HW2_Gabriel

February 19, 2017

1 Homework 2 - Hückel Theory and Argus Lab

Gabriel Fior - 03642356

In this homework, we had to do the following: 1. Calculate energy levels of HOMO/LUMO levels 2. Determine HOMO/LUMO wavefunctions and their electron density (and plot them) 3. Compare results with ArgusLab

```
In [27]: import numpy as np
         import matplotlib.pyplot as plt
         import os
         %matplotlib inline
```

```
In [99]: alpha=-6.6 #eV
         beta=-2.7 #eV
         N= 10 #available e- in naphthalene
```

Here we determine the Hamiltonian of the system, defined by:

$$
\begin{align}
H_{ij} = \alpha \quad & \text{if } i = j \tag{1}\\
H_{ij} = \beta \quad & \text{if i and j are next neighbors} \tag{2}\\
H_{ij} = 0 \quad & \text{otherwise} \tag{3}\\
& \tag{4}
\end{align}
$$

```
In [47]: # determine hamiltonian => alpha if i=j, beta if first neighbours, 0 otherwise
         H = np.zeros((N,N))
         for i in range(N):
             for j in range(N):
                 if i==j:
                     H[i,j] = alpha
                 elif j==(i-1) or j==(i+1):
                     H[i,j] = beta

         #additional neighbors, according to image from homework 1
         #C5 neighbor of C10 and vice-versa
         H[4,-1]  = beta
         H[-1,0] = beta
         H[-1,4] = beta
         H[0,-1] = beta
         print H
```

```
[[-6.6 -2.7  0.   0.   0.   0.   0.   0.   0.  -2.7]
 [-2.7 -6.6 -2.7  0.   0.   0.   0.   0.   0.   0. ]
 [ 0.  -2.7 -6.6 -2.7  0.   0.   0.   0.   0.   0. ]
 [ 0.   0.  -2.7 -6.6 -2.7  0.   0.   0.   0.   0. ]
 [ 0.   0.   0.  -2.7 -6.6 -2.7  0.   0.   0.  -2.7]
 [ 0.   0.   0.   0.  -2.7 -6.6 -2.7  0.   0.   0. ]
 [ 0.   0.   0.   0.   0.  -2.7 -6.6 -2.7  0.   0. ]
 [ 0.   0.   0.   0.   0.   0.  -2.7 -6.6 -2.7  0. ]
 [ 0.   0.   0.   0.   0.   0.   0.  -2.7 -6.6 -2.7]
 [-2.7  0.   0.   0.  -2.7  0.   0.   0.  -2.7 -6.6]]
```

Below we calculate the eigenvalues and eigenvectors of the hamiltonian in order to get the energies and the corresponding wave functions (molecular orbitals) as coefficients ck (coeff_k)

```
In [104]: Ek, coeff_k = np.linalg.eig(H)  # c_ik eigenvectors, E_k their eigenvalues

          indices_sorted = np.argsort(Ek) #sort in ascending energies
          Ek.sort()

          sorted_coeff_k = coeff_k[indices_sorted]
          print 'energies sorted: ' + str(Ek)
```

```
energies sorted: [-12.81749422 -10.96869177 -10.11749422  -9.3         -8.26869177
  -4.93130823  -3.9         -3.08250578  -2.23130823  -0.38250578]
```

Since we have 10 available electrons, we can fill up until the 5th orbital. We have the 1s2, 2s2 and 2p6 totally filled. Therefore, our top most filled level (HOMO) is the 5th level (Ek[4]) and our lowest unnocupied level (LUMO) is the 6th level (Ek[5])

```
In [108]: E_gap = Ek[np.int(N/2)] - Ek[np.int(N/2 - 1)]
          print 'Egap : ' +str(E_gap)+' eV'
```

```
Egap : 3.33738353925 eV
```

2 Calculate wave functions

From the website http://winter.group.shef.ac.uk/orbitron/AOs/1s/equations.html, we have that the wave functions for the 2pz orbital can be constructed as follows

$$\phi_s = R_{1_s} Y_{1_s} = \frac{1}{2\sqrt{6}} \rho Z^{3/2} \exp(-\rho/2))(\frac{\sqrt{3} * z/r}{\sqrt{4\pi}}) \tag{5}$$

and the electron density is given by

$$n = \phi_{1_s}^2 \tag{6}$$

```
In [109]: #Calculate wave function
          def wavefunction(x,y,z):

              Z_eff = 3.136 #orbital specific, got a mean number for Carbon from wikipedia
              n = 2 #2p orbitals
              r = np.sqrt(x**2 + y**2 + z**2) #radial coordinate
              rho = 2*Z_eff*r/n / 52.9 #conversion between Bohr radius and atomic units
              R = 1./(2.*np.sqrt(6))*rho*Z_eff**(1.5)*np.exp(-rho/2)
              Y = np.sqrt(3)*z/r /np.sqrt(4.*np.pi)
              Psi_pz = R * Y

              return Psi_pz
```

