\right\} + \frac{1}{2}\sum_{ij\leq F}^{N} \langle ij|\frac{1}{r}|ij\rangle_{AS}\right] |\Phi_0\rangle,\end{aligned}$$

and we calculate these expressions using the generalized Wick's theorem, using our new vacuum state $|\Phi_0\rangle$. We set up the expressions

$$\begin{aligned}\langle\Phi_0| \left\{\hat{a}^\dagger_p \hat{a}_q\right\} |\Phi_0\rangle = 0, \\ \langle\Phi_0| \left\{\hat{a}^\dagger_p \hat{a}^\dagger_q \hat{a}_s \hat{a}_r\right\} |\Phi_0\rangle = 0\end{aligned}$$

and what remains of the expected value of the energy will be

$$\begin{aligned}\langle\Phi_0|\hat{H}|\Phi_0\rangle &= \sum_{i\leq F}^{N} \langle i|\hat{h}_0|i\rangle \langle\Phi_0|\Phi_0\rangle + \frac{1}{2}\sum_{ij\leq F}^{N} \langle ij|\frac{1}{r}|ij\rangle_{AS} \langle\Phi_0|\Phi_0\rangle \\ &= \left\langle 1,+\frac{1}{2}\middle|\hat{h}_0\middle|1,+\frac{1}{2}\right\rangle + \left\langle 1,-\frac{1}{2}\middle|\hat{h}_0\middle|1,-\frac{1}{2}\right\rangle \\ &\quad + \frac{1}{2}\left\langle 1,+\frac{1}{2}1,-\frac{1}{2}\middle|\frac{1}{r}\middle|1,+\frac{1}{2}1,-\frac{1}{2}\right\rangle - \frac{1}{2}\left\langle 1,+\frac{1}{2}1,-\frac{1}{2}\middle|\frac{1}{r}\middle|1,-\frac{1}{2}1,+\frac{1}{2}\right\rangle \\ &\quad + \frac{1}{2}\left\langle 1,-\frac{1}{2}1,+\frac{1}{2}\middle|\frac{1}{r}\middle|1,-\frac{1}{2}1,+\frac{1}{2}\right\rangle - \frac{1}{2}\left\langle 1,-\frac{1}{2}1,+\frac{1}{2}\middle|\frac{1}{r}\middle|1,+\frac{1}{2}1,-\frac{1}{2}\right\rangle \\ &= \left\langle 1,+\frac{1}{2}\middle|\hat{h}_0\middle|1,+\frac{1}{2}\right\rangle + \left\langle 1,-\frac{1}{2}\middle|\hat{h}_0\middle|1,-\frac{1}{2}\right\rangle \\ &\quad + \frac{1}{2}\left\langle 1,+\frac{1}{2}1,-\frac{1}{2}\middle|\frac{1}{r}\middle|1,+\frac{1}{2}1,-\frac{1}{2}\right\rangle - 0 \\ &\quad + \frac{1}{2}\left\langle 1,-\frac{1}{2}1,+\frac{1}{2}\middle|\frac{1}{r}\middle|1,-\frac{1}{2}1,+\frac{1}{2}\right\rangle - 0 \\ (*) &= 2\langle 1|\hat{h}_0|1\rangle + \langle 11|\frac{1}{r}|11\rangle\end{aligned}$$

where we have identified the indices $p, q, r, s, \ldots, i, j, k, \ldots, a, b, c, \ldots$ as unique **sets** of quantum numbers. In $(*)$ we rewrite the terms so that they only depend on the principal quantum number, n. The exchange terms in the two-body potential become zero as we integrate over spin, because our two-body operator operates only on the spatial dimensions of the wave function. We know that our basis is the eigenbasis of the one-body part of our Hamiltonian, and the we have the two-body part tabulated, and we can calculate the expression for the expected value of the ground state. Given $\langle 11|\hat{v}|11\rangle = \frac{5Z}{8}$ and the exchange integrals become zero as we are integrating over spin aswell, the energy becomes

$$\mathrm{E}[\Phi_0] = \langle\Phi_0|\hat{H}|\Phi_0\rangle = -\frac{Z^2}{2} - \frac{Z^2}{2} + 2\frac{1}{2}\frac{5Z}{8} = -Z^2 + \frac{5Z}{8} = -Z(Z - \frac{5}{8}) = -\frac{11}{4}(\text{a.u.}).$$

1.c. Limiting ourselves to one-particle-one-hole excitations

First we find the general expression for the integral $\langle\Phi_0|\,\hat{H}\,|\Phi_i^a\rangle$, where i denotes the hole-state and a denotes the particle state above the Fermi level. We write the integral as

$$\langle\Phi_0|\,\hat{H}\,|\Phi_i^a\rangle = \langle\Phi_0|\,\hat{H}\,\hat{a}_a^\dagger\,\hat{a}_i\,|\Phi_0\rangle\,,$$

and again set our vacuum to be the ground state and use Wick's generalized theorem to find the expectation values,

$$\begin{aligned}\langle\Phi_0|\left\{\hat{a}_p^\dagger\,\hat{a}_q^\dagger\,\hat{a}_s\,\hat{a}_r\right\}\hat{a}_a^\dagger\,\hat{a}_i\,|\Phi_0\rangle &= 0,\\ \langle\Phi_0|\left\{\hat{a}_p^\dagger\,\hat{a}_q\right\}\hat{a}_a^\dagger\,\hat{a}_i\,|\Phi_0\rangle &= \delta_{pi}\delta_{qa},\\ \langle\Phi_0|\,\hat{a}_a^\dagger\,\hat{a}_i\,|\Phi_0\rangle &= 0.\end{aligned}$$

