

H A M E K A

QUANTUM MECHANICS

A
*Conceptual
Approach*

QUANTUM MECHANICS

QUANTUM MECHANICS

A Conceptual Approach

HENDRIK F. HAMEKA

 **WILEY-INTERSCIENCE**

A John Wiley & Sons, Inc. Publication

Copyright © 2004 by John Wiley & Sons, Inc. All rights reserved.

Published by John Wiley & Sons, Inc., Hoboken, New Jersey.
Published simultaneously in Canada.

No part of this publication may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, scanning, or otherwise, except as permitted under Section 107 or 108 of the 1976 United States Copyright Act, without either the prior written permission of the Publisher, or authorization through payment of the appropriate per-copy fee to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, 978-750-8400, fax 978-646-8600, or on the web at www.copyright.com. Requests to the Publisher for permission should be addressed to the Permissions Department, John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, (201) 748-6011, fax (201) 748-6008.

Limit of Liability/Disclaimer of Warranty: While the publisher and author have used their best efforts in preparing this book, they make no representations or warranties with respect to the accuracy or completeness of the contents of this book and specifically disclaim any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives or written sales materials. The advice and strategies contained herein may not be suitable for your situation. You should consult with a professional where appropriate. Neither the publisher nor author shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages.

For general information on our other products and services please contact our Customer Care Department within the U.S. at 877-762-2974, outside the U.S. at 317-572-3993 or fax 317-572-4002.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print, however, may not be available in electronic format.

Library of Congress Cataloging-in-Publication Data:

Hameka, Hendrik F.

Quantum mechanics : a conceptual approach / Hendrik F. Hameka.

p. cm.

Includes index.

ISBN 0-471-64965-1 (pbk. : acid-free paper)

1. Quantum theory. I. Title.

QC174.12.H353 2004

530.12-dc22

2004000645

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

To Charlotte

CONTENTS

Preface	xi
1 The Discovery of Quantum Mechanics	1
I Introduction, 1	
II Planck and Quantization, 3	
III Bohr and the Hydrogen Atom, 7	
IV Matrix Mechanics, 11	
V The Uncertainty Relations, 13	
VI Wave Mechanics, 14	
VII The Final Touches of Quantum Mechanics, 20	
VIII Concluding Remarks, 22	
2 The Mathematics of Quantum Mechanics	23
I Introduction, 23	
II Differential Equations, 24	
III Kummer's Function, 25	
IV Matrices, 27	
V Permutations, 30	
VI Determinants, 31	

VII	Properties of Determinants, 32	
VIII	Linear Equations and Eigenvalues, 35	
IX	Problems, 37	
3	Classical Mechanics	39
I	Introduction, 39	
II	Vectors and Vector Fields, 40	
III	Hamiltonian Mechanics, 43	
IV	The Classical Harmonic Oscillator, 44	
V	Angular Momentum, 45	
VI	Polar Coordinates, 49	
VII	Problems, 51	
4	Wave Mechanics of a Free Particle	52
I	Introduction, 52	
II	The Mathematics of Plane Waves, 53	
III	The Schrödinger Equation of a Free Particle, 54	
IV	The Interpretation of the Wave Function, 56	
V	Wave Packets, 58	
VI	Concluding Remarks, 62	
VII	Problems, 63	
5	The Schrödinger Equation	64
I	Introduction, 64	
II	Operators, 66	
III	The Particle in a Box, 68	
IV	Concluding Remarks, 71	
V	Problems, 72	
6	Applications	73
I	Introduction, 73	
II	A Particle in a Finite Box, 74	

III	Tunneling, 78	
IV	The Harmonic Oscillator, 81	
V	Problems, 87	
7	Angular Momentum	88
I	Introduction, 88	
II	Commuting Operators, 89	
III	Commutation Relations of the Angular Momentum, 90	
IV	The Rigid Rotor, 91	
V	Eigenfunctions of the Angular Momentum, 93	
VI	Concluding Remarks, 96	
VII	Problems, 96	
8	The Hydrogen Atom	98
I	Introduction, 98	
II	Solving the Schrödinger Equation, 99	
III	Deriving the Energy Eigenvalues, 101	
IV	The Behavior of the Eigenfunctions, 103	
V	Problems, 106	
9	Approximate Methods	108
I	Introduction, 108	
II	The Variational Principle, 109	
III	Applications of the Variational Principle, 111	
IV	Perturbation Theory for a Nondegenerate State, 113	
V	The Stark Effect of the Hydrogen Atom, 116	
VI	Perturbation Theory for Degenerate States, 119	
VII	Concluding Remarks, 120	
VIII	Problems, 120	
10	The Helium Atom	122
I	Introduction, 122	

