TEXTBOOK

Wolfgang Cassing

Theoretical Physics Compact III

Quantum Mechanics

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Quantum Mechanics

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Dedicated to Prof. Dr. Achim Weiguny

Preface

This book provides a textbook on quantum mechanics and is in particular suited for bachelor students in their second or third year of studies in theoretical physics. In Part I a short summary of classical mechanics and its limits is given by pointing out those physical observations, that are in conflict with (or opposed to) interpretations within classical mechanics. Early attempts to extend the classical physics by additional boundary conditions are discussed as well.

In Part II the *Elementary Quantum Mechanics* for a single particle is introduced and the statistical interpretation of its wave function, which results from the Schrödinger equation in the presence of external forces. It is shown how to translate classical observables in phase-space representation to quantum mechanical operators acting in an abstract Hilbert space of wave functions. Observable quantities like momentum, angular momentum or energy then are defined by expectation values of their corresponding operators. Contrary to classical mechanics the sequence of measurements on different observables in general cannot be exchanged; this is reflected in commutators between operators that have the same algebra as the Poisson brackets in classical mechanics. A prominent example is the uncertainty relation between position and momentum, which states that the product of the uncertainty in position and the uncertainty in momentum has a lower limit in quantum mechanics and is increasing in time for free wave packets. Another example is the angular momentum, whose components do not commute and reflect the fact that the order of rotations cannot be exchanged. In line with the observations in the Stern-Gerlach experiments a spin is attributed to electrons and described by an internal degree of freedom with the same algebra as the angular momentum. This finally results in the Pauli equation that describes the dynamics of charged spin 1/2 particles e.g. in an external electromagnetic field.

The general properties of quantum mechanics then are illustrated by a couple of examples including the infinite (and finite) square well, the quantum mechanical tunnelling through a finite potential well as well as problems with crystal (periodic) symmetries leading to finite

energy bands in solid state materials. The problem of the harmonic oscillator is solved algebraically and its spectrum is derived as well as its eigenfunctions in one and three dimensions. In case of radial symmetry the radial Schrödinger equation is derived and solved explicitly for the case of the hydrogen atom. Apart from bound states of the single-particle problem, furthermore, continuum states are investigated in the framework of scattering theory and an alternative formulation of quantum mechanics is found in terms of the Lippmann-Schwinger equation, which is more appropriate for scattering problems due to the explicit implementation of proper boundary conditions. In this context the scattering amplitude and the differential cross section are introduced, that describe the scattering probability in quantum theory. The Born series is set up for the scattering amplitude and investigated in leading order approximation. Finally, the scattering amplitude is derived in angular momentum representation and scattering phase shifts are introduced, that define the S-matrix for elastic scattering (and fixed angular momentum).

The *Mathematical Foundations of Quantum Mechanics* are addressed in Part III of this book that aims at a rigid formulation of many-particle problems in quantum physics. To this aim in particular self-adjoint, unitary and projection operators are discussed in detail. In this context the possible many-body states are characterized with respect to their particle-exchange symmetry (in case of identical particles) which leads to the classification of fermions and bosons, which differ by a minus-sign in their wave function for the exchange of two particles. The Pauli principle, furthermore, states that fermions can only occupy a state (with given quantum numbers) once, whereas there is no limitation for bosons. This distinction is not possible in classical mechanics, since the particles can be distinguished by their trajectories in phase space, but has severe consequences for many-body systems close to their ground state.

In Part IV of this book the *Quantum Mechanics of Many-Body Systems* is addressed and the different pictures for the time-evolution of the system are pointed out, i.e. the Schrödinger picture, the Heisenberg picture and the Dirac picture, which are equivalent, but have different advantages depending on the problem under consideration. In order to obtain a flexible and convenient formulation of the many-particle

problem the particle number representation for fermions and bosons is introduced, which differ in the commutation relations for the particle creation and annihilation operators. It is shown how to compute observables in this representation and examples for ground states of bosons and fermions are presented. Furthermore, the quantization of the electromagnetic field is formulated, which—as in case of matter fields—has a particle interpretation (photons) in addition to the wave properties. The interactions between matter and the radiation field are calculated in leading order, too.

Systematic Approximation Methods are in the focus of Part V of this book, which starts with a formal formulation of scattering theory for many-body systems and introduces the concept of the S-matrix and T-matrix. In particular the T-matrix is shown to follow a general Born-series, which can be solved either by iteration or a systematic expansion in powers of the interaction. Explicit formulae for the ground state of many-body systems are presented. The Hartree-Fock approach is derived and discussed in detail, which has a wide application in atomic and nuclear physics as well as in theoretical chemistry. The approach basically focusses on the properties of ground states of atoms and molecules as well as nuclei and is an effective one-body theory, where the individual two-body interactions are summed up in an effective Hartree-Fock mean field. Residual interactions between pairs of fermions with time-reversed quantum numbers are finally incorporated in the BCS theory, which allows to describe superconductivity in metals and nuclei at low temperatures.

Acknowledgements This book results from the collaboration with many students and collaborators throughout about 35 years of common teaching and research. It follows the drafts of my teacher Prof. Dr. Achim Weiguny to whom this volume is dedicated. Special thanks go to my daughter Marie for preparing some of the figures and helpful comments on notations and presentations.

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About This Book

This book provides a textbook on quantum mechanics and is in particular suited for bachelor students in their second or third year of studies in theoretical physics.

After a short summary of classical mechanics and its limits the elementary quantum mechanics for a single particle is introduced in terms of the Schrödinger equation, which is solved for a couple of representive examples. Apart from bound states of the single-particle problem continuum states are investigated in the framework of scattering theory. In this context the scattering amplitude and the differential cross section are introduced, that describe the scattering in quantum theory.

The mathematical foundations of quantum mechanics are addressed in the second part of this book, that aims at a rigid formulation of many-particle problems in quantum physics. For a flexible and convenient formulation of the many-particle problem the particle number representation for fermions and bosons is introduced. Furthermore, a formal formulation of scattering theory for many-body systems is presented in terms of the S-matrix and T-matrix. In particular the T-matrix is shown to follow a general Born-series, which can be solved by iteration. The Hartree-Fock approach is derived and discussed in detail, while residual interactions between pairs of fermions with time-reversed quantum numbers are finally incorporated in the BCS theory, which allows to describe superconductivity in metals and nuclei at low temperatures.

The author is a retired Professor of Theoretical Physics at the university of Giesen and has shared the responsibility for the introduction of Bachelor and Master courses in Physics since 2005. His expertise is the phase-space dynamics of classical and quantum many-body systems, which in part is published in a book on transport theories. Moreover, he has written a series of textbooks in Theoretical Physics.

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Introduction

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1. Principles of Classical Physics

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Before coming to the actual formulation of quantum mechanics we briefly summarize the basic concepts and equations of classical mechanics. Furthermore, classical statistics is discussed with respect to the concept of identical particles and the basic assumptions for experimental measurements in classical physics are pointed out in order to be confronted with the different perspectives in quantum mechanics.

1.1 Motion of Mass Points

In classical physics a system of *N* mass points is fully characterized by the positions and velocities of the particles as a function of time

$$\{q_i(t), \dot{q}_i(t)\}; i = 1, 2, \ldots, 3N. \tag{1.1}$$

To each mass point (particle) a trajectory is assigned, which can be determined by integrating Newton's equations of motion. The solution is unique as soon as the positions and velocities of all particles are determined (measured) at some time t_0 assuming that all internal and external forces are known.

With respect to the formulation of quantum theory we write the equations of motion using a characteristic function for the system, the **Lagrange function**

$$L = L(q_i, \dot{q}_i; t) \tag{1.2}$$

as

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_i}\right) - \frac{\partial L}{\partial q_i} = 0. \tag{1.3}$$

If the forces are derived from a potential

$$V = V(q_i;t) \tag{1.4}$$

by forming the negative gradient, then L has the form

$$L = T - V, \tag{1.5}$$

where

$$T = \sum_i \frac{m_i}{2}\dot{q}_i^2 \tag{1.6}$$

is the non-relativistic kinetic energy. By substituting (1.4), (1.5) and (1.6) into (1.3) one immediately regains Newton's equations of motion. In case of velocity-dependent forces (example: **Lorentz force**), V has to be generalized to

$$V = V(q_i, \dot{q}_i;t). \tag{1.7}$$

Instead of working with the $r = 3N$ 2nd order differential equations (1.3) in the **Lagrange formalism**, one can also use $2r$ differential equations of first order in the **Hamilton formalism**. For the transformation to the Hamilton formalism **canonical momenta** are introduced by,

$$p_i = \frac{\partial L}{\partial \dot{q}_i}, \tag{1.8}$$

which reduce to the usual momenta

$$p_i = m_i \dot{q}_i \tag{1.9}$$

if V does not depend on $\dot{q}_i$. With the help of the **Hamilton function**, which is obtained by a **Legendre transformation**,

$$H = H(q_i, p_i; t) = \sum_i \dot{q}_i p_i - L, \tag{1.10}$$

the equations of motion then can be written as

$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \dot{p}_i = -\frac{\partial H}{\partial q_i}. \tag{1.11}$$

Furthermore:

$$\frac{\partial H}{\partial t} = -\frac{\partial L}{\partial t}. \tag{1.12}$$

For the proof one forms the complete differential of $H(q_i, p_i; t)$.

Note: Instead of the explicit equations of motion one can alternatively employ the **variation principle** for the action *S*,

$$\delta S(t_1, t_2) = \delta \int_{t_1}^{t_2} L(q_i, \dot{q}_i; t)\ dt = 0, \tag{1.13}$$

with the boundary conditions

$$\delta q_i(t_1) = \delta q_i(t_2) = 0. \tag{1.14}$$

1.2 Poisson Brackets, Conservation Laws

An observable of the system (example: *z*-component of angular momentum, mean square radius) can be represented as

$$F = F(q_i, p_i; t). \tag{1.15}$$

For the total change in time of *F* one obtains:

$$\begin{aligned} \frac{dF}{dt} &= \sum_i \left(\frac{\partial F}{\partial q_i} \frac{dq_i}{dt} + \frac{\partial F}{\partial p_i} \frac{dp_i}{dt} \right) + \frac{\partial F}{\partial t} \\ &= \sum_i \left(\frac{\partial F}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial F}{\partial p_i} \frac{\partial H}{\partial q_i} \right) + \frac{\partial F}{\partial t} \end{aligned} \tag{1.16}$$

$$= \{F, H\} + \frac{\partial F}{\partial t}\,.$$

In general, the expression

$$\{F_1, F_2\} = \sum_i \left(\frac{\partial F_1}{\partial q_i}\,\frac{\partial F_2}{\partial p_i} - \frac{\partial F_1}{\partial p_i}\,\frac{\partial F_2}{\partial q_i} \right) \tag{1.17}$$

is denoted by the **Poisson bracket** of the quantities F_1, F_2. For an observable *F*, that not explicitly depends on time (example: *z*-component of the angular momentum), its change in time is determined by the Poisson bracket with *H*,

$$\frac{dF}{dt} = \{F, H\} \quad \text{if} \quad \frac{\partial F}{\partial t} = 0. \tag{1.18}$$

Examples:

(i) **Fundamental Poisson brackets** $\{q_i, p_j\} = \delta_{ij}$

(ii) **Hamilton's equations**

$$\begin{aligned} \dot{q}_i &= \partial H/\partial p_i = \{q_i, H\} \\ \dot{p}_i &= -\partial H/\partial q_i = \{p_i, H\} \end{aligned}$$

(iii) $dH/dt = \{H, H\} + \partial H/\partial t = \partial H/\partial t.$

From (iii) the conservation law of energy arises if *H* is not explicitly dependent on *t* and has the form $H = T + V(q_i)$.

For a closed system the fundamental mechanical quantities—energy, momentum and angular momentum - are conserved quantities. This is a direct consequence of the **invariance** of the Lagrange function - and thus of the physical system—with respect to **time translation**, **space translation** and **space rotation**. Since momentum and angular momentum for a system of *N* particles does not depend explicitly on time *t*, then from (1.16) or (1.18) follows for a conserved quantity *G*

$$\frac{dG}{dt} = \{G, H\} = 0. \tag{1.19}$$

Conservation laws imply that for the considered observable the Poisson bracket with the Hamilton function vanishes.

1.3 Identical Particles Classical Statistics

Particles with the same physical properties (same mass, same charge, etc.) are called **identical particles**. In classical physics identical particles are **distinguishable** based on their trajectories: numbering e.g. two identical particles at a time t_0 by 1 and 2, then at a later time $t > t_0$ the particles can be identified again as 1 or 2 by following their motion along the respective trajectory, which is unique.

If there are a lot of identical particles (like H_2 molecules in a macroscopic volume), the system is described using statistical methods (probability statements), although in principle all physical properties of the system are fixed for all times, if the initial conditions are known. Statistics methods are used for practical reasons: if it is not possible to measure or calculate all physical variables of the system or if statements about certain quantities are practically uninteresting (e.g. the positions of all molecules in a macroscopic volume).

1.4 Fundamental Interactions

The forces acting between mass points can be reduced to a few fundamental types of interactions, that partially are described in the context of **field theories**:

(i) the **gravitational interaction,** which couples to the mass of the particles and is essential for the motion of macroscopic bodies (especially celestial objects);

(ii) the **electromagnetic interaction**, which couples to the charge and the magnetic moment of the particles. It is important for problems in both macroscopic and microscopic dimensions;

(iii) the **weak interaction** which e.g. is responsible for the β decay;

(iv) the **strong interaction**, which describes the nuclear forces between the nucleons by the exchange of mesons. It is fundamentally based on the exchange of **colored** gluons coupling to the **color charge** of quarks in quantum chromodynamics (QCD).

Note: (ii) and (iii) are also referred to as **electroweak interaction**, which is based on the exchange of a massless vector particle (the photon γ) as well as massive vector bosons (W^+, W^0, W^-, Z^0).

This book primarily focuses on electromagnetic interactions.

1.5 Concept of Measurement in Classical Physics

In order to carry out a measurement of a physical system, the system (object) to be examined must interact with a detector. The detector changes its state (e.g. in the form of a mechanical pointer) and, in principle, the system (object) to be examined is also inversely influenced by the measurement process.

On the basis of classical physics the following fundamental statements are assumed about the measurement process:

1. The reaction of the measurement process on the object can in principle be calculated according to the laws of classical physics.
2. The perturbations—caused by a measurement on the object - can be made arbitrarily small. With a suitable setup of the measurement the impact on the object can therefore be neglected.
3. Measurements of different properties (observables) on the same system do not interfere with each other.

Example: If we measure positions and momenta at some time t_0 of a system of mass points we obtain certain numerical values. If we carry out the same measurement again at a later time $t > t_0$ we obtain in

principle those values, which can be calculated from the first measurement using the equations of motion.

The concept described above is indeed applicable to macroscopic phenomena. We can determine the position of a macroscopic object using e.g. a photograph. In principle the state of the macroscopic object is changed because light interacts with it when the image is taken (radiation pressure). However, this change can be made arbitrarily small within the framework of classical physics by exposing the object increasingly weakly or using a more sensitive film. As a condition for this assumption all physical variables have to change **continuously**.

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2. Limits of Classical Physics

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Classical physics has proven to be valid when applied to macroscopic objects (e.g. celestial mechanics) and macroscopic fields (e.g. deflection of an electron beam in an electric or magnetic field). However, in the following we will discuss some characteristic experiments, where explanations—based on classical physics—definitely fail.

2.1 The Photoelectric Effect

Experimentally one finds that e.g. electrons are emitted from an alkali metal, if the metal is irradiated with UV light. In detail it is stated:

(1) The electric current density is proportional to the intensity of the incident radiation as expected according to classical physics. But:

(2) The energy of the emitted electrons does not depend on the intensity of radiation (in particular not from the distance between the light source and the metal), but only on the frequency ν of the light and the metal used. With the help of a counter-voltage it can be shown, that the energy of the electrons increases linear with the frequency and that no electrons are emitted below a (material-dependent) cutoff frequency ν_c, independent of the radiation intensity.

(3) Above the respective cut-off frequency ν_c the electron emission starts instantaneously.

Point (2) together with (3) cannot be explained in classical wave theory; specifically point (3) shows that the process is not based on a continuous collection of radiation energy in the metal.

Einstein's explanation is based on the hypothesis that the incident radiation can be viewed as a stream of light quanta (photons) with the energy $h\nu$. These photons can be absorbed individually by the metal electrons; if the energy $h\nu$ of the photons is larger than the binding energy of the electrons in the metal, the electrons can leave the metal after absorbing a photon. The kinetic energy then is

$$E_{kin} = \frac{1}{2}\ m\ v^2 = h\nu - W, \tag{2.1}$$

where W is the minimum binding energy of electrons in the metal considered. Einstein's hypothesis is confirmed by experiment qualitatively and quantitatively; in particular (2.1) explains the cutoff frequency. The proportionality constant h in (2.1) turns out to be identical to that known from the radiation of black bodies (**Planck's constant**).

2.2 The Compton Effect

We consider the scattering of light on free (or very weakly bound) electrons (see Fig. 2.1) and assume that the incident radiation is monochromatic. One observes that the wavelength of the scattered light differs from that of the incident light; for the deviation in wavelength one finds,

$$\Delta\lambda = d(1 - \cos\ \vartheta) = \lambda' - \lambda, \tag{2.2}$$

where the constant d is independent of the wavelength λ of the incident light and ϑ is the angle between the direction of observation and the direction of propagation of the incident radiation.

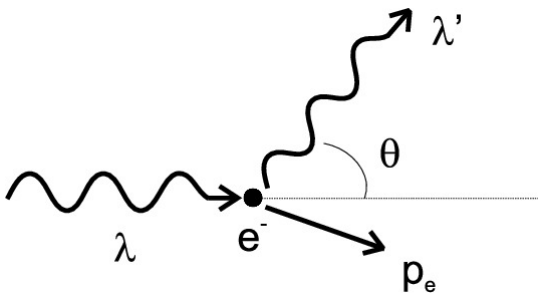

Fig. 2.1 Kinematics for photon scattering (with wavelength λ) on an electron at rest

This finding can be easily explained within the framework of Einstein's photon hypothesis: Since photons (in vacuum) travel with the velocity of light *c*, they cannot have a finite rest mass; accordingly the relativistic energy-momentum relation is:

$$E = pc. \tag{2.3}$$

If energy and frequency are linked via $E = h\nu$, then the magnitude of the momentum of the photon is:

$$p = \frac{h\nu}{c}. \tag{2.4}$$

The properties of the photons $(E, \mathbf{p})$ are the same as those of the wave packet $(\nu, \mathbf{k})$ and linked by:

$$E = h\nu; \quad \mathbf{p} = \hbar\mathbf{k}; \quad k = |\mathbf{k}| = \frac{2\pi}{\lambda} = \frac{2\pi\nu}{c}; \; \hbar = \frac{h}{2\pi}. \tag{2.5}$$

To explain (2.2) one only needs the conservation laws of energy and momentum. If the light (the photon) interacts with an electron at rest, then the following holds for the individual elementary process:

$$\mathbf{p} = \mathbf{p}' + \mathbf{p}_e, \tag{2.6}$$

$$E + mc^2 = E' + \sqrt{(m^2c^4 + p_e^2c^2)}, \tag{2.7}$$

with $\mathbf{p}'$ denoting the momentum of the photon after scattering and $\mathbf{p}_e$ the momentum of the electron after scattering. We write (2.7) as

$$p_e^2 = \tfrac{1}{c^2}\left(E + mc^2 - E'\right)^2 - m^2c^2 \tag{2.8}$$

and square (2.6)

$$p_e^2 = p^2 + p'^2 - 2\ \mathbf{p}\cdot\mathbf{p}' = \tfrac{1}{c^2}\left(E^2 + E'^2 - 2\ EE'\cos\vartheta\right). \tag{2.9}$$

Then follows

$$E - E' = \tfrac{EE'}{mc^2}\left(1 - \cos\vartheta\right) = \tfrac{2\pi\hbar c}{\lambda\lambda'}\left(\lambda' - \lambda\right) \tag{2.10}$$

or with (2.5)

$$\Delta\lambda = \lambda' - \lambda = \tfrac{h}{mc}\left(1 - \cos\vartheta\right). \tag{2.11}$$

Indeed, the factor $h/(mc)$ agrees with the experimentally determined constant d in (2.2).

The explanation of the Compton effect within the framework of Einstein's **photon hypothesis** implies that the scattered photon and the scattered electron occur simultaneously. This could be confirmed by coincidence measurements.

It is instructive to compare these results with the predictions of classical theory. According to Maxwell's theory, the electron under consideration is accelerated by the electric field of the incident radiation, whereas the electric field of the incident radiation looses energy and momentum. The energy absorbed by the accelerated electron is emitted again in the form of a spherical wave of the same frequency. Since the total momentum of the emitted radiation is zero for symmetry reasons, the momentum law requires that the electron takes up momentum in the direction of the incident radiation ($\mathbf{k}$-direction). If the electron initially was at rest, it then should move in the $\mathbf{k}$-direction. This is in contradiction to the experimental observation

that scattered electrons also have momentum components perpendicular to the $\mathbf{k}$-direction.

Note: The frequency of the absorbed and emitted light is only the same in the rest frame of the electron under consideration; the frequencies observed in the laboratory system are different due to the Doppler effect as soon as the electron is in motion. The corresponding shift in wavelength $\Delta\lambda$ depends on the angle ϑ as in equation (2.11), however, for the factor d in (2.2) one doesn't get the correct value in classical theory!

The experiments outlined in (2.1) and (2.2) show that light has a particle character; on the other hand, interference and diffraction experiments show phenomena, that can only be understood in terms of waves. Light thus presents itself in two forms, as a particle or as a wave, respectively, according to the experiment under consideration. This **wave-particle duality** is incompatible with the ideas of classical physics.

If the electromagnetic radiation contradicts the classic wave pattern by showing particle aspects, it is to be expected that inversely mass points under certain conditions also show a wave character. This is indeed the case as one can see from the

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2.3 Electron Diffraction on Crystals

If one shoots electrons of defined energy E and momentum $\mathbf{p}$ on a single crystal one observes **Laue diagrams** on a screen behind the crystal similar to the scattering of X-rays on crystals. If the structure of the crystal is known (lattice constant, crystal symmetry) one can—in analogy to X-ray diffraction—determine a wavelength λ from the Laue diagram. One finds empirically that λ is related to the energy E or the magnitude of the momentum $\mathbf{p}$ of the electrons according to ($p = |\mathbf{p}|$)

$$\lambda = \frac{h}{p} \tag{2.12}$$

(**de Broglie relation**), or using the wave number $k = 2\pi/\lambda$

$$\mathbf{p} = \hbar\mathbf{k}; \quad \hbar = \frac{h}{2\pi}, \tag{2.13}$$

in agreement with (2.5) for the case of photons!

The results reported above are compatible with other experimental observations and also for other particles (e.g. neutrons, helium atoms) and force us **to attribute wave properties to matter, which obviously contradicts the ideas of classical physics**.

Apart from the wave-particle dualism, which is insolvable for classical physics, there is further experimental evidence for the duality for matter and electromagnetic radiation and for the limits of classical physics: In the atomic domain there are situations in which physical quantities (example: energy of a particle) can only assume **discrete** values (excited states of atoms) in contrast to the classical theory.

2.4 Quantization of the Energy of Bound States

Characteristic for the emission and absorption of electromagnetic radiation by matter is the existence of **sharp spectral lines**. Absorption and emission spectra for a given system (atom, molecule, atomic nucleus) are the same; every system has a characteristic spectrum that can be used to identify it (detection of trace elements).

