Abstract: The accurate atomic potential determination is an essential task in the molecular simulations, e.g. Grand Canonical Monte Carlo (GCMC). The so-called ab-initio simulations using the quantum mechanics would be of great interest in the computational physics. The numerical simulation of the adsorption phenomenon requires knowing the interactions parameters between the atoms that make up the systems and it sustains the potential that it would be exploited either. In the present communication, the determination of the interaction parameters for the molecular simulation purposes have been extracted by means of solving the Schrödinger’s equation using the finite element method. The Partial Differential Equation (PDE) implementation of the Schrödinger has been successfully achieved via COMSOL MP.

Keywords: Schrödinger equation; Wave function; Custom PDE; FEA; Hydrogen atom

1 Introduction

There is a bunch of studies pertaining to the purification of water by means of the physically- or chemically-motivated ways. The physical adsorption can be addressed as a prominent method of purification. The adsorption is a surface phenomenon in which the particles or molecules (adsorbate) bind to the top layer of a material (adsorbent) [1]. However, the physisorption deals with the Van der Waals interactions between adsorbent and adsorbate, whereas, the chemisorption handles the chemical bonds that are involved between the adsorbate and adsorbent.

To achieve the physisorption adsorption, it is necessary to know the values of the parameters of molecules interactions. The determination of these parameters can be done via the quantum mechanics involving the Schrödinger equation. The Lennard-Jones’ molecular parameters, i.e. $\epsilon$ and $\sigma$ are usually determined from physical properties such as the critical constants, second virial coefficient, viscosity and crystal properties [2, 3]. The empirical potentials are customarily applied to perform the molecular simulations, e.g. Grand Canonical Monte Carlo (GCMC). The most commonly-used pairwise additive potential has been proposed by Lennard Jones (Equation 1). This potential is increasingly used to determine the intermolecular parameters for simple molecules ($H_2$, $O_2$, $N_2$, $CO$, $CH_4$) [3], in which we add the interaction terms in some cases potential iodide (KI) molecule [4, 5].

$$U_{LJ}^{ij}(r) = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right]$$  \hspace{1cm} (1)

However, there are some additional potentials such as the Morse’s potential (Equation 2) [6, 7]. The aforementioned potential takes advantage of four parameters and it provides the smaller separation distances between the atoms as well.

$$U^M(r_{ij}) = D \left[ \exp(-2\beta(r_{ij} - r_c)) - 2\exp(-\beta(r_{ij} - r_c)) \right] + E_\infty$$ \hspace{1cm} (2)

where, $D$, $r_{ij}$, $r_c$, $\beta$ and $E_\infty$ are the dissociation energy, internuclear separation, mean bond length and constants extracted from the spectroscopic data, respectively. One can also address some further potentials, e.g. Rydberg’s potential, Buckingham’s potential, Murrel-Mottram’s potential and
Biswas-Hamann’s potential (See appendix A for more details). The COMSOL MP is used to solve the Schrödinger’s equation in the case of the hydrogen molecule herein [8, 9]. The paper is organized as following: The second section deals with the methods and theory about Schrödinger’s equation. The use of Comsol Multiphysics has been brought in the third section. The Results and discussion in fourth section. At last, some conclusions and outlooks are discussed.

2 Methods and theory

The adsorption of different molecules, e.g. H₂, Pb and Cd, on different forms of carbon-based materials are of great interest in the adsorption society (See Figure 1, Figure 2 and Figure 3).

Figure 1: Typical illustration of nanotube.

Figure 2: Typical illustration of graphite (slit-shaped).

Figure 3: Typical illustration of conical shapes [10].

The above-mentioned adsorptions may be carried out by means of the chemical or physical methods. For physical method, the real problem is the definition of the interaction potential of the molecules that they should be adsorbed. Thus, different methods are presented in the literature to determine the potential that is best for a particular molecule including Density Functional Theory (DFT) methods. The finite element method can be utilized to solve the Schrödinger’s equation as well. In the quantum mechanics, the Schrödinger’s equation can be described as a PDE and it highlights how the quantum state of a physical system changes within time. It was formulated in late 1925 by the Australian physicist Erwin Schrödinger [11]. This equation has different forms for a specific situation. Thus, it may be time-independent, time-dependent, 1-D, 3-D, 1-particle and N-particles. The general Schrödinger equation is displayed as Equation 3.

