H. Haken
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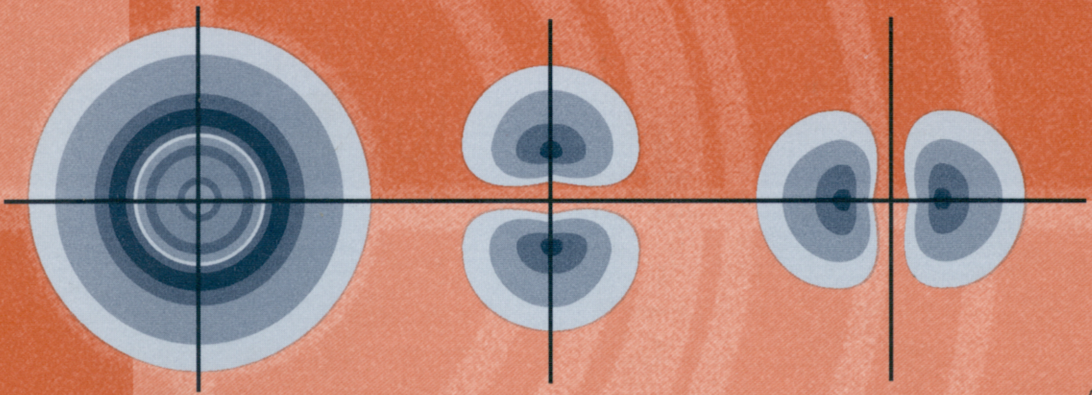
The Physics of Atoms and Quanta

Introduction to Experiments and Theory

Sixth Edition



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Fundamental Constants of Atomic Physics in the International System of Units (SI)

Permeability Constant of Vacuum	μ_0	$= 4\pi \cdot 10^{-7}\,\mathrm{Vs\,A^{-1}\,m^{-1}}$ $= 1.256637 \ldots \cdot 10^{-6}\,\mathrm{Vs\,A^{-1}\,m^{-1}}$
Permittivity Constant of Vacuum	ε_0	$= (\mu_0 c^2)^{-1}$ $= 8.8541878 \ldots \cdot 10^{-12}\,\mathrm{As\,V^{-1}\,m^{-1}}$
Velocity of Light in Vacuum	c	$= 2.99792458 \cdot 10^{8}\,\mathrm{ms^{-1}}$
Boltzmann's Constant	k	$= 1.380658 \cdot 10^{-23}\,\mathrm{JK^{-1}}$
Faraday Constant	F	$= 9.6485309 \cdot 10^{4}\,\mathrm{C\,mol^{-1}}$
Elementary Charge	e	$= 1.6021773 \cdot 10^{-19}\,\mathrm{C}$
Rest Mass of the Electron	m_0	$= 9.1093897 \cdot 10^{-31}\,\mathrm{kg}$
Specific Charge of the Electron	e/m_0	$= 1.75881962 \cdot 10^{11}\,\mathrm{C\,kg^{-1}}$
Rest Mass of the Proton	m_p	$= 1.6726231 \cdot 10^{-27}\,\mathrm{kg}$
Planck's Constant	h	$= 6.626755 \cdot 10^{-34}\,\mathrm{Js}$
	$\hbar$	$= h/2\pi = 1.0545887 \cdot 10^{-34}\,\mathrm{Js}$
Rydberg Constant	R_∞	$= 1.0973731534 \cdot 10^{7}\,\mathrm{m^{-1}}$
Bohr Radius	a_0	$= 0.529177249 \cdot 10^{-10}\,\mathrm{m}$
Bohr Magneton	μ_B	$= 9.2740154 \cdot 10^{-24}\,\mathrm{Am^2}\,(= \mathrm{J/T})$
Nuclear Magneton	μ_N	$= 5.0507866 \cdot 10^{-27}\,\mathrm{Am^2}$
Compton Wavelength of the Electron	λ_c	$= 2.42631058 \cdot 10^{-12}\,\mathrm{m}$
Fine Structure Constant	α	$= 7.29735308 \cdot 10^{-3}$
Avogadro's number	N_A	$= 6.022045 \cdot 10^{23}\,\mathrm{mol^{-1}}$

Energy Conversion Table see inside back cover

Energy Conversion Table

	J	eV	cm^{-1}	K
1 Joule (J) =	1	$6.24146 \cdot 10^{18}$	$5.03404 \cdot 10^{22}$	$7.24290 \cdot 10^{22}$
1 eVolt (eV) =	$1.60219 \cdot 10^{-19}$	1	$8.06548 \cdot 10^{3}$	$1.16045 \cdot 10^{4}$
1 cm^{-1} =	$1.98648 \cdot 10^{-23}$	$1.23985 \cdot 10^{-4}$	1	1.43879
1 K =	$1.38066 \cdot 10^{-23}$	$8.61735 \cdot 10^{-5}$	$6.95030 \cdot 10^{-1}$	1

Explanation

The energy E is quoted in Joule (J) or watt-seconds (Ws)

$$1\ \mathrm{J} = 1\ \mathrm{Ws}\ .$$

In spectroscopy, one frequently quotes the term values in wavenumbers $\bar{\nu} = E/hc$.

The conversion factor is

$$E/\bar{\nu} = hc = 1.98648 \cdot 10^{-23}\ \mathrm{J/cm^{-1}}\ .$$

Another energy unit, especially in collision experiments, is the electron volt (eVolt, eV). The voltage V is given in volts, and the energy conversion factor is obtained from $E = \mathrm{e}V$:

$$E/V = e = 1.60219 \cdot 10^{-19}\ \mathrm{J/V}\ .$$

In the case of thermal excitation with the heat energy kT, the absolute temperature is a measure of the energy. From $E = kT$ we obtain the conversion factor

$$E/T = k = 1.38066 \cdot 10^{-23}\ \mathrm{J/K}\ .$$

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Hermann Haken Hans Christoph Wolf

The Physics of Atoms and Quanta

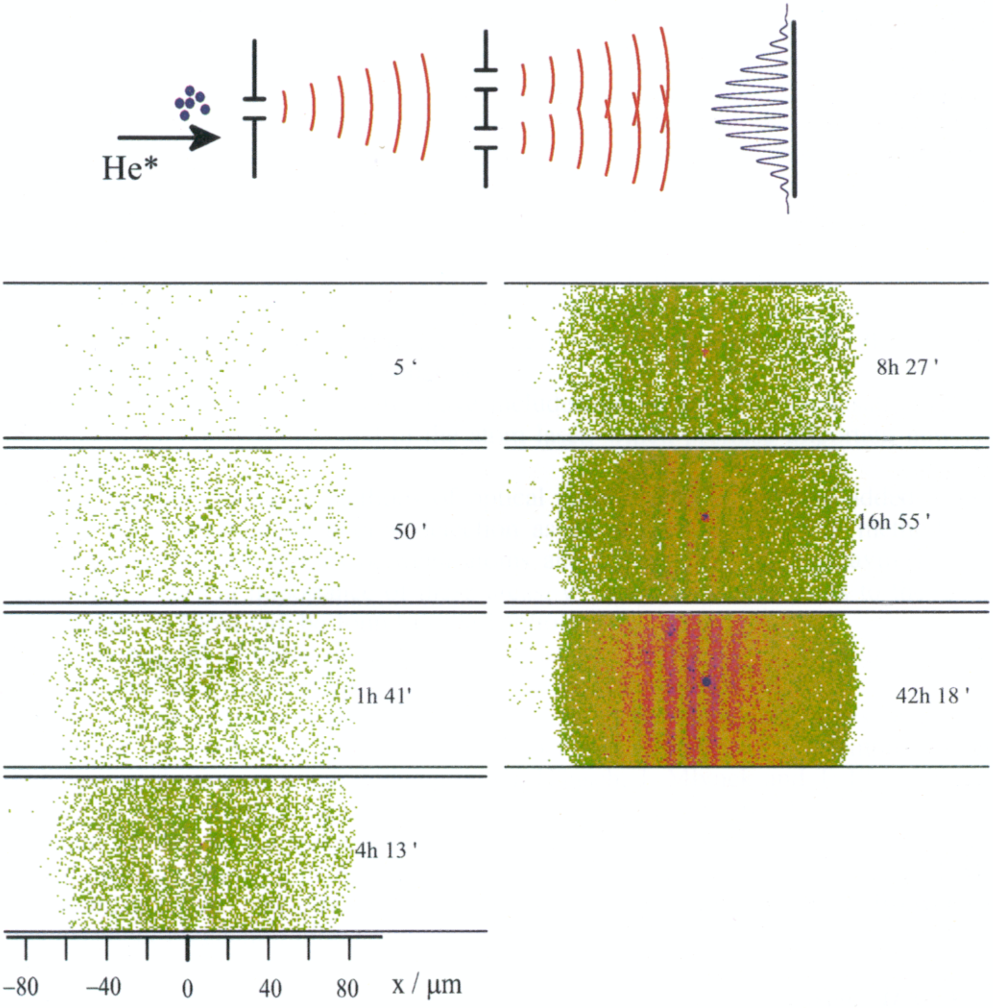
Introduction to Experiments and Theory

Translated by William D. Brewer

Sixth Revised and Enlarged Edition
With 287 Figures,
29 Tables, 173 Problems and Solutions

Springer

A Fundamental Experiment in Quantum Physics:
The Wave-Particle Dualism of Matter



When helium atoms all having the same direction and velocity are passed through a double-slit apparatus, each atom produces a strictly localised *point* of impact on a screen behind the slits; the atoms appear to be essentially particles. If the experiment is allowed to run for a longer time, so that a large number of impact points is registered on the screen, then an interference pattern appears, analogous to that seen in Young's double-slit experiment with light; the helium atoms thus behave in this case as waves. The seven images show the measured intensity distribution on the screen as a function of time (5′ to 42 h 18′) after starting the experiment. This experiment demonstrates the wave-particle dualism of matter in an impressive fashion. How quantum theory bridges the apparent contradiction: pointlike particle on the one hand, extended wave on the other, is a subject treated in this book. These experiments on helium atoms were carried out by O. Carnal, J. Mlynek: Phys. Rev. Lett. *66*, 2689 (1991) and Ch. Kurtsiefer, T. Pfau, J. Mlynek: Nature *386*, 150 (1997). More details are given in Sect. 6.6.

Preface to the Sixth Edition

Since a new edition of our book has once again become necessary, we have as before taken the opportunity to include the latest developments in atomic and quantum physics. These areas continue to yield new and fascinating experimental and theoretical results which are of fundamental importance and are also extremely interesting to students of science. As a result of newly developed experimental methods and theoretical techniques, it has also become possible to find solutions to some long-established problems. In this spirit we have added an entire new chapter dealing with entangled wavefunctions, the Einstein-Podolsky-Rosen paradox, Bell's inequalities, the paradox of Schrödinger's cat and the concept of decoherence. In addition, we have treated new ideas relating to quantum computers and the numerous quantum-physical schemes for constructing them. These new concepts exemplify the rapidly-developing area of quantum information.

Finally, in this new chapter we have included the experimental realisation of the Bose-Einstein condensation and of the atom laser, which promise important new applications.

In Chap. 22, "Modern methods of optical spectroscopy", we have added a new section on nondestructive photon detection as an example of efficient methods for investigating the interactions between atoms and photons in resonant cavities. Considering the current importance of these areas, we emphasize references to the original literature. These can be found in the Bibliography.

In treating all of these subjects, we have as usual made an effort to give a readily understandable description, in line with the tradition of this book.

