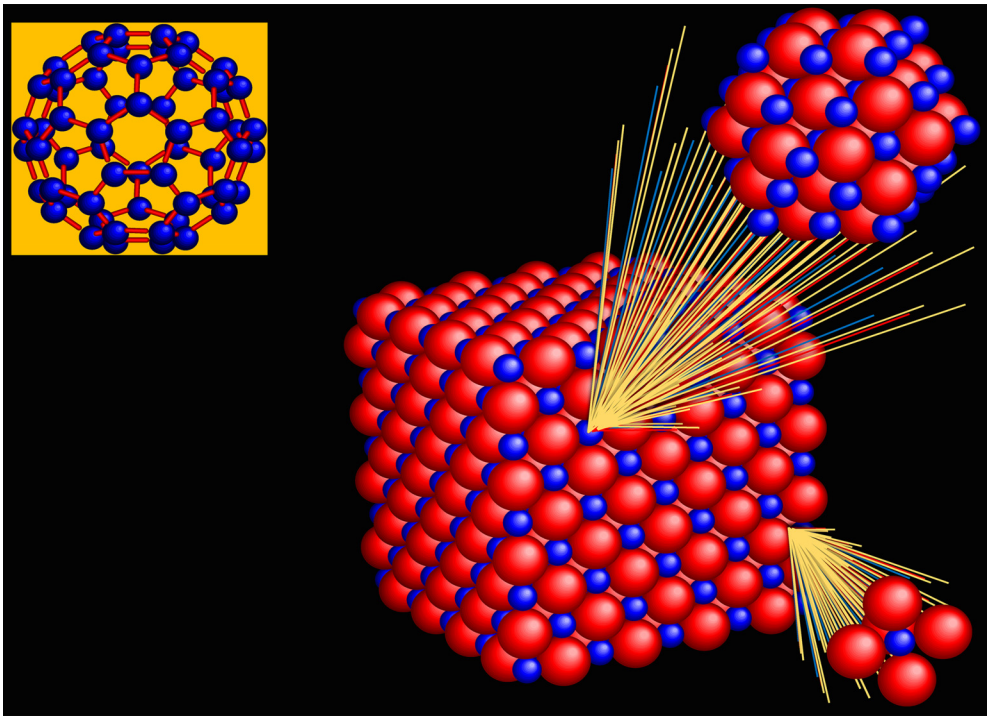
Current Natural Sciences

Patrice MÉLINON and Michel BROYER

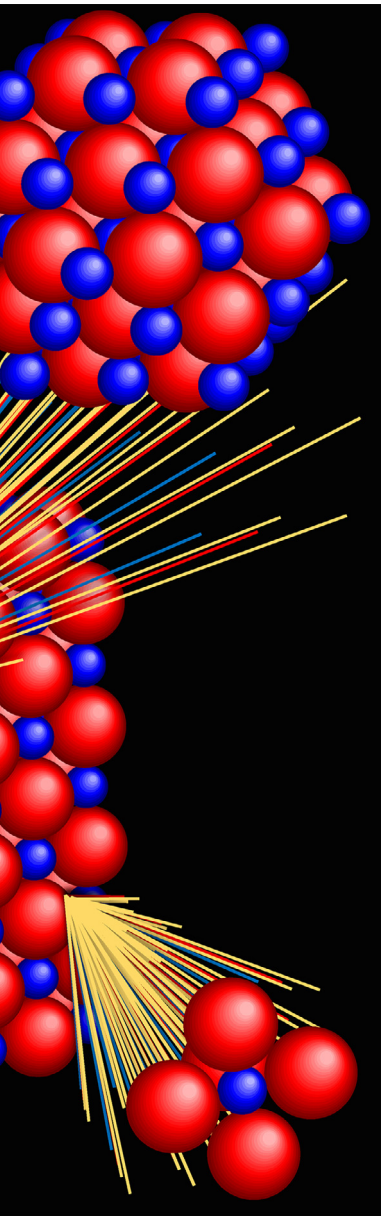
Atomic Clusters

Introduction to the Nano World



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Current Natural Sciences



Atomic Clusters

Introduction to the Nano World

Patrice MÉLINON and Michel BROYER

The spectacular development of nanotechnologies over the last twenty years has introduced all kinds of nano-objects or nanoparticles into everyday life. The remarkable properties of these nano-materials explain why they are used as much in cosmetics and lubricants as in most high-tech components.

The aim of this book is to describe the basic principles governing nanoscience, and nanophysics in particular. The authors show how the physics and chemistry of atoms influence the properties of nano-objects. They also describe how the properties of macroscopic materials are modified when their size decreases.

This first volume is devoted to aggregates or nanoparticles in the ground state. It shows how binding energy and symmetry properties govern the arrangement of atoms according to their electronic structure. It also explains the influence of metal bond complexity on the properties of transition metal nanoparticles. Applications are given for insulator-metal transition, magnetism and catalysis.

A second volume will describe the influence of the temperature, the excited states of aggregates and their optical properties. The authors come from different backgrounds, Michel Broyer from atomic and molecular physics and Patrice Mélinon from condensed matter. They were both pioneers in aggregate and work at Lyon I University.

Michel Broyer is a former student at ENS Ulm and professor at Lyon I University, where he is developing optical spectroscopy of aggregates. He has won numerous prizes and awards, including the prestigious Franco-German Gentner Kastler Prize and honorary member of the Institut Universitaire de France.

Patrice Mélinon developed pioneering experiments in Lyon on nanoparticles deposited on surfaces. He is Director of Research at CNRS and a former expert for Micro and NanoTechnologies. He is also author of a book with B. Masenelli "Small fullerenes and Superfattices" (2011).

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Patrice Mélinon and Michel Broyer

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Table of Content

Foreword **ix**

Constants and units **xiii**

1 Introduction **1**
1.1 Cluster physics: a young science 1
1.2 Size effect, role of the surface 3
1.2.1 Geometrical consideration 3
1.2.2 Generalization 4
1.3 Kubo conductivity criterion for metallic clusters 4
1.4 Examples of some of the more specific remarkable size effects 5
1.4.1 The discovery of carbon fullerenes 5
1.4.2 Metal insulator transition in clusters of specific systems 7
1.4.3 Magnetism 8
1.4.4 Heterogeneous catalysis 9
1.5 Small disgression on the law in 1/R 9
1.6 Conclusion 10

2 Cohesion of a cluster: origin, chemical bond **11**
2.1 Introduction 11
2.2 Cohesion of a metallic cluster: case of simple metals 11
2.2.1 Hamiltonian and cohesive energy in a simple metal . . 12
2.2.2 Jellium model 12
2.2.3 Macroscopic approach: liquid drop model 14
2.2.4 Tight binding: TBSMA model 17
2.2.5 Hückel's model of quantum chemistry 23
2.2.6 Realistic model 27
2.3 Cohesive energy in pure covalent elements 29
2.3.1 Introduction 29
2.3.2 Geometry in bulk phase 30
2.3.3 Cohesive energy 31

2.3.4 Geometry of covalent clusters: some general considerations . . . 39
2.3.5 Carbon clusters . . . 39
2.3.6 Silicon, germanium and tin clusters in sp^3 hybridization . . . 51
2.4 Cohesion of ionic systems . . . 54
2.4.1 Introduction . . . 54
2.4.2 Ionic bonding in the bulk phase . . . 55
2.4.3 Structures of the solid phase . . . 55
2.4.4 Pauling's rules [Pauling (1929)] . . . 65
2.4.5 Ionic compounds concerned . . . 67
2.4.6 Colored centers . . . 67
2.5 Ionic bonding in clusters . . . 69
2.5.1 General . . . 69
2.5.2 Colored centers in clusters . . . 71
2.5.3 Madelung constant in clusters . . . 75
2.5.4 Rigid model . . . 75
2.6 Cohesive energy of ionocovalent clusters . . . 77
2.6.1 Pauling ionicity . . . 77
2.6.2 Ionicity of Phillips [Phillips and Vechten (1969)] . . . 78
2.6.3 Phase transition . . . 79
2.7 Cohesion in van der Waals compounds . . . 81
2.7.1 Classical treatment . . . 81
2.7.2 Quantum approach . . . 82
2.7.3 Van der Waals energy in a cluster . . . 84

3 Shell effects in metallic clusters 87
3.1 Introduction . . . 87
3.2 Experimental results . . . 88
3.2.1 Some anomalies in the mass spectra . . . 88
3.2.2 Cohesive energy in clusters: Experimental methods and results . . . 90
3.2.3 Analogy with atoms and nuclei . . . 92
3.3 Electronic shells for electronic systems . . . 94
3.3.1 Master equation . . . 95
3.3.2 The model of the hydrogen atom . . . 95
3.3.3 Case of clusters: choice of V(**r**) potential . . . 96
3.3.4 Deformation of the droplet - Jahn Teller effect . . . 116
3.3.5 Calculations with a harmonic potential: Clemenger-Nilsson model . . . 118
3.4 Geometric shells . . . 118
3.4.1 General remarks . . . 118
3.4.2 Observation of geometric magic numbers . . . 119
3.5 Broken bond model . . . 120
3.5.1 Binding energy . . . 120

3.5.2 Geometric shells . . . 132
3.5.3 Experimental results . . . 136
3.6 Other models . . . 138
3.7 Conclusion . . . 138
3.8 Appendix: highlighting the magic numbers . . . 139

4 Insulator metal transition in clusters 141
4.1 Insulator Metal Transition in condensed matter . . . 141
4.1.1 Introduction: from atom to solid, energy bands, definitions . . . 141
4.1.2 Problem-related to the definition of metal . . . 143
4.1.3 Atomic approach of the metallic character: the "catastrophe" of the electric polarizability . . . 147
4.1.4 Macroscopic approach by electrical conductivity . . . 148
4.1.5 Approach in the context of band theory (Mott) . . . 150
4.1.6 Mott-Hubbard transition in a non mono electronic system . . . 151
4.1.7 Size effect: experimental problems . . . 155
4.2 Insulating Metal Transition in metal clusters . . . 155
4.2.1 Metal Insulator Transition due to electronic confinement . . . 156
4.2.2 Consideration of degeneracies in the framework of the shell model . . . 157
4.2.3 Experimental results . . . 161
4.2.4 Insulator-metal transition in divalent metals . . . 167
4.3 Insulator metal transition in semiconductors . . . 173
4.3.1 Change of coordination . . . 173
4.4 Electronic confinement in semiconductors . . . 173
4.4.1 Experimental observations . . . 174
4.4.2 Confinement in a box . . . 175
4.4.3 Wannier exciton: Efros's model [Efros and Efros (1982)] 176
4.4.4 More sophisticated models . . . 177
4.4.5 Clusters of ligand-free semiconductors . . . 178
4.4.6 Conclusion on semiconductors . . . 178
4.5 Overall conclusion . . . 181
4.6 Appendix . . . 182
4.6.1 Bohr radius a_H . . . 182
4.6.2 Quantum unit of conductance . . . 182
4.6.3 Ioffe Regel criterion [Gurvitch (1981)] . . . 183
4.6.4 IPES versus PES . . . 184
4.6.5 Mott insulator: an example NiO . . . 185

