

Methodology Article

Before You Click: Understanding the Potential Energy Surface of Water

Vaijayanthi Bhashyam* 

Department of Chemistry, Gargi College, University of Delhi, Delhi, India

Abstract

Students and researchers pursuing molecular modeling or computational chemistry use readily available software such as Schrodinger, Gaussian, Arguslab, Hyperchem etc. to facilitate the visualization of molecules and calculation of their energy. A variety of computational tools form the basis of working of such software. The first step in using most of these software programs is to optimize the geometry of the input molecule. During such optimization procedure, the software searches for parameters of geometry such as bond length, bond angle and dihedral angle which results in the molecule's minimum energy and hence the most stable geometry. While it is pertinent for the student to be able to choose the right computational tool to obtain reliable results, the visualization of potential energy diagram of the molecule is equally important. It may be appropriately said that the core of all the computational tools is rooted in a deep understanding of potential energy diagrams or potential energy surfaces (PESs). Potential energy surfaces are multidimensional graphs of potential energy against the various independent variables of geometrical parameters. They can span from three-dimensional representations (with two dimensions for the independent variables and one for energy) to more complex, higher-dimensional forms. A PES is often compared to a landscape, with hills, valleys, and ridges corresponding to high and low energy configurations. It is a challenge for undergraduate students to understand the PESs of polyatomic molecules as they have always dealt with potential energy diagrams that are of two dimensions only. This article discusses a simplified approach to grasp the concept of PES for polyatomic molecules, using water—the simplest polyatomic molecule—as an example. A three-dimensional PES graph is created in MS Excel using values calculated from the free molecular modeling software, ArgusLab. Additionally, the process of reducing the 3D plot to a 2D plot through slicing is also explained.

Keywords

Computational Chemistry, Potential Energy Surface, Water, Polyatomic Molecule, Slicing

1. Introduction

Chemistry education for undergraduates has undergone a significant transformation with the introduction of computational methods and molecular modeling. These advancements have enabled the visualization of molecules, both large and small, thanks to the progress in computer technology. Various

software programs such as Schrodinger, Gaussian, Quantum Espresso, Arguslab, and Hyperchem, have been developed to facilitate the visualization and calculation of energy of molecules or groups of molecules. The introduction of these software programs at the undergraduate level of chemistry curric-

*Corresponding author: b.vaijayanthi@gargi.du.ac.in (Vaijayanthi Bhashyam), bvaijayanthi@yahoo.com (Vaijayanthi Bhashyam)

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ulum and suitable training can prepare these students to pursue computational chemistry/molecular modeling as their career.

The selection of appropriate calculation methods (called tools of computational chemistry) is important to get reliable results. Most interactive software programs use semi-empirical or ab initio methods, with the former being more commonly preferred. The first step in any of these software is to optimize the structure proposed by the user. During such optimization procedure, the software program searches for that combination of bond lengths, bond angles, and dihedral angles which result in the molecule's minimum energy, thereby yielding the most stable or optimized geometry.

2. Methods

ArgusLab 4.0.1, a free molecular modeling software was used for the calculations. Single point energy calculations using AM1 were carried out and the heat of formation so obtained were noted and plotted.

3. Results

While undergraduate students need to grasp the underlying theory behind these computational tools, the visualization of potential energy diagrams is equally important. To comprehend the structure of a molecule and the dynamics of chemical reactions, it is crucial to know potential energy as it relates to the molecule's geometry. The understanding of potential energy diagrams serves as a foundation for various computational techniques. Scientists have been constantly working on calculating the vibrational spectrum of various molecules. [1]

Numerous publications are available that focus on potential energy diagrams, specifically known as potential energy surfaces (PES). Advancements in computational techniques and ab initio methods have been increasingly contributing to a better and more accurate PES enabling detailed studies of complex molecular systems. It is now possible to have deeper insights into fundamental processes like hydrogen bonding and molecular solvation.

The simplest polyatomic molecule that we can think of, is water. The PES of water helps in exploring various molecular properties such as vibrational spectra [2], isotope effects [3], and reaction dynamics. [4]

A large amount of work has been done on water. From a simple understanding of the intramolecular potential of water [5] to hydrogen bonding [6, 7] in water, many different methods such as ab initio [8], molecular mechanics, and molecular dynamics [4, 9, 10] have been used. The simulated PES of water has been used to study the thermodynamic and structural aspects of water. [11] Scientists have studied the structure of water dimer [12-14], trimer [15], and protonated water [16] using neural network potentials. Ion solvation by water has also been studied. [17-19] This article specifically discusses the simulation of the PES of water in small bits,

along with the visualization of the larger picture of water PES. Condensed phase simulations of water and ice. [20] During the last few decades many model potentials based on different types of force fields for simulation of water have been published. [21]

3.1. Plot of Potential Energy Against Geometrical Parameters

Frequently, students have encountered two-dimensional graphs of potential energy diagrams. (Figure 1) [22] These graphs depict the potential energy of a diatomic molecule on the vertical axis and the bond length on the horizontal axis. Upon examining these graphs, numerous questions arise. Are these curves similar for all molecules? How do they change for a polyatomic molecule? How does the curve or plot change from one molecule to another? How do we interpret these curves, and how and why are they significant in understanding molecular mechanisms?

