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# Springer Handbook

of Atomic, Molecular,  
and Optical Physics

Gordon W. F. Drake (Ed.)

With CD-ROM, 288 Figures and 111 Tables



Springer

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Editor:  
Dr. Gordon W. F. Drake  
Department of Physics  
University of Windsor  
Windsor, Ontario N9B 3P4  
Canada

Assistant Editor:  
Dr. Mark M. Cassar  
Department of Physics  
University of Windsor  
Windsor, Ontario N9B 3P4  
Canada

Library of Congress Control Number: 2005931256

ISBN-10: 0-387-20802-X e-ISBN: 0-387-26308-X  
ISBN-13: 978-0-387-20802-2 Printed on acid free paper

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Printed in Germany.

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Production and typesetting: LE-TeX GbR, Leipzig  
Handbook coordinator: Dr. W. Skolaut, Heidelberg  
Typography, layout and illustrations: schreiberVIS, Seeheim  
Cover design: eStudio Calamar Steinen, Barcelona  
Cover production: *design&production* GmbH, Heidelberg  
Printing and binding: Stürtz GmbH, Würzburg

SPIN 10948934 100/3141/YL 5 4 3 2 1 0

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# Handbook of Atomic, Molecular, and Optical Physics

*Editor*

**Gordon W. F. Drake**

Department of Physics, University of Windsor, Windsor, Ontario, Canada  
gdrake@uwindsor.ca

*Assistant Editor*

**Mark M. Cassar**

Department of Physics, University of Windsor, Windsor, Ontario, Canada  
cassar@uwindsor.ca

*Advisory Board*

**William E. Baylis** – Atoms

Department of Physics, University of Windsor, Windsor, Ontario, Canada  
baylis@uwindsor.ca

**Robert N. Compton** – Scattering, Experiment

Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA  
ahd@ornl.gov

**M. Raymond Flannery** – Scattering, Theory

School of Physics, Georgia Institute of Technology, Atlanta, Georgia, USA  
flannery@eikonol.physics.gatech.edu

**Brian R. Judd** – Mathematical Methods

Department of Physics, The Johns Hopkins University, Baltimore, Maryland, USA  
juddbr@pha.jhu.edu

**Kate P. Kirby** – Molecules, Theory

Harvard-Smithsonian Center for Astrophysics, Cambridge, Massachusetts, USA  
kirby@cfa.harvard.edu

**Pierre Meystre** – Optical Physics

Optical Sciences Center, The University of Arizona, Tucson, Arizona, USA  
pierre@rhea.opt-sci.arizona.edu

## Foreword by Herbert Walther

The Handbook of Atomic, Molecular and Optical (AMO) Physics gives an in-depth survey of the present status of this field of physics. It is an extended version of the first issue to which new and emerging fields have been added. The selection of topics thus traces the recent historic development of AMO physics. The book gives students, scientists, engineers, and other interested people a comprehensive introduction and overview. It combines introductory explanations with descriptions of phenomena, discussions of results achieved, and gives a useful selection of references to allow more detailed studies, making the handbook very suitable as a desktop reference.

AMO physics is an important and basic field of physics. It provided the essential impulse leading to the development of modern physics at the beginning of the last century. We have to remember that at that time not every physicist believed in the existence of atoms and molecules. It was due to Albert Einstein, whose work we commemorate this year with the world year of physics, that this view changed. It was Einstein's microscopic view of molecular motion that led to a way of calculating Avogadro's number and the size of molecules by studying their motion. This work was the basis of his PhD thesis submitted to the University of Zurich in July 1905 and after publication became Einstein's most quoted paper. Furthermore, combining kinetic theory and classical thermodynamics led him to the conclusion that the displacement of a microparticle in Brownian motion varies as the square root of time. The experimental demonstration of this law by Jean Perrin three years later finally afforded striking proof that atoms and molecules are a reality. The energy quantum postulated by Einstein in order to explain the photoelectric effect was the basis for the subsequently initiated development of quantum physics, leading to a revolution in physics and many new applications in science and technology.

The results of AMO physics initiated the development of quantum mechanics and quantum electro-

dynamics and as a consequence led to a better understanding of the structure of atoms and molecules and their respective interaction with radiation and to the attainment of unprecedented accuracy. AMO physics also influenced the development in other fields of physics, chemistry, astronomy, and biology. It is an astonishing fact that AMO physics constantly went through periods where new phenomena were found, giving rise to an enormous revival of this area. Examples are the maser and laser and their many applications, leading to a better understanding of the basics and the detection of new phenomena, and new possibilities such as laser cooling of atoms, squeezing, and other nonlinear behaviour. Recently, coherent interference effects allowed slow or fast light to be produced. Finally, the achievement of Bose–Einstein condensation in dilute media has opened up a wide range of new phenomena for study. Special quantum phenomena are leading to new applications for transmission of information and for computing. Control of photon emission through specially designed cavities allows controlled and deterministic generation of photons opening the way for a secure information transfer.

Further new possibilities are emerging, such as the techniques for producing attosecond laser pulses and laser pulses with known and controlled phase relation between the envelope and carrier wave, allowing synthesis of even shorter pulses in a controlled manner. Furthermore, laser pulses may soon be available that are sufficiently intense to allow polarization of the vacuum field. Another interesting development is the generation of artificial atoms, e.g., quantum dots, opening a field where nanotechnology meets atomic physics. It is thus evident that AMO physics is still going strong and will also provide new and interesting opportunities and results in the future.



**Prof. Dr. Herbert Walther**

## Preface

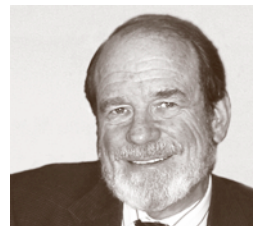
The year 2005 has been officially declared by the United Nations to be the International Year of Physics to commemorate the three famous papers of Einstein published in 1905. It is a fitting tribute to the impact of his work that the *Springer Handbook of Atomic, Molecular, and Optical Physics* should be published in coincidence with this event. Virtually all of AMO Physics rests on the foundations established by Einstein in 1905 (including a fourth paper on relativity and his thesis) and his subsequent work. In addition to the theory of relativity, for which he is best known, Einstein ushered in the era of quantum mechanics with his explanation of the photoelectric effect, and he demonstrated the influence of molecular collisions with his explanation of Brownian motion. He also laid the theoretical foundations for all of laser physics with his discovery (in 1917) of the necessity of the process of stimulated emission, and his discussions of the Einstein–Podolsky–Rosen Gedanken experiment (in 1935) led, through Bell’s inequalities, to current work on entangled states and quantum information. The past century has been a Golden Age for physics in every sense of the term.

