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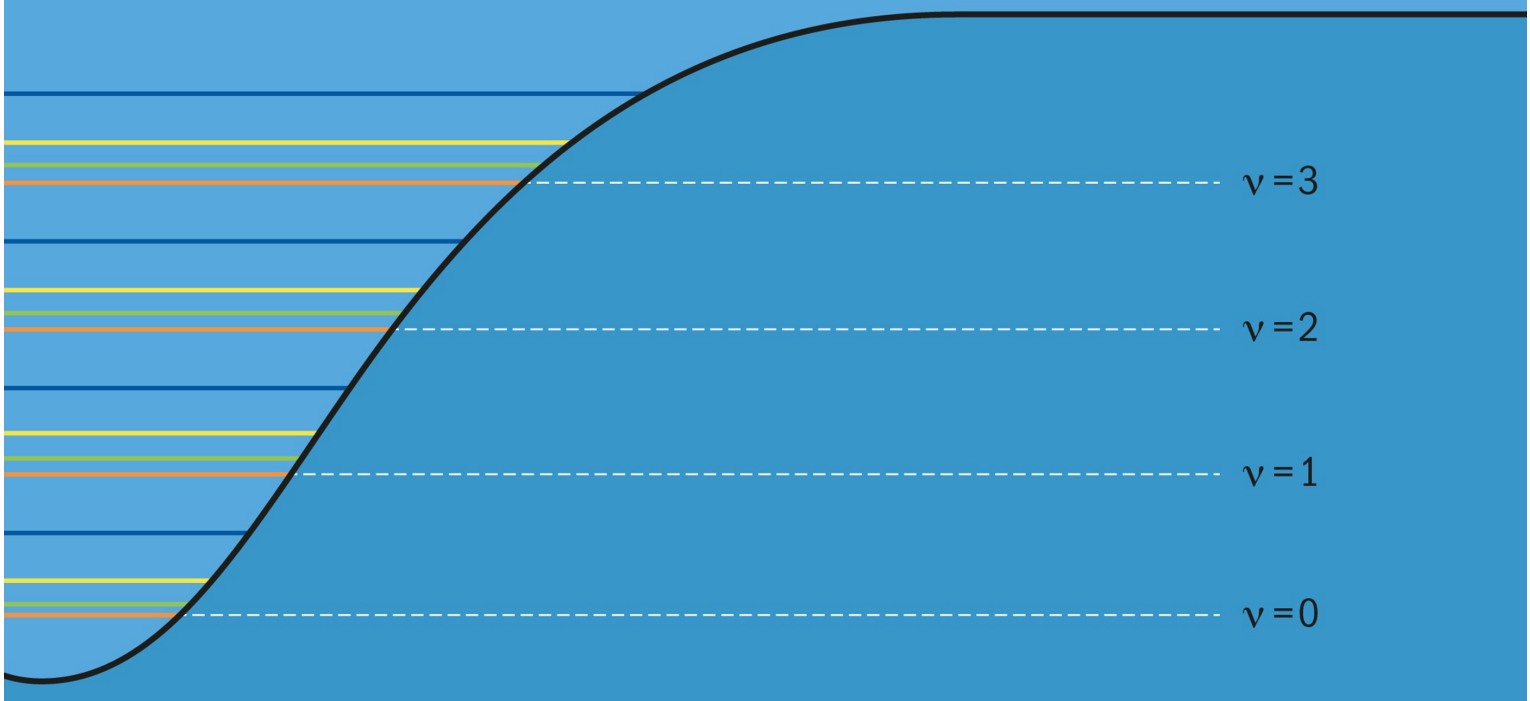
Atomic and Molecular Physics

