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Phase-Space Dynamics of Diatomic Molecules as Morse Oscillator

Dipak Adhikari[1,2], Ravi Karki, Kapil Adhikari[3], Nurapati Pantha[2], Narayan prasad Adhikari[2]

[1] *Department of Physics, Prithvi Narayan Campus, Tribhuvan University, Pokhara, Nepal*
[2] *Central Department of Physics, Tribhuvan University, Kirtipur, Kathmandu, Nepal*
[3] *Faculty of Science and Technology, Gandaki University, Nepal*

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Abstract

A diatomic molecule in motion is modeled by the Morse oscillator. It enhances the straightforward harmonic oscillator model, which assumes that the molecule dissociates at a certain energy and that the vibrational modes converge with rising energy. Most of its features may be described analytically, and it is frequently used to describe the spectroscopy of diatomic molecules and anharmonic vibrational dynamics. Studies have been conducted into the diatomic molecules' behavior as a Morse Oscillator in phase space. Three main types of trajectory categories are investigated. Open trajectory indicates the unbounded motion, whereas closed trajectory represents the periodic motion. Another trajectory is known as the homoclinic orbit aided to separate these motions. The trajectory with energy more than dissociation energy is found to be open, whereas the trajectory with energy less than dissociation energy is found to be closed.

Keywords: Anharmonic; Homoclinic orbit; Morse Potential; Phase space; Separatrix; Trajectory

1. Introduction

A potential energy function known as the Morse potential is named after physicist Philip M. Morse [1]. The intermolecular force between two atoms of a diatomic molecule was initially described by it. It clearly takes into account bond breaking's effects, such as the presence of unbound states. As a result, it provides a more accurate representation of the molecule's vibrational structure than the quantum harmonic oscillator [2]. It also explains how real bonds are anharmonic. The functional form of Morse potential is

$$V(r) = D(1 - e^{-\alpha q})^2 \quad (1)$$

where D is the molecule's dissociation energy, and q is the distance between the two atoms. The depth of the potential well is represented by D, and its width is controlled by α. A wide well is represented by a small α and a narrow well by a large α [3,4]. Figure 1 illustrates the nature of the Morse potential curve and demonstrates how real molecules do not exactly follow the law of simple harmonic motion.
Real bonds are elastic but do not follow Hooke's law because they are not homogeneous enough.
Phase space refers to the set of position and momentum coordinates (q, p) that characterize a dynamical system. It is a very important concept in physics that integrates classical and quantum mechanics. According to classical mechanics, phase space is the space of all potential states of a physical system. The term" state" should be understood to include both the position (q) and momenta (p) of all the objects in the system. As a result, both the system's position and momentum are necessary to predict its future behavior [5,6]. The concept of phase space was developed in the late 19th century by Ludwig Boltzmann, Henri Poincar´e, and Josiah Willard Gibbs [7].

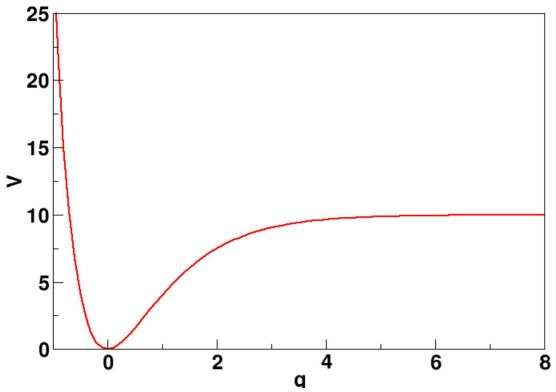

Figure 1: Morse potential curve

*Corresponding author. Tel.: +977- 9846060098

E-mail address: adipak098@gmail.com

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Phase trajectory is the path of a point in a phase space that depicts how the state of a dynamical system changes with time. The Hamiltonian of the system $H\ (q,p,t)$ which depends on generalized coordinates, generalized conjugate momenta of the system, and time can completely, describes the me-

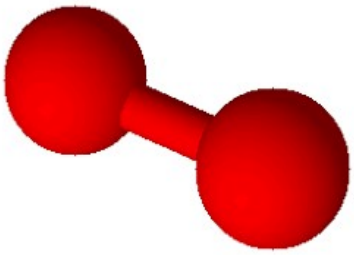

Figure 2: Structure of oxygen molecule

chanical system. The information concerning the path taken by the system is given by the analysis of q with respect to t but gives no details about how the system is moving. In contrast, analyzing p with respect to *t* reveals the time evolution of the system's momentum and, consequently, its energy, but does not provide its position. The investigation of the system's position and momentum evolution without an explicit correlation to time is made possible by the analysis of p with respect to q.

