CHAPTER 1

1. INTRODUCTION

1.1 AN OVERVIEW OF CATALYSIS

A catalyst alters the rate of a chemical reaction without being consumed. Catalysed reactions have lower activation energy than uncatalysed reactions. The function of a catalyst is to split up the main reaction into two or more steps. The potential energy barrier in each step is reduced compared to single step of the main reaction. Hence catalyst helps to cross the barrier in two or more steps. A catalyst increases rate of a reaction without modifying the overall standard Gibbs Free energy change of the reaction. The model is depicted in figure 1. The initial and final states of the reaction energetically remains the same. The catalytic processes are classified into two types, 1.Heterogeneous and 2.Homogeneous catalysis. In heterogeneous catalysis, the catalyst and reactants are in different phases. Typical example involves a solid catalyst with reactants as either liquids or gases. A homogeneous catalyst can function in the same phase of reactants.

Fig.1. Potential energy diagram for catalyzed and uncatalyzed reactions.

Substances that increase the rate of reaction are called positive catalysts or simply catalysts, while substances that decrease the rate of reaction are called negative catalysts or inhibitors. In some reactions one of the reaction products is a catalyst for the reaction; this phenomenon is called self-catalysis or autocatalysis. Some substances that are not themselves catalysts but increase the activity of a catalyst when added with it; such substances are called promoters.
Essential criteria for good catalyst

a. chemically inert
b. large surface area
c. specific in activity
d. Economically feasible

Heterogeneous catalysis involves process which consists of three main steps: adsorption of reactants on the catalyst surface, reaction on the surface and the desorption of the products. A nano-material based catalyst is an example of heterogeneous catalyst. The catalytic activity of nanoparticles are influenced by its structure and properties.

1.2 Nanoparticles

Nanoparticles possess nano dimensional lattice parameters. There is no accepted international definition for nanoparticles; it can be quoted as a particle having one or more dimensions of the order of 100 nm or less. The name Nano is derived from the Latin word “nannus” meaning dwarf. Nanoparticle research is currently an area of intense scientific research due to variety of potential applications. Nanoparticles effectively bridge between bulk material and atomic or molecular structure. One of the earliest nano size objects was made of gold by Faraday when he prepared colloidal gold and called it divided metals\(^1\).

The properties of materials change as their size approach to nano scale and the percentage of atoms at the surface of material become significant. The distinguishing feature of nanoparticles irrespective of their detailed structure is that they possess a large surface area to volume ratio and a large fraction of atoms that are co-ordinatively unsaturated compared to the bulk. These surface atoms are responsible for many unique properties of nanoparticles. This effect specific to small size of nanoparticle is called quantum size effect\(^2\). This nano dimensional structures show pronounced features in their electrical property (conductivity.), optical property (colour and transparency), physical property (hardness and melting point) and chemical property (reactivity and reaction rate).The chemical activity of material increases when it approaches the nano scale. Nanoparticles are essential components of heterogeneous catalysis. The atoms with reduced coordination found at the surface have
modified chemical property and can be active sites for various reactions. Therefore nanoparticles are attractive as catalysts.

Recently there is considerable variety in the type of nanoparticle system that have been fabricated and studied. Since nanoparticle possesses unique beneficial chemical, physical and mechanical properties, they can be used in wide variety of applications\(^3\). They include computer chips, insulation materials, cutting tools, low cost flat panel displays, high sensitivity sensors, long lasting medical implants, electrochromic display devices.

### 1.3 Gold Nano particles

Bulk Gold is very popular for being chemically inert. It is one of the most stable and precious metals in the group 8. When the size of gold is decreased to nano meter range, it becomes highly active, which is schematically shown in Fig.2. Those nano meter size particle of gold in a fluid suspension is called gold nano particle. The characteristics of gold Nano particles are due to their shape and size. Due to their unique physical, optical and electronic properties and functional activity, they are utilized in high technology applications.

1. **Electronics**: Gold Nano-particles are used to connect conductors, resisters, and are important components in electronic chips.

2. **Biomedical**: They have a wide variety of bio medical applications due to its bio compatibility and ease of conjugation to bio-molecule. They are used in photodynamic therapy, therapeutic agent delivery used to detect diagnosis of heart diseases, cancers etc.

3. **Sensors**: They are used as sensors in Surface Enhanced Raman spectroscopy (SERS), detection of protein, pollutant and as a colorimetric sensor in food industry.

4. **Probes**: The gold Nano particle probes are extremely stable, have a long shelf life and are non-toxic. They create an enhanced assay signal making them useful for transmission electron microscopy.

5. **Catalysis**: Gold Nano particles are widely used as catalysts for a variety of chemical reactions, such as selective oxidation, reduction reactions.
1.3.1 Catalysis by gold Nano-particles

Gold Nano-particles are active catalysts at room temperature. Nano gold, either protected by organic ligand or supported on solid surfaces have attractive applications in catalysis. Some of them are

1. Oxidation of carbon monoxide: Nano gold has the best low temperature activity for CO oxidation. This reaction is an effective approach to solve pollution problem by CO.
2. Oxidation of alkanes and alkenes: Nano gold is capable of catalysing the oxidation of methane, propane, and propene
3. Water gas shift reaction (WGS): CO+H₂O↔CO₂+H₂
   The WGS reaction is widely used to generate hydrogen. Gold Nano particles are one of the best catalysts for WGS reaction.
4. Reactions with oxides of nitrogen: NO and NO₂ are present in exhausts of diesel and petrol engines. In order to minimize the toxicity of these gases, gold catalysts are used to reduce them to N₂.
5. Other applications involve vapour phase epoxidation of propene, oxidation of glycol, reaction between CS₂ and NaBH₄ and also catalyse reduction of 4 nitrophenol.

Gold based catalysts are highly explored in various chemical reactions due to its greater availability and relatively low and stable cost as compared with platinum group metals (PGM)
1.3.2 Need of gold Nano clusters

Gold in the bulk phase has been regarded as least reactive and inert when compared with other transition metals\textsuperscript{4}, because it has higher ionization potential of 9.2 eV. When Nano gold is dispersed over metal oxide support, it become highly active catalyst for different oxidation reactions especially CO to CO\textsubscript{2} oxidation\textsuperscript{5}. The catalytic activity critically depends on the size of the particles. The activity depends not only on the size but also on the oxidation state of the cluster and nature of the support\textsuperscript{4,6,19}. In the case of supported gold particles, the oxygen vacancies (F-center) on the support play an important role in the catalytic activity. The number of low coordinated sites and surface roughness affects the activity of gold. The gold-support interface perimeter and charge transfer between gold and support also play an essential role in the activation of Nano size gold clusters\textsuperscript{7}. Various gold species like 2-3 nm Au NPs, gold bilayer structures, sub nanometer gold clusters, low-coordinated gold atoms at the perimeter sites of gold particles, gold cations and pairs of gold atoms and gold cations are expected to be act as active sites. Au Nano particles larger than 5nm are generally not active, but exhibit bulk behaviour.

The large surface area of the nanoparticles gives access to more reacting molecules and higher turnover numbers. The surface areas are characterized by the geometry, bond angles, bond lengths, and low coordinated sites. The electronic distribution on the surface varies with different geometries. The nanoparticles can be used in colloidal solutions, which improve the accessibility of reacting molecules to the surface. Unprotected gold nanoparticles have a tendency to merge and form large clusters. Hence obtaining the Au NPs with smaller size and lower number of atoms is a great challenge for desired reactions. Designing of thermodynamically favourable model may open a solution for the new catalyst development.

1.3.3 CO Oxidation by gold catalysts

Gold was considered inactive till the 80', In 1987 Haruta showed that Au NPs are active for the CO oxidation

\[ \text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2 \]

The main applications of Gold-nanoparticle-based catalyst for CO oxidation reactions are
1 CO oxidation in catalytic exhausts

80% of vehicle pollution in the earth comes from the engine cold-start. Now days this is a major cause of air pollution. So Au NPs can play an important role to reduce the pollution from vehicle exhaust.

2 Purification of hydrogen for fuel cell

Consider the Methanol reforming reaction in fuel cell

\[ \text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow 3 \text{H}_2^+ \text{CO}_2 + \varepsilon(\text{CO}) \]

The CO formed in this reaction adversely affect the Pt electrode of fuel cell and hence its efficiency. Problem of poisoning of the Pt anode by CO can also be solved by Au NPs

Au Nano particles supported on transition metal oxides are active catalysts for oxidation reactions at low temperature\(^4\). Gold is inert in the bulk form but becomes active in the nano state and have a potential application in the oxidation of CO from automotive exhaust. CO oxidation is important due to the concern of environmental protection. CO gas should be removed from car exhaust and from hydrogen gas used for fuel cells. The oxide support has a vital role because bare gold is not enough active. There will be partial electron transfer from the F center defect of the support to metal cluster. Then the metal gets charged and leading to the activation of O-O bond of the molecule adsorbed on the cluster\(^8\). The activation weakens the O-O bond and lowers the barrier for reaction with CO and subsequent formation of CO\(_2\)\(^9\). The mechanism of CO oxidation on gold is affected by several factors such as oxidation state of Au, quantum size effect\(^{18}\), support induced strain\(^{19}\), oxygen spill over to and from the support and low coordinated Au atoms on the Nano particles.

