European J of Physics Education Volume 5 Issue 1 2014 Acosta, Tapia, Cab

Restricted Closed Shell Hartree Fock Roothaan Matrix Method Applied to Helium Atom using Mathematica

César R. Acosta[1]*
J. Alejandro Tapia[1]
César Cab[1]

[1]Av. Industrias no Contaminantes por anillo periférico Norte S/N
Apdo Postal 150 Cordemex
Physics Engineering Department
Universidad Autónoma de Yucatán

**crenan@uady.mx*

(Received: 20.12. 2013, Accepted: 13.02.2014)

Abstract
Slater type orbitals were used to construct the overlap and the Hamiltonian core matrices; we also found the values of the bi-electron repulsion integrals. The Hartree Fock Roothaan approximation process starts with setting an initial guess value for the elements of the density matrix; with these matrices we constructed the initial Fock matrix. The Mathematica software was used to program the matrix diagonalization process from the overlap and Hamiltonian core matrices and to make the recursion loop of the density matrix. Finally we obtained a value for the ground state energy of helium.

Keywords: STO, Hartree Fock Roothaan approximation, spin orbital, ground state energy.

Introduction

The Hartree Fock method (Hartree, 1957) also known as Self Consistent Field (SCF) could be made with two types of spin orbital functions, the Slater Type Orbitals (STO) and the Gaussian Type Orbital (GTO), the election is made in function of the integrals of spin orbitals implicated. We used the STO to construct the wave function associated to the helium atom electrons. The application of the quantum mechanical theory was performed using a numerical method known as the finite element method, this gives the possibility to use the computer for programming the calculations quickly and efficiently (Becker, 1988; Brenner, 2008; Thomee, 2003; Reddy, 2004).

It is known that the effects of electron spin produces an antisymmetric wave function and that the charge of the nuclei is screened by the other electrons, then the effective charge that affect the interactions electron-nuclei and electron-electron is ζ, all of this effects are considered on the Hartree Fock Roothaan approximation. Dealing with Restricted Closed shell approximations means that we are considering only an even number of electrons, with all electrons paired such that $n=N/2$ spatial orbitals are doubly occupied (Szabo, 1996; Levine, 2008; Bransden, 2003).

Hartree Fock Roothaan equations

The initial point of view of this approach is the independent particle model, according to which each electron moves in an effective potential which takes into account the attraction of the nucleus and the average effect of the repulsive interaction due to the others electrons and their spin (Hartree, 1957; Rosetti, 1974; Szabo, 1996; Levine, 2008; Bransden, 2003).

The general procedure for finding a wave function of order zero (ground state) of a set of electrons, is to multiply the hydrogen-like wave function of each one electron

$$\psi^{(0)} = f_1(r_1,\theta_1,\varphi_1)\, f_2(r_2,\theta_2,\varphi_2)\cdots f_n(r_n,\theta_n,\varphi_n)$$

Where the hydrogen-like orbitals are

$$f = R_{nl}(r)\,Y_l^m(\theta,\varphi)$$

Where $R_{nl}(r)$ is the radial function and $Y_l^m(\theta,\varphi)$ are spherical harmonics. This wave function has total nuclear charge Ze, with Z number of protons and e the charge of an electron.

Each electron in a many electron system is described by its own wave function (Bransden, 2003). According with this approach the trial wave function of the *N*-electrons is a Slater determinant Φ, which is a function of spatial orbitals and spin states. The central modification made at this point is to assume that an electron in a multi-electron atom not perceive the whole nuclear charge, as this is partially shielded by the other electrons. Therefore it is proposed an antisymmetric wave function of the form (Szabo, 1996; Levine, 2008; Bransden, 2003)

$$\Phi_H = g_1(r_1,\theta_1,\varphi_1)\, g_2(r_2,\theta_2,\varphi_2)\cdots g_n(r_n,\theta_n,\varphi_n)$$

Where g_n represent the spin orbital, but now depends of shielded nucleus charge ζ, which can be expressed as a Linear combination of Atomic Orbitals (LCAO), depending on the base functions (χ) as follows

$$g_n = \sum_{i=1} c_i \chi_i \tag{1}$$

Where the base function χ are a complete set of Slater Type Orbitals (STO), which is defined in atomic units as

$$\chi = \frac{(2\zeta)^{n+\frac{1}{2}}}{\left[(2n)!\right]^{\frac{1}{2}}} r^{n-1} e^{-\zeta r} Y_l^m(\theta,\phi) \tag{2}$$

in this STO n represents the principal quantum number of the electron orbital for which the function χ is defined, and ζ is an effective electron charge (Rosetti, 1974).

