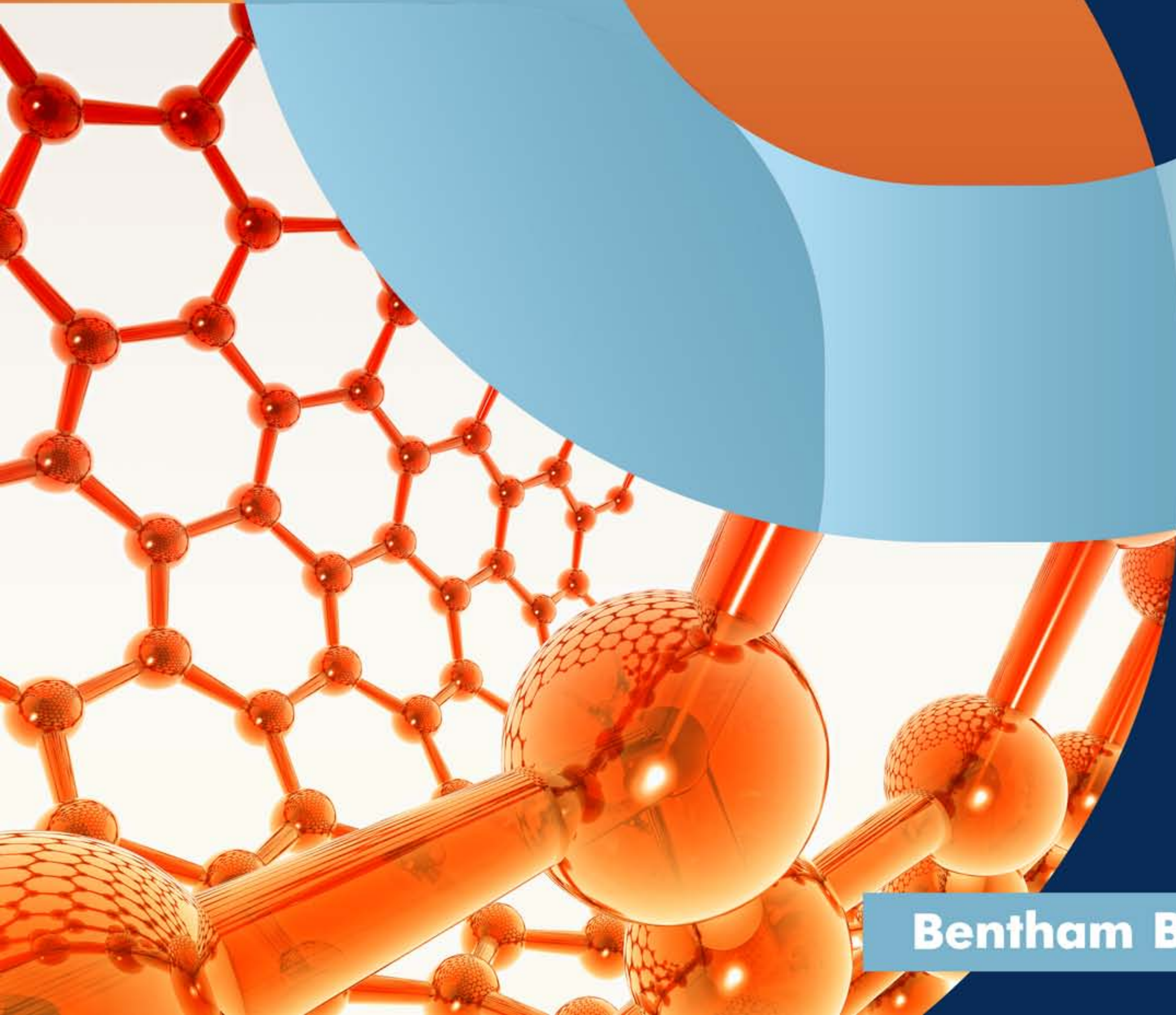

DFT-BASED STUDIES ON ATOMIC CLUSTERS

Ambrish Kumar Srivastava
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DFT-Based Studies on Atomic Clusters

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DFT-Based Studies on Atomic Clusters

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FOREWORD

Atomic clusters are usually a bunch of atoms whose dimensions are in between a molecule and a bulk material. Presumably, their properties may be quite different as compared to bulk material. This makes them interesting to explore by experimental and theoretical methods. Despite several technological advances, there are several difficulties in experimental studies on atomic clusters. This is where theoretical methods play a pivotal role. Among various available methods, density functional theory (DFT) is quite popular due to its better compromise between computational cost and accuracy. This is the reason that the DFT-based methods are frequently used to study a variety of atomic clusters.

It gives me immense pleasure to write the foreword of this book. ‘DFT-based studies on atomic clusters’ provides a very important and contemporary account of the research on atomic clusters using popular DFT methods. The book is divided into seven chapters. The first chapter introduces atomic clusters and provides a quick survey of density functional theory and its role in the study of atomic clusters. The next chapter discusses the optimization of atomic clusters using various algorithms. The subsequent chapters cover the applications of DFT methods on different themes. An exclusive chapter on molecular clusters has also been included for completeness. The book is concluded in the last chapter, and some future directions are also mentioned. The contents of the book are systematically and concisely presented. Several illustrations in the form of graphics and tables are included for the convenience of readers. Overall, this book is very useful to Ph.D. students and young researchers, among others, who are interested in exploring a miraculous world of atomic clusters by means of density functional theory.

I wish you all the best.

January 10, 2023

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PREFACE

Atomic clusters are collections of a few to a few thousand atoms, which possess unusual structures and interesting properties. For instance, fullerene is an atomic cluster of 60 carbon atoms with a spherical ball structure. The clusters are formed by most of the elements of the periodic table. However, there are several challenges in the experimental observation of clusters. This is where theoretical methods come in, and density functional theory (DFT) is more popular among them. The basic idea of writing a book on atomic clusters comes from our previous Bentham book entitled "DFT-Based Studies on Bioactive Molecules". Considering the increasing scope of theoretical studies, we studied several atomic clusters using various DFT methods. However, we always felt the need for a book dealing with atomic clusters and DFT methods.

This book entitled "DFT-Based Studies on Atomic Clusters" aims to fill a gap between DFT and atomic clusters. The book aims to introduce readers and researchers to the interesting world of atomic clusters, their properties, and their widespread scientific and technological applications explored by DFT. The book comprises seven chapters. The first chapter gives a background of atomic clusters, their types, and characteristics. It also provides some basics of DFT, its methods, and applications. After choosing an appropriate method, the very first step of a DFT study is geometry optimization. The second chapter discusses various optimization algorithms for local and global optimization of atomic clusters. The subsequent three chapters focus on the application of DFT on various transition metal-doped Cu clusters for CO_2 adsorption, endohedral metallofullerenes and their intermediates, coinage metal dimers and their interactions with nucleic acid bases, respectively. These are followed by an exclusive chapter on molecular clusters with a particular emphasis on H_2 adsorption by alkaline earth metal oxide clusters. The book is finally concluded in the last chapter, and some future perspectives are offered.

We are very thankful to Rabia Maqsood, manager of Bentham Books, for the support at every level and Prof. Neeraj Misra for writing the Foreword for this book.

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CHAPTER 1

Atomic Clusters: An Introduction

Abstract: An assembly of a few to thousands of atoms or molecules is referred to as a cluster. This chapter exclusively deals with atomic clusters and their classifications based on the nature of bonding and the number of constituents. The size effect, surface phenomena, and variation of properties with the size of atomic clusters have also been discussed. The difficulties in cluster experiments have been highlighted. Various theoretical methods to study the clusters have been mentioned, with the main focus on the density functional theory (DFT). The accuracy of various DFT methods and choosing appropriate methods have been particularly discussed. Finally, the way to perform DFT-based studies on clusters is also explored. This chapter provides a brief introduction to what the book is all about.

