

AMES GRANT
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**SIMULATION STUDIES FOR SURFACES
AND MATERIALS STRENGTH**

Semiannual Progress Report
for
Cooperative Agreement NCC2-297
for the period
May 1, 1987 - October 31, 1987

Submitted to

National Aeronautics and Space Administration
Ames Research Center
Moffett Field, California 94035

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(NASA-CR-181535) SIMULATION STUDIES FOR
SURFACES AND MATERIALS STRENGTH Semiannual
Progress Report, 1 May - 31 Oct. 1987
(Eloret Corp.) 42 p

N88-12557

CSCL 07D

Unclas

G3/25 0110988

In accordance with the original proposal, during this period investigations were carried out in two general areas. (i) A new and realistic potential energy function comprising angle dependent terms was employed to describe the potential surface of the $N + O_2$ system. The potential energy parameters were obtained from high level *ab initio* results using a non-linear fitting procedure. It was shown that the potential function is able to reproduce a large number of points on the potential surface with a small rms deviation. (ii) An literature survey was conducted during this time to analyze exclusively the status of current small cluster research. This survey turned out to be quite useful in understanding and finding out the existing relationship between theoretical as well as experimental investigative techniques employed by different researchers. Additionally, in this review the importance of the role played by computer simulation studies in small cluster research, was documented.

I. A Model Potential for the $N + O_2$ System

In this study a model potential function was used to generate the potential energy surface associated with the $N + O_2 \rightarrow NO + O$ reaction. About 60 points on this potential energy surface have been calculated by S. Walch [J. Chem. Phys., **86**, 6946 (1987)], using a high level *ab initio* technique. In order to approximate this potential surface we considered a potential energy function comprising two- and three-body interactions. The two-body part was represented by a generalized Morse function. For example, for two particles i and j separated by r_{ij} it is expressed as:

$$u(r_{ij}) = A \cdot \exp(-b_1 r_{ij}) - B \cdot \exp(-b_2 r_{ij})$$

where, A , B , b_1 and b_2 denote the two-body parameters to be evaluated from fitting

to *ab initio* results.. In this reaction there are two different types of interactions; therefore, we obtained two different sets of parameters for $O - O$ and $N - O$ interactions. Using the *ab initio* results, the parameters were calculated for the $O - O$ pair potential as: $A = 2755$. eV, $B = 350.5$ eV, $b_1 = 5.056$ and $b_2 = 2.884$, and for the $N - O$ pair potential as: $A = 5294$. eV, $B = 313.7$ eV, $b_1 = 5.965$ and $b_2 = 2.871$. With these parameters now the Morse function can reproduce the *ab initio* values with a rms deviation of less than 0.009 eV.

For the three-body part we used a new angle dependent function:

$$w(r_{ij}, r_{ik}, r_{jk}) = Z(h_i + h_j + h_k)$$

where, Z is the three-body intensity parameter; h_i , h_j and h_k represent corresponding angle dependent parts for particles i , j and k ; for example for atom i it is given by:

$$h_i = \alpha_i \cdot f_{ij} \cdot f_{ik} \cdot (\cos\Theta_{jik} + \beta_i)^2$$

Parameters α_i and β_i have to be calculated for the i th atom (i. e., separately for N and O). Θ_{jik} denotes the angle at the vertex i . f_{ij} and f_{ik} represent cut off functions and are expressed as:

$$f_{ij} = \frac{1}{2} - \frac{1}{\pi} \arctg(\lambda_{ij} \cdot (r_{ij} - c_{ij}))$$

Here, the parameters λ and c are for each individual pair ij , ik or jk . Accordingly, the three-body function contains 9 parameters to be determined. The process of parameter evaluation is a long and cumbersome procedure. In this particular case we used a non-linear fitting program and the three-body potential parameters were calculated as: $Z = 0.98864$ eV, $\alpha_O = 5.3718$, $\alpha_N = 4.7693$, $\beta_O = 0.32167$, $\beta_N = 1.2223$, $\lambda_{OO} = 11.316$, $\lambda_{NO} = 2.1802$, $c_{OO} = 10.523$ and $c_{NO} = 1.6938$. Now, the potential energy function using these fitted parameters is able to reproduce the *ab initio* results (60 points) with an rms deviation of 0.075 eV.

The *arctg* function employed for the cut-off makes the potential quite realistic by asymptotically converging to zero in all directions. For calculating time depen-

dent features, therefore, the use of the potential in molecular dynamics procedures (where, derivatives are needed), is expected to be a straightforward procedure.

II. Properties of Small Clusters

As a result of an extensive literature survey, in this part, a general review paper on small clusters was prepared. The review provides a comprehensive picture of the microcluster research conducted during recent years. In the paper, we analyzed achievements and limitations of various investigative methods, and indicated some missing links in the collaboration between experimental and theoretical research. Special emphasis was given to *ab initio* and semiempirical methods and their connections to computer simulation studies. High level *ab initio* calculations even for clusters of very small sizes are still limited by the current computer capacities. Parametrized model potentials, however, seem to overcome this difficulty. Despite their present qualitative nature, computer simulation studies, as it stands now, are becoming more and more an integral part of the identification and characterization methods used in choosing appropriate models, as well as in the interpretation of experimental observations. It is shown that one of the important shortcomings in the small cluster research based on computer simulations, is due to the unavailability of realistic potential functions describing the interactions among the atoms in the cluster.

In the first chapter of this review, following the introduction, background information which includes various review articles closely related to microcluster research, is presented. Also is included in Chapter I a section on important definitions and classification schemes for small clusters. In Chapter II, in addition to a quick review of the synthesis and experimental characterization techniques of small clusters, theoretical investigative methods (mostly based on first principles) are included along with common computer simulation techniques employed in small cluster re-

search. The present status of the structural and electronic properties of clusters along with their chemical reactivity are reviewed and analyzed comparatively in Chapter III. Chapter IV contains some important limitations and shortcomings of various experimental as well as theoretical investigation methods along with recent achievements in cluster research activities to date. Also included are our conclusions and future projections for microcluster science.

This study was conducted in collaboration with Dr. C. W. Bauschlicher Jr. and a shortened version of the manuscript entitled "Properties of Small Clusters" is included as an addendum.

ADDENDUM

Properties of Small Clusters

I. Introduction

The large increase in number of scientific publications on microclusters during the last 5-6 years is perhaps the most vivid indication of the rising importance of this field. Today, not only the catalytic chemist, but also scientists from many other disciplines are involved with studies related to small clusters. This field constitutes one of the important areas where experiments and theoretical work go hand in hand and benefit considerably from each others' results. Because the characterization of microclusters is believed to furnish additional information about the fundamental mechanism of catalysis and many important chemical reactions, properties of small clusters, in recent years, have become a subject of intense theoretical and experimental investigations (Gole 1986). This growing interest is at present not only a technological one, but also has established academic roots. Since small cluster research is involved with microscopic level investigations, the results that it produces are extremely valuable in the understanding of various very important processes such as nucleation, epitaxy, catalysis, crystal growth and photographic chemistry. Atoms in a microcluster have, in general, different surroundings with respect to those in the bulk state. For example, the average number of nearest neighbors of an atom in a cluster does not always correspond to its chemical valence and it differs also from the number of nearest neighbors in the corresponding crystal (Koutecky and Fantucci 1986). Many quantities (such as the temperature, surface tension, surface area and even the volume) that are used in the description of macroscopic systems, become ill-defined as the cluster size decreases. Therefore, in the classical nucleation approach, for instance, one encounters many difficulties in calculating properties of small clusters from thermodynamical considerations (Pound 1985; Hagena 1987). While the contribution coming from atoms located at surfaces to many intensive properties is negligible in the description of a macroscopic system, it plays an important part in the case of small clusters.

The most popular question asked in microcluster work is: "how do the different material properties vary as a function of the cluster size?". Today, it is well known that many characteristics associated with small clusters vary non-monotonically going from a dimer to the bulk state. For example, intriguing variations in the chemical reactivity and selectivity are the two significant features over which the catalytic chemist would like to obtain complete control. Microstructures display curious crystallographic anomalies which can not be found in the bulk. Pentagonal structures exist for small dimension phases. Energy and stability calculations show that these structures are energetically favored when they are compared to normal bulk structures. In many instances, researchers dealing with small clusters reported the existence of icosahedral and polyicosahedral structures which looked like an amorphous structure (Farges et al. 1985; and Renou and Gillet 1981). Electronic excitations and ionization characteristics of microclusters were also found to be quite different from respective processes in the bulk (Hermann et al. 1986; and Baetzold 1981). Undoubtedly, a thorough understanding of small cluster properties and associated processes at atomic dimensions will provide an enormous advantage in manipulating various technologically important reactions in the directions desired. From an academic viewpoint, on the other hand, the evolution of the structural, electronic and other properties as atoms form progressively larger clusters leading to a macroscopic size solid has long been a challenging problem for solid state and theoretical physicists. An enormous amount of experimental and theoretical work has been conducted to resolve how these various properties of the solid state evolve. These intensified efforts, during the last decade in particular, have resulted in an overwhelming advancement in microcluster research. While many long standing problems related to small clusters have been solved, many new ones, however, were added to our list. Today, in gas-phase cluster research, for instance, we can generate clusters (neutral or ionic) from practically any element. Characterization techniques have been developed to such a state that for structural identifications in a variety of cases atomic level resolutions are possible. Very fundamental steps have been taken toward the understanding of chemical reactivity. The availability of supercomputers, on the other hand, furnished tremendous help in understanding microcluster prop-

erties via accurate *ab initio* calculations along with detailed computer simulation methods. Their contribution to small cluster research is at present making an impact by providing atomistic level information (unavailable by experimental means) to solve many problems related to stability and other structural properties. Theoretical methods along with atomistic computer simulation techniques are on their way to becoming an integral part of the characterization procedures by providing sound models and contributing to the interpretation of many experimental observations.

This article is designed to provide a rather general picture of the microcluster research conducted during recent years. The main purpose of the paper is to address both experimentalists and theoreticians, indicating achievements and limitations of various investigative techniques, as well as to point out missing links in the collaboration between theory and experimental research. Because of the length restriction, only a small number of the papers on microclusters available in the literature were cited in this article. Therefore, we unavoidably failed to include many outstanding articles in our reference list. In this chapter, following background information which includes various review articles closely related to microcluster research, a general definition and classification schemes are presented. In Chapter II, in addition to a quick review of the synthesis and experimental characterization techniques of small clusters, theoretical investigative methods (mostly based on first principles) are included along with common computer simulation techniques employed in small cluster research. The present status of the structural and electronic properties of clusters along with their chemical reactivity are reviewed and analyzed comparatively in Chapter III. Chapter IV contains some important limitations and shortcomings of various experimental as well as theoretical investigation methods along with recent achievements in cluster research activities to date. Also included are our conclusions and future projections in the microcluster science.

The large body of scientific literature on microcluster research which has been accumulated within a short time, suffers from various problems of disparate terminology. For better communication, common acronyms employed in experimental and theoretical microclusters research are presented in Appendices I and II, respectively.

