P.-G. Reinhard, E. Suraud

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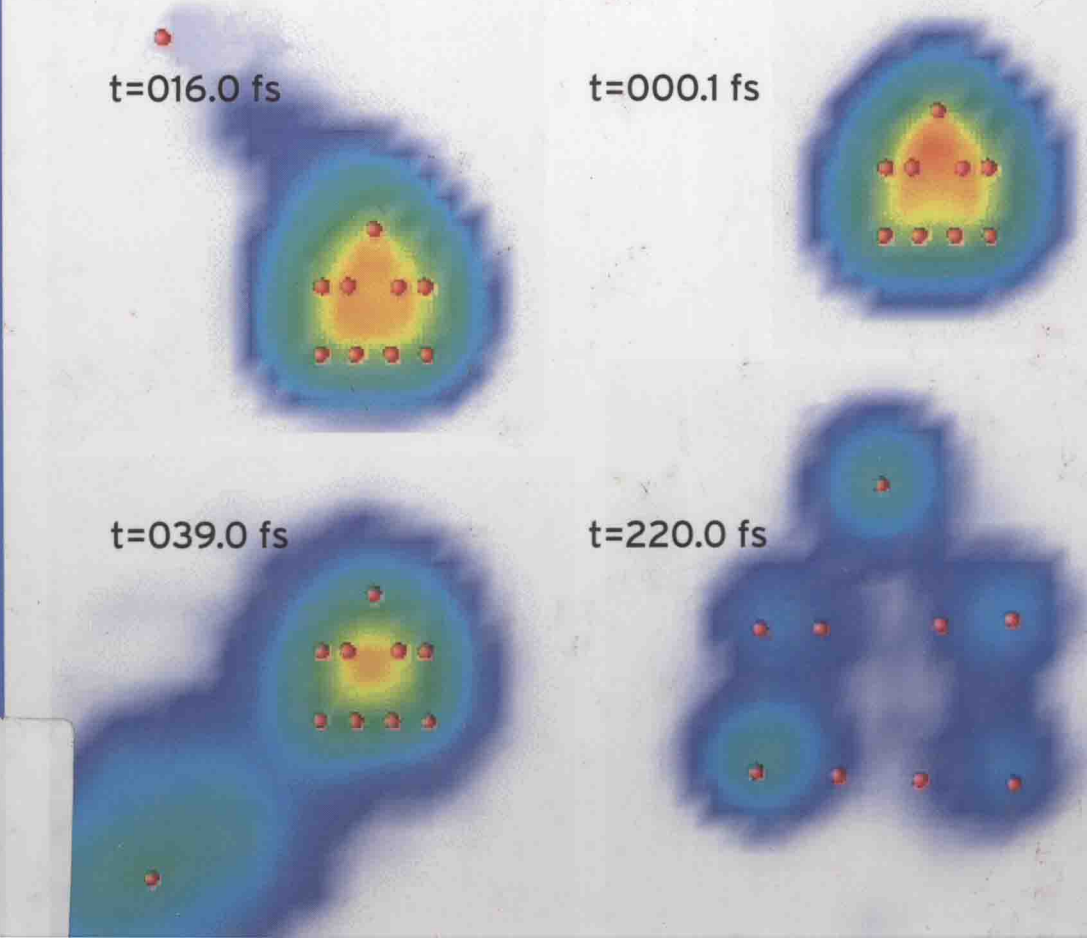
Introduction to Cluster Dynamics



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Cover Picture
The cover picture shows four snapshots from a collision of an Ar^{8+} ion on the cluster Na^{+}_{9}. The ions (Na^{+} and Ar^{8+}) are indicated by red dots. The electronic density is drawn in colour scale with dark yellow representing the highest value. The time steps are arranged counterclockwise. The sequence starts at the upper right panel showing the unperturbed ground state of Na^{+}_{9}. The approaching Ar^{8+} and its first polarizing effects on the electron cloud are seen in the next time slot (upper left panel). Short after the encounter (lower left panel), one notes that the Ar^{8+} takes away a sizeable amount of cluster electrons. The thus highly ionized cluster undergoes a Coulomb fragmentation. The last snapshot (lower right) demonstrates the global expansion of the cluster.