Once again, we express our gratitude to those students, colleagues and other readers of the book who have made a number of suggestions for its improvement. Our special thanks go to our colleagues Th. Hänsch, J. Mlynek and T. Pfau for providing us with coloured figures of their newest experimental results. We thank Ms. Irmgard Möller for her quick and careful preparation of the new parts of the manuscript. We are grateful to Springer-Verlag, in particular Dr. H.J. Kölsch and Mr. C.-D. Bachem for their efficient cooperation as always, and Prof. W.D. Brewer for his excellent translation of the new chapters.

Stuttgart, March 2000 *H. Haken H.C. Wolf*

Preface to the Fourth Edition

This fourth edition contains a few additional figures. Otherwise only typographical errors have been removed.

The final chapter on Fundamentals of the Quantum Theory of Chemical Bonding is continued in an extended way in the textbook *Molecular Physics and Elements of Quantum Chemistry* by the same authors. This book contains, in particular, a profound presentation of group theory as applied to atoms and molecules. Furthermore, the interaction between atoms and molecules and light is treated in detail.

We thank again Springer-Verlag, in particular Dr. H. J. Kölsch and Mr. C.-D. Bachem for their excellent cooperation as always, and Prof. W. D. Brewer for his continuous support in translating our German text.

Stuttgart, February 1994 *H. Haken H. C. Wolf*

Preface to the First Edition

A thorough knowledge of the physics of atoms and quanta is clearly a must for every student of physics but also for students of neighbouring disciplines such as chemistry and electrical engineering. What these students especially need is a coherent presentation of both the experimental and the theoretical aspects of atomic and quantum physics. Indeed, this field could evolve only through the intimate interaction between ingenious experiments and an equally ingenious development of bold new ideas.

It is well known that the study of the microworld of atoms caused a revolution of physical thought, and that fundamental ideas of classical physics, such as those on measurability, had to be abandoned. But atomic and quantum physics is not only a fascinating field with respect to the development of far-reaching new physical ideas. It is also of enormous importance as a basis for other fields. For instance, it provides chemistry with a conceptual basis through the quantum theory of chemical bonding. Modern solid-state physics, with its numerous applications in communication and computer technology, rests on the fundamental concepts first developed in atomic and quantum physics. Among the many other important technical applications we mention just the laser, a now widely used light source which produces light whose physical nature is quite different from that of conventional lamps.

In this book we have tried to convey to the reader some of the fascination which atomic and quantum physics still gives a physicist studying this field. We have tried to elaborate on the fundamental facts and basic theoretical methods, leaving aside all superfluous material. The text emerged from lectures which the authors, an experimentalist and a theoretician, have given at the University of Stuttgart for many years. These lectures were matched with respect to their experimental and theoretical contents.

We have occasionally included in the text some more difficult theoretical sections, in order to give a student who wants to penetrate further into this field a self-contained presentation. The chapters which are more difficult to read are marked by an asterisk. They can be skipped on a first reading of this book. We have included chapters important for chemistry, such as the chapter on the quantum theory of the chemical bond, which may also serve as a starting point for studying solid-state physics. We have further included chapters on spin resonance. Though we explicitly deal with electron spins, similar ideas apply to nuclear spins. The methods of spin resonance play a fundamental role in modern physical, chemical and biological investigations as well as in medical diagnostics (nuclear spin tomography). Recent developments in atomic physics, such as studies on Rydberg atoms, are taken into account, and we elaborate the basic features of laser light and nonlinear spectroscopy. We hope that readers will find atomic and quantum physics just as fascinating as did the students of our lectures.

The present text is a translation of the second German edition *Atom- and Quantenphysik*. 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. Our thanks also go to Dr. J. v. Schütz and Mr. K. Zeile for the critical reading of the manuscript, to Ms. S. Schmiech and Dr. H. Ohno for the drawings, and to Mr. G. Haubs for the careful proofreading. We would like to thank Mrs. U. Funke for her precious help in typing new chapters. Last, but not least, we wish to thank Springer-Verlag, and in particular H. Lotsch and G.M. Hayes, for their excellent cooperation.

Stuttgart, February 1984 *H. Haken H.C. Wolf*

Contents

Appendix

List of the Most Important Symbols Used

The numbers of the equations in which the symbols are defined are given in parentheses; the numbers in square brackets refer to the section of the book. The Greek symbols are at the end of the list.

$\mathbf{A}$	Vector potential
A	Amplitude or constant
A	Mass number (2.2) or area
a	Interval factor or fine structure constant (12.28) and hyperfine splitting (20.10)
a_0	Bohr radius of the H atom in its ground state (8.8)
$\mathbf{B}$	Magnetic induction
b^+, b	Creation and annihilation operators for the harmonic oscillator
b	Constant, impact parameter
C	Constant
c	Velocity of light, series expansion coefficient
c.c.	Complex conjugate
$\mathbf{D}$	Dipole moment
d	Constant
dV	Infinitesimal volume element
$\mathbf{E}$	Electric field strength
E	Energy, total energy, energy eigenvalue
E_{kin}	Kinetic energy
E_{pot}	Potential energy
E_{tot}	Total energy
e	Proton charge
$-e$	Electron charge
e	Exponential function
$\mathbf{F}$	Electric field strength (14.1)
$\mathbf{F}, F$	Total angular momentum of an atom, including nuclear angular momentum and corresponding quantum number (20.6)
F	Amplitude of the magnetic induction [14.4, 14.5]
f	Spring constant
g	Landé g factor (12.10, 16, 21, 13.18, 20.13)
$\mathcal{H}$	Hamilton function, Hamiltonian operator
H_n	Hermite polynomial
h	Planck's constant
$\hbar$	$= h/2\pi$
$\mathbf{I}, I$	Nuclear angular momentum and corresponding quantum number (20.1)
I	Abbreviation for integrals [16.13] or intensity
i	Imaginary unit ($\mathrm{i} = \sqrt{-1}$)
$\mathbf{J}, J$	Total angular momentum of an electron shell and corresponding quantum number (17.5)
$\mathbf{j}, j$	Total angular momentum of an electron and corresponding quantum number [12.7]
$\hat{j}$	Operator for the total angular momentum
k	Boltzmann's constant, force constant
$\mathbf{k}$	Wavevector
$\mathbf{L}, L$	Resultant orbital angular momentum and corresponding quantum number (17.3)
L_n	Laguerre polynomial (10.81)
$\mathbf{l}, l$	Orbital angular momentum of an electron and corresponding quantum number
$\hat{l}$	Angular momentum operator
m, m_0	Mass
m	Magnetic quantum number
m_l	– for angular momentum
m_s	– for spin
m_j	Magnetic quantum number for total angular momentum
m_0	Rest mass, especially that of the electron

N, n	Particle number, particle number density
N	Normalisation factor
n	Principal quantum number or number of photons or an integer
P	Spectral radiation flux density (5.2) or probability
P_l^0	Legendre polynomial
P_l^m	($m \neq 0$) Associated Legendre function
$p, \bar{p}$	Momentum, expectation value of momentum
Q	Nuclear quadrupole moment (20.20)
Q, q	Charge
$R(r)$	Radial part of the hydrogen wavefunction
$\mathbf{r}$	Position coordinate (three-dimensional vector)
r	Distance
$\mathbf{S}$	Resultant spin (17.4)
S	Symbol for orbital angular momentum $L = 0$
$\mathbf{s}, s$	Electron spin and corresponding quantum number (12.15)
$\hat{\mathbf{s}}$	Spin operator $= (\hat{s}_x, \hat{s}_y, \hat{s}_z)$
T	Absolute temperature
T_1	Longitudinal relaxation time
T_2	Transverse relaxation time
t	Time
u	Spectral energy density (5.2), atomic mass unit [2.2]
V	Volume, potential, electric voltage
$\bar{V}$	Expectation value of the potential energy
v	Velocity, particle velocity
x	Particle coordinate (one-dimensional)
$\bar{x}$	Expectation value of position
$Y_{l,m}(\theta, \phi)$	Spherical harmonic functions (10.10, 48 – 50)
Z	Nuclear charge
α	Fine structure constant [8.10] or absorption coefficient (2.22)
β	Constant
Γ	Decay constant
γ	Decay constant or linewidth gyromagnetic ratio (12.12)

∇^2	Laplace operator $= \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$
ΔE	Energy uncertainty
Δk	Wavenumber uncertainty
Δp	Momentum uncertainty
Δt	Time uncertainty (= finite measurement time)
ΔV	Finite volume element
$\Delta \omega$	Uncertainty in the angular frequency
Δx	Position uncertainty
$\delta(x)$	Dirac delta function (see mathematics appendix)
$\delta_{\mu,\nu}$	Kronecker delta symbol: $\delta_{\mu,\nu} = 1$ for $\mu = \nu$, $\delta_{\mu,\nu} = 0$ for $\mu \neq \nu$
ε	Dimensionless energy (9.83)
$\varepsilon^{(n)}$	Energy contributions to perturbation theory
ε_0	Permittivity constant of vacuum
θ	Angle coordinate (10.2)
κ	Defined in (10.54)
λ	Wavelength (exception: expansion parameter in [15.2.1, 2]) Mean free path [2.4.3]
$\boldsymbol{\mu}, \mu$	Magnetic moment (12.1)
μ	Reduced mass (8.15)
μ_B	Bohr magneton (12.8)
μ_N	Nuclear magneton (20.3)
ν	Frequency [8.1]
$\bar{\nu}$	Wavenumber [8.1]
ξ	Dimensionless coordinate (9.83)
ϱ	Charge density, density of states, mass density; or dimensionless distance
σ	Scattering coefficient, interaction cross section (2.16)
τ	Torque (12.2)
Φ	Phase
ϕ	Phase angle, angle coordinate
$\phi(x)$	Wavefunction of a particle
$\phi_\uparrow, \phi_\downarrow, \phi$	Spin wavefunctions
ψ	Wavefunction
Ψ	Wavefunction of several electrons
$\hat{\Omega}$	Generalised quantum mechanical operator
Ω	Frequency [14.4, 14.5, 15.3]
ω	Angular frequency $2\pi\nu$, or eigenvalue [9.3.6]
$\triangleq$	means "corresponds to"

1. Introduction

1.1 Classical Physics and Quantum Mechanics

Atomic and quantum physics, which are introduced in this book, are essentially products of the first third of this century. The division of classical physics into branches such as mechanics, acoustics, thermodynamics, electricity, and optics had to be enlarged when – as a consequence of the increasing knowledge of the structure of matter – atoms and quanta became the objects of physical research. Thus, in the twentieth century, classical physics has been complemented by atomic physics and the physics of light or energy quanta. The goal of atomic physics is an understanding of the structure of atoms and their interactions with one another and with electric and magnetic fields. Atoms are made up of positively charged nuclei and negatively charged electrons. The electromagnetic forces through which these particles interact are well known in classical physics.

The physics of atomic nuclei cannot be understood on the basis of these forces alone. A new force – the nuclear or strong force – determines the structures of nuclei, and the typical binding energies are orders of magnitude larger than those of the electrons in atoms. The study of nuclei, of elementary particles, and the whole of high energy physics thus form their own branches of physics. They will not be treated in this book.

1.2 Short Historical Review

The word *atom* comes from the Greek and means "the indivisible", the smallest component of matter, which cannot be further divided. This concept was introduced in the 5th and 4th centuries B.C. by Greek natural philosophers. The first atomic theories of the structure of matter were those of *Democrites* (460 – 370 B.C.), *Plato* (429 – 348), and *Aristotle* (384 – 322). It required more than two millenia until this speculative atomism grew into an exact atomic physics in the modern sense.

