Molecular Dynamic Simulation on the Collision of a diatomic Hydrogen Molecule with Copper Atomic Cluster (cu9)

A Thesis Submitted to the University of Khartoum for the Degree of M. Sc. In Physics

by

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Abstract

This study has provided valuable information about the kinetic of collision of a diatomic Hydrogen/ Deuterium molecules with Copper atomic cluster (cu₉) at different temperatures scales. The minimum geometry of the cluster was obtained by using thermal quenching method.

The reactive channel of the Cu₉ (T) and H₂ (v,j) molecules collision system is studied via quasi classical molecular dynamics simulation techniques (MD). The potential energy representing the reaction was chosen to be the embedded-atom potential model (EAM), that represent the interaction between the atoms in the cluster. The interaction between the molecule and the cluster was modeled by LEPS (London- Eyring- Polany- Sato) potential energy function. Both channels, the reactive (dissociate adsorption of the molecule on the cluster) and the non-reactive (in elastic scattering of the molecule from the cluster) are considered. Dissociative chemisorption probability, reaction cross section, and rate constant were computed as a function of the initial rovibrational states of molecule (vᵢ, jᵢ), collision energy, impact parameter, and cluster's temperature. The studies demonstrated that among all function's changes, the increment of translation energy enhance the reactivity. The H₂ / D₂ isotopic effect on the dissociation probability was also studied. The reaction cross section shows a significant strong isotope effects for the cluster and that the hydrogen molecule was always have a greater cross section than heavier deuterium molecule. The inelastic scattering probability was studied as a function of the collision energy of the molecule and the impact parameter. As expected, in the non reactive channel at higher translation energy the dissociation probability increases and the inelastic scattering probability decreases.

Key Words : Molecular Dynamics Simulation, Clusters, Dissociative Chemisorptions, Copper, Hydrogen, Deuterium.
دراسة منظومة تصادم جزيء الهيدروجين \( \text{(H}_2 \text{)} \) ذاتي الذرة مع عقد (مجموعة) ذرة من النحاس تتألف من 9 ذرات (Cu) باستخدام تقنية محاكاة (نموذج) ميكانيكا الجزيئات (/md)

بحث: ماجستر
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المستخلص

هذه الدراسة وفرت معلومات عن منظومة تصادم جزيء الهيدروجين \( \text{(H}_2 \text{)} \) ذاتي الذرة مع عقد (مجموعة) ذرة النحاس (Cu) في درجات حرارة مختلفة (T). تم إيجاد أصغر شكل هندسي للعقود باستخدام تقنية الإخماد الحراري.

تمت دراسة المسار التفاعلي لمنظمة تصادم جزيء الهيدروجين (\( \text{(H}_2 \text{)} \)) مع عقود النحاس الذري (Cu) من خلال تقنية شبة تقليدية هي محاكاة (نموذج) ميكانيكا الجزيئات (MD). تم اختيار طاقة الوضع للتفاعل (EAM) التي تمثل التفاعل (التفاعل) بين ذرات عقود النحاس، أما التفاعل (التفاعل) بين الجزيئات والعقد الذري فتم تمثيله أو نمذجته بدولة طاقة الوضع لـ Cu، وتم تحليل هذه النمذجة باستخدام (LEPS) وهو متعدد الفعال و ذاتية.

تتمثل فكرة التمثيلية للانحلال الإحلالي للجزيء في العقود الذري للنحاس، بينما يمثل المسار التصادمي للفعال (الاستطاعات الغير مرنة لجزيء من العقود الذري للنحاس).

تم حساب كل من احتمالية الانحلال الكيميائي الإحلالي، مقاطع التفاعل المستعرض للعقد الذري، ثابت المعدل التفاعلي كمود وحالة الابتعاثية للجزيء (Eo, \( \text{v} \)), و طاقة التفاعل، و معامل التصادم، و درجة حرارة العقود. أثبتت الدراسة أن زائدة في طاقة أرسال الجزيء وبالتالي طاقة التصادم يقابلها زيادة منتظمة في المقطع التفاعلي وبالتالي زيادة في احتمالية انحلال الجزيء. كما تمت دراسة ظاهرة تأثير النظارية للهيدروجين والمدروبيوم (D/D) على احتمالية الانحلال (أو التفكك) وأثبت قابلية عالية للانحلال نفوذ قابلية التفاعل المدروبيوم. تم حساب معدل التفاعل الذي أظهر عدم الاعتماد على زيادة عدد الكم الإحاثي (Eo) وزيادة متهدفة عند ازدياد عدد الكم الذري (Eo) كما أظهرت كل الدراسات السابقة الذكر عدم اعتمادها على التغيير في درجة حرارة عقود النحاس في المدى المذكور. كما تم أيضا دراسة احتمالية الاستطاعة الغير مرنة للجزيء كداخلية في طاقة تصادم الجزيء، ومعامل التصادم، و كما هو متوقع فإن زيادة طاقة الأرسال للجزيء المرسل يصبحها زيادة في احتمالية الأمثلة التصادمي وضع في أمثلة التصادمي.

كلمات مفتاحية: نمذجة (محاكاة) ديناميكية الجزيئات، العوامل (المجموعات) الذرية، الامثلة الكيميائي الإحلالي (التككي)، النحاس، الهيدروجين، المدروبيوم
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<td>E</td>
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<tr>
<td>Q</td>
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<td>$R_{A,B}$</td>
<td>Distance between atoms</td>
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<tr>
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</tr>
<tr>
<td>$r_{ij}$</td>
<td>Distance between atom I and atom j</td>
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<tr>
<td>T</td>
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<td>U,V</td>
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$V_s$ Attractive term

$\nu_f$ Final vibertional state

$\nu_i$ Initial vibertional state

$V(X_A, X_B, \{ X_C \})$ LEPS potential energy

$\alpha$ Parameter controlling the width of potential well

$\Delta$ Sato parameter

**ABBREVIATIONS**

DOF Degree of free Dom

EAM Embedded Atom Model

LEPS London –Eyring –Polyani –Sato

MD Molecular Dynamics Simulation

MC Monte Carlo

PEC Prediction evaluation correction

PES Potential Energy Surface
Chapter 1

Introduction

Much progress has been made in the recent years in theoretical and experimental descriptions of cluster reactions, especially more attention was paid to probe the kinetic and energetic of metal cluster-molecule reactions\(^1\). This focus on reactivity should be distinguished from the fast amount of researches, which has focused on the structure and energetic of pure metal and semiconductor cluster.

Cluster is a basic building block of nanotechnology electronic, nanosience. The ability to generate metal colloids with narrow size distribution means that it is possible to design nanoparticles, and to study the matter properties from the small cluster size. Also clusters can be used as model for heterogeneous catalysis reactions on bulk metal surfaces\(^2,3\).

Copper is one of the abundant elements in the nature, cheap, and considered as important metallic catalysts in hydrogenation reactions, where the surface generally lowers the activation barrier to bond breaking and stabilizes reaction intermediates which eventually proceed to form reaction products. On the other hand hydrogen with its small size, the most abundant element in the universe (make up 90% of the universe by weight) and the only stable neutral two body system which has special significance in quantum mechanics, all this make it with it is heavier isotope deuterium one of the highest fertile ground for experimentalists\(^4\).

Hydrogen chemisorptions play a very important role in understanding of various catalytic reactions in which hydrogen molecule adsorb dissociatively on transition metal surface. These studies was important in processes using catalysis such as: Petroleum refining processing, catalytic cracking, breaking long chain hydro carbons into smaller pieces, catalytic converter in auto mobile (decreased the pollution), Ammonia and Methanol synthesis, manufacture of margarine, and olefin polymerization, also in metal dispersion, and in metal imbrittlement\(^5,6\).
The interaction of hydrogen with copper cluster is still poorly characterized in both of theoretical and experimental studies. Because of the differences in the potential energy models selected to describe these interactions, the results was equivocal in determining the dissociation activation barrier, and the adsorption positions of the hydrogen atoms on Cu cluster sides.

Techniques of computer experiment or computer simulations, with the advent of high-speed computers, altered the picture by inserting a new element right in between experiment and theory. Where they simulate the experiments which may be expensive or difficult and sometimes impossible to be done in laboratory (for example in extremes conditions). They successfully fill the gap between the experimental observations and theoretical modeling\(^{(7)}\). One of these simulations techniques is the molecular dynamic (MD) techniques where the time evolution of a set of interacting atoms is followed by integrating their equations of motion; this is done by solving it numerically on a computer following the laws of classical, quasiclassical or quantum mechanics.

In our study the result of a quasiclassical simulation study of the interaction of hydrogen and deuterium molecules with Cu\(_9\) atomic cluster was presented. Both channel, the reactive (dissociative adsorption of molecule on cluster) and non reactive (scattering of the molecule from the cluster), were considered. This work provided a MD simulation result of two processes:

\[
\text{H}_2 \ (v_{i,j}) + \text{Cluster} \rightarrow \{ \text{H}_2 \ (v_{f,j}) \}_{\text{adsorbed}} \rightarrow \text{H} + \text{H} + \text{Cluster},
\]

and the process of inelastic scattering of the molecule from the cluster:

\[
\text{H}_2 (v_{i,j}) + \text{Cluster} \rightarrow \text{H}_2 (v_{f,j}) + \text{Cluster}, \quad \text{(8)}
\]

The dynamics of interaction between a molecule and cluster depends on the relative partners (molecule and cluster) and on their degrees of freedom (DOF), mainly in the internal one. It is of no doubt a formidable task to obtain a full theoretical description, which include all full DOF. Away around this would be for us to choose model systems for which the influence of certain DOF is minimized. Alternatively, we choose only those DOF on which we can exert considerable control. In this work the molecule translation energy, initial rovibrational state, cluster temperature and the reaction impact parameter were selected to be the controlled DOF of the collision system.
The goal of this simulation is to study the collision of H\textsubscript{2} molecules with Cu\textsubscript{9} atomic cluster, which include study of dissociative chemisorption probability, reaction cross section, reaction rate constant as function of collision energy, impact parameter, and cluster temperature. Also, H\textsubscript{2} / D\textsubscript{2} (isotopic effect) and inelastic scattering probability were studied. Before the collision, the copper cluster was prepared at desired temperatures T (K), and the H\textsubscript{2} molecule was prepared at specific initial vibrational (v\textsubscript{i}) and initial rotational (j\textsubscript{i}) states.

The general idea of the computer simulation MD predictor corrector method that solves numerically the equations of motion of the system was described in the second chapter. The selected potential energy surfaces that compute for the hydrogen molecule atoms and the cluster atom potential V\textsubscript{EAM} (Embedded atom potential) and the LEPS (London –Eyring –Polyani –Sato) which represents the molecule – cluster potential energy surface V\textsubscript{LEPS} were included in the third chapter. In the forth chapter the cluster physics model selection, and the classical trajectory calculations as a theoretical tools were provided. In the fifth chapter the results of the reaction cross section, rate constant at different initial roviberalional states and different temperatures were discussed for both of hydrogen and deuterium isotopes. The conclusion was given in chapter six and references were given at the end of the thesis.
Chapter 2
Molecular Dynamics Simulation

A computer simulation, computer model or a computational model is a computer program that try to simulate theoretical model of a particular system. Also it is the control of designing a model of an actual or theoretical physical system by performing the model on a digital computer and analyzing the perform output. Computer simulation has become a useful part of modeling many natural systems in physics. In sciences computational (Physics, chemistry and biology), and in human systems computational (economics and social science - the computational sociology) as well as in engineering were useful to gain insight into the operation of those systems. In such simulations the model behavior will change each simulation according to the set of initial parameters assumed for the environment. Traditionally, the formal modeling of systems has been via a mathematical model, which attempts to find analytical solutions enabling the prediction of the behavior of the system from a set of parameters and initial conditions. Recently computer simulations were carried out in the hope of understanding the properties of assemblies of molecules in terms of their structure and the microscopic interactions between them, also to enable us to learn something new that cannot be found out in other ways.

Computer simulations act as a bridge between microscopic length and time scales and the macroscopic world of the laboratory. At the same time, the hidden details behind bulk measurements can be revealed. Also, it can be the link between theory and experiment, where scientists may test a theory by conducting a simulation using the same model, or test the model by comparing with experimental results. Simulations may also carry out on the experiments that are difficult or impossible in the laboratory (for example, working at extremes of temperature or pressure).

2-1 Computer Simulation Method

There are many different types of computer simulation; the common feature they all share is the attempt to generate a sample of representative scenarios for a model in which a complete account of all possible states would be impossible. Computer models can be classified according to several criteria including:
• Stochastic or deterministic
• Steady-state or dynamic
• Continuous or discrete
• Local or distributed.

The two main families of simulation technique are molecular dynamics (MD) (Deterministic) and Monte Carlo (MC) (Stochastic), additionally; there is a whole range of hybrid techniques which combine features from both. In molecular dynamics the positions are obtain by numerically solving differential equations of motion and so, the positions are connected in time the positions tell dynamics of individual molecules as in motion picture. A molecular scale simulation consists of three principle steps:
1. Construction of model.
2. Calculation of molecular trajectories (these steps constitutes the simulation properties).
3. Analysis of those trajectories to obtain property values.

2-1-1 Stochastic Methods

In this method stochastic elements were used to compute quantities of interest. Stochastic models such as Monte Carlo simulations which they use random number generators to model chance or random events, Markov chain where the outcome of random event series depends only on the outcome of immediately previous event.

Monte Carlo (MC) is the purely stochastic method, it is typically performed on a fixed number of molecules N placed in fixed volume V and maintained at constant absolute temperature T. In Monte Carlo simulation, ensemble averages are evaluated by accumulating the integral at randomly generated values of independent variables of atomic positions \( r^N \). On the other hand, the positions are generated stochastically such that a molecular configuration \( r^N \) depends only on the previous configuration. The importance sampling scheme devised by Metropolis et al\(^9\), this method involves the following principle steps: First, assign initial positions \( r_i \) to the N molecules and compute the total potential energy. Then hypothesize a new configuration by arbitrarily disciplining one molecule and proposing that it was moved from \( r \) through a randomly chosen distance and direction to a new position \( r' \). If we reject the proposed
configuration, we count the old configuration as the new one and repeat the process using some other arbitrary chosen molecule. For each configuration generated by this procedure, we evaluate property integrand and accumulate them in running sums. To obtain sufficient precision for average, a few million configurations are generally needed.

2-1-2 Deterministic Methods

The idea behind these methods is the use of intrinsic dynamics of the model to propagate the system. In such kind of methods one can deal with all degrees of freedom. Such that, for collection of particles governed by classical mechanics with a trajectory \((x_n(t), p_n(t))\) in phase space for fixed initial points \(x_1(0), x_2(0), \ldots, x_n(0)\) and momenta \(p_1(0), p_2(0), \ldots, p_n(0)\), the equations of motion of such system will be discreted to generate a path in phase space along which properties can be computed. One of the deterministic methods is the well known molecular dynamics method.