Background

During the last few years, parallel to the large number of individual scientific papers dealing with microclusters, many extensive review articles have appeared in the literature. The critical nucleus, perhaps best expressed by the number of papers published or by the number of scientists working on a specific subject, was reached long ago for the field of microcluster science to be recognized as a separate discipline. Already, the division of microcluster science into distinct sub-disciplines is taking place. A large portion of the recent literature devoted to microclusters is involved with metal clusters. In a recent article, for instance, Morse (1986) reviews exclusively isolated small homo- and heteronuclear clusters of transition metals. This article, which includes over 500 references, provides a comprehensive coverage of the recent literature on the measured and calculated properties of dimers and trimers as well as on ionic clusters. Koutecky and Fantucci (1986), on the other hand, in an article on the theoretical aspects of clusters, critically review different types of computational techniques which have been used to calculate various electronic and structural properties of small clusters. Their review contains microclusters of metal atoms along with some selected results for Si and Ge clusters. A large amount of theoretical data based on the various level of computations which have been collected from over 350 papers published in recent years, were also included in this paper. A recent review by Gole (1986) constitutes a comprehensive collection of various preparation and identification techniques for probing isolated small metal clusters. In this paper, he mainly compares available spectroscopic methods used in small cluster research and critically discusses different problems encountered in the gas phase experiments for small and intermediate size metal clusters. The article contains a large amount of experimental data (including energetics and spectroscopic results) for pure and mixed metal clusters collected from 150 references. In a recent article by Castle-

man and Keesee (1986) the formation and characterization procedures of ionic clusters have been reviewed. In this comprehensive article the researchers have critically analyzed and compared structural and electronic properties of cluster ions along with their chemical reactivity. This paper also contains important aspects of photodissociation and spectroscopic techniques employed in cluster ion research. Experimental results obtained from matrix isolations have been the primary subject of another recent review article by Moskovits (1986). In this article, he presents a detailed comparison of different measurement techniques and preparation procedures employed in characterization experiments related to matrix research. This review, despite its specific orientation, includes the results of about 100 recent scientific papers. Whetten et al. (1985) review different research activities on the physical and chemical properties of clusters of transition metals. The article comprises recent work related mainly to the molecular beam and flow techniques, as well as synthetic methods such as matrix isolation and cold flow condensation of laser-vaporization plasma. Also, presented in the paper is a critical assessment of experimental measurements of rovibronic and magnetic properties as well as binding energies of dimers and trimers. Supported particles and their relation to the area of catalytic chemistry has been the subject of a review article by Poppa (1984). Thermodynamic, morphological, crystallographic and electronic properties of small clusters have been analyzed as a function of particle size, type of support and type of gaseous environment. For different systems, in the article, chemical properties of supported particles are correlated with their observed physical characteristics. Furthermore, cluster-support interactions in vacuum and in other gaseous environments are considered and related to preparation and sintering processes. The article also covers new integrated characterization techniques employed exclusively in supported cluster research. Jortner (1984) in his review analyzes dynamics and relaxation properties as well as the nature of thermal and electronic states of isolated microclusters. He mainly covers non-metallic particles with emphasis on the interrelationship between the characteristics of molecular and condensed phases. In the article, the gas-phase clusters are classified based on their bonding states. Also, the process of dissociation and the microscopic solvation effect related to excited states of organic clusters are discussed. A recent article by Phillips (1986) covers microclusters of inert gases, metals and semi-metals. In this review paper he analyzes energetics, kinetics as well as the bonding behavior of small clusters in relation to their stabilities and structural properties.

The area of metal cluster complexes has been the subject of several recent review articles. Farrar and Goudsmit (1986) discuss particularly the structure and morphological aspects of metal cluster complexes. The article includes empirical rules that are frequently used to account for the particular stability of complexes based on aggregates of specific shapes. Poe (1986), on the other hand, covers the kinetics of reactions and photoreactions involving metal cluster complexes. For carbonyls, in particular, he presents a systematic analysis for the reactivity of clusters with respect to the various reaction paths. Petz (1986) in his recent article has reviewed exclusively transition-metal complexes with derivatives of divalent silicon, germanium, tin and lead as ligands. In this extensive paper, preparation techniques and the most important spectroscopic features of these complexes, along with their chemical and structural properties are included. Bradley (1986) covers organometallic chemistry of metal clusters. In his review are included a summary of homogeneous catalysis by metal cluster compounds along with discussions on the analogy between the reactivity and structure of ligands on metal clusters versus adsorbate on metal crystal surfaces. Applications of metal cluster complexes to the synthesis of new catalytic materials have been the subjects of recent papers by Brenner (1986) and Gates (1986). These interesting papers include discussions on the possibility of producing catalysts of uniform cluster size distribution by denuding a cluster complex from its ligands and retaining the metal core on a catalyst support material. A comprehensive book edited by Gates et al. (1986) contains a critical evaluation of the recent literature and the prospect of metal clusters in catalysis. Also included in this book are recent methods for the synthesis and characterization of small clusters used by catalytic chemist.

The use of zeolites as supports for small clusters was the subject of a recent article by Gallezot (1986). His review paper includes preparation and characterization methods for metal clusters

trapped in zeolites. Also, in the article Gallezot examines catalytic properties of particles in relation to their physical, morphological and electronic properties. In a recent paper on covalent group IV atomic clusters Brown et al. (1987) examined exclusively microclusters of carbon, silicon and germanium which represent an interesting sequence because of the decreasing importance of π -bonding with increasing atomic number in these covalent systems. Their work includes a systematic analysis of structural and electronic properties and the way these properties vary as the size of clusters increases. In another recent paper by Honeycutt and Anderson (1987) molecular dynamics results on melting and freezing of small Lennard-Jones clusters were presented. This paper is devoted exclusively to computer simulation studies and includes a critical comparison of their results with other simulation results from the recent literature. Low and high energy structures of small clusters and their transition behavior were systematically analyzed. Particular attention is given in this paper to the analysis of the coexisting features of various minimum energy configurations.

Definitions and Classifications

Microclusters may be defined as aggregates of atoms (or molecules) held under different conditions. In general, it is anticipated that properties of microclusters are different from their bulk or crystalline state properties. A precise description of microclusters may be achieved by using four different classification schemes based on the *composition*, *surroundings*, *size* and the *level structure* of the cluster.

(i) *Classification with respect to composition*: In this scheme clusters may be categorized into two parts as *homonuclear* and *heteronuclear* clusters. Homonuclear clusters are monatomic systems and constitute the simplest category. They are used very frequently in small cluster research because of their importance in understanding the general behavior of microclusters. Heteronuclear clusters, on the other hand, include alloys and molecular species. The types of atoms which constitute a cluster are perhaps the most important factors responsible for cluster characteristics. A priori, the composition reflects the types of bondings (such as covalent, metallic, Van der Waals, etc.) and interactions operational among the atoms in the cluster. While in the case of a homonuclear cluster only one types of interaction is expected, for heteronuclear cases different type of bonding combinations may exist.

(ii) *Classification with respect to the surroundings*: Environmental effects on properties of microclusters may be quite significant. In this respect clusters may be reviewed in two basic categories, *isolated clusters* and *trapped clusters*. Isolated clusters are those with no (or negligible) environmental influence acting upon them. In general, gas-phase clusters under low pressure conditions may be included in this group. In this case, of course, forces operational among the clusters in the gas phase, as well as interactions between the carrier gas molecules and the clusters, should be negligible. Because of the need to understand many specific properties associated with microclusters and to sort out environmental effects, isolated small cluster research has gained a tremendous momentum during the last decade. Trapped clusters, on the other hand, were the subject of many earlier studies conducted by catalytic chemists. In those cases, the clusters were under the influence of some environmental effects (produced by interactions between the cluster atoms and the neighboring atoms of the support) which might have altered various physical and chemical properties of the cluster with respect to its isolated condition. Examples for trapped clusters include clusters in matrices, in zeolites, in polymers, in solutions, or clusters deposited on substrate surfaces.

(iii) *Classification with respect to sizes*: One of the most common classification schemes for microclusters is that based on size. In general, *very small clusters* are defined as those containing 2 to 10 atoms; *small size clusters* are with 10 to 10^2 atoms; *medium size clusters* contain 10^2 to 10^3 atoms; *large clusters* are with 10^3 to 10^4 atoms while clusters containing atoms more than 10^5 are classified as *very large clusters*. Even though the boundaries in this classification scheme are

somewhat arbitrary and depend very much on the type of atomic species involved, there are many differences not only in properties of clusters in going from one group to the other, but also in their preparation and characterization techniques as well. While, properties of clusters in the very large size group resemble bulk properties, many characteristics of very small size and small size clusters deviate sharply from their bulk qualities.

(iv) *Classification with respect to level structures:* In the description of microclusters, the thermodynamic and electronic state of particles play an important role. In this classification scheme, in general, clusters may be grouped in two categories, namely *neutral* and *ionic* species. Most of the small cluster research is involved with neutral particles which are often assumed to be in their ground state. However, for characterization purposes, in many of the gas-phase experiments in particular, clusters in their higher (rotational, vibrational and electronic) levels of excitations are used. In this respect, melted clusters, for instance, may be classified as thermally excited neutral particles. Primarily in gas-phase cluster experiments negatively or positively charged particles are used. Single or multiple ionization of particles is utilized in association with various characterization and separation techniques in isolated small cluster research.

Since the inception of microcluster research the word "small cluster" has been adopted and used interchangeably with the word "microcluster". This tradition is kept in this article. Wherever necessary, however, special efforts are made to distinguish "small clusters" from *small size clusters* indicating the size category.

II. Formation, Characterization and Investigation Methods

Generation:

Among the methods of producing small clusters, condensation in free jets is the most widely used technique in generating gas-phase microclusters. Generation of isolated small clusters in their "equilibrium" morphology, free of environmental effects and for a time period allowing proper separation and identification is a challenging problem even for permanent gases or van der Waals systems. In general, the thermodynamic state of the gas prior to its expansion and the nozzle dimensions determine the cluster characteristics. Related to the condensation phenomenon in free jets, however, Hagena (1987) recently analyzed condensation theories and concluded that the present state of these theories is inadequate to provide a definitive prediction about the clustering conditions of metal vapors in free jet experiments. Conditions for producing cluster beams for materials with high boiling temperatures are rather different from those for permanent gases. For producing cluster beams for a metal (or semiconductor), the material must be heated (for example, using a Knudsen cell effusion procedure) well above its melting point to obtain vapor pressure high enough for a dynamic expansion. In most of the recent experiments, the beams are generated by the laser vaporization of the appropriate metal in a flow of helium carrier gas. Metal clusters and the carrier gas, then, pass through a nozzle into a fast-flow reaction channel to form the cluster beam as the mixture flows into a vacuum (Morse and Smalley 1984). One of the critical parameters within a laser vaporization cluster source is the dimension of the channel connecting the cluster source to the expansion chamber. Within this channel the laser-induced plasma should recombine, hot atoms should thermalize and form clusters. The binding energy released in the cluster formation must be dissipated in collisions with the carrier gas. Over the short times involved, only a very small portion of the excess energy of the vaporization pulse can be transferred to the nozzle walls, most remain as heat in the helium carrier gas (Heath et al. 1985). Another technique, called "Multiple Expansion Cluster Source" which is used to produce microclusters of metals, has been employed by Bowles et al. (1981). These researchers were able to form clusters of Cu, Ag, Au and Ni as an aerosol supported in an inert gas

which is then expanded through an orifice into a vacuum chamber where the cluster beam is formed.

For generating ions, the clusters in the beam are ionized by electron impact or by laser photons to produce positively charged particles, or an electron attachment method must be used for obtaining negatively charged particles before they reach the detection chamber. Also, cluster ions may be produced from ionic gaseous atoms (or molecules) which subsequently undergo clustering reactions (Castleman and Keesee 1986). Another method to produce ionized particles uses a liquid metal ion source (LMIS). In this technique a liquid meniscus of a metal is submitted to a very intense electric field that produces a beam of charged particles (Joyes et al., 1986).

In general, two problems are associated with cluster beam generation techniques: first is the difficulty of preparing a sample of specific cluster size with adequate purity and abundance, and second is the limited time available for the observation of clusters in the generated beam. The latter problem is related to the thermodynamic state of the particles in the beam. Schumacher et al. (1984) argue that the nonequilibrium state of the clusters in the beam must be taken into consideration when assigning stability of clusters in relation to their abundance in the size distribution. Also, for the structural determination of gas-phase microclusters in particular the thermal state of the beam is an important consideration. In an article by Gspann (1986) larger metal clusters formed in the condensing flow of pure vapors were found to remain an extended amount of time in a liquid state under high vacuum conditions.

In order to overcome the difficulty mentioned above and to obtain more specific information about the stability and size of clusters in the beam studies, a separation step is introduced prior to the final detection step. In general, separation of clusters in the beam is a difficult problem. For separation of ionic clusters the most popular method is a combined technique which involves ionization and mass separation steps. It is, however, cumbersome to use this method for producing neutral clusters because it should contain an additional neutralization step for the ionic species. Other methods which are best suited for smaller size clusters, employ beam deflection procedures. These methods are based on magnetic-, electric- crossjet- or photo-deflection techniques and do not involve ionization steps (Kappes and Schumacher 1985; Gspann 1984; and Keesee et al., 1984). Some of these techniques for generating a neutral, mass-selected cluster beam have been examined by Arnold et al. (1985). Their discussions include charge exchange of mass-selected cluster ions, velocity selection of neutral clusters produced by gas aggregation method and deflection of clusters in electric fields. Abe et al. (1982) have shown that aggregation techniques can be used to produce efficiently very large clusters of metals. Also, Muhlback et al. (1981) and Sattler et al. (1981) have employed mass aggregation techniques to generate significant amounts of small to intermediate size clusters of Sb, Bi and Pb. They also have found that variation of the type of inert gas as well as the system temperature can influence strongly the size distribution and the beam intensity. Recent attempts to solve problems associated with cluster beam techniques, include confining and accumulating cluster ions of the desired size in an ion trap. The device used for this purpose is the "Penning Trap" where a combination of static, magnetic and electric fields is used to establish a three-dimensional trapping potential. In such a device cluster ions would be almost at rest in space, confined in a small volume, and could be studied at leisure (Kluge et al. 1986).

