Calculation of the Molecular Orbitals of H2O by LCAO with Matlab

Student Project Mattia Moroder

1 Introduction

In this project the molecular orbitals of water are calculated by means of LCAO (Linear Combination of Atomic Orbitals). Documentation about LCAO can be found here and documentation about LCAO for H2O here.

2 The LCAO_H2O.m file

The *LCAO_H2O.m* file is divided into two main parts. In the first one, the eigenenergies and the eigenvectors (the coefficient vectors) of the molecular orbitals are computed. In the second one the atomic orbitals 1s, 2s, 2px, 2py, 2pz (of oxygen) and the calculated molecular orbitals are plotted in 3D.

2.1 Calculations

First of all, some atomic constants are defined. Then the atomic orbitals are defined at the positions of the two hydrogen atoms and the oxygen atom (taken from jmol). Cartesian coordinates are used. Successively the overlap matrix S is evaluated and printed.
For calculating the H matrix the strategy explained here is applied: the Hamilton Operator isn't directly applied on the orbital wavefunctions. Instead, it is decomposed in a hydrogen-like Hamiltonian part (for which the eigenenergies are well known) and a part containing only two potential terms. This facilitates calculations since the Laplacian hasn't to be calculated. Having S and H, we solve the eigenvalue problem $\hat{S}^{-1} \cdot \hat{H} \cdot \vec{c} = E \cdot \vec{c}$
where $\vec{c}$ is the coefficient vector telling how much every atomic orbital contributes to a molecular orbital and E is the corresponding energy.

2.2 Plots

For the plots, the atomic orbitals were redefined by setting the Bohr radius a_0 equal 1 because Matlab has some troubles when plotting very small vectors.
The 7 molecular orbitals are calculated by multiplying $\vec{c}$ with the atomic orbitals.
It is important to notice that for 3D plotting the variables x,y and z have to be three-dimensional arrays. Those are obtained with *meshgrid*. With *isosurface* the surface on which electrons are found with a certain probability is plotted. Two different colors are used for indicating the phase of the wave function. All figures can be rotated an zoomed.
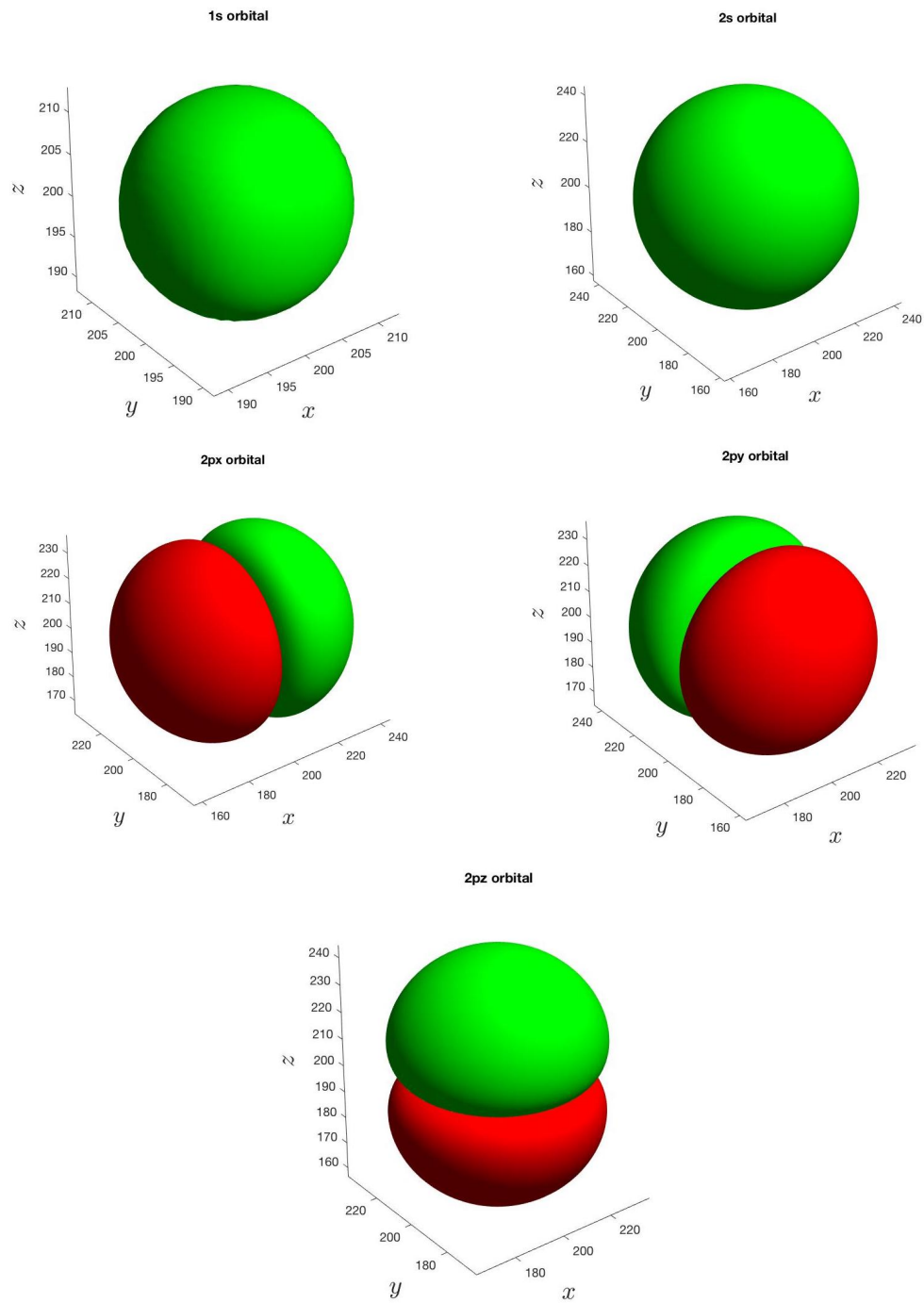
3 Results

