

On the computational quantum mechanics from Schrödinger to Kohn-Sham equation via 3D-FEM

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Résumé :

La détermination des paramètres d'interactions entre les molécules est très importante pour les simulations moléculaires. Pour déterminer ces potentiels, on utilise généralement l'équation de Schrödinger. Mais le problème rencontré réside dans la résolution des équations aux dérivées partielles (EDPs) multidimensionnelles générées après l'application de l'opérateur Hamiltonien sur chaque électron. Ainsi, l'objectif de cette communication est de résoudre l'équation de Kohn-Sham par la méthode des éléments finis en 3D dans le cas des systèmes mono-électronique, plus précisément le cas de l'atome d'hydrogène.

Abstract :

The accurate atomic potential determination is an essential task in the molecular simulations. The so-called ab-initio simulations using the quantum mechanics are of great interest in the computational physics and computational mechanics. Basically, the potential interactions can be obtained by means of the Schrödinger's equation. The main obstacle in the quantum mechanics is the solution of this equation whose application leads to the multi-dimensional PDEs with the Hamiltonian operator for every single electron. The Kohn-Sham's method which establishes the Density Functional Theory, is widely used in the quantum mechanics field. Basically, the 3D finite element method can be used to solve the Schrödinger's equation for the mono-electronic cases. In the present contribution, the solution of the Schrödinger's equation as well as KS model have been brought via the numerical implementations under 3D finite element method and eigenvalue problem solvers.

Mots clefs : Quantum mechanics, Schrödinger's equation, Kohn-Sham method, self-consistency, 3D-FEM

1 Brief presentation of Schrödinger's equation

In the quantum mechanics, the Schrödinger's equation can be described as a Partial Differential Equation and it represents how the quantum state of a physical system varies within time. It was formulated in late 1925 by the Erwin Schrödinger [1]. This equation may be time-independent, time-dependent, 1-D, 3-D, 1-particle and N-particles. The general Schrödinger equation is displayed as below :

$$H\Psi = E\Psi \quad \text{on} \quad \Omega \subset \mathbb{R}^N \quad (1)$$

Where H is Hamiltonian operator of system, E represent energy, and ψ is quantum mechanical wave function, respectively. However, the definition of the expression of Hamiltonian depends on the number of nuclei and electron system (monoatomic or polyatomic). Equation (1) can be re-written as below :

$$H\Psi =$$

$$\overbrace{\left[\underbrace{-\sum_{k=1}^N \frac{\hbar^2}{2M_k} \nabla_k^2}_{\text{Nuclear kinetic energy}} \underbrace{-\sum_{i=1}^n \frac{\hbar^2}{2m_e} \nabla_i^2}_{\text{Electron kinetic energy}} \underbrace{-\frac{1}{4\pi\epsilon_0} \sum_{k=1}^N \sum_{i=1}^n \frac{z_k e}{R_{ik}}}_{\text{Electron/nuclear attraction}} + \underbrace{\frac{1}{4\pi\epsilon_0} \sum_{i=1}^n \sum_{j \neq i}^n \frac{e^2}{r_{ij}}}_{\text{Electron/electron repulsion}} + \underbrace{\frac{1}{4\pi\epsilon_0} \sum_{k=1}^N \sum_{k < l}^N \frac{z_k z_l}{R_{kl}}}_{\text{Nuclear/nuclear repulsion}} \right]}_{E=\text{Energy eigenvalue}} \Psi$$

$$= E\Psi \quad \text{on} \quad \Omega \subset \mathbb{R}^N \quad (2)$$

where, \hbar , M_k , m_e , R_{ik} , R_{kl} , r_{ij} and e are the Plank constant over 2π , the mass of k^{th} nucleus, mass of an electron, distance between the electron and nuclei, distance between nuclei, distance between electrons and electron charge, respectively.

1.1 Schrödinger's equation solution for the hydrogen atom H

Basically, the Schrödinger's equation is described by means of atomic units due to its advantage in the computational physics and its simplicity. The simplest form of the above-mentioned equation can be extracted for hydrogen atom, i.e. H and hydrogen cation, i.e. H_2^+ . The aforementioned cases involves only an electron and as a consequence, the Schrödinger's PDE gets reduced to the well known PDEs whose application leads to the only 3-Dimension. Let's get started with the simplest case in which the analytical solution is comprehensively studied, i.e. hydrogen atom. The hydrogen atom contains only an electron and one can readily write the Schrödinger's equation as following :

$$\left[-\frac{\hbar}{2m_e} \left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial x_3^2} \right) + V(x_1, x_2, x_3) \right] \Psi = E\Psi \quad \text{on} \quad \Omega \subset \mathbb{R}^3 \quad (3)$$

where,

$$V(\vec{r}) = -\frac{e}{4\pi\epsilon_0 r} = -\frac{e}{4\pi\epsilon_0 \sqrt{x_1^2 + x_2^2 + x_3^2}} \quad (4)$$

Equation (3) and Equation (4) can be re-written under the atomic units considerations as :

$$\left[-\frac{1}{2} \left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial x_3^2} \right) + V(x_1, x_2, x_3) \right] \Psi = E\Psi \quad \text{where} \quad V(\vec{r}) = -\frac{e}{r} = -\frac{e}{\sqrt{x_1^2 + x_2^2 + x_3^2}} \quad (5)$$

Basically, the distance and energy units in the atomic units considerations are in [*bohr*] and [*eV*], respectively. The geometrical configuration of the hydrogen atom has been shown in Figure 1.