This experimental finding does not fit into the framework of the classical theory, in which the energy is a continuous quantity. A convenient explanation is provided by the following hypothesis (N. Bohr): atoms (molecules, atomic nuclei) can only exist in certain **stationary states**, which have a well-defined energy. When interacting with electromagnetic radiation only **discontinuous** transitions between the stationary states are possible, resulting in sharp spectral lines in the emission pattern; the energy difference between the states under consideration corresponds to the energy of the emitted (absorbed) photon,

$$E_i - E_j = h\nu_{ij}. \tag{2.14}$$

A further experimental confirmation of energy quantization is provided by the **Frank-Hertz experiment** on inelastic collisions of electrons on atoms: Monoenergetic electrons are scattered from the atoms of a target, the energy of the scattered electrons is measured (by a counter voltage) and from this the energy loss is determined. Let T be the

kinetic energy of the incoming electrons, E_0, E_1, . . . the energies of the stationary states of the target atoms. Since all atoms are practically in the ground state with energy E_0 (according to the experimental conditions), according to Bohr's hypothesis the atoms cannot absorb energy as long as $T \leq E_1 - E_0$, i.e. the collision is elastic. If $T \geq E_1 - E_0$, atoms can reach the first excited state and the electrons lose the energy $E_1 - E_0$ (inelastic scattering). This is exactly what is observed; with increasing energy *T* higher excitations are observed, too.

An analog experiment in nuclear physics is **Coulomb excitation**, in which protons move close to a nucleus and—with a loss of energy—excite the nucleus to low lying states.

2.5 Quantization of Orientation

We consider the deflection of a beam of paramagnetic atoms with the magnetic moment μ in an inhomogeneous magnetic field $\mathbf{B}$ (**Stern-Gerlach experiment**). The force acting on the dipole moments is

$$\mathbf{F} = \nabla(\overrightarrow{\mu} \cdot \mathbf{B}), \tag{2.15}$$

since the potential energy is $-(\mu \cdot \mathbf{B})$ (see electrodynamics). For the sake of simplicity we assume that (by appropriate shaping of the magnets) only B_z and $\partial B_z/\partial z$ are non-zero. Then only the force in the *z* direction acts on the particles with strength:

$$|\mathbf{F}| = F_z = \mu_z \frac{\partial B_z}{\partial z}\,. \tag{2.16}$$

If the magnetic moments are initially oriented statistically, then all values for μ_z are possible between $\pm\mu$ $(\mu = |\overrightarrow{\mu}|)$. Accordingly, the deflection angle can continuously vary between the extreme angles belonging to $\mu_z = \pm\mu$. On the screen—placed perpendicular to the beam behind the magnet in the direction of the beam—one would therefore expect—according to the classical theory—the image shown in Fig. 2.2a; the length of the line depends on the kinetic energy of the atoms, the strength of the magnetic field and the distance between the

magnet and the screen. Figure 2.2b shows the trivial result for the case $\mu = 0$.

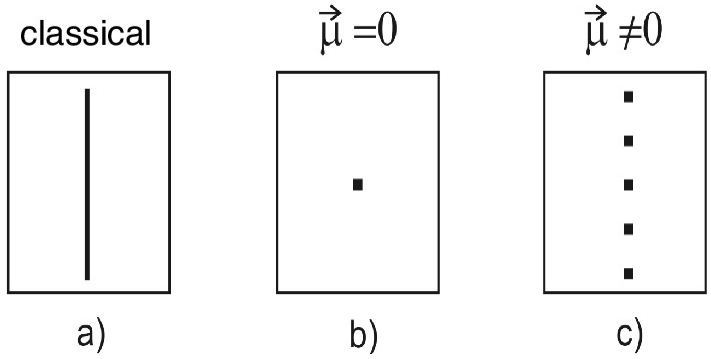

Fig. 2.2 The classical expected spatial distribution of the atoms (**a**); result for the case $\mu = 0$ (**b**); result for the case of angular momentum l=2$\hbar$ (**c**)

Experimentally the case (*c*) is found, i.e. a sequence of equidistant points along the *z* direction, symmetrical to the original beam direction. Apparently only certain discrete values of μ_z are realized; since the magnetic moment is directly related to the angular momentum of the atoms, this implies that the *z* component of the angular momentum of the atoms can only have certain discrete (integer) values (in units of $\hbar$).

Note: Figure 2.2 (*c*) refers to the case of orbital angular momentum $l = 2\hbar$; in the case of spins (half integers) the central point is omitted.

The wave-particle duality as well as the quantization of certain physical properties show that classical physics fails at the atomic level. The classical theory must be replaced by a new theory—the **quantum theory**—which, of course, must include the classical physics as a limiting case, since this has been proven valid for macroscopic systems. **The fact that the wave-particle duality shows up both for matter as well as for electromagnetic radiation, implies that a quantum theory is needed not only for matter but also for radiation**.

In the following we will first examine the quantum theory of matter using the example of a single particle. Then we formulate the quantum theory abstractly and axiomatically; this abstract formulation will also show how to deal with the multi-particle problem and how to quantize the electromagnetic field.

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3. Beginning of Quantum Theory: Matter Waves

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In this chapter we briefly discuss Bohr's model of the atom and the concept of matter waves.

3.1 Bohr's Model of the Atom

The first attempt to solve the problems of classical physics was to add certain **quantum postulates** to mechanics. This reduced the possible continuum of classic paths to certain **permitted** paths. Despite some successes (quantitative description of the hydrogen atom, etc.), this attempt had to be abandoned because it.

(1) failed in some concrete cases (aperiodic motions, i.e. scattering states; **anomalous Zeeman effect**) and

(2) is not free from contradictions: on the one hand, the concept of an orbit in form of **allowed orbits** is required, on the other hand, in a transition between two **allowed orbits** the particles should reach their state discontinuously, i.e. not along a classic path.

3.2 Matter Waves

The second attempt, which ultimately led in the right direction, goes back to the observation of interference phenomena from material

beams. Experiments like the electron diffraction on crystals suggest to attribute a wave to a monoenergetic particle beam; the most simple approach - for geometrical reasons - is a plane wave

$$\sim \exp\left(i[\mathbf{k}\cdot\mathbf{r} - \omega t]\right). \tag{3.1}$$

We now have to link the known properties of the particles—in our case the energy E and the momentum $\mathbf{p}$—to the quantities characterizing the wave, i.e. angular frequency ω and wave vector $\mathbf{k}$. According to experimental finding by **de Broglie** (2.12) we connect $\mathbf{k}$ and $\mathbf{p}$ by

$$\mathbf{p} = \hbar\mathbf{k}. \tag{3.2}$$

The analogy to photons suggests that the (kinetic) energy of the particles with the angular frequency $\omega = 2\pi\nu$ to be given by

$$E = \hbar\omega \tag{3.3}$$

due to the Lorentz invariance of the phase in (3.1). The frequency ω is certainly independent of the direction of $\mathbf{k}$ due to spatial isotropy, it thus can only depend on the magnitude of $\mathbf{k}$. So we have to find the dispersion law

$$\omega = \omega(k) \tag{3.4}$$

for material particles, that replaces the relationship for photons

$$\omega = kc. \tag{3.5}$$

To this aim we consider a wave packet (i.e. a superposition of plane waves)

(3.6)

$$\psi(\mathbf{r};t) = \int d^3k\ \varphi(\mathbf{k})\ \exp\ (i[\mathbf{k}\cdot\mathbf{r} - \omega t]),$$

and assume that $\varphi(\mathbf{k})$ is only significantly different from zero in the neighborhood of $\mathbf{k} \approx \mathbf{k}_0$. Then we can expand the phase as:

$$\mathbf{k}\cdot\mathbf{r} - \omega t \approx \mathbf{k}_0\cdot\mathbf{r} - \omega_0 t + (\mathbf{k}-\mathbf{k}_0)\cdot(\mathbf{r} - \mathbf{v}_g t) + \cdots \tag{3.7}$$

with

$$\mathbf{v}_g = \left.\frac{\partial\omega}{\partial\mathbf{k}}\right|_{\mathbf{k}=\mathbf{k}_0}. \tag{3.8}$$

Equation (3.6) then gives the approximate result

$$\psi(\mathbf{r};t) \approx a(\mathbf{r};t)\ \exp\ (i[\mathbf{k}_0\cdot\mathbf{r} - \omega_0 t]) \tag{3.9}$$

with the amplitude

$$a(\mathbf{r};t) = \int d^3k\ \varphi(\mathbf{k})\ \exp\ \{i(\mathbf{k}-\mathbf{k}_0)\cdot(\mathbf{r} - \mathbf{v}_g t)\}. \tag{3.10}$$

Equation (3.9) represents a plane wave modulated with the amplitude (3.10) with wave vector $\mathbf{k}_0$ and frequency ω_0 and should be more suitable to describe an experimentally realizable particle beam, which is always localized in space and time contrary to an infinitely extended plane wave.

The amplitude $a(\mathbf{r};t)$ now has a maximum for such values of $(\mathbf{r}, t)$, for which the oscillating exp-factor in (3.10) becomes stationary, i.e. for

$$\mathbf{r} = \mathbf{v}_g t. \tag{3.11}$$

The maximum of the amplitude therefore moves with the **group velocity** $\mathbf{v}_g$ in space. It now makes sense to compare this group velocity with the velocity $\mathbf{v}$,

$$\mathbf{v}_g = \frac{\partial\omega}{\partial\mathbf{k}} = \mathbf{v} = \frac{\mathbf{p}}{m} = \frac{\hbar\mathbf{k}}{m} = \frac{\partial\omega}{\partial k}\,\mathbf{e}_k. \tag{3.12}$$

Due to (3.2) we get the (non-relativistic) relation by integration w.r.t. k,

$$\omega(k) = \frac{\hbar}{2\,m}k^2, \tag{3.13}$$

where a possible integration constant is omitted here because in $\psi(\mathbf{r};t)$ it only would provide a constant phase.

The **dispersion relation** (3.13) is in fact confirmed by diffraction experiments with electrons or other atomic particles and thus the interpretation (3.12) of the group velocity. We notice that (3.13) is precisely the classical (non-relativistic) energy-momentum relation for a free particle corresponding to:

$$E = \hbar\omega = \frac{p^2}{2\,m}. \tag{3.14}$$

3.3 Wave Equation of Free Particles

We now want to set up a wave equation for the motion of free particles. The desired equation must meet the following general criteria:

(1) It must be **linear and homogeneous**; the solutions then satisfy the **superposition principle** as necessary for interference phenomena: if ψ_1 and ψ_2 are solutions of the (required) wave equation, then the linear combination $\lambda_1\psi_1 + \lambda_2\psi_2$ is a solution, too.

(2) It must be a **first-order differential equation in time** such that $\psi(\mathbf{r};t)$ completely describes the state of the physical system: if ψ is known at any time t_0, then the temporal evolution for ψ follows from the wave equation in a unique way.

Such a wave equation can be obtained by taking the following partial derivatives of the plane wave (3.1).

(3.15)

$$\frac{\partial^2\psi}{\partial r^2} = -k^2\psi$$

$$\frac{\partial\psi}{\partial t} = -i\omega\ \psi \tag{3.16}$$

and account for the dispersion relation (3.13). From (3.15) and (3.16) directly follows

$$i\hbar\frac{\partial}{\partial t}\ \psi = -\frac{\hbar^2}{2\,m}\Delta\psi, \tag{3.17}$$

i.e. the **Schrödinger equation** for free particles.

Note: The wave equation for electromagnetic radiation is different from (3.17) because it is of second order with respect to time. This is a consequence of the different dispersion relations $\omega(k)$. The analogy of wave theory for matter and for radiation becomes more transparent when comparing (3.17) with the Maxwell equations for the components of $\mathbf{E}$ and $\mathbf{B}$, which in line with (3.17) are first-order differential equations with respect to time: the state of the free radiation field is uniquely determined, if all components of $\mathbf{E}$ and $\mathbf{B}$ are fixed at some time t_0. This comparison also shows that the description of matter not necessarily must succeed with a single function $\psi(\mathbf{r};t)$; we will indeed see later that we require several (at least 2) wave functions as soon as we include the electron spin in the theory.

3.4 Continuity Equation

Since in non-relativistic classical physics the mass of a system is a conserved quantity, it makes sense to ask whether we can derive a corresponding conservation law from the wave Eq. (3.17). To this aim we consider the conjugate-complex equation to (3.17)

$$-i\hbar\frac{\partial}{\partial t}\ \psi^* = -\frac{\hbar^2}{2\,m}\Delta\psi^*, \tag{3.18}$$

multiply (3.17) from the left by ψ^*, (3.18) by ψ and consider the difference:

$$i\hbar\frac{\partial}{\partial t}(\psi^*\psi) = \frac{\hbar^2}{2\,m}\{[\Delta\psi^*]\psi - \psi^*[\Delta\psi]\}. \tag{3.19}$$

With the identity

$$[\Delta\psi^*]\psi - \psi^*[\Delta\psi] = \nabla\cdot\{\psi\ \nabla\psi^* - \psi^*\nabla\psi\} \tag{3.20}$$

this results in a **continuity equation** of the form

$$\frac{\partial}{\partial t}(\psi^*\psi) + \nabla\cdot\left(\frac{\hbar}{2im}[\psi^*\nabla\psi - \psi\ \nabla\psi^*]\right) = 0. \tag{3.21}$$

3.5 Interpretation of Matter Waves

We identify

$$\rho(\mathbf{r};t) \equiv \psi^*(\mathbf{r};t)\psi(\mathbf{r};t) \tag{3.22}$$

with the **particle density** and

$$\mathbf{j}(\mathbf{r};t) \equiv \frac{\hbar}{2im}\{\psi^*(\mathbf{r};t)\nabla\psi(\mathbf{r};t) - \psi(\mathbf{r};t)\ \nabla\psi^*(\mathbf{r};t)\} \tag{3.23}$$

with the **particle current density.** Gauß's theorem then gives

$$\frac{\partial}{\partial t}\left(\int d^3r\ \psi^*(\mathbf{r};t)\psi(\mathbf{r};t)\right) = 0, \tag{3.24}$$

assuming that $\mathbf{j}$ for $r\to\infty$ drops faster than $1/r^2$. Equation (3.24) involves the conservation of the total mass or particle number. Since for real physical systems the mass or particle number is always finite, we get the constraint

$$\int d^3r\ \psi^*(\mathbf{r};t)\psi(\mathbf{r};t) < \infty. \tag{3.25}$$

This implies that $\psi(\mathbf{r};t)$ is a square-integrable complex function, i.e. $\psi \epsilon \mathscr{L}_2$.

Since Eq. (3.17) is homogeneous, we can choose the normalization constant in (3.25) arbitrarily. We can therefore describe also a **single** particle with the wave function $\psi(\mathbf{r};t)$. The position of the particle in the classical sense we can identify with the center of mass

$$< \mathbf{r} >= \frac{\int d^3r \ \psi^* \mathbf{r} \ \psi}{\int d^3r \ \psi^* \psi} = \frac{(\psi, \mathbf{r}\psi)}{(\psi, \psi)}, \tag{3.26}$$

where the scalar product

$$(\phi, \psi) := \int d^3r \ \phi^*(\mathbf{r}) \psi(\mathbf{r}) \tag{3.27}$$

is the dot-product defined in the space $\mathscr{L}_2$ for $\phi, \psi \ \epsilon \mathscr{L}_2$.

3.6 Criticism of the Concept of Matter Waves

The concept of spatially **smeared** particles (developed above) proves to be misleading. The following considerations will show this:

(1) Describing a particle with a defined mass *m* and charge *e* by a spatially sharply localized wave packet at time $t = t_0$, then this wave packet disintegrates in time.

(2) Within the framework of a strict wave theory, in diffraction experiments the intensity of the diffraction image should decrease with a decrease of the incoming matter wave, but the structure of the diffraction image should remain. Experimentally one observes something completely different: on a photographic plate behind the diffracting object individual points appear for low beam intensity; **only a measurement over a long period of time results in a statistical distribution of the individual points, which reflect the structure of a diffraction pattern**.

In summary, we have discussed Bohr's model of the atom and the early concepts of matter waves for a particle. The failures of these early concepts have been pointed out and will pave the wave to a proper formulation of quantum mechanics.

Part II
Elementary Quantum Mechanics

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4. Quantum Theory of a Particle

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In this chapter we will present a discussion of the Schrödinger equation—without and with external forces—and investigate the properties of stationary states.

4.1 Statistical Interpretation of the Wave Function

The results of diffraction experiments at very low intensity (see Sect. 3.6) suggests a statistical interpretation of the wave function $\psi(\mathbf{r};t)$. Following a suggestion from Born we normalize by

$$\int d^3r \ |\psi(\mathbf{r};t)|^2 = (\psi,\psi) = 1 \tag{4.1}$$

and interpret

$$|\psi(\mathbf{r};t)|^2 \tag{4.2}$$

as **probability density**, i.e. as the probability that the particle can be found at position $\mathbf{r}$ at time t in a respective measurement of its position. If we use the **Schrödinger equation** in the form (3.17) the continuity Eq. (3.21) still holds, but $j(\mathbf{r};t)$ now has to be interpreted as **probability current density**. Then

$$\int_F \mathbf{j}\cdot\mathbf{df} \tag{4.3}$$

is the probability that a particle passes through the surface F per unit of time. The relation following from (3.21) for $(V\to\infty)$

$$\frac{d}{dt}\left(\int_V d^3r \ |\psi(\mathbf{r};t)|^2\right) = 0 \tag{4.4}$$

shows the conservation of the overall probability, that particles can be found somewhere in space (time independence of the norm).

This statistical interpretation should be interpreted in such a way that $\psi(\mathbf{r};t)$ does not describe a single particle (as assumed in the naive theory of matter waves), but the **state of a quantum mechanical ensemble of particles**, i.e. a large number of particles with the same internal properties for the same experimental conditions. As an example we mention the motion of electrons in a large number of hydrogen atoms, which are all exposed to the same electrostatic field.

Accordingly, the quantity—already introduced in (3.26):

$$< \mathbf{r} >= \frac{\int d^3r \ \psi^* \mathbf{r} \ \psi}{\int d^3r \ \psi^* \psi} \tag{4.5}$$

has not to be identified with the position of a particle, but as an **average** of a sufficiently large number of position measurements of the ensemble under consideration.

This **statistical interpretation** is in full agreement with diffraction experiments as discussed in Sect. 2.3. A diffraction experiment with an electron beam of sufficiently high intensity is equivalent to a multitude of experiments with a single electron of a quantum mechanical ensemble. One therefore obtains a diffraction pattern corresponding to the probability distribution that is determined by the wave function $\psi(\mathbf{r};t)$. Reducing the intensity of the incident electron beam (or photon beam) more and more, the diffraction pattern finally disappears; instead one registers (in the detector) a sequence of well-defined hits, for which the wave function $\psi(\mathbf{r};t)$ can not make a statement.

The temporal evolution of a quantum mechanical ensemble of free particles is determined by the Schrödinger equation (3.17). Since this is a 1st order differential equation with respect to time *t*, the specification of the wave function $\psi(\mathbf{r};0)$ at time $t = 0$ is sufficient to clearly determine the state of the ensemble at later times $t \neq 0$. In this sense quantum mechanics is also a strictly causal theory.

4.2 Schrödinger Equation of a Particle in the Presence of External Forces

In the presence of external forces we must extend the Schrödinger equation (3.17) without violating the fundamental properties quoted in Sect. 3.3. The extension then has to be of the form:

$$i\hbar\frac{\partial}{\partial t} \ \psi = O \ \psi, \tag{4.6}$$

where *O* is a linear operator to be determined. We can restrict the possible approaches for *O* by requiring that the statistical interpretation of $|\psi|^2$ should continue to hold. As in Sect. 3.4 we get from (4.6):

$$i\hbar\frac{\partial}{\partial t}\int d^3r\ \psi^*\psi = \int d^3r\ \{\psi^* O\ \psi - (O\psi)^*\psi\}. \tag{4.7}$$

The conservation of the total probability requires

$$(\psi, O\psi) = \int d^3r\ \psi^* O\ \psi = \int d^3r\ (O\psi)^*\psi = (O\psi, \psi). \tag{4.8}$$

Now let ψ_1 and ψ_2 be two different solutions to (4.6) then—due to the linearity of O—must hold

$$O(c_1\psi_1 + c_2\psi_2) = c_1 O\psi_1 + c_2 O\psi_2 \tag{4.9}$$

for arbitrary complex numbers c_1 and c_2. By inserting in (4.8) $\psi = c_1\psi_1 + c_2\psi_2$ we directly get:

$$(O\psi_1, \psi_2) = \int d^3r\ (O\psi_1)^*\psi_2 = \int d^3r\ \psi_1^* O\ \psi_2 = (\psi_1, O\psi_2). \tag{4.10}$$

An operator with the property (4.10) is called **hermitian**.

To get the detailed structure of the hermitian operator O we recall that the right side of the free Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\ \psi = -\frac{\hbar^2}{2m}\Delta\ \psi \tag{4.11}$$

originates from the kinetic energy $E = \hbar^2 k^2/(2m)$ of the free particle. Thus attributing in quantum mechanics the **differential operator** to the momentum in the form

$$\mathbf{p} = -i\hbar\nabla, \tag{4.12}$$

we can write (4.11) as

$$i\hbar\frac{\partial}{\partial t}\ \psi = \hat{T}\ \psi, \tag{4.13}$$

where

$$\hat{T} \equiv -\frac{\hbar^2}{2m}\Delta \equiv \frac{p^2}{2m} \tag{4.14}$$

is the kinetic energy operator. For simplicity we denote the operator of the kinetic energy in quantum mechanics again by *T*, i.e. $\hat{T} = T$. - In case of a conservative force (e.g. electrostatic field) the form (4.13) suggests to use as a Schrödinger equation:

$$i\hbar \frac{\partial}{\partial t}\ \psi(\mathbf{r};t) = (T+V)\psi(\mathbf{r};t) = \left(-\frac{\hbar^2}{2\,m}\Delta + V(\mathbf{r})\right)\psi(\mathbf{r};t). \tag{4.15}$$

Here the potential *V*, in which the particle should move, appears as a real multiplicative operator. Then

$$H = T + V \tag{4.16}$$

is the operator corresponding to the Hamilton function in quantum mechanics. We therefore write (4.15) also in the form

$$i\hbar \frac{\partial}{\partial t}\ \psi = H\ \psi. \tag{4.17}$$

The **Hamilton operator** *H* is hermitian since *V* is assumed to be real.

In the case of the velocity-dependent Lorentz force let's adopt the classical rule and replace (with a real vector potential **A**)

$$\mathbf{p} \to \mathbf{p} - \frac{e}{c}\ \mathbf{A}. \tag{4.18}$$

We then obtain the general Schrödinger equation for a particle of mass *m* and charge *e* in the form (in cgs -Gauss units)

$$i\hbar \frac{\partial}{\partial t}\ \psi(\mathbf{r};t) = \left[\frac{1}{2\,m}\left\{-i\hbar\nabla - \frac{e}{c}\ \mathbf{A}(\mathbf{r};t)\right\}^2 + e\Phi(\mathbf{r};t)\right]\psi(\mathbf{r};t) \equiv H\ \psi(\mathbf{r};t). \tag{4.19}$$

The connection to the electric field $\mathbf{E}(\mathbf{r};t)$ and the magnetic field $\mathbf{B}(\mathbf{r};t)$ is given by (see electrodynamics)

$$\mathbf{B}(\mathbf{r};t) = \nabla \times \mathbf{A}(\mathbf{r};t), \tag{4.20}$$

$$\mathbf{E}(\mathbf{r};t) = -\nabla\Phi(\mathbf{r};t) - \frac{\partial}{\partial t}\mathbf{A}(\mathbf{r};t).$$

The considerations above should not be understood as a derivation of the Schrödinger equation, but only as a heuristic introduction to quantum theory in the framework of the correspondence between classical and quantum mechanical observables. A stricter mathematical formulation is presented in Chaps. 9 and 10.

