WILEY-VCH

Phuong Mai Dinh, Paul-Gerhard Reinhard, and Eric Suraud

An Introduction to Cluster Science

PHYSICS TEXTBOOK

Phuong Mai Dinh
Paul-Gerhard Reinhard
Eric Suraud

An Introduction to Cluster Science

Related Titles

Cundari, T.R., Boyd, D.B. (eds)

Reviews in Computational Chemistry, Volume 25
2 edn

2007
ISBN: 978-0-470-17998-7, Also available in digital formats

Barone, V. (ed.)

Computational Strategies for Spectroscopy
From Small Molecules to Nano Systems

2011
ISBN: 978-0-470-47017-6, Also available in digital formats

Komatsuzaki, T., Berry, R., Leitner, D.M. (eds)

Advancing Theory for Kinetics and Dynamics of Complex, Many-Dimensional Systems
Clusters and Proteins, Advances in Chemical Physics Volume 145

2011
ISBN: 978-0-470-64371-6, Also available in digital formats

Hadjichristidis, N., Hirao, A., Tezuka, Y., Du Prez, F. (eds)

Complex Macromolecular Architectures
Synthesis, Characterization, and Self-Assembly

2011
ISBN: 978-0-470-82513-6

Gonsalves, K., Halberstadt, C., Laurencin, C.T., Nair, L.S. (eds)

Biomedical Nanostructures

2008
ISBN: 978-0-471-92552-1

Vollath, D.

Nanomaterials
An Introduction to Synthesis, Properties and Applications

2008
ISBN: 978-3-527-31531-4

Hirscher, M. (ed.)

Handbook of Hydrogen Storage
New Materials for Future Energy Storage

2010
ISBN: 978-3-527-32273-2, Also available in digital formats

Grunenberg, J. (ed.)

Computational Spectroscopy
Methods, Experiments and Applications

2011
ISBN: 978-3-527-32649-5, Also available in digital formats

Rubahn, H.

Basics of Nanotechnology
3 edn

2008
ISBN: 978-3-527-40800-9

Phuong Mai Dinh
Paul-Gerhard Reinhard
Eric Suraud

An Introduction to Cluster Science

WILEY-VCH
Verlag GmbH & Co. KGaA

Authors

Phuong Mai Dinh
Université Paul Sabatier
Laboratoire de Physique Théorique
Toulouse
France

Paul-Gerhard Reinhard
Universität Erlangen
Institut für Theoretische Physik
Erlangen
Germany

Eric Suraud
Université Paul Sabatier
Laboratoire de Physique Théorique
Toulouse
France

Cover Design
Physics meets art: The background of the cover represents a detail of a church window (© jorisvo/fotolia.com). The shining colors of church windows reflect their content in metallic particles, in modern words metallic nanoclusters.

Physics meets biology: illustrative example of gold nanoclusters attached to a DNA molecule. The presence of nobel metal nanoparticles in biological environments results in significant radiobiological and immunological effects the essential physical insights into which could be obtained through the molecular dynamics simulations, see http://www.mbnexplorer.com/.

Library of Congress Card No.:
applied for

British Library Cataloguing-in-Publication Data:
A catalogue record for this book is available from the British Library.

Bibliographic information published by the Deutsche Nationalbibliothek
The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at http://dnb.d-nb.de.

Hardcover ISBN 978-3-527-41246-4
Softcover ISBN 978-3-527-41118-4
ePub ISBN 978-3-527-67570-8
Mobi ISBN 978-3-527-67569-2

Cover Design Simone Benjamin, McLeese Lake, Canada
Typesetting le-tex publishing services GmbH, Leipzig
Printing and Binding Markono Print Media Pte Ltd, Singapore

Printed in Singapore

Printed on acid-free paper

To Philippe, Elisabeth, and Evelyne

Contents

Preface

Cluster science developed as an independent branch of science only a few decades ago. Since then its remarkable achievements have turned it into a major branch of science bridging the gap between microscopic and macroscopic worlds. Cluster science joins efforts from physicists and chemists and has led to impressive technological developments, opening the door to the nanoworld. It is now an established field of research with an impressive network of connections to neighboring scientific domains such as material science, but also to more remote ones such as, in particular, biology. We aim in this short book at addressing both these aspects, first, presenting cluster science as such, and second, indicating the connections to other fields of research.