\[ H \psi = E \psi \]  

Where \( H \) is Hamiltonian operator of system, \( E \) represent energy, and \( \psi \) is quantum mechanical wave function. However, the definition of the expression of Hamiltonian depends on the number of nuclei and electron system studied (monatomic or polyatomic). If we consider the case of an atom (N nuclei and n electron) expression of the Hamiltonian is given by Equation 4.

\[
H = -\sum_{k=1}^{N} \frac{\hbar^2}{2M_k} \nabla_k^2 - \sum_{i=1}^{n} \frac{\hbar^2}{2m_e} \nabla_i^2 - \frac{1}{4\pi\varepsilon_0} \sum_{k=1}^{N} \sum_{i=1}^{n} \frac{z_ke}{R_{ik}} + \frac{1}{4\pi\varepsilon_0} \sum_{i=1}^{n} \sum_{j=1}^{n} \frac{e^2}{r_{ij}} + \frac{1}{4\pi\varepsilon_0} \sum_{k<l}^{N} \frac{z_kz_l}{R_{kl}}
\]  

(4)

Where the equation parameters are:

\( \hbar = \frac{h}{2\pi} \), \( h \) is Plank’s constant.

\( M_k \) is the mass of \( k^{th} \) nuclei and \( m_e \) is the mass of an electron.

\( R_{ik} \) is distance between the electron and nuclei.

\( R_{kl} \) is distance between nuclei.

\( r_{ij} \) is distance between electron.
\( e \) is charge of the electron.

\( z_k \) and \( z_l \) are charge of \( k^{th} \) and \( l^{th} \) nuclei.

By applying the condition of Born-Oppenheimer [12] “when we consider the nuclei set”, the Hamiltonian is decoupled part in nuclear and electronics. The resolution of the electronic part allows for the wave function and the energy of the system. In addition, this is the square of the wave function that has a physical meaning and represents the probability of finding an electron. Thus, the validation of the 3D model of the hydrogen was performed by solving the Schrödinger’s equation from COMSOL software, the electrostatic potential in Cartesian coordinates is given by Equation 6.

3 Results

3.1 Hydrogen atom

To make the adsorption of different molecules by numerical simulations, it is useful to determine the parameters of interaction between different atoms that make up the system, this will define the adequate potential to explain the phenomenon.

This article shows how to calculate molecule hydrogen ion the interaction parameters by solving the Schrödinger’s equation and using the finite elements method.

The 2D model of atom hydrogen is treated by exploiting the cylindrical coordinates \((\rho, \phi, z)\). Thus, we must define the Laplacian in cylindrical coordinates and the electronic wave function \(\psi\) as the product of two function, one with a radial and z-coordinate dependence, and the other an angular dependence \((\psi = \psi_1(\rho,z)\psi_2(\phi))\) [13], the results of the model in 2D are presented in Figure 1.

In the case of the resolution of the Schrödinger equation and 3D Cartesian coordinate of the hydrogen atom, the Hamiltonian should be formulated as:

\[
H = -\frac{\hbar^2}{2m_e} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V(x, y, z)
\]

where \( V(x, y, z) = -\frac{e^2}{4\pi \epsilon_0 \sqrt{x^2 + y^2 + z^2}} \).

\[
-\nabla \cdot (e\nabla u + au) + \beta \nabla u + au = d_u u \quad (6)
\]

where the coefficient values of PDE equation (Equation 6) are: \( e = \frac{\hbar^2}{2m_e}, \alpha = 0, a = V, d_u = 1 \).

However, the solution is more accurate when more mesh density is used, this means that more RAM memory is required during the computations (Figure 1, Figure 2).

![Figure 1: Mesh density of the hydrogen atom model in 2D.](image1)

![Figure 2: Mesh (6804786 Degree Of Freedoms (DOFs)) density of 3D the hydrogen atom model.](image2)

However, to validate the model, a comparison has been made with the 2D model that is located in the model library COMSOL. To solve the problem in 3D, it is very important to define the boundary conditions in COMSOL Multiphysics properly,
and also define the terms of the various coefficients of eigenvalue PDE (Equation 6).

The resolution of the equation for the hydrogen atom shows different forms of atomic orbitals.