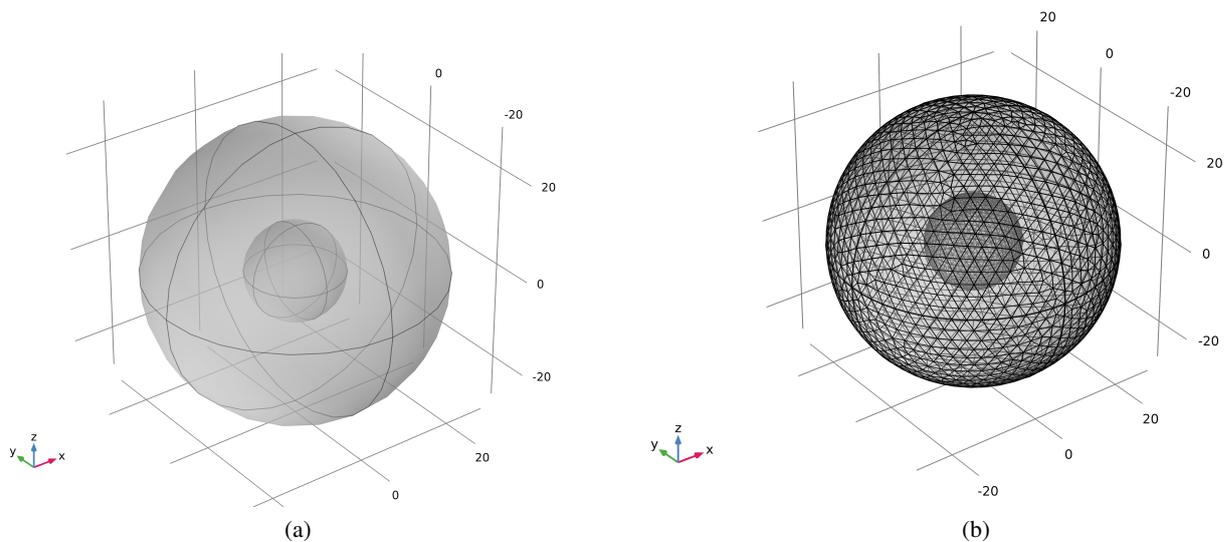


FIGURE 1 – a) Geometrical configuration of hydrogen atom (inside radius=9.4486 [*bohr*]= 0.5 [*nm*] and outside radius= 28.3459 [*bohr*]=1.5 [*nm*]), b) 3D-FEM mesh density including very fine mesh densities at the atom nucleus.

As shown in Figure 1, the 3D-FEM model contains two spheres with very high mesh density and high mesh density including 0.5 [*nm*] and 1.5 [*nm*]. The solution of Equation (5) by means of the required boundary conditions can be done via 3D finite element analysis using eigenvalue problem solvers [2, 3, 4, 5]. As pointed out earlier, the state field variable is known as the wave function. The wave function can be linked to the electron probability density and electron presence probability in the quantum mechanics. Basically, the solution of the Schrödinger's equation gives rise the wave function distribution determination via the finite element analysis or Density Functional Theory software in the computational physics and quantum mechanics communities. The solution of equation via the FEM entails the eigenvalue problem solvers. To pursue the numerical solution of the above-mentioned equation, the relevant boundary conditions must be taken into account. The Dirichlet boundary condition for the outer surfaces can be applied and this relies on the fact that there is more unlikely to find the electron outside the second sphere (far beyond 1.5 [*nm*] from the atom nucleus). The numerical solutions of the Schrödinger equation have been provided in Figure 2 and Figure 3. In Figure 2 and Figure 3, the projection of the wave function on the XY, XY and ZX planes have been brought via 3D-FEM. Additionally, the isosurface illustrations of wave function outcomes for different values of energy have been presented to highlight the possible orbital shape under various energy values.

The numerical solutions for the hydrogen atom can be simply compared to those obtained by the analytical solution and recently experimental observations (Figure 4).