Cluster science: a young field with a long history and a promising future Clusters were recognized in technological applications well before they were identified as physical objects. It was well known to Roman craftsmen and into the Middle Ages that immersing small pieces of a noble metal into a glass allowed for beautiful colors to then reside within the glass. More recently, photography became possible when realizing that small aggregates, namely "small" pieces of matter, of AgBr had a remarkable sensitivity to light, which with a proper chemical treatment, allowed to record and print images. However, over these many centuries, the idea of clusters as a subject of scientific research remained absent. One major reason was that one did not know how to isolate and to identify such microscopically small objects from a carrier environment, for example a glass in the Middle Ages, or more recently a gel. It has only been during the last quarter of the twentieth century that researchers have succeeded in producing in a controlled manner aggregates of various (controlled) sizes, thus opening the door to dedicated studies of clusters, also known as nanoparticles. For example, studies of clusters of various sizes allowed for the first time to systematically track the transition between atom/molecule and a bulk material. Within a few decades, cluster physics has become a lively domain of research, and has "invaded" many other domains where it is now fully admitted that clusters do play a major role. As typical examples, let us cite the many potential applications of nanosystems in material science in the race for miniaturization, as well as in medicine for drug delivery and imaging. We could also mention astrophysics with the composition of the interstellar medium, or climate science with aerosols. Cluster science has thus a promising future which motivates us to present its many facets in this book. Thereby we try to stay at an introductory level to address a broad readership.

Cluster science: a merger between physics and chemistry Clusters are constituted from atoms and interpolate between small molecules and bulk materials. As such, they thus call for expertise from chemistry – chemistry of small molecules but also solid-state chemistry – as well as from physics – atomic and molecular physics and solid-state physics. Indeed, the cluster community formed as a merger between various fields of physics and chemistry, including researchers involved in the study of other finite systems, such as nuclei or helium droplets. From this somewhat heterogeneous background emerged an original and rich scientific field primarily dedicated to the study of clusters themselves. Cluster science indeed developed over the last few decades into a somewhat specific domain. The study of clusters themselves made tremendous progress, reaching now in some cases a remarkable degree of detail, for example, even a time-resolved account of the dynamical response to a dedicated excitation. This high degree of detail was made possible partly because of the growing versatility of lasers over the same period of time and to the fact that clusters may have a strong coupling to light, especially clusters made out of metallic material. We will see many examples along that line throughout this book, both in the study of clusters themselves as well as in applications to other fields.

Cluster science: an interface between many domains A fascinating aspect of cluster science is that clusters play a role in several somewhat unexpected scenarios. This holds, for example, in astrophysics where it was recently realized that the composition of cosmic dust is “full” of clusters, whose influence on light signals received on earth may be crucial. But this also holds in terms of applications, for example, in drug delivery on specific targets in the human body. But they may be essential building blocks of new materials as well. The range of “applications” is thus enormous, from the largest times and distances in the universe to nanosized devices and materials, with an excursion into mesoscopic constituents of living cells in the human body. These apparently remote domains of scientific knowledge happen to share common objects, namely clusters. It is thus certainly an important issue to understand the properties of these fascinating objects.

The aim of this book is to introduce the reader to these many aspects of cluster science. The domain is huge and cannot be covered in depth within the limited size of the present book which should be an introductory text. It nonetheless indicates the wide range of cluster physics. We thus have confined the presentation to the basic aspects of clusters, being well aware that some aspects and many details are missing. This book is not meant to be an exhaustive review but rather a survey to motivate the reader to go deeper into the material. We have thus tried to supply relevant citations, mostly to textbooks or review papers and, when found helpful, to the proper specific citation. A strong underlying idea was to precisely cover general characteristics, often on a schematic basis, as well as some actual recent scientific results in order to enlighten the ever-developing nature of the field. The book thus consists of two parts of about equal size. The first half of the book (Chapters 1 to 3) includes a general introduction and provides the basic notions and keywords in experiments and theory. These notions should suffice for further reading of papers in the field. The last three chapters (Chapters 4 to 6) gather a collection of illustrative results. These chapters cover both properties of clusters themselves and their applications in various domains of science from astrophysics to material science and biology.

A book is always the result of numerous interactions with many colleagues. It is obvious that our project would not have converged without these many interactions. We would thus like to acknowledge the help of all these colleagues and tell them how much they helped, long ago or more recently, both in terms of science and personal contacts. We would, in particular, like to mention here: E. Artacho, M. Bär, M. Belkacem, D. Berger, G.F. Bertsch, S. Bjornholm, C. Bordas, M. Brack, F. Calvayrac, B. and M. Farizon, F. Fehrer, T. Fennel, G. Gerber, E. Giglio, C. Guet, B. von Issendorf, H. Haberl, J.M. L'Hermite, P. Klüpfel, U. Kreibig, J. Kohanoff, C. Kohl, S. Kümmel, E. Krotscheck, P. Labastie, F. Lépine, F. Marquardt, K.-H. Meiwes-Broer, B. Montag, M. Moseler, J. Navarro, V. Nesterenko, A. Pohl, L. Sanche, L. Serra, R. Schmidt, A. Solov'yov, F. Spiegelman, F. Stienkemeier, J. Tiggesbäumker, C. Toepffer, C. Ullrich, R. Vuilleumier, Z.P. Wang, P. Wopperer, F.S. Zhang, and G. Zwicknagel. Finally we would like to mention that this book emerges from a long-standing collaboration between the authors. This would not have been possible without the help of funding from the French–German exchange program PROCOPE, the Institut Universitaire de France, and the Alexander-von-Humboldt Foundation. We are thankful to these institutions to have supported us in our common efforts.