These yield the following expectation value for the general integral

$$\langle\Phi_0|\,\hat{H}\,|\Phi_i^a\rangle = \langle i|\,\hat{h}_0\,|a\rangle + \sum_{k\leq F}^{N}\langle ik|\,\frac{1}{r}\,|ak\rangle_{AS}\,, \tag{1.4}$$

where $\langle ii|\,\frac{1}{r}\,|ai\rangle_{AS} = 0$, giving

$$\begin{aligned}\langle\Phi_0|\,\hat{H}\left|\Phi_{1,+\frac{1}{2}}^{2,+\frac{1}{2}}\right\rangle &= \left\langle 1,+\frac{1}{2}\right|\hat{h}_0\left|2,+\frac{1}{2}\right\rangle + \left\langle 1,+\frac{1}{2}1,-\frac{1}{2}\right|\frac{1}{r}\left|2,+\frac{1}{2}1,-\frac{1}{2}\right\rangle_{AS},\\ \langle\Phi_0|\,\hat{H}\left|\Phi_{1,-\frac{1}{2}}^{2,-\frac{1}{2}}\right\rangle &= \left\langle 1,-\frac{1}{2}\right|\hat{h}_0\left|2,-\frac{1}{2}\right\rangle + \left\langle 1,-\frac{1}{2}1,+\frac{1}{2}\right|\frac{1}{r}\left|2,-\frac{1}{2}1,+\frac{1}{2}\right\rangle_{AS},\\ \langle\Phi_0|\,\hat{H}\left|\Phi_{1,+\frac{1}{2}}^{3,+\frac{1}{2}}\right\rangle &= \left\langle 1,+\frac{1}{2}\right|\hat{h}_0\left|3,+\frac{1}{2}\right\rangle + \left\langle 1,+\frac{1}{2}1,-\frac{1}{2}\right|\frac{1}{r}\left|3,+\frac{1}{2}1,-\frac{1}{2}\right\rangle_{AS},\\ \langle\Phi_0|\,\hat{H}\left|\Phi_{1,-\frac{1}{2}}^{3,-\frac{1}{2}}\right\rangle &= \left\langle 1,-\frac{1}{2}\right|\hat{h}_0\left|3,-\frac{1}{2}\right\rangle + \left\langle 1,-\frac{1}{2}1,+\frac{1}{2}\right|\frac{1}{r}\left|3,-\frac{1}{2}1,+\frac{1}{2}\right\rangle_{AS}.\end{aligned}$$

A diagrammatic representation of $\langle\Phi_0|\,\hat{H}\,|\Phi_i^a\rangle$ is given in Figure 1.4.

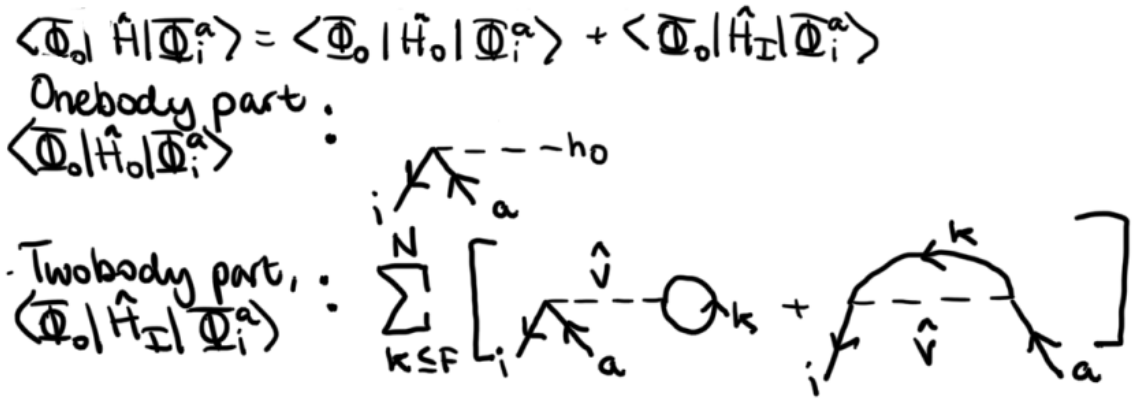

Figure 1.4: *Diagrammatic representation of* $\langle\Phi_0|\,\hat{H}\,|\Phi_i^a\rangle$.

Now, we want to find the general expression for the expected values between all 1p1h-states,

$$\langle\Phi_i^a|\,\hat{H}\left|\Phi_j^b\right\rangle = \langle\Phi_0|\,\hat{a}_i^\dagger\,\hat{a}_a\,\hat{H}\,\hat{a}_b^\dagger\,\hat{a}_j\,|\Phi_0\rangle\,.$$

Again we use Wick's generalized theorem, yielding

$$\langle\Phi_0|\,\hat{a}_i^\dagger\,\hat{a}_a\Big\{\hat{a}_p^\dagger\,\hat{a}_q^\dagger\,\hat{a}_s\,\hat{a}_r\Big\}\,\hat{a}_b^\dagger\,\hat{a}_j\,|\Phi_0\rangle = \delta_{pa}\delta_{qj}\delta_{sb}\delta_{ri} - \delta_{pa}\delta_{qj}\delta_{si}\delta_{rb} + \delta_{pj}\delta_{qa}\delta_{si}\delta_{qr} - \delta_{pj}\delta_{qa}\delta_{sr}\delta_{qi},$$
$$\langle\Phi_0|\,\hat{a}_i^\dagger\,\hat{a}_a\Big\{\hat{a}_p^\dagger\,\hat{a}_q\Big\}\,\hat{a}_b^\dagger\,\hat{a}_j\,|\Phi_0\rangle = \delta_{ij}\delta_{pa}\delta_{qb} - \delta_{ab}\delta_{pj}\delta_{qi},$$
$$\langle\Phi_0|\,\hat{a}_i^\dagger\,\hat{a}_a\,\hat{a}_b^\dagger\,\hat{a}_j\,|\Phi_0\rangle = \delta_{ab}\delta_{ij}.$$