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Introduction to Cluster Dynamics

To our families

Preface

Cluster physics, and even more so cluster dynamics, is a young and fast developing field of science. It addresses fundamental questions in physics and chemistry, but leads also to new technological developments. Because it is such a recent field and also because it has links to many areas in physics and chemistry, cluster science is not yet routinely taught in universities, at least not as a well identified field. Thus there are only few textbooks presenting the topic as such and even less books with a sufficient treatment of dynamics. The aim of this book is to try to fill this gap whereby we concentrate on dynamical aspects. The material presented here stems from lectures given by the authors at undergraduate and graduate levels, both in France and in Germany. The presentation is thus to a large extent tutorial, particularly in the first chapters.

Cluster science was recognized as an independent field of physics and chemistry only in the last decades of the twentieth century. This recognition is, to a large extent, connected to the experimental capability of producing free clusters without constraining environments such as substrates or matrices. The discovery of fullerenes which are large carbon cages with C_{60} as the most famous example was an important step in this direction, also in view of the technological applications of carbon compounds. Somewhat surprisingly, it turns out that clusters had been known and used for centuries, for example by craftworkers (exploiting their remarkable optical properties) or in photography (exploiting photosensitive AgBr clusters embedded in a film). In spite of these important applications, it was only at the beginning of the twentieth century that the notion of a cluster as an independent object was suggested by G. Mie in the context of the optical response. Decades later, many investigations were performed on deposited or embedded clusters and clusters finally became a central object of investigations in the late twentieth century. As already mentioned, cluster physics opens numerous technological applications, in particular in relation to carbon compounds (for example with the so called carbon nanotubes). But the impact of cluster physics is not only focused on applications. Clusters constitute special objects with specific properties which require specific investigations, both from experimental and theoretical sides. But they also have an extremely important and unique property: they are scalable. One can vary the size of a cluster from the dimer close to the bulk. Clusters thus provide a useful laboratory for investigating the structure of matter and in particular how matter properties do evolve with size. They constitute, so to say, a bridge between microscopic and macroscopic worlds.

As cluster physics is a merger between various fields of physics and chemistry, it would be illusory to conceive an introductory book covering all the many facets. We shall focus on one particular aspect, namely cluster dynamics. Even then, there is far too much material for one book like this. We aim here at a tutorial introduction reporting basic experimental and theoretical tools without entering too deeply into the details covered by the various subfields. And we

will illustrate our discussions with results directly taken from the most recent researches in the field, in order to keep contact with these rapid developments. Such a choice implies a certain degree of superficiality and incompleteness. We try to avoid technicalities in order to focus on physical insights. Some more involved, but necessary, details will be outlined in a few appendices. Even with such simplifying assumptions, one is bound to make choices, which de facto eliminate or less fully cover some aspects. Our bias here goes into three (physically motivated) directions. First, we shall devote a large fraction of our discussions and examples to the particular case of metal clusters. The reason is that they have played an important role in cluster studies, that many complementing experimental results are available for these systems, and that the metallic bonding gives these systems systematic behaviors, which are not so easily found in other types of clusters. Metal clusters thus constitute ideal examples of illustration of physical concepts, particularly in the context of a textbook. The second bias concerns our focus on dynamical questions. Many different theoretical methods, with origins in various fields of physics and chemistry, have been developed to describe clusters. In the case of dynamics, the task becomes so involved that only few of these methods are really applicable to practical problems, in particular when one wants to exploit the above mentioned scalability of clusters. This gives naturally more weight to time-dependent density functional theory as the presently most efficient theoretical method for describing truly dynamical processes in clusters. Of course, we also discuss examples obtained with other techniques when applicable. The third bias concerns an experimental tool. Laser excitation as a doorway to dynamical processes will acquire a large weight in the examples. This, again, is natural as the fast progress of laser technology stimulates research in cluster dynamics very much.