The Hartree-Fock-Roothaan equations based on the STO functions are

$$F_{rs} = H_{rs}^{core} + \sum_{t=1}^{b}\sum_{u=1}^{b} P_{tu}\left[\langle rs|tu\rangle - \frac{1}{2}\langle ru|ts\rangle\right] \tag{3}$$

in equation (3) F_{rs} represents a general element of the Fock Matrix, $\langle rs|tu\rangle$ are the electronic repulsion integrals and P_{tu} are the elements of the density matrix, that are written as

$$P_{tu} = 2\sum_{j=1}^{n/2} c_{tj}^{*} c_{uj} \quad ; \quad t = 1, 2, \ldots, b \quad ; \quad u = 1, 2, \ldots, b \tag{4}$$

electronic repulsion due to the charge and spin of the electrons expressed in the spin orbital χ are given by the integrals

$$\langle rs|tu\rangle = \iint \frac{\chi_r^*(1)\chi_s(1)\chi_t^*(2)\chi_u(2)}{r_{12}} d\tau_1 d\tau_2 \tag{5}$$

These integrals represent the expected value of the interaction $1/r_{12}$ relative to the state $\chi_r(i)\chi_s(j)$ such that the electron *i* is in spin-orbital χ_r and the electron *j* is in spin-orbital χ_s. The H_{rs}^{core} are the elements of the Hamiltonian operator that are given by

$$H_{rs}^{core} = \langle \chi_r(1)|\hat{H}^{core}|\chi_s(1)\rangle \tag{6}$$

Where the Hamiltonian operator written in function of the screened charge ζ is

$$\hat{H}^{core} = -\frac{1}{2}\nabla^2 - \frac{Z}{r} \tag{7}$$

The Roothaan eigenvalue equation is then expressed as

$$\sum_{s=1}^{b} c_{si}\left(F_{rs} - \varepsilon_i S_{rs}\right) = 0 \quad \Rightarrow \quad Determinant\left(F_{rs} - \varepsilon_i S_{rs}\right) = 0 \tag{8}$$

Finally the elements of the overlapping matrix are the integrals given by

$$S_{rs} = \langle \chi_r|\chi_s\rangle = \int \chi_r^*(r,\theta,\varphi)\chi_s(r,\theta,\varphi)d\tau \tag{9}$$

Integral evaluation

There are two kinds of integrals, the one-electron as are the overlapping integral S_{rs} and the Hamiltonian core H_{rs}^{core}, and the two-electron given by the electron repulsion integral $\langle rs|tu\rangle$, each one has different treatment.

For the one-electron integrals, we used the formula shown below, that can be obtained integrating by parts

$$\int_0^\infty x^b e^{-qx} dx = \frac{b!}{q^{b+1}} \tag{10}$$

and for two-electron integral we used (10) and additionally these two ones

$$\int x^2 e^{-bx} dx = -e^{-bx}\left(\frac{x^2}{b}+\frac{2x}{b^2}+\frac{2}{b^3}\right) \tag{11}$$

$$\int x e^{-bx} dx = -\frac{e^{-bx}}{b^2}(bx+1) \tag{12}$$

Since in the application of equation (5) to the spin orbital of two electrons recursively we have the integral that is shown below

$$A = \int_0^\infty e^{-ar_1} r_1^2 dr_1 \int_0^\infty \frac{e^{-br_2}}{r_{12}} r_2^2 dr_2 \tag{13}$$

This integral can be transformed to an evaluation formula as is described next.