These leads to the following general expression for the Hamiltonian between two 1p1h-states,

$$\begin{aligned}
\langle\Phi_i^a|\,\hat{H}\,\Big|\Phi_j^b\Big\rangle &= \langle a|\,\hat{h}_0\,|b\rangle\,\delta_{ij} - \langle j|\,\hat{h}_0\,|i\rangle\,\delta_{ab} + \sum_{k\leq F}^{N}\langle k|\,\hat{h}_0\,|k\rangle\,\delta_{ab}\delta_{ij} \\
&\quad + \frac{1}{4}\Big[\langle aj|\,\frac{1}{r}\,|ib\rangle_{AS} - \langle aj|\,\frac{1}{r}\,|bi\rangle_{AS} + \langle ja|\,\frac{1}{r}\,|bi\rangle_{AS} - \langle ja|\,\frac{1}{r}\,|ib\rangle_{AS}\Big] \\
&\quad + \sum_{k\neq i\leq F}^{N}\Big[\langle ak|\,\frac{1}{r}\,|bk\rangle_{AS}\,\delta_{ij} - \langle jk|\,\frac{1}{r}\,|ik\rangle_{AS}\,\delta_{ab}\Big] \\
&\quad + \frac{1}{2}\sum_{kl\leq F}^{N}\langle kl|\,\frac{1}{r}\,|kl\rangle_{AS}\,\delta_{ab}\delta_{ij} \\
&= \langle a|\,\hat{h}_0\,|b\rangle\,\delta_{ij} - \langle j|\,\hat{h}_0\,|i\rangle\,\delta_{ab} + \sum_{k\leq F}^{N}\langle k|\,\hat{h}_0\,|k\rangle\,\delta_{ab}\delta_{ij} \\
&\quad + \langle aj|\,\frac{1}{r}\,|ib\rangle_{AS} + \sum_{k\neq i,j\leq F}^{N}\Big[\langle ak|\,\frac{1}{r}\,|bk\rangle_{AS}\,\delta_{ij} - \langle jk|\,\frac{1}{r}\,|ik\rangle_{AS}\,\delta_{ab}\Big] \\
&\quad + \frac{1}{2}\sum_{kl\leq F}^{N}\langle kl|\,\frac{1}{r}\,|kl\rangle_{AS}\,\delta_{ab}\delta_{ij}.
\end{aligned}$$

A diagrammatic representation of $\langle\Phi_i^a|\,\hat{H}\,\Big|\Phi_j^b\Big\rangle$ is given in Figure 1.5.

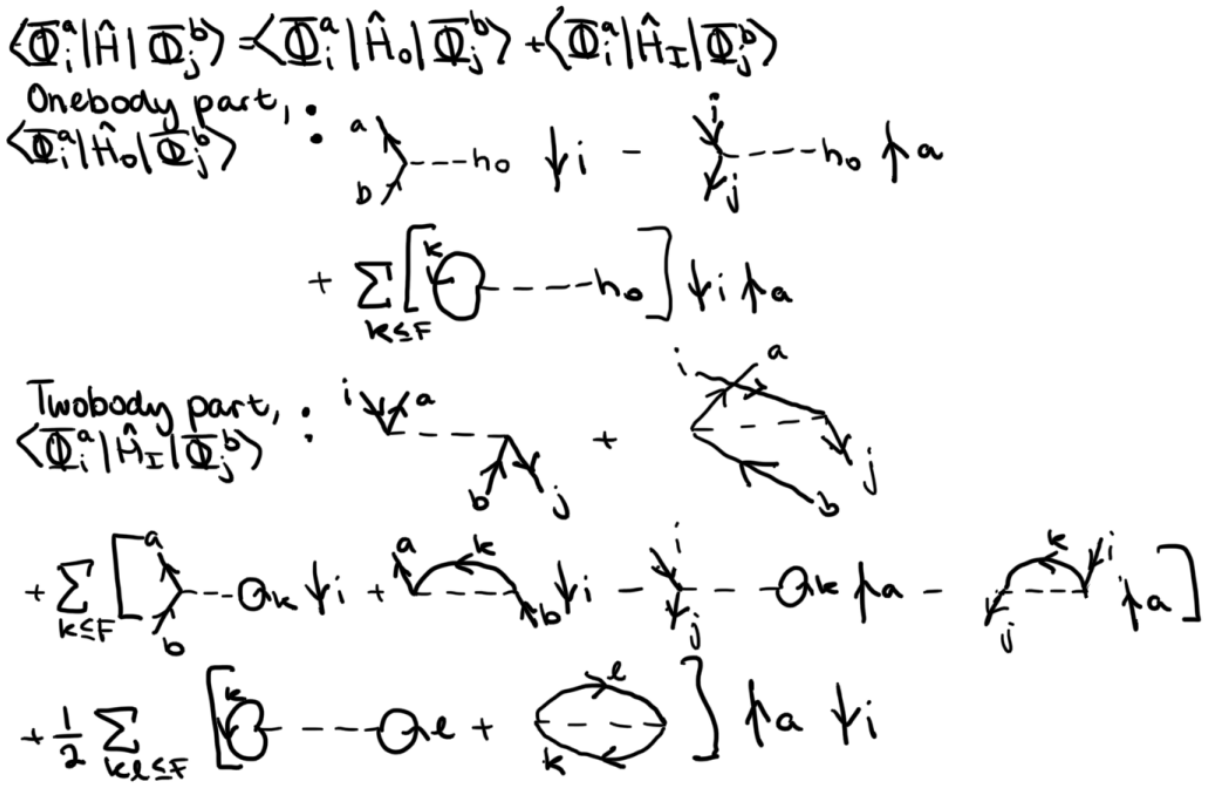

Figure 1.5: *Diagrammatic representation of* $\langle \Phi_i^a | \hat{H} \left| \Phi_j^b \right\rangle$.

