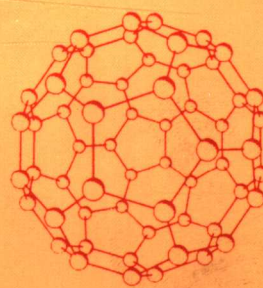
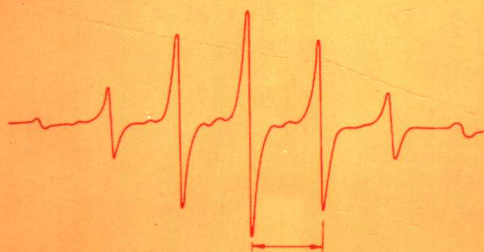
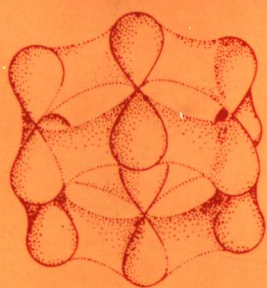


Haken · Wolf

# Molecular Physics and Elements of Quantum Chemistry

Introduction  
to Experiments and Theory

分子物理学和量子化学基础



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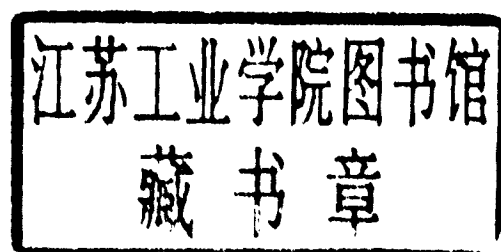
Hermann Haken   Hans Christoph Wolf

# Molecular Physics and Elements of Quantum Chemistry

Introduction  
to Experiments and Theory

Translated by William D. Brewer

With 261 Figures and 43 Tables



Springer

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## Preface

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 his or her 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 continue to fulfil 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 this 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 and H.C. Wolf*

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## 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
$A$	Vector Potential
$b$	Einstein Coefficient
$b_k^+, b_k$	Creation and Annihilation Operators for Bose Particles (7.47) ff.
$B$	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 (11.131) ff.
$c$	Velocity of Light in Vacuum
$c, C$	Concentration
$c_i$	Expansion Coefficient
$C, C_\phi, C_n$	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
$e$	Unit Vector
$E$	Energy
	Fine Structure Constant (ESR)
	Identity Operator
$E$	Electric Field Strength
$\bar{E}$	Energy Expectation Value
$E_{el}$	Electronic Energy
$E_{kin}, E_{pot}$	Kinetic or Potential Energy
$E_{rot}$	Rotational Energy
$E_{vib}, E_v$	Vibrational Energy
$\Delta E$	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
$\hbar = h/2\pi$	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
$k$	Wavevector
$l$	Mean Free Path
	Angular Momentum Quantum Number
$L$	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
$m$	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)
$n_{\lambda}$	Number of Quanta in the State $\lambda$
$N$	Number Density (Number per Unit Volume)
$N$	Angular Momentum of Molecular Rotation
$N_A$	Avogadro's Number
$p$	Pressure
	Electronic State in an Atom
	Linear Momentum, Momentum Operator
$p$	Electric Dipole Moment
	Linear Momentum, Momentum Operator
$p_{\mu,\kappa}$	Momentum Matrix Element (16.113)
$\bar{p}$	Expectation Value of Momentum
$P$	Momentum, Projection Operator (6.58)
$P$	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
$\mathbf{r}$	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
$S$	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
$\bar{x}$	Expectation Value of Position (4.16)
$Z$	Nuclear Charge, Number of Initial States
$\alpha$	Absorption Coefficient Polarisability Function of Moments of Inertia (11.72) Spin Function Angle
$\beta$	Hyperpolarisability Magnetic Polarisability (3.36) Optical Polarisability (3.14) Function of Moments of Inertia (11.72) Expansion Function with Respect to Time Spin Function
$\gamma$	Magnetogyric Ratio
$\Gamma$	Representation of a Group Linewidth
$\delta$	Chemical Shift (NMR)
$\delta(x)$	Dirac Delta Function
$\delta_{ij}$	Kronecker Delta Symbol
$\Delta$	Difference Symbol