These applications highlight the importance Au NPs as a catalyst in CO oxidation but there are a lot of difficulties arise while choosing the catalyst. The main issues are based on size and shape of the active Au NPs. Some of them are;

- The actual samples display size and shape distributions
- The very small nanoparticles (< 1 nm) are not easily visualisable
- Some minority NPs can provide the activity of a catalyst
But the researchers overcome these difficulties and finally concluded the main features of Au NPs to act as a good catalyst are as follows,

- It should be active at room temperature
- The Size of NPs < 5 nm
- They can be easily supported on reducible oxide: TiO$_2$ > CeO$_2$ > Al$_2$O$_3$
- The maximum activity is found around 2-3 nm

In 2008 Herzing and coworkers\textsuperscript{12} reported that “High catalytic activity for carbon monoxide oxidation is correlated with the presence of bilayer clusters that are ~ 0.5 nano meter in diameter and contain only ~ 10 gold atoms”. A good agreement for this result was reported by Chen-Goodman. Their studies have shown that a bilayer Au structure is a critical feature for catalytically active Au nanoparticles, along with low coordinated Au sites, support-to-particle charge transfer effects, and quantum size effects.

But in 2010 Liu, Schuth et al reported a disagreement with these studies. According to them “For the current catalyst, gold nano clusters have diameters larger than 1 nm and bilayer structures and/or diameters of about 0.5 nm are not mandatory to achieve the high activity”. Based on all these results finally researchers specified the main features of Au NPs for CO oxidation.\textsuperscript{13} as follows;

**Main conclusions about the active Au NPs for the oxidation of CO**

- The active Au particles size is 1.5 - 3 nm
- Bigger particles are not or very few active
- Au catalyst supported on TiO$_2$ is more active for the desired reaction\textsuperscript{16}
1.4 Mechanism of CO oxidation

There are several proposed mechanisms for the reaction. They are mainly categorised into two, (1) mechanism involving only Au NPs and CO, (2) mechanism involving the interaction with the support\textsuperscript{15}. Many factors such as kinetic, temperature studies and kinetic isotope effect reinforce these mechanisms\textsuperscript{17}. Kinetic studies show a reaction rate $\alpha [\text{CO}] [\text{O}_2]$, indicating that CO and O\textsubscript{2} are adsorbed on the surface until saturation and the reaction of the adsorbed CO and O\textsubscript{2} is the rate determining step\textsuperscript{18}. The heterogeneously catalysed CO oxidation frequently requires adsorption of both reactants on the surface of the catalyst, i.e. it follows a Langmuir-Hinshelwood mechanism. It involves the dissociation of dioxygen O\textsubscript{2}, the reaction between the adsorbed species CO and O, and the desorption of the product, CO\textsubscript{2}. Typical catalysts for oxidation reactions form bonds of medium strength with oxygen\textsuperscript{20}. It involves the adsorption of both oxygen molecule and CO. Carbon monoxide, CO, is isoelectronic with N\textsubscript{2}. The substantial dissociation energy of 1077.10 kJ/mol corresponds to the short bond length of 1.1282 Å and the high molecular vibration frequency of 2143 cm\textsuperscript{-1}. The CO molecule has a remarkably small dipole moment of $\mu = 0.112$ D with the positive end on oxygen. The mechanism of CO oxidation involves the following steps. The schematic diagram is shown in Fig.3.

1. $\text{O}_2 (g) \rightarrow \text{O}_2 (ad)$
2. $\text{O}_2 (ad) \rightarrow 2\text{O}(ad)$
3. $\text{CO}(g) \rightarrow \text{CO}(ad)$
4. $\text{CO}(ad) + \text{O}(ad) \rightarrow \text{CO}_2(ad)$
5. $\text{CO}_2(ad) \rightarrow \text{CO}_2(g)$

Fig.3. Schematic diagram representing CO oxidation on Au NPs
Bulk gold is the noblest of all metals and on other hand Au is used as the best in catalysis. Among the main factors that determine the efficiency of Au catalysts is the shape of Au nanoparticles. The shape of Au nanoparticles has a key role in every aspect of their functionality, from sensing and biolabeling applications to plasmonics and photonics, in which an electronic states transformation occurs. The probability of such a transition depends on the density of states and the dipole matrix elements. For a given size, both wave functions and energies depend critically on the nanoparticle shape. For example, the lowest excitation energy for a cubic nanoparticle is 10% higher than that of a spherical nanoparticle of the same volume.

Gold nanoparticles are often found in their equilibrium shape and at the thermodynamic limit, this is a polyhedron enclosed by faces of various crystal orientations. Nanoparticle shape is often found to change upon exposure to some interacting environment. In the case of Au nanoparticles upon exposure to CO, a change in their shape has been observed both experimentally and theoretically. This is due to the dependence of interface tension of a metal in equilibrium with a gas to the surface tension, the adsorption energy, and the coverage of adsorbates. In order to predict the equilibrium shape in an interacting environment, it is necessary to have a systematic calculation of adsorption energies for all relevant surfaces.

These properties of gold Nano clusters were widely studied using computational method, which is the best tool for the theoretical investigation of catalyst surfaces.

1.5 Computational chemistry

Computational chemistry involves the use of computers to solve chemical problems. The commonly investigated problems are prediction of molecular geometry, energy of molecules, determination of reaction intermediates and transition states, visualization of orbital interactions, chemical reactivity, and calculation of IR, UV, and NMR spectra, the interaction of a substance with an enzyme, the physical properties of a substance. The schematic diagram is given in Fig.4.
Computational chemistry is used in a number of different ways. One important way is to model a molecular system prior to synthesizing in laboratory. This is very useful information, because synthesizing a single compound requires months of labour and raw materials, and generate toxic wastes. A second use of computational chemistry is in understanding a problem more completely. There are some properties of a molecule that can be obtained computationally more easily than by experiment such as molecular bonding. Thus many experimental chemists are now using computational modelling to gain additional understanding of the compounds being examined in the laboratory.

Energy is one of the most useful concepts in science. The analysis of energetics can predict what molecular processes are likely to occur. All computational chemistry techniques define energy such that that system with the lowest energy is the most stable. Thus, finding the stable shape of a molecule corresponds to finding the shape with the lowest energy. Computational results can be related to thermodynamics. It is possible to correlate the results of computation such as internal energy, free energy etc. to the various contributions to entropy.

Quantum mechanics is one of the mathematical description of the behaviour of electron. It can predict any property of an individual atom or molecule exactly. Two equivalent formulations of QM were devised by Schrodinger and Heisenberg. And Schrodinger equation is the basis for all computational chemistry methods.

Computational chemistry is fairly cheap and fast compared to experiment. It is environmentally safe. It does not replace the experiments but minimize the difficulties. Computational chemistry is useful in studying the properties of a material in material science.
Semiconductors, superconductors, plastics, ceramics etc. can be investigated by the use of computational chemistry.

### 1.5.1 Computational methods

The main tools available for computational studies are\(^{10,11}\):

1. **Molecular mechanics (MM):** It is the quick and simple method used for a geometry optimization. It also derives relationship between energy and structural parameter. Large molecules can be easily optimized in seconds on a powerful computer.

2. **Ab initio calculations:** The word Ab initio means “from the beginning”. These calculations are based on solving Schrodinger equation. It is more pure in relation to theory. The molecular energy and wave function can be calculated by solving Schrodinger equation. From the wave function analysis, the electronic distribution over the molecule is obtained and it helps to predict, which parts of it are likely to be attacked by nucleophiles or electrophiles.

3. **Semi empirical calculations (SE):** They use the same Schrodinger equation as Ab initio method. Calculations are possible for moderate sized molecules. It is the mixing of theory and experiment that makes the method semi-empirical. SE calculations are slower than MM and faster than Ab initio calculations.