4.3 Stationary States

If the Hamiltonian H does not depend on t (closed system), the time dependence in $\psi(\mathbf{r};t)$ is separated by the Ansatz

$$\psi(\mathbf{r};t) = \varphi(\mathbf{r})\ \exp\{-\tfrac{i}{\hbar}Et\}. \tag{4.21}$$

One then obtains the time-independent Schrödinger equation from (4.19)

$$H\ \varphi(\mathbf{r}) = E\ \varphi(\mathbf{r}) \tag{4.22}$$

for calculating the **stationary** states $\varphi(\mathbf{r})$. We briefly prove some **fundamental properties**:

(1) E **is real since** H **is hermitian**. For the proof we form

$$(\varphi, H\varphi) = \int d^3r\ \varphi^* H\ \varphi = E\ \int d^3r\ \varphi^*\varphi = E(\varphi,\varphi) \tag{4.23}$$

and after complex conjugation of (4.22) obtain

$$(H\varphi,\varphi) = \int d^3r (H\varphi)^*\varphi = E^* \int d^3r\ \varphi^*\varphi = E^*(\varphi,\varphi). \tag{4.24}$$

Due to the hermiticity of H, the difference results in

$$0 = (E - E^*)\int d^3r\ \varphi^*\varphi = (E-E^*)(\varphi,\varphi) \tag{4.25}$$

thus

$$E = E^*, \tag{4.26}$$

since the normalization integral (φ,φ) is $\neq 0$.

(2) For any time-independent operator *F*—such as e.g. the position operator $\mathbf{r}$ —holds that

$$(\psi, F\psi) = \int d^3r\ \psi^*(\mathbf{r};t) F\ \psi(\mathbf{r};t) = \int d^3r\ \varphi^*(\mathbf{r}) F\ \varphi(\mathbf{r}) = (\varphi, F\varphi) \tag{4.27}$$

is independent of *t* (**stationary**). In particular we have

$$\psi^*\psi = \varphi^*\varphi \tag{4.28}$$

and

$$\psi^*\nabla\psi - \psi\ \nabla\psi^* = \varphi^*\nabla\varphi - \varphi\ \nabla\varphi^*. \tag{4.29}$$

(3) **Orthogonality**:

For solutions φ_1, φ_2 of (4.22) to different values $E_1 \neq E_2$ holds:

$$(\varphi_1, \varphi_2) = \int d^3r\ \varphi_1^*\varphi_2 = 0. \tag{4.30}$$

Proof: We start from

$$\varphi_2^*(H - E_1)\varphi_1 = 0; \quad \varphi_1[(H - E_2)\varphi_2]^* = 0 \tag{4.31}$$

and form $\int d^3r \cdots$ For the difference of the resulting equations we obtain

$$(E_2 - E_1) \int d^3r\ \varphi_2^*\varphi_1 = (E_2 - E_1)(\varphi_2, \varphi_1) = 0 \tag{4.32}$$

due to the hermiticity of H. Since $E_1 \neq E_2$ the proof completes.

(4) **Degeneracy**

Among the stationary states there are also those, that belong to the same eigenvalue in energy *E*, but differ in some other physical properties. Such solutions from (4.22) are called **degenerate**. Any linear combination of such solutions then is again a solution of (4.22) to the same value *E*; in particular, degenerate solutions are in general not orthogonal to each other. However, by suitable linear combinations an orthogonal set can always be obtained from the degenerate solutions (**Schmidt orthogonalization**).

Such degeneracies occur in connection with symmetries of *H*. We give a simple **example**: For the free Schrödinger equation ($V \equiv 0$), $H = T$ is invariant with respect to the **parity** operation

$$\mathbf{r} \to -\mathbf{r} \tag{4.33}$$

and the solutions

$$\exp\left(+i\mathbf{k}\cdot\mathbf{r}\right),\ \ \exp\left(-i\mathbf{k}\cdot\mathbf{r}\right) \tag{4.34}$$

are (twofold) degenerate. They differ physically from each other in the different direction of the momentum.

In summarizing this chapter we have introduced the statistical interpretation of the Schrödinger equation—without and with external forces—and investigated the properties of stationary states.

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5. Operators and Expectation Values

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In this chapter we will introduce the rules to translate classical observables in phase-space representation to hermitian operators in the formal space of wavefunctions (Hilbert space). It is furthermore proven that the classical equations of motion also hold for the expectation values of the corresponding quantum operator (Ehrenfest theorem). The formal translation of the Poisson brackets in classical mechanics to commutators in quantum physics is derived and it is shown, that the commutators follow the same algebra as the Poisson brackets.

5.1 Quantum Mechanical Analogue of the Classical Equations of Motion

In Sect. 4.2 we have assigned linear operators to various classical observables, which act in the space of wave functions $\psi(\mathbf{r};t)$. As an example we have introduced the position operator $\mathbf{r}$ as a multiplication by $\mathbf{r}$ and interpreted—with the condition (4.1)—its **expectation value**

$$< \mathbf{r} >= \int d^3r \ \psi^*(\mathbf{r};t) \ \mathbf{r} \ \psi(\mathbf{r};t) = (\psi, \mathbf{r}\psi) \tag{5.1}$$

as the average of a very large number of position measurements on the ensemble considered. We want to calculate now the temporal evolution of $< \mathbf{r} >$ and, for the sake of simplicity, assume that the Hamilton operator of the particle has the form

$$H = -\frac{\hbar^2}{2\,m}\Delta + V(\mathbf{r}). \tag{5.2}$$

For the temporal evolution of $< \mathbf{r} >$—the operator $\mathbf{r}$ itself is independent of time—we find by using the Schrödinger equation (4.17)

$$\frac{d}{dt} < \mathbf{r} >= \int d^3r \ \left\{[\frac{\partial}{\partial t} \ \psi^*]\mathbf{r} \ \psi + \psi^*\mathbf{r} \ [\frac{\partial}{\partial t} \ \psi]\right\} = \frac{i}{\hbar}\int d^3r \ \left\{[H\psi]^*\mathbf{r} \ \psi - \psi^*\mathbf{r} \ [H\psi]\right\}. \tag{5.3}$$

Due to the hermiticity of H we can rewrite

$$\frac{d}{dt} < \mathbf{r} >= \frac{i}{\hbar}\int d^3r \ \psi^*(H \ \mathbf{r} - \mathbf{r} \ H)\psi = \frac{i}{\hbar}(\psi, (H \ \mathbf{r} - \mathbf{r} \ H)\psi). \tag{5.4}$$

For the further evaluation of (5.3) we have to calculate the **commutator**

$$[H, \mathbf{r}] := H\ \mathbf{r} - \mathbf{r}\ H. \tag{5.5}$$

Since $\mathbf{r}$ and $V(\mathbf{r})$ are pure multiplicative operators they commute with each other, *V* does not contribute to (5.5); it remains to investigate

$$[\Delta, \mathbf{r}] = ? \tag{5.6}$$

Since operators like $\partial/\partial y$ and *x* commute with respect to their action on $\psi(\mathbf{r};t)$,

$$\left[\frac{\partial}{\partial y},\ x\right]\psi(\mathbf{r};t) = 0, \tag{5.7}$$

only

$$\left[\frac{\partial^2}{\partial x^2},\ x\right]\psi(\mathbf{r};t) \tag{5.8}$$

can contribute to (5.3). For this we get

$$\left[\frac{\partial^2}{\partial x^2}x - x\frac{\partial^2}{\partial x^2}\right]\psi(\mathbf{r};t) = \frac{\partial}{\partial x}\left(x\frac{\partial}{\partial x} + 1\right)\psi(\mathbf{r};t) - x\ \frac{\partial^2}{\partial x^2}\psi(\mathbf{r};t) = 2\frac{\partial}{\partial x}\psi(\mathbf{r};t). \tag{5.9}$$

In total we get from (5.3)

$$\frac{d}{dt} < \mathbf{r} >= -\frac{i\hbar}{m}\ \int d^3r\ \psi^*\nabla\psi = \frac{1}{m}\ \int d^3r\ \psi^*(-i\hbar\nabla)\psi \tag{5.10}$$

and finally with (4.12)

$$\frac{d}{dt} < \mathbf{r} >= \frac{1}{m} < \mathbf{p} >. \tag{5.11}$$

The classical relationship between velocity and momentum also holds for the expectation values of the corresponding quantum mechanical operators.

Based on the result above we now follow the same procedure for the time derivative of the momentum $< \mathbf{p} >$

$$\frac{d}{dt}(\psi, \mathbf{p}\psi) = \frac{d}{dt} < \mathbf{p} >= \frac{i}{\hbar}\int d^3r\ \psi^*[H,\ \mathbf{p}]\psi. \tag{5.12}$$

Since $-\hbar^2\Delta \equiv p^2$ and every operator commutes with itself, only the contribution from the potential energy remains in the commutator (5.12):

$$[V,\ \mathbf{p}] \equiv V\ \mathbf{p} - \mathbf{p}\ V = i\hbar\nabla V. \tag{5.13}$$

This gives the quantum mechanical analogue to the classical equations of motion after forming the expectation values,

$$\frac{d}{dt} < \mathbf{p} >= - < \nabla \ V > . \tag{5.14}$$

5.2 Hermitian Representation of Operators

We now want to extend the considerations above to arbitrary observables and note:

(1) Every classical observable *F* can be represented as a function of position and momentum coordinates $\mathbf{r}_{kl}$ and $\mathbf{p}_{kl}$ and possibly of time *t*,

$$F(\mathbf{r}_{kl}, \mathbf{p}_{kl}; t). \tag{5.15}$$

(2) We have assigned the classical variables $\mathbf{r}_{kl}$ and $\mathbf{p}_{kl}$ in quantum theory to the operators $\mathbf{r}$ and $\mathbf{p} = -i\hbar\nabla$, which act in the space of wave functions (that will be denoted later as **Hilbert space**).

The quantization rule for position and momentum suggests to assign to every observable *F* an operator

$$F(\mathbf{r}, \mathbf{p}; t). \tag{5.16}$$

In the non-relativistic theory, *t* plays the role of a parameter, and is not an operator! We'll come back to this point later. When translating classical observables to operators

$$F(\mathbf{r}_{kl}, \mathbf{p}_{kl}; t) \rightarrow F(\mathbf{r}, \mathbf{p}; t) \tag{5.17}$$

the following points should be noted:

(i) The above quantization rule refers to **cartesian coordinates**. To illustrate this point, let us consider the Schrödung equation of a free particle in 2 dimensions:

$$i\hbar \frac{\partial}{\partial t} \ \psi(x, y; t) = -\frac{\hbar^2}{2\,m} \left\{ \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right\} \psi(x, y; t). \tag{5.18}$$

Converting (5.18) to polar coordinates *r*, φ, we get

$$i\hbar \frac{\partial}{\partial t} \ \psi(r, \varphi; t) = -\frac{\hbar^2}{2\,m} \left\{ \frac{\partial^2}{\partial r^2} + \frac{1}{r} \ \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \varphi^2} \right\} \psi(r, \varphi; t). \tag{5.19}$$

If we start from the classical Hamilton function in polar coordinates,

$$H_{kl} = \frac{1}{2\,m} \left\{ p_r^2 + \frac{1}{r^2} p_\varphi^2 \right\}_{kl} \tag{5.20}$$

and adopt the rule for quantization, we obtain

$$(p_r)_{kl} \to p_r = -i\hbar\frac{\partial}{\partial r}; \qquad (p_\varphi)_{kl} \to -i\hbar\frac{\partial}{\partial \varphi}. \tag{5.21}$$

In contrast to (5.19) the Schrödinger equation would read as

$$i\hbar\frac{\partial}{\partial t}\ \psi(r,\varphi;t) = -\frac{\hbar^2}{2\,m}\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r^2}\frac{\partial^2}{\partial \varphi^2}\right)\psi(r,\varphi;t). \tag{5.22}$$

To avoid such ambiguities in quantization, we always refer to the quantization rule formulated in (5.17) in cartesian coordinates.

(ii) Since the expectation values of the operators

$$< F >= \int d^3r\ \psi^* F(\mathbf{r},\mathbf{p};t)\psi \tag{5.23}$$

have a direct physical interpretation and must be real, the operators have to be hermitian:

$$(\psi, F\psi) = \int d^3r\ \psi^* F\ \psi = \int d^3r\ (F\psi)^*\psi = (F\psi,\psi) \tag{5.24}$$

for every wave function $\psi(\mathbf{r};t)$ of the particle. Except for the elementary operators for position and momentum therefore are allowed: polynomials (with real coefficients) in $\mathbf{r}$ (e.g. potential energy of an oscillator) or $\mathbf{p}$ (e.g. kinetic energy of a particle), but also mixed polynomials like

$$\mathbf{l} \equiv \mathbf{r}\times\mathbf{p} = -(\mathbf{p}\ \times\mathbf{r}) \tag{5.25}$$

such as the operator of the orbital angular momentum. On the other hand,

$$\mathbf{r}\cdot\mathbf{p} \tag{5.26}$$

is not a hermitian operator. In the transition from the classical mechanics to quantum mechanics we must **symmetrize** and replace

$$\mathbf{r}_{kl}\cdot\mathbf{p}_{kl} \to \tfrac{1}{2}(\mathbf{r}\cdot\mathbf{p} + \mathbf{p}\cdot\mathbf{r}). \tag{5.27}$$

The reason for the necessity of symmetrization is the non-commutativity of the hermitian operators $\mathbf{r}$ and $\mathbf{p}$,

$$[x_i,\ p_j] = i\hbar\delta_{ij};\quad i,j = 1,2,3. \tag{5.28}$$

This—in contrast to (5.25)—becomes effective in the scalar product (5.26) or (5.27). For the *x* component one finds—due to the hermiticity of $\mathbf{r}$ and $\mathbf{p}$—e.g.:

$$\int d^3r\ \psi_1^*\ p_x x\ \psi_2 = \int d^3r\ (p_x\psi_1)^* x\ \psi_2 = \int d^3r\ (x\ p_x\psi_1)^*\psi_2 \neq \int d^3r\ (p_x x\psi_1)^*\psi_2, \tag{5.29}$$

because of (5.28). In analogy it is easy to prove that the form (5.27) is hermitian.

A practical example of the symmetrization performed in (5.27) is the transformation of

$$(\mathbf{A}\cdot\mathbf{p})_{kl} \tag{5.30}$$

into quantum theory as

$$\tfrac{1}{2}(\mathbf{A}\cdot\mathbf{p}+\mathbf{p}\cdot\mathbf{A}). \tag{5.31}$$

From (5.30) one obtains explicitly

$$\tfrac{1}{2}(\mathbf{A}\cdot\mathbf{p}+\mathbf{p}\cdot\mathbf{A}) = \mathbf{A}\cdot\mathbf{p}+\tfrac{1}{2}\nabla\cdot\mathbf{A} \neq \mathbf{A}\cdot\mathbf{p}. \tag{5.32}$$

The above statements have to be followed in the actual calculations with (4.19)!

Note: Even with the demand for hermiticity the quantization rule is not unique in all cases. We consider e.g. the classical quantity

$$(p_x x)^2_{kl}, \tag{5.33}$$

for which we can specify 2 hermitian operators:

$$\tfrac{1}{2}(p_x^2x^2+x^2p_x^2) \neq \tfrac{1}{4}(p_x x + x\ p_x)^2. \tag{5.34}$$

Such—formally possible—hermitian operators we will not encounter in practice and therefore discard a deeper investigation of these ambiguities.

5.3 Ehrenfest's Theorem; Conservation Laws

The investigations in Sect. 5.1 can now easily be generalized for the time evolution of the expectation value of any observable represented by a hermitian operator

$$F = F(\mathbf{r},\mathbf{p};t). \tag{5.35}$$

The following holds:

$$\frac{d}{dt} < F >= \int d^3r\left\{\left(\frac{\partial}{\partial t}\ \psi^*\right)F\ \psi + \psi^* F\left(\frac{\partial}{\partial t}\ \psi\right) + \psi^*\frac{\partial F}{\partial t}\ \psi\right\}$$

$$= -\tfrac{i}{\hbar} < [F,\ H] > + < \tfrac{\partial F}{\partial t} >. \tag{5.36}$$

If we compare (5.36) with (1.16) we find that for quantum mechanical expectation values the same relationships hold as for the corresponding classical observables when using the commutator [,] instead of the corresponding Poisson bracket $\{,\}$ (apart from the factor $-i/\hbar$).

For a time-independent observable *G*, according to (5.36), we get

$$\frac{d}{dt} < G >= 0 \qquad \rightarrow < G >= \text{const.} \tag{5.37}$$

if

$$[G, H] = 0. \tag{5.38}$$

In analogy to classical mechanics (cf. (1.19)) we call such an observable a **conserved quantity**.

The **Ehrenfest theorem** is the statement, that for the expectation values of operators the same equations of motion hold as for the classical observables, i.e. since—in case of small fluctuations—the quantum mechanical equations of motion merge to the classical equations of motion. To this aim we consider the temporal change in the expectation value of the momentum (5.14) and expand $< \nabla\ V(\mathbf{r}) >$ in $\mathbf{r}$ around the expectation value $< \mathbf{r} >$,

$$\frac{d}{dt} < \mathbf{p} >= - < \nabla V(\mathbf{r}) >= - < \sum_{n=0}^{\infty} \nabla_n \frac{1}{n!} [(\mathbf{r} - < \mathbf{r} >) \cdot \nabla]^n V(\mathbf{r})|_{\mathbf{r}=<\mathbf{r}>} >$$

$$= -\nabla V(< \mathbf{r} >) - \tfrac{1}{2} \nabla \left[\sigma_x^2 \tfrac{\partial^2}{\partial x^2} + \sigma_y^2 \tfrac{\partial^2}{\partial y^2} + \sigma_z^2 \tfrac{\partial^2}{\partial z^2} \right] V(\mathbf{r})|_{<\mathbf{r}>} - \cdots \tag{5.39}$$

with

$$\sigma_x^2 =< x^2 > - < x >^2 \; ; \; \sigma_y^2 =< y^2 > - < y >^2 \; ; \; \sigma_z^2 =< z^2 > - < z >^2. \tag{5.40}$$

In the case of vanishing fluctuations σ_i^2 in the local positions just the classical force $-\nabla V(< \mathbf{r} >)$ remains. On the other hand, for the harmonic oscillator (in any dimension) the 2nd partial derivative is a constant, such that the correction terms with the gradients always disappear. In this special case the classical equations of motion for the expectation values of the operators $< \mathbf{r} >$ and $< \mathbf{p} >$ also hold identically.

5.4 Algebra of Commutators

In the following we will present **calculation rules for commutators**, that arise directly from the definition and are used frequently: For any linear operators *A*, *B*, *C* we have

$$[A, B] = -[B, A]$$

$$[A, B + C] = [A, B] + [A, C]$$

$$[A, BC] = [A, B]C + B[A, C] \tag{5.41}$$

$$[A,[B,C]]+[B,[C,A]]+[C,[A,B]]=0.$$

Example: $[p_x^2,\ x]=p_x[p_x,\ x]+[p_x,\ x]p_x=2\hbar/i\ p_x$.

Note: The rules (5.41) also hold for the Poisson brackets (see classical mechanics). The identity of the algebras is a prerequisite for the compatibility of classical physics and quantum mechanics in the limit of large actions!

In summarizing this chapter we have introduced the rules to translate classical observables in phase-space representation to hermitian operators in Hilbert space. It has, furthermore, been proven that the classical equations of motion also hold for the expectation values of the corresponding quantum operator (Ehrenfest theorem). The formal translation of the Poisson brackets in classical mechanics to commutators in quantum physics has been derived and it was shown, that the commutators follow the same algebra as the Poisson brackets.

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6. Expectation Values and Fluctuations of Observables

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In this chapter we will investigate the connection between the possible expectation values of an observable *A* and its fluctuations in context with its commutator [*A*, *H*]. Furthermore, we will establish the relationship between momentum conservation and translational invariance as well as the conservation of angular momentum and rotational invariance in quantum theory. In addition we will introduce the 'spin' of electrons (or related fermions) and explore its properties with respect to rotations.

6.1 Expectation Values

In Chap. 4 (Eq. (4.5)) we have interpreted the expectation value (normalized according to (4.1))

$$< \mathbf{r} >= \int d^3r \ \psi^* \mathbf{r} \ \psi = (\psi, \mathbf{r}\psi) \tag{6.1}$$

as the average value for the position, that can be found for many measurements in the ensemble described by ψ. We have, furthermore, interpreted

$$|\psi(\mathbf{r};t)|^2 \equiv w(\mathbf{r};t) \tag{6.2}$$

as the probability density for a position measurement to find particles at position $\mathbf{r}$ at time *t*. Since *t* plays the role of a parameter we will suppress *t* in the following equations. We can also write Eq. (6.1) as

$$< \mathbf{r} >= \int d^3r \ w(\mathbf{r})\mathbf{r} \tag{6.3}$$

with

$$\int d^3r \ w(\mathbf{r}) = 1. \tag{6.4}$$

We now want to investigate the general case of an arbitrary observable.

First of all a short preliminary remark on the definition of **average**. For a series of *N* experiments for a certain quantity *X* with the values x_i measured with the probability (relative

probability) w_i, the average of the quantity X is defined by

$$< X >= \sum_{i=1}^{N} x_i w_i, \tag{6.5}$$

where

$$\sum_{i=1}^{N} w_i = 1. \tag{6.6}$$

If for X a continuum of values x is possible, then in (6.5) and (6.6) we have to replace the summation by an integration; this corresponds to the case of the quantity position $\mathbf{r}$ discussed above. Of course, a combination of both cases is also possible (continuous and discrete values of the quantity X).

Examples: Energy of a particle in a finite potential; energy spectra of the H atom (see Sect. 7.6).

Let's look at the point above for the expectation value of the momentum

$$< \mathbf{p} >= \int d^3r \ \psi^* \tfrac{\hbar}{i} \nabla \psi = (\psi, \mathbf{p}\psi). \tag{6.7}$$

This obviously doesn't have the desired form since ∇ is not a multiplicative operator. To regain the form of an average value here and in other cases we need to investigate the

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6.2 Hermitian Eigenvalue Problem of Operators

For the sake of simplicity, let's consider for now such hermitian operators $A(\mathbf{r}, \mathbf{p})$, whose eigenvalue problem

$$A(\mathbf{r}, \mathbf{p})\chi_n(\mathbf{r}) = a_n \chi_n(\mathbf{r}) \tag{6.8}$$

has only discrete, non-degenerate eigenvalues a_n $(n = 0, 1, 2, \ldots)$. In this case the solutions χ_n are square integrable (cf. various examples from Sect. 7.6) and without any limitation of generality we can assume,

$$\int d^3r \ |\chi_n(\mathbf{r})|^2 = 1. \tag{6.9}$$

For the interpretation of the expectation value of A in a state $\psi(\mathbf{r};t)$ as the average value in the sense of Eqs. (6.5) and (6.6) it is now essential, that the system of eigenfunctions χ_n of A is complete: every square-integrable function must have an expansion within the functions χ_n, in particular $\psi(\mathbf{r};t)$,

$$\Psi(\mathbf{r};t) = \sum_{n=0}^{\infty} c_n(t)\chi_n(\mathbf{r}). \tag{6.10}$$

The convergence of the series in (6.10) is to be understood as the **convergence on average** (see Chap. 9). Since the functions χ_n are orthogonal (see Sect. 4.3 (Eq. (4.30))) and normalized (6.9) we find for the expansion coefficients:

$$c_n(t) = \int d^3r \ \chi_n^*(\mathbf{r})\psi(\mathbf{r};t) = (\chi_n, \psi). \tag{6.11}$$

Example: The Hamilton operator of the one-dimensional harmonic oscillator has a discrete, non-degenerate, complete spectrum.

For an ensemble in the state $\psi(\mathbf{r};t)$ we get for the expectation value of the observable *A*:

$$< A >= \int d^3r \ \psi^* A \ \psi = \sum_{n=0}^{\infty} a_n |c_n(t)|^2 \tag{6.12}$$

with

$$1 = \int d^3r \ \psi^* \psi = \sum_{n=0}^{\infty} |c_n(t)|^2, \tag{6.13}$$

taking into account (6.8) and (6.10) as well as the orthogonality of the $\chi_n(\mathbf{r})$. Equations (6.12) and (6.13) now allow for the desired interpretation of $< A >$:

The possible values of the observable *A* of a particle in a measurement of the ensemble are the eigenvalues a_n. The probability (relative probability for many individual measurements), with which one of the values a_n is measured, is given by $|c_n(t)|^2$.