3.1 Atomic Orbitals

Figure 1: Plots of the atomic orbitals used for the calculations

## 3.2 $\hat{S}$ and $\hat{H}$ Matrices

$$\hat{S} = \begin{pmatrix} 0.998 & 0.371 & 0.060 & -0.547 & 0.279 & 0.218 & 0 \\ 0.371 & 0.998 & 0.060 & -0.547 & -0.279 & 0.218 & 0 \\ 0.060 & 0.060 & 0.986 & 0.185 & 0 & 0 & 0 \\ -0.547 & -0.547 & 0.185 & 0.998 & 0 & 0 & 0 \\ 0.279 & -0.279 & 0 & 0 & 0.997 & 0 & 0 \\ 0.218 & 0.218 & 0 & 0 & 0 & 0.997 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

$$\hat{H} = 10^{-17} \cdot \begin{pmatrix} -1.510 & -0.742 & -6.182 & 3.278 & -1.524 & -1.461 & 0 \\ -0.803 & -1.347 & -6.182 & 3.278 & 1.524 & -1.461 & 0 \\ -3.598 & -3.588 & -107.869 & -3.287 & 0 & -0.094 & 0 \\ 0.333 & 0.243 & -20.456 & -6.567 & 0 & 0.255 & 0 \\ -0.197 & 0.152 & 0 & 0 & -4.920 & 0 & 0 \\ -0.602 & -0.567 & -0.094 & 0.255 & 0 & -7.188 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -7.095 \end{pmatrix}$$

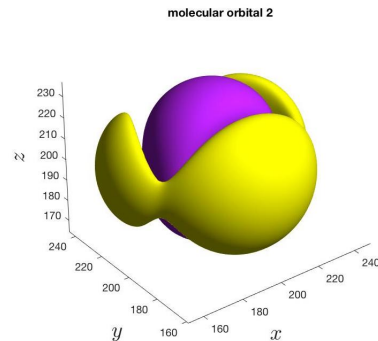## 3.3 Calulculated MOs and Comparison with TEXTBOOK VALUES

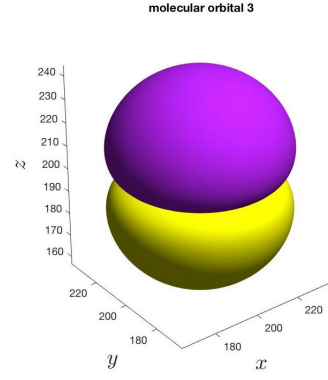$$\vec{c_1} = \begin{pmatrix} -0.0035 \\ -0.0035 \\ 1 \\ -0.0019 \\ 0 \\ 0.0025 \\ 0 \end{pmatrix} \qquad E_1 = -6384 eV \tag{1}$$

