METAL CLUSTERS

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PREFACE

Research in atomic and molecular clusters is an interdisciplinary enterprise involving experimental and theoretical chemists and physicists. It has exploded rapidly in importance over the past 10 years, peppering scientific meetings with a barrage of symposia. It has engendered a Gordon conference and rumors (one hopes false ones) that a journal is being planned entitled *Cluster Science*.

Of all the research involving atomic and molecular clusters, the largest portion is dedicated to the study of aggregates of metal atoms. This is perhaps because this territory offers the greatest scope both in terms of chemical and physical challenge and possible utility in the field of catalysis. This book is the first attempt to cover this territory widely. Being the first of its kind, the book is in part a somewhat didactic general introduction to the field, as well as a monograph summarizing the research accomplishments realized to date.

The book travels from theory, through inorganic chemistry, past physical chemistry and chemical physics, ending in catalysis. Chapter 2 outlines the molecular orbital techniques used to predict the electronic and geometrical structure of metal clusters. It considers, in addition, the confidence with which one may carry over the results obtained with aggregates containing a few atoms to larger metal crystallites and metal crystal surfaces. In Chapter 3 the structures of stable metal cluster complexes are discussed and illustrated. The empirical rules that are currently used to account for the particular stabilities of complexes based on metal aggregates of specific shapes and nuclearity is presented. Chapter 4 discusses the kinetics of reaction and photoreaction involving metal cluster complexes, especially carbonyls. Much of its contents has not been compiled or reviewed elsewhere. The organometallic chemistry of metal clusters is reviewed in Chapter 5, including a summary of homogeneous catalysis by metal cluster compounds and a discussion of the analogy between the reactivity and structure of ligands on metal clusters versus adsorbate on metal crystal surfaces. Chapter 6 is a thorough review of the methods used to generate metal clusters in the gas phase, mainly through the use of molecular beam techniques. The results of laser-based spectroscopic techniques are presented, as well as preliminary studies involving reactions of metal clusters of various size with chlorine. Clusters frozen in noble gas matrices form the central theme of Chapter

7. Both naked metal aggregates and clusters with adsorbate attached are discussed. An introduction is also included to the very recent experiments probing the gas phase reactivity of metal clusters of various sizes toward adsorbate. Zeolites are ideal supports for very tiny metal clusters. Their molecular size pores and cavities will only admit the smallest aggregates. Chapter 8 reviews much of what is known regarding the structure of metal clusters enclosed in zeolites. The final two chapters present a review of applications of metal cluster complexes to the creation of new catalytic materials. The possibility of making catalysts of uniform cluster size distribution by denuding a cluster complex of its ligands and retaining the metal core on a catalyst support material is an exciting one. The two chapters discuss this quest and present the outcome of tests of catalysts made in this manner.

As usual, this volume rests on the efforts of many individuals, not all of whom can be acknowledged here. Thanks are due foremost to the contributors whose material forms the substance of the book; to my students and collaborators: Dr. John Hulse, Dr. Robert Lipson, William Limm, Dr. Therese Mejean, Andrew Kirkwood, Dr. Peter McBreen, Dr. Dorit Hall, Douglass Miller, Carolyn Preston, and David Zargarian, who have taught me much. Special thanks are due to my wife Linda who encouraged me to complete the task.