5 Complex metals **187**
5.1 Introduction . . . 187
5.1.1 Atomic structure of metals . . . 187
5.1.2 Structure of metals and phase diagram in the solid . . 188
5.1.3 Relationship between the structure of the clusters and that of the solid phase . . . 190
5.1.4 Fermi surfaces, conductivity, metallicity in solids . . . 191
5.2 Experimental methods . . . 195
5.2.1 Geometric structure . . . 195
5.2.2 Cohesive energy: CID . . . 198
5.3 Alkaline metals, noble metals, reminders of the case of gold . . . 199
5.4 Trivalent metals . . . 202
5.4.1 A chameleon metal: the boron . . . 203
5.4.2 Aluminum . . . 204
5.4.3 Gallium . . . 208
5.5 Transition metals . . . 210
5.5.1 Ferromagnetism: iron, cobalt, nickel . . . 210
5.5.2 A complex transition metal: manganese . . . 210
5.5.3 A simple transition metal: ruthenium . . . 211
5.5.4 Palladium . . . 214
5.5.5 Platinum . . . 214
5.6 Semi-metals or metalloids . . . 215
5.6.1 Antimony: tetraheral units . . . 216
5.7 Heavy elements of column IV . . . 220
5.7.1 Tin . . . 220
5.7.2 Lead . . . 221
5.8 Strongly correlated systems: NiO . . . 222
5.9 Lanthanides . . . 223
5.10 Conclusion . . . 225

6 Dipole and electrical polarizability **227**
6.1 Introduction . . . 227
6.2 Experimental measurements . . . 228
6.2.1 Measurement of the electrical polarizability in the absence of a permanent dipole . . . 229
6.2.2 Measurement of the electric dipole . . . 231
6.2.3 Comparison with magnetic measurements . . . 234
6.3 The case of atoms . . . 235
6.3.1 Reminders . . . 235
6.3.2 Atomic polarizability . . . 235
6.3.3 Results . . . 239
6.3.4 Evolution of the polarizability as a function of R_{at}^3 . . . 239
6.4 Alkaline dimers: ellipsoidal jellium . . . 240
6.5 Metallic clusters . . . 243

6.5.1 Cluster electrical dipole 243
6.5.2 Polarizability 245
6.6 Covalent systems 249
6.6.1 Carbon clusters 249
6.6.2 Silicon clusters 256
6.7 Ionic compounds 259
6.7.1 Small clusters 260
6.7.2 Large clusters 262
6.7.3 Point charge model 263
6.8 Ionocovalent compounds 263
6.9 Conclusion 263
6.10 Appendix 264
6.10.1 Field induced by a dipole 265
6.10.2 Thomas Fermi in a system without interaction 266
6.10.3 Local electron density 268
6.10.4 RPA approximation in the Thomas Fermi model 269
6.10.5 Thomas Fermi in a system with interaction 271

7 Magnetism **273**
7.1 Some definitions 273
7.2 Preamble 273
7.3 Atomic and molecular magnetism 273
7.3.1 Atomic magnetism 273
7.3.2 Measurement of atomic magnetic moments 279
7.4 Magnetism in the dimer 280
7.4.1 Molecular physics approach 280
7.4.2 Heisenberg's effective Hamiltonian 282
7.5 Magnetism in n-mers 286
7.6 Magnetism in solid 286
7.6.1 Origin of ferromagnetism 286
7.6.2 Orbital magnetism 288
7.6.3 Itinerant magnetism: Stoner criterion 289
7.7 Weiss Domains 292
7.8 Magnetism in clusters 293
7.8.1 Measurement of magnetism in clusters 293
7.8.2 Superparamagnetism 298
7.8.3 Very small sizes 299
7.8.4 Intermediate sizes 300
7.8.5 Large sizes: surface effects 304
7.9 Magnetism in clusters: case of non-ferromagnetics 307
7.9.1 Free clusters of paramagnetic systems 307
7.9.2 Supported or clusters with ligands of diamagnetic systems: the case of gold 307

7.10 Magnetic susceptibility of small metal clusters in the framework of the Kubo model . . . 312
7.10.1 Case of bulk metal . . . 312
7.10.2 Case of small monovalent metal clusters . . . 314
7.11 Conclusion . . . 314

8 Heterogeneous catalysis 317
8.1 Introduction . . . 317
8.2 Gas phase catalysis . . . 319
8.3 Heterogeneous catalysis . . . 321
8.3.1 Definition . . . 321
8.3.2 Issue . . . 323
8.3.3 Principle of a laboratory measurement . . . 323
8.4 The 1/R law: a specificity in catalysts . . . 325
8.5 Geometric effect . . . 325
8.5.1 Coordinance in the bulk phase . . . 325
8.5.2 Coordination in large clusters . . . 327
8.6 Substrate effect . . . 329
8.6.1 Large clusters . . . 329
8.6.2 Small clusters . . . 330
8.7 Size effect . . . 331
8.8 Activity and selectivity . . . 333
8.9 Cluster morphology: dynamic aspect . . . 334
8.9.1 Dynamics on the surface . . . 335
8.9.2 Large clusters: thermodynamic aspect . . . 336
8.9.3 Small clusters . . . 338
8.10 New catalysts: gold . . . 340
8.10.1 Large clusters . . . 340
8.10.2 Small clusters . . . 342
8.11 Conclusion . . . 342

Conclusion 345

Annex: *Ab initio* models 347

References 363

Foreword

Clusters: Introduction to the nano world

The nanotechnologies (or nano-world) concern objects of the order of the nanometer (nm) that is to say of the billionth of a meter. In fact, nano-objects have dimensions that vary between a few nm and a few hundred nm. They contain between a few tens of atoms and a few tens or hundreds of thousands of atoms. The spectacular development of nanotechnologies during the last twenty years has introduced into everyday life all sorts of nano-objects or nano-particles used in cosmetics, and lubricants, as well as in the components of the most high-tech objects, medicine, textiles, food, etc. The properties of nano-objects are very different from those of other materials. The remarkable properties of nanoparticles (antioxidant agents for example) have generated their massive use in food and clothing. Public health issues require knowledge of the properties of these nanoparticles to anticipate any health problems. These nano-objects are invading our environment. Their small size gives them particularly interesting properties for all kinds of applications in physics, chemistry, biology, mechanics, etc. Scientists are interested in their properties. The field of nano-objects is becoming more and more vast and one can write a book just on the catalysis of the nanoparticles or their magnet properties, or on their optical properties, another synthesizing and processing them, etc. We have chosen to focus on the basic properties and the understanding of the fundamental aspects of these intermediary nano-objects between the atom and the macroscopic matter. We will limit ourselves in this book to the clusters of N identical atoms with N ranging from a few atoms to a few tens of thousands even if in some cases we will focus on clusters constituted by two types of atoms for example the ionic systems $(NaCl)_N$. The clusters of atoms are part of the nano-objects. They are a little simpler and therefore easier to understand. They are in some way the prototypes of nano-objects.

The physics of atomic aggregates has been developed since the 1970s thanks to the development of sources and in particular laser vaporization sources allowing to produce, in molecular beam, aggregates of almost any atom, particularly of the most refractory metals or materials. These aggregates (clusters) could be studied by laser spectroscopy associated with mass spectrometry, techniques which have also been continuously improved since the 70s. Then

from the 1990s, these clusters produced in a very controlled way could be deposited on surfaces for solid physics-type measurements (electron microscopy, *STM*, X-ray diffraction, etc.) or for applications. At the same time, chemical synthesis methods have been developed and allow the production of ligand-protected clusters (or nanoclusters) in solution. Similarly, the *ab initio* computational methods inspired by the density functional theory (DFT) have greatly benefited from the spectacular improvement of the computing power of computers.

However, even though there are a great number of journal articles and compilations by a great number of authors, there is no textbook with a clear guiding thread which is here to understand how one goes from the properties of the atom to those of condensed matter and how these "intermediate objects" acquire particular properties. It is thus a very multidisciplinary subject. It requires knowledge of basic atomic physics, essentially the properties of the wave functions of the fundamental states from the simplest atoms (alkalis) to the most complex (transition metals, even rare earths). Indeed, the wave function, often complex, of the atoms of the periodic table contains "in germ" all the ingredients that determine the properties of the condensed phase. Similarly, it plays an essential role in the intermediary state that the aggregates constitute. This subject also requires knowledge of solid-state physics and crystallography. Indeed, one can see the clusters as atom by atom building up, which is the "bottom up" point of view, or as a reduction of size from a massive phase, which is the "top down" point of view. Similarly, the notions of chemical bonding are very important. We are really in the field of Physical Chemistry including "Chemical Physics" and "Physical Chemistry" fields. The cluster topic also concerns "*ab initio*" calculations, which are sometimes called "quantum chemistry" in reference to the eminently quantum character of the wave function. To illustrate these multidisciplinary aspects, one can quote the units of energy where one will learn to juggle with the electron Volt, the kilocalories per mole, the cm^{-1}, the Hartree, the Rydberg, the Joule, the Kelvin degree, etc. To assist the reader, a summary of the units and unit systems used will be given at the beginning of the book.

This book is intended for Master's students in Physics or Chemistry who are interested in nano-objects. Indeed, the explosion of nanosciences around the years 2000 and the following, reinforces the need for a book on the basic principles that determine the properties of these aggregates or nanoparticles. It is therefore also intended for researchers and teachers who are embarking on nanosciences or who at some point in their research have to work on this subject. The topic of aggregates remains very vast and we have divided the book into 2 volumes. Volume 1 is dedicated to the cluster properties in the ground state or ambient temperature. Volume 2 will deal with the properties in the excited states and will include, among other things, the influence and role of the temperature. Volume 1 begins with a short introduction, Chapter 2 focuses on the energy of cohesion in the ground state, Chapter 3 concerns the effects of electron and atomic shells especially in the simplest systems,

chapter 4, the transition insulating metal according to the size, chapter 5, the complex metals, chapter 6, the dipole and the polarizability of the bare-clusters, chapter 7, the magnetic properties, and finally chapter 8 the catalysis by the clusters. An appendix will deal with *ab initio* theoretical calculation methods, in particular the density functional theory.

Constants and units

Summary

The physics of aggregates being multidisciplinary, it uses heterogeneous systems of units, in particular for the units of energy as well as the notations of physical quantities. We will define the systems of units and the symbols used in this book which are sometimes not the usual symbols.

The four fundamental constants in the sense of Einstein

By convention, $\hbar = h/2\pi$ is given.

$\hbar = 1.054\,571\,726(47) \times 10^{-34}$ J · s, $\hbar = h/2\pi$ Planck's constant reduced in joules-seconds
$h = 6.626\,070\,040(81) \times 10^{-34}$ J · s, h Planck's constant in joules-secondes
$k_B = 1.38064852(79) \times 10^{-23}$ JK^{-1} Boltzman constant
$c = 2.997\,924\,58 \times 10^{8}$ m · s^{-1}, speed of light in vacuum in meters per second
$G = 6.67408(31) \times 10^{-11}$ m^3.kg^{-1}.s^{-2} gravitational constant which we will not use hereafter.

Physical constants used in the book in SI units

One recalls that the SI system is composed of seven basic units: the meter (m), the kilogram (kg), the second (s), the ampere (A), the kelvin (K), the candela (cd) and the mole (mol).

