He_atom

October 3, 2022

1 Using He_2^4 atom to Demostrate Hartree-Fock SCF Method

1.1 Expectation value for neutral Helium atom; He_2^4

$$\langle\Psi|\hat{H}|\Psi\rangle = 2\langle\psi|\hat{h}|\psi\rangle + \langle\psi\psi|\hat{V}_{12}|\psi\psi\rangle$$

1.2 Hartree-Fock energy:

$$E^{HF} = min_{\Psi}\langle\Psi|\hat{H}|\Psi\rangle$$

- Reference:

  Am. J. Phys. 2021, 89, 426. "A first encounter with the Hartree-Fock self-consistent-field method"

1.2.1 Pseudo-code:

1. Import libraries
2. Parameters setting
3. Main part: HF-SCF iteration
4. Plot results

[80]:
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# 1. Import libraries

import numpy as np
import matplotlib.pyplot as plt
%matplotlib inline
```

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# 2. Parameters setting

# Atomic number, i.e. the number of protons in the nucleus of an atom
Z = 2

# Number of SCF itrations
num_iter = 20

# Parameters from Table 1
#  two orbital energies
eps_1 = - (Z ** 2) / 2
eps_2 = - (Z ** 2) / 8
#  Cloulomb and Exchange integrals
I_1111 = (5/8) * Z
I_1112 = (2**12 / 7**4) * (np.sqrt(2) / 27) * Z
I_1122 = (16 / 9**3) * Z
I_1212 = (17 / 3**4) * Z
I_1222 = (2**9 / 5**5) * (np.sqrt(2)/27) * Z
I_2222 = (77/2**9) * Z
```

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# 3. Main part: HF-SCF iteration

# Initialization of the HF SCF procedure:
theta = 0
f_theta = []
f_theta.append([0, theta])

f_total_energy = []
f_orbital_energy = []

# Loop for carrying out the iterative SCF procedure:
for i in range(num_iter):
    c_1 = np.cos(theta) # Eq.(16)
    c_2 = np.sin(theta) # Eq.(17)
    # print(c_1,c_2)

    # Calculation of the two-electron energy [Eq.(13)]:
    total_energy = 2 * ( eps_1 * c_1**2 + eps_2 * c_2**2 ) \
    + I_1111 * c_1**4 + 4 * I_1112 * c_1**3 * c_2 \
    + 2 * ( 2 * I_1122 + I_1212) * c_1**2 * c_2**2 \
    + 4 * I_1222 * c_1 * c_2**3 \
    + I_2222 * c_2**4
    f_total_energy.append([i,total_energy])

    # Calculation of the matrix elements of the Fock matrix:
    # Eq.(23)
    F_11 = eps_1 + I_1111 * c_1**2 \
    + 2 * I_1112 * c_1 * c_2 + I_1212 * c_2**2
    # Eq.(24)
    F_12 = I_1112 * c_1**2 + 2 * I_1122 * c_1*c_2 \
    + I_1222 * c_2**2
    # Eq.(25)
    F_21 = F_12
    # Eq.(26)
    F_22 = eps_2 + I_1212 * c_1**2 \
    + 2 * I_1222 * c_1 * c_2 + I_2222 * c_2**2
    '''
        Calculation of the lower of the two roots of the characteristic␣
↪polynomial of the Fock matrix, using the quadratic formula:
    '''
    orbital_energy = 0.5*(F_11 + F_22) \
    - np.sqrt( 0.25*(F_11 - F_22)**2 + F_12**2 )
    f_orbital_energy.append([i+1, orbital_energy])

    '''
        For a given Fock matrix and orbital energy, Eq.(22) corresponds to a␣
↪simple linear system for c_1 and c_2. By analytically solving this system,␣
↪an explicit expression for the polar angle theta is obtained. This␣
↪expression is used in the following for updating theta:
    '''
    theta = np.arctan ((orbital_energy - F_11)/F_12)
    f_theta.append([i+1, theta])

# Change variable datatype in order to plot figures
f_theta = np.array(f_theta)
f_total_energy = np.array(f_total_energy)
f_orbital_energy = np.array(f_orbital_energy)