The meaning of the word *atom* becomes less subject to misinterpretation if it is translated into Latin: an *individuum* is the smallest unit of a large set which possesses all the essential characteristics of the set. In this sense, an atom is in fact indivisible. One can, to be sure, split a hydrogen atom into a proton and an electron, but the hydrogen is destroyed in the process. For example, one can no longer observe the spectral lines characteristic of hydrogen in its optical spectrum.

Atomism as understood by modern science was first discovered for *matter*, then for *electricity*, and finally for *energy*.

The *atomism of matter*, the recognition of the fact that all the chemical elements are composed of atoms, followed from chemical investigations. The laws of constant and multiple proportions, formulated by *J. L. Proust* ca. 1799 and by *Dalton* ca. 1803, can be explained very simply by the atomic hypothesis:

The reaction equations

14 g nitrogen + 16 g oxygen yield 30 g NO and

14 g nitrogen + 32 g oxygen yield 46 g NO_2

mean: the atomic weights of nitrogen and oxygen are related as 14 : 16.

Only whole atoms are react with one another. The first atomic model (*W. Prout*, 1815) assumed that the atoms of all elements are put together out of hydrogen atoms. As a heuristic principle this hypothesis finally led to a scheme for ordering the elements based on their chemical properties, the *periodic system* of *L. Meyer* and *D. I. Mendeleev* (1869). More about this subject may be found in introductory textbooks on chemistry.

About the same time (1808), it was found by *Gay-Lussac* that not only the weights but also the *volumes* of gaseous reactants occur as ratios of small integers. In the above example,

1 volume nitrogen + 1 volume oxygen yield 2 volumes NO

1 volume nitrogen + 2 volumes oxygen yield 2 volumes NO_2.

Similar observations led to the *hypothesis of Avogadro* (1811): Equal volumes of gases under similar conditions (pressure, temperature) contain equal numbers of molecules.

Continued investigations of gases in the course of the 19th century led to the *atomism of heat*, that is, to the explanation of heat in general and of the thermodynamic laws in particular as consequences of atomic motion and collisions. In about 1870, the first theory to encompass a whole branch of physics, the *kinetic theory of gases*, was completed by the physicists *Clausius* and *Boltzmann*.

The *atomism of electricity* was discovered in 1833 by the English scientist *Michael Faraday*. Based on the quantitative evaluation of exceedingly careful measurements of the electrolysis of liquids, he formulated his famous laws:

> The quantity of an element which is separated is proportional to the quantity of charge transported in the process,

and

> various elements are separated into equivalent weights by the same quantity of charge.

From this, *Faraday* concluded:

> There are "atoms" of electricity – it was only after 70 years that their mass and charge could be determined –

and

> these "atoms" of electricity – the electrons – are bound to atoms of matter.

The discovery of the *atomism of energy* can be dated exactly: on December 14, 1900, *Planck* announced the derivation of his laws for black body radiation in a lecture before the Physical Society in Berlin. In order to derive these laws, he assumed that the energy of harmonic oscillators can only take on discrete values – quite contradictory to the classical view, in which the energy values form a continuum.

This date can be called the birth date of quantum theory. The further development of atomic and quantum physics is the subject of this book.

Our knowledge of the structure of atoms was influenced strongly by the investigation of optical spectra. After *Kirchhoff* and *Bunsen* had shown, about 1860, that optical spectra are characteristic of the elements which are emitting or absorbing the light, *Balmer* (1885) succeeded in finding an ordering principle in atomic spectra, expressed in the formula (8.1) which bears his name and which describes the spectral lines emitted from hydrogen atoms. As a result of the atomic model proposed by *Rutherford* (1911), *Bohr* was able, in 1913, to formulate the basic principles of the quantisation of electron orbits in atoms. These quantisation rules were considerably extended by *Sommerfeld*. A parallel development was the concept of matter waves, carried out by *De Broglie*. The actual breakthrough was attained by *Born, Heisenberg, Schrödinger, Pauli, Dirac,* and other researchers in the decade between 1920 and 1930.

The problems of atomic physics which are of current interest in research are:

- an increasingly detailed description of the structure of electronic shells of atoms and their excitations,
- the interactions between atoms and radiation fields, for example in view of their applications in optical pumping (Chap. 21) and in laser physics (Chap. 22),

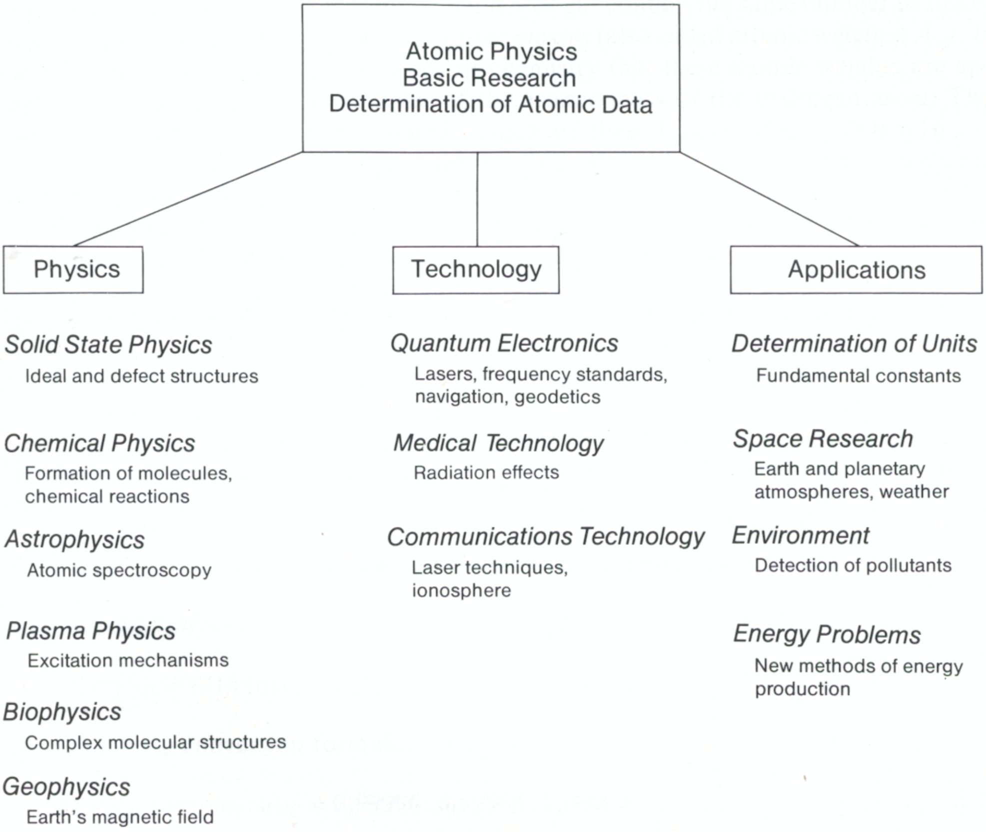


Fig. 1.1. The relevance of atomic physics for other disciplines of science and technology

- the interactions of atoms among themselves due to collisions in the gas phase and during the formation of molecules,
- the physical principles which lead to the formation of condensed phases from single atoms, and their properties.

Thus molecular and solid state physics are based on atomic physics, and chemistry as well makes constant use of its laws and principles.

Atomic physics is furthermore a basic science for many other disciplines of research, technology, and applications. A few examples are shown in Fig. 1.1.

The following chapters do not give a historical or a chronological presentation; they do, however, show the general line of developments and discoveries. An inductive approach is often used. It is of little use in physics to content oneself with the acquisition of factual knowledge. A physicist must learn to analyse, to explain, and to extract the essentials from experimental findings. In this way, one develops models for nature. In the process, it is important to recognise relationships to other experimental results and to be able to predict the outcome of new experiments. The predictions must then be experimentally tested. Because of this process, physics is not a dead, finalised science, but rather is in a constant state of development, since new experimental techniques open up new areas of research while, on the other hand, the process of developing physical concepts gives the impulse for ever newer experiments.

2. The Mass and Size of the Atom

2.1 What is an Atom?

An atom is the smallest unchangeable component of a chemical element. *Unchangeable* means in this case *by chemical means*; i.e., by reactions with acids or bases or the effect of moderate temperatures, atoms may only be slightly changed, namely, in their degree of ionisation. Moderate temperatures refers here to temperatures whose equivalent energy kT (k is Boltzmann's constant, T the temperature in K) is not larger than a few electron volts (eV) (see Table 8.1).

2.2 Determination of the Mass

Beginning with *Dalton*'s law of constant and multiple proportions, and *Avogadro*'s hypothesis, according to which equal volumes of gas contain the same number of molecules or atoms, we introduce *relative atomic masses* (also called atomic weights) A_{rel}. It was first discovered with the methods of chemistry that these atomic weights are approximately whole-number multiples of the atomic mass of the hydrogen atom. The relative atomic masses of nitrogen and oxygen are then $A_{\text{rel}}(\text{N}) \simeq 14$, $A_{\text{rel}}(\text{O}) \simeq 16$.

For this reason, an atomic mass unit has been defined, 1 u (abbreviation for unit, previously also referred to as 1 amu), which is approximately equal to the mass of a hydrogen atom. Since 1961 the unit of atomic mass has been based on the carbon atom ^{12}C with $A_{\text{rel}} = 12.00000\,\text{u}$ and is thus no longer exactly equal to the mass of the H atom. The use of C as base substance was found to be expedient for the experimental precision determination of atomic masses by chemical means. We have as definition

$$\begin{aligned}1\,\text{u} = 1/12 &\text{ of the mass of a neutral carbon atom with nuclear charge 6}\\ &\text{and mass number 12, i.e., } {}^{12}_{6}\text{C}\,. \end{aligned} \qquad (2.1)$$

Earlier scales were defined somewhat differently: the old "chemical" scale was based on oxygen in the naturally occurring isotope mixture:

$$1\,\text{amu}_{\text{chem}} = 1/16\,(\text{average mass of O atoms in the natural isotopic mixture})$$

and the old "physical" scale was based on the oxygen isotope ^{16}O:

$$1\,\text{amu}_{^{16}\text{O}} = 1/16\,(\text{mass of an } {}^{16}\text{O atom})\,.$$

The following conversion formulae hold:

$$\text{amu}_{\text{chem}} : \text{amu}_{^{16}\text{O}} : \text{u}_{^{12}\text{C}} = 0.99996 : 0.99968 : 1.00000 \qquad (2.2)$$

and

$$A_{\mathrm{rel,chem}} : A_{\mathrm{rel},{}^{16}\mathrm{O}} : A_{\mathrm{rel},{}^{12}\mathrm{C}} = 1.00004 : 1.00032 : 1.00000 \,. \tag{2.3}$$

The absolute atomic masses can be obtained from the relative masses using the concept of the mole.

1 mole of a substance is, according to *Avogadro*, as many grams as the relative atomic weight (in the case of molecules, as the correspondingly defined relative molecular weight). Thus, 1 mole of the carbon isotope ${}^{12}_{6}\mathrm{C}$ is 12 grams. 1 mole of any substance contains the same number (N_A) of atoms (molecules).

The number N_A which is defined in this way is called Avogadro's number (in the German literature, it is called the Loschmidt number after the Austrian physicist *Loschmidt* who determined it in 1865 by measurements on gases). Experimental methods for its determination will be discussed in the following section.

The absolute atomic mass m_{atom} can therefore be obtained by measuring Avogadro's number. We have:

$$\text{Mass of an atom} = \frac{\text{Mass of 1 mole of the substance}}{N_A} \,. \tag{2.4}$$

The determination of atomic masses is thus based on the determination of Avogadro's number; the size of the latter depends evidently on the choice of the base substance for the mole. N_A is currently defined as the number of carbon atoms in 12.000 g of isotopically pure ${}^{12}_{6}\mathrm{C}$.