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$\epsilon$	Dielectric Constant
	Extinction Coefficient
	Infinitesimal Parameter
$\eta$	Quantum Yield
$\theta$	Spherical Polar Coordinate
$\Theta$	Inertial Tensor, Moment of Inertia (11.52)
$\Theta_{\mu\kappa}$	Transition Dipole Matrix Element (16.120) ff.
$\lambda$	Quantum Number of Orbital Angular Momentum (13.2)
	Eigenvalue of a Determinant; Index which Distinguishes Plane Waves with Different Wavevectors $k_\lambda$
$\Lambda$	Total Orbital Angular Momentum (13.4)
$\mu$	Transition Matrix Element (15.6)
	Magnetic Moment
	Permeability Constant
$\xi_i$	Displacement from the Rest Position
$\pi$	(Orbital) Molecular Orbital (Linear Combination, in particular of $p_z$ -Functions)
$\varrho(E)$	Energy Density
$\varrho$	Density
	Spin Density (ESR)
$\sigma$	Inversion Operator, Spin Matrices
	Diamagnetic Shielding Factor (NMR)
$\bar{\sigma}$	Inversion-Translation Operator
$\sum$	Summation Symbol
$\Sigma$	Molecular Term Symbol
$\phi$	Wavefunction, Spherical Polar Coordinate
$\Phi$	Wavefunction
$\chi$	Wavefunction (Especially Oscillator Functions)
$\chi(R), \chi_1(R)$	Character of $R$ in a Reducible or Irreducible Representation
$\psi$	Wavefunction
$\Psi$	Wavefunction of Several Electrons
$\omega$	Circular Frequency $2\pi\nu$
$\Omega$	Total Electronic Angular Momentum
$\Omega$	Solid Angle
$\nabla$	Nabla Operator
$\nabla^2$	Laplace Operator

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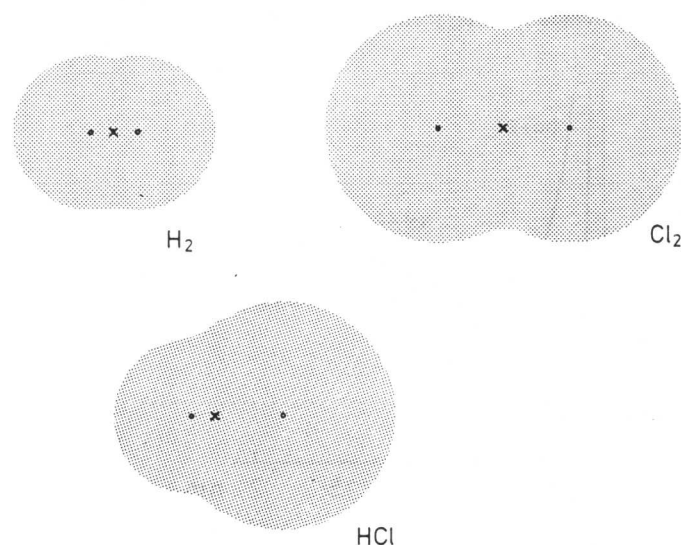
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# 1. Introduction

## 1.1 What is a Molecule?

When two or more atoms combine to form a new unit, that new particle is termed a *molecule*. The name is derived from the Latin word *molecula*, meaning "small mass". A molecule is the smallest unit of a chemical compound which still exhibits all its properties, just as we have seen the atom to be the smallest unit of a chemical element. A molecule may be decomposed by chemical means into its component parts, i.e. into atoms. The great variety of materials found in the world of matter is a result of the enormous variety of possible combinations in which molecules may be constructed out of the relatively few types of atoms in the Periodic Table of elements.