molecular orbital 1
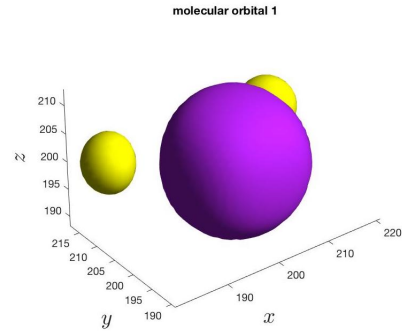
$$\vec{c_2} = \begin{pmatrix} -0.0603 \\ -0.0588 \\ 0.0112 \\ -0.4854 \\ 0.0001 \\ 0.8702 \\ 0 \end{pmatrix} \qquad E_2 = -468.1132 eV \tag{2}$$
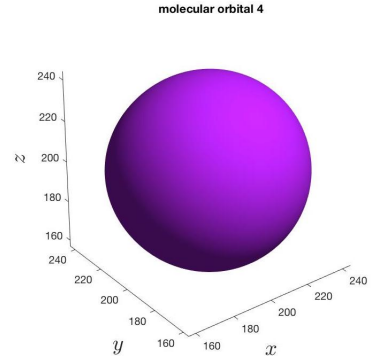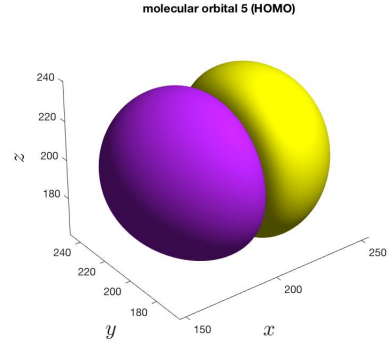

molecular orbital 2

$$\vec{c_3} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0.0009 \\ 1 \end{pmatrix} \qquad E_3 = -443.1471 eV$$
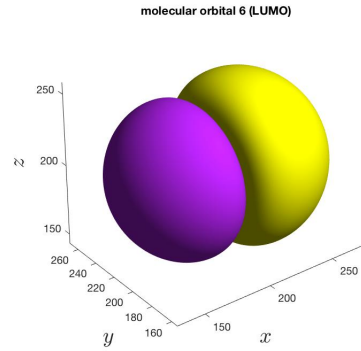

molecular orbital 3

$$\tag{3}$$

$$\vec{c_4} = \begin{pmatrix} -0.0085 \\ -0.0082 \\ -0.0204 \\ 0.9775 \\ 0 \\ 0.2095 \\ 0 \end{pmatrix} \qquad E_4 = -380.7321 eV$$

molecular orbital 4

$$\tag{4}$$
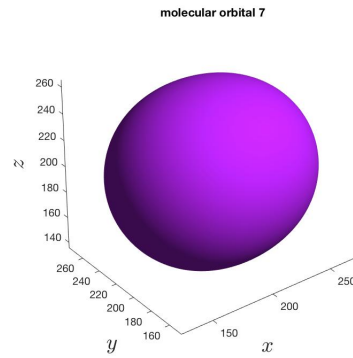
$$\vec{c_5} = \begin{pmatrix} -0.0889 \\ 0.0853 \\ 0.0002 \\ -0.0013 \\ -0.9924 \\ 0.0005 \\ 0 \end{pmatrix} \qquad E_5 = -293.3509 eV$$

molecular orbital 5 (HOMO)

$$\tag{5}$$

$$\vec{c_6} = \begin{pmatrix} -0.8115 \\ 0.5803 \\ 0.0084 \\ -0.0263 \\ -0.0616 \\ 0.0152 \\ 0 \end{pmatrix} \qquad E_6 = -74.8981 eV$$

molecular orbital 6 (LUMO)

$$\tag{6}$$

$$\vec{c_7} = \begin{pmatrix} 0.5733 \\ 0.8009 \\ -0.0496 \\ 0.1427 \\ -0.0088 \\ -0.0839 \\ 0 \end{pmatrix} \qquad E_7 = -43.6906 eV$$

molecular orbital 7

$$(7)$$

4 Remarks and advice for using the program

I have not been able to find another work in which the molecular orbitals of water are calculated by LCAO using the 7 atomic orbitals I used. In this work, where the Hartree-Fock method is applied, many molecular orbitals have the same shape as those that I have computed, but their energies are different. This is also true when comparing my results to those of Michael Stadlhofer's student project. The one thing those three works have in common is the very large energy spacing between E_1 and E_2.

The program takes about 25 minutes to make the calculations and the plots (on a MacBook Pro). Speed can be increased by lowering the *accuracy* for the plot (line 145). Making *minval* smaller (line 15) increases the accuracy of the calculations along with the computing time and if it becomes too small the integrals tend to diverge.