A primer

Luciano Colombo



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To my family

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Foreword

There are many excellent books teaching physics at different levels of difficulty. However, if we look not only for good physics but *also* for attractive and pleasing ways to present the challenging physical questions, as well as the ways to face and solve them, we soon come to the conclusion that except for some celebrated cases, there are not many. Yet, to feel that what is being learned is something which is not really that difficult but something natural or even relatively simple, is what makes a reader feel comfortable with new notions and, at the end, drives him/her to rethink about these ideas and thus, discover that in fact things are not that simple and what is being read is a clever answer to a complex problem. But this is the way for many of us to learn, as in one of those Chekhov plays so full of real life insight although apparently nothing extraordinary or unusual happens. We must feel at home with new concepts to experience the need to go to the heart of the problem. The gift to be able to explain complex concepts in simple words is the result of long practice in polishing from unnecessary complications and reducing the problem to their very fundamental nature. Professor Colombo is an accomplished communicator as any reader of this book will agree. The present volume, which is the first of a series of three aiming to present a broad coverage of atomic, molecular, solid-state and statistical physics, typically at an undergraduate level, will be enjoyed by everyone trying to enter into the realm of atoms and molecules and how we understand them.

The first chapter ('The overall picture') already sets the tone. Do atoms exist?, What are atoms made of?, these are the *simple* questions opening the book. In about a dozen pages we start being told about such fundamental things as the law of multiple definite proportions and Avogadro's number, the different experimental realizations providing support for the atomistic picture, the constituents of atoms and the experimental observations pointing to failures of classical physics when dealing with small enough objects, and eventually leading to the wave–matter duality and the development of the matter waves equation and its probabilistic interpretation. This is really a long trip dealing with difficult notions which could discourage many readers but which is absorbing and thought-provoking in the author's hands.

The volume consists of three main parts: 'Preliminary concepts', 'Atomic physics' and 'Molecular physics'. The first part contains two chapters which provide the appropriate historical perspective leading to the contemporary view of atomic and molecular physics, as well as the necessary mathematical background. As discussed above, the first chapter is a guided tour through the physical developments which led from the atomistic hypothesis to the shaping of the new language needed to properly describe atoms and molecules based on the wave–matter duality. The second chapter ('Essential quantum mechanics') introduces the basic notions and mathematical tools, i.e. the basic ingredients of the language which will be used in the rest of the book. All through this chapter, which is thus an introduction to essential quantum mechanics, effort is made in underlining how the new language is related to notions in classical physics, but also what are the subtle new ideas emerging, as for instance

the far-reaching consequences of the concept of indistinguishability of identical particles in quantum mechanics leading to the Pauli principle. This chapter concludes with the introduction of perturbation theory, a wonderful tool which will be extensively used in the two main parts of the book.

The second part ('Atomic physics'), containing three chapters, deals with the physical description of atoms and their interaction with radiation. It begins with application of the machinery developed in chapter 2 to the simplest atomic system, the hydrogen atom. The study leads to the important concept of atomic orbital, a basic ingredient of our knowledge of atomic and molecular physics and chemistry. Atomic orbitals describe the movement of the electron in the field of charged nuclei and this leads naturally to the study of the magnetic interactions occurring in one-electron atomic systems. The effect of uniform and non-uniform magnetic fields is considered and leads to another extremely important concept, the electron spin. This concept is clearly introduced, showing how it can provide an explanation for the famous Stern–Gerlach experiment. A simple, intuitive explanation of its origin is presented although it is already pointed out that, only in a relativistic version of quantum mechanics, can the spin concept be naturally accounted for. This chapter is completed with the introduction of the spin–orbit coupling effects and the fine and hyperfine structure of one-electron atoms spectra. This is followed by a chapter dealing with the interaction of one-electron atoms with electromagnetic radiation. The elementary theory of absorption and emission of radiation is developed for both spontaneous and stimulated processes and selection rules for allowed transitions are worked out. Finally, the LASER concept is qualitatively presented. The third and last chapter of this part deals with the extension of most of these ideas to many-electron atoms by taking into account electron–electron (Coulomb and exchange) interactions at different levels of sophistication. For instance using the so-called central-field approximation readers are naturally led to the main concepts behind the periodic table of elements. However, more sophisticated approaches to the electron–electron interactions are needed in order to be able to fully understand atomic spectra, and the Hartree, Hartree–Fock and configuration interaction methods are discussed. This part concludes with the development of selection rules for optical transitions and the effect of external magnetic fields on multi-electron atoms. It is certainly a long journey full of unexpected surprises but also lucid rationalizations made appealing by the clarity of the exposition.