4. **Density functional theory (DFT):** It is also based on Schrodinger equation. DFT does not calculate the wave function but derives the electronic density distribution directly. DFT calculations are faster than Ab initio but slower than SE. DFT is relatively new technique.
2.1 Computational details

Density functional theory was used for the theoretical study of anionic, neutral and cationic gold clusters. All molecular geometries were optimized by Gaussian 09 programme. DFT is opted because it maintains good quality and computing time ratio. We used B3LYP exchange correlation hybrid functional. Hybrid functionals are a class of approximations to the exchange-correlation energy functional in density functional theory (DFT). One of the most commonly used versions is B3LYP, which stands for Becke, 3-parameter, Lee-Yang-Parr. The basis set used is LanL2DZ (The Los Alamos National Laboratory basis sets), which gives consistent results for different systems.

2.2 Density functional theory (DFT)

DFT is the most popular and versatile computational method to investigate the electronic structure of many body systems. It is highly useful for the investigation of systems of increasing size and complexity. DFT is based on two theorems proposed by Hohenberg and Kohn in 1964. According to the theorem the ground state energy of a system of interacting electrons in an external potential is a function of the electron density. In this theory, the properties of a many-electron system can be determined by using functionals (here electron density). DFT provides description of the chemical bond between a surface and a molecule which is essential for understanding surface chemical reactivity and catalysis. DFT calculations for solid state systems are in good agreement with experimental data. The cost of this computational method is comparatively lower than traditional methods. DFT can predict Molecular structures, vibrational frequencies, atomization energies, ionization energies, electric and magnetic properties, reaction paths. The ultimate goal of most approaches in quantum chemistry is the solution of time independent Schrödinger equation.

The general form of Schrödinger equation is given below

\[ \hat{H}\Psi_i(\vec{r}_1, \ldots, \vec{r}_n, \vec{R}_1, \ldots, \vec{R}_N) = E\Psi_i(\vec{r}_1, \ldots, \vec{r}_n, \vec{R}_1, \ldots, \vec{R}_N) \rightarrow (1) \]

Where \( \hat{H} \) is the Hamiltonian operator, \( \Psi_i \) is the wave function of the \( i \)th state of the system and \( E \) is the total energy of the system. From Schrödinger equation the ground state energy of a system of interacting electrons in an external potential is a function of the electron density

\[ E(\rho) = T(\rho) + V_{ex}(\rho) + V_{ee}(\rho) \rightarrow (2) \]
The energy function contains three terms, $T(\rho)$ - the kinetic energy, $V_{\text{ext}}(\rho)$ - the interaction with external potential and $V_{\text{ee}}(\rho)$ - electron–electron interaction.

**Applications of density functional theory**

DFT is used to determine various properties which can also be found using experimental set up. The various applications of DFT are listed below.

1. **Structural properties**: DFT can predict the best possible crystal structure. It also determines geometry of various organic molecules, defect structure, grain boundary, surface structure and adsorption mode of molecules.
2. **Mechanical properties**: It can calculate various mechanical properties of a given material such as elastic modulus, compressibility and thermal expansion coefficient.
3. **Transport properties**: DFT can calculate migration barrier to diffusion and from this, diffusion rate of vacancy and interstitial can be estimated.
4. **Optical properties**: Optical spectra can be estimated using DFT hence luminescence and fluorescence of materials can be found.
5. **Chemical properties**: Various chemical properties such as rate of reaction, formation energy, chemisorption of different gases can be established using DFT.
6. **Electrical properties**: Band structure, dipole moment, conductivity of materials, electron affinity and ionization energies can be calculated for any given system.
7. **Phase transformations**: The phase transformation that takes place under mechanical strain, crystal structure changes can be predicted by DFT.
8. **Magnetic properties**: Magnetic susceptibility, polarizability and frequency-dependent optical rotation parameter etc. are calculated using DFT.

**2.2.1 DFT and Catalysis**

In catalysis the aim of DFT is to develop concepts that are useful to understanding which properties determine the activity and selectivity of a catalyst. It is also useful in the calculations for the development of a new catalyst. Metals and metal oxide surfaces have applications in catalysis. The adsorption sites and binding energies of these surfaces have been determined using DFT. In homogeneous catalysis the formation of ion pairs plays an important role in the mechanism. And their studies mainly carried out using IR spectroscopy. The assignment of IR band can be calculated by DFT. By this method the many electron
problems can be solved accurately and efficiently. Different properties of a catalyst such as ionization potential, electron affinity can be calculated using DFT

2.3 Gaussian

Gaussian is a computer program for computational chemistry. It is a widely used for the determination of electronic structure. The name originates from Gaussian type orbitals to speed up calculations compared to those using Slater-type orbitals. The current version of the program is Gaussian 09. Gaussian software is useful in solving different chemical problems such as (1) geometry optimization and reaction modelling (2) vibrational analysis (3) molecular properties like electrostatic potential, electron density etc. Gaussian is used to study reactions in a wide variety of chemical environments. Gaussian 09’s models can be applied to both stable species and compounds which are difficult or impossible to observe experimentally (short-lived intermediates and transition structures). Spectroscopy is a fundamental tool for investigating molecular structures and properties. However, observed spectra are often difficult to interpret. Gaussian 09 can also compute relevant spectroscopic constants and related molecular properties with excellent accuracy. This combination of experimental observation and theoretical computation can yield very accurate structural and spectral data for compounds of interest. Gaussian 09 can predict a variety of spectra including IR and Raman, NMR, UV/Visible, Vibrational circular dichroism (VCD), Raman optical activity (ROA), Electronic circular dichroism (ECD), Optical rotary dispersion (ORD), Hyperfine spectra (microwave spectroscopy), Franck-Condon, Herzberg-Teller and Franck-Condon/Herzberg-Teller analyses. The accuracy of calculations is highly dependent on the basis set used. Chiral molecules are of great importance in many researches. Gaussian 09 can also study chirality with several techniques. Steady-state spectroscopy is one of the most fundamental tools for investigating equilibrium structures and potential energy surfaces for different electronic states. However, interpreting such experimental data is often not straightforward but Gaussian 09 is capable for predicting the optical spectra. For example, the time-dependent DFT method produces high quality descriptions of excited state systems (comparable to DFT for the ground state). Gaussian 09 computes the most important tensors which contribute to hyperfine spectra. Calculations can suggest regions in which to look for transitions, which can make experiments more efficient. Theoretical results are also useful for making spectral assignments for observed peaks, which can be difficult or impossible to determine solely from the experimental data. Accurate predictions of ΔG are vital to
understanding many chemical reactions. Gaussian 09 offers a variety of very accurate energy methods for predicting thermochemical quantities. In addition to ΔG and ΔH, we can predict heats of formation, atomization energies, ionization potentials, electron affinities and proton affinities for a wide range of compounds at the highest accuracy. In addition to the spectroscopic features, Gaussian 09 also provides several other features for studying Photochemistry and other Excited State Processes. Solvent Effects can also be taken into account when optimizing structures and predicting most molecular properties. Gaussian 09 is a powerful program offering sophisticated modelling capabilities.

2.4 Basis Set Terminology

A basis set is a set of functions used to create the molecular orbitals, which are expanded as a linear combination of such functions with the weights or coefficients to be determined. Normally, the functions are atomic orbitals and they are centered on atoms. Sometimes, the functions centered on bonds or lone pairs are also used.

2.5 Graphical user interface (GUI)

In computing, graphical user interface (GUI) is a type of user interface that allows users to interact with electronic devices through graphical icons. The actions in GUI are usually performed through direct manipulation of the graphical elements. Besides in computers, GUIs can be found in hand-held devices such as MP3 players, portable media players, gaming devices etc. Designing the visual composition and temporal behavior of GUI is an important part of software application programming in the area of human-computer interaction. A GUI uses a combination of technologies and devices to provide a platform that the user can interact with, for the tasks of gathering and producing information.

2.6 Secure Shell (SSH)

Secure Shell (SSH) is a cryptographic network protocol for secure data communication, remote command-line login, remote command execution, and other secure network services between two networked computers that connects, via a secure channel over an insecure network, a server and a client. The input data is created and can be transferred to the super computer. The data to be sent to a particular port of supercomputer can be forwarded from particular port of remote machine using separately prepared (and coded) communication pathway.
2.7 Chemissian

Chemissian is an analysing tool of molecules electronic structure and spectra. It can manipulate molecular orbital energy-level diagrams, calculated and experimental UV-VIS electronic spectra, Natural transition orbitals, electronic/spin density maps, calculation of population and valence, analysis of electron density distribution, bond order and bond length of different compounds. Chemissian has a user-friendly graphical user interface.

2.8 Gaussum

GaussSum is a Graphical user interface (GUI) application that can analyse the output of Gaussian to extract and calculate useful information. This includes the progress of the SCF cycles, geometry optimisation, density of states spectrum UV-Vis/IR/Raman spectra, MO levels, MO contributions and more. GaussSum is written by Noel O'Boyle, and grew from work he carried out during his PhD in Prof. Han Vos' research group at Dublin City University, Ireland.