Another procedure to prepare microclusters for further investigation is the matrix isolation technique. In this method microclusters are trapped in a solid environment. To eliminate or rather minimize undesired environmental effects due to the cluster-matrix interaction, in general matrices of rare gas solids are utilized in this technique. The process of the matrix isolation of clusters involves a step of co-condensing of a vapor with a rare gas onto a cold surface. In general, the technique is performed in two different ways. Dilute atomic vapor of a metal in a rare gas environment is cocondensed below $10^{\circ}K$. Then, by relaxing the matrix, absorbed metal atoms are permitted to diffuse and form microclusters. In the second case, a rare gas mixed with metal vapor containing gas-phase clusters are used directly in the cocondensation process. In general, depending on the

type of identification method which would follow the isolation step, the incoming clusters may be ionized and mass selected prior to deposition. Nonuniform size distributions in the study of matrix trapped microclusters also create problems for the identification methods. To overcome this difficulty, therefore, in many of the recent experiments mass select gas-phase clusters are employed for the matrix isolation. Also, for the preparation of the small to intermediate size clusters, seeded beam or gas aggregation techniques (based on a liquid helium cooled differential pumping), which provide a narrow size distribution of the particles, are employed (Schulze et al. 1984). In a recent work by Heimbrook et al. (1987), a pulsed laser vaporization combined with matrix isolation technique was employed to investigate properties of various microclusters of metals. The method was found to be very suitable for analyzing geometrical, electronic and vibrational behavior of a wide range of transient species, for mixed heteronuclear clusters and alloys. In recent years, the physical and chemical behavior of small metal clusters dispersed in polymeric thin film matrices, has gained considerable interest from fundamental as well as technological viewpoints. In an exclusive article by Kay (1986) different procedures for synthesis along with important properties of metal clusters trapped in polymeric matrices were outlined. In the earlier matrix isolation techniques it has been, in general, assumed that trapped clusters conserve their gas phase properties and the interaction between the atoms in the cluster and the surrounding matrix is negligible. Jacox (1987) systematically analyzed the effect of rare-gas matrices on the electronic energy level of various dimers. His findings indicate that the matrix effect is small for neon and increases for heavier rare-gases. However, for trimers and larger clusters it has been shown that the matrix can play an important role in the structural properties of trapped clusters. For example, Kernisant et al. (1985) using ESR spectra, have demonstrated the effect of various matrices on the structure of Ag_3 .

Another important method for the generation of small clusters is based on well characterized metal-cluster complexes (Brenner 1986; and Farrar and Goudsmit 1986). If the ligands of these metal-cluster complexes are stripped (for example, by thermolysis or laser photolysis) the core collapses and forms the more strongly bound "bare" metal cluster. This preparation technique generally provides quite uniform size distributions.

For the preparation of microclusters supported on substrates, the most commonly used technique is the vapor deposition. In the recent past, many experimental techniques have been developed for the preparation as well as for the characterization of substrate deposited small clusters. Most of these experiments were performed for model catalytic studies with UHV-evaporated metal clusters. In a study by Poppa et al. (1985) small clusters of Pd were grown by deposition from the vapor phase under UHV conditions. Their results indicate that the crystallinity, cleanliness, stoichiometry and structural perfection of the support surface play a major role in determining the structural properties of the cluster.

Characterization Techniques:

In general, for the characterization of microclusters, the above preparation procedures are coupled with one or more identification techniques and constitute one single integrated characterization experiment.

Time-of-flight mass spectrometry (TOFMS) is an important technique which is used quite frequently for the analysis of gas-phase generated small clusters during the time of their flight from the reaction chamber to the vacuum. Today, in many of the TOFMS measurements a photoionization step is added to provide particle size specificity together with spectroscopic data. For probing cold gas-phase metal clusters spectroscopic information comes, in general, from two different types of laser techniques. (i) The "fluorescence excitation spectrum" is obtained by exciting molecular fluorescence with a tunable dye laser. Since for cooled particles only a few vibrational and rotational levels

of the ground electronic state are populated, the excitation spectrum probes the level structure of the excited electronic state. (ii) "Photoluminescence or dispersed emission spectroscopy", on the other hand, uses a non-tunable exciting laser held at a specific absorption frequency and the emitted fluorescent light is dispersed to give an emission spectrum. Here, the emission spectrum is used to probe the level structure of the ground electronic state (Gole 1986). A combination of photoluminescence and excitation spectroscopy is the *laser induced atomic fluorescence spectroscopy* which is suitable for studying bound-free transitions. Multiphoton ionization spectroscopy is another very useful technique for the characterization of small clusters in supersonic jets. A variation of this method which is called resonant two-photon ionization spectroscopy (R2PI) has been used in different cluster studies by Whetten et al. (1985), Trevor et al. (1985), Rohlfing et al. (1984), Langridge-Smith et al. (1984), and Leutwyler et al. (1981). In this technique, first, one or more photons are tuned into resonance with an electronic transition, exciting a bound state of the neutral particle. Then, an additional photon excites the particle to its ionization, producing a cation. The mass analyzed ion current, in these experiments, is monitored as a function of the frequency of the first exciting laser. Measurements of the ion signal as a function of the irradiation frequency (if data are carefully analyzed taking into account photofragmentation and saturation effects) can provide information about the cluster rovibronic properties (Kappes and Schumacher 1985, and Schumacher et al. 1984). In order to prevent the fragmentation of the produced ion, in more recent (two-color) experiments, two different lasers are used to excite and ionize. The photoionization and dissociative ionization of several different potassium clusters along with their fragmentation patterns were investigated systematically by Brechignac et al. (1987).

Photodetachment and photoelectron spectroscopy have proved to be powerful methods for the characterization of some small cluster negative ions. Basic principles of the photodetachments of negative ions have been well documented by Feigerle et al. (1981) and Stevens et al. (1983). Recently, Leopold et al. (1987) have investigated mass-selected copper cluster anions by photoelectron spectroscopy. They obtained measurements for vertical electron binding energies and adiabatic electron affinities as a function of cluster size. Zheng et al. (1986) conducted laser photodetachment studies on silver and copper negative ion beams obtained from a supersonic metal cluster source. Their measurements also include electron affinities of small metal clusters as a function of the cluster size. In these measurements the temperature of the cluster ion and, for the case of Ag particles, photofragmentation are among the experimental problems cited. Structural characterization methods based on electron diffraction techniques are among the most effective experimental tools available for research on clusters. For crystalline clusters it can often determine in detail the atomic arrangement, cluster size and density. For amorphous or liquid like clusters, however, the diffraction information is somewhat more limited. It has been shown that computer simulation studies now can provide supplementary evidence of considerable value for filling in details not resolved by the diffraction analysis (Bartell 1986).

Among the X-Ray techniques EXAFS is the most widely used technique for structural characterization of small clusters deposited on substrate surfaces, carbon films and for micro-particles trapped in zeolites or matrices (Gallezot 1986; Kay 1986; Poppa 1984). In general, EXAFS, which requires synchrotron radiation, provides an accurate and powerful technique to probe the local structure and surface geometry. Interpretation of EXAFS data is somewhat cumbersome. It is based on the single scattering theory and accordingly structural parameters are calculated by Fourier transform methods. Structural information obtained from EXAFS data is in the form of a pair correlation function. For various size clusters EXAFS provides accurate nearest neighbor distances and coordination numbers. Furthermore, it appears to be a particularly adequate technique to investigate bimetallic particles since the signal-to-noise ratio is quite high (Bommannavar et al., 1985).

Another important technique to determine the structure and morphology of supported clusters is the radial electron distribution method which is based on X-ray scattering measurements. RED provides the complete set of interatomic distances present in the cluster as opposed to EXAFS which

probes mainly the first coordination sphere around the absorbing atom. These techniques have been compared in articles by Poppa (1984) and Gallezot (1983). Many of the techniques developed for analysis of crystalline surfaces have been adapted for the characterization of supported clusters. In supported small cluster research (such as in model studies on catalysis) UHV-based integrated devices are being used for characterization as well as for preparation purposes. One of the most important advantages of such integrated techniques is to provide an excellent analytical environment, including high-energy-resolution/high sensitivity electron and infrared spectroscopy methods and high-spatial-resolution electron microscopy (and diffraction) to characterize the system in great detail (Poppa 1984). Furthermore, UHV-integrated techniques can also furnish the highly desired control of the cleanliness of the experimental environment that is necessary for the stoichiometry and morphology of the substrate surfaces as well as for the structure, size and the habit for the supported particles.

In general, insulating supports (bulk or thin films) are used for the study of small metal particles. It is well recognized that surface properties of a substrate play an important role in the chemical and physical interaction between the support and the particle, therefore they can interfere in many of the detection procedures such as high resolution electron microscopy measurements. Furthermore, defects (such as ledges, kinks and point defects) and their distribution at substrate surfaces alter the adatoms-surface interactions which, in turn, affect significantly the nucleation and growth characteristics. The influence of the substrate surface geometry has been investigated systematically by Honjo and Yagi (1980).

Many of the techniques for probing bulk surfaces are also used for the study of supported small clusters. Recent techniques employed in characterization studies of supported clusters can broadly be classified in two groups. (i) High spatial resolution techniques that have limited analytical power, include micro-area electron diffraction, TEM, STEM and STED. (ii) Large area methods are based on various spectroscopic and diffraction techniques as well as thermal desorption and work function measurements (such as UPS, XPS, IRS LEED, SIMS, TPD, EXAFS and AES). Often two or more of these techniques are combined to form powerful experimental approaches. These experiments integrate in some way TEM imaging techniques of high spatial resolution with standard surface analytic techniques of low detection limit and high structural sensitivity. They add particle size, number density and habit information to electron spectroscopy, work function, thermal desorption and electron diffraction studies (Poppa 1984). The most commonly used integrated experimental techniques in supported cluster research include the TPD/AES *Dual-Chamber System* (Doering et al. 1982), the XPS/AES/WF/TPD *System* (Poppa 1983), the UHV *in situ* TEM/TED *Stage* (Moorhead et al. 1980, and Metois et al. 1977) and the UHV *in situ* STED *System* (Anton and Poppa 1982, and Poppa 1983). Recent advances in the analytical probing techniques based on electron microscopy were the subject of a review paper by Venables et al. (1987). In this article the authors review limitations as well as achievements of techniques like STM, SEM, REM, HREM and STEM.

Ab initio and Semiempirical Methods

In this section we review *ab initio* techniques along with some semiempirical methods for calculating the stability and electronic structure of microclusters. Koutecky and Fantucci (1986) have given an overview of the status of the calculation of small metal clusters prior to 1986, and in his recent review of small transition metal clusters, Morse (1986) has made a detailed comparison of the calculated and experimental results. The *ab initio* methods loosely divide into the SCF/MCSCF/CI, or molecular orbital (MO), and density functional approaches. The MO approaches have proven to yield extremely accurate results for small molecules, in many cases rivaling the accuracy possible in experiment. With the current methods and supercomputers, the size of the system that can be treated is large compared to only a few years ago. However MO methods suffer from the rapid growth in work with problem size. Hence as the system size increases it is common to make more approximations either in the orbital basis set, or in the treatment of correlation. Both of these

approximations naturally reduce the accuracy of the method. The density functional approaches were developed based upon the assumption that the exchange and correlation energy can be approximated by functions of the electron density. This approximation greatly reduces the work relative to the MO methods. The local spin density version of this approach appears to yield a reliable view of metals (Fu et al. 1985), and thus suggests that the approximation is quite good. However, when LSD is applied to molecules, the computed dissociation energies are too large, for example LSD yields an F_2 dissociation energy a factor of two larger than experiment (Wimmer 1987); this is in distinct contrast to accurate MO calculations (Langhoff et al. 1986) which are in almost perfect agreement with experiment. It is likely that part of problem with the LSD method is due to the far more rapid changes in electron density that occur in molecules. As discussed by Koutecky and Fantucci (1986), several efforts are underway to incorporate the gradient of the electron density into the evaluation of the exchange and correlation energy. Until some of these problems are resolved it appears that the LSD method can treat larger systems than the MO method, but the intrinsic accuracy is lower.