The third part deals with Molecular physics. Now, things become more complex since there are many electrons *and* nuclei. This means that one needs to introduce some approximation in order to keep the problems manageable. This is the Born–Oppenheimer approximation, which is the beginning of the excursion through the molecular world. The rest of this chapter is devoted to the analysis of the two main sources of stability in molecules: ionic and covalent bonding. Whereas ionic bonding can be understood from a purely classical, Coulombic perspective, covalent bonding can only be understood from a purely quantum mechanical approach. The simplest molecule, H_2, is used to discuss this extraordinarily important concept which lies at the basis of modern chemistry. Having set the basis for understanding the electronic motion in diatomic molecules it is time to progress and consider the inner molecular

motions, i.e. rotations and vibrations, which in the case of diatomic molecules can be discussed with great accuracy, including the roto-vibrational coupling. In that way the rotational and vibrational spectra used to characterize diatomic molecules is described and later completed by the consideration of light scattering experiments like Raman and Rayleigh scattering. Finally, an extension to polyatomic molecules is presented leading to the introduction of the very useful concept of normal vibrational mode. In the final chapter of this part, the electronic structure of polyatomic molecules is discussed. Analysis of the simple H_2^+ molecular ion leads to the introduction of several important concepts such as molecular orbital, overlap and resonance integrals, bonding and antibonding levels and electronic configuration, which are at the basis of the modern theory of the chemical bonding. The linear combination of the atomic orbitals approach, a formalism which has strong roots in solid-state theory and very well suited to fully exploit the symmetry properties of the molecules is used throughout the chapter. The nature of the molecular orbitals for different homonuclear and heteronuclear diatomic molecules as well as polyatomic molecules is discussed so that the reader is acquainted with many aspects of the conceptual framework commonly used to discuss the electronic structure of molecular systems (hybridisation, electronic delocalisation, etc).

This book provides a guide to understanding the physics of atoms and molecules in a vivid and pedagogical way. Throughout the book the mathematical formalism is kept to a minimum level compatible with rigor without leading to unnecessarily long derivations which would distract the reader from the conceptual framework. When such mathematical digressions are useful they are given in a series of appendices.

One could naively think that if we are able to understand something we should also be able to explain it to others. This is unfortunately not so simple. Being able to expose in a clear, consistent and engaging way is something requiring long dedication. Professor Colombo has wholly succeeded in this purpose and provided us with a nice and attractive approach to atomic and molecular physics. The level of the book is typically that for an undergraduate series of lectures and thus will be well suited for an audience of students in physics, chemistry, materials sciences and engineering having a good background in classical physics and calculus. The good balance between fundamental understanding and formal treatment will also make it appropriate for graduate students or scientists in other fields needing to acquire a good grasp of atomic or molecular physics.

Those who will have their first exposure to atomic and molecular physics through this book are very lucky. There is no that doubt readers of this book will be eagerly waiting for the next two volumes.

ENRIC CANADELL
Institute of Materials Sciences of Barcelona
Consejo Superior de Investigaciones Científicas
Bellaterra, June 2019

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Author biography

Luciano Colombo

Luciano Colombo received his doctoral degree in physics from the University of Pavia (I) in 1989 and then he was a post-doc at the École polytechnique fédérale de Lausanne (CH) and at the International School for Advanced Studies (I). He became assistant professor (tenured) at the University of Milano (I) in 1990, next moving to the University of Milano-Bicocca (I) in 1996 for an equivalent position. Since 2002 he has been full professor of theoretical condensed matter physics at the University of Cagliari (I) and since 2015 fellow of the 'Istituto Lombardo—Accademia di Scienze e Lettere' (Milano, I). He has been the principal investigator of several research projects addressed to solid-state and materials physics problems, the supervisor of more than 80 students (at bachelor, master, and PhD level), and the mentor of about 20 post-docs. He is the author, or coauthor, of more than 250 scientific articles and 6 books. More about him can be found at: http://people.unica.it/lucianocolombo.