2.9 Geometry Optimization

In the field of computational chemistry geometry optimization is the process of finding an arrangement in space of a collection of atoms according to some computational model of chemical bonding. The net inter-atomic force on each atom is acceptably close to zero and the position on the potential energy surface is a stationary point. The optimized structures often correspond to a substance as it is found in nature. And the geometry of such a structure can be used in a variety of experimental and theoretical investigations in the fields of chemical structure, thermodynamics, chemical kinetics, spectroscopy and others. It is also called energy minimization. Typically this process is used to find the geometry of a particular arrangement of the atoms that represents a local or global energy minimum.

2.10 Ionization Potential

The ionization potential is the lowest energy that is necessary to remove one electron from substance A. It is an important property to determine reactivity of atoms and molecules.

\[ A \rightarrow A^+ + e^- \]
After this reaction, ion A+ and electron e- are separated by an infinite distance and do not interact. The ionization potential can be calculated as the difference between total energies of neutral atom and ion (total energy of free electron e- is zero).

\[ \text{IP} = \text{E}_{\text{tot}} (A+) - \text{E}_{\text{tot}} (A) \]

### 2.11 Electron Affinity

It is the binding energy of an extra electron to a neutral system. It is an opposite process of ionization potential.

\[ \text{A}^+ + e^- \rightarrow \text{A}^- \]

The electron affinity can be calculated by measuring the difference between energies of neutral system and its anion. The free electron energy is considered as zero.

\[ \text{EA} = \text{E}_{\text{tot}} (A) - \text{E}_{\text{tot}} (A^-) \]

### 2.12 Density Of States

The electronic d-band properties are important factors for the emerging catalytic activity of Au nano-clusters. The important d-band parameters are d-band width, apparent spin-orbit splitting, and d-band center position. The d-band width and spin-orbit splitting values decrease steeply with decreasing number of atoms and the band narrowing is caused by hybridization of fewer wave-functions of valence electrons. The d-band center position shifts to the higher binding energy side with decreasing the cluster size. The rapid increase of d-band centre position is due to the dynamic final-state effect, which results in higher binding energy shifts of core and valence states due to a positive hole created after photoelectron emission. The d-band center shifts apart from the Fermi-level with decreasing the cluster size. Such behaviour is ascribed to the contraction of average Au-Au bond length with decreasing the cluster size.

According to d-band model, adsorbate energy levels interact with metal’s d-band to produce bonding and anti-bonding states. The position of the d-band center influences strength of the interaction and the occupancy of the resulting states, which are directly related to the adsorption energy. For bulk Au, the d-band lies relatively deep below the Fermi-level and as a result the antibonding state is thought to be filled, making interaction between the adsorbate
and bulk Au repulsive. According to theoretical studies, with the reduction of the cluster size and increasing the number of less coordinated atoms, the d-band tends to move closer to Fermi-level. Below the certain cluster size the anti-bonding state becomes higher than EF, reducing the potential barriers for adsorption and dissociation.

DOS of a system is described as the number of states per interval of energy at each energy level that are available to be occupied by the electrons. A high DOS at specific energy level means that there are many states available for occupation. A DOS of zero means that no states can be occupied at that energy level.
Chapter 3

SCOPE AND OBJECTIVES OF THE WORK

Gold based catalysts are highly explored in the area of chemical reaction due to its greater availability and relatively low and stable prize as compared with platinum group metals. Computational chemistry plays an important role to avoid the experimental difficulties and cost during the investigation on the activity of gold Nano particles. The present study aims to investigate;

- Optimization of stable gold clusters \((\text{Au})x\) where \((x=4\) to 28\)
- Investigation of symmetry and point group of these clusters.
- Predicting the surface reactivity of Au clusters
- Calculation of DOS, UV-Visible, IR etc.
- Calculation of ionization potential, electron affinity, average bond length, average bond order, chemical hardness, electrophilic power etc.
- Adsorption of CO molecules on these clusters and investigation of adsorption energies
- The reaction of CO oxidation is to be carried out on these gold clusters.
- How specifically the size and shape of Au NPs control the reactivity
Chapter 4  Results and Discussions

4.1 Structure of Gold Clusters

The modelled geometries were allowed to relax their configurations through geometry optimization to find out the ground state global minimum configuration of a particular model. All the geometry optimisation calculations were computed using DFT/ B3LYP/ LanL2DZ level of theory. After finding the global minimum, the final configuration was assigned as a stable configuration of that particular cluster. The nine different shapes such as square, triangle, hexagon, extended hexagon, unequal hexagon, extended pentagon, three – three matrix, three – two matrix, and three – four matrix with dissimilar number of gold atoms were constructed with ranging from Auₙ (n=4-28). Structural, vibrational and their electronic properties etc are summarized. All the constructed gold cluster models were presented in two-dimensional. In the catalytic environment, the two dimensional monolayer is having enhanced catalytic activity.

4.2 Tilted square type clusters

The optimized structures of neutral gold clusters Auₙ(n= 4,9,16,25) possessed square\(^{26}\) type geometry and are shown in fig 5.

![Optimized geometries of tilted square gold clusters](image)

Fig5: optimized geometries of tilted square gold clusters

From the DFT calculations, it is clear that all the four geometries possess D\(_{2h}\) symmetry. Various properties of these clusters were analysed and listed in table 1

<table>
<thead>
<tr>
<th>Cluster name</th>
<th>Binding energy</th>
<th>Average Coordination no</th>
<th>Average bond length</th>
<th>Average bond order</th>
<th>IP (eV)</th>
<th>EA (eV)</th>
<th>Chemical hardness</th>
<th>Electrophilic power</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au₄</td>
<td>-1.16</td>
<td>2.5</td>
<td>2.80</td>
<td>0.47</td>
<td>7.94</td>
<td>2.61</td>
<td>2.66</td>
<td>5.23</td>
</tr>
<tr>
<td>Au₉</td>
<td>-1.48</td>
<td>3.55</td>
<td>2.77</td>
<td>0.34</td>
<td>6.59</td>
<td>3.12</td>
<td>1.68</td>
<td>6.84</td>
</tr>
<tr>
<td>Au₁₆</td>
<td>-1.63</td>
<td>4.12</td>
<td>2.79</td>
<td>0.29</td>
<td>6.47</td>
<td>4.11</td>
<td>1.38</td>
<td>10.9</td>
</tr>
<tr>
<td>Au₂₅</td>
<td>-1.70</td>
<td>4.48</td>
<td>2.8</td>
<td>0.41</td>
<td>6.33</td>
<td>4.60</td>
<td>1.17</td>
<td>14.18</td>
</tr>
</tbody>
</table>

Table1: Properties of tilted square gold clusters
From the table 1 it can be seen that the binding energy of tilted square clusters follows a decreasing trend from lower number of gold atoms to higher number. But in the case of average coordination number, \( \text{Au}_{25} \) possessed a higher value and a lower value for \( \text{Au}_4 \). That indicates average coordination number increases with increase in number of atoms. All the four clusters showed almost same average bond length irrespective of the size (2.8Å). Lower bond length or higher bond order indicates the inertness of species. When the chemical bond becomes weak the bond length increases, then the involving electrons are loosely held on the bond and it becomes readily available for the desired catalytic process. Average bond order is higher for \( \text{Au}_4 \) (0.473) and lower for \( \text{Au}_{16} \) (0.295). Hence it is found that \( \text{Au}_{16} \) is more active than \( \text{Au}_4 \). Bulk gold possesses an ionization potential of 9.2eV, and it is inert. But nano gold particles show difference in IP when compared with bulk. The IP decreases with increasing number of atoms in the cluster. The lowest IP is observed for \( \text{Au}_{25} \) cluster. The variation of electron affinity showed an opposite trend from that was observed in ionization potential. It is increased as the size of the cluster increased. The chemical hardness followed an increasing trend and electrophilic power followed a decreasing trend with number of atoms in the cluster.

**UV-Visible spectrum**

![UV-Visible spectrum of tilted square gold clusters](image)

Fig 6 shows the UV-Visible spectrum for square type clusters. The UV-Visible spectrum of gold clusters was calculated using Time dependent (TD-DFT) method. The spectrum shows a maximum molar absorptivity around 204nm for \( \text{Au}_4 \) cluster. The maximum molar
absorptivity at 404nm, 410nm, 615nm were observed for Au\textsubscript{9}, Au\textsubscript{16}, and Au\textsubscript{25} respectively. The molar absorptivity maxima show a red shift from the lower wavelength to higher region as the number of atoms in the cluster increases.