We consider Cr_2 , perhaps the most difficult transition metal dimer, to illustrate some of problems associated with calculation of transition metal clusters. Early density functional work was rather unsuccessful, for example Harris and Jones (1979) predicted a $^1\Sigma_g^+$ ground state for Cr_2 with a bond length of 3.66Å, instead of $^1\Sigma_g^+$ with an equilibrium distance, r_e , of 1.6788Å (Michalopoulos et al. 1982). With improved formulations of the density functional approach, it was found that if the symmetry of the calculations were lowered from $D_{\infty h}$ to $C_{\infty v}$, the correct ground state was predicted and the computed bond length was in good agreement with experiment (Baykara et al. 1984). In the transition metal dimers, the overlap of the orbitals on the two centers is significantly higher for the σ and π orbitals than for the δ orbitals (Bauschlicher et al. 1986) by reducing the symmetry, the δ orbitals are allowed to localize. Thus, both the relatively strong σ and π bonds and the weak δ bonds can be described. In CASSCF calculations the δ bonding is found to be much weaker than either the σ or π bonding (Walch et al. 1983). Thus at the experimental r_e , both the density functional and MO approaches agree that the δ bonding is much weaker than the σ and π bonding. While the qualitative view of the bonding is the same from the LSD and MO approaches, the CASSCF calculations predict shallow well with a long (3.06Å) bond arising from 4s-4s bonding (Goodgame and Goddard 1981). The deep well, with its short bond length arising from 3d-3d bonding, appears only as a bump in repulsive part of the potential (Walch et al. 1983). This result might be considered as a failure for the MO approach. However, it is well known that the CASSCF approach describes the atomic 3d-3d exchange more accurately than the large correlation associated with the metal-metal bonds (Bauschlicher et al. 1986). In other systems, this limitation is corrected by the addition of more extensive correlation in a CI calculation which more correctly balances the treatment of exchange and correlation. For Cr_2 the appropriate CI calculation would contain 57 million configurations in only a modest basis set and is therefore not currently possible.

Since the error in the CASSCF approach is quite understandable, Goodgame and Goddard (1985) proposed a correction. They assumed that the largest contribution to the bonding that was neglected in the CASSCF was due to Cr^-Cr^+ . They therefore corrected the CI Hamiltonian elements that corresponded to this bonding based upon the computed error in the ionization potential minus the electron affinity. This approach leads to a deep well with 3d-3d bonding, and an r_e in agreement with experiment. However the potential has a weakly bound outer well corresponding to 4s-4s bonding. This second well and the overall shape of the potential is quite different from that computed using the LSD method. It is possible that Moskovits et al. (1985) have seen this outer well in experiment.

While questions still remain about the exact shape of the Cr_2 potential, it is clear that the transition metals are very difficult to treat from a computational point of view. The addition of extensive correlation in CI calculations is in general not possible and this reduces the MO approach to more qualitative methods, while the LSD method must artificially lower the symmetry to try an

balance the treatment of the weak and strong bonds. In light of these problems it is not surprising to find that a rather limited number of calculations have been performed for clusters of transition metal atoms. These have been restricted to those systems where the MO approaches do relatively well for the dimers; CASSCF calculations have been performed for Sc_3 , Sc_3^+ and Ti_3^+ to get qualitative insight into the nature of the bonding and how this changes to from that in the dimer (Walch and Bauschlicher 1985). Also a comparison between the bonding in Sc_3 and Y_3 has been made by Walch (1987). Using the density functional approaches larger cluster have been considered such as fifteen atom clusters of V, Cr and Fe (Salahub and Messmer 1981, Lee et al. 1984). The structure of these fifteen atom clusters was not optimized because of the computational cost.

Unlike the open d transition metals, the accuracy of calculations on the closed d shell group IB metals is much higher, as are calculations on simple metals or the non-metals. For these systems much higher accuracy is possible and much larger systems have been treated. While they are perhaps not as interesting as catalysts as the open d transition metals, there is experimental work for comparison and it is likely that insight into the nature of the bonding and reactivity of the small metal clusters will come through a combination of theory and experiment on these systems. Therefore we devote the remainder of this section to these systems.

Calculations on Cu_2 with large basis sets, including extensive correlation (using the CPF approach) and accounting for relativistic effects yield excellent results for the Cu_2 bond length, dissociation energy and vibrational frequency (Scharf et al. 1985, and Werner and Martin 1985). It is possible to apply only a slightly lower level of theory to Cu_3 . The bonding is expected to be dominated by the 4s electrons, which would result in a prediction of an equilateral triangle structure with a $^2E'$ ground state. This structure naturally Jahn-Teller distorts to form 2B_2 and 2A_1 states. The separation between these states is sufficiently small that Cu_3 is a fluxional molecule. The experiments of Moskovits (1985) were interpreted as yielding a symmetric stretch of 354 cm^{-1} , while Truhlar et al. (1986) had fitted the fluorescence spectrum of Rohlfing and Valentini (1986) with a pseudorotation barrier of 95 cm^{-1} and a Jahn-Teller stabilization energy of 221 cm^{-1} leading to the symmetric stretch frequency of 270 cm^{-1} . The computed result (Langhoff et al. 1986) for the symmetric stretch of 268 cm^{-1} is strong support for the assignment of Truhlar et al. (1986). In addition the computed pseudorotation barrier and Jahn-Teller stabilization (59 and 280 cm^{-1}) also support the assignment of Truhlar et al. The *ab initio* calculations have also shown that the IP must be in the upper half of the experimental range (Powers et al. 1983).

$X\alpha$ calculations (Post and Baerends 1982) yields a Cu-Cu bond length in Cu_3 that is 0.2\AA longer than the CPF value, (based upon Cu_2 calculations the CPF value is expected to be slightly longer than experiment) and an angle of an 60° , that is, it does not show the Jahn-Teller distortion. A local spin density calculation (Wang 1985) has the 2B_2 structure to be 0.154 eV above the 2A_1 state, this contradicts the experimental observation that Cu_3 is a fluxional molecule and the ESR data that indicates the 2B_2 is the lower of the two states (Howard et al. 1985). The Anderson-Hückel approach (Anderson 1978) predicts Cu_3 is linear contradicting the experimental results. The DIM approach (Richtsmeier et al. 1980) however yields results which are in excellent agreement with the CPF work. The agreement between the DIM and CPF results supports the use of this semiempirical method for this particular system. Thus for Cu_3 only the MO approach supplies a sufficiently accurate description of the bonding to allow differentiation between two different experimental values for the symmetric stretch.

It is possible to treat the isovalent Ag_3 and AgCu_2 to the same level of accuracy as Cu_3 (Walch et al. 1986). As expected the bonding in these three systems is very similar. Ag_3 has a 2B_2 ground state, with one bond angle greater than 60° , as does Cu_3 . However, the most stable structure of AgCu_2 is the 2A_1 state with a Cu-Ag-Cu bond angle of less than 60° . This arises because the optimal Cu-Cu bond length is shorter than that for Ag-Cu, thus the 2A_1 state becomes favored. Since Li_3 is also isovalent and has a 2B_2 ground state, the longer bond for Li_2 than for CuLi would imply that

the isovalent CuLi_2 system would have a 2B_2 state. However, the low IP of Li_2 and modest EA of Cu leads to a large ionic contribution to the bonding and a 2A_1 ground state (Bauschlicher et al. 1987).

The most stable Be_3 structure is an equilateral triangle. Since Cu_3 is only slightly distorted from this structure, one might initially expect that Cu_2Be and Be_2Cu would have similar structures. However, both systems are linear, which arises because Be forms 2s-2p hybrid orbitals to allow the formation of two bonds (Bauschlicher et al. 1987). As illustrated by the CuLi_2 and Cu-Be dimers, and the work of Rao et al. (1986) on Li_xMg and Li_xAl clusters, the bonding in the mixed component systems can be very different from the single component clusters.

To consider larger clusters further simplifications must be made. Therefore, a great deal of work has been directed at Li, Be and Al clusters. The work on these clusters have fallen into several basic categories. In some calculations the geometry and bond length are taken to be that of the bulk and the convergence of some properties with the number of atoms is studied. This approach principally started as a method for studying the convergence properties of the cluster model approach for treating a metal surface. Since it is known that small clusters do not have the geometry of the bulk, extensive work has been performed for small clusters where all geometric parameters are optimized. To study larger clusters it is quite common to take an intermediate position, where some constraints are imposed on the structure, and the remaining degrees of freedom are optimized. (In general, optimized means the minimization of total energy with respect to the atomic positions).

Li, with only one valence electron, is the simplest system to treat and has therefore attracted the most attention. Koutecky and coworkers (Koutecky and Fantucci 1986, and references therein) using SCF/CI approaches, have performed a very large number of calculations on Li clusters. They have considered the question of the ground state and equilibrium geometry. One interesting feature of this work is that the small clusters remain planar till Li_7 , where upon they become three-dimensional (3D). A similar observation has been made for Na clusters using the LSD approach (Martins et al. 1985). If one views the bonding in metals from a two-body interaction point of view, one would expect Li_4 to become a tetrahedron, and all larger clusters to be 3D as well. This important observation seems to be ignored in much of the modeling work which is based only on a two-body potential, and therefore must find the close-packed structures the most stable. The work of Brucat et al. (1986) shows that the reactivity of Nb clusters depends more strongly on the number of atoms in the cluster than the charge state of the cluster (the neutral and the +1 ion display similar reactivity) suggests that shape of the cluster plays a very important role in the cluster reactivity. Thus studies which strive to optimize all degrees of freedom could be very important in the understanding of cluster reactivity.

In order to address the question of change in bond length with cluster size and relaxation of the layers in larger clusters, Li clusters containing up to 35 atoms were studied (Bagus et al. 1985). To make the calculation tractable, the geometry was taken to be body centered cubic like and only the Li-Li bond length was optimized. This work shows a relaxation of the layers similar to that observed for metal surfaces, the bond lengths for the atoms with fewer neighbors contract. While this should be an important observation for larger clusters, it does not address the structure and bonding in smaller clusters.

McAdon and Goddard (1987) have also considered the bonding in Li clusters using a GVB approach. Their view of the bonding is that one electron bonds are formed and the electrons are located between the atoms. They considered three high symmetry thirteen atom clusters, those which are a fragment of the bulk, fcc- or hcp-like, and the icosahedron. These three structures are the ones which are commonly picked because the limited number of degrees of freedom make them ideal for study. However, based upon the rules which McAdon had developed to describe the bonding, they were able to predict several lower symmetry structures which are more stable. This

type of chemical understanding of the nature of metal-metal bonds is extremely important, since it will help to eliminate the need to consider every possible state and structure.

Another interesting feature of the work of McAdon and Goddard is that even though they find one electron bonds, the most stable state arises when the neighboring electrons are low spin coupled. This is in disagreement with Pacchioni and Koutecky (1986), who for example find sextet ground states for several high symmetry Li_{13} structures. One of the problems associated with an MO approach is that at low levels of treatment it describes the higher spin states better. This is a problem for metal clusters since there can be many low-lying spin states close in energy. Thus when one of the high spin states is found to be the ground state, the question of the level of correlation treatment is naturally a concern. While McAdon and Goddard were limited to only an MCSCF treatment, one assumes that if more extensive correlation were added the low spin states would be further stabilized. This leads one to suggest that the SCF/CI approach used by Pacchioni and Koutecky introduced a bias toward the high spin states at the SCF level that the CI could not overcome. (See the discussion of spin states in McAdon and Goddard (1987).)

It is well known that Be_2 is weakly bound (0.94 kcal/mole per atom) (Lengsfeld et al. 1983) Be_3 is more strongly bound (8.33 kcal/mole per atom), and Be_4 is another factor of two more strongly bound (Harrison and Handy 1986). This increase in the binding energy with cluster size is due to an increased number of bonds that can amortize the hybridization energy. In Be_2 two atoms must hybridize to form one bond, in Be_3 , three atoms hybridize to form three bonds, while in Be_4 four atoms hybridize and six bonds are formed (Bauschlicher et al. 1982). This dramatic increase in binding energy with cluster size is different from Li, which can bond without hybridizing. Also, Be_4 is a tetrahedron, and Be clusters become three dimensional much sooner than Li clusters. Once the cluster reaches the point where the Be atoms are hybridizing, the binding energy per atom begins to increase more slowly, with Be_4 , Be_5 and Be_6 having very similar values, and Be_7 having a D_e per atom only 18% larger than Be_4 (Marino and Ermler 1987).