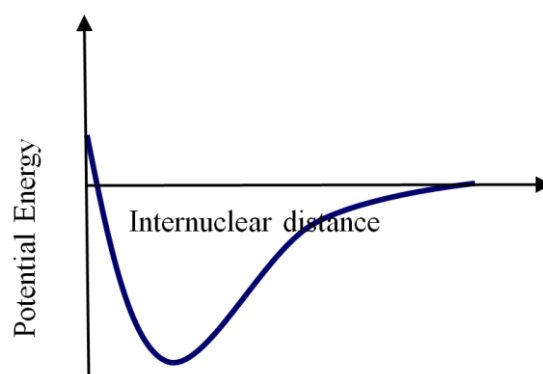


Figure 1. Potential Energy Diagram of a diatomic molecule.

3.1.1. Water as an Example

To find answers to the above questions, let us explore what shape this diagram takes when applied to water. In the case of water, there are three atoms resulting in two O-H bond lengths and one H-O-H bond angle. For convenience, the atoms are numbered (Figure 2). The potential energy of water depends on the potential variations of these two bond lengths and the bond angle. Assuming that the two O-H bond lengths are equal since they are identical, the potential energy appears to depend only on two independent variables, bond length and bond angle. Any particular combination of bond length and bond angle is different from another one leading to a different energy value, making the potential energy diagram for water a three-dimensional graph. The third dimension represents the energy, while the first two dimensions represent the variables of bond length and bond angle. These diagrams are referred to as potential energy surface (PES) or potential energy surfaces since the resulting plot resembles a surface (in this case, two-dimensional). Additionally, there can be potential energy diagrams of higher dimensions for

molecules with 4 or more atoms, such as 4D, 5D, and so on, with 3D, 4D, and higher-dimensional coordinates representing the potential energy thus resulting in higher-order surfaces. HOF is an example that gives rise to a 4D graph with a resultant 3D surface. It may be imagined how difficult it is to visualize the PES of molecules even slightly bigger than H₂O or HOF for an undergraduate student.

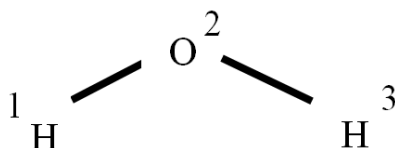


Figure 2. Water molecule.

(i). Fixing the Bond Length

Fixing a few of the variables can simplify such complex potential energy diagrams. Here, the simplest molecule – water – is taken into consideration. If one variable, say, bond length, is fixed, the potential energy diagram can be reduced to a two-dimensional graph which will be simply a plot of potential energy as a function of the other variable, bond angle. To begin with, let us fix the bond length at 1 Å. Based on our previous knowledge of water structure, the optimal bond angle is 104° 91'. Using a molecular modeling software like Arguslab (a freeware), we can calculate the single point energy of a particular geometry of water. One can use the heat of formation values to be representing potential energy in order to observe the trend in energy as a function of geometrical parameters. The potential energies of different geometries of water can be computed by changing the bond angle within a range of 70° to 180° which are the angles chosen randomly on either side of the optimum angle and at a fixed bond length of 1 Å. This allows us to plot a graph of Potential Energy against bond angle at a bond length of 1 Å. Figure 3a shows such a plot in Excel with Potential energy calculated using ArgusLab. A minimum corresponding to an angle of 104.5° may be observed in the plot which is close to the universally accepted bond angle for water.

(ii). Fixing the Bond Angle

It is important to note that in the previous analysis, the bond length was fixed at 1 Å. Similar graphs may be plotted by fixing the bond length at different values and obtaining the energy for a range of bond angles. All of these plots show a similar shape (Figure 3b). Though potential energy has been calculated for more combinations of bond length and bond angle, only a few of them are shown in Figure 3b for clarity. It may be seen from this graph that the lowest energy of each curve appears around a bond angle of 104.5°.

Instead of fixing the bond length, if we now fix the bond angle (say at 104.5°) and vary the bond length, a plot such as that shown in Figure 3c is obtained. The minimum is obtained at 0.96 Å. Several such plots of potential energy vs bond

length may be obtained for varying bond angles. Figure 3d shows such diagrams.

Which of these plots represents the real water molecule, and how can we determine that? To assess this, we need to analyse the curves obtained.