The book is primarily written for undergraduate students in their last-year course. It should also be useful for graduate students and, because we have included most recent developments, the book might also be used by researchers. In order to merge both aspects, namely tutorial introduction and account of the latest developments, we have decided to start at an elementary level and to finish with up to date developments. The first four chapters thus require only elementary notions of quantum physics and basic knowledge of solid state and molecular physics. The last chapter is devoted to discussions of actual research with bias on dynamical problems. This chapter probably requires a deeper knowledge of the field, but should in principle be accessible to a reader having gone through the first four chapters. Finally the text is complemented by several appendices providing more details on several key methods.

The first chapter, *About clusters*, is meant to be propaedeutic. It aims at introducing clusters in relation to atoms, molecules and condensed matter. It provides a first overview of cluster structure, its chemical classification, and a few simple dynamical features. Metal clusters are discussed separately at the end of the chapter, addressing especially the dominant optical response. It is assumed that the reader has here a basic knowledge of atomic physics and chemistry. Crucial input from these fields is supplied in an appendix.

The second chapter, *From clusters to numbers: experimental aspects*, discusses the various experimental methods in cluster physics, focusing the discussions on cluster production and analyzing tools (by means of various spectroscopies). The basic setups are introduced accompanied by a brief discussion of their practical handling. The typical results from each area are presented and discussed. At the end, the reader should have a good oversight of structural and dynamical properties of the various sorts of clusters. A lot of material does exist for C_{60} and for metal clusters, in which dynamical effects are especially well documented. These will

dominate in the presentation. Results from other species will also be listed where available.

The third chapter, *The cluster many-body problem: a theoretical perspective*, gives a brief overview of the basic theoretical concepts for the computation of cluster structure and dynamics. A detailed discussion of the various levels of approximation for ions and electrons, and of their validity, is presented. This chapter also gives many results as examples, complementing (and, when possible, in direct relation with) the experimental findings from the previous chapter, emphasizing again observables in direct relation to cluster dynamics.

Chapter 4, *Gross properties and trends*, summarizes the results of experiments and theory from a general point of view. Typical time-, length- and frequency-scales are worked out. Trends with system size, material density, and strength of excitation are established. Electronic and ionic shell effects are addressed. Because of the numerous available systematics a strong bias on metal clusters exists in this chapter. The close relation between metal clusters and nuclei is also discussed.

The last chapter, *New frontiers in cluster dynamics*, deals with the most recent developments, in particular with dynamics in the regime of high excitations. It covers the transient regime where the dynamics can still be sorted in terms of multi-photon processes. It continues to the most violent excitation processes in strong laser fields or in ionic collisions which lead to high ionization states and to fast cluster fragmentation by Coulomb explosion. This corresponds to a very active field of research nowadays. The chapter has thus an open end.

The five chapters are complemented by eight appendices containing various practical and theoretical data. The titles of the appendices are to a large extent self explanatory: Appendix A *Conventions of notations, symbols, units, acronyms*, Appendix B *Gross properties of atoms and solids*, Appendix C *Some details on basic techniques from molecular physics and quantum chemistry*, Appendix D *More on pseudo-potentials*, Appendix E *More on density functional theory*, Appendix F *Fermi gas model and semiclassics*, Appendix G *Linearized TDLDA and related approaches* and Appendix H *Numerical considerations*.