Presentation of the 'Primer series'

This is the first volume of a series of three books that, as a whole, account for an introduction to the huge field usually referred to as 'condensed matter physics': they are respectively addressed to atomic and molecular physics, to solid state physics, and to statistical methods for the description of classical or quantum ensembles of particles. They are based on my 20 year experience of teaching undergraduate courses on these topics for bachelor-level programs in physical and engineering sciences at the University of Cagliari (Italy).

The volumes are called 'Primers' to underline that the pedagogical aspects have been privileged over those of completeness. In particular, I selected the contents of each volume so to keep limited its number of pages and so that the topics actually covered correspond to the *syllabus* of a typical one-semester course.

More important, however, was the choice of the style of presentation: I wanted to avoid an excessively formal treatment, preferring instead the exploration of the underlying physical features and always placing phenomenology at the centre of the discussion. More specifically, the main characteristics of this book series are:

- emphasis is always given to the physical content, rather than to formal proofs, i.e. mathematics is kept at the minimum level possible, without affecting rigour or clear thinking;
- an in-depth analysis is presented about the merits and faults of any approximation used, incorporating as well a thorough discussion of the conceptual framework supporting any adopted physical model;
- prominence is always on the underlying physical basis or principle, rather than to applications;
- when discussing the proposed experiments, the focus is given to their conceptual background, rather than to the details of the instrumental setup.

Despite the tutorial approach, I nevertheless wanted to follow the Italian academic tradition, which provides even the elementary introduction to condensed matter physics at a quantum level. I hope that my efforts have optimally combined ease-of-access and rigour, especially conceptual.

The intentionally non-encyclopaedic content and the tutorial character of these 'Primers' should facilitate their use even for students not specifically enrolled in a university *curriculum* in physics. I hope, in particular, that my textbooks could be accessible to students in chemistry, materials science and also of many engineering branches. In view of this, I have included a brief outline of non-relativistic quantum mechanics in the first 'Primer', a subject that does not appear in the typical engineering *curricula*. For the rest, classical mechanics, elementary thermodynamics and Maxwell theory of electromagnetism are used, to which all students of natural and engineering sciences are normally exposed.

Each 'Primer' is organised in parts, divided into chapters. This structure is tailored to facilitate the planning of a one-semester course: these volumes aim at

being their main teaching tool. More specifically, each part identifies an independent teaching module, while each chapter corresponds to about two weeks of lecturing.

I cannot conclude this general introduction without thanking the many students who, over the years, have attended my courses in condensed matter physics at the University of Cagliari. Through the continuous exchange of ideas with them I have gradually understood how best to organise my teaching and the corresponding study material. As a matter of fact, the contents that I have collected in these volumes were born from this very fruitful dialogue.

Luciano Colombo
Cagliari, June 2019

Introduction to: 'Atomic and Molecular Physics: a primer'

Atoms are the basic building blocks of any material system: their physics rules over the behaviour of basically everything. Therefore, even if we limit ourselves to just consider what is found on our planet, the atomistic picture is really needed to understand at the most fundamental level the physical behaviour of organic and inorganic matter, biological molecules and systems, as well as geological materials.

Accordingly, some substantial basic notion on atomic physics must be recognised as inalienable from a modern undergraduate course in physics, as well as in materials science, chemistry, and, likely, engineering too. Since the first step in atomic aggregation consists in the formation of molecules, any tutorial introduction to the topic must also necessarily contain an introduction to molecular physics.

This state of affairs defines the main goal of this volume, namely: to present a modern and unified tutorial account of the fundamental physics of atoms and molecules. A modern approach does require the use of quantum mechanics, while a unified perspective dictates looking at a molecule as a bound system of atoms, still retaining some of their properties. Both features are fully exploited in this volume.

