

Numerical Study of Density Functional Theory of Multi-electronic Atoms: Case of Carbon and Helium

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Abstract The ab-initio method based on density functional theory was used via local density approximation (LDA) to analyze the electronic structure of helium atoms and carbon. This involves calculating physical properties of these atoms such as effective potential, electron density and radial wave functions in both the ground state and the first three excited states. Thus, taking into account the structural complexity of the system, the calculations were carried out implicitly by the finite element method via the MATLAB software in deterministic mode. At the end of the study, the results obtained are consistent and revealing. They have shown that the effective potential of the helium atom decreases with position both in its ground state and in its first three excited states, so for the carbon atom, they have shown that these two states evolve in the same way. Regarding the electron density, the results revealed that at each radius of an atomic orbital, the electron density passes through a maximum for the helium atom while for carbon, the results show a succession of two and three peaks. Finally, with regard to radial wave functions, the results showed that the 1s orbital is closer to the nucleus than the 2s, 2p and 3s orbitals for the helium atom. For the carbon atom, the results confirm the information provided by the electron density. From the results it can be concluded that the effective potential of a multielectronic atom decreases with position and that the densest orbitals are those near the nucleus.

Keywords: Schrodinger equation DFT, implicit method, finite-difference approach, MATLAB

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1. Introduction

During the last fifty years, solid-state physics has experienced an impressive boom both in the field of theory and in implementations of this theory [1,2]. It is about the application of quantum mechanics to molecular systems in order to extract the different physicochemical properties such as structural, elastic, thermal, magnetic, optical and electronic properties [3,4]. According to [5,6], several formalisms or quantum approaches have been put in place to try to solve the problem. Mainly, we can distinguish three approaches: (i) the first purely empirical consisting in making experimental observations and carrying out measurements to obtain the values of the parameters which make it possible to describe the properties of the given system; (ii) the second semi-empirical consists in introducing a theoretical modeling but requires experimental studies to adjust the values of the modeling parameters and (iii) the third, the ab-initio approach, consists of starting from the fundamental laws of quantum physics and electromagnetism, and some basic characteristics defining the system to determine, explain or predict its structures and properties [7-8]. Among these approaches,

the ab-initio approach has become a basic tool since the approach is to calculate the properties of complex systems from the fundamental laws governing the elementary constituents of these systems [9]. This approach has now been able to replace experiments that are very expensive or even impractical in the laboratory or very dangerous [10]. In ab-initio calculations, the approach consists in first determining the megatonic and ionic structures of the system and then deducing the values of the characteristic parameters [11,12]. This new method of calculation, which uses the computer tool, is based on density functional theory (DFT). It is a method which makes it possible to study the electronic structures of systems composed of several atoms and to deduce their physicochemical properties. Combined with numerical physics methods, DFT forms the basis of several of the most efficient and widely used ab-initio computational methods to determine the values of the parameters that define the properties of various materials and structures [13]. DFT is derived from the work of [14], followed by that of [15]. DFT makes it possible to tackle the problem of the electronic structure of ion-electron systems by using electron density as the main basic quantity [13-16]. The ab initio methods of numerical physics based on DFT have made it possible to obtain results that are interesting and

difficult, if not impossible, to obtain with other approaches. The application of these methods and their extensions are particularly promising for nanosciences and nanotechnologies [17,18]. This is why interest in FTD and its applications is growing worldwide today [19,20]. It is in this same vein that the present study was initiated. This involves analyzing the electronic structure of multielectronic atoms such as Helium and Carbon through the ab-initio method which is based on the density functional theory using the local density approximation (LDA). This is a way of describing matter in its ground state no longer by going through the wave functions of the N electrons but rather by considering the electron density of these. This requires solving the Schrödinger equation, which is an N-body problem whose resolution is difficult, if not impossible, to obtain analytically [21]. Thus, the putting into practice of ab-initio methods, such as those based on DFT, generally require numerical methods with adequate computer resources [1]. These methods can therefore be considered to be within the framework of digital physics. The use of computer tools and methods, means that the modeling of real compounds (with possibly complex structures) becomes perfectly possible with means and within deadlines which remain "reasonable" and more precise, making it possible to obtain very quickly the results. properties of many solids [22,23]. It makes it possible to explain and predict the structures and properties of materials knowing a few parameters such as the atomic numbers of the constituent atoms [14-24]. In practice, it allows the creation of a large number of materials currently used in industry and new technologies. In this study we used the MATLAB code in deterministic mode to do our calculations. The results obtained provided a better understanding of the organization of matter at the atomic scale in the case of helium and carbon. The choice of these atoms is no accident. It obeys well-defined rules: (i) they are atoms made up of several electrons; (ii) they have paramagnetic and ferromagnetism properties; (iii) their total energies calculated in their ground and excited states corroborate with those found by Slater's method and (v) several works in the literature testify to the targeting of these two atoms. Among these works, we can cite among others [25,26,27,28] for the carbon atom and [29-34] for the helium atom.

