

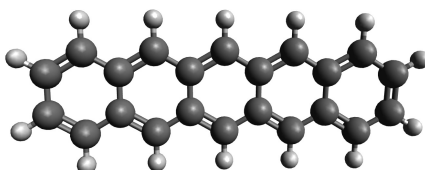
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<https://www.ur.de/physics/wilhelm/teaching/sose24-computational-nanoscience>

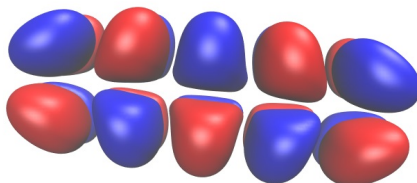
Computational Nanoscience: Solution to Exercise Sheet No. 5

Exercise 5.1: HOMO and LUMO of pentacene

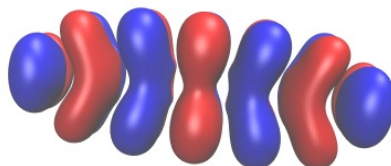
(a) A screenshot from Avogadro:



(b) A screenshot of the HOMO (isovalues $\pm 0.01 \text{ a.u.}^{-3/2}$, a.u.: atomic unit of length)



A screenshot of the LUMO (isovalues $\pm 0.01 \text{ a.u.}^{-3/2}$)



- (c) The HOMO has less nodal planes (6 nodal planes, 1 horizontal, 4 vertical and 1 in the plane of the atoms) than the LUMO (7 nodal planes). Therefore, we expect a higher kinetic energy for the LUMO and thus, a higher energy eigenvalue of the LUMO than the HOMO is expected. This principle is quite general for organic molecules with HOMO and LUMO π orbitals, see e.g. page 627 of Organic Chemistry by T. W. Graham Solomons, Craig B. Fryhle, Scott A. Snyder or <https://www.masterorganicchemistry.com/2017/05/05/the-pi-molecular-orbitals-of-benzene/>.
- (d) The discussions follows points from the lecture (arguments already have been given orally in the videos and will be repeated here).
- Do the molecular orbitals $\psi_n(\mathbf{r})$ from Hartree-Fock have any physical meaning? No.
 - What is the reason we nevertheless use them for a comparison to an experiment?

The closed-shell Hartree-Fock equations

$$\int F(\mathbf{r}, \mathbf{r}') \psi_n(\mathbf{r}') d\mathbf{r}' = \varepsilon_n \psi_n(\mathbf{r}), \quad (1)$$

$$F(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') \left(-\frac{\hbar^2}{2m} \nabla_{\mathbf{r}}^2 - \sum_A \frac{Z_A e^2}{|\mathbf{r} - \mathbf{R}_A|} + V_H(\mathbf{r}) \right) + V_x(\mathbf{r}, \mathbf{r}'), \quad (2)$$

$$V_H(\mathbf{r}) = 2e^2 \sum_{m=1}^{N/2} \int d^3\mathbf{r}' \frac{|\psi_m(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|}, \quad V_x(\mathbf{r}, \mathbf{r}') = -e^2 \sum_{m=1}^{N/2} \frac{\psi_m(\mathbf{r}) \psi_m(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (3)$$

are a Schrödinger type equation for a single electron in ‘some’ external potential

$$V_{\text{ext}}(\mathbf{r}, \mathbf{r}') = \left(-\sum_A \frac{Z_A e^2}{|\mathbf{r} - \mathbf{R}_A|} + V_H(\mathbf{r}) \right) \delta(\mathbf{r} - \mathbf{r}') + V_x(\mathbf{r}, \mathbf{r}') \quad (4)$$

of nuclei and other electrons (Hartree potential and exchange potential are not the exact potential caused by the other electrons!). Still the external potential $V_{\text{ext}}(\mathbf{r}, \mathbf{r}')$ from Hartree-Fock captures some of the most important physics, as the Coulomb interactions between an electron in a state $\psi_n(\mathbf{r})$ and the electron density (Hartree potential) and the atomic nuclei. Therefore, it is not surprising that eigenfunctions ψ_n from upper equations have the same shape as measurements from STM. (Still, a proper theoretical description and definition of single-electron wavefunctions is missing, we will do it in the *GW* chapter.)

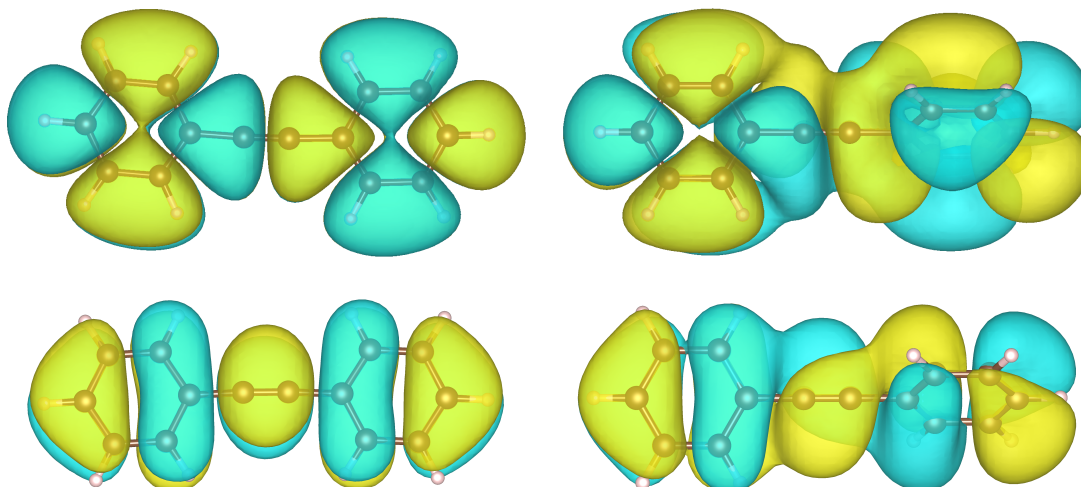
- Which contributions in the Hartree-Fock equations cause the spatial shape of the molecular orbitals? The kinetic energy and the external potential. Other contributions are rather smooth and do not influence the shape of $\psi_n(\mathbf{r})$ much.

Exercise 5.2: Helical Orbitals in Diphenylacetylene

- (a) The benzene rings tend to have orbitals above and below the plane of the ring. Therefore, we can expect that for planar geometry, when the planes of the two rings are aligned, the delocalisation of orbitals from one benzene ring into the other ring leads to a reduction in the energy of the electrons.

In the twisted geometry, such delocalisation requires deformation of the orbitals, which we can associate with increase in energy.

- (b) The molecular orbitals have the following structure



Left column : planar geometry, lowest unoccupied orbital on the top, highest occupied orbital on the bottom. Right column : Same as left column, but for twisted geometry.

- (c) In the images above, the HOMO orbital in the twisted geometry has rotation in clockwise direction (when looking from the centre of the triple bond to the left benzene ring), while the LUMO orbital has anti-clockwise direction.
- (d) In the case when the two benzene rings are perpendicular, we can expect that the orbital will be without helical rotation on the triple bond.

One way to rationalize this is by considering both the clockwise and anti-clockwise rotation in such geometry. Since the benzene rings are perfectly perpendicular, the system has mirror symmetry along the axis of the triple bond. Therefore, energy of the two rotating orbitals will be strictly identical, and so the symmetric orbital will be a combination of both, where no rotation is observed.