Despite this history of unparalleled progress, the field of AMO Physics continues to advance more rapidly than ever. At the time of publication of an earlier Handbook published by AIP Press in 1996 I wrote “The ever increasing power and versatility of lasers continues to open up new areas for study.” Since then, two Nobel Prizes have been awarded for the cooling and trapping of atoms with lasers (Steven Chu, Claude Cohen-Tannoudji, William D. Phillips in 1997), and for the subsequent achievement of Bose–Einstein condensation in a dilute gas of trapped atoms (Eric A. Cornell, Wolfgang Ketterle, Carl E. Wieman in 2001). Although the topic of cooling and trapping was covered in the AIP Handbook, Bose–Einstein condensation was barely mentioned. Since then, the literature has exploded to nearly 2500 papers on Bose–Einstein condensation alone. Similarly, the topics of quantum information and quantum computing barely existed in 1995, and have since become rapidly growing segments of the physics literature. Entirely new topics such as “fast light” and “slow light” have emerged. Techniques for both

high precision theory and measurement are opening the possibility to detect a cosmological variation of the fundamental constants with time. All of these topics hold the promise of important engineering and technological applications that come with advances in fundamental science. The more established areas of AMO Physics continue to provide the basic data and broad understanding of a great wealth of underlying processes needed for studies of the environment, and for astrophysics and plasma physics.

These changes and advances provide more than sufficient justification to prepare a thoroughly revised and updated *Atomic, Molecular and Optical Physics Handbook* for the Springer Handbook Program. The aim is to present the basic ideas, methods, techniques and results of the field at a level that is accessible to graduate students and other researchers new to the field. References are meant to be a guide to the literature, rather than a comprehensive bibliography. Entirely new chapters have been added on Bose–Einstein condensation, quantum information, variations of the fundamental constants, and cavity ring-down spectroscopy. Other chapters have been substantially expanded to include new topics such as fast light and slow light. The intent is to provide a book that will continue to be a valuable resource and source of inspiration for both students and established researchers.

I would like to acknowledge the important role played by the members of the Advisory Board in their continuing support of this project, and I would especially like to acknowledge the talents of Mark Cassar as Assistant Editor. In addition to keeping track of the submissions and corresponding with authors, he read and edited the new material for every chapter to ensure uniformity in style and scientific content, and he composed new material to be added to some of the chapters, as noted in the text.



Prof. Gordon W. F. Drake

February 2005

Gordon W. F. Drake

---

## List of Authors

**Nigel G. Adams**

University of Georgia  
Department of Chemistry  
Athens, GA 30602-2556, USA  
e-mail: [adams@chem.uga.edu](mailto:adams@chem.uga.edu)

**Miron Ya. Amusia**

The Hebrew University  
Racah Institute of Physics  
Jerusalem, 91904, Israel  
e-mail: [amusia@vms.huji.ac.il](mailto:amusia@vms.huji.ac.il)

**Nils Andersen**

University of Copenhagen  
Niels Bohr Institute  
Universitetsparken 5  
Copenhagen, DK-2100, Denmark  
e-mail: [noa@fys.ku.dk](mailto:noa@fys.ku.dk)

**Nigel R. Badnell**

University of Strathclyde  
Department of Physics  
Glasgow, G40NG, United Kingdom  
e-mail: [n.r.badnell@strath.ac.uk](mailto:n.r.badnell@strath.ac.uk)

**Thomas Bartsch**

Georgia Institute of Technology  
School of Physics  
837 State Street  
Atlanta, GA 30332-0430, USA  
e-mail: [bartsch@cns.physics.gatech.edu](mailto:bartsch@cns.physics.gatech.edu)

**Klaus Bartschat**

Drake University  
Department of Physics and Astronomy  
Des Moines, IA 50311, USA  
e-mail: [klaus.bartschat@drake.edu](mailto:klaus.bartschat@drake.edu)

**William E. Baylis**

University of Windsor  
Department of Physics  
Windsor, ON N9B 3P4, Canada  
e-mail: [baylis@uwindsor.ca](mailto:baylis@uwindsor.ca)

**Anand K. Bhatia**

NASA Goddard Space Flight Center  
Laboratory for Astronomy & Solar Physics  
Code 681, UV/Optical Astronomy Branch  
Greenbelt, MD 20771, USA  
e-mail: [anand.k.bhatia@nasa.gov](mailto:anand.k.bhatia@nasa.gov)

**Hans Bichsel**

University of Washington  
Center for Experimental Nuclear Physics and  
Astrophysics (CENPA)  
1211 22nd Avenue East  
Seattle, WA 98112-3534, USA  
e-mail: [bichsel@npl.washington.edu](mailto:bichsel@npl.washington.edu)

**Robert W. Boyd**

University of Rochester  
Department of Physics and Astronomy  
Rochester, NY 14627, USA  
e-mail: [boyd@optics.rochester.edu](mailto:boyd@optics.rochester.edu)

**John M. Brown**

University of Oxford  
Physical and Theoretical Chemistry Laboratory  
South Parks Road  
Oxford, OX1 3QZ, England  
e-mail: [john.m.brown@chem.ox.ac.uk](mailto:john.m.brown@chem.ox.ac.uk)

**Henry Buijs**

ABB Bomem Inc.  
585, Charest Boulevard East  
Suite 300  
Québec, PQ G1K 9H4, Canada  
e-mail: [henry.l.buijs@ca.abb.com](mailto:henry.l.buijs@ca.abb.com)

**Philip Burke**

The Queen's University of Belfast  
Department of Applied Mathematics  
and Theoretical Physics  
Belfast, Northern Ireland BT7 1NN, UK  
e-mail: [p.burke@qub.ac.uk](mailto:p.burke@qub.ac.uk)



**Denise Caldwell**

National Science Foundation  
Physics Division  
4201 Wilson Boulevard  
Arlington, VA 22230, USA  
e-mail: [dcaldwel@nsf.gov](mailto:dcaldwel@nsf.gov)

**Mark M. Cassar**

University of Windsor  
Department of Physics  
Windsor, ON N9B 3P4, Canada  
e-mail: [cassar@uwindsor.ca](mailto:cassar@uwindsor.ca)