While in classical physics the measured values of an observable form a continuum—according to the considerations above—observables in quantum theory may have **discrete values** (the eigenvalues). This is in accordance with energy and quantization of orientation (see Chap. 2). Whether an observable is discrete and/or has continuous eigenvalues, must be checked in each concrete case by solving the eigenvalue Eq. (6.8).

We now consider the case where an observable *B* has a complete, discrete spectrum which, however, can still be degenerate; an example is the spectrum of the angular momentum (6.4). The eigenvalue problem for $B = B(\mathbf{r}, \mathbf{p})$ we then can write as

$$B \ \chi_{n,l}(\mathbf{r}) = b_n \chi_{n,l}(\mathbf{r}), \tag{6.14}$$

where $b_n \neq b_m$ for $n \neq m$; the index *l* numbers the degenerate solutions to the eigenvalue b_n. The solutions $\chi_{n,l}$ are chosen such that

$$\int d^3r \ \chi^*_{n,l} \ \chi_{n',l'} = \delta_{nn'} \delta_{ll'} \tag{6.15}$$

(the orthogonality with respect to *n* follows automatically from the hermiticity of *B*); the solutions, which are degenerate with respect to *n*, are orthogonalized according to Schmidt's method. Since the spectrum was assumed to be complete, we can expand ψ as

$$\psi(\mathbf{r};t) = \sum_{n,l} d_{nl}(t) \chi_{n,l}(\mathbf{r}) \tag{6.16}$$

with

$$d_{nl}(t) = \int d^3r \ \chi^*_{n,l}(\mathbf{r}) \psi(\mathbf{r};t) = (\chi_{n,l}, \psi). \tag{6.17}$$

In analogy to (6.12), (6.13) we find:

$$< B >= \int d^3r \ \psi^* B \ \psi = \sum_n \ b_n \ \sum_l |d_{nl}(t)|^2, \tag{6.18}$$

with

$$1 = \int d^3r \ \psi^* \psi = \sum_n \sum_l |d_{nl}(t)|^2. \tag{6.19}$$

The sum $\sum_l |d_{nl}(t)|^2$ is to be interpreted as the probability to encounter the eigenvalue b_n in a single measurement.

In the case of a continuous spectrum non-normalizable eigenfunctions occur; as an important example we will examine the particle momentum in Sect. 6.3. Finally, there is also the case of a partly discrete—partly continuous spectrum, e.g. the energy spectrum of the *H* atom.

6.2.1 Fluctuations of Observables

The **mean-square fluctuation**

$$(\Delta x)^2 :=< (x- < x >)^2 >=< x^2 > - < x >^2 \tag{6.20}$$

is a useful measure for the spreading of measured data, i.e. the deviation from the average. If we apply this to the measured values of an observable *A* we get the mean-square fluctuation of an observables *A* in the state $\psi(\mathbf{r};t)$:

$$(\Delta A)^2 = \int d^3r \ \psi^*(A - \int d^3r \ \psi^* A \ \psi)^2 \psi = \int d^3r \ \psi^* A^2 \psi - \left(\int d^3r \ \psi^* A \ \psi\right)^2 \geq 0 \tag{6.21}$$

$$= (\psi, A^2\psi) - (\psi, A\psi)^2.$$

Of particular interest is the case

$$\Delta A = 0, \tag{6.22}$$

i.e. for each individual measurement on a particles of the ensemble we get a well-defined value with the probability 1 (**sharp value**). We are now investigating, when this is the case, i.e. when

$$(\psi, A^2\psi) = \int d^3r \ \psi^* A^2 \psi = \left(\int d^3r \ \psi^* A \ \psi\right)^2 = (\psi, A\psi)^2. \tag{6.23}$$

Equation (6.23) is written more compactly as

$$(\psi, A^2\psi) = (A\psi, A\psi) = (\psi, A\psi)^2, \tag{6.24}$$

where A is assumed to be hermitian. With the definition

$$\bar{\psi} \equiv A\psi \tag{6.25}$$

we find alternatively

$$(\psi, \bar{\psi})^2 = (\bar{\psi}, \bar{\psi}) = (\bar{\psi}, \bar{\psi})(\psi, \psi) \tag{6.26}$$

as the case of **Schwarz's inequality for scalar products** (Chap. 9), in which this reduces to an equation. This only occurs if

$$A\psi = a\psi, \tag{6.27}$$

i.e. $\bar{\psi}$ is proportional to ψ.

Result: The observable A has a well-defined value with probability 1 only if the state function ψ is also an eigenfunction of the operator A; the measured value then is a corresponding eigenvalue of A. We get the same result by inserting (6.10) in (6.21). The demand (6.22) then is:

$$(\Delta A)^2 = \sum_{n=0}^{\infty} \left\{ a_n - \sum_{m=0}^{\infty} a_m |c_m(t)|^2 \right\}^2 |c_n(t)|^2 = 0. \tag{6.28}$$

Equation (6.28) is fulfilled if and only if

$$|c_m(t)| = 1 \tag{6.29}$$

for $m = k$ (fixed) and = 0 otherwise, such that ψ at time t of the measurement must have the form:

$$\Psi(\mathbf{r};t) = c_k(t)\chi_k(\mathbf{r}) \tag{6.30}$$

for arbitrary but fixed k.

As the expectation value $< A >$ also ΔA in general is time-dependent, such that the spreading of the measured values is not constant in time.

Only if A is a conserved quantity, $[H, A] = 0$, apart from $< A >$ also the probabilities $|c_n(t)|^2$ and thus also ΔA remain constant.

Proof If $[H, A] = 0$, we have

$$A\chi_n = a_n\chi_n, \tag{6.31}$$

thus also $H\chi_n$ is eigenfunction of A with eigenvalue a_n,

$$H\ A\chi_n = A\ H\chi_n = a_n H\chi_n. \tag{6.32}$$

If there is no degeneracy, $H\chi_n$ must—up to a numerical factor—match χ_n,

$$H\chi_n = E_n\chi_n;\ E_n \text{ real.} \tag{6.33}$$

Then we get from (6.11):

$$\frac{d}{dt}\ c_n(t) = \int d^3r\ \chi_n^* \frac{\partial}{\partial t}\ \psi = -\frac{i}{\hbar}\int d^3r\ \chi_n^* H\psi = -\frac{i}{\hbar}\int d^3r\ (H\chi_n)^*\psi$$

$$= -\tfrac{i}{\hbar}E_n c_n(t) \tag{6.34}$$

with the solution

$$c_n(t) = c_n(0)\ \exp\left\{-\tfrac{i}{\hbar}E_n t\right\}. \tag{6.35}$$

Thus

$$|c_n(t)|^2 = |c_n(0)|^2 \tag{6.36}$$

is time-independent and therefore also ΔA. For an observable *B* with a degenerate, discrete spectrum (cf. (6.14)), one can prove in analogy that

$$\tfrac{d}{dt}\sum_k |d_{nk}(t)|^2 = 0 \tag{6.37}$$

for the case of $[H, B] = 0$.

We thus have obtained the general result, that for a conserved quantity in addition to the expectation value also the relative probabilities and the fluctuations of the measured values are constant in time.

6.2.2 Commuting Operators

We show that two observables—represented by operators *A*, *B*—can be measured simultaneously sharp, if $[A, B] = 0$, and vice versa. We make the (simplifying) assumption that *A* and *B* have purely discrete spectra. To this aim we prove that

(1) commuting (hermitian) operators have a common **system of eigenfunctions**, i.e. not just individual eigenfunctions like l^2 and l_z for $l = 0$ (see below). If χ_n are eigenfunction of *A* to the eigenvalue a_n,

$$A\chi_n = a_n\chi_n, \tag{6.38}$$

then due to $[A, B] = 0$:

$$AB\chi_n = B\ A\chi_n = a_n B\chi_n, \tag{6.39}$$

such that $B\chi_n$ is also eigenfunction of *A* with eigenvalue a_n. If now a_n is not degenerate, then $B\chi_n$ must be proportional to χ_n, such that

$$B\chi_n = b_n\chi_n. \tag{6.40}$$

If a_n is *f*-fold degenerate,

$$A\chi_{nk} = a_n\chi_{nk}; \qquad k = 1, \ldots, f, \tag{6.41}$$

only follows due to (6.39)

$$B\chi_{nk} = \sum_{l=1}^{f} \alpha_{kl}\chi_{nl}. \tag{6.42}$$

But now we can always diagolnalize the hermitian *f*-dimensional matrix

$$(\chi_{nk}, B\chi_{nk'}) = B^n_{kk'} \equiv \int d^3r\ \chi^*_{nk} B\ \chi_{nk'} = (B^n_{kk'})^* \tag{6.43}$$

by a linear transformation of the χ_{nk}. The resulting linear combinations of the χ_{nk} then are simultaneous eigenfunctions of *A* and *B*; q.e.d.

(2) Conversely, if *A* and *B* have a common system of eigenfunctions,

$$A\chi_n = a_n\chi_n; \quad B\chi_n = b_n\chi_n, \tag{6.44}$$

we can commute *A* and *B*. We prove the statement by considering

$$B\ A\chi_n = b_n a_n \chi_n \quad \text{and} \quad \mathrm{AB\chi_n = a_n b_n \chi_n}; \tag{6.45}$$

for the difference follows:

$$(BA - AB)\chi_n = 0. \tag{6.46}$$

Since the χ_n form a complete system (otherwise one could not interpret *A*, *B* as observables), the **operator relation** follows:

$$[B, A] = 0. \tag{6.47}$$

6.2.3 Summary

(1) An operator *A*—representing an observable—must be hermitian and have a complete spectrum of eigenfunctions in the Hilbert space $\mathscr{H}$.

(2) Measured values of the observable *A* are the real eigenvalues a_n; they can be discrete and/or continuous.

(3) The probability of measuring a value a_n is given by the square of the expansion coefficient of ψ with respect to the eigenfunction χ_n belonging to a_n, if a_n is not degenerate; otherwise one has to sum over the contributions from the degenerate eigenfunctions.

(4) The fluctuation of the measured values is determined by the mean-square deviations: $(\Delta A)^2 = < A^2 > - < A >^2$.

(5) The expectation value $< A >$, ΔA and the probabilities are exactly constant in time if $[A, H] = 0$..

(6) Two observables can be measured simultaneously **sharp**, if and only if they commute.

To (4) $\Delta A = 0$ if and only if the wave function $\psi(\mathbf{r};t)$ at time t—of the start of the measurement—is an eigenfunction of A.

6.3 Momentum

6.3.1 Hermiticity

For the x component of the momentum (by partial integration) the following holds:

$$\int dxdydz\ \psi_1^*\left(\frac{\hbar}{i}\ \frac{\partial}{\partial x}\ \psi_2\right) = \int dxdydz\ \left(\frac{\hbar}{i}\ \frac{\partial}{\partial x}\ \psi_1\right)^*\psi_2$$

$$+\frac{\hbar}{i}\ \int dy\ dz\ \left(|\psi_1^*\psi_2|_{x=-\infty}^{x=+\infty}\right). \tag{6.48}$$

If the functions ψ_1, ψ_2 vanish at infinity, the integrated term in (6.48) vanishes and we get:

$$\int d^3r\ \psi_1^*\left(\tfrac{\hbar}{i}\ \tfrac{\partial}{\partial x}\ \psi_2\right) = \int d^3r\left(\tfrac{\hbar}{i}\ \tfrac{\partial}{\partial x}\ \psi_1\right)^*\psi_2. \tag{6.49}$$

The operator $\mathbf{p}$ is thus hermitian in the space of functions ψ, which together with their partial derivatives are square-integrable.

In analogy to $\mathbf{p}$ the kinetic energy operator

$$T \equiv -\tfrac{\hbar^2}{2\,m}\Delta = \tfrac{p^2}{2\,m} \tag{6.50}$$

is hermitian in the space of the functions ψ, which, together with their 1st and 2nd partial derivatives, are square integrable. We have seen in Chap. 4 that this property of T (generally: H, cf. Chap. 7) is necessary for the probability interpretation of $\psi^*\psi$.

6.3.2 Translation

We consider an infinitesimal translation in space ($\epsilon \ll 1$)

$$\mathbf{r} \to \mathbf{r} - \epsilon\mathbf{a}; \tag{6.51}$$

the connection between $\psi(\mathbf{r};t)$ and $\psi(\mathbf{r} - \epsilon\mathbf{a};t)$ in the Hilbert space we get by Taylor expansion

$$\psi(\mathbf{r} - \epsilon\mathbf{a};t) = \psi(\mathbf{r};t) - \epsilon\mathbf{a}\cdot\nabla\psi(\mathbf{r};t)\cdots \approx (1 - \epsilon\mathbf{a}\cdot\nabla)\psi(\mathbf{r};t). \tag{6.52}$$

For a **finite** translation in **a** the higher terms of the Taylor expansion must be taken into account:

$$\psi(\mathbf{r}-\mathbf{a};t)=\sum_{n=0}^{\infty}\frac{1}{n!}(-\mathbf{a}\cdot\nabla)^n\psi(\mathbf{r};t)=\exp\{-\mathbf{a}\cdot\nabla\}\psi(\mathbf{r};t)$$

$$=\exp\left(-\tfrac{i}{\hbar}\mathbf{a}\cdot\mathbf{p}\right)\psi(\mathbf{r};t)=\psi'(\mathbf{r};t). \tag{6.53}$$

The operator $\exp(-i/\hbar\ \mathbf{a}\cdot\mathbf{p})$ therefore represents a **translation** in the space of wave functions ψ, i.e. the Hilbert space $\mathscr{H}$. The **generators** of such a translation in $\mathscr{H}$ are the components of the momentum $\mathbf{p}$.

The operators

$$\tau(\mathbf{a})=\exp\left(-\tfrac{i}{\hbar}\mathbf{a}\cdot\mathbf{p}\right) \tag{6.54}$$

form an **abelian group** (like the translations (6.51)) since the components of $\mathbf{p}$ commute with each other and the group properties hold:

(1) With $\tau(\mathbf{a}_1)$ and $\tau(\mathbf{a}_2)$ then also $\tau(\mathbf{a}_1)\tau(\mathbf{a}_2)=\tau(\mathbf{a}_1+\mathbf{a}_2)$ is a translation operator.

(2) Associativity: $\tau(\mathbf{a}_1)[\tau(\mathbf{a}_2)\tau(\mathbf{a}_3)]=[\tau(\mathbf{a}_1)\tau(\mathbf{a}_2)]\tau(\mathbf{a}_3)$

(3) The identity is $\tau(0)=1$

(4) For every operator $\tau(\mathbf{a})$ there is an inverse $\tau(-\mathbf{a})$ since $\tau(\mathbf{a})\tau(-\mathbf{a})=1$.

The proofs follow directly from (6.53).

We call a physical system **translation invariant** if

$$[\tau(\mathbf{a}),H]=0. \tag{6.55}$$

Thus if ψ is a solution of the Schrödinger equation

$$i\hbar\tfrac{\partial}{\partial t}\ \psi=H\psi, \tag{6.56}$$

also $\tau(\mathbf{a})\psi$ is a solution of the Schrödinger equation because of

$$i\hbar\tfrac{\partial}{\partial t}(\tau(\mathbf{a})\psi)=\tau(\mathbf{a})H\psi=H(\tau(\mathbf{a})\psi). \tag{6.57}$$

Equation (6.55) is satisfied if and only if

$$[H, \mathbf{p}] = 0. \tag{6.58}$$

If $[T, \mathbf{p}] = 0$, (6.58) is only possible for a single particle if *V* is constant in space. Conversely: If a particle moves in a space-dependent potential $V = V(\mathbf{r})$, then the translation invariance is destroyed. For several particles, translation invariance (as will be discussed later) implies that the interaction *V* between the particles only depends on the relative distance of the particles:

$$V = V(\mathbf{r}_{ik}); \quad \mathbf{r}_{ik} = \mathbf{r}_i - \mathbf{r}_k \tag{6.59}$$

for any two particles *i*, *k* of the system.

6.3.3 Eigenvalue Problem

The momentum has a **continuous eigenvalue spectrum**; the eigenfunctions are plane waves

$$\mathbf{p} \ \exp{(i\mathbf{k}\cdot\mathbf{r})} = \hbar\mathbf{k} \ \exp{(i\mathbf{k}\cdot\mathbf{r})} \tag{6.60}$$

with $\hbar\mathbf{k}$ as the eigenvalue. They are also eigenfunctions to *T*,

$$T \ \exp{(i\mathbf{k}\cdot\mathbf{r})} = \tfrac{\hbar^2 k^2}{2\,m} \exp{(i\mathbf{k}\cdot\mathbf{r})}, \tag{6.61}$$

and thus form a simultaneous system of eigenfunctions of the commuting operators *T* and $\mathbf{p}$.

The orthogonality relation reads

$$\int d^3r \ \exp{(i\mathbf{k}\cdot\mathbf{r})}^* \exp{(i\mathbf{k}'\cdot\mathbf{r})} = \int d^3r \ \exp{(i[\mathbf{k}'-\mathbf{k}]\cdot\mathbf{r})} = 0 \ \text{ for } \ \mathbf{k} \neq \mathbf{k}', \tag{6.62}$$

but for $\mathbf{k} = \mathbf{k}'$ the integral (6.62) diverges; the eigenfunctions to the operator $\mathbf{p}$ thus are not square-integrable and therefore cannot be considered as wave functions of the free particle in the strict sense, but useful because they provide a 'dense' or 'complete' basis in $\mathscr{H}$ (see Chap. 9).

6.3.4 Momentum Representation

We now want to show that the interpretation of the expectation value $< \mathbf{p} >$ is possible as a statistical average, although the spectrum of $\mathbf{p}$ is continuous and the eigenfunctions cannot be normalized. The decisive point is that the plane waves form a **complete basis** in $\mathscr{H}$. For the quantitative formulation of this fact we limit ourselves to a single dimension (*x*). The completeness of the basis of the plane waves then states that every square-integrable function $\psi(x;t)$ can be represented as

$$\psi(x;t) = \lim_{a\to\infty} \int_{-a}^{a} \tfrac{1}{\sqrt{2\pi}} \exp{(ikx)} \tilde{\psi}(k;t) \ dk. \tag{6.63}$$

Equation (6.63) is—in analogy to (6.10)—to be understood in the sense of mean-square convergence (not point-like). The **Fourier transform** $\tilde{\psi}(k;t)$ can be calculated from $\psi(x;t)$,

$$\tilde{\psi}(k;t) = \lim_{b\to\infty} \tfrac{1}{\sqrt{2\pi}} \int_{-b}^{b} \exp{(-ikx)} \psi(x;t) \ dx, \tag{6.64}$$

and is itself square-integrable. In the Fourier transformation—defined in the context of (6.63) and (6.64)—the normalization is preserved which, however, is the underlying requirement for the Fourier transform (6.64) to preserve the probability interpretation of $\psi^*\psi$, *i.e.*. $(\psi,\psi)=(\tilde{\psi},\tilde{\psi})$:

$$\int_{-\infty}^{\infty} dx\ |\psi(x;t)|^2 = \int_{-\infty}^{\infty} dk\ |\tilde{\psi}(k;t)|^2. \tag{6.65}$$

To explain (6.65) we consider

$$\lim_{a\to\infty}\lim_{b\to\infty}\ (2\pi)^{-1}\int_{-\infty}^{\infty} dx \int_{-a}^{a} dk' \int_{-b}^{b} dk\ \ \exp\ (i(k-k')x)\ \ \tilde{\psi}^*(k';t)\tilde{\psi}(k;t). \tag{6.66}$$

For $k\neq k'$ we do not get any contributions to the $\int dx$ because of (6.62). We express this fact using the δ- distribution,

$$\delta(k-k') = \tfrac{1}{2\pi}\int_{-\infty}^{\infty} dx\ \ \exp\ \{i(k-k')x\}, \tag{6.67}$$

then:

$$\int_{-\infty}^{\infty} dx\ |\psi(x;t)|^2 = \lim_{a\to\infty}\lim_{b\to\infty}\int_{-a}^{a} dk' \int_{-b}^{b} dk\ \delta(k-k')\tilde{\psi}^*(k';t)\tilde{\psi}(k;t)$$

$$= \int_{-\infty}^{\infty} dk\ \tilde{\psi}^*(k;t)\tilde{\psi}(k;t) = 1. \tag{6.68}$$

If the derivative $\partial/\partial x\ \ \psi$ exists and is itself square-integrable—this is the case for all solutions of the Schrödinger equation, since the operator of the kinetic energy *T* is always contained in *H* —then holds,

$$p_x\psi(x;t) = \lim_{a\to\infty}\ \tfrac{1}{\sqrt{2\pi}}\int_{-a}^{a} dk\ \hbar\ k\ \tilde{\psi}(k;t)\ \exp\ (ikx), \tag{6.69}$$

and $k\tilde{\psi}(k;t)$ is also square integrable. This implies—in analogy to (6.68):

$$< p_x > = \lim_{a\to\infty}\lim_{b\to\infty}\int_{-a}^{a} dk' \int_{-b}^{b} dk\ \delta(k-k')\ \ \tilde{\psi}^*(k';t)\ \hbar\ k\ \tilde{\psi}(k;t)$$

$$= \int_{-\infty}^{\infty} dk\ \ \tilde{\psi}^*(k;t)\ \ \hbar k\ \ \tilde{\psi}(k;t). \tag{6.70}$$

The generalization of (6.63)–(6.70) to the 3-dim. case is trivial.
In view of the statistical interpretation of quantum theory we consider

$$< \mathbf{p} >= \int d^3k \ \hbar\mathbf{k} \ \tilde{\psi}^*(\mathbf{k};t)\tilde{\psi}(\mathbf{k};t) \tag{6.71}$$

with

$$1 = \int d^3k \ \tilde{\psi}^*(\mathbf{k};\mathbf{t})\tilde{\psi}(\mathbf{k};t). \tag{6.72}$$

If one interprets $\tilde{\psi}^*(\mathbf{k};t)\tilde{\psi}(\mathbf{k};t)$ as the **probability density** to encounter the considered particle of the ensemble at time *t* with the momentum $\hbar\mathbf{k}$, then $< \mathbf{p} >$ can also be interpreted as an average in the statistical sense.

6.3.5 Periodic Boundary Conditions

If we want to avoid the use of the δ-function in practice, we can instead of the entire 3-dim. space consider a sufficiently large (but finite) normalization volume. To simplify the notation, let's consider again only a single dimension (x). In order to keep p_x hermitian in the finite interval $[-b/2, b/2]$, the wave functions $\psi(x;t)$ must fulfill certain boundary conditions. According to (6.48) the hermiticity of p_x (due to partial integration) requires

$$\psi_1^*\psi_2\Big|_{-b/2}^{b/2} = 0, \tag{6.73}$$

such that

$$\frac{\psi_1^*(b/2)}{\psi_1^*(-b/2)} = \frac{\psi_2(-b/2)}{\psi_2(b/2)} \tag{6.74}$$

for any square-integrable functions ψ_1, ψ_2 in $[-b/2, b/2]$. Equation (6.74) leads to the periodic boundary conditions (except for a phase factor)

$$\psi(b/2) = \psi(-b/2) \tag{6.75}$$

for the functions permitted. The eigenfunctions of p_x can now be normalized

$$u_n = \frac{1}{\sqrt{b}} \ \exp\ (ik_n x) \tag{6.76}$$

with

$$k_n = 2\pi \ \frac{n}{b}; \quad n = 0, \pm1, \pm2, \pm3, \ldots \tag{6.77}$$

and the eigenvalues of p_x are discrete: $\hbar k_n$.

Any function, that is square-integrable in $[-b/2, b/2]$, then can be represented as a Fourier series

$$\psi(x;t) = \sum_{n=-\infty}^{\infty} c_n(t)u_n(x) \tag{6.78}$$

with

$$c_n(t) = \frac{1}{\sqrt{b}} \int_{-b/2}^{b/2} dx \;\; \psi(x;t) \, \exp\,(-ik_n x). \tag{6.79}$$

6.3.6 Uncertainty Relation

Since *x* and p_x do not commute

$$[p_x, x] = \frac{\hbar}{i}, \tag{6.80}$$

they cannot be measured sharp at the same time, so it's safe to expect

$$\Delta p_x \neq 0, \tag{6.81}$$

if $\Delta x = 0$ and $\Delta x \neq 0$ if $\Delta p_x = 0$.