Phase-space dynamics refers to the analysis of *p* with respect to q. It simply uses p and q to represent the system's Hamiltonian or equations of motion. The system's behavior can then be graphically represented by plotting the resulting equation in momentum space, called phase space trajectory. Every phase point on the phase space plot depicts the entire physical state of the system under investigation, which is one advantage of phase-space dynamics. The nature of this study is computational and pedagogical. This work presents a case study of an oxygen molecule treated as a Morse oscillator. A simple molecular structure of oxygen is shown in figure 2.

2. Materials and Method

2.1 Hamiltonian

The Hamiltonian is constant and equal to the sum of the kinetic and the potential energies (the Morse potential). The Morse potential defines one degree of freedom of the Hamiltonian system. To generate a phase plot, it is necessary to derive the Hamiltonian in terms of p and q. The Hamiltonian function is given by,

$$H(p,q) = \frac{p^2}{2m} + D(1 - e^{-q\alpha})^2 \qquad (2)$$

2.2 Region of Bounded Motion: Periodic orbits

The motion in q of trajectories with energy greater than *D* is unbounded. Motions that satisfy $0 < h < D$ on their trajectory are considered periodic. These periodic orbits' level sets are provided by

$$h = \frac{p^2}{2m} + D(1 - e^{-q\alpha})^2 \qquad (3)$$

and they encircle the point of stable equilibrium $(q,p) = (0,0)$. Turning points are the two unique points where the periodic orbits cross the q-axis, $q_+ > 0$ and $q_- < 0$. These turning points are calculated by

$$q_+ = -\frac{1}{\alpha}\log\left(1 - \sqrt{\frac{h}{D}}\right) > 0 \qquad (4)$$

$$q_- = -\frac{1}{\alpha}\log\left(1 + \sqrt{\frac{h}{D}}\right) < 0 \qquad (5)$$

The level curve with energy equal to the dissociation energy h = D has the form:

$$D = \frac{p^2}{2m} + D(1 - e^{-\alpha q})^2 \qquad (6)$$

and is a separatrix connecting the saddle point. It is referred to as a homoclinic orbit in the language of Hamiltonian dynamics that separates bounded and unbounded motion.

For $h = D$ i.e. the energy of the homoclinic orbit, or separatrix , $T(D) = \infty$, which is the "period of a separatrix". For $h = 0$, which is the energy of the elliptic equilibrium point. In this case,

$$T(0) = \pi\frac{\sqrt{2m}}{\alpha\sqrt{D}}$$

2.2 Expressions for q(t) and p(t),

For $0 < h < D$, $q(t)$ is given by

$$q(t) = \frac{1}{\alpha}\log\frac{\sqrt{Dh}\cos\left(\sqrt{\frac{2(D-h)}{m}}\alpha t\right)+D}{D-h} \qquad (7)$$

Differentiating the expression for $q(t)$ will give the expression for $p(t)$ through the relation $q\cdot = \frac{p}{m}$

The homoclinic orbit, corresponding to $h = D$. The integral expression for the homoclinic orbits is

$$q_0(t) = \frac{1}{\alpha}\log\frac{1+\frac{2D}{m}\alpha^2t^2}{2} \qquad (8)$$

Similarly, we obtain $p_0(t)$ from the relation

$$q^{\cdot} = \frac{p}{m} \text{ as, } p_0(t) = \frac{4mD\alpha t}{2D\alpha^2 t^2 + m} \quad (9)$$

Increasing the total energy h to the value of D and beyond results in unbounded motion (For $0 < D < h$), trajectories retain the turning point q_-, while q_+ becomes infinite. The expression for q_- is identical to low energies and is obtained from (2) by setting $p = 0$ and solving for q.