**Kelly Chance**

Harvard-Smithsonian Center for Astrophysics  
60 Garden Street  
Cambridge, MA 02138-1516, USA  
e-mail: [kchance@cfa.harvard.edu](mailto:kchance@cfa.harvard.edu)

**Raymond Y. Chiao**

366 Leconte Hall  
U.C. Berkeley  
Berkeley, CA 94720-7300, USA  
e-mail: [chiao@physics.berkeley.edu](mailto:chiao@physics.berkeley.edu)

**Lew Cocke**

Kansas State University  
Department of Physics  
Manhattan, KS 66506, USA  
e-mail: [cocke@phys.ksu.edu](mailto:cocke@phys.ksu.edu)

**James S. Cohen**

Los Alamos National Laboratory  
Atomic and Optical Theory  
Los Alamos, NM 87545, USA  
e-mail: [cohen@lanl.gov](mailto:cohen@lanl.gov)

**Bernd Crasemann**

University of Oregon  
Department of Physics  
Eugene, OR 97403-1274, USA  
e-mail: [berndc@uoregon.edu](mailto:berndc@uoregon.edu)

**David R. Crosley**

SRI International  
Molecular Physics Laboratory  
333 Ravenswood Ave., PS085  
Menlo Park, CA 94025-3493, USA  
e-mail: [david.crosley@sri.com](mailto:david.crosley@sri.com)

**Derrick Crothers**

Queen's University Belfast  
Department of Applied Mathematics and  
Theoretical Physics  
University Road  
Belfast, Northern Ireland BT7 1NN, UK  
e-mail: [d.crothers@qub.ac.uk](mailto:d.crothers@qub.ac.uk)

**Lorenzo J. Curtis**

University of Toledo  
Department of Physics and Astronomy  
2801 West Bancroft Street  
Toledo, OH 43606-3390, USA  
e-mail: [ljc@physics.utoledo.edu](mailto:ljc@physics.utoledo.edu)

**Alexander Dalgarno**

Harvard-Smithsonian Center for Astrophysics  
60 Garden Street  
Cambridge, MA 02138, USA  
e-mail: [adalgarno@cfa.harvard.edu](mailto:adalgarno@cfa.harvard.edu)

**Abigail J. Dobbyn**

Max-Planck-Institut für Strömungsforschung  
Göttingen, 37073, Germany

**Gordon W. F. Drake**

University of Windsor  
Department of Physics  
401 Sunset St.  
Windsor, ON N9B 3P4, Canada  
e-mail: [gdrake@uwindsor.ca](mailto:gdrake@uwindsor.ca)

**Joseph H. Eberly**

University of Rochester  
Department of Physics and Astronomy  
and Institute of Optics  
Rochester, NY 14627-0171, USA  
e-mail: [eberly@pas.rochester.edu](mailto:eberly@pas.rochester.edu)

**Guy T. Emery**

Bowdoin College  
Department of Physics  
15 Chestnut Rd.  
Brunswick, ME 04011, USA  
e-mail: [gemery@bowdoin.edu](mailto:gemery@bowdoin.edu)

**Volker Engel**

Universität Würzburg  
Institut für Physikalische Chemie  
Am Hubland  
Würzburg, 97074, Germany  
e-mail: [voen@phys-chemie.uni-wuerzburg.de](mailto:voen@phys-chemie.uni-wuerzburg.de)

**Paul Engelking**

University of Oregon  
Department of Chemistry  
and Chemical Physics Institute  
Eugene, OR 97403-1253, USA  
e-mail: [engelki@uoregon.edu](mailto:engelki@uoregon.edu)

**Kenneth M. Evenson<sup>†</sup>****James M. Farrar**

University of Rochester  
Department of Chemistry  
120 Trustee Road  
Rochester, NY 14627-0216, USA  
e-mail: [farrar@chem.rochester.edu](mailto:farrar@chem.rochester.edu)

**Gordon Feldman**

The Johns Hopkins University  
Department of Physics and Astronomy  
Baltimore, MD 21218-2686, USA  
e-mail: [gordon.feldman@jhu.edu](mailto:gordon.feldman@jhu.edu)

**Paul D. Feldman**

The Johns Hopkins University  
Department of Physics and Astronomy  
3400 N. Charles Street  
Baltimore, MD 21218-2686, USA  
e-mail: [pdf@pha.jhu.edu](mailto:pdf@pha.jhu.edu)

**Charlotte F. Fischer**

Vanderbilt University  
Department of Electrical Engineering  
Computer Science  
PO BOX 1679, Station B  
Nashville, TN 37235, USA  
e-mail: [charlotte.f.fischer@vanderbilt.edu](mailto:charlotte.f.fischer@vanderbilt.edu)

**Victor Flambaum**

University of New South Wales  
Department of Physics  
Sydney, 2052, Australia  
e-mail: [v.flambaum@unsw.edu.au](mailto:v.flambaum@unsw.edu.au)

**M. Raymond Flannery**

Georgia Institute of Technology  
School of Physics  
Atlanta, GA 30332-0430, USA  
e-mail: [ray.flannery@physics.gatech.edu](mailto:ray.flannery@physics.gatech.edu)

**David R. Flower**

University of Durham  
Department of Physics  
South Road  
Durham, DH1 3LE, United Kingdom  
e-mail: [david.flower@durham.ac.uk](mailto:david.flower@durham.ac.uk)

**A. Lewis Ford**

Texas A&M University  
Department of Physics  
College Station, TX 77843-4242, USA  
e-mail: [ford@physics.tamu.edu](mailto:ford@physics.tamu.edu)

**Jane L. Fox**

Wright State University  
Department of Physics  
3640 Colonel Glenn Hwy  
Dayton, OH 45419, USA  
e-mail: [jane.fox@wright.edu](mailto:jane.fox@wright.edu)

**Matthias Freyberger**

Universität Ulm  
Abteilung für Quantenphysik  
Albert Einstein Allee 11  
Ulm, 89069, Germany  
e-mail: [matthias.freyberger@uni-ulm.de](mailto:matthias.freyberger@uni-ulm.de)

**Thomas Fulton**

The Johns Hopkins University  
The Henry A. Rowland Department  
of Physics and Astronomy  
Baltimore, MD 21218-2686, USA  
e-mail: [Thomas.Fulton@jhu.edu](mailto:Thomas.Fulton@jhu.edu)

