INF5620 - Numerical methods for partial differential equations

Problem set 3

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- For the Github repository containing programs and results, follow this link: `https://github.com/UiO-INF5620/INF5620-evenmn/tree/master/assignment_3`

1 Introduction

The aim of this project is to study Hartree-Fock restricted and unrestricted. Many-particle system, the system is defined by the total wave function $|\Phi\rangle = |\phi_1\phi_2\cdots\phi_N\rangle$ where ϕ_i is a single particle function (SPF). Electrons

2 Theory

Write down some general formulas here, Wave functions for restricted and unrestricted HF ex.

2.1 Energy expression

The Hamiltonian of the system is assumed to on the form

$$\hat{H} = \hat{h}(i) + \hat{w}(i,j) \tag{1}$$

where $\hat{h}$ is the kinetic energy operator and $\hat{w}$ is the potential energy. We want to find the total energy of the system, which is given by $\langle\Phi|\hat{H}|\Phi\rangle$. If we consider the kinetic energy, we can easily see that the kinetic energy of particle i is given by $T_i = \langle\phi_i|\hat{h}|\phi_i\rangle$. For the potential it gets more complicated, since we have interaction between all the particles. We also need to make sure that the braket is anti-symmetric as we look at a system of fermions (electrons). For one electron pair i and j we therefore get the potential

$$V_{i,j} = \frac{1}{2}\langle \phi_i\phi_j|\hat{w}|\phi_i\phi_j - \phi_j\phi_i\rangle$$

with negative sign in the ket to get an anti-symmetric braket. Consider now a system of $N+1$ electrons, the total energy is given by

$$E = \langle \Phi|(\hat{h}(i) + \hat{w}(i,j))|\Phi\rangle = \sum_{i=0}^{N}\langle \phi_i|\hat{h}|\phi_i\rangle + \frac{1}{2}\sum_{i=0}^{N}\sum_{\substack{j=0\\ j\neq i}}^{N}\langle \phi_i\phi_j|\hat{w}|\phi_i\phi_j - \phi_j\phi_i\rangle.$$

We can apply this formula to find an expression for the UHF-energy. By plugging in the general for the UHF wave function from above, we obtain

$$\begin{aligned}
E_{UHF} &= \langle \Phi_{UHF}|\hat{H}|\Phi_{UHF}\rangle && (2)\\
&= \sum_{i,\sigma}\langle \phi_i^\sigma|\hat{h}|\phi_i^\sigma\rangle + \frac{1}{2}\sum_{i,j,\sigma,\tau}\langle \phi_i^\sigma\phi_j^\tau|\hat{w}|\phi_i^\sigma\phi_j^\tau - \phi_j^\tau\phi_i^\sigma\rangle && (3)\\
&= \sum_{i,\sigma}\langle \phi_i^\sigma|\hat{h}|\phi_i^\sigma\rangle + \frac{1}{2}\sum_{i,j,\sigma,\tau}\langle \phi_i^\sigma\phi_j^\tau|\hat{w}|\phi_i^\sigma\phi_j^\tau\rangle - \frac{1}{2}\sum_{i,j,\sigma}\langle \phi_i^\sigma\phi_j^\sigma|\hat{w}|\phi_j^\sigma\phi_i^\sigma\rangle. && (4)
\end{aligned}$$

Note that we do not have a sum over τ in the last term, but both τs are replaced by σs. This is because the last term represents the exchange energy, and only particles with the same spin can exchange energy. Here we can also see why the anti-symmetric bra needs to have negative sign: fermions cause repulsive "exchange force", and with the standard positive force direction the exchange energy should be negative for fermions.

2.2 UHF equations

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2.3 section3

2.4 Restricted Hartree-Fock