Below we initialize the xy grid where the wavefunctions are going to be defined, and also the molecule is localized.

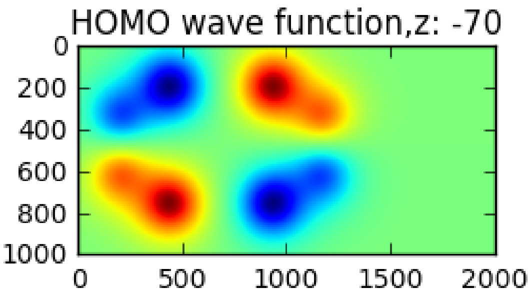
```
In [110]: width = 1000
          length = 500
          step = 0.5

          gridX = np.arange(0,width,step)
          gridY = np.arange(0,length,step)
          x,y = np.meshgrid(gridX,gridY,sparse = True)

          N = 10 #number of atoms

          r = np.zeros((N,2)) #holds [x,y] position of each atom

          d = 140
          h = 0.5*d
          w = np.sqrt(3)*0.5*d

          #positions of atoms in molecule
          r[0] = [w, 2*h+d]
          r[1] = [0,h+d]
          r[2] = [0,h]
          r[3] = [w,0]
          r[4] = [2*w,h]
          r[5] = [3*w,0]
          r[6] = [4*w,h]
          r[7] = [4*w,h+d]
          r[8] = [3*w,2*h+d]
          r[9] = [2*w,h+d]
```

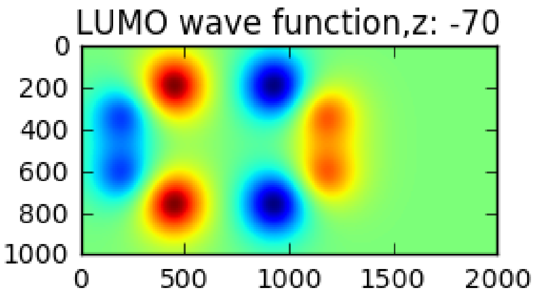
```
         #we recenter the molecule so that the image is better localized in the grid and the pl
         r[:,0] += 100
         r[:,1] += 100
```

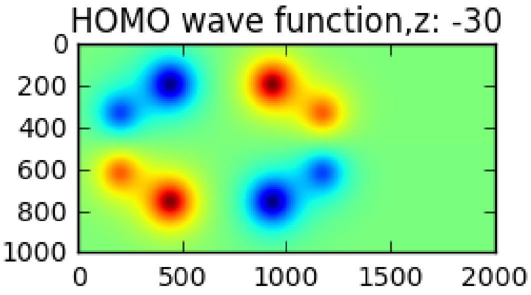
```
In [166]: rho = np.zeros((length/step,width/step))
          #list_energies = []
          list_z=[]
          list_rhos=[]

          for z in (-70,-30,1,10,50,80,100):
              list_energies=[]
              rho = np.zeros((length/step,width/step))
              for E in range(6):

                  Psi_k = np.zeros((length/step,width/step))

                  for n in range(N):

                      xnew = x - r[n,0]
                      ynew = y - r[n,1]
                      Psi_k += coeff_k[n,indices_sorted[E]] * wavefunction(xnew, ynew, z)

                  #if E <= 5:
                  rho += 2 * (Psi_k)**2

                  list_energies.append([z,E,Psi_k])
              list_z.append([z,list_energies])
              list_rhos.append(rho)
```