Keywords: Atomic clusters, Density functional theory, Fullerene, Size effect, Theoretical methods.

1.1. INTRODUCTION

The word 'cluster' stands for 'aggregates' or a 'bunch' or 'collection' of something. Atoms constitute molecules, but what do molecules constitute? One might say it is probably a bulk material. But this is not as simple as it appears. Rather it leads to a very fundamental question. *How many molecules are needed to behave as bulk materials?* Irrespective of the scale, molecules and bulk materials both are made up of atoms in a very specific fashion. For instance, the H_2O molecule contains H and O atoms so does ice or water. However, it is not known how many H_2O molecules or H and O atoms are there in 1 cc of ice or 250 ml of water. Let's leave this question right here and focus on the collections of atoms beyond the scale of molecules. This is what may be referred to as a 'cluster'.

The earliest mention of 'clusters' was probably made by Robert Boyle in 1661 in his book "The Sceptical Chymist". In the 20th century, the term "cluster" was used by F. A. Cotton in the early 1960s for the compounds having metal-metal bonds. Although clusters have attracted interest in the early 1930s [1], most of the developments in this field happened in the last five decades. Now, it is well known that the clusters are formed by most, if not all, of the elements in the

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periodic table, including the inert gases. The atmosphere contains several clusters of molecules. The clusters of carbon are found to be in soot and even in space. These clusters have several intriguing properties, which lead to their various applications. For instance, the clusters of the coinage metals (Cu, Ag, and Au) are found in stained glass windows.

1.2. CLUSTERS, MOLECULES AND NANOPARTICLES

In this context, clusters are referred to as finite aggregates containing a few to a few thousand constituents, *i.e.*, atoms or molecules. Thus, their size may vary from a few Å to nanometers. Therefore, they can be considered as intermediates between a typical molecule and bulk material, as shown in Fig. (**1.1**). Considering the composition and size, molecules and nanoparticles are also 'finite aggregates' of atoms, like clusters. For instance, at least two atoms can constitute a small molecule such as O_2, and hundreds or thousands make a macromolecule such as hemoglobin. Further, hundreds of thousands of atoms may form nanoparticles having size in nanometers. The definition of cluster overlaps with those of molecules and nanoparticles. There is no systematic way to distinguish them, unfortunately! There are certain facts, however, that can be useful 'sometimes' for such distinction. These facts often work as a rule of thumb.

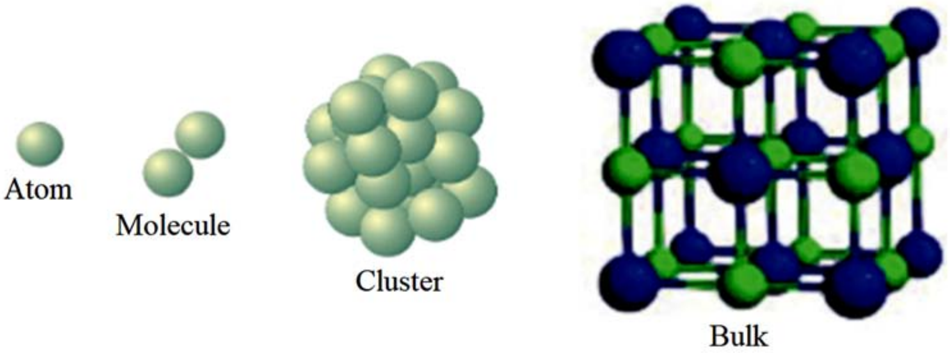

Fig. (1.1). Cluster as intermediate between molecule and bulk.

Molecules or compounds are known to exist in nature under ambient conditions, whereas clusters are formed in the laboratory under extreme conditions or vacuum. Molecules, being stable, interact weakly with each other, while clusters interact more strongly, in general, to form larger clusters. Molecules, by nature, have fixed size and composition, but those of clusters can be easily varied. The structures of molecules adopt specific geometries, unlike clusters, which may possess numerous geometries, *i.e.*, isomers. In molecules, atoms share their electrons to form covalent bonds, but clusters exhibit a variety of bonds, including van der Waals, metallic, covalent, and ionic bonds. As a matter of fact, molecules differ from clusters in several ways.

To differentiate clusters and nanoparticles is even more challenging. In clusters, size and composition can be controlled with atomic precision, *i.e.*, one atom at a time. On the contrary, the number of atoms in a nanoparticle cannot be determined with the same precision. For small clusters consisting of a few atoms, the properties vary unevenly and change widely with the addition of a single atom. With the increase in the size of a few hundred to thousand atoms (typically in the nanometer range), the variation in properties is less drastic. Over the years, the size of clusters has been increased, and that of nanoparticles has been reduced, making both close to each other, and the term 'nanoclusters' is often used to mediate between them.

The differences mentioned above are often derived from experience. There are no strict boundaries to separate clusters from molecules and nanoparticles. A good example is Buckminsterfullerene (C_{60}), named after Buckminster Fuller, an American architect. It is a hollow spherical ball-like cluster of 60 carbon atoms that are arranged in the form of 12 pentagons and 20 hexagons, as shown in Fig. (**1.2**). It was theoretically predicted by E. Osawa in 1970 [2] and experimentally synthesized by Kroto *et al.* in 1985 [3]. It is a highly stable cluster with the dimension of the order of 1 nm. Interestingly, it has most of the properties of a molecule, and it can be realized as a nanoparticle. It can be regarded as a 'nanocluster' [4].

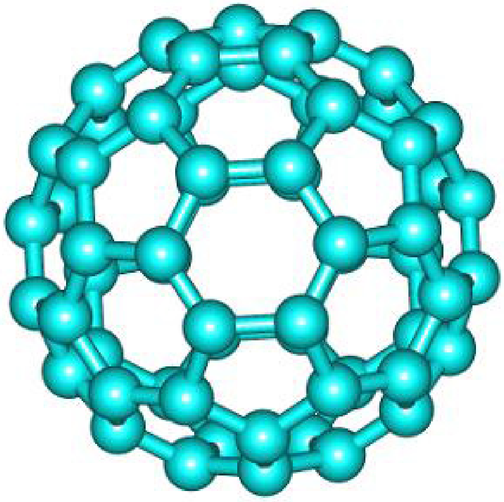

Fig. (1.2). C_{60}: an example of cluster, molecule, and nanoparticle.

CHAPTER 2

Structural Optimization of Atomic Clusters

Abstract: This chapter exclusively addresses the algorithms employed to perform geometry optimization of clusters. These algorithms can be broadly classified into two groups: gradients-based algorithms and gradient-free algorithms. Gradient-based algorithms use the gradient of potential energy functions to give local minima. On the contrary, gradient-free algorithms are inspired by natural processes, which exploit some mathematical models, which lead to global minimum. Although there are a variety of gradient-free algorithms, some of the most popular ones include genetic algorithm, particle swarm, simulated annealing, *etc*. The strengths and weaknesses of all these algorithms have been also discussed.

Keywords: Artificial bee colony, Gradient, Genetic algorithm, Geometry optimization, Global minimum, Garticle swarm, Local minima, Neural network, Simulated annealing.