We know that r_{12} represents the distance between the two electrons and that dr_2 is the differential radial in the space of the electron 2, then we have

$$A = \int_0^\infty e^{-ar_1} r_1^2 dr_1 B \tag{14}$$

Where B is given by

$$B = \left[\frac{1}{r_1}\int_0^{r_1} r_2^2 e^{-br_2} dr_2 + \int_{r_1}^\infty r_2 e^{-br_2} dr_2\right]$$

Then applying (\ref{11}) to the first part of B and (12) to the second part, we have

$$B = \frac{2}{b^3 r_1} - e^{-br_1}\left(\frac{1}{b^2}+\frac{2}{b^3 r_1}\right) \tag{15}$$

Substituting (15) in (14) and simplifying we obtain

$$A = \frac{2}{b^3}\int_0^\infty e^{-ar_1} r_1 dr_1 - \frac{1}{b^2}\int_0^\infty e^{-(a+b)r_1} r_1^2 dr_1 - \frac{2}{b^3}\int_0^\infty e^{-(a+b)r_1} r_1 dr_1 \tag{16}$$

Using equation (10) to evaluate (16), finally obtain a formula for the electron repulsion integral, as

$$A = \frac{2}{b^3 a^2} - \frac{2}{(a+b)^3 b^2} - \frac{2}{(a+b)^2 b^3} \tag{17}$$

Therefore, if we want to calculate the *ground state of helium atom* with the SCF procedure, using the orbitals exponent $\zeta_1 = 1.45$ y $\zeta_2 = 2.91$ (Roetti, 1974), the spin orbital functions are, according with equation (2)

$$\chi_1 = 2\zeta_1^{\frac{3}{2}} e^{-\zeta_1 r} Y_0^0 \tag{18}$$

$$\chi_2 = 2\zeta_2^{\frac{3}{2}} e^{-\zeta_2 r} Y_0^0 \tag{19}$$

Applying (5) to the state $\langle 11|11\rangle$, we have

$$\langle 11|11\rangle = \int\int \frac{\chi_1^*(1)\chi_1(1)\chi_1^*(2)\chi_1(2)}{r_{12}} d\tau_1 d\tau_2$$

Substituting spin orbital χ_1 and simplifying

$$\langle 11|11\rangle = 16\zeta_1^6 \int e^{-2\zeta_1 r_1} \left(Y_0^0\right)^2 d\tau_1 \int \frac{e^{-2\zeta_1 r_2} \left(Y_0^0\right)^2}{r_{12}} d\tau_2 \tag{20}$$

with $d\tau_1 = r_1^2 Sin\theta_1 dr_1 d\theta_1 d\phi_1$, $d\tau_2 = r_2^2 Sin\theta_2 dr_2 d\theta_2 d\phi_2$ and

$$\int_0^{\pi} \left(Y_0^0\right)^2 \sin\theta d\theta \int_0^{2\pi} d\phi = 1$$

Equation (20) is written as

$$\langle 11|11\rangle = 16\zeta_1^6 \int_0^{\infty} e^{-2\zeta_1 r_1} r_1^2 dr_1 \int_0^{\infty} \frac{e^{-2\zeta_1 r_2}}{r_{12}} r_2^2 dr_2$$

Then using (17) with $a = b = 2\zeta_1$

$$\langle 11|11\rangle = \frac{5}{8}\zeta_1 = 0.9062 \tag{21}$$

for the state $\langle 22|22\rangle$, we have the same result, but with ζ_2

$$\langle 22|22\rangle = \frac{5}{8}\zeta_2 = 1.8188 \tag{22}$$

Again applying (5) to the state $\langle 12|12\rangle$, we have

$$\langle 12|12\rangle = \iint \frac{\chi_1^*(1)\chi_2(1)\chi_1^*(2)\chi_2(2)}{r_{12}} d\tau_1 d\tau_2$$

Substituting spin orbitals χ_1, χ_2 and simplifying

$$\langle 12|12\rangle = 16\zeta_1^3\zeta_2^3 \int_0^\infty e^{-(\zeta_1+\zeta_2)r_1} r_1^2 dr_1 \int_0^\infty \frac{e^{-(\zeta_1+\zeta_2)r_2}}{r_{12}} r_2^2 dr_2$$

with $a = b = (\zeta_1 + \zeta_2)$ substituting in (17) and simplifying

$$\langle 12|12\rangle = \frac{20\zeta_1^3\zeta_2^3}{(\zeta_1+\zeta_2)^5} = 0.9536 \tag{23}$$

Once again applying (5) to the state $\langle 11|22\rangle$, we have

$$\langle 11|22\rangle = \iint \frac{\chi_1^*(1)\chi_1(1)\chi_2^*(2)\chi_2(2)}{r_{12}} d\tau_1 d\tau_2$$

