H. Haken
H.C. Wolf

Molecular Physics and Elements of Quantum Chemistry

Introduction to Experiments and Theory

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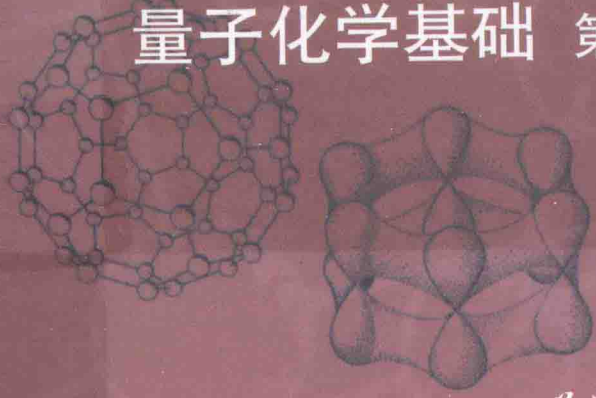
Second Edition

分子物理学和量子化学基础 第2版



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Hermann Haken Hans Christoph Wolf

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Translated by William D. Brewer
Second Enlarged Edition
With 306 Figures, 43 Tables, 133 Problems
and Web-based Solutions
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Fundamental Constants of Atomic Physics in the International System of Units (SI)

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Permeability Constant of Vacuum	μ_0	$= 4\pi \cdot 10^{-7}\ \mathrm{V\,s\,A^{-1}\,m^{-1}}$
		$= 1.256637\ldots \cdot 10^{-6}\ \mathrm{V\,s\,A^{-1}\,m^{-1}}$
Permittivity Constant of Vacuum	ε_0	$= (\mu_0 c^2)^{-1}$
		$= 8.8541878\ldots \cdot 10^{-12}\ \mathrm{A\,s\,V^{-1}\,m^{-1}}$
Velocity of Light	c	$= 2.99792458 \cdot 10^{8}\ \mathrm{m\,s^{-1}}$
Boltzmann's Constant	k	$= 1.380658R - 23\ \mathrm{J\,K^{-1}}$
Faraday Constant	F	$= 9.6485309 \cdot 10^{4}\ \mathrm{C\,mol^{-1}}$
Elementary Charge	e	$= 1.6021773 \cdot 10^{-19}\ \mathrm{C}$
Electron Rest Mass	m_0	$= 9.1093897 \cdot 10^{-31}\ \mathrm{kg}$
Specific Charge of the Electron	e/m_0	$= 1.75881962 \cdot 10^{11}\ \mathrm{C\,kg^{-1}}$
Proton Rest Mass	m_P	$= 1.6726231 \cdot 10^{-27}\ \mathrm{kg}$
Planck's Constant	h	$= 6.6260755 \cdot 10^{-34}\ \mathrm{J\,s}$
	$\hbar$	$= h/2\pi = 1.0545887 \cdot 10^{-34}\ \mathrm{J\,s}$
Rydberg Constant	R_∞	$= 1.0973731534 \cdot 10^{7}\ \mathrm{m^{-1}}$
First Bohr Radius	a_0	$= 0.529177249 \cdot 10^{-10}\ \mathrm{m}$
Bohr Magneton	μ_B	$= 9.2740154 \cdot 10^{-24}\ \mathrm{A\,m^2}$
Nuclear Magneton	μ_N	$= 5.0507866 \cdot 10^{-27}\ \mathrm{A\,m^2}$
Compton Wavelength of the Electron	λ_e	$= 2.42631058 \cdot 10^{-12}\ \mathrm{m}$
Fine Structure Constant	α	$= 7.29735308 \cdot 10^{-3}$
Avagadro Constant (Loschmidt's Number)	N_A	$= 6.0221367 \cdot 10^{23}\ \mathrm{mol^{-1}}$

Energy Conversion Table see inside back cover

Molecular Physics and Elements of Quantum Chemistry

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by Hermann Haken, Hans Christoph Wolf

Preface to the Second Edition

Since the publication of the first edition of this book, there have been many important new developments in the field of molecular physics. The new methods and results which are most significant for students are treated extensively in this second edition. Among these are in particular single-molecule spectroscopy and the field of molecular electronics, which is in a stage of rapid development, including the areas of electroluminescence and organic light-emitting diodes. In addition, we have extended and corrected the earlier material in a number of places. We have also included exercises in this new edition; they will allow students to deepen their understanding and offer a basis for further individual study. The complete solutions to the exercises can be found on the Internet under www.springeronline.com/3-540-40792-8.