We pose by convention $e^2 = \frac{q_e^2}{4\pi\epsilon_0}$

$m_e = 9.10938356 \times 10^{-31}$ kg electron rest-mass
$m_p = 1.67262 \times 10^{-27}$ kg proton mass
mass ratio proton/electron: 1836.15267389(17)
Fine structure constant $\alpha = e^2/\hbar c$ $\alpha = 7.297\,352\,5698(24) \times 10^{-3}$ (dimensionless)

$q_e = 1.602\,176\,565(35) \times 10^{-19}\,\mathrm{C}$ or in ampere second A.s atomic unit of charge (elementary electric charge) (C for Coulomb)
Bohr radius (atomic unit of length) is the characteristic length separating the electron from the proton $a_0 = \frac{\hbar^2}{m_e e^2}$
$a_0 = 0.529\,177\,210\,92(17) \times 10^{-10}\,\mathrm{m}$
$\epsilon_0 = 8.854187817 \times 10^{-12}\,\mathrm{Fm}^{-1}$ or in $\mathrm{A}^2.\mathrm{s}^4\mathrm{kg}^{-1}.\mathrm{m}^{-3}$, vacuum dielectric constant (F for Faraday, A for Ampère)
$\mu_0 = 4\pi \times 10^{-7} = 12.566370614 \times 10^{-7}\,\mathrm{kg.m.s}^{-2}.\mathrm{A}^{-2}$, magnetic permeability of vacuum
ϵ_0 et μ_0 are related to the fundamental constant c by the relation $c^2\epsilon_0\mu_0 = 1$
μ_B the Bohr magneton is a physical constant that relates the magnetic moment of the electron to its angular momentum $\mu_B = \frac{q_e\hbar}{2m_e}$
$\mu_B = 927.4009994(57) \times 10^{-26}\,\mathrm{JT}^{-1}$ or $A.m^2$ (T for Tesla)
$G_0 = 7.7480917310(18) \times 10^{-5}\,\mathrm{S}$ or in $\mathrm{m}^{-2}.\mathrm{kg}^{-1}.\mathrm{s}^3.\mathrm{A}^2$ quantum conductance, S for Siemens
$N_A = 6.022140857(74) \times 10^{23}\,\mathrm{mol}^{-1}$Avogadro's number
Infinite Rydberg constant R_∞ is a wavenumber. This is related to an energy constant called the Rydberg energy (constant) R_y corresponding to the ionization energy of a hydrogen system in which the mass of the nucleus is considered infinite, by the relation $Ry = hcR_\infty$ et $R_y = \frac{1}{2}\alpha^2 m_e c^2$ or $R_\infty = \frac{m_e\alpha^2 c}{2h}$.
$R_\infty = 1.0973731568508 \times 10^7\,\mathrm{m}^{-1} = 13.605693009(84)\,\mathrm{eV}$
As a general rule, we use the Rydberg energy (constant) R_H corresponding to the ionization energy of the hydrogen atom. This one is linked to R_{infty} by a corrective term taking into account the mass of the proton $R_H = R_y \frac{1}{1+m_e/m_p}$
$R = 8.3144598(48)\,\mathrm{Jmol}^{-1}\mathrm{K}^{-1}$ molar (ideal) gas constant
$\sigma = 5.670367(13) \times 10^{-8}\,\mathrm{Wm}^{-2}\mathrm{K}^{-4}$ or in $\mathrm{kg.s}^{-3}.\mathrm{K}^{-4}$ Stefan-Boltzmann's constant, W for Watt, K for Kelvin
$g_S = 2,00231930436182$ Landé's factor for the electron
$q_e/m_e = 1.758820024(11) \times 10^{11}\,\mathrm{C/kg}$ electron charge/mass ratio, C for Coulomb
The Debye noted D unit of dipole moment belongs to the *CGS* system and has the value $1D = 3.33564 \times 10^{-30}\,\mathrm{C.m}$

Energy units

Energy definition

The energy E, a fundamental quantity of physics, can be expressed in terms of fundamental constants

$E = m_e c^2 = h\nu = k_B T$ or in reduced units energy expressed in amu (atomic mass unit) or in kg, in Herz (or in m^{-1} more commonly in cm^{-1} by the relation $\nu = c/\lambda$) or in Kelvin. We also have other secondary relations:

$E = q_e V$ (or the electron volt noted eV) and the Joule, energy provided by a power of 1 watt during one second (homogeneous with kinetic energy) as well as the calorie/per mole which involves the Avogadro number used in calorimetry. The energy E, a fundamental quantity of physics, can be expressed in terms of fundamental constants $E = m_e c^2 = h\nu = k_B T$ or in reduced units energy expressed in amu (atomic mass unit) or in kg, in Hertz (or in m^{-1} more commonly in cm^{-1} by the relation $\nu = c/\lambda$) or in Kelvin.

We also sometimes use the system of atomic units defined by
$m_e = 1$, $\hbar = 1$, $e^2 = \frac{q_e^2}{4\pi\epsilon_0} = 1$

We then have $\alpha = \frac{e^2}{\hbar c}$ et $a_0 = \frac{\hbar^2}{m_e e^2} = 1$

The energy $E_h = m_e \alpha^2 c^2 = 1$ is the unit of energy in this system and is called the Hartree. We verify that $E_h = 2R_y$: the Hartree is two Rydbergs.

Conversion of energy units

The various tables give the correspondences for the energy units (CODATA reference 2014 [Mohr *et al.* (2008); Tiesinga *et al.* (2021)]). The conversions in bold type are the most frequently used.

1amu =	1eV =
$\mathbf{1.660539040(20) \times 10^{-27} kg}$	$1.0735441105(66) \times 10^{-9}$amu
$1.08095438(62) \times 10^{13}$K	$3.674932248(23) \times 10^{-2} E_h$
$2.2523427206(10) \times 10^{23}$Hz	$2.417989262(15) \times 10^{14}$Hz
$1.492418062(18) \times 10^{-10}$J	$8.065544005(50) \times 10^{5} m^{-1}$
	$= \mathbf{8065.544005(50) cm^{-1}}$
$3.4231776902(16) \times 10^{7} E_h$	$\mathbf{1.6021766208(98) \times 10^{-19} J}$
$931.4940954(57) \times 10^{6}$eV	$1.16045221(67) \times 10^{4}$K
$7.5130066166(34) \times 10^{14} \mathrm{m}^{-1}$	$1.782661907(11) \times 10^{-36}$kg

1Hartree =	1Herz =
$2.9212623197(13) \times 10^{-8}$amu	$4.4398216616(20) \times 10^{-24}$amu
27.211 386 02(17) eV	$4.4398216616(20) \times 10^{-24}$amu
$6.579683920711(39) \times 10^{15}$Hz	$4.135667662(25) \times 10^{-15}$eV
$2.194746313702(13) \times 10^{7} \mathrm{m}^{-1}$	$3.335640951 \times 10^{-9} \mathrm{m}^{-1}$
$4.359744650(54) \times 10^{-18}$J	$6.626070040(81) \times 10^{-34}$J
$3.1577513(18) \times 10^{5}$K	$4.7992447(28) \times 10^{-11}$K
$4.850870129(60) \times 10^{-35}$kg	$7.372497201(91) \times 10^{-51}$kg

1Joule =	1Kelvin =
$6.700535363(82) \times 10^{9}$amu	$9.2510842(53)x10^{-14}$amu
$6.241509126(38) \times 10^{18}$eV	$\mathbf{8.6173303(50)x10^{-5}}$eV
$2.293712317(28) \times 10^{17} E_h$	$3.1668105(18)x10^{-6} E_h$
$1.509190205(19) \times 10^{33}$Hz	$2.0836612(12)x10^{10}$Hz

$5.034116651(62) \times 10^{24}\mathrm{m}^{-1}$	$69.503457(40)\mathrm{m}^{-1}$
$7.2429731(42) \times 10^{22}\mathrm{K}$	$1.38064852(79) \times 10^{-23}\mathrm{J}$
$\mathbf{1.112650056 \times 10^{-17}}\mathrm{kg}$	$1.53617865(88) \times 10^{-40}\mathrm{kg}$

1Kg =	$1\mathrm{m}^{-1}$ =
$\mathbf{6.022140857(74) \times 10^{26}}\mathrm{amu}$	$1.33102504900(61) \times 10^{-15}\mathrm{amu}$
$5.609588650(34) \times 10^{35}\mathrm{eV}$	$\mathbf{1.2398419739(76) \times 10^{-6}}\mathrm{eV}$
$2.061485823(25) \times 10^{34} E_h$	$4.556335252767(27) \times 10^{-8} E_h$
$1.356392512(17) \times 10^{50}\mathrm{Hz}$	299792458Hz
$4.524438411(56) \times 10^{41}\mathrm{m}^{-1}$	$1.986445824(24) \times 10^{-25}\mathrm{J}$
$8.987551787 \times 10^{16}\mathrm{J}$	$1.43877736(83) \times 10^{-2}\mathrm{K}$
$6.5096595(37) \times 10^{39}\mathrm{K}$	$2.210219057(27) \times 10^{-42}\mathrm{kg}$

other units
1cal=$2.6131952590564 \times 10^{+19}$ eV
1eV=$3.8267327959301 \times 10^{-20}$ cal
1eV=23.060 9 kcal/mole used in calorimetry
1 kcal/mole=0.043 363 4 eV
1 kcal/mole=349.757 cm^{-1}
1 kcal/mole= 4.18400 kJ/mole
1 kcal/mole=503.228 K
1 kcal/mole=$1.048\,54 \times 10^{+13}$Hz

Electrostatic/magnetism analogy

The physics of aggregates being multidisciplinary, it uses heterogeneous systems of units, in particular for the units of energy as well as the notations of physical quantities. We will define the systems of units and the symbols used in this book which are sometimes not the usual symbols.

The total electrostatic dipole moment noted μ_{dip} is written

$$\boldsymbol{\mu_{dip}} = \int_V \rho(\boldsymbol{r}) \boldsymbol{r} d^3 r \tag{1}$$

$\rho(r)$ is the density of charges including all the electrons and nuclei, at a position r in the aggregate, the sum being done on the whole volume. For the magnetic dipole, by analogy with electrostatics (although the point magnetic charges are fictitious, the calculation remains correct), one can write an analogous relation knowing that the magnetic moment is a vector quantity

$$\boldsymbol{\mu_{eff}} = \frac{1}{2c} \int_V \boldsymbol{r} \times J(\boldsymbol{r}) d^3 r \tag{2}$$

J is the current density

Chapter 1

Introduction

1.1 Cluster physics: a young science

It is very important to first define the objects of interest and their dimensions. Atomic or molecular clusters are sets of few units to few tens of thousands of atoms or small molecules. From the dimensional point of view, the cluster is situated in the current terminology between the atom and the nanoparticle: atom (10^{-10}m)→ molecule (10^{-9}m)→ cluster ($10^{-9} - 10^{-8}$m)→ nanoparticle (10^{-8}m)→ colloid ($10^{-8} - 10^{-6}$m)→ solid. There is often an overlap between the term aggregate or cluster and the term nanoparticle, but a nanoparticle is generally larger by a factor of about 10. In this book, we will mainly focus on clusters of atoms, except in the case of ionic clusters or in the case of mixed clusters made of two atoms, such as silicon and carbon or gold and silver. The cluster physics, which can be called "Physics of Divided Matter" is to be compared with atomic and molecular physics on the one hand and condensed matter physics on the other. It is a question of understanding how we go from the properties of the atom to those of the solid. It is sometimes said that the cluster properties can change if the number of atoms changes by a single unit, that is to say, that this is the domain where "every atom counts". And we will see that this is often verified ...