This Primer is divided into three parts: the first one provides a brief historical introduction on early atomic physics and outlines the kernel of non-relativistic quantum mechanics, the second one is addressed to atomic physics, and the third one deals with molecules. Eight appendices are added to the text, each focussed on some technical development which, at first reading, can be skipped without compromising the general understanding of the arguments developed in the main text. A bibliography is added to each chapter as a guideline for further reading.

The volume contains many figures, most of which are 'conceptual', i.e. they are basically intended to provide a graphical representation of the main ideas and concepts developed in the written part. Tables with numerical values of important physical properties are included as well, in the attempt to provide the reader with information useful to 'quantify' the physical results presented. Finally, a list of all the mathematical symbols used in the volume is given at the beginning as an orientation guide while reading.

List of symbols

α	fine structure constant
$\alpha(\omega)$	absorption coefficient (Beer law)
α_{elec}	electric dipole polarizability
α_{hf}	hyperfine splitting constant
Γ	loss factor of a LASER device
ε_0	vacuum permittivity
μ_{B}	electron Bohr magneton
μ_{N}	nuclear magneton
μ_0	vacuum permeability
ζ	atomic valence
$\xi(r)$	spin–orbit coupling constant (hydrogenic atoms)
ξ_{LL}	orbit–orbit coupling constant (vector model of the atom)
ξ_{LS}	spin–orbit coupling constant (vector model of the atom)
ξ_{SS}	spin–spin coupling constant (vector model of the atom)
$\phi_{nlm}(\mathbf{r})$	Slater-type orbital
$\varphi(\mathbf{r})$	single-electron spin-orbital
χ_{A}	antisymmetric total spin wavefunction of an electron system
χ_{S}	symmetric total spin wavefunction of an electron system
$\psi_{\text{ab}}(\mathbf{r})$	anti-bonding molecular orbital
$\psi_{\text{b}}(\mathbf{r})$	bonding molecular orbital
$\psi_{nlm_l}(\mathbf{r})$	single-electron hydrogenic wavefunction
$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots)$	generic total space wavefunction of an electron system
Ψ_{A}	antisymmetric total space wavefunction of an electron system
Ψ_{S}	symmetric total space wavefunction of an electron system
ω_0	fundamental oscillation frequency of a diatomic molecule (harmonic approximation)
a_0	Bohr radius
A	mass number
$\mathbf{A}$	vector potential for the electromagnetic field
A_{21}	Einstein coefficient for spontaneous emission
B	rotational constant in a diatomic molecule
B_{12}	Einstein coefficient for stimulated absorption
B_{21}	Einstein coefficient for stimulated emission
c	speed of light
d_{elec}	induced electric dipole moment
e	electron charge (absolute value)
E_{ab}	molecular energy in an anti-bonding state
E_{b}	molecular energy in a bonding state
E_{diss}	dissociation energy of a diatomic molecule
$E_{\text{e}}^{(\mathbf{R})}$	electronic energy of a molecule in the nuclear configuration $\mathbf{R}$
E_{GS}	ground state energy (both in atomic and molecular systems)
E_{n}	nuclear (vibrational+rotational) energy of a molecule
E_{so}	spin–orbit interaction energy
$E_{\text{p}}(R)$	potential energy of a diatomic molecule (R is the internuclear distance)
E_{rot}	rotational energy of a molecule
E_{vib}	vibrational energy of a molecule
E_{T}	total energy of a molecule

