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Clusters and Colloids
From Theory to Applications
Edited by Günter Schmid
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The cover shows a high resolution microscopic image of a single gold colloid (about 11 x 13 nm), protected by a shell of P(m-C,H,SO,Na) ligands. The picture has kindly been provided by Prof. J. O. Bovin and A. Carlsson, University of Lund, which is gratefully acknowledged.

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1 General Introduction

Günter Schmid

The continuous reduction in size of a solid finally leads to a situation where the original solid state properties can be only partially observed or may be even completely lost, as these properties are exclusively the result of the cooperation between an infinite number of building blocks. Further reduction of size finally leads to typical molecular behavior. On the other hand, even here are structural relations to the bulk occasionally detectable. For instance, the arrangements of the sp$^3$ hybridized carbon atoms in cyclohexane or in adamantane can easily be traced back to the diamond lattice, whereas benzene or phenanthrene represent derivatives of the graphite lattice. However, neither cyclohexane, benzene, nor phenanthrene have chemical properties which are comparable with those of the carbon modifications they originate from. The existence of the above mentioned C$_6$, C$_{10}$ or C$_{14}$ units is only made possible by the saturation of the free valencies by hydrogen atoms. Comparable well known examples for other elements are numerous, for instance the elements boron, silicon, and phosphorous. Figure 1-1 illustrates some of the relations between elementary and molecular structures.

Carbon atoms with sp$^2$ hybridization offer a fascinating example for the transition from the infinite crystal lattice to the molecular state. In this case, not 6, 10, or 14, but 60 carbon atoms are used as cutouts of the lattice, and the free valencies are not saturated by hydrogen atoms: such nano sized cutouts are too small to exist as a stable graphitic structure and consequently they create a spheric shape consisting of five- and six membered rings with altogether 60 vertices, the famous soccer-like so-called fullerene, C$_{60}$.

If a piece of metal is reduced to a size of a few thousand atoms we enter the world of metal colloids, unique particles which were already handled by Michael Faraday in the last century. Smaller units of a few hundred or dozen atoms are usually called 'clusters'. This term is also well tried for small molecular species consisting of only a few metal atoms. Metals, especially transition metals, offer an exceptional opportunity to study the pathway which leads from the bulk to the molecular state and finally to mononuclear complexes (Figure 1-2).

The present book aims for a general overview of our present knowledge in the field of cluster and colloid science, without calling on completeness. On the contrary, it is intended to elucidate developments, highlights, and the actual situation. The broadness of this field is documented by chapters with a mainly theoretical background, sections where the physics of small metal particles dominate,
Figure 1-1. Structural relations between the bulk and the molecular state of some elements.
1-1 a) The graphite lattice, a') the fullerene molecule $\text{C}_{60}$, formally derived from a $\text{C}_{60}$ cutout of a graphite layer, and a'') the skeleton of the phenanthrene molecule as a representative of aromatic systems.
1-1 b) The diamond lattice and the molecular structures of the molecules, b') adamantane, and b'') cyclohexane. The chair configuration of its $\text{C}_6$-skeleton can be easily recognized in b') and b).
1-1 c) The crystal structure of the rhombohedral boron modification consisting of linked icosahedra. c') Most boranes derive from the icosahedral building block. $[\text{B}_n\text{H}_{12}]^{2-}$ consists of a complete icosahedron. (The hydrogen atoms are omitted)
General Introduction

and others in which the syntheses of clusters and colloids are described. The syntheses, physical and chemical properties, and first applications as well as the structures of these nano sized particles are treated. The generation and the properties of 'isolated clusters' ('naked clusters'), which are only available in so-called cluster beams, are not intended to be described in this book. They are of special interest in physics, however, they can never be isolated as stable materials. The description of the various and complicated cluster beam techniques as well as the discussion of the physical properties of clusters in beams would exceed the frame of this book considerably.

Where does the scientific importance and the fascination for clusters and colloids originate from? There are several answers to this question, not the least of which is due to subjectively different views. For many scientists, the synthesis of isolable metal clusters is a big challenge, whereas others are interested in structural details or physical properties. A possible application in catalysis is a further motive to employ oneself with small and reactive metal particles. All these different interests are finally based on a mutuality to which the known and the expected properties are based on: that is, the dramatic reduction of freely mobile electrons on the path from the bulk to the cluster. However, such a miniaturization also affects numerous other properties, for instance the melting point. This can be demonstrated with the element gold: the melting point of bulk gold is 1064°C, whereas that of a 1.5 nm gold particle is decreased to about 500–600°C. Of much more importance is the change in the electronic properties on the way from the bulk to the nano sized species. This can be followed best in an imaginary experiment. If a threedimensional piece of metal is reduced to a layer of only a few atoms in thickness, the original electrons, which were freely mobile in three dimensions, now can only move in two dimensions: a quantum wall has been generated. Further reduction to a quantum wire leads to the one dimensional case. If finally a quantum wire was to be cut into a piece which was as short as it was thick, then an electronically zero dimensional quantum dot would result. In such a quantum dot, the last few 'metallic' electrons are fenced and, due to quantum size effects, they behave like electrons in a box and differ generally from electrons in the bulk. These electrons determine the physical and chemical characteristics of metal clusters and colloids to a significant extent.

