FYS-KJM4480 - Quantum Mechanics for Many-Particle Systems

Project 1

Even Marius Nordhagen

October 11, 2017

- 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 use unrestricted Hartree-Fock (UHF) and restricted Hartree-Fock (RHF) to estimate the energy of various molecules. Firstly we go throught the theory of UHF and RHF and find which equations we need to solve, secondly we solve these equations numerically. We use the quantum chemistry package Psi4 to find the Hamiltonian and the number of occupied up-spin states and down-spin states, and from this we use the theory presented in the project text. We expect the UHF method to give more accurate energies than the RHF method, but on the other hand it is way more expensive. To verified the computed energies, we compare them to the energies of Psi4, which has inbuilt UHF- and RHF methods.

2 Theory

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

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. Total Slater determinants for RHF and UHF:

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

$$|\Phi_{UHF}\rangle = |\varphi_1^{\uparrow}\cdots\varphi_{N\uparrow}^{\uparrow}\bar{\varphi}_1^{\downarrow}\cdots\bar{\varphi}_{N\downarrow}^{\downarrow}\rangle \tag{3}$$

2.1 Energy expression

The Hamiltonian of the system is assumed to have the form

$$\hat{H} = \hat{h}(i) + \hat{w}(i,j) \tag{4}$$

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 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

$$\begin{aligned} E_{UHF} &= \langle\Phi_{UHF}|\hat{H}|\Phi_{UHF}\rangle \\ &= \sum_{i,\sigma}\langle\varphi_i^{\sigma}|\hat{h}|\varphi_i^{\sigma}\rangle + \frac{1}{2}\sum_{i,j,\sigma,\tau}\langle\varphi_i^{\sigma}\varphi_j^{\tau}|\hat{w}|\varphi_i^{\sigma}\varphi_j^{\tau} - \varphi_j^{\tau}\varphi_i^{\sigma}\rangle \\ &= \sum_{i,\sigma}\langle\varphi_i^{\sigma}|\hat{h}|\varphi_i^{\sigma}\rangle + \frac{1}{2}\sum_{i,j,\sigma,\tau}\langle\varphi_i^{\sigma}\varphi_j^{\tau}|\hat{w}|\varphi_i^{\sigma}\varphi_j^{\tau}\rangle - \frac{1}{2}\sum_{i,j,\sigma}\langle\varphi_i^{\sigma}\varphi_j^{\sigma}|\hat{w}|\varphi_j^{\sigma}\varphi_i^{\sigma}\rangle. \end{aligned} \tag{5}$$

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

$$\left[\hat{h} + \sum_{\tau} \hat{v}_H^{\tau} - \hat{v}_{EX}^{\sigma}\right] \varphi_i^{\sigma} = \sum_j \lambda_{j,i}^{\sigma} \varphi_j^{\sigma} \tag{6}$$

where

$$\hat{v}_H^{\tau}\psi = \sum_j (\cdot\, \varphi_j^{\tau} | \hat{w} | \psi \varphi_j^{\tau}), \qquad \hat{v}_{EX}^{\sigma}\psi = \sum_j (\cdot\, \varphi_j^{\sigma} | \hat{w} | \varphi_j^{\sigma} \psi) \tag{7}$$

so all the objects in the square brackets are operators, which means we can define a new operator

$$\hat{f}^{\sigma} = \hat{h} + \sum_{\tau} \hat{v}_H^{\tau} - \hat{v}_{EX}^{\sigma}. \tag{8}$$

We have the following relation

$$\delta\varphi_i^{\sigma}(\vec{r}) = \sum_p \varphi_p^{\sigma}(\vec{r})(\varphi_p^{\sigma} | \delta\varphi_i^{\sigma}) \equiv \sum_p \varphi_p^{\sigma}(\vec{r}) \eta_{p,i}^{\sigma}. \tag{9}$$

It is sufficient to vary the bra in the braket because...

Recall the UHF energy from equation (5) and write out δE_{UHF}:

$$\begin{aligned} \delta E_{UHF} = &\sum_{i,\sigma} \langle \delta\varphi_i^{\sigma} | \hat{h} | \varphi_i^{\sigma} \rangle + \frac{1}{2} \sum_{i,j,\sigma,\tau} \langle \delta\varphi_i^{\sigma} \varphi_j^{\tau} | \hat{w} | \varphi_i^{\sigma} \varphi_j^{\tau} \rangle \\ &- \frac{1}{2} \sum_{i,j,\sigma} \langle \delta\varphi_i^{\sigma} \varphi_j^{\sigma} | \hat{w} | \varphi_j^{\sigma} \varphi_i^{\sigma} \rangle. \end{aligned} \tag{10}$$