2.1. INTRODUCTION

As mentioned in Chapter 1, the first step of the DFT study is to find the structure(s) of clusters. This is usually done by a process known as structural or geometry optimization. By optimization, we "generally" mean to find a configuration of atoms in a cluster corresponding to its minimum potential energy, be it local or global. For further discussion on geometry optimization, the readers may refer to the previous book [1]. Within the framework of DFT, the process of structural optimization is displayed in Fig. (**2.1**). It can be seen that a self-consistent method is used after guessing an initial structure or input geometry. If it does not meet the optimization criteria, one needs to choose a new input geometry according to the optimization algorithm. An optimization algorithm, for our purposes, is a special method or program to find the optimized structure(s). These optimization algorithms can be classified into two major groups: gradient-based algorithms and gradient-free algorithms.

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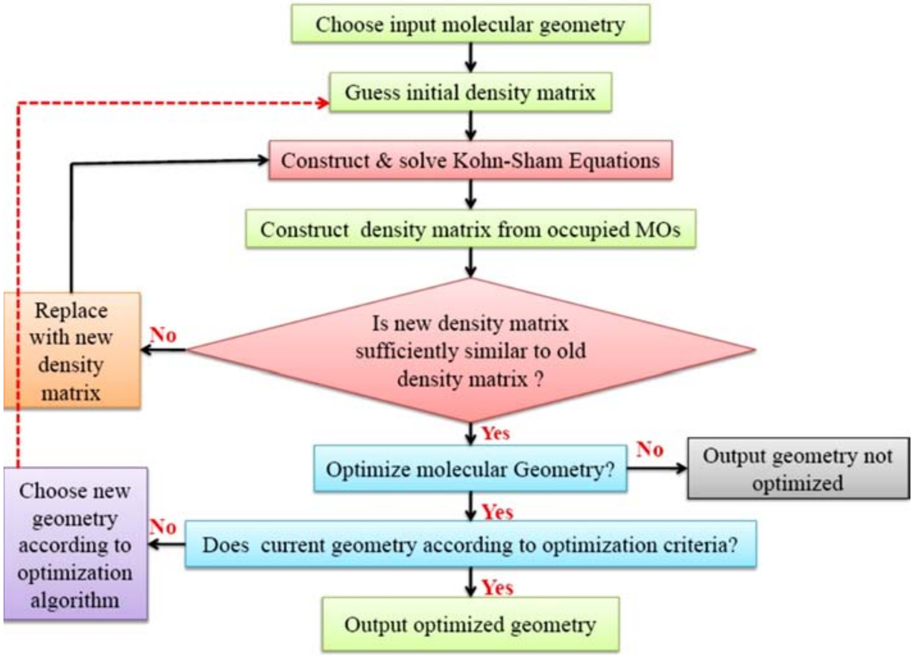
Choose input molecular geometry
Guess initial density matrix
Construct & solve Kohn-Sham Equations
Construct density matrix from occupied MOs
Is new density matrix sufficiently similar to old density matrix ?
No
Replace with new density matrix
Yes
Optimize molecular Geometry?
No
Output geometry not optimized
Yes
Does current geometry according to optimization criteria?
No
Choose new geometry according to optimization algorithm
Yes
Output optimized geometry

Fig. (2.1). Flowchart for geometry optimization of clusters using DFT-based methods.

2.2. GRADIENT-BASED ALGORITHMS

It is based on the gradient of a potential energy function in a $3N$-dimensional space, commonly known as a potential energy surface of a cluster of N atoms. Consider a dimer whose potential energy (V) curve is shown in Fig. (**2.2**). P_i and P_0 are the points corresponding to input geometry with the potential energy V_i and an inter-atomic distance R_i, and optimized geometry with V_o and an inter-atomic distance of R_0. Considering the vibration of atoms, we have,

$$V - V_o = \frac{k}{2}(R - R_O)^2 \tag{2.1}$$

For point P_i,
$$\left(\frac{\partial V}{\partial R}\right)_i = k(R_i - R_O) \tag{2.2}$$

In general, we get,
$$\left(\frac{\partial^2 V}{\partial R^2}\right) = k \tag{2.3}$$

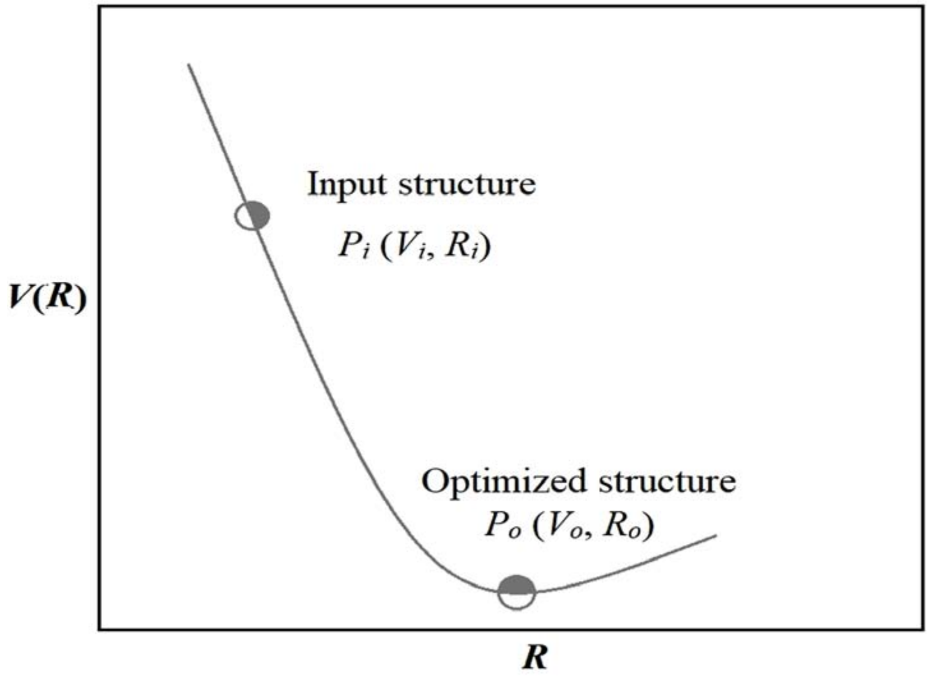

Fig. (2.2). Potential energy function with respect to the interatomic distance for a dimer.

Substituting eq. (2.3) in eq. (2.2) leads to,

$$R_O = R_i - \left(\frac{\partial V}{\partial R}\right)_i \Big/ \left(\frac{\partial^2 V}{\partial R^2}\right) \qquad \textbf{(2.4)}$$

Generalizing the above treatment for a 3*N*-dimensional space such that V≡E and R≡q, the initial matrices for the derivative of energy (gradient matrix, g_i) and force constant (Hessian matrix, H_i) with respect to geometry can be expressed as:

$$\boldsymbol{g}_i = \begin{pmatrix} (\partial E/\partial q_1)_i \\ (\partial E/\partial q_2)_i \\ \vdots \\ (\partial E/\partial q_N)_i \end{pmatrix} \qquad \textbf{(2.5)}$$

CHAPTER 3

Adsorption of CO_2 on Transition Metal-Doped Cu Clusters: A DFT Study

Abstract: Activation of CO_2 is the first step towards its reduction to more useful chemicals. Electrochemical CO_2 reduction reactions can lead to high value-added chemical and materials production while helping decrease anthropogenic CO_2 emissions. In studies, it was found that copper metal clusters can reduce CO_2 to more than thirty different hydrocarbons and oxygenates, yet they lack the required selectivity. Density functional theory (DFT)-based studies are carried out on copper clusters, doped clusters, nano-structures and Cu-based alloy catalysts to assess the activity and selectivity of CO_2 reduction to generate carbon monoxide (CO), formic acid (HCOOH), formaldehyde (H2C=O), methanol (CH_3OH) and methane (CH_4). In this chapter, we will discuss the effect of the adsorption of CO_2 on (Sc, Ti, V) metal-doped clusters. DFT studies carried out for these clusters showed a high CO_2 adsorption energy, a low activation barrier for its dissociation, and a facile regeneration of the clusters. The reaction energies (dopant-dependent), the mechanisms for reaction, dissociation barriers for $CO_{2,}$ and less desorption energies (dopant dependent) for carbon monoxide (CO) during the activation of CO_2 with Cu_3X clusters (X= first row transition metals) are discussed in the chapter. C_6Li_6 is not capable of capturing CO_2 molecules but is effective in their storage. The interaction of $CO_2$with superalkalis such as FLi_2, OLi_3, and NLi_4 and non-metallic superalkalis such as F_2H_3, $O_2H_{5,}$ and N_2H_7 is also included due to its applications.