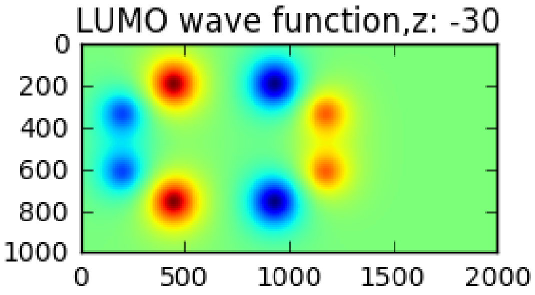
```
/Users/gabrielfior/anaconda/lib/python2.7/site-packages/ipykernel/__main__.py:1: VisibleDeprecat
  if __name__ == '__main__':
/Users/gabrielfior/anaconda/lib/python2.7/site-packages/ipykernel/__main__.py:8: VisibleDeprecat
/Users/gabrielfior/anaconda/lib/python2.7/site-packages/ipykernel/__main__.py:11: VisibleDepreca
```

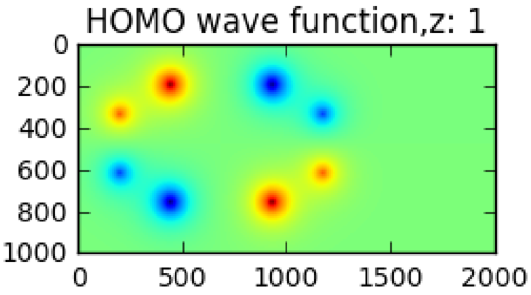
```
In [167]: #list_energies
          for i in range(len(list_z)):
              plt.figure(i)

              plt.subplot(121)
              plt.imshow(list_z[i][1][-2][2])
              plt.title('HOMO wave function,z: '+str(list_z[i][1][-2][0]))
              plt.subplot(122)
              plt.imshow(list_z[i][1][-1][2])
              plt.title('LUMO wave function,z: '+str(list_z[i][1][-2][0]))
              plt.tight_layout()
              plt.show()
          #print len(list_z[0][1][-1])
```