For unbounded trajectories, it is not possible to define a (finite) period, but we can obtain an expression for t as a function of position as

$$t(q) = \frac{1}{\alpha}\sqrt{\frac{m}{2(h-D)}}\log\left(\frac{h-D+De^{-\alpha q}+\sqrt{(h-D)\{h-D(1-e^{-\alpha q})^2\}}}{\sqrt{hD}\ e^{-\alpha q}}\right) \quad (10)$$

An expression for $q(t)$ is given by

$$q(t) = \frac{1}{\alpha}\log\frac{\sqrt{hD}e^{2\beta t} - 2De^{\beta t} + \sqrt{hD}}{2(h-D)e^{\beta t}} \quad (11)$$

Where $\beta = \alpha\sqrt{\frac{2(h-D)}{m}}$. Using the relation $q^{\cdot} = \frac{p}{m}$ yields the expression of $p(t)$ [3,10].

2.2 Methodology

The current study is both computational and theoretical in nature. It mainly concentrates on Phase space dynamics of diatomic molecule. Using the Morse Potential, the necessary Hamiltonian is obtained and computational calculation is performed by Euler's algorithm. Plotting the trajectories is done with the help of Xmgrace and gnuplot.

3. Results and Discussion

3.1 Morse oscillator over Harmonic oscillator

The two atoms of a diatomic molecule oscillate about their equilibrium point and have a balance distance. When the gap widens, the chemical link between two atoms is shattered. The harmonic oscillator, which depicts the vibrations of the two atoms along a bond direction traveling through the centers of masses, is the most basic model for the motion of a diatomic molecule. But unlike the approximate approach for low vibrational quantum numbers provided by a harmonic oscillator (Hooke's law), the behaviors of molecules do not fit this model. Instead, an exponential form of potential explains how to bond breaking affects molecule vibrations better than a harmonic oscillator. The Morse potential is a particular kind of exponential potential that acts as a useful model for the potential energy of a diatomic molecule. Therefore, the laws/equations of simple harmonic motion do not quite apply to real molecules. The ideal simple harmonic parabola and the potential curve for anharmonic extension and compression of a typical diatomic molecule (O_2) are shown in Figure 3. The anharmonic potential is shown by the full line curve, while the harmonic potential is shown by the dotted curve. This figure clearly demonstrates how the Morse oscillator differs from the harmonic oscillator.

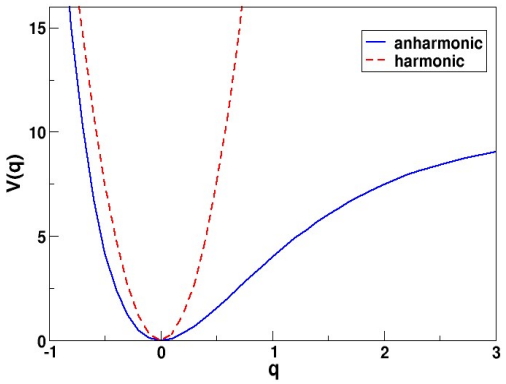

Figure 3: Curve comparison between harmonic and anharmonic potential

3.2 Phase space trajectory

The phase-space trajectories of the Morse oscillator for $D = 10.0, \alpha = 1.0$, $m = 8.0$, as well as for various values of the Hamiltonian or energy (h) of the system are depicted in figures 4, 5, 6 and 7. The equilibrium point at the origin is shown by the black dot in figure 4 with energy $h = 0$. The periodic orbits of the oscillator at different energies, $h = 3.0$ and $h = 7.0$, are represented by the blue and green trajectories, respectively. These paths are closed and are referred to as close trajectories. Figure 5 shows the unbounded motion of the oscillator at different energies, $h = 11.0$ and $h = 15.0$, as represented by blue and green trajectories. These paths are open and are referred to as open trajectories. The oscillator no longer exhibits 'back and forth' motion as a result of the open trajectory. The open trajectory's clear meaning is that the system's momentum never reaches zero and always moves in the same direction. The purple trajectory in figure 6 represents the homoclinic orbit. It stands for the oscillator's maximum energy, below which the atom continues to oscillate 'back and forth' motion and above which the molecule dissociates into its constituent atoms. The phase-space trajectory that depicts the oscillator's