II	Experimental Developments, 123	
III	Pauli's Exclusion Principle, 126	
IV	The Discovery of the Electron Spin, 127	
V	The Mathematical Description of the Electron Spin, 129	
VI	The Exclusion Principle Revisited, 132	
VII	Two-Electron Systems, 133	
VIII	The Helium Atom, 135	
IX	The Helium Atom Orbitals, 138	
X	Concluding Remarks, 139	
XI	Problems, 140	
11	Atomic Structure	142
I	Introduction, 142	
II	Atomic and Molecular Wave Function, 145	
III	The Hartree-Fock Method, 146	
IV	Slater Orbitals, 152	
V	Multiplet Theory, 154	
VI	Concluding Remarks, 158	
VII	Problems, 158	
12	Molecular Structure	160
I	Introduction, 160	
II	The Born-Oppenheimer Approximation, 161	
III	Nuclear Motion of Diatomic Molecules, 164	
IV	The Hydrogen Molecular Ion, 169	
V	The Hydrogen Molecule, 173	
VI	The Chemical Bond, 176	
VII	The Structures of Some Simple Polyatomic Molecules, 179	
VIII	The Hückel Molecular Orbital Method, 183	
IX	Problems, 189	
	Index	191

PREFACE

The physical laws and mathematical structure that constitute the basis of quantum mechanics were derived by physicists, but subsequent applications became of interest not just to the physicists but also to chemists, biologists, medical scientists, engineers, and philosophers. Quantum mechanical descriptions of atomic and molecular structure are now taught in freshman chemistry and even in some high school chemistry courses. Sophisticated computer programs are routinely used for predicting the structures and geometries of large organic molecules or for the identification and evaluation of new medicinal drugs. Engineers have incorporated the quantum mechanical tunneling effect into the design of new electronic devices, and philosophers have studied the consequences of some of the novel concepts of quantum mechanics. They have also compared the relative merits of different axiomatic approaches to the subject.

In view of the widespread applications of quantum mechanics to these areas there are now many people who want to learn more about the subject. They may, of course, try to read one of the many quantum textbooks that have been written, but almost all of these textbooks assume that their readers have an extensive background in physics and mathematics; very few of these books make an effort to explain the subject in simple non-mathematical terms.

In this book we try to present the fundamentals and some simple applications of quantum mechanics by emphasizing the basic concepts and by keeping the mathematics as simple as possible. We do assume that the reader is familiar with elementary calculus; it is after all not possible to explain the Schrödinger equation to someone who does not know what a derivative or an integral is. Some of the mathematical techniques that are essential for understanding quantum mechanics, such as matrices and determinants, differential equations, Fourier analysis, and so on are

described in a simple manner. We also present some applications to atomic and molecular structure that constitute the basis of the various molecular structure computer programs, but we do not attempt to describe the computation techniques in detail.

Many authors present quantum mechanics by means of the axiomatic approach, which leads to a rigorous mathematical representation of the subject. However, in some instances it is not easy for an average reader to even understand the axioms, let alone the theorems that are derived from them. I have always looked upon quantum mechanics as a conglomerate of revolutionary new concepts rather than as a rigid mathematical discipline. I also feel that the reader might get a better understanding and appreciation of these concepts if the reader is familiar with the background and the personalities of the scientists who conceived them and with the reasoning and arguments that led to their conception. Our approach to the presentation of quantum mechanics may then be called historic or conceptual but is perhaps best described as pragmatic. Also, the inclusion of some historical background makes the book more readable.

I did not give a detailed description of the various sources I used in writing the historical sections of the book because many of the facts that are presented were derived from multiple sources. Some of the material was derived from personal conversations with many scientists and from articles in various journals. The most reliable sources are the original publications where the new quantum mechanical ideas were first proposed. These are readily available in the scientific literature, and I was intrigued in reading some of the original papers. I also read various biographies and autobiographies. I found Moore's biography of Schrödinger, Constance Reid's biographies of Hilbert and Courant, Abraham Pais' reminiscences, and the autobiographies of Elsasser and Casimir particularly interesting. I should mention that Kramers was the professor of theoretical physics when I was a student at Leiden University. He died before I finished my studies and I never worked under his supervision, but I did learn quantum mechanics by reading his book and by attending his lectures.

Finally I wish to express my thanks to Mrs. Alice Chen for her valuable help in typing and preparing the manuscript.

HENDRIK F. HAMEKA