The simplest molecules are diatomic and homonuclear; that is, they are made up of two atoms of the same type, such as  $\text{H}_2$ ,  $\text{N}_2$ , or  $\text{O}_2$ . In these cases, one should imagine the electron distribution as shown in Fig. 1.1 (upper part): there are electrons which belong equally to both atoms, and they form the chemical bond. The next simplest group is that of diatomic molecules containing two different atoms, so-called heteronuclear molecules, such as  $\text{LiF}$ ,  $\text{HCl}$ , or  $\text{CuO}$ ; see Fig. 1.1 (lower part). In these molecules, in addition to chemical bonding by shared electrons, which is termed homopolar or covalent bonding, another bonding mechanism is important: heteropolar or ionic bonding.



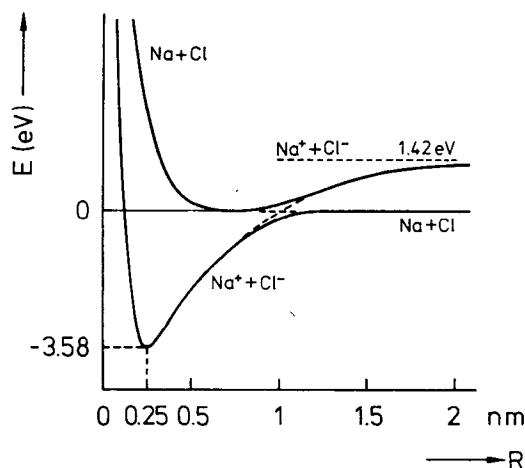
**Fig. 1.1.** Electron distributions in the small molecules  $\text{H}_2$ ,  $\text{Cl}_2$ , and  $\text{HCl}$ , shown schematically. The nuclear separations are 0.74 Å in  $\text{H}_2$ , 1.27 Å in  $\text{HCl}$ , and 1.99 Å in  $\text{Cl}_2$



We shall explain some of the basic concepts of molecular physics at this point by using as an example the molecule NaCl (in the gas phase). Figure 1.2 shows the potential energy of the system sodium + chlorine as a function of the distance between the atomic nuclei. At large internuclear distances, the interaction between a neutral sodium and a chlorine atom is quite weak and the potential energy of the interaction is thus nearly zero; a slight attractive interaction can, however, be caused by the weak mutual polarisation of the electronic charge clouds. If we bring the neutral atoms close together, at a distance of ca. 0.6 nm a repulsive interaction occurs. This fact can be used to define the size of the atoms, as discussed in more detail in I. (We denote the book *The Physics of Atoms and Quanta*, by H. Haken and H.C. Wolf, as I. We assume knowledge of the atomic physics treated in that book and will refer to it repeatedly in the following.)

At an internuclear distance of 1.2 nm, however, the state in which an electron from the sodium atom passes onto the chlorine atom becomes more energetically favored, and the system  $\text{Na}^+/\text{Cl}^-$  is thus formed by charge transfer. When the distance is further decreased, the effective interaction potential becomes practically the same as the attractive Coulomb potential between the two ions. An equilibrium state is finally reached at a distance of 0.25 nm, due to the competition between this attractive potential and the repulsion of the nuclei and the closed electronic shells of the ions; the repulsion dominates at still smaller distances. This equilibrium distance, together with the electron distribution corresponding to it, determine the size of the molecule.

Continuing through molecules containing several atoms, such as  $\text{H}_2\text{O}$  (water),  $\text{NH}_3$  (ammonia), or  $\text{C}_6\text{H}_6$  (benzene), with 3, 4, or 12 atoms, respectively, we come to large molecules such as chlorophyll or crown ethers, and finally to macromolecules and polymers such as polyacetylene, which contain many thousands of atoms and whose dimensions are no longer measured in nanometers, but instead may be nearly in the micrometer range. Finally, biomolecules such as the giant molecules of deoxyribonucleic acids (DNA), which are responsible for carrying genetic information (see Sect. 20.6), or molecular functional units such as the protein complex of the reaction centre for bacterial photosynthesis (cf. the schematic representation in Fig. 1.3), are also objects of study in molecular physics. These molecules will be treated in later sections of this book, in particular in Chap. 20.



**Fig. 1.2.** The potential energy  $E$  for NaCl and  $\text{Na}^+\text{Cl}^-$  as a function of their internuclear distance  $R$ , in the gas phase