Substituting spin orbitals χ_1, χ_2 and simplifying

$$\langle 11|22\rangle = 16\zeta_1^3\zeta_2^3 \int_0^\infty e^{-2\zeta_1 r_1} r_1^2 dr_1 \int_0^\infty \frac{e^{-2\zeta_2 r_2}}{r_{12}} r_2^2 dr_2$$

with $a = 2\zeta_1$ and $b = 2\zeta_2$ substituting in (17) and simplifying

$$\langle 11|22\rangle = \zeta_1^3\zeta_2^3 \left[\frac{1}{\zeta_1^2\zeta_2^3} - \frac{1}{(\zeta_1+\zeta_2)^3\zeta_2^2} - \frac{1}{(\zeta_1+\zeta_2)^2\zeta_2^3} \right] = 1.1826 \tag{24}$$

Again applying (5) to the state $\langle 11|12\rangle$, we have

$$\langle 11|12\rangle = \iint \frac{\chi_1^*(1)\chi_1(1)\chi_1^*(2)\chi_2(2)}{r_{12}} d\tau_1 d\tau_2$$

Substituting spin orbitals χ_1, χ_2 and simplifying

$$\langle 11|12\rangle = 16\zeta_1^{\frac{9}{2}}\zeta_2^{\frac{3}{2}} \int_0^\infty e^{-2\zeta_1 r_1} r_1^2 dr_1 \int_0^\infty \frac{e^{-(\zeta_1+\zeta_2)r_2}}{r_{12}} r_2^2 dr_2$$

with $a = 2\zeta_1$ and $b = \zeta_1 + \zeta_2$ substituting in (17) and simplifying

$$\langle 11|12\rangle = 16\zeta_1^{\frac{9}{2}}\zeta_2^{\frac{3}{2}}\left[\frac{(3\zeta_1+\zeta_2)^3-4(\zeta_1+\zeta_2)\zeta_1^2-4(3\zeta_1+\zeta_2)\zeta_1^2}{2(3\zeta_1+\zeta_2)^3(\zeta_1+\zeta_2)^3\zeta_1^2}\right] \tag{25}$$

it's easy to observe that

$$\langle 11|12\rangle = \langle 12|11\rangle = \langle 11|21\rangle = \langle 21|11\rangle = 0.9033 \tag{26}$$

Finally applying (5) to the state $\langle 12|22\rangle$, we have

$$\langle 12|22\rangle = \iint \frac{\chi_1^*(1)\chi_2(1)\chi_2^*(2)\chi_2(2)}{r_{12}} d\tau_1 d\tau_2$$

Substituting spin orbitals χ_1, χ_2 and simplifying

$$\langle 12|22\rangle = 16\zeta_1^{\frac{3}{2}}\zeta_2^{\frac{9}{2}}\int_0^\infty r_1^2 e^{-(\zeta_1+\zeta_2)r_1}dr_1\int_0^\infty \frac{e^{-2\zeta_2 r_2}}{r_{12}} r_2^2 dr_2$$

with $a=\zeta_1+\zeta_2$ and $b=2\zeta_2$ substituting in (17) and simplifying

$$\langle 12|22\rangle = 16\zeta_1^{\frac{3}{2}}\zeta_2^{\frac{9}{2}}\left[\frac{1}{4\zeta_2^3(\zeta_1+\zeta_2)^2}-\frac{1}{2(\zeta_1+3\zeta_2)^3\zeta_2^2}-\frac{1}{4(\zeta_1+3\zeta_2)^2\zeta_2^3}\right]$$

it's easy to observe that

$$\langle 12|22\rangle = \langle 22|12\rangle = \langle 21|22\rangle = \langle 22|21\rangle = 1.2980 \tag{27}$$

The one-electron integrals are simpler than the two-electron integrals, then for the overlapping integrals, we have that $S_{11}=\langle\chi_1|\chi_1\rangle=1$; $S_{22}=\langle\chi_2|\chi_2\rangle=1$, and for $S_{12}=\langle\chi_1|\chi_2\rangle$, utilizing (9)

$$S_{12}=\langle\chi_1|\chi_2\rangle = 4\zeta_1^{\frac{3}{2}}\zeta_2^{\frac{3}{2}}\int_0^\infty e^{-(\zeta_1+\zeta_2)r}r^2dr$$

