Synopsis

Atomic clusters are aggregates of atoms consisting of a few to a few hundred atoms. Because of the wide range of their possible sizes, compositions and charge states, atomic clusters constitute virtually a new ‘phase’ of matter with properties distinct from those of an atom and the corresponding bulk. Difference in properties with respect to the bulk arises primarily because of two reasons: first, unlike bulk, the number of atoms on the surface of a cluster is a substantial fraction of the total number of atoms; second, the arrangement of atoms in a cluster is generally very different from that in the corresponding bulk. The most extraordinary feature of atomic clusters is an extreme size-dependence of their structural, electronic, magnetic, chemical, and optical properties. Addition or removal of even one atom or an electron can substantially alter their physical and chemical properties [1].

For an ease of analysis and understanding, atomic clusters can be classified in various ways. Clusters can be classified as small, medium-sized and large depending on the number of constituent atoms. Another convenient classification is based on the types of the constituent atoms and the nature of bonding between them. One talks about (i) semiconductor clusters such as Ge_N, Si_N, (ii) ionic clusters, such as [Na_NCl_M]^{(N-M)+}, (iii) rare gas clusters, e.g., Ar_N, (iv) metal clusters with metallic bonding such as Na_N and Au_N, (v) molecular clusters, e.g., (CO)_N.

During the last three decades, metal clusters have been the most extensively explored class of clusters by experimental and theoretical means. Metal clusters can be further subdivided into simple metal, noble metal, transition metal (TM), and mixed or alloy clusters. We term clusters composed of group-IA (alkali), group-II and group-IIIA metal elements as simple metal clusters [1–3]. Clusters of group-IB elements are termed noble metal clusters. Although they share many properties of the simple metal clusters, there can be significant differences also, most notably in case of Au clusters. A characteristic feature of simple metal clusters is a greater stability of clusters having certain specific number of valence electrons compared to their neighbors. In 1984, Knight et al measured the mass abundance spectrum of Na_N clusters which showed strongly size-dependent abundance [4]. Particularly sharp drops in intensity were observed just after N = 8, 20, 40, 58 and 92. In the mass abundance spectrum of gas phase clusters peaks of higher intensity indicate higher stability of these clusters with respect to their neighbors. Thus Na_N clusters at N = 8, 20, 40, 58 and 92 were more stable. These clusters are termed magic clusters. Magic clusters were also observed in other experiments on various simple metal and noble metal clusters [1]. In order to explain the enhanced stability of
metal clusters of specific sizes, several simple quantum mechanical models have been
invoked. These models are known as shell models [1,5]. The underlying assumption
of all these models is that the valence electrons of all the metal atoms are confined
within a finite region of space defined by the ‘volume’ of the cluster. Using spherically
symmetric confining potentials, such as the 3D harmonic oscillator potential, one
obtains the following sequence of one electron orbitals 1S\(^2\), 1P\(^6\), (1D\(^{10}\) 2S\(^2\)), (1F\(^{14}\)
2P\(^6\)), (1G\(^{18}\) 2D\(^{10}\) 3S\(^2\)), (1H\(^{22}\) 2F\(^{14}\) 3P\(^6\)) .... One-electron orbitals within parentheses
are degenerate in energy. Completely filled electronic shells will result when there
are 2, 8, 20, 40, 70, 112 ... electrons in the cluster. If the confining potential is
of hard-wall form, magic clusters occur for valence electron counts of 18, 34, 58,
68, 92 etc. in addition to 2, 8, 20, 40 and 70 [1]. We know that atoms with filled
electronic shells exhibit enhanced stability. Similarly, it was argued that stability of
magic clusters is due to their closed electronic shells. Experiments were performed to
measure other properties directly related to the electronic structure, e.g., ionization
potential, electron affinity and polarizability. Sharp drops in the ionization potential
have been observed at sizes just after the magic sizes. Also, low values of electron
affinity were seen at the magic sizes. All these experimental observations indicate
that stability of magic clusters is an electronic feature [1,6].