2-1-3 Advantages and area of application of simulation method

A simulation is an imitation of some real thing, state of affairs, or process. The act of simulating something generally entails representing certain key characteristics or behaviors of a selected physical or abstract system.

Simulation is used in the modeling of natural systems or human systems in order to gain insight into their functioning, also include simulation of technology for performance optimization, health care, safety engineering, city and urban planning, testing, training flight, education and games. It can be used to show the eventual real effects of alternative conditions and courses of action.

- Deterministic methods are generally easier and faster to apply and readily lead themselves to computer applications.
- Many kinds of small errors tend to accumulate with time and so become apparent.
- When generate trajectories, the existence of an explicit time variable allows us to estimate the length needed for a run. The duration must be at least several multiples of relaxation time for the lowest phenomenon being studied.
- It is more efficiently evaluates such properties as the heat capacities, compressibility, and interfacial properties. Also configuration properties, provides entrance to dynamics quantities such as transport coefficients and time correlation functions.

2-2 Molecular Dynamics Simulation

Molecular dynamics (MD) simulation is computational method or a form of computer simulation, where atoms and molecules are allowed to interact for a period of time under known laws of physics. This is done by generating a molecular trajectories over finite time. The molecular dynamics method was first introduced by Alder et al. (10) in the middle of the last century to study the interactions of hard spheres. Since it is impossible to find the properties of such complex systems analytically, because molecular systems generally consist of a vast number of particles, MD simulation circumvents this problem by using numerical methods.

MD represents an interface between laboratory experiments and theory, and can be understood as a "virtual experiment", generate information at the microscopic level including atomic positions and velocities; also it is a special discipline of molecular modeling. It addresses numerical solutions of Newton's, Lagrangian's, and Hamiltonian equations of motion on an atomistic or similar model of molecular system to obtain information about its time dependent properties.

Molecular dynamics is concerned with molecular motion, where it is inherent to all chemical processes, such as simple vibrations, bond stretching and angle bending. Chemical reactions, hormone-receptor binding, and other complex processes are associated with many kinds of intra- and intermolecular motions. The driving force for chemical processes is described by thermodynamics. The mechanism by which chemical processes occur is described by kinetics. Thermodynamics dictate the energetic relationships between different chemical states, whereas the sequence or rate of events that occur as molecules transform between their various possible states is described by kinetics.
Conformational transitions and local vibrations are the usual subjects of molecular dynamics studies, which alter the intramolecular degrees of freedom in a step-wise fashion. The steps in molecular dynamics represent the changes in atomic position, $r_i$, over time (i.e. velocity) as seen in Fig. (2-1).

The force on an atom can be calculated from the change in energy between its current position and its position a small distance away. This can be recognized as the derivative of the energy with respect to the change in the atom's position:

$$\frac{dE}{dr_i} = F_i$$  \hspace{1cm} (2-1)
Energies can be calculated using either molecular mechanics or quantum mechanics methods. Molecular mechanics energies are limited to applications that do not involve strong changes in electronic structure such as bond making/breaking, while quantum mechanical energies can be used to study dynamic processes involving chemical changes.

Knowledge of the atomic forces and masses can then be used to solve for the positions of each atom along a series of extremely small time steps (on the order of femtoseconds = 10^{-15} seconds). The resulting series of snapshots of structural changes over time gives the simulation trajectory. The use of this method to compute trajectories can be more easily seen when Newton's equation is expressed in the following form:

\[- \frac{dE}{dr_i} = m_i \frac{d^2r_i}{dt^2}\]  \hspace{1cm} (2-2)

Since trajectories are not directly obtained from Newton's equation due to lack of an analytical solution, the atomic accelerations are firstly computed from the forces and masses and the velocities are next calculated from the accelerations based on the following relationship:

\[a_i = \frac{d v_i}{dt}\]  \hspace{1cm} (2-3)

Lastly, the positions are calculated from the velocities:

\[v_i = \frac{d r_i}{dt}\]  \hspace{1cm} (2-4)

A trajectory between two states can be subdivided into a series of sub-states by small time steps, "delta t" (e.g. 1 femtosecond).

The initial atomic positions at time "t" is used to predict the atomic positions at time "t + \Delta t". The positions at "t + \Delta t" are used to predict the positions at "t + 2* \Delta t ", and so on Fig. (2-3).
Molecular dynamics has no defined point of termination other than the amount of time that can be practically covered. Unfortunately, the current picosecond order of magnitude limit is often not long enough to follow many kinds of state to state transformations, such as large conformational transitions in proteins.

**2-2-1 Standards Molecular Dynamics Simulation Models**

**2-2-1-1 Microcanonical ensemble (NVE)**

In the microcanonical, or NVE ensemble, the system is isolated from changes in moles (N), volume (V) and energy (E). It corresponds to an adiabatic process with no heat exchange. A microcanonical molecular dynamics trajectory may be seen as an exchange of potential and kinetic energy, with total energy being conserved. For a system of N particles with coordinates $X$ and velocities $V$, the following pair of first order differential equations may be written in Newton's notation as

\[ F(x) = -\nabla U(x) = M\ddot{x}(t) \]  \hfill (2-5)

\[ V(t) = \dot{x}(t) \]  \hfill (2-6)

**2-2-1-2 Canonical ensemble (NVT)**

In the canonical ensemble, moles (N), volume (V) and temperature (T) are conserved. It is also sometimes called constant temperature molecular dynamics (CTMD). In NVT, the energy of endothermic and exothermic processes is exchanged with a thermostat.
2-2-1-3 Isothermal-Isobaric (NPT) ensemble

In the isothermal-isobaric ensemble, moles (N), pressure (P) and temperature (T) are conserved. In addition to a thermostat, a barostat is needed.

2-2-1-4 Generalized ensembles

The replica exchange method is a generalized ensemble. It was originally created to deal with the slow dynamics of disordered spin systems. It is also called parallel tempering. The replica exchange MD (REMD) formulation tries to overcome the multiple-minima problem by exchanging the temperature of non-interacting replicas of the system running at several temperatures.

2-2-2 Molecular dynamics time average Method

Since integral over all system is generally extremely difficult to calculate because one must calculate all possible states of the system, molecular dynamics simulation calculate the points in the ensemble sequentially in time. So to calculate an ensemble average, the molecular dynamics simulations must pass through all possible states corresponding to the particular thermodynamic constraints. Another way, as done in an MD simulation, is to determine a time average of A, which is expressed as

\[
\langle A \rangle_{\text{time}} = \lim_{\tau \to 0} \frac{1}{\tau} \int_{t=0}^{\tau} A(P_N^X(t), r_N^X(t))dt \approx \frac{1}{M} \sum_{i=1}^{M} A(P_N^N, r_N^N)
\]  

Where \( \tau \) is the simulation time, M is the number of time steps in the simulation and \( A(p_N^N, r_N^N) \) is the instantaneous value of A.

The dilemma appears to be that one can calculate time averages by molecular dynamics simulation, but the experimental observables are assumed to be ensemble averages. Resolving this leads us to one of the most fundamental axioms of statistical mechanics, the ergodic hypothesis, which states that the time average equals the ensemble average.

The Ergodic hypothesis states

\[
\langle A \rangle_{\text{ensemble}} = \langle A \rangle_{\text{time}}
\]  

(2-8)
The basic idea is that if one allows the system to evolve in time indefinitely, that system will eventually pass through all possible states. One goal, therefore, of a molecular dynamics simulation is to generate enough representative conformations such that this equality is satisfied. If this is the case, experimentally relevant information concerning structural, dynamic and thermodynamic properties may then be calculated using a feasible amount of computer resources. Because the simulations are fixed duration, one must be certain to sample a sufficient amount of phase space.

2-2-2-1 Average potential energy

$$V = \langle V \rangle = \frac{1}{M} \sum_{i=1}^{M} V_i$$  \hspace{1cm} (2-9)

Where M is the number of configurations in the molecular dynamics trajectory and $V_i$ is the potential energy of each configuration.

2-2-2-2 Average kinetic energy

$$K = \langle K \rangle = \frac{1}{M} \sum_{j=1}^{M} \left\{ \sum_{i=1}^{N} \frac{m_i}{2} v_i \cdot v_i \right\}_j$$  \hspace{1cm} (2-10)

where M is the number of configurations in the simulation, N is the number of atoms in the system, $m_i$ is the mass of the particle i and $v_i$ is the velocity of particle i.

2-2-2-3 Temperature

The temperature is directly related to the kinetic energy by the well known equitation formula

$$K = \frac{3}{2} N k_B T$$  \hspace{1cm} (2-11)

for practical purpose it is also common to define "instantaneous temperature" $T(t)$ proportional to instantaneous Kinetic energy $K(t)$.

2-2-2-4 Pressure

The pressure measurement based on the Clausius viral function
\[ PV = NK_bT - \frac{1}{D} \left( \sum_i r_i \left[ \frac{dv(r_i)}{dr} \right] \right) \]  

(2-12)

where D is the dimensionality of the system and \( \nu(r_i) \) is the potential energy associated with the system. A molecular dynamics must be sufficient long so that enough representative conformation have been sampled.

### 2-2-3 The structure and important aspects M.D starting point

Molecular dynamics simulation is in many respects very similar to real experiments, that is to say we follow exactly the same approach. Firstly we prepare a sample (model system consisting of N particles). Secondly we solve the equation of motion numerically and due to the complicated nature of this equation and also there is no analytical solution to it, this is done until the properties of this system no longer change with time (equilibrated system). Finally we perfume the actual measurement.

To construct a molecular dynamics simulation program it must be as simple as possible to illustrate a number of important features of simulation and it is constructed as follows:

1- Select the parameter that specifies the conditions of the run (e.g. initial temperature, number of particle, density, time step, etc).
2- Initialize the system (i.e. we select initial positions and velocities).
3- Compute the force on all particles.
4- Integrate the equation of motion. These two steps (3 & 4) represent the core of the simulation, and they are prepared until the time evolution of the system for the desired length of time is computed.
5- After completing the central loop, compute and print the average of measured equation, and stop.

In order solve the problem in computer first of all we need to discretize the trajectories that is to say instead of considering

\[(r_i(t), v_i(t)) \geq 0\]  

(2-13)

For continuous time we consider a sequence of state
Numerous numerical discretization methods have been developed. All these algorithms assume the position, velocities and acceleration can be approximated by a Taylor series expansion

\[
(r(t + \delta t) = r(t) + v(t)\delta t + \frac{1}{2} a(t)\delta t^2 + ...)
\]

\[
v(t + \delta t) = v(t) + a(t)\delta t + \frac{1}{2} b(t)\delta t^2 + ...
\]

\[
a(t + \delta t) = a(t) + b(t)\delta t + ...
\]

Where \( r \) is the position, \( v \) is the velocity (the first derivative with respect to time), \( a \) is the acceleration (the second derivative with respect to time), etc.

2-2-4 M.D. Integration of time Algorithm

2-2-4-1 Verlet algorithm

The Verlet algorithm uses positions and accelerations at time \( t \) and the positions from time \( t-\Delta t \) to calculate new positions at time \( t+\Delta t \). The Verlet algorithm uses no explicit velocities. The advantages of the Verlet algorithm are: it is straightforward, and the storage requirements are modest. The disadvantage is that the algorithm is of moderate accuracy.

To derive the Verlet algorithm one can write

\[
r(t + \delta t) = r(t) + v(t)\delta t + \frac{1}{2} a(t)\delta t^2
\]

\[
r(t - \delta t) = r(t) - v(t)\delta t + \frac{1}{2} a(t)\delta t^2
\]

Summing these two equations, one obtains

\[
r(t + \delta t) = 2r(t) - r(t - \delta t) + a(t)\delta t^2
\]
2-2-4-2 The Leap-frog algorithm

\[
\begin{align*}
    r(t + \delta t) &= r(t) + v(t + \frac{1}{2} \delta t) \delta t \quad (2-21) \\
    v(t + \frac{1}{2} \delta t) &= v(t - \frac{1}{2} \delta t) + a(t) \delta t \quad (2-22)
\end{align*}
\]

In this algorithm, the velocities are first calculated at time \( t+1/2 \delta t \); these are used to calculate the positions, \( r \), at time \( t+\delta t \). In this way, the velocities leap over the positions, and then the positions leap over the velocities. The advantage of this algorithm is that the velocities are explicitly calculated, however, the disadvantage is that they are not calculated at the same time as the positions. The velocities at time \( t \) can be approximated by the relationship:

\[
v(t) = \frac{1}{2} \left[ v(t - \frac{1}{2} \delta t) + v(t + \frac{1}{2} \delta t) \right] \quad (2-23)
\]

2-2-4-3 The Velocity Verlet algorithm

This algorithm yields positions, velocities and accelerations at time \( t \). There is no compromise on precision.

\[
\begin{align*}
    r(t + \delta t) &= r(t) + v(t) \delta t + \frac{1}{2} a(t) \delta t^2 \quad (2-24) \\
    v(t + \delta t) &= v(t) + \frac{1}{2} \left[ a(t) + a(t + \delta t) \right] \delta t 
\end{align*}
\]

2-2-4-4 Beeman’s algorithm

This algorithm is closely related to the Verlet algorithm

\[
\begin{align*}
    r(t + \delta t) &= r(t) + v(t) \delta t + \frac{2}{3} a(t) \delta t^2 - \frac{1}{6} a(t - \delta t) \delta t^2 \quad (2-26) \\
    v(t + \delta t) &= v(t) + v(t) \delta t + \frac{1}{3} a(t) \delta t + \frac{5}{6} a(t) \delta t + \frac{1}{6} a(t) \delta t 
\end{align*}
\]
The advantage of this algorithm is that it provides a more accurate expression for the
velocities and better energy conservation. The disadvantage is that the more complex
expressions make the calculation more expensive.

2-2-4-5  General predictor- corrector Algorithms:

Predictor-corrector algorithms were first introduced into molecular dynamics by
Rahman (9). From the current position $r(t)$ and velocity $v(t)$ the steps are as follows:
1- Predict the position $r(t + \Delta t)$ and velocity $v(t + \Delta t)$ at the end of the next step.
2- Evaluate the forces at $(t + \Delta t)$ using the predicted position.
3- Correct the predictions using some combination of the predicted and previous
values of position and velocity.