Figure 1-2. Illustration of the transition from a) bulk metal via b) colloids and clusters to c) small molecular cluster species.
Another factor deserves consideration if we are to discuss the properties and applications of metal clusters and colloids. Most of the investigated species do not exist without being influenced by a surrounding media. In practice, most of the clusters and colloids described in this book are protected by a shell of ligand molecules or they are embedded in cages or matrices like polymers or solids, in order to separate them from each other to prevent coalescence. Ligand molecules, as well as cages, chemically interact with the surface atoms of the metal particles and so have a remarkable influence on their electronic character. Just as the electronic states of single metal atoms or ions in simple complexes are determined by the ligand field, the surface atoms of a cluster or colloid will be affected by their environment as well. Consequently, we have to realize that the properties of 'naked' clusters must be considerably different from those of ligated or somehow fenced metal particles.

This book tries to regard most of these aspects. Internationally recognized scientists describe those fields of cluster and colloid research in which they have been working for many years and therefore are endowed with fundamental knowledge. The book is intended for those scientists working in research as well as in practice who wish to gain a fundamental insight into one or more areas of the world of small metal particles. However, it is addressed to advanced students in physics, chemistry, or materials sciences as well.
2 Electronic Structures of Metal Clusters and Cluster Compounds

Notker Rösch and Gianfranco Pacchioni

2.1 Introduction

Inorganic chemists understand the term “cluster” differently than physical chemists or physicists do. It is no wonder then that the objects designated in these fields as clusters have very different characteristics and that their investigations give rise to quite different concepts and require many diverse methods, both experimental and theoretical. In the following, we will focus our attention on the electronic structures of those metal clusters and metal cluster compounds which represent the most important systems in each area. It will become clear that despite their often very different characteristics, the same, or at least rather similar, concepts and methods in theoretical chemistry may be profitably applied to both types of metal clusters. By highlighting both their similarities and their differences, the juxtaposition of these two classes of metal clusters will provide a more lucid view on each of them.

In the newly emerging field of cluster science, as an offspring of physical chemistry and physics, the term “cluster” refers to a new form in the aggregation of matter which lies intermediate between the molecular and the solid state. Thus, cluster science will provide information on how the properties of a solid gradually evolve as atoms are brought together to form increasingly larger units. Given this general definition, it might be difficult to distinguish between a molecule and a small cluster. For instance, one may wish to exclude a tetrahedron of four phosphorus atoms or a ring of eight sulphur atoms from the class of clusters. In fact, the P$_4$ and S$_8$ molecular units exist in various aggregation states (solid, liquid, and vapour) and may be more properly considered as homonuclear molecules. In this contribution, the term “cluster” will be used to designate aggregates of atoms, not necessarily of the same element, which do not exist in measurable quantities in an equilibrium vapor. In this respect, the fullerenes would be considered as large molecules while Na$_n$ aggregates certainly belong to the category of clusters.

Even within the field of inorganic chemistry, the term “cluster” is used to designate a wide variety of molecular entities. The boranes (e.g. [B$_{12}$H$_{12}$]$^2^-$), the basic Fe$_3$S$_4$ unit contained in the iron-sulphur proteins, the transition metal carbonyls (e.g. [Ni$_5$(CO)$_{12}$]$^2^-$), the “metal-only” clusters like Bi$_9^{4^+}$, Ge$_9^{2^-}$, and
Pb$_2^+$, the ternary chalcides of general formula [M$_2$Mo$_6$X$_8$] (Chevrel phases), and such cage molecules as P$_4$ (the basic component of white phosphorus) are all examples of “cluster cages” but with completely different characteristics.

Undoubtedly, the metal clusters form a unique and exciting subgroup of inorganic cluster compounds. More than a thousand examples of ligated metal clusters have been reported in the literature since the first examples of polynuclear complexes containing metal-metal bonds were discovered about 30 years ago. This number gives an idea of the exceptional growth which has taken place in this area of inorganic chemistry. It is useful to classify an inorganic cluster as “a compound containing a finite group of metal atoms which are held together entirely, mainly, or at least to a significant extent, by bonds directly between metal atoms”. [1] This definition, originally proposed by Cotton in 1966, is valuable from a conceptual point of view, although it is difficult to apply since there is generally no simple way to establish the existence or to measure the strength of a metal–metal bond within a cluster compound. Thus, the distinction between a metal cluster and other metal containing inorganic compounds where metal–metal bonds are completely absent is not always straightforward. Actually, characterizing the nature and the extent of the metal–metal interactions in metal clusters is one of the most challenging problems for theoreticians and will be discussed at length below.