Recently several different groups have considered clusters containing thirteen or more Be atoms, and as the clusters get larger the level of approximation naturally decreases. One question which has concerned these studies is the spin of the ground state. In a study of a D_{3h} geometry Be_{13} cluster, a $^3E''$ state was predicted to be the lowest (Pacchioni and Koutecky 1984). More recently it was found that increasing the size of the basis set favored the lowest singlet state ($^1A'_1$) more than the triplet state (Bauschlicher and Pettersson 1986); distortion of the cluster (Bauschlicher and Pettersson 1986) and correlation (Pacchioni and Koutecky 1984) also favor the singlet state. Rohlfing and Binkley (1987) have also found that including correlation, using the perturbation theory, stabilizes the low spin states of both the O_h and D_{3h} forms of Be_{13} . Using only the SCF approach Pettersson and Bauschlicher (1986) were able to extend their work to include Be_{55} . Based upon Be_{13} and the work of McAdon and Goddard (1987) on Li clusters, Pettersson and Bauschlicher (1986) concluded that the true ground state of Be_{13} and Be_{55} should arise from the lowest spin (one exception being that unpaired electrons in degenerate orbitals should be high spin coupled). More recent calculations on Be_{51} and Be_{57} support this assumption, where singlet ground states were found at the SCF level (Ross et al. 1987). Furthermore, Pettersson and Bauschlicher (1986) assume that the correlation energy in the fcc- and hcp-like structure were the essentially same since they had the same number of bonds; this has subsequently been supported by the calculations of Rohlfing and Binkley (1986). It was found that the lowest structure in both the Be_{13} and Be_{55} was fcc-like, not the hcp-like structure which might have been guessed from the structure of bulk Be. However, the difference between hcp and fcc becomes smaller as the cluster size increases. Leading to the prediction that for a very large cluster the hcp would be more stable at the SCF level.

The Be_{13} work might suggest that it is always better to consider the lowest spin state. However, the recent exhaustive study of small Be clusters by Marino and Ermler (1987) shows that even using a large basis set and including correlation some clusters do appear to have high-spin ground states.

Small Al clusters have been studied in several series of MO calculations (Koutecky and Fantucci 1986, Upton 1986, Bauschlicher and Pettersson 1986, Bauschlicher and Pettersson 1987, Pettersson et al. 1987). One conclusion reached in all the studies is that Al has more stringent basis set requirements than Li or Be; a 3d polarization function must be included in the basis set. Al, like Li, does not become 3D for Al_4 , and the planar structures remain low-lying even for the larger clusters. Because the Al clusters do not become close packed immediately, they were used in a study where MO calculations were used to calibrate a modeling approach which included both two and three-body interaction potentials (Pettersson et al. 1987). While it is now clear that additional work on the form of the potential is required, the results strongly suggest that a synergism between the computational methods is possible and desirable.

Another interesting feature of the Al clusters is the ground state symmetry of Al_3 . In this system, a degenerate $^4E'$ state Jahn-Teller distorts to become two nondegenerate states (4A_2 and 4B_1). In addition there is a $^2A'_1$ state with a computed energy between the two Jahn-Teller components. As discussed above, one would expect that improved treatments would lower the $^2A'_1$ state relative to the quartet states, leading to a prediction of a doublet ground state. This is in agreement with magnetic deflection experiments (Cox et al. 1986), but contradicting the ESR spectrum obtained in matrix isolation (Howard et al. 1985). It is possible that the states are sufficiently close in energy that the matrix environment reverses the two states. Given the very small energy difference between the states it is possible that under different conditions that all three states could be present. It seems unlikely that this situation is unique to Al_3 and leads to the suggestion that perhaps the clusters should not be viewed as having only one structure, but as being more fluxional in nature. More electronic structure calculations and more modeling is needed to determine the extent of this problem and its possible consequences in the chemistry of the clusters.

The interaction of one metal atom with H_2 has been studied by several groups (for example Blomberg and Siegbahn 1983, Siegbahn et al. 1984, and Rappe and Upton 1986) and the next step is to consider the reaction of clusters of metal atoms with some molecule. However, this is a very large task, and people have considered the chemisorbed products of such a reaction. High symmetry Be_{13} and Al_{13} clusters with two and six adsorbate atoms have been studied (Bauschlicher 1985 and Partridge and Bauschlicher 1986) as well as Al_3 - Al_6 clusters with two H atoms (Upton 1986). The Al_3 - Al_6 clusters show that Al_6 is the smallest cluster that will adsorb an H_2 , in agreement with experiment. This is interesting since the cohesive energy, EA and IP for the clusters are quite similar. The determining factor in chemisorption appears to be the energy required to excite to a state which can bond two H atoms, and the disruption of the Al-Al bonding caused by the H bonding. The larger clusters appear to have sufficient Al-Al bonding and low-lying states capable of H chemisorption that the process becomes favorable. The thirteen atom work lead to the suggestion that, unlike metal surfaces, the three-fold hollow adsorption sites might become favorable over four-fold hollow sites because of the extra degree of freedom in the cluster, namely the relaxation of the metal-metal bond lengths.

In addition to the work on metal clusters, calculations have been performed on non-metal clusters, with C (for example Lüthi and Almlöf 1987, Shibuya and Yoshitani 1987, and Newton and Stanton 1986) and Si (Raghavachari 1986, and Pacchioni and Koutecky 1986) being the most studied. A great deal of recent effort has been directed at the very interesting experimental observation of Kroto et al. (1985) that C_{60} appeared to be far more stable than any of the nearby clusters. Since the cluster appeared to be so much more stable, it was suggested to have a soccerball shape. Further, they found that C_{60}La was stable leading to the suggestion that the carbon sphere surrounded the La. More recent experiments by Cox et al. (1986) have found that if the intensity of the ionizing laser is increased, the difference in the mass spectrum signal for C_{60} and the nearby clusters is reduced. That is the intensity of the mass spectrum signal is not directly related to the concentration of the neutral species. Further, the C_{60}La^+ signal was only 1-2% of the C_{60}^+ , hence the failure of Kroto et al. to observe C_xLa_2 is not surprising. This lead Cox et al. to suggest that C_{60}La is not a

soccerball surrounding the La atom. This also leads to questions about the original interpretation of the C_{60} structure. Many computational methods have been applied to the study of C_{60} (see Shibuya and Yoshitani 1987 and references therein) with the highest level of theory being used by Lüthi and Almlöf (1987). In this work they considered the question of the stability of C_{60} relative to other structures as well as relative to 60 carbon atoms. For the planar molecules they used graphite-like structures with dangling bonds and with the dangling bonds tied off with hydrogens. They found that they could fit cluster data to determine the C-C, C-H and dangling bond energy. At this SCF level with a double zeta basis set, the C_{60} soccerball is more stable than a 60 atom planar sheet. However, the binding energy per C atom in the soccerball is smaller than that for a planar sheet where the dangling bonds are tied off with hydrogen. Therefore it is concluded that while the soccerball is more stable than other 60 atom clusters, the angle strain and inhibited delocalization makes it less stable than an infinite graphite sheet. It is not possible to add polarization functions to the full C_{60} molecule, so they tested their importance for corannulene ($C_{20}H_{10}$), a bowl shaped fragment of C_{60} with the dangling bonds tied off with hydrogen. While the d functions are more important for the bowl shape than the planar molecules, the difference is not sufficiently large to make C_{60} more stable than the graphite. It is interesting to note that Newton and Stanton (1986), based upon semiempirical methods, also concluded that the soccerball was the most stable 60 atom cluster. Thus theory seems to support the view of Kroto et al., that a likely structure for C_{60} is that of a soccerball. Only a few years ago, this size cluster was not tractable in *ab initio* calculations.

The work on Si clusters (Raghavachari 1986) follows along the lines of the small metal clusters. A detailed study of the basis set and correlation requirements is made and appropriate level of treatment is applied to the larger clusters. As in the metal clusters the geometry of the small clusters cannot be considered as fragments of bulk. As the cluster size increases, three dimensional clusters with singlet ground states quickly become the most stable.

In addition to treating free clusters, people have recently begun to consider the metal support interaction. One example of this work is the study of Cu on MgO(100) (Bacalis and Kunz 1985). In this work the support was modelled by five atoms and a charge array. The Cu adsorption site was determined and Cu in a Mg vacancy was studied. A Be_4 cluster on a Cu_{18} cluster was used to investigate a Be cluster on a Cu(100) surface (Bauschlicher et al. 1987). It is expected that such studies could be performed in which the adsorbed metal or the support were varied to give some insight into the bonding. We expect that these calculations will become more common in the near future.

Calculations for the transition metal diatomics indicate that for transition metal clusters only qualitative information is possible at the present time and it will probably be some time before accurate calculations are possible. The simple metal work shows that for small clusters accurate calculations are possible. For some properties it has been shown that correlation can be ignored, and hence quite large clusters can be considered at the SCF level. This has allowed the study of the convergence of some cluster properties to that of the bulk. However, for such questions as the binding energy, correlation must be included. Perhaps the most severe case of this is that Mg_4 is not bound at the SCF level, and only becomes bound with the inclusion of correlation (Chiles et al. 1981). It has also been found that different clusters have different basis set requirements; Be clusters require a good description of the 2p, while Al clusters require a 3d function. So even these simple metal clusters can require extensive treatments to accurately compute their properties. However, with improved methods, a better understanding of the bonding and an improved interface between the *ab initio* and modeling approach, the calculation of the properties of small metal clusters should become an even more important component of the study of small clusters.

The applicability and associated level of success of different *ab initio* methods in predicting properties of small to very small clusters of atoms have shown enormous improvements during the last four to five years. Despite this tremendous development, a systematic classification of the achieve-

ments and limitations in predicting properties of small metal clusters, such as structure, binding energy, electronic state, ionization potential and reactivity, is not currently possible. However, it is not impossible that this goal will be achieved in the next few years for, at least, the non-transition metal clusters.

Semiempirical methods in general, start with the basic ideas used in *ab initio* methods, but reduce the complexity by many approximations. They further reduce the work by approximating many of the required matrix elements with information deduced from experiment. The parameters used to approximate the matrix element can be fine tuned based upon application of the method to molecular systems for which experimental data exists. It is probably not surprising that for a series of n related compounds, if the semiempirical methods are calibrated for $n-1$, they can do quite well for the n^{th} ; in general, this appears to be the case for organic systems where many well understood examples can be used to calibrate the methods. However, this does not appear to be the case when such methods are applied to clusters. As emerges in the Morse (1986) review, the semiempirical methods do not work too well for the transition metal clusters. As discussed above, application of the Anderson-Hückel approach incorrectly predicts a linear Cu_3 , while the DIM method correctly describes the same system. For C_{60} where one might guess that the semiempirical methods would be reliable, the *ab initio* results (Lüthi and Almlöf 1987) and the semiempirical results (Newton and Stanton 1986) yield the same conclusions. At the present time it appears that caution must be used in applying semiempirical methods to interpret the chemistry of metal clusters. It is hoped that as more experimental and accurate *ab initio* data becomes available to calibrate these methods their reliability will increase to a point similar to that for carbon chemistry.

Computer simulation methods

Computer simulation techniques based on atomistic considerations provide a useful approach to the study of small clusters. Despite the fact that presently many of the computer simulation calculations are at a qualitative level, nevertheless, they contribute considerably to our understanding of microscopic structures and related processes. Simulation studies not only help scientists to gain proper intuition, in fact, they are becoming an important tool to aid in the interpretation of many experimental observations. There are three common "atomic level" computer simulation methods which can be used in small cluster research: Molecular Dynamics, Monte-Carlo and Statics.

In the molecular dynamics technique the classical equation of motion is solved numerically for a collection of N atoms which constitute the cluster. Depending on the potential energy function used and the type of the system to be simulated, a variety of numerical algorithms are available for this purpose (Beeman 1976, Evans and Morriss 1984). The method generates a time-order series of atomic coordinates representing the motion of every atom in the system. Kinetic energies are incorporated with the calculation scheme; therefore temperature effects are intrinsically included in the result. In principle, molecular dynamics calculations with a sufficient number of iterations can simulate any time dependent (nonequilibrium) as well as equilibrium quantity. Using velocities of particles evaluated in every step, one can obtain the velocity autocorrelation function from which the frequency distribution spectrum for the microcluster can be calculated.

Monte-Carlo techniques employed in small cluster simulations are, in general, based on the Metropolis procedure (Wood and Erpenbeck 1976 and James 1980). Starting from an initial configuration, atoms in the cluster are randomly displaced according to the Maxwell-Boltzmann distribution. After the generation of a sufficient number of Monte-Carlo steps (ensuring that the phase space is sampled ergotically) the desired quantities are calculated as ensemble averages from position dependent quantities estimated in every step. By this method any equilibrium quantity can be calculated as a function of temperature which is introduced via the Maxwell-Boltzmann factor.

