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http://www.physik.uni-regensburg.de/forschung/evers/courses/2021/comp_nanoscience.phtml

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 tunneling 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.

 (b) Compute and plot the HOMO and the LUMO of pentacene. Paste screenshots of HOMO and LUMO to your solution pdf file. There is a video (5. Hartree-Fock: 5.7 Plotting Hartree-Fock molecular orbitals) with instructions how to plot molecular orbitals using the program vmd.

 Hint: Plot the isosurface of the HOMO and the LUMO at an appropriate value $\pm \psi_0$ (see as a reference value e. g. Fig. 3 in [1]). You can use the very small default basis sets in Turbomole (def-SVP) to minimize the computation time. In general, the spatial shape of the molecular orbitals is already converged with very small basis sets.

 (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?

 (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?

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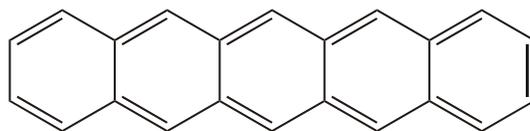
Figure 1: Molecular structure of pentacene. Carbon atoms are displayed, hydrogen atoms are not displayed (it is easiest if you enable automatic H atoms in avogadro; then you can just put the double bonds as drawn in this figure).

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.

   Hint: Relax the geometry towards the geometry with lowest Hartree-Fock energy using `jobex`. Enter `eiger` for displaying the eigenvalues of the last step in the geometry optimization.

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

   Hint: In order to perform a Hartree-Fock calculation for a charged molecule, choose the charge when you're asked '`Enter the charge of the molecule`' during the extended Hückel guess.

(c) Discuss: Why is the ionization potential of N_2 larger than the ionization potential of O_2?

(d) Discuss: Should the numerical values from (a) and (b) match according to Koopmans' theorem?

(e) Discuss: Which method, (a) or (b), do you consider more reliable for computing the ionization potential?

(f) Is method (b) also working for determining the ionization potential of a periodic system, for example an aluminum unit cell with periodic boundary conditions?