# Relationship between total energy and theta
f_theta_E = np.array([
    f_theta[0:len(f_theta) - 1, 1] ,
    f_total_energy[:,1]
    ])
f_theta_E = np.transpose(f_theta_E)
f_theta_E = f_theta_E[f_theta_E[:,0].argsort()]
```

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# 4. Plot result
fig, ax = plt.subplots(2,2, figsize=(10,10))

ax[0, 0].plot(f_theta[0:10,0],f_theta[0:10,1],'k',marker='o')
ax[0, 1].plot(f_total_energy[:,0],f_total_energy[:,1],'k',marker='o')
ax[1, 0].plot(f_orbital_energy[:,0],f_orbital_energy[:,1],'k',marker='o')
ax[1, 1].plot(f_theta_E[:,0],f_theta_E[:,1],'k',marker='o')

ax[0, 0].set_title('theta')
ax[0, 1].set_title('total energy')
ax[1, 0].set_title('orbital energy')
ax[1, 1].set_title('Total energy vs. theta')

ax[0, 0].set_xlabel('Iteration number')
ax[0, 1].set_xlabel('Iteration number')
ax[1, 0].set_xlabel('Iteration number')
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ax[1, 1].set_xlabel('rad')

ax[0, 0].set_ylabel('rad')

ax[0, 1].set_ylabel('Eh')
ax[1, 0].set_ylabel('Eh')
ax[1, 1].set_ylabel('Eh')

# save figure for different tests
PATH = '../aux/'
name = 'Z2'
fig.savefig(PATH + name + '.png')
```

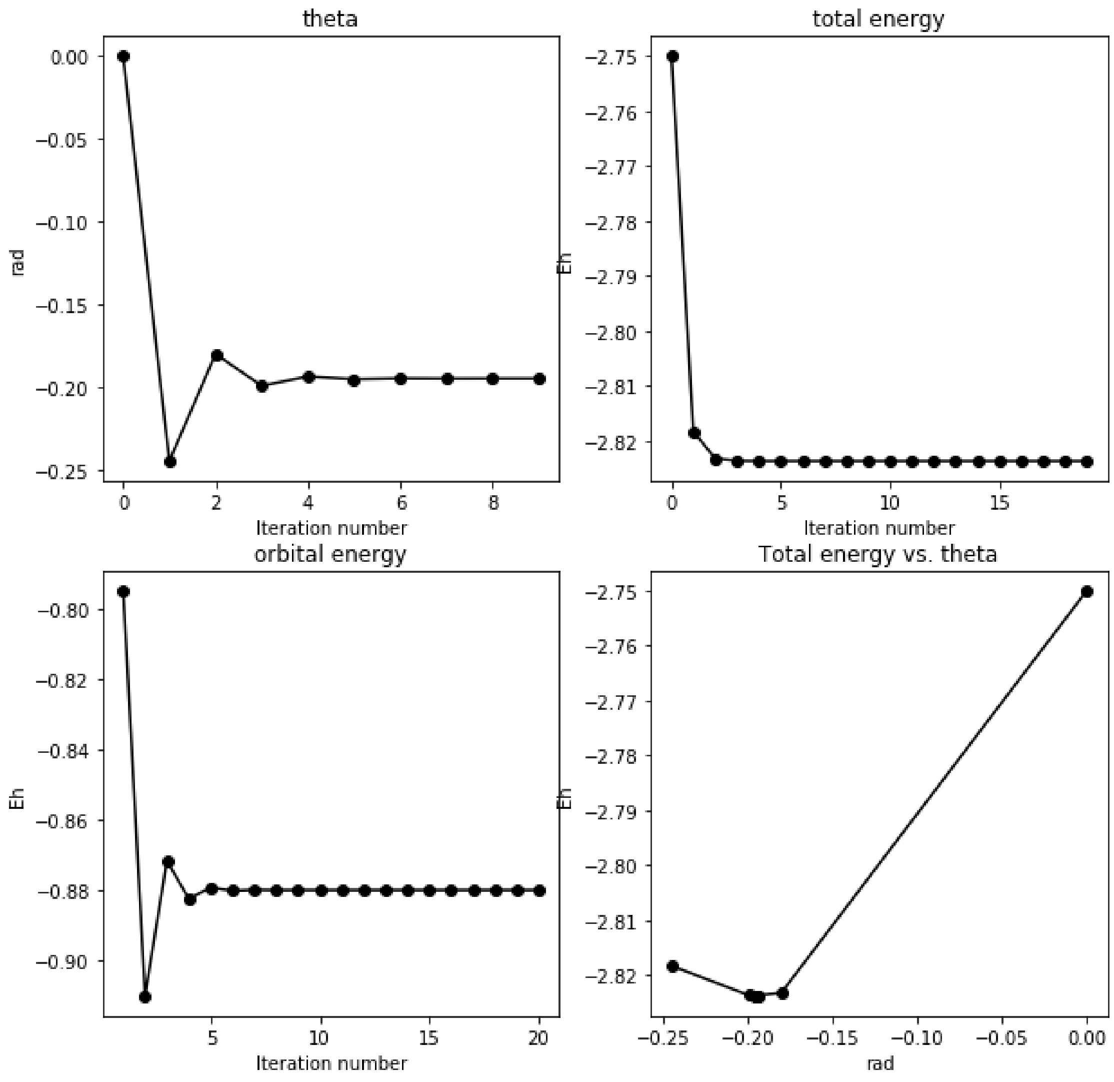
theta
rad
Iteration number
total energy
Eh
Iteration number
orbital energy
Eh
Iteration number
Total energy vs. theta
Eh
rad