**Density of states**

The Fig 7 is a plot of density of states for the gold clusters. The d-band width and spin-orbit splitting values decrease steeply with decreasing number of atoms\textsuperscript{20}. The d-band center shifts apart from the Fermi-level with decreasing the cluster size. The density of states shows an increase in trend with the number of atoms Au\textsubscript{4} to Au\textsubscript{25}. From the graph it is also clear that the d-band center position shifts to the higher binding energy side with decreasing the cluster size.

![Density of states plot](image)

**Fig7**: Density of states of tilted square gold clusters

**4.3 Triangular gold clusters**\textsuperscript{21}

Gold clusters Au\textsubscript{n}(n=6,10,15,21) of triangular shape were optimized and is shown in Fig 8

![Optimized geometries](image)

**Fig8**: Optimized geometries of triangular gold clusters
Au$_6$ possessed a D$_{3h}$ point group of symmetry and all the other configurations have D$_2$ symmetry. Different properties of these clusters were tabulated in table 2.

<table>
<thead>
<tr>
<th>Cluster name</th>
<th>Binding energy</th>
<th>Average Coordination no</th>
<th>Average bond length</th>
<th>Average bond order</th>
<th>IP (eV)</th>
<th>EA (eV)</th>
<th>Chemical hardness</th>
<th>Electrophilic power</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au$_6$</td>
<td>-1.50</td>
<td>3</td>
<td>2.74</td>
<td>0.39</td>
<td>8.45</td>
<td>2.15</td>
<td>3.15</td>
<td>4.46</td>
</tr>
<tr>
<td>Au$_{10}$</td>
<td>-1.46</td>
<td>3.6</td>
<td>2.78</td>
<td>0.33</td>
<td>7.38</td>
<td>3.21</td>
<td>1.58</td>
<td>10.62</td>
</tr>
<tr>
<td>Au$_{15}$</td>
<td>-1.57</td>
<td>4</td>
<td>2.8</td>
<td>0.31</td>
<td>6.91</td>
<td>3.62</td>
<td>1.42</td>
<td>10.56</td>
</tr>
<tr>
<td>Au$_{21}$</td>
<td>-1.67</td>
<td>4.28</td>
<td>2.76</td>
<td>0.37</td>
<td>6.25</td>
<td>3.83</td>
<td>1.21</td>
<td>10.52</td>
</tr>
</tbody>
</table>

Table2: Properties of triangular gold clusters

From the table 2, binding energy shows decreasing trend and average coordination number shows an increasing trend with increase in number of atoms. Initially the average bond length shows a slight increase and then remains constant as the number of atoms increases. In triangular geometry, the lower member Au$_6$ possess a higher bond order and then it decreases with number and finally the bond order is increased for Au$_{21}$. There is an increase in the electron affinity from the lower number to higher number. The higher clusters were co-ordinatively unsaturated than the lower clusters and hence they showed more electron affinities.

**UV-Visible spectrum**

![UV-Visible spectrum](image)
The UV-Visible spectrum shows maximum at 310nm for Au₆, 410nm for Au₁₀, 510 nm for Au₁₅ and 515nm for Au₂₁. From the spectrum it is very clear that there is a shift towards the higher wavelength as the number of atoms in the cluster increases. This is called red shift and is caused mainly by Doppler effect.

**Density of states**

Fig10: Density of states of triangular gold clusters

DOS of a system is described as the number of states per interval of energy at each energy level that are available to be occupied by the electrons. The rapid increase of d-band centre position is due to the dynamic final-state effect, which results in higher binding energy shifts of core and valence states due to a positive hole created after photoelectron emission. The width of the band is decreased with decrease in number of atoms. It is very clear from fig 10.

**4.4 Hexagonal Gold clusters**

The optimized geometries of hexagonal shaped clusters Auₙ (n= 7, 19) are sown in Figure 11.

Fig11: Optimized geometries of hexagonal gold clusters
Among these nano clusters, Au$_7$ possess D$_{2h}$ point group and Au$_{19}$ possess D$_{6h}$ point group.

<table>
<thead>
<tr>
<th>Cluster name</th>
<th>Binding energy</th>
<th>Average Coordination no</th>
<th>Average bond length</th>
<th>Average bond order</th>
<th>IP (eV)</th>
<th>EA (eV)</th>
<th>Chemical hardness</th>
<th>Electrophilic power</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au$_7$</td>
<td>-1.38</td>
<td>3.42</td>
<td>2.81</td>
<td>0.34</td>
<td>6.82</td>
<td>3.58</td>
<td>1.50</td>
<td>8.61</td>
</tr>
<tr>
<td>Au$_{19}$</td>
<td>-1.67</td>
<td>4.42</td>
<td>2.81</td>
<td>0.30</td>
<td>6.60</td>
<td>4.15</td>
<td>1.33</td>
<td>11.29</td>
</tr>
</tbody>
</table>

Table 3: Properties of hexagonal gold clusters

The binding energies of Au$_7$ and Au$_{19}$ were found to be -1.385 and -1.671 respectively. So it decreases with number of atoms. Average coordination number is found to be higher for Au$_{19}$. The average coordination number and bond length are responsible for the activity of catalysts in catalytic reactions. Cluster with the shorter bond length is tightly held together and the cluster is said to be contracted cluster. This is due to that of the valence electrons in the adjacent electrons overlapping causes the shrinkage of bond length. IP and EA shows the general trend like other clusters. Chemical hardness decrease from Au$_7$ to Au$_{19}$. The effect of molecular environment generally results in an increased hardness in atoms. The extent of this effect depends on the kind of coordination as well as the bond distances. The shortening of bond distances results in an exponential increase of this parameter. The electrophilic power is increased with number of atoms in the cluster.

**UV-Visible spectrum**

![UV-Visible spectrum of hexagonal gold clusters](image)

Fig 12: UV-Visible spectrum of hexagonal gold clusters.
The optical absorption spectrums of the hexagonal gold clusters were studied using Time Dependent Density functional theory (TD-DFT) and are plotted in fig 12. As the number of atoms in the cluster increases there is a shift from higher energy to lower energy region. So Au_{19} have a peak at higher wavelength region when compared with Au_{7} cluster.

**Density of states**

![Density of states of hexagonal gold clusters](image)

Fig13: Density of states of hexagonal gold clusters

The electronic d-band properties are important factors for the emerging catalytic activity of Au nano-clusters. The important d-band parameters are d-band width, apparent spin-orbit splitting, and d-band center position. Here the band width is higher for Au_{19} cluster. When the size of the cluster is decreased, the band width is decreased. And the d-band center position shifts to the higher binding energy side with decreasing the cluster size. From the plot of DOS, the number of states in each energy level that are available to be occupied by the electrons can be studied.

**4.5 Extended hexagonal shaped clusters**

Gold nano clusters having 10, 13, 16, 19, 22, 25 and 28 number of atoms possess an extended hexagonal shaped geometry.
Figure 14 shows the optimized structure of the clusters. All the clusters having $D_{2h}$ symmetry. And their properties are tabulated in table 4.

<table>
<thead>
<tr>
<th>Cluster name</th>
<th>Binding energy</th>
<th>Average Coordination no</th>
<th>Average bond length</th>
<th>Average bond order</th>
<th>IP (eV)</th>
<th>EA (eV)</th>
<th>Chemical hardness</th>
<th>Electrophilic power</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au$_{10}$</td>
<td>-1.574</td>
<td>3.8</td>
<td>2.79</td>
<td>0.33</td>
<td>7.58</td>
<td>2.91</td>
<td>2.33</td>
<td>5.91</td>
</tr>
<tr>
<td>Au$_{13}$</td>
<td>-1.577</td>
<td>3.69</td>
<td>2.83</td>
<td>0.30</td>
<td>6.91</td>
<td>3.64</td>
<td>1.49</td>
<td>9.81</td>
</tr>
<tr>
<td>Au$_{16}$</td>
<td>-1.614</td>
<td>4.12</td>
<td>2.77</td>
<td>0.30</td>
<td>6.67</td>
<td>3.78</td>
<td>1.51</td>
<td>8.80</td>
</tr>
<tr>
<td>Au$_{19}$</td>
<td>-1.639</td>
<td>4.21</td>
<td>2.79</td>
<td>0.31</td>
<td>6.53</td>
<td>3.84</td>
<td>1.25</td>
<td>9.67</td>
</tr>
<tr>
<td>Au$_{22}$</td>
<td>-1.661</td>
<td>4.27</td>
<td>2.8</td>
<td>0.31</td>
<td>6.35</td>
<td>3.92</td>
<td>1.37</td>
<td>10.3</td>
</tr>
<tr>
<td>Au$_{25}$</td>
<td>-1.668</td>
<td>4.32</td>
<td>2.82</td>
<td>0.30</td>
<td>6.51</td>
<td>3.81</td>
<td>1.34</td>
<td>9.90</td>
</tr>
<tr>
<td>Au$_{28}$</td>
<td>-1.684</td>
<td>4.35</td>
<td>2.75</td>
<td>0.31</td>
<td>6.18</td>
<td>4.00</td>
<td>1.08</td>
<td>11.9</td>
</tr>
</tbody>
</table>

Table 4: Properties of extended hexagonal gold clusters

The binding energy for Au$_{10}$ is -1.574 eV and it moves on decreasing up to -1.684 eV for Au$_{28}$ cluster. Like other geometries, extended hexagonal clusters are also showing an increase in average coordination number along with an increase in number of atoms. Average bond length and bond order show almost a constant value. There is a decrease in IP and a linear increase in EA from Au$_{10}$ to Au$_{28}$. As the number of atoms increases, chemical hardness shows a decrease and electrophilic power shows an increase in tendency.
UV-Visible spectrum

From the UV spectrum (fig 15), it is very clear that there is a sharp increase in the molar absorptivity from \( \text{Au}_{10} \) to \( \text{Au}_{28} \) as well as there is a shift in the peak position towards the right (i.e. higher wavelength).