We can now write down the Hamiltonian matrix as

$$\begin{pmatrix} \langle \Phi_0 | \hat{H} | \Phi_0 \rangle & \langle \Phi_0 | \hat{H} \left| \Phi_{1,+\frac{1}{2}}^{2,+\frac{1}{2}} \right\rangle & \langle \Phi_0 | \hat{H} \left| \Phi_{1,-\frac{1}{2}}^{2,-\frac{1}{2}} \right\rangle & \langle \Phi_0 | \hat{H} \left| \Phi_{1,+\frac{1}{2}}^{3,+\frac{1}{2}} \right\rangle & \langle \Phi_0 | \hat{H} \left| \Phi_{1,-\frac{1}{2}}^{3,-\frac{1}{2}} \right\rangle \\ \left\langle \Phi_{1,+\frac{1}{2}}^{2,+\frac{1}{2}} \right| \hat{H} | \Phi_0 \rangle & \left\langle \Phi_{1,+\frac{1}{2}}^{2,+\frac{1}{2}} \right| \hat{H} \left| \Phi_{1,+\frac{1}{2}}^{2,+\frac{1}{2}} \right\rangle & \left\langle \Phi_{1,+\frac{1}{2}}^{2,+\frac{1}{2}} \right| \hat{H} \left| \Phi_{1,-\frac{1}{2}}^{2,-\frac{1}{2}} \right\rangle & \left\langle \Phi_{1,+\frac{1}{2}}^{2,+\frac{1}{2}} \right| \hat{H} \left| \Phi_{1,+\frac{1}{2}}^{3,+\frac{1}{2}} \right\rangle & \left\langle \Phi_{1,+\frac{1}{2}}^{2,+\frac{1}{2}} \right| \hat{H} \left| \Phi_{1,-\frac{1}{2}}^{3,-\frac{1}{2}} \right\rangle \\ \left\langle \Phi_{1,-\frac{1}{2}}^{2,-\frac{1}{2}} \right| \hat{H} | \Phi_0 \rangle & \left\langle \Phi_{1,-\frac{1}{2}}^{2,-\frac{1}{2}} \right| \hat{H} \left| \Phi_{1,+\frac{1}{2}}^{2,+\frac{1}{2}} \right\rangle & \left\langle \Phi_{1,-\frac{1}{2}}^{2,-\frac{1}{2}} \right| \hat{H} \left| \Phi_{1,-\frac{1}{2}}^{2,-\frac{1}{2}} \right\rangle & \left\langle \Phi_{1,-\frac{1}{2}}^{2,-\frac{1}{2}} \right| \hat{H} \left| \Phi_{1,+\frac{1}{2}}^{3,+\frac{1}{2}} \right\rangle & \left\langle \Phi_{1,-\frac{1}{2}}^{2,-\frac{1}{2}} \right| \hat{H} \left| \Phi_{1,-\frac{1}{2}}^{3,-\frac{1}{2}} \right\rangle \\ \left\langle \Phi_{1,+\frac{1}{2}}^{3,+\frac{1}{2}} \right| \hat{H} | \Phi_0 \rangle & \left\langle \Phi_{1,+\frac{1}{2}}^{3,+\frac{1}{2}} \right| \hat{H} \left| \Phi_{1,+\frac{1}{2}}^{2,+\frac{1}{2}} \right\rangle & \left\langle \Phi_{1,+\frac{1}{2}}^{3,+\frac{1}{2}} \right| \hat{H} \left| \Phi_{1,-\frac{1}{2}}^{2,-\frac{1}{2}} \right\rangle & \left\langle \Phi_{1,+\frac{1}{2}}^{3,+\frac{1}{2}} \right| \hat{H} \left| \Phi_{1,+\frac{1}{2}}^{3,+\frac{1}{2}} \right\rangle & \left\langle \Phi_{1,+\frac{1}{2}}^{3,+\frac{1}{2}} \right| \hat{H} \left| \Phi_{1,-\frac{1}{2}}^{3,-\frac{1}{2}} \right\rangle \\ \left\langle \Phi_{1,-\frac{1}{2}}^{3,-\frac{1}{2}} \right| \hat{H} | \Phi_0 \rangle & \left\langle \Phi_{1,-\frac{1}{2}}^{3,-\frac{1}{2}} \right| \hat{H} \left| \Phi_{1,+\frac{1}{2}}^{2,+\frac{1}{2}} \right\rangle & \left\langle \Phi_{1,-\frac{1}{2}}^{3,-\frac{1}{2}} \right| \hat{H} \left| \Phi_{1,-\frac{1}{2}}^{2,-\frac{1}{2}} \right\rangle & \left\langle \Phi_{1,-\frac{1}{2}}^{3,-\frac{1}{2}} \right| \hat{H} \left| \Phi_{1,+\frac{1}{2}}^{3,+\frac{1}{2}} \right\rangle & \left\langle \Phi_{1,-\frac{1}{2}}^{3,-\frac{1}{2}} \right| \hat{H} \left| \Phi_{1,-\frac{1}{2}}^{3,-\frac{1}{2}} \right\rangle \end{pmatrix} \tag{1.5}$$

Inserting the values for each matrix element, and diagonalizing it, yields a ground state energy of -2.8386 atomic units for the helium atom, which is not too far from the exact value, -2.9037 atomic units of energy. For further reference to this FCI-based method, I rename it **Configuration Interaction 1p1h** (CI1p1h).

1.d. Moving to the beryllium atom

We will represent the beryllium atom using the same basis as for the Helium atom. The nucleus of the Beryllium atom has the electric charge, $Z = 4e$. This will alter the eigenvalues of our single-particle states, and also the interactions between the electrons (the magnitude of the "static" electric field is increased). The beryllium atom contains four electrons. Our ansatz for the ground state, $|\Phi_0\rangle$, is given by filling our single-particle basis set with electrons

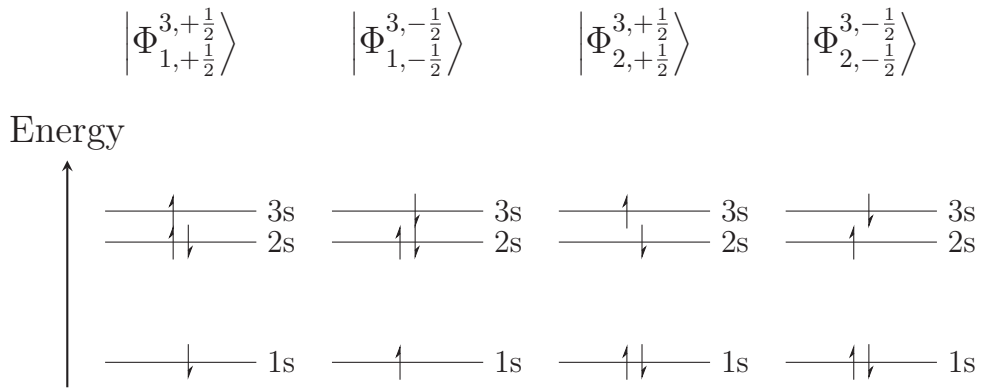

Figure 1.7: *Schematic drawing of all possible singly-excited states, $|\Phi_i^a\rangle$ for the beryllium atom in the hydrogen-like single-particle basis.*