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May, 1986

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INTRODUCTION

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The study of metal clusters is now decidedly a recognizable discipline, manifesting all the earmarks of a field of study in the process of unification, like a cosmic dust-cloud on its way to becoming a star. It has symposia and conferences organized in its name and is attended by participants whose backgrounds are so different that their presence in the same room would have been unexpected were it not for the cluster connection. Their perspectives and language have also changed. Organometallic chemists talk of the similarity between cluster complexes and molecules absorbed on metal surfaces. The same group is now aware of developments in heterogeneous catalysis and appreciate the connection between the chemistry of a metal cluster complex and reactions on large metal crystallites such as one might encounter in supported catalysts. Likewise, surface chemists using techniques such as ultraviolet photoelectron spectroscopy, electron energy loss spectroscopy, or surface infrared spectroscopy use metal cluster complexes as models on the basis of which to interpret their data. Chemical physicists studying the spectra of transition-metal diatomics produced in supersonic nozzle beams and detected by resonant two-photon ionization allude in their discussions to metal-metal multiple bonding, a concept begotten by and normally the concern of organometallic chemists. The products of organometallic synthesis are now finding their way into the hands of both chemical physicists, who wish to use them as precursers for making metal clusters in the gas phase (1) by photolysis, and catalysists, who hope to use these substances for making catalysts of uniform metal particle-size distribution by decomposing metal cluster carbonyls that have been adsorbed on oxide supports (2).

A brief historical synopsis of the study of metal clusters helps to bring it into perspective. Before 1960 metal clusters were studied mainly in the context of catalysis with little physical characterization, except for surface area studies and measurements of percent dispersion; the latter giving some idea of the cluster sizes involved. Some remarkable insights nevertheless were achieved regarding the role of multiple surface sites in catalysis which is sometimes referred to as ''structure sensitivity'' (3). Likewise, some commendable efforts were made in understanding the structure of the metal aggregates residing in the catalyst, as for example, in the classic electron microscopic studies of Prestridge and coworkers (4).

A major milestone in the study of clusters occurred in 1955 when Longuet-Higgins and coworkers (5) predicted the icosahedral structure of $B_{12}H_{12}^{-2}$. This prediction was confirmed experimentally as one of the many score of important chemical discoveries that were made in the fifties, sixties, and early seventies in the study of the structure and chemistry of boranes (6). Although the boranes formed the first major group of cluster compounds about which precise chemical and structural information was acquired, they will be almost totally ignored in this book. Not because they are unimportant; quite the contrary, they are so important that several excellent monographs dedicated to them already exist (6).

The 1960s also produced the first cluster carbonyls such as $Co_4(CO)_{12}$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$, and the famous $Re_2Cl_8^{-2}$ ion which was shown by Cotton to possess the now famous metal-metal quadruple bond (7). This launched a field in its own right, culminating in the synthesis of dozens of triply and quadruply bonded bimetal complexes (8).

The 1960s, as well, saw the development of modern techniques of surface analysis for the study of molecules adsorbed on single crystal metal surfaces. In discussions on the vibrational and electronic data obtained therefrom more and more use is made of transition-metal complexes as models for molecules adsorbed on metals.

Enormous advances were made in the 1970s in the synthesis of large cluster complexes. Premier among the players here were the late Paolo Chini and coworkers (9). Compounds such as $Rh_{13}(CO)_{24}H_x^{5-x}$, $Pt_{26}(CO)_{32}^{-2}$, $Pt_{38}(CO)_{44}H_x^{-2}$, and $[Pt_3(CO)_6]^{-2}$ were reported.

The similarities between what surface scientists observe and what organometallic chemists synthesize prompted the late Earl Muetterties to formulate the ''surface cluster analogy'' (10) in the mid-1970s. This statement alerted both camps (surface chemists and cluster chemists) to the presence of each other. Many fundamental questions arise as a consequence. For example, Why are small naked metal clusters such good catalysts, whereas cluster carbonyls, often containing approximately the same number of metal atoms, are usually rather indifferent catalysts? How many metal atoms must a cluster contain before its properties are indistinguishable from the bulk? (This last question, it was soon realized, was really a family of questions since the answer depended dramatically on whether one was interested in a cluster's chemical, optical, electronic, or magnetic properties among others.)

Several strategies were employed in the 1970s in an attempt to address these questions. Theoreticians began to apply molecular orbital techniques (11) in improving the level of understanding of both the nature of the metal-metal bonding within clusters and the adsorbate—metal bond. Matrix isolation techniques were used to make both naked and adsorbate-covered metal clusters which could then be studied using a wide variety of spectroscopic methods (12). The related technology of metal vapor synthesis was developed (13). The new techniques, developed originally for surface science, began to be employed in the 1970s to study "real" catalysts. These methods, such as EXAFS (extended X-ray absorption, fine structure spectroscopy), revolutionize structural analysis of catalysts and catalyst materials (14).

