

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 use unrestricted Hartree-Fock (UHF) and restricted Hartree-Fock (RHF) to estimate the energy of various molecules. Firstly we go through 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 verify 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:

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

where each orbit φ is double occupied.

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

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

Total Slater determinant:

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

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

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

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 bracket 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 bracket. 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

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

Note that we do not have a sum over τ in the last term, but both τ s are replaced by σ s. 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

$$\left[\hat{h} + \sum_{\tau} \hat{v}_H^{\tau} - \hat{v}_{EX}^{\sigma} \right] \varphi_i^{\sigma} = \sum_j \lambda_{j,i}^{\sigma} \varphi_j^{\sigma} \quad (7)$$

where

$$\hat{v}_H^{\tau} \psi = \sum_j (\cdot \varphi_j^{\tau} | \hat{w} | \psi \varphi_j^{\tau}), \quad \hat{v}_{EX}^{\sigma} \psi = \sum_j (\cdot \varphi_j^{\sigma} | \hat{w} | \varphi_j^{\sigma} \psi) \quad (8)$$

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

$$\hat{f}^{\sigma} = \hat{h} + \sum_{\tau} \hat{v}_H^{\tau} - \hat{v}_{EX}^{\sigma} \quad (9)$$

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

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

$$\hat{f}^{\sigma} \varphi_i^{\sigma} = \sum_j \lambda_{i,j}^{\sigma} \varphi_j^{\sigma} \quad (11)$$

2.3 Roothan-Hall equations

We have just seen the UHF equations on non-canonical form (equation (11)), but it is better to have them on canonical form (transform to eigenvalue problems):

$$\hat{f}^{\sigma} \varphi_i^{\sigma} = \epsilon_i^{\sigma} \varphi_i^{\sigma}. \quad (12)$$

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

$$\varphi_p^{\sigma} = \sum_p \psi_p U_{p,q}^{\sigma}. \quad (13)$$

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

$$S_{p,q} = (\psi_p|\psi_q). \quad (14)$$

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

$$(pr|qs) \equiv (\psi_p\psi_q|\hat{w}|\psi_r\psi_s) \quad (15)$$

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

$$h_{q,p} = (\psi_q|\hat{h}|\psi_p), \quad D_{r,s}^\sigma = \sum_j U_{r,j}^\sigma (U_{s,j}^\sigma)^* \quad (16)$$

respectively. From this we can derive some useful relations

$$\begin{aligned} (\psi_p|\hat{h}|\varphi_i^\sigma) &= (\psi_p|\hat{h}|\sum_i \psi_i U_{i,q}^\sigma) \\ &= \sum_i (\psi_p|\hat{h}|\psi_i) U_{i,q}^\sigma \\ &= \sum_i h_{p,i} U_{i,q}^\sigma. \end{aligned} \quad (17)$$

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

$$\begin{aligned} (\psi_p|\hat{v}_H^\tau|\varphi_i^\sigma) &= (\psi_p|\hat{v}_H^\tau|\sum_i \psi_i U_{i,q}^\sigma) \\ &= \sum_i \left(\sum_j (\psi_p\varphi_j^\tau|\hat{w}|\psi_i\varphi_j^\tau) \right) U_{i,q}^\sigma \\ &= \sum_i \left(\sum_j (pi|jj) \right) U_{i,q}^\sigma \\ &= \sum_i h_{p,i} U_{i,q}^\sigma. \end{aligned} \quad (18)$$

$$\begin{aligned}
(\psi_p|\hat{v}_{EX}^\sigma|\varphi_i^\sigma) &= (\psi_p|\hat{v}_{EX}^\sigma|\sum_i \psi_i U_{i,q}^\sigma) \\
&= \sum_i \left(\sum_j (\psi_p \varphi_j^\sigma|\hat{w}|\varphi_j^\sigma \psi_i) \right) U_{i,q}^\sigma \\
&= \sum_i \left(\sum_j (pj|ji) \right) U_{i,q}^\sigma \\
&= \sum_i h_{p,i} U_{i,q}^\sigma.
\end{aligned} \tag{19}$$

$$\begin{aligned}
(\psi_p|\varphi_i^\sigma) &= (\psi_p|\sum_i \psi_i U_{i,q}^\sigma) \\
&= \sum_q (\psi_p|\psi_q) U_{q,i}^\sigma \\
&= \sum_q S_{p,q} U_{q,i}^\sigma
\end{aligned} \tag{20}$$

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

$$F^\sigma = h + J(D^\uparrow + D^\downarrow) - K(D^\sigma) \tag{21}$$

where $J(D)_{p,q} = \sum_{r,s} (pq|rs) D_{s,r}$ and $K(D)_{p,q} = \sum_{r,s} (ps|rq) D_{s,r}$.

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

$$F(D)U = SU\epsilon \tag{22}$$

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

$$F^\sigma(D^\uparrow, D^\downarrow)U^\sigma = SU^\sigma\epsilon^\sigma \tag{23}$$

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.