The science of clusters is relatively young because until recently we did not know how to produce clusters with a well-controlled number of atoms. It is from the 1980s, that we could produce these bare clusters in molecular jets, thanks to the laser vaporization sources developed first by RE. Smalley from 1981 [Dietz *et al.* (1981)]. At the same time, chemists have been able to control more precisely the clusters protected by ligands in the liquid phase. On small systems, one can reach atomic precision as for $Au_{25}(SG)_{18}$ for example (SG acronym of the ligand, glutathiol). Of course, for such small sizes, ligands play an important role in the properties and must be taken into account. However, nanoparticles in the liquid phase have played an essential role in the understanding of optical properties. Moreover, research on clusters has benefited not only from synthetic methods but also from optical spectroscopy and mass spectrometry methods. Finally, for the clusters deposited on surfaces,

the improvement of electron microscopes played an important role, and especially the discovery of the tunneling microscope by Binning and Rohrer in 1982 allowed not only to observe these particles in comfortable conditions (in the air) but also to manipulate them as attested by the famous figure of the IBM logo obtained by Don Eigler of the IBM laboratory with xenon atoms or the writing of "NIST" with *73* cobalt atoms (figure 1.1).

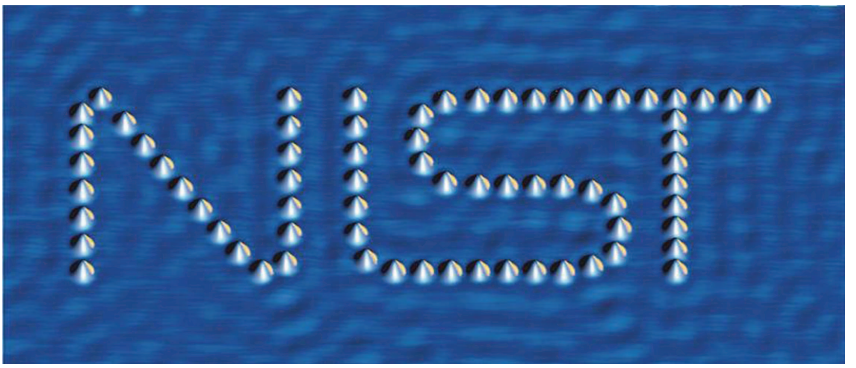


FIG. 1.1 – Image obtained by very low-temperature manipulation of 73 cobalt atoms to write the "NIST" logo [Celotta *et al.* (2014)]. Reprinted by permission from AIP Publishing, Review of Scientific Instruments, COPYRIGHT 2014.

The study of clusters is in essence multidisciplinary because it lies at the crossroads of several disciplines, atomic and molecular physics, chemistry, solid state physics, and nuclear physics from which it borrows a number of concepts (notably the liquid drop model and the so-called "shell" structure). It is difficult to know when this discipline was born but it was popularized by the famous sentence pronounced by Richard Feynman in 1959 during a conference of the American Chemical Society "there is plenty of room at the bottom". This sentence translates the fact that the border between the properties of the atom and the solid was far enough to imagine an intermediate world, a noman's land, populated by giant molecules, "clusters" with surprising and unknown properties at the time. These properties, of which we will give some examples in a non-exhaustive way in the introduction, will be taken up and studied later. They are sufficiently important to justify downstream research called "nanotechnology" which since the end of the 1990s has spread to all disciplines including physics, chemistry, biology, and medicine.

It is difficult to know the first effects of size observed, the name given to these specific properties, studied in the literature. We can quote the work of Takagi [Takagi (1954)] who as early as 1954 highlighted the dependence in $1/R$ of the melting temperature of small particles and this by validating a theoretical prediction given by Pawlow in 1909 [Pawlow (1909)]. We can therefore start cluster physics in the 50s. It was also known that small particles of the platinum group should be used for heterogeneous catalysis. However, it was difficult to control the size of these small particles.

1.2 Size effect, role of the surface

1.2.1 Geometrical consideration

The most trivial phenomenon in a cluster of N atoms is that the number of atoms on the surface is large compared to the number of atoms in the volume especially when compared to a bulk material. It is expected that some properties depend on the ratio between the number of atoms on the surface and the total number of atoms. We can easily estimate this ratio. We call r_s the average radius occupied by an atom. It is defined by the relation:

$$V = \frac{4}{3}\pi R^3 = \frac{4}{3}\pi r_s^3 N \tag{1.1}$$

We deduce that $R = r_s N^{1/3}$. If N_s is the number of atoms on the surface, then the surface S is $S = N_s \pi r_s^2 = 4\pi R^2$, this is valid if the aggregate is big enough and has a structure close to the sphere. We deduce that $N_s = 4N^{2/3}$ and the ratio is (figure 1.2):

$$\frac{N_s}{N} = \frac{4}{N^{1/3}} = 4\frac{r_s}{R} \tag{1.2}$$

We thus obtain a dependence in *1/R*. Figure 1.2 shows this dependence compared to reality for an icosahedral structure that we will discuss in the following. The dependence in *1/R* is quite well verified for clusters beyond a hundred atoms for compact structures like icosahedra. Indeed the above formula gives $N_s/N > 1$ if N>64, which is obviously absurd. It is easy to understand that this ratio tends towards 1 for small N because as soon as the number of atoms is lower or of the order of *10*, all the atoms are on the surface. We will see

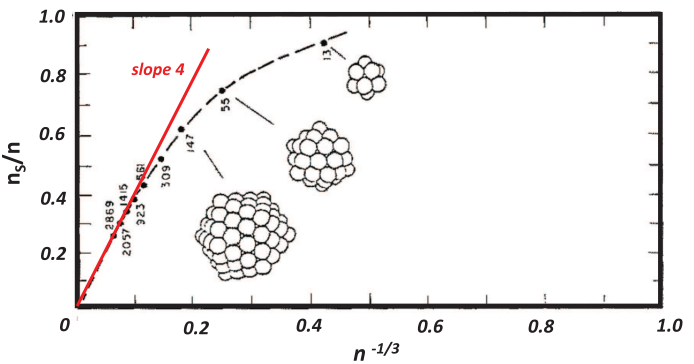


FIG. 1.2 – Surface-to-volume ratio in *1/R* for assumed spherical clusters (asymptote of slope 4) and icosahedral clusters. [Jortner (1992)]. In the original figure, n is the total number of atoms and $n^{-1/3}$ is proportional to *1/R*, n_s is the number of atoms on the surface.

later that the dependence in *1/R* plays an important role even if it can sometimes be fortuitous. It is even sometimes observed while the notion of surface cannot be defined, for example for $N<10$, $N_s/N = 1$ whatever N is, and yet the law in *1/R* can still be applied by extending the definition of R by the relation $R = r_s N^{1/3}$. We can consider this law in *1/R* as a scaling factor. The interesting properties will be those which deviate from this general law in *1/R*.

1.2.2 Generalization

The size effects obey a universality class. To any particle, we can associate a wavelength. Let us take an example, the interaction of a photon and a cluster. In a massive solid, the wavelength of the photon is very small compared to the characteristic length of the solid (its dimension). In a cluster of small size, this is not the case. In all generality and by using the general law used in statistical physics one will write that a physical phenomenon X can develop

$$X = \left(\frac{X_{bulk}}{1 + \frac{\xi(R)}{2R}} \right)^{1/2S} = X_{bulk} \left(1 - \frac{\xi(R)}{2R} + \frac{\xi(R)}{4R^2}^2 - \dots \right)^{1/2S} \tag{1.3}$$

with $S=1/2$ for a Fermionic system, ξ is a characteristic length called correlation length, the dependence in *1/R* appears at the first order development by admitting that the characteristic length does not depend itself on R.

1.3 Kubo conductivity criterion for metallic clusters

Materials are generally classified into three categories, conductors (no gap), semiconductors (band gap less than *2* eV), and insulators (band gap greater than *2* eV). For metals, we know that the metal bond is characterized by the delocalization of electrons. In the solid, we can consider in first approximation that the electrons are free and confined in the volume of the solid. We use the Fermi-Dirac statistics and the electrons populate the levels below the Fermi level E_F. The density of states in a parallelepiped is then given by:

$$\rho(E) = VAE^{1/2} \tag{1.4}$$

V is the volume of the cluster and A a constant $A = \frac{1}{2\pi^2}(\frac{2m_e}{\hbar^2})^{3/2}$, m_e being the mass of the electron

We can assume at this point that there is no degeneracy other than the 2-degeneracy due to the electron spin. This assumes that the clusters are deformed with respect to a sphere and this is generally the case for clusters deposited on a support. Then the average δ gap at the Fermi level E_F between the energy levels is:

$$\delta = \frac{4E_F}{3N} \tag{1.5}$$

E_F is given by $E_F = 3/2(N/VA)^{2/3}$ and in this model, E_F is independent of N because the volume is proportional to N, $V = (4/3)\pi r_s^3 N = (4/3)\pi R^3$. We can notice that E_F varies in $1/r_s^2$. E_F is of the order of a few eV (3.24 eV for sodium, *5.49* eV for silver). For a macroscopic piece of metal, N is of the order of Avogadro's number and the gap between the energy levels is totally negligible as compared to k_BT (k_B Boltzmann constant, T the temperature). We say that there is no energy gap. In a cluster, we immediately notice that as soon as the number of atoms is lower than *100*, the gap between the energy levels becomes of the order of k_BT. This is the Kubo's criterion [Kubo (1962)]:

If $\delta > k_BT$, then the cluster becomes semiconducting. For sodium clusters of *100* atoms at room temperature ($k_BT = 0.025$ eV), the Kubo's criterion is largely in favor of a semiconductor because $\delta = 0.04$ eV. If we take into account the degeneracies which depend on the geometry of the cluster, the gap is even higher.

However, everything depends on which properties we are interested in. With respect to the gap between the energy levels, small clusters are clearly "semiconducting". This is why these small clusters like Ag_8 or the small gold clusters [Zheng *et al.* (2012)] fluoresce. But if we are interested in the bond between atoms, the electrons remain delocalized in the first approximation. We say that the bond remains metallic. We can therefore always use to some extent the approximation of free electrons in a box, more precisely a sphere. This will give fruitful images (physical interpretations) as we will see in chapter 3 for the effects of electronic shells. We will find these collective effects even at small sizes for the optical properties in small clusters. Of course for optics, in small systems, the geometry will also play an important role as we will see later.

1.4 Examples of some of the more specific remarkable size effects

In paragraphs 1.2 and 1.3, we have described phenomena that obey laws of scale. But cluster physics also shows remarkable properties and some "surprises". In this paragraph, we will just evoke them in a non-exhaustive way because these effects will be treated in detail in the following chapters.

1.4.1 The discovery of carbon fullerenes

Carbon is known to exist in two forms in its condensed phase, graphite, and diamond, graphite being the more stable form and diamond metastable. This element is known to give different types of covalent bonds related to *sp*, sp^2, sp^3 hybridizations depending on the position of its neighbors. One could say that carbon "plays" with its neighbors, *sp* for 2 neighbors (linear form), sp^2 (graphite) for 3, and sp^3 (diamond) for 4. What happens when we have a very small number of atoms. *A priori*, each time we add an atom the structure changes because we have to take into account the external atoms. In 1991,

R.E. Smalley and his collaborators discovered a new class of molecules, the fullerenes of carbon, which are cage molecules made up of pentagons and hexagons, the most famous and the most stable is the C_{60} made up of *12* pentagons and *20* hexagons. The C_{60} will then be synthesized in a condensed phase, as well as other fullerenes. We will come back to these structures in chapter 2 and to the type of bonding, but it is interesting to note that these cage structures had been predicted by crystallographers as early as 1970 [Hoard *et al.* (1970); Jemmis and Jayasree (2003)], (see figure 1.3). However it was still necessary to observe and synthesize them for carbon.