The existence of the electronic shells in simple metal clusters and their dominat-
ing role in governing stability provides a very exciting possibility that clusters may
exhibit electronic and chemical features similar to elemental atoms. Leuchtner et al
studied reactivity of Al\(^{-}\)\(_n\) clusters with oxygen [7]. All the anionic clusters reacted
with O\(_2\) except for Al\(^{-}\)\(_{13}\), Al\(^{-}\)\(_{23}\) and Al\(^{-}\)\(_{37}\). With three valence electrons per Al atom,
Al\(^{-}\)\(_{13}\), Al\(^{-}\)\(_{23}\) and Al\(^{-}\)\(_{37}\) have 40, 70 and 112 valence electrons respectively. Therefore
their non-reactive behavior can be understood in terms of closed electronic shells.
This experiment demonstrated that the electronic shell structure plays a decisive
role in determining the reactivity of simple metal clusters. Since non-reactive be-
haviour is also well known for inert gas atoms due to their closed shells, Al\(^{-}\)\(_{13}\) can
be regarded as an analogue of those atoms. This led to the idea of ‘superatoms’. The most recent definition of superatoms as given by the proponents Castleman and
Khanna is as follows. A superatom is a cluster not only mimicking some properties
of an elemental atom but a motif that is stable in chemical assembly and may also
demonstrate new chemical features beyond the analogue atom [8]. Various com-
bined theoretical and experimental studies revealed that Al\(_{13}\) and Al\(_{14}\) behave as a
halogen and an alkaline earth element respectively [9–12]. Al\(^{-}\)\(_{7}\) was shown to be-
have as a multi valence superatom in a way similar to a C atom [13]. Thus, simple
quantum mechanical shell models provide us with an elegant electron counting rule through which we can understand the electronic and chemical properties of simple metal clusters. Electronic properties of noble metal clusters, particularly Cu and Ag, are also understood within shell models [6]. Recently, it has been shown that the conventional shell sequence in spherical metal clusters as discussed so far can be modified by structural distortions which can lead to species with enhanced stability at unconventional electron counts. For example, CuAl$^{-}_{22}$ with 68 valence electrons was shown to have reduced reactivity against O$_2$ [14]. In the spherical shell model, 68 electrons correspond to a closed 2D$^{10}$ shell, with an empty 3S$^2$. However, the origin of the enhanced stability of CuAl$^{-}_{22}$ was shown to be due to splitting of the 2D$^{10}$ shell because of a structural distortion of the cluster. This deformation can be understood in terms of a crystal field like splitting of degenerate shells into subshells.

Recently, the idea of superatoms has been extended to ‘magnetic superatoms’. VCs$_8$ is the first example of a magnetic superatom in which atomic $d$ electrons localized on the V atom provide a moment of 5 $\mu_B$ whereas delocalized electrons from the $s$-valence states of the Cs and V atoms form a filled shell of 1S$^2$1P$^6$. This provides stability to the cluster [15]. It has been shown that two and three units of VCs$_8$ do not coalesce when they are brought in contact. They are found to retain their structural identity, magnetic moment and form a stable dimers and trimers.

Despite having great success, there are cases where shell models cannot explain the properties of all-metal clusters as observed in various experimental and theoretical studies [16,17]. There are other simple electron counting rules in chemistry like the Hückel rule and Wade-Mingos rules which account for stability of electronic systems. According to the Hückel rule, planar and cyclic hydrocarbons having $(4n+2)$π electrons have enhanced stability. These hydrocarbons are known as aromatic compounds. Benzene, i.e., C$_6$H$_6$ is one of the classic examples. Recently, Li et al [16] have shown that the concept of aromaticity can be used in explaining the enhanced stability of bimetallic LiAl$_4^-$, NaAl$_4^-$, and CuAl$_4^-$ clusters. After that, numerous studies have been devoted to finding stable cluster motifs using aromaticity as a guiding principle. Although aromaticity is a widely used term, a precise quantitative and well-accepted definition of this quantity is still missing. For quantitative estimation of aromaticity, different criteria have been proposed by different authors [17]. These can be based on structural, energetic, reactivity, electronic or magnetic properties. The most popular criterion used to identify an aromatic cluster is perhaps the nucleus independent chemical shift (NICS), a magnetic measure. Clusters with negative values of NICS are classified as aromatic. while clusters with positive values of NICS
are classified as anti-aromatic [18,19].

Motivated by the interesting concept of superatom, a major part of my thesis is devoted to identifying stable clusters which behave as magnetic superatoms. The detailed study of structural, electronic and magnetic properties of a single 3d TM doped alkaline earth and aluminum clusters using first-principles approach based on density functional theory forms a major part of this thesis. In addition, I have studied V doped silver clusters using first-principle calculations. This work is motivated by recent experiments performed by Janssens et al on these clusters [20]. This thesis is organized as follows.