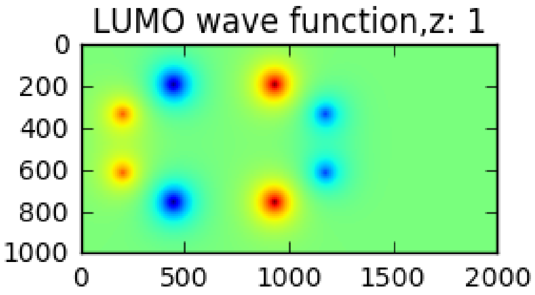

HOMO wave function,z: -70
0
200
400
600
800
1000
0
500
1000
1500
2000

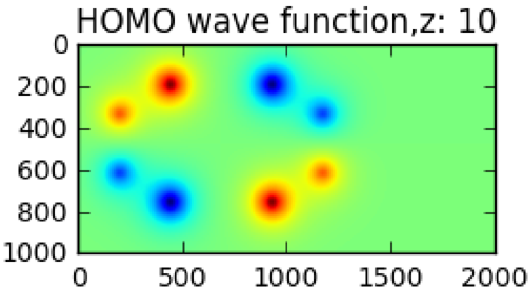

LUMO wave function,z: -70
0
200
400
600
800
1000
0
500
1000
1500
2000

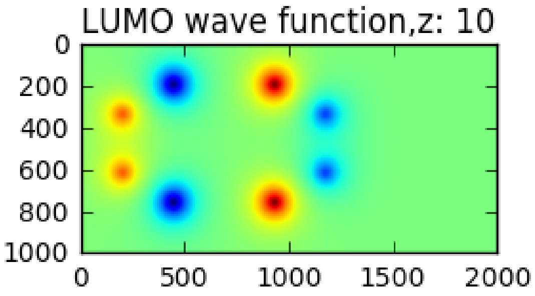

HOMO wave function,z: -30
0
200
400
600
800
1000
0
500
1000
1500
2000

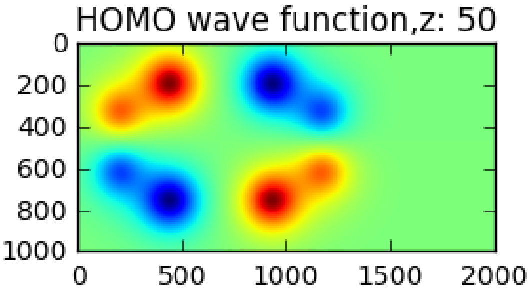

LUMO wave function,z: -30
0
200
400
600
800
1000
0
500
1000
1500
2000

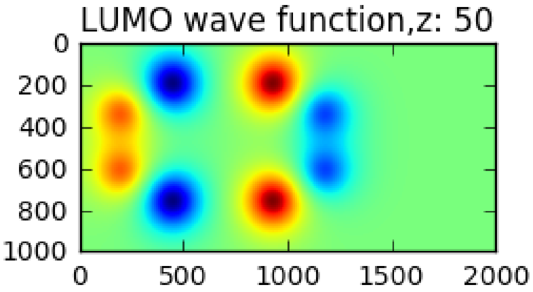

HOMO wave function,z: 1
0
200
400
600
800
1000
0
500
1000
1500
2000

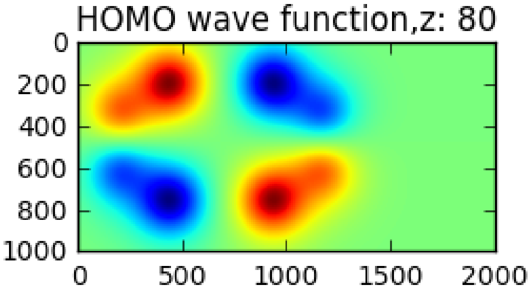

LUMO wave function,z: 1
0
200
400
600
800
1000
0
500
1000
1500
2000

