7. Conclusions and Future Perspectives

The goal of the present thesis is to gain fundamental understanding of atomic structure, bonding, electronic and chemical properties of isolated and supported metallic clusters and their interactions with gas molecules. These studies have implications towards elucidating microscopic aspects of several condensed-phase phenomena and designing new materials for heterogeneous catalysis. While bare and doped lead clusters were used as models for elucidating the evolution of geometric and electronic structures and bonding, gold cluster models were used to study and differentiate the electronic and chemical properties of pure, doped and supported clusters. Throughout the work standard codes of density functional theory, within the plane-wave based pseudo-potential framework were used as tools to illustrate the physico-chemical behavior of all the systems considered in this thesis and compared with available experimental data whenever available.

The evolution of geometric and electronic structure of $\text{Pb}_n$ and $\text{Pb}_n^+$ clusters ($n = 2\ldots15$) has been elucidated and compared with other Group IV elemental clusters. The results suggest that unlike $\text{Si}$, $\text{Ge}$, and $\text{Sn}$ clusters, which favour less compact prolate shape in the small size range, $\text{Pb}$ clusters favour compact spherical structures consisting of fivefold or sixfold symmetries. The central feature of these studies showed that spin orbit coupling effect is quite important to describe the energetics of these clusters. The relative stability of $\text{Pb}_n$ clusters, analyzed based on the calculated binding energies and second difference in energy suggests that $n = 4, 7, 10$ and $13$ clusters are more stable than their respective neighbours, which is in good agreement with experimental observations. Charged $\text{Pb}_n^+$ clusters also showed compact growth pattern as those observed for neutrals with small local distortions. Based on the fragmentation pattern it is seen that while smaller clusters favor monomer evaporation, larger ones fragment into two stable daughter products. The experimental observations of large abundance for $n = 7$ cluster and lowest abundance of $n = 14$ cluster...
have been demonstrated from their fragmentation pattern. The results were subsequently tested and verified by Waldschmidt *et al.* [368], in their work on surface-induced dissociation studies on the energetics and structure of lead clusters. The chemical stability of these clusters was analyzed by evaluating their energy gap between the highest occupied and lowest unoccupied molecular orbitals and adiabatic ionization potentials. Albeit higher binding energy of $\text{Pb}_{13}$, the lower ionization potential was explained based on its electronic structure through the density of states and electron shell filling model of spherical clusters.

Considering the fact that introduction of an impurity atom can play a very important role in the modification of electronic and geometrical properties of homoatomic clusters, the structural and electronic properties of $\text{Pb}_nM$ $(M = C, Al, In, Mg, Sr, Ba$ and $\text{Pb}$; $n = 8, 10, 12$ and $14$) clusters were studied. The results revealed that the location of the impurity atom depends on the nature of interaction between the impurity atom and the host cluster and the size of the impurity atom. While the impurity atoms smaller than $\text{Pb}$, favor to occupy the endohedral position, the larger atoms form exohedral capping of the host cluster. Based on the interaction energy of the $M$ atoms with $\text{Pb}_n$ clusters, it was found that $p – p$ interaction dominates over the $s – p$ interaction and smaller size atoms interact more strongly. The stability analysis of these clusters suggests that while the substitution of $\text{Pb}$ by $C$ or $Al$ enhances the stability of the $\text{Pb}_n$ clusters, $Mg$ lowers the stability. The energy gap analysis revealed that while the substitution of $Mg$ atom widens the HLG, all other elements reduce the gap of the $\text{Pb}_nM$ clusters. The unusual increase in the interaction energy of $Mg$ with $\text{Pb}_{12}$ and the largest HOMO–LUMO gap of $Mg\text{Pb}_{12}$ cluster has been explained based on the 50 electrons rule for icosahedral structures. Further investigations of the stability of $\text{Pb}_nM$ clusters revealed that the interplay between the atomic and electronic structure is crucial to understand the stability of these clusters. Further fragmentation behavior of the bimetallic cluster ions $\text{Sn}_n\text{Pb}^+$ and $\text{Pb}_n\text{Sn}^+$ were investigated which were more amenable for
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contemporary experiments. A systematic theoretical study of the structure and electronic properties of $Sn_{n-1}Pb$ and $Pb_{n-1}Sn$ ($n = 2 - 13$) clusters was done. Fragmentation studies have revealed that, for $Sn_nPb^+$ first the single lead atom is split off; in contrast the $Pb_nSn^+$ clusters dissociate mainly in fragments retaining the single tin atom, which is in full accordance with the low-energy surface-induced dissociation patterns of $Sn_nPb^+$ and $Pb_nSn^+$ clusters which were carried out by Waldschmidt et al. [392]. For larger collision energies the complete set of smaller tin fragment ions $Sn_{n-m}^+$ with $m < n$ is found for $Sn_nPb^+$, whereas the $Pb_nSn^+$ clusters decay into two series of $Pb_{n-m}Sn^+$ and $Pb_{n-m}^+$ fragments with $m < n$. Though it might be a computationally expensive exercise, global minimum methods should be used to test all the possible isomers chosen after using Mote Carlo, or after annealing quenching sequences.

