Exercise Sheet 5

Due: 28.05.24 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 both the notebook (`.ipynb`), as well as an exported pdf.
- Submit all your files in the Übungsgruppenverwaltung, only once for your group.

1 Restricted Hartree-Fock

In the restricted, closed shell setting, two spin orbitals ϕ with spin up and down are paired and share the same spatial orbital φ (this only works for systems with even numbers of numbers), for instance

$$\phi_1(x) = \varphi_1(r)\alpha(w) \quad \text{and} \quad \phi_2(x) = \varphi_1(r)\beta(w).$$

Write down the energy in the restricted Hartree-Fock approximation. The sums should only go up to $N/2$, where N is the number of electrons. Remember that some integrals vanish due to spin. (8 pts)

2 Diagonalization of the overlap matrix

In the LCAO ansatz (linear combination of atomic orbitals), the molecular orbitals are given by

$$\phi_i = \sum_\alpha C_{\alpha i}\chi_\alpha.$$

The overlap matrix S of the atomic orbitals χ is defined as

$$S_{\alpha\beta} = \langle\chi_\alpha|\chi_\beta\rangle.$$

Show that C diagonalizes S, i.e., prove that $C^\dagger SC = \mathbb{I}$. (6 pts)

3 Understanding PySCF logging

Perform a restricted Hartree-Fock calculation PySCF with verbosity set to 9. Use the molecule HF (hydrogen fluoride) with the 6-31G* basis. Comment on every line of the output and explain what it means. You can group repeating blocks and only comment once. (6 pts)