An enterprise such as a book is necessarily the result of numerous interactions with many colleagues. They all have played an important role in the process, many of them on our way of learning cluster physics and some of them specifically giving advice for writing this book. We would thus like to acknowledge the help of all these colleagues and tell them how much they helped us and brought to us, both in terms of science and personal contacts. We would in particular like to mention here: J. Alonso, M. Belkacem, G. F. Bertsch, S. Bjornholm, M. Brack, A. Bulgac, F. Calvayrac, M. Chabot, J. P. Connerade, G. Gerber, B. Gervais, E. Giglio, E. K. U. Gross, C. Guet, H. Haberland, J. M. L'Hermite, P. H. Hervieux, B. Huber, B. von Issendorf, U. Kreibig, S. Kümmel, P. Labastie, M. Manninen, K.-H. Meiwes-Broer, V. Nesterenko, G. Pastor, R. Poteau, R. Schmidt, L. Serra, L. Schweikhard, F. Stienkemeier, J. Tiggesbäumker, C. Toepffer, C. Ullrich, D. Vernhet, K. Wohrer, and G. Zwicknagel. 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.

Paul-Gerhard Reinhard and *Eric Suraud*

September 2003

Contents

1 About clusters

Although we usually do not realize it, clusters belong to our everyday life. They have been exploited practically in many situations without people being aware of the underlying details. The tailoring of fine dispersed pieces of material (clusters !) inside bulk has, for example, been turned to an art by craft-workers for centuries. Already the Romans knew, empirically, how to play with the size of dispersed particles in a glass to produce various shining colors. Depending on the size of the gold inclusions, a glass could thus exhibit red as well as yellow reflections, for an example see [KV93]. In a different domain, photography also represents a typical application of cluster physics. Depending on the size of the AgBr clusters deposited on the film, they will more or less quickly and finely respond to light and thus perpetuate the properties of the produced image. Early photographers of the nineteenth century quickly realized and controlled such physical behaviors. Still, even at that time, clusters were not considered as objects of scientific studies, even not recognized as specific objects. The work of Mie at the turn of the twentieth century probably constitutes one of the earliest speculations on the existence and specificity of metal clusters — or rather, because the word "cluster" did not exist in this context at that time, of "small particles" [Mie08]. The question raised by Mie concerned the response of small metal particles to light, and how this response might depend on the size of the considered particle. Let us quote Mie: "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 submicroscopical particles; thus, in a way, one could investigate by optical means how gold particles are composed of atoms". A non negligible part of today's investigations on clusters relies on, or is very close to, Mie's intuition. As we shall see throughout this book, light represents a particularly useful means for the investigation of both structure and dynamics of clusters. And the response of clusters to light is indeed extremely sensitive to their properties. The beautiful achievements of Roman and later glass makers precisely reflect such properties. And photography, as well, is an art dealing with light.

The inspiring intuition of Mie did not suffice to promote cluster science to the status of a well recognized field of physics. Indeed the times of the early twentieth century were busy with the identification and analysis of "elementary" constituents of matter and only simple molecules seemed in reach of understanding in the mid century, or alternatively the other extreme, namely the problem of bulk material, of course with other techniques than the ones used in atomic physics. Modern cluster physics, as we know it today, only appeared in the last quarter of the twentieth century with the possibility of producing free clusters and tracking such small particles with several, still developing, techniques. This allowed the initiation of studies on clusters as such, which was an important step for the field. Indeed, embedded

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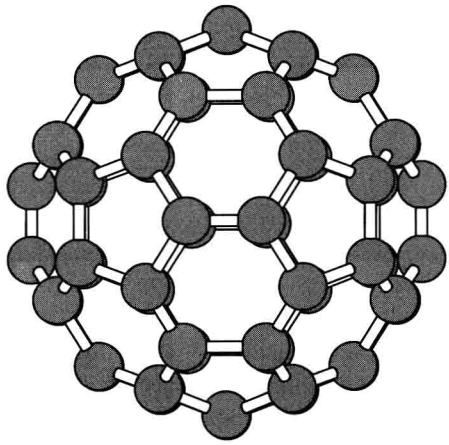