3.1.2. Potential Energy Surface of Water

By examining various plots and analyzing the data obtained, we can identify trends and correlations.

It is interesting to note that the variation of potential energy as a function of both bond length and bond angle can be plotted in a single diagram using the latest spreadsheet software. The resultant plot is known as a potential energy surface and abbreviated as PES. Figure 4 depicts the potential energy diagram of water (ref) for the chosen range of bond length and bond angles which are the independent geometrical parameters.

By visualizing the PES, we gain a comprehensive understanding of the relationships between different variables and the corresponding potential energy values. It provides a holistic representation of the system under consideration, allowing us to analyze and interpret its behavior. An analogy that helps understand the potential energy diagram is imagining a towel being flown away by wind.

3.2. Stationary Points

A graph of PES provides a convenient way to determine the potential energy for any combination of bond length and bond angles. It is important to note that every point on the graph is not equally important. In fact, points on a PES at which the slope is zero are of utmost significance. Such points are called stationary points. In the case of water, a stationary point of significance is the minimum and at this point,

$$\partial E / \partial R = 0 = \partial E / \partial A$$

where R and A represent the bond length and bond angle respectively; in Figure 4, it is represented by a *. In basic chemistry, we learn that the most stable structure corresponds to a minimum point on the graph. For water, this minimum occurs at a bond length of 0.96 Å and a bond angle of 104.5° which corroborates with the experimental results.

3.3. Reducing the Dimensionality of PES - Slicing

Potential energy surfaces of larger molecules are not visualizable as they involve more dimensions. Hence, a simplification of the PES involves cutting slices across the multi-dimensional PES. [23] Cutting the PES perpendicular to a coordinate and parallel to other coordinates, results in a slice with a constant value for the former coordinate. Slicing the PES of water will simply result in the two-dimensional graphs that we started with. Slicing across the bond length axis, gives Figure 3a while slicing across the bond angle axis, gives

Figure 3b. It is interesting to note that either we start with the slices and build the loaf (the PES) or we make the loaf and to simplify it, cut it into slices. Water is an excellent example to understand the slicing of PES diagrams.

4. Discussion

Simplification of PES by slicing makes it easier for undergraduate students to clearly understand the energy changes of a molecule as a function of its coordinates. **Figures 3b and 3d** indicate that the bond angle in water is around 100° for any of the bond lengths considered and the bond length is around 1 \AA for any of the bond angles considered. There is a good enough correlation between experiment and theoretical calculation. For further understanding, the PES of HOF may

be plotted keeping one of the variables fixed at a particular value and varying the other two. It is believed that an undergraduate student will understand the concept of PES through water as an example.

5. Conclusion

A simple way to understand the potential energy surfaces has been discussed. Visualization/imagination of potential energy surfaces of polyatomic molecules is expected to be easier after the present exercise with water. Simplifying complex potential energy surfaces by the process of slicing has also been explained. Students may be intrigued to compute and hence plot the potential energy surface of HOF after fixing one of the three variables.