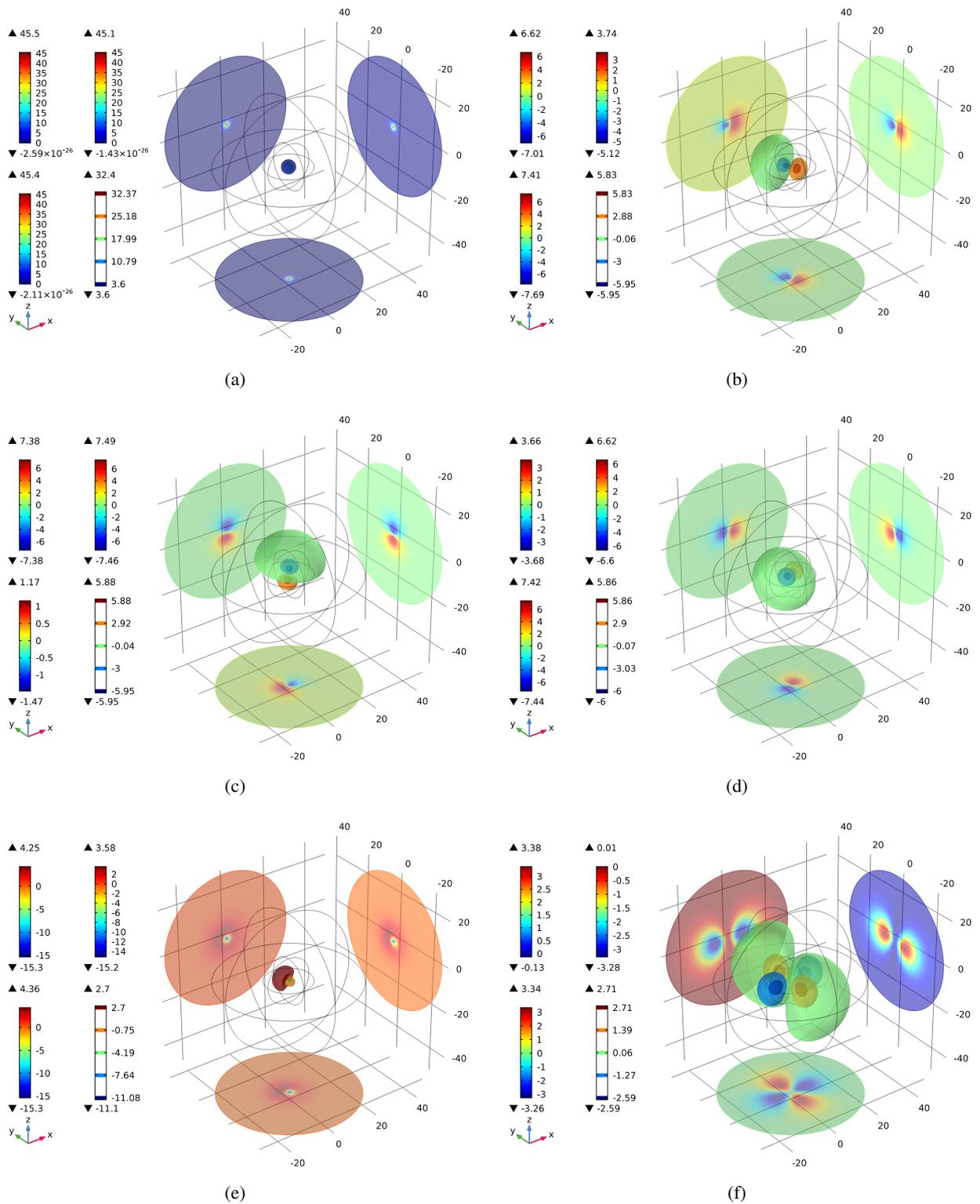


FIGURE 2 – YZ-plane slice plot, XY-plane slice plot, ZX-plane slice plot and isosurface plot of wave function ψ for a) $E_1 = -0.49655$ [Hartree] = -13.512 [eV], b) $E_2 = -0.12496$ [Hartree] = -3.4003 [eV] c) $E_3 = -0.12496$ [Hartree] = -3.4003 [eV], d) $E_4 = -0.12496$ [Hartree] = -3.4003 [eV], e) $E_5 = -0.12496$ [Hartree] = -3.4003 [eV] and f) $E_6 = -0.055496$ [Hartree] = -1.5101 [eV].

One of the main issue in the quantum mechanics is that one can get the realistic electron density via the

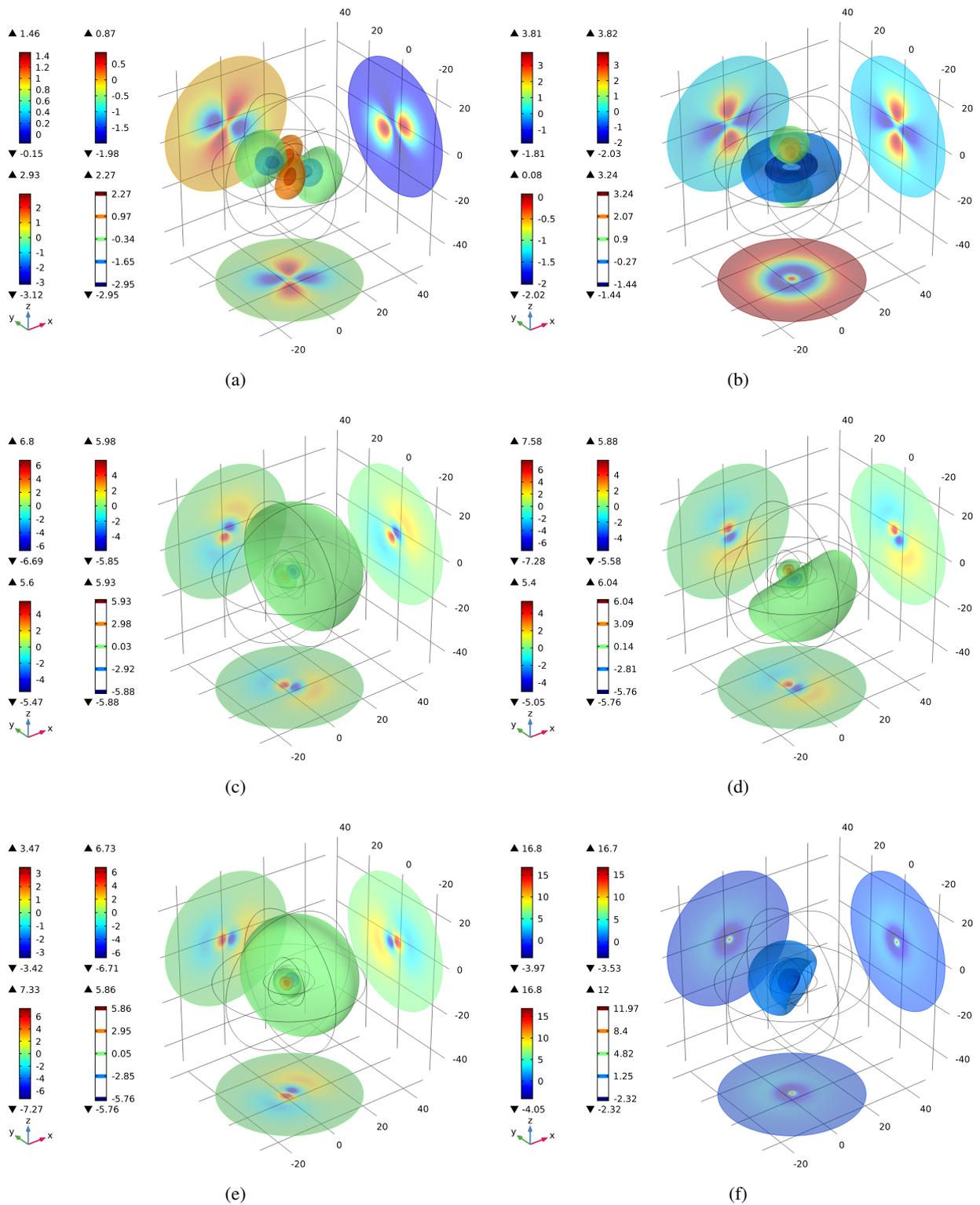


FIGURE 3 – YZ-plane slice plot, XY-plane slice plot, ZX-plane slice plot and isosurface plot of wave function ψ for a) $E_7=-0.055496$ [*Hartree*]=-1.5101 [eV], b) $E_8=-0.055496$ [*Hartree*]=1.5101 [eV] c) $E_9=-0.055496$ [*Hartree*]=1.5101 [eV], d) $E_{10}=-0.055496$ [*Hartree*]=1.5101 [eV], e) $E_{11}=-0.055355$ [*Hartree*]=-1.5063 [eV] and f) $E_{12}=-0.0550719$ [*Hartree*]=-1.4986 [eV] .

computational methods. That is why it is also called ab-initio method in the computational physics and