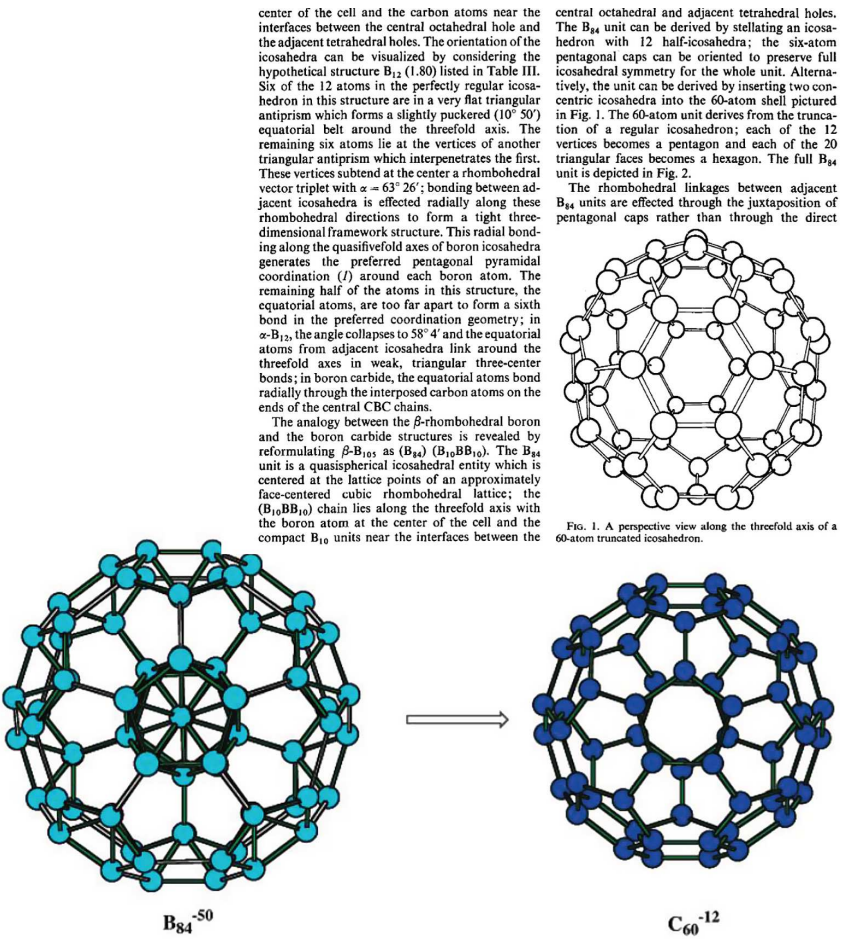


FIG. 1.3 – Facsimile of part of a 1970 publication by Hoard *et al* [Hoard *et al.* (1970)] showing the analogy between the B_{84} element constituting boron in the rhombohedral phase and the 60-atom structure that can exist in carbon. The $B_{84} \rightarrow C_{60}$ transformation is shown in the bottom figure (from the original figure by Jemmis and collaborators [Jemmis and Jayasree (2003)].

Moreover, the discovery of C_{60} stimulated research on carbon nanostructures. Nanotubes, then graphene were discovered and synthesized. There was a Nobel Prize in Chemistry for C_{60} and a Nobel Prize in Physics for graphene (2010).

1.4.2 Metal insulator transition in clusters of specific systems

The atoms of divalent metals have an external electronic shell s^2, it is a complete shell that leads in principle to a complete s-band in the solid. However, these metals are excellent conductors. This is due to the fact that in the solid the empty p-band (excited state) mixes with the s-band, resulting in a non-complete sp-band in the solid, thus a conductor (figure 1.4). If we go back to the small clusters, the dimer has a bond mainly of Van der Waals type. The case of mercury, whose atom has the highest gap, has been well documented [Brechignac *et al.* (1988); Busani *et al.* (1998)].

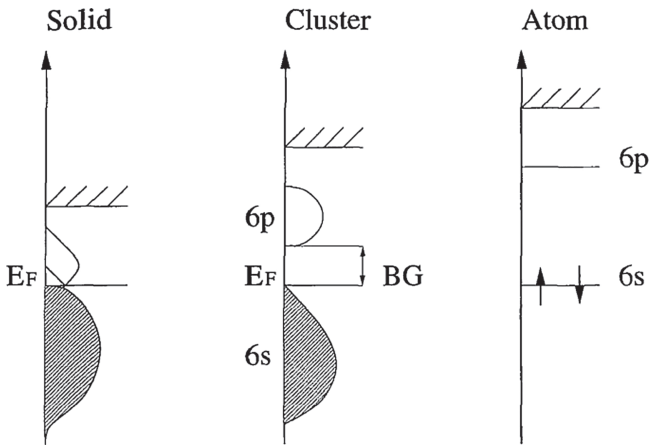


FIG. 1.4 – Transition from atom to solid in mercury with the formation of the *sp* band.

This effect was observed in a spectacular way in mercury and one can see the s-band and the p-band approaching progressively and then joining at about 400 atoms [Busani *et al.* (1998)]. One thus observes a progressive metal-insulator transition. We will return to these metals in the following.

Conversely, silicon, which is a semiconductor, becomes "metallic" below a certain size by a change of crystallographic structure [Sattler and Nalwa (2002)], *i.e.* greater compactness and a greater number of neighbors (higher than 4) in the small clusters (see chapter 2). This number of neighbors is clearly greater than *4*. This means that there is no energy gap in the small clusters of silicon as in the macroscopic phase. But as they are small systems there can

still be significant energy gaps. We can also compare this phenomenon with the metallic phase of silicon at high pressure, thus more compact.

1.4.3 Magnetism

Any student of physics learns that only three simple elements are ferromagnetic at room temperature in the macroscopic phase: iron, cobalt, and nickel (to which one could add gadolinium which has a Curie temperature of *292* K). This is explained by Stoner's theory of itinerant magnetism which takes into account the high electron density and a high exchange integral. However, by reducing the size, ferromagnetism can appear on other metals, and this is at room temperature because the Curie temperature depends on the size. The most surprising case is that of gold, a noble metal reputed to have no ferromagnetism in the solid. In the case of free clusters, the theory predicts ferromagnetism in small gold clusters, which nevertheless, as shown in figure 1.5, remains very weak compared to that of iron (see chapter 7). This ferromagnetism of gold is observed experimentally in small gold clusters encapsulated in a polymer matrix [Luo *et al.* (2007)].

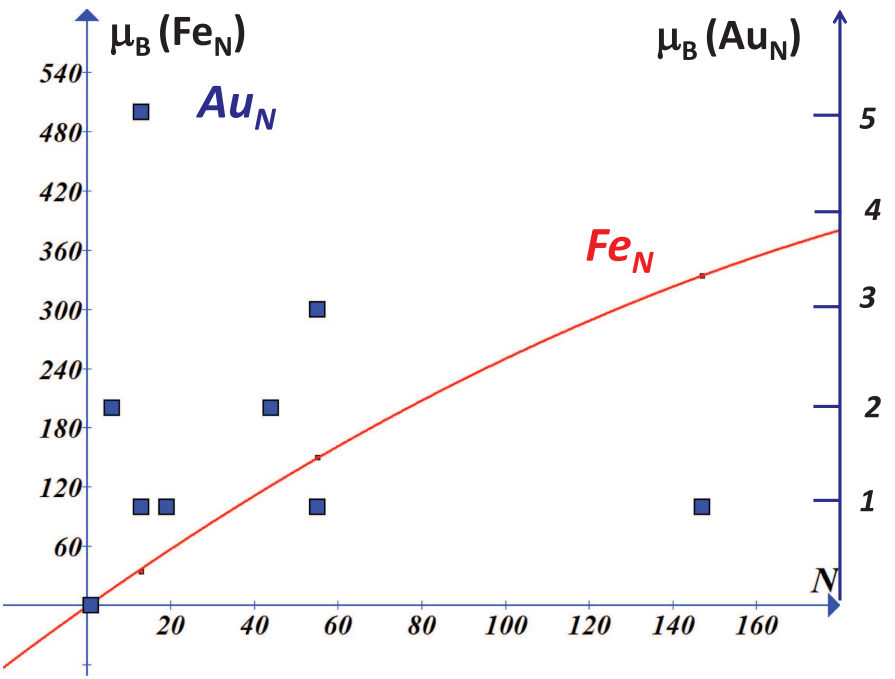


FIG. 1.5 – Calculated values of the total magnetic moment expressed in Bohr magnetons for iron Fe_N clusters [R. Singh and P. Kroll (2008)] and gold Au_N clusters [Luo *et al.* (2007)]. Contrary to iron the total magnetic moment does not increase with the number of atoms but depends strongly on the symmetry of the particle. Its origin is very different from that of iron.

1.4.4 Heterogeneous catalysis

A heterogeneous catalyst is a piece of material that drastically increases the rate of a chemical reaction without being changed at the end. The catalyst is said to undergo a cycle of chemical reactions at the end of which the desired reaction has taken place and the catalyst has returned to its initial state. This makes it possible to start again and to recycle the catalyst continuously. In fact, it is the surface of this catalyst that is important because the reactants get trapped there. It is therefore necessary that the catalyst has the maximum surface area to present to the reacting gases. From this point of view, "divided matter", nanoparticles, and clusters, are essential for heterogeneous catalysis and this has been known for a long time. For monoatomic elements, the science of clusters will allow us to understand classical catalysts like the elements of the platinum group: Ru, Rh, Pd, Re, Ir, Pt. On the other hand, noble metals, and particularly gold have a low reactivity (in popular imagery, gold is unalterable). For gold clusters, it is not the same. Japanese chemist Haruta [Haruta (1997)] showed 1997 that supported gold clusters catalyze the oxygen oxidation of carbon monoxide. This catalytic activity takes place specifically on the corners and edges of the nanoparticles and is dependent on the support. For small clusters free of any support, *CO* oxidation was also predicted and observed.

1.5 Small disgression on the law in 1/R

As we introduced in 1.2, the main size effect follows a law in 1/R. The meaning of R is not as trivial as it seems. In many books, one will find (we will also use it abusively hereafter) the notion of the surface over volume (*i.e. 1/R* for a sphere). *A priori* this property would seem to indicate that the relevant criterion is the ratio between the number of atoms on the surface and the number of atoms in volume. This is true for very large sizes ($> 20\,\text{nm}$) when this ratio is negligible but absurd for small sizes for two reasons

- The surface-to-volume ratio means the ratio of the number of surface atoms to the total number of atoms which integrates not only the volume atoms but also the surface atoms, why recount the surface atoms?
- In a compact system (Kepler's theorem) one must have at least *13* atoms to introduce a volume atom, that is to say, an atom in volume surrounded by *12* neighbors on the surface.

As we will see later, the law in *1/R*, if we neglect the magic numbers, is valid for sizes as small as ... the dimer! (see for example the ionization potential). In this case, where is the surface, where is the volume?