Keywords: Adsorption, Catalysts, Copper clusters, Materials, Regeneration.

3.1. INTRODUCTION

CO_2 reduction is an urgent problem for society due to increased CO_2 emission from the combustion of fossil fuels. Severe problems of climate crisis arise due to the rise of its atmospheric aggregation and reduced pH of the hydrosphere [1 - 8]. To avoid and solve this problem, CO_2 capture, storage, or recycling to commercially useful chemical compounds, such as CH_3OH, might be a solution [1, 7, 9 - 14]. Although the hydrogenation of CO_2 to CH_3OH is possible in a thermodynamic manner, it is inhibited by other kinetic obstacles [15].

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In recent years, due to the demand for sustainable fuel solutions, alternative options for increased fossil fuel consumption, such as CO_2 utilization, have been necessary. The reduction of CO_2 means either a reduction of CO_2 emissions in the atmosphere or a chemical reduction of CO_2 for enriched products. The reduction of CO_2 in the atmosphere is caused by carbon capture and storage (CCS), while another use is to recycle the CO_2 waste and employ it for zero waste emission [16]. In this regard, two processes can be opted: (1) hydrogenation to HCOOH or CH_3OH [17] carried out homogeneously in liquid and catalytic phase in a reversible manner, which is used for effective hydrogen storage, and [18] (2) reduction of CO_2 to CO, which is used as feedstock for the synthesis of fuels (Fischer–Tropsch process) [19]. In this process, heterogeneous cobalt-based catalysts in the gas phase and elevated temperatures are used [20]. Yet the unfavorable thermodynamics of the reaction is the major limitation to the effective use of CO_2 reduction. The first step is the transfer of the first electron to the CO_2 molecule with 1.9 eV energy, which is a thermodynamically favorable step in hydrogenation [21] and is possible with active and rare earth metal-based catalysts. The electrochemical CO_2 reduction reaction (eCO_2RR) is used to convert CO_2 because the eCO_2RR could attain a carbon-neutral energy cycle if combined with electricity from sustainable resources. The main challenge in the electrochemical CO_2 reduction reaction is how to activate the competitive CO_2-reducing pathways, such as the hydrogen evolution reaction (HER) and the conversion of CO_2 to a particular product with high selectivity. The slight difference in the electrochemical potentials (ECPs) of CO_2 reduction forms different products. For example, the ECP for the transformation of CO_2 to ethylene is −0.34 V, while the ECP for the transformation of CO_2 to CH_3OH is −0.38 V. These values are taken relative to the standard hydrogen electrode (SHE) [22, 23].

Gas phase clusters have well-defined, precise geometric structures. These clusters are used to find out the sites for the catalytic activity of the catalysts [24 - 26]. These clusters reveal the role of cluster size and geometry, dopants, charge state, and the reaction mechanism [27 - 30]. The widely used catalysts are noble metal-based and transition metal catalysts, as they are relatively stable under reactive conditions. The combination of different metals has various synergistic effects. Among various clusters, copper is the most promising metal for CO_2 reduction. Cu is widely used in coupling reactions and the hydrogenation of CO_3^{2-} to CH_3OH [31 - 33]. Cu catalysts hydrogenate CO_2 to CHOH, which is used for the selectivity of good CH_3OH at low temperatures [34, 35].

DFT studies are carried out on copper surfaces (111, 211), small to medium-sized copper clusters Cu_n ($n = 13, 15, 19, 55, 79$) and metal-mediated reduction of CO_2 to CO [36 - 40]. The cationic copper clusters are used to facilitate dissociative H_2

adsorption in CO_2 hydrogenation [41, 42]. Cu nanoparticles and nanoclusters deposited on ZnO are more active than conventional catalysts. A combined experimental and computational study showed that Cu_4 clusters are highly reactive and have lower bond barrier energy for the reduction of CO_2 to CH_3OH [43, 44]. The effect on the size of the cluster and support has been investigated in reactivity toward CO_2.

3.2. COMPUTATIONAL DETAILS

DFT studies are carried out using various software such as Q-Chem 5.3 [45] with TPSSh/ def2-TZVP [46, 47]+D3 method, and Siesta [48] and CASTEP package [49]. In CASTEP, GGAPBE functional is used to calculate the electronic wave functions with a plane-wave basis set, as well as ultra pseudopotentials inside the ionic cores. The cut-off energy, Monkhorst–Pack k points sampling, is initiated according to the predictive model. For activation barriers of CO_2 dissociation, the transition states are searched by linear synchronous transit (LST)/quadratic synchronous transit (QST) method. Further nudged elastic band (NEB) calculations are carried out using transition state (TS) conformers. VASP [50] is used for structural and energy calculations with spin-polarized DFT level with Grimme's-D3 dispersion correction and Perdew– Burke–Ernzerhof (PBE) exchange-correlation functional with a kinetic energy cutoff (E_{cut}) according to the structural parameters. The energies, zero point energies, and entropies are computed with free energy corrections.

The electronic structure calculations are carried out with Wiberg bond indexes, natural charges [51, 52], energy decomposition analysis (EDA) [53], and frontier molecular orbitals (FMO). In a study, reaction energies are calculated from the lower energy bare gas phase clusters with CO_2 molecules. Tamkin library [54] is used to estimate the free energies calculated at different temperatures. The free energies are calculated using the computational hydrogen electrode (CHE) method [55].

The Gibbs free energy of each step is calculated by:

$$\Delta G = \Delta S + \Delta E_{ZPE} - T\Delta S + \Delta G_{solv} + \Delta GU \qquad \textbf{(3.1)}$$

where ΔE - reaction energy, ΔE_{ZPE} - change in zero-point energy (ZPE), ΔS - change in entropy, and T - temperature (300 K).

DFT is used to estimate the stability of studied adsorbates and clusters. VASPsol [56] calculates the solvation-free energy ΔGsolv. ΔGU is the free energy correction. For joint proton-electron transfer (CPET), the ΔGU term can be calculated by:

CHAPTER 4

DFT Studies on Intermediates for Sizeable Endohedral Metallofullerenes

Abstract: “Endohedral metallofullerenes (EMFs)”, also known as metallofullerenes, are the hybrid molecules of spherical nanocarbons. The structure of EMFs consists of atomic metal(s) or metal-containing clusters enclosed inside the fullerenes. These unique EMFs have potential applications in various fields. Smalley and coworkers first reported the EMFs in 1985 [1], soon after C_{60} was discovered. In this chapter, we will discuss the computational studies carried out for the various types of EMFs and their potential role in industrial applications. Endohedral metallofullerenes $M@C_{44}$ containing several different gap atoms of scandium and titanium family are experimentally detected. Dispersion-corrected DFT was carried out to study C_{44} and its fullerene derivatives to calculate the binding properties and interactions. Results showed that the computational and experimental studies agreed well with C_{44} and its endohedral compounds. Results predicted that C_{44} D_2 (89) isomer is suitable for forming endohedral compounds. The binding affinity of the endohedral atom and its enclosure showed good profusion of these clusters. The DFT studies are used to study different characteristics of the doped C_{44}-D_2 (89) to the tri and tetra anions of empty C_{44}-D_2 clusters. These metal−cage bonds possess partial (ionic and covalent) interactions. The aromaticity of the cage is estimated with nucleus-independent chemical shift (NICS(0)), as it plays a vital role in balancing the endohedral species.