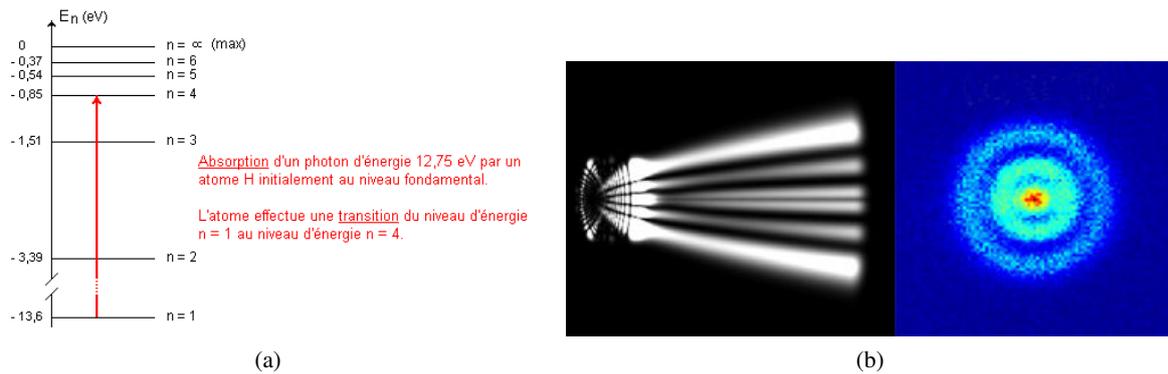


FIGURE 4 – a) Hydrogen atom energy level illustration in [eV] and b) Experimental observation of unresonated hydrogen atom [6].

mechanics communities. It is straightforward to emphasize that the wave function has not the physical meaningful interpretation in a general manner. As a matter of fact, the wave function square can be considered as the probability density, i.e. $|\psi|^2 := \psi \times \psi$. The latter definition can be applied to determine the probability of electron presence in the quantum mechanics (Figure 5).

1.2 Schrödinger's equation solution for the hydrogen cation H_2^+

The hydrogen molecule ion is also the simplest molecule. The main reason behind this fact is that it involves only an electron like hydrogen atom. Similarly, the electronic Schrödinger equation exactly can be extracted [7, 8, 9, 10]. Moreover, the numerical solution can be realized via the Schrödinger's equation either.

In Figure 6a, the molecular structure of hydrogen molecule is exhibited. The H_2^+ illustration has been depicted in Figure 6b. As illustrated in Figure 6b, two protons are labeled H_1 and H_2 . The distances from each proton to the electron e are denoted as r_1 and r_2 , respectively. r is the distance between H_1 and H_2 . Therefore, the Hamiltonian for the hydrogen molecular ion without the Born-Oppenheimer approximation is given by :

$$H = \underbrace{-\frac{\hbar^2}{2M}(\nabla_1^2 + \nabla_2^2)}_{\text{Nuclear energy kinetics}} \underbrace{-\frac{\hbar^2}{2m_e}\nabla_e^2}_{\text{Electron energy kinetics}} \underbrace{-\frac{e^2}{4\pi\epsilon_0 r_1} - \frac{e^2}{4\pi\epsilon_0 r_2}}_{\text{Nuclear/electron attraction}} \underbrace{+\frac{e^2}{4\pi\epsilon_0 r}}_{\text{Nuclear/nuclear repulsion}} \quad (6)$$

Evidently, this Hamiltonian yields the multi-dimensional PDE equation and it can not be handled in an usual manner like that done for the hydrogen atom case study. The Born-Oppenheimer approximation can be used in H_2^+ case in the sense that the mass of nuclei is too much greater than the electron mass and the first part in Equation (6) vanishes as below :

$$H = \underbrace{-\frac{\hbar^2}{2M}(\nabla_1^2 + \nabla_2^2)}_{\approx 0} \underbrace{-\frac{\hbar^2}{2m_e}\nabla_e^2}_{\text{Electron energy kinetics}} \underbrace{-\frac{e^2}{4\pi\epsilon_0 r_1} - \frac{e^2}{4\pi\epsilon_0 r_2}}_{\text{Nuclear/electron attraction}} \underbrace{+\frac{e^2}{4\pi\epsilon_0 r}}_{\text{Nuclear/nuclear repulsion}} \Rightarrow \quad (7)$$

$$H = -\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{e^2}{4\pi\epsilon_0 r_1} - \frac{e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r}$$

Once again, we take advantage of the Schrödinger's equation, $H\psi = E\psi$ with the extracted Hamiltonian