Figure 1.1: Ionic structure of the famous C_{60} cluster. The 60 atoms are arranged as 12 pentagons and 20 hexagons yielding a truncated icosahedron. That shape consists in 12 vertices bound together by 20 equilateral (and equal) triangles. At each vertex of the icosahedron, 5 triangles meet. Truncating these vertices by a plane, leads to the pentagonal faces. The total number of vertices becomes 60. For this C_{60}, 120 symmetry operations can be identified. And this high degree of symmetry has long been used by artists, the actual name of "Buckminster fullerenes" going back to the architect Richard Buckminster Fuller, renowned for his geodesic domes based on pentagons and hexagons.

clusters (as the fine gold particles in Roman glasses), or clusters deposited on surfaces, were experimentally accessible since long and of course the subject of numerous studies. But these rarely concentrated on the clusters, independently from the matrix or substrate. The case was more or less appended to surface or material science and did not constitute a true independent field. The capability of producing free clusters from dedicated sources, allowed the true starting of cluster science on a systematic basis. One of the startup events was the identification of C_{60} clusters, the famous fullerenes [YPC$^+$87, Kro87], with their remarkable geometry shown in Figure 1.1. At about the same time, free metal clusters had been produced and investigated, see e.g. [KCdH$^+$84]. The many original results obtained from then on for metal clusters, carbon clusters and, increasingly, other materials, established cluster physics as an independent, although cross-disciplinary, field among the well defined branches of physics and chemistry. Of course the production and analysis of free clusters gave new impetus to activities on deposited or embedded clusters as well. At the same time, amazing developments in the nanoscopic analysis of surfaces opened new views and much refined analysis of supported clusters. An example is given in Figure 1.2 showing in detail Ag nano-clusters sitting on a HOPG surface. As we will see, the combination of these quickly developing methods of nano-analysis with nano-particles, called clusters, constitutes a powerful tool for fundamental and applied physics.

The physics and chemistry of clusters, with its many facets covering free as well as embedded or deposited clusters, addresses an impressive set of problems, ranging from fundamental to applied ones. In all that, clusters are a species of their own asking for specific understanding of their properties. Although molecular and solid state physics, as well as chemistry or nuclear physics, do add helpful aspects, clusters belong to none of these fields and thus require devoted methods, both at the experimental and theoretical levels. A specific feature is, e.g., that cluster size can be varied systematically between atoms and bulk: they are, so to say, "scalable" objects. Clusters thus play an essential role from a fundamental physical point of view. They do represent an exceptional opportunity for testing the many-body problem, which is a generic quantum mechanical task and lies at the heart of the understanding of most complex systems. Bear in mind that solid state physics deals with virtually infinite, although

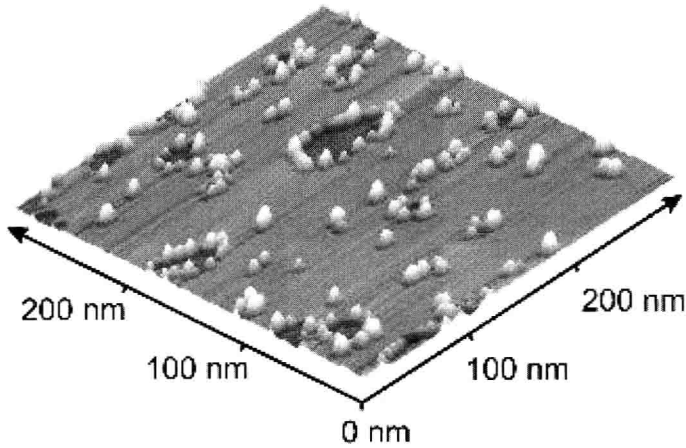

Figure 1.2: Topography of silver nanoparticles deposited on highly oriented pyrolytic graphite (HOPG), recorded with an *in situ* scanning tunneling microscope (STM). From [LMP+00].