Keywords: Clusters, Doping, DFT, Metallofullerenes, Interactions.

4.1. INTRODUCTION

Endohedral metallofullerenes (EMFs) are the molecular species in which metal is confined within a fullerene carbon cage. Smalley and coworkers first reported the EMFs in 1985, soon after C_{60} was discovered [1]. The fullerenes led to another discovery of internally doped compounds as endohedral fullerenes (EFs) in which different types of metals were put inside the fullerene. Endohedral metallofullerenes are used in solar cells, quantum computing, magnetic materials, and biomedical applications [2 - 5]. The encapsulated clusters and their cages can be tuned for physicochemical properties. The cluster/cage interactions determine

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the reactivity and structure of the EMFs. The first stable EMF, La@C_{82}, was detected by Smalley *et al*. Later on, the mono-EMFs and di-EMFs were discovered. Sc3N@C_{80} is the third most desired fullerene, which is prepared using the Kratschmer-Huffman method. These cluster fullerenes have wide applications in next-generation photovoltaic devices. The other potential biomedical applications of cluster fullerenes include them as diagnostic and therapeutic agents. Endohedral fullerenes consisting of atoms, ions, molecules, or clusters encapsulated in the C_{60} cage show particular structures. The physicochemical properties are due to the encapsulated clusters and their cages. The structure and reactivity of the EMFs are determined by the cluster/cage interactions [6]. Previous studies showed that fullerene cages can be modified by encapsulating various species [7 - 12], and the unusual properties of EMFs are used for biomedical [13 - 15] and photovoltaics applications [16].

These types of EMFs are synthesized by laser evaporation of graphite rods with doped metal in the gas phase. The accumulation and propensity of the combined species for buckyball cages with more than 60 carbon atoms are provided by mass spectrometry (MS) [17, 18]. It is seen that the negative charge of the fullerene cage is increased by the doped metal, which further increases the activity of EMFs [19, 20]. The fullerenes with less than 60 carbon atoms are also exploited due to their constrained compositions and atypical properties [20]. These smaller fullerenes defy the isolated pentagonal rule (IPR) [21]. The IPR states that all pentagons are surrounded by hexagons only. These fullerenes with small sizes can form large EMFs, such as M@C_n (n=28, 36, 44, 50) [20]. EMFs such as M@C_{28} and larger M@C_{36} with group 4 atoms show stability [20, 21], but the explanation for the stability is still unknown. Also, these EMFs are not aromatic, and there is no known method to stabilize M@C_{44} and M@C_{50} endohedral fullerenes [22 - 24]. Yet the stable structure of M@C_{28} and M@C_{36} EMFs may be due to electron donation from metal to the outer cage [25]. The oxidation state of the enclosed atom is determined by the ionization potential (IP).

4.2. COMPUTATIONAL DETAILS

The computational studies were carried out to study the electronic properties of EMFs M@C_{44} with endohedral transition metals (scandium (Sc), yttrium (Y), and lanthanum (La)) and group 4 (titanium (Ti), zirconium (Zr), and hafnium (Hf)) elements with density functional theory (DFT) [26]. The Perdew−Burke−Ernherzof (PBE) [27, 28] functional with effective core potential (ECP) def2- TZVP [29] basis set was used for the groups 5 and 6 elements. TURBOMOLE 6.5 package [30] was used to calculate the lower minima structures, and dispersion correction method D3(BJ) [31] was used to calculate the binding energies of the EMFs. The theoretical calculations were validated by the experimental studies. The structural, vibrational, and energetic properties of buckyball [32, 33] and endohedral compound Ar@C_{60} [34, 35] were measured with dispersion-corrected terms as it was observed that the dispersion-corrected structures gave much more accurate results. Various potential energy surface (PES) structures were scanned for the two isomers with D_2 symmetry and the geometrical restraints within the hollow gap of EMFs.

The structure of endohedral species (center of the cage) was shifted by 1 Å off-center along different directions. The optimized geometries with spin multiplicity (2), with real vibrational frequency and lower minima, were reported and analyzed further. The vertical ionization energies (VIEs) and vertical electron affinities (VEAs) for the EMFs and the two potential C_{44} isomers were calculated. The binding energies (BE_{ZPE}) are calculated by;

$$BE_{ZPE} = E_{ZPE}(M@C44) - E(M) - E_{ZPE}(C44) \qquad \textbf{(4.1)}$$

where $E_{ZPE}(M@C_{44})$ is the energy of the globally minimized M@C_{44} compound with the ZPE correction, $E_{ZPE}(C_{44})$ is the optimized zero point energy (ZPE) for the optimized state $C_{44}^{-}D_2$, and E(M) is the endohedral atom energy (ground state). Hirshfeld population analysis was used to obtain the distribution of charges. G09 [36] software program was used to carry out the single point calculations at PBED3(BJ)/def2-TZVP level. Gaussview 5.0 program [37] was used to plot the electrostatic potential (ESP) maps (0.01 au-isosurface) and frontier orbitals (HOMO, LUMO) from 0.02 au values. The aromaticity of all the M@C_{44} compounds was determined by the indices NICS(0). The computational studies with appropriate methods were used to calculate the nuclear magnetic resonance (NMR) isotropic constituent. The ADF software with scalar relativistic DFT [38] appropriate functionals and basis sets was used for the analysis of selected segments. The calculations involved the PBE functional and GGA with [39] DFT-D3 to include the weak London dispersion effects [39]. Calculations regarding the relativistic effects were included through ZORA Hamiltonian [40], and unrestricted DFT methods were used for unpaired electrons.

4.3. RESULTS AND DISCUSSION

(89) isomer structures of C_{44} [23] were generated, out of which, some structures were hollow [41, 42], and few were already synthesized earlier [41]. Two isomers exhibiting D_2 symmetry were considered suitable geometries [43, 44]. The fullerene C_{44}-D_2 (89) violated the IPR [23, 24] and formed 4 triple sequentially fused pentagon (TSFP) units separated by 4 clusters of each 3 hexagons. See Fig. (**4.1**) [45].

CHAPTER 5

DFT Studies on Nucleic Acid Base (NAB)−M_2/M_2^{2+} Complexes

Abstract: Metal clusters, atomically precise aggregates of metal atoms, when prepared in the gas phase, produce only “magic numbers” sizes. Small-sized metal clusters (2 nm (<~100 atoms)) have different geometric and electronic properties as compared to bulk metal structures. Metal clusters are used as new functional nanomaterials in various applications. In this chapter, the interactive properties of different nucleic acid bases (NAB) with M_2/M_2^{2+} (M = Ag, Au, and Cu) are studied by theoretical means. Transition metals have a great affinity toward nucleic acids, which makes them suitable candidates for metal ion sensing, removal of toxic metal ions, and the construction of functional metal nanostructures. The highly significant symmetric dinuclear metal-mediated homo base pairs structures with significant stabilities play a vital role in various applications. Metal-nucleobase complexes have wide applications, such as sensors, bidirectional nucleobases, logic gates, and nanowires. A logic gate programs cells for biomedical and environmental applications. In this chapter, the electronic and optoelectronic properties of M_2 and M_2^{2+} with various NAB pairs, such as adenine−thymine (AT), adenine−uracil (AU), adenine thymine (ATAT) Watson Crick (WCST) stacking pairs, adenine−adenine stacking pairs (AAST), and adenine−adenine hydrogen bonding (AAHB) (M = Ag, Au, Cu), are studies, along with their applications.

