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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.

(a) Create the geometry of pentacene with Avogadro, see Fig. 1 for the molecular geometry. **[1]**

(b) 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. **[6]**

(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? **[2]**

(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? **[3]**

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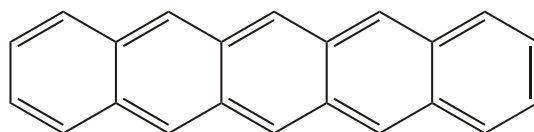
Figure 1: Molecular structure of pentacene. Carbon atoms are displayed, hydrogen atoms are not displayed (it is easiest if you enable automatic H atoms in Avogadro; then you can just put the double bonds as drawn in this figure).

Exercise 5.2: Helical Orbitals in Diphenylacetylene

Diphenylacetylene is a carbohydrate molecule consisting of two benzene rings connected by carbon triple bond chain. We will investigate its molecular orbitals in HF in two distinct geometries - planar and twisted, whose visualisations and coordinates are given below
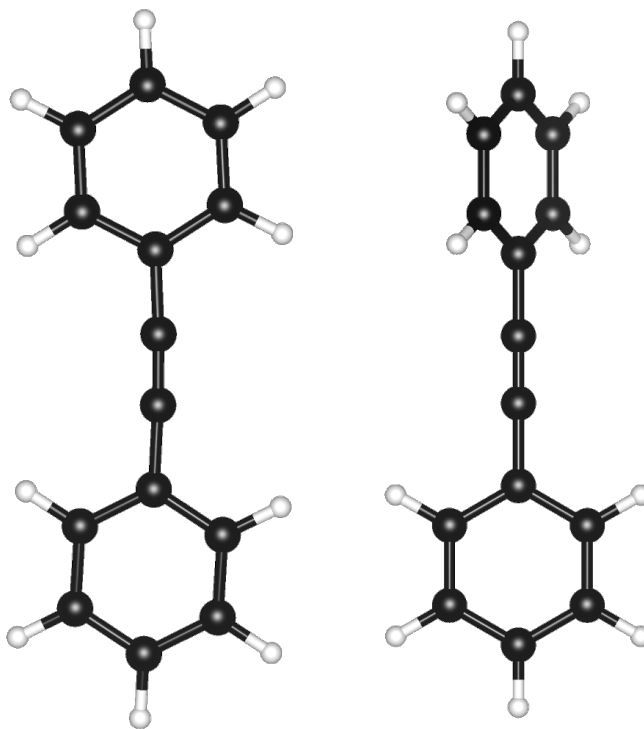
24				24			
Planar				Twisted			
C	7.97016	4.98674	4.99767	C	7.97485	5.00101	4.99803
C	7.37670	5.67743	6.05755	C	7.27560	6.20895	4.99934
C	5.98752	5.77920	6.13671	C	5.88117	6.20882	5.00031
C	5.18923	5.19022	5.15663	C	5.18324	5.00231	4.99987
C	5.77962	4.49783	4.09813	C	5.88020	3.79500	4.99839
C	7.17034	4.39539	4.01790	C	7.27445	3.79365	4.99750
H	7.99264	6.14077	6.82354	H	7.81390	7.15424	4.99971
H	5.52884	6.31869	6.96070	H	5.33774	7.15048	5.00147
H	4.10621	5.27114	5.21686	H	4.09593	5.00273	5.00071
H	5.15578	4.03953	3.33455	H	5.33587	2.85384	4.99806
H	7.62154	3.85613	3.18883	H	7.81197	2.84787	4.99652
C	10.59702	4.86954	4.89429	C	10.59888	5.00086	4.99728
C	9.39527	4.90049	4.92082	C	9.41746	5.00058	4.99765
C	12.02701	4.88130	4.90685	C	12.04150	5.00179	4.99723
C	12.70220	5.49749	5.96425	C	12.74066	5.60733	6.04250
C	14.09697	5.52810	5.98124	C	14.13508	5.60888	6.04170
C	14.81895	4.94223	4.94146	C	14.83302	5.00553	4.99688
C	14.14661	4.32426	3.88584	C	14.13639	4.40017	3.95237
C	12.75086	4.29309	3.86770	C	12.74204	4.39787	3.95179
H	12.14595	5.95816	6.77662	H	12.20227	6.08007	6.86097
H	14.61963	6.00991	6.80326	H	14.67835	6.08107	6.85650
H	15.90651	4.96810	4.95358	H	15.92047	5.00716	4.99669
H	14.71092	3.86887	3.07657	H	14.68085	3.92953	3.13740
H	12.23526	3.81229	3.04097	H	12.20461	3.92384	3.13336

(a) Before any calculation, can you estimate which geometry will have smaller energy? **[2]**

(b) Use the same basis set and computational parameters as in (b) to evaluate the molecular orbitals of the twisted and planar geometry **[4]**

(c) Along the carbon chain in the twisted geometry, we observe rotation of the direction of otherwise planar *p*-type orbitals. These helical orbitals have number of interesting properties, among one of them is the dependence of the direction of rotation of the different orbitals. Compare the rotation in HOMO and LUMO. **[1]**

(d) In the planar geometry, the orbital helix is not observed - do you expect there to be another geometry, where the orbitals remain planar as well? **[1]**