**Chapter 1** This chapter is an introduction to the topic of atomic clusters and superatoms. In this I review the literatures on atomic clusters, various shell models, and shell effects in simple metal and noble metal clusters. In addition, the concepts of superatom, magnetic superatom, cluster assembled materials (CAM’s), and aromaticity in all-metal clusters are reviewed.

**Chapter 2** is about the underlying theory and techniques of calculations used in this thesis. Density functional theory is reviewed. Techniques for solving the Kohn-Sham equations using both localized and plane wave basis sets, and the concept of pseudopotential are discussed. An evolutionary algorithm for finding the global minima of clusters is also discussed.

**Chapter 3** In this chapter the electronic and magnetic properties of 3d TM doped calcium clusters are presented. We have found TiCa\(_8\) and FeCa\(_8\) to have enhanced stability as indicated by large gaps between the highest occupied and lowest unoccupied molecular orbitals (HL gap), hardness (\(\eta\)) and adiabatic spin excitation energy (\(\Delta E_{\text{spin}}\)). In addition, FeCa\(_8\) is found to have a magnetic moment of 4 \(\mu_B\). The stability of TiCa\(_8\) is understood from the fact that it has 20 valence electrons, a magic number. Most striking feature of this chapter is the stability of FeCa\(_8\) at an unconventional electron count of 24. We have shown that the origin of this stability is an interplay between crystal field effect and Hund’s coupling. FeCa\(_8\) is identified as a magnetic superatom in the same spirit as VCs\(_8\) [21].

**Chapter 4** extends our search for magnetic superatoms by investigating the electronic and magnetic properties of the TMSr\(_8\) clusters. TiSr\(_8\) and CoSr\(_8\) are found to have enhanced stability within the TMSr\(_8\) clusters. The enhanced stability of TiSr\(_8\) is understood in a way similar to TiCa\(_8\). Because of the low magnetic moment
of 1 $\mu_B$, CoSr$_8$ is not found to be an attractive candidate for magnetic superatom. Most strikingly, FeSr$_8$ does not emerge as a cluster with enhanced stability. We have discussed the reasons behind this. Furthermore, we have shown that the ground state electronic configuration of a TMSr$_8$ cluster is also determined by the combined effect of Hund’s coupling and crystal field effect [22].

**Chapter 5** explores the possibility of finding clusters with enhanced stability and finite magnetic moment within the CrSr$_N$ and MnSr$_N$ ($N=4-12$) series. Motivation for studying these clusters originated from the study of TMSr$_8$ clusters. We found that CrSr$_9$ and MnSr$_{10}$ have enhanced stability as indicated by their hardness, second order energy difference ($\Delta_2(N)$) and $\Delta E_{\text{spin}}$. CrSr$_9$ and MnSr$_{10}$ are found to have magnetic moments of 4$\mu_B$ and 5$\mu_B$ respectively. Again, the origin of stability and magnetic moment in CrSr$_9$ and MnSr$_{10}$ clusters is the combined effect of crystal field and Hund’s coupling. CrSr$_9$ and MnSr$_{10}$ are also found to behave as magnetic superatoms [22].

**Chapter 6** focuses on the electronic and magnetic properties of a single Cr, Mn, Fe, Co and Ni doped Al clusters in search of magnetic superatoms. While we have not been able to identify any possible candidates for magnetic superatoms in these series, we have found some very interesting properties in them. We have found that FeAl$_4$, and CoAl$_3$ clusters have enhanced stability as indicated by their second order energy difference, hardness and adiabatic spin excitation energy. However, they have no net magnetic moment. Most importantly we found that spherical shell models cannot describe the electronic structure of TM doped aluminum clusters, in contrast to binary TM doped alkali and alkaline earth clusters. In fact we have shown that stability of FeAl$_4$, and CoAl$_3$ can be associated with their aromatic behaviour as revealed by their negative NICS values [23].

**Chapter 7** investigates the evolution in the atomic structure, bonding characteristics, stability, and the spin magnetic moment of neutral and cationic VAg$_N$ clusters. This work is motivated by the experimental study of the VAg$_5^+$ clusters in which VAg$_5^+$ and VAg$_7^+$ were found to be stable [20]. We found that VAg$_5^+$ and VAg$_7^+$ have enhanced stability in agreement with the experiments, indicated by their large HL gap and $\Delta_2(N)$. In addition we show that the stability of VAg$_5^+$ and VAg$_7^+$ can be explained in terms of exchange splitting within the 1D shell orbitals of these clusters [24].