The static method, on the other hand, is based on a simple minimization technique to find the configuration of a cluster corresponding to the nearest energy minimum. It is a temperature

independent approach and it can be regarded as the $T = 0^\circ K$ case. Because of the simplicity of the static method and its small demand of computation time, it is used quite frequently to obtain local minima. Depending upon the initial configuration chosen, however, this method can provide only one of the many configurational energy levels associated with the cluster. Even for clusters in the smaller size regimes, finding the cluster configuration corresponding to the lowest energy level (the ground state) may turn out to be a quite difficult job, in particular if the gross structure or the symmetry group of the ground state can not be guessed initially. In order to increase the probability of finding the global minimum, a rather large number of initial guesses must be made and even then, minima located in narrow catchment regions may easily be missed. On the other hand, if one uses physical intuition, usually as a set of growth rules deduced from the behavior of macroscopic systems, to generate configurations which are likely to lead to the global minimum, the general tendency is to miss low-symmetry solutions (Wille 1987).

All three of these simulation methods are based on some type of a potential energy function which describes the total interaction energy among the atoms as a function of their positions in the cluster. In general, finding an appropriate potential energy function constitutes the most important and difficult part in these simulation techniques, which are basically long iterative procedures. Therefore, it is necessary to describe the total potential energy of the system in terms of semiempirical or model potential functions with simple analytic forms. While for smaller size clusters more complex functions (perhaps even functions based on first principles) can be utilized, in the case of larger clusters the computational time becomes prohibitively long, requiring the use of functions with simplest possible forms to represent the interactions among the atoms in the cluster.

Based on the Born-Oppenheimer approximation, if it is assumed that a function $\Phi(\vec{r}_1, \dots, \vec{r}_N)$ exists to describe the total potential energy of an isolated system of N atoms as a function of their positions, then, without any loss of generality the function Φ can be expanded as:

$$\begin{aligned} \Phi = & \sum_i^N \sum_{j < i}^N u(\vec{r}_i, \vec{r}_j) + \sum_i^N \sum_{j < i}^N \sum_{k < i}^N u(\vec{r}_i, \vec{r}_j, \vec{r}_k) + \dots \\ & \dots + \sum_i^N \dots \sum_{i < \dots < n}^N u(\vec{r}_i, \dots, \vec{r}_n) + \dots \end{aligned}$$

where, $u(\vec{r}_i, \vec{r}_j)$, $u(\vec{r}_i, \vec{r}_j, \vec{r}_k)$ and $u(\vec{r}_i, \dots, \vec{r}_n)$ denote the two-body, three-body and n -body interactions, respectively. In this so called many body expansion of Φ , it is usually believed that the series has a quick convergence, therefore, the higher moments may be neglected. Otherwise this equation can not be employed for systems containing more than only a few atoms.

In the earlier calculations, in general, the higher terms including even the three-body part were omitted, and the total potential energy, Φ , was approximated only by the sum of two-body interactions. This approach, which may be regarded as a first order approximation, not only simplified the statistical mechanical formalisms used in calculating various thermodynamical properties, but, more importantly, it enabled many earlier researchers to run simulation calculations with relatively smaller and less powerful computers. In most of the simulation calculations which are carried out considering this first order approximation, Lennard-Jones type functions were employed to mimic two-body interactions. Despite the fact that those so called Lennard-Jones systems may only represent microclusters of rare gases where the role of many-body forces are minimal, they provided a very useful understanding about many properties of microclusters in a systematic way that could not be acquired easily by other means. Recent studies, however, indicated that, particularly in the case of systems containing atoms other than those with close-shell structures, this first order approximation is inappropriate and produces results inconsistent with many experiments due to neglect of many-body interactions (Finnis and Sinclair 1984). Therefore, in more recent simulation

studies, in addition to two-body interactions, three-body interactions also are being considered in the calculation of potential energies (Feuston et al. 1987). As anticipated, the type of potential energy function used in a modeling procedure dictates many properties of small clusters, such as the stability and the energetics and, of course, the distribution of the configurational energy levels, as well.

Using the Lennard-Jones function to represent two-body interactions Hoare and Pal (1971) performed static calculations to find stable configurations of various sizes of microclusters and their corresponding energy values. Almost the same calculations were recently repeated by Pang et al. (1986), for clusters of rare gas atoms in an attempt to analyze the stability of small clusters as a function of their size. Despite the fact that these two calculations, for many cases, produced similar results, for a few cases (for 6, 8 and 9 atoms clusters) the results obtained by Pang et al. (1986) produced somewhat higher energy values than Hoare and Pal's findings, indicating that they do not correspond to the energetically lowest configurations. This may represent an example of the above mentioned difficulty associated with the static method in finding the lowest energy configuration even in the case of smaller size clusters. Hoare and McInnes (1976) calculated as many as possible configurations (for clusters containing up to 13 atoms), corresponding to various energy minima using the Lennard-Jones and Morse functions. One of the most important features of their results was the extreme sensitivity of the number of possible stable configurations to the range and softness of the pair potential. They also showed that in the case of the Lennard-Jones results non-crystallographic configurations predominate among the calculated minimum energy structures. Recently, Wille (1987) calculated minimum energy structures of microclusters containing up to 25 Lennard-Jones atoms. He used a simulated annealing method, a variant of the Monte-Carlo technique, to calculate configurations corresponding to the ground states of clusters with different sizes. In the process of simulated annealing the system is started in a random initial configuration at a sufficiently high temperature. After a certain number of Monte-Carlo steps the temperature is reduced by a prescribed factor, and then, the process is repeated until no further improvements have been made over a number of iterations. This method was found to be particularly useful in obtaining global minima. Yang and Bambakidis (1978) calculated structural stability of small clusters employing a two-body Morse interaction potential. They used a static method and calculated energies for icosahedral and cubo-octahedral geometries as a function of the cluster size. While for smaller cluster sizes the icosahedral structure was found to be energetically more stable, in the case of larger cluster sizes ($N > 3400$) the cubo-octahedral structure becomes more favorable.

Tsai and Abraham (1978), using a Monte-Carlo simulation technique, calculated the structure and thermodynamics of binary microclusters of Lennard-Jones atoms as a function of cluster size, composition and temperature. In this work the authors analyzed the internal energy, instantaneous snapshot pictures of the microcluster's atomic configuration, and the single-particle pair distribution function. Melting properties for microclusters up to 13 atoms were investigated by Etters and Kaelberer (1977) employing a Monte-Carlo technique based on Lennard-Jones pair interactions. They found that the melting temperature depends strongly on the cluster size and the transition is rather gradual. In this study they have also emphasized the importance of the statistical sampling in determining properties around the melting transition where fluctuations play a significant role. Franke (1987) employing a "Path-Integral Monte-Carlo" method based on quantum statistical mechanics, investigated thermodynamical and geometrical properties of rare gas clusters. His results indicate the importance of the zero point energy to the structure of the 13-atom cluster. He found that in the entire temperature region he studied a rather slow melting process is taking place. The number of configurations contributing to the partition function was found to be growing continuously and no transition point could be recognized. In another model calculation Pal and Hoare (1987) simulated the dynamics of nitrogen microclusters based on the assumed free rotation of N_2 molecules within a solid-like harmonic vibrating structure. Calculated results were compared with experimental measurements and consistencies were found for certain temperature ranges.

Simulation calculations using both molecular dynamics and Monte-Carlo techniques were carried out by Heidi et al. (1987) and Jellinek et al. (1986) in an effort to investigate solid liquid changes in 13-particle clusters of argon. Calculations indicated the existence of two forms, a solid-like phase and a liquid-like phase with finite range of total energies. Clusters spend long time intervals in each phase, undergoing spontaneous transitions from one form to the other in the course of their time evolution. In another simulation study by Quirke and Sheng (1984) the melting behavior of small clusters of atoms was investigated using a Monte-Carlo method based on Lennard-Jones potentials. They found a smooth melting transition from an icosahedral microcrystal to an inhomogeneous liquid. A systematic simulation study of microclusters containing 13 - 147 atoms was recently carried out by Honeycutt and Andersen (1987) using constant temperature and constant energy calculations alternatingly. A molecular dynamics procedure based on the Lennard-Jones potential was employed and, for some cases, it was combined with the stochastic collision technique of Andersen (1980). They investigated minimum energy structures of small clusters along with their equilibration characteristics at elevated temperatures and coexisting phases. Calculated results showed a strong dependence on the type of the ensemble (microcanonical or canonical) used in the simulation procedure. The ensemble dependence they found, decreases as the cluster size increases. This outcome may be expected because (i) fluctuations about mean values become more and more important as N , the number of atoms in the cluster, decreases; and (ii) the two ensembles used in the calculations have different fluctuation characteristics (Hill 1963, 1964).

Based on a statics method, the energetically most favorable structures of microclusters (up to 13 atoms) have been calculated by Halicioglu and White (1980), (1981) using a potential energy function comprising two- and three-body interactions. Structural changes were parametrically analyzed and the effect of the intensity of the three-body interactions on the minimum energy configurations was investigated. It has been concluded that three-body interactions play a significant role in the minimum energy structures of clusters. Employing a molecular dynamics technique based on two- and three-body interactions Polymeropoulos and Brickmann (1982), and (1983) calculated stabilities of microclusters of varying sizes and showed the significance of the three-body interactions by correlating the calculated results with experiments. Their findings suggest that the occurrence of clusters corresponding to "magic numbers" for xenon and the absence of such stable clusters for argon is due to the three-body triple-dipole interactions. In another more recent study Polymeropoulos and Brickmann (1985) analyzed ionized rare-gas clusters containing up to 26 atoms employing a combined molecular dynamics and Monte-Carlo technique. Calculated results for cluster stabilities were found to be in fair agreement with experimental measurements. Their simulation results indicate that the ionization process plays an important role in the structure and stability of gas-phase clusters.

Blaisten-Barojas and Andersen (1985) analyzed the effect of three-body interactions on the structure of small clusters and found that the coordination number in the cluster diminishes as the three-body strength increases, resulting in a global expansion of the cluster. In another investigation by Halicioglu et al. (1985) the influence of the three-body forces on the vibrational properties for triatomic clusters was analyzed, parametrically. They investigated the frequency distribution spectra for linear and triangular shapes when both are equally stable energetically. In a recent article Blaisten-Barojas and Levesque (1986) investigated microclusters of silicon considering two- and three-body interactions. Their calculations (performed at $T = 0^\circ K$) for Si clusters produced rather open structures as minimum energy configurations, in particular for smaller size clusters, reflecting the existence of strong three-body forces operational among silicon atoms. Using an empirical potential energy function (Finnis-Sinclair potential) Marville and Andreoni (1987) have calculated the cohesive energy of transition-metal clusters as a function of the cluster size. They have examined energetics and the structural parameters of microclusters at the static limit and analyzed the validity of the potential function for structural simulation studies.

III. Important Properties of Small Clusters

In this section some of the common properties of microclusters (such as structural, electronic and energetic properties as well as chemical reactivity) are reviewed and analyzed. One of the most significant and popular features of small cluster investigations is the analysis of various properties as a function of cluster size. Any property associated with a small cluster is expected to converge to its parent bulk value as the cluster size approaches macroscopic dimensions. In many studies (experimental and theoretical) it has been clearly demonstrated that this convergence has a non-monotonic character and has different slopes for different properties. Depending on the atomic species involved deviations from the linearity in cluster properties are most pronounced in the *very small* and *small* size clusters regions. Many of the electronic properties and related level structures of small clusters have already been discussed in the section devoted to *ab initio* methods in Chapter II. In general, structural and electronic properties as well as magnetism and energetics of clusters are very closely interconnected, therefore, it is difficult to analyze them independently (Rao and Jena 1985). While the positions of atomic nuclei in a microcluster determine the electronic states, the distribution of electrons, in turn, plays an important role in the energetics; accordingly, it affects the shape and the overall geometry of the cluster along with its magnetic quality.

