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Modeling of Diatomic Molecule using The Morse Potential and The Verlet Algorithm

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Abstract. Performing molecular modeling usually uses special software for Molecular Dynamics (MD) such as: GROMACS, NAMD, JMOL etc. Molecular dynamics is a computational method to calculate the time dependent behavior of a molecular system. In this work, MATLAB was used as numerical method for a simple modeling of some diatomic molecules: HCl, H_2 and O_2. MATLAB is a matrix based numerical software, in order to do numerical analysis, all the functions and equations describing properties of atoms and molecules must be developed manually in MATLAB. In this work, a Morse potential was generated to describe the bond interaction between the two atoms. In order to analyze the simultaneous motion of molecules, the Verlet Algorithm derived from Newton's Equations of Motion (classical mechanics) was operated. Both the Morse potential and the Verlet algorithm were integrated using MATLAB to derive physical properties and the trajectory of the molecules. The data computed by MATLAB is always in the form of a matrix. To visualize it, Visualized Molecular Dynamics (VMD) was performed. Such method is useful for development and testing some types of interaction on a molecular scale. Besides, this can be very helpful for describing some basic principles of molecular interaction for educational purposes.

Keywords: Diatomic Molecule, MATLAB, Molecular Dynamic.
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INTRODUCTION

Observing microscopic behavior gives us an understanding of how material works. There are many interesting structural and dynamic phenomena which occur at molecular scale. Studying molecular behavior and more complete interactions on a molecular scale can be derived by experimental studies with simulation. Simulation allows us to study the behavior of materials under a wide range of physical conditions, which are not always easily accessible, safe, or affordable experimentally such as at extremely high temperature and pressure. In common work, simulations involving large ensembles of atoms and molecules, employ special software for molecular dynamics (MD) such as GROMACS, NAMD, JMOL etc. Molecular dynamics (MD) is a computational method to calculate the time dependent behavior of molecular systems. MD is extensively used in chemistry, molecular biology and some areas of materials research. In this work numerical method was done using MATLAB for modeling of some diatomic molecules. Numerical analysis is important factor for simulation In order to obtain some insight about the model of diatomic molecule.

A diatomic molecule is the easiest to study. In this work, the interaction and the energy between two atoms was described by the Morse Potential. It provides a useful approximation for the potential energy of a diatomic molecule. Besides, the Morse potential is superior to the harmonic oscillator model in that it can account for anharmonicity and bond dissociation. In order to develop the system by one time step to predict the new atom positions and velocities at the end of the step, the Verlet algorithm was operated. It is the simplest algorithms for solving differential equations numerically, which differ in complexity and accuracy. Both the Morse potential and Verlet algorithm were integrated using MATLAB to describe some diatomic molecules interaction.

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Unlike special software used in MD which provides some equations and database of atom with their properties and also random generator, MATLAB is a matrix based numerical software. Generally people are more familiar with this software than some special software used in MD. Developing numerical analysis of diatomic molecule with MATLAB would open the opportunity for more people to study molecular dynamics. Another language program such as C++ or Fortran is also possible to operate numerical analysis of some diatomic molecules. But in some researches and educational purposes, MATLAB is better known, especially in Department of Physics, Parahyangan Catholic University.

MATLAB which is a high-level programming language is often used for numerical computation techniques to solve problems involving mathematical operations elements, matrices, optimization, approximation etc [1]. This means in order to do numerical analysis of a diatomic molecule interaction under certain circumstance, a physical condition based on convenient mathematical and physical equation has to be built manually. This method is helpful to explain the basic principle of atomic interaction for educational purposes.

THEORY

In this section, the basic theory of molecular dynamics (MD) used in this work during simulation is explained.

Interatomic Potential

Modeling the atomic potential is one of the most important parts of a molecular dynamics numerical method. This particular investigation deals with atoms that are free to vibrate within the molecules. The two atoms that can form a bond will do so to create a diatomic molecule when they approach each other closely. The Morse potential is a convenient model for the potential energy of a diatomic molecule. The energy stored in the bond between the two atoms is given as a function of x, the norm of the interatomic distance x:

$$\mathrm{V}_{(\mathrm{x})} = D(1 - e^{-B(x-x_0)})^2 - D \tag{1}$$

D is the pair potential well depth, B is an adjustable parameter which determines the range of the interparticle forces and x_0 is the equilibrium separation between atoms [2]. In a diatomic molecule, there is only one nuclear coordinate, namely, the interatomic distance x. In this case, the potential energy describes the potential energy of the system, $V_{(x)}$, as the two atoms are brought closer together, or are separated from one another [3].