As a simple example, consider the following predictor corrector based on Euler's
method (9):

The force evaluation would actually be done in the previous step $(t + \Delta t)$ and stored for
use in the current step, so this algorithm meets the goals of requiring only one force
evaluation per step while providing an algorithm of higher order than Euler's method.
The advantages of the general predictor–corrector algorithm that it was simple to
implement, and offer great flexibility in that many choices are possible for both the
prediction and correction steps. Also, it provides good stability because the corrector
step amounts to a feedback mechanism that can dampen instabilities which might be
introduced by the predictor. The disadvantage of predictor- corrector algorithms is that
each E-step requires force calculations and P(EC)$^n$ simulation will perform nearly n
times slower than the P(EC) simulation.

2-2-4-6  Gear’s predictor- corrector algorithms:

Those commonly used in molecular dynamics are often taken from the collection of
methods by Gear (9). The one used in the programs consists of the following steps:
1- Predict molecular positions $r_i$ at time $t + \Delta t$ using a fifth- order Taylor series based
on positions and their derivatives at time. Thus, the derivatives $\dot{r}_i$, $\ddot{r}_i$, $r_i^{(iii)}$, $r_i^{(iv)}$, $r_i^{(v)}$, are
needed at each step; these are also predicted at time $t + \Delta t$ by applying Taylor.
Expansions at $t$:
- \( r_i(t + \Delta t) = r_i(t) + \dot{r}_i(t) \Delta t + \ddot{r}_i(t) \frac{(\Delta t)^2}{2!} + r_i(t) \frac{(\Delta t)^3}{3!} + \dot{r}_i(t) \frac{(\Delta t)^4}{4!} + r_i(t) \frac{(\Delta t)^5}{5!} \) 

(2-28)

- \( \dot{r}_i(t + \Delta t) = \dot{r}_i(t) + \ddot{r}_i(t) \Delta t + \frac{\dddot{r}_i(t)}{2!} \frac{(\Delta t)^2}{2!} + r_i(t) \frac{(\Delta t)^3}{3!} + \dot{r}_i(t) \frac{(\Delta t)^4}{4!} \) 

(2-29)

- \( \dddot{r}_i(t + \Delta t) = \dddot{r}_i(t) + \frac{\dddot{r}_i(t)}{2!} \Delta t + \frac{\dddot{r}_i(t)}{3!} \Delta t^3 + \frac{\dddot{r}_i(t)}{4!} \Delta t^4 \) 

(2-30)

- \( r_{ij}(t + \Delta t) = r_{ij}(t) + \frac{\dddot{r}_{ij}(t)}{2!} \Delta t + \frac{\dddot{r}_{ij}(t)}{3!} \Delta t^3 \) 

(2-31)

- \( r_{ij}(t + \Delta t) = r_{ij}(t) + \frac{\dddot{r}_{ij}(t)}{2!} \Delta t \) 

(2-32)

- \( r_{ij}(t + \Delta t) = \frac{\dddot{r}_{ij}(t)}{2!} \) 

(2-33)

2- Evaluate the intermolecular force \( F_i \) on each molecule at time \( t + \Delta t \) using the predicted positions. For continuous potential energy functions \( U(r_{ij}) \) that act between atoms \( i \) and \( j \), the force on each molecule is given by:

\[
F_i = - \sum_{j \neq i} \frac{\partial U(r_{ij})}{\partial r_{ij}} \hat{r}_{ij} \tag{2-34}
\]

Where \( \hat{r}_{ij} \) is the unit vector in the \( r_{ij} \)-direction. Evaluation of forces is time consuming because the sum in (2-34) must be performed for each molecule \( i \) in the system. However, there are several ways to save time; one is that Newton’s third law can be applied.

\[
F_i(r_{ij}) = - F_i(r_{ij}) \tag{2-35}
\]

3-Correct the predicted position and their derivatives using discrepancy \( \Delta \dot{r}_i \) between the predicted acceleration and that given by the evaluated force \( F_i \) with the force at \( t + \Delta t \) obtained from (2-34). Newton’s second law can be used to determine the accelerations \( \ddot{r}_i(t + \Delta t) \). The difference between the predicted accelerations and evaluated accelerations is the formed,

\[
\Delta \dot{r}_i = \left[ \ddot{r}_i(t + \Delta t) - \frac{\dot{r}_i}{\Delta t} \right] \tag{2-36}
\]

In gear’s algorithms for second-order differential equations, this difference term is used to correct all predicted positions and their derivatives; thus,

\[
r_i = r_i + \Delta R2 \tag{2-37}
\]

\[
\dot{r}_i \Delta t = \dot{r}_i \Delta t + \alpha_1 \Delta R2 \tag{2-38}
\]
\[ \frac{\dot{p}(\Delta t)^2}{2!} = \frac{\ddot{p}(\Delta t)^2}{2!} + \alpha_2 \Delta R^2 \]  \hspace{1cm} (2-39)

\[ \frac{r_i(\Delta t)^3}{3!} = \frac{(r_i)^p}{3!} + \alpha_3 \Delta R^2 \]  \hspace{1cm} (2-40)

\[ \frac{r_i(\Delta t)^4}{4!} = \frac{(r_i)^p}{4!} + \alpha_4 \Delta R^2 \]  \hspace{1cm} (2-41)

\[ \frac{r_i(\Delta t)^5}{5!} = \frac{(r_i)^p}{5!} + \alpha_5 \Delta R^2 \]  \hspace{1cm} (2-42)

Where \( \alpha_i \) parameters promote numerical stability of the algorithm, and depend on order of the differential equations to be solved and on the order of Taylor series predictor.

The program in this study was introduced by Voter et al. \(^{(11)}\). The package was prepared to run under the operating systems UNIX.
Chapter 3
Atomic Reactions and Potential Energy Surfaces (PES)

In recent years a variety of experimental studies was performed to probe the kinetic and energetic of metal cluster–molecule reactions. Most of the surface molecule studies involving Hydrogen have been computed semi-empirically. The simulation contained in this work makes use of a pair wise description for atom and molecules interaction by using the semi empirical method, which contains the two body potential and many body potential.

3-1 Atomic Reactions

A molecular dynamics simulation requires the definition of a potential function, or a description of the terms by which the particles in the simulation will interact. The best choices of methods will be one of three:


B- Semi Empirical Methods.

C- Theoretical Methods.

3-2 Potentials Energy Surfaces (PES) theoretical methods
3-2-1 Ab-initio methods

Ab-initio quantum-mechanical gives a formula to calculate the potential energy of a system of atoms or molecules. The properties of the system in ab-intio calculations are:

- Calculating the wave-functions for electrons moving around the nucleus of atoms, i.e., for nuclei in the close neighborhood of the reaction coordinate.
- Produce a large amount of information that is not available from the empirical methods, such as density of states information.
Advantage of using ab-initio methods is the ability to study reactions that involved breakage or formation of covalent bonds. The disadvantage of ab-initio methods is that computational is very expensive and also it yield poor geometries and energetic, especially for transition metal system, because it doesn’t properly accounts for electron correlation \(^{(10)}\).

A popular package for ab-initio molecular dynamics is the Car-Parrinello Molecular Dynamics (CPMD) package based on the density functional theory.

3-2-2 Density Functional Theory (DFT)

The more interest recent and perspective appears is that of the density functional theory. The basic advantage of it is that the total electronic energy is directly tied to electron density so that each electron is considered as moving in effective low potential of nuclei and other electron. DFT methods such as Bech’es exchange potential (BB), Local density approximation (LDA), and general gradient MM approximation (GGA) show a detectable progress and they considered as efficient and accurate computational methods in the studies of reaction on transition metal.

3-2-3 Hybrid QM/MM

These methods are known as mixed or hybrid of: quantum-mechanical (QM) methods, which are very powerful, expensive, and accurate. And the classical or molecular mechanics methods (MM), which are faster, but require wide parameterization; and energy estimates obtained are not very accurate. A new class of method Hybrid QM/MM has emerged that combines the good points of QM (accuracy) and MM (speed) these good points becomes the most advantage of the Hybrid methods. It is useful in investigating phenomenon such as hydrogen tunneling, which occur in transfer in the enzyme liver alcohol dehydrogenase.

3-2-4 Coarse-graining and reduced representations

In these methods used "pseudo-atoms" to represent groups of atoms tackle the problem which obtain in MD simulations system such as:
- Very large systems may require such large computer resources that they cannot easily be studied by traditional all-atom methods.

- Simulations of processes on long timescales (beyond about 1 microsecond) are expensive, because they require so many time steps.

When coarse-graining is done at higher levels, the accuracy of the dynamic description may be less reliable. But very coarse-grained models have been used successfully to examine a wide range of questions in structural biology.

3-2-5 Semi-empirical potentials

Semi-empirical potentials make use of the matrix representation from quantum mechanics. However, the values of the matrix elements are found through empirical formulae where some integrals are replaced by empirical parameters. These methods are applied for very large system where only valence electrons are usually considered.

The advantages of semi-empirical potentials are that are faster than ab-initio or DFT calculations, and they are used to determine the energy contributions of the orbital. The disadvantages of semi-empirical potentials are that they are generally less accurate and they give a very poor approximation for the new function. There are a wide variety of semi-empirical potentials, such as tight-binding potentials, Stillinger-Weber potential, Tersoff's potential.

3-2-6 Empirical potentials

Empirical potentials used in chemistry are frequently called force fields, while those used in materials physics are called just empirical or analytical potentials, they can be divided into:

1- Two body potentials (The interatomic potentials).
2- Many body potentials.

3-2-6-1 Two body potentials (The interatomic potentials)

The potential functions representing the non-bonded interactions are usually "pair potentials", in which the total potential energy of a system can be calculated from the
sum of energy contributions from pairs of atoms. These non-bonded interactions, because they are nonlocal and involve at least weak interactions between every pair of particles in the system, are normally the bottleneck in the speed of MD simulations.

An example of a calculated pair potential is the non-bonded Lennard-Jones potential (also known as the 6-12 potential), used for calculating van der Waals forces.

\[
U(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right]
\]

(3-1)

Another example is the Morse potential functions expressing the core-core repulsion between atom i and j separated by the distance \(R_{ij}\).

\[
\phi_{ij}(R_{ij}) = D_{eq} \left( 1 - e^{-\alpha(R_{eq} - r_{eq})} \right)^2
\]

(3-2)

\(D_{eq}, r_{eq}\) are the potential depth, minimum distance at equilibrium and "\(\alpha\)" represent parameter controlling the width of potential well (Morse parameter).

### 3-2-6-2 Many body potentials:

Many-body potentials, has been implemented for a wide range of materials, involves a sum over groups of three atoms. The PES was chosen to used in this work is the:

\[
V = V_{EA} + V_{LEPS}
\]

(3-3)

Where the \(V_{EA}\) is the Embedded Atom potential. \(V_{LEPS}\) is the interaction between gas atoms and the cluster, and among the gas interaction of the diatomic molecule.

### 3-2-6-2-1 Embedded-atom potential method (EAM)

This developed by Daw and Baskes\(^{(11,12)}\) and determined empirically to describe the interaction between atoms in cluster, where the energy of each atom is computed from the energy needed to embed the atom in the local-electron density as provided by the other atoms of the metal, and the energetics of an arbitrary arrangement of atoms can be calculated quickly. The starting point of EAM is the observation of that the total electron density in a metal is reasonable approximated by linear superposition of contributions from the individual atoms. The electron density in the vicinity of each atom can then be express as a sum of the density contributed by the atom in question.
plus the electron density from all the surrounding atoms. By making a simplification
that this background electron density is a constant, the energy associated with the
electron density of an atom plus the background density is constant. In addition, there
is an electrostatic energy contribution due to the core – core overlap.

The Embedded Atom potential is:

\[ V_{EAM} = \sum \phi(r_i) + \sum F(\rho) \tag{3-4} \]

\[ E_{total} = V_{EAM} = \sum_i F_i(\rho_{h,i}) + \frac{1}{2} \sum_{j(i(h))} \phi_j(R_{ij}) \tag{3-5} \]

\( F(\rho_{h,i}) \) represent the energy of embedding atom i in background the host electron
density \( \rho_{h,i} \) due to the remaining atoms at the systems. \( \phi_j(R_{ij}) \) is the core- core pair
repulsive atom i and j separated by distance( \( r_{ij} \)).

The atomic densities was calculated from the Hartree–Fock calculations

\[ \rho^q(R) = n_s \rho_s + n_d \rho_d \tag{3-6} \]

Where \( n_s \) and \( n_d \) are the number of the outer s and d electrons and the \( \rho_s \) and \( \rho_d \) are
the densities associated with the s and d wave functions.

The observations, along with the columbic origin of the pair interaction term, suggest
that the pair interaction between atoms of type i and j in terms of effective charges is
given by:

\[ \phi_i(R) = \frac{z_i(R) z_j(R)}{R} \tag{3-7} \]

Where a simple parameterized form for \( (R) = Z_0(1 + \beta R)^{r-\alpha R} \). In this work and in
similar way to that of Hartree Fock

\[ \rho^q_i(r_{ij}) = r_{ij}^6 \left[ e^{-\beta r_{ij}} + 512 e^{-2\beta r_{ij}} \right] \tag{3-8} \]

or

\[ \rho(r) = r^6 \left[ e^{-\beta r} + 512 e^{-2\beta r} \right] \tag{3-9} \]

is used to express the atomic density and

\[ \phi_i(r_{ij}) = D_e \left[ 1 - \exp\left[-\alpha (r_{ij} - r_e)\right] \right] - D_e \tag{3-10} \]

Where \( \phi_i(r_{ij}) \) is the Morse potential function expressing the core – core interaction
function.

This calculation methods for \( \rho^q_i(r_{ij}) \) and \( \phi(r) \) was firstly used by Voter and Chen(13).

\( D_e, r_e \) and \( \alpha \) are respectively, the depth of the potential, the distance to the minimum
and a measure of the curvature of the minimum which is usually used for cluster while the other forms are used for the bulk.

3-2-6-2-2 (London –Eyring –Polyani –Sato) potential (LEPS)

From the Semi-empirical potential energy surface i.e. in which some integrals are replaced by empirical parameter, $V_{LEPS}$ potential energy surface was chosen to represent the Diatomic (AB) – cluster interaction system. $V_{LEPS}$ was the modified four –body (London –Eyring –Polyani –Sato) potential first introduced by McCreery and wolken$^{14}$,and later it has been widely used to study the dynamics of gas – surface and gas–cluster reaction

$$V_{LEPS}(X_A, X_B, X_C) = Q_{AB} + Q_{AC} + Q_{BC} - \left[J_{AB}^2 + (J_{AC} + J_{BC})^2 - J_{AB}(J_{AC} + J_{BC})\right]^{1/2} \quad (3-11)$$

Where Q and J are the coulomb and exchange integrals respectively. The subscripts A,B labeling the molecule atoms C represent the cluster and $X_A, X_B, X_C$ are their coordinate respectively. The LEPS parameters values were chosen to be that of Lee and Depresto$^{15}$.