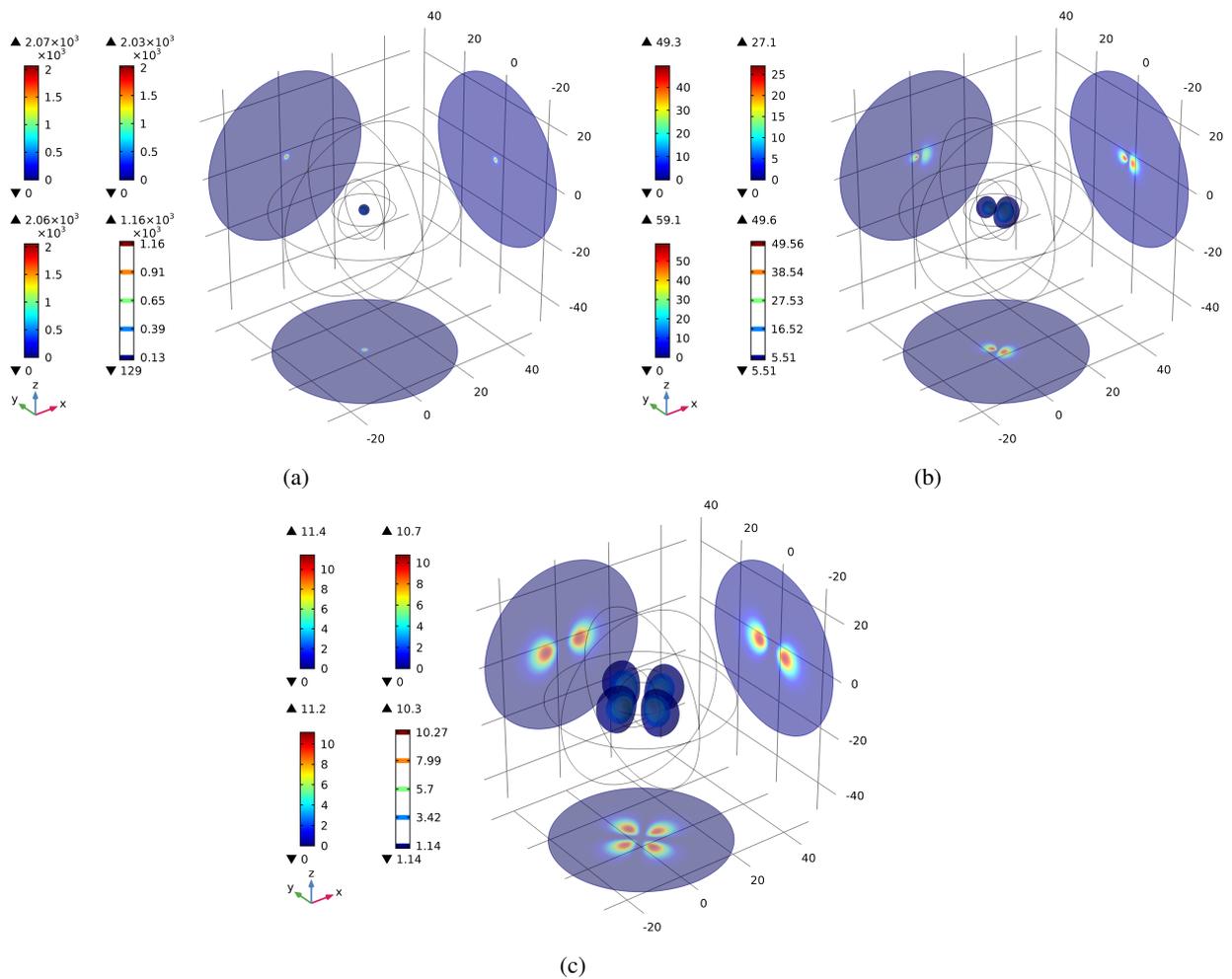


FIGURE 5 – Probability density ($|\psi|^2$) for hydrogen atom at a) $E_1=-13.512$ [eV], b) $E_2=-3.4003$ [eV] and c) $E_6=-1.5101$ [eV].

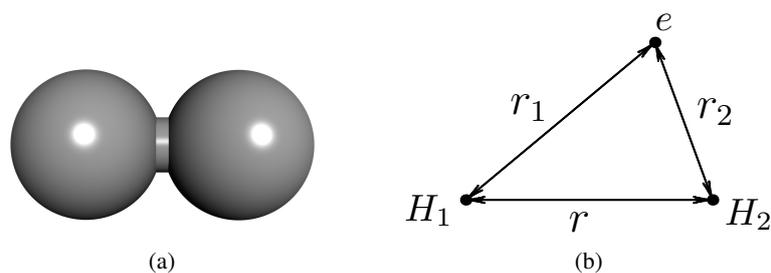


FIGURE 6 – a) Hydrogen molecule, H_2 molecular illustration and b) Hydrogen cation, H_2^+ illustration for Schrödinger's equation description [11].

and we arrive at the PDE equation whose application can prepare the solution of wave function and other relevant quantum mechanics parameter like those described earlier herein.

$$\left[-\frac{\hbar^2}{2m_e} \left(\frac{\partial}{\partial x_1} + \frac{\partial}{\partial x_2} + \frac{\partial}{\partial x_3} \right) - \frac{e^2}{4\pi\epsilon_0 r_1} - \frac{e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r} \right] \psi = E\psi \quad \text{on } \Omega \subset \mathbb{R}^3 \quad (8)$$

It is of great importance to note that the accurate and computationally affordable solution of Equation

(8) can be carried out via the atomic units. Hence, one can infer the following PDE for computation purposes via FEM :

$$\left[-\frac{1}{2} \left(\frac{\partial}{\partial x_1} + \frac{\partial}{\partial x_2} + \frac{\partial}{\partial x_3} \right) - \frac{e^2}{r_1} - \frac{e^2}{r_2} + \frac{e^2}{r} \right] \psi = E\psi \quad \text{on } \Omega \subset \mathbb{R}^3 \quad (9)$$

One main issue is to obtain the potential interaction between atoms. This can be handled via 3D-FEM parametric computations in the sense that the distance between first and second proton can be gradually varied, e.g. from 1 [pm]=0.001 [nm] to 1000 [pm]=1 [nm]. These 3D-FEM computations of Equation (9) give rise the potential interaction which is substantially required at atomic scale (Figure 7). Consequently, one can obtain very important plot, i.e. potential energy versus distance for the molecular simulation at atomic scale.