**Alexander L. Gaeta**

Cornell University  
Department of Applied and Engineering Physics  
Ithaca, NY 14853-3501, USA  
e-mail: [a.gaeta@cornell.edu](mailto:a.gaeta@cornell.edu)

**Alan Gallagher**

JILA, University of Colorado and National Institute  
of Standards and Technology  
Quantum Physics Division  
Boulder, CO 80309-0440, USA  
e-mail: [alang@jila.colorado.edu](mailto:alang@jila.colorado.edu)

**Thomas F. Gallagher**

University of Virginia  
Department of Physics  
382 McCormick Road  
Charlottesville, VA 22904-4714, USA  
e-mail: [tfg@virginia.edu](mailto:tfg@virginia.edu)

**Muriel Gargaud**

Observatoire Aquitain des Sciences de l'Univers  
2 Rue de l'Observatoire  
33270 Floirac, France  
e-mail: [gargaud@obs.u-bordeaux1.fr](mailto:gargaud@obs.u-bordeaux1.fr)

**Alan Garscadden**

Airforce Research Laboratory  
Area B  
1950 Fifth Street  
Wright Patterson Air Force Base,  
OH 45433-7251, USA  
e-mail: [alan.garscadden@wpafb.af.mil](mailto:alan.garscadden@wpafb.af.mil)

**John Glass**

British Telecommunications  
Solution Design  
Riverside Tower (pp RT03-44)  
Belfast, Northern Ireland BT1 3BT, UK  
e-mail: [john.glass@bt.com](mailto:john.glass@bt.com)

**S. Pedro Goldman**

The University of Western Ontario  
Department of Physics & Astronomy  
London, ON N6A 3K7, Canada  
e-mail: [goldman@uwo.ca](mailto:goldman@uwo.ca)

**Ian P. Grant**

University of Oxford  
Mathematical Institute  
24/29 St. Giles'  
Oxford, OX1 3LB, UK  
e-mail: [ipg@maths.ox.ac.uk](mailto:ipg@maths.ox.ac.uk)

**Donald C. Griffin**

Rollins College  
Department of Physics  
1000 Holt Ave.  
Winter Park, FL 32789, USA  
e-mail: [griffin@vanadium.rollins.edu](mailto:griffin@vanadium.rollins.edu)

**William G. Harter**

University of Arkansas  
Department of Physics  
Fayetteville, AR 72701, USA  
e-mail: [wharter@uark.edu](mailto:wharter@uark.edu)

**Carsten Henkel**

Universität Potsdam  
Institut für Physik  
Am Neuen Palais 10  
Potsdam, 14469, Germany  
e-mail: [carsten.henkel@quantum.physik.uni-potsdam.de](mailto:carsten.henkel@quantum.physik.uni-potsdam.de)

**Eric Herbst**

The Ohio State University  
Departments of Physics  
191 W. Woodruff Ave.  
Columbus, OH 43210-1106, USA  
e-mail: [herbst@mps.ohio-state.edu](mailto:herbst@mps.ohio-state.edu)

**Robert N. Hill**

355 Laurel Avenue  
Saint Paul, MN 55102-2107, USA  
e-mail: [rnhill@fishnet.com](mailto:rnhill@fishnet.com)

**David L. Huestis**

SRI International  
Molecular Physics Laboratory  
Menlo Park, CA 94025, USA  
e-mail: [david.huestis@sri.com](mailto:david.huestis@sri.com)

**Mitio Inokuti**

Argonne National Laboratory  
Physics Division  
9700 South Cass Avenue  
Building 203  
Argonne, IL 60439, USA  
e-mail: [inokuti@anl.gov](mailto:inokuti@anl.gov)

**Takeshi Ishihara**

University of Tsukuba  
Institute of Applied Physics  
Ibaraki 305  
Tsukuba, 305-8577, Japan

**Juha Javanainen**

University of Connecticut  
Department of Physics  
Unit 3046  
2152 Hillside Road  
Storrs, CT 06269-3046, USA  
e-mail: [jj@phys.uconn.edu](mailto:jj@phys.uconn.edu)

**Erik T. Jensen**

University of Northern British Columbia  
Department of Physics  
3333 University Way  
Prince George, BC V2N 4Z9, Canada  
e-mail: [ejensen@unbc.ca](mailto:ejensen@unbc.ca)

**Brian R. Judd**

The Johns Hopkins University  
Department of Physics and Astronomy  
3400 North Charles Street  
Baltimore, MD 21218, USA  
e-mail: [juddbr@pha.jhu.edu](mailto:juddbr@pha.jhu.edu)

**Alexander A. Kachanov**

Research and Development  
Picarro, Inc.  
480 Oakmead Parkway  
Sunnyvale, CA 94085, USA  
e-mail: [akachanov@picarro.com](mailto:akachanov@picarro.com)

**Isik Kanik**

California Institute of Technology  
Jet Propulsion Laboratory  
Pasadena, CA 91109, USA  
e-mail: [isik.kanik@jpl.nasa.gov](mailto:isik.kanik@jpl.nasa.gov)

**Savely G. Karshenboim**

D.I.Mendeleev Institute for Metrology (VNIIM)  
Quantum Metrology Department  
Moskovsky pr. 19  
St. Petersburg, 190005, Russia  
e-mail: [sek@mpq.mpg.de](mailto:sek@mpq.mpg.de)

**Kate P. Kirby**

Harvard-Smithsonian Center for Astrophysics  
60 Garden Street MS-14  
Cambridge, MA 02138, USA  
e-mail: [kkirby@cfa.harvard.edu](mailto:kkirby@cfa.harvard.edu)

**Sir Peter L. Knight**

Imperial College London  
Department of Physics  
Blackett Laboratory  
Prince Consort Road  
London, SW7 2BW, UK  
e-mail: [p.knight@imperial.ac.uk](mailto:p.knight@imperial.ac.uk)

**Manfred O. Krause**

Oak Ridge National Laboratory  
125 Baltimore Drive  
Oak Ridge, TN 37830, USA  
e-mail: [mok@ornl.gov](mailto:mok@ornl.gov)

**Kenneth C. Kulander**

Lawrence Livermore National Laboratory  
7000 East Ave.  
Livermore, CA 94551, USA  
e-mail: [kulander@llnl.gov](mailto:kulander@llnl.gov)