2. Materials and Methods

2.1. Problem Formulation

The density functional theory finds its roots in the Thomas-Fermi model which, from 1927, gives a very simple relation giving the total energy of an atomic or molecular system from its electron density alone (Parr and Yang, 1989). Then completed by Dirac who adds the exchange energy to it, this model suffers in the eyes of chemists from a congenital defect: the molecule is less stable than the atom. The first calculations attributable to the density functional theory date back to the X α calculations introduced by Slater in 1951. However, the corresponding equations being obtained at the time by an approximation of the Hartree-Fock method, (also called ab initio by theoretical chemists), it did not seem conceivable

that the X α method could lead to better results than those obtained from the Hartree-Fock method [7]. The density functional theory was in fact born in 1964 with the publication by Hohenberg and Kohn of their famous theorems: the first establishes, by reasoning by the absurd, that the ground state of an electronic system does not depend on than its sole density. It is only later that this theorem will be generalized to degenerate ground states, as well as to the excited states lowest in their class of symmetry. The second theorem is the analogue of the variational principle, and shows that the density is stationary for the ground state. But the existence of this stationary solution did not make it possible to make precise calculations, and it is the method proposed the following year by Kohn-Sham which will make possible calculations that are both less cumbersome than calculations by Hartree-Fock, and with suitable precision: the originality of the Kohn-Sham method is to obtain the kinetic energy from orbitals representing a system of electrons without interactions having the same density, and which will obey to a Schrodinger-type equation [35]. The energy of electronic interaction, which on the other hand is obtained by density alone, is divided into two contributions: classical Coulomb energy, and exchange-correlation energy. The latter in fact contains everything that is not contained in this kinetic energy KS and Coulomb energy, namely mainly the energy, which finds its origin in the quantum nature of electrons, the correlation energy, which translates the non-independence of electrons in their movements, as well as the difference between the kinetic energy calculated from orbitals representing a system without interaction and the real kinetic energy of the systems of interacting electrons [36]

2.2. DFT Formalism

The Theory of Functional Density has become, over the last decades, a theoretical tool that has taken a very important place among the methods used for the description and analysis of physical and chemical properties for complex systems, particularly for systems containing a large number of electrons [37]. DFT is a reformulation of the N-body quantum problem and as the name suggests, it is a theory that only uses electron density as the fundamental function instead of the wave function as is the case in the method by Hartree and Hartree-Fock. The main goal of DFT is to replace the multielectronic wave function with electron density as the base quantity for calculations. While the multielectronic wave function depends on 3N variables (where N is the total number of particles in the system), the density is a function of three variables that it is an easier quantity to process as long as it is mathematically conceptually [4]. The DFT allows us to solve the Schrödinger equation with N bodies by only involving the observable $\rho(\vec{r})$ defined in the physical space R^3 which replaces a space of configurations with 3N variables in which is defined the wave function (Hartree-Fock) [38]. The formalism of the DFT is based on the theorem of Hohenberg and Kohn. The most common version, the local density approximation (LDA), often gives results as good as those of Hartree-Fock-type methods, for less computation times.

The Hamiltonian of a system of N electrons moving in a fixed external potential is given by equation (1) [39].

$$\begin{aligned} H = & T_N + T_e + V_{N-N} + V_{N-e} + V_{e-e} \\ = & -\frac{\hbar^2}{2M} \sum_k \Delta_k - \frac{2}{2m} \sum_i \Delta_i + \frac{1}{2} \sum_k \sum_{l \neq k} \frac{e^2}{4\pi\epsilon_0 |\vec{R}_k - \vec{R}_l|} \\ & - \sum_k \sum_{i \neq k} \frac{z_k e^2}{4\pi\epsilon_0 |\vec{R}_k - \vec{r}_i|} + \frac{1}{2} \sum_i \sum_{j \neq i} \frac{e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|} \end{aligned} \quad (1)$$

T_N : kinetic energy of nuclei; T_e : kinetic energy of electrons;

V_{N-N} : potential nucleus-nucleus repulsion energy;

V_{N-e} : potential electron-nucleus attraction energy;

V_{e-e} : electron-electron repulsion potential energy

r_i, r_j : electron positions i et (j) respectively.

R_k, R_l : positions of the nuclei (k) et (l) respectively;

z_k, z_l : atomic numbers of nuclei (k) et (l) respectively;

e : electron charge; m : electron mass; M : core mass.

2.3. Basic Equations

Electrons are defined as indistinguishable and inseparable particles. In this reality, an electron cannot be located as much as an individual particle. Each particle has the probability of being present in a volume element. The electron density $\rho(\vec{r})$ is the probability of finding one of the N electrons in the element of volume $d^3\vec{r}$. Therefore, it is defined as the multiple integral on the space and spin coordinates of all electrons, represented by relation (2) [7].

$$\rho(\vec{r}) = N \int dr_1 \dots \int dr_{n-1} \Psi^*(r_1 \dots r_{n-1}, r_n) \Psi(r_1 \dots r_{n-1}, r_n) \quad (2)$$

$\rho(\vec{r})$ is a positive function depending only on the 3 coordinates (x, y, z) of space which tends to zero when r tends to infinity and whose integral over all space gives the number N of electrons.

2.3.1. Hohenberg and Kohn Equations

Once the electron density is defined, it is necessary to lay the foundations of the DFT, expressed for the first time by Hohenberg and Kohn in 1964 on which rests all the DFT which can be summed up in two theorems [14].

• First theorem

The first theorem is used to establish a correspondence between the electron density $\rho(\vec{r})$ of a polyelectronic system in the ground state and the external potential $V_{ext}(r)$ of the nucleus so as to be able to describe the value of any observable as a unique functional of the exact electron density specific to this ground state. The consequence of this theorem is that the variation of the external potential then implies a variation of the electron density. It allows to define a universal functional of the electron density, $F_{HK}[\rho(r)]$ called Hohenberg-Kohn functional, such that the energy of the atom is written according to equation (3) [7]

$$E[\rho(r)] = F_{HK}[\rho(r)] + \int \rho(r) v_{ext}(r) d^3r \quad (3)$$

where $F_{HK}[\rho(r)]$ is the unknown universal functional given by the relation (4)

$$\begin{aligned} F_{HK}[\rho(r)] \\ = T_s[\rho(r)] + \frac{1}{2} \iint \frac{\rho(r)\rho(r')}{|r-r'|} d^3r d^3r' + E_{xc}[\rho(r)] \end{aligned} \quad (4)$$

$T_s[\rho(r)]$: Sum of the kinetic energies of the negatons;

The second term is the Coulomb interaction potential energy;

