# *Laser-Molecule Interaction*

## *Laser Physics and Molecular Nonlinear Optics*

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# LASER-MOLECULE INTERACTION

The discovery of laser technology a few short decades ago has revolutionized both science and industry, paving the way for a growing number of practical applications in all aspects of daily life. This developing interest in expanding the potential of laser physics has resulted in an important new focus on light-matter interaction and given rise to the field of *nonlinear optics.*

*Laser-Molecule Interaction* presents the first cohesive treatment of both the fundamentals of laser science and the study of nonlinear optics. The authors, Jean René Lalanne, André Ducasse, and Stanisław Kielich, are pioneers in the field who have contributed greatly to the study of the interaction of lasers with matter and its practical applications in the world.

An important new approach to the study of laser physics and molecular nonlinear optics, *Laser-Molecule Interaction* provides easy access to complex concepts in both an analytical and uniquely practical way. Because mastery of laser-matter interaction requires knowledge in three fields of physics, the authors begin with a broad review of quantum mechanics, tensor calculus, and statistical physics, followed by an in-depth treatment of the operation and properties of the laser. This combined knowledge is then applied to the study of laser-molecule interaction and its implications for the future of nonlinear optics.

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Throughout the text, chapters are logically organized to provide a quick, complete reference on all aspects of laser-molecule interaction and on related linear and nonlinear processes. Important concepts are reinforced by 35 original problems with solutions, which allow readers to test their understanding of the subject matter and optimize their progress.

Designed for scientists, engineers, and advanced students in physics, chemical physics, and laser research, *Laser-Molecule Interaction* serves as an excellent self-teaching book, classroom text, or reference source.

**About the authors**

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# *Foreword*

While as far as we know, lasers have been with us for only a few decades, nonlinear optics has been part of our world since the beginning. The domain has never been as lively, exciting, and promising as it is now. Some of the most fundamental concepts, such as, the requirement of a population inversion for lasers are shaken, and the first experimental demonstrations are on their way. A larger number of techniques have now been perfected to the point of becoming the essential laboratory tools as well as the key components of a growing field of applications ranging from telecommunications to medical diagnostics and therapeutics.

The studies of nonlinear optics have really started with the discovery of the laser, and while most of the individuals who were part of the pioneering efforts are still with us, at least three new generations of researchers and engineers have joined over the years. Every day adds another family of new young investigators eager to push the limits, exercise their creativity, and add their contribution to the field. The industry that has developed around the discoveries in the field is finally reaching maturity, and the demand for highly qualified engineers is growing every day.

The authors of this book recognized these needs two decades ago. Their interest and motivation to educate at all levels ranging from undergraduate to seasoned engineers has been constant since then. This interest is illustrated by the numerous lectures, topic schools, and teaching materials that they have developed and continuously improved during their long collaboration. Their book *Laser Molecule Interaction* reflects the passion to educate demonstrated by Jean-René, André, and Stanislaw. It represents the results of numerous, sometimes extremely challenging discussions on the basic concepts and of better ways to introduce them. The content of this book is also the result of a constant challenge and critique by the two generations of students that have been exposed to the material presented. As a former colleague and occasional participant in the discussions and lectures, I am delighted to finally see that the authors have decided to broaden their audience by publishing the results of their long effort in an original book.

If this book allows a better and faster understanding of sometimes difficult concepts, triggers motivation, and develops an increased interest of the reader to the field of nonlinear optics, as I am firmly convinced that it will, the authors will have reached their longstanding goal. I wish them success, and I also hope that the reader will find as much interest and fun reading this book as I have experienced while sharing many years of my professional life with the authors.