We will show below that always holds

$$\boxed{\Delta p_x \Delta x \geq \frac{\hbar}{2}.} \tag{6.82}$$

To this aim we consider the function

$$f(\alpha) = \int d^3r \;\; |(x - < x >)\psi + i\alpha(p_x - < p_x >)\psi|^2 \geq 0, \tag{6.83}$$

which can be written explicitly as:

$$f(\alpha) = \int d^3r \;\; \psi^*(x - < x >)^2\psi + \alpha^2 \int d^3r \;\; ([p_x - < p_x >]\psi)^*(p_x - < p_x >)\psi$$

$$+i\alpha \;\; \int d^3r\{\psi^*(x - < x >)(p_x - < p_x >)\psi - ([p_x - < p_x >]\psi)^*(x - < x >)\psi\}. \tag{6.84}$$

The first term in (6.84) is $(\Delta x)^2$; the second results in $(\Delta p_x)^2$ using that p_x is hermitean; in the linear term in α we can (with the help of (6.80)) transform the 2nd part:

$$\int d^3r([p_x - < p_x >]\psi)^*(x - < x >)\psi = \int d^3r \;\; \psi^*(p_x - < p_x >)(x - < x >)\psi$$

$$= \int d^3r \;\; \psi^*(x - < x >)(p_x - < p_x >)\psi + \frac{\hbar}{i} \;\; \int d^3r \;\; \psi^*\psi, \tag{6.85}$$

such that (if ψ is normalized) this term contributes to $f(\alpha)$ by $-\alpha\hbar$. In total we get

$$f(\alpha) = (\Delta x)^2 + \alpha^2(\Delta p_x)^2 - \alpha\hbar \geq 0. \tag{6.86}$$

Since $f(\alpha)$ is positive semidefinite (by construction), $f(\alpha)$ can have at most a single real zero. This implies that for the discriminant must hold:

(6.87)

$$4(\Delta p_x)^2(\Delta x)^2 - \hbar^2 \geq 0,$$

thus

$$\Delta x \;\; \Delta p_x \geq \tfrac{\hbar}{2}. \tag{6.88}$$

For a plane wave $\Delta p_x = 0$, such that according to (6.82) $\Delta x = \infty$: the location of the particle is completely undetermined! The equal sign in (6.82) appears for the case of a Gaussian wave packet, which is briefly sketched below.

At time $t = 0$ let

$$\psi(x;0) = \tfrac{1}{\sqrt{b}} \;\; \tfrac{1}{\sqrt[4]{\pi}} \; \exp\left\{-\tfrac{x^2}{2b^2} + ik_0 x\right\}; \tag{6.89}$$

the associated Fourier transform is

$$\tilde{\psi}(k;0) = \;\; \tfrac{\sqrt{b}}{\sqrt[4]{\pi}} \; \exp\left\{-\tfrac{1}{2}(k-k_0)^2 b^2\right\}. \tag{6.90}$$

Since for a free particle $[H, p] = 0$, $H = T$, the expectation value of the momentum and its mean square fluctuation are constant in time. With (6.90) we obtain (after performing the k integration) using

$$I_0 = \int_{-\infty}^{\infty} \exp\left(-\alpha x^2\right) \, dx = \sqrt{\frac{\pi}{\alpha}};$$

$$\tfrac{d^n}{d\alpha^n} I_0 = (-1)^n \textstyle\int_{-\infty}^{\infty} x^{2n} \exp\left(-\alpha x^2\right) \, dx \tag{6.91}$$

$$< p_x >= \hbar k_0; \quad \Delta p_x = \tfrac{\hbar}{b\sqrt{2}} \tag{6.92}$$

for all times t. On the other hand $< x >$ and Δx change in time. To see this we transform the Schrödinger equation of the free particle to the **momentum representation**

$$i\hbar \tfrac{\partial}{\partial t} \tilde{\psi}(k;t) = \tfrac{\hbar^2 k^2}{2\,m} \tilde{\psi}(k;t); \tag{6.93}$$

Equation (6.93) can be integrated with the initial condition (6.90):

$$\tilde{\psi}(k;t) = \exp\left(-\tfrac{i\hbar k^2 t}{2\,m}\right) \tilde{\psi}(k;0). \tag{6.94}$$

The back transformation into the **position representation** results in:

$$\psi(x;t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \tilde{\psi}(k;t) \exp{(ikx)} dk$$

$$= \frac{1}{\sqrt[4]{\pi}} \frac{1}{\sqrt{b + \frac{i\hbar t}{mb}}} \exp\left\{ \frac{2ib^2 k_0 x - x^2 - \frac{i\hbar t k_0^2 b^2}{m}}{2b^2(1 + \frac{i\hbar t}{mb^2})} \right\} \tag{6.95}$$

or

$$|\psi(x;t)|^2 = \frac{1}{b(t)} \frac{1}{\sqrt{\pi}} \exp\left\{ -\frac{(x - v_0 t)^2}{b(t)^2} \right\} \tag{6.96}$$

with

$$b(t)^2 = b^2 + \left[\frac{\hbar t}{mb} \right]^2 \text{ and } \mathrm{v}_0 = \frac{\hbar \mathrm{k}_0}{\mathrm{m}}. \tag{6.97}$$

With (6.96) we get

$$< x >= v_0 t; \Delta x = \frac{b(t)}{\sqrt{2}}. \tag{6.98}$$

Equations (6.92) and (6.98) show that for $t = 0$

$$\Delta x \ \Delta p_x = \frac{\hbar}{2}, \tag{6.99}$$

however, for $t \neq 0$ the product $\Delta x \ \Delta p_x > \hbar/2$ since the uncertainty in position grows while the uncertainty in momentum remains constant. This

6.3.7 Disintegration of Wave Packets

is not limited to the Gaussian form (6.89), but holds in general. For a force-free particle we always have $(H = T)$:

$$\frac{d}{dt} < p_x >= \frac{i}{\hbar} < [H, p_x] >= 0, \tag{6.100}$$

such that

$$\frac{d}{dt} < x >= \frac{<p_x>}{m} = \text{const.} \tag{6.101}$$

We can therefore always choose the coordinate system in a way that

$$< x >= 0; < p_x >= 0. \tag{6.102}$$

Then according to (5.36):

$$\frac{d}{dt}(\Delta x)^2 = \frac{d}{dt} < x^2 >= \frac{i}{\hbar} < [T, x^2] > \tag{6.103}$$

and

$$\frac{d^2}{dt^2}(\Delta x)^2 = \frac{i}{\hbar}\frac{d}{dt} < [T, x^2] >= -\frac{1}{\hbar^2} < [T, [T, x^2]] >. \tag{6.104}$$

Since $T = p^2/(2m)$ we need:

$$[p_x^2, x^2] = x[p_x^2, x] + [p_x^2, x]x = \frac{2\hbar}{i}(xp_x + p_x x) \tag{6.105}$$

and

$$[p_x^2, [p_x^2, x^2]] = \frac{2\hbar}{i}[p_x^2, xp_x + p_x x] = \frac{2\hbar}{i}([p_x^2, x]p_x + p_x[p_x^2, x])$$

$$= \frac{2\hbar}{i}\{p_x[p_x, x]p_x + [p_x, x]p_x^2 + p_x^2[p_x, x] + p_x[p_x, x]p_x\} = -8\hbar^2 p_x^2. \tag{6.106}$$

This results in (6.104)

$$\frac{d^2}{dt^2}(\Delta x)^2 = \frac{2}{m^2} < p_x^2 >= \text{const} \ > 0, \tag{6.107}$$

such that $(\Delta x)^2$ grows quadratically with *t*, i.e. **every wave packet disperses in time**.

6.3.8 Reduction of Degrees of Freedom

In classical physics we can reduce the number of degrees of freedom of a system with the help of constraints. For example, if a particle is supposed to move on the surface of a sphere, we can reduce the equations of motion in 3 dimensions with the additional condition

$$r_{kl.} = \text{const}; (p_r)_{kl.} = 0 \tag{6.108}$$

to a 2-dimensional problem in the degrees of freedom ϑ, φ. **Due to the uncertainty relation for position and momentum or generally for canonically conjugate variables this freezing of degrees of freedom in quantum mechanics in general is not possible!** An important example is the **spontaneous emission** of photons, which results precisely from the fact, that the degrees of freedom of the radiation field in quantum theory cannot be frozen.

6.4 The Orbital Angular Momentum

6.4.1 Hermiticity

The angular momentum operator

$$\mathbf{l} = \mathbf{r} \ \times \ \mathbf{p} \tag{6.109}$$

does not require any symmetrization in the sense of (5.27), since for every component l_i the relevant components of $\mathbf{r}$ and $\mathbf{p}$ commute, e.g.

$$l_z = xp_y - yp_x = p_y x - p_x y. \tag{6.110}$$

The space of functions in which $\mathbf{l}$ is hermitian can be either specified with respect to cartesian coordinates or with respect to polar coordinates (see Sect. 6.4.4).

6.4.2 Rotations

In analogy to Sect. 6.3.2 we consider an infinitesimal rotation, e.g. around the z axis:

$$(x, y, z) \to (x + \epsilon y, -\epsilon x + y, z). \tag{6.111}$$

A Taylor expansion of $\psi(x + \epsilon y, -\epsilon x + y, z;t)$ around (x, y, z) then gives:

$$\psi(x + \epsilon y, -\epsilon x + y, z;t) = \psi(x, y, z;t) - \epsilon\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\psi = \left(1 - \frac{i\epsilon}{\hbar}l_z\right)\psi(x, y, z;t). \tag{6.112}$$

For a finite rotation φ around the z axis we have (as in Sect. 6.3.2)

$$\psi(R_\varphi \mathbf{r};t) = \sum_{n=0}^{\infty} \frac{1}{n!}\left\{-\frac{i}{\hbar}\varphi l_z\right\}^n \psi(\mathbf{r};t) = \exp\left\{-\frac{i}{\hbar}\varphi l_z\right\}\psi(\mathbf{r};t). \tag{6.113}$$

When rotating about an arbitrary axis by $\overrightarrow{\varphi}$, the generalization of (6.113) reads:

$$\psi_\varphi(\mathbf{r};t) = \exp\left\{-\frac{i}{\hbar}\overrightarrow{\varphi}\cdot\mathbf{l}\right\}\psi(\mathbf{r};t). \tag{6.114}$$

The operators

$$\hat{R}(\overrightarrow{\varphi}) = \exp\left(-\frac{i}{\hbar}\overrightarrow{\varphi}\cdot\mathbf{l}\right), \tag{6.115}$$

which represent rotations in the space of the wave functions ψ (like the translations), form a group which, however (unlike the translations), is **not abelian**: finite rotations about different axes are generally not interchangeable in their order. Since the components of $\mathbf{l}$ are the **generators** of the rotations, this implies

$$[l_i, l_j] \neq 0 \quad \text{for} \quad \mathrm{i} \neq \mathrm{j}. \tag{6.116}$$

We call a physical system **rotationally invariant** if

$$[\hat{R}(\overrightarrow{\varphi}), H] = 0. \tag{6.117}$$

If ψ is a solution of the Schrödinger equation,

(6.118)

$$i\hbar\frac{\partial}{\partial t}\ \psi = H\psi,$$

then also $\hat{R}(\overrightarrow{\varphi})\psi$:

$$i\hbar\frac{\partial}{\partial t}(\hat{R}(\overrightarrow{\varphi})\psi) = \hat{R}(\overrightarrow{\varphi})H\psi = H(\hat{R}(\overrightarrow{\varphi})\psi). \tag{6.119}$$

Equation (6.117) is fulfilled if and only if

$$[\mathbf{l}, H] = 0. \tag{6.120}$$

Since p^2 is a scalar, p^2 commutes with $\hat{R}(\overrightarrow{\varphi})$, thus also

$$[T, \mathbf{l}] = 0. \tag{6.121}$$

Furthermore, $|\mathbf{r}|$ (for several particles $|\mathbf{r}_{ij}|$) is a scalar, such that

$$[V, \mathbf{l}] = 0, \tag{6.122}$$

if

$$V = V(|\mathbf{r}|) \text{ or } V = V(|\mathbf{r}_{ij}|). \tag{6.123}$$

6.4.3 Active and Passive Transformations

When describing spatial transformations (rotations, translations) the following perspectives are equivalent:

(1) A rotation (translation) of the physical system (**active transformation**), i.e. a rigid rotation (translation) of the wave function ψ **in the Hilbert space** $\mathscr{H}$.

(2) equivalent to (1) is (see Fig. 6.1) a (**passive**) inverse coordinate transformation (rotation, translation), i.e. a transformation of the coordinate system of an observer (passive transformation) in **3-dimensional space**.

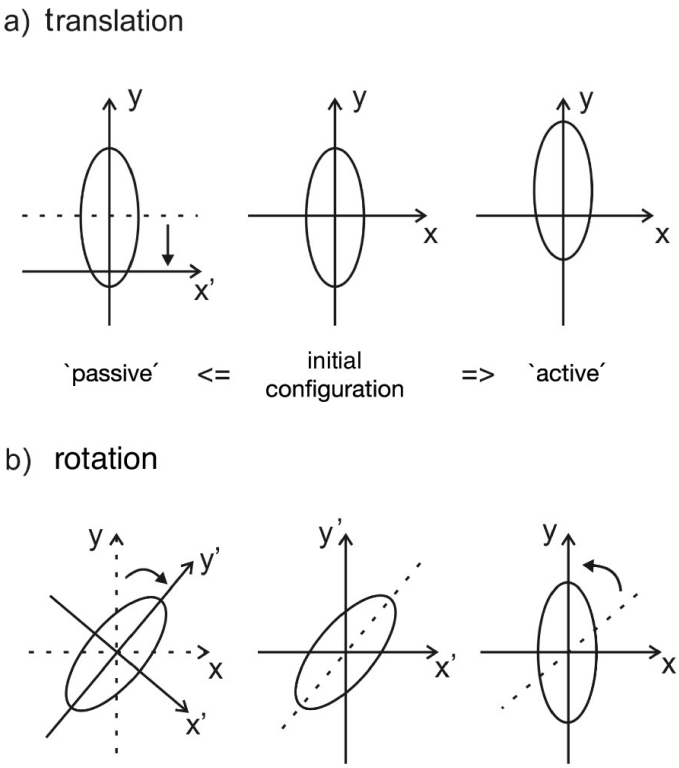

Fig. 6.1 Illustration of 'passive' and 'active' transformations

For a scalar wave function ψ, which assigns a complex number to every point in space, due to the equivalence of the perspectives (1) and (2) then holds

$$\psi(s^{-1}\mathbf{r};t) = S\psi(\mathbf{r};t) = \psi'(\mathbf{r};t); \tag{6.124}$$

where *s* stands for a rotation (translation) of the coordinate system in 3-dimensional space, the operator *S* for the corresponding transformation of the wave function ψ in the Hilbert space $\mathscr{H}$.

For a vector field—e.g. the vector potential $\mathbf{A}(\mathbf{r};t)$—the situation is a little more complicated than in (6.124), since the components of **A** (as a vector) also change when performing a rotation. In this case we get:

$$s\mathbf{A}(s^{-1}\mathbf{r};t) = S\mathbf{A}(\mathbf{r};t) = \mathbf{A}'(\mathbf{r};t). \tag{6.125}$$

To find the explicit form of the operator *S*, an infinitesimal transformation, e.g. around the *z* axis, is sufficient. Then we get

$$A'_x(\mathbf{r};t) = A_x(\overrightarrow{\rho};t) - \epsilon A_y(\overrightarrow{\rho};t)$$

$$A'_y(\mathbf{r};t) = \epsilon A_x(\overrightarrow{\rho};t) + A_y(\overrightarrow{\rho};t)$$

$$A'_z(\mathbf{r};t) = A_z(\overrightarrow{\rho};t) \tag{6.126}$$

with

$$\overrightarrow{\rho} \equiv s^{-1}\mathbf{r} = (x + \epsilon y, -\epsilon x + y, z). \tag{6.127}$$

We carry out the Taylor expansion of $A_i(\overrightarrow{\rho};t)$ around $\mathbf{r} = (x, y, z)$ in analogy to (6.112). Then (6.126) can be written as

$$\mathbf{A}'(\mathbf{r};t) = \left(1 - \tfrac{i}{\hbar}\epsilon[l_z + s_z]\right)\mathbf{A}(\mathbf{r};t) \tag{6.128}$$

where the 3×3 matrix s_z is defined by

$$s_z \begin{pmatrix} A_x \\ A_y \\ A_z \end{pmatrix} = \hbar \begin{pmatrix} -iA_y \\ iA_x \\ 0 \end{pmatrix}, \tag{6.129}$$

which leads to the explicit form

$$s_z = \hbar \begin{pmatrix} 0 & -i & 0 \\ i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \tag{6.130}$$

The matrices for rotations around the *x*, *y* axes are:

$$s_x = \hbar \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -i \\ 0 & i & 0 \end{pmatrix} s_y = \hbar \begin{pmatrix} 0 & 0 & i \\ 0 & 0 & 0 \\ -i & 0 & 0 \end{pmatrix}. \tag{6.131}$$

For a rotation about any axis with $\overrightarrow{\varphi}$ we obtain

$$\mathbf{A}'(\mathbf{r};t) = \exp\left\{-\tfrac{i}{\hbar}\overrightarrow{\varphi}\cdot[\mathbf{l} + \mathbf{s}]\right\}\mathbf{A}(\mathbf{r};t). \tag{6.132}$$

Equation (6.132) suggests that $\mathbf{s}$ has the character of angular momentum. In fact one finds commutation relations as for the components of $\mathbf{l}$,

$$[s_x, s_y] = i\hbar s_z, \quad [s_z, s_x] = i\hbar s_y, \quad [s_y, s_z] = i\hbar s_x. \tag{6.133}$$

Furthermore, using the representations (6.130) and (6.131) one finds directly:

$$s^2 = s_x^2 + s_y^2 + s_z^2 = 2\hbar^2 1_{3x3}, \quad = 2\hbar^2 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \tag{6.134}$$

such that (anticipating the results of Sect. 6.4.4) we can assign **spin** 1 (in units of $\hbar$) to the vector field $\mathbf{A}$. Since the operators s_x, s_y, s_z—in contrast to the components of $\mathbf{l}$—do not depend on the position coordinates, the spin obviously describes an **internal property** of the system described by the vector field $\mathbf{A}(\mathbf{r};t)$.

Note: In addition to the radiation field **A** there are other physical systems that are described by vector fields like e.g. the ρ and ω meson, which, however, in contrast to the radiation field (photon γ) are massive, *i.e.*. $m_\omega \approx m_\rho \approx 780\ MeV/c^2$. In the weak interaction the vector fields W^+, W^-, W^0, Z^0 with masses around 90 GeV/c^2 play the dominant role.

6.4.4 Commutation Relations; Eigenvalues

From the definition (6.109) one calculates directly:

$$[l_x, l_y] = i\hbar l_z, \quad [l_z, l_x] = i\hbar l_y, \quad [l_y, l_z] = i\hbar l_x \tag{6.135}$$

or short

$$[l_n, l_m] = i\hbar \epsilon_{nmk} l_k$$

with the completely antisymmetric tensor ϵ_{nmk} of rank 3. One also finds

$$[l^2, l_i] = 0 \quad \text{for} \quad \mathrm{i} = \mathrm{x}, \mathrm{y}, \mathrm{z} \tag{6.136}$$

as a result of the fact that l^2 is a scalar quantity. From (6.135) and (6.136) it follows that l^2 and one of the components l_i form a common system of eigenfunctions. For the following considerations we choose $l_z = l_3$ and search for the solutions of

$$l^2 \psi_{\lambda\mu} = \lambda \psi_{\lambda\mu}; \quad l_z \psi_{\lambda\mu} = \mu \psi_{\lambda\mu}. \tag{6.137}$$

In a first step we want to investigate, which eigenvalues (λ, μ) are possible at all within the framework of the commutation rules (6.135) and using the hermiticity of the components l_i as well as the normalization of the solutions $\psi_{\lambda\mu}$. In a second step the eigenfunctions $\psi_{\lambda\mu}$ of the orbital angular momentum will be constructed explicitly.

For the determination of the possible eigenvalues λ, μ it is useful to introduce—instead of l_x, l_y—the linear combinations

$$l_\pm = l_x \pm i l_y. \tag{6.138}$$

Then it follows that

$$[l^2, l_z] = [l^2, l_\pm] = 0 \tag{6.139}$$

due to (6.136) and from (6.135) we obtain

$$[l_z, l_\pm] = \pm l_\pm, \tag{6.140}$$

where, to simplify the notation, the units are chosen such that $\hbar$= 1 (natural units). With the operators $l_\pm$, l_z we can write l^2 as:

$$l^2 = l_+ l_- + l_z^2 - l_z = l_- l_+ + l_z^2 + l_z. \tag{6.141}$$

From (6.140) and (6.139) now follows:

$$l^2(l_\pm \psi_{\lambda\mu}) = \lambda(l_\pm \psi_{\lambda\mu}),$$

$$l_z(l_\pm \psi_{\lambda\mu}) = (\mu \pm 1)(l_\pm \psi_{\lambda\mu}), \tag{6.142}$$

if we apply the operators l_+, l_- to Eq. (6.137). Thus using the operators l_+, l_-, the quantum number μ can be increased or decreased by 1 each, i.e.

$$l_\pm \psi_{\lambda\mu} \sim \psi_{\lambda\mu\pm1}. \tag{6.143}$$

If one assumes an arbitrary angular momentum eigenstate $\psi_{\lambda\mu}$, the question is whether this increase or decrease of the quantum numbers is infinitely possible or stops after a finite number of steps (which may depend on λ). In addition we have to investigate whether the new emerging state can be normalized.

If we use (6.138), (6.141) and the hermiticity of l_i, we get:

$$(l_+ \psi_{\lambda\mu}, l_+ \psi_{\lambda\mu}) = (\psi_{\lambda\mu}, l_- l_+ \psi_{\lambda\mu}) = (\lambda - \mu^2 - \mu)(\psi_{\lambda\mu}, \psi_{\lambda\mu}) \tag{6.144}$$

and after multiple applications of l_+ finally:

$$(l_+^{m+1}\psi_{\lambda\mu}, l_+^{m+1}\psi_{\lambda\mu}) = (\lambda - \ mu^2 - \mu) \cdots (\lambda - [\mu + m]^2 - [\mu + m])(\psi_{\lambda\mu}, \psi_{\lambda\mu}). \tag{6.145}$$

For fixed λ, μ now the factor

$$(\lambda - \mu^2 - \mu) \cdots (\lambda - [\mu + m]^2 - [\mu + m]) \tag{6.146}$$

becomes negative for sufficiently large *m*; since the normalization of the possible eigenfunctions is $\psi_{\lambda\mu}$, $l_+\psi_{\lambda\mu}$, $l_+\psi_{\lambda\mu} \cdots$ has to be positive, we come to a contradiction unless the series stops for a value $m_0 + 1$, i.e.

(6.147)

$$l_+^{m_0+1}\psi_{\lambda\mu} = 0$$

or with (6.145) we get

$$\lambda - [\mu + m_0]^2 - [\mu + m_0] = 0. \tag{6.148}$$

The series of angular momentum eigenfunctions generated from $\psi_{\lambda\mu}$ according to $m = m_0$ must stop!