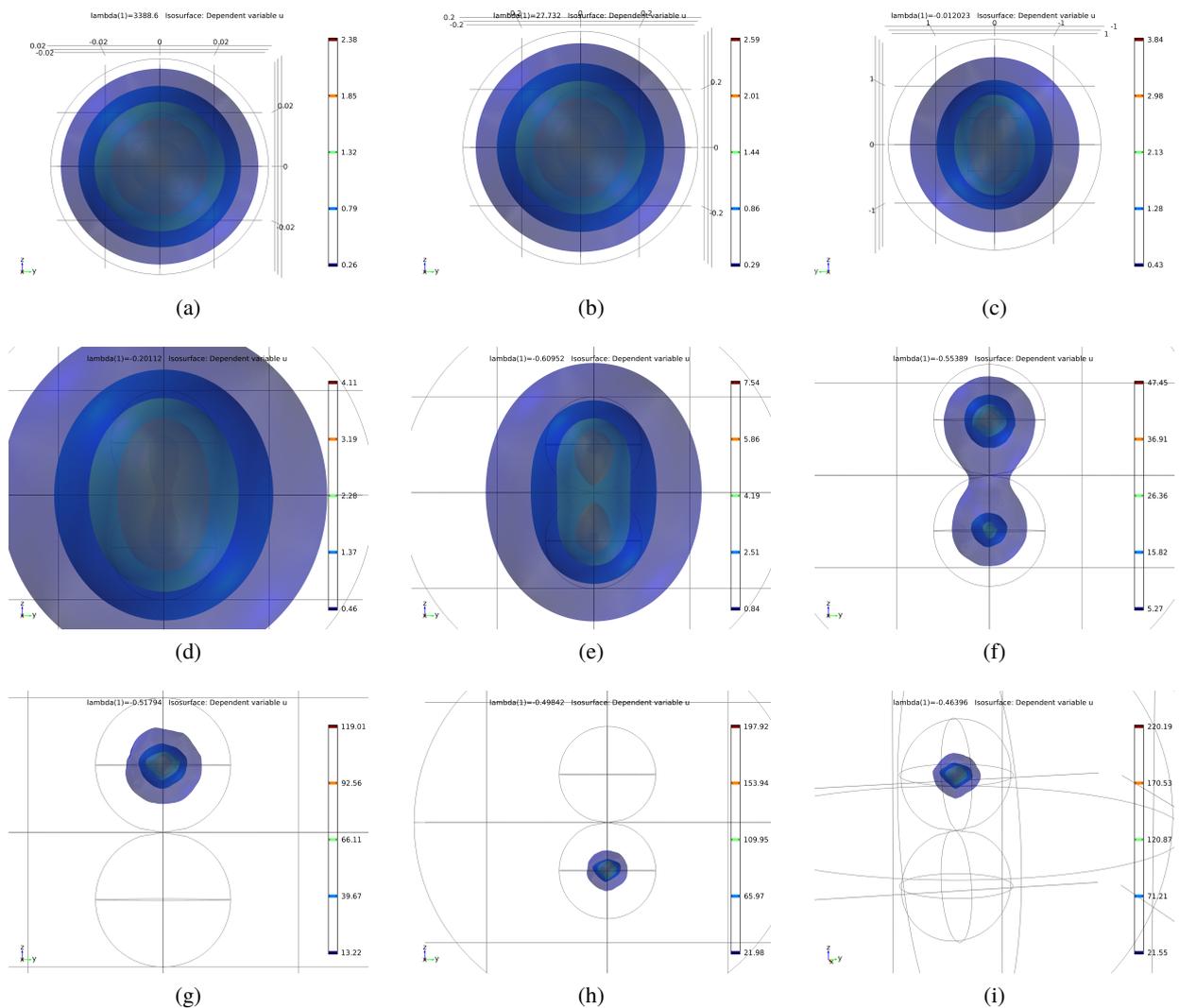


FIGURE 7 – Wave function distribution outcomes for H_2^+ [11], a) Proton distance = 0.01 [Å]=1 [pm]=0.001 [nm], b) Proton distance = 0.1 [Å]=10 [pm]=0.01 [nm], c) Proton distance = 0.45 [Å]=45 [pm]=0.045 [nm], d) Proton distance = 0.50 [Å]=50 [pm]=0.050, e) Proton distance = 1 [Å]=100 [pm]=0.1 [nm], f) Proton distance = 3 [Å]=300 [pm]=0.3 [nm], g) Proton distance = 5 [Å]=500 [pm]=0.5 [nm], h) Proton distance = 8 [Å]=800 [pm]=0.8 [nm] and i) Proton distance = 10 [Å]=1000 [pm]=1 [nm].

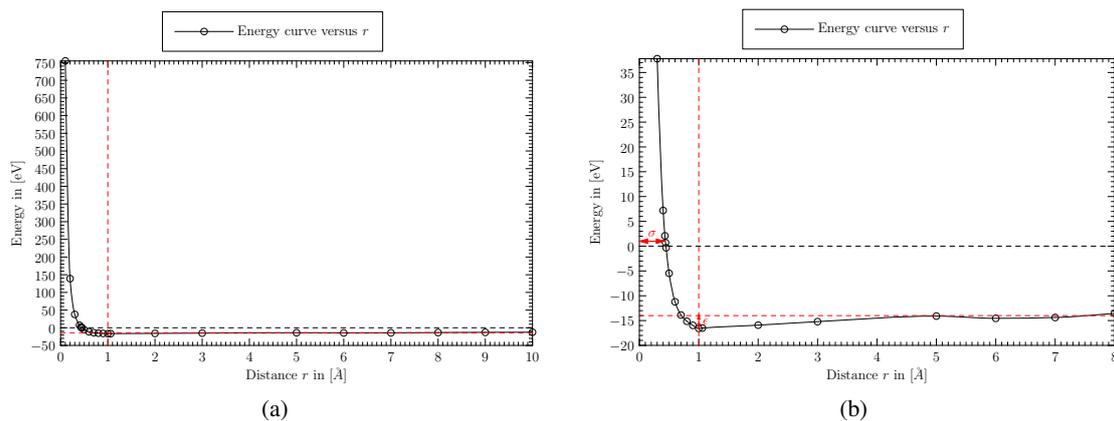


FIGURE 8 – Potential energy versus proton distance, a) Global curve trend and b) Detailed curve [11].

In Figure 8a and Figure 8a, the potential interaction curve is plotted versus proton distance. This curve can be approximately fitted to the semi-empirical potential expressions in the literature, e.g. Lennard-Jones, $\sigma=0.44$ [Å] and $\varepsilon=3.023$ [eV]. Let us get started with more complex cases, e.g. hydrogen molecule H_2 and carbon dioxide CO_2 . The main problem of these molecules is that the Hamiltonian is getting more complex and the Schrödinger's equation turns to be multi-dimensional PDE. For instance, the number of dimensions for H_2 and CO_2 molecules are equal to $3 \times 2=6$ and $3 \times (6 + 2 \times 8)=66$ dimensions, respectively. Therefore, the problem gets more and more complex and the Schrödinger's equation solution would not be the feasible choice.

2 Kohn-Sham's equation description

2.1 Brief Kohn-Sham's equation description and assumptions

The Kohn-Sham's equation would reduce the complexities coming from the Schrödinger's equation by means of some assumptions and approximations. The Kohn-Sham's Ansatz provides mono-electronic PDE for every single electron in the molecule. This equation can be written as below :

$$\left[-\frac{1}{2}\nabla^2 + V_S(r) \right] \psi_i(r) = \varepsilon_i \psi_i(r) \quad \text{where} \quad V_S(r) := V_H(r) + V_{EXT}(r) + V_{XC}(r) \quad \text{for} \quad i = 1, \dots, N \quad (10)$$

where, V_S , V_H , V_{EXT} , V_{XC} , ε_i and N are the Kohn-Sham effective potential, Hartree potential, external potential, exchange-correlation potential, energy at i and number of electrons in the molecule, respectively. The Equation (10) sustains system of non-linear PDEs, e.g. a system of two PDEs for the hydrogen molecule and a system of 22 PDEs for the CO_2 molecule. These equations can be numerically solved by means of Density Functional Theory and/or finite element method [12, 13, 14].