Metal clusters are the most interesting from several points of view, although a great deal of attention has also been given to clusters of semiconducting materials [2–6] and to Van der Waals clusters [7, 8] over the past decade. In the following, we will discuss the electronic structures of both gas phase (or “naked”) metal clusters and inorganic metal cluster compounds. Rather than attempting to give an exhaustive review, we will highlight the key concepts and methods and then discuss the theoretical results, mostly from a quantum chemical point of view, for important examples in each class of metal cluster. This implies two obvious restrictions for our presentation. First, when one is interested in the transition to the bulk limit, it is natural to discuss clusters using concepts and methods derived from condensed matter theory. Although we will occasionally mention such methods, we will not explore them in any great detail. Furthermore, gas phase clusters (and in several cases also inorganic clusters) have interesting and novel dynamic properties as a consequence of their unusual geometric and electronic properties. These aspects of clusters are beyond the scope of this presentation.

2.2 The Description of the Clusters Electronic Structure

The role of theory in cluster research is twofold. On the one hand, theory must be able to provide a basis for understanding the chemical and physical properties of small metal aggregates, whether naked or ligated, and to rationalize any observed trends. On the other hand, theory is also expected to furnish quantita-
2.2 The Description of the Clusters Electronic Structure

tive answers and to have a definite predictive power. An obvious question among
the many that may be posed to theory is the one already mentioned concerning
the amount of metal–metal bonding. Another important one is about the geometry
of a cluster and its relation to the other characteristics of the cluster. It is
clear from these considerations that one would like to apply highly accurate
methods as well as qualitative schemes. Also, methods which are able to describe
not only small but also large clusters as well, and even extended systems will have
a special appeal. It should be remembered that the quantitative description of
metal compounds, and especially those of the transition metals, is still quite a
challenge for all computational methods, despite the substantial progress which
has been made in the recent past, at least for mononuclear complexes. [9, 10]

Given the complexity of the systems and the diversity of the questions still
open in the field of metal clusters, it is no wonder that essentially all the methods
available from the ample arsenal of quantum chemistry have been applied to clus-
ter problems. We will not give an extensive overview of the many different
methods (let alone aim for completeness) and leave aside most technical aspects.
This information can be found in specialized publications (e.g. [11–15]), from
which some are even devoted to the electronic structures of clusters. [16, 17]
Instead, we will summarize the basic features of the methods and comment on
their applicability to the description of both naked and ligated metal clusters.
We will start the discussion with wave function based methods and then proceed
to density functional methods. Although the latter have only recently gained
a broader acceptance for chemical applications, they have a rich tradition in
the metal cluster field, particularly due to their solid state heritage. We will
also briefly mention simplified approaches to the electronic structure of metal
clusters.

First principle quantum chemical methods, whether wave function based ("ab
initio") or density based, are aimed at solving the electronic Schrödinger equa-
tion without any reference to adjustable parameters or empirical data. In their
standard form, they invoke the Born-Oppenheimer separation of electronic and
nuclear motion and employ a nonrelativistic Hamiltonian which does not include
any explicit reference to spin-dependent terms. Many quantum chemical methods
are based on the variational principle which, for computational convenience, is
implemented in algebraic form via either one-electron functions built from linear
combinations of atomic orbitals or n-electron functions constructed from Slater
determinants. [11, 12]

2.2.1 Wave Function Based Methods

The basis for all wave function based ab initio methods is the Hartree-Fock (HF)
approach. [11, 12] It makes use of a single-determinant ansatz constructed from
one-electron spin orbitals. These orbitals describe the motion of each electron
within the field of the nuclei and the mean field of the remaining n–1 electrons.
The mean field is not known a priori, but depends on the orbitals which are
determined self-consistently from the eigenvalue problem of the Fock operator.
Therefore, the resulting iterative procedure is referred to as a self-consistent field (SCF) technique. In the case of metal clusters, one is often faced with an open shell system in which at least one set of degenerate spin orbitals is not fully occupied. The familiar form of the restricted HF (RHF) theory must then be replaced by a more complicated formalism. Often, one resorts to unrestricted HF (UHF) theory which allows different spatial orbitals for different spins at the expense of employing a wave function which is not an eigenfunction of the total spin operator.\[12, 17\] For computational efficiency, the molecular orbitals are usually constructed as a linear combination of atomic Gaussian type basis functions (GTO). In this way, the accuracy of the description of a metal cluster is very dependent on the choice of the basis set (see \[18\] for a comprehensive description of \textit{ab initio} basis sets). The number of integrals which have to be computed in the HF method formally scales with $N^4$ where $N$ is the number of basis functions. This means that the treatment of clusters having more than about 20 atoms becomes difficult, even with the computational facilities available today. This problem can be partially overcome by using a “direct” SCF approach. Here, the storage requirement is significantly reduced by following a strategy whereby the integrals are evaluated upon demand as required for constructing the change in the Fock operator during the iteration process.\[19, 20\]