Corresponding considerations can be made when employing l_-. We obtain in analogy to (6.148) the condition

$$\lambda - [\mu - n_0]^2 + [\mu - n_0] = 0, \tag{6.149}$$

thus

$$l_-^{n_0+1}\psi_{\lambda\mu} = 0. \tag{6.150}$$

Solving (6.148) and (6.149) for μ, λ we find:

$$\mu = \tfrac{n_0 - m_0}{2}\hbar, \tag{6.151}$$

$$\lambda = \tfrac{1}{2}(m_0 + n_0)\left(\tfrac{[m_0+n_0]}{2} + 1\right)\hbar^2. \tag{6.152}$$

We therefore have found the possible eigenvalues for l^2, l_z:

$$\lambda = j(j+1)\hbar^2; j = 0, \tfrac{1}{2}, 1, \tfrac{3}{2}, 2, \tfrac{5}{2}, \cdots \tag{6.153}$$

and

$$\mu/\hbar = -j, -j+1, \ldots, +j. \tag{6.154}$$

For every angular momentum quantum number j then there are $(2j+1)$ values of μ (in agreement with the Stern-Gerlach experiments in Chap. 2). In the following we want to show that for the orbital angular momentum $\mathbf{l}$ only the values $j = 0, 1, 2, \ldots$ occur, which we will refer to below as l.

6.4.5 Eigenfunctions for l^2, l_z

To construct the eigenfunctions to l^2 and l_z it is useful to introduce polar coordinates r, ϑ, φ. The components l_i then are written as:

$$l_z = -i\hbar\tfrac{\partial}{\partial\varphi}; l_\pm = \hbar\,\exp\,(\pm i\varphi)\left[\pm\tfrac{\partial}{\partial\vartheta} + i\ \ \cot\,\vartheta\ \ \tfrac{\partial}{\partial\varphi}\right], \tag{6.155}$$

and for l^2 follows:

$$l^2 = -\hbar^2\left(\frac{1}{\sin\vartheta}\ \frac{\partial}{\partial\vartheta}\ \sin\vartheta\ \frac{\partial}{\partial\vartheta} + \frac{1}{\sin^2\vartheta}\ \frac{\partial^2}{\partial\varphi^2}\right). \tag{6.156}$$

Since the coordinate *r* does not occur in (6.155) and in (6.156), we omit *r* in the following. Due to

$$l_z\ \exp(im\varphi) = -i\hbar\frac{\partial}{\partial\varphi}\exp(im\varphi) = m\hbar\ \exp(im\varphi) \tag{6.157}$$

we can use the Ansatz for the solutions of

$$l^2\chi_{lm}(\vartheta,\varphi) = l(l+1)\hbar^2\chi_{lm}; l_z\chi_{lm}(\vartheta,\varphi) = m\hbar\ \chi_{lm}(\vartheta,\varphi) \tag{6.158}$$

involving the product function:

$$\chi_{lm}(\vartheta,\varphi) = f_{lm}(\vartheta)\exp(im\varphi). \tag{6.159}$$

The possible eigenvalues are now restricted by the fact, that for a scalar function $\psi(r)$ must hold:

$$\psi(r,\vartheta,\varphi+2\pi) = \psi(r,\vartheta,\varphi). \tag{6.160}$$

This implies for (6.159)

$$\exp(im2\pi) = 1\ \rightarrow\ m\,\text{is an integer}, \tag{6.161}$$

such that the possible values of *l, m* are given by

$$l = 0,1,2,\ldots; -l \le m \le l. \tag{6.162}$$

At this point we can briefly address the question of the hermiticity of l_z. The requirement

$$(\psi_1, l_z\psi_2) = (l_z\psi_1, \psi_2) \tag{6.163}$$

leads (after partial integration $(\int d^3r = \int d\varphi\ sin\vartheta\ d\vartheta\ r^2dr)$ with respect to φ) to

$$\psi_1^*(r,\vartheta,2\pi)\psi_2(r,\vartheta,2\pi) = \psi_1^*(r,\vartheta,0)\psi_2(r,\vartheta,0). \tag{6.164}$$

The function domain, in which l_z is hermitian, thus must have the property,

$$\psi(r,\vartheta,2\pi) = \exp(i\alpha)\psi(r,\vartheta,0), \tag{6.165}$$

where α is an arbitrary real number (but fixed for all ψ). By (6.160), however, the condition (6.165) is always fulfilled.

We now turn to the calculation of $f_{lm}(\vartheta)$; first we consider the case $m = l$. Then we have

$$l_+ f_{ll}(\vartheta) \exp(il\varphi) = 0, \tag{6.166}$$

which (with (6.155)) leads to the differential equation

$$\left(\frac{\partial}{\partial\vartheta} - l \cot\vartheta\right) f_{ll}(\vartheta) = 0. \tag{6.167}$$

The solution of (6.167) is (up to a normalization factor)

$$f_{ll}(\vartheta) \sim (\sin\vartheta)^l. \tag{6.168}$$

Starting from (6.168) one now obtains by applying l_-

$$\chi_{lm}(\vartheta,\varphi) \sim (l_-)^{l-m} \chi_{ll}(\vartheta,\varphi). \tag{6.169}$$

This provides a complete construction procedure for the eigenfunctions $\chi_{lm}(\vartheta,\varphi)$.

To gain some more insight into the structure of the χ_{lm}, we use (with $\frac{d}{d(cos\vartheta)} = -\frac{1}{\sin\vartheta}\ \frac{d}{d\vartheta}$) the identity:

$$l_-[\exp(il\varphi) f(\vartheta)] = \exp(i(l-1)\varphi)\left[-\frac{d}{d\vartheta} - l \cot(\vartheta)\right] f(\vartheta)$$

$$= \exp(i(l-1)\varphi)\left[(\sin\vartheta)^{1-l} \tfrac{d}{d(\cos\vartheta)} (\sin\vartheta)^l\right] f(\vartheta), \tag{6.170}$$

from which we get:

$$l_-^2[\exp(il\varphi) f(\vartheta)] = l_-\left\{\exp(i(l-1)\varphi)\left[(\sin\vartheta)^{1-l} \frac{d}{d(\cos\vartheta)} (\sin\vartheta)^l\right] f(\vartheta)\right\}$$

$$= \exp(i(l-2)\varphi)\left\{(\sin\vartheta)^{2-l} \tfrac{d}{d(\cos\vartheta)} (\sin\vartheta)^{l-1} (\sin\vartheta)^{1-l} \tfrac{d}{d(\cos\vartheta)} (\sin\vartheta)^l f(\vartheta)\right\}. \tag{6.171}$$

Thus we can write (6.169) as

$$\chi_{lm}(\vartheta,\varphi) \sim \exp(im\varphi)(\sin\vartheta)^{-m} \frac{d^{l-m}}{d(\cos\vartheta)^{l-m}} (\sin\vartheta)^{2l}. \tag{6.172}$$

The functions $f_{lm}(\vartheta)$ therefore are polynomials of degree l in $\sin\vartheta$, $\cos\vartheta$.

By a twofold partial integration with respect to the variable $\cos\vartheta$ it can be shown that in addition to l_z also l^2 is hermitian in the space of functions χ_{lm}. Then

the orthogonality of the χ_{lm} follows from their property as eigenfunctions to l^2, l_z:

$$\left[\int_0^{2\pi} d\varphi\left(\int_{-1}^{1} d(\cos\vartheta)\ \chi^*_{lm}\chi_{l'm'}\right)\right] = 0 \tag{6.173}$$

for $l \neq l'$ and/or $m \neq m'$.

To determine the normalization constants, we start again with the case $m = l$. The functions

$$c_l(\sin\vartheta)^l \exp(il\varphi) \tag{6.174}$$

are normalized to 1 when using (determining the still free phase)

$$c_l = (-1)^l\sqrt{\tfrac{(2l+1)!}{4\pi}}\tfrac{1}{2^l l!}. \tag{6.175}$$

For the case $m \neq l$ we assume the relation in analogy to (6.144).

$$(l_-\chi_{lp}, l_-\chi_{lp}) = (l(l+1) - p^2 + p)(\chi_{lp}, \chi_{lp}) = (l-p+1)(l+p)(\chi_{lp}, \chi_{lp}). \tag{6.176}$$

Using the usual phase convention we obtain from (6.176) for the normalized χ_{lp} :

$$\chi_{l,p-1} = \tfrac{1}{\sqrt{(l-p+1)(l+p)}} l_-\chi_{lp}. \tag{6.177}$$

Starting from the already normalized functions χ_{ll} the normalized functions are obtained by iteration of (6.177):

$$\chi_{lm}(\vartheta,\varphi) = \sqrt{\tfrac{(l+m)!}{(2l)!(l-m)!}}(l_-)^{l-m}\chi_{ll}(\vartheta,\varphi). \tag{6.178}$$

The standard solutions are therefore explicitly:

$$Y_{lm}(\vartheta,\varphi) = (-1)^l/(2^l l!)\sqrt{\frac{(2l+1)(l+m)!}{4\pi(l-m)!}}$$

$$\times \exp(im\varphi)(\sin\vartheta)^{-m}\tfrac{d^{l-m}}{d(\cos\vartheta)^{l-m}}(\sin\vartheta)^{2l}. \tag{6.179}$$

Summary: For the functions $Y_{lm}(\vartheta,\varphi)$ the following holds:

$$\begin{aligned} l^2 Y_{lm} &= l(l+1)Y_{lm}; l_z Y_{lm} = mY_{lm}; \\ l_\pm Y_{lm} &= \sqrt{(l\pm m+1)(l\pm(-m))}Y_{lm\pm1} \end{aligned} \tag{6.180}$$

and

$$\int_0^{2\pi} d\varphi \ \int_{-1}^{1} d(\cos\vartheta) \ Y_{lm}^* Y_{l'm'} = \delta_{ll'}\delta_{mm'}. \tag{6.181}$$

6.4.6 Angular Momentum Representation

The spherical harmonics $Y_{lm}(\vartheta,\varphi)$ form a complete system of functions on the unit sphere. Therefore every square-integrable function $\psi(\mathbf{r})$ can be expanded in an (on average convergent) series

$$\psi(\mathbf{r}) = \sum_{l=0}^{\infty}\sum_{m=-l}^{l} g_{lm}(r) Y_{lm}(\vartheta,\varphi). \tag{6.182}$$

For the expansion coefficients $g_{lm}(r)$ follows (due to the orthonormalization of the Y_{lm}) :

$$g_{lm}(r) = \int_0^{2\pi}\int_{-1}^{1} d\varphi \ d(\cos\vartheta) \ Y_{lm}^*(\vartheta,\varphi)\psi(r,\vartheta,\varphi). \tag{6.183}$$

For an ensemble in the state ψ the expectation values for l^2 and l_z

$$(\psi, l^2\psi) = < l^2 > = \sum_{l=0}^{\infty} l(l+1)\hbar^2 \sum_{m=-l}^{l}\int_0^{\infty} r^2 dr \ |g_{lm}(r)|^2;$$

$$< l_z > = \sum_{l=0}^{\infty}\sum_{m=-l}^{l} m\hbar \ \int_0^{\infty} r^2 dr \ |g_{lm}(r)|^2 \tag{6.184}$$

with the normalization

$$1 = \sum_{l=0}^{\infty}\sum_{m=-l}^{l}\int_0^{\infty} r^2 dr \ |g_{lm}(r)|^2. \tag{6.185}$$

Thus we can interpret the integral

$$\int_0^{\infty} r^2 dr \ |g_{lm}(r)|^2 \tag{6.186}$$

as probability to find—in a simultaneous measurement of l^2 and l_z of a particle described by ψ—the values $l(l+1)$ and m.

If the ensemble is prepared in such a way that ψ already is an eigenfunction of l^2 to the eigenvalue $l(l+1)$, then in a measurement of l_z only the $(2l+1)$ discrete values $-l \le m \le l$ can be found. Thus the eigenvalues of l^2 are $(2l+1)$-fold degenerate. Conversely: If ψ is an eigenfunction of l_z with eigenvalue m, then for a measurement of l^2 only the eigenvalues $l(l+1)$ with $l \ge |m|$ can be found.

In an eigenstate ψ_{lm} to l^2 and l_z the components l_x, l_y are not sharp due to (6.135). For the mean square of the fluctuation, which for symmetry reasons are the same for l_x and l_y, one immediately finds:

$$(\psi_{lm}, (\Delta l_x)^2 \psi_{lm}) = \int d^3r \ \psi^*_{lm} l_x^2 \psi_{lm} = \tfrac{1}{2}(\psi_{lm}, (l^2 - l_z^2)\psi_{lm}) = \tfrac{1}{2}\{l(l+1) - m^2\}\hbar^2, \tag{6.187}$$

if one considers that

$$\int d^3r \ \psi^*_{lm} l_x \psi_{lm} = 0 \tag{6.188}$$

because of (6.138), (6.142) and (6.173). Equation (6.187) shows that there is exactly a single state in which, in addition to l^2, all 3 components l_i can be measured sharply, i.e. the case $l = m = 0$.

6.4.7 Angle–Angular Momentum Uncertainty

Accordingly to (6.80) the following commuation rule holds for the angle φ and the component l_z,

$$[l_z, \varphi] = \tfrac{\hbar}{i}. \tag{6.189}$$

Due to the analogy of (6.189) and (6.80) one is tempted to conclude from (6.189) the relation (in analogy to (6.82)),

$$\Delta\varphi \ \Delta l_z \geq \tfrac{\hbar}{2}. \tag{6.190}$$

However, Eq. (6.190) cannot be valid in general because for eigenfunctions of l_z the fluctuation $\Delta l_z = 0$, while $\Delta\varphi \leq 2\pi$ is always finite! The error in the conclusion is due to the fact that—in the derivation of (6.82) from (6.80)—it was assumed in (6.85) (without explicit mentioning), that with ψ also $x\psi$ belongs to the function space in which p_x is hermitian. Exactly this prerequisite, necessary for the proof in Sect. 5.2, is not fulfilled for the case of the angular momentum l_z and the angle φ: according to the previous analysis l_z is hermitian in the space of periodic functions $\psi(r, \vartheta, \varphi)$ with

$$\psi(r, \vartheta, \varphi) = \psi(r, \vartheta, \varphi + 2\pi) \tag{6.191}$$

but then $\varphi\psi(r, \vartheta, \varphi)$ is not periodic and the requirements for the proof in Sect. 5.3 are not fulfilled. This clarifies that (6.190) cannot hold in general as the example above has shown.

The way to arrive at correct uncertainty relations for angular momentum and angles is already outlined by the discussion above. One must replace the observable φ by a periodic function, e.g. $\cos\varphi$ or $\sin\varphi$. Then we obtain

$$[l_z, \cos\varphi] = -\tfrac{\hbar}{i} \ \sin\varphi \tag{6.192}$$

$$[l_z, \sin\varphi] = \tfrac{\hbar}{i} \ \cos\varphi, \tag{6.193}$$

and with ψ the function $\sin\ \varphi\ \psi$ or $\cos\ \varphi\ \psi$ is also periodic.

6.5 The Spin–Intrinsic Angular Momentum

6.5.1 Experimental Observations

If we carry out a **Stern-Gerlach experiment** (see Chap. 2) with hydrogen atoms, which are all in the ground state, we observe a (symmetric) splitting of the primary beam into two secondary beams. This finding is in contrast to the previous considerations on the quantum theory of a point-like particle, according to which no splitting would be expected in the Stern-Gerlach experiment, since

(i) in the ground state of the *H* atom (see Sect. 7.6.5) the electron has the orbital angular momentum $\mathbf{l} = 0$, such that no permanent magnetic moment results from the orbital motion of the electron in the atom;

(ii) the induced magnetic moment (diamagnetism)—even for strong magnetic fields—is not sufficient to split the beam of the size found experimentally.

The results of the Stern-Gerlach experiment can be easily explained, if we assign an intrinsic angular momentum (**spin**)—and thus a corresponding magnetic moment—to the electron. This intrinsic angular momentum of the particle is an **internal property** independent of the coordinate system without a classical analogue; in particular, it cannot be transformed away by translating to another coordinate system. Since the primary beam splits exactly into 2 secondary beams only the 2 values $m_s = +1/2, -1/2$ (in units of $\hbar$) are possible for the *z* component of the spin. This implies that a spin $s = 1/2$ (in units of $\hbar$) can be assigned to the electron.

Other hints for the spin of the electron are provided by the fine structure of spectral lines, the **Einstein-de Haas effect** as well as the **anomalous Zeemann effect**. Other elementary particles also have **spin 1/2 :** nucleons, muons, quarks, neutrinos; on the other hand, **spin 0**: pions, kaons, η; **Spin 1**: photons, gluons, vector mesons ρ, ω, ϕ etc.

6.5.2 The Pauli Spin Matrices

The explanations above show that a scalar wave function—depending only on $(\mathbf{r}, t)$—is not sufficient for a description of an ensemble of electrons; we have to assign an additional (internal) degree of freedom to the electron. This additional degree of freedom can only be characterized by two values $m_s = +1/2$ or $m_s = -1/2$. A mathematical description of such a degree of freedom is possible in terms of a 2-dimensional vector space, its basis vectors

$$\begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{or} \quad \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{6.194}$$

are assigned to the states (denoted by: **spin up** or **spin down**) with $m_s = +1/2$ or $m_s = -1/2$.

Operators that act in the space spanned by (6.194) can be represented by 2×2 matrices. Since the operator of the *z* component of the spin S_z should have the eigenvalues $\pm 1/2$ (in units of $\hbar$), its representation is obvious

$$S_z = \tfrac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{6.195}$$

We can flip the electron spin (spin flip) using the operators

$$S_+ = \frac{1}{2}\begin{pmatrix} 0 & 2 \\ 0 & 0 \end{pmatrix}; S_- = \frac{1}{2}\begin{pmatrix} 0 & 0 \\ 2 & 0 \end{pmatrix}. \tag{6.196}$$

This gives (cf. the operators $l_\pm$ from Sect. 6.4)

$$S_+ \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}; S_+ \begin{pmatrix} 1 \\ 0 \end{pmatrix} = 0, \tag{6.197}$$

or

$$S_- \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}; S_- \begin{pmatrix} 0 \\ 1 \end{pmatrix} = 0. \tag{6.198}$$

Every operator acting in the space defined by (6.194) can be written as a linear combination of S_z, S_+, S_- and the identity matrix $1_{2\times 2}$, e.g. the operators

$$S_x = \frac{1}{2}(S_+ + S_-) = \frac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; S_y = \frac{1}{2i}(S_+ - S_-) = \frac{1}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \tag{6.199}$$

which together with S_z are the cartesian components of the **spin vector**

$$\mathbf{S} = \begin{pmatrix} S_x \\ S_y \\ S_z \end{pmatrix}. \tag{6.200}$$

In the **standard representation** we define the components of the σ-matrices by

$$\mathbf{S} = \frac{1}{2}\ \boldsymbol{\sigma}, \tag{6.201}$$

which are called **Pauli spin matrices** with the three components:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{6.202}$$

The following properties hold for these matrices, which follow directly from the definition (6.202):

(i) **Normalization**

$$\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = 1_{2\times 2} = E_2 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \tag{6.203}$$

such that

$$\vec{\sigma}^2 = 3E_2 \;\Rightarrow\; S^2 = \tfrac{3}{4}\; E_2 = \tfrac{1}{2}\big(1+\tfrac{1}{2}\big)E_2 \tag{6.204}$$

in accordance with (6.153).
(ii) **Commutators**

$$\sigma_x\sigma_y - \sigma_y\sigma_x = 2i\;\sigma_z \tag{6.205}$$

or

$$[S_x, S_y] = i\;S_z \tag{6.206}$$

as expected for angular momenta (cf. (6.135)).
(iii) **Anti-commutators**

$$[\sigma_x, \sigma_y]_+ = \sigma_x\sigma_y + \sigma_y\sigma_x = 0. \tag{6.207}$$

6.5.3 Spinors

We can now define an arbitrary state of a set of particles with spin 1/2 by a two-component wave function (**spinor**)

$$\Psi(\mathbf{r};t) = \psi_u(\mathbf{r};t)\begin{pmatrix}1\\0\end{pmatrix} + \psi_d(\mathbf{r};t)\begin{pmatrix}0\\1\end{pmatrix} = \begin{pmatrix}\psi_u(r;t)\\ \psi_d(r;t)\end{pmatrix}. \tag{6.208}$$

The operation of the spin operators on spinors follows directly from Sect. 6.5.2, e.g.

$$\sigma_x\Psi = \begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}\begin{pmatrix}\psi_u\\ \psi_d\end{pmatrix} = \begin{pmatrix}\psi_d\\ \psi_u\end{pmatrix}; \tag{6.209}$$

the operators of position and momentum (as well as all operators built from $\mathbf{r}$ and $\mathbf{p}$, such as angular momentum) are given by a multiplication with the identity matrix

$$E_2 = \begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix} \tag{6.210}$$

and thus become operators in the space of spinors (6.208).

Example:

(6.211)

$$\mathbf{r}\ \Psi = \begin{pmatrix} \mathbf{r} & 0 \\ 0 & \mathbf{r} \end{pmatrix} \cdot \begin{pmatrix} \psi_u \\ \psi_d \end{pmatrix} = \begin{pmatrix} \mathbf{r}\psi_u \\ \mathbf{r}\psi_d \end{pmatrix}.$$

We define the **norm of** Ψ as

$$(\Psi, \Psi) = \int d^3r\ (\psi_u^* \psi_d^*) \begin{pmatrix} \psi_u \\ \psi_d \end{pmatrix} = \int d^3r\ \{|\psi_u|^2 + |\psi_d|^2\}. \tag{6.212}$$

For spinors Ψ, that are normalized to 1 according to (6.212), we can e.g. interpret

$$\int_V d^3r\ |\psi_u|^2 \tag{6.213}$$

as the probability to find an electron in the volume V with the spin component $m_s = +1/2$. If we discard the information about spin then

$$\int_V d^3r\ \{|\psi_u|^2 + |\psi_d|^2\} \tag{6.214}$$

is the probability of finding an electron in the volume V.

The definition of the expectation value of an observable in a state Ψ follows from (6.209) to (6.212). It is explained by a few **examples**:

(i) Position:

$$< \mathbf{r} >= (\Psi, \mathbf{r}\Psi) = \int d^3r\ \{(\psi_u^* \psi_d^*)\} \begin{pmatrix} \mathbf{r}\psi_u \\ \mathbf{r}\psi_d \end{pmatrix} = \int d^3r\ \mathbf{r}\{|\psi_u|^2 + |\psi_d|^2\}; \tag{6.215}$$

(ii) Spin:

$$< S_z >= (\Psi, S_z\Psi) = \tfrac{1}{2}\ \int d^3r\ \{(\psi_u^* \psi_d^*) \begin{pmatrix} \psi_u \\ -\psi_d \end{pmatrix}\} = \tfrac{1}{2}\ \int d^3r\ \{|\psi_u|^2 - |\psi_d|^2\} \tag{6.216}$$

or

$$< S_x >= (\Psi, S_x\Psi) = \tfrac{1}{2}\ \int d^3r \{(\psi_u^* \psi_d^*) \begin{pmatrix} \psi_d \\ \psi_u \end{pmatrix}\} = \tfrac{1}{2}\ \int d^3r\ \{\psi_u^* \psi_d + \psi_d^* \psi_u\}. \tag{6.217}$$

Of course, operator products are also possible, such as e.g. the spin-orbit coupling $\mathbf{l} \cdot \mathbf{S} = l_x S_x + l_y S_y + l_z S_z$, which follows from the relativistic theory and explains the fine structure of the spectral lines.

6.5.4 Rotation of Spinors

In analogy to Sect. 6.4 we conclude the following property of a spinor Ψ in rotations:

$$\Psi'(\mathbf{r};t) = \hat{S}\Psi(\mathbf{r};t) \tag{6.218}$$

with

$$\hat{S} = \exp\left\{-\frac{i}{\hbar}\overrightarrow{\varphi}\cdot[\mathbf{l}+\mathbf{S}]\right\} = \sum_{n=0}^{\infty}\frac{1}{n!}\left(-\frac{i}{\hbar}\overrightarrow{\varphi}\cdot[\mathbf{l}+\mathbf{S}]\right)^n, \tag{6.219}$$

where $\mathbf{S}$ now consists of the 2×2 Pauli matrices introduced in Sect. 6.5.2 (6.195), (6.199). According to (6.125)–(6.127) we obtain for the transformation behavior of the spinor components ψ_u, ψ_d in rotations, e.g. around the *x* axis by the angle φ

$$\begin{pmatrix}\psi'_u\\ \psi'_d\end{pmatrix}(\mathbf{r};t) = \begin{pmatrix}\cos\left(\frac{\varphi}{2}\right) & -i\,\sin\left(\frac{\varphi}{2}\right)\\ -i\,\sin\left(\frac{\varphi}{2}\right) & \cos\left(\frac{\varphi}{2}\right)\end{pmatrix}\begin{pmatrix}\psi_u\\ \psi_d\end{pmatrix}(\overrightarrow{\rho},t) \tag{6.220}$$

where $\overrightarrow{\rho}$ arises from $\mathbf{r}$ by the inverse rotation, i.e. $\overrightarrow{\rho} = s^{-1}\mathbf{r}$.