This corresponds to that a single particle function (SPF) in Slater determinant is multiplied with δ, and delta transforms that SPF to another SPF:

$$\sum_{i,\sigma} \delta\varphi_i^{\sigma} = \varphi_a^{\sigma}. \tag{11}$$

We therefore obtain

$$\delta E_{UHF} = \langle \varphi_a^{\sigma} | \hat{h} | \varphi_i^{\sigma} \rangle + \frac{1}{2} \sum_{j,\tau} \langle \varphi_a^{\sigma} \varphi_j^{\tau} | \hat{w} | \varphi_i^{\sigma} \varphi_j^{\tau} \rangle - \frac{1}{2} \sum_j \langle \varphi_a^{\sigma} \varphi_j^{\sigma} | \hat{w} | \varphi_j^{\sigma} \varphi_i^{\sigma} \rangle \tag{12}$$

If we set this to zero, we get

$$\begin{aligned} \delta E_{UHF} &= \langle \varphi_a^{\sigma} | \hat{h} | \varphi_i^{\sigma} \rangle + \frac{1}{2} \sum_{j,\tau} \langle \varphi_a^{\sigma} \varphi_j^{\tau} | \hat{w} | \varphi_i^{\sigma} \varphi_j^{\tau} \rangle - \frac{1}{2} \sum_j \langle \varphi_a^{\sigma} \varphi_j^{\sigma} | \hat{w} | \varphi_j^{\sigma} \varphi_i^{\sigma} \rangle \\ &= \langle \varphi_a^{\sigma} | \hat{h} + \sum_{\tau} \hat{v}_H^{\tau} - \hat{v}_{EX}^{\sigma} | \varphi_i^{\sigma} \rangle \\ &= \langle \varphi_a^{\sigma} | \hat{f}^{\sigma} | \varphi_i^{\sigma} \rangle = 0 \end{aligned} \tag{13}$$

This result makes sense: if we set the perturbation $\delta E_{UHF} = 0$, the Fock operator should remain unchanged.

Now we want to find the non-canonical UHF equation. $\eta^{\sigma}_{i,j}$ is zero for all i's except for $i = a$:

$$\langle\varphi^{\sigma}_a|\hat{f}^{\sigma}|\varphi^{\sigma}_i\rangle - \sum_j \lambda^{\sigma}_{j,i}(\varphi^{\sigma}_a|\varphi^{\sigma}_j) = 0 \quad \Rightarrow \quad \hat{f}^{\sigma}\varphi^{\sigma}_i(r) = \sum_j \lambda^{\sigma}_{j,i}\varphi^{\sigma}_i(r) \tag{14}$$

2.3 Roothan-Hall equations

We have just seen the UHF equations on non-canonical form (equation (14)), but it is better to have them on canonical form (transform to eigenvalue problems):

$$\hat{f}^{\sigma}\varphi^{\sigma}_i = \epsilon^{\sigma}_i\varphi^{\sigma}_i. \tag{15}$$

For numerical treatment, it can be useful to consider the molecular orbitals φ^{σ}_p as a sum over atomic orbital basis functions ψ_p:

$$\varphi^{\sigma}_p = \sum_p \psi_p U^{\sigma}_{p,q}. \tag{16}$$

We cannot guarantee orthonormal basis functions, thus we will have a overlap represented by the overlap matrix

$$S_{p,q} = (\psi_p|\psi_q). \tag{17}$$

In the implementation we will use Psi4 to find the required matrices and compare the energies. Psi4 uses Mulliken notation:

$$(pr|qs) \equiv (\psi_p\psi_q|\hat{w}|\psi_r\psi_s) \tag{18}$$

and so will we do to short down the calculations. We now define the Hamiltonian matrix and the density matrix

$$h_{q,p} = (\psi_q|\hat{h}|\psi_p), \qquad D^{\sigma}_{r,s} = \sum_j U^{\sigma}_{r,j}(U^{\sigma}_{s,j})^* \tag{19}$$

respectively. From this we can derive some useful relations where we are projecting the equations above onto atomic orbitals, i.e. we need to switch indexes from occupied to unoccupied.

$$\begin{aligned}(\psi_p|\hat{h}|\varphi^{\sigma}_i) &= (\psi_p|\hat{h}|\sum_q \psi_q U^{\sigma}_{q,i} \\ &= \sum_i (\psi_p|\hat{h}|\psi_q)U^{\sigma}_{q,i} \\ &= \sum_i h_{p,q}U^{\sigma}_{q,i}.\end{aligned} \tag{20}$$