F	Faraday constant
g_j	Lande' g-factor
g_{L}	orbital g-factor
g_{N}	nuclear g-factor
g_{S}	spin g-factor
$G(\omega)$	gain factor of a LASER device
h	Planck constant
$\hbar$	$\hbar = h/2\pi$
H_{AA}	Coulomb integral in a diatomic molecule
H_{AB}	resonance integral in a diatomic molecule
I	moment of inertia of a molecule
$I_{\alpha}^{1\mathrm{b}}$	single-electron Hartree–Fock integral
$I_{\alpha\beta}^{2\mathrm{b,d}}$	two-electron Hartree–Fock integral (direct term)
$I_{\alpha\beta}^{2\mathrm{b,ex}}$	two-electron Hartree–Fock integral (exchange term)
$I_{nl,n'l'}$	Coulomb integral calculated for the pair of nl and $n'l'$ hydrogenic states
j	total angular momentum quantum number (single electron)
j_{tot}	total angular momentum quantum number for the full set of electrons
$\mathbf{J}$	total (orbital+spin) angular momentum vector (single electron)
$\mathbf{J}_{\mathrm{tot}}$	total (orbital+spin) angular momentum vector for the full set of electrons
$\mathbf{k}$	wavevector of an electromagnetic wave
k_{B}	Boltzmann constant
$K_{nl,n'l'}$	exchange integral calculated for the pair of nl and $n'l'$ hydrogenic states
l	orbital angular momentum quantum number (single electron)
l_{tot}	total orbital angular momentum quantum number for the full set of electrons
$\mathbf{L}$	orbital angular momentum vector (single electron)
L_z	z-component of the orbital angular momentum vector (single electron)
$\mathbf{L}_{\mathrm{tot}}$	total orbital angular momentum vector for the full set of electrons
m_l	orbital magnetic quantum number (single electron)
$m_{l_{\mathrm{tot}}}$	total orbital magnetic quantum number for the full set of electrons
m_{e}	electron mass
m_{p}	proton mass
m_s	spin magnetic quantum number (single electron)
$m_{s_{\mathrm{tot}}}$	total spin magnetic quantum number for the full set of electrons
$\mathbf{M}_{\mathrm{L}}$	orbital magnetic moment vector (single electron)
$\mathbf{M}_{\mathrm{L}_{\mathrm{tot}}}$	total orbital magnetic moment vector for the full set of electrons
$\mathbf{M}_{\mathrm{N}}$	nuclear magnetic moment vector of an atom
$\mathbf{M}_{\mathrm{S}}$	spin (or intrinsic) magnetic moment vector (single electron)
$\mathbf{M}_{\mathrm{S}_{\mathrm{tot}}}$	total spin (or intrinsic) magnetic moment vector for the full set of electrons
$\mathbf{M}_{\mathrm{J}_{\mathrm{tot}}}$	total magnetic moment vector of an atom (electron contribution)
$n^{2S+1}L_J$	spectroscopic symbol for atomic levels (with $n = 1, 2, 3, \ldots$ and $L = S, P, D, \ldots$)
n_{d}	degree of degeneracy of an hydrogen quantum state
$\mathbf{N}$	total nuclear angular momentum vector of an atom
$\mathcal{N}_{\mathrm{A}}$	Avogadro number
$P_{nl}(r)$	radial distribution function (or radial probability)
$\mathcal{P}_{1\to 2}$	probability per unit time for a quantum transition from state '1' to state '2'
$R_{nl}(r)$	hydrogen radial wavefunction
$\bar{R}_{nl}(r)$	radial central-field wavefunction in a multi-electron atom

$\mathcal{R}_{\mathrm{H}}$	Rydberg constant for the hydrogen atom (infinite nuclear mass approximation)
$\bar{\mathcal{R}}_{\mathrm{H}}$	Rydberg constant for the hydrogen atom with finite nuclear mass
s	spin quantum number (single electron)
s_{tot}	total spin quantum number for the full set of electrons
$\mathbf{S}$	spin angular momentum vector (single electron)
S_z	z-component of the spin angular momentum vector (single electron)
S_{AB}	overlap integral in a diatomic molecule
$\mathbf{S}_{\mathrm{tot}}$	total spin angular momentum vector for the full set of electrons
V_{cf}	central-field potential
V_{ee}	electron–electron Coulomb interaction potential
V_{ne}	nucleus–electron Coulomb interaction potential
V_{nn}	nucleus–nucleus Coulomb interaction potential
V_{TF}	Thomas–Fermi potential
w	atomic weight
W_α	ionisation work (electron accommodated on the φ_α spin-orbital)
$Y_{lm_l}(\theta, \phi)$	spherical harmonic function
Z	atomic number