symmetric, samples while in molecular or nuclear physics the systems never contain more than a few hundreds of constituents. Clusters bridge the gap. But the interest in them is not purely fundamental. As outlined above, clusters play a role in many practical situations like photography or artwork. More precisely, they have applications in many fields of science as, e.g., astrophysics, chemistry or material science. For example, clusters seem to play an important role in the formation mechanisms and the properties of cosmic dust [CTB89]. Carbon clusters are also expected to be present in the interstellar medium. The most striking property of clusters for applications in chemistry is their size. Indeed, because clusters may be quite small, but not too small, they can exhibit a large and tunable surface to volume ratio. They may thus provide ideal catalysts and play a crucial role in reaction kinetics [SAH+99]. A typical example of application here is photography. In material science, the discovery of fullerenes and carbon nanotubes opened the way to the design of new materials [Kai01]. This breakthrough renewed chemistry and physics of carbon to such a level that this field is almost becoming independent from the mother field of cluster physics, probably in part because of its many industrial applications.

Cluster physics with its many achievements now belongs to one of the most active fields in physics, and offers, through related domains like the physics of nanotubes or fullerenes, one of the fastest developing areas in applied as well as in fundamental science. It is close to impossible to cover in a single book all the topics related to cluster physics. We shall thus focus here on one important aspect of the field: cluster dynamics. As in atomic and molecular physics, detailed studies on the dynamics of quantum many-body systems were boosted by the rapid progress of laser technology and the possibility of studying electronic motion at the femtosecond (fs) level. Clusters add to these studies the variability of sizes, as discussed

above. Of course, the field of cluster science is so recent that we shall devote a large part of the book to the principle methods of cluster physics, experimental ones (in Chapter 2) as well as theoretical ones (in Chapter 3). Before that, we are going discuss in this chapter here the nature of clusters in relation to more established objects such as atoms and molecules, on the one side, and bulk, on the other side. Not surprisingly, we shall see that size turns out to be a key quantity, influencing many cluster properties. And we shall see that clusters are more than just big molecules or "small" pieces of bulk. They are indeed objects of their own, and cluster physics thus has to combine expertise from various fields of physics and chemistry into an excitingly new area of research.

1.1 Atoms, molecules and solids

Before considering clusters made of atoms, it is useful to briefly summarize what we need to know on the more "traditional" systems such as atoms, molecules and solids. Clusters range between these extremes and we shall see that understanding binding mechanisms between atoms or inside bulk provides the necessary keys to understand binding of clusters. Starting point is the atoms, then we discuss their combination in terms of molecules and in the infinite limit in terms of solids. We can then address clusters. For all species, we give here a brief overview with bias on the electronic structure, mostly at a qualitative level. For more thorough discussions, we refer the reader to standard textbooks of atomic, molecular, chemical physics or solid-state physics as cited at the relevant places.

1.1.1 Atoms

1.1.1.1 Qualitative aspects

Atoms consist of a central nucleus and a neutralizing electronic cloud. The atomic number Z labels the charge of the nucleus which is the number of protons inside the nucleus. The other constituents are the neutrons which, however, play a negligible role for the electronic problem, at least at the level we are interested in. For our purpose, we can safely reduce the effect of the nucleus to that of a point charge Ze (thus neglecting hyper-fine structure as effects of finite size and magnetic coupling [YH96]). Electrons are then supposed to feel only the Coulomb field of the (point-) nucleus. At the level of the fine structure, there are the relativistic effects on the electrons as spin-orbit splitting and Breit interaction [Wei78]. These are, in fact, crucial for heavy elements or when going for quantitative details of bonding. Nonetheless, we neglect fine structure in the discussions of this book to keep the presentation simple.