$E_{xc}[\rho(r)]$: exchange-correlation energy

• Second theorem

The second theorem is a variational principle analogous to that proposed in the Hartree-Fock approach for a functional of the wave function, but applied this time to a functional of the electron density. This second theorem states that for any multi-electronic system with an electron number N and an external potential $V_{ext}(r)$; the universal functional $F_{HK}[\rho]$, expressing energy as a function of electron density, reaches its minimum value when the electron density $\rho(r)$ corresponds to the exact density of the ground state $\rho_0(r)$. Minimization of energy goes through the use of the Lagrange formalism, i.e., by establishing a Lagrangian given by equation (5) [40].

$$L[\rho] = E[\rho] - \mu \left[\int \rho(r) dr - N \right] \quad (5)$$

where μ is the Lagrange multiplier; the minimization of the Lagrangian implies the relation (6):

$$\frac{\delta}{\delta \rho(r)} \left\{ E[\rho] - \mu \left[\int \rho(r) dr - N \right] \right\} = 0 \quad (6)$$

As the differential of a functional is expressed by relation (7), we can thus rewrite equation (6) in the form of relation (8)

$$\delta F = \int \frac{\delta F}{\delta f(x)} \delta f(x) dx \quad (7)$$

$$\int \left\{ \frac{\delta E[\rho]}{\delta \rho(r)} - \mu \right\} \delta \rho(r) dr = 0 \quad (8)$$

This named relation, fundamental equation of the density functional theory, implies relations (9) and (10)

$$\mu = \frac{\delta E[\rho]}{\delta \rho(r)} \quad (9)$$

$$\mu = v_{ext} + \frac{\delta F_{HK}[\rho]}{\delta \rho(r)} \quad (10)$$

2.3.2. Kohn-Sham Equations

Kohn and Sham assume that there is a fictitious system of N independent electrons with the same electron density as the real system of interacting electrons. The interest comes from the fact that the expressions of kinetic energy and potential energy for this system are known, the only indeterminate term is the exchange-correlation term. Then they proposed separations according to relation (11) [15].

$$T_{el}[\rho(r)] = T_s[\rho(r)] + (T_{el}[\rho(r)] - T_s[\rho(r)]) \quad (11)$$

where $T_s[\rho(r)]$ is the kinetic energy of an electron gas without interaction which calculated by reintroducing an orbital description according to the relation (12)

$$T_s[\rho(r)] = \sum_i^n \int dr \Psi_i^*(r) \left[-\frac{1}{2} \Delta \right] \Psi_i(r) \quad (12)$$

$$\begin{aligned} & v_{el-el}[\rho(r)] \\ & = E_H[\rho(r)] + (v_{el-el}[\rho(r)] - E_H[\rho(r)]) \end{aligned} \quad (13)$$

$E_H[\rho(r)]$ is the Coulomb energy of electron-electron interaction, or the Hartree energy defined by equation (14):

$$E_H[\rho(r)] = \frac{1}{2} \int dr dr' \frac{\rho(r)\rho(r')}{|r-r'|} \quad (14)$$

The functional which is defined by relation (15) can also be written by relation (16)

$$F_{HK}[\rho(r)] = T_{el}[\rho(r)] + v_{el-el}[\rho(r)] \quad (15)$$

$$F_{HK}[\rho(r)] = T_s[\rho(r)] + E_H[\rho(r)] + E_{xc}[\rho(r)] \quad (16)$$

$E_{xc}[\rho(r)]$ is the correlation exchange term defined by relation (17)

$$\begin{aligned} E_{xc}[\rho(r)] = & \{v_{el-el}[\rho(r)] - E_H[\rho(r)]\} \\ & + \{T_{el}[\rho(r)] - T_s[\rho(r)]\} \end{aligned} \quad (17)$$

This term includes the kinetic energy correlation for an interacting electron gas and the Hartree energy correction in the electron-electron interaction [26].

The density functional defined by equation (3) then relates to relation (18)

$$\begin{aligned} E[\rho(r)] = & T_s[\rho(r)] + \frac{1}{2} \int dr dr' \frac{\rho(r)\rho(r')}{|r-r'|} \\ & + \int dr v_{ext}(r)\rho(r) + E_{xc}[\rho(r)] \end{aligned} \quad (18)$$

Applying the variational principle to this functional leads to equation (19):

$$\begin{aligned} \frac{\partial E[\rho(r)]}{\partial \rho(r)} = & \frac{\partial T_s[\rho(r)]}{\partial \rho(r)} + \int \frac{\rho(r')}{|r-r'|} dr \\ & + v_{ext}(r) + \frac{\partial E_{xc}[\rho(r)]}{\partial \rho(r)} \end{aligned} \quad (19)$$

Determining the ground state of the system then amounts to solving a set of equations called Kohn-Sham equations defined by relation (20) which can also be denied by equation (21) [41].

$$\left[\begin{aligned} & -\frac{1}{2} \Delta + v_{ext}(r) + \int dr' \frac{\rho(r')}{|r-r'|} \\ & + \frac{\partial E_{xc}[\rho(r)]}{\partial \rho(r)} \end{aligned} \right] \Psi_i(r) = \varepsilon_i \Psi_i(r) \quad (20)$$

$$\left[-\frac{1}{2} \Delta + v_{eff}(r) \right] \Psi_i(r) = \varepsilon_i \Psi_i(r) \quad (21)$$

$V_{eff}(r)$: effective potential is defined by relation (22)

$$V_{eff}(r) = V_{ext}(r) + \int \frac{dr' \rho'(r)}{|r-r'|} + V_{xc}[\rho(r)] \quad (22)$$