The functions $Q_{A,B}$ and $J_{A,B}$ are determined from a Morse and anti-Morse from for the individual A-B interaction by:

$$Q_{A,B} + J_{A,B} = V_{A,B} = \left[\alpha R - \alpha \alpha\right] - 2 \exp\left[-\alpha \alpha\right] \quad (3-12)$$

$$Q_{A,B} - J_{A,B} = \left[\frac{1 - \Delta_{A,B}}{2(1 + \Delta_{A,B})}\right] \left[\exp\left[-\alpha \alpha\right] + 2 \exp\left[-\alpha \alpha\right]\right] \quad (3-13)$$

where $R = |x_A - x_B|$

for the A-C term, the analogous equations are

$$Q_{A,C} + J_{A,C} \equiv V_{A,C} = V_r - V_a \quad (3-14)$$

$$Q_{A,C} + J_{A,C} = \left[\frac{(1 - \Delta_{A,C})}{2(1 + \Delta_{A,C})}\right] \left[\exp\left[-\alpha \alpha\right] + 2 \exp\left[-\alpha \alpha\right]\right] \quad (3-15)$$

Where $V_r$ and $V_a$ are the repulsive and attractive terms respectively, for the A–C interaction. These are given by

$$V_r = D_H \exp\left[-\alpha \alpha (r_A - r_C)\right] + \sum_k D_k (R_k - r_2) \quad (3-16)$$

$$V_a = 2D_H \exp\left[-\alpha \alpha (r_A - r_C)\right] + \sum_k 2D_k \exp\left[-\alpha (R_A - r_2)\right] \quad (3-17)$$
Where $R_{A,K} = |x_A - x_K|$ and $K$ indicates the atom in the cluster. The summation in Eq. (3-17) extended over all the atoms in the cluster.

The variable $r_s$ in these equations is related to the valence electron density of the cluster at the position of atom $A$ by

$$r_s = \left\{ \frac{3}{4\pi m(x_A)} \right\}^{\frac{1}{3}}$$  \hspace{1cm} (3-18)

$$\rho(x_A) = \sum_k N_{4s} \rho_{4s}(r_{A,K})$$ \hspace{1cm} (3-19)

Where $N_{4s}$ is modeled by the summed atomic Hartree –Fock densities from the 4s valence electrons. In this work the parameters used were tabulated in set of table (3-1) where we can classify them into two categories:

<table>
<thead>
<tr>
<th>H-H terms</th>
<th>LEPS-DePristo</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_e$ (eV)</td>
<td>4.745</td>
</tr>
<tr>
<td>$\alpha_e$ (Å)</td>
<td>1.943</td>
</tr>
<tr>
<td>$r_e$ (Å)</td>
<td>0.741</td>
</tr>
<tr>
<td>$\Delta_{H,H}$</td>
<td>0.000</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>H/D-H terms</th>
<th>LEPS-DePristo</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_H$ (eV)</td>
<td>1.2</td>
</tr>
<tr>
<td>$\alpha_H$ (Å)</td>
<td>3.253</td>
</tr>
<tr>
<td>$r_H$ (Å)</td>
<td>3.98</td>
</tr>
<tr>
<td>$\Delta_{H,Co}$</td>
<td>0.24</td>
</tr>
</tbody>
</table>

Table (3-1). The LEPS potential energy parameter

1- The set of parameters for the Hydrogen molecule before interacting.

2- The set of parameters for the Hydrogen atoms after interacting with the cluster which also classified into two sets:

A- The set of parameter associated with the LEPS interaction potential between the Hydrogen atoms in the hydrogen molecule while they were connected to the cluster.

B- The set of parameter associated with the LEPS interaction potential between the Hydrogen atoms and the cluster's atoms.
Chapter 4
Model Selection

In the last decade the understanding of the melting process of small atomic and molecular clusters, its structure and dynamics has been a subject of intense research activities, and many theoretical and experimental studies \(^{(2,3)}\).

In the model chosen by our work: H-H bond was taken to be perpendicular to the line or plane in which the Cu atoms were located. The initial separation between the diatomic and the cluster was chosen to be 8.5 Å and the initial moment and coordinate were chosen in accordance with a quasi classical prescription developed by Porter\(^{(16)}\). The geometrical structure of the most stable Cu cluster is identified using Molecular dynamic and Thermal Quenching simulation technique \(^{(17,18)}\). Calculations were done for 500 trajectory in a grid of translation energy \(E_t\) and impact parameter \(b\) with \(\Delta E = 0.01\text{eV}\) and \(\Delta b = 0.25\text{Å}\).

![Diagram of the collision of Hydrogen molecule with Copper atomic cluster.](image)

The four distances monitored in this collision are:

1- The distance between the two atoms in the molecules.
2- The distance between the molecules center of mass and the cluster center of mass.
3- The distance between the first molecule and the cluster center of mass.
4- The distance between the second molecule and the cluster center of mass.
4-1 Collision Model Selection:

In this study Morse potential, L E PS potential, and E.A potential that used to represent the potential energy associated with the reaction was shown as a schematic diagram in Fig (4-2).

![Diagram showing collision system potentials]

Fig. (4-2). A schematic diagram shows all potentials energies of the collision system.

When a diatomic molecule prepared in a certain initial quantal state, interact with metal clusters, a number of processes can occur as schematically diagramed Fig (4-3):

1- Some may be adsorbed as molecules, or as dissociated atoms, then after adsorption they may diffuse, or migrate.
   \[ H_2(v,j)+\text{cluster} \rightarrow [H_2(v,j)]_{\text{ads}} \rightarrow [H+H]_{\text{diss}} \rightarrow [H_2(v,j)]_{\text{recom}} \]

2- Some may undergo dissociative scattering i.e atomic fragmentation then going back into the gas face after recombining with the fragmented/or dissociated atoms.

3- Some undergo Elastic scattering (diffraction)
   \[ H_2(v,j)+\text{Cluster} \rightarrow H_2(v,j)+\text{Cluster} \]

4- And some may also undergo Inelastic scattering:
   i) By excitation of the molecular internal degree of freedom (DOF) e.g rotation and/or vibration
   ii) By excitation of the surface phonons and/or surface electron-hole
   \[ H_2(v,j)+\text{Cluster} \rightarrow H_2(v',j')+\text{Cluster} \]
Fig. (4-3). A schematic diagram of several reactions that may occur when a diatomic molecule, prepared in a certain initial quantum mechanical state, interacts with a metal surface.

4-2 Cluster and Cluster Physics:

Clusters are aggregates of atoms or molecules; it can also be said that they bridge the gap between small molecules and bulk materials (2-10^9) where n can be as high as 6 or 7 atoms) (2,3) as shown Fig. (4-4).

The scientific study of cluster is fairly recent; the earliest reference to cluster was made by Robert Boyle in 1961\(^9,20\).

Fig. (4-4) A schematic diagram that represent the size relationships of atomic, molecular, and solid state physics.
clusters are formed by most of the elements in the periodic table, some cluster (H$_2$O cluster) are found in the atmosphere, they can be subdivided according to the type of the constitutes atoms, some example of different types of clusters\(^{(2)}\):

1- Metal cluster: metallic elements from a cross the periodic table forms a wide variety of clusters, where the boning is metallic. Metal clusters may be composed of single metallic element or more than one metal.

2- Semiconductor cluster: this class of cluster includes compound semiconductor clusters. Also it made up of the elements (such as carbon, silicon and germanium) which are semiconductor in solid state.

3- Ionic clusters: it can be gained when the electronegativity different between two elements in a compound semiconductor cluster, increase, so the polarity of the bonds increase until the bonding can better be described as ionic, or electrostatic in nature.

4- Rare gas clusters: at low temperature, it is possible to form cluster of the rare gas elements (Helium or Radon).

5- Molecular clusters: it can be formed by supersonic expansion of molecular vapor.

6- Cluster molecules: one can compose molecules from the Cluster.

Clusters may be homogenous, that is Composed only one kind of atom or molecule, or heterogeneous, made of more kind of atom or molecule. It can be made in laboratory by making a vapor of the elementary component particles and letting them aggregate, or by knocking them directly out of a solid.

The field of cluster science studies the chemical reactions that occur on or within clusters. As example hydrogen molecule striking a cluster of nickel atoms may dissociate into hydrogen atoms that become strongly bound to the nickel cluster. Other kind of reaction of cluster that have been studied is the recombination of the atoms of diatomic molecule imbedded in cluster that dissociated by adsorbing sufficient energies from the cluster. These examples of reaction have important counterparts in chemistry of catalysis.

4-2-1 Clusters Usage

There is an experimental and theoretical interest in study of elemental clusters in gas
phase or in solid state due to:

- Intrinsic properties of clusters.
- The central position that they occupy between molecular and condensed matter science.
- They span a wide range of particle size, from molecular to the microcrystalline.
- Constitute a new type of material (nano particles).
- The study of the evolution of the geometric and electronic of materials.

4-2-2 Structures of cluster and their chemical and physical properties

Cluster may offer ways to make altogether new kinds materials, carry out chemical reactions in new way, gain new kinds of understanding for the behavior of bulk matter, learning how bulk properties emerge from properties of clusters. The quantum effects which occur in such material of finite size and dimension, lead to their special properties. Also, cluster make mechanical, electronic, optical and other properties, good potential candidates as new building materials for electronic devices, it can, and do, adopt new atomic arrangements, which may be forbidden in the bulk. Also, the patterns of atoms on cluster’s surface were energetically favorable.

4-2-3 Clusters Application

- Clusters were used as a model for heterogeneous catalysis on bulk metal surface.
- Nanotechnology industry.
- Build devices, and play a pivotal role as components for a variety of electronic, magnetic and optical devices.
- The field of organic and bio-organic nanoscience.
- The scientific study of cluster find new field of research.
- Physicists, chemists and materials scientists, they develop methods of synthesis.
- Advances in techniques for the synthesis of cluster engineered materials containing controlled nanostructures, provide the capability of preparing new
classes of materials with enhanced optical, magnetic, chemical sensor and photocatalytic properties.

- Development of high tech materials to obtain useful properties not found in naturally-occurring substances.
- Electronic industry, where making devices like transistors smaller and more efficient.

4-2-4 General considerations

Theory has played an important role in the development and application of cluster science. Since many cluster properties such as: cluster geometries, binding energies and energy barriers are not easily measured directly from experiment, theoretical models and computational method have been very useful in helping to interpret some problems. The field of clusters serves as testing for theoretical method, and testing the range of validity of theoretical models derived from the extremes of atomic molecular and solid state physics.

Resemble of the large bulk, a cluster of atoms depends on the type of atoms constituting it and on the type of it's physical properties. Many properties of clusters depend on the fraction of atoms lying on the surface of it. This high surface to bulk ratio which has made metal nanoclusters so important, it works as a source of finely dispersed metal for application in heterogeneous catalysis. More generally, the size dependent behavior of cluster properties suggests very exciting prospect of using nanoclusters as building blocks to construct nano (electronic, magnetic or optical) devices with perfect characteristics.

4-2-5 Some of the fascinating feature of cluster

There is currently a strong interest in the prospect of producing new materials consisting of small atomic cluster, because of their unique features such as: size effects, cluster-surface analogy, nanoscience, which are describe in more details in following paragraphs:
• **Size effects**

The theoretical and experimental study of the size dependent evolution of the geometric and electronic structures of cluster, and their chemical and physical properties show that the size of cluster, as well as the type of particles from which it is composed, is an important parameter for modification the properties of the cluster\(^{(1-6)}\).

• **The Cluster-Surface Analogy**

Since clusters have high percentage of their atoms on the surface, there is strong link between the chemistry and physics of cluster and of the surface of bulk matter. As surface atoms have lower coordination number (fewer nearest neighbors) than interior (bulk) atoms, there is the possibility of cluster surface rearrangements. This is analogous to the reconstruction observed for bulk surface, which lower the cluster’s surface energy by forming additional surface bonds. Clusters may also be stabilized by the coordination of legends to their surface. The reactivity of under–coordinated surface atoms makes cluster of interest as models for heterogeneous catalysis on bulk metal surface. In fact, since metal cluster are small metal particles, they can be used as very finely dispersed metal for catalysis.

• **Nanoscience**

The fields of nanoscience study the particles and structures with dimensions of the order of nanometer (10\(^{-9}\)m). The scientific study of clusters play very important role as components in novel electronic, magnetic and optical nanodevices. Also they develop improved methods of synthesis, stabilization and assembly of single nanocluster and arrays of nanoclusters.

**4-2-6 Metal cluster**

Most studies of cluster reactivity have been performed on transition metals, those element in the middle of the periodic table which has in completely filled d orbital\(^{(1-8)}\). The interest on transition metal cluster reactivity comes from the desire to model and gain full understanding of the fundamental processes which occur in heterogeneous
catalysis, where their activity can be controlled by varying the composition of the catalyst. The surface of a metallic catalyst generally lowers the activation barrier to bond breaking and stabilizes reaction which eventually proceeds to form reaction products. In typical industrial catalytic processes, reactor gases are passed through a bed containing finely divided metal particles. The reactivity of the catalyst depends only on their total surface area, so smaller particles slow greater activity catalytic processes taking place on the surface of metal particles and solid, then it is necessary to study chemical processes, where bond breaking and formation on the surface of clusters. Cluster reactivity can be made more specific by carefully controlling the internal energy.

4-2-7 The Spherical Cluster Approximation

In the spherical cluster approximation (SCA), an N-atom cluster is modeled by sphere. This becomes a better approximation as the cluster gets larger and enables equations to be derived for the number of surface atom and the fraction of surface atoms. In the large cluster limit for a spherical cluster composed of N atoms, the cluster radius ($R_C$), surface area ($S_C$), and volume ($V_C$) can be related to the radius ($R_a$), surface area ($S_a$) and volume ($V_a$) of the constituent atoms, as follows.