And evaluating with (10) it is obtain

$$S_{12}=4\zeta_1^{\frac{3}{2}}\zeta_2^{\frac{3}{2}}\left[\frac{2}{(\zeta_1+\zeta_2)^3}\right]=0.8366 \tag{28}$$

The Hamiltonian core operator ($\hat{H}^{core}$), for helium atom, are obtained using (7)

$$\hat{H}^{core} = -\frac{1}{2}\nabla^2 - \frac{2}{r} \tag{29}$$

Since each element of the Hamiltonian is calculated with (6)

$$H_{11}^{core} = \left\langle \chi_1 \left| -\frac{1}{2}\nabla^2 - \frac{2}{r} \right| \chi_1 \right\rangle$$

Where the Laplacian for this element is

$$\nabla^2\left(e^{-\zeta_1 r}\right) = \frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial}{\partial r}\left(e^{-\zeta_1 r}\right)\right]$$

Then integral for the Hamiltonian core element H_{11}^{core} is

$$H_{11}^{core} = 4\zeta_1^3\int_0^\infty \left(e^{-\zeta_1 r}\right)\left[\frac{\zeta_1}{2r}\left(2-\zeta_1 r\right) - \frac{2}{r}\right]\left(e^{-\zeta_1 r}\right) r^2\,dr$$

Simplifying and evaluating using (10), it is observed too that H_{22}^{core} has the same expression

$$H_{11}^{core} = \frac{1}{2}\zeta_1^2 - 2\zeta_1 = -1.8488 \quad \Rightarrow \quad H_{22}^{core} = \frac{1}{2}\zeta_2^2 - 2\zeta_2 = -1.5860 \tag{30}$$

Then the integral for the Hamiltonian core element H_{12}^{core} is

$$H_{12}^{core} = 4\zeta_1^{\frac{3}{2}}\zeta_2^{\frac{3}{2}}\int_0^\infty \left(e^{-\zeta_1 r}\right)\left[\frac{\zeta_2}{2r}\left(2-\zeta_2 r\right) - \frac{2}{r}\right]\left(e^{-\zeta_2 r}\right) r^2\,dr$$

Which is evaluated using (10)

$$H_{12}^{core} = 4\zeta_1^{\frac{3}{2}}\zeta_2^{\frac{3}{2}}\left[\frac{\zeta_1\zeta_2 - 2\zeta_1 - 2\zeta_2}{\left(\zeta_1+\zeta_2\right)^3}\right]$$

$$H_{12}^{core} = -1.8826 = H_{21}^{core} \tag{31}$$

Matrix Method Description (MMD)

As we can see the overlapping matrix (*S*) is not orthogonal,

$$S = \begin{bmatrix} 1 & 0.8366 \\ 0.8366 & 1 \end{bmatrix} \tag{32}$$

That is because the non-diagonal elements are different from cero. Therefore the procedure initiates with the diagonalization of matrix *S*, in this particular example the eigenvalues are $S = \{1.8366, 0.1634\}$, here it is *extremely important* to note that the eigenvalues and their eigenvector associated, must be sorted from lowest to highest, this is to arrange the spin orbitals in the same sense.

$$\lambda_1 = 0.1634 \quad □ \quad \text{eigenvector } \vec{v}_1 = \left(-0.707106781, 0.707106781\right)$$

Therefore, we build a unitary matrix (U) with the sorted eigenvectors *taken as columns* of *U*

$$U = \begin{bmatrix} -0.707106781 & 0.707106781 \\ 0.707106781 & 0.707106781 \end{bmatrix}$$

What we have done is to find a basis, complete and orthogonal, but not orthonormal. If we want to facilitate all the operations involved in the SCF procedure, we must work with a unitary transformation matrix (*X*), then all the elements of matrix *U* must be divided by its corresponding eigenvalue's squared root.

$$X = \begin{bmatrix} \dfrac{u_{11}}{\sqrt{\lambda_1}} & \dfrac{u_{12}}{\sqrt{\lambda_2}} \\ \dfrac{u_{21}}{\sqrt{\lambda_1}} & \dfrac{u_{22}}{\sqrt{\lambda_2}} \end{bmatrix}$$

For the helium this matrix (*X*) is

$$\boldsymbol{X} = \begin{bmatrix} -1.749278568 & 0.521768326 \\ 1.749278568 & 0.521768326 \end{bmatrix} \tag{33}$$

An additional matrix (*D*) is the one built with the eigenvalues in the principal diagonal

$$\boldsymbol{D} = \begin{bmatrix} 0.1634 & 0 \\ 0 & 1.8366 \end{bmatrix}$$

Some matricial proof we can make is that $XDX^{\dagger} = I$, and $UDU^{\dagger} = S$.