The HF method provides a transparent interpretation of the $n$-electron wave function. According to Koopmans’ theorem, the one-electron energies are directly related to the ionization potentials.\[11, 12\] In general, the method yields acceptable results for the properties of clusters near the equilibrium configuration, provided the HOMO-LUMO gap is not too small. Unfortunately, this is not the case for many naked metal clusters. Although it may not be a problem for ligated clusters, they tend to be too large for this level of theory. A severe limitation to the HF mean field approach is that it ignores the spatial correlation of the electrons. Thus, the absolute values of observable properties, in particular the binding energies and vibrational frequencies, deviate considerably from their experimental values.\[12\] Another disadvantage with respect to metal clusters is the well known fact that the HF method incorrectly describes dissociation when it is accompanied by a change in spin multiplicity.\[12\]

In order to improve the mean field description of the electronic structure one has to go beyond the single-configuration approach.\[12, 13\] Two main strategies have been developed to introduce correlation effects. In the first case, one employs methods based on many-body perturbation theory (MBPT).\[12, 21\] They allow the treatment of so-called dynamical correlation effects in cases where the HF method already provides a reasonable description of the ground state. However, these perturbation theoretical methods are not variational, that is the calculated value for the energy does not provide an upper bound to the true energy of the system.

An alternative is represented by methods where one mixes one-electron configurations to obtain a many-determinant wave function.\[12\] These configurations are generated by distributing the electrons among the mean field spin orbitals. If one takes all the possible “substitutions” (single, double, triple, etc.) into account, one obtains in principle the exact solution to the Schrödinger equation.
This approach is called full configuration interaction (full CI). The energy difference between the full CI and the SCF solutions is defined as the correlation energy.

In practice, however, such calculations are hardly feasible for systems containing more than $10^{-15}$ electrons because post-HF methods scale as at least $N^2$. Thus, one has to resort to limited multi-determinant expansions of the $n$-electron wave function. This "truncated" CI introduces only part of the correlation energy with the main consequence being that the method is not size consistent: the energy of a system and its separated components are not described on an equal footing. This represents a serious drawback when studying the change in cluster stability as a function of cluster size and ultimately precludes the investigation of large clusters and thus the convergence to the bulk cohesive energy. [14] Another limitation is that the interpretation of the CI wave function is often less facile.

The problems of size consistency can be removed by employing multi-configuration SCF (MCSCF) techniques. [22] The MCSCF wave function is a truncated CI expansion in which both the coefficients of the atomic orbitals in the one-electron wave functions and the coefficients of the determinants in the CI expansion are simultaneously optimized. The underlying equations are considerably more complicated than those of either the HF or the CI methods. For this reason, MCSCF and its variant GVB [23] and CASSCF [4] techniques have so far been applied only to clusters of relatively small size. [17]

Nevertheless, these methods provide the only viable alternative for naked transition metal clusters since they can treat the nondynamical correlation effects of the near-degeneracy problems which typically occur in these systems. For clusters of simple metals, the previously mentioned MBPT methods are applicable when one configuration dominates the multi-determinant expansion. Post-HF techniques yield much better values for the various measurable properties of a cluster. The allowed optical transition energies play a particularly important role among these because they often permit the indirect determination of the geometry of a gas phase metal cluster. [25] In this context, the only computational approaches which allow for an accurate description of the excited states are the CI or MCSCF methods. Since the electronic properties of small metal clusters depend strongly on the details of the geometric structure, a geometry optimization should only be performed with a method that includes a description of the correlation effects. However, due to the availability of analytical gradient techniques, most of the geometry optimization studies on clusters have so far been performed at only the HF level of theory. [17, 25]

Since the computational effort required for post-HF ab initio methods is quite substantial, one often treats only the valence electrons explicitly and replaces the atomic cores by analytical effective core potentials (ECP). [17, 26] This technique is also referred to as a pseudopotential approach. A variety of strategies for the design of ECP's has been suggested. [27–30] Although these techniques have allowed the description of relatively large naked metal clusters, their application to ligated clusters is still scarce and restricted to low nuclearity complexes. For certain properties the ECP technique represents a considerable restriction, in particular when the polarization of the core is not negligible; however, more sophisti-
cated formalisms are being developed to include appropriate corrections. [17, 31] ECP's also provide a convenient way for treating heavier atoms by incorporating relativistic effects. [29] These are important for clusters of the heavy elements in general and in particular for clusters of gold and mercury. [32] Relativistic corrections may be as large as correlation effects in gold cluster compounds. [33]