Metal clusters were made and studied in nozzle beams first by Gole and coworkers (15) and by Schumacher and his group (16). The latter developed resonant two-photon ionization specifically for the study of alkali clusters (17). They were also able to measure the ionization potential of sodium clusters as a function of cluster size up to Na_{19} and discovered unusually stable and unusually unstable alkali cluster sizes (so-called magic numbers) among the aggregates they produced. Cluster distributions surpassing Na_{60} have now been achieved (18). Richard Smalley and his group (19) refined the nozzle-beam technique for studying just about any metal. Using an ingenious laser ablation method, researchers have now produced and studied cluster beams of a large number of metals. Two other groups—Argonne and Exxon—have developed this method further.

Most recently, the nozzle-beam technique has been turned toward the study of chemical reactions. Metal hydride, metal oxide, metal sulfide formation, and alkane dehydrogenation are among the reactions studied as a function of cluster size (20).

Enormous progress has been made in the past 20 years in metal cluster research; yet the goals now remain largely the same as then. In the fields of catalysis, chemistry, and physics the aim is to discover how a chemical process depends on cluster size; how the chemistry of a metal changes with its state of aggregation; and how structural, electronic, optical, and magnetic properties vary with cluster size, eventually reaching those of the bulk metal. Although for organometallic chemists the size of the largest soluble cluster complex and the general rule governing the sizes and structures of stable complexes remain unanswered questions, the generation of cluster complexes with unusually high catalytic activity is also still an unrealized goal.

For theory, too, the future holds its challenges. Even clusters as small as diatomics may prove difficult species to get right, as illustrated by the controversies surrounding Cr_2 (21).

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SOME TOPICS IN COMPUTATIONAL TREATMENT OF METAL CLUSTERS

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2.1 INTRODUCTION

The recent explosion of interest in small metal particles has been accompanied by widespread application of various theoretical methods to the problem. The variety of methods (and sometimes different results) are almost as numerous as the different groups attacking the problem. The methods that are applied have limitations even though several man-years of development may have been associated with any particular approach. These limitations often lead to differing calculated results, which have sparked numerous controversies in the field. This is characteristic of a young and growing area. I will attempt here to categorize the different theoretical approaches that have been used to study transition- and noble-metal clusters. Only some of the more obvious features of each method will be discussed since great detail is not needed for an overview of this field. Several applications of the methods to current relevant problems will be discussed, illustrating some strong and weak points associated with the various methods.

2.2 METHODS

2.2.1 Ab Initio Methods

Ab initio methods occupy a central place in theoretical studies of electronic structure. If a sufficiently flexible basis set is used with the full self-consistent-field (SCF) computational apparatus available in contemporary computer programs, excellent agreement with experiment can be obtained (1). Rarely can this limit be approached, however, for problems involving transition-metal multiple-atom clusters, and so the selection of basis sets and the use of approximation become crucial.

Ab initio methods are those in which the wavefunction is solved by accurately evaluating all of the integrals in the $2N$-electron Hamiltonian.

$$\hat{H} = \sum_{i}^{N} -\frac{\nabla_i^2}{2} + \sum_{i=1}^{N}\sum_{k=1}^{M} -\frac{Z_k}{r_{ik}} + \sum_{j>i}^{N}\frac{1}{r_{ij}} + \sum_{l>k}^{M}\frac{Z_l Z_k}{R_{lk}} \tag{2.1}$$

Here M centers containing Z electrons and separated by a distance R_{lk} interact with $2N$ electrons having nuclear-electron separation r_{ik}. At the first level of approximation the wavefunction Ψ is expressed as an antisymmetrized (2) product of spin orbitals ϕ_i in a single Slater determinant.

$$\Psi = \mathcal{A}\prod_{i=1}^{N} \phi_i \tag{2.2}$$

Crucial at this stage is the choice of the form of the molecular orbitals (ϕ_i) since they are expanded as a linear combination of basis orbitals, χ_i. This basis set (3) may contain one function per atomic orbital (minimal), two per atomic orbital (double-zeta), or more per atomic orbital (extended). In addition, functions of a higher angular momentum quantum number (polarization) may be used to augment the description of each atomic orbital. Clearly, to account properly for changes in shape of the orbitals in a molecular or cluster environment, double-zeta or larger basis sets must be used.