Although this discussion seems sterile, it is to be noted that the ratio *1/R* does not correpond to the notion of surface and volume but the notion of "ball" in the sense of topology (in Euclidean space the ball is the volume bounded by a two-dimensional spherical shell). Thus, the electronic cloud around a dimer can be assimilated to a ball of radius R, R being the "cut off" of the extension of

the electronic cloud. Even if in common language we can speak of surface and volume, it is the symmetry breaking in space at the cluster/vacuum interface that defines the *1/R* property. It is therefore not surprising that the law in 1/R is universal and this is for sizes much smaller than *N=13* atoms. In other words, the radius of a cluster is defined by the size of the global electronic cloud. It is in this spirit that the radius of an atom is defined.

1.6 Conclusion

The list of effects is not exhaustive, but it shows the richness of the field, which goes far beyond the expected scale effects. As some speakers said at the first conferences on the field in the 80's or 90's, "Small is different" as well "Small is beautiful" And it is indeed the case. We will illustrate this in the following by describing recently discovered properties of clusters. In volume 1 we will focus on clusters in the ground state, *i.e.* at relatively low temperature, typically near room temperature. This means that in this part, the coupling with phonons will hardly be discussed. In volume 2, we will describe the thermal effects. The energy of phonons being low compared to the cohesion energy, we will talk about a cluster in a weakly excited state. We will study the influence of the temperature and we will have to revisiting the thermodynamic and statistical models because the approximation of large numbers is not valid anymore. In particular, we will be interested in changes of state such as melting and we will see that for such small systems, it is difficult to define the temperature and the thermometer that measures it. The rest of this book will be devoted to excited states in the range of a few eV, interaction with light, optical properties, collective excitations of the surface plasmon type, then fragmentation or Coulombic explosion in highly excited states, and finally electronic dynamics at different time scales.

Chapter 2

Cohesion of a cluster: origin, chemical bond

2.1 Introduction

The binding energy of a cluster is the simplest parameter to calculate because this quantity involves only the fundamental state. It is therefore the parameter that can be calculated with the greatest accuracy. In this chapter, we will deal with different types of bonds, metallic, covalent, ionic, and van der Waals. Concerning the metallic bond, it is well known in solid-state physics that it is the most complex bond to describe since it is essentially quantum in nature (it involves, among other things, the energy of the Fermi gas of electrons). Starting from the observation of several experimental mass spectra showing cluster distributions or relative intensities of cluster populations as a function of their size, it is clear that metallic clusters have different properties from those of the bulk phase. We recall that in the bulk phase, the cohesive energy is defined at zero temperature as the energy necessary to break all the bonds, *i.e.* the energy required to transform the solid into a perfect gas where all the atoms are without interaction. This same definition will be used for clusters.

The metallic bond is treated here in the simplest model corresponding to the delocalization of the s-electrons. For all these models we assume that the temperature is zero, so $k_B T = 0$. Consequently, free energy and enthalpy will be confused. It will be the same for the other types of bonds

2.2 Cohesion of a metallic cluster: case of simple metals

The simple metals are the alkaline and alkaline-earth metals where the bond is due to the s-electrons. It also concerns in first approximation the noble metals, copper, silver, and gold.

2.2.1 Hamiltonian and cohesive energy in a simple metal

The metal bond is purely quantum and arises from the optimal overlap of valence electron orbitals (figure 2.1). In a simple metal with a spherical valence electron orbital, the maximum overlap will occur for a well-defined crystal structure where the overlap is maximal. It can be shown in topology [Bambah (1954)] that in the 3D Euclidean space the maximal covering is of the centered cubic type although the maximal compactness is in its dual structure *i.e.* face-centered cubic (Kepler conjecture proved by Hales [Hales (2005)]). All the alkaline metals in normal conditions are cubic-centered.

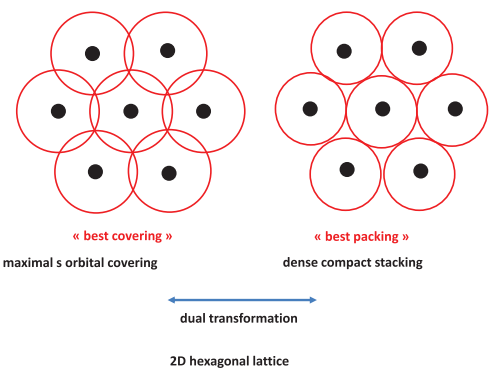


FIG. 2.1 – Covering the plane by circles, comparison between optimal covering and the most compact stacking. In a *2D* network, the most compact stacking is the hexagonal structure.

Let us write the Hamiltonian in a crystal of N metallic atoms of valence Z in the Born Oppenheimer approximation (the nuclei are fixed in space)

$$H = \sum_{i=1}^{N} \frac{-\hbar^2 \nabla_i^2}{2m_e} - \sum_{i,j} \frac{Z_i e^2}{|r_i - R_j|} + \frac{1}{2} \sum_{i,j \neq i} \frac{e^2}{|r_i - r_j|} + \frac{1}{2} \sum_{i,j \neq i} \frac{Z_i Z_j e^2}{|R_i - R_j|} \quad (2.1)$$

$$H = E_c + U^{en} + U^{ee} + U^{nn} \quad (2.2)$$

$e^2 = q_e^2/4\pi\epsilon_0$, E_c is the kinetic energy of the electrons, U^{en} is the total Coulombic interaction, U^{nn} the nuclear repulsion, U^{ee} is the Coulombic repulsion between electrons. It is not possible to solve formally equation 2.1 because the term U^{ee} does not permit the calculation of the eigenfunctions of H. Among all the approximations of quantum models, the theory of the density functional [Kohn (1999)] occupies a central place to compute the cohesive energy of a system in an *ab initio* scheme (without any prerequisite parameters).

2.2.2 Jellium model

The Jellium model called the uniform electron gas model (or homogeneous) consists in treating the problem of a gas of electrons distributed in a sphere

positively and uniformly charged, of volume Ω, called "background". The Hamiltonian is written

$$\hat{H} = \hat{H}_{\text{el}} + \hat{H}_{\text{back}} + \hat{H}_{\text{el-back}} \tag{2.3}$$

Where the first term decomposes into two parts: the kinetic energy of the electron gas and the electron-electron repulsion, respectively.

$$\hat{H}_{\text{el}} = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i<j}^{N} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \tag{2.4}$$

The second term designates the interaction of the "background" of positive charges with themselves

$$\hat{H}_{\text{back}} = \frac{e^2}{2} \int_{\Omega} \mathrm{d}\mathbf{R} \int_{\Omega} \mathrm{d}\mathbf{R}' \, \frac{n(\mathbf{R})n(\mathbf{R}')}{|\mathbf{R} - \mathbf{R}'|} = \frac{e^2}{2} \left(\frac{N}{\Omega}\right)^2 \int_{\Omega} \mathrm{d}\mathbf{R} \int_{\Omega} \mathrm{d}\mathbf{R}' \, \frac{1}{|\mathbf{R} - \mathbf{R}'|} \tag{2.5}$$

The last term designates the electron-"background" interaction of positive charge

$$\hat{H}_{\text{el-back}} = \int_{\Omega} \mathrm{d}\mathbf{r} \int_{\Omega} \mathrm{d}\mathbf{R} \, \frac{\rho(\mathbf{r})n(\mathbf{R})}{|\mathbf{r} - \mathbf{R}|} = -e^2 \frac{N}{\Omega} \sum_{i=1}^{N} \int_{\Omega} \mathrm{d}\mathbf{R} \, \frac{1}{|\mathbf{r}_i - \mathbf{R}|} \tag{2.6}$$

For a simple metal in the free electron approximation (the electrons do not interact with each other), we obtain the kinetic energy E_c by applying the Fermi-Dirac statistics, E_F being the Fermi level energy

$$E_c/N = \frac{3}{5} E_F = \frac{1.1050\hbar^2}{m r_s^2} \tag{2.7}$$

that we can express in Rydberg

$$E_c/N = \frac{2.21}{(r_s/a_0)^2} \tag{2.8}$$

$a_0 = \frac{\hbar^2}{m_e e^2} = 0.529$ Å is the Bohr radius, the energy is expressed in Rydberg (1Ryd=13.6 eV), r_s is the Wigner Seitz radius, *i.e.* the radius of the sphere occupied by an atom 'on average')

$$H = \sum_{i=1}^{N} \frac{-\hbar^2 \bigtriangledown_i^2}{2m} = \frac{\hbar^2 k^2}{2m} = E_c \tag{2.9}$$

The free electron model consists of retaining only the first term of equation 2.3. We can improve the free electron model. For that, we consider that the nuclei form a positive homogeneous jellium (the "background"). In the framework of the Hartree-Fock approximation, we can take into account the exchange term

[Kohn (1999)] due to the antisymmetric character of the wave function. This amounts to adding in the jellium model the exchange term U_{exc} (in Rydberg units) which is written

$$U_{exc}/N = -\frac{0.4582e^2}{r_s} = -\frac{0.916}{(r_s/a_0)} \tag{2.10}$$

One will thus have in the model of Jellium with correction Hartree-Fock (One will find the demonstration in the reference [Neil W. Ashcroft (1976)]).

$$E_{c,HF}/N = \frac{2.21}{(r_s/a_0)^2} - \frac{0.916}{(r_s/a_0)} \tag{2.11}$$

There remains the correlation term E_{corr} which cannot be computed formally. The simplest analytical form is given by Wigner [Wigner (1938)] within the case of large values of r_s the asymptotic form

$$E_{corr,W}/N = -\frac{0.865}{(r_s/a_0) + 14.75} \tag{2.12}$$

These corrective terms of the free electron model will play an important role later for the ionic bond for example.

2.2.3 Macroscopic approach: liquid drop model

2.2.3.1 Cohesive energy

As we have seen in the introduction if we assume at the first approximation that the particle is spherical, the properties of low-dimensional objects are related to the radius of curvature , it is the liquid drop model. This model is used in nuclear physics to explain the mass of atomic nuclei and is originally known as the model of Gamow and Weizsacker [Weizsäcker (1935)]. It does not take into account the existence of facets whose presence is inherent to the crystallographic structure of the cluster. We use a macroscopic approach inspired by solid-state physics. In this model of the spherical liquid drop the cohesive energy is written as a volume term minus the excess surface free energy. This energy is the product of the surface tension γ by the surface S (we remind that there is only one component)

$$E_{cluster} = E_{bulk} - S\gamma \tag{2.13}$$

E_{bulk} is the total cohesive energy in a bulk phase. Let r_s be the Wigner-Seitz radius of the atom ($v_0 = 4/3\pi r_s^3$), the surface S is written

$$S = N^{2/3} 4\pi r_s^2 \tag{2.14}$$

where N is the number of atoms. By normalizing, we deduce the energy per atom

$$E_{cluster}/N = E_{coh} - \frac{4\pi r_s^2 \gamma}{N^{1/3}} \tag{2.15}$$

TAB. 2.1 – Cohesive energy per atom and surface energy for some elements according to theoretical calculations of Perdew and collaborators [Perdew *et al.* (1990)].

element	$\pi r_s^2 \gamma$	$E_{coh,theo}$	$4\pi r_s^2 \gamma / E_{coh}$
Li	1.21	1.63	0.74
Na	0.89	1.11	0.80
K	0.75	0.93	0.81
Rb	0.69	0.85	0.81
Cs	0.66	0.80	0.83
Cu	2.80	3.49	0.88
Ag	2.50	2.95	0.85
Au	3.00	3.81	0.79

