MOLECULAR CLUSTERS: A BRIDGE TO SOLID-STATE CHEMISTRY

Despite the fact that clusters can be viewed as solids at the nanoscale, molecular cluster chemistry and solid-state chemistry traditionally have been considered as separate topics. Such treatment makes it difficult to appreciate commonalities of structure and bonding. This book connects the electronic structure models of small clusters with conceptually analogous models of solid-state materials, thereby creating a bridge. The approach also establishes boundary conditions on the electronic structure of nanoclusters: species that lie in-between the two. Although the focus is on clusters, sufficient attention is paid to solid-state compounds at each stage of the development to establish the interrelationship between the two topics. Comprehensive coverage of cluster types by composition, size, and ligation is provided, as is a synopsis of selected research.

Written in an accessible style with numerous illustrations, exercises, problems and solutions to aid comprehension, this book is suitable for graduate students and researchers in inorganic chemistry, physical chemistry, materials science, and condensed matter physics.

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MOLECULAR CLUSTERS
A Bridge to Solid-State Chemistry

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Preface

Who, what, where, why, when and how – the elementary prescription for a news squib is also appropriate for a preface.

Who? The book is intended primarily as a text for advanced undergraduates and graduate students. It can also serve the needs of research workers in the wide area of nanochemistry, as molecular clusters and extended solid-state materials constitute the structural “bookends” of nanoparticles: species that are not large enough to be treated with solid-state concepts but too large to follow the simple rules of molecular clusters. Those interested in a wide-ranging introduction to models of electronic structure applicable to delocalized, three-dimensional systems will also find it useful.

What? This text circumscribes a non-traditional area of inorganic chemistry. The focus is on a class of compound that exhibits cluster bonding. Emphasis is on connections between the problems of small molecular clusters, where the vast majority of atoms are found at the surface, to large crystals, where most atoms are found in the bulk. A review of bonding in molecular compounds (Chapter 1) is followed by the fundamentals of cluster bonding in p-block clusters (Chapter 2) and transition-metal clusters (Chapter 3). After making connections with organometallic chemistry (Chapter 4), mixed p–d-block clusters are developed (Chapter 5). A bonding model for periodic extended structures (Chapter 6) is developed in the style of Chapter 1. Chapter 7 then illustrates some of the similarities and differences between the bonding of clusters and related solid-state structures. The finale (Chapter 8) abstracts a selection of recent research to illustrate real connections between clusters and solid-state systems.

Where? Time will tell where this text will fit in the curricula of relevant departments. Presently, there is no common course in chemistry that it could serve as a primary text. However, since the mid-1990s a first-year graduate course along the lines of the material contained within this text has been offered at Notre Dame.
Preface

Drafts of the present text have been used twice in Chem 616 “Solid-state and cluster chemistry” further developing the material herein.

Why? In inorganic texts solid-state chemistry appears ancillary to the main emphasis of molecular chemistry. The title of one first-year chemistry text proclaims chemistry a “molecular science.” Clusters fare less well. Service on standard inorganic exam committees reveals many teachers of inorganic chemistry who are uncomfortable with both solid-state and cluster chemistries. The conceptual barrier involves the delocalized bonding networks required for an understanding of electronic structure. This book attempts to smooth the transition between simple localized bonding models and the delocalized ones by using clusters to bridge molecular and solid-state chemistries. From the localized two-center bonds of three-connect clusters to the band structure of metals, cluster bonding provides a unifying paradigm.

When? Both solid-state chemistry and main-group cluster chemistry can be considered mature areas. Transition-metal cluster chemistry is of more recent origin; however, it too has been well defined in a number of edited works. There are texts on solid-state chemistry and one on cluster chemistry but there is no text that exploits connections between the two using simple models. Simplified models are the tools of the working chemist but the power of the simple models within an area also creates barriers to inter-area understanding. The time is right to show that the molecular and solid-state boundary conditions on clusters reveals the exciting problems of structure and properties that remain to be discovered in the region lying between small clusters and bulk materials – nanoparticles.

How? The text is representative, not comprehensive, and we attempt to balance simplification and detail. Additional sources are gathered at the end of each chapter but this list is far from complete. Literature is cited when it is felt the reader might benefit from following the original arguments or when a more comprehensive monograph provides access to the details of a given topic or area. For non-chemists the Appendix contains an outline of the fundamental concepts of chemistry prerequisite to the body of the text. With the exception of Chapter 8, each chapter includes worked exercises and homework problems at the end of the chapter. A number of problems are drawn from the research literature to illustrate the approach advocated. They are challenging by design and a few of the solutions are not published.

Caveats. Those familiar with cluster chemistry will mark the absence of cluster synthesis, framework dynamics and reactivity. Considerable information exists and these topics for selected cluster types are well developed in cluster reviews and edited volumes. However, our focus on electronic structure is deliberate. We wished to compare and contrast geometric and electronic structure across the large sweep of element composition and cluster size up to and including bulk materials. To keep the book of manageable size relative to a typical one-semester advanced course yet
still bridge the disparate areas encompassed in “cluster chemistry” we chose a focus consistent with our scope. The approach is unabashedly qualitative but we hope the reader finds the material an hors d’oeuvre leading to more satisfying entrées in the literature of the many broad topics touched upon.

Thank yous. First, we owe an intellectual debt to the masters of both cluster and solid-state chemistries from whom the models presented arose. Some are acknowledged by name in the text where appropriate. Many others, unacknowledged, created and described the magnificent bodies of chemistry, experimental and theoretical, which constitute the foundations of this work. That is the nature of science – most of us are ants piling our grains of chemistry so that those with longer sight can see even farther.

One of us (TF) held a Leverhulme Visiting Professorship at the University of Bath in the spring of 2004 during which the writing of this book was begun. Dr. Andrew S. Weller made this happen. Many thanks to Andy and his department for both a productive and pleasant sojourn in England. We are also grateful to the CNRS and the NSF for the support of our independent research as well as a joint project of cooperative research which facilitated our writing efforts. Our thanks go to Nancy Fehlner who read the entire manuscript in its final form as well as Dr. Mouna Ben Yahia who kindly performed some theoretical calculations to check qualitative (sometimes not) ideas we had in mind. Still, it is highly unlikely we have produced an error-free book – entropy rules – and the errors that remain are ours.