Gold, which is inert in the bulk, is found to be highly active in its nano form and the chemical reactivity of the $Au$ clusters can be tuned by the incorporating a dopant in it. The atomic and electronic structure of $Au_{n-1}Al$ ($n = 2 - 7$) clusters are elucidated with a view to understand how chemical bonding influences the stability and structure of small size $Au$ clusters. The optimized geometries of $Au_{n-1}Al$ clusters indicate that the substitution of $Au$ by $Al$ results an early onset of three-dimensional structures from tetramer onwards. Based on the energetics, $Au_5Al$ and $Au_5Al$ clusters are found to be extraordinary stable. The oxidation of $Au_{n-1}Al$ clusters undergoes via dissociative mechanism, albeit significant charge transfer from $Al$ to $Au$. Moreover, the $O_2$ molecule prefers to attach at the $Al$ site rather than at the $Au$ site.

On the basis of the above results $CO$ oxidation behavior of $Au-Al$ nano-composites in three different size ranges; (i) a small cluster $Al_6Au_8$, (ii) a mid-sized cluster $Al_{13}Au_{42}$, and (iii) a periodic slab of $Au(111)$ surface, where the $Au$ atoms in the second layer is substituted by $Al$ atoms has been carried out. While the $Al_6Au_8$ forms a cage like structure
with both the Au and Al atoms on the surface of the cage, Al$_{13}$Au$_{42}$ forms core-shell type symmetric icosahedral structure. For the Al substituted Au(111) surface, the ionic relaxation results in compression between the interlayer separations. The charge distribution analysis suggests that in all cases Al atoms donate electronic charges to the Au atoms. This has been corroborated by the red shift in the density of states spectrum, a signature of more negative charge state whence a higher chemical reactivity. The CO oxidation was investigated through both Eley-Rideal (E-R) and Langmuir-Hinshelwood (L-H) mechanism. The interaction of O$_2$ molecule with these systems occurs non-dissociative way with elongation of the O – O bond. Further interaction with CO molecule leads to the formation of CO$_2$ spontaneously. On contrary, the CO$_2$ evolution by co-adsorption of O$_2$ and CO molecules undergoes through an intermediate complex of higher energy. On the basis of the results it is inferred that the efficient CO oxidation of the Al – Au nanocomposite is due to negatively charged surface Au atoms. The results showed an improved oxidation behavior of Au in presence of Al atoms, be it inside the core for core-shell type structure or at the sub-surface layer for periodic slabs. As a future perspective the results obtained on the steps of the catalytic oxidation of CO on a metallic surface at fixed chemical potentials of the reactants by DFT calculations, might be fed into kinetic Monte Carlo simulations to obtain detailed information of the reaction under experimental pressure and temperature conditions and at real time scales. Studies on the catalyst stability and coverage effects (multiple CO and O$_2$ adsorption) will be carried out in future.

Motivated by the pioneering work of Haruta et al, which showed low temperature CO oxidation of supported Au clusters these studies, a systematic study on the adsorption of Au$_n$($n = 1 \rightarrow 6$) clusters on a regular α – Al$_2$O$_3$(0001) surface and the role of support on the structure and reactivity of metal clusters was carried out by studying the interaction of O$_2$ with the deposited clusters. The results reveal that Au atom binds weakly on the Al$_2$O$_3$
surface and it favors to connect with one of the Al atoms on the surface layer. Despite weak interaction, there is a diffusion barrier for Au atoms on the support. The adsorption studies results revealed clustering of atoms with Au – Au bonds is more favorable in comparison to dispersion on the alumina surface albeit a kinetic barrier that exists between these two configurations. In general, Au\textsubscript{n} clusters preferentially adsorb with a puckered conformation on the Al\textsubscript{2}O\textsubscript{3} surface. The adsorption energies of Au\textsubscript{n} clusters showed strong odd-even variations on Al\textsubscript{2}O\textsubscript{3} surface, with local maxima at \( n = 2, 4, 6 \) which were established to be stable by experiment. The charge transfer is further reflected by red shift in the energy levels of the density of states spectrum, a signature for higher chemical reactivity. Further reaction of oxygen molecules with these Au\textsubscript{n}/Al\textsubscript{2}O\textsubscript{3} systems shows dissociative chemisorptions is more favorable than molecular adsorption.

With the understanding and knowledge gained on the interactions of O\textsubscript{2} CO on deposited Au\textsubscript{n} clusters and experience on handling CO oxidation over different systems, future studies would be carried out on a few similar reactions. A natural continuation of these studies is to determine a better support by trying different support oxide surfaces. One of our immediate interests is to study and gain insights on the enhanced activity of water shift reaction (\( CO + H_2 O \rightarrow CO_2 + H_2 \)), on deposited Au\textsubscript{n} clusters on various oxide surfaces. Further, the preferential oxidation of CO, which is important in proton exchange membrane fuel cells is being studied on different catalysts like Pt/Al\textsubscript{2}O\textsubscript{3}, Pt/A – zeolite, Au/Fe\textsubscript{2}O\textsubscript{3} etc. We would extend these studies on deposited gold clusters as probable catalyst candidates for this reaction using a combination of DFT modeling techniques and explain the performance of Au and Pt catalysts. Another project of near future is to give a mechanistic rationale for the recent experimental results that have shown the potential of gold/carbon as good candidate for the direct epoxidation of propene and larger alkenes. A concluding remark: computational modeling of materials for various applications has emerged from the
convergence of many different computational methods and the introduction of high-performance computers and the fundamental insight into various mechanisms of different processes can only be realized by breakthroughs in theoretical insight and computational methods.