All the values founded in previous section (Szabo, 1996, Levine, 2008, Bransden, 2003, Roetti, 1974), are part of the Fock matrix, then each element of this matrix are calculated using (3)

$$\begin{aligned} F_{11} = H_{11}^{core} \quad & + P_{11}\left(\langle 11|11\rangle - \frac{1}{2}\langle 11|11\rangle\right) + P_{12}\left(\langle 11|12\rangle - \frac{1}{2}\langle 12|11\rangle\right) \\ & + P_{21}\left(\langle 11|21\rangle - \frac{1}{2}\langle 11|21\rangle\right) + P_{22}\left(\langle 11|22\rangle - \frac{1}{2}\langle 12|21\rangle\right) \end{aligned}$$

$$F_{11} = -1.8488 + 0.4531P_{11} + 0.9033P_{12} + 0.7058P_{22} \tag{34}$$

$$\begin{aligned} F_{12} = H_{12}^{core} \quad &+P_{11}\left(\langle 12|11\rangle - \frac{1}{2}\langle 11|12\rangle\right) + P_{12}\left(\langle 12|12\rangle - \frac{1}{2}\langle 12|12\rangle\right) \\ &+P_{21}\left(\langle 12|21\rangle - \frac{1}{2}\langle 11|22\rangle\right) + P_{22}\left(\langle 12|22\rangle - \frac{1}{2}\langle 12|22\rangle\right) \end{aligned}$$

$$F_{12} = -1.8826 + 0.45165P_{11} + 0.8391P_{12} + 0.6490P_{22} = F_{21} \tag{35}$$

$$\begin{aligned} F_{22} = H_{22}^{core} \quad &+P_{11}\left(\langle 22|11\rangle - \frac{1}{2}\langle 21|12\rangle\right) + P_{12}\left(\langle 22|12\rangle - \frac{1}{2}\langle 22|12\rangle\right) \\ &+P_{21}\left(\langle 22|21\rangle - \frac{1}{2}\langle 21|22\rangle\right) + P_{22}\left(\langle 22|22\rangle - \frac{1}{2}\langle 22|22\rangle\right) \end{aligned}$$

$$F_{22} = -1.5860 + 0.7058P_{11} + 1.2980P_{12} + 0.9094P_{22} \tag{36}$$

At this point we must obtain an initial guess at the density matrix *P*, which commonly are zeros or ones (we have taken ones), therefore the initial matrix *F* is

$$F = \begin{bmatrix} 0.2134 & 0.05715 \\ 0.05715 & 1.3272 \end{bmatrix}$$

Transforming the matrix *F* to the orthonormal space using *X*, this is what we mean $F1 = X^{\dagger}FX$. Now we must diagonalize the Fock matrix *F1*, again eigenvalues and eigenvectors associated must be sorted from lowest to highest.

$$\varepsilon_1 = 0.202241 \quad □ \quad \text{eigenvector } \vec{v}_1 = \left(-0.237268, -0.971444\right)$$

$$\varepsilon_2 = 4.61274 \quad □ \quad \text{eigenvector } \vec{v}_2 = \left(-0.971444, -0.237268\right)$$

The matrix obtained named *C1*, is in the orthonormal space

$$C1 = \begin{bmatrix} 0.237268 & -0.971444 \\ -0.971444 & -0.237268 \end{bmatrix} \tag{37}$$

Then *C* in the initial space is obtained with *C=XC1*

$$C = \begin{bmatrix} -0.921916 & 1.57553 \\ -0.0918216 & -1.82313 \end{bmatrix}$$

with the matrix *C*, using (4) we build the new matrix *P*, here it is important to observe the upper limit of the summation (*n/2*), because it implies that the matrix *C* is trim to the half of columns,

$P = 2C_R C_R^{\dagger}$, where C_R is a trim matrix of C. This upper limit of the summation implies that n must be even, or as is referred in the literature, Restricted Closed Shell.

$$P = 2\begin{bmatrix} -0.921916 \\ -0.0918216 \end{bmatrix}\begin{bmatrix} -0.921916 & -0.0918216 \end{bmatrix} = \begin{bmatrix} 1.69986 & 0.169304 \\ 0.169304 & 0.0168624 \end{bmatrix}$$

If matrix P is the same as the previous density matrix or within a specified criterion, then the procedure has converged. If not, we must calculate again the Fock matrix, using (34), (35) and (36) and do all the steps described in this section (MMD).