What remains is the non-relativistic many-electron problem in the central field of the nucleus. It is well known that the electrons arrange themselves in shells around the nucleus. The quantitative understanding of the arrangement of these shells is a non-trivial problem, except for the case of the hydrogen atom where the problem reduces to one single electron in a central field. The case of many-electron atoms quickly becomes complex because of the two-body coulomb interactions between electrons. It is usually treated in a mean-field approximation where each electron is supposed to feel the net effect of all other electrons as one common central mean field. This allows one to sort electrons in shells denoted by their orbital angu-

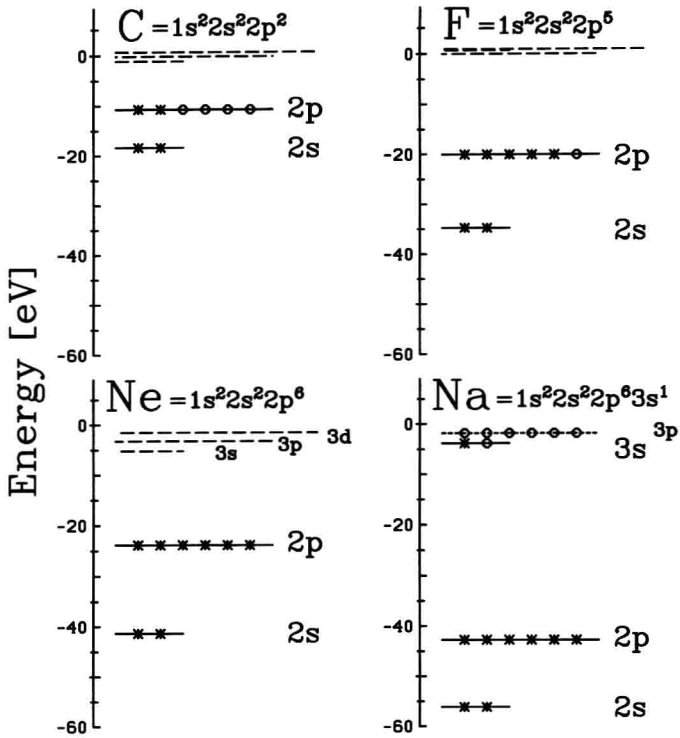

Figure 1.3: Level schemes for the C, F, Ne, and Na atoms. Open circles and/or dashed lines indicate empty states, crosses occupied states. The same energy scale is used for all 4 atoms for better comparison. The spectroscopic notation is given for each atom.

lar momentum and sorted according to increasing single-electron energy. Without entering details which can be found elsewhere (see [Wei78] and Appendix B), we want to remind the basic "Aufbau" principle of electronic shells. Let's imagine that we fill the atom successively, electron by electron. The first electron will feel only the nuclear attraction as a pure Coulomb field. But already the second electron experiences both the nuclear attraction and the repulsion due to the first electron. Both electrons will stabilize to form the most deeply lying electronic level, the $1s$ shell, filled with these two electrons and distinguished by spin up or down. The third electron has to fight the conflicting influence of the attracting nucleus and the two repelling $1s$ electrons. It will feel a screened nuclear charge $(Z-2)|e|$ and form, together with the next electron to come, the $2s$ electronic shell. Because the nuclear charge is screened, the $2s$ shell is much less bound than the $1s$ shell of the pure nuclear field. Mind also that the Pauli principle does hinder these $2s$ electrons to approach the nucleus in the area occupied by the $1s$ electrons. The $2s$ shell will thus be pushed outside the $1s$ one. Carrying on, the building principle works in a similar way. Electrons do gather in shells, characterized by a principal ($n = 1, 2, 3 \ldots$) and an orbital quantum number ($l = 0 \equiv s$, $l = 1 \equiv p$, $l = 2 \equiv d$, $l = 4 \equiv f \ldots$) where each l shell contains $2(2l+1)$ electrons. In light atoms (lighter than Ca (Z=20)) the sequence of successively occupied shells is $1s, 2s, 2p, 3s, 3p, 4s, 3d \ldots$. An example, for the electronic structures of Carbon (C), Fluorine (F), Neon (Ne), and Sodium (Na), is given in Figure 1.3. The single-electron energies have been obtained by density-functional methods as discussed in Chapter 3 which suffices for the purpose of the schematic discussion