2.2.2 Density Functional Methods

Density functional methods for finite electronic systems were suggested some time ago, [15, 34, 35] but only in the last decade have these techniques found wider acceptance for chemical applications. [36, 37] Density functional theory (DFT) starts from the assertion that the ground state energy of an electronic system can be expressed as a unique functional of the density \( \rho \) and that it fulfills a variational principle. [38, 39] A convenient technique for solving this minimization problem is provided by the Kohn-Sham (KS) formalism [40] which results in a one-electron Schrödinger equation with a density dependent effective local potential. A very appealing aspect of this formalism is its simplicity; yet it incorporates exchange and correlation effects on an equal footing. Limitations of DFT are that the fundamental form of the energy functional is known only approximately and that, in contrast to wave function based methods, there is no hierarchy in the approximations which can provide for systematic improvements.

The most common choice for the energy functional starts from its separation into three terms: a kinetic energy contribution of a "noninteracting" reference system, the classical Coulomb interaction of the charge distribution under study, and a remainder which comprises the exchange and correlation effects. [15] Various approximations have been suggested to treat the latter term, [15, 34, 37] whereby a popular choice is to assume the same functional form as in a weakly inhomogeneous electron gas. This approach is called the local density approximation (LDA) and several parametrizations have been suggested. If one takes only the exchange interaction into account, then the famous \( q^{1/3} \) dependence of the "exchange-correlation" potential, well known from the \( \chi \alpha \) formalism, [41] is obtained. It should be noted that the "correlation energy" in DFT is defined differently than in \textit{ab initio} methods. The relationship of the exchange-only approximation in LDA to the HF formalism has been the subject of an intense and controversial debate which has not reached a definite conclusion. [42] At this level, the method provides good results for bond lengths and vibrational frequencies. [37] However, the values for binding energies may be in serious error; in many cases, they are too large. This deficiency is related to the LD approximation. Improvements can be made by choosing a more sophisticated form for the exchange-correlation functional in that it also depends on the gradients of the electronic density. These so-called nonlocal corrections do not affect the local character of the effective one-electron potentials. This aspect of the theory is currently undergoing intense development. [34, 37, 43, 44]

In the LDA methods, the one-electron functions are usually expanded into atomic basis sets whereby numerical orbitals, GTO's, Slater-type orbitals (STO),
2.2 The Description of the Clusters Electronic Structure

and the very special linearized muffin tin orbitals (LMTO) are used. [37] The use of GTO's or STO's facilitates a direct comparison between the one-electron functions in the LDA to those in HF theory. In contrast to HF, however, Koopmans' theorem is not valid here. [15] In order to relate the one-electron energies in DFT to ionization potentials or core level binding energies one must resort to Slater's transition state procedure. [41]

The local spin density (LSD) approximation is an extension of the above method to spin-polarized cases in which different densities are defined for electrons with up and down spins. [15, 34] This is particularly important for the study of transition metal clusters with magnetic ground states, such as clusters of Co, Fe, Ni, etc. In the following, the term 'local density functional (LDF) methods' will be used as a joint designation of DFT methods that employ either the LD or the LSD approximation. Density functional based methods have been further augmented by including pseudopotentials and relativistic effects, as well as energy gradients for geometry optimization. [37, 45] The molecular dynamics (MD) approach of Car and Parrinello [46] provides a useful tool for determining the global energy minimum of a system by simultaneously solving the KS equations as the nuclear positions vary.

The various computational schemes based on DFT are attractive alternatives to conventional ab initio methods and particularly for the study of large clusters since the computational effort increases with the number of basis functions as roughly $N^3$. They allow an accurate treatment of transition metal clusters where the standard HF technique is not easily applicable. Furthermore, they provide a natural way for describing the transition from the molecular to the metallic regime since DFT theory underlies most of the first principle methods for solid state band structure calculations. [47] Although the method is still restricted to ground state properties, possible extensions for the treatment of excited states are under discussion. [34]

2.2.3 Simplified Methods

Over the past 25 years, a large variety of approximations have been introduced to treat the electronic structure problem for large systems. Many of these methods try to simplify the HF-SCF formalism by restricting themselves to the valence electrons and by drastically reducing the number of integrals which have to be explicitly calculated. [48, 49] In order to compensate for these crude approximations, parameters are introduced and adjusted to fit various experimental quantities. Several strategies have been followed and an important distinction between these is in their treatment of the electron-electron interaction. This interaction either is considered only implicitly as in Hückel and extended Hückel (EH) methods [11] or is treated similar to that in HF theory within the zero differential overlap (ZDO) methods. [48, 49] The EH method has been widely used in the study of ligated metal clusters, [50] and it also provides a framework to rationalize electron counting rules. [51] These very simplified techniques have a special merit when one investigates those aspects of the electronic structure
which are governed by topological factors. Details of this will be discussed in later sections. It should be pointed out, however, that the reliability of these methods for quantitative predictions is in general very limited, especially when applied to transition metal clusters.

