

In recent years, Rydberg atoms have been the subject of intense study, becoming the testing ground for several quantum mechanical problems. This book provides a comprehensive description of the physics of Rydberg atoms, highlighting their remarkable properties by reference to their behavior in a wide range of physical situations.

Beginning with a brief historical overview, the basic properties, creation and detection of Rydberg atoms are described. The effects of blackbody radiation are discussed, as are optical excitation in static electric fields, ionization by pulsed electric fields, Rydberg spectroscopy in high magnetic fields, and microwave excitation and ionization. The collisions of Rydberg atoms with neutral atoms and molecules, charged particles, and other Rydberg atoms are dealt with in detail. The powerful method of multichannel quantum defect theory is presented, and used in the description of autoionizing Rydberg states, interseries interactions and double Rydberg states.

In addition to providing a clear introduction to the basic properties of Rydberg atoms, experimental and theoretical research in this extensive field is reviewed. The books will therefore be valuable to both graduate students and established researchers in physics and physical chemistry.

Cambridge University Press
0521021669 - Rydberg Atoms
Thomas F. Gallagher
Frontmatter
[More information](#)

**Cambridge Monographs on
Atomic, Molecular, and Chemical Physics
3**

General editors: A. Dalgarno, P. L. Knight, F. H. Read, R. N. Zare

RYDBERG ATOMS

Cambridge University Press
0521021669 - Rydberg Atoms
Thomas F. Gallagher
Frontmatter
[More information](#)

*Cambridge Monographs on
Atomic, Molecular, and Chemical Physics*

1. R. Schinke *Photodissociation Dynamics*
2. L. Frommhold *Collision-induced Absorption in Gases*
3. T. F. Gallagher *Rydberg Atoms*

Cambridge University Press
0521021669 - Rydberg Atoms
Thomas F. Gallagher
Frontmatter
[More information](#)

RYDBERG ATOMS

THOMAS F. GALLAGHER

*Jesse W. Beams Professor of Physics
Department of Physics, University of Virginia*



Cambridge University Press
0521021669 - Rydberg Atoms
Thomas F. Gallagher
Frontmatter
[More information](#)

CAMBRIDGE UNIVERSITY PRESS
Cambridge, New York, Melbourne, Madrid, Cape Town, Singapore, São Paulo

Cambridge University Press
The Edinburgh Building, Cambridge CB2 2RU, UK

Published in the United States of America by Cambridge University Press, New York

www.cambridge.org
Information on this title: www.cambridge.org/9780521385312

© Cambridge University Press 1994

This publication is in copyright. Subject to statutory exception
and to the provisions of relevant collective licensing agreements,
no reproduction of any part may take place without
the written permission of Cambridge University Press.

First published 1994
This digitally printed first paperback version 2005

A catalogue record for this publication is available from the British Library

Library of Congress Cataloguing in Publication data

Gallagher, Thomas F.
Rydberg atoms / Thomas F. Gallagher.
p. cm.
ISBN 0-521-38531-8
1. Rydberg states. I. Title.
QC454.A8S27 1994
539.7—dc20 93-37132 CIP

ISBN-13 978-0-521-38531-2 hardback
ISBN-10 0-521-38531-8 hardback

ISBN-13 978-0-521-02166-1 paperback
ISBN-10 0-521-02166-9 paperback

Contents

Preface	xiii
1 Introduction	1
References	9
2 Rydberg atom wavefunctions	10
References	26
3 Production of Rydberg atoms	27
Excitation to the Rydberg states	27
Electron impact	29
Charge exchange	31
Optical excitation	32
Collisional–optical excitation	35
References	37
4 Oscillator strengths and lifetimes	38
Oscillator strengths	38
Radiative lifetimes	45
References	49
5 Black body radiation	50
Black body radiation	50
Black body induced transitions	53
Black body energy shifts	55
Initial verification	57
Temperature dependent measurements	59
Suppression and enhancement of transition rates	61
Level shifts	64
Experimental manifestations and uses	65
Far infrared detection	66
References	68
6 Electric fields	70
Hydrogen	70
Field ionization	83
Nonhydrogenic atoms	87
Ionization of nonhydrogenic atoms	95
References	101

viii	<i>Contents</i>	
7 Pulsed field ionization		103
Hydrogen		104
Nonhydrogenic atoms		105
Spin orbit effects		115
References		119
8 Photoexcitation in electric fields		120
Hydrogenic spectra		120
Nonhydrogenic spectra		135
References		141
9 Magnetic fields		143
Diamagnetism		143
Quasi Landau resonances		147
Quasi classical orbits		153
References		160
10 Microwave excitation and ionization		162
Microwave ionization of nonhydrogenic atoms		164
Microwave multiphoton transitions		168
Hydrogen		182
Ionization by circularly polarized fields		190
References		193
11 Collisions with neutral atoms and molecules		195
A physical picture		196
Theory		198
Experimental methods		205
Collisional angular momentum mixing		208
The effects of electric fields on ℓ mixing		212
ℓ mixing by molecules		213
Fine structure changing collisions		215
n changing collisions by rare gases		216
n changing by alkali atoms		220
n changing by molecules		221
Electron attachment		230
Associative ionization		239
Penning ionization		243
Ion-perturber collisions		243
Fast collisions		245
References		247