The present best value for N_A is

$$N_A = (6.022045 \pm 0.000005) \cdot 10^{23}\,\mathrm{mole}^{-1} \,.$$

With this value, we can write (2.4) in the form

$$m_{\mathrm{atom}} = \frac{A_{\mathrm{rel},{}^{12}\mathrm{C}}}{N_A}\,[\mathrm{gram}] \,. \tag{2.5}$$

For the conversion of the mass unit u into other units the following relations hold:

$$1\,\mathrm{u} = (1.660565 \pm 0.000005) \cdot 10^{-27}\,\mathrm{kg} = 931.478\,\frac{\mathrm{MeV}}{c^2} \,. \tag{2.6}$$

This last conversion results from the mass-energy equivalence $E = mc^2$. MeV is a measure of energy (see Table 8.1), c is the velocity of light. Numerical values for masses m, relative atomic masses A_{rel}, and the mass number A of a few atoms are shown in Table 2.1.

Table 2.1. Mass number, mass, and relative atomic mass of several atoms

	Mass number A	Mass m [kg]	A_{rel}
H atom	1	$1.67342 \cdot 10^{-27}$	1.007825
C atom	12	$19.92516 \cdot 10^{-27}$	12.000000
O atom	16	$26.5584 \cdot 10^{-27}$	15.99491

The mass number A of an atom is the integer which is closest to its relative atomic mass A_{rel}. It is found in nuclear physics that A is equal to the number of nucleons (protons and neutrons) in the atomic nucleus.

2.3 Methods for Determining Avogadro's Number

2.3.1 Electrolysis

In electrolytic decomposition of salts from a solution, the amount of salt decomposed is proportional to the charge which flows through the electrolyte. For one mole of a monovalent substance, a charge of 96485 As (ampere-seconds) is required. This is the Faraday constant F. Thus, since each ion carries one elementary charge e, we have the relation $N_{\mathrm{A}} = F/e$. The elementary charge e denotes the charge on a single electron (see Sect. 6.3). For example, in order to electrodeposit one mole or 63.5 g of copper from a solution of $\mathrm{CuSO_4}$ in water, $2N_{\mathrm{A}}$ electrons are necessary, since the copper ion is doubly positively charged. By weighing the amount of material deposited and measuring the electric current as well as the time, one can obtain the constant N_{A}.

2.3.2 The Gas Constant and Boltzmann's Constant

The universal gas constant R and Boltzmann's constant k are related through the equation $k = R/N_{\mathrm{A}}$.

The gas constant can be determined by means of the ideal-gas law $pV = RT$; the Boltzmann constant, for example, from sedimentation equilibria (*Perrin,* 1908). In the latter method, the density distribution of small suspended particles in a liquid, determined by the simultaneous action of gravity and the Brownian molecular motion, is given by the equation

$$n_h = n_0\,\mathrm{e}^{-mgh/kT}, \tag{2.7}$$

where n_h is the number of particles in a unit volume at a height h, n_0 the number of particles in a unit volume at height $h = 0$, m the mass of the particles, g the acceleration of gravity, k the Boltzmann constant, and T the absolute temperature. In Fig. 2.1, a model

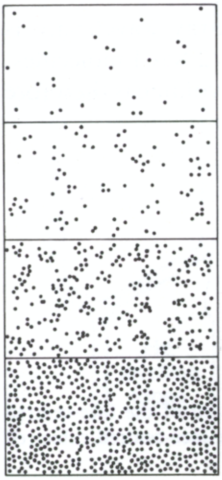


Fig. 2.1. Sedimentation equilibrium: distribution of suspended mastix spheres of 0.6 μm diameter at four different heights in the field of view of a microscope (after *Perrin*)

experiment demonstrating sedimentation is shown. The formula given by (2.7) is a special case of the famous Boltzmann distribution. Since we will use this distribution in numerous places in this book, we will give an explicit general formula for it here. The exact derivation may be found in texts on statistical physics. According to the Boltzmann distribution, the number of particles with energies in the interval $E \dots E+dE$ in thermal equilibrium is given by

$$n_E dE = NZ(T)\,\mathrm{e}^{-E/kT} g(E)\,dE\,, \tag{2.8}$$

where, generalising (2.7), the following quantities appear: N is the total number of particles, $Z(T)$ is the *partition function*. The latter ensures that, integrating over the whole energy range, one obtains the total particle number N, i.e., $\int n_E dE = N$. It is therefore given by $Z(T)^{-1} = \int \exp(-E/kT)\,g(E)\,dE$. Finally, $g(E)$ is the *density of states*; it is necessary since, for example, particles with the same energy can be moving in different directions, i.e., there can be more than one state with the energy E.

A completely satisfactory definition of $g(E)$ only becomes possible with the help of quantum mechanics. Using quantum numbers, of which we will later encounter a number of examples, one can count the number of "states" in the interval $E \dots E+dE$.

2.3.3 X-Ray Diffraction in Crystals

With x-radiation of a known wavelength, one can determine the lattice constant, or the volume of an atom or molecule in a crystal. The volume of a mole V_{mol} is then N_A times the atomic volume. For one mole one thus has

$$N_A V_{\mathrm{atom}} = V_{\mathrm{mol}} = M/\varrho\,, \tag{2.9}$$

where M denotes the molar mass and ϱ the mass density.

Figure 2.2 illustrates the principle; it shows a section of a NaCl lattice. NaCl crystallises in the face-centred cubic structure. The NaCl lattice can be built up from two face-centred cubic lattices containing the Na^+ and the Cl^- ions. These ions occupy the corners of cubes of side $a/2$, where a is the edge length of the Na^+ or Cl^- unit cell. The unit cell is the smallest unit of a crystal, in the sense that the crystal structure consists of a repetition of this element in each of the three dimensions of space.

The size of a can be determined by x-ray diffraction if the x-ray wavelength is known (Sect. 2.4.5). In a cube of volume $(a/2)^3$, there are $4/8 = 1/2$ NaCl molecules, since each ion belongs to 8 cubes. The number of molecules per unit volume is therefore

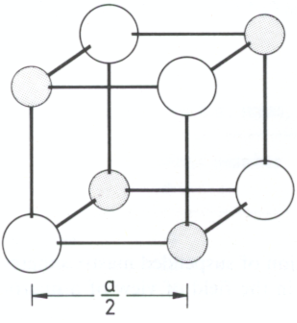


Fig. 2.2. Section of a NaCl lattice. The unit cell of the face-centred cubic lattice is a cube of side a. It contains one face-centred cubic cell each of Na^+ and of Cl^- ions

$$n = (1/2)(2/a)^3 . \tag{2.10}$$

When we set this equal to the quotient $N_A/V_{mol} = N_A \varrho/M$, we obtain

$$N_A = \frac{4M}{a^3 \varrho} = \frac{4 \cdot 58.4}{(5.63)^3 \cdot 10^{-24} \cdot 2.16} = 6.05 \cdot 10^{23}\,\mathrm{mol}^{-1} \quad \text{or} \tag{2.11}$$

$$6.05 \cdot 10^{26}\,(\mathrm{kmol})^{-1} \quad \text{with} \quad a = 5.63 \cdot 10^{-8}\,\mathrm{cm} \quad \text{and} \quad \varrho = 2.16\,\mathrm{gcm}^{-3} .$$

The accuracy of a measurement of N_A by this method is about $5 \cdot 10^{-6}$ (relative uncertainty). The density ϱ cannot, up to now, be determined with greater accuracy. However, the lattice constant a can be obtained with much greater accuracy using an x-ray interferometer of Si single crystals, resulting in a relative error of $6 \cdot 10^{-8}$. This method becomes an absolute technique for determining N_A if the measurement of the x-ray wavelength is made using a mechanically ruled grating and can thus be related to the meter directly. This becomes possible with the method of grazing-incidence diffraction; in the normal-incidence method, the mechanically prepared rulings are too wide relative to the wavelength.

2.3.4 Determination Using Radioactive Decay

Among the many other methods with which N_A has been determined, we will only mention here that of *Rutherford* and *Royds* from the year 1909.

In the experimental setup shown in Fig. 2.3, a radon source is contained in the interior of the glass tube A. The α particles which are emitted by this source can pass through the thin walls of tube A. In the second, thick-walled tube B, the α particles,

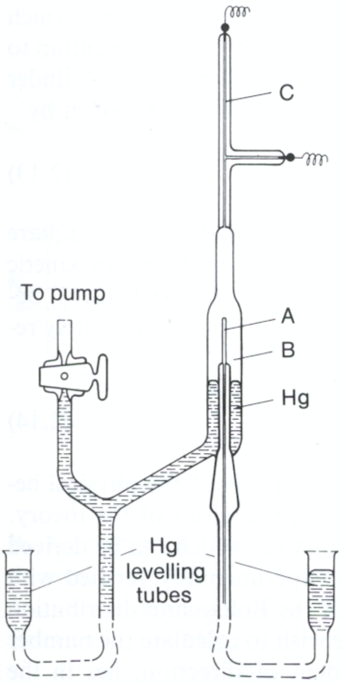


Fig. 2.3. Experimental arrangement of *Rutherford* and *Royds*: Phil. Mag. **17**, 281 (1909). The thin-walled glass tube A contains the α-active gas radon, ${}^{222}_{86}\mathrm{Rn}$. The helium atoms which collect after some days in the evacuated space B are compressed into the capillary C and detected in the spectrum of a gas discharge. The mercury levelling vessels serve to compress the gases

which are the atomic nuclei of helium atoms, collect as He gas. Through ionisation processes in the source, in the glass walls, and in the gas, electrons are set free which can combine with the α particles and make them into He atoms. Ignition of a gas discharge in tube C excites these atoms and causes them to emit light; spectral analysis shows that the gas is, in fact, helium.

In this manner, it was demonstrated that α particles are helium nuclei. If one measures the quantity of gas which is formed in a certain time, and knows the decay rate of the source (e.g., by counting with a Geiger counter or scintillation detector), one can determine the number of atoms per unit volume and thus N_A.

2.4 Determination of the Size of the Atom

2.4.1 Application of the Kinetic Theory of Gases

The kinetic theory of gases describes the macroscopic state variables of gases such as pressure and temperature on an atomic basis. Its application to the explanation of the macroscopically measurable quantities relevant to gases also leads to a determination of the size of the atoms. To understand this, we must first recall the arguments which provide convincing evidence for the correctness of the kinetic theory.

The ideal-gas law states

$$pV = nRT\,, \tag{2.12}$$

where p is the pressure, V the volume, n the number of moles, R the universal gas constant, and T the temperature.