The second term of this equality is the Hartree potential, which can be in the form of an average of an interaction potential given by equation (23):

$$V_H(r_i) = \int v(r_i) \frac{d\Omega_i}{4\pi} \quad (23)$$

Where $v(r_i)$ is an interaction potential given by equation (24)

$$v(r_i) = \sum_{j \neq i}^n \int \frac{|\Psi_j|^2}{|\vec{r}_j - \vec{r}_i|} dv_j \quad (24)$$

2.4. Numerical Resolution

There are two ways of looking at an atomic system, either from its electron cloud via electron density, or through nuclei via external potential. Hohenberg and Khon have shown that there is a one-to-one correspondence between the external potential and the electron density, that is, one seems to be the image of the other. Thus, by knowing the electron density, the Hamiltonian operator can be determined and through the latter, the different properties of the molecule or material can be calculated [42]. On the other hand, the fact that the total energy of a system in the ground state is a functional $E[\rho(r)]$ of the electron density allowed Hohenberg and Khon to express this functional according to the expression (25) [7].

$$E[\rho(r)] = F_{HK}[\rho(r)] + \int \rho(r) V_{ext}(r) d^3r \quad (25)$$

Knowledge of the functional $F_{HK}[\rho(r)]$ makes it possible to determine the total energy the charge density of the ground state for a given external potential, using the variational principle. Unfortunately, the theorem of Hohenberg and Khon does not give any indication of the form of and that this functional $F_{HK}[\rho(r)]$ remains unknown to this day. There is no exact formulation to express kinetic energy as an electron density functional. The equations of Khon and Sham present the only solution to this problem and which are established with the objective of providing the foundations necessary to effectively exploit the theorems of Hohenberg and Khon [43,44]. To do this, they introduced a further development which consists in replacing the real interactive system with a fictitious characterized in all respects by the same density as the system of interacting electrons. Schrödinger equation to be solved in the framework of the Kohn and Sham approach is of the following form (26) [45]

$$\left[-\frac{1}{2} \Delta + V_{eff}(r) \right] \Psi_i(r) = \varepsilon_i \Psi_i(r); i = 1, \dots, N \quad (26)$$

Solving the Kohn and Sham equations requires the choice of a basis for the wave functions that can be taken as a linear combination of orbitals called Kohn-Sham orbitals (KS) written in the form defined by l'equation (27)

$$\Psi_i(r) = \sum_i C_{ij} \varphi_j(r) \quad (27)$$

Where the $\varphi_j(r)$ are the basic functions and the C_{ij} the expansion coefficients. Solving the Kohn and Sham equations comes down to determining the C_{ij} coefficients for the occupied orbitals that minimize the total energy. This resolution is done numerically in an iterative manner following 6 steps [1]:

- i) We choose an initial density $\rho_0(r)$;
- ii) We determine the Kohn-Sham potential $V_{\text{eff}}(r)$;
- iii) Solve the second Kohn-Sham equation giving the functions $\Psi_i(r)$ and corresponding eigenvalues ε_i ;
- iv) We calculate a new density $\rho(r)$ from the functions $\Psi_i(r)$;
- v) We check the convergence criterion (by comparing the old and the new density). If the criterion is not yet

satisfied, we start the cycle again. The most used convergence criteria are based on the difference between the energies or the densities corresponding to the α^{th} et $(\alpha - 1)^{\text{th}}$ iteration as shown in equation (28)

$$\left\{ \begin{array}{l} |E_\alpha - E_{\alpha-1}| < \gamma_E \\ \text{ou} \\ \left| \iiint d^3r [\rho_\alpha(r) - \rho_{\alpha-1}(r)] \right| < \gamma_\rho \end{array} \right. \quad (28)$$

γ_E and γ_ρ being the values of the tolerances (precisions) that we choose from the start.

vi) Finally, the different physical quantities are calculated (Energy, forces, etc.); End of process.

All of these steps are shown schematically by the algorithm shown in Figure 1.