**Paul G. Kwiat**

University of Illinois at Urbana-Champaign  
Department of Physics  
1110 West Green Street  
Urbana, IL 61801-3080, USA  
e-mail: [kwiat@uiuc.edu](mailto:kwiat@uiuc.edu)

**Yuan T. Lee**

Academia Sinica  
Institute of Atomic and Molecular Science  
PO BOX 23-166  
Taipei, 106, Taiwan

**Stephen Lepp**

University of Nevada  
Department of Physics  
4505 Maryland Pkwy  
Las Vegas, NV 89154-4002, USA  
e-mail: [lepp@unlv.edu](mailto:lepp@unlv.edu)

**Maciej Lewenstein**

ICFO–Institut de Ciències Fotòniques  
C. Jordi Ginora 29 Nexus II  
Barcelona, 08034, Spain  
e-mail: [maciej.lewenstein@icfo.es](mailto:maciej.lewenstein@icfo.es)

**James D. Louck**

Los Alamos National Laboratory  
Retired Laboratory Fellow  
PO BOX 1663  
Los Alamos, NM 87545, USA  
e-mail: [jimlouck@aol.com](mailto:jimlouck@aol.com)

**Joseph H. Macek**

University of Tennessee and Oak Ridge National  
Laboratory  
Department of Physics and Astronomy  
401 Nielsen Physics Bldg.  
Knoxville, TN 37996–1200, USA  
e-mail: [jmacek@utk.edu](mailto:jmacek@utk.edu)

**Mary L. Mandich**

Lucent Technologies Inc.  
Bell Laboratories  
600 Mountain Avenue  
Murray Hill, NJ 07974, USA  
e-mail: [mandich@lucent.com](mailto:mandich@lucent.com)

**Edmund J. Mansky**

Oak Ridge National Laboratory  
Controlled Fusion Atomic Data Center  
Oak Ridge, TN 37831, USA  
e-mail: [edmundmansky@intdata.com](mailto:edmundmansky@intdata.com)

**Steven T. Manson**

Georgia State University  
Department of Physics and Astronomy  
Atlanta, GA 30303, USA  
e-mail: [smanson@gsu.edu](mailto:smanson@gsu.edu)

**William C. Martin**

National Institute of Standards and Technology  
Atomic Physics Division  
Gaithersburg, MD 20899–8422, USA  
e-mail: [wmartin@nist.gov](mailto:wmartin@nist.gov)

**Jim F. McCann**

Queen's University Belfast  
Dept. of Applied Mathematics  
and Theoretical Physics  
Belfast, Northern Ireland BT7 1NN, UK  
e-mail: [j.f.mccann@qub.ac.uk](mailto:j.f.mccann@qub.ac.uk)

**Ronald McCarroll**

Université Pierre et Marie Curie  
Laboratoire de Chimie Physique  
11 rue Pierre et Marie Curie  
75231 Paris Cedex 05, France  
e-mail: [mccarrol@ccr.jussieu.fr](mailto:mccarrol@ccr.jussieu.fr)

**Fiona McCausland**

Northern Ireland Civil Service  
Department of Enterprise Trade and Investment  
Massey Avenue  
Belfast, Northern Ireland BT4 2JP, UK  
e-mail: [fiona.mccausland@detini.gov.uk](mailto:fiona.mccausland@detini.gov.uk)

**William J. McConkey**

University of Windsor  
Department of Physics  
Windsor, ON N9B 3P4, Canada  
e-mail: [mcconk@uwindsor.ca](mailto:mcconk@uwindsor.ca)

**Robert P. McEachran**

Australian National University  
Atomic and Molecular Physics Laboratories  
Research School of Physical Sciences  
and Engineering  
Canberra, ACT 0200, Australia  
e-mail: [robert.mceachran@anu.edu.au](mailto:robert.mceachran@anu.edu.au)

**James H. McGuire**

Tulane University  
Department of Physics  
6823 St. Charles Ave.  
New Orleans, LA 70118–5698, USA  
e-mail: [mguire@tulane.edu](mailto:mguire@tulane.edu)

**Dieter Meschede**

Rheinische Friedrich–Wilhelms–Universität Bonn  
Institut für Angewandte Physik  
Wegelerstraße 8  
Bonn, 53115, Germany  
e-mail: [meschede@iap.uni-bonn.de](mailto:meschede@iap.uni-bonn.de)

**Pierre Meystre**

University of Arizona  
Department of Physics  
1118 E, 4th Street  
Tucson, AZ 85721-0081, USA  
e-mail: [meystre@physics.arizona](mailto:meystre@physics.arizona)

**Peter W. Milonni**

104 Sierra Vista Dr.  
Los Alamos, NM 87544, USA  
e-mail: [pwm@lanl.gov](mailto:pwm@lanl.gov)

**Peter J. Mohr**

National Institute of Standards and Technology  
Atomic Physics Division  
100 Bureau Drive, Stop 8420  
Gaithersburg, MD 20899-8420, USA  
e-mail: [mohr@nist.gov](mailto:mohr@nist.gov)

**David H. Mordaunt**

Max-Planck-Institut für Strömungsforschung  
Göttingen, 37073, Germany

**John D. Morgan III**

University of Delaware  
Department of Physics and Astronomy  
Newark, DE 19716, USA  
e-mail: [jdmorgan@udel.edu](mailto:jdmorgan@udel.edu)

**Michael S. Murillo**

Los Alamos National Laboratory  
Theoretical Division  
PO BOX 1663  
Los Alamos, NM 87545, USA  
e-mail: [murillo@lanl.gov](mailto:murillo@lanl.gov)

**Evgueni E. Nikitin**

Technion-Israel Institute of Technology  
Department of Chemistry  
Haifa, 32000, Israel  
e-mail: [nikitin@techunix.technion.ac.il](mailto:nikitin@techunix.technion.ac.il)

**Robert F. O'Connell**

Louisiana State University  
Department of Physics and Astronomy  
Baton Rouge, LA 70803-4001, USA  
e-mail: [roconnell@phys.lsu.edu](mailto:roconnell@phys.lsu.edu)

**Francesca O'Rourke**

Queen's University Belfast  
Department of Applied Mathematics and  
Theoretical Physics  
University Road  
Belfast, BT7 1NN, UK  
e-mail: [s.orourke@qub.ac.uk](mailto:s.orourke@qub.ac.uk)

**Ronald E. Olson**

University of Missouri-Rolla  
Physics Department  
Rolla, MO 65409, USA  
e-mail: [olson@umr.edu](mailto:olson@umr.edu)