one-by-one, always filling the lowest unoccupied single-particle basis function. We therefore get

$$|\Phi_0\rangle = \hat{a}^\dagger_{1,+\frac{1}{2}}\,\hat{a}^\dagger_{1,-\frac{1}{2}}\,\hat{a}^\dagger_{2,+\frac{1}{2}}\,\hat{a}^\dagger_{2,-\frac{1}{2}}\,|0\rangle\,,$$

as our ground state in second quantization, where again $|0\rangle$ denotes the true vacuum state. Figure 1.6 displays a schematic drawing of the ground state for beryllium.

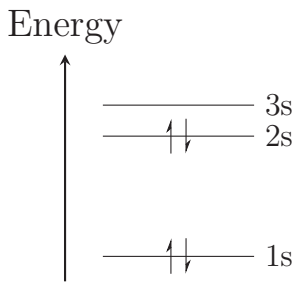

Figure 1.6: *Schematic drawing of our anzats for the ground state of beryllium in $\mathscr{H}_{3n0}$.*

The singly-excited states from our ansatz for the ground state, $|\Phi_0\rangle$, becomes

$$\begin{aligned}
\left|\Phi^{3,+\frac{1}{2}}_{1,+\frac{1}{2}}\right\rangle &= \hat{a}^\dagger_{3,+\frac{1}{2}}\,\hat{a}_{1,+\frac{1}{2}}\,|\Phi_0\rangle \\
\left|\Phi^{3,-\frac{1}{2}}_{1,-\frac{1}{2}}\right\rangle &= \hat{a}^\dagger_{3,-\frac{1}{2}}\,\hat{a}_{1,-\frac{1}{2}}\,|\Phi_0\rangle \\
\left|\Phi^{3,+\frac{1}{2}}_{2,+\frac{1}{2}}\right\rangle &= \hat{a}^\dagger_{3,+\frac{1}{2}}\,\hat{a}_{2,+\frac{1}{2}}\,|\Phi_0\rangle \\
\left|\Phi^{3,-\frac{1}{2}}_{2,-\frac{1}{2}}\right\rangle &= \hat{a}^\dagger_{3,-\frac{1}{2}}\,\hat{a}_{2,-\frac{1}{2}}\,|\Phi_0\rangle\,,
\end{aligned}$$

and they are all schematically drawn in Figure 1.7.

We have that the ground state ansatz energy of the Beryllium atom in the hydrogen-like basis set is $\langle\Phi_0|\,\hat{H}\,|\Phi_0\rangle$ is -13.7160 atomic units.
Our ansatz for the ground state and the four singly-excited states in Figure 1.6 gives our many-body basis for an FCI (full configuration interaction) calculation that yielded a ground state energy of beryllium that is -14.3621 atomic units of energy, whereas the exact energy is given as -14.6674 atomic units.

1.e. Hartree-Fock

We have the hydrogen-like single-particle basis states $1s, 2s, 3s$ that may contain two electrons each due to the spin quantum number. The original hydrogen-like basis set will be denoted $|\lambda\rangle$ where $\lambda \in \left\{\left(1,+\frac{1}{2}\right),\left(1,-\frac{1}{2}\right),\left(2,+\frac{1}{2}\right),\left(2,-\frac{1}{2}\right),\left(3,+\frac{1}{2}\right),\left(3,-\frac{1}{2}\right)\right\}$. We define the unitary transformation

$$|p\rangle = \sum_{\lambda} C_{p\lambda} |\lambda\rangle , \tag{1.6}$$

where the new basis is just as orthonormal as the original basis. This is because a unitary transformation always preserves the inner product. We will vary the coefficients of this new basis such that we obtain a minimum in the expected value of the Hartree-Fock (HF) ground state ansatz, $\mathrm{E}\left[\Phi^{HF}\right] = \left\langle \Phi^{HF} \right| \hat{H} \left| \Phi^{HF} \right\rangle$. We write the Hartree-Fock ground state energy as

$$\mathrm{E}\left[\Phi^{HF}\right] = \sum_{i=1}^{N} \langle i| \hat{h}_0 |i\rangle + \frac{1}{2} \sum_{i=1,j=1}^{N} \langle ij| \hat{v} |ij\rangle_{AS} ,$$

where the i, j indices indicate HF single-particle states below the Fermi level. We can then rewrite this expression in terms of our original basis

$$\mathrm{E}\left[\Phi^{HF}\right] = \sum_{i}^{N} \sum_{\alpha,\beta} C^*_{i\alpha} C_{i\beta} \langle \alpha| \hat{h}_0 |\beta\rangle + \frac{1}{2} \sum_{ij}^{N} \sum_{\alpha\gamma\beta\delta} C^*_{i\alpha} C^*_{j\gamma} C_{i\beta} C_{j\delta} \langle \alpha\gamma| \hat{v} |\beta\delta\rangle_{AS} ,$$

where the α-, β-, $\gamma-$ and δ-sums sums over all single-particle states in the original basis, as in Equation 1.6. We also know that the new HF single-particle basis is orthonormal,

$$\langle p|q\rangle = \delta_{pq} = \sum_{\alpha\beta} C^*_{p\alpha} C_{p\beta} \langle \alpha|\beta\rangle = \sum_{\alpha\beta} C^*_{p\alpha} C_{p\beta} \delta_{\alpha\beta} = \sum_{\alpha} C^*_{p\alpha} C_{p\alpha},$$

and we'll use this together with the single-particle energies of the HF basis set, ϵ_i^{HF}, to define the set of Lagrange multipliers as $\lambda_i = \epsilon_i^{HF}$. We define a new functional $F\left[\Phi^{HF}\right]$ which is the energy functional of the HF ground state with the constraints of the Lagrange multipliers,

