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<https://www.ur.de/physics/wilhelm/teaching/sose24-computational-nanoscience>

## Computational Nanoscience: Exercise Sheet No. 5

### Exercise 5.1: HOMO and LUMO of pentacene

In 2005, Repp *et al.* [1] reported images of molecular orbitals of pentacene experimentally by a scanning tunnelling microscope (STM). Calculate the spatial structure of pentacene's highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) from Hartree-Fock in vacuum and compare them to the experimental results.

- Create the geometry of pentacene with Avogadro, see Fig. 1 for the molecular geometry. [1]
- Compute and plot the HOMO and the LUMO of pentacene. Use def2-SVP basis set and carry only the energy/MO calculation on coordinates from Avogadro, i.e. use the following input file

```
&GLOBAL
  RUN_TYPE ENERGY
  PROJECT_NAME HF
&END GLOBAL
&FORCE_EVAL
  METHOD QS
  &DFT
    &XC
      &HF
        FRACTION 1.0
      &END HF
    &XC_FUNCTIONAL NONE
  &END XC_FUNCTIONAL
&END XC
&QS
  METHOD GAPW
  ! All overlaps are considered
  MIN_PAIR_LIST_RADIUS -1.0
&END QS
&POISSON
  PERIODIC NONE
  POISSON_SOLVER ANALYTIC
&END POISSON
BASIS_SET_FILE_NAME def2-svp.1.cp2k
POTENTIAL_FILE_NAME POTENTIAL
&SCF
  ! Make sure that LUMO is also considered
  ADDED_MOS 1
```

```

&END SCF
&PRINT
  &MO_CUBES
    FILENAME MO
    NHOMO 1
    NLUMO 1
  &END MO_CUBES
&END PRINT
&END DFT
&SUBSYS
&CELL
  ! Leave sufficient room for the whole chain
  ABC 25.0 15.0 10.0
  PERIODIC NONE
&END CELL
&TOPOLOGY
  &CENTER_COORDINATES
&END CENTER_COORDINATES
  COORD_FILE_FORMAT XYZ
  ! Here you can change the molecule that is being investigated
  COORD_FILE_NAME pentacene.xyz
&END TOPOLOGY
&KIND H
  BASIS_SET def2-SVP
  POTENTIAL ALL
&END KIND
&KIND C
  BASIS_SET def2-SVP
  POTENTIAL ALL
&END KIND
&END SUBSYS
&END FORCE_EVAL

```

Molecular orbitals can be plotted with jmol program. Using it to open the cube file directly should work, but you can also control the isosurface value used in the jmol program by running it in the directory with the saved cube file, then opening the in-program console and running

```
isosurface pentacene cutoff 0.01 sign "pentacene.cube"
```

where instead of 0.01 you put your chosen isosurface value and instead of "pentacene.cube" the name of the cube file with the orbital data. See also <https://chemapps.stolaf.edu/jmol/docs/> for reference. [4]

- (c) Have a look at the spatial structure of the HOMO and the LUMO. Can you give a quick argument based on the orbital shape, why indeed the energy of the HOMO is lower than the energy of the LUMO? [1]

- (d) Discuss: Do the molecular orbitals  $\psi_n(\mathbf{r})$  from Hartree-Fock have any physical meaning? What is the reason we nevertheless use them for a comparison to an experiment? Which contributions in the Hartree-Fock equations cause the spatial shape of the molecular orbitals? [2]

### References:

- [1] J. Repp, G. Meyer, S. M. Stojković, A. Gourdon, and C. Joachim: Molecules on Insulating Films: Scanning-Tunneling Microscopy Imaging of Individual Molecular Orbitals, [Phys. Rev. Lett. 94, 026803 \(2005\)](#).

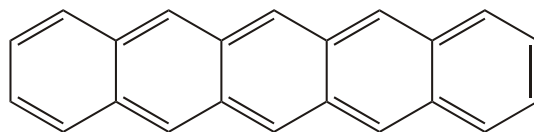


Figure 1: Molecular structure of pentacene. Carbon atoms are displayed, hydrogen atoms are not displayed (it is easiest if you enable automatic H atoms in Avogadro; then you can just put the double bonds as drawn in this figure).

### Exercise 5.2: Ionization potential and Koopmans' theorem

The experimental values of  $N_2$  and  $O_2$  are 15.58 eV ( $N_2$ ) and 12.07 eV ( $O_2$ ). Compute the ionization potential of  $N_2$  and  $O_2$  in two different ways:

- (a) Calculate the energy of the highest occupied molecular orbital (HOMO) from Hartree-Fock in eV. Check the basis set convergence. [4]

**Hint:** Relax the geometry towards the geometry with lowest Hartree-Fock energy using the following input file

```
&GLOBAL
  RUN_TYPE GEO_OPT
  PROJECT_NAME O2
&END GLOBAL
&FORCE_EVAL
  METHOD QS
  &DFT
    &XC
      &HF
        FRACTION 1.0
      &END HF
    &XC_FUNCTIONAL NONE
  &END XC_FUNCTIONAL
&END XC
&QS
  METHOD GAPW
  ! All overlaps are considered
  MIN_PAIR_LIST_RADIUS -1.0
```

```

&END QS
&POISSON
  PERIODIC NONE
  POISSON_SOLVER ANALYTIC
&END POISSON
BASIS_SET_FILE_NAME def2-qzvpp.1.cp2k
BASIS_SET_FILE_NAME def2-tzvpp.1.cp2k
POTENTIAL_FILE_NAME POTENTIAL
! Following two lines can be commented for N2
UKS
MULTIPLICITY 3
&PRINT
  &MO
    &EACH
      QS_SCF 0
    &END EACH
  ENERGIES
&END MO
&END PRINT
&END DFT
&SUBSYS
&CELL
  ! Leave sufficient room for the whole chain
  ABC 10.0 10.0 10.0
  PERIODIC NONE
&END CELL
&TOPOLOGY
  &CENTER_COORDINATES
  &END CENTER_COORDINATES
  COORD_FILE_FORMAT XYZ
  ! Here you can change the molecule that is being investigated
  COORD_FILE_NAME O2.xyz
&END TOPOLOGY
&KIND 0
  BASIS_SET def2-QZVPP
  POTENTIAL ALL
&END KIND
&KIND N
  BASIS_SET def2-QZVPP
  POTENTIAL ALL
&END KIND
&END SUBSYS
&END FORCE_EVAL

```

Here, we use def2-QZVPP and def2-TZVPP basis sets to check for convergence. The PRINT section by default prints the information at every iteration level, but since we only require energy of final relaxed molecule, we can put QS\_SCF 0.

- (b) Calculate the difference between the Hartree-Fock energy of  $X_2$  and  $X_2^+$  in eV. Check basis set convergence. [4]

**Hint:** In order to perform a Hartree-Fock calculation for a charged molecule, use `CHARGE` keyword in the DFT section. Due to odd number of electrons, include `UKS` keyword for both molecules and leave `MULTIPLICITY` keyword commented (do not impose specific multiplicity).

- (c) Discuss: Why is the ionization potential of  $N_2$  larger than the ionization potential of  $O_2$ ? [1]
- (d) Discuss: Should the numerical values from (a) and (b) match according to Koopmans' theorem? [1]
- (e) Discuss: Which method, (a) or (b), do you consider more reliable for computing the ionization potential? [1]
- (f) Is method (b) also working for determining the ionization potential of a periodic system, for example an aluminium unit cell with periodic boundary conditions? [1]