The main assumptions and definitions in the Kohn-Sham's equation can be summarized as below :

- The electron density definition, $n(r)$,
- The ground state electron density completely determines all properties of an atomic system [15, 16],

- The existence of an energy functional which takes its minimum at the ground state electron density $n_0(r)$ [15, 16],

In Equation (10), there are several terms. The first term is the effective potential whose value is equal to the sum of Hartree potential, external potential and exchange-correlation potential. These potentials can be denoted as :

$$V_{\text{EXT}} := \sum_{A=1}^M \frac{Z_A}{|R_A - r|} \quad (11a)$$

$$V_{\text{H}} := \int_{\Omega \subset \mathbb{R}^3} \frac{n(r')}{|r - r'|} dr' \quad \text{or} \quad \nabla \cdot (-\nabla (V_{\text{H}})) = 4\pi n(r) \quad (11b)$$

$$V_{\text{XC}} := \frac{\delta E_{\text{XC}}}{\delta n(r)} \quad \text{where} \quad E_{\text{XC}} := \int_{\Omega \subset \mathbb{R}^3} \epsilon(n(r)) n(r) dr \quad (11c)$$

The exchange-correlation potential, V_{XC} is not well known in the Density Functional Theory based on the Kohn-Sham's equation. Consequently, there is a bunch of equations dealing with this term in the quantum mechanics community, e.g. Fermi's approximation, Local Density Approximation (LDA) and Generalized Gradient Approximation (GGA).

$$E_{\text{XC}} := \begin{cases} \int_{\Omega} \epsilon(n(r)) n(r) dr, & \mathbf{LDA} \\ \int_{\Omega} f(n(r), \nabla n(r)) dr, & \mathbf{GGA} \end{cases} \quad (12)$$

In the next section, the numerical scheme of the Kohn-Sham's equation is represented. It is of great importance to recall that the Kohn-Sham convergence can be handled via the self-consistency condition. We talk about it in the next section.

3 Kohn-Sham's equation numerical scheme

The Kohn-Sham's equation can be solved by means the illustrated flowchart in Figure 9. The starting point is the computation of initial electronic density. Afterwards, the initial density is utilized to reach the solution for Kohn-Sham equations. It is required to note that there is a non-linear PDE for every single electron and one should deal with a system of non-linear PDEs. This leads to the wave function for each electron ψ_i . It is necessary to use these wave functions to compute again new electronic density. The Kohn-Sham's Ansatz is applied here to verify whether the new electronic density coincides with the previous iteration. This condition should be rigorously verified to get the solution. This issue is a vital stage in the computations of the DFT method.

Basically, the computation of the Hartree potential can be done in an implicit manner using Poisson's equation. Actually, the solution of the Poisson's equation for the Hartree potential is substantially more computationally affordable than the explicit one. Let us take into account the case of the hydrogen molecule. The Kohn-Sham's equation can be denoted as :

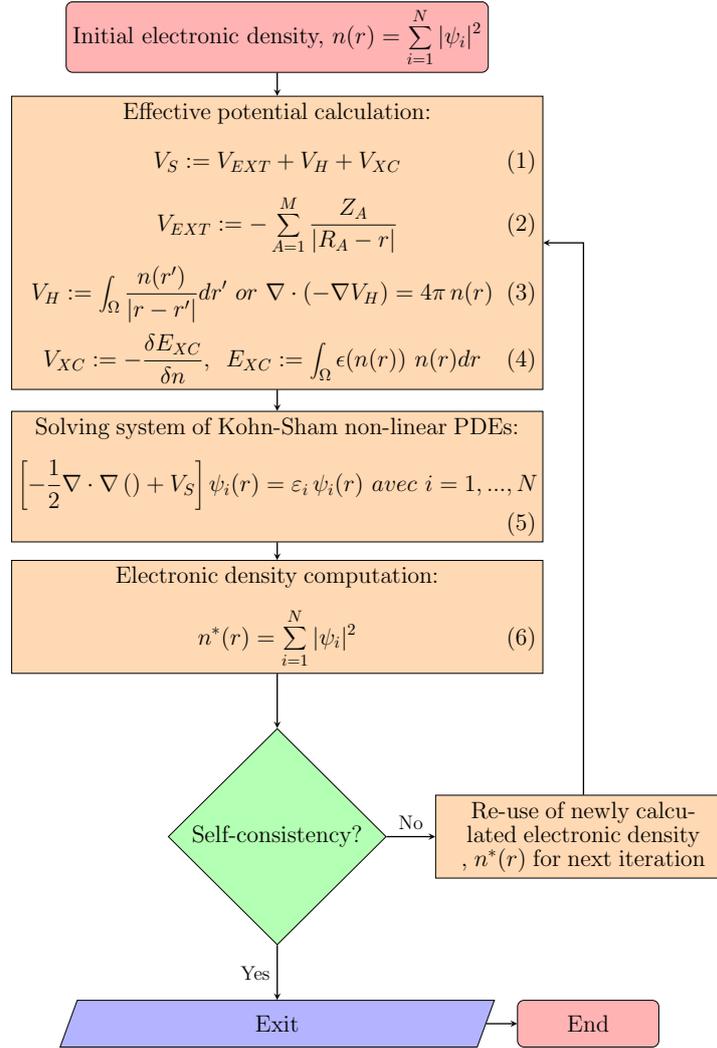


FIGURE 9 – Kohn-Sham’s method numerical scheme indicating self-consistent field algorithm.

$$\left[-\frac{1}{2} \nabla^2 + V_S(r) \right] \psi_1(r) = \epsilon_1 \psi_1(r) \quad \text{on } \Omega \subset \mathbb{R}^3 \quad (13a)$$

$$\left[-\frac{1}{2} \nabla^2 + V_S(r) \right] \psi_2(r) = \epsilon_2 \psi_2(r) \quad \text{on } \Omega \subset \mathbb{R}^3 \quad (13b)$$

$$n(r) = \psi_1^2(r) + \psi_2^2(r) \quad (13c)$$

$$\nabla \cdot (-\nabla (V_H)) = 4\pi n(r) \quad \text{on } \Omega \subset \mathbb{R}^3 \quad (13d)$$

$$V_S(r) := V_H(r) + V_{EXT}(r) + V_{XC}(r) \quad (13e)$$

$$V_{XC}(r) = V_X(r) + \overbrace{V_C(r)}^{V_C(r)=0} = V_X(r) = \left(\frac{3n(r)}{\pi} \right)^{\frac{1}{3}} \quad (13f)$$

It is well worth mentioning that Equation (13f) deals with the Thomas-Fermi assumption (1927) pertaining to the exchange-correlation potential. In fact, $V_{XC}(r)$ can be divided into the summation of two counterparts. The first one can be called as $V_X(r)$ and the second one can be named as $V_C(r)$. In the Thomas-Fermi’s exchange-correlation potential, there is only the first counterpart. As pointed out, the

accurate definition of exchange-correlation function for the molecules is an open problem.