The results on the Schrödinger’s equation solution for a hydrogen atom have been made to an eigenvalue of $-2 \times 10^{-18} [J]$. The solution gives the minimum value of the energy near to $-2.180 \times 10^{-18} [J]$ (0.50 [Hartree]) ($\approx -2.176 \times 10^{-18} [J]$ (0.499 [Hartree]) which is the energy of the hydrogen atom in the ground state) Figure 3 and Figure 4.

The following result gives the wave function and eigenvalue $-5.450 \times 10^{-19} [J]$ (0.125 [Hartree]) ($\approx -5.44 \times 10^{-19} [J]$ (0.125 [Hartree]) energy levels of hydrogen atom for n=2) for quantum number (n=2) for hydrogen (Figure 5 and Figure 6).

The following outcomes provide the wave function and eigenvalue $2.422 \times 10^{-19} [J]$ (0.056 [Hartree]) ($\approx 2.417 \times 10^{-19} [J]$ (0.055 [Hartree]) energy levels of hydrogen atom for n=3) for the quantum number (n=3) for hydrogen (Figure 7 and Figure 8).

Figure 3: Atomic orbital shape, eigenvalue and wave function for the ground state of the hydrogen atom in 2D.

Figure 4: Atomic orbital shape, eigenvalue and wave function for the ground state of the hydrogen atom in 3D.

Figure 5: Atomic orbital shape, eigenvalue and wave function of the hydrogen atom in 2D.

Figure 6: Atomic orbital shape, eigenvalue and wave function of the hydrogen atom in 3D.
The hydrogen molecular ion $H^+_2$

The hydrogen molecule ion is the simplest molecule and the only molecule for which we can solve the electronic Schrödinger equation exactly [14, 15, 16, 17].

The two protons are labeled $H_1$ and $H_2$, and the distance from each proton to the electron $e$ are $r_1$ and $r_2$, respectively. $r$ is the distance between $H_1$ and $H_2$. So, the Hamiltonian for the hydrogen molecular ion without the Born-Oppenheimer approximation is given by:

$$H = -\frac{\hbar^2}{2M} \left( \nabla_1^2 + \nabla_2^2 \right) - \frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{e^2}{4\pi \varepsilon_0 r_1} - \frac{e^2}{4\pi \varepsilon_0 r_2} + \frac{e^2}{4\pi \varepsilon_0 r} \tag{7}$$

The Born-Oppenheimer shows that the Hamiltonian for electronic motion given by Equation 8, because the mass of nuclei are so much greater than that of electrons, that the velocity of nuclei will be much smaller than that of the electron.

$$H = -\frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{e^2}{4\pi \varepsilon_0 r_1} - \frac{e^2}{4\pi \varepsilon_0 r_2} + \frac{e^2}{4\pi \varepsilon_0 r} \tag{8}$$

The first term is the electronic kinetic energy, the two other terms are the electrostatic attractions of the electrons to each nuclear, and the last term is the nuclear electrostatic repulsion. Solving this Schrödinger’s equation in the case of hydrogen ion shows the influence of the distance between the nuclei.

Figure 10: Atomic orbital shape, eigenvalue $E = 124.788662$ [Hartree] and wave function of the hydrogen ion in 3D, $r = 0.05$ [Å].

The Figure 10 show that, when $r \to 0$ the two nuclei close each other, therefore share the same electronic orbital.
Figure 11: Atomic orbital shape, eigenvalue $E = 27.732068$ [Hartree] and wave function of the hydrogen ion in 3D, $r = 0.1\,\text{Å}$.

The above results (Figure 10 and Figure 11) show that when the distance between the nuclei is very low the electron is trapped between the two cores, and interacts equiprobable manner.

Figure 12: Atomic orbital shape, eigenvalue $E = -0.609516$ [Hartree] and wave function of the hydrogen ion in 3D, $r = 1\,\text{Å}$.

The above result (Figure 12) shows that there is a distance where the interaction between the electron and the nucleus becomes very strong, at this distance the energy of system is the lowest. In this case the electron is in orbit around the two nuclei.

Figure 13: Atomic orbital shape, eigenvalue $E = -0.498417$ [Hartree] and wave function of the hydrogen ion in 3D, $r = 8\,\text{Å}$.

