Exercise Sheet 6

Due: 04.06.24 14h00

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General Regulations.

- Please hand in your solutions in groups of up to two people.
- Your solutions to theoretical exercises can be either handwritten notes (scanned), or typeset using LaTeX. In case you hand in handwritten notes, please make sure that they are legible and not too blurred or low resolution.
- For the practical exercises, always provide the (commented) code as well as the output, and don't forget to explain/interpret the latter. Please hand in an exported PDF of your notebook.
- Submit all your files in the Übungsgruppenverwaltung, only once for your group.

1 Visualization of AOs and MOs

(a) Visualize the atomic orbitals (AOs) of an HF (hydrogen fluoride) molecule using the `6-31G(d,p)` basis set. Label the orbitals with the corresponding atom and quantum numbers.

Hint: You can use `mol.eval_gto("GTOval", coords)` to evaluate the Gaussian-type orbitals (GTOs) at `coords`. (3 pts)

(b) Perform a Hartree-Fock calculation on the molecule and visualize the resulting molecular orbitals (MOs). Which of these orbitals are occupied? (3 pts)

(c) Compute the electron density and plot it. Most of the density will be located at the heavier fluorine. Subtract the initial guess and plot the difference. (3 pts)

2 PCA on Fock matrix

In this exercise, we want to apply principal component analysis (PCA) to the Fock matrices that we obtain during the Hartree-Fock procedure. You can use the implementation of PCA from the `scikit-learn` library.

(a) Perform a Hartree-Fock calculation on a water molecule using the `6-31G(2df,p)` basis set. Repeat the calculation with all four combinations of with/without DIIS and with/without damping. Record the number of iterations needed for convergence in each case.

Hint: If you are using DIIS, you can set the damping by passing a float to `mf.diis_damp`. Damping without DIIS can be achieved by specifying `mf.damp` and setting `mf.diis_start_cycle` to a large number (see https://pyscf.org/user/scf.html#converging-scf-iterations). (4 pts)

(b) Save the upper triangular part of the Fock matrices obtained in the previous step. Why is the upper triangular part sufficient?

Hint: To save the Fock matrices, you can define a callback function `callback(envs)` that reads out the Fock matrix `envs['fock']` and pass it to `mf.callback`. (3 pts)

(c) Perform PCA on all Fock matrices of different methods combined. Plot the trajectories in the first two principal components in one plot. Explain the differences between the trajectories. (4 pts)