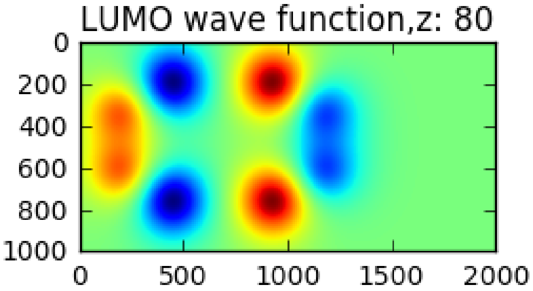

HOMO wave function,z: 10
0
200
400
600
800
1000
0
500
1000
1500
2000

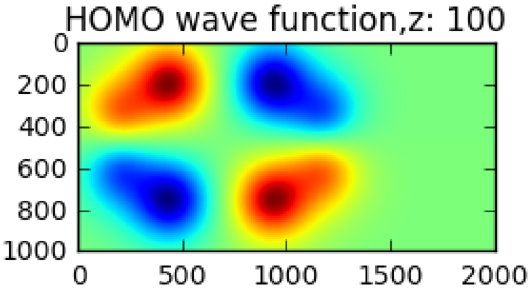

LUMO wave function,z: 10
0
200
400
600
800
1000
0
500
1000
1500
2000

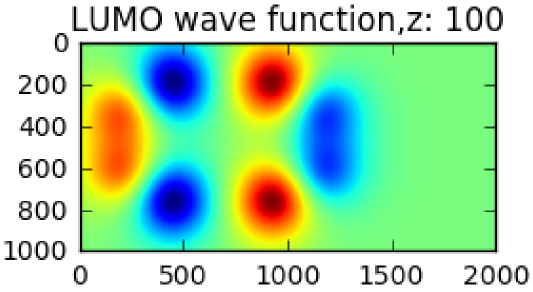










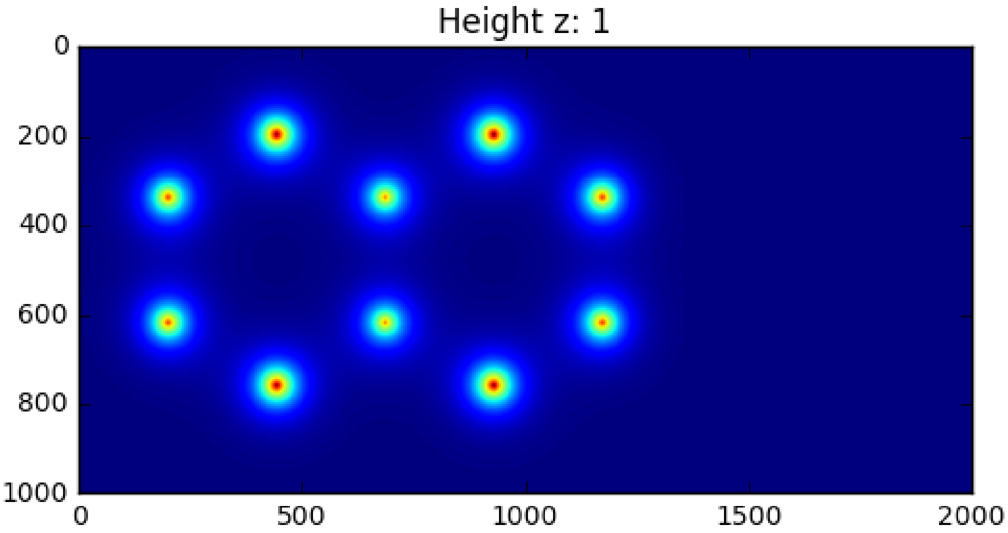


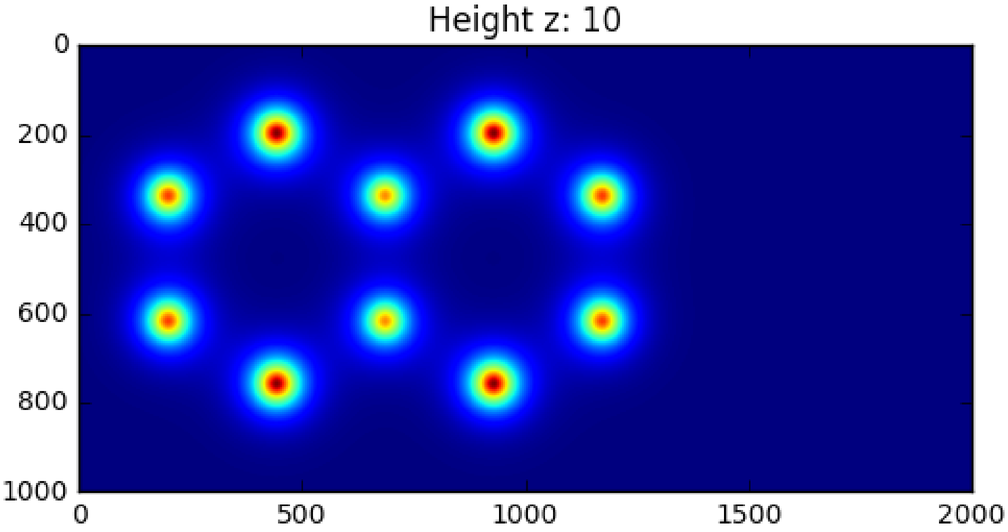
In the images above, one can notice that, for the low heights z (1,10) the atom positions can be directly noticed. As the height increases, the wave function get smeared out.

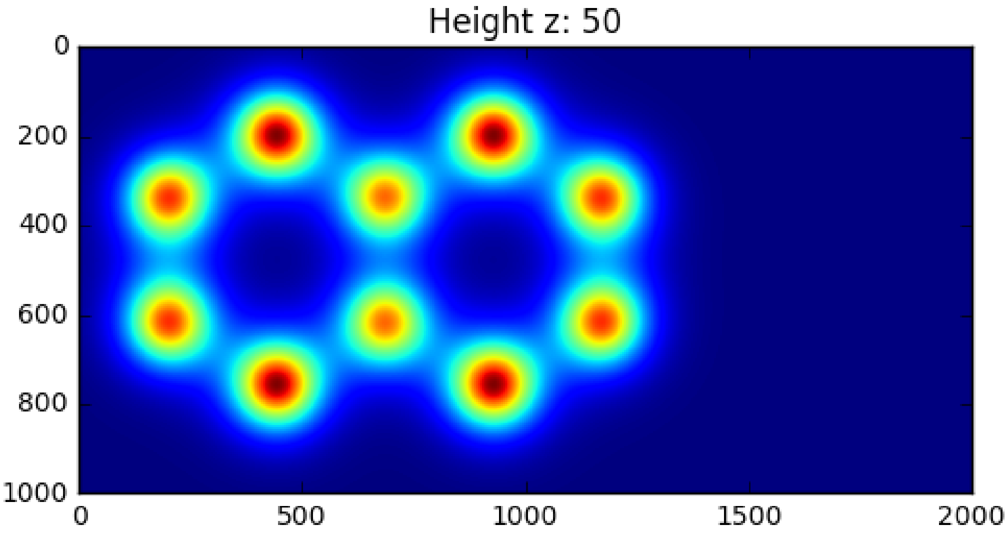
Below I plot the electron charge density ρ, which was obtained by summing up the absolute value of the wave function up to the HOMO level.