$$\mathrm{F}\left[\Phi^{HF}\right] = \mathrm{E}\left[\Phi^{HF}\right] - \sum_{i=1}^{N} \epsilon_i^{HF} \sum_{\alpha} C^*_{i\alpha} C_{i\alpha},$$

and we minimize this with respect to the coefficient $C^*_{i\alpha}$. We use the classical extreme-finding method of differentiating with respect to the variable we want to find the extreme with respect to, and setting it equal to zero,

$$\frac{\mathrm{d}F\left[\Phi^{HF}\right]}{\mathrm{d}C^*_{i\alpha}} = 0,$$

where we treat $C_{i\alpha}$ and $C^*_{i\alpha}$ as independent variables. This becomes a set of equations

$$\begin{aligned}
\frac{\mathrm{d}F\left[\Phi^{HF}\right]}{\mathrm{d}C^*_{i\alpha}} &= \sum_{\beta} C_{i\beta} \langle \alpha| \hat{h}_0 |\beta\rangle + \frac{1}{2} \sum_{j}^{N} \sum_{\gamma\beta\delta} C^*_{j\gamma} C_{i\beta} C_{j\delta} \langle \alpha\gamma| \hat{v} |\beta\delta\rangle_{AS} \\
&\quad + \frac{1}{2} \sum_{j}^{N} \sum_{\gamma\beta\delta} C^*_{j\gamma} C_{i\beta} C_{j\delta} \langle \alpha\gamma| \hat{v} |\beta\delta\rangle_{AS} - \epsilon_i^{HF} C_{i\alpha} \\
&= \sum_{\beta} C_{i\beta} \left\{ \langle \alpha| \hat{h}_0 |\beta\rangle + \sum_{j}^{N} \sum_{\gamma\delta} C^*_{j\gamma} C_{j\delta} \langle \alpha\gamma| \hat{v} |\beta\delta\rangle_{AS} \right\} - \epsilon_i^{HF} C_{i\alpha},
\end{aligned}$$

which simply gives the eigenvalue problems

$$\sum_\beta C_{i\beta}\left\{\langle\alpha|\,\hat{h}_0\,|\beta\rangle + \sum_j^N\sum_{\gamma\delta} C^*_{j\gamma}C_{j\delta}\,\langle\alpha\gamma|\,\hat{v}\,|\beta\delta\rangle_{AS}\right\} = \epsilon_i^{HF}C_{i\alpha}$$
$$\sum_\beta C_{i\beta}\,\hat{h}^{HF}_{\alpha\beta} = \epsilon_i^{HF}C_{i\alpha},$$

where we have defined the HF matrix element, $\hat{h}^{HF}_{\alpha\beta}$, as

$$\hat{h}^{HF}_{\alpha\beta} = \langle\alpha|\,\hat{h}_0\,|\beta\rangle + \sum_j^N\sum_{\gamma\delta} C^*_{j\gamma}C_{j\delta}\,\langle\alpha\gamma|\,\hat{v}\,|\beta\delta\rangle_{AS}\,. \tag{1.7}$$

The first term in the HF matrix element is simply the expectation value of $\hat{h}_0$ between the states from our original basis $\langle\alpha|$ and β. This yields zero unless $|\alpha\rangle = |\beta\rangle$. The second term is the weighted sum of all electron-electron interactions (where one of the outgoing electrons are in the $|\alpha\rangle$ state, and one of the incoming are in the $|\beta\rangle$ state) between states for all electrons below the Fermi level. They are weighted with the linear expansion coefficients of the remaining electron states, defined in Equation 1.6.

The second term deserves a closer examination. We write it out as '

$$\sum_j^N\sum_{\gamma\delta} C^*_{j\gamma}C_{j\delta}\,\langle\alpha\gamma|\,\hat{v}\,|\beta\delta\rangle_{AS} = \sum_j^N\sum_{\gamma\delta}\Big[C^*_{j\gamma}C_{j\delta}\,\langle\alpha\gamma|\,\hat{v}\,|\beta\delta\rangle - C^*_{j\gamma}C_{j\delta}\,\langle\alpha\gamma|\,\hat{v}\,|\delta\beta\rangle\Big].$$

We treat these two expressions differently, and first we will deal with the direct term, written as

$$\sum_j^N\sum_{\gamma\delta} C^*_{j\gamma}C_{j\delta}\,\langle\alpha\gamma|\,\hat{v}\,|\beta\delta\rangle = \sum_j^N\sum_{\gamma\delta} C^*_{j\gamma}C_{j\delta}\int \mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2\phi^*_\alpha(\mathbf{r}_1)\phi^*_\gamma(\mathbf{r}_2)\,\hat{v}(\mathbf{r}_1,\mathbf{r}_2)\phi^*_\beta(\mathbf{r}_2)\phi^*_\delta(\mathbf{r}_2),$$

where we have omitted the spin part of the wave functions for simplicity. We then move on to insert the coefficents and the sums over γ and δ into the integral as shown

$$\sum_j^N\sum_{\gamma\delta} C^*_{j\gamma}C_{j\delta}\,\langle\alpha\gamma|\,\hat{v}\,|\beta\delta\rangle = \sum_j^N\int \mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2\phi^*_\alpha(\mathbf{r}_1)\left(\sum_\gamma C^*_{j\gamma}\phi^*_\gamma(\mathbf{r}_2)\right)\hat{v}(\mathbf{r}_1,\mathbf{r}_2)\phi_\beta(\mathbf{r}_1)\left(\sum_\delta C_{j\delta}\phi_\delta(\mathbf{r}_2)\right).$$

Now we recognize the terms $\sum_\gamma C^*_j\gamma\phi^*_\gamma(\mathbf{r})$ and $\sum_\delta C_{j\delta}\phi_\delta(\mathbf{r})$ as the HF single-particle states, $\phi^*_j(\mathbf{r})$ and $\phi_j(\mathbf{r})$, respectively, and the integral becomes

$$\sum_j^N\sum_{\gamma\delta} C^*_{j\gamma}C_{j\delta}\,\langle\alpha\gamma|\,\hat{v}\,|\beta\delta\rangle = \sum_j^N\int \mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2\phi^*_\alpha(\mathbf{r}_1)\phi^*_j(\mathbf{r}_2)\,\hat{v}(\mathbf{r}_1,\mathbf{r}_2)\phi_\beta(\mathbf{r}_1)\phi_j(\mathbf{r}_2)).$$