We are grateful to Mr. C.-D. Bachem and Dr. Th. Schneider of the Springer-Verlag for their continuous and very agreeable cooperation during the preparation of the book. We thank our colleague Prof. W. D. Brewer for his competent translation.

Stuttgart, February 2004 *H. Haken · H.C. Wolf*

Preface to the First Edition

This textbook is intended for use by students of physics, physical chemistry, and theoretical chemistry. The reader is presumed to have a basic knowledge of atomic and quantum physics at the level provided, for example, by the first few chapters in our book *The Physics of Atoms and Quanta*. The student of physics will find here material which should be included in the basic education of every physicist. This book should furthermore allow students to acquire an appreciation of the breadth and variety within the field of molecular physics and its future as a fascinating area of research.

For the student of chemistry, the concepts introduced in this book will provide a theoretical framework for that entire field of study. With the help of these concepts, it is at least in principle possible to reduce the enormous body of empirical chemical knowledge to a few fundamental rules: those of quantum mechanics. In addition, modern physical methods whose fundamentals are introduced here are becoming increasingly important in chemistry and now represent indispensable tools for the chemist. As examples, we might mention the structural analysis of complex organic compounds, spectroscopic investigation of very rapid reaction processes or, as a practical application, the remote detection of pollutants in the air.

The present textbook concerns itself with two inseparably connected themes: chemical bonding and the physical properties of molecules. Both have become understandable through quantum mechanics, which had its first successes in the elucidation of atomic structure. While the question of chemical bonding is mainly connected with the ground state of the electrons and its energy as a function of the internuclear separation of the bonded atoms, an explanation of other physical properties of molecules generally requires consideration of excited states. These can refer both to the electronic motions and to those of the nuclei.

The theoretical investigation of these themes thus requires the methods of quantum mechanics, and their experimental study is based on spectroscopic methods, in which electromagnetic waves over a wide spectral range serve as probes. In this way, it becomes possible to obtain information on the structure of a molecule, on its electronic wavefunctions and on its rotations and vibrations. We include here the theoretical and experimental determination of binding energies and the energies of excited states. In the theoretical treatment, we shall meet not only concepts familiar from atomic physics, but also quite new ones, among them the Hartree-Fock approximation, the Born-Oppenheimer approximation, and the use of symmetry properties

in group theory. These ideas likewise form the basis of the quantum theory of solids, which is thus intimately connected to molecular physics.

In spite of the central importance held by the combination of molecular physics and quantum chemistry, there previously has been no textbook with the aim we have set for the present one. That fact, along with the extremely positive reception of our introductory text *The Physics of Atoms and Quanta* by students, teachers and reviewers, has stimulated us to write this book. We have based it on lecture courses given over the past years at the University of Stuttgart. We have again taken pains to present the material in a clear and understandable form and in a systematic order, treating problems from both an experimental and from a theoretical point of view and illustrating the close connection between theory and experiment.

Anyone who has been concerned with molecular physics and quantum chemistry will know that we are dealing here with practically limitless fields of study. An important, indeed central task for us was therefore the choice of the material to be treated. In making this choice, we have tried to emphasise the basic and typical aspects wherever possible. We hope to have succeeded in providing an overview of this important and fascinating area of research, which will allow the student to gain access to deeper aspects through study of the published literature. For those who wish to delve deeper into the great variety of research topics, we have provided a list of literature sources at the end of the book. There, the reader will also find literature in the area of reaction dynamics, which is presently experiencing a period of rapid development, but could not be included in this book for reasons of internal consistency. In addition, we give some glimpses into rather new developments such as research on photosynthesis, the physics of supramolecular functional units, and molecular microelectronics.