As a proof, note that $\hat{S}$ can also be written as

$$\hat{S} = \exp\left(-\frac{i}{\hbar}\varphi l_x\right)\exp\left(-\frac{i}{\hbar}\varphi S_x\right), \tag{6.221}$$

since the operators $\mathbf{l}$, $\mathbf{S}$ act in different spaces and consequently $[\mathbf{l},\ \mathbf{S}] = 0$. We can therefore consider separately:

$$\exp\left(-\frac{i}{\hbar}\varphi S_x\right)\Psi = \exp\left(-i\ \frac{\varphi}{2}\ \sigma_x\right)\Psi = \sum_{n=0}^{\infty}\frac{1}{n!}\left(-i\ \frac{\varphi}{2}\ \sigma_x\right)^n\Psi \tag{6.222}$$

$$= \left(\cos\left(\frac{\varphi}{2}\right)\cdot E_2 - i\ \sin\left(\frac{\varphi}{2}\right)\cdot\sigma_x\right)\Psi,$$

since according to (6.203):

$$\sigma_x^2 = E_2, \sigma_x^3 = \sigma_x\ \text{ etc.} \tag{6.223}$$

The transformation behavior of the spinor components differs from that of the components of a vector field in that the angle $\varphi/2$ occurs in (6.222). This has the particular consequence that in a rotation by $\varphi = 2\pi$

$$\Psi \to \Psi' = \exp(-i\pi)\Psi = -\Psi, \tag{6.224}$$

while for a vector field $\mathbf{A}$ we have:

$$\mathbf{A} \to \mathbf{A}' = \mathbf{A}. \tag{6.225}$$

6.5.5 Pauli Equation

The time evolution of the spinor Ψ is determined by a Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\ \Psi = H\ \Psi, \tag{6.226}$$

where H can now contain spin-dependent terms. The internal angular momentum $\mathbf{S}$ is linked to a magnetic moment

$$\overrightarrow{\mu_s} = \frac{e}{mc}\mathbf{S} \tag{6.227}$$

as the **Einstein—de Haas experiment** shows explicitly. In a magnetic field $\mathbf{B}$ such a magnetic moment has the energy

$$-\overrightarrow{\mu_s}\cdot\mathbf{B}. \tag{6.228}$$

Then the Hamiltonian is

$$H = \frac{1}{2\,m}\left(\mathbf{p} - \frac{e}{c}\ \mathbf{A}\right)^2 + e\Phi - \frac{e}{mc}\mathbf{S}\cdot\mathbf{B}. \tag{6.229}$$

Since from the definition of the spin matrices it follows that

$$(\Psi, \mathbf{S}\Psi) = (\mathbf{S}\Psi, \Psi), \tag{6.230}$$

also the (non-relativistic) Hamiltonian (6.229) for an electron with spin is hermitian, if the components of the spinors Ψ drop fast enough in the asymptotic region. Then we get:

$$\frac{d}{dt}(\Psi, \Psi) = 0, \tag{6.231}$$

such that the norm (Ψ, Ψ) remains constant in time.

If $[H, \mathbf{l} + \mathbf{S}] = 0$, we obtain—as in Sect. 6.4—that with Ψ also $\hat{S}\Psi$ is a solution of (6.226) (**rotational invariance**).

Additions:

(1) One might attempt to determine the internal magnetic moment of the electron classically by describing the electron as a homogeneous sphere of charge $-e$ with the classical electron radius $r_0 = e^2/(mc^2)$ rotating around a principle axis. For a quantitative explanation of the Stern-Gerlach experiments from Sect. 6.5.1 then an orbital velocity $v \approx 200\ \ c$ at the equator of the sphere would be required; This clearly marks the end of a classical description!

(2) The electron spin inevitably follows from relativistic quantum theory, the **Dirac theory**, from which the Pauli equation (6.226) with the Hamilton operator (6.229) results in the non-relativistic limit.

In summarizing this chapter we have investigated the connection between the possible expectation values of an observable *A* and its fluctuations in context with its commutator [*A*, *H*]. Furthermore, we have established the relationship between momentum conservation and translational invariance as well as the conservation of angular momentum and rotational

invariance in quantum theory. In addition we have introduced the ‘spin’ of electrons (or related fermions) and explored its properties with respect to rotations.

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7. Motion of a Particle with External Forces

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In this chapter we will discuss the quantum mechanics of a single particle in an external potential and classify the possible solutions. As examples we calculate the wave functions for an infinite and a finite well and for potentials that are periodic in space. Furthermore, the harmonic oscillator problem will be examined in detail as well as the motion of a charged particle (and its spin) in a magnetic field. The bound states and energy levels of the hydrogen atom will close this chapter.

7.1 General Properties of the Wave Function

The following discussion refers to the Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\ \psi = H\ \psi \tag{7.1}$$

with local potentials, i.e.

$$H = T + V; V = V(\mathbf{r}); \tag{7.2}$$

here ψ is a scalar function (not a two or more component spinor). Furthermore, due to the 2nd derivatives in $\mathbf{r}$ in the kinetic energy operator **the wave function ψ must be continuous together with its first derivatives as long as the potential V remains finite**.

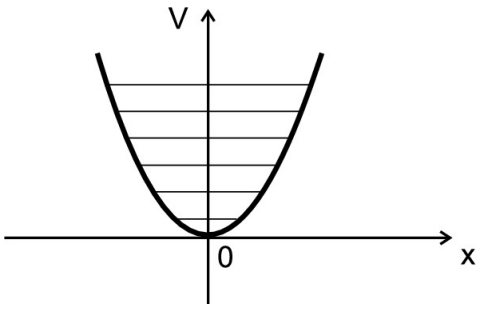

Fig. 7.1 Example for a potential that only allows for closed orbits

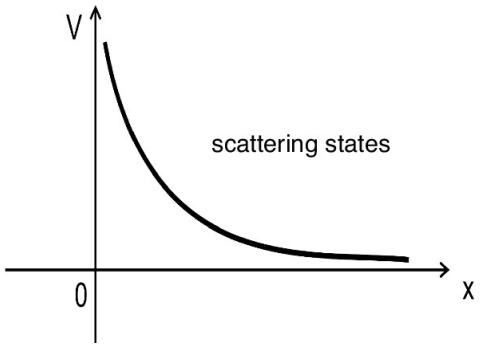

Fig. 7.2 Example for a potential that only allows for open orbits

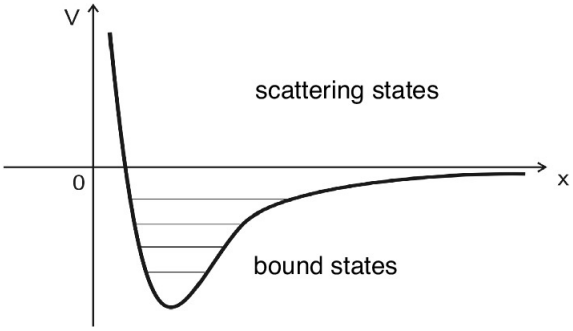

Fig. 7.3 Example for a potential that has bound as well as scattering states

7.1.1 Classification of Solutions

It is useful to differentiate the following cases for the shape of the potential:

(1) If all classical orbits are closed, the eigenvalue spectrum of H is purely discrete and all eigenfunctions can be normalized. An example is the harmonic oscillator (Fig. 7.1).

(2) If the classical system only has open orbits, the energy spectrum is purely continuous and the eigenfunctions cannot be normalized. Example: repulsive Coulomb potential (Fig. 7.2).

(3) The potential V has the shape as shown in Fig. 7.3:
This case corresponds to e.g. the potential between the atoms of a diatomic molecule. Bound states as well as continuum states show up.

(4) The α—decay of an atomic nucleus is determined by a potential of the form shown in Fig. 7.4 (here x is the distance between the α particle and the remaining nucleus):

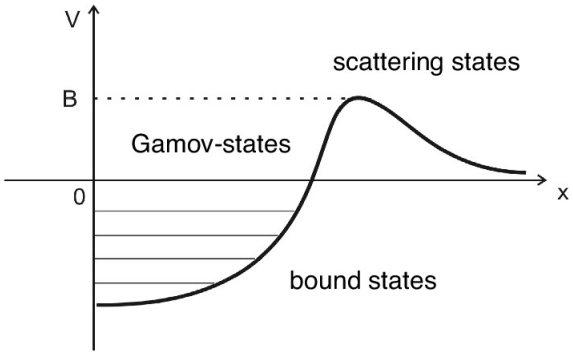

Fig. 7.4 Example for a potential that has bound states, scattering states as well as resonant Gamov states

The barrier stems (a) from the Coulomb repulsion and (b) from the centrifugal term of the kinetic energy (see Sect. 7.6). In such a case we have—apart from bound states $(E < 0)$ and scattering states $(E > 0)$—a third type of possible states in the range $0 < E < B$: states that are within the barrier can only exist for a finite time τ until they decay by tunneling (**Gamov states**). Classically, the situation is completely different: a particle with $0 < E < B$ is either on a closed orbit within the barrier or on an open trajectory outside the barrier. A transition (at fixed energy) from one type of orbit type to the other is impossible. In classical physics there would be no α—decay (or spontaneous nuclear fission).

7.1.2 The Wronski Determinant

It is often possible to reduce the stationary Schrödinger equation to a one-dimensional problem, which is determined by a differential equation of the form

$$\xi'' + (\epsilon - U(x))\xi = 0 \tag{7.3}$$

with $\epsilon = 2mE/\hbar^2, U(x) = 2mV(x)/\hbar^2$. Let's consider 2 solutions ξ_1, ξ_2 with eigenvalues ϵ_1, ϵ_2; then from (7.3) we get the relationship

$$\xi_2\xi_1'' - \xi_1\xi_2'' = (\epsilon_2 - \epsilon_1)\xi_1\xi_2. \tag{7.4}$$

We now show with (7.4) that square integrable solutions cannot be degenerate. We provide the proof indirectly: If $\epsilon_1 = \epsilon_2$, we would have (7.4):

$$\xi_2\xi_1'' - \xi_1\xi_2'' = 0 = W(\xi_1, \xi_2)', \tag{7.5}$$

i.e. the **Wronski determinant**

$$W(\xi_1, \xi_2) \equiv \xi_2\xi_1' - \xi_1\xi_2' = \text{const.} \quad \forall \text{x}. \tag{7.6}$$

In line with the assumption of square integrability the functions ξ_1, ξ_2 must vanish at infinity; thus the constant of integration itself is zero:

$$W(\xi_1, \xi_2) \equiv \xi_2\xi_1' - \xi_1\xi_2' = 0. \tag{7.7}$$

This directly leads to

$$\xi_1 = \text{const. } \xi_2, \tag{7.8}$$

i.e. the two solutions agree except for a normalization factor, in contradiction to the assumption.

With the help of (7.4) we can also make statements about the zeros of the solutions of (7.3). We consider 2 real solutions of (7.3) ξ_1, ξ_2—the solutions of the real differential equation (7.3) can always be chosen real—and let $\epsilon_2 > \epsilon_1$; we then integrate (7.4) over an interval whose endpoints *a*, *b* are two consecutive zeros of ξ_1, therefore:

$$\xi_2\xi_1'|_a^b - \xi_1\xi_2'|_a^b = \xi_2\xi_1'|_a^b = (\epsilon_2 - \epsilon_1)\int_a^b \xi_1\xi_2 \, dx. \tag{7.9}$$

In the interval [*a*, *b*] ξ_1 has a uniform sign, e.g. $\xi_1 > 0$. Then the following relations hold at the endpoints:

$$\xi_1'(a) \geq 0; \quad \xi_1'(b) \leq 0. \tag{7.10}$$

It now follows that $\xi_2(x)$ must have at least 1 zero between 2 successive zeros of $\xi_1(x)$. If $\xi_2(x) > 0 \ (< 0)$ in between the zeros *a*, *b* of $\xi_1(x)$, then the right side according to (7.9) will be $> 0 \ (< 0)$, while the left side with (7.10) turns out to be $\leq 0 \ (\geq 0)$: contradiction! Now if ξ_1, ξ_2 disappear at the boundaries $x \to \pm\infty$ (bound states), the n_1 zeros of $\xi_1(x)$ divide the interval $[-\infty, \infty]$ in $(n_1 + 1)$ subintervals. Since $\xi_2(x)$ in each of these intervals has at least 1 zero point, the function $\xi_2(x)$, which leads to the higher eigenvalue $\epsilon_2 > \epsilon_1$ (by assumption), must have at least $(n_1 + 1)$ zero points.

7.2 Simple Examples

7.2.1 The Infinite Potential Well

The most simple model system in quantum mechanics is the one-dimensional infinite potential well. It consists of a potential-free area which is surrounded by two infinitely high potential walls:

$$V(x) = \infty \qquad \text{for } \ \mathrm{x} < 0 \tag{7.11}$$

$$V(x) = 0 \qquad \text{for } \ 0 < \mathrm{x} < \mathrm{a}$$

$$V(x) = \infty \qquad \text{for } \ \mathrm{x} > \mathrm{a}.$$

The classical range is restricted to the interval $0 < x < a$ and the potential belongs to the 1st class of potentials. We will see that the energy quantization in this example results directly from the restriction of the classical range.

Outside the classical region the potential is too strong, such that apart from the trivial solution $\psi = 0$ no other solutions may exist. Inside the potential, however, we have a free system described by the stationary Schrödinger equation

$$-\frac{\hbar^2}{2\,m}\frac{\partial^2}{\partial x^2}\psi(x) = E\psi(x). \tag{7.12}$$

The general solution of this equation is

$$\psi(x) = A\,\sin\,(kx) + B\,\cos\,(kx), \tag{7.13}$$

with the wave number $k = \sqrt{2mE}/\hbar$. The coefficients *A* and *B* must be derived from the continuity conditions of the wave function. Since the potential is no longer finite, the derivative of the wave function is not continuous, but the wave function itself continues to be continuous and therefore must disappear at the edges of the potential, i.e. $\psi(0) = 0$ and $\psi(a) = 0$.

The first condition leads to $B = 0$ since $\cos\,(0) = 1$. The second condition can only be fulfilled if $\sin\,(ka) = 0$. Therefore, the wave number only allows certain discrete values:

$$\sin\,(ka) = 0 \quad \Rightarrow \quad ka = n\pi, \tag{7.14}$$

where *n* is an integer number. The energy then can also only take discrete values. The last free coefficient *A* follows from the normalization. The energies and wave functions of the infinite potential well therefore are (see Fig. 7.5):

$$E_n = \frac{\hbar^2\pi^2}{2\,ma^2}n^2, \qquad \psi_n(x) = \sqrt{\frac{2}{a}}\,\sin\,\left(\frac{\pi n}{a}x\right). \tag{7.15}$$

In the more realistic case of the finite potential well, the wave function does not have to disappear at the edges, but can penetrate into the classically forbidden area and drops here exponentially ($\sim\exp\,(-\kappa x)$ with real $\kappa = \sqrt{2m(V_0 - E)}/\hbar$) for $E < V_0$. In this case the derivative of the wave function is also continuous again.

In general, every potential can be approximated by many constant potentials. In this case one has to determine two coefficients per section and has two boundary conditions from the continuity conditions. Since the wave function must also be normalizable, one has to determine $2N$ coefficients (for *N* potential sections) from $2N + 1$ boundary conditions. The system thus is overdetermined and solutions only exist for certain discrete energy eigenvalues.

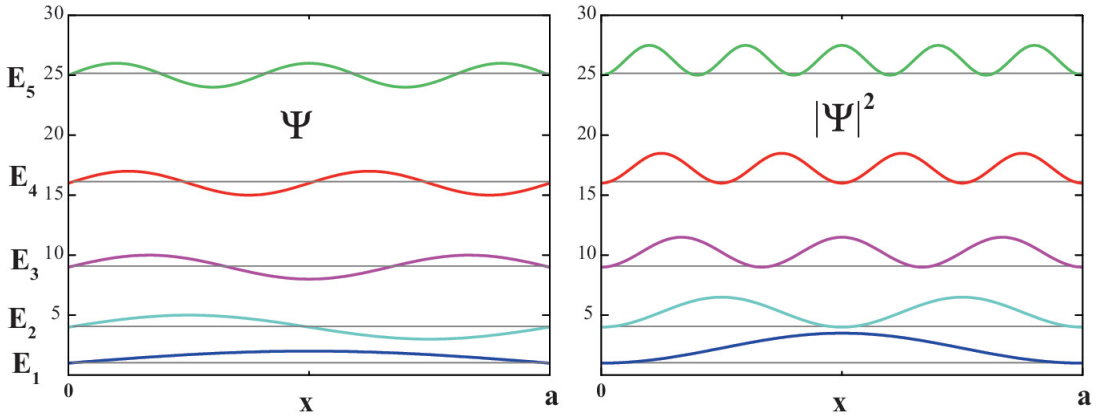

Fig. 7.5 Illustration of the wave functions $\psi(x)$ and the associated energy levels of an infinite potential well (left) and the densities $|\psi(x)|^2$ (right)

7.2.2 The Finite Potential Well

In the previous section we have discussed an example with a discrete spectrum and now want present an example with a continuous spectrum. The potential should be a single finite potential well,

$$V_I(x) = 0 \qquad \text{for} |\mathrm{x}| > \mathrm{a} \tag{7.16}$$

$$V_{II}(x) = V_0 > 0 \qquad \text{for} -\mathrm{a} \leq \mathrm{x} \leq \mathrm{a}.$$

A particle, coming from the left, moves to the right in direction of the potential well. There are two classical options: If the energy of the particle is larger than the step ($E > V_0$), it can pass the step; if the energy is smaller, the particle is reflected. Quantum mechanically, both possibilities can occur.

For the wave function (I) in front of the step, we choose a plane wave traveling to the right for the incoming wave and a plane wave traveling to the left for the reflected wave,

$$\psi^I_{x<-a}(x) = \psi_{in}(x) + \psi_R(x) = e^{ikx} + Re^{-ikx}. \tag{7.17}$$

The amplitude of the incoming wave here is set to 1. For the wave function behind the step (*III*) we only take a plane wave running to the right, since the particle cannot be reflected at infinity,

$$\psi^{III}_{x>a}(x) = \psi_T(x) = Te^{ikx}. \tag{7.18}$$

The wave function in the well for $E < V_0$ has to be taken as

$$\psi^{II}_{|x|<a}(x) = A_{II} \exp(-\kappa x) + B_{II} \exp(+\kappa x) \tag{7.19}$$

with $\kappa = \sqrt{2m(V_0 - E)}/\hbar)$ for $E < V_0$. For $E > V_0$ we have the basis solutions $\exp(\pm i\tilde{k}x)$ with $\tilde{k} = 2\,m(E - V_0)/\hbar^2$. The overall solution then emerges from the solution of the Schrödinger equation by exploiting the continuity conditions:

$$\psi^I(-a) = \psi^{II}(-a), \qquad \psi^{II}(a) = \psi^{III}(a), \tag{7.20}$$

$$\frac{\partial}{\partial x}\psi^I(-a) = \frac{\partial}{\partial x}\psi^{II}(-a), \qquad \frac{\partial}{\partial x}\psi^{II}(a) = \frac{\partial}{\partial x}\psi^{III}(a)$$

for the four complex coefficients R, T, A_{II}, B_{II}. Their explicit evaluation is straight forward for $E < V_0$ and $E > V_0$ (but lengthy and serves as a good exercise).

Of particular interest is the **reflection coefficient** *R* and the **transmission coefficient** *T*, which indicate the amplitude for reflection at the step or transmission. The conservation of probability here requires $|R|^2 + |T|^2 = 1$. Figure 7.6 shows the shape of the probability density $|\psi(x)|^2$ for an energy $0 < E < V_0$. The density oscillates in the region before the well (I) due to the interference between the incoming and reflected wave; in the classically forbidden region (II) it drops roughly exponentially and becomes a constant ($|T|^2$) in the region III.

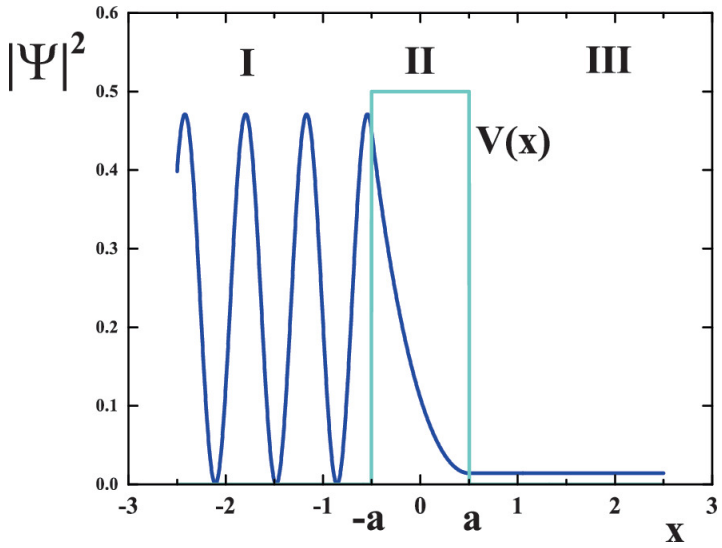

Fig. 7.6 Illustration of the probability density $|\psi(x)|^2$ for the potential well in case of $0 < E < V_0$

In distinction to classical mechanics the particle can bypass the potential well with a certain probability even if the necessary energy is missing. This effect is called **tunnelling**. The inverse case is also possible: If the energy of the particle is higher than the potential step, it would classically always pass the step. In quantum mechanics it can also be reflected in this case! Fig. 7.7 shows the reflection $|R|^2$ and the transmission $|T|^2$ probability as a function of the energy of the particle (in units of V_0). For small energies the reflection dominates, while for large energies the transmission is becoming more and more likely. For certain discrete energies the step becomes completely transparent; these energies correspond to the energy levels of the infinite potential well (7.15).

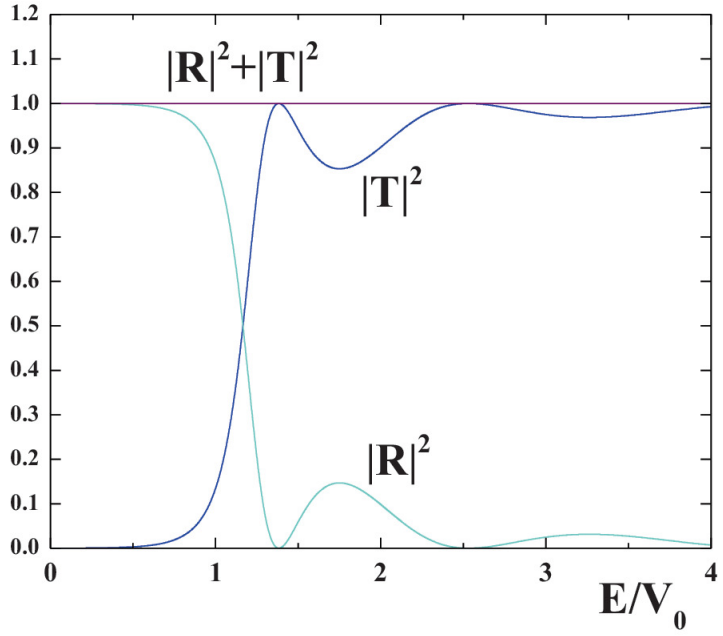

Fig. 7.7 Illustration of the energy dependence of the reflection and transmission probabilities $|R|^2$ and $|T|^2$

7.3 Periodic Potentials

7.3.1 Crystal Symmetry

For studying the motion of an electron in a crystal it is expedient to employ the periodicity of the grid. We here assume an ideal grid; grid disturbances (local shifts), edge effects therefore are neglected. The grid periodicity can then be formulated as

$$V(\mathbf{r}) = V(\mathbf{r} + \mathbf{R}_m), \tag{7.21}$$

where $\mathbf{R}_m$ is a displacement vector which transfers the crystal lattice into itself.