Structural and Electronic Properties:

Unfortunately, detailed configurational analysis of a cluster on an atomic scale is a very difficult task. For gas-phase clusters, in general, structural information comes from electron diffraction studies. For trapped clusters, on the other hand, techniques such as EXAFS or XANES along with electron diffraction techniques are employed. While for trapped clusters structural property measurements can be conducted at leisure, one faces difficulties in analyzing and sorting out associated environmental effects due to the interactions between the atoms in the cluster and the surrounding atoms. Howard et al. (1985) analyzed this environmental effect on the structure of very small clusters of coinage metals trapped in various matrices. In the case of gas-phase clusters, on the other hand, the environmental effect is minimal. However, the timing of the measurement is often restricted depending on the type of the experimental technique and equipment utilized. In general, the time lapse between the generation of a cluster in the gas phase and the measurement step is quite short, therefore, findings related to the stability of small clusters and their equilibrium conditions are open to various criticisms (Schumacher et al., 1984; Brown 1987). The equilibrium condition is an important consideration in correlating the abundance ratio of a particular species in the beam with its stability. Since different size clusters may dissociate (or associate) at different rates, the abundance ratio in the beam at a nonequilibrated state may not always reflect the stability of gas-phase clusters at their equilibrated state. The relationship between the magic numbers and relative stabilities of clusters was analyzed recently by Phillips (1985) and the role of the kinetics in this analogy was found to be very significant. Furthermore, Kappes et al. (1986) have analyzed the relationship between the measured ion abundances in the cluster beam and thermodynamic stabilities of neutral ions. In this paper, they have also investigated the structural and bonding characteristics of various isolated alkali clusters.

Theoretical investigations indicate that small clusters exhibit different geometrical structures with varying degrees of symmetry corresponding to metastable states which, in many cases, are nearly degenerate with the ground state configuration. Earlier calculations based on model pair interactions (representing small clusters of rare gases) by Hoare and Pal (1971), (1972), Hoare and McInnes (1976) and by Etters et al. (1977) produced varying geometrical configurations for a small cluster all corresponding to different energy minima. In general, simulation calculations indicate that for clusters with atoms interacting via two-body potentials (Lennard-Jones or Morse), the icosahedral symmetry is energetically more favorable than the cubo-octahedral structure in the smaller size regimes, while for larger clusters the opposite prevails (see also Yang and Bambakidis 1978). These calculated results are consistent with the electron diffraction experiments by Lee and Stein (1985) on gas-phase argon clusters. Also, in another paper by the same authors (Lee and

Stein 1987) structural variations of argon clusters were studied both experimentally and by model calculations. Their results indicate that the icosahedral configuration changes to fcc as the size is increased over 3000 atoms per cluster. The same conclusion was also reached in a more recent paper by Honeycutt and Andersen (1987) where they also have investigated the phenomenon of transitions (coexistence) back and forth between two or more types of structures. Furthermore, Beck et al. (1987), Heidi et al. (1987), Jellinek et al. (1986) and Berry et al. (1984) in their investigation on the melting and freezing behavior of finite clusters, have also found that different phases can coexist over a range of temperatures.

In another calculation based on a parametrical analysis, Halicioglu and White (1980), (1981) used a model potential function comprising two- and three-body interactions for clusters containing 3-13 atoms. Due to the inclusion of three-body interactions in these calculations various open structures such as linear, two-dimensional planar and ring structures as well as three-dimensional species were found to be energetically stable species with comparable energies. Changes in the energetically most stable structures as a function of the three-body intensity were found to occur abruptly. Results clearly indicate that configurations of microclusters vary from compact three-dimensional structures to open two- and even one-dimensional forms as the three-body intensity increases progressively from zero to larger values. MNDO calculations carried out for small carbon clusters by Newton and Stanton (1986) also indicate that for certain size regimes planar and polyhedral carbon clusters may be nearly degenerate. More recently, Pettersson et al. (1987) calculated energetically stable structures of Al clusters employing an *ab initio* all electron approximation. Among different stable structures, for each cluster, some were found to be nearly degenerate. As another interesting outcome, these high level calculations indicate that for Al₄ and Al₅ two dimensional structures are energetically more stable than the three-dimensional more compact forms. Extensive lists for the energetics of various metal clusters with different symmetries are given in two recent articles by Koutecky and Fantucci (1986). Two important conclusions may be drawn from theoretical investigations on the structure and stability of microclusters: (i) In general, a number of different stable structures are likely to be found energetically in near degeneracy with the ground state configuration. (ii) The energetically lowest configuration does not have to be associated with a three-dimensional high symmetry structure.

The first conclusion mentioned above, can be recognized as the main cause of the fluxional nature of small clusters that produces an additional difficulty in the structural determination of isolated small clusters. Kondow (1987) in his article points out the existence of various metastable cluster structures having similar stabilities. In general, it is anticipated that fluxionality of clusters is inversely proportional to its size. There are several direct experimental results indicating the fluxional character of small metal clusters. Smith et al. (1986) have investigated structural changes and atomic rearrangements in small gold clusters. Wallenberg et al. (1986) analyzed structural rearrangements in small Pt clusters using a recent HREM technique. They investigated the influence of the electron beam on the structural changes of smaller particles in connection with phenomena such as crystal growth and particle coalescence. In another recent experimental work, Iijima and Ichihashi (1986) investigated dynamic behavior of ultrafine gold particles around 20 Å in size at a level of atomic resolution by electron microscope. It was emphasized that structural fluctuation of small gold particles takes place when they are exposed to electron beam irradiation. They found that the shape of the clusters continuously changed in every few tenths of a second and these structural variations were often accompanied by rotational and translational motion. This structural fluctuation phenomenon was called "quasi-melting" of small clusters by Marks et al. (1986). They analyzed the energetics associated with the dynamical fluctuations of the particles among different configurations and they tried to attribute this phenomenon to the reduction of surface energy anisotropy as the temperature is raised. Small clusters of benzene molecules were described by Stance et al. (1987) in terms of a liquid-like rather than solid-like state.

Clusters of group IV elements exhibit very interesting properties in terms of both structural

and electronic aspects. While characteristics of germanium clusters resemble silicon (Bloomfield et al. 1985; Heath et al. 1985), clusters of carbon display very different structural properties (Brown et al. 1987; Kroto et al. 1985). Carbon clusters, in general, appear to have more open structures relative to silicon and germanium clusters, perhaps because of the strong π -bonding which encourages linear or monocyclic ground state configurations. Energy minimization calculations, also, indicate that generally three-dimensional structures are more stable for silicon clusters whereas the corresponding small clusters of carbon were found to be linear or planar (Brown et al. 1987; Newton and Stanton 1986). It has also been found that calculated equilibrium structures of small silicon clusters deviate significantly from those of the corresponding crystalline fragments. Some preliminary calculations indicate that the crossover to the bulk structure occurs for clusters of several hundred silicon atoms (Brown et al. 1987; Tomanek and Schluter 1986). A fascinating structure for carbon clusters which consist of 60 carbon atoms was proposed by Kroto et al (1985). The structure of C_{60} (buckminsterfullerene) is spherical and based on an icosahedron and truncated at each pentagonal apex. Recent HREM observation of partially graphitized carbon by Iijima (1987) has revealed a spherical C_{60} structure which resembles the 60-carbon cluster proposed by Kroto et al. (1985). In the photofragmentation experiments on silicon cluster ions, Bloomfield et al. (1985) determined relative cross sections in individual fragmentation channels. Fragmentation experiments were carried out by exposing the mass selected ionized silicon clusters to an intense beam of pulsed laser radiation. Their findings indicate that the clusters dissociated at near melting temperatures and the fragmentation spectra were shown to be temperature dependent. In a recent study based on molecular dynamics calculations, Feuston et al. (1987) analyzed the ground state and finite temperature configurations of silicon clusters. Their results suggest that the magic numbers in the fragmentation spectra for silicon clusters are determined by the topology and energetics of high temperature structures rather than by the structure and energies of the ground state.

In the structural characterization of microclusters bond length measurements play an important role. In the majority of the experimental studies, it has been found that the nearest neighbor distance contracts as the cluster size decreases. However, clusters with atoms of group II, in particular, exhibit a reverse trend, the nearest neighbor distance expands as the cluster size decreases (Brechignac and Cahuzac 1986). Investigations on the nearest neighbors distance measurements for metals, in general, are conducted using the EXAFS technique. For small metal clusters such as Au (Balerna et al. 1985 and De Crescenzi et al. 1985), Cu, Ag (Howard et al. 1985), Fe and Cr (Montano et al. 1985) varying degrees of contractions of interatomic distances have been reported both for clusters trapped in matrices or deposited on various substrates. On the other hand, in some cases, observations in experiments on substrate supported clusters were interpreted as an expansion in the lattice parameters (Heinemann and Poppa 1985; Heinemann et al. 1983). However, in another article Gallezot et al. (1985) suggest that some of these observations may be explained as a diffraction phenomenon rather than an actual increase of the interatomic distances in clusters.

Heteronuclear clusters which are also called "Compound Clusters" have a special and important place in small cluster research. In many instances, for example, small intermetallic clusters generated in the gas phase exhibit unusual properties (Martin 1986). Various structural and electronic properties of compound clusters involving Li, Na, Mg and Al atoms were calculated by Rao et al. (1986) employing *ab initio* methods. They found that the equilibrium geometries of a homonuclear microcluster can be significantly altered by replacing one of its constituent atoms with a different atomic species. According to their results, clusters of Li_2Al and Li_2Mg exhibit linear configurations as the energetically most stable structure, whereas, Li_3 forms an isosceles triangle. In another study based on computer simulations by Tsai and Abraham (1978) the compositional distribution of the binary species was found to be an important factor in cluster packing geometry. In a more recent experimental investigation on binary systems Sattler (1986) studied clusters of heavy metals (Bi, Pb and Sb) generated by a simultaneous inert gas condensation technique. He analyzed, in this study, the size distribution of clusters in the beam, adsorption probabilities and cluster reactivities as a function of cluster size and the number of foreign atoms in the cluster. Martin (1985) investigated

compound clusters of Cs by allowing the gas-phase generated Cs clusters to combine with O₂, Cl₂ and S₈. By varying the partial pressure of constituent elements in the gas phase, he studied in one experiment the stability of a broad range of cluster compositions. Results he obtained indicate that for Cs compound clusters (either charged or neutral) the stability is higher for clusters with even numbers of electrons.

Thermodynamic properties such as the melting point and the vapor pressure of microclusters also display considerable deviations as a function of cluster size. For smaller size clusters vapor pressure increases as the melting point drops. As Poppa (1984) outlined in his review, such important thermodynamic property variations associated with cluster dimensions must be taken into consideration in the context of sintering and dispersion studies in the supported cluster research. In recent computer simulation studies it has been found that in the smaller size regimes a temperature interval, ΔT_c , exists where solid-like and liquid-like structures can coexist (Beck et al. 1987, Honeycutt and Andersen 1987). This temperature interval was defined as $\Delta T_c = T_m - T_f$ where T_m denotes the upper bound of stability for the solid and T_f is the lower bound of stability for the liquid. Beck et al. (1987) found that ΔT_c is not a simple function of the cluster size, but generally increases as the size decreases. Other computer simulation investigations by Heidi et al. (1987); Jellinek et al. (1986); Quirke and Sheng (1984) and Etters and Kaelberer (1977) on the melting properties of rare gas clusters indicate that, in general, melting behavior exhibits strong dependence on the size of the cluster.

Multiply charged microclusters exhibit some degree of instability which is inversely proportional to their size. In these clusters it has been shown by Sattler (1985) that repulsive forces of the charges are operational and overcome the cohesive energy of the cluster causing a so called *Coulomb explosion*. The minimum number of atoms required for a stable charged cluster is a material characteristic and depends on the ionization state of the particle. For various elements Morse (1986) in his recent review article lists the minimum number of atoms necessary for a cluster to stabilize a charge. Based on mass spectroscopic analysis of positively and negatively charged CO₂ clusters Knapp et al. (1985) found that the size distributions of these species (both being produced from the same ensemble of neutral clusters) are completely dissimilar. Furthermore, different *magic numbers* in the two types of mass spectra indicate that the geometrical structures of these cluster ions are non-identical and depend on the sign of the charge.