![UV-Visible spectrum](image)

**Fig15:** UV-Visible spectrum of extended hexagonal gold clusters

Density of states

DOS spectrum of extended hexagonal clusters was plotted in fig 16. Density of states as well as band width increases sharply with increase in number of atoms.

![Density of states](image)

**Fig16:** DOS of extended hexagonal gold clusters
**4.6 Unequal hexagon**

The DFT study gives five different unequal hexagonal shapes for Au clusters having 12, 14, 16, 18 and 21 number of atoms. Au\textsubscript{12} and Au\textsubscript{18} possess D\textsubscript{3h} symmetry and others (Au\textsubscript{14}, Au\textsubscript{16}, Au\textsubscript{21}) possess D\textsubscript{2h}, C\textsubscript{s} and C\textsubscript{2v} respectively. The corresponding geometries are shown in fig 17. All the properties of these clusters are tabulated in table 5.

![Fig17: Optimized geometries of unequal hexagonal gold clusters](image)

<table>
<thead>
<tr>
<th>Cluster name</th>
<th>Binding energy</th>
<th>Average Co-ordination no</th>
<th>Average bond length</th>
<th>Average bond order</th>
<th>IP (eV)</th>
<th>EA (eV)</th>
<th>Chemical hardness</th>
<th>Electrophilic power</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au\textsubscript{12}</td>
<td>-1.61</td>
<td>4</td>
<td>2.8</td>
<td>0.32</td>
<td>7.41</td>
<td>3.37</td>
<td>2.01</td>
<td>7.20</td>
</tr>
<tr>
<td>Au\textsubscript{14}</td>
<td>-1.61</td>
<td>4.14</td>
<td>2.79</td>
<td>0.32</td>
<td>6.98</td>
<td>3.97</td>
<td>1.50</td>
<td>9.94</td>
</tr>
<tr>
<td>Au\textsubscript{16}</td>
<td>-1.65</td>
<td>4.25</td>
<td>2.79</td>
<td>0.33</td>
<td>7.14</td>
<td>3.89</td>
<td>1.62</td>
<td>9.36</td>
</tr>
<tr>
<td>Au\textsubscript{18}</td>
<td>-1.64</td>
<td>4.27</td>
<td>2.78</td>
<td>0.36</td>
<td>6.57</td>
<td>4.05</td>
<td>1.38</td>
<td>11.5</td>
</tr>
<tr>
<td>Au\textsubscript{21}</td>
<td>-1.68</td>
<td>4.47</td>
<td>2.81</td>
<td>0.35</td>
<td>7.03</td>
<td>4.26</td>
<td>1.26</td>
<td>11.19</td>
</tr>
</tbody>
</table>

Table 5: Properties of unequal hexagonal gold clusters

There is a slight increase in the binding energy and average coordination number from lower number to higher number. There is not much difference in average bond length and bond order for these clusters. Like other geometries IP shows an increase in value and EA decreases as the number of atoms increases. The same pattern was observed for chemical hardness and electrophilic power.

**UV-Visible spectrum**

Fig18 gives the corresponding UV spectrum for unequal hexagonal clusters. From the spectrum it is clear that from Au\textsubscript{12} to Au\textsubscript{18} there is a sharp increase in intensity of the peak and a slight shift towards the higher wavelength. And Au\textsubscript{21} shows a large shift (red shift) when compared with other clusters.
Density of states

A plot of DOS vs Energy is given in the Fig19. The density of states as well as band width shows an increase in trend with the increase in number of atoms. From the graph it is observed that Au$_{21}$ possess a maximum band width and higher density of states.

![Density of states graph](image)

---

**Fig18:** UV-Visible spectrum of unequal hexagonal gold clusters

**Fig19:** DOS of unequal hexagonal gold clusters
4.7 Extended pentagon

The optimized geometries $\text{Au}_n$ ($n=5, 8, 13, 15$) of extended pentagonal shape is shown below. All these geometries having the same $C_{2v}$ point group of symmetry.

![Fig20: Optimized geometries of extended pentagonal gold clusters](image)

### Table 6: Properties of extended pentagonal gold clusters

<table>
<thead>
<tr>
<th>Cluster name</th>
<th>Binding energy</th>
<th>Average Coordination no</th>
<th>Average bond length</th>
<th>Average bond order</th>
<th>IP (eV)</th>
<th>EA (eV)</th>
<th>Chemical hardness</th>
<th>Electrophilic power</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Au}_5$</td>
<td>-1.25</td>
<td>2.4</td>
<td>2.72</td>
<td>0.57</td>
<td>7.57</td>
<td>3.25</td>
<td>2.15</td>
<td>6.79</td>
</tr>
<tr>
<td>$\text{Au}_8$</td>
<td>-1.49</td>
<td>3.5</td>
<td>2.8</td>
<td>0.33</td>
<td>7.40</td>
<td>3.01</td>
<td>2.19</td>
<td>6.17</td>
</tr>
<tr>
<td>$\text{Au}_{13}$</td>
<td>-1.60</td>
<td>4.0</td>
<td>2.8</td>
<td>0.31</td>
<td>6.93</td>
<td>3.62</td>
<td>1.51</td>
<td>8.72</td>
</tr>
<tr>
<td>$\text{Au}_{15}$</td>
<td>-1.64</td>
<td>4.13</td>
<td>2.8</td>
<td>0.30</td>
<td>6.65</td>
<td>4.03</td>
<td>1.44</td>
<td>10.39</td>
</tr>
</tbody>
</table>

Table 6 gives the details regarding the properties of these clusters. The properties such as BE, average coordination number, EA and electrophilic power shows a sharp increase with increase in number of atoms. But average bond order, IP and chemical hardness shows a decrease in trend with increase in number of atoms.

#### UV-Visible spectrum

![Fig21: UV-Visible spectrum of extended pentagonal gold clusters](image)
The UV-Visible spectrum is shown in fig21, in which $\text{Au}_5$ shows maximum intensity around 367 nm. $\text{Au}_8$, $\text{Au}_{13}$, $\text{Au}_{15}$ possess maximum intensities around 383, 452 and 499 nm respectively. Hence it is very clear that there is large shift towards higher excitation energy with in number of atoms in the cluster.

**Density of states**

![Density of states graph]

Fig.22: DOS of extended pentagonal gold clusters

The d-band center position shifts to the higher binding energy side with decreasing the cluster size. There is a narrowing of the d band from higher number cluster to lower number and is due to hybridization of fewer wave-functions of valence electrons. The sharp change in DOS is very clear from $\text{Au}_8$ to $\text{Au}_{13}$.

**4.8 Three – three matrix**

![Cluster diagrams]

Fig23: Optimized geometries of three-three matrix gold clusters
Au\textsubscript{n} clusters having n=12, 18 and 21 was optimized and possess a three – three stacking arrangement of atoms two dimensionally. Among this Au\textsubscript{21} having C\textsubscript{2v} symmetry and other two geometries having C\textsubscript{2h} symmetry.

<table>
<thead>
<tr>
<th>Cluster name</th>
<th>Binding energy</th>
<th>Average Co-ordination no</th>
<th>Average bond length</th>
<th>Average bond order</th>
<th>IP (eV)</th>
<th>EA (eV)</th>
<th>Chemical hardness</th>
<th>Electrophilic power</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au\textsubscript{12}</td>
<td>-1.54</td>
<td>3.83</td>
<td>2.80</td>
<td>0.40</td>
<td>6.95</td>
<td>3.85</td>
<td>1.54</td>
<td>9.42</td>
</tr>
<tr>
<td>Au\textsubscript{18}</td>
<td>-1.60</td>
<td>4.11</td>
<td>2.78</td>
<td>0.33</td>
<td>6.78</td>
<td>4.12</td>
<td>1.32</td>
<td>11.21</td>
</tr>
<tr>
<td>Au\textsubscript{21}</td>
<td>-1.63</td>
<td>4.19</td>
<td>2.79</td>
<td>0.32</td>
<td>6.65</td>
<td>4.22</td>
<td>1.21</td>
<td>12.19</td>
</tr>
</tbody>
</table>

Table 7: Properties of three-three matrix gold clusters

The properties show a similar increasing and decreasing trend depending on the number of atoms are same as that of previously discussed geometries.