We now will describe general properties of the stationary solutions for the potential (7.21),

$$\left\{-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) - E\right\}\psi(\mathbf{r}) = 0, \tag{7.22}$$

which follow directly from the periodicity of *V*. For simplicity we limit ourselves—due to the separation of the wave function $\psi(\mathbf{r}) \equiv \psi_x(x)\psi_y(y)\psi_z(z)$—to a one-dimensional model. The essential statements also hold in the three-dimensional case.

7.3.2 One-Dimensional Periodic Potential

We consider the differential equation

$$\psi'' + (\epsilon - U(x))\psi = 0 \tag{7.23}$$

with

$$\epsilon = \frac{2m}{\hbar^2}E; U(x) = \frac{2m}{\hbar^2}V(x) \tag{7.24}$$

and

$$U(x) = U(x+a), \tag{7.25}$$

where a is the length of the **unit cell**.
It will now be shown that the solutions of (7.23) can always be chosen such that

$$\psi(x+a) = \lambda\psi(x) \tag{7.26}$$

or (after iteration)

$$\psi(x+na) = \lambda^n\psi(x). \tag{7.27}$$

If $\psi_1(x)$, $\psi_2(x)$ are two linearly independent solutions of (7.23) to the energy ϵ, then the functions $\psi_1(x+a)$, $\psi_2(x+a)$, which are also solutions of (7.23) to the energy ϵ due to the periodicity (7.25), can be represented as

$$\psi_1(x+a) = C_{11}\psi_1(x) + C_{12}\psi_2(x);$$

$$\psi_2(x+a) = C_{21}\psi_1(x) + C_{22}\psi_2(x). \tag{7.28}$$

To satisfy (7.26) we must diagonalize the matrix C_{ik}; the eigenvalues λ result from

$$(C_{11}-\lambda)(C_{22}-\lambda) - C_{12}C_{21} = \lambda^2 - (C_11 + C_22)\lambda - C_12C_21 + C_11C_22 = 0. \tag{7.29}$$

This is a quadratic equation for λ; about its solutions λ_1, λ_2 we can make the general statement:

$$\lambda_1\lambda_2 = 1. \tag{7.30}$$

We prove Eq. (7.30) using the Wronski determinant. Then for any two solutions ψ_1, ψ_2 of (7.23) for the same energy ϵ holds:

$$\psi_2\psi_1'' - \psi_1\psi_2'' = 0, \tag{7.31}$$

i.e., the Wronski determinant is constant

$$W(\psi_1,\psi_2) = \psi_2\psi_1' - \psi_1\psi_2' = \text{const}. \tag{7.32}$$

On the other hand, (7.28) gives

$$W(\psi_1(x+a),\psi_2(x+a)) = W(\psi_1(x),\psi_2(x)) \begin{pmatrix} C_{11} & C_{12} \\ C_{21} & C_{22} \end{pmatrix} \tag{7.33}$$

leading to

$$C_{11}C_{22} - C_{12}C_{21} = 1 = \lambda_1\lambda_2. \tag{7.34}$$

The only physically interesting solutions are those for which $|\lambda| = 1$, otherwise—due to (7.27)—ψ would grow beyond all limits for $x \to \pm\infty$. Therefore we can write the solutions as

$$\lambda_1 = \exp\,(ika);\ \lambda_2 = \exp\,(-ika);\ k\,\text{real}. \tag{7.35}$$

Writing the phase in (7.35) as $\varphi = ka$ is reasonable in view of

$$\tau(a)\psi = \exp\,(-\tfrac{i}{\hbar}ap_x)\psi = \lambda\psi. \tag{7.36}$$

Obviously, it is sufficient to consider values *k* in the interval

$$-\tfrac{\pi}{a} \le k \le \tfrac{\pi}{a}. \tag{7.37}$$

We thus have shown that all (physically meaningful) solutions from (7.23) can be chosen such that

$$\psi(x+na) = \exp\,(i\ nka)\psi(x) \tag{7.38}$$

with $n = 0, \pm1, \pm2, \pm3, \ldots$. ψ then must have the following structure:

$$\psi(x) = \exp\,(ikx)v_k(x) \tag{7.39}$$

with

$$v_k(x) = v_k(x+a). \tag{7.40}$$

The statement formulated in (7.39) and (7.40) is called **Bloch's theorem**.

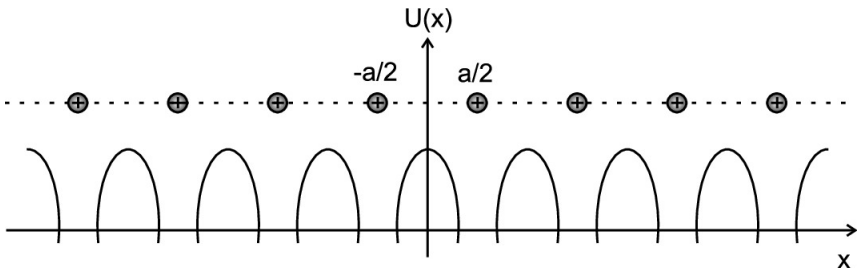

Fig. 7.8 Periodic potential for the case of a crystal in the direction of symmetry

The most simple model for the motion of an electron in the lattice of a crystal is the assumption of a spatially constant potential *U*, which can be obtained by averaging over the periodic potential assumed above (Fig. 7.8). The solutions for the constant potential are

$$\psi_0(x) = \exp\,(ikx) \tag{7.41}$$

with *k* from (7.37). If we compare with (7.39)–(7.40), we may interpret the Bloch function as grid-periodically modulated plane waves.

For an infinitely extended crystal the possible *k* values are continuous in the interval (7.37). In case of a finite crystal we account for the periodic boundary conditions (see Sect. 6.3.5) and obtain (choosing the boundary points to be symmetrical to $x = 0$)

$$\exp\,\left(ik\left(x - \tfrac{L}{2}\right)\right) v_k\left(x - \tfrac{L}{2}\right) = \exp\,\left(ik\left(x + \tfrac{L}{2}\right)\right) v_k\left(x + \tfrac{L}{2}\right) \tag{7.42}$$

for $L = na$ (length of the crystal), according to the Bloch theorem

$$\exp\,(ikL) = 1 \;\;\Rightarrow\;\; k = \tfrac{2\pi n}{L} \,\text{for integers n.} \tag{7.43}$$

We then obtain discrete *k* values in the interval (7.37) (**1. Brillouin zone**).

7.3.3 Energy Bands

We choose the coordinate origin such that

$$U(x) = U(-x). \tag{7.44}$$

With $\psi(x)$ then also $\psi(-x)$ is a solution of (7.23) to the energy ϵ such that the functions

$$\psi_\pm(x) = \psi(x) \pm \psi(-x) \tag{7.45}$$

are also solutions for the same energy (solutions with **positive and negative parity**). Any Bloch solution ψ_B (with the property (7.38)) we then can write as a linear combination of ψ_+ and ψ_-:

$$\psi_B(x) = A\;\psi_+(x) + B\;\psi_-(x). \tag{7.46}$$

Together with (7.38) the continuity of ψ_B, ψ_B' at the edge points of the unit cell, e.g. $x = \pm\left(\frac{a}{2}\right)$ requires:

$$\psi_B\left(\tfrac{a}{2}\right) = \exp\,(ika)\;\psi_B\left(-\tfrac{a}{2}\right) \tag{7.47}$$

and

$$\psi_B'\left(\tfrac{a}{2}\right) = \exp\,(ika)\;\psi_B'\left(-\tfrac{a}{2}\right). \tag{7.48}$$

Inserting (7.46) in (7.47), (7.48) and considering

(7.49)

$$\psi_+\left(\tfrac{a}{2}\right) = \psi_+\left(\tfrac{a}{2}\right); \psi_-\left(\tfrac{a}{2}\right) = -\psi_-\left(-\tfrac{a}{2}\right),$$

we get

$$A[1-\exp(ika)]\psi_+\left(\tfrac{a}{2}\right) + B[1+\exp(ika)]\psi_-\left(\tfrac{a}{2}\right) = 0 \tag{7.50}$$

$$[A[1+\exp(ika)]\psi'_+\left(\frac{a}{2}\right) + B[1-\exp(ika)]\psi'_-\left(\frac{a}{2}\right) = 0.$$

Here we have used

$$\psi'_\pm(x) = \tfrac{d}{dx}\{\psi(x) \pm \psi(-x)\} \tag{7.51}$$

as well as the fact that d/dx is odd in the transformation $x \to -x$. The condition for a solution of (7.50) is:

$$[1-\exp(ika)]^2\psi_+\left(\tfrac{a}{2}\right)\psi'_-\left(\tfrac{a}{2}\right) = [1+\exp(ika)]^2\psi'_+\left(\tfrac{a}{2}\right)\psi_-\left(\tfrac{a}{2}\right). \tag{7.52}$$

If we introduce the Wronski determinant at the position $a/2$,

$$W = \psi_+\left(\tfrac{a}{2}\right)\psi'_-\left(\tfrac{a}{2}\right) - \psi'_+\left(\tfrac{a}{2}\right)\psi_-\left(\tfrac{a}{2}\right), \tag{7.53}$$

Eq. (7.52) turns to

$$[1-\exp(ika)]^2 = 4\exp(ika)\psi'_+\left(\tfrac{a}{2}\right)\psi_-\left(\tfrac{a}{2}\right)/W \tag{7.54}$$

or

$$\cos(ka) = 2\ \psi'_+\left(\tfrac{a}{2}\right)\ \psi_-\left(\tfrac{a}{2}\right)/W + 1. \tag{7.55}$$

The right side of (7.55) depends on the energy ϵ, to which ψ_+, ψ_- are solutions of the Schrödinger equation. We can also write (7.55) as

$$\cos(ka) = f(\epsilon). \tag{7.56}$$

Now since $-1 \leq \cos(ka) \leq +1$, only such values ϵ are possible as solutions of (7.23) with

$$-1 \leq f(\epsilon) \leq +1. \tag{7.57}$$

Since the solutions of (7.23) are continuous in ϵ the function $f(\epsilon)$ will also be a continuous function of ϵ. It can therefore—depending on the specific form of $f(\epsilon)$—give related energy ranges for which (7.57) is fulfilled (**permitted energy bands**), as well as those for which (7.57) is not fulfilled (**forbidden energy bands**). A typical case is shown in Fig. 7.9.

Whereas any energy is possible for free electrons, the periodic potential modifies the spectrum to a sequence of permitted and forbidden energy bands.

7.3.4 Periodic Box Potential

As an example for the general considerations above we consider the following (analytically solvable) potential:

$$U(x) = U_0 \text{for} -\tfrac{\mathrm{b}}{2} \leq \mathrm{x} \leq \tfrac{\mathrm{b}}{2} \tag{7.58}$$

$$U(x) = 0 \text{for} -\frac{\mathrm{a}}{2} \leq \mathrm{x} \leq -\frac{\mathrm{b}}{2} \text{and} \frac{\mathrm{b}}{2} \leq \mathrm{x} \leq \frac{\mathrm{a}}{2}$$

with (see Fig. 7.10)

$$U(x + a) = U(x). \tag{7.59}$$

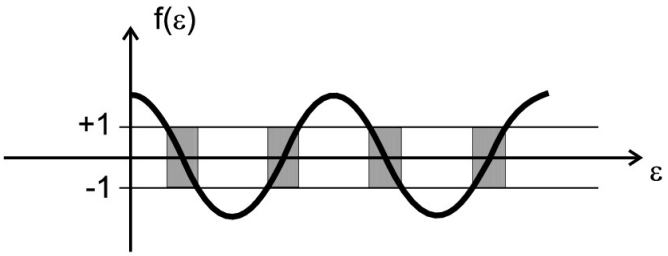

Fig. 7.9 Energy bands in crystals (allowed areas hatched)

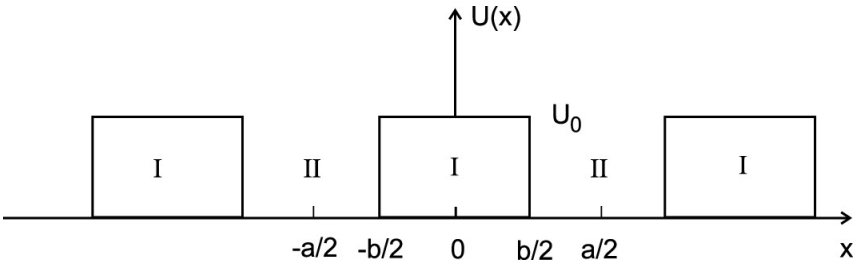

Fig. 7.10 Illustration of the periodic box potential discussed in the text

The solutions of (7.23) in the area I ($E < V_0$) are:

$$\psi_{\pm}^{I} = \exp\,(\kappa x) \pm \exp\,(-\kappa x) \tag{7.60}$$

with the abbreviation

$$\kappa^2 = \tfrac{2m}{\hbar^2}(V_0 - E) = U_0 - \epsilon; \tag{7.61}$$

the general Bloch solution in the area I then is (according to (7.57)):

$$\psi^{I}(x) = 2\{A_I \cosh\,(\kappa x) + B_I \sinh\,(\kappa x)\}. \tag{7.62}$$

In region II

(7.63)

$$\psi_{\pm}^{II}(x) = \exp(ikx) \pm \exp(-ikx)$$

with

$$k^2 = \frac{2m}{\hbar^2}E = \epsilon, \tag{7.64}$$

thus:

$$\psi^{II}(x) = 2\{A_{II}\cos(kx) + i\ B_{II}\sin(kx)\} = A_{II}\psi_+(kx) + B_{II}\psi_-(kx). \tag{7.65}$$

The conditions (7.47), (7.48) only refer to $\psi^{II}(x)$ and its derivative:

$$\psi^{II}\left(\tfrac{a}{2}\right) = \exp(ika)\ \psi^{II}\left(-\tfrac{a}{2}\right) \tag{7.66}$$

and

$$\psi^{II'}\left(\tfrac{a}{2}\right) = \exp(ika)\ \psi^{II'}\left(-\tfrac{a}{2}\right). \tag{7.67}$$

In addition we have the continuity of ψ, ψ' at $x = b/2$ as the connection between areas I and II,

$$\psi^{II}\left(\tfrac{b}{2}\right) = \psi^{I}\left(\tfrac{b}{2}\right) \tag{7.68}$$

and

$$\psi^{II'}\left(\tfrac{b}{2}\right) = \psi^{I'}\left(\tfrac{b}{2}\right). \tag{7.69}$$

This gives 4 homogeneous equations for the 4 unknowns A_I, B_I, A_{II}, B_{II}. In order to obtain a non-trivial solution for this system of equations its determinant must disappear. The result (after some lengthy calculation) is:

$$\cos(ka) = \cosh(\kappa b)\cos(k[a-b]) + \frac{\kappa^2 - k^2}{2\kappa k}\sinh(\kappa b)\sin(k[a-b]) = f(\epsilon), \tag{7.70}$$

and the right side of (7.70) gives the function $f(\epsilon)$ from (7.56) (see Fig. 7.9).

7.4 The Harmonic Oscillator

7.4.1 One-Dimensional Case

We are looking for the eigenvalues of the Hamilton operator

$$H = \frac{1}{2m}p_x^2 + \frac{1}{2}\ m\ \omega^2 x^2 \tag{7.71}$$

and the associated eigenfunctions. For the solution of the eigenvalue equation

(7.72)

$$H\ \psi_\lambda = E_\lambda \psi_\lambda$$

we proceed in analogy to Sect. 6.4: instead of p_x and x with

$$[p_x, x] = \tfrac{\hbar}{i} \tag{7.73}$$

we use the operators

$$a = \sqrt{\tfrac{m\omega}{2\hbar}}\, x + i \tfrac{1}{\sqrt{2\hbar m\omega}}\, p_x; \tag{7.74}$$

$$a^\dagger = \sqrt{\frac{m\omega}{2\hbar}}\, x - i \frac{1}{\sqrt{2\hbar m\omega}}\, p_x,$$

for which follows from (7.73)

$$[a, a^\dagger] = 1. \tag{7.75}$$

The inverse of (7.74) gives

$$\tfrac{1}{2}(a + a^\dagger)\sqrt{\tfrac{2\hbar}{m\omega}} = x, \qquad -\tfrac{i}{2}(a - a^\dagger)\sqrt{2\hbar m\omega} = p_x. \tag{7.76}$$

The Hamiltonian H can be expressed in the operators a, $a^\dagger$ and achieves the simple form:

$$H = \tfrac{p_x^2}{2\,m} + \tfrac{m}{2}\omega^2 x^2 = \hbar\omega\big(a^\dagger a + \tfrac{1}{2}\big). \tag{7.77}$$

We now determine the spectrum of the operator

$$N = a^\dagger a \tag{7.78}$$

according to Sect. 6.4 by computing the commutation relations

$$[N, a] = -a \tag{7.79}$$

$$[N, a^\dagger] = a^\dagger \tag{7.80}$$

that follow directly from (7.75) and the definition (7.78).

We now assume that we have found a normalized eigenfunction ψ_λ with eigenvalue λ of the operator N (note $[H, N] = 0$) :

$$N\ \psi_\lambda = \lambda\ \psi_\lambda \quad \text{with}\ \ (\psi_\lambda, \psi_\lambda) = 1. \tag{7.81}$$

Then by applying a $(a^\dagger)$ to ψ_λ we can decrease (increase) the eigenvalue by one:

$$N(a\psi_\lambda) = a(N-1)\psi_\lambda = (\lambda - 1)(a\psi_\lambda). \tag{7.82}$$

For the norm of $(a\psi_\lambda)$ follows:

$$(a\psi_\lambda, a\psi_\lambda) = (\psi_\lambda, a^\dagger a\psi_\lambda) = \lambda, \tag{7.83}$$

if one exploits the hermiticity of x and p_x and the definition (7.74). In analogy we get:

$$N(a^\dagger\psi_\lambda) = (\lambda + 1)(a^\dagger\psi_\lambda) \tag{7.84}$$

with

$$(a^\dagger\psi_\lambda, a^\dagger\psi_\lambda) = \lambda + 1. \tag{7.85}$$

Since the norm of $a\psi_\lambda$ cannot be negative, the eigenvalue must be $\lambda \geq 0$ due to (7.83). By applying $a^\dagger$ to ψ_λ repeatedly we get normalizable eigenfunctions of N with the eigenvalues $\lambda + 1$, $\lambda + 2$, $\lambda + 3, \ldots$; there is no upper limit to the spectrum. Downwards, however, there is a limit: a μ times application of a to ψ_λ results in

$$(a^\mu\psi_\lambda, a^\mu\psi_\lambda) = \lambda(\lambda-1)(\lambda-2)\cdots(\lambda-\mu+1). \tag{7.86}$$

Since the left side in (7.86) cannot become negative, λ must be an integer (non-negative) number, such that the sequence

$$\psi_\lambda, a\psi_\lambda, a^2\psi_\lambda, \ldots \tag{7.87}$$

after $\mu = \lambda$ steps stops,

$$a^{\lambda+1}\psi_\lambda = 0; \quad \lambda = 0, 1, 2, 3, \ldots \tag{7.88}$$

Thus the operator N has the eigenvalues

$$n = 0, 1, 2, 3, \ldots, \tag{7.89}$$

such that we get an equidistant spectrum for H that is unlimited upwards:

$$E_n = \hbar\omega\left(n + \tfrac{1}{2}\right);\ n = 0, 1, 2, 3, \ldots \tag{7.90}$$

The operator N has the property of counting the excitations of energy $\hbar\omega$, which a certain oscillator state ψ_n contains. The state of lowest energy—the **ground state**—has the energy

$$E_0 = \tfrac{1}{2}\hbar\omega \tag{7.91}$$

(zero point energy) and can be characterized by

$$a\psi_0 = 0. \tag{7.92}$$

The occurrence of the zero point energy (7.91) is typical for quantum theory and a direct consequence of the non-commutability of x and p_x and thus the position-momentum uncertainty: classically the oscillator may have the momentum $(p_x)_{kl.} = 0$ at $x_{kl.} = 0$ (rest position).

Starting from the ground state ψ_0, whose existence we will show in Sect. 7.4.2 in the form of a spatial representation, the excited states can be constructed as

$$a^\dagger\psi_0,\ \ a^{\dagger 2}\psi_0, \ldots,\ \ a^{\dagger n}\psi_0, \ldots \tag{7.93}$$

The operator $a^\dagger$ therefore generates excitations of the oscillator energy $\hbar\omega$—it is therefore denoted as **creation operator**—. Conversely, the **annihilation operator** a leads from a state with the excitation energy $n\hbar\omega$ to an energetically lower state with exitation energy $(n-1)\hbar\omega$.

If ψ_0 is normalized,

$$(\psi_0, \psi_0) = 1, \tag{7.94}$$

we get by iteration of (7.85)

$$(a^{\dagger n}\psi_0, a^{\dagger n}\psi_0) = 1 \cdot 2 \cdot 3 \cdots = n!; \tag{7.95}$$

Thus the normalized eigenfunctions are:

$$\psi_n = \tfrac{1}{\sqrt{n!}}(a^\dagger)^n\psi_0. \tag{7.96}$$

In this normalization we get (except for an insignificant phase factor):

$$a^\dagger\psi_n = \sqrt{n+1}\psi_{n+1}; a\psi_n = \sqrt{n}\psi_{n-1}. \tag{7.97}$$

7.4.2 Spatial Representation

We first determine the ground state wave function $\psi_0(x)$, which is defined by (7.92), i.e.

$$a\psi_0 = \left\{ \sqrt{\tfrac{m\omega}{2\hbar}}\, x + \sqrt{\tfrac{\hbar}{2\,m\omega}}\, \tfrac{d}{dx} \right\} \psi_0 = 0. \tag{7.98}$$

With the dimensionless coordinate

$$\xi = \sqrt{\tfrac{m\omega}{\hbar}}\, x \tag{7.99}$$

we get from (7.98)

$$\left\{ \tfrac{d}{d\xi} + \xi \right\} \psi_0(\xi) = 0 \tag{7.100}$$

with the solution

$$\psi_0(\xi) = c_0 \, \exp\, (-\tfrac{1}{2}\ \xi^2). \tag{7.101}$$

For the normalization

$$\int_{-\infty}^{\infty} |\psi_0|^2 dx = 1, \tag{7.102}$$

the constant c_0 (with $\int \exp\,(-\xi^2) d\xi = \sqrt{\pi}$) amounts to:

$$c_0^2 = \sqrt{\tfrac{m\omega}{\pi\hbar}}. \tag{7.103}$$

To determine the eigenfunctions of the excited states we express $a^\dagger$ in terms of ξ and $d/d\xi$:

$$a^\dagger = \tfrac{1}{\sqrt{2}} \left(\xi - \tfrac{d}{d\xi} \right) \tag{7.104}$$

and obtain (taking into account (7.96)):

$$\psi_n = \tfrac{c_0}{\sqrt{n! 2^n}} ((\xi - \tfrac{d}{d\xi})^n \, \exp\, (-\tfrac{\xi^2}{2})). \tag{7.105}$$

Then

$$\psi_n \sim \psi_0 \cdot (\text{polynomial of degree n}), \tag{7.106}$$

where even and odd polynomials alternate, i.e. ψ_n has positive parity for *n* even and negative parity for *n* odd (see Fig. 7.11). The lowest order **Hermite polynomials** read:

(7.107)

$$H_0(x) = 1$$

$$H_1(x) = 2x$$