Toulouse	*Phuong Mai Dinh,*
Erlangen	*Paul-Gerhard Reinhard and*
Toulouse	*Eric Suraud*

March 2013

Units

We list here a few basic physical constants and units (data taken from [1]). We use the Gaussian system of units for electromagnetic properties (dielectric constant $\epsilon_0 = 1/4\pi$).

Electron mass:	$m_e = 0.0156\,\text{eV fs}^2 a_0^{-2} = 0.5\,\text{Ry}^{-1} a_0^{-2}\hbar^2$ $= 1\,\text{Ha}^{-1} a_0^{-2}\hbar^2$
Light velocity:	$c = 5670\, a_0\,\text{fs}^{-1} = 274.12\,\text{Ry}\, a_0 = 137.06\, a_0\,\text{Ha}^{-1}$
Fine structure constant:	$\alpha = \frac{e^2}{\hbar c} = 0.007297 = \frac{1}{137.03}$
Charge:	$e^2 = 1\,\text{Ha}\,\text{a}_0 = 2\,\text{Ry}\,\text{a}_0 = 14.40\,\text{eV Å} = 27.2\,\text{eV}\,\text{a}_0$
Bohr energy:	$E_B = \frac{e^4 m_e}{2\hbar^2} = \frac{\alpha^2 m_e c^2}{2} = 13.604\,\text{eV} = 1\,\text{Ry} = \frac{1}{2}\,\text{Ha}$
Bohr radius:	$a_0 = \frac{\hbar^2}{m_e c^2} = 0.5291\,\text{Å} = 0.05291\,\text{nm}$ $= 0.5291 \times 10^{-10}\,\text{m}$
Bohr magneton:	$\mu_B = \frac{\hbar e}{2 m_e} = 5.788\,\text{eV T}^{-1}$
Boltzmann constant:	$k_B = 8.6174 \times 10^{-5}\,\text{eV K}^{-1}$
Energy scales:	$1\,\text{Ha} = 2\,\text{Ry} = 27.2\,\text{eV}$ $1\, h\,\text{GHz} = 4.136 \times 10^{-6}\,\text{eV};\ 1\frac{hc}{\text{cm}} = 0.1240 \times 10^{-3}\,\text{eV}$
Time scales:	$1\,\text{fs} = 10^{-15}\,\text{s} = 1.519\frac{\hbar}{\text{eV}} = 20.66\frac{\hbar}{\text{Ry}} = 41.32\frac{\hbar}{\text{Ha}}$ $1\,\frac{\hbar}{\text{Ha}} = 0.5\,\frac{\hbar}{\text{Ry}} = 0.0242\,\text{fs}$
Laser intensity:	$I = \frac{c}{8\pi}\lvert E_0\rvert^2;\ \frac{I}{\text{W cm}^{-2}} = 27.8\left\lvert\frac{E_0}{\text{V cm}^{-1}}\right\rvert^2$
Scale factors:	$\hbar c = 1.9731 \times 10^{-7}\,\text{eV m} = 1973.1\,\text{eV Å} = 274.12\,\text{Ry}\, a_0$ $\frac{\hbar^2}{m_e} = 1\,\text{Ha}\, a_0^2 = 2\,\text{Ry}\, a_0^2 = 7.617\,\text{eV Å}^2$

In dynamics, one simultaneously treats energy, distance and time scales, so that one has to consider proper combinations of these three quantities. Some standard packages are:

- eV, a_0 and fs
- Ry, a_0, $\hbar$ Ry^{-1} ($1\,\hbar$ Ry^{-1} = 0.0484 fs)
- Ha, a_0, $\hbar$ Ha^{-1} ($1\,\hbar$ Ha^{-1} = 0.0242 fs, called the atomic unit).