**UV-Visible spectrum**

The maximum intensity for Au\textsubscript{12} is around 410 nm and the peak intensity increases and the peak is shifted towards right when the cluster is having 18 number of atoms. Au\textsubscript{21} possess a maxima at 546 nm and there is notable shift from other two.

![UV-Visible spectrum](image)

Fig. 24: UV-Visible spectrum of three-three matrix gold clusters
Density of states

Fig25: DOS of three-three matrix gold clusters

Like other geometries DOS and band width shows an increase in trend with increase in number of atoms. Au$_{21}$ having a higher DOS at specific energy level and Au$_{12}$ having the least. It is shown in fig25

4.9 Three – two matrix

The optimized geometries of Au$_{10}$, Au$_{12}$ and Au$_{13}$ having a three – two matrix type arrangement of atoms and is shown in figure. Au 12 and Au 13 possess a D$_{2h}$ symmetry and Au$_{10}$ possess C$_{2v}$ symmetry.

![Optimized geometries of three-two matrix gold clusters](image)

Table 8: Properties of three-two matrix gold clusters

<table>
<thead>
<tr>
<th>Cluster name</th>
<th>Binding energy</th>
<th>Average Coordination no</th>
<th>Average bond length</th>
<th>Average bond order</th>
<th>IP (eV)</th>
<th>EA (eV)</th>
<th>Chemical hardness</th>
<th>Electrophilic power</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au$_{10}$</td>
<td>-1.57</td>
<td>3.6</td>
<td>2.79</td>
<td>0.34</td>
<td>7.65</td>
<td>2.99</td>
<td>3.49</td>
<td>1.74</td>
</tr>
<tr>
<td>Au$_{12}$</td>
<td>-1.56</td>
<td>3.83</td>
<td>2.81</td>
<td>0.31</td>
<td>6.9</td>
<td>3.84</td>
<td>2.32</td>
<td>6.08</td>
</tr>
<tr>
<td>Au$_{13}$</td>
<td>-1.58</td>
<td>3.69</td>
<td>2.78</td>
<td>0.33</td>
<td>6.00</td>
<td>5.06</td>
<td>1.07</td>
<td>11.22</td>
</tr>
</tbody>
</table>

Table8: Properties of three-two matrix gold clusters
**UV-Visible spectrum**

![UV-Visible spectrum graph](image)

Fig27: UV-Visible spectrum of three-two matrix gold clusters

A small red shift in the peak is observed from $\text{Au}_{10}$ to $\text{Au}_{13}$. $\text{Au}_{10}$, $\text{Au}_{12}$, $\text{Au}_{13}$ having maximum intense peak at 378, 400 and 420 nm respectively.

**Density of states**

![Density of states graph](image)

Fig28: DOS of three-two matrix gold clusters

There is not much difference in the number of atoms in the clusters. Hence there is no differentiable change in the Density of state spectrum.

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4.10 Three – four matrix

After the DFT analysis for geometry optimization to find out the global minimum configuration, the following clusters were obtained with three – four stacking of atoms two dimensionally.

![Fig29: Optimized geometries of three-four matrix gold clusters](image)

All the structural properties such as BE, average coordination number, average bond length, average bond order, IP, EA, chemical hardness and electrophilic power were evaluated and listed as follows.

<table>
<thead>
<tr>
<th>Cluster name</th>
<th>Binding energy</th>
<th>Average Coordination number</th>
<th>Average bond length</th>
<th>Average bond order</th>
<th>IP (eV)</th>
<th>EA (eV)</th>
<th>Chemical hardness</th>
<th>Electrophilic power</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au_{11}</td>
<td>-1.56</td>
<td>3.63</td>
<td>2.79</td>
<td>0.35</td>
<td>7.06</td>
<td>3.88</td>
<td>1.55</td>
<td>9.53</td>
</tr>
<tr>
<td>Au_{14}</td>
<td>-1.61</td>
<td>4</td>
<td>2.80</td>
<td>0.38</td>
<td>6.98</td>
<td>3.91</td>
<td>1.57</td>
<td>9.58</td>
</tr>
<tr>
<td>Au_{17}</td>
<td>-1.65</td>
<td>4.23</td>
<td>2.81</td>
<td>0.37</td>
<td>6.91</td>
<td>3.98</td>
<td>1.42</td>
<td>10.25</td>
</tr>
<tr>
<td>Au_{24}</td>
<td>-1.70</td>
<td>4.41</td>
<td>2.81</td>
<td>0.40</td>
<td>6.83</td>
<td>4.18</td>
<td>1.36</td>
<td>11.25</td>
</tr>
</tbody>
</table>

Table9: Properties of three-four matrix gold clusters

As the cluster size increases from Au_{11} to Au_{24}, there is a large increase in the binding energy. Average coordination number increases from 3.36 to 4.41 from Au_{11} to Au_{24}. There is a slight increase in average bond length when moves from lower to higher cluster. The average coordination number and bond length are responsible for the activity of catalysts in catalytic reactions. Cluster with the shorter bond length is tightly held together and the cluster is said to be contracted cluster. For the adsorption of gas molecules, the surface coordinative unsaturated sites will have more attraction towards gas molecules. In clusters due to surface relaxation, the coordination number of a particular atom may vary. Here the average coordination number could help to predict favourable adsorption on the surface. The average bond order increases with increase in number of atoms. As the cluster size increases from Au_{11} to Au_{24} the IP value corresponds to those clusters decreases. Catalysts having higher ionization potentials are commonly less reactive. Bulk gold possesses an ionization potential of 9.2eV, and it is inert. But Nano gold particles show difference in IP when compared with
bulk, and are active catalysts. Electron affinity is an important property that governs the electron transfer between catalyst and reactant in catalytic reactions. EA for these clusters shows a linear increase with increase in size of the cluster. Chemical hardness increase from $\text{Au}_{11}$ to $\text{Au}_{24}$ and electrophilic power shows an opposite behaviour.

**UV-Visible spectrum**

![UV-Visible spectrum](image)

Fig30: UV-Visible spectrum of three-four matrix gold clusters

The UV-Visible spectrum of three-four matrix clusters is plotted in Fig30. $\text{Au}_{11}$ cluster possess maximum molar absorptivity at 418 nm and it is shifted to 420 nm for $\text{Au}_{14}$ and it again shifted to 485 nm for $\text{Au}_{17}$ and finally the maxima for $\text{Au}_{24}$ is around 490 nm. As the number of atoms increases there is a shift in the intensity towards the higher wavelength region and is called red shift.

**Density of states**

DOS of a system is described as the number of states per interval of energy at each energy level that are available to be occupied by the electrons. The d-band width and spin-orbit splitting values decrease steeply with decreasing number of atoms and the band narrowing is caused by hybridization of fewer wave-functions of valence electrons\textsuperscript{29}. The d-band center position shifts to the higher binding energy side with decreasing the cluster size. In this DOS spectrum, it is seen that a higher DOS is observed for $\text{Au}_{24}$ and lower for $\text{Au}_{11}$. The position of the d-band center influences strength of the interaction and the occupancy of the resulting states, which are directly related to the adsorption energy. A high DOS at specific energy
level means that there are many states available for occupation. A DOS of zero means that no states can be occupied at that energy level.

![Density of States (DOS) graph for different matrix gold clusters](image)

**Fig. 31:** DOS of three-four matrix gold clusters
4.11 CO OXIDATION OVER GOLD NANO CLUSTERS

4.11.1 CO adsorption on Au

For calculation, all the previously discussed Au nano clusters were used. CO molecule is placed in every possible adsorption sites on these clusters and was optimized. Clusters having the lowest value for adsorption energy are energetically favourable and they are selected for further reaction of CO oxidation. The optimized CO adsorption modes on these clusters were shown in Fig.32.