Keywords: Bioimaging, Coinage metals, Nucleobases, Nanowires, Sensors.

5.1. INTRODUCTION

Metal-organic hybrid complexes are used for many fundamental biological processes. Nanotechnology has opened the biosensing, bioimaging, and medicinal applications with metal-nucleobase interactions such as copper (Cu)-mediated enzymes that are used to regulate the transport of oxygen, communication between neurons [1], and iron in hemoglobin and oxygen transport processes [2]. Other potential materials are silver clusters with DNA stabilization [3 - 5] and gold clusters with thiolate protection [6, 7]. Various properties and possibilities of these systems are still unexplored due to their stability in solution, which hinders their potential applications. Group 11 coinage metal clusters (Cu, Ag, and Au) have been explored widely, and they interact easily with organic and biological

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species [8, 9]. The electronic structure of these metals has an outermost shell with a single s-type electron and a d-type closed shell, which is energetically below. When these metal atoms accumulate with atomic combinations on a nanometric scale, the electron-electron interactions occur in the shell model (mean free type) [10]. The delocalized band is formed by 1s electron, but it shows a filled electron shell due to the quantum nature of the model. The stability of closed shells in nanosystems increases the stability. Magic sizes are defined by the increased stability of a given number of atoms.

Due to the conductivity and notable thermal duplex stability, nucleobase pair−metal ion complexes have been a topic of research in recent years [11 - 17]. These complexes have applications as quantum wires [11], biosensors [18], bidirectional nitrogenous bases [19], and logic gates [20]. The logic gates act as the binary choices of biological entities, which are targeted to program cells for sustainable sensors and medical usage [21 - 23]. DNA carries genetic information, and this regular and canonical information can be used to generate novel bioinspired functionalized materials. DNA-metal complexes have metal-nucleobase bonds [22], whereas the metal-nucleobase pair complexes have twofold complementary hydrogen bonds between nucleic acids. Many experimental and theoretical investigations have been carried out in recent years on dinuclear metal-nucleobase pairs and metal ion-nucleobase complexes such as dinuclear Ag ions complexes and diverse bases [23 - 29]. *Mandal et al*. [30 - 32] carried out studies on dinuclear (CuII and HgII) complexes that have synthetic nucleobase (9-ethyl-1, N6-ethenoadenine). Results showed that binuclear tritium (T)-mercury (Hg) II 2-A pair of nucleobases form (M-N) parallel bonds (two sets) with ligands (anionic), which compensate the charge of metal ions partially. The term “aurophilic bonding/interactions” for gold (Au+-Au+) was introduced in 1988 [33, 34]. In 1993, Vicente *et al*. [35] introduced “nucleophilicity” for (Ag, Au, and Cu) cations having weak closed-shell interactions. The term was further extended by *Pyykkö* [36] (1994) to “metallophilic interactions” for metal atoms with closed-shell interactions. These metallophilic interactions are close to the hydrogen bonding and weaker than the covalent bonding. These metallophilic interactions are stronger compared to the van der Waals forces. Metallophilic interactions influence and increase the structural characteristics of metal compounds. In the case of aurophilic and argentophilic bonding, the aurophilic bonding is stronger as Au has strong relativistic effects. The distance between Au-Au and Ag-Ag is very close in coinage metal families [37, 38].

In previous studies, various metal ions-artificial DNA frameworks were used for self-fabricated metal assembly [4, 9]. A magnetic chain is formed by DNA−metal complexes to self-assemble the metal centers and form the nanodevices, such as semiconductors, nanowires, and molecular magnets. DNA is most suitable for logic gates applications due to its affinity, nontoxicity, use of biological (RNAs-metal) entities, and biodegradability. Experimental studies showed that the polymerization reactions in nucleobases with G quadruplex DNA sequence [39] output signal produces several logic gates. The cost-effective logic gates are designed by non-labeled oligomer probes to initiate the luminescent signal [40, 41]. Another study was carried out on (mono and binuclear) nucleobase interactions by the relative cooperation of the double strands of DNA [30]. Tanaka and Shionaya [4] studied fully synthesized metal-mediated base pairs entangled metal interactions with monomeric ligand-bearing nucleosides. The studies on nucleobase stacking pairs to assist Cu^{2+}, Ni^{2+}, and Pd^{2+} metal ions showed the potential utility of Cu^{2+}. Studies showed that these resulted in metallo-base pairs becoming uniform with no net charges, as these complexes are responsible for the deprotonation of the coordinating moieties. This property of metallo-nucleobase complexes can be widely used in electronics [40 - 42]. Due to the potential applications of NAB−M_2/M_2^{2+} complexes, computational studies have been carried out on M_2 and M_2^{2+} with numerous NAB pairs combinations, such as AT, AU, AAHB, ATAT (WCST) and AAST stacking pairs. DFT studies have been carried out to calculate the global descriptors and HL gap of the studied complexes. The HL represents the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital). The structural stability of complexes is carried out by the DOS, and chemical bonding is analyzed by the PDOS, which are density of states and partial density of states, respectively. The time-dependent density functional theory (TDDFT) studies are carried out for absorption energies and excitation energies in water. Water as a solvent is used to conduct the studies on arabino-furanosyl nucleosides with the pairing of Watson−Crick bases [44]. These complexes are widely used in biosensors and bioelectronics applications.

5.2. COMPUTATIONAL METHOD

Various conformational structures for (NAB)−M_2/M_2^{2+} complexes are optimized by DFT with B3LYP [45] functional and 6-31G** basis set. CAM-B3LYP [46] functional with a 6-31G** basis set is used for the stacking pairs of (AAST and WCST) with the G09 software program [47]. Los Almos effective-core potential LANL2DZ [48] is used for coinage metal clusters, and the 6-31G** basis set is used for other atoms. Basis set superposition error (BSSE)-corrected energies [49] are used for the calculations. Gaussview [50] program was used to envisage the optimized geometries. The optimized structures were considered to have no negative vibrational frequency and lower minima. All the DFT and TDDFT studies were carried out with water (($\varepsilon = 78.39$) as a solvent, and the TDDFT calculations used the conductor-like screening model [51] to calculate the absorption and the emission wavelength [52].

CHAPTER 6

Molecular Clusters and Hydrogen Storage by Clusters of Alkaline Earth Metal Oxides

Abstract: This chapter is exclusively devoted to molecular clusters. Molecular clusters refer to finite aggregates of molecules or compounds. In such clusters, molecules are usually bound by hydrogen bonding, van der Waals, or similar weak interactions. We have shown some examples of molecular clusters, such as the clusters of H_2O and LiF molecules. Alkaline-earth metal oxide clusters such as $(BeO)_N$, $(MgO)_N$, and $(CaO)_N$ have specifically been discussed, and their hydrogen storage behavior have been explored using various DFT methods such as B3LYP, PBE-D3, M06-2X, *etc*. B3LYP is a hybrid functional. PBE-D3 is a dispersion-corrected GGA functional, whereas M06-2X is a meta GGA functional, as discussed in Chapter 1. It was found that small $(BeO)_N$ clusters prefer planar structures due to partially covalent Be-O bonds, unlike ionic Mg-O and Ca-O bonds. Although all these clusters can effectively adsorb H_2 molecules, smaller clusters serve as better adsorbents due to the high percentage mass ratio.

Keywords: Adsorption energy, Alkaline-earth metal oxides, Binding energy, DFT study, Hydrogen storage, H_2O clusters, LiF clusters, Molecular clusters.

