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/evenmn/master/tree/master/FYSKJM4480/Project1`

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 Slater determinant $|\Phi\rangle = |\phi_1\phi_2\cdots\phi_N\rangle$ where ϕ_i is a single particle function (SPF). Electrons

2 Theory

For both RHF and UHF we can split up the wave function in a spin part and a position part:

$$\phi_{p,\sigma}(x) = \varphi_p(\vec{r})\chi_\sigma(s) \tag{1}$$

where each orbit φ is double occupied.

$$|\Phi_{RHF}\rangle = |\phi_{1\uparrow}\phi_{1\downarrow}\cdots\phi_{N\uparrow}\phi_{N\downarrow}\rangle = |\varphi_1\cdots\varphi_N\bar{\varphi}_1\cdots\bar{\varphi}_N\rangle \tag{2}$$

$$\phi_{p,\sigma}(x) = \varphi_p^\sigma(\vec{r})\chi_\sigma(s) \tag{3}$$

Total Slater determinant:

$$|\Phi_{RHF}\rangle = |\varphi_1^\uparrow\cdots\varphi_{N\uparrow}^\uparrow\bar{\varphi}_1^\downarrow\cdots\bar{\varphi}_{N\downarrow}^\downarrow\rangle \tag{4}$$

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

$$\hat{H} = \hat{h}(i) + \hat{w}(i,j) \tag{5}$$

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 UHF wave function from above, we obtain

$$\begin{aligned} E_{UHF} &= \langle\Phi_{UHF}|\hat{H}|\Phi_{UHF}\rangle \\ &= \sum_{i,\sigma}\langle\varphi_i^\sigma|\hat{h}|\varphi_i^\sigma\rangle + \frac{1}{2}\sum_{i,j,\sigma,\tau}\langle\varphi_i^\sigma\varphi_j^\tau|\hat{w}|\varphi_i^\sigma\varphi_j^\tau - \varphi_j^\tau\varphi_i^\sigma\rangle \\ &= \sum_{i,\sigma}\langle\varphi_i^\sigma|\hat{h}|\varphi_i^\sigma\rangle + \frac{1}{2}\sum_{i,j,\sigma,\tau}\langle\varphi_i^\sigma\varphi_j^\tau|\hat{w}|\varphi_i^\sigma\varphi_j^\tau\rangle - \frac{1}{2}\sum_{i,j,\sigma}\langle\varphi_i^\sigma\varphi_j^\sigma|\hat{w}|\varphi_j^\sigma\varphi_i^\sigma\rangle. \end{aligned} \tag{6}$$

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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Recall the UHF energy from equation (6) and write out δE_{UHF}:

$$\delta E_{UHF} = \sum_{i,\sigma} \langle \delta\varphi_i^\sigma | \hat{h} | \varphi_i^\sigma \rangle + \frac{1}{2} \sum_{i,j,\sigma,\tau} \langle \delta\varphi_i^\sigma \varphi_j^\tau | \hat{w} | \varphi_i^\sigma \varphi_j^\tau \rangle \\ - \frac{1}{2} \sum_{i,j,\sigma} \langle \delta\varphi_i^\sigma \varphi_j^\sigma | \hat{w} | \varphi_j^\sigma \varphi_i^\sigma \rangle. \tag{7}$$

2.3 Roothan-Hall equations

2.4 Restricted Hartree-Fock

With the restrictions $U = U^\uparrow = U^\downarrow$ and $N = N^\uparrow = N^\downarrow$ the UHF equations are still valid. The Roothan-Hall equation for RHF is

$$F(D)U = SU\epsilon \tag{8}$$

where the Fock-operator is $F = h + J(D) - 1/2K(D)$ and the density matrix reads $D = 2U_{occ}U_{occ}^H$. Similarly for UHF we have the Roothan-Hall equation

$$F^\sigma(D^\uparrow, D^\downarrow)U^\sigma = SU^\sigma\epsilon^\sigma \tag{9}$$

with $F = h + J(D^\uparrow + D^\downarrow) - K(D^\sigma)$ and $D = U_{occ}^\uparrow(U_{occ}^\uparrow)^H + U_{occ}^\downarrow(U_{occ}^\downarrow)^H$. As we can see, RHF is like a more general version of UHF with $D^\uparrow = D^\downarrow = D$ and $U_{occ}^\uparrow = U_{occ}^\downarrow = U$, and a solution of RHF Roothan-Hall equations will therefore also be a solution of the UHF Roothan-Hall equations.