First the cluster volume is assumed to be simply the volume of an atom multiplied by the number of atoms in the cluster:

$$V_C = NV_a$$  \hspace{1cm} (4-1)

This represents a significant oversimplification, since it does not take into account the fact that hard spheres cannot pack to fill space exactly. Expressing equation (4-1) in terms of the cluster and atomic radii, we have:

$$\frac{3}{4} \pi R_C^3 = N \left( \frac{4}{3} \pi R_a^3 \right)$$  \hspace{1cm} (4-2)

Which can be rearranging to give the following relationship between cluster and atomic radius:

$$R_C = N^{\frac{1}{3}} R_a$$  \hspace{1cm} (4-3)

The surface area of the cluster is then related to that of an atom as follows:

$$S_C = 4\pi R_C^2 = 4\pi \left( N^{1/3} R_a \right)^2 = N^{2/3} S_a$$  \hspace{1cm} (4-4)
In the limit of large cluster, the number of surface atoms \(N_s\) in a cluster is given by dividing the surface area of the cluster by the cross-sectional area of an atom \(A_a\):

\[
N_s = \frac{4\pi N^{2/3} R_a^2}{\pi R_a^2} = 4N^{2/3}
\]  

(4-5)

many properties of clusters depend on the fraction of atoms \(F_s\) which lie on the surface of the cluster. For pseudo-spherical cluster this quantity is given by:

\[
F_s = \frac{N_s}{N} = 4N^{1/3}
\]  

(4-6)

4-8-2 Technological application of the metal clusters

Here some types of metal cluster was mentioned briefly, which have already led to some important recent technological application of clusters and promise to open up whole new wide field of nanotechnology in the future:

4-2-8-1 Metal colloids

Colloids are a dispersion of particles (generally sub-micron in size) of one material in another. A dispersion of solid in liquid (e.g. a pssivated metal cluster in water or an organic solvent) or solid in another solid (such as in stained glass). Ability to generate metal colloids with narrow size distributions means that it is possible to design arrays of nanoparticles.

4-2-8-2 Semi conductor quantum dots

The development of semiconductor was beginning in the recent years, Quantum dots with their small size (nanometer dimensions) can be packed on to a computer chip, and promise great sensitivity from measuring currents and local field, may eventually be used as single- electron switching devices on transistor. Nano cluster technology usage in computers give a hand in increasing memory capacity, increasing processor and communication speed. It may also be used in optical computers, where digital information is transmitted as light pulses traveling a long optical fibers, as they open up the possibility of manufacturing very small, high efficient, quantum dot lasers which operate at low power.
4-2-8-3 Supported clusters

Studies of supported clusters offer the possibility of studying many processes (such as catalysis) on the nanometer scale.

In our study we were interested in transition metal copper (Cu₉) cluster. Its configuration is represented in fig (4-5) below. The different Cuₙ configurations (n=6,7,8,9,10) was tabulated in table (4-1)

![Cu₉ configuration](image)

Fig.(4-5) The most stable isomers of Cu₉, Double Capped Octahedron

4-3 Quasi classical selection of initial coordinates and momenta or a rotating Morse oscillator\(^{(16)}\)

The classical orbits of a rotating Morse oscillator are calculated by means of Hamilton-Jacoby theory after truncating the Hamiltonian to permit analytical solution. Except at very high J, the approximate analytic orbit for the radial coordinate is in good agreement with that obtained by numerical integration of the exact equations of motion. Bohr quantization gives an expression for the rotation- vibration energy correct through quadratic terms in \(v + \frac{1}{2}\) and \(J(J+1)\), where \(v\) and \(J\) are the vibrational and rotational quantum numbers, respectively. The principal result is an analytic prescription for obtaining values of the coordinates and momenta, given \(v\), \(J\), and a set of random numbers, that facilitates properly weighted quasi classical selection of initial states of diatomic molecules in trajectory calculations.
Table 4-1  Cu(6, 7, 8, 9, 10) Geometrics, structures, bond lengths, and the Minimum energy of the most stable Cu_n (n=6, 7, 8, 9, 10).

The use of classical trajectory calculations as a theoretical tool for studying the molecular dynamics of diatomic molecules has revived an interest in the classical mechanics of the Mores oscillator. Slater has given an expression for the classical orbit of a non-rotating mores oscillator from which the probability density for the displacement can be easily obtained. Rankin and Miller have solved the non-rotating mores oscillator problem by means of action-angle variables.
This chapter derived several useful classical formulas for a rotating oscillator who's Hamiltonian has been truncated to allow analytic solution of the dynamical problem. The accuracy of the orbit calculated from the truncated Hamiltonian is assessed by comparison with the results of a numerical integration of the exact equations of motion.

Applying the rules of Bohr quantization to obtain quasi classical formulas, namely classical expressions for a Morse oscillator with a quantum-mechanically allowed internal energy and rotational angular momentum.

The classical Hamiltonian for a rotating Morse oscillator with angular momentum \( L \) and reduced mass \( \mu \) is:

\[
H = \frac{P_r^2}{2\mu} + \frac{L^2}{2\mu r^2} + D \left(1 - e^{-\alpha(r - r_e)}\right)^2
\]  

(4-7)

Where \( D, \alpha, \) and \( r_e \) are the usual Morse parameters. Taking exponential variable to be:

\[
\xi = e^{-\alpha(r - r_e)}
\]  

(4-8)

Then the expansion of \( 1/r^2 \) about \( r = r_e \) is equivalent to expanding about \( \xi = 1 \):

\[
\frac{1}{r^2} = \frac{1}{r_e^2} + \frac{2}{\alpha r_e^3} (\xi - 1) - \frac{1}{\alpha r_e^4} \left(1 - \frac{3}{\alpha r_e}\right)(\xi - 1)^2 + ....
\]  

(4-9)

Neglecting powers of \( \xi - 1 \) greater than two, we have for the Hamiltonian:

\[
H = \frac{P_r^2}{2\mu} + \frac{L^2}{2\mu r_e^3} + \frac{L^2}{\alpha \mu r_e^3} (\xi - 1) + \left[D - \frac{L^2}{2\alpha \mu r_e^3} \left(1 - \frac{3}{\alpha r_e}\right)\right] \times (\xi - 1)^2
\]  

(4-10)

Solving for \( P_r \) at a fixed energy \( E \) gives:

\[
P_r = \mu \dot{\xi} = \pm (2\mu)^{1/2} (a + b\xi + c\xi^2)^{1/2}
\]  

(4-11)

Where:

\[a = E - D - AL^2\]
\[b = 2D - BL^2\]
\[c = -D + CL^2\]

\[
A = \frac{1}{2\mu r_e^3} \left[1 - \frac{3}{\alpha r_e} \left(1 - \frac{1}{\alpha r_e}\right)\right]
\]

\[
B = \frac{1}{\mu \alpha r_e^3} \left[1 - \frac{3}{2\alpha r_e}\right]
\]
\[ C = \frac{1}{2\mu \alpha r_e^3} \left[ 1 - \frac{3}{\alpha r_e} \right] \]  

(4-12)

Transformation to action angle variables and solution of the equations of motion:

To solve the dynamical problem, we transform to a system of conjugate variables \((Q_j, P_j)\) in which the momenta \(P_j\) are constants of the motion. Since \(H\) is independent of time, the generator of such a transformation is Hamilton's characteristic function, namely:

\[ W(r, \theta, \phi, P_1, P_2, P_3) = W_r + W_\theta + W_\phi, \ldots \]  

(4-13)

Where:

\[ W_r = \int P_r dr = -\left(\frac{2\mu}{\alpha}\right)^{\frac{1}{2}} \int \left( a + b \xi + c \xi^2 \right) \]  

(4-14a)

\[ W_\theta = \int P_\theta d\theta = \int \left( L^2 - \frac{M^2}{\sin^2 \theta} \right)^{\frac{1}{2}} d\theta \]  

(4-14b)

\[ W_\phi = \int P_\phi dr = M\phi \]  

(4-14c)

The new coordinates are given by:

\[ Q_i = \frac{\partial W}{\partial P_i} \]  

(4-15)

We therefore need the derivatives:

\[ \frac{\partial W_r}{\partial a} = -\left(\frac{\mu}{2}\right)^{\frac{1}{2}} \frac{1}{\alpha \sqrt{-a}} \arcsin \left( \frac{b \xi + 2a}{\xi \sqrt{b^2 - 4ac}} \right) \]  

(4-16a)

\[ \frac{\partial W_r}{\partial b} = \left(\frac{\mu}{2}\right)^{\frac{1}{2}} \frac{1}{\alpha \sqrt{-c}} \arcsin \left( \frac{2c \xi + b}{\sqrt{b^2 - 4ac}} \right) \]  

(4-16b)

\[ \frac{\partial W_r}{\partial c} = \left(\frac{\mu}{2}\right)^{\frac{1}{2}} \frac{1}{\alpha 2(-c)^{\frac{1}{2}}} \arcsin \left( \frac{2c \xi + b}{\sqrt{b^2 - 4ac}} \right) - \frac{1}{2c \alpha} |P_r| \]  

(4-16c)

\[ \frac{\partial W_\theta}{\partial L} = q_L = \arccos \left( \frac{\cos \theta}{\sqrt{1 - \lambda^2}} \right) \]  

(4-17a)

\[ \frac{\partial W_\theta}{\partial M} = -\arccos \left( \frac{\lambda \cot \theta}{\sqrt{1 - \lambda^2}} \right) \]  

(4-17b)

\[ \frac{\partial W_\phi}{\partial M} = \phi \]  

(4-18)

Where:
We take as the conserved momenta three quantities that are proportional to the action variables,

\[ P_i \equiv N = \frac{1}{2\pi} \oint P_i dr = \frac{1}{\pi} \left( \frac{2\mu}{\alpha} \right)^{\frac{1}{2}} \int_\alpha^\beta (a + b\xi + c\xi^2) \frac{d\xi}{\xi} = \frac{2\mu}{\alpha} \left( \frac{b}{2\sqrt{-c}} - \sqrt{-a} \right) \]

\[ P_2 \equiv L = \left( \frac{P_\theta^2}{\sin^2 \theta} + \frac{P_\phi^2}{\sin^2 \phi} \right)^{\frac{1}{2}} \]

\[ P_3 \equiv M = P_\phi \]

Where \( \xi, \tilde{\xi} \) are the roots of \( P_r = 0 \)

\[ \xi = (2c)^{\frac{1}{2}} \left[ b - \sqrt{b^2 - 4ac} \right] \]

(4-23a)

And

\[ \tilde{\xi} = (2c)^{\frac{1}{2}} \left[ b + \sqrt{b^2 - 4ac} \right] \]

(4-23b)

From Eqs. (4-15) – (4-23) we obtain the equations of transformation to the new variables,

\[ Q_\psi = \left( \frac{\partial W}{\partial \psi} \right)_{L,M} \left( \frac{\partial W}{\partial \psi} \right)_{b,c} \frac{\partial N}{\partial \alpha} \right|_{b,c} = -\arcsin \left( \frac{b\xi + 2a}{\xi\sqrt{b^2 - 4ac}} \right) \]

\[ Q_\phi = \left( \frac{\partial W}{\partial \psi} \right)_{N,M} \left( \frac{\partial W}{\partial \psi} \right)_{b,c} \left( \frac{\partial N}{\partial \alpha} \right)_{b,c} + \left( \frac{\partial N}{\partial \psi} \right)_{b,c} \frac{dc}{dl} + \left( \frac{\partial W}{\partial \psi} \right)_{a,b} \frac{dc}{dl} + \left( \frac{\partial W}{\partial \psi} \right)_{a,b} \frac{dc}{dl} + \left( \frac{\partial W}{\partial \psi} \right)_{a,b} \frac{dc}{dl} \]

\[ \left( \frac{\partial W}{\partial L} \right)_{M} = qL - L \left\{ \frac{\mu}{2} \left[ \frac{1}{\alpha} \frac{1}{\sqrt{-c}} \left( \frac{bc}{c} + 2B \right) \right] \arcsin \left( \frac{b\xi + 2a}{\xi\sqrt{b^2 - 4ac}} \right) + \arcsin \left( \frac{2c\xi + b}{\sqrt{b^2 - 4ac}} \right) + \frac{c}{c\alpha} \right\} \]

(4-25)

\[ Q_M = \left( \frac{\partial W}{\partial \psi} \right)_{N,L} \left( \frac{\partial W}{\partial \psi} \right)_{L} + \frac{\partial W}{\partial \psi} = \phi - \arcsin \left( \frac{\lambda \cot \theta}{\sqrt{1 - \lambda^2}} \right) \]

(4-26)

In Eqs.(4-24)–(4-26), the old coordinates \( \xi, \theta, \phi \) are held constant in all the differentiations. The time derivatives of the new coordinates are given by Hamiltonian's equation,

\[ \frac{\partial \psi}{\partial H} \]

(4-27)
Thus we find that $Q_M$ is constant and that $Q_N$ and $Q_L$ are proportional to the time:

$$\dot{Q}_N = \left(\frac{\partial E}{\partial N}\right)_{L,M} = a\left(\frac{2}{\mu}\right)^{\frac{1}{2}} \sqrt{-a} \equiv \omega_N$$  \hspace{1cm} (4-28a)

$$\dot{Q}_L = \left(\frac{\partial E}{\partial L}\right)_{N,M} = 2L \left[ A + \left(\frac{a}{c}\right)^{\frac{1}{2}} \left( B + \frac{b}{2c} \right) \right] \equiv \omega_L$$  \hspace{1cm} (4-28b)

$$\dot{Q}_M = \left(\frac{\partial E}{\partial M}\right)_{N,L} \equiv \omega_M = 0$$  \hspace{1cm} (4-28c)

Solution of the equation of motion thus takes the simple form:

$$Q_N(t) = \delta_N + \omega_N t \hspace{1cm} (4-29a)$$

$$Q_L(t) = \delta_L + \omega_L t \hspace{1cm} (4-29b)$$

$$Q_M(t) = \delta_M \hspace{1cm} (4-29c)$$

The radial orbit is easily obtained from Eqs. (4-24) and (4-29a):

$$r(t) = r_e \frac{1}{\alpha} \ln \left\{ -2a \left[ b + \sqrt{b^2 - 4ac \sin(\omega_N t + \delta_N)} \right] \right\}^{-1}$$  \hspace{1cm} (4-30)

The orbit for $\theta$ is obtained from Eqs. (4-17a), (4-25) and (4-29b):

$$\theta(t) = \arccos \left[ \sqrt{1 - \lambda^2} \cos(\omega_L t + \delta_N + L \Delta_L) \right]$$  \hspace{1cm} (4-31)

Where:

$$\Delta_L = \left(\frac{\mu}{2}\right)^{\frac{1}{2}} \frac{1}{\alpha \sqrt{-c}} \left( \frac{bc}{c} + 2B \right) \left[ \arcsin \left( \frac{b \xi + 2a}{\xi \sqrt{b^2 - 4ac}} \right) + \arcsin \left( \frac{2c \xi + b}{\sqrt{b^2 - 4ac}} \right) \right] + \frac{c}{\xi \alpha} \left(2 \mu^{\frac{1}{2}} (a + b \xi + c \xi^2)^{\frac{1}{2}} \right)$$  \hspace{1cm} (4-32)

And

$$\xi = \left( -2a \left[ b + \sqrt{b^2 - 4ac \sin(\omega_N t + \delta_N)} \right] \right)$$  \hspace{1cm} (4-33)

Finally, from Eqs. (4-26) and (4-29c) we obtain for the orbit of $\phi$:

$$\phi(t) = \delta_N + \arccos \left( \frac{\lambda \cot \left[ \theta(t) \right]}{\sqrt{1 - \lambda^2}} \right)$$  \hspace{1cm} (4-34)