4 Numerical experiments

In this section, the numerical outcomes for Kohn-Sham's equation for hydrogen molecule using Thomas-Fermi mathematical expression (Equation (13f)) are presented as a LDA (Local Density Approximation) subgroup definition. Basically, the use of the Thomas-Fermi as exchange-correlation potential is limited to the numerical experiments herein. In Figure 10, the wave functions and electronic density distributions have been displayed using 3D-FEM as long as adaptive meshing algorithm. The adaptive meshing technique makes more accurate results during the computations. This issue has been added to all PDEs of Kohn-Sham's equations.

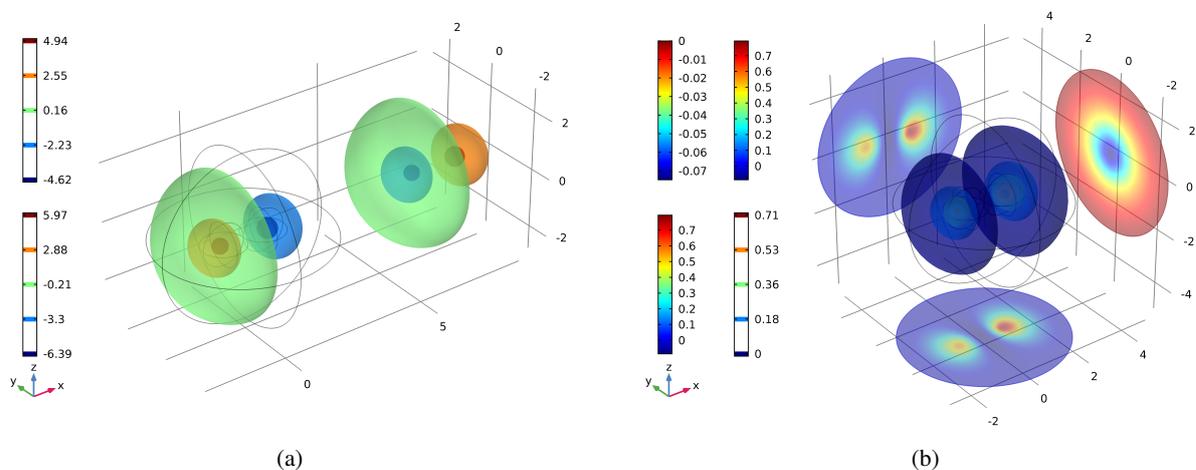


FIGURE 10 – Kohn-Sham's equation outcomes using Thomas-Fermi approximation for $V_{XC}(r)$, a) Wave functions distributions, ψ_1 and ψ_2 and b) Electronic density on YZ, XY and ZY planes and isosurface plot for H₂.

The extracted outcomes via the finite element analysis demonstrates that it is quite possible to fully implement the Kohn-Sham equation into the general purpose finite element method packages using the self-consistency conditions involving the iterative algorithm. The main challenge would be the accurate determination of eigenvalues using the finite element method. To achieve this assignment, it is required to use the most relevant eigensolvers and sufficient mesh density at the required zones next to the atom nuclei. The latter matter can be done via the adaptive meshing. It is quite possible to investigate its benefits and there are some contributions dealing with this issue in the literature, e.g. [13, 14]

5 Conclusion

The present contribution demonstrate that the 3D-FEM can be used to achieve the solution of the Schrödinger's equation as well as Kohn-Sham's equation. The difficulties stemming from the multi-dimensional issues of the Schrödinger's equation have been highlighted and emphasized herein. The numerical solutions via Eigenvalue solvers and adaptive meshing have been utilized to obtain the Energy levels, 3D-wave function distributions and electronic density for the simple cases in the current study. This substantiates that the computational mechanics can be applied to solve the quantum mechanics problems. The next contributions should be focused on the accuracy for the numerical solutions and very

precise exchange-correlation potentials for the molecules. The most interesting aspect is that the Local Density Approximation and Generalized Gradient Approximations can be easily handled in the present 3D-FEM numerical scheme by means of the MATLAB-COMSOL code applied to reach the solutions in the present work. This issue can not be readily carried out in the current available DFT softwares.

6 Acknowledgments

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Nomenclature

Constants

ϵ_0 $\frac{1}{\mu_0 C^2}$ Permittivity of free space 8.8542×10^{-12} in [$C^2/N.m^2$]

\hbar $\frac{h}{2\pi}$ $1.054571628 \times 10^{-34}$ in [$J.s$]

e Charge on an electron 1.60218×10^{-19} in [C]

h Plank's constant $6.62606896 \times 10^{-34}$ in [$J.s$]

M Mass of nucleus in [au]

M Mass of the nuclei in [Kg]

m_e Mass of electron 9.1094×10^{-31} in [Kg]

Scalar quantities

ψ Wave function in [$-$]

ϵ_i energy in [$Hartree$]

E Energy eigenvalue in [J]

$f(n(r), \nabla n(r))$ Generalized Gradient Approximation function

$n(r)$ electronic density potential in [$-$]

r distance between the first proton and second proton in [$bohr$]

r_1 distance between the first proton to the electron in [$bohr$]

r_2 distance between the second proton to the electron in [$bohr$]

V_C second counterpart of V_{XC} in [$Hartree$]

V_{EXT} external potential in [$Hartree$]

V_H Hartree potential in [$Hartree$]

V_S effective Kohn-Sham's potential in [$Hartree$]

V_{XC} exchange-correlation potential in [$Hartree$]

V_X first counterpart of V_{XC} in [$Hartree$]

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