We are now ready to define a new operator, the direct HF term operator, $\hat{v}_j^{HF(dir)}$, defined as

$$\hat{v}_j^{HF(dir)}(\mathbf{r}_1) = \int \mathrm{d}\mathbf{r}_2\phi^*_j(\mathbf{r}_2)\,\hat{v}(\mathbf{r}_1,\mathbf{r}_2)\phi_j(\mathbf{r}_2),$$

which can be interpreted as an electric potential from the electron occupying the jth HF single-particle state. and our direct term becomes

$$\sum_j^N\sum_{\gamma\delta} C^*_{j\gamma}C_{j\delta}\,\langle\alpha\gamma|\,\hat{v}\,|\beta\delta\rangle = \int \mathrm{d}\mathbf{r}_1\phi^*_\alpha(\mathbf{r}_1)\,\hat{v}_j^{HF(dir)}(\mathbf{r}_1)\phi_\beta(\mathbf{r}_1).$$

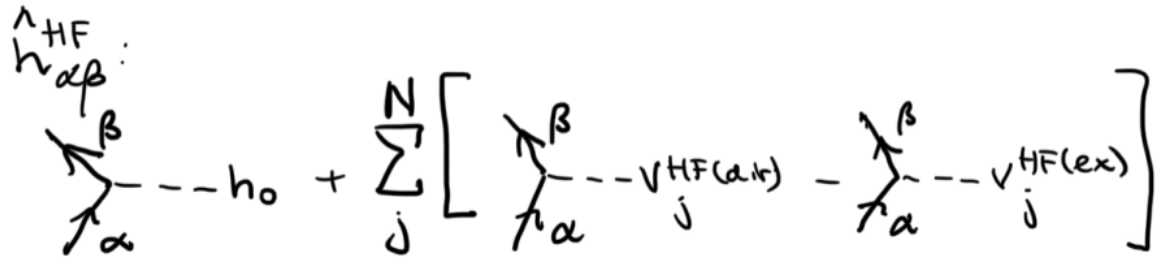

Figure 1.8: *Diagrammatic representation of* $\hat{h}^{HF}_{\alpha\beta}$.

This term is called the **Coulomb term** in Szabo & Ostlund. The next term is a bit trickier, but similarly to the first derivation, it can be shown that

$$-\sum_{j}^{N}\sum_{\gamma\delta} C^*_{j\gamma}C_{j\delta}\,\langle\alpha\gamma|\,\hat{v}\,|\delta\beta\rangle = \sum_{j}^{N}\int \mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2\phi^*_\alpha(\mathbf{r}_1)\left(\sum_\gamma C^*_{j\gamma}\phi^*_\delta(\mathbf{r}_2)\right)\hat{v}(\mathbf{r}_1,\mathbf{r}_2)\left(\sum_\delta C_{j\delta}\phi_\delta(\mathbf{r}_1)\right)\phi_\beta(\mathbf{r}_2)$$
$$= \sum_{j}^{N}\int \mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2\phi^*_\alpha(\mathbf{r}_1)\phi^*_j(\mathbf{r}_2)\,\hat{v}(\mathbf{r}_1,\mathbf{r}_2)\phi_j(\mathbf{r}_1)\phi_\beta(\mathbf{r}_2)$$

which can be interpreted as the previous term, but now there has also been an exchange of electrons between the single-particle states. This comes from the antisymmetrical nature of the Slater determinants. We define a new operator, called the exchange HF operator, such that its effect on two states is

$$\langle\alpha|\,\hat{v}^{HF(ex)}_j(\mathbf{r}_1,\mathbf{r}_2)\,|\beta\rangle = \int \mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2\phi^*_\alpha(\mathbf{r}_1)\phi^*_j(\mathbf{r}_2)\,\hat{v}(\mathbf{r}_1,\mathbf{r}_2)\phi_j(\mathbf{r}_1)\phi_\beta(\mathbf{r}_2),$$

and we write the Hartree-Fock operator in second quantization as

$$\hat{h}^{HF}_{\alpha\beta} = \left[\hat{h_0} + \sum_{j}^{N}(v_j^{H\hat{F}(dir)} - v_j^{H\hat{F}(ex)})\right]\hat{a}^\dagger_\alpha\,\hat{a}_\beta,$$

and its diagrammatic form is show in Figure 1.8.

1.f. The Hartree-Fock matrices

Before our first iteration of the HF algorithm, we define our initial guess of the HF basis to simply be the original hydrogen-like basis, that is,

$$C_{i\alpha} = \delta_{i\alpha}.$$

Before we write the HF matrix, (Equation 1.7), before the first iteration, we map the indices of the original basis $\left\{\left(1,+\frac{1}{2}\right),\left(1,-\frac{1}{2}\right),\left(2,+\frac{1}{2}\right),\left(2,-\frac{1}{2}\right),\left(3,+\frac{1}{2}\right),\left(3,-\frac{1}{2}\right)\right\}$ onto $\{0,1,2,3,4,5\}$ where the quantum numbers in the first representation is directly mapped ($\left(1,+\frac{1}{2}\right)\rightarrow 0, \left(1,-\frac{1}{2}\right)\rightarrow 1,\dots$) onto the combined quantum numbers in the second representation. We also remind ourselves of

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

for the original hydrogen-like basis, here represented with the greek indices for the quantum numbers representing them. We define ϵ_α to be the energy of the single-particle state $|\alpha\rangle$, and in our new representation $\alpha\in\{0,1,2,3,4,5\}$.