Simplified methods based on DFT have also been suggested. A rather simple, but very effective one used for the description of some cluster properties, like the "magic numbers" for gas phase clusters, is the jellium model. [52] This approximation does not provide any insight into the nature of the chemical bonding between the atoms and, in particular, it neglects all details of the nuclear framework. The jellium model can be used to extract information on only the topological aspects of the cluster geometry. [51] Other approximate DFT based schemes have been developed and applied to the investigation of cluster stability and geometry and include the embedded atom [53] and the effective medium theory. [54] These approximate methods will be discussed further below in context with special aspects of the cluster electronic structure.

2.3 Structure and Properties of Naked Clusters

We will discuss metal clusters of both the main group and transition metal elements, although such a distinction is not really necessary; in fact, many of the features typical of metal clusters and also their size effects have been observed for both transition metal as well as simple metal clusters. However, an obvious, but important difference is that the latter are much easier to treat theoretically and, indeed, have been studied at a much higher level of accuracy. Thus, a coherent understanding of size effects in main group clusters will also be very helpful in the description of transition metal clusters.

It has become quite apparent that the properties of small naked clusters are dominated by their very different average atomic coordination compared to that in the bulk. The low coordination in the clusters is the origin of several peculiar properties, including the large oscillations and discontinuities observed as function of the cluster size. The rationalization of these discontinuities represents one of the main goals of cluster theory. The second basic question that has attracted the attention of both chemists and physicists is that concerning the size which is required for a cluster to exhibit bulk-like character. There seems to be general agreement [17, 55, 56] that this question does not have a unique answer. As the cluster size increases, some physical properties converge to the crystalline value more rapidly than others. Many chemically interesting properties reach values within a few percent of their bulk limit for clusters containing about 100 atoms. On the other hand, pronounced cluster size dependent variations are observed for clusters having less than 100 atoms. [56]
2.3 Structure and Properties of Naked Clusters

2.3.1 The Theoretical Description of Metal Clusters

The need for theory in cluster research is quite evident since there are several properties and characteristics of bare clusters that are not easily determined experimentally, such as the geometry of stable isomers and the energy barriers which separate different structures on a potential energy hypersurface. The most serious problem to constructing a theory capable of giving an adequate description of a cluster's electronic structure is the requirement that it treats a very small cluster of only a few atoms at a comparable level of accuracy as a large metallic aggregate with typical bulk-like properties. In other words, one would like to have a theory that can extrapolate correctly to both the molecular (or atomic) and the bulk limits. Clearly, this is not a simple task and, so far, most of the theoretical approaches used in cluster theory have been derived from theories which were developed to describe one or the other extreme.

Band structure theories used for the treatment of bulk metals are based on the concept of translational symmetry and on the itinerant electron model and are therefore not applicable in the case of finite clusters where structural anisotropy, small dimensions, and anomalies in the electronic structure are common. At the molecular level, clusters are better described with the methods of quantum chemistry at either the semiempirical, the \textit{ab initio}, or the density functional level. [17, 57–59] In some cases, even simple considerations based on the symmetry and topology of a cluster provide useful qualitative information. The problem with these simplified methods is that they can, at best, fulfill the first requirement for a cluster theory of qualitative understanding, yet in no way can they satisfy the second requirement of quantitative prediction. Both types of theory, qualitative and quantitative (or at least semiquantitative), have been and continue to be used in the study of naked clusters, and their success largely depends on the property or on the problem under investigation. There are few areas in modern science where the role of theory is so pivotal as it is in cluster research. Experiments need to be substantiated by theory and theory is continuously being challenged by new experimental findings. The combined use of theory and experiment is one of the reasons for the impressive advances which have been achieved in this field over the past 15 years. It is not a mere coincidence that in several cases theoretical predictions on cluster structures and properties have anticipated the experimental findings.

2.3.2 Structure, Bonding, and Stability

2.3.2.1 Geometrical Structures

Without any doubt, the question concerning the structure of metal clusters is one of the most intriguing. Unfortunately, as mentioned previously, it is also one of the most difficult to probe directly by experiment. The only available techniques
are electron diffraction from gas phase clusters or information from low temperature matrix studies (e.g. absorption, Raman, ESR, EXAFS). [55, 56] From the very beginning then, the main goal of the theoretical study of clusters has been the prediction of their structures.