Verlet Alghorithm

The molecular dynamics method solves Newton's equations of motion for atoms by taking a small step in time and using approximate numerical methods to predict the new atom positions and velocities at the end of the step. At the new positions, the atomic forces are recalculated and another step in time is made. This procedure is repeated many thousands of times in a typical simulation. The approximate numerical method used to advance the system by one time step is known as an integration algorithm [4]. There exist many different algorithms for solving differential equations numerically, which differ in complexity and accuracy. One of the simplest is the Verlet algorithm [5]. Below is the time integration operation via the Verlet algorithm.

$$m_i \ddot{x}_i(t) = F_i(x(t)) \tag{2}$$

By Input of two third-order Taylor expansions for the positions $x(t)$ to equation (2) derives the Verlet algorithm:

$$x_i(t+h) = 2x_i(t) - x_i(t-h) + \frac{F_i(t)}{m_i} h^2{}_i \tag{3}$$

Discretizing the trajectory $x(t)$, here is introduced the increment h which defines the time distance between the discretization points along the trajectory.

SIMULATION & ANALYSIS

In this work, numerical methods were performed on a simple interaction of diatomic molecules (table 1). In order to build the condition describing the molecule movement using MATLAB, some equations must be derived. The vibrational motion of diatomic molecules interacting via the Morse function is simulated using classical-mechanical equations of motion. First, describe the atoms as masses m_1 and m_2 which are considered to be connected via a massless ideal spring with spring constant k (**FIGURE 1**).

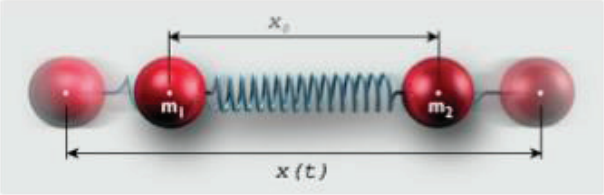

FIGURE 1. Representation of diatomic molecule at their equilibrium distance x_0 and at some generic position $x(t)$ at time t [6].

With the condition created above, it would be easier to solve the Newton's equation of motion for two atoms by applying the Verlet algorithm to the Morse potential and its harmonic approximation. By substituting the first and second derivative of equation (3) to equation (2), the following generated equation is obtained below:

$$x(t+h) = \frac{2}{1+a}x(t) - \frac{1-a}{1+a}x(t-h) + \frac{1}{1+a}\frac{h^2}{m}F(x(t)) \tag{4}$$

As diatomic molecule has 2 atoms, here m is $\frac{m_1 m_2}{m_1 + m_2}$

When an atom is displaced from its equilibrium position in a molecule, it is subject to a restoring force which increases with the displacement. A spring follows a same law (Hooke's law); the chemical bond is therefore formally similar to a spring that has weights (atoms) attached to its two ends. The function of $F(x(t))$ represents the spring force acting between the two masses describing diatomic molecule vibration.

$$F(x(t)) = -k(x(t) - x_0) \tag{5}$$

In order to determine the force acting between the two atoms and to find the equilibrium position x_0 corresponding to the average energy stored in the bond, It is necessary to calculate the first derivative of the Morse potentia $V_{(x)}$ (equation 1) with respect to x.

$$F(x) = 2BDe^{-B(x-x_0)}[e^{-B(x-x_0)} - 1] \tag{6}$$

TABLE 1. The constants of diatomic molecules used in Morse potential [7]

Molecules	m (AMU)	x_m [10^{-10}m]	B [10^{10} m^{-1}]	D [eV]
HCl	H = 1 Cl = 35	1.275	1.869	4.618
O_2	16	1.208	2.655	5.214
N_2	14	1.098	2.691	9.905

The second step is to compute all of the equations above to analyze the interaction of diatomic molecules. The experiment was carried out at room temperature 300 K to analyze the interaction of two atoms forming a diatomic molecule as function of position (equation 4). As results, MATLAB generated the trajectory of a diatomic molecule under three conditions: harmonic oscillation, anharmonic oscillation and dissociation. Both harmonic force and the Morse force (equation (5) & (6)) are the most influential factor to determine the trajectory.