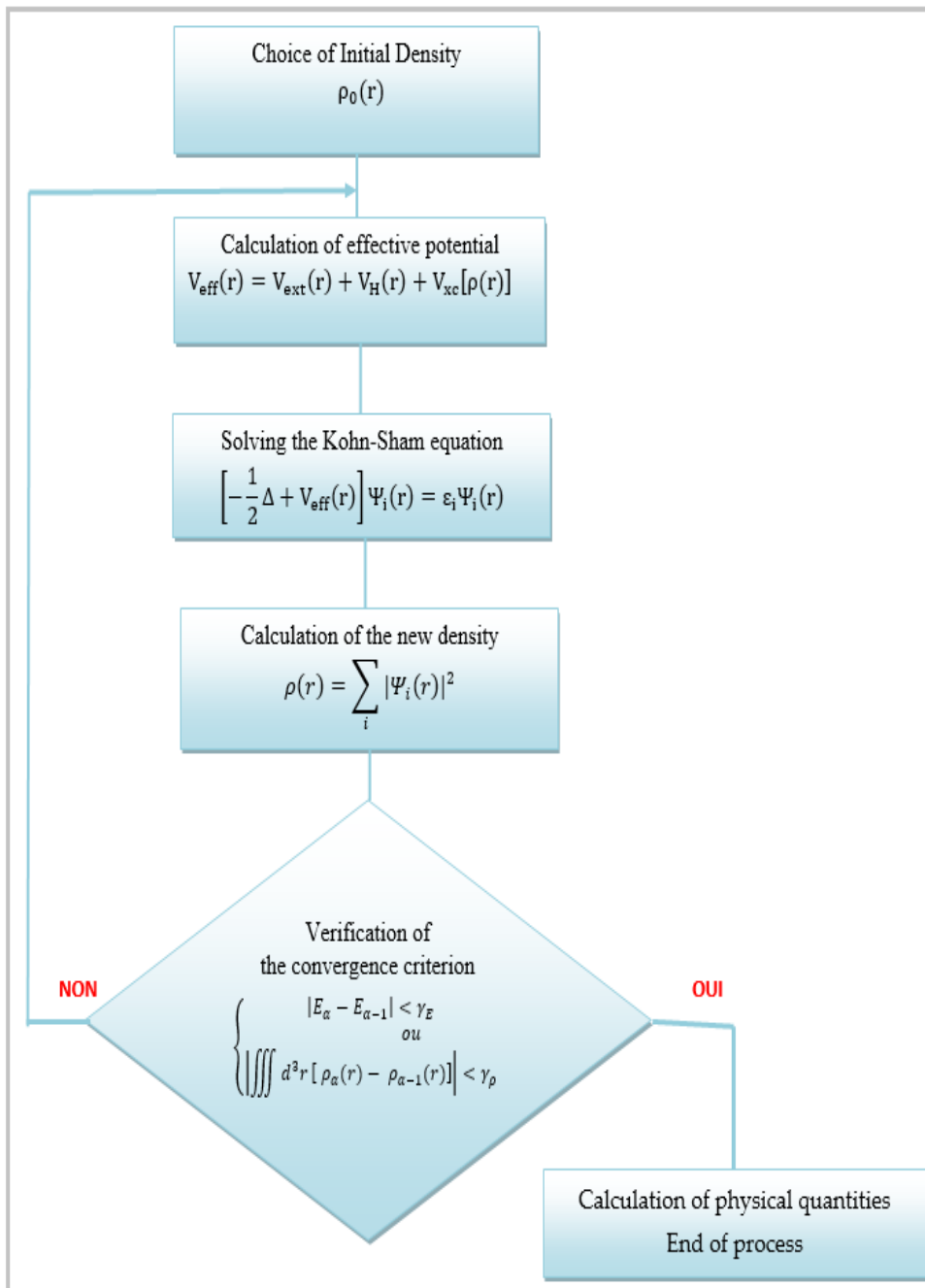


Figure 1. Iterative process used in solving Kohn-Sham equations

Due to the structural complexity of the system, we have linearized the basic equations implicitly and solved numerically by the finite element method using Matlab software. MALAB (MATrix LABORatory) is programming software that makes it as easy as possible to transcribe a mathematical problem into computer language, using writing as close as possible to scientific natural language. A sequential resolution of the problem using this computer program, made it possible to quickly obtain

interesting and difficult results, if not impossible, to obtain with other approaches such as the analytical one.

3. Results and Discussion

Below we present the graphical results relating to the effective potential, electron density and radial wave function for helium and carbon atoms.

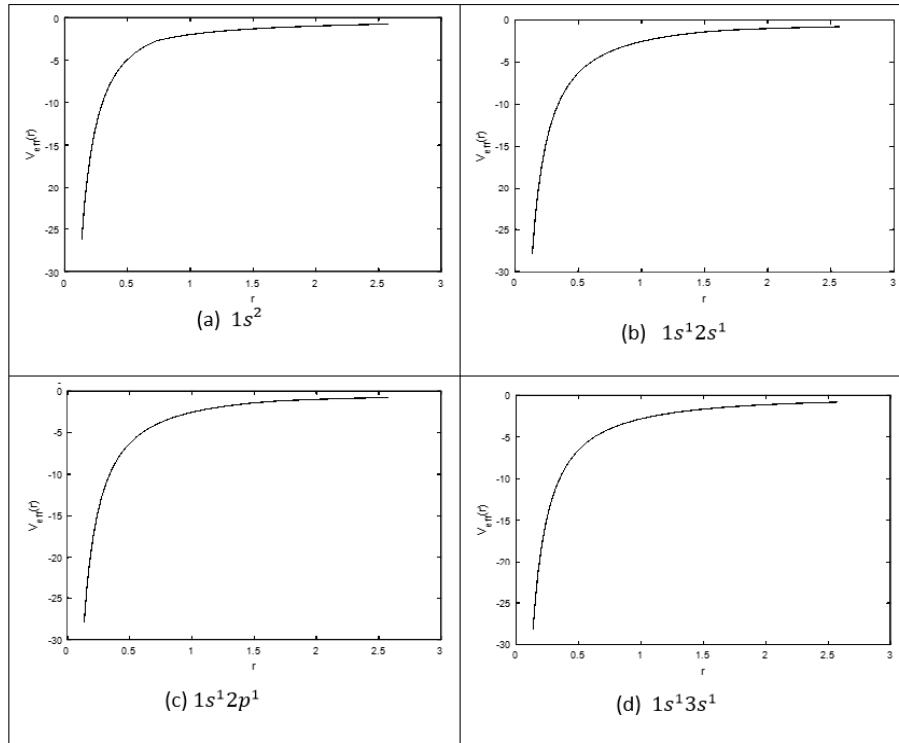


Figure 2. Variations depending on the position of the effective potential of the helium atom in its ground state (a) and its first three excited states (b, c, d)