At constant temperature, this is Boyle's law. Equation (2.12) can also be derived kinetically. To do this, one calculates the number of particles in a given volume which collide with a unit surface of the walls per unit time and thereby transfer momentum to the walls (this is the number of particles contained in the so-called Maxwellian cylinder of length v). The pressure which is exerted by the gas on the walls is then given by

$$p = (1/3)Nm\overline{v^2}\,, \tag{2.13}$$

where m is the mass of the particles (gas atoms or molecules), $\overline{v^2}$ is their mean-square velocity, and N is the number of particles per unit volume. Since the mean kinetic energy $m\overline{v^2}/2$ of a free particle in thermal equilibrium is equal to $(3/2)\,kT$, (2.13) becomes $p = NkT$. This equation is identical to the ideal-gas law, as one immediately recognises upon multiplication by the molar volume V_{mol}:

$$pV_{\mathrm{mol}} = NV_{\mathrm{mol}}kT = N_A kT = RT\,. \tag{2.14}$$

The demonstration that the kinetic theory gives a good description of the physical behaviour of gases is provided by experimental testing of the predictions of the theory. For example, the distribution of the molecular velocities in a gas which can be derived from the kinetic theory (Maxwell distribution) has been experimentally verified with great accuracy. This distribution is again a special case of the Boltzmann distribution [cf. (2.8)]. Here the energy of a particle is $E = mv^2/2$. We wish to calculate the number of particles, $n(v)\,dv$, whose *absolute* velocity, independent of direction, lies in the interval $v \dots v+dv$. Thus we must recalculate the density function $g(E)$ in terms of a new density function $\tilde{g}(v)$, using the condition

$$g(E)\,dE = \tilde{g}(v)\,dv\,.$$

Since the calculations yield no physical insights, we will only give the end result, the Maxwellian velocity distribution:

$$n(v)\,dv = n_0 v^2 \sqrt{\frac{2}{\pi}} \left(\frac{m}{kT}\right)^{3/2} \mathrm{e}^{-mv^2/2kT} dv \tag{2.15}$$

with $n(v)\,dv$ being the number of particles with a velocity in the interval $v \dots v+dv$ and n_0 the total number of particles. In the experimental test of the velocity distribution, the relative number of gas atoms with a given velocity v is measured.

2.4.2 The Interaction Cross Section

The size of an atom in a gas may be measured from the *interaction cross section* with which the atom collides with other atoms. The derivation of the concept *interaction cross section* is illustrated in Fig. 2.4. A beam of atoms of type 1 (beam cross-sectional area A, particle radius r_1, particle number density N_0) strikes a layer made of atoms of type 2 (layer thickness Δx, particle radius r_2, particle number density n). We ask, "How many atoms of type 1 collide with those of type 2 and are deflected from their course, so that they do not pass undisturbed through the layer?" This interaction cross section is thus frequently referred to in physical language as a *scattering cross section*.

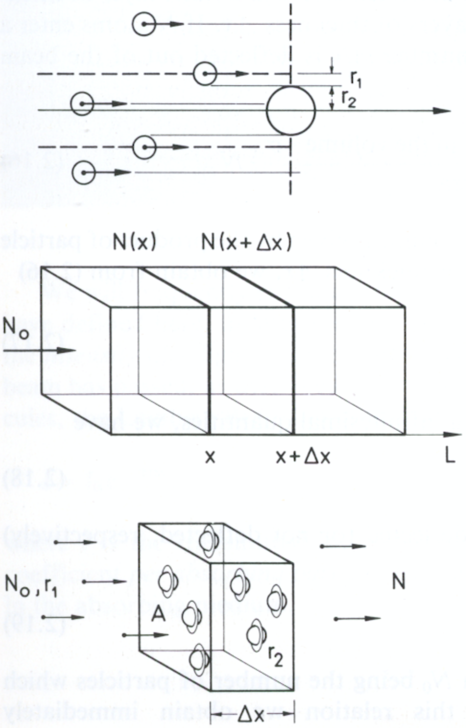


Fig. 2.4. Definition and measurement of interaction cross sections. *Upper part:* The interaction cross section of particles with radius r_1 with those of radius r_2 is found to be $(r_1+r_2)^2\pi$. *Centre part:* Out of N_0 particles which reach the volume element of thickness Δx from the left, N pass through undeflected. In this manner, the interaction cross section may be experimentally determined. *Lower part:* Derivation of (2.20). The radii of particles 1 and 2 are combined into the radius (r_1+r_2)

The problem corresponds roughly to the following macroscopic situation: someone is standing in front of a forest and shoots a bullet from a rifle. The probability that the bullet will pass through the forest undeflected is larger, the smaller the thickness and the density of the trees. If one shoots repeatedly and counts the number of undeflected bullets relative to the total number fired, it is possible to determine the thickness of the trees (that is, their interaction cross section). In order to do so, one must know their density. Naturally, one would not use such a method for a real forest. In atomic physics, it is, however, necessary, since it is not possible to put a meter stick up to an atom as it is to a tree. The same problem occurs in a number of contexts in physics: for example, in nuclear physics, a collision between two particles can be used to determine the interaction cross section for a nuclear or particle reaction. In atomic physics, we shall see that the interaction between a light quantum and an atom is described by a cross section. Because of its wide application in many areas of physics, the concept of the interaction cross section will be treated in some detail here.

A collision between atoms of radii r_1 and r_2 leads to a deflection of the atoms out of their initial directions when it occurs within an area $\sigma = (r_1 + r_2)^2 \pi$ (see Fig. 2.4). We may thus combine the deflection of both colliding particles into a common cross section. The probability of a collision is then given as the quotient of the number of favorable to the number of possible cases:

$$W = \frac{\text{Area of all the interaction cross sections in the volume of the beam}}{\text{Total area } A} .$$

This is valid under the assumption that the areas πr^2 of various particles which are located behind one another do not overlap. This is fulfilled for a sufficiently small layer thickness. In order to calculate the number of deflected atoms in a finite layer of thickness L, we first divide up the layer into thin layers of thickness Δx. If N atoms enter a thin layer at the position x (see Fig. 2.4), a number ΔN is deflected out of the beam after passing through the distance Δx:

$$\Delta N = -WN = -\frac{\text{Total number of atoms in the volume} \cdot \sigma}{\text{Total area}} \cdot N . \tag{2.16}$$

Since the total number of atoms in a given volume is given by the product of particle number density n with the area A and the layer thickness Δx, we obtain from (2.16)

$$\Delta N = -\frac{nA\,\Delta x\,\sigma}{A} N . \tag{2.17}$$

If we replace differences by the corresponding infinitesimal quantities, we have

$$dN/N = -n\sigma\,dx . \tag{2.18}$$

To obtain the number of atoms which are deflected (or not deflected, respectively) along the entire length x, we integrate (2.18):

$$\ln N = -n\sigma x + \ln N_0 . \tag{2.19}$$

Here, $\ln N_0$ is a constant of integration, with N_0 being the number of particles which are incident at the point $x = 0$. From this relation we obtain immediately

$N = N_0 \exp(-n\sigma x)$ as the number of particles which are still present after a distance x, or, after passing through a total length L

$$N = N_0 \mathrm{e}^{-n\sigma L} . \tag{2.20}$$

The number of deflected atoms is correspondingly

$$N_{\mathrm{scatt}} = N_0(1 - \mathrm{e}^{-n\sigma L}) . \tag{2.21}$$

The product $n\sigma = \alpha$ is also denoted as the (macroscopic) *scattering coefficient* and σ as the (microscopic) total interaction cross section.

From a measurement of σ follows, according to $\sigma = (r_1 + r_2)^2 \pi$, the quantity $(r_1 + r_2)$. In the case of identical atoms with $r = r_1 = r_2$, we have thus determined r, i.e., the *size* of the atoms.

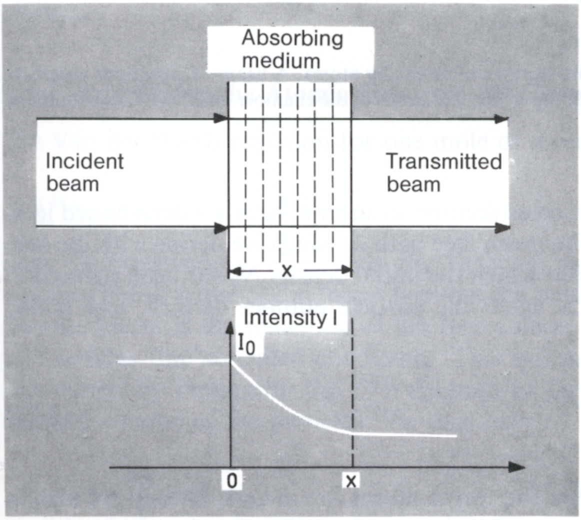


Fig. 2.5. Attenuation of a light beam on passing through an absorbing medium

We will frequently encounter the concept of the interaction cross section, which we have defined here, in later sections of this book. Figure 2.5 shows the dependence of the *intensity* of a light beam on the thickness of absorbing medium through which the beam has passed, as described by (2.20). For the absorption of *light* by atoms or molecules, the Lambert-Beers law is valid:

$$I = I_0 \mathrm{e}^{-n\alpha x} , \tag{2.22}$$

where I is the transmitted intensity, I_0 the incident intensity, and α the absorption coefficient *per absorbing particle*. n is again the number density of atoms or molecules in the absorbing medium.

2.4.3 Experimental Determination of Interaction Cross Sections

Interaction cross sections can be directly measured by collision experiments using an atomic beam and a gas target. An apparatus for such measurements is shown in Fig. 2.6.

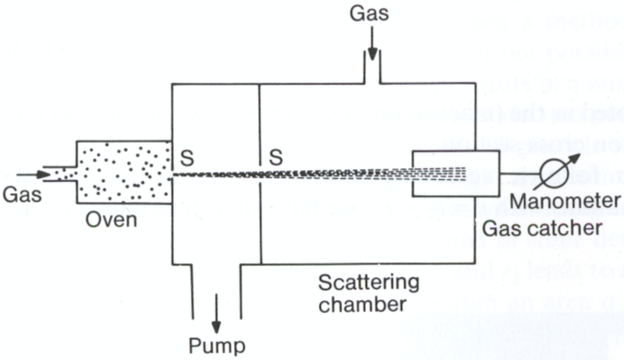


Fig. 2.6. Setup for measuring scattering cross sections of atoms by atoms. A beam of gas atoms enters the scattering chamber through the slits S. Scattering by the gas atoms in the chamber leads to an attenuation of the beam which arrives at the catcher

Frequently, however, interaction cross sections or atomic sizes are determined indirectly. For example, one measures the mean free path λ, which we define with the help of (2.20): λ is the distance L or x, after which the initial density N_0 has been reduced to N_0/e. Thus, with (2.20), where n is again the particle number density, and taking $r_1 = r_2 = r$,

$$\lambda = \frac{1}{4\pi r^2 n} = \frac{1}{\sigma n}. \tag{2.23}$$

Up to now, we have assumed that the target atoms are at rest. If they are also in motion, the expression for λ must be modified somewhat. We give the result without derivation:

$$\lambda = \frac{1}{4\pi\sqrt{2}r^2 n}. \tag{2.24}$$

The mean free path thus defined enters into macroscopically measurable quantities, for example the viscosity η. The viscosity is in fact a measure of the momentum transfer between atoms or molecules in gases or liquids and therefore also depends on the frequency of collisions between the particles. The mean free path can thus also be macroscopically determined. The detailed relation is (without derivation)

$$\eta = \tfrac{1}{3}\varrho\lambda\bar{v}, \tag{2.25}$$

where η is the viscosity, ϱ the density, λ the mean free path, and $\bar{v}$ the mean velocity of the particles. The quantity η can be measured, e.g., from the flow velocity through a capillary.

Another method for measuring λ results from thermal conductivity in gases. The latter also depends on the frequency of collisions between the particles and the energy transfer which thus occurs. Here we have – likewise without derivation – a relation between the heat flow dQ/dt and the thermal gradient dT/dx which produces it:

$$dQ/dt = -\lambda_{\mathrm{TC}} \cdot A \cdot dT/dx\,, \tag{2.26}$$

where dQ is the differential quantity of heat, λ_{TC} the thermal conductivity, and A the cross-sectional area of the heat transport medium. The thermal conductivity λ_{TC} depends upon the mean free path according to the relation

$$\lambda_{\mathrm{TC}} = \frac{n}{2} k \bar{v} \lambda\,. \tag{2.27}$$

Table 2.2 on p. 20 contains some values for atomic radii. Further details and the derivations which we have passed over here may be found in standard texts on experimental physics.