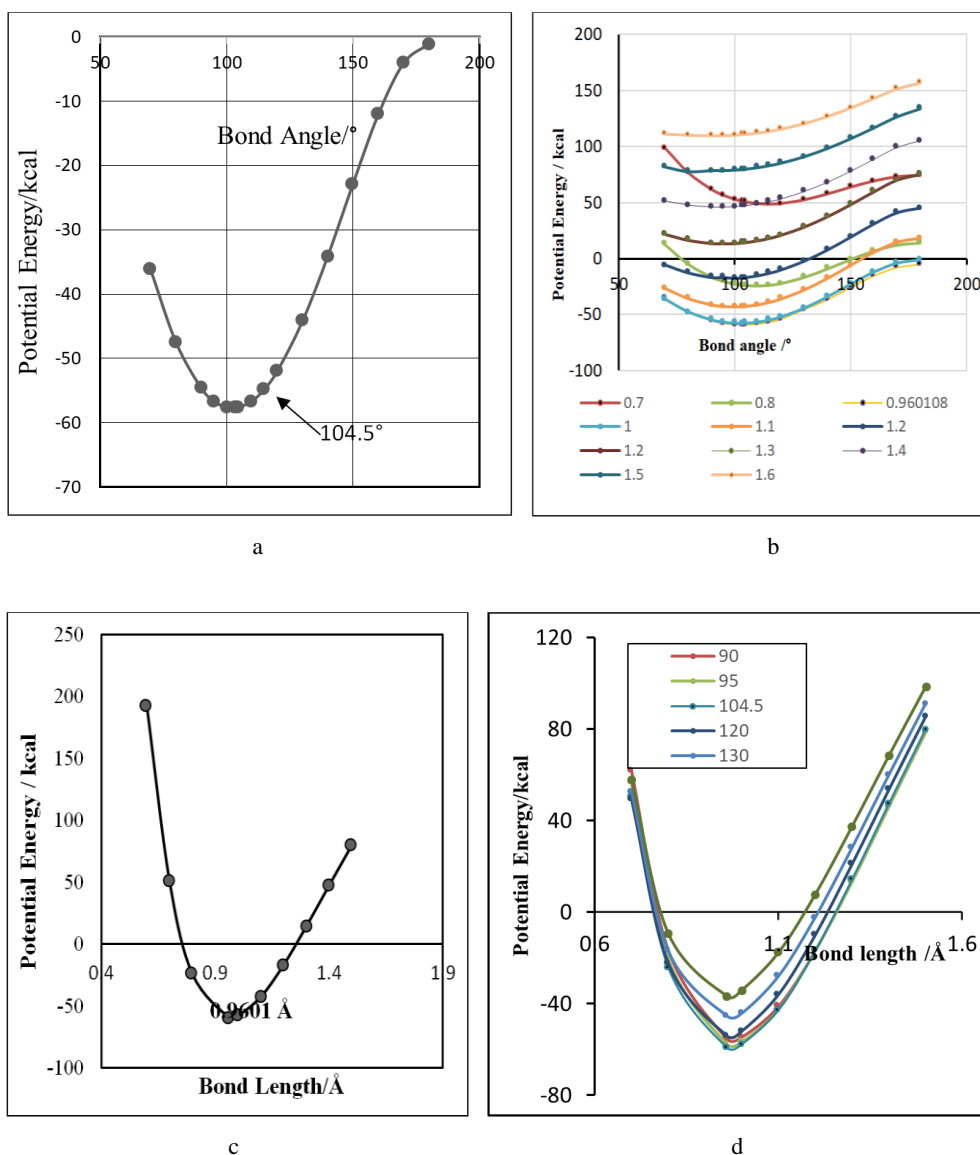


Figure 3. a: Potential Energy as a function of bond angle at a bond distance of 1.0 \AA ; (b) Potential Energy against bond length of water at different bond angles (in $^\circ$); (c) Potential Energy as a function of Bond Length at a fixed bond angle of 104.5° ; (d) Potential Energy as a function of Bond Angle at fixed bond lengths.

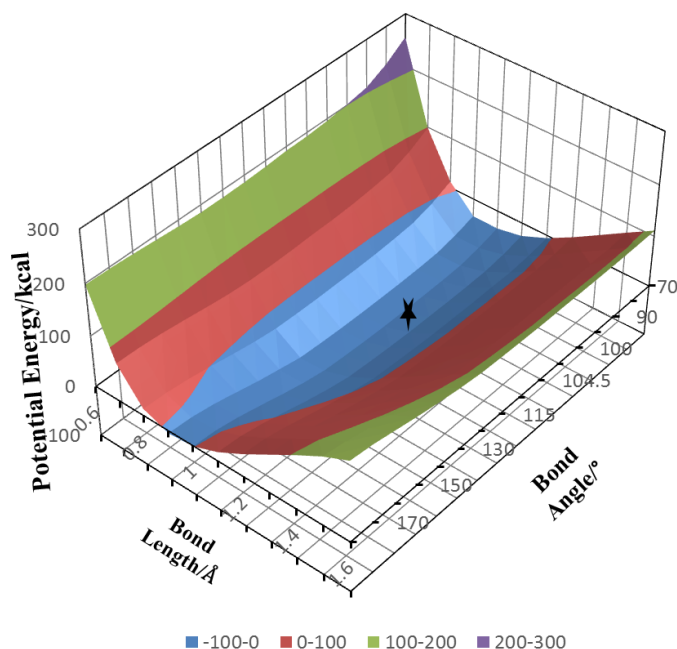


Figure 4. Potential Energy Surface of Water.

Abbreviations

PES Potential Energy Surfaces

Supplementary Material

The supplementary material can be accessed at <https://doi.org/10.11648/j.ijtc.20251301.14>

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Author Contributions

Vaijayanthi Bhashyam is the sole author. The author read and approved the final manuscript.

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Data Availability Statement

The data supporting the outcome of this research work has been is available as supplementary material.

Conflicts of Interest

The authors declare no conflicts of interest.

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Biography



Vaijayanthi Bhashyam is an Associate Professor working at Gargi College (University of Delhi), India. She completed at Ph.D. from the Department of Chemistry, University of Delhi in 1992 and Masters in Chemistry from IIT (Delhi) in the year 1987. Basically a physical chemist, her fields of interest are computational chemistry, molecular modeling and analytical chemistry.

Research Field

Vaijayanthi Bhashyam: Computational chemistry, Analytical Chemistry