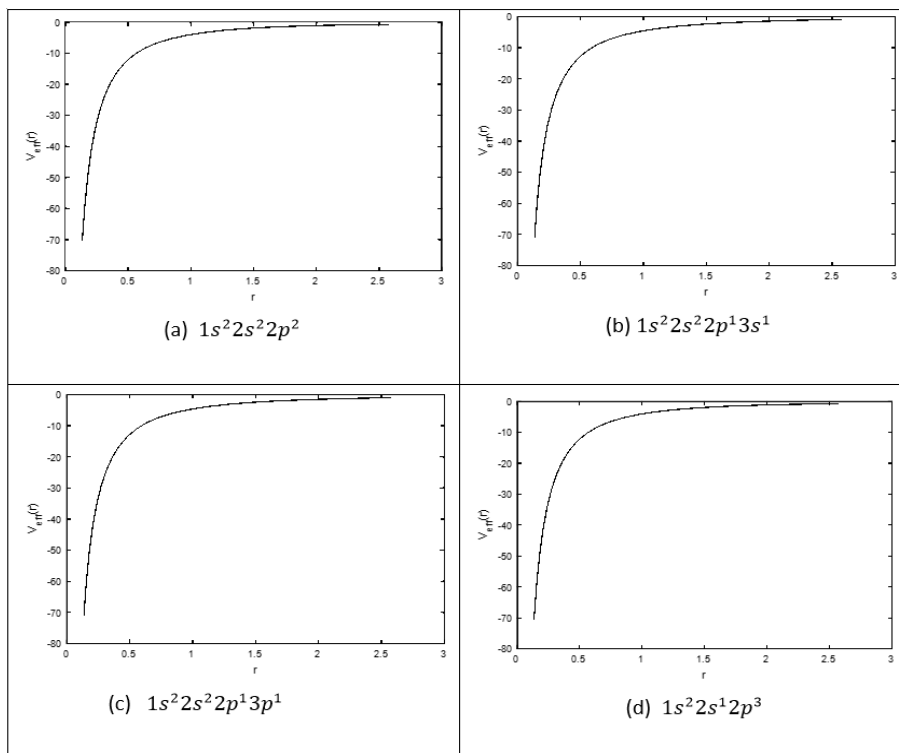


Figure 3. Variations depending on the position of the effective potential of the carbon atom in its ground state (a) and its first three excited states (b, c, d)

3.1. Effective Potential

In Figure 2 and Figure 3, we can see the variations in the effective potential as a function of the position for the helium and carbon atoms respectively in the ground state and in the first three excited states. Thus, the analysis in Figure 2 shows that there is a very rapid growth in the region of the heart represented here by the 1s orbital. In the outer region we noticed a

slight increase in the effective potential. This allows us to conclude that the effective potential of the helium atom decreases with position. Reading Figure 3 shows that the effective potential of the carbon atom in its ground state as in excited states changes in the same way. It increases very rapidly in the area near the nucleus, but as we move away from the nucleus it begins to stabilize to tend towards a limit value for all four states studied.

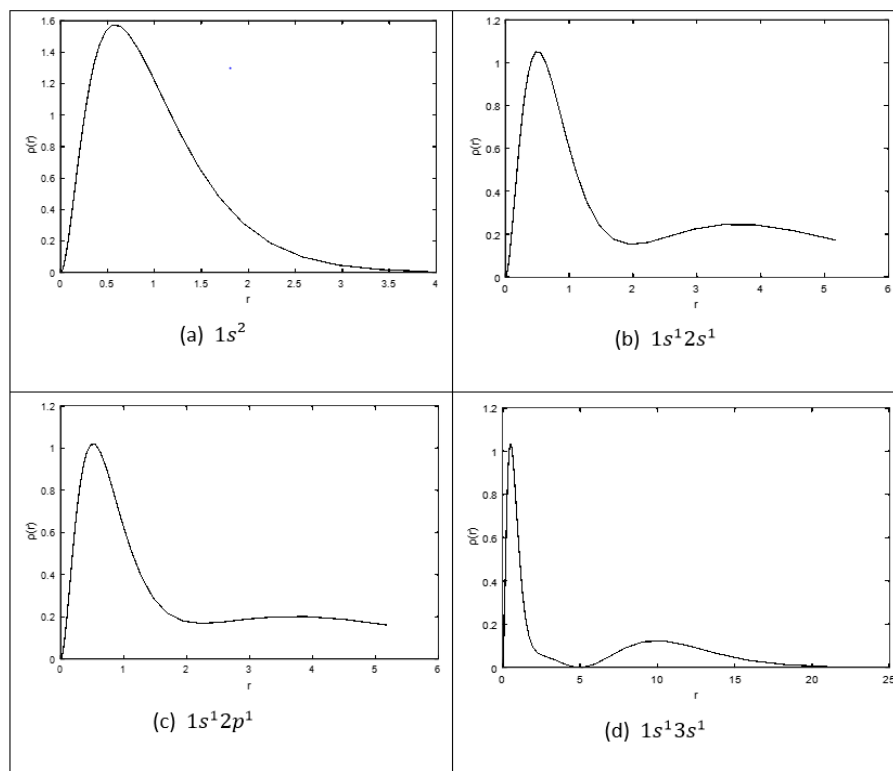


Figure 4. Variations depending on the position of the electron density of the helium atom in its ground state (a) and its first three excited states (b, c, d)