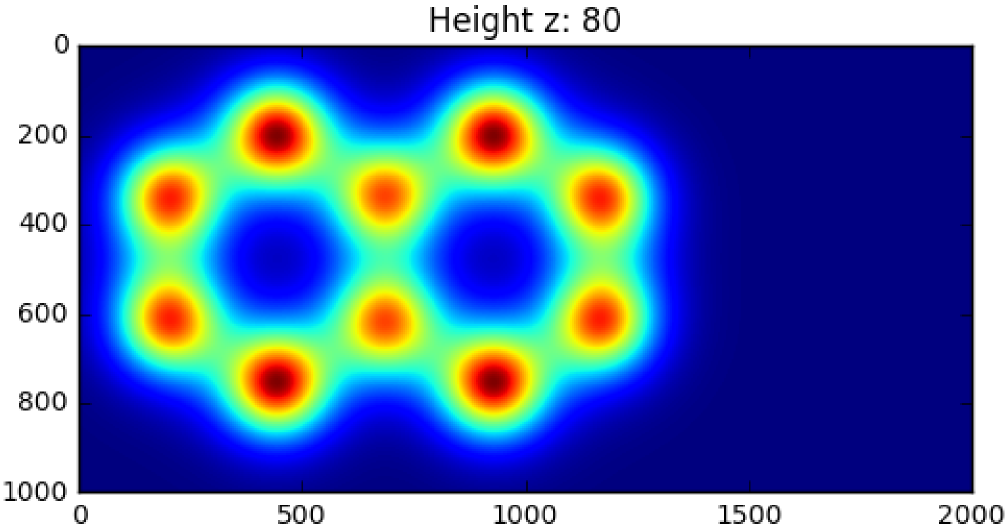
```
In [165]: print len(list_rhos)
          for i,j in zip(range(len(list_rhos)),(1,10,50,80,100)):
              plt.imshow(list_rhos[i])
              plt.title('Height z: '+str(j))
              plt.show()
```