The book is thus intended to fulfill a dual purpose: on the one hand to give an introduction to the well-established fundamentals of the field of molecular physics, and on the other, to lead the reader to the newest developments in research.

This text is a translation of the second German edition of *Molekülphysik and Quantenchemie*. We wish to thank Prof. W. D. Brewer for the excellent translation and the most valuable suggestions he made for the improvement of the book.

We thank our colleagues and those students who have made a number of useful suggestions for improvements. In particular, we should like to thank here all those colleagues who have helped to improve the book by providing figures containing their recent research results. The reader is specifically referred to the corresponding literature citations given in the figure captions. We should also mention that the present text makes reference to our previous book, *The Physics of Atoms and Quanta*, which is always cited in this book as I.

Last but not least we wish to thank Springer-Verlag, and in particular Dr. H. J. Kölsch and C.-D. Bachem for their always excellent cooperation.

Stuttgart, January 1995 *H. Haken · H.C. Wolf*

List of the Most Important Symbols Used in this Book

a	Hyperfine Coupling Constant (ESR)
	Einstein Coefficient
a_k^+, a_k	Creation and annihilation Operators for Fermi Particles (7.50) ff.
A	One-Dimensional Irreducible Representation
$\boldsymbol{A}$	Vector Potential
b	Einstein Coefficient
b_k^+, b_k	Creation and Annihilation Operators for Bose Particles (7.47) ff.
$\boldsymbol{B}$	Magnetic Field Strength
	Magnetic Flux Density
B	Rotational Constant (9.13)
	One-Dimensional Irreducible Representation
B_k^+, B_k	Creation and Annihilation Operators for Vibrational Quanta (11.132) ff.
c	Velocity of Light in Vacuum
c, C	Concentration
c_i	Expansion Coefficient
C, C_ϕ, C_n	Rotation Operators (Rotation of $2\pi/n$)
$\bar{C}_n$	Helicity Operator
d	Electronic State in an Atom
D	Determinant
	Fine Structure Constant (19.35)
	Centrifugal Stretching Coefficient (9.25)
D, D_e, D_0	Dissociation Energy
e	Elementary Charge
$\boldsymbol{e}$	Unit Vector
E	Energy
	Fine Structure Constant (ESR)
	Identity Operator
$\boldsymbol{E}$	Electric Field Strength
$\bar{E}$	Energy Expectation Value
E_{el}	Electronic Energy
$E_{\text{kin}}, E_{\text{pot}}$	Kinetic or Potential Energy
E_{rot}	Rotational Energy
$E_{\text{vib}}, E_{\text{V}}$	Vibrational Energy

ΔE	Energy Difference
f	Oscillator Strength
	Number of Degrees of Freedom
	Electronic State in an Atom
F	Vibrational Term
$F_{l,m}$	Spherical Harmonic Functions
g	g-Factor (Magnetic)
G	Rotational Term
h	Order of a Group
$\hbar \doteq h/2\pi$	Planck's Constant (h = Planck's Quantum of Action)
H	Hamilton Function, Hamiltonian Operator
$H_{k,k}$	Matrix Element of the Hamiltonian Operator (7.16)
i	Imaginary Unit
i	Inversion Operator
I	Intensity
J	Rotational Quantum Number
	Spin-Spin Coupling Constant (NMR)
k	Boltzmann Constant
	Spring Constant, Force Constant
	Component of a Wavevector, Integer
$\boldsymbol{k}$	Wavevector
l	Mean Free Path
	Angular Momentum Quantum Number
$\boldsymbol{L}$	Angular Momentum
	Angular Momentum Operator
L_{l+m}	Laguerre Polynomial
$L_{\pm}$	Creation or Annihilation Operator for the z-Component of Angular Momentum
m	Mass, Magnetic Quantum Number
$\boldsymbol{m}$	Magnetic Moment
m_0	Rest Mass of the Electron
m_r	Reduced Mass
M	Magnetic Quantum Number
	Molecular Mass
n	Index of Refraction
	Principal Quantum Number
n_i	Number of Times the i-th Irreducible Representation Occurs in a Reducible Representation (6.47)
n_λ	Number of Quanta in the State λ
N	Number Density (Number per Unit Volume)
$\boldsymbol{N}$	Angular Momentum of Molecular Rotation
N_A	Avogadro's Number