**Barbara A. Paldus**

Skymoon Ventures  
3045 Park Boulevard  
Palo Alto, CA 94306, USA  
e-mail: [bpaldus@skymoonventures.com](mailto:bpaldus@skymoonventures.com)

**Josef Paldus**

University of Waterloo  
Department of Applied Mathematics  
200 University Avenue West  
Waterloo, ON N2L 3G1, Canada  
e-mail: [paldus@scienide.uwaterloo.ca](mailto:paldus@scienide.uwaterloo.ca)

**Gillian Peach**

University College London  
Department of Physics and Astronomy  
London, WC1 E6BT, UK  
e-mail: [g.peach@ucl.ac.uk](mailto:g.peach@ucl.ac.uk)

**Ruth T. Pedlow**

Queen's University Belfast  
Department of Applied Mathematics  
and Theoretical Physics  
University Road  
Belfast, Northern Ireland BT7 1NN, UK  
e-mail: [r.pedlow@qub.ac.uk](mailto:r.pedlow@qub.ac.uk)

**David J. Pegg**

University of Tennessee  
Department of Physics  
Nielsen Building  
Knoxville, TN 37996, USA  
e-mail: [djpegg@utk.edu](mailto:djpegg@utk.edu)

**Ekkehard Peik**

Physikalisch-Technische Bundesanstalt  
Bundesallee 100  
Braunschweig, 38116, Germany  
e-mail: [ekkehard.peik@ptb.de](mailto:ekkehard.peik@ptb.de)

**Ronald Phaneuf**

University of Nevada  
Department of Physics  
MS-220  
Reno, NV 89557-0058, USA  
e-mail: [phaneuf@unr.edu](mailto:phaneuf@unr.edu)

**Michael S. Pindzola**

Auburn University  
Department of Physics  
Auburn, AL 36849, USA  
e-mail: [pindzola@physics.auburn.edu](mailto:pindzola@physics.auburn.edu)

**Eric H. Pinnington**

University of Alberta  
Department of Physics  
Edmonton, AB T6H 0B3, Canada  
e-mail: [pinning@phys.ualberta.ca](mailto:pinning@phys.ualberta.ca)

**Richard C. Powell**

University of Arizona  
Optical Sciences Center  
Tucson, AZ 85721, USA  
e-mail: [rcpowell@email.arizona.edu](mailto:rcpowell@email.arizona.edu)

**John F. Reading**

Texas A&M University  
Department of Physics  
College Station, TX 77843, USA  
e-mail: [reading@physics.tamu.edu](mailto:reading@physics.tamu.edu)

**Jonathan R. Sapirstein**

University of Notre Dame  
Department of Physics  
319 Nieuwland Science  
Notre Dame, IN 46556, USA  
e-mail: [jsapirst@nd.edu](mailto:jsapirst@nd.edu)

**Stefan Scheel**

Imperial College London  
Blackett Laboratory  
Prince Consort Road  
London, SW7 2BW, UK  
e-mail: [s.scheel@imperial.ac.uk](mailto:s.scheel@imperial.ac.uk)

**Axel Schenzle**

Ludwig-Maximilians-Universität  
Department für Physik  
Theresienstraße 37  
München, 80333, Germany  
e-mail: [axel.schenzle@physik.uni-muenchen.de](mailto:axel.schenzle@physik.uni-muenchen.de)

**Reinhard Schinke**

Max-Planck-Institut für Dynamik &  
Selbstorganisation  
Bunsenstr. 10  
Göttingen, 37073, Germany  
e-mail: [rschink@gwdg.de](mailto:rschink@gwdg.de)

**Wolfgang P. Schleich**

Universität Ulm  
Abteilung für Quantenphysik  
Albert Einstein Allee 11  
Ulm, 89069, Germany  
e-mail: [wolfgang.schleich@uni-ulm.de](mailto:wolfgang.schleich@uni-ulm.de)

**David R. Schultz**

Oak Ridge National Laboratory  
Physics Division  
Oak Ridge, TN 37831-6373, USA  
e-mail: [schultz@mail.phy.ornl.gov](mailto:schultz@mail.phy.ornl.gov)

**Michael Schulz**

University of Missouri-Rolla  
Physics Department  
1870 Miner Circle  
Rolla, MO 65409, USA  
e-mail: [schulz@umr.edu](mailto:schulz@umr.edu)

**Peter L. Smith**

Harvard University  
Harvard-Smithsonian Center for Astrophysics  
60 Garden Street  
Cambridge, MA 02138, USA  
e-mail: [plsmith@cfa.harvard.edu](mailto:plsmith@cfa.harvard.edu)

**Anthony F. Starace**

The University of Nebraska  
Department of Physics and Astronomy  
116 Brace Laboratory  
Lincoln, NE 68588-0111, USA  
e-mail: [astarace1@unl.edu](mailto:astarace1@unl.edu)

**Glenn Stark**

Wellesley College  
Department of Physics  
106 Central Street  
Wellesley, MA 02481, USA  
e-mail: [gstark@wellesley.edu](mailto:gstark@wellesley.edu)

**Allan Stauffer**

Department of Physics and Astronomy  
York University  
4700 Keele Street  
Toronto, ON M3J 1P3, Canada  
e-mail: [stauffer@yorku.ca](mailto:stauffer@yorku.ca)

**Aephraim M. Steinberg**

University of Toronto  
Department of Physics  
Toronto, ON M5S 1A7, Canada  
e-mail: [steinberg@physics.utoronto.ca](mailto:steinberg@physics.utoronto.ca)

**Stig Stenholm**

Royal Institute of Technology  
Physics Department  
Roslagstullsbacken 21  
Stockholm, SE-10691, Sweden  
e-mail: [stenholm@atom.kth.se](mailto:stenholm@atom.kth.se)

**Jack C. Straton**

Portland State University  
University Studies  
117P Cramer Hall  
Portland, OR 97207, USA

**Michael R. Strayer**

Oak Ridge National Laboratory  
Physics Division  
Oak Ridge, TN 37831-6373, USA  
e-mail: [strayer@csep2.phy.ornl.gov](mailto:strayer@csep2.phy.ornl.gov)

**Carlos R. Stroud Jr.**

University of Rochester  
Institute of Optics  
Rochester, NY 14627-0186, USA  
e-mail: [stroud@optics.rochester.edu](mailto:stroud@optics.rochester.edu)