Now recall the Hartree potential $\hat{v}_H^\tau$ and the exchange potential $\hat{v}_{EX}^\sigma$ from section (2.2):

$$\begin{aligned}(\psi_p|\hat{v}_H^\tau|\varphi_i^\sigma) &= (\psi_p|\hat{v}_H^\tau|\sum_q \psi_q U_{q,i}^\sigma) \\ &= \sum_q \Big(\sum_j (\psi_p \varphi_j^\tau|\hat{w}|\psi_q\varphi_j^\tau)\Big) U_{q,i}^\sigma \\ &= \sum_q \Big(\sum_j (pq|jj)\Big) U_{q,i}^\sigma \\ &= \sum_q \Big(\sum_{r,s} (pq|rs) D_{s,r}^\tau \Big) U_{q,i}^\sigma \end{aligned} \tag{21}$$

$$\begin{aligned}(\psi_p|\hat{v}_{EX}^\sigma|\varphi_i^\sigma) &= (\psi_p|\hat{v}_{EX}^\sigma|\sum_q \psi_q U_{q,i}^\sigma) \\ &= \sum_q \Big(\sum_j (\psi_p \varphi_j^\sigma|\hat{w}|\varphi_j^\sigma\psi_q)\Big) U_{q,i}^\sigma \\ &= \sum_q \Big(\sum_j (pj|jq)\Big) U_{q,i}^\sigma \\ &= \sum_q \Big(\sum_{r,s} (ps|rq) D_{s,r}^\sigma \Big) U_{q,i}^\sigma \end{aligned} \tag{22}$$

$$\begin{aligned}(\psi_p|\varphi_i^\sigma) &= (\psi_p|\sum_i \psi_i U_{i,q}^\sigma) \\ &= \sum_q (\psi_p|\psi_q) U_{q,i}^\sigma \\ &= \sum_q S_{p,q} U_{q,i}^\sigma \end{aligned} \tag{23}$$

We use the 3 first derivations above to define the UHF Fock matrix:

$$F^\sigma = h + J(D^\uparrow + D^\downarrow) - K(D^\sigma) \tag{24}$$

where $J(D)_{p,q} = \sum_{r,s}(pq|rs)D_{s,r}$ and $K(D)_{p,q} = \sum_{r,s}(ps|rq)D_{s,r}$. From the canonical UHF equation in (15), we have now seen how to project the left-hand-side, and we get similar projecting for the right-hand-side:

$$\epsilon^\sigma(\psi_p|\varphi_i^\sigma) = \epsilon^\sigma \sum_q S_{p,q} U_{q,i}^\sigma \tag{25}$$

So the UHF Roothan-Hall equation transforms to a generalized eigenvalue problem:

$$F^\sigma(D^\uparrow, D^\downarrow)U^\sigma = SU^\sigma\epsilon^\sigma \tag{26}$$

with $D^\uparrow = U^\uparrow_{occ}(U^\uparrow_{occ})^H$ and $D^\downarrow = U^\downarrow_{occ}(U^\downarrow_{occ})^H$.

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. By choosing $D^\uparrow = D^\downarrow = (1/2)D$, we will only get one Fock operator independent of the spin, which is the RHF. Starting from the UHF Fock operator (equation (24)), we get

$$\begin{aligned} F &= h + J(D^\uparrow + D^\downarrow) - K(D^\sigma) \\ &= h + J(D) - \frac{1}{2}K(D). \end{aligned} \tag{27}$$

where equation (27) is the RHF Fock operator. Similarly the RHF Roothan-Hall equation can easily be derived from the UHF Roothan-Hall equation in (26):

$$\begin{aligned} F^\sigma(D^\uparrow, D^\downarrow)U^\sigma &= SU^\sigma\epsilon^\sigma \\ F(D)U &= SU\epsilon \end{aligned} \tag{28}$$

where the density matrix now reads $D = 2U_{occ}U^H_{occ}$.

As we can see, RHF is like a more general version of UHF with $D^\uparrow = D^\downarrow = D$ and $U^\uparrow_{occ} = U^\downarrow_{occ} = U$, and a solution of UHF Roothan-Hall equations will therefore also be a solution of the RHF Roothan-Hall equations.

3 Conclusion

Please see the github repository for the implementation. I wish I could show some beautiful figures here, but I did not manage to solve the project properly. I think the implementation is sort of correct, but I have not included the SCF iteration lopps for UHF and RHF as I should. This gives a major error, but I believe the iteration loops would have fixed it. Nevertheless I had some problems with the combination Jupyter notebook and Psi4, and eventually I decided to write all the code in python, hope it is okay.