The first semiquantitative \textit{ab initio} investigations on cluster structures were performed on Li clusters, whereby the computational simplicity of these systems was exploited. [60–63] If one surmises that metal clusters are the "seed" for crystal growth, it is logical to expect that they will assume the most compact structure for any given nuclearity, that is, a tetrahedron for the tetramer or an octahedron for the hexamer. In these cases, the driving force which determines the shape of a small metal aggregate would be the tendency to maximize the coordination. Therefore, it came as some suprise when one found that the most stable structures for low nuclearity Li clusters, [61, 63] and of alkali metal clusters in general, [64–66] were not the most compact ones. The tetramers Li₄, Na₄, K₄, etc., assume, in fact, a nearly planar rhombic structure. This theoretical prediction was confirmed in recent years by thermodynamic data on matrix isolated Li₄ [67] and by photodetachment experiments on gas phase Li₄ (see Section 2.3.5). Even more astonishing was the finding that Li₆ is not an octahedron but rather an edge-bridged planar triangle, with a pentagonal pyramid being very close in energy. [68, 69] The theoretical prediction that Li₇ should have a bipyramidal pentagonal form was confirmed by ESR spectroscopy on matrix isolated Li clusters. [70] The appearance of cluster structures having pentagonal symmetry has opened new horizons for the understanding of cluster growth. Based on \textit{ab initio}, density functional, and Car-Parrinello calculations, stable isomers with pentagonal or icosahedral symmetry have also been proposed for larger size clusters (e.g. Li₁₃ [71]) and clusters of other elements (e.g. Be₇, [72] Mg₇, [73] Ni₇, [74] Nb₇, [75] and Cu₆, Ag₆ as well as Au₆ [76] all exhibit pyramidal or bipyramidal pentagonal arrangements). Given the difficulty of determining the structure of gas phase clusters, it is not surprising that discrepancies between theory and experiment still exist. For instance, based on vibrational autodetachment studies on Au₆, [77] it was suggested that the neutral cluster has a planar ring structure.

Using the large amount of theoretical data available for the alkali metal clusters, an "aufbau" algorithm for cluster growth was proposed but met with little success. [17] The idea that the growth sequence starts from some given "seed" structure, like a tetrahedron or a rhombus, does not seem valid. Alkali metal clusters derived from condensed tetrahedra do not correspond to the absolute minima on the potential energy surface. While heptamers prefer a pentagonal bipyramid structure, the octamer has a tetrahedral shape which cannot be derived by simply adding an atom to the heptamer. Substantial rearrangement of the atoms must take place as a cluster grows, and the dynamics of cluster growth can certainly be quite complicated when several channels compete. Similar qualitative conclusions about the most stable structures of alkali metal clusters have been obtained at very different levels of theory (graph theory, Extended Hückel, jellium, semiempirical, Hartree-Fock, valence bond, density functional, etc.). [17] Thus, it seems that the leading interaction mechanism is the overlap between the outer s orbitals of the alkali atoms with little (but not negligible) mixing of the
empty p orbitals (hybridization). This causes the bonding to be nondirectional and so the geometry may be predicted on the basis of topological arguments.

Even more complex are the clusters formed from metal atoms which have more than one electron in the valence shell, that is, those from the majority of the elements of the periodic table. Since these atoms undergo substantial rehybridization in their cluster bond formation, the geometrical shape cannot be predicted by simple topological schemes. An illustrative example is provided by the alkaline earth metal clusters [72, 73, 78–86] whose atoms have a \((ns)^2 (np)^0\) configuration. Only closed shell interactions in the form of van der Waals forces would occur if a change in configuration did not take place. True chemical bonds can only be formed after promoting one electron from the valence s to the valence p shell. This is what actually happens in small alkaline earth metal clusters like Be\(_4\) and Be\(_5\). The potential energy curves for the interactions between the Be atoms in forming Be\(_4\) and Be\(_5\) clusters exhibit an interesting double minimum feature (Fig. 2-1). [81, 83]

The Be atoms are in their atomic \((2s)^2 (2p)^0\) configuration at longer interatomic distances and the interactions are very weak. As the separation decreases,
the atoms begin to modify their electronic configuration and the 2p levels become populated. This corresponds to an electron promotion and the related energetic cost shows up as an increase in the total energy. As the distances decrease further, the price paid to change the Be configuration is overcompensated for by the formation of strong directional bonds. Thus, an energy barrier results at an interatomic distance of about 2.5–3 Å (Fig. 2-1) and the potential surface exhibits a deep minimum at a Be–Be separation close to the bulk value of 2.29 Å. [81, 83] This behavior is typical for all small alkaline earth clusters, but the balance between the energy necessary to promote electrons from the s to the p shell and the energy gain due to the bond formation depends strongly on the cluster geometry. The interaction of four Be atoms to form a rhombic cluster is much less favorable than that for a tetrahedron, as shown by an analysis of the wavefunction. The formation of the sp hybrids requires the average coordination of the Be atoms to be as high as possible. Thus, completely different bonding mechanisms have been identified in the formation of Li₄ and Be₄. This is also generally true for clusters of different elements and accounts for the different geometrical structures observed for tetrabers of different elements. [17]