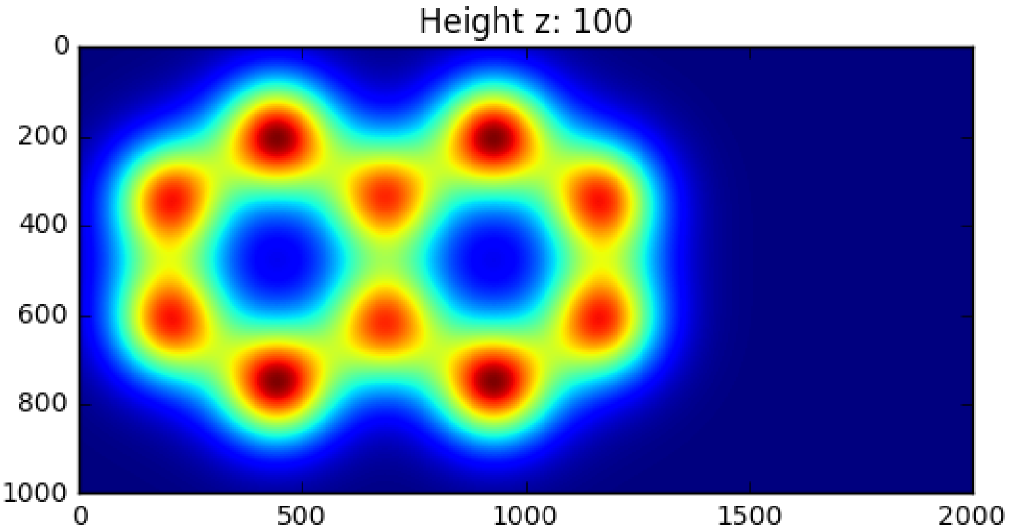
5


Height z: 1
0
200
400
600
800
1000
0
500
1000
1500
2000


Height z: 10
0
200
400
600
800
1000
0
500
1000
1500
2000


Height z: 50
0
200
400
600
800
1000
0
500
1000
1500
2000


Height z: 80
0
200
400
600
800
1000
0
500
1000
1500
2000



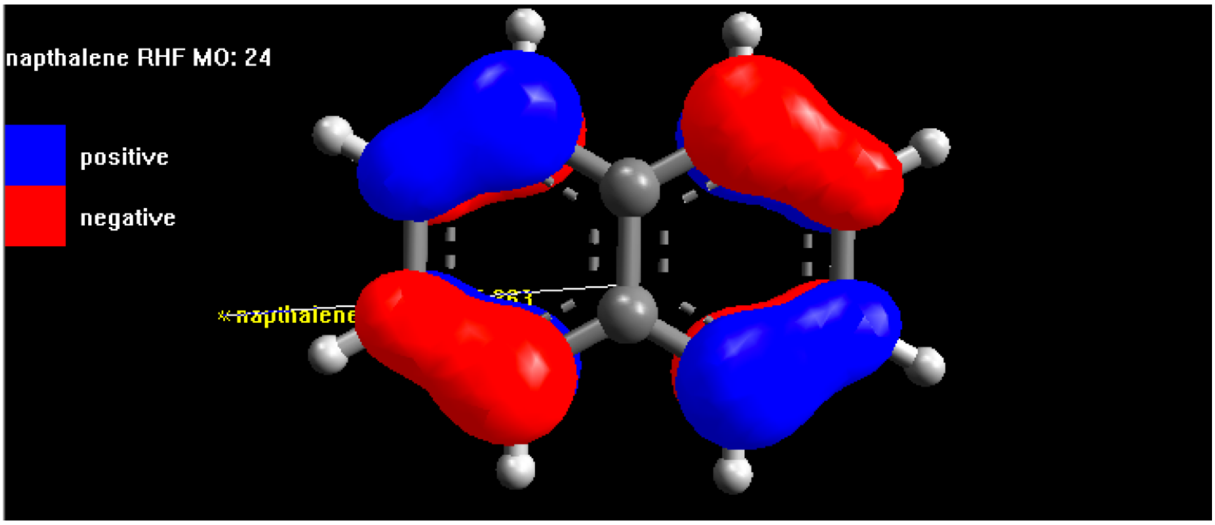
The final step is to compare my results with ArgusLab. As can be seen in the images below, the plots of the HOMO/LUMO orbitals agree very well, specially if you see that in both calculations the sign of the wave function changes (going from blue to red, when z goes from a negative value to a positive value), and vice-versa.

LUMO orbital calculated for Naphtalene by Argus

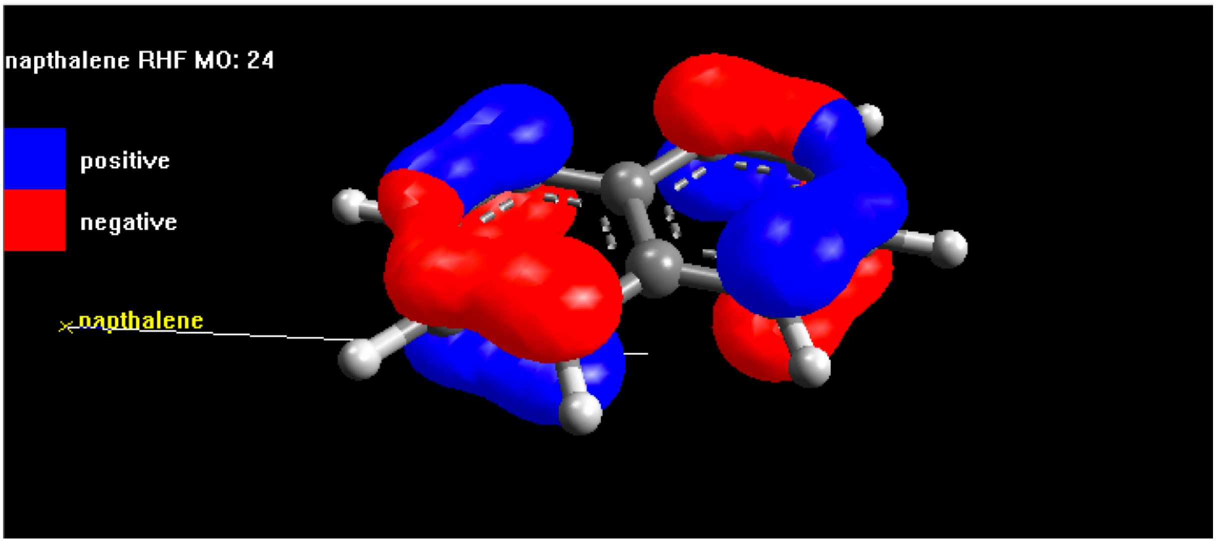
HOMO orbital calculated for Naphtalene by Argus

```
In [ ]:
```

HOMO


napthalene RHF MO: 24
positive
negative
napthalene

LUMO


napthalene RHF MO: 24
positive
negative
napthalene