The Cartesian components of the linear momentum can be expressed in terms of the variables (and thus through Eqs. (4-29) as function of $t$) and of the constant angular momenta. Transformation to the polar coordinates:
$x = r \sin \theta \cos \phi (29a)$
$y = r \sin \theta \sin \phi (29b)$
$z = r \cos \theta (29c)$
gives for the conjugate momenta:

\[ P_r = \mu r = P_x \sin \theta \cos \phi + P_y \sin \theta \cos \phi + P_z \cos \theta \] (4-36a)

\[ P_\theta = \mu \theta r^2 = P_r \cos \theta \cos \phi + P_y r \cos \theta \sin \phi + P_z r \cos \theta \] (4-36b)

\[ P_\phi = \mu \phi r^2 \sin^2 \theta = -P_r \sin \theta \sin \phi + P_y r \sin \theta \cos \phi \] (4-36c)

In matrix form, the transformation is:

\[
\begin{pmatrix}
P_x \\
P_y \\
P_z
\end{pmatrix} =
\begin{pmatrix}
\sin \theta \cos \phi & \cos \theta \cos \phi & -\sin \phi \\
\sin \theta \sin \phi & \cos \theta \sin \phi & \cos \phi \\
\cos \theta & -\sin \theta & 0
\end{pmatrix}
\begin{pmatrix}
P_r \\
P_\theta / r \\
P_\phi / r \sin
\end{pmatrix}
\] (4-37)

From Eqs. (4-17a) and (4-26), we find that:

\[ \sin \theta = \left( \sin^2 q_L + \lambda^2 \cos^2 q_L \right)^{1/2} \] (4-38a)

\[ \cos \theta = \sqrt{1 - \lambda^2 \cos q_L} \] (4-38b)

\[ \sin \phi = \frac{\sin q_L \cos Q_M + \lambda \cos q_L \sin Q_M}{\left( \sin^2 q_L + \lambda^2 \cos^2 q_L \right)^{1/2}} \] (4-38c)

\[ \cos \phi = -\frac{\sin q_L \sin Q_M - \lambda \cos q_L \cos Q_M}{\left( \sin^2 q_L + \lambda^2 \cos^2 q_L \right)^{1/2}} \] (4-38d)

Substitution of Eqs. (4-38) into Eq. (4-37) gives after some algebrate simplification:

\[
\begin{pmatrix}
P_x \\
P_y \\
P_z
\end{pmatrix} = p_r \begin{pmatrix}
-\sin q_L \sin Q_M + \lambda \cos q_L \cos Q_M \\
\sin q_L \cos Q_M + \lambda \cos q_L \sin Q_M \\
\end{pmatrix} + L / r \begin{pmatrix}
-\cos q_L \sin Q_M - \lambda \sin q_L \cos Q_M \\
\cos q_L \cos Q_M - \lambda \sin q_L \sin Q_M \\
-\sqrt{1 - \lambda^2 \sin q_L}
\end{pmatrix}
\] (4-39)

In Eqs. (4-39), the "intermediate" variable $q_L$ is given by:

\[ q_L = Q_L + L \Delta_L \] (4-40)

$P_r$ is given by Eq. (4-11), $r$ is given by:
\[ r = r_c - \frac{1}{\alpha} \ln \xi \]  
\[ (4-41) \]

\( \Delta_L \) is given by Eq. (4-32) and \( \xi \) by:
\[ \xi = (-2a) \left[ b + \sqrt{b^2 - 4ac \sin Q_N} \right]^{-1} \]  
\[ (4-42) \]

From Eqs. (4-35) and (4-38), the components of \( r \) are found to be given by:
\[
\begin{pmatrix}
  x \\
  y \\
  z
\end{pmatrix} = r \begin{pmatrix}
  -\sin q_L \sin Q_M + \lambda \cos q_L \cos Q_M \\
  \sin q_L \cos Q_M + \lambda \cos q_L \sin Q_M \\
  \sqrt{1 - \lambda^2} \cos q_L
\end{pmatrix}
\]  
\[ (4-43) \]

Classical radial distribution:
The radial density function is obtained in the usual way:
\[ P(r)dr = \frac{2}{T_r} \frac{dP}{dr} \]  
\[ (4-44) \]

Since \( P_r = \mu r \) and since \( T_r = 2\pi / \omega_N \) we have:
\[ P(r) = \frac{\alpha}{\pi} (-2a\mu)^{\frac{1}{2}} |P_r|^{-1} \]  
\[ (4-45) \]

The (cumulative) radial distribution function is:
\[ D(r) = \int_{r<}^r P(r')dr' = \frac{1}{\pi} (-2a\mu)^{\frac{1}{2}} \int_{r<}^r P_r^{-1}dr' \]  
\[ (4-46) \]

From Eqs. (4-11) and (4-46) we obtain:
\[ D(r) = \frac{\sqrt{-\alpha}}{\pi} \int_{\xi}^{\xi_0} \left( a + b\xi' + c\xi'^2 \right)^{-\frac{1}{2}} \frac{d\xi'}{\xi'} = \frac{1}{2} - \frac{1}{\pi} \arcsin \left( \frac{b\xi + 2a}{\xi \sqrt{b^2 - 4ac}} \right) \]  
\[ (4-47) \]

Where a, b, c are given by Eqs. (4-12) and \( \xi \) by Eqs. (4-8).
The derivation of \( D(r) \) directly from the above results is trivial. Inspection of Eqs. (4-8), (4-23), and (4-24) shows that \( r \) goes from \( r< \) to \( r> \) as \( Q_N \) goes from \( -\pi/2 \) to \( \pi/2 \).

Thus, with boundary condition \( D(r<) = 0 \), it follows that:
\[ D(r) = \frac{1}{\pi} [Q_N(r) - Q_N(r_c)] \]  
\[ (4-48) \]

Which is the same result as Eq. (4-47). The radial density is therefore
\[ P(r) = \frac{1}{\pi} \frac{dQ_N}{dr} = -\frac{\alpha \xi}{\pi} \frac{dQ_N}{d\xi} = \frac{\alpha \sqrt{-a}}{\pi} (a + b \xi + c \xi^2)^{1/2} \]  

which is equivalent to Eq. (4-45).

The Bohr–Sommerfeld quantization rule is:

\[ N = \left( v + \frac{1}{2} \right) \hbar \]  

(4-50)

Where \( v \) is the vibrational quantum number and \( N \) is given by Eq. (4-20). To compare with the quantum–mechanical eigenvalues for rotating Morse oscillator, we use Eq. (4-12) to expand \( b/2\sqrt{-c} \) in powers of \( L^2 \):

\[ \frac{b}{2\sqrt{-c}} = D \frac{3}{2} - FL^4 - GL^6 + \cdots \]  

(4-51)

Where:

\[ F = \frac{3}{4\mu \alpha \omega_e^2 D^{3/2}} \left( 1 - \frac{1}{\alpha \omega_e} \right) \]  

(4-52)

\[ G = \frac{1}{32\mu \alpha \omega_e^6 D^{3/2}} \left( 5 - \frac{3}{\alpha \omega_e} \right) \left( 1 - \frac{3}{\alpha \omega_e} \right) \]

Solving Eq. (4-20) for \( a \), substituting the definition of \( a \) from Eq. (4-12), and using Eq. (4-50) for \( N \), we obtain for \( E \)

\[ E = D + AL^3 - \left[ \left( v + \frac{1}{2} \right) \frac{\hbar a}{(2\mu)^{1/2}} - D^{1/2} + FL^2 + GL^4 \right]^2 \]  

(4-53)

Writing out Eq. (4-53) to the fourth power of \( L \), substituting the definitions for all constants, and setting \( L^2 = J(J+1)\hbar^2 \) gives the quasiclassical selection of initial coordinates and momenta:

\[ E_{\omega,\alpha} = \frac{\hbar^2}{2\mu \omega_e^2} J(J+1) + \hbar \omega_e \left( v + \frac{1}{2} \right) - \frac{\hbar^2 \omega_e^2}{4D} \left( v + \frac{1}{2} \right)^2 - \frac{\hbar^4}{4\mu \alpha \omega_e^6 D^{3/2}} [J(J+1)]^2 \]  

\[ - \frac{3}{4\mu \alpha \omega_e^2 D} \left[ 1 - \frac{1}{\alpha \omega_e} \right] \hbar^2 \omega_e \left( v + \frac{1}{2} \right) J(J+1) \]  

(4-54)

Which is in agreement with the quantum-mechanical results. Thus the value of \( v \) found from a classical trajectory for a diatomic molecule by the prescription

\[ v = -\frac{1}{2} + \frac{2}{\hbar} \int_{\xi_c}^r p_r \, dr \]  

(4-55)
Is unambiguously the vibrational”quantum number”even when separation of vibration and rotation is a poor assumption, since inserting of \( v \) from Eq.(4-54) and \( J \) from the expression

\[
J = \frac{1}{2} \left( 1 + \frac{4L^2}{\hbar^2} \right)^{1/2}
\]

Into Eq. (4-54)correctly gives the (unseparable)rotation-vibration energy.

There are several equivalent methods by which the radial coordinate \( r \) can be selected at random. The radial distribution function \( D(r) \) given in Eq. (4-47) can be set equal to a number \( R \) chosen randomly, from the closed interval \((0,1)\) with uniform density, and the result solved for \( r \) with the assistance of Eq. (4-8). Alternatively, one can set \( \delta_n = 0 \) and \( \omega_n t = 2\pi R \) in Eq. (4-30). Both of these methods lead to:

\[
r = r_c - \frac{1}{\alpha} \ln \left\{ \left( -2a \right) \left[ b + \sqrt{b^2 - 4ac \sin(2\pi R)} \right]^{-1} \right\}
\]

While these methods are adequate for \( r \), they are not so easy to apply in the case of \( \theta, \phi \), and the components of \( P \).

Since the independent angle variables \( Q_n, Q_L \) and \( Q_M \) [see Eqs. (4-29)] all range from 0 to \( 2\pi \) and are at most liner in \( t \), it is clear that one need merely to set:

\[
Q_n = 2\pi R_1, \\
Q_L = 2\pi R_2, \\
Q_M = 2\pi R_3,
\]

where \( R_1 \) are mutually random numbers with flat distribution in the closed interval \((0,1)\). The component of \( r \) and \( p \) calculated from Eqs, (4-39) (4-43) then have the properly weighted distribution for a rotating Morse oscillator. The quasiclassical selection is implemented by the use Eq.(4-50)and

\[
L^2 = j(j+1)\hbar^2
\]

in the evaluation of the constant \( a, b, \) and, \( c \) by means of Eq.(4-12).

This prescription is analogous to the situation in quantum mechanics when the values of the momenta (here the action variables) are sharp and the value of their conjugate coordinate (here the angle variables) are therefore completely random.
Chapter 5
Results and Discussion

5-1 Collision Method

The study of the reactivity of metal cluster with Hydrogen and Deuterium has provided valuable information about the chemisorption probability, reactivity cross section and rate constant. In this work some representative results are discussed and displayed for the reactive and non reactive channels of the interaction of H₂/D₂ molecules with a non rotating and non translating Cu₉ cluster Fig(5-1). The most stable isomer with Double Capped Octahedron structure was chosen. The potential energy that associated with forces at each atom in the collision was represented by the potential energy surface given by:

\[ V = V_{EA} + V_{LEPS} \]  \hspace{1cm} (5-1)

Where the \( V_{EA} \) is the Embedded Atom potential. \( V_{LEPS} \) is the interaction potential between gas atoms and the cluster, and among the gas interaction of the diatomic molecule.

The Cu₉ cluster was prepared at a given initial temperature \( T \) defined as:

\[ T(k) = \frac{2\langle E_k \rangle}{(3n - 6)K_B} \]  \hspace{1cm} (5-2)

Where \( E_k \) is a total kinetic energy of the cluster, \( K_B \) is Boltzmann constant, \( n \) is the number of atoms cluster, \( \langle \rangle \) stand for time average. The lowest energy structure of Cu₉ cluster is obtained by using the Voter etal(11) version of the EA model, and it’s average bond length distance \( \langle d \rangle \) was taken to be 2.449 Å.

The dynamical calculation were carried out using the classical trajectory technique, where the time evolution of the molecule cluster collision system is generated by solving numerically the Hamiltonians equations of motion for all atoms in the system. Totally 500 trajectory were run for each set of initial conditions by employing Hamming’s modified fourth-order predictor-corrector algorithm with step size of \( 10^{-15} \) s upon which the system was equilibrated, and the origin of the coordinate system was placed at the center of mass of the cluster. For a particular cluster temperature and rovibrational state of the hydrogen molecule the dissociation probability is given by:

\[ P_{\nu,j,T}(b,E_{\nu}) = \frac{N_{\nu,j,T}(b,E_{\nu})}{N} \]  \hspace{1cm} (5-2)
Where \( \mathcal{N}_{(v, j)}(b, E_{tr}) \) is the number of effective trajectories, "N" is the number of all trajectories (N=500). The calculations were done for a set of translation energies \( E_{tr} \) with \( \Delta E=0.01\text{eV} \), and impact parameter \( b \) with \( \Delta b=0.25\text{Å} \) for each translation energy.

The reaction cross section was obtained with the use of:

\[
\sigma_{v, j}(E_{tr}) = 2\pi \int_{0}^{b_{\text{max}}} P(b, E_{tr}) \, db \quad (5-4)
\]

Where for a particular cluster temperature, \( b_{\text{max}} \) represent the least impact parameter beyond which the dissociation probability tend to zero (\( P_{v,j,T}(b, E_{tr})=0 \)), in our work \( b_{\text{max}} \) ranges in \( 2.5 - 3.5 \text{Å} \).

The reaction rate constant was obtained by:

\[
K(T) = \left( \frac{1}{\mu \pi} \right)^{1/2} \left( \frac{2K_{\mu}T}{\sigma(E)} \right)^{1/3} \int_{0}^{\infty} \sigma(E) \exp \left( \frac{-E}{K_{\mu}T} \right) dE \quad (5-5)
\]

Where \( \mu \) is the collision reduced mass.

Fig. (5-1) A schematic diagram represents the reaction factor, which changes during the reactions.

