

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 L^AT_EX. 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 Gaussian basis sets

Atomic basis sets are available online in the “EMSL basis set exchange” database. The details of the Pople 6-31G* basis set of Nitrogen are presented in this way¹:

```
01: #BASIS SET: (10s,4p,1d) -> [3s,2p,1d]
02: N S
03: 4173.5110000 0.0018348
04: 627.4579000 0.0139950
05: 142.9021000 0.0685870
06: 40.2343300 0.2322410
07: 12.8202100 0.4690700
08: 4.3904370 0.3604550
09: N SP
10: 11.6263580 -0.1149610 0.0675800
11: 2.7162800 -0.1691180 0.3239070
12: 0.7722180 1.1458520 0.7408950
13: N SP
14: 0.2120313 1.0000000 1.0000000
15: N D
16: 0.8000000 1.0000000
```

Please explain the following lines and numbers in the description of the basis set:

- | | |
|--|---------|
| (a) line 01 | (2 pts) |
| (b) line 02 and the numbers in lines 03-08 | (2 pts) |
| (c) lines 15 and 16 | (2 pts) |
| (d) lines 09-14 | (2 pts) |

¹If you need more information about basis sets you can read up in Jensen, Introduction to Computational Chemistry, Chapter 5.

2 Geometric investigation of restricted Hartree-Fock

In this exercise, we want to further investigate the geometric structure of restricted Hartree-Fock.

- (a) Consider a N_2 molecule. Choose a random axis and rotate the molecule around this axis with an angle $\varphi \in [0, 2\pi)$. For each angle, calculate the converged Fock matrix with the restricted Hartree-Fock algorithm and the **sto-3g** basis set. Investigate how the components of the Fock matrix change under this rotation. Which part is invariant? Which part transforms like a vector?

Hint: What components in the Fock matrix correspond to which orbitals in the basis set? (6 pts)

- (b) Now consider an Ethane molecule. Rotate the molecule randomly in 3d space and save the converged Fock matrices. Make an interactive 3d PCA plot of the upper triangular part of the Fock Matrix. Interpret the resulting geometry. (6 pts)