The Schröedinger equation is solved (4) by minimizing the energy through the variation of the molecular orbitals. The energy is

$$\begin{aligned}
E &= \sum_{i=1}^{N} 2\epsilon_i - \sum_{i,j=1}^{N} (2J_{ij} - K_{ij}) + V_N \\
\epsilon_l &= \left\langle \phi_l \left| \frac{-\nabla_i^2}{2} + \sum_{k=1}^{M} \frac{-Z_k}{r_{ik}} \right| \phi_l \right\rangle + \sum_j (2J_{lj} - K_{lj}) \qquad (2.3) \\
J_{ij} &= \left\langle \phi_i(1)\phi_i(1) \left| \frac{1}{r_{12}} \right| \phi_j(2)\phi_j(2) \right\rangle \\
K_{ij} &= \left\langle \phi_i(1)\phi_j(1) \left| \frac{1}{r_{12}} \right| \phi_i(2)\phi_j(2) \right\rangle
\end{aligned}$$

where ϵ_i is the orbital energy, J_{ij} is the coulomb integral, K_{ij} is the exchange integral, and V_N represents the nuclear repulsion. This simplest solution corresponds to two electrons per orbital and is termed *restricted Hartree-Fock*. At this level of solution the results may be easily transferred to a conceptual molecular orbital picture, but some ground-state properties often do not agree well with experiment as we will see later. Correlation effects, which allow electrons to interact instantaneously with each other rather than with the average field of the other electrons, may be introduced by the addition of a linear combination of Slater determinants. This approach, called CI (configuration interaction), improves calculated ground-state properties and permits dissociation to the proper atomic limits. Of course, this extension greatly increases the computational problem.

The application of pseudopotentials (or effective potentials) can greatly reduce the computational demands of a given problem. In this approach, a potential function is added to the Hamiltonian in equation (2.1) that will allow elimination of explicit treatment of core orbitals. The pseudopotential is usually chosen so as to lead to a computed spectrum of eigenvalues that will match the experimental spectrum of the atom or solid band structure. Goddard et al. (5) have pointed out several potential problems with this approach, including one of the most damaging for problems of interest here. That problem is whether choosing the correct eigenvalue spectrum guarantees that the correct shape and sizes of valence orbitals will be obtained. He advocates an ab initio effective-potential method that fits the effective potential to an all-electron ab initio calculation and therefore gives the correct shape of the valence orbitals.

One of the major problems with restricted Hartree-Fock calculations is that at the dissociation limit ionic states are formed. This problem is exemplified by the textbook example for H_2, where at infinite separation the wavefunction contains equal ionic and covalent contributions, whereas only covalent contributions are desired. One solution to this problem is the *unrestricted Hartree-Fock* theory in which different spatial functions are used for the pairs of up- and down-spin orbitals. Alternatively, valence-bond methods that contain only covalent contributions at large distances may be used.

The generalized valence-bond method (GVB) developed by Goddard and coworkers (1,5) has the correct dissociation limit and solves for the optimal orbitals as in Hartree-Fock theory. For H_2, the Hartree-Fock wavefunction

$$\Psi^{\text{HF}} = \mathcal{A}[\phi_1\phi_2(\alpha\beta)], \qquad \langle\phi_1|\phi_2\rangle = 0 \tag{2.4}$$

is replaced by a wavefunction in which $\langle\phi_1|\phi_2\rangle \neq 0$. By use of this prescription the singlet electron pairs are allowed to correlate

$$\Psi^{\text{GVB}} = \mathcal{A}[\phi_1'\phi_2'(\alpha\beta - \beta\alpha)], \qquad \langle\phi_1'|\phi_2'\rangle \neq 0 \tag{2.5}$$

This modifies slightly the form of the variational equations to be solved but automatically includes some of the correlation effects in the solution. In addition, further configuration interaction calculations may be carried out to obtain more of the correlation energy.