The helium atom

Our HF matrix for helium becomes, after putting in the numerical values for the respective interactions and single-particle energies, then

$$\hat{h}^{HF(0)} = \begin{pmatrix} -0.75 & 0 & 0.1787 & 0 & 0.0880 & 0 \\ 0 & -0.75 & 0 & 0.1787 & 0 & 0.0880 \\ 0.1787 & 0 & 0.2956 & 0 & 0.1787 & 0 \\ 0 & 0.1787 & 0 & 0.2956 & 0 & 0.1787 \\ 0.0880 & 0 & 0.1787 & 0 & 0.1642 & 0 \\ 0 & 0.0880 & 0 & 0.1787 & 0 & 0.1642 \end{pmatrix},$$

and after diagonalization of it, our HF single-particle energies become (tabulated in Table 1.3) $1s^{HF(0)} = -0.7832$ a.u., $2s^{HF(0)} = 0.0396$ a.u. and $3s^{HF(0)} = 0.4534$ a.u. of energy, and the ground state energy becomes -2.8292 a.u. of energy. In Section 1.c we calculated the energy of the ground state ansatz in our hydrogen-like single-particle basis to be -2.75 a.u., and the CI1p1h calculation yielded an approximation to the ground state energy that is -2.8386 a.u.. One iteration of the HF algorithm is ~ 0.01a.u. farther away from the true ground state compared with the CI1p1h calculation.

HF single-particle state	Energy (atomic units)
$\|0^{HF(0)}\rangle$	-0.7832
$\|1^{HF(0)}\rangle$	-0.7832
$\|2^{HF(0)}\rangle$	0.0396
$\|3^{HF(0)}\rangle$	0.0396
$\|4^{HF(0)}\rangle$	0.4534
$\|5^{HF(0)}\rangle$	0.4534

Table 1.3: *Single-particle energies of the HF single-particle states after one iteration of the HF algorithm.*

The beryllium atom

For beryllium, the first HF matrix becomes

$$\hat{h}^{HF(0)} = \begin{pmatrix} -3.909 & 0 & 0.3917 & 0 & 0.1892 & 0 \\ 0 & -3.909 & 0 & 0.3917 & 0 & 0.1892 \\ 0.3917 & 0 & 0.1928 & 0 & 0.4452 & 0 \\ 0 & 0.3917 & 0 & 0.1928 & 0 & 0.4452 \\ 0.1892 & 0 & 0.4452 & 0 & 0.5269 & 0 \\ 0 & 0.1892 & 0 & 0.4452 & 0 & 0.5269 \end{pmatrix},$$

and the first diagonalization yields $\left\{1s^{HF(0)}, 2s^{HF(0)}, 3s^{HF(0)}\right\} = \{-3.9507, -0.1040, 0.8657\}$ a.u of energy for the HF single-particle energies after one iteration. The ground state energy after the first iteration becomes -14.4998 a.u. of energy. In Section 1.d we found the ground state ansatz energy, given hydrogen-like single-particle states, to be -13.7160 a.u., and the CI1p1h calculation yielded a ground state energy of -14.3621 a.u.. After just one iteration of the HF algorithm, the ground state energy is a quite much better (of magnitude ~ 0.1) approximation to the true ground state energy.

1.g. Results from the Hartree-Fock iterative scheme

Table 1.4 yields the energies in the HF scheme (the second last row) given a convergence in the single-particle energies where the previous iteration had a summed difference lower than 10^{-10}. Compared with just one iteration of the HF scheme, the difference is quite small. In the case of the helium atom, given our basis set, the best method seems to be the CI1p1h method for approximating the ground state energy. Compared to the exact ground state energy (given in the last row of Table 1.4) of -2.9037 a.u., we are quite far off with all the methods, but on the other hand, we only use six basis function. By just using six basis functions we manage to find an approximation to the ground state with a relative error of approximately 2% (see Table 1.5 for all relative errors). For the beryllium atom, we find that the HF scheme yields the best approximations to the ground state energy, with an improvement of almost half the error of the CI1p1h method.
Why did the HF outperform the CI1p1h method for the beryllium atom and not for helium atom? A possible explanation may be the size of the hydrogen-like basis set. We use six basis functions (1s, 2s and 3s, all with degeneracy 2 because of the spin quantum numbers), all of s-character. Beryllium has four electrons, and the lowest unoccupied single-particle state for the beryllium atom would be one of the three single-particle states of p-character. These are not to be found in our single-particle basis set, and therefore, the CI1p1h were not expected to sufficiently cover the excited states of beryllium. As for helium, the lowest unoccupied single-particle state, the 2s orbital, is in our basis set, and therefore the CI1p1h method works better for helium compared with the HF method. The method only excludes the doubly excited states for a full CI in our basis, while for beryllium 3p3h and 4p4h states are also possible, leaving more configurations omitted in our CI1p1h method compared with a full CI. The HF-algorithm minimizes the energy functional as we vary the coefficients with respect to our basis set, and therefore it may be able to replicate some of the true nature of beryllium even though our basis does not cover many single-particle states. It certainly outperforms our CI1p1h method for beryllium.

Method	Energy approx. helium (a.u.)	Energy approx. beryllium (a.u.)
Ground state ansatz	-2.75	-13.7160
CI1p1h	-2.8386	-14.3621
Hartree-Fock (1 iteration)	-2.8292	-14.4998
Hartree-Fock (converged)	-2.8311	-14.5083
Exact energy	-2.9037	-14.6674

Table 1.4: *Approximations to the ground state energy of the helium and beryllium atoms, given with three different methods (and after the first iteration in the Hartree-Fock method).*

Method	Δ (helium)	δ (helium)	Δ (beryllium)	δ (beryllium)
Ground state ansatz	0.1537 a.u.	5.3%	0.9514 a.u.	6.5%
CI1p1h	0.0651 a.u.	2.2%	0.3053 a.u.	2.1%
Hartree-Fock (1 iteration)	0.0745 a.u.	2.6%	0.1676 a.u.	1.1%
Hartree-Fock (converged)	0.0726 a.u.	2.5%	0.1591 a.u.	1.1%

Table 1.5: *Absolute (Δ) and relative (δ) errors (percentage errors) of the ground state approximation given the different methods (including after one iteration of the HF scheme).*

Cooperation and discussion

To a large extent, I have been discussing the project with Håkon Kvernmoen and Aleksandar Davidov.