1
Clusters in Nature

Clusters, also called nanoparticles, are special molecules. They are composed from the same building blocks, atoms or small molecules, stacked in any desired amount. This is similar to a bulk crystal. In fact, one may view clusters as small pieces of bulk material. It has only been within the past few decades that clusters have come into the focus of intense investigations. During these few decades, cluster science has developed into an extremely rich and promising field of research. As often in science, technological applications of clusters existed before they were identified and understood. One of the most famous and oldest examples of the application of clusters in technology is the coloring of glass by immersing small gold clusters into the glass itself. The process allowed for some tuning of colors depending on the inclusions' size. This technology dates back to Roman times, where there is evidence craftmen had perfectly mastered this versatile technique. In scientific terms, such a phenomenon just reflects the size dependence of the optical response (that is, the color) of gold clusters in a glass matrix (although that prosaic formulation certainly does not give sufficient credit to the marvelous impressions attained that way). Another example of early applications is found in traditional photography which started about two centuries ago. The emulsion of a photographic film contains a dense distribution of AgCl (later AgBr) clusters whose special optical properties allowed to store information from light impulses and to visualize it later by chemical reduction. Progress in sensitivity and resolution was tightly bound in properly handling the cluster properties, where for a long time photographers did not even know that they were dealing, in fact, with clusters.

Figure 1.1 exemplifies clusters with an ancient and with a modern view. Figure 1.1a shows a church window from the St. Etienne cathedral in Bourges (France), whose impressive colors (not visible here, but which can be appreciated from the book cover) were fabricated to a large extent by Au clusters embedded in glass. Figure 1.1b was recorded with the most modern achievements of scanning tunneling microscopes (STM). It shows in detail Ag nanoparticles sitting on a highly oriented pyrolytic graphite (HOPG) surface. From the given length scale, we read off for this case cluster sizes in the range of a few nanometers, which corresponds to system sizes of about 100–10 000 Au atoms. As we will see, the combination of these quickly developing methods of nanoanalysis with nanoparticles, called clusters, constitutes a powerful tool for fundamental and applied physics.

An Introduction to Cluster Science, First Edition. Phuong Mai Dinh, Paul-Gerhard Reinhard, and Eric Suraud.

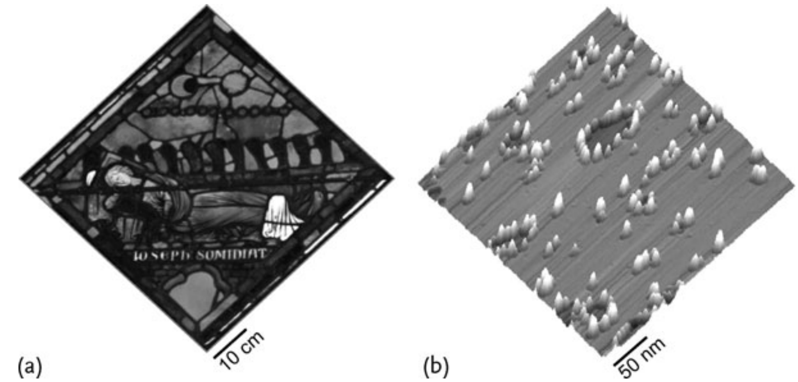

Figure 1.1 (a) Glass window of the St. Etienne cathedral in Bourges, France. Colors of church windows reflect their content in metallic particles. (b) Topography of silver nanoparticles deposited on (HOPG), recorded with an *in situ* scanning tunneling microscope (STM), from [2].

A first theoretical study which these days plays a basic role in cluster physics goes back to G. Mie in the early twentieth century [3]. Mie considered the question of the response of small metal particles to light, and how this optical response might depend on the size of the considered particle. It is interesting to quote Mie who turned out to develop a remarkable intuition of the future of cluster science: "Because gold atoms surely differ in their optical properties from small gold spheres", it would "probably be very interesting to study the absorption of solutions with the smallest submicroscopic particles; thus, in a way, one could investigate by optical means how gold particles are composed of atoms." This apparently simple and "reasonable" statement actually covers a large fraction of today's activities in cluster science as the interaction with light is a key tool for the investigation of cluster structure and dynamics.

In spite of Mie's intuition, the study of clusters as physical individual objects remained rather limited for the subsequent decades. Most investigations concerned clusters in contact with an environment (embedded or deposited). This limitation was due to the difficulty to create isolated clusters in a controlled manner. During the last quarter of the twentieth century, the capability of producing free clusters from dedicated sources finally triggered the emergence of cluster science on a systematic basis. The identification of the remarkable C_{60} clusters, the famous fullerenes [4], and the first systematic investigations of metal clusters [5] were impressive boosters. From then on, cluster science rapidly grew to an independent, although cross-disciplinary, field among the well-defined branches of physics and chemistry, ranging from fundamental research to applications in the context of nanotechnology.

Grossly speaking, clusters can be considered as large molecules or small pieces of bulk material. Their properties thus can be understood to some extent by methods from molecular and solid-state physics. Nonetheless, clusters represent a species of their own. One of the possibly most specific aspects of clusters is the fact that one can deliberately vary cluster size. Clusters are, so to say, "scalable" objects which