2.4.4 Determining the Atomic Size from the Covolume

The Van der Waals equation for one mole of a real gas states

$$(P + a/V^2)(V - b) = RT\,. \tag{2.28}$$

Here the expression a/V^2 denotes the "internal pressure" which adds to the external pressure P and is due to the forces between the particles. Another correction due to the internal forces is the reduction of the free volume V of the gas by the volume of the gas particles (the so-called covolume). This quantity b, which can be experimentally determined by measuring the P-V diagram of the equation of state, is equal to the fourfold volume of the particles. We thus have

$$b = 4 \cdot \frac{4\pi}{3} \cdot r^3 \cdot N_{\mathrm{A}}\,. \tag{2.29}$$

2.4.5 Atomic Sizes from X-Ray Diffraction Measurements on Crystals

The famous experiment of *von Laue, Friedrich*, and *Knipping* in 1912 on the diffraction of x-radiation in crystals yielded:

- the final proof that crystals are built up of atoms,
- the wavelength of x-radiation,
- the lattice constant of crystals – and with it, information on the size of the atoms in the crystal.

Figure 2.7 shows the experimental set-up schematically. For an exact derivation of the interference conditions, one would have to treat the interference from a three-dimensional lattice. Here we will use the simplified method of *Bragg* (1913) to illustrate how the lattice constants can be determined.

X-ray diffraction may be regarded as a reflection of x-radiation by the so-called lattice planes at certain specular angles. A lattice plane is a plane in a crystal which is occupied by atoms. In a crystal there is a large number of families of parallel and equi-

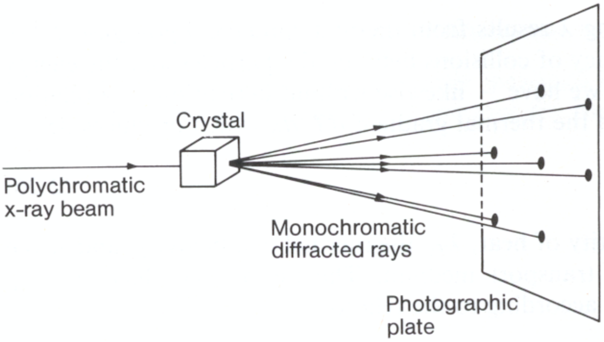


Fig. 2.7. X-ray diffraction from a single crystal after *von Laue*; schematic of the experimental arrangement. X-radiation with a continuous distribution of wavelengths (polychromatic or white x-radiation) is diffracted by a single crystal. The conditions for interference from a three-dimensional lattice yield constructive interference at particular directions in space and at particular wavelengths. One thus observes interference maxima, which correspond to certain discrete wavelengths (monochromatic x-radiation)

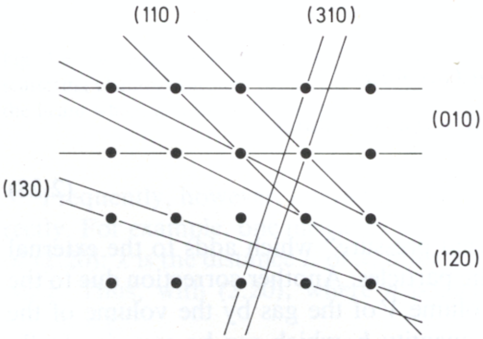


Fig. 2.8. Simple cubic lattice with several lattice planes. These are characterised by the *Miller Indices*. The spacing between two parallel lattice planes decreases with increasing Miller indices

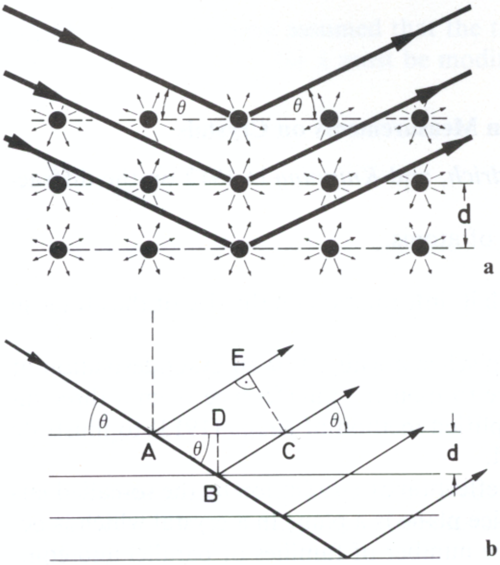


Fig. 2.9 a, b. Derivation of the Bragg Law of Reflection. The horizontal lines symbolise lattice planes, from which the incident x-radiation arriving at angle θ is scattered. **a)** Each atom of a lattice plane acts as a scattering centre. **b)** The derivation of the Bragg condition for the reflection of x-radiation from a lattice plane

distant lattice planes. They are distinguished from one another by their spacing, by the density of atoms within the planes, and by their orientations within the crystal lattice (see Fig. 2.8). According to Huygens' principle, each atom which is struck by the incident x-radiation acts as the source point for a new elementary wave (Fig. 2.9a). These elementary waves produce constructive interferences at certain angles. The reflection condition is derived as follows: amplification occurs when the path difference Δ between two adjacent beams corresponds to a whole multiple of the wavelength, $n\lambda$. For the path difference Δ we have, according to Fig. 2.9b,

$$\Delta = \mathrm{AB} + \mathrm{BC} - \mathrm{AE} = 2\mathrm{AB} - \mathrm{AE} = \frac{2d}{\sin\theta} - 2\mathrm{AD}\cos\theta \,. \tag{2.30}$$

With the relation $\mathrm{AD} = d/\tan\theta$, one obtains from (2.30)

$$\Delta = 2\frac{d}{\sin\theta}(1-\cos^2\theta) \,,$$

or, finally, the condition for constructive interference

$$\Delta = 2d\sin\theta = n\lambda \,. \tag{2.31}$$

The various methods of observing x-ray diffraction from crystals which are used in practice differ in the following ways:

- In the *Laue* method one uses a single crystal, a particular value of the angle of incidence, and x-radiation with a continuous spectrum ("polychromatic" x-rays). The condition for constructive interference is fulfilled for individual *points* in the plane of observation for particular wavelengths.
- In the *Bragg* rotating-crystal method one also uses a single crystal, but monochromatic x-rays. The crystal is rotated, so that the angle of incidence varies through a continuous range of values. The condition for constructive interference is fulfilled for various lattice planes successively.
- In the *Debye-Scherrer* method (Figs. 2.10, 11), the sample is polycrystalline or powdered. The x-rays are monochromatic. Since each lattice plane occurs in all possible orientations relative to the incident beam, one obtains interference *cones* whose intersection with the plane of observation gives interference rings.

Equation (2.31) relates the wavelength of the x-rays to the lattice constant or the spacing of the lattice planes. The x-ray wavelength can be measured by other means than with crystal interferences. Its measurement can be directly correlated to the meter by utilising x-ray interference at grazing incidence from a diffraction grating. Since it is not possible to manufacture diffraction gratings with a grating constant of the order of x-ray wavelengths, one uses coarse gratings, for example with 50 lines/mm, and lets the x-radiation strike the grating at a grazing angle of less than 1°. Since the index of refraction of x-rays is somewhat smaller than 1, total reflection occurs when the angle of incidence is sufficiently small. The effective grating constant is then the projection of the actual line spacing at this angle. It is sufficiently small to permit the measurement of the x-ray wavelength.

We make two additional remarks concerning x-ray diffraction.

- In practice, x-ray diffraction is much more complicated than indicated above. The exact intensity distribution in the diffraction pattern must be carefully determined, and account must be taken of the fact that the scattering centres are not points, but instead are electronic shells with a finite extension. A complete, quantitative ana-

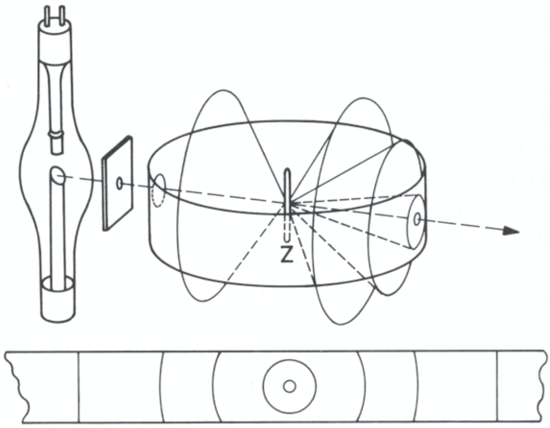


Fig. 2.10. Debye-Scherrer method: x-ray diffraction of monochromatic x-radiation by a polycrystalline sample Z. On the film, the intersections of the diffraction cones from the various families of lattice planes appear as rings. To generate monochromatic x-radiation, one uses either the socalled characteristic x-ray lines (Fig. 18.3), or a single crystal may be employed as a monochromator according to the principle of (2.31)

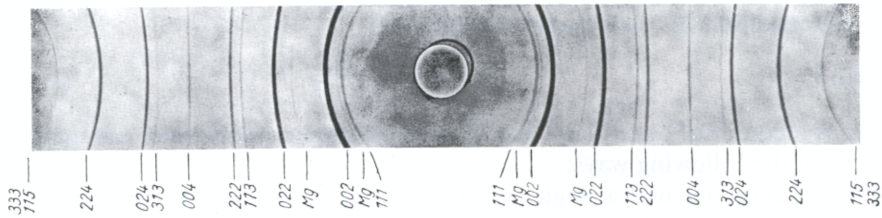


Fig. 2.11. Debye-Scherrer diagram of MgO [from Gerthsen, Kneser, Vogel: *Physik*, 13th ed. (Springer, Berlin, Heidelberg, New York 1978) Fig. 12.37]

lysis of x-ray diffraction patterns leads finally to an exact determination of the electron density with the sample crystal lattice. From it, we obtain not only the spacing between the atoms in the lattice, but also their sizes and even their shapes. Figures 2.12 and 2.13 illustrate experimentally determined electron density distributions in crystals. A contour map of this type raises the question, "Where does an atom have its boundary?", and this leads in turn to the question,

"What do we really mean by the *size* of an atom?"

– In the case of hard spheres, the size can be defined exactly. For atoms, the concept "size" cannot be defined without reference to the method of measurement. Various methods are sensitive to different properties of the atom, which depend on the "size of the atom" in differing ways.

Let us consider the methods of investigation described above once more in light of this remark.

From the viscosity η one obtains a measure of the interatomic distance in the presence of thermal motion. Because the atoms are not perfectly hard spheres, the radius determined in this manner will, however, be a function of the velocity. Furthermore, the results depend on the shape of the atom; the spatial extension of the electronic shells of atoms and molecules deviates more or less strongly from a spherical shape, in general.

The covolume b in the real-gas law is derived under the assumption that the atoms are elastic spheres. The lattice plane spacing d measures an equilibrium distance between the particles in the crystal lattice.