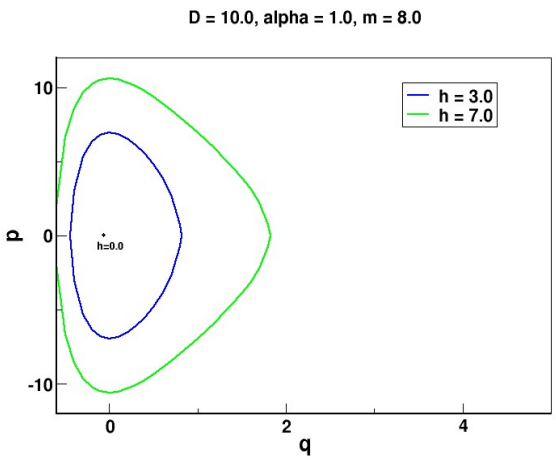

Figure 4: Periodic orbits

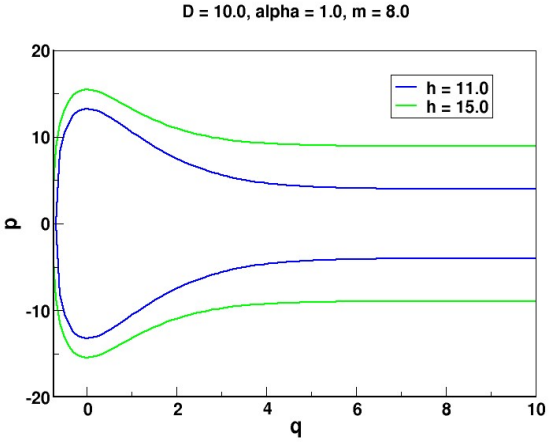

Figure 5: Unbounded orbits

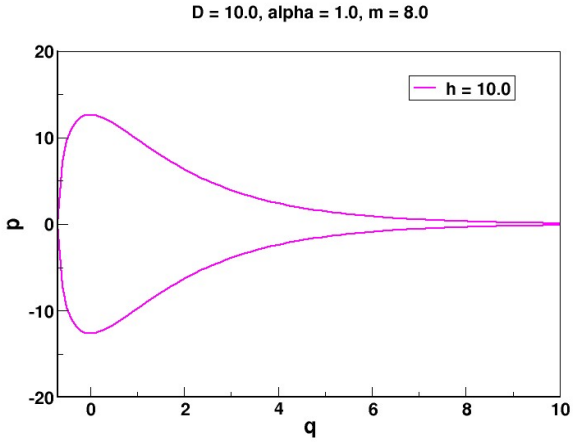

Figure 6: Homoclinic orbits

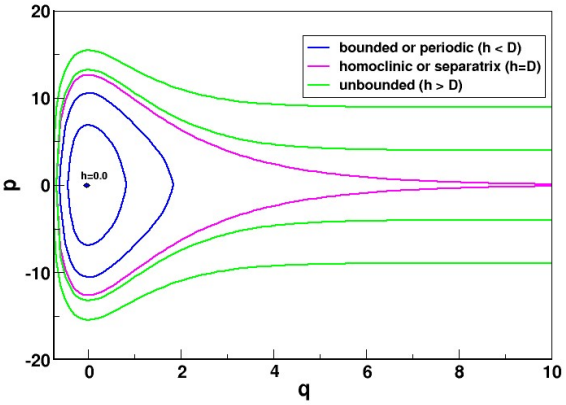

Figure 7: Comparison of orbits

motion at the boundary when it transitions from a 'back and forth' to a dissociation state is called separatrix. The purple trajectory in figure 6 is very close in energy to the separatrix and it is extremely close to it in shape. In figure 7, all of the trajectories with various energies are compared.

4. Conclusions

The phase space trajectories of the diatomic molecules have been investigated using the Morse potential. Three different categories of trajectories have been identified. The first one, which represents periodic motion, is closed or bounded. The second one is a homoclinic orbit and the third one is an open or unbounded trajectory that depicts unbounded motion. The motion in q of trajectories with energy greater than D is unbounded. The homoclinic orbit, which described by trajectories with energy h satisfies the relation $0 < h < D$.

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