Starting with zero time at the beginning of each trajectory the molecule was launched towards the cluster with specified collision energy \( E_{tr} \) ranging from 0 to 1 eV with \( \Delta E=0.01\text{eV} \). At each energy the initial impact parameter \( b \) was sampled systematically on the range 0 to \( b_{\text{max}} \) with \( \Delta b=0.25\text{Å} \). The H-H and H-cluster distance were monitored for each collision. The trajectory is terminated either when the H-H distance exceeds the value of \( 2.223\text{Å} \) (three times the equilibrium H-H bond length) or when the hydrogen molecule approximately reaches the same region after departing from the cluster. The initial separation between the diatomic molecule and the cluster was chosen to be \( 8.5\text{Å} \) and the molecule was sent toward the cluster with initial
roviberal state chosen to be \( v_i = 0 \) and \( j_i = 0 \). The initial vibrational \( v \) and rotational \( j \) states of the diatomic were specified via standard quasi classical method for each temperature which developed by Portor \(^{16} \). To test the effect of the rovibrational state in the reaction we considered a different value for them and report the changes happen to the chemisorptions probability and cross section for each value. The changes in the reaction properties with the increment of cluster’s temperature were also examined.

5-2 Direct, Indirect dissociation, and Inelastic scattering

5-2-1 Direct Dissociation

In this collision model the molecule started its motion when the distance between its center of mass (CM) and the cluster–CM is 8.5 Å. When the distance approximately approached 4 Å at time \( 16 \times 10^{-14} \) s the molecule starts to interact with the cluster. As seen from the Fig.(5-2) when the molecule reached this distance the molecule starts to rotates and vibrates. At this time the distance between \( H_1 - H_2 \) also started to increase till they dissociated. The reaction was held at \( 0.0 \text{eV} < E_{cm} < 1 \text{eV} \) and impact parameter \( 0.0 \text{Å} < b < 3.5 \text{Å} \). Some of molecules reaches the cluster with relatively high translation energy and then dissociate immediately by the time they reach the cluster’s surface, as shown in Fig(5-2) the dissociation occurs at \( 23 \times 10^{-14} \) s, this was called the Direct Dissociation. Molecules arrive at cluster’s surface with low collision energy some of them may not dissociate, and the rest may dissociate after a few time.

![Direct Dissociation](image)

**Fig. (5-2) Direct Dissociation in the collision of the Cu\(_9^+ + H_2\); \((E_t = 0.5 \text{ eV})\), CM-CM the distance between center of mass of the molecule and the center of mass of the cluster.**
5-2-2 Indirect Dissociation

Same as the direct dissociation when the molecule–cluster distance (CM–CM) reached 4 Å, at time $16 \times 10^{-14}$ s, the molecules that reached the cluster with low translation energy attach themselves to the surface of the cluster. They rotate and vibrate while searching for the active site of the cluster to break the bond or till they gain enough energy from the cluster’s atoms allowing them to dissociate. This may cause a resonance for some period of time at the surface of the cluster and this type of reactions was called Indirect Dissociation Reaction, Fig (5-3) below. The time taken by this type of reaction before dissociation is about $50 \times 10^{-14}$ s which about twice times that the direct dissociation.

![Indirect Dissociation](image)

Fig. (5-3) Indirect Dissociation in the collision of the Cu$_9$ + H$_2$; (Etr =0.05 eV)

5-2-3 Inelastic Scattering

It may occur for all translation energies that molecules reach the cluster and they inelastically scatter back as shown from Fig.(5-4). In the same manner as the previous types of reaction, the molecule reach the cluster at 4 Å at time $16 \times 10^{-14}$ s but the H–H bond distance never breaks down and the molecule rotates and vibrates while retuning back to its initial distance. This type of interaction was called inelastic scattering, it is independent on the translation energy of the impinging molecule as well as it depends directly on the reaction impact parameter.
Fig. (5-4) Inelastic scattering in the collision of the Cu$_9$ + H$_2$; (E$_{tr}$ = 0.5 eV)

5-3 Reaction cross section of H$_2$ molecule on the Cu$_9$ (0K) cluster at (v=0, j=0) roviberalational state

The reactive cross section of H$_2$ molecule in the ground state with the non rotating and non translating Cu$_9$ (0K) cluster as function of collision energy. In the low energy region (starting from 0.01eV) reactivity was presented in Fig (5-5) increase rapidly and reaches to a maximum value near 0.05eV. As the collision energy increases further, the cross section decrease and has minimum value near 0.35eV beyond which the reaction cross section increase monotonically.

Fig. (5-5) Dissociative chemisorptions reaction cross section of H$_2$(v=0,j=0)+Cu$_9$(0K).
The peak in low energy region represent the complex formation of H₂ molecule with cluster, that is, the molecule attaches itself to the surface of the cluster and then searches for the active–site to break its bond or till it gain enough energy to dissociate, this resonance enhance the reactivity.

The minimum area (E_{tr}=0.25eV) confirm the existence of the activation barrier associated with this type of reactions. This results was tend to be in a good correspondence with that reached before in the Cu + H₂ (1,21) and Ni + H₂ (18,22,23) dissociative adsorption reactions.

**5-4 Dissociative adsorption of H₂ and Cu₉ at different initial (v,j) roviberalional states**

This collision system was investigated for several initial (v, j) states of the H₂ with the most stable Cu₉ cluster. Reactivity at (v=0, j=0), (v=0, j=3), (v=0, j=5), (v=0, j=10), (v=1,j=0), (v=3, j=0) at T(0k) are displayed in Fig (5-6 ). From the below display, when compared between the (v=0, j=0,3,5,10), the cross section is beginning from low E_{tr} but it increased clearly at high E_{tr}, and show more reactivity with increase of the rotational state.

![Fig. (5-6)](image)

Fig. (5-6) . Reactive cross section of the H₂(v, j)+Cu₉(0K)collision system as function of the collision energy, H₂ molecule is in different initial rovibrational state.
The increment of the reaction cross section with the translation energy is noticeable, moreover the area of the activation barrier reported at $v=0, j=0$ was near to disappear. It is seen that from the above figure and for all cases of different $v_i, j_i$, the cross sections display a small but non zero threshold value of translation energy below $0.4\text{eV}$, and above which they increase monotonically with the increase of $E_{tr}$. The higher initial rovibrational energy of the molecule lower the value of the threshold energy, and the larger the cross sections of the dissociative adsorption. While an increase of the probability to break the H-H bond with an increase of total energy, the activation barrier encountered by the impinging molecule decreases with an increase of $v_i, j_i$. In contract, it is very clear that the cross section increase monotonically by increase of $v_i, j_i$ where the roviberalional is more effective. This was also experimentally proved for Cu (13) $^{(1)}$ and Cu (100) $^{(5)}$ however it is well established by know that the chemisorption of Hydrogen molecule in Copper cluster is an activated process.

To summarize; increasing of the rovibrational quantum number has enhanced effect on increasing and the reactivity and the dissociative chemisorptions cross section. At $(v=0, j=0)$, $(v=0, j=3)$, $(v=0, j=5)$ there no recordable different in the cross section will it is highly noticeable for $(v=0, j=10)$, incrementing the rotational state from 0 to 10 does not change much the total energy of the molecule. Generally it can be said that the reactivity is insensitive to the rotational states. On the other hand as seen from Fig (5-6) the cross section are hindered by rotational states of the molecule more than the viberalional states that is to say the higher roviberalional states the higher the reaction cross section.
At lower collision energies these rotational states have approximately the same reactivity, while the difference was more pronounced at higher collision energies \( \geq 0.3 \text{eV} \).

Despite the fact that the \((v=0, j=10)\) state has more energy \((E_{vj}=-3.731 \text{eV})\) than \((v=3, j=0)\) state \((E_{vj}=-3.962 \text{eV})\), the \((v=3, j=0)\) state is more reactive, which a dramatically increase in the cross section founded with increase of the vibrational state in all the value of the translation energy for the both state \((v=0, j=10)\) and \((v=3, j=0)\), as shown the below Fig (5-8):

![Fig. (5-8) Reactive cross section of the \( \text{H}_2(v, j) + \text{Cu}_9(0K) \): \( \text{H}_2(v=0, j=10) \), \( \text{H}_2(v=3, j=0) \)]

5-5 Isotopic Effects (\( \text{H}_2 / \text{D}_2 \))

To study the difference in the reactivity of \( \text{H}_2 \) molecule to that of the heaviest isotope \( \text{D}_2 \) molecule with copper cluster (\( \text{Cu}_9 \)) the reaction cross section for both of them, and the result are plotted in the Fig (5-9).

As seen from the Fig(5-9) the reaction cross sections of \( \text{H}_2/\text{D}_2 \) molecules in the ground state with the most stable isomers of \( \text{Cu}_9 \) cluster are present as function of the collision energy. In the low-energy region (starting from 0.01eV) reactivity increases rapidly and reaches to a maximum value near 0.09eV. As the collision energy increases
further, the cross sections decrease and have minimum values near 0.25eV, beyond this energy; the curves increase monotonically.

**Fig. (5-9).** Dissociation cross section of the reaction H\textsubscript{2}/D\textsubscript{2}(v=0, j=0)+Cu\textsubscript{9} (T=0K)

When comparing the calculated results for the dissociation of D\textsubscript{2}-Cu\textsubscript{9} with that H\textsubscript{2}-Cu\textsubscript{9}, from the first look to the graph, it is immediately observed that the cross section demonstrate a strong isotope effects for the cluster and that the hydrogen molecule was always have a greater cross section than heavier deuterium molecule, moreover the deuterium follow the hydrogen in its maximum and minimum location on the reaction cross section curve, also the figure shows that the cross section for the same translation energy for both D\textsubscript{2} and H\textsubscript{2} molecules was hindered by energy barrier and that energy barrier for the D\textsubscript{2} molecule dissociation have no sharp minima like that for H\textsubscript{2}. This explained like follow: since D\textsubscript{2} travel at much lower velocity than H\textsubscript{2} then the steering energy will become more effective for D\textsubscript{2} more than H\textsubscript{2} leading it to overcome the activation barrier. Also from our calculations for hydrogen and the other calculation\textsuperscript{(1,22,24)}, the dissociation of hydrogen is activation process and that a certain amount of energy must be fed to translation Degree Of Free Dom (DOF) of the impinging hydrogen molecule before dissociative can occur. The same conclusion again was reach for Deuterium Fig (5-10). Again and as what was reported for H\textsubscript{2} molecule it is so clear that the D\textsubscript{2} reaction cross section increase monotonically with the increment of
the vibrational states from 0 to 10, however the rotation states have a significant
effects in minimizing barrier more than the vibrational states can do. Interestingly the
quantum state \((v=3,j=0)\) for Deuterium have larger cross section than Hydrogen
\((v=0,j=3)\)and it was clear that the isotopic effect, although it is very significant but, it
can be neglected if compared to the roviberalational effect Fig(5-11).

![Graph showing dissociation cross section as function of translation energy for H2/D2](image)

Fig. (5-10). Dissociation cross section as function of translation energy for H2/D2
\((v=0,3, j=0,3)+Cu9(0K)\)

The reaction rate constants are calculated by using the same set of LEPS parameters. It
is clear that the rate constant shows increase with increase of the vibartional number.
As expected D2 molecule have less rate constant than H2 molecule. The ratio of the rate
constant of Hydrogen to that of Deuterium at some definite rovibartional state was
tabulated in table (5-1).

<table>
<thead>
<tr>
<th>Cu9 + H2/D2 (vi,ji)</th>
<th>Rate constant ( \times 10^{-10} \text{ (cm}^3/\text{s}) )</th>
<th>Ratio of the Rate constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(v=0,j=0)</td>
<td>1.503</td>
<td>1.49</td>
</tr>
<tr>
<td>D(v=0,j=0)</td>
<td>1.004</td>
<td></td>
</tr>
<tr>
<td>H(v=3,j=0)</td>
<td>3.485</td>
<td>1.13</td>
</tr>
<tr>
<td>D(v=3,j=0)</td>
<td>3.095</td>
<td></td>
</tr>
</tbody>
</table>

Table (5-1) The reaction rate constant in the collision system Cu9 H2/D2 (vi,ji) at
\(T=0K\)
5-6 Dissociation adsorption probability of H$_2$ molecule and Cu$_9$ cluster

In this work the dissociation probability of molecule as function of the impact parameter for small range of molecule translation energy ($0.01 < E_t < 1.0 \text{ eV}$) was investigated. As seen in Fig (5-11), the molecules that reach the cluster with high translation energy (for example 0.8 eV) will have greater dissociation probability when interacting with atoms near the center of mass of the cluster i.e. at impact parameter $b=0 \text{ Å}$. This probability decrease successively with the increase in the impact parameter till it reach its minimum value at 4.25 $\text{ Å}$. The molecule interact at lower translation energy (as example 0.01 eV) have the least dissociation probability, but they dissociate at large impact parameter than the former one which clearly sign for the area of indirect dissociation explaining before. As for the rovibertional states $v=0,j=0$ this probability increase with the increase of the rotational states a rovibertonal state as seen in Fig (5-12), (5-13), (5-14). With high translation energy (0.8 eV) the dissociation probability was greater for all rovberational state than that for $v=0,j=0$ rovberational state. Interestingly this true for all translation energies from 0.1 eV to 0.6 eV, again this probability decrease successively with the increase in the impact parameter till it reach its minimum value at $5 \text{ Å}$, and at lower translation energy (0.01 eV was selected) have the least dissociation probability when interacting with atoms near the center of mass of the cluster.

![Fig. (5-11) Reaction probability as function of impact parameter for different value of $E_t$ (eV) for Cu$_9$ atomic cluster at (0K) at ($v=0,j=0$)](image-url)
Again and as expected the roviberational state is more dominant in increasing the dissociation probability than the rotational state, see Fig (5-12).

Fig. (5-12). Reaction probability as function of impact parameter for different value of H$_2$ molecule translation energy (eV) for Cu$_9$ atomic cluster at (0K) at (v=0,j=5)

Fig. (5-13). Reaction probability as function of impact parameter for different value H$_2$ of molecule translation energy (eV) for Cu$_9$ atomic cluster at (0K) at (v=0,j=10)
Fig. (5-14) Reaction probability as function of impact parameter for different value of H₂ molecule Eᵣ (eV) for Cu₉ atomic cluster at (0K) at (v=3,j=0)

Also the D₂ isotopic effect on the dissociation probability was studied and deuterium provided for the same incidence energy Eᵣ the locations of minima for the dissociative probability curve of D₂ are shifted more towards higher rotational state (j=0,3), as comparing with those of H₂ (j=0,3), which H₂ exhibiting higher chemisorption probability than D₂ in the higher region, because D₂ travels at much lower velocity than H₂ for the same translation energy Eᵣ steering will be more effective for D₂ than for H₂, as displayed in Fig(5-11) and Fig(15).

Fig. (5-15) Reaction probability as function of impact parameter for different value of D₂ molecule Eᵣ (eV) for Cu₉ atomic cluster at (0K) at (v=0,j=0)
5-7 The reaction rate constant

To test the effect of the rovibartional states of the molecule on the Rate Constant calculations were done for different values of it as represented in table (5-2).