	<i>Contents</i>	ix
12 Spectral line shifts and broadenings		250
Theory		250
Experimental methods		254
Measurements of shifts and broadening		255
References		267
13 Charged particle collisions		269
State changing collisions with ions		269
Na $nd \rightarrow n\ell$ transitions		270
Depopulation of the Na ns and np states		272
Theoretical descriptions		275
Electron loss		276
Charge exchange		279
Electron collisions		285
References		288
14 Resonant Rydberg–Rydberg collisions		290
Two state theory		294
Box interaction strength approximation		295
Exact resonance approximation		296
Numerical calculations		298
Intracollisional interference		301
Calculation of cross sections		301
Experimental approach		302
n scaling laws		303
Orientation dependence of \mathbf{v} and \mathbf{E} and intracollisional interference		306
Velocity dependence of the collisional resonances		307
Transform limited collisions		312
References		313
15 Radiative collisions		314
Initial experimental study of radiative collisions		317
Theoretical description		321
References		339
16 Spectroscopy of alkali Rydberg states		340
Optical measurements		341
Radiofrequency resonance		343
Core polarization		348
Fine structure intervals		352
Quantum beats and level crossing		355
References		363

x	<i>Contents</i>	
17	Rf spectroscopy of alkaline earth atoms	365
	Theoretical description of series perturbation and nonadiabatic effects in core polarization	365
	Experimental methods	373
	Low angular momentum states and series perturbations	375
	Non adiabatic core polarization	376
	References	380
18	Bound He Rydberg states	381
	Theoretical description	381
	Experimental approaches	384
	Quantum defects and fine structure	391
	References	393
19	Autoionizing Rydberg states	395
	Basic notions of autoionizing Rydberg states	395
	Experimental methods	399
	Experimental observations of autoionization rates	408
	Electron spectroscopy	411
	References	413
20	Quantum defect theory	415
	Quantum defect theory (QDT)	415
	Geometrical interpretation of the quantum defect surface	421
	Normalization	422
	Energy constraints	423
	Alternative $\underline{\mathbf{R}}$ matrix form of QDT	424
	The role of QDT	427
	References	428
21	Optical spectra of autoionizing Rydberg states	429
	The shake up satellites	434
	Interacting autoionizing series	440
	Comparison between experimental spectra and $\underline{\mathbf{R}}$ matrix calculations	448
	References	451
22	Interseries interaction in bound states	453
	Perturbed Rydberg series	453
	Properties of perturbed states	457
	Continuity of photoexcitation across ionization limits	460
	Forced autoionization	461
	References	464

Cambridge University Press
0521021669 - Rydberg Atoms
Thomas F. Gallagher
Frontmatter
[More information](#)

	<i>Contents</i>	xi
23	Double Rydberg states	466
	Doubly excited states of He	467
	Theoretical descriptions	469
	Laser excitation	480
	Experimental observations of electron correlation	482
	References	491
	Index	493

Preface

My intent in writing this book is to present a unified description of the many properties of Rydberg atoms. It is intended for graduate students and research workers interested in the properties of Rydberg states of atoms or molecules. In many ways it is similar to the excellent volume *Rydberg States of Atoms and Molecules* edited by R. F. Stebbings and F. B. Dunning just over a decade ago. It differs, however, in covering more topics and in being written by one author. I have attempted to focus on the essential physical ideas. Consequently the theoretical developments are not particularly formal, nor is there much emphasis on the experimental details.

The constraints imposed by the size of the book and my energy have forced me to limit the topics covered in this book to those of general interest and those about which I already knew something. Consequently, several important topics which might well have been included by another author are not included in the present volume. Two examples are molecular Rydberg states and cavity quantum electrodynamics.

Finally, it is a great pleasure to acknowledge the fact that this book would never have been written without the efforts of many people. First I would like to acknowledge the help of my colleagues in the Molecular Physics Laboratory of SRI International (originally Stanford Research Institute). They had the confidence that our initial experiments would develop into a productive research program, and they completed my education as a physicist. My colleagues at the University of Virginia have continued to provide both a critical audience and the encouragement necessary to undertake the writing of this book.

My collaborators have contributed substantially to my understanding of Rydberg atoms, and it is a pleasure to acknowledge the contributions of L. A. Bloomfield, W. E. Cooke, S. A. Edelstein, F. Gounand, R. M. Hill, R. Kachru, R. R. Jones, D. J. Larson, D. C. Lorents, L. Noordam, P. Pillet, K. A. Safinya, W. Sandner, and R. C. Stoneman. In addition I have been the beneficiary of the insights of my students, post doctoral fellows, and visitors. Without all of their contributions this book could not have been written.

I am indebted to Tammie Shifflett, Bessie Truzy, Warrick Liu, and Sibyl Hale for their careful typing of the manuscript, and it is a pleasure to acknowledge the encouragement of James Deeny, Rufus Neal, and Philip Meyler of the Cambridge

Cambridge University Press
0521021669 - Rydberg Atoms
Thomas F. Gallagher
Frontmatter
[More information](#)

xiv

Preface

University Press. Finally, the gentle prodding of my mother, Margaret Gallagher, and the patience of my wife, Betty, played important roles in the completion of this book.

Charlottesville, Virginia
November, 1993

T. F. Gallagher