Chemical Reactivity

The chemical reactivity of small clusters constitutes a subject of great importance in catalysis related areas. Like other properties, chemical reactivity of a cluster depends on its size, structure as well as on its electronic state. Model studies in catalysis are generally based on a systematic investigation of the chemical reactivity of clusters deposited on substrate surfaces (Bond 1985; Del Angel et al. 1985; Poppa 1984). Unfortunately, many of these investigations are faced with the difficulty of sorting out and understanding the strong cluster-support interactions which affect greatly the chemical reactivity. In order to avoid these environmental effects, in recent years, studies on the chemical reactivity of small isolated clusters have been conducted. In those studies, after the cluster beam is generated, a reagent is injected in the gas stream and the resulting products along with the remaining clusters are measured by a suitable mass spectroscopic technique (Moskovits 1986). Recently, Brucat et al. (1986) analyzed the charge dependence of chemisorption patterns for transition metal clusters. They found a remarkable parallel in the reactivity of positive metal clusters when compared to the corresponding neutrals. Other studies include the gas phase reaction of Fe clusters with H₂ and D₂ (Whetten et al. 1985; Richtsmeier et al. 1985; Geusic et al. 1985). Findings have indicated that the chemical reaction is not a monotonic function of the cluster size. While Fe₁₀, Fe₁₁ and Fe₁₂ exhibit an increased reactivity, Fe₁₇ was found to be very inactive. In another investigation Whetten et al. (1985) analyzed the size dependence of the chemical reaction

taking place between isolated Fe clusters (upto Fe_{15}) and O_2 . Also, among recent studies, chemical reactions between Pt clusters and various hydrocarbon molecules were systematically investigated by Trevor et al. (1985). A comprehensive coverage of chemical reactivity of neutral and ionic metal clusters is included in the recent review article by Morse (1986).

IV. Conclusion

In this section an outline of progress made in microcluster research to date is presented. Achievements and limitations of techniques used in various cluster studies as well as the credibility of results, along with the difficulties encountered in investigations and interpretations are discussed. The present state of collaboration between theory and experiments is also analyzed.

Experimentally, the field of isolated metal clusters has exhibited a rapid progress in recent years. Various cluster sources have been developed. Intense beams with high purity have made it possible to study neutral and ionic clusters of practically any element. Despite advanced separation procedures, however, preparation techniques (for both gas-phase and matrix isolation) depending on the type and composition of microclusters, still suffer from problems associated with non-uniform size distribution of neutral clusters. This non-uniformity also affects adversely various identification methods. Difficulties encountered in PES due to non-uniform size distribution seem to become manageable, at least, by using mass-selected metal cluster ions (Zheng et al. 1986; Kermisant 1985). Problems associated with equilibration and structural fluctuations of isolated small clusters particularly in gas-phase research are being recognized now and need further investigation. Recent experiments have indicated the importance of matrix-cluster interactions in the quantitative interpretation of spectroscopic results (Bechthold and Schober 1987; Bechthold et al. 1986; Moskovits and Limm 1986). Correlation between the cluster ionization potential and the rate of chemical reactivity is not yet well established (Brucat et al. 1986). In some cases, predissociation seems to be an important limitation in gas phase spectroscopic identification techniques (Moskovits and Limm 1986). In supported cluster research, in general, surface properties interfere with detection procedures. Interactions between the cluster and the substrate continue to be a problem, especially in the interpretation of various experimental observations. At the present time, it seems that research on clusters deposited on substrate surfaces needs more support from theory. On the other hand, integrated experimental techniques have been used successfully to analyze structural characteristics along with the chemical reactivity of clusters deposited on substrates (Poppa et al. 1986; Poppa 1984). EM techniques and their relation to STM are gaining interest in supported cluster research. Probably, over the next few years, several new combination instruments will emerge that will combine STM with some form of EM (Venables et al. 1987). A microscopic level understanding of the catalytic activity and/or selectivity is still at a very early stage. Unusual surface structures of clusters are still believed to be playing the most important role. New ideas and an increased involvement of theory are urgently needed in these areas.

Significant developments in small cluster research have also taken place in theoretical studies as well as in simulation techniques. Highly accurate *ab initio* calculations have now become feasible with the availability of supercomputers which also allow long iterative simulation calculations for microclusters of varying sizes. Theoretical calculations based on first principles have now started making an impact in a variety of investigations (ranging from structural to electronic properties) particularly for dimers and trimers. Calculations have not only reproduced experimental results correctly, but also provided new information about non-observable properties of these small clusters. Results from *ab initio*, semiempirical and computer simulation calculations indicate that in many cases small to very small size clusters possess a number of low lying energy states corresponding to different configurations and symmetries (Pettersson et al. 1987). This near degeneracy situation is very closely related to the fluxional character of small clusters. In the literature to date, except for the trimer case perhaps, not much attention has been paid to the fluxional nature of small isolated clusters. Configurational energy states and their distribution associated with a microcluster,

like other cluster properties, depend on the atomic species in the cluster as well as on its size. Unfortunately, at the present time, we do not have any practical means of calculating the distribution of the energy levels associated with a given cluster which could furnish information about the fluctuating nature of the cluster. If a microcluster is associated with narrowly spaced low-lying configurational energy states, it is very likely that at finite temperatures structural fluctuations would take place. However, the degree of these structural fluctuations has not yet been correlated either with the composition or size of the clusters. Furthermore, at the present time, we have very little information about the energy barriers separating these low lying states. Computer simulation studies based on Lennard-Jones systems provide some qualitative insight about the spread in the distribution of the configurational energy states along with some indirect information about the energy barriers. If the spread is large and the energy states are narrowly spaced and accessible (with low barriers separating them), then, the structure is fluxional and no preferred geometry can be assigned. Accordingly, the time average of the structure is rather liquid-like (Beck et al. 1987; Honeycutt and Andersen 1987; Jellinek et al. 1986; Hoare 1979). In the study of small clusters, it seems that the possibility of fluctuating structures is a very important issue. In particular, in the interpretation of various experimental observations, the assumption of a cluster as a rigid structure with atoms vibrating about their "sites" (inherited from macroscopic solid state physics) should be very carefully reconsidered.

In general, accurate *ab initio* calculations are employed in finding the energetically most stable (ground state) configuration of microclusters. In these calculations, results are obtained via an optimization procedure which is basically an energy minimization. Then, analogies are sought between these calculated results representing the ground state configuration at the static limit ($T = 0^\circ K$) and experimental observations (such as abundance ratio or magic numbers). In this whole procedure several important points are generally overlooked. (i) Even for clusters containing small numbers of atoms, to find the configuration corresponding to the global minimum (the ground state), a careful scanning of the phase space is required. With a limited number of points, it is very easy to miss deep minima, in particular, belonging to small catchment areas (Wille 1987). (ii) The assumption that the ground state configuration of a cluster must have a high symmetry should not always be taken for granted. Recent calculations have indicated that low symmetry forms may also be the ground state (McAdon and Goddard III 1987; Pettersson et al. 1987). (iii) The often presumed similarities between the structures of ionic clusters and their neutral counterparts need further elaboration. The generalization of this assumption should be avoided, particularly, if the energetics of low lying states are unknown.

High level *ab initio* calculations even for clusters of very small sizes are still difficult. Parametrized models, however, seem to become feasible in this respect (Pettersson et al. 1987). One of the shortcomings in the small cluster research based on computer simulations is due to the unavailability of realistic potential functions describing the interactions among the atoms in the cluster. Simulation results show strong dependence on the functional form of the potential. While results obtained by simple pair potentials have provided an enormous amount of understanding and conceptualization of microcluster properties, they do not in general, furnish quantitative information. However, the recent use of three-body interactions (in addition to pair interactions), has improved simulation results considerably, even for covalently bonded systems (Feuston et al. 1987; Blaisten-Barojas and Levesque 1986). In calculating average values for small clusters at finite temperatures simulation results were found to be ensemble dependent (Honeycutt and Andersen 1987). Probably, the role played by fluctuations in this dependence is significant (Hill 1963, 1964). Despite their qualitative nature, computer simulation studies, as it stands now, are becoming more and more an integral part of the identification and characterization method used in choosing appropriate models, as well as in the interpretation of experimental observations (Bechthold and Schober 1987; Gallezot et al. 1985).

The question: "when does a cluster become a bulk?" still remains unanswered. The assumption

that properties of microclusters lie intermediate between atomic properties and bulk characteristics is changing. In the very small size regime, in particular, many properties of clusters exhibit varying degrees of fluctuations depending on the type of atoms forming the cluster (Gole 1986). Perhaps, because of the availability of advanced integrated equipment, experimental developments appear to outpace theoretical advancements in small cluster research. During the last few years, in particular, experiments have generated an overwhelming amount of data which still need careful interpretation at atomistic levels. What seem to be missing at the moment are sound and reliable models which can describe experimental observations in a more unified and consistent manner. Despite the existing and ever increasing collaborative efforts between theory and experiments, microcluster research needs even more involvement of theory in order to properly analyze and sort out many of the experimental observations in a more fundamental way.

Presently, it is our hope that the theory will eventually provide the highly desired unified models that can be used universally in the interpretation of many experimental observations. This probably will be accomplished via highly accurate *ab initio* calculations that can be extended beyond the very small size regimes, and/or by means of computer simulation studies based on highly reliable model potential functions.

APPENDIX I.

Acronyms Used in Experimental Microcluster Research:

AES: Auger Electron Spectroscopy
ARPES: Angle-Resolved Photoelectron Spectroscopy
CTEM: Conventional Transmission Electron Microscopy
DTA: Differential Thermal Analysis
EELS: Electron Energy Loss Spectroscopy
EPR: Electron Paramagnetic Resonance
ESCA: Electron Spectroscopy for Chemical Analysis
ESR: Electron Spin Resonance
EXAFS: Extended X-Ray Absorption Fine Structure
FEM: Field Emission Microscopy
HREELS: High Resolution Electron Energy Loss Spectroscopy
HREM: High Resolution Electron Microscopy
ICB: Ionized Cluster Beam
IETS: Inelastic Electron Tunnelling Spectroscopy
ISS: Ion Scattering Spectroscopy
LEED: Low Energy Electron Diffraction
LIAF: Laser Induced Atomic Fluorescence
LMIS: Liquid Metal Ion Source
MS: Mass Spectrometry
NMR: Nuclear Magnetic Resonance
PDL: Pumped Dye Laser
PES: Photoelectron Spectroscopy
R2PI: Resonant Two-Photon Ionization
RED: Radial Electron Distribution
REM: Reflection Electron Microscopy
REMPI: Resonantly Enhanced Multi-Photon Ionization
RRS: Resonance Raman Spectroscopy
RS: Raman Spectroscopy
SAXS: Small Angle X-Ray Scattering
SEM: Scanning Electron Microscopy
SERS: Surface Enhanced Raman Spectroscopy
SIMS: Secondary Ion Mass Spectroscopy
SRS: Stimulated Raman Scattering
STED: Scanning Transmission Electron Diffraction
STEM: Scanning Transmission Electron Microscopy
STM: Scanning Tunnelling Microscopy
TED: Transmission Electron Diffraction
TEM: Transmission Electron Microscopy
TOFMS: Time of Flight Mass Spectroscopy
TPD: Temperature Programed Desorption
TPI: Two-Photon Ionization
UHV: Ultrahigh Vacuum
UPS: Ultraviolet Photoelectron Spectroscopy
WAXS: Wide Angle X-Ray Scattering
WF: Work Function
XPS: X-Ray Photoelectron Spectroscopy
XRD: X-Ray Diffraction
XRF: X-Ray Fluorescence

APPENDIX II.

Acronyms Used in Theoretical Microcluster Research:

AREP: Averaged Relativistic Core Potential
CAS-SCF: Complete Active Space-Self-Consistent Field
CI: Configuration Interaction
CNDO: Complete Neglect of Differential Overlap
CPF: Coupled Pair Functional method
CVP: Core-Valence Polarization
DIM: Diatomics in Molecules
DVM: Discrete Variational Method
EA: Electron Affinity
EH: Extended Huckel
ECP: Effective Core Potential (Pseudopotential)
GMO: Generalized Molecular Orbital
GVB: Generalized Valence Bond
HFS: Hartree-Fock-Slater
IP: Ionization Potential
LCAO: Linear Combination of Atomic Orbitals
LCGTO: Linear Combination of Gaussian-Type Orbitals
LD: Local Density
LSD: Local Spin Density
MC-SCF: Multi-Configurational Self-Consistent Field
MRD-CI: Multi-Reference Diexcited Configuration Interaction
MEH: Modified Extended Huckel
MINDO: Modified Intermediate Neglect of Differential Overlap
NRMP: Non-Relativistic Model Potential
POL-CI: Polarized Configuration Interaction
RECP: Relativistic Effective Core Potential
RHF: Restricted Hartree-Fock
SC-CMS: Self Consistent Cellular Multiple Scattering
SC-LSD: Self-Consistent Local Spin Density
SCF: Self Consistent Field
SH: Simple Huckel
STO: Slater-Type Atomic Orbitals
UHF: Unrestricted Hartree-Fock

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