6.1. INTRODUCTION

Parallel to atomic clusters, molecular clusters can be considered finite aggregates of molecules. The constituent molecules of clusters may be of the same type or may be different. Based on the number of constituent molecules, *i.e*., 2, 3, 4…, these clusters are dimer, trimer, tetramer, and so forth. Evidently, the molecule itself is a monomer for the clusters. In molecular clusters, molecules are mainly held together by hydrogen bonding, van der Waals interactions, dipole-dipole interactions, dipole-induced dipole interactions, *etc*. The study of molecular clusters is of the same fundamental importance as atomic clusters. To illustrate this, the structures of $(H_2O)_N$ [1] are displayed in Fig. (**6.1**) for $N = 2\text{-}5$. In these clusters, H_2O molecules are linked together by hydrogen bonding. Similarly, hydrogen bonding is also responsible for the structure and properties of water, an important substance for life, as a solvent and in its various phases. In the case of

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$(H_2O)_2$ dimer, there exists a hydrogen bonding between O of one molecule and H of the other. The question is, how many H_2O molecules are needed for its clusters to behave as water (liquid), ice (solid), or vapor (gas)? This is, of course, the fundamental question, as already mentioned in Chapter 1. Another interesting aspect is to analyze the structure and properties of molecular clusters as a function of the size, which will presumably help in understanding the bulk growth mechanism at the molecular scale. For instance, the structure of the $(H_2O)_{100}$ cluster [2] resembles an icosahedron, as displayed in Fig. (**6.2**). For an interesting account, the readers can go through Ref [3].

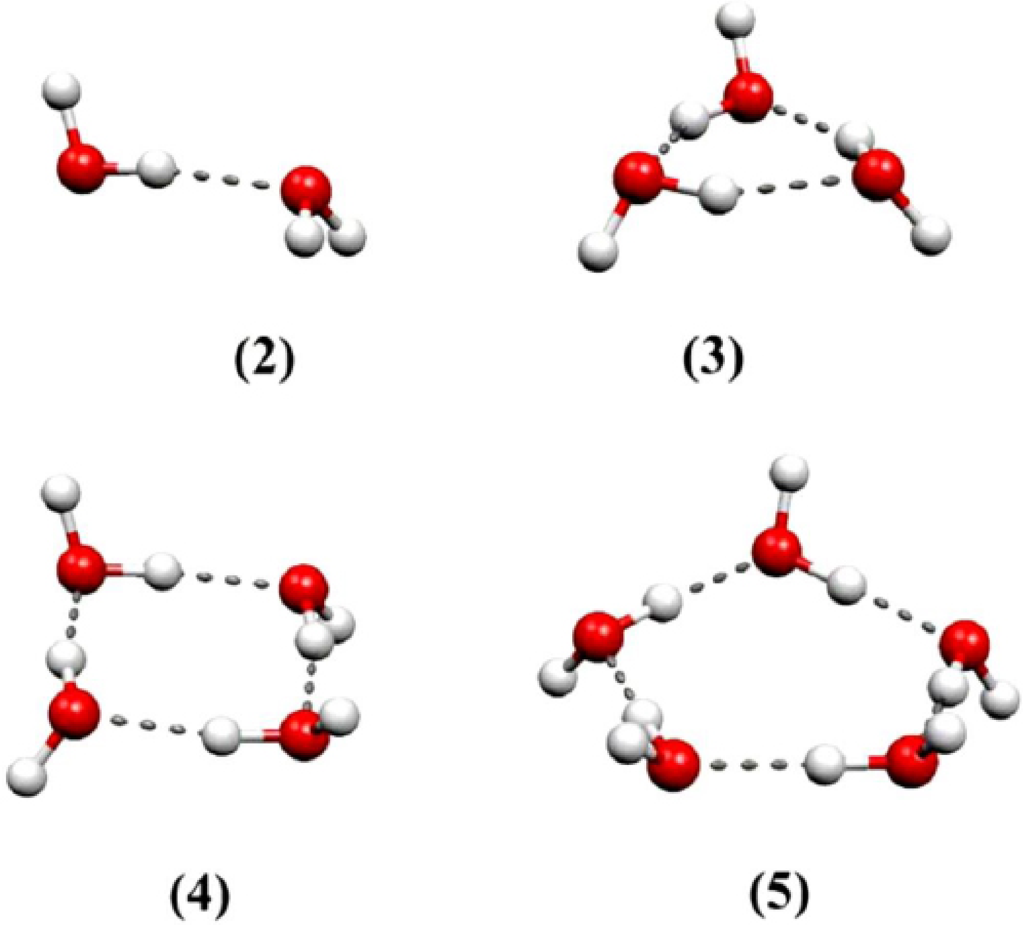
(2) (3) (4) (5)

Fig. (6.1). Equilibrium structures of $(H_2O)_N$ clusters for $N = 2\text{-}5$ from Ref [1].

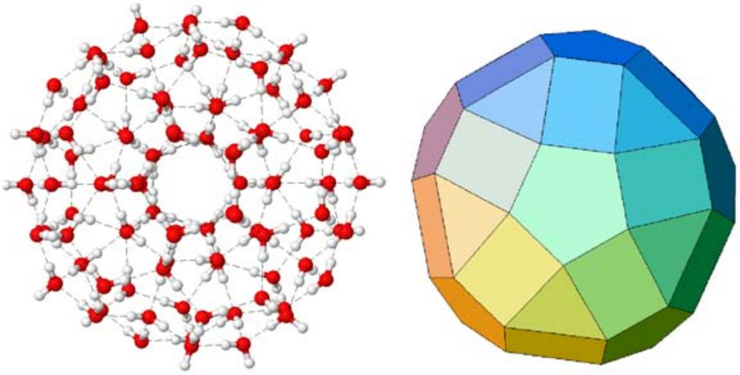

Fig. (6.2). Model structure of the $(H_2O)_{100}$ cluster from Ref [2]. (left) resembling an icosahedron (right).

Another interesting example is $(LiF)_N$ clusters, which are stabilized by dipole-dipole interactions. The planar structures of $(LiF)_N$ clusters [4] for $N = 2, 3, 5, 7$, and 9 are displayed in Fig. (**6.3**). One can see that the structure of $(LIF)_2$ is square planar, whereas that of $(LiF)_3$ is hexagon ring. Some new insights into the structure of $(LIF)_2$ and $(LiF)_3$ have been provided by Srivastava and Misra [5 - 8], which is beyond the scope of this book. The structures of $(LiF)_N$ for $N = 5, 7$, and 9 were obtained by fusing two, three, and four $(LiF)_3$ clusters, respectively. When these $(LiF)_3$ clusters are placed coaxially, they lead to the formation of nanotube structures [9], as shown in Fig. (**6.4**).

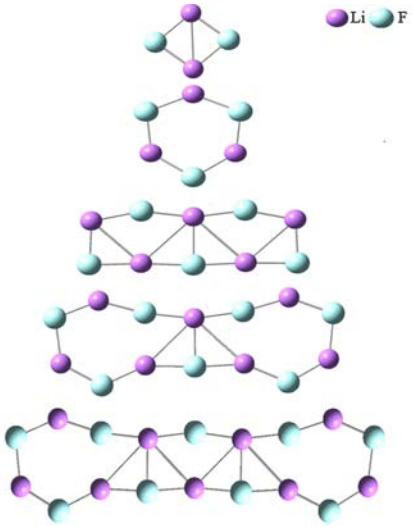

Fig. (6.3). Planar structures of $(LiF)_N$ clusters for $N = 2, 3, 5, 7$, and 9 from Ref [4].