Results and Conclusion

The necessary steps to perform all the matrix process have been programmed in Mathematica (**M**), which is showed in appendix (A), however some particularities of the software must be commented.

- The vectors in **M** are defined as rows, but the operations with a matrix are with columns. Then it is necessary to take the transpose of this vector.
- **M** sorts the eigenvalues from highest to lowest, then it is necessary to make additional steps to reverse this fact. The solution we found was to build an object with two different entities, a scalar as first element and a vector as second element. Then when we calculate the transformation matrix (*U*), must be referred to the second element (step 6). But when we calculate the unitary matrix (*X*), the denominator is referred to the first element (the scalar value in step 8). Again the scalar value was used in step 9.
- The solution described in the previous item was applied again in step 14, for the construction of Fock matrix.
- In steps 10 and 11 we checked that *U* and *X* were correctly builded, with the obtainment of *S* and *I*.
- In step 18 we calculate C_R, and this is because the upper limit of the summation is *n/2*.
- The Hartree-Fock-Roothaan Energy founded is in agreement with the value reported (Szabo, 1996, Levine, 2008).
- The two-electron repulsion integrals were made with an evaluation formula that we construct (17).

For teaching this concepts in college it is necessary to have enough knowledge in quantum mechanics, electromagnetic theory and linear algebra, that is because all the spin orbitals must form an orthonormal basis and electron's repulsion integrals are constructed with those spin orbitals. Special attention must have the Hamiltonian that is obtained with the Schrödinger equation.

Acknowledgement

The present work was supported by grant FOMIX 2011-09 No. 170297.

References

Bransden, B. H., & Joachain, C. J. (2003). *Physics of atoms and molecules*. Pearson Education India.

Brenner, S. C., & Scott, R. (2008). *The mathematical theory of finite element methods* (Vol. 15). Springer.

Bukowski, R., Sadlej, J., Jeziorski, B., Jankowski, P., Szalewicz, K., Kucharski, S. A., ... & Rice, B. M. (1999). Intermolecular potential of carbon dioxide dimer from symmetry-adapted perturbation theory. *The Journal of chemical physics*, *110*(8), 3785-3803.

Carey, G. F., & Oden, J. T. (1981). *Finite elements. 1. An introduction*. Prentice-Hall.

Hartree, D. R. (1957). *The calculation of atomic structures* (pp. 25-25). New York: J. Wiley.

Levine, I. N. (2000). *Quantum chemistry* (Vol. 5). Upper Saddle River, NJ: Prentice Hall.

Reddy, J. N. (2004). *Nonlinear finite element analysis*. Oxford University Press, New York.

Szabo, A. (1996). Modern Quantum Chemistry: Introduction To Advanced Electronic Structure Theory Author: Attila Szabo, Neil S. Ostlund, Publ.

Thomée, V. (1990). Finite difference methods for linear parabolic equations. *Handbook of numerical analysis.*, *1*, 5.