BERNARD COUILLAUD

*Coherent Inc.*
*March 1995*

# *Preface*

Light-matter interaction is now a privileged field of physics. The invention of the *laser* in 1959 has greatly contributed to the highly spectacular development of this field during the past 30 years. In particular, the first observation of coherent generation of a harmonic optical wave by P. A. Franken in 1961 gave rise to a novel optics—*nonlinear optics*—the unceasing development of which has achieved remarkable proportions in the domain of fundamental research as well as in that of practical applications. Thus, there is no exaggeration in the statement that the applications of the laser and nonlinear optics extend to practically all the domains of science and technology (in 1992, the laser market has exceeded the "gigadollar" level). This remarkable diversity of applications has resulted in an unceasing growth of the number of scientific publications and international conferences; many researchers in a great variety of specialities have become directly involved in nonlinear optics—often like Monsieur Jourdain,* speaking in prose unwittingly!

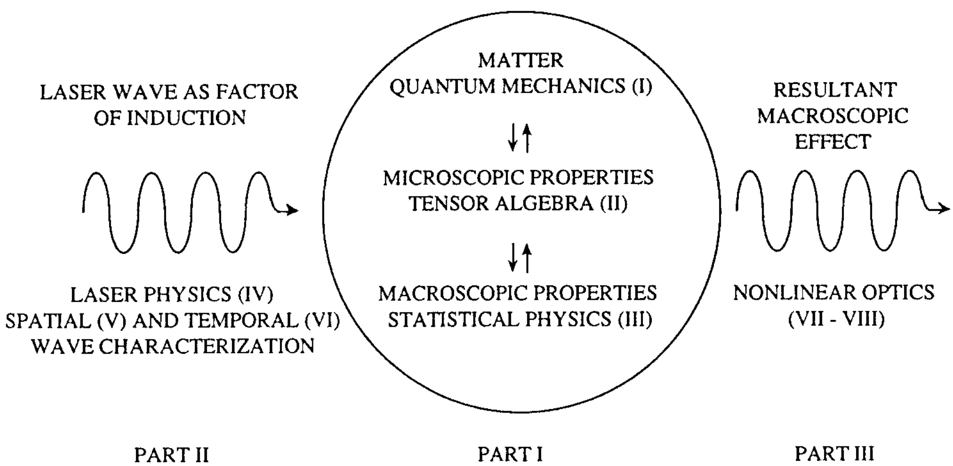
In 1970, when one of us (SK) had been invited as Associated Professor to Bordeaux University 1, we profited by our activities in fundamental research, often led jointly and always directed toward the laser and its interaction with matter, to promote a line of training in laser science and nonlinear optics. Thus, in the course of 25 years, we have contributed to the education and updating of about a thousand teachers (of the universities and other higher education establishments) as well as researchers and engineers. It is just this experience in teaching, summarized in the publication of a monograph by one of us (JRL) as the result of courses read at the Commissariat à l'Energie Atomique, that we now propose to transmit more widely by way of the present book, characterized as follows:

- This book is primarily intended for students of the second and third cycles of universities and schools of engineering. More exactly, we have written it essentially for the use of students preparing doctoral theses in *Chemical Physics*. Certainly, too, it will also prove useful for students of physics and junior researchers as an introductory handbook on the laser and its interaction with matter and, obviously, for wider circles of readers, many

*Molière, in *Le Bourgeois gentilhomme*.

of whom have already visited our laboratories, with the aim of obtaining first-hand knowledge of the laser, its operation, and possibilities.

- It is by no means conceived as an exhaustive presentation of nonlinear optics; in fact, there exist about a dozen books in English, written for physicists, which the reader will find cited in our bibliography. However, they consistently deal *either* with the laser *or* with nonlinear optics. We, on the other hand, have preferred *to deal with these two subjects jointly* since they are inseparable in practice. We have thus decided to restrict ourselves to the presentation of only certain examples characteristic of the very numerous nonlinear "effects" induced by lasers. Moreover, with regard to the specific requirements of the readers for whom our book is destined, we have decided to give priority to examples of *laser-molecule interaction*, which we chose for the title of our book.
- The book is intended to be *self-consistent*. Correct mastery of laser-matter interaction presupposes the acquisition of knowledge in three fields of physics; thus, the reader will be presented with the fundamentals of quantum mechanics, tensor calculus, and statistical physics as they intervene throughout our book and with a necessarily limited list of works of reference on these subjects which, if needed, may help the general reader to achieve a better assessment of laser technique.
- The few works of reference cited in each chapter fall into two categories: (1) basic works on the subject dealt with in the respective chapter, and (2) introductory articles in published widely read reviews such as *La Recherche*, *Physics Today*, or *Laser Focus World*. The references cited in the second category will direct the reader wishing for further specialization to the many original scientific papers produced in the course of all these years, the perusal of which is, in many cases, by no means easy.
- Our book contains about *35 original problems together with their solutions*, thereby providing the student with a handy tool for testing his or her newly acquired knowledge and also constituting a valuable addition to the examples discussed in the text. The book is conceived as follows:



The roman numbers in parentheses denote the chapters. The three parts are of equal length.

Part I provides a partial review of the description of microsystems and an introduction to their nonlinear optical properties. Chapter I gives quantum mechanical description of the microsystem in the absence of a laser wave, first isolated then in interaction with its environment. Chapter II contains an introduction to nonlinear optics starting from a *tensorial description* of the optical properties of microsystems. Susceptibility tensors are discussed as to their structure and reduction. The tensorial expressions for electric n-poles and the fields radiated by them are presented. Chapter III is devoted to the transition from the microscopic to the macroscopic. The fundamentals of *statistical physics* are reviewed briefly. The calculation of the mean values of tensorial quantities at thermal equilibrum is performed on a variety of examples leading to the description of spherically symmetric (isotropic) macroscopic systems. Thus, at the end of Part I, the reader may have become familiar with the tensorial description of the optical properties of matter and acquired mastery of the mathematical and physical concepts and procedures that will enable him to start on the study of laser waves and their properties in applications to macroscopic systems.

Part II, which comprises Chapters IV, V, and VI, deals with the *laser*. In Chapter IV, its operation and the properties of fundamental wave emitted are discussed on the basis of Einstein's phenomenological approach of wave-matter amplifying interaction. Chapter V deals with the *spatial properties* of the laser wave related to the geometry of the cavity containing the amplifying medium, as well as the surface and angular energy concentrations one can obtain using the transformations undergone by laser beams when traveling through. Chapter VI gives a presentation of *different types of laser operation* (continuous-wave and pulsed) and of the *time structure* of the waves. The parameter *time* is given the attention it deserves with regard to its very important role in laser physics, particularly in the time-resolved spectroscopy and in physics of high intensities. We expect Part II may provide the reader with sufficient experimental mastery of optical sources—by no means a matter of just "pressing the right switch" but often requiring optimization in the course of experiment.

In Part III the results already established are combined to give a basic treatment of laser-molecule interaction. Chapter VII is devoted to the application of the density operator formalism to *stationary resonant laser-molecule interaction* in a semiclassical approach in which the laser wave is treated classically whereas the material system is dealt with in accordance with quantum mechanics. Expressions for the nonlinear polarization, susceptibility, and light refractive index are derived and their applications in Lamb laser theory, saturated absorption spectroscopy, and laser manipulation of microscopic systems are discussed. Finally, Chapter VIII is entirely devoted to a presentation of *nth-order susceptibility*. Its properties are made apparent in some examples of nonlinear interaction involving weak and strong as well as stationary and nonstationary energy transfer, such as harmonics generation and scattering, optical Kerr effect, degenerate four-wave mixing, and photon echo.

Inevitably, our book is the result of a compromise: In our attempts to adhere throughout to the level of principles, we deliberately limited the subject matter and sacrificed bulk in order to achieve better understanding. We hope that our book, which is of the nature of an introduction, may stimulate the reader to supplementary, more highly specialized studies.

We wish to express our indebtedness to B. Couillaud, our longtime friend and associate; to all our colleagues teaching within the curriculum on lasers; to F. Boisard, who enabled us to set up this line of teaching; and to B. Veyret and R. Perrier, who have helped us on many occasions. Also, we wish to thank N. Robineau who prepared the manuscript for the printers. The authors would also like to gratefully acknowledge K. Flatau, their friend, for his help in the preparation of Part I of this book.

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