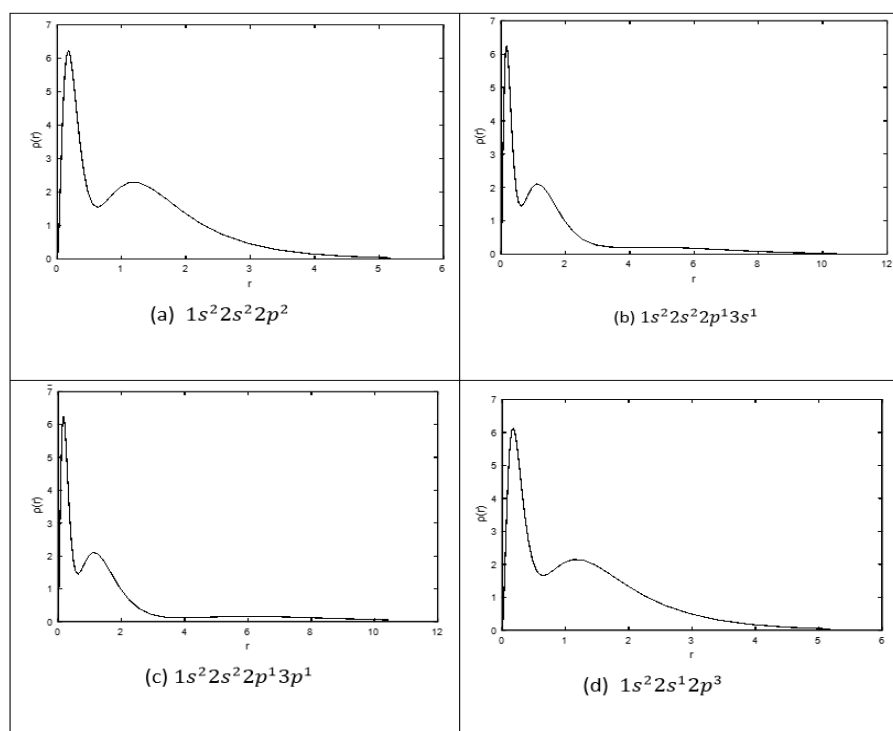


Figure 5. Variations depending on the position of the electron density of the carbon atom in its ground state (a) and its first three excited states (b, c, d)

3.2. Electron Density

Figure 4 and Figure 5 illustrate the evolution of electron density following the position of the helium and carbon atoms in the ground state and in the first three excited states, respectively. The analysis of Figure 4 shows that at each radius of an atomic orbital, the electron density passes through a maximum. In the ground state all the electrons are in the 1s orbital, this gives a very dense orbital characterized by a maximum of the electron density higher than all the maxima found for this orbital in the excited states. At the excited states $1s^12s^1$ and $1s^12p^1$ we have two electron density maxima; the electrons have reached the radii of the 1s and 2s orbitals. In its states the 1s orbital is denser than the 2s and 2p orbitals and has a maximum electron density much greater than the maximum in the 2s or 2p orbital. In the excited state $1s^13s^1$ the 3s orbital is small compared to the 1s orbital which is larger and closer to the nucleus. The electron density in this state goes through a maximum at the radius of the 1s orbital, at the radius of the 3s orbital we also have a maximum of the very small electron density before the maximum found at the radius of the 1s orbital. The analysis of Figure 5 in the four states studied shows a succession of two and three peaks. In the ground

state and in the excited state $1s^22s^12p^3$ we have two electron density maxima, the electrons have reached the radii of the 1s, 2s and 2p orbitals. The maximum electron density at the smallest position is greater than the other maxima. The 1s orbital is denser than the 2s and 2p orbitals. In the excited states $1s^22s^22p^13s^1$ and $1s^22s^22p^13p^1$, we have three maxima. The third maximum appears at the radius of the 3s orbital.

3.3. Radial Wave Functions

In Figure 6 and Figure 7, we have a presentiment of the variations of the radial wave functions as a function of the position for the helium and carbon atoms respectively in the ground state and in the first three excited states. This is to describe the regions of space where the electrons of helium and carbon atoms are likely to be found. Analysis of Figure 6 shows that the 1s orbital is closer to the nucleus than the 2s, 2p and 3s orbitals. The 2s and 2p orbitals have their electrons farther from the nucleus than those of the 1s orbital but closer than the electron in the 3s orbital. The analysis of Figure 7 confirms information provided by the electron density. It also shows the negative part of the radial wave function.

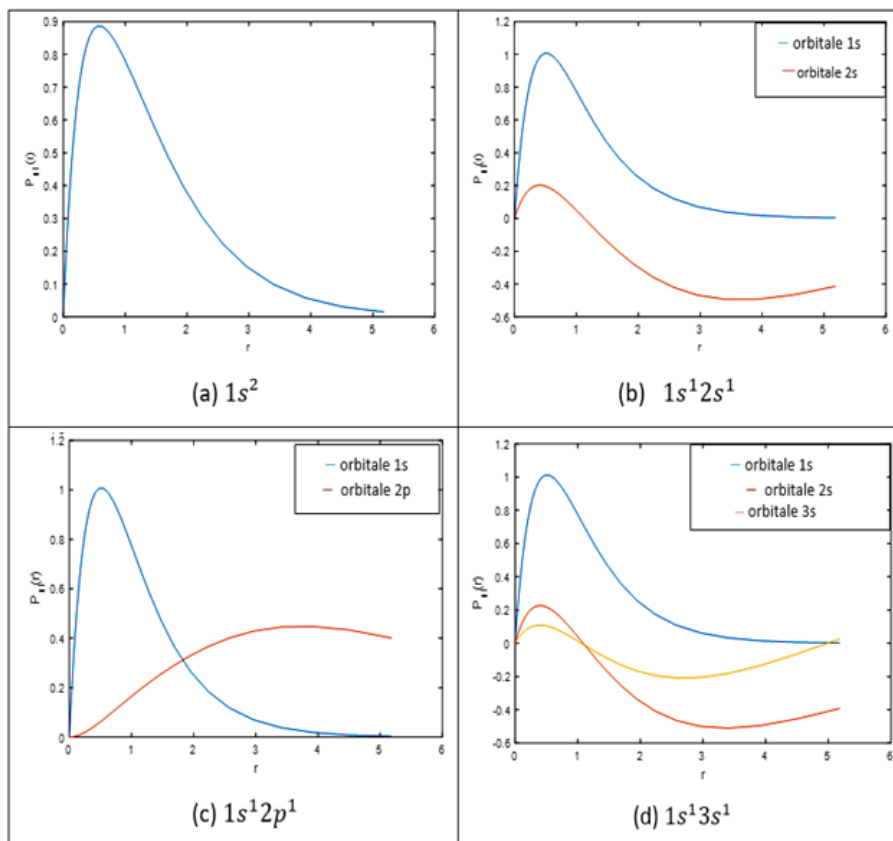


Figure 6. Variations depending on the position of the radial wave functions of the helium atom in its ground state (a) and its first three excited states (b, c, d)