Figure 14: Atomic orbital shape, eigenvalue $E = -0.463957$ [Hartree] and wave function of the hydrogen ion in 3D, $r = 10\,\text{Å}$.

However, when the distance between the cores becomes very large, the electron orbit is in between one of the two nuclei (Figure 13 and Figure 14).

### 3.2.1 Lennard-Jones Potential of $H_2^+$

The Lennard-Jones potential is function of distance between the centers of two particles, and for the molecule hydrogen it is represent by Figure 15 and Figure 16. These results have found numerically by PDE
method, the bonding energy has a minimum at $R_e = 1$ Å (Figure 16) and the experimental value is 1.06 Å [18, 16]. When the internuclear separation $r = R_e$, the energy of system is lowest, and dissociation energy $\epsilon = 3.02$ [eV] and experimental value is 2.78 [eV].

![Energy curve versus $r$](image1)

**Figure 15:** Molecule hydrogen ion energy versus $r$ (separation of two protons).

![Energy curve versus $r$](image2)

**Figure 16:** Lennard-Jones parameters of hydrogen ion, $\sigma = 0.44$ Å, $\epsilon = 3.023$ [eV].

### 4 Conclusions and outlooks

We have validate the 3D model of the hydrogen atom by solving the Schrödinger’s equation and used this model to determine the parameters of Lennard Jones in the case of the molecule of hydrogen ion by finite elements methods. Moreover, the effect of the distance between the protons are well demonstrated that the mesh are not made very well. The next problem to solve is to determine by exploiting the finite element method and COMSOL software, settings interactions potential Lennard-Jones among two molecules of hydrogen, and using the approach used in the case Hydrogen molecule ion.

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### References


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Appendices

A Potential equations

A.1 Buckingham potential

The Buckingham (Equation 9) potential is a formula which describes the Pauli repulsion energy and Van der Waals energy for the interaction of two atoms that are directly bonded as a function of the interatomic distance r.

\[ U^{BK}(r_{ij}) = A \exp(-B r_{ij}) - \frac{C}{r_{ij}^6} \] (9)

Where A, B, C are constants. The first term of this equation is a repulsion and the second is an attraction. This equation in theoretical study of equation of state for gaseous helium, neon and argon.

A.2 Rydberg potential

The Rydberg potential was proposed by Rydberg to evaluate the vibration spectrum of diatomic molecules, the same properties are obtained with the Morse potential.

\[ U^{Ryd}(r_{ij}) = -\gamma \left[ 1 + a \left( \frac{r_{ij} - R}{R} \right) \right] \times \exp \left( -a \left( \frac{r_{ij} - R}{R} \right) \right) \] (10)

A.3 Biswas-Hamann potential

The Biswas–Hamann potential (Equation 11) have two distinct parts a repulsive term and an attractive terms.

\[ U^{BH}(r_{ij}) = A \exp(-\alpha r_{ij}) + B \exp(-\beta r_{ij}) \] (11)

A.4 Murrel-Mottram

The Murrel-Mottram potential function exist as a summation of 2-body and a 3-body term [19]. For 2-body term the parameters \( \gamma_{MM} \) and \( a \) are determined by fitting phonon and elastic constant data, and the lattice energies and lattice constant of crystalline phase, this equation displayed as Equation 12.

\[ U^{MM}(r_{ij}) = -\gamma_{MM} \left[ 1 + a \left( \frac{r_{ij} - R}{R} \right) \right] \times \exp \left( -a \left( \frac{r_{ij} - R}{R} \right) \right) \] (12)

Nomenclature

Constants

\( \epsilon_0 \) \( \frac{1}{\mu_0} \) Permittivity of free space \( 8.8542 \times 10^{-12} \) in \( [C^2/N.m^2]\)

\( \epsilon_{ij} \) Parameter of Lennard-Jones in \([J]\)

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

\( \sigma_{ij} \) Distance at which the two particles are at equilibrium in \([m]\)

\( e \) Charge on an electron \( 1.60218 \times 10^{-19} \) in \([C]\)

\( M \) Mass of the nuclei in \([kg]\)

\( m_e \) Mass of electron \( 9.1094 \times 10^{-31} \) in \([kg]\)
**Scalar quantities**

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