E_{coh} is the cohesive energy per atom in the solid ($E_{coh} = E_{solid}/N$). Knowing that

$$N = \frac{d^3}{(2r_s)^3} \tag{2.16}$$

d is the diameter of the liquid drop (d=*2R*) we can also write R^3/r_s^3. We finally have the relation

$$E_{cluster}/N = E_{coh} - \frac{4\pi r_s^3 \gamma}{R} \tag{2.17}$$

This means that the energy of a cluster per atom (relation 2.17) varies in *1/R*. We will now estimate the "surface" term $4\pi r_s^2 \gamma$ which implies the knowledge of γ. For this, it is wise to know the ratio between the surface term $4\pi r_s^2 \gamma$ and the volume term E_{coh}. As said before (equations 2.7 and 2.10) the cohesive energy in the Jellium model is written

$$E_{coh} = \frac{1.1050\hbar^2}{m_e r_s^2} - \frac{0.4582e^2}{r_s} + E_{corr} \tag{2.18}$$

Table 2.1 gives some theoretical values of E_{coh} and $4\pi r_s^2 \gamma$ calculated by Perdew within the jellium model [Perdew *et al.* (1990)] (see paragraph 2.2.4)

We see that the term $4\pi r_s^2 \gamma / E_{coh}$ is on average equal to *0.82*. We thus obtain the empirical formula. In the same way, we see that the surface energy "destabilizes" the system, its contribution being negative. As we will see later, the cluster will try to minimize the surface energy when this is possible, hence a particular form of equilibrium. In this case, there are no facets (sphere model) and the surface energy is an average value.

$$E_{cluster}/N = E_{coh}(1 - 0.82N^{-1/3}) \tag{2.19}$$

We can define a dimensionless parameter E_{norm} which traduces the ratio of the energy of the liquid drop to the energy in a bulk phase

$$E_{norm} = E_{cluster}/E_{bulk} \tag{2.20}$$

TAB. 2.2 – Experimental cohesive energies per atom for sodium clusters compared to the liquid drop model. The value *N=94* is extrapolated from the reference [Borggreen *et al.* (1999)], the value *N*=15 corresponds to an extrapolated value of the reference [Bréchignac *et al.* (1989)], *A (eV)* experimental value, *B(eV)* liquid drop model, *C (eV) TBSMA* model (see text). For the *TBSMA* and liquid drop models the reference is fixed by the value in the bulk solid.

N	$E_{cluster}$A (eV)	$E_{cluster}$ B (eV)	$E_{cluster}$C (eV)
∞ (bulk)	1.33	1.33	1.33
94	0.9	1.09	0.86
15	0.8	0.89	0.82
2	0.75	0.46	0.54

then

$$E_{norm} = (1 - 0.82N^{-1/3}) \tag{2.21}$$

This very simple formula contains a formalism derived from the density functional where the contribution of the kinetic and correlation exchange terms of a uniform electron gas of density $n = 3/4\pi r_s^3$ is calculated exactly. This is the contribution of the surface energy and the term "0.82" in equation 2.21

The liquid drop model predicts well a decrease of the cohesive energy with the size of the cluster. It remains to estimate the degree of accuracy of our model. Table 2.2 gives some experimental values compared to the liquid drop and *TBSMA* ("Tight Binding Second Moment Approximation") models that we will expose later.

The general trend is correct. If the agreement is not perfect, it is nevertheless remarkable to have a "quasi-universal" law for all these metals. This is due to the fact that the surface energy is associated with the dangling bonds at the surface, so this dangling bond energy is proportional to the cohesive energy, hence a quasi-constant ratio (table 2.1). Of course, this point of view is simplistic because the electronic cloud reorganizes itself on the surface. This extremely simple formula can be verified in certain cases including more complex noble metals (gold).

Figure 2.2 shows that the *1/R* dependence (here in $1/N^{1/3}$) for gold clusters is verified theoretically (figure 2.2), whatever the sophistication of the quantum chemical calculations. Thus, the agreement for small gold clusters (see figure 2.2) is reasonable (see equations 2.22 and 2.23 below). Thus for the PBE-D3 model (see figure 2.2) we have the following equation

$$E_{cluster}/N = 3.38(1 - 0.83N^{-1/3}) \tag{2.22}$$

in the liquid drop model (E_{coh}=3.81 eV [Wang *et al.* (2002)])

$$E_{cluster}/N = 3.81(1 - 0.82N^{-1/3}) \tag{2.23}$$

This corresponds approximately to the PBE-D3+$\Delta(SO)$ model in figure 2.2.

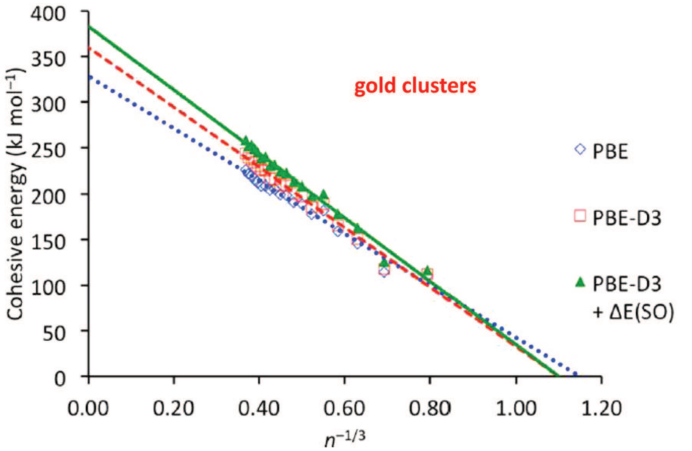


FIG. 2.2 – Cohesive energies calculated as a function of $N^{-1/3}$ for Au_N *2<N<20* clusters using different quantum chemical "*PBE*" models (the generalized gradient approximation (*GGA*) in the form of Perdew Burke Ernzerhof functional) "*PBE-D3*" and "*PBE-D3+SO*" structural parameters are given by a "high-level *CCSD(T)-F12*-type" model [Chan and Yim (2013)]. For the conversion of energy unit 1eV = 96.487kJ/mole. Reprinted by permission from American Chemical Society, Journal of Chemical Theory and Computation, COPYRIGHT 1993.

2.2.4 Tight binding: TBSMA model

2.2.4.1 Cohesive energy

In the broken bond model used in crystallography, the cohesive energy of an atom is proportional to the number of bonds and therefore to the number of first Z neighbors (coordination).

$$E_{coh} = Z \times E_{at} \tag{2.24}$$

E_{at} is the cohesive energy of an atom by coordination. This intuitive model derived from classical physics overestimates the energy.

In the tight-binding model which is "quantum" and in second moment approximation (called "TBSMA") the cohesive energy can be calculated from the method of moments. We call moment of n- order of a function $\rho(E)$ the mathematical quantity

$$\mu_n = \int \rho(E) E^n dE \tag{2.25}$$

Physically we can calculate μ_n from the equation

$$\mu_n = \sum_r < r \mid H^n \mid r > \tag{2.26}$$

The order n of the moment μ_n is equal to the total number n of paths that can be made starting from an atom and returning to this atom. We will consider

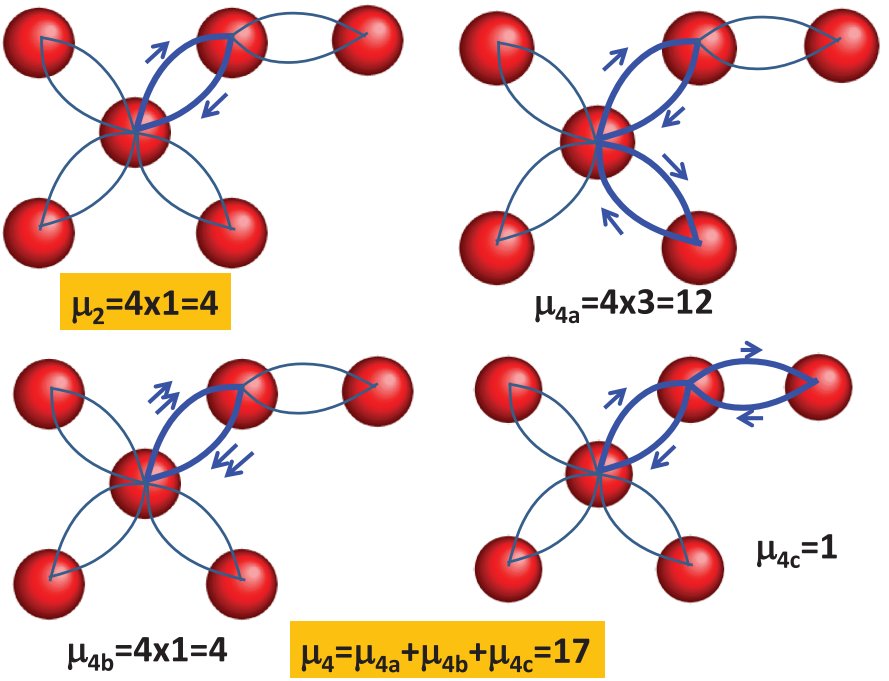


FIG. 2.3 – Example of paths in the six-atom cluster shown in the figure (normalized in β units). The moment is calculated for the central atom. The total second-order moment is 4 (there are four neighbors), this moment corresponds to a closed path from the neighboring atom and back to the starting point. Note that in this structure there is no third-order moment. The fourth order moment for illustration is decomposed in all possible trajectories knowing that one can travel twice the same path (μ_{4b}), describe a trajectory between two first neighbors (μ_{4a}) or between a first and a second neighbor (μ_{4c}). We will verify that in the case of a diamond structure (each atom has four neighbors) the fourth-order moment is 28. The atom having only one neighbor has a second-order moment of 1.

the number of paths between an atom and one of its first neighbors, which is *2*. An example is given in figure 2.3.

In the "Tight Binding" or Hückel's models, the only non-zero matrix elements between first neighbors are noted β, we will have a very simple relation (see figure 2.3)

$$\mu_2 = Z\beta^2 \tag{2.27}$$

where Z is the number of first neighbors

In addition to the treatment limited to the first neighbors, we can simplify the problem by taking a constant density of states $\rho(E)$ characterized by its width W.

$$\rho(E) = \frac{2}{W} \text{ if } -W/2 < E < 0 \tag{2.28}$$

$$\rho(E) = 0 \text{ if } E > 0 \tag{2.29}$$

For a simple monovalent metal, this band is half filled, and the second-order moment is written according to equation 2.25

$$\mu_2 = \int_{-W/2}^{W/2} \rho(E) E^2 dE = \frac{W^2}{12} \tag{2.30}$$

The cohesive energy of electronic origin that we consider here coincides with the cohesive energy of the system, it writes

$$E_{coh,e} = E_{coh} = \int_{-W/2}^{0} E\rho(E) dE = -\frac{W}{4} \tag{2.31}$$

Using equations 2.30 et 2.31

$$|E_{coh}| = \frac{\sqrt{3}}{2} \mu_2^{1/2} \tag{2.32}$$

Equation 2.27 gives us the value of μ_2

$$E_{coh} = \frac{\sqrt{3}}{2} Z^{1/2} \beta \tag{2.33}$$

β is an energy that involves the overlap between the orbitals of neighboring atoms, it is often called the overlap integral or the hopping integral. Contrary to the broken bond model where the dependence is in Z, the TBSMA model gives a dependence in $Z^{1/2}$

However, in all cases, the cohesive energy is expected to be maximum when the surface of the polyhedron is minimal and the surface of each facet is as compact as possible. Indeed the cohesive energy increases with Z even if it is only in $Z^{1/2}$.