2.2.2 X_α Methods

There are several variations of calculations carried out in the X_α scheme. The starting point is an equation derived by Slater (6) in which the exchange terms in the Hartree-Fock equations are replaced by the X_α potential

$$V_{X_\alpha} = -6\alpha\left(\frac{3}{4\pi}\rho\right)^{1/3} \tag{2.6}$$

derived from the free-electron theory. In this equation ρ is the electron density and α is a parameter for each atom. The one-electron Hartree-Fock-Slater equation is

$$\{-\nabla_1^2 + V_c(1) + V_{X_\alpha}(1)\}\phi_i(1) = \epsilon_i\phi_i(1) \tag{2.7}$$

where ϵ_i and ϕ_i are the eigenvalue and the molecular spin orbital, respectively, ∇_1^2 represents the kinetic energy operator, and $V_c(1)$ is the coulomb term (6). Note the use of the local energy-independent X_α potential to replace the nonlocal energy-dependent exchange potential of the Hartree-Fock equations in this procedure. The procedure considerably reduces the computational complexity of the problem to be solved compared to the Hartree-Fock method. All electrons are treated in this method, and apparently some electron-correlation contribution is provided by the X_α potential. The eigenvalues computed in X_α theory do not have the same meaning as eigenvalues computed in Hartree-Fock theory, where in the Koopmans' theorem approximation their negative value gives the ionization potential. Of course, this approximation neglects relaxation processes inherit in the ionization process. In the X_α methods a transition-state method is used to compute the ionization potentials

$$-\mathrm{IP} = \frac{\partial \langle E_{X_\alpha} \rangle}{\partial n_i} \tag{2.8}$$

where $\langle E_{X_\alpha} \rangle$ is the statistical total energy and n_i is the occupation number of the ith orbital. This procedure accounts for relaxation effects inherent in the ionization (7).

The most commonly used form of the theory (SCF-X_α-SW) makes muffin-tin approximations in which spherical potentials are used to partition space around a given molecule or cluster. This approximation has given good eigenvalues and wavefunctions but does not presently permit computation of an accurate energy. This is a limitation for many applications of the theory. Also, the spherical potentials of the muffin tin make it more appropriate for high-symmetry problems. Some work has been done using the overlapping spheres method in which more asymmetric spatial potentials are treated to divide space. This introduces an arbitrary choice of the degree of overlap. Other versions of the X_α theory have to permit computation of the total energy. These include the LCAO-X_α (8) and discrete variational methods (9).

2.2.3 Semiempirical Methods

Semiempirical methods of quantum chemistry are generally aimed at understanding the trends within a series of like structures after the parameters are fixed by comparison with experiment for some model species. Thus, the numerous integrals in equation (2.2) are replaced by their effective corresponding experimental counterparts. These methods are much less sophisticated than the procedures we have described before but they remain an important tool in quantum chemistry. Conceptual models are most easily derived from them, and the essential symmetry properties of wavefunctions are retained at this level.

The CNDO (complete neglect of differential overlap) (10) and MINDO (modified intermediate neglect of differential overlap) (11) methods exemplify one line of development of the theory. The central approximations of this method involve

$$\left\langle \chi_i(1)\chi_l(1) \left| \frac{1}{r_{12}} \right| \chi_j(2)\chi_k(2) \right\rangle = \langle il|jk\rangle = \langle ii|jj\rangle \delta_{il}\cdot\delta_{jk} \tag{2.9}$$

$$S_{ij} = \langle \chi_i|\chi_j\rangle = \delta_{ij}$$
$$\delta_{ij} = \text{Krönicker delta}$$