Under harmonic oscillation, the trajectory is shown in **FIGURE 2**. The graph shows that the harmonic and the Morse trajectory coincide. At this condition, the atoms in a molecule vibrate about their equilibrium positions and

these vibrations have small amplitudes. It was happened where the initial position ($x(-h)$) is at around to its equilibrium position (x_0). It causes the restoring force exerted on the atom to be proportional to the displacement of the atom from its equilibrium position.

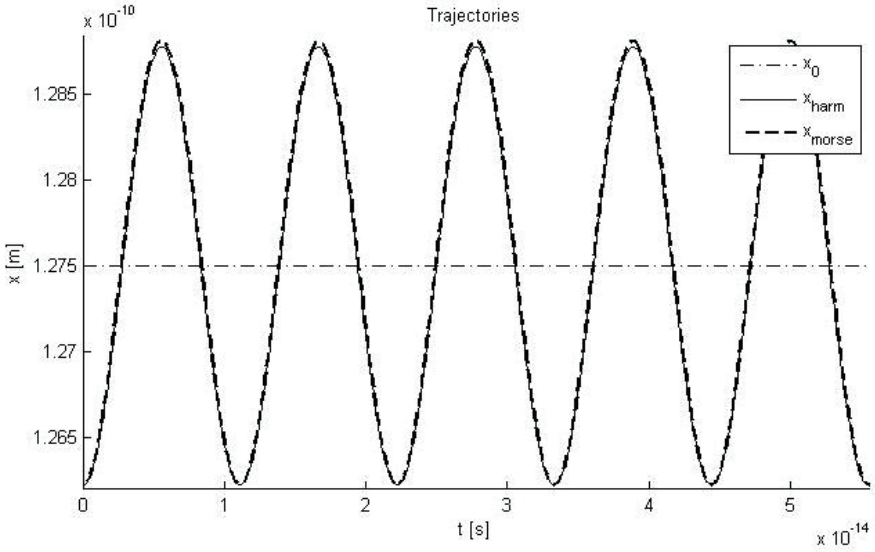

FIGURE 2. Trajectory of diatomic molecule (HCl) plotted using MATLAB under harmonic oscillation. x_0 is the equilibrium position, x_{harm} is trajectory of a harmonic oscillator and x_{morse} is trajectory of a Morse oscillator.

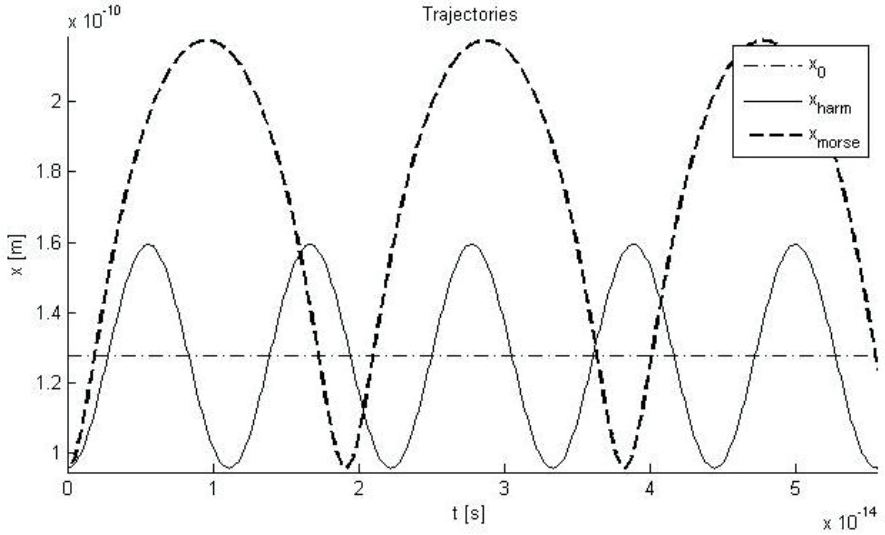

FIGURE 3. Trajectory of diatomic molecule (HCl) plotted using MATLAB under anharmonic oscillation. x_0 is the equilibrium position, x_{harm} is trajectory of a harmonic oscillator and x_{morse} is trajectory of a Morse oscillator.