![Fig.32: CO adsorption on gold clusters](image)

All the properties of these clusters were listed in table

<table>
<thead>
<tr>
<th>Cluster name</th>
<th>$E_{ads}$ (eV)</th>
<th>$v_{CO}$ (cm$^{-1}$)</th>
<th>$d_{C-Au}$ (Å)</th>
<th>$d_{C-O}$ (Å)</th>
<th>NBO(O)</th>
<th>NBO(C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au$_4$</td>
<td>-1.45</td>
<td>2056.78</td>
<td>1.95</td>
<td>1.16</td>
<td>-0.378</td>
<td>0.486</td>
</tr>
<tr>
<td>Au$_5$</td>
<td>-1.05</td>
<td>2020.12</td>
<td>1.98</td>
<td>1.16</td>
<td>-0.389</td>
<td>0.487</td>
</tr>
<tr>
<td>Au$_7$</td>
<td>-1.05</td>
<td>2020.78</td>
<td>1.98</td>
<td>1.16</td>
<td>-0.389</td>
<td>0.493</td>
</tr>
<tr>
<td>Au$_{10}$</td>
<td>-1.90</td>
<td>2052.79</td>
<td>1.97</td>
<td>1.16</td>
<td>-0.375</td>
<td>0.498</td>
</tr>
<tr>
<td>Au$_{12}$</td>
<td>-1.62</td>
<td>2050.82</td>
<td>2.00</td>
<td>1.16</td>
<td>-0.382</td>
<td>0.493</td>
</tr>
<tr>
<td>Au$_{12a}$</td>
<td>-0.93</td>
<td>2033.46</td>
<td>2.00</td>
<td>1.16</td>
<td>-0.386</td>
<td>0.503</td>
</tr>
<tr>
<td>Au$_{14}$</td>
<td>-1.14</td>
<td>2036.11</td>
<td>1.98</td>
<td>1.16</td>
<td>-0.379</td>
<td>0.506</td>
</tr>
<tr>
<td>Au$_{17}$</td>
<td>-0.83</td>
<td>2035.46</td>
<td>2.00</td>
<td>1.16</td>
<td>-0.381</td>
<td>0.506</td>
</tr>
<tr>
<td>Au$_{18}$</td>
<td>-2.03</td>
<td>2049.95</td>
<td>1.99</td>
<td>1.16</td>
<td>-0.381</td>
<td>0.491</td>
</tr>
</tbody>
</table>

Table.10: Properties of CO adsorption on Au

The adsorption energy of the clusters should have higher negative value for favourable adsorption of CO molecule. A negative value of $E_{ads}$ denotes an exothermic adsorption
process which means that the adsorption of CO molecules on the Au surface is energetically favourable, while a positive value of $E_{\text{ads}}$ denotes an endothermic adsorption process, implying that the adsorption of the CO molecules on Au surface is energetically unfavourable$^{28,30}$. Among the clusters Au$_{18}$ possess the lowest value for adsorption energy (-2.03915). The CO stretching frequencies are also changing when adsorbed to Au. Vibration analysis confirms that the optimized configurations are stable. The bond length of CO is predicted to be 1.16 Å which is in good agreement with available experimental data and theoretical results (1.15 Å)$^{24}$. The NBO charges were also calculated because charge distribution on carbon atoms is important for finding the adsorption sites on Au. The NBO charges for free CO is calculated as 0.496 for both C and O. When it is adsorbed to Au, the NBO charges were changing due to some charge transfer between CO and Au.

4.11.2. O$_2$ adsorption on Au

Oxygen molecule is adsorbed on these stable gold clusters in different adsorption sites. And the most favourable adsorption modes are given in Fig.33.

![Fig.33: O$_2$ adsorption on gold clusters](image)

The various properties of these geometries are tabulated in table

<table>
<thead>
<tr>
<th>Cluster name</th>
<th>$E_{\text{ads}}$ (eV)</th>
<th>$d_{O-Au}$ (Å)</th>
<th>$d_{o-o}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au$_4$</td>
<td>-0.77</td>
<td>2.13</td>
<td>1.31</td>
</tr>
<tr>
<td>Au$_5$</td>
<td>-2.22</td>
<td>2.21</td>
<td>1.32</td>
</tr>
<tr>
<td>Au$_7$</td>
<td>-2.13</td>
<td>2.20</td>
<td>1.33</td>
</tr>
<tr>
<td>Au$_{10}$</td>
<td>-1.63</td>
<td>2.16</td>
<td>1.31</td>
</tr>
<tr>
<td>Au$_{12}$</td>
<td>-1.67</td>
<td>2.17</td>
<td>1.36</td>
</tr>
<tr>
<td>Au$_{12a}$</td>
<td>-1.01</td>
<td>2.13</td>
<td>1.37</td>
</tr>
<tr>
<td>Au$_{14}$</td>
<td>-1.00</td>
<td>2.24</td>
<td>1.36</td>
</tr>
<tr>
<td>Au$_{17}$</td>
<td>-1.87</td>
<td>2.58</td>
<td>1.27</td>
</tr>
<tr>
<td>Au$_{18}$</td>
<td>-1.78</td>
<td>2.14</td>
<td>1.32</td>
</tr>
</tbody>
</table>

Table.11: Properties of O$_2$ adsorption on Au
The predicted adsorption energies of O$_2$ molecule on these clusters were slight higher (more negative) than adsorption energies for CO. The bond length of free O$_2$ molecule is predicted to be 1.270 Å. When it is adsorbed to Au nano cluster, the bond is elongated to 1.3 Å. Some significant distortions of the Au cluster are caused by the strong adsorption of O$_2$ which also provides more degrees of freedom for reaction sites. The most energetically favourable configuration is characterized by O$_2$ parallel to Au nano clusters. Among these clusters Au$_5$ possess more negative value for adsorption energy. So Au$_5$ is selected for discussing CO oxidation mechanism. The bond length of O$_2$ adsorbed on on Au$_5$ is elongated to 1.32 which means the O$_2$ is activated.

4.1.2 CO oxidation reaction mechanisms

Generally, there are two well established mechanisms for CO oxidation with O$_2$, namely, the Langmuir–Hinshelwood (LH) mechanism and the Eley–Rideal (ER) mechanism$^{28}$. The LH mechanism involves the co-adsorption of CO and O$_2$ molecules on the catalyst surface before reaction, reaction of the co-adsorbed CO and O$_2$ molecules, formation of a peroxo-type complex intermediate and desorption of the generated CO$_2$ molecule from the catalyst surface$^{23}$. In the ER mechanism, the CO molecules directly react with the adsorbed and activated O$_2$ (atomic O), where the activation of O$_2$ is the rate-limiting step. Here the mechanism involving molecular oxygen is selected for discussing the CO oxidation mechanism.

4.1.3 CO oxidation on Au$_5$ cluster

The CO oxidations on all the above discussed Au clusters were carried out and Au$_5$ is selected to discuss the mechanism. The reaction energy profile for CO oxidation on Au$_5$ cluster is given in figure 34. The initial geometry of pure Au$_5$ cluster is changing in each step of the reaction. This distortion in geometry will give more degrees of freedom for reaction sites. So the flexibility in shape of the catalyst during each step of the reaction is favourable for better activity. The relative free energy is compared with pure Au$_5$ cluster which is assumed to be zero. The adsorption of CO molecule and O$_2$ molecule on Au$_5$ is thermodynamically favourable. Because both having a negative value of relative free energy. But O$_2$ adsorption is more favourable because it is having more negative value than CO adsorption. When both CO and O$_2$ together adsorbed to Au$_5$, the relative free energy again decreases and there is a possibility for transfer of oxygen atom to CO molecule. Then the O$_2$ bond is dissociated and CO$_2$ is formed in the intermediate step. The next step is the
deformation of the Au$_5$ cluster which is an endothermic in nature. The relative free energy is increasing in this step. Finally the desorption of CO$_2$ is thermodynamically favourable, because the relative free energy is decreasing in this step.

Fig. 34: Reaction energy profile for CO oxidation on Au$_5$ cluster
Summary and Conclusion

- For Au\(_x\) (x = 4-28) different structures were created, from that the most stable configurations were identified using DFT/ B3LYP/ LanL2DZ.
- From the calculated Ionization potential, Electron affinity, average bond length, average bond order, chemical hardness and electrophilic power of the gold clusters, it is deduced that the cluster having optimum number of Au\(_n\) atoms will exhibit enhanced catalytic property.
- Density of States for the gold nano clusters was deduced.
- UV-Visible and IR spectrum of these nano clusters were studied.
- Various two dimensional shapes of Au cluster surface was optimized. All the different shapes possessed almost similar catalytic properties irrespective of the shape.
- From these studies the information on the activity of nano gold for CO oxidation reaction was postulated.
- CO oxidation is carried out over some selected Au nano clusters which possessed good adsorption energy values.
- Au\(_5\) nano cluster is selected for discussing mechanism of CO oxidation because it possessed good adsorption energies for CO and O\(_2\) adsorption. Some structural distortions of the catalyst during the course of the reaction was observed.
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