When one goes from Be to heavier alkaline earth elements like Mg and Ca, the situation becomes even more complex since the tendency to form hybrid sp orbitals decreases as a group is descended. Indeed, it has been shown [80, 82] that in order to correctly describe the bonding in clusters of the heavier alkaline earth metals, one has to employ large basis sets which include not only p but also d polarization functions. Furthermore, correlation has to be taken into account simultaneously.

The special situation with clusters formed from atoms having a fully occupied s valence shell is of particular interest since in these cases, the non-metal to metal transition may occur more suddenly than with other metals. To use band structure terminology, closed shell atoms can form stable aggregates only via an overlap of the filled valence s-band with a low lying empty band (most likely of p character). The energy gap between the s- and the p-like level manifolds will decrease as the cluster size increases until a certain particle size is reached at which point the overlap will occur. Here, measurable changes in the electronic structure should take place and possibly be accompanied by a sudden change in some properties, such as the cohesive energy and the ionization potential. Whereas this transition has been theoretically predicted to take place with very small sized Be clusters, [81, 83] it seems to require 50 or more atoms in the case of Hg. [87]

Various techniques have been employed to theoretically determine metal cluster structures. In general, structural optimization is performed by standard minimization techniques which make use of first and second order derivatives of the total energy with respect to the nuclear displacements. This procedure may be used in connection with semiempirical, [88] ab initio, or DF-type electronic structure calculations (e.g. [57]) and is well suited for finding local minima which lie close to the starting configuration. An alternative approach is that of a molecular dynamics (MD) simulation based either on empirical many-body potentials or on the density functional MD method as proposed by Car and Parrinello. [46]
The problem with empirical many-body potentials lies in the choice of the parameters used to define the interatomic force fields. [89] Since empirical potentials are usually derived by fitting bulk properties, their application to finite systems can lead to incorrect answers. However, successful examples of empirical potential functions which incorporate cluster size dependent effects, such as the sp hybridization in Be clusters, [90] have been reported.

Much more appealing for the purpose of structure determination is the computationally expensive Car-Parrinello method, [46] where the relaxations of both the electronic and the nuclear degrees of freedom are treated simultaneously. The applications of this procedure to Na [91] and Mg [73] clusters containing up to 20 atoms have confirmed the earlier predictions based on standard ab initio methods for the existence of stable pentagonal forms, the oscillatory behavior of many properties (in particular for low nuclearity clusters), and the abundance of structural isomers with similar binding energies in clusters whose sizes do not correspond to specially stable situations ("magic numbers"). Finally, simulated annealing calculations have further demonstrated that the cluster geometry is not determined by a tendency for denser packing, but rather by the requirement for a more favorable electronic configuration.

Since the latter procedure is quite expensive, approximate treatments have been designed for transition metal clusters based on the embedded atom method (EAM). [53] In EAM, the dominant contribution to the energy of the metal is viewed as the energy of an atom embedded in the local electron density of its environment, supplemented by short range two-body interactions and possibly other terms. The basic idea underlying this method is similar to the effective medium theory [54, 92, 93] and both procedures find their roots in density functional theory. Applications of these techniques to transition metal clusters of medium to very large size (up to 5000 atoms) have been reported. It has been suggested that low nuclearity Ni and Pd clusters (up to about 20 atoms) tend to maximize the minimum coordination at any atom. [94] On the other hand, clusters containing from a few hundred to a few thousand atoms exhibit transitions from icosahedral to decahedral and finally to face-centered cubic polyhedra. [95]

### 2.3.2.2 The Jellium Model

The idea that clusters which exhibit high stability correspond to particular "closed shell" electronic configurations is basic for the use of the jellium model. It is well known that the mass spectra of Na$_n$ clusters in molecular beams show a higher abundance, indicating greater stability, of masses corresponding to $n = 2, 8, 20, 40, 58, 92$, etc. [52] This sequence of "magic numbers" has been rationalized by Knight and coworkers by means of the jellium model. [52] The jellium model describes the cluster electronic structure by considering only the valence electrons which are assumed to move "freely" in a smooth attractive mean field potential. A crucial approximation is that the detailed positions of nuclei do not play a significant role. An important characteristic of the jellium approach is its separa-