One notices that a diatomic molecule which was actually bound using a harmonic potential would never dissociate. The Morse potential realistically leads to dissociation. This is caused as its exponential component follows the shape determined potential functions over a wider range of interatomic distances than does the harmonic oscillator. This fact resulted to anharmonic oscillation and also dissociation when the distance between two atoms is long enough.

Anharmonic oscillation arises when the vibrational amplitude becomes large. Then, the bond is not capable of exerting a restoring force that is proportional to its displacement (**FIGURE 3)**. An anharmonic oscillation occurs

when the molecule is tested at high temperature. For example the effect of anharmonity is the thermal expansion of a solid [8,9]. The energy of a system of two atoms depends on the distance between them. At large distances the total energy decreases following the an exponential curve, this condition is called dissociation.

The last step of this work is to visualize the trajectory of diatomic molecules. As the data obtained by MATLAB is still in matrix form, it is necessary useful to do visualization with the help of VMD (Visualized Molecular Dynamic) [10]. VMD processed the matrix data to be visualized based on the condition created in simulation with MATLAB.

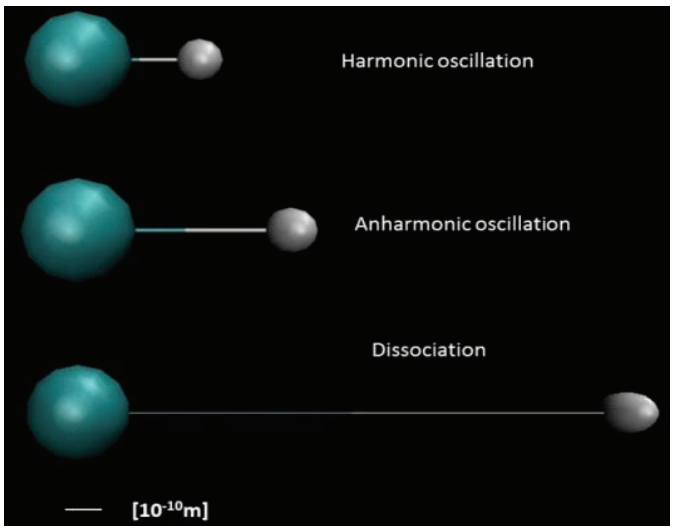

FIGURE 4. Visualization of HCl molecule by VMD under harmonic oscillation, anharmonic oscillation and dissociation. Green represents Cl atom and white represents H atom.

During the experiments some diatomic molecules were visualized (**TABLE 1**). But in this paper only HCl molecule is shown in **FIGURE 4**. Under harmonic oscillation, VMD showed that the HCl molecule vibrates with a small amplitude due to its initial position ($x(-h)$) is at around to its equilibrium position (x_0). Under anharmonic oscillation when the distance between two atoms is large enough, both atoms still well interacted showed by the vibration. There was no vibration under dissociation showing that there is no interaction when two atoms dissociate.

CONCLUSION

This experiment shows that MATLAB is not just a powerful tool to solve some mathematical problems such as matrices, optimization, approximation etc. But it showed that MATLAB was also a good tool as numerical analysis for a simple diatomic molecule. With the right operation applied, some conditions under numerical method using MATLAB could represent the behavior of molecule as in real life. For example, describe the interaction of HCl molecule under anharmonic condition which usually occurs at high temperature.

Developing the conditions representing molecular scale with MATLAB manually was not easy. But it showed how the equation and function work together. Which means this can be helpful to explain the basic principle of atomic interaction for educational purposes. With MATLAB many people would allow to study the basics of molecular dynamics considering that more people are familiar with MATLAB than with some MD software such as NAMD, GROMAC, JMOL etc.

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