2.2.4.2 Evolution of the interatomic distance with the size in the TBSMA approximation

In the previous paragraph, we calculated the electronic cohesive energy assimilated to the cohesive energy. We can now calculate the cohesive energy in a more precise way. For that, we suppose that all the atoms of the cluster are equivalent with a distance r between each neighbor. The number of first neighbors is noted as Z.

The simplest model consists of representing the potential between two atoms using a two-body potential. To calculate the total energy, we need two terms, one representing the attraction energy given by equation 2.31, the energy of electronic origin, and the other given by a term of repulsion. Moreover, it is necessary to introduce a dependence of energy with the distance r. We will discuss these two terms.

i) Attractive energy
This energy of electronic origin (hence the index "e") is given by equation 2.33

$$E_{coh,e} = \frac{\sqrt{3}}{2}\sqrt{Z} \times \beta \tag{2.34}$$

The overlap term β depends on the distance r. This dependence is also a function of the type of orbitals involved through their spatial and angular extensions. The simplest way to represent the dependence in r is to take an empirical law of exponential type

$$\beta = \beta_0 \exp(-qr) \tag{2.35}$$

β_0 is a constant supposed to be known, q is a positive real number (be careful not to confuse it with the charge) and depends on the element constituting the cluster. The attractive energy is written

$$E_{coh,e} = \frac{\sqrt{3}}{2}\sqrt{Z} \times \beta_0 \exp(-qr) \tag{2.36}$$

ii) Repulsion energy
This energy noted $E_{rep,e}$ comes from the repulsion of the electronic clouds and nuclei when r is smaller than the distance d between the atoms. For two atoms we will choose an empirical potential of exponential form with a positive real coefficient p supposed to be known. This repulsion is additive when the number of first neighbors increases.

$$E_{rep,e} = ZC \exp(-pr) \tag{2.37}$$

The term C is a constant assumed to be known. We deduce from it the cohesive energy

$$E_{coh}(r) = E_{coh,e} - E_{rep,e} = \frac{\sqrt{3}}{2}\sqrt{Z} \times \beta_0 \exp(-qr) - ZC \exp(-pr) \tag{2.38}$$

The equilibrium distance d is classically defined by the condition

$$\frac{\delta E_{coh}(r)}{\delta r} = 0 \mid_{r=d} \tag{2.39}$$

Then

$$\exp((p-q)d) = \frac{p}{q}\sqrt{Z}\frac{2}{\sqrt{3}}\frac{C}{\beta_0} \tag{2.40}$$

In order to remove the C constant, we can introduce the cohesive energy in the bulk phase noted E_{solid}. This term is obtained for the particular case $Z = Z_\infty$ and $d = d_\infty$, Z_∞ and d_∞ being the number of first neighbors and the interatomic distance in the solid. So we have the particular case,

$$\exp((p-q)d_\infty) = \frac{p}{q}\sqrt{Z_\infty}\frac{2}{\sqrt{3}}\frac{C}{\beta_0} \tag{2.41}$$

Either by combining equations 2.40 and 2.41, we get

$$\exp(p-q)(d_\infty - d) = \left(\frac{Z_\infty}{Z}\right)^{1/2} \tag{2.42}$$

We thus obtain a relation between the interatomic equilibrium distance d in a small particle and its value in the bulk phase d_∞.

$$d = d_\infty - \frac{1}{2(p-q)} \ln \frac{Z_\infty}{Z} \tag{2.43}$$

Experience shows that *(p-q)* is in general a positive term. In a small particle, Z represents the average number of first neighbors summed over all atoms. Its value cannot exceed Z_∞ in the bulk phase (except change of bond type with size), that is $Z < Z_\infty$. We deduce that the distance d is always smaller than d_∞. This effect is called the contraction phenomenon. It is verified in the case of simple metals (alkaline and noble metals). Figure 2.4 shows the value obtained in the case of copper. These values are deduced from the X-ray absorption spectroscopy (*EXAFS*). For copper reasonable values of p and q are respectively $p = 9d_\infty^{-1}$ and $q = 3d_\infty^{-1}$. Equation 2.43 gives for the dimer (Z=1), d=2.35Å to be compared to the experimental value d=2.23Å (see figure 2.4). For a particle of 55 atoms (Z=*7.85*) we will have d=2.51Å a value very close to the solid one. This is confirmed if we look at curve 2.4 which tends very quickly towards its asymptotic value. This property is quite general for metals and our model, even if it is very simple, explains why the interatomic distance in the dimer is generally smaller than this same distance in the condensed phase. This property reflects the fact that with many neighbors, atoms are constrained and subject to the repulsion of the electronic clouds of more atoms (in a dimer the electronic clouds can more easily be deformed). In fact, this property is quite general for metals. There are exceptions such as mercury and the elements of the same column Zn and Cd (see table 2.3) which we will come back to in another chapter. It should be noted that the contraction of the distances when the size decreases can be interpreted by a simple phenomenological model based on the surface stress and the Laplace equation. It can be shown that the surface stress f_s can be written in a homogeneous and isotropic system (face-centered cubic for example) [Mays *et al.* (1968); Vermaak *et al.* (1968)]

$$f_s = -\frac{3}{2}\frac{\Delta d_\infty}{d_\infty}\frac{R}{K} \tag{2.44}$$

where K is the modulus of compressibility related to the Laplace pressure P inside the particle of radius R and volume V

$$K = \frac{-\Delta V}{PV} \tag{2.45}$$

Surface stress is responsible for the contraction of the particle.

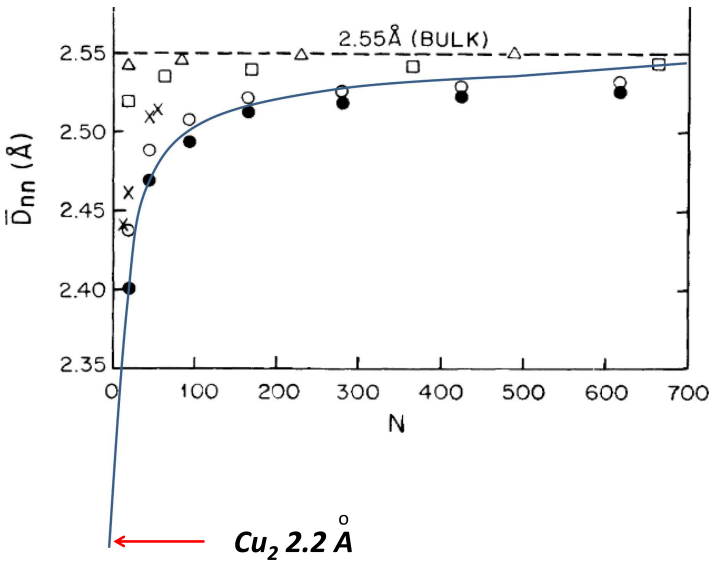


FIG. 2.4 – Variation of the interatomic distance as a function of size for copper clusters. These distances are obtained from the analysis of the EXAFS structure of copper clusters dispersed in a solid argon matrix at a temperature of *4.2 K*. Under these conditions, it is assumed that the matrix plays no role (no pressure on the clusters). From reference [Jiang *et al.* (1987)]. The original measurements are from Montano *et al* [Montano *et al.* (1986)]. Reprinted by permission from American Physical Society, Physical Review B, COPYRIGHT 1987.

TAB. 2.3 – Experimental values of the distance between first neighbors in the solid and in the dimer for some metals (in Å). For the solid, the data are taken from reference [1] [Kittel (2005)]. [2] [Huber (2013)], [3] [Lim *et al.* (2005)], [4] [Johnson (2020)], [5] [Jules and Lombardi (2003)], [6] [Sontag and Weber (1982)], [7] [Gerber and Broida (1976)]. We note that the contraction occurs except for the divalent elements of the zinc column where the *sp* hybridization will play a fundamental role (see the chapter insulator-metal transition). The mercury dimer has a large size because of the Van der Waals character, thus not a very binding, of the bond. It is the same for the elements of the same column *Cd* and *Zn*.

	Li	Na	K	Rb	Cs
bulk	3.02[1]	3.66[1]	4.52[1]	4.84[1]	5.24[1]
dimer	2.67 [2]	3.08 [2]	3.92 [3]	4.18 [3]	4.65[3]
	Al	Ag	Au	Ba	Pt
bulk	2.86[1]	2.89[1]	2.88[1]	4.35[1]	2.77[1]
dimer	2.7[4]	2.53[5]	2.47 [5]		2.33 [5]
	Sb	Bi	Hg	Cd	Zn
bulk	2.91[1]	3.07[1]	3.01[1]	2.98[1]	2.67[1]
dimer	2.48[6]	2.66 [7]	3.63 [5]	4.07 [5]	4.19 [5]

2.2.4.3 Cohesive energy

We have all the ingredients to calculate the cohesive energy of a cluster. For convenience, the cohesive energy will be normalized to the energy in the bulk phase. The reader will check from equations 2.38 and 2.43, that it is possible to write

$$E_{coh} = \left(\frac{p-q}{p}\right)^{-1} E_{bulk} \left[\left(\frac{Z}{Z_\infty}\right)^{1/2} \exp q(d_\infty - d) - \frac{q}{p}\frac{Z}{Z_\infty} \exp p(d_\infty - d\right)\Bigg] \tag{2.46}$$

Simplifying this expression by using the form $exp(ab) = (\exp(a))^b$ leads to the equation

$$E_{coh} = E_{bulk} \left(\frac{Z}{Z_\infty}\right)^{(p-2q)/2(p-q)} \tag{2.47}$$

Note that in general $p > 2q$ is a realistic condition. If $p >> q$, the previous equation is reduced to the assymptotic law such as we have defined in equation 2.33.

$$E_{coh} = E_{bulk} \left(\frac{Z}{Z_\infty}\right)^{1/2} \tag{2.48}$$

Z is related to the size and requires knowledge of the structure of the lattice, the polyhedron, and the possible position of the atoms if the polyhedron is incomplete (geometrical magic number). We can recalculate the equilibrium form obtained in this formalism from the TBSMA model. Intuitively, this model seeks to maximize the compactness and will give similar results to the model of broken bonds (since $p > 2q$). This has importance for the stability related to the geometrical shells. There will be an excess of "stability" for perfect polyhedra.

In the case of sodium, reasonable values of p and q are respectively $p = 7.75 d_\infty^{-1}$ and $q = 1.65 d_\infty^{-1}$. We will take a structure where $Z_\infty = 12$ (the bulk phase is cubic centered, but the observation of the magic numbers is in favor of a twelve neighbors structure (icosahedron, see next paragraph). Using $E_{bulk} = 1.33\,\text{eV}$, we can for example calculate the cohesive energy defined for sodium clusters of *2*, *15*, and *94* atoms as defined in table 2.2. These clusters do not correspond to closed atomic shells structures. We can in first approximation roughly estimate Z by taking its value for neighboring polyhedra namely *N=13 (Z=7)* and *N=55 (Z=7.85)*. The results are given in table 2.2 column C.

2.2.5 Hückel's model of quantum chemistry

2.2.5.1 Introduction

The *TBSMA* model is based on the hypothesis of the existence of energy bands. It is thus explicitly a model from solid-state physics where the notion of periodicity is acquired. This formalism is questionable in the case of small particles