**Arthur G. Suits**

State University of New York  
Department of Chemistry  
Stony Brook, NY 11794, USA  
e-mail: [arthur.suits@sunysb.edu](mailto:arthur.suits@sunysb.edu)

**Barry N. Taylor**

National Institute of Standards and Technology  
Atom Physics Division  
100 Bureau Drive  
Gaithersburg, MD 20899-8401, USA  
e-mail: [barry.taylor@nist.gov](mailto:barry.taylor@nist.gov)

**Aaron Temkin**

NASA Goddard Space Flight Center  
Laboratory for Solar and Space Physics  
Solar Physics Branch  
Greenbelt, MD 20771, USA  
e-mail: [aaron.temkin-1@nasa.gov](mailto:aaron.temkin-1@nasa.gov)

**Sandor Trajmar**

California Institute of Technology  
Jet Propulsion Laboratory  
3847 Vineyard Drive  
Redwood City, 94063, USA  
e-mail: [trajmar@comcast.net](mailto:trajmar@comcast.net)

**Elmar Träbert**

Ruhr-Universität Bochum  
Experimentalphysik III/NB3  
Bochum, 44780, Germany  
e-mail: [traebert@ep3.rub.de](mailto:traebert@ep3.rub.de)

**Turgay Uzer**

Georgia Institute of Technology  
School of Physics  
837 State Street  
Atlanta, GA 30332-0430, USA  
e-mail: [turgay.uzer@physics.gatech.edu](mailto:turgay.uzer@physics.gatech.edu)



**Karl Vogel**

Universität Ulm  
Abteilung für Quantenphysik  
Albert Einstein Allee 11  
Ulm, 89069, Germany  
e-mail: *karl.vogel@uni-ulm.de*

**Jon C. Weisheit**

Washington State University  
Institute for Shock Physics  
PO BOX 64 28 14  
Pullman, WA 99164, USA  
e-mail: *weisheit@wsu.edu*

**Wolfgang L. Wiese**

National Institute of Standards and Technology  
100 Bureau Drive  
Gaithersburg, MD 20899, USA  
e-mail: *wiese@nist.gov*

**Martin Wilkens**

Universität Potsdam  
Institut für Physik  
Am Neuen Palais 10  
Potsdam, 14469, Germany  
e-mail: *martin.wilkens@physik.uni-potsdam.de*

**David R. Yarkony**

The Johns Hopkins University  
Department of Chemistry  
Baltimore, MD 21218, USA  
e-mail: *yarkony@jhu.edu*

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# Springer Handbook of Atomic, Molecular, and Optical Physics

## Organization of the Handbook

**Part A** gathers together the mathematical methods applicable to a wide class of problems in atomic, molecular, and optical physics. The application of angular momentum theory to quantum mechanics is presented. The basic tenet that isolated physical systems are invariant to rotations of the system is thereby implemented into physical theory. The powerful methods of group theory and second quantization show how simplifications arise if the atomic shell is treated as a basic structural unit. The well established symmetry groups of quantum mechanical Hamiltonians are extended to the larger compact and noncompact dynamical groups. Perturbation theory is introduced as a bridge between an exactly solvable problem and a corresponding real one, allowing approximate solutions of various systems of differential equations. The consistent manner in which the density matrix formalism deals with pure and mixed states is developed, showing how the preparation of an initial state as well as the details regarding the observation of the final state can be treated in a systematic way. The basic computational techniques necessary for accurate and efficient numerical calculations essential to all fields of physics are outlined and a summary of relevant software packages is given. The ever present one-electron solutions of the nonrelativistic Schrödinger equation and the relativistic Dirac equation for the Coulomb potential are then summarized.

**Part B** presents the main concepts in the theoretical and experimental knowledge of atomic systems, including atomic structure and radiation. Ionization energies for neutral atoms and transition probabilities of selected neutral atoms are tabulated. The computational methods needed for very high precision approximations for helium are summarized. The physical and geometrical significance of simple multipoles is examined. The basic nonrelativistic and relativistic theory of electrons and atoms in external magnetic fields is given. Various properties of Rydberg atoms in external fields and in collisions are investigated. The sources of hyperfine structure in atomic and molecular spectra are outlined, and the resulting energy splittings and isotope shifts given. Precision oscillator strength and lifetime measurements, which provide stringent experimental tests of fundamental atomic structure calculations, are discussed. Ion beam spectroscopy is introduced, and individual applications of ion beam techniques are detailed. A basic description of neutral collisional line shapes is given, along with a discussion of radiation transfer in a confined atomic vapor. Many qualitative features of the Thomas–Fermi model are studied and its later outgrowth into general density functional theory delineated. The Hartree–Fock and multiconfiguration Hartree–Fock theories, along with configuration interaction methods, are discussed in detail, and their application to the calculation of various atomic properties presented. Relativistic methods for the calculation of atomic structure for general many-electron atoms are described. A consistent diagrammatic method for calculating the structure of atoms and the characteristics of different atomic

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processes is given. An outline of the theory of atomic photoionization and the dynamics of the photon–atom collision process is presented. Those kinds of electron correlation that are most important in photoionization are emphasized. The process of autoionization is treated as a quasibound state imbedded in the scattering continuum, and a brief description of the main elements of the theory is given. Green’s function techniques are applied to the calculation of higher order corrections to atomic energy levels, and also of transition amplitudes for radiative transitions of atoms. Basic quantum electrodynamic calculations, which are needed to explain small deviations from the solution to the Schrödinger equation in simple systems, are presented. Comparisons of precise measurements and theoretical predictions that provide tests of our knowledge of fundamental physics are made, focussing on several quantitative tests of quantum electrodynamics. Precise measurements of parity nonconserving effects in atoms could lead to possible modifications of the Standard Model, and thus uncover new physics. An approach to this fundamental problem is described. The problem of the possible variation of the fundamental constants with time is discussed in relation to atomic clocks and precision frequency measurements. The most advanced atomic clocks are described, and the current laboratory constraints on these variations are listed.