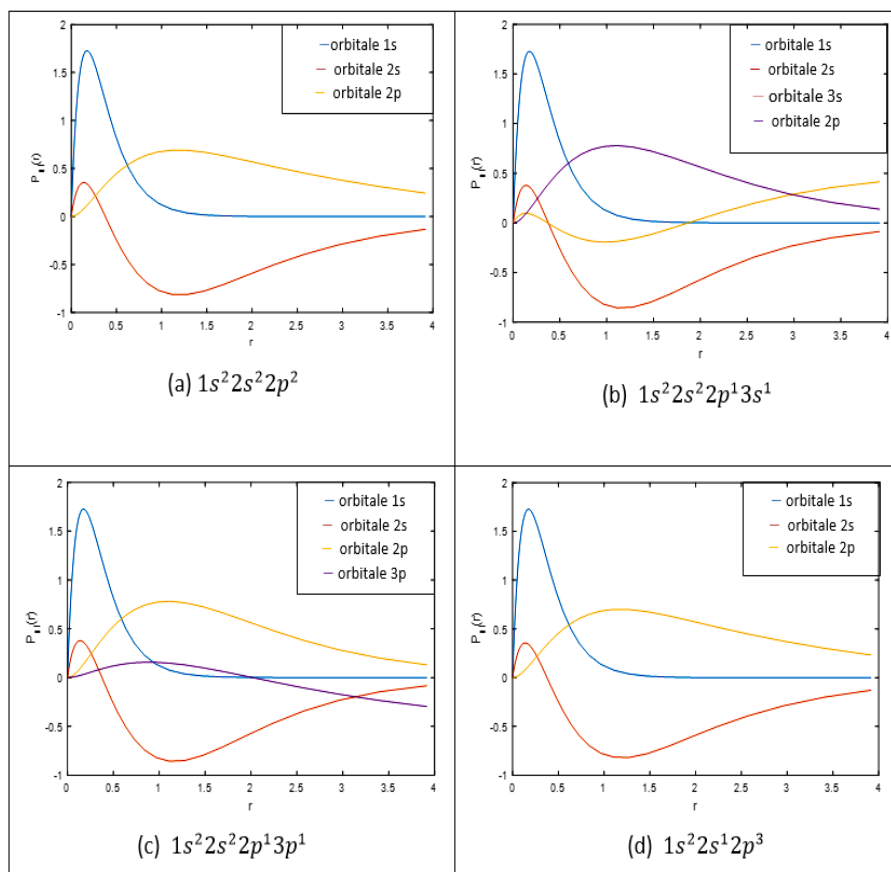


Figure 7. Variations depending on the position of the radial wave functions of the carbon atom in its ground state (a) and its first three excited states (b, c, d)

4. Conclusion

Nowadays, the density functional theory has established itself as a relatively fast and reliable way to simulate the electronic and structural properties for all the elements of the periodic table. In this work, we are interested in the study of the electronic structure of helium and carbon atoms in the approximation of the density functional theory. To this end, we have developed a MATLAB code based on this same theory to determine physical quantities such as the effective potential, the electron density and the radial wave functions of these atoms in their ground state and certain excited states. At the end of the study, the results obtained are consistent and revealing. For the helium atom, there is a very rapid growth of the effective potential in the region of the heart represented here by the 1s orbital. In the outer region we noticed a slight increase in the effective potential. This allows us to conclude that the effective potential of the helium atom decreases with position. For the carbon atom, the effective potential in its ground state as in excited states, evolves in the same way. There is a very rapid increase in potential in the area near the nucleus, but as we move away from the nucleus, it begins to stabilize to tend towards a limit value for all four states studied. Regarding the electron density, we note that in the ground state all the electrons are in the 1s orbital, this gives a very dense orbital characterized by a maximum greater than all the maxima found for this orbital in the excited states. At the excited states $1s^1 2s^1$ and $1s^1 2p^1$, we have two maxima, the electrons have reached the radii of the 1s and 2s orbitals. In these states

the 1s orbital is denser than the 2s and 2p orbitals and has a much higher maximum than that obtained in the 2s or 2p orbital. In the excited state $1s^1 3s^1$ the 3s orbital is small compared to the 1s orbital which is larger and closer to the nucleus. The electron density in this state passes through a maximum at the radius of the 1s orbital; at the radius of the 3s orbital we also have a very small maximum compared to that found at the radius of the 1s orbital. Regarding the carbon atom, we note that in the ground state and in the excited state $1s^2 2s^1 2p^3$, we have two maxima of the electron density, the electrons reached the radii of the 1s, 2s and 2p orbitals. The maximum electron density at the smallest position is greater than the other maxima. The 1s orbital is denser than the 2s and 2p orbitals. In the excited states $1s^2 2s^2 2p^1 3s^1$ and $1s^2 2s^2 2p^1 3p^1$, we have three maxima. The third maximum appears at the radius of the 3s orbital. Finally, with respect to radial wave functions, it is a question of describing the regions of space where the electrons of helium and carbon atoms are likely to be found. Thus, we note that for the helium atom, the 1s orbital is closer to the nucleus than the 2s, 2p and 3s orbitals. The 2s and 2p orbitals have their electrons farther from the nucleus than those of the 1s orbital but closer than the electron in the 3s orbital. For the carbon atom, the results confirm the information provided by its electron density. They also show the negative part of the radial wave function. Ultimately, we conclude that the effective potential of a multielectronic atom decreases with position and that the densest orbitals are those near the nucleus. The density functional theory is therefore a good approximation for the treatment of the electronic structure of multielectronic

atoms. However, to give this study all its quintessence, it is imperative to validate these results by exploiting other ab-initio methods such as the linearized augmented plane wave method (FP-LAPW) and the linearized muffin-tin orbitals method (FP-LMTO).

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Competing Interests

The authors declare no competing interests.

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