p	Pressure
	Electronic State in an Atom
	Linear Momentum, Momentum Operator
$\boldsymbol{p}$	Electric Dipole Moment
	Linear Momentum, Momentum Operator
$p_{\mu,\kappa}$	Momentum Matrix Element (16.113)
$\overline{p}$	Expectation Value of Momentum
P	Momentum, Projection Operator (6.58)
$\boldsymbol{P}$	Momentum Operator
P_l^0	Legendre Polynomial
P_l^m	$(m \neq 0)$ Associated Legendre Function
Q	Class of a Group
r	Radial Distance, Particularly of Electrons
$\boldsymbol{r}$	Radius Vector
R	Distance of Nuclei
	Ideal Gas Constant
	Generalised Group Operation
$\hat{R}$	Reducible Representation Matrix
R_e	Equilibrium Distance or Bond Length
S	Overlap Integral (4.43)
	Spin Quantum Number
$\boldsymbol{S}$	Resultant Spin
	Spin Operator
S_m	Rotation-Inversion Operator
$S_m(j)$	$(m = \pm 1/2)$ Spin Function
S_+	Raising Operator for the z-Component of Total Spin
T	Temperature
	Electronic Term
T_1, T_2	Relaxation Times
v	Velocity
	Vibration Quantum Number
V	Potential
	Potential Energy
	Volume
$w_{\mu,\kappa}$	Transition Probability per Second
W	Energy
	Total Transition Probability
x_e	Anharmonicity Constant
$\overline{x}$	Expectation Value of Position (4.16)
Z	Nuclear Charge, Number of Initial States
α	Absorption Coefficient
	Polarisability
	Function of Moments of Inertia (11.72)

	Spin Function
	Angle
β	Hyperpolarisability
	Magnetic Polarisability (3.36)
	Optical Polarisability (3.14)
	Function of Moments of Inertia (11.72)
	Expansion Function with Respect to Time
	Spin Function
γ	Magnetogyric Ratio
Γ	Representation of a Group
	Linewidth
δ	Chemical Shift (NMR)
$\delta(x)$	Dirac Delta Function
δ_{ij}	Kronecker Delta Symbol
Δ	Difference Symbol
ε	Dielectric Constant
	Extinction Coefficient
	Infinitesimal Parameter
η	Quantum Yield
θ	Spherical Polar Coordinate
Θ	Inertial Tensor, Moment of Inertia (11.52)
$\boldsymbol{\Theta}_{\mu\kappa}$	Transition Dipole Matrix Element (16.120) ff.
λ	Quantum Number of Orbital Angular Momentum (13.4)
	Eigenvalue of a Determinant; Index which Distinguishes Plane Waves with Different Wavevectors k_λ
Λ	Total Orbital Angular Momentum (13.7)
μ	Transition Matrix Element (Sect. 15.1)
	Magnetic Moment
	Permeability Constant
ξ_i	Displacement from the Rest Position
π	(Orbital) Molecular Orbital (Linear Combination, in particular of p_z-Functions)
$\varrho(E)$	Energy Density
ϱ	Density
	Spin Density (ESR)
σ	Inversion Operator, Spin Matrices
	Diamagnetic Shielding Factor (NMR)
$\overline{\sigma}$	Inversion-Translation Operator
$\sum$	Summation Symbol
Σ	Molecular Term Symbol
ϕ	Wavefunction, Spherical Polar Coordinate
Φ	Wavefunction
χ	Wavefunction (Especially Oscillator Functions)
$\chi(R)$, $\chi_1(R)$	Character of R in a Reducible or Irreducible Representation

ψ	Wavefunction
Ψ	Wavefunction of Several Electrons
ω	Circular Frequency $2\pi\nu$
$\boldsymbol{\Omega}$	Total Electronic Angular Momentum
Ω	Solid Angle
∇	Nabla Operator
∇^2	Laplace Operator

Contents