<table>
<thead>
<tr>
<th>Cu₉ + H₂/D₂(vᵢ,jᵢ)</th>
<th>Rate constant ( \times 10^{-10} (cm^3 / s) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(v=0, j=0)</td>
<td>1.503</td>
</tr>
<tr>
<td>H(v=0, j=3)</td>
<td>0.84</td>
</tr>
<tr>
<td>H(v=0, j=5)</td>
<td>0.739</td>
</tr>
<tr>
<td>H(v=0, j=10)</td>
<td>1.104</td>
</tr>
<tr>
<td>H(v=3, j=0)</td>
<td>3.485</td>
</tr>
<tr>
<td>H(v=1, j=0)</td>
<td>1.774</td>
</tr>
<tr>
<td>D(v=0, j=0)</td>
<td>1.004</td>
</tr>
<tr>
<td>D(v=3, j=0)</td>
<td>3.095</td>
</tr>
</tbody>
</table>

Table (5-2) The reaction rate constant in the collision system Cu₉ H₂/D₂ (vᵢ,jᵢ) at (T=0K)

On the other hand all these rate constants are calculated by using the same set of parameters of the LEPS function. It is clear that the rate constant shows independence on the increase of the vibartional number, in contrast it increases rapidly with the increase of the rotational number.

5-8 Effects of cluster's formation temperature in the dissociation cross section

At temperatures below 900K the rate constant show weak changes with temperature see Fig. (5-16). The reaction of the molecule H₂ with Cu₉ cluster for different temperatures (T=303K, 802K, 1059K) were studied and founded that increase the temperature of the cluster increase the collision energy of Cu atom and the molecule, so there is more energy available in the system to break the H-H bond. As a result this negative effect on the reactivity is removed. Thus reactivity of H₂ molecule on the cluster at several TK temperatures approximately has same value; this means that the chemisorption of H₂ molecule on the copper cluster does not depend on the temperature of the cluster as seen in the Fig. (5-16).
Fig. (5-16). Dissociation cross section of the reaction H\textsubscript{2} (v=0, j=0) + Cu\textsubscript{9} (T=0K, 302K, 802K, 1059K)

The low sensitivity towards temperature can explained like that: at that temperature scales there are small number of active sites on the cluster that can leads to a direct dissociative chemisorption or there are several sites but the reaction was dynamically constrained i.e. there are specific requirement in the impact parameter or in molecule orientation, also it can be caused by the decreases in the initial trapping of the H/D molecule on the cluster surface, as in table (5-3) for the ratio of the reaction rate for H and D.

Fig. (5-17) Dissociation cross section of the reaction H\textsubscript{2}/D\textsubscript{2} (v=0, j=0) + Cu\textsubscript{9} (T=0K, 303K, 802K, 1059K)
Table (5-3). The reaction rate constant in the collision system Cu₉ H₂/D₂ (0, 0) at
(T=303 K, 802 K, 1059 K)

<table>
<thead>
<tr>
<th>Cu₉+H₂/D₂ (vᵢ,jᵢ)</th>
<th>Rate constant ( \times 10^{-10} (\text{cm}^3/\text{s}) ) (T=303K)</th>
<th>Rate constant ( \times 10^{-10} (\text{cm}^3/\text{s}) ) (T=802 K)</th>
<th>Rate constant ( \times 10^{-10} (\text{cm}^3/\text{s}) ) (T=1059 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(v=0,j=0)</td>
<td>1.503</td>
<td>0.850</td>
<td>1.903</td>
</tr>
<tr>
<td>D(v=0,j=0)</td>
<td>1.004</td>
<td>1.093</td>
<td>1.05</td>
</tr>
</tbody>
</table>

5-9 The Probability of Inelastic Scattering

The probability of the inelastic scattering of H molecule from the Cu₉ cluster was
calculated and the values were plotted via histogram graph Fig (5-17). The inelastic
scattering was plotted for two different translation energy: \( E_t=0.5 \text{eV} \) and \( 1.0 \text{eV} \). For
each one of this translation energy the inelastic scattering was studied at two different
impact parameters \( b=0 \) Å and \( b=3.5 \) Å. The molecule were sent towards the cluster with initial rovibrational state (v=0,j=0),
and after collision they reflect with a different final rovibrational states (vᵢ=1or2,jᵢ=1-15) depend on its translation energy and the collision impact parameter. At fixed
translation Energy \( E_t=0.5 \text{eV} \) and fixed impact parameter \( b=0 \) Å Fig.(5-17), the
probabilities of scattering with vibration state \( vᵢ=1(pᵢ=1) \) is always greater than
probability of scattering \( vっております. The reverse is true that is to say with the reduction in translation
energy and while the dissociative adsorption decreases the inelastic probability
increases. The inelastic scattering probability was increase with the increase of the
impact parameter. The inelastic scattering probability was decrease with increase of the roviberalational state as seen in the below tables (5-4), (5-5), (5-6).

<table>
<thead>
<tr>
<th>$b = 0 \text{ Å}$</th>
<th>$b = 3.5 \text{ Å}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{tr}} = 0.5$</td>
<td>$P_{v=1} = 0.652$</td>
</tr>
<tr>
<td></td>
<td>$P_{v=2} = 0.034$</td>
</tr>
<tr>
<td>$E_{\text{tr}} = 1.0$</td>
<td>$P_{v=1} = 0.37$</td>
</tr>
<tr>
<td></td>
<td>$P_{v=2} = 0.11$</td>
</tr>
</tbody>
</table>

Table (5-4) The inelastic scattering probability of $H(v = 0, |j = 0)$

<table>
<thead>
<tr>
<th>$b = 0 \text{ Å}$</th>
<th>$b = 3.5 \text{ Å}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{tr}} = 0.5$</td>
<td>$P_{v=1} = 0.104$</td>
</tr>
<tr>
<td></td>
<td>$P_{v=2} = 0.054$</td>
</tr>
<tr>
<td>$E_{\text{tr}} = 1.0$</td>
<td>$P_{v=1} = 0.077$</td>
</tr>
<tr>
<td></td>
<td>$P_{v=2} = 0.052$</td>
</tr>
</tbody>
</table>

Table (5-5) The inelastic scattering probability of $H(v = 0, |j = 10)$

Table (5-6) The inelastic scattering probability of $H(v = 0, |j = 3)$
Fig. (5-17). Probability of the inelastic scattering of the Hydrogen molecule \( \text{H}_2(v=0,j=0) \) from \( \text{Cu}_9(T=0K) \) cluster at different translations energy and impact parameters; (1) \( E_{tr}=0.5\text{eV}, b=0\text{Å} \); (2) \( E_{tr}=0.5\text{eV}, b=3.5\text{Å} \); (3) \( E_{tr}=1\text{eV}, b=0\text{Å} \); (4) \( E_{tr}=1\text{eV}, b=3.5\text{Å} \).
Fig. (5-18). Probability of the inelastic scattering of the Hydrogen molecule $H_2(v=0,j=5)$ from Cu$_9$ (T=0K) cluster at different translations energy and impact parameters; (a) $E_{tr}=0.5$eV, $b=0$ Å; (b) $E_{tr}=0.5$eV, $b=3.5$ Å; (c) $E_{tr}=1$eV, $b=0$ Å; (d) $E_{tr}=1$eV, $b=3.5$ Å.
Fig. (5-19). Probability of the inelastic scattering of the Hydrogen molecule $\text{H}_2$ ($v=0, j=10$) from Cu$_9$ (T=0K) cluster at different translations energy and impact parameters; (a) $E_t=0.5\text{eV}$, $b=0\text{Å}$; (b) $E_t=0.5\text{eV}$, $b=3.5\text{Å}$; (c) $E_t=1\text{eV}$, $b=0\text{Å}$; (d) $E_t=1\text{eV}$, $b=3.5\text{Å}$
Fig. (5-20). Probability of the inelastic scattering of the Hydrogen molecule \( \text{H}_2(v=3,j=0) \) from Cu\(_9\) (T=0K) cluster at different translations energy and impact parameters; (1)\( E_t=0.5\text{eV}, \ b=0\text{Å} \); (2)\( E_t=0.5\text{eV}, \ b=3.5\text{Å} \); (3) \( E_t=1\text{eV}, \ b=0\text{Å} \); (4) \( E_t=1\text{eV}, \ b=3.5\text{Å} \).
Fig.(5-21). Probability of the inelastic scattering of the Deuterium molecule $D_2(v=0,j=0)$ from Cu$_9$ (T=0K) cluster at different translations energy and impact parameters; (1) $E_{tr}=0.5$eV, $b=0$ Å; (2) $E_{tr}=0.5$eV, $b=3.5$ Å; (3) $E_{tr}=1$eV, $b=0$ Å; (4) $E_{tr}=1$eV, $b=3.5$ Å.
Chapter 6
Conclusion

In this work results of a quasi classical simulation study of the interaction of $\text{H}_2$ molecule with a Cu$_9$ cluster were reported. Both channels, the reactive (dissociative adsorption of the molecule on the cluster) and non reactive (scattering of the molecule from the cluster), were considered. The processes were examined as function of the initial quantal rovibartional state of molecule, collision energy and impact parameter.

The dynamics of interaction between a molecule and a surface depend on the relative partners (molecule and cluster) and on the internal DOF (Degree Of Freedom) of molecule and cluster. It is of no doubt a formidable task to obtain a full theoretical description, which include all full DOF. A way around this we choose a model system for which the influence of certain DOF is minimized was chosen. Moreover, we selectively work on those DOF which can exert considerable control.

Several factors that influence the reaction Hydrogen molecule and Copper cluster were studied: the geometry of the reaction patterns, cluster temperature, H/D isotopic effect, molecular translational energy, impact parameter and molecular rovibrational quantum number as internal DOF of the molecule.

From the monitored data there was three types of reaction process recorded; one was named as the direct dissociation and it was the case when the molecules reaches the cluster with relatively high translation energy and then dissociate immediately by the time they reach the cluster surface. The second type was indirect dissociation when some of molecules, that reached the cluster with low translation energy, attaches them self to the surface of the cluster rotating and vibrating while searching for the active sites of the cluster to break the bond or till they gain enough energy from the cluster atoms allowing them to dissociate, this cause a resonance for some period of time at the surface of the cluster. The third types was inelastic scattering, it may occur for all translation energies that the molecule by the time they reach the cluster with initial $v_i$, $j_i$ rovibrational states, they reflect back with different final $v_f$, $j_f$ rovibrational states.

In the reactive channel the reaction dissociation cross section of H$_2$ molecule in the Cu cluster was investigated. At the region of low molecule translation energy the reaction cross-section increase rapidly and reached a maximum value then it show a dramatically decrease to some minimum value with the further increase of the collision
translation energy demonstrating the existence of reaction threshold. As the energy increases further, the reaction cross section started to increase monotonically again. As expected and experimentally proved\(^{(1,9,21)}\), it was seen that for all cases of different \(v_i\), \(j_i\) rovibrational states the cross section display a small but non zero threshold (dynamical activation barriers) value for the molecule translation energy below which there was minimum probability of dissociation adsorption and above which it increase monotonically with the increase of \(E_n\) molecule translational energy. The activation barrier encountered by impinging molecule decrease with the increase of \(v_{i,j_i}\). Parallel to that, it is very clear that the reaction cross section increase monotonically by increasing of \(v_i, j_i\) quantum rovibrational states, this is also experimentally proved \(^{(1,22,23)}\) for Cu(100)\(^{(5)}\). However by this simulation studies and with that experimentally and theoretically proved it is well established by now that the chemisorption of Hydrogen molecule in copper cluster/surface is an activated process. Also the strong isotopic \(H_2/D_2\) effect was illustrated, and that for a given rovibartional states and fixed number of Cu atoms and specific cluster formation temperature there is more influence for the lighter isotope \(H_2\) than on the heavier isotope \(D_2\). However, it becomes less important at higher molecular rovibartional quantum states i.e. at higher incident energies.

In this work the effect of the initial rovibrational states of the translating molecule was investigated by increasing successively both of vibration and rotational states \((v=0, j=0;3;5;10)\) and \((v=1;3,j=0)\). It is very clear that from the monitored and plotted data, the cross section increase monotonically with increase of \(v_i, j_i\). It was also seen that the vibartional effect exerting more influence than that of the rotational in increasing of the reaction cross section. Also the dissociation of \(D_2\) at different rovibrational states was studied and provided that for the same \(E_n\) incidence energy of \(H_2\) the locations of minima of \(D_2\) was shifted more towards higher rotational state \((j=0,3)\), as comparing with those of \(H_2\) \((j=0,3)\), which indicate that \(H_2\) exhibiting higher chemisorption probability than \(D_2\) in the higher region, because \(D_2\) travels at much lower velocity than \(H_2\) for the same translation energy \(E_n\) steering will be more effective for \(D_2\) than for \(H_2\).

In correspondence calculations of the reaction rate constant and as expected \(D_2\) molecule have less rate constant than \(H_2\) molecule. Generally we find that the ratio of rate constants for \(H_2\) molecule to that of \(D_2\) molecule vary from one to two order of
magnitude. This calculations was founded to be in a good accord with that for Cu\textsubscript{13} cluster\textsuperscript{(1)}, Cu\textsubscript{7}\textsuperscript{(21)} and Cu and Pd surface. Reaction rate also increase with the increment of initial rovibatioal state.

As expected with high translation energy molecules will have greater dissociation probability when interacting with atoms near the center of mass of the cluster i.e. at impact parameter $b=0$ Å. This probability decrease successively with the increase in the impact parameter till it reach its minimum value for the impact parameter $b>4$ Å. The molecule interact at lower translation energy have the least dissociation probability, but they dissociate at large impact parameter than the former one.

As for the rovibertional states $v=0,j=0$ this probability increase with the increase of the rotational states and rovibertonal state. With high translation energy the dissociation probability was greater for all rovibertional state than that for $v=0,j=0$. This is true for all translation energies from 0.1eV to 0.6eV, again this probability decrease successively with the increase in the impact parameter, and at lower translation energy (0.01eV was selected) have the least dissociation probability when interacting with atoms near the center of mass of the cluster. Again and as expected the viberational state is more dominate in increasing the dissociation probability than the rotational state.

As we look forward there was clear insensitivity of dissociation cross section to the increases of cluster formation temperatures for both isotopes H\textsubscript{2} and D\textsubscript{2}. This is also true for the rate constants calculations. At different rovibrational states it has been also noticed this insensitivity toward the increase of the cluster temperatures.

Future work:

1- Energizing the system by increasing the rovibrational energy ($v=0,j=0$) to ($v=n,j=m$).

1- Increasing the cluster temperature for higher than the melting temperature.

3- Increasing the cluster size Cu\textsubscript{10} to Cu\textsubscript{14}.
7- References


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