Appendix 1: Mathematica Programming

```
(*1.- Clear Global memory *)
ClearAll["Global`*"]

(*2.- Define the matrix H^core *)
HC={{-1.8488,-1.8826},{-1.8826,-1.5860}};
" H^core = "MatrixForm[HC]

(*3.- Define the overlapping matrix S *)
S={{1,0.8366},{0.8366,1}};
"Overlapping matrix S = "MatrixForm[S]

(*4.- Define an object that is composed of a scalar (eigenvalue) in the first column and a vector
(eigenvector) in the second column, which are obtained by diagonalizing the matrix S *)
{eigenvals,eigenvecs}=Eigensystem[S];

(*5.- Assign to a variable 'so' the object organized from lowest to highest *)
"Sorted object that was obtained from the diagonalization of the overlapping matrix"
so=SortBy[Transpose[{eigenvals,eigenvecs}],First]

(*6.- Take the element in the second row of the organized object  'so' that are the eigenvectors and with
these form a matrix *)
MMS={so[[1,2]],so[[2,2]]};
"Eigenvectors of the sorted object defined as rows = "MatrixForm[MMS]

(*7.- The transformation matrix U, is formed with the transpose of MMS (the eigenvectors are written as
column vectors)*)
U=Transpose[MMS];
"U = "MatrixForm[U]

(*8.- The transformation matrix X is obtained by dividing the eigenvector's columns of U between its
corresponding eigenvalue's square root *)
X={{U[[1,1]]/Sqrt[so[[1,1]]],U[[1,2]]/Sqrt[so[[2,1]]]},{U[[2,1]]/Sqrt[so[[1,1]]],U[[2,2]]/Sqrt[so[[2,1]]]}};
"Transformation Matrix X = "MatrixForm[X]
"Matrix Transpose of X = "MatrixForm[Transpose[X]]
(*9.- The diagonal matrix DS is formed with the eigenvalues of S *)
DS={{so[[1,1]],0},{0,so[[2,1]]}};
"Diagonal Matrix of eigenvalues of DS = "MatrixForm[DS]
(*10.- Proof that the Matrix multiplication of U with DS and with the transpose of the matrix U returns us
S *)
" Proof U.DS.U^† = "MatrixForm[U.DS.Transpose[U]]

(*11.- Proof that the Matrix multiplication of X with DS and with the transpose of the matrix X returns us
the Unitary matrix *)
" Proof X.DS.X^† = "MatrixForm[X.DS.Transpose[X]]

(*12.- Define the initial matrix P *)
P={{1,1},{1,1}};
"P = "MatrixForm[P]
```

```
(*13.- The loop to find the lowest energy is initiated *)
For[i=1,i<=7,i++,
Frs={{HC[[1,1]]+0.4531P[[1,1]]+0.9033P[[1,2]]+0.7058P[[2,2]],HC[[1,2]]+0.45165P[[1,1]]+0.8391P[[1,
2]]+0.6490P[[2,2]]},{HC[[2,1]]+0.45165P[[1,1]]+0.8391P[[1,2]]+0.6490P[[2,2]],HC[[2,2]]+0.7058P[[1,1
]]+1.2980P[[1,2]]+0.9094P[[2,2]]}};

Print["Fock Matrix Frs] = " MatrixForm[Frs]];
F1=Transpose[X].Frs.X;
Print["Transformed Fock Matrix F1 = " MatrixForm[F1]];

(*14.- Diagonalize the Fock matrix transform F1 and sort the eigenvalues and their eigenvectors
associated, from lowest to highest *);
Clear[eigenvals,eigenvecs]
{eigenvals,eigenvecs}=Eigensystem[F1];
so=SortBy[Transpose[{eigenvals,eigenvecs}],First];
(*15.- matrix NF1 is formed with the eigenvectors sorted, taken from object 'so' with the eigenvectors as
rows *);
NF1={so[[1,2]],so[[2,2]]};
(*16.- The matrix of coefficients C1 is formed with the transpose of NF1 (the eigenvectors are placed as
columns)*);
C1=Transpose[NF1];
Print["Matrix of coefficients in orthonormal espace C1 = " MatrixForm[C1]];
(*17.- Place the matrix of coefficients C1 in the initial vectorial space, the matrix C is formed *);
CM=X.C1;
Print["Matrix of coefficients C = " MatrixForm[CM]];
(*18.- The elements values of the matrix P are calculated again, with the trimmed matrix C *);
CR=Transpose[Transpose[CM][[1;;1]]];
Print["Trimmed matrix CR = "MatrixForm[CR]];
P=2CR.Transpose[CR];
Print["P = "MatrixForm[P]];
(*19.- The Hartree-Fock-Roothaan Energy is calculated for the new values of matrix P *);
EHF
=0.5(P[[1,1]](Frs[[1,1]]+HC[[1,1]])+P[[1,2]](Frs[[1,2]]+HC[[1,2]])+P[[2,1]](Frs[[2,1]]+HC[[2,1]])+P[[2,
2]](Frs[[2,2]]+HC[[2,2]]));
Print["Hartree-Fock-Roothaan Energy = ",EHF];
Print[Style[{"Finish Loop ",i},FontColor -> Red]];
]
(*20.- Displays the last energy calculated *)
Print["Optimal energy of the system EHF = ", EHF];
```