**Part C** begins with a discussion of molecular structure from a theoretical/computational perspective using the Born–Oppenheimer approximation as the point of departure. The key role that symmetry considerations play in organizing and simplifying our knowledge of molecular dynamics and spectra is described. The theory of radiative transition probabilities, which determine the intensities of spectral lines, for the rotationally-resolved spectra of certain model molecular systems is summarized. The ways in which molecular photodissociation is studied in the gas phase are outlined. The results presented are particularly relevant to the investigation of combustion and atmospheric reactions. Modern experimental techniques allow the detailed motions of the atomic constituents of a molecule to be resolved as a function of time. A brief description of the basic ideas behind these techniques is given, with an emphasis on gas phase molecules in collision-free conditions. The semiclassical and quantal approaches to nonreactive scattering are outlined. Various quantitative approaches toward a description of the rates of gas phase chemical reactions are presented and then evaluated for their reliability and range of application. Ionic reactions in the gas phase are also considered. Clusters, which are important in many atmospheric and industrial processes, are arranged into six general categories, and then the physics and chemistry common to each category is described. The most important spectroscopic techniques used to study the properties of molecules are presented in detail.

**Part D** collects together the topics and approaches used in scattering theory. A handy compendium of equations, formulae, and expressions for the classical, quantal, and semiclassical approaches to elastic scattering is given; reactive systems and model potentials are also considered. The dependence of scattering processes on the angular orientation of the reactants and products is discussed through the analysis of scattering experiments which probe atomic collision theories at a fundamental level.

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The detailed quantum mechanical techniques available to perform accurate calculations of scattering cross sections from first principles are presented. The theory of elastic, inelastic, and ionizing collisions of electrons with atoms and atomic ions is covered and then extended to include collisions with molecules. The standard scattering theory for electrons is extended to include positron collisions with atomic and molecular systems. Slow collisions of atoms or molecules within the adiabatic approximation are discussed; important deviations from this model are presented in some detail for the low energy case. The main methods in the theoretical treatment of ion-atom and atom-atom collisions are summarized with a focus on intermediate and high collision velocities. The molecular structure and collision dynamics involved in ion-atom charge exchange reactions is studied. Both the perturbative and variational capture theories of the continuum distorted wave model are presented. The Wannier theory for threshold ionization is then developed. Studies of the energy and angular distribution of electrons ejected by the impact of high-velocity atomic or ionic projectiles on atomic targets are overviewed. A useful collection of formulae, expressions, and specific equations that cover the various approaches to electron-ion and ion-ion recombination processes is given. A basic theoretical formulation of dielectronic recombination is described, and its importance in the interpretation of plasma spectral emission is presented. Many of the equations used to study theoretically the collisional properties of both charged and neutral particles with atoms and molecules in Rydberg states are collected together; the primary approximations considered are the impulse approximation, the binary encounter approximation, and the Born approximation. The Thomas mass-transfer process is considered from both a classical and a quantum perspective. Additional features of this process are also discussed. The theoretical background, region of validity, and applications of the classical trajectory Monte Carlo method are then delineated. One-photon processes are discussed and aspects of line broadening directly related to collisions between an emitting, or absorbing, atom and an electron, a neutral atom or an atomic ion are considered.

**Part E** focuses on the experimental aspects of scattering processes. Recent developments in the field of photodetachment are reviewed, with an emphasis on accelerator-based investigations of the photodetachment of atomic negative ions. The theoretical concepts and experimental methods for the scattering of low-energy photons, proceeding primarily through the photoelectric effect, are given. The main photon-atom interaction processes in the intermediate energy range are outlined. The atomic response to inelastic photon scattering is discussed; essential aspects of radiative and radiationless transitions are described in the two-step approximation. Advances such as cold-target recoil-ion momentum spectroscopy are also touched upon. Electron-atom and electron-molecule collision processes, which play a prominent role in a variety of systems, are presented. The discussion is limited to electron collisions with gaseous targets, where single collision conditions prevail, and to low-energy impact processes. The physical principles and experimental methods used to investigate low energy ion-atom collisions are outlined. Inelastic processes which occur in collisions between fast, often highly charged, ions and atoms, are described. A summary of the methods commonly employed in scattering experiments

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involving neutral molecules at chemical energies is presented. Applications of single-collision scattering methods to the study of reactive collision dynamics of ionic species with neutral partners are discussed.

**Part F** presents a coherent collection of the main topics and issues found in quantum optics. Optical physics, which is concerned with the dynamical interactions of atoms and molecules with electromagnetic fields, is first discussed within the context of semiclassical theories, and then extended to a fully quantized version. The theoretical techniques used to describe absorption and emission spectra using density matrix methods are developed. Applications of the dark state in laser physics is briefly mentioned. The basic concepts common to all lasers, such as gain, threshold, and electromagnetic modes of oscillation are described. Recent developments in laser physics, including single-atom lasers, two-photon lasers, and the generation of attosecond pulses are also introduced. The current status of the development of different types of lasers – including nanocavity, quantum-cascade and free-electron lasers – are summarized. The important operational characteristics, such as frequency range and output power, are given for each of the types of lasers described. Nonlinear processes arising from the modifications of the optical properties of a medium due to the passage of intense light beams are discussed. Additional processes that are enabled by the use of ultrashort or ultra-intense laser pulses are presented. The concept of coherent optical transients in atomic and molecular systems reviewed; homogeneous and inhomogeneous relaxation in the theory are properly distinguished. Multiphoton and strong-field processes are given a theoretical description. A discussion of the generation of sub-femtosecond pulses is also included. General and specific theories for the control of atomic motion by light are presented. Various traps used for the cooling and trapping of charged and neutral particles and their applications are discussed. The fundamental physics of dilute quantum degenerate gases is outlined, especially in connection with Bose–Einstein condensation. de Broglie optics, which concerns the propagation of matter waves, is presented with a concentration on the underlying principles and the illustration of these principles. The fundamentals of the quantized electromagnetic field and applications to the broad area of quantum optics are discussed. A detailed description of the changes in the atom–field interaction that take place when the radiation field is modified by the presence of a cavity is given. The basic concepts needed to understand current research, such as the EPR experiment, Bell’s inequalities, squeezed states of light, the properties of electromagnetic waves in cavities, and other topics depending on the nonlocality of light are reviewed. Applications to cryptography, tunneling times, and gravity wave detectors are included, along with recent work on “fast light” and “slow light.” Correlations and quantum superpositions which can be exploited in quantum information processing and secure communication are delineated. Their link to quantum computing and quantum cryptography is given explicitly.

**Part G** is concerned with the various applications of atomic, molecular, and optical physics. A summary of the processes that take place in photoionized gases, collisionally ionized gases, the diffuse interstellar medium, molecular clouds, circumstellar shells, supernova ejecta, shocked regions, and the early

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