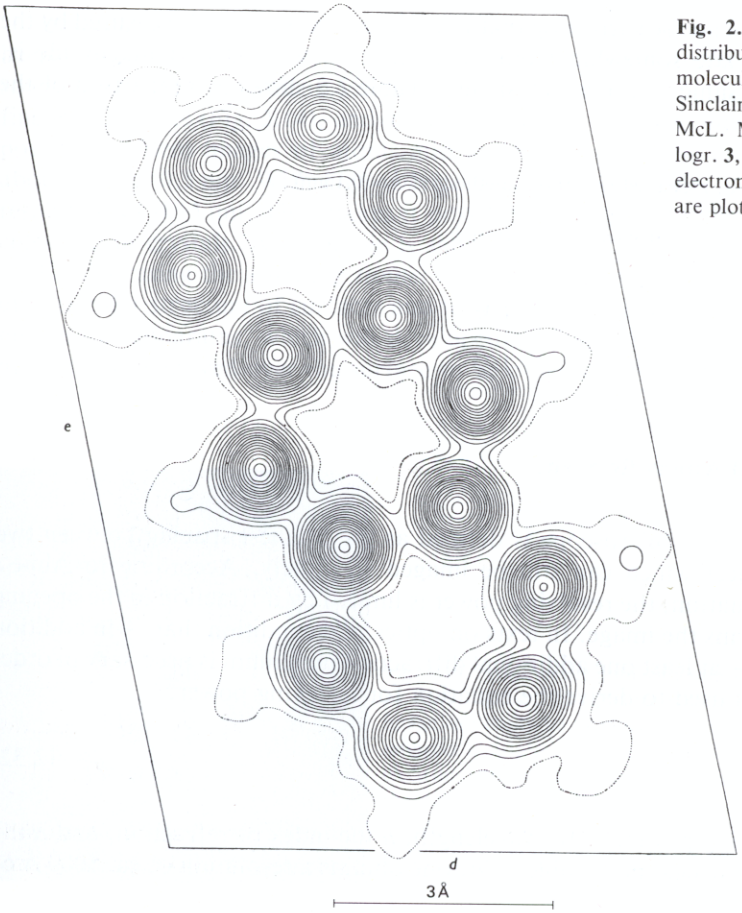


Fig. 2.12. The electron density distribution in the anthracene molecule determined by V. L. Sinclair, J. M. Robertson, A. McL. Mathieson: Acta Crystallogr. **3**, 254 (1950). Lines of equal electron density ("contour lines") are plotted

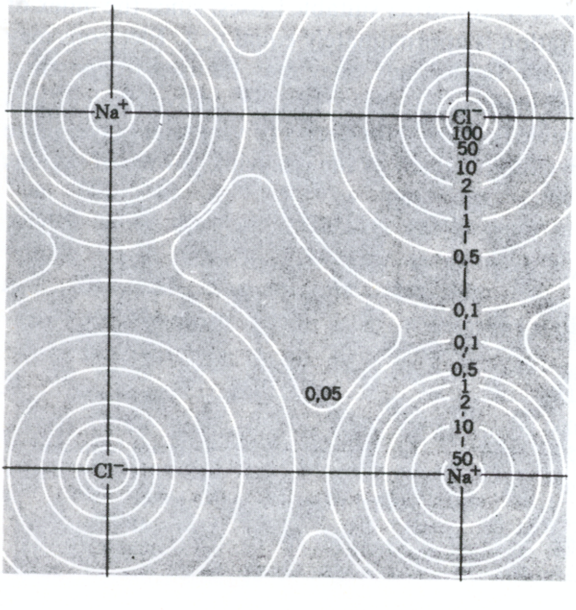


Fig. 2.13. Distribution of the electron density in the basal plane of NaCl from x-ray analysis by Schoknecht: Z. Naturforsch. **12a**, 983 (1957). The solid curves are again lines of equal electron density

It should therefore not be surprising that the values of atomic radii measured by the various methods deviate somewhat from each other – the order of magnitude is, however, always the same – a few Ångstroms. Table 2.2 shows a comparison of the measured values.

Table 2.2. Atomic radii [Å], measured by various methods (1 Å = 0.1 nm)

	from η	from d	from b
Neon	1.18	1.60	1.2
Argon	1.44	1.90	1.48
Krypton	1.58	1.97	1.58
Xenon	1.75	2.20	1.72

2.4.6 Can Individual Atoms Be Seen?

The *resolving power* of a microscope is defined as the smallest spacing between two structures in an object which can still be imaged separately. According to Abbé's theory of image formation, the resolving power is limited by diffraction in the opening of the lens which forms the image. In texts on optics, the condition that – in addition to the zeroth order – at least one additional diffraction maximum is necessary in order to form an image, is used to derive the equation for resolving power,

$$d = \frac{\lambda}{n \sin \alpha}, \tag{2.32}$$

where d is the resolving power, λ the wavelength, n the index of refraction, and α the angular opening of the lens. For visible light, one obtains a resolution of ca. 5000 Å or 500 nm.

For other types of electromagnetic radiation, the theoretical resolving power cannot be reached. For x-rays, it is not possible to construct suitable lenses, since the index of refraction of all substances for x-radiation is approximately equal to 1. Electrons may be deflected by electric and by magnetic fields; thus, they may be used to construct lenses for electrons and to form images. Because of the unavoidable "lens aberrations", however, it is only possible to work with beams of very small divergence in electron microscopes. Table 2.3 gives an overview of the resolving powers of various methods of image formation.

Table 2.3. Resolving powers for various wavelengths

	Resolving Power [Å]		Remarks
	theory	practice	
Light	ca. 5000	ca. 5000	
Dark field	ca. 500	ca. 500	No image formation, only diffraction pattern
X-rays ($\lambda = 1$ Å)	1	several 100	No lenses
Electrons (100000 Volt $\triangleq \lambda = 0.037$ Å)	0.04	0.7	Lens aberrations

In recent years, great success in the effort to form images of individual atoms has been obtained with special types of electron microscopes: with the *field emission microscope* it has been possible to visualize single atoms or large molecules on the tips of fine metal points (Fig. 2.14), and with the *scanning electron microscope* it has proved possible to form images of atoms and molecules. Here the attainable resolution is about 5 Å or 0.5 nm. With *high-voltage electron microscopes*, one can now obtain a resolution of 0.15 nm. This makes it possible to image the individual atoms in molecules and in crystals. An example is shown in Fig. 2.15.

Finally, using the *scanning tunnel microscope*, it is possible to resolve the atomic or molecular structure of surfaces and to make the individual structural elements visible. In this apparatus, which was developed by *Binnig* and *Rohrer*, an extremely fine metal point is moved over the surface to be observed at a distance of less than 1 nm.

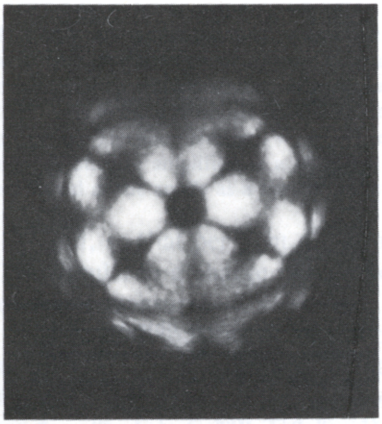


Fig. 2.14. Image of the point of a tungsten needle with a field emission microscope, developed by *F. W. Müller*. The picture was provided by the Leybold-Heraeus Co. in Cologne. The image can easily be produced as a lecture demonstration. The various lattice planes which intersect the tip of the needle have differing emission probabilities for the field emission of electrons; this produces the geometric pattern of light and dark regions. This pattern reflects the crystal lattice geometry. Barium atoms were then vapour-deposited onto the tungsten needle. Where they are present, the emission probability is increased, so that they appear as bright points in the image. During the vapour deposition one can observe them falling onto the point like snowflakes. It can be shown in this manner that individual atoms become visible

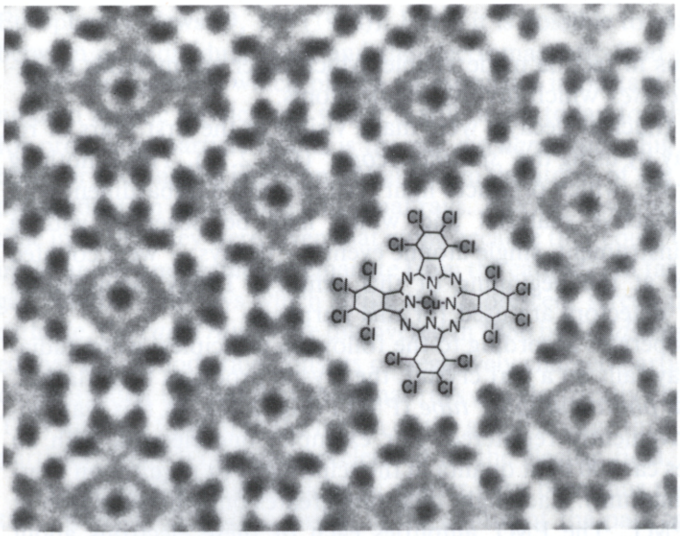


Fig. 2.15. An electron microscope picture of hexa-deca-chloro-copper-phthalocyanin molecules. The molecules were produced as a ca. 10 monolayer thick, crystalline growth-layer on the alkali halide crystal which serves as substrate. The image formation and processing were done with a 500 kV high-resolution electron microscope and with a special image enhancement technique. The central copper atoms are especially clear, as are the 16 peripheral chlorine atoms. (The picture was kindly placed at our disposal by Prof. *N. Uyeda*, Kyoto University)

The tunnel current between the substrate and the point is a measure of the distance, of the charge density, and of the electrical work function for charges leaving the substrate. These quantities change from place to place on an atomic scale; thus, one can obtain a picture of the substrate surface. In Fig. 2.16, the atomic structure of single molecules of copper phthalocyanine is shown.

The imaging and manipulation of individual atoms or molecules on solid surfaces has become possible with this instrument. More details are given in Haken and Wolf, *Molecular Physics and Elements of Quantum Chemistry*, Sect. 2.1.

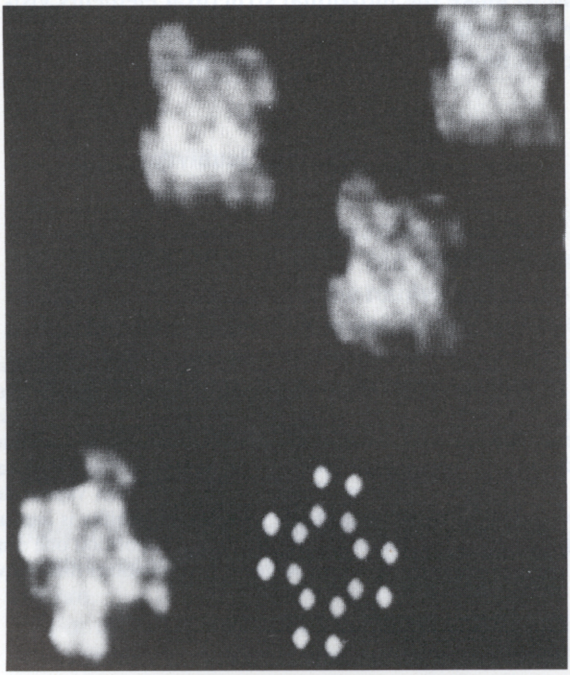


Fig. 2.16. A picture obtained with the scanning tunnel microscope, showing copper phthalocyanine molecules on a copper substrate surface. From P.H. Lippel, R.J. Wilson et al., Phys. Rev. Lett. **62**, 171 (1989). At the lower right, the calculated charge density 2 Å above the molecular plane is shown

Individual atoms can thus in fact be made visible. Much older are methods of experimentally observing *processes* which involve single atoms.

Single atomic processes (nuclear decays) were made visible in the first years of research into radioactive decay by using the *"spinthariscope"* (Fig. 2.17). This is nothing more than a fluorescent screen, which produces light flashes upon bombardment with decay products from radioactive material and which may be observed with a magnifying lens. With this instrument, single atomic events – decays – were counted in Rutherford's laboratory at the beginning of this century. Today, scintillation detectors or semiconductor detectors are used for this purpose.