CHAPTER 7

Atomic Clusters: Conclusions, Prospects and Perspectives

Abstract: This chapter provides a summary of the book and offers some future perspectives.

Keywords: Atomic clusters, DFT study, Future scope, Molecular clusters, Nanoclusters.

7.1. INTRODUCTION

Atomic clusters have been a subject of continuous exploration due to their interdisciplinary nature and interesting properties. These properties are often size-dependent, and therefore, it provides a unique opportunity to tailor the properties by controlling their size. Having size in the range of nanometers, the clusters with $10\text{-}10^6$ atoms or molecules are often referred to as nanoclusters, which may possess crystalline as well as non-crystalline shapes. The shape of nanocrystals may take face-centered cubic, octahedral, or truncated octahedral structures, whereas the non-crystalline nanostructures are usually icosahedra, decahedra, polytetrahedral, and polyicosahedra. The basic parameters in the research of atomic clusters or nanoclusters include the composition, size, and structure. In all these aspects, theoretical studies often dominate over experimental studies for being cost-effective and giving accurate results. In the recent past, density functional theory (DFT) has taken the lead in the study of atomic clusters with varying sizes, as shown graphically in Fig. (**7.1**). This book tried to capture the essence of the research on atomic clusters using DFT methods in a concise form comprising seven chapters including this one. Herein, we provide an overall summary of previous chapters along with some future scope and directions.

In Chapter 1, we provided an introduction to atomic clusters, which may be ionic, covalent, metallic, *etc.*, depending on the type of constituents and nature of bonding with several examples. We classify these clusters into small, medium, and large clusters according to their size or the number of constituents. We also

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discussed how theoretical methods play an important role in the study of clusters. In particular, we mentioned salient features of density functional theory and their applications in the study of clusters.

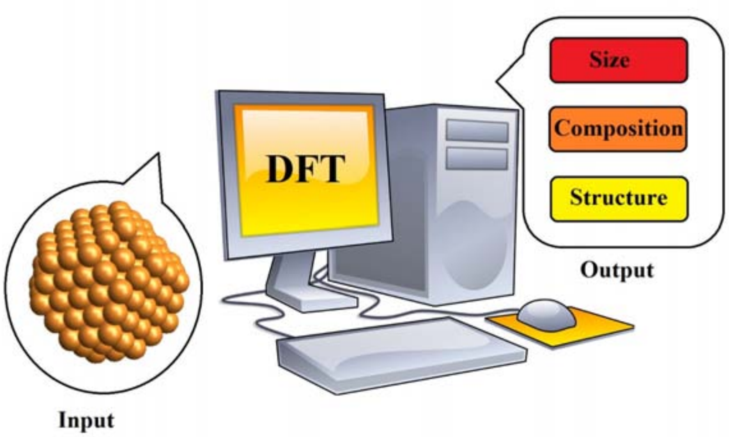

Fig. (7.1). The workflow of DFT study on atomic clusters. DFT takes an input structure and provides output parameters.

In Chapter 2, we discussed optimization algorithms for atomic clusters. These algorithms are used to obtain the structures of clusters corresponding to either local minima or global *i.e.*, minimum in their potential energy surface (PES), as shown in Fig. (**7.2**). These optimization algorithms can be broadly classified into two groups: gradient-based algorithms such as the Berny algorithm and gradient-free algorithms such as the genetic algorithm.

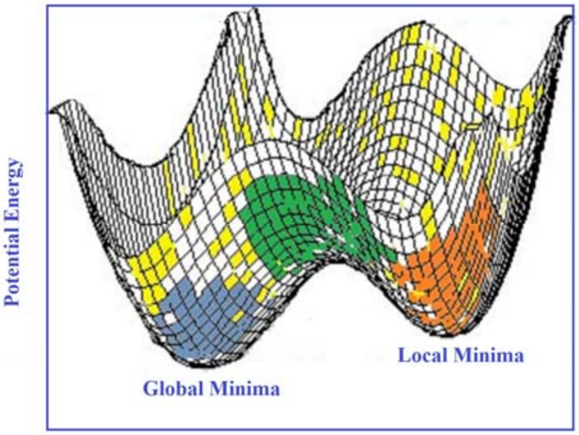

Fig. (7.2). A potential energy surface (PES) of clusters having global and local minima.

It is evident that the electrochemical CO_2 reduction (CO_2R) integrated renewable energy sources are used to produce fuels that are used to sustain the global energy economy. These sources are used not only as flow resources of conventional fossil-derived resources but can also be used to store energy from natural intrinsic electric motors (wind, sun) (see Fig. (**7.3**)). With the discovery of CO_2 reduction to hydrocarbons on copper electrodes with comparatively large Faradaic efficiencies [1], efforts have been made to develop and understand the reaction mechanism of CO_2R on Cu. Since Cu has a unique ability to catalyze the electrochemical conversion of CO_2 to potentially useful fuels and chemicals, we have discussed the adsorption of CO_2 on transition metal doped Cu clusters, their mechanisms, catalytic surface, composition, structures, the choice of electrolyte ions and pH, and the design of electrochemical cell in Chapter 3.

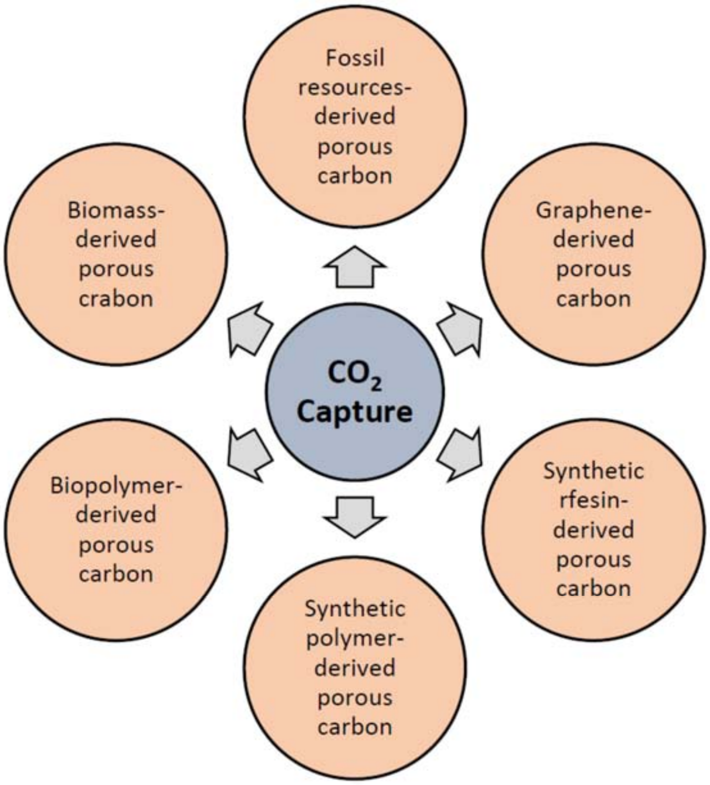
Fossil resources-derived porous carbon
Biomass-derived porous crabon
Graphene-derived porous carbon
CO₂ Capture
Biopolymer-derived porous carbon
Synthetic rfesin-derived porous carbon
Synthetic polymer-derived porous carbon

Fig. (7.3). Representation of various precursor-derived porous carbon materials for CO_2 adsorption. Cited by Gunawardene, O.H.P.; Gunathilake, C.A.; Vikrant, K.; Amaraweera, S.M. Carbon Dioxide Capture through Physical and Chemical Adsorption Using Porous Carbon Materials: A Review. *Atmosphere***2022**, *13*, 397.

In recent years, computational methodologies and atomistic pathways have been developed to analyze the possible CO_2R pathways [2 - 4]. Despite challenges,

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