A scintillation detector operates according to the following principles: when radiation from a radioactive decay falls on a NaI crystal, the crystal produces light flashes, which can be amplified in a *photomultiplier tube* (PMT) (Fig. 2.18). In this way, individual events can be conveniently registered. For example: one electron with an energy of 10000 eV produces ca. 200 light quanta in the scintillator (it requires on average about 50 eV per light quantum). Each light quantum creates one photoelectron at the photocathode of the PMT. The PMT amplifies each of these electrons about

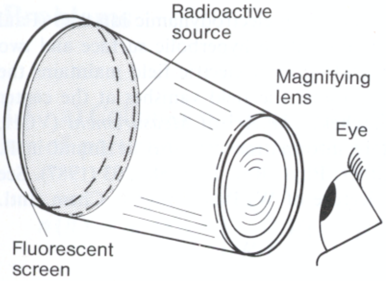


Fig. 2.17. Spinthariscope, schematic illustration. The fluorescent screen scintillates due to the irradiation from the radioactive source. The scintillation processes may be observed through the magnifying lens

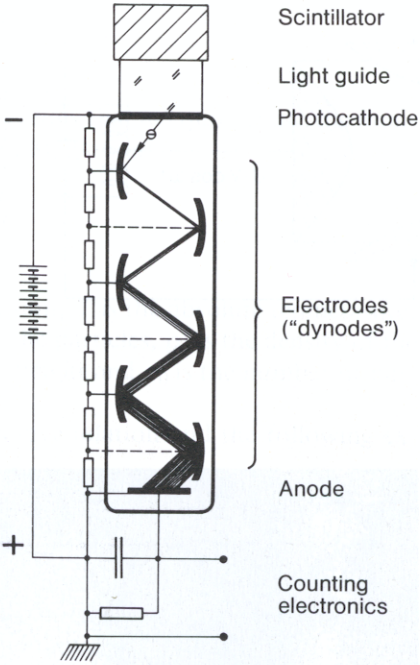


Fig. 2.18. Schematic diagram of a scintillation detector. The light flashes which are produced in the scintillator by the incident radiation pass through the light guide to the photocathode of an electron multiplier tube. The photoelectrons which are released by the cathode are amplified in a series of steps and registered at the anode as a current pulse ▶

10^5-fold, so that per light quantum, about 10^5 electrons are released from the anode. This results in a charge per incident electron (beta particle) of $3 \cdot 10^{-12}$ C, which can easily be measured.

Individual ions can be caught in an *electromagnetic ion trap*, stored there, and spectroscopically studied as isolated particles. An ion trap is shown in Fig. 2.19. It localizes the particle by making use of inhomogeneous electromagnetic fields of suitable geometry (quadrupole field). The localized ion can be excited to luminescence with narrow-band laser light; Fig. 2.20 shows an example. Thus, the interaction between the radiation field and individual ions can be investigated. Such studies are also the goal in the development of the one-atom maser, as described by *H. Walther* (e.g. H. Walther: Europhysics News **19**, 105 (1988)). Here, it is possible to observe the energy exchange between an individual atom and the electromagnetic field in a resonant cavity.

An arrangement which played an especially important role in the early period of modern atomic physics and which is still in use today for the excitation of atoms and for producing particle beams is the *gas discharge tube*, Fig. 2.21. It can be employed both for exciting the emission of light from the atoms of the gas inside the tube and for the production of cathode and canal rays. *Plücker* described *cathode rays* for the first time in 1859. They were given that name because they could be observed through a hole in the anode and seemed to emanate from the cathode. In fact, they are generated in the gas volume. The rays which strike the fluorescent screen in front of the hole in the cathode, the *canal rays*, were discovered in 1886 by *Goldstein*. In 1897, *Thomson* showed that the cathode rays consists of negatively charged particles – the *electrons*. *Wien* demonstrated in 1900 that the canal rays are electrically charged atoms, that is, ions. They also are formed in the region of the gas discharge through collisions with charged particles which have been accelerated by the electric field.

Atoms as the basic particles of matter have been thus theoretically and experimentally detected and made visible in the course of the past century.

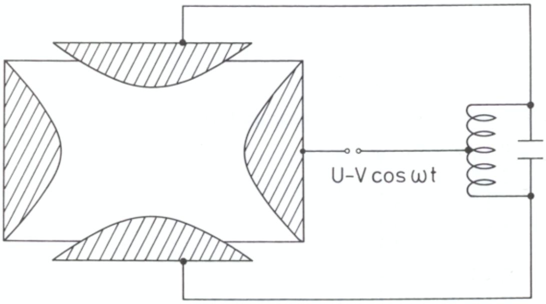


Fig. 2.19. Schematic view of an electrodynamic ion trap (Paul trap). It is made of a ring with a hyperbolic surface and two hyperbolic caps. A high-frequency electric field maintains the ions on small circular orbits; the field vanishes at the center point. From P.E. Toschek, *The Art of Measurement* (VCH, Weinheim 1988). More information can also be found in F. Diedrich and H. Walther: Phys. Rev. Lett. **58**, 203 (1987). See also the Nobel prize lecture of W. Paul: Angew. Chem. Intl. Ed. **29**, 739 (1990)

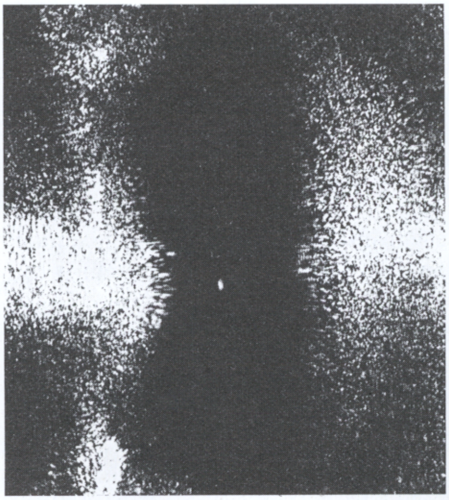


Fig. 2.20. Imaging of individual atoms. In the center of an ion trap, a barium ion has been localized and excited by laser light to resonance fluorescence; it becomes visible as a luminous spot. From P.E. Toschek and W. Neuhauser: *Atomic Physics* 7, ed. by D. Kleppner and F.M. Pipkin (Plenum, New York 1981)

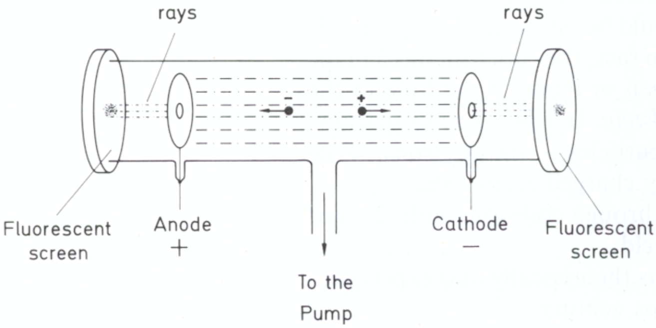


Fig. 2.21. A gas discharge tube for producing cathode rays. Between the cathode and the anode is a potential difference of several thousand volts. The fluorescence which appears in the tube and the formation of cathode rays depend strongly on the gas pressure. In the field-free region between the cathode and the fluorescent screen one observes the canal beam, which consists of positive ions. The cathode and canal rays produced in this manner were particularly important in the early period of atomic physics for the investigation of charge, mass, and scattering cross sections of electrons and ions

Problems

2.1 a) Colloidal particles are dispersed in a liquid. Show that at equilibrium, the number of particles per cm^3 is given by a Boltzmann distribution:

$$n(h) = n_0 \exp - \left[\frac{N_A}{RT} V(\varrho - \varrho')gh \right] ,$$

where N_A is Avogadro's number, R is the gas constant, T is the absolute temperature, V is the volume of the particles, ϱ is the density of the particles, ϱ' is the density of the liquid, g is the acceleration due to gravity, h is the height and n_0 is the number of particles at the height $h = 0$.

b) Determine Avogadro's number, using the above relation and the following experimental data:

$n_0 = 134$ particles/cm^3, $n(h = 0.0030$ cm$) = 67$ particles/cm^3, $\varrho = 1.23$ g/cm^3, $\varrho' = 1.00$ g/cm^3, $T = 293$ K, particle diameter $= 4.24 \cdot 10^{-5}$ cm.

Hint: To derive an expression for $n(h)$, use the barometric altitude formula: $dp = -\varrho(h)g\,dh$. Treat the particles as heavy, non-interacting molecules of an ideal gas and use the ideal gas equation $pV = RT$ to obtain the relation between dp and $d\varrho$ or dn.

2.2 Liquid helium (atomic weight 4.003) has a density $\varrho = 0.13$ g/cm^3. Estimate the radius of a He atom, assuming that the atoms are packed in the densest possible configuration, which fills 74% of the space.

2.3 Canal rays, i.e., positive ion rays are generated in a gas discharge tube. How often does an ion ($r = 0.05$ nm) collide with an atom of the ideal filler gas ($r = 0.1$ nm) if it travels 1 m in a straight path through the discharge tube and if the pressure in the tube is 1 mbar? 10^{-2} mbar? 10^{-4} mbar and the temperature $T = 300$ K? (1 mbar corresponds to 10^2 Pa).

Hint: The ions do not have a Maxwell-Boltzmann velocity distribution. All the particles are assumed to have the same velocity.

2.4 The covolume of helium gas was determined from pressure-volume diagrams to be $b = 0.0237$ litre/mole. The covolume of mercury is 0.01696 litre/mole. What is the size of the atoms in the two gases?

2.5 a) Why are monochromatic x-rays used for the Debye-Scherrer method, and how are they produced? Does the diffraction cone with the smallest apex angle represent the smallest or the largest lattice plane spacing? How large is this spacing if a first-order angle $\alpha = 5°$ is measured between the surface of the cone and the undiffracted beam? (Assume that the quantum energy of the x-rays is 50 keV, $E_{\text{x-ray}} = 50$ keV).

b) The angle of maximum intensity of the first order reflection of x-rays with wavelength $\lambda = 2.1$ Å from the cleaved surface of a NaCl crystal is measured to be $\theta = 22°10'$. Calculate the lattice constant of the NaCl crystal. Use the result to derive Avogadro's number. The density of NaCl is $\varrho = 2.163$ g cm^{-3}.

2.6 Monochromatic x-rays ($\lambda = 0.5$ Å) fall on a sample of KCl powder. A flat photographic plate is set up 1 m from the powder and perpendicular to the beam. Calculate the radii of the sections of the Bragg diffraction cone (Fig. 2.10) for first- and second-order diffraction, assuming a lattice-plane spacing of 3.14 Å.

2.7 A tight bunch of slow neutrons (2 eV), which is produced in a nuclear reactor, lands on a crystal with a lattice spacing of 1.60 Å. Determine the Bragg angle for first-order diffraction.

Hint: Use (7.1) for the wavelength of the neutrons.

2.8 Atoms of an unknown element are deposited onto a perfectly planar crystal surface and are to be studied using a scanning tunneling microscope. The microscope employs a tungsten needle tip. What is the minimum size of the unknown atoms (r_x), and how far apart must they be spaced, in order that they can be distinguished (take e.g. the criterion that the minimum measureable height $\Delta h = 30\%$ of the W atomic diameter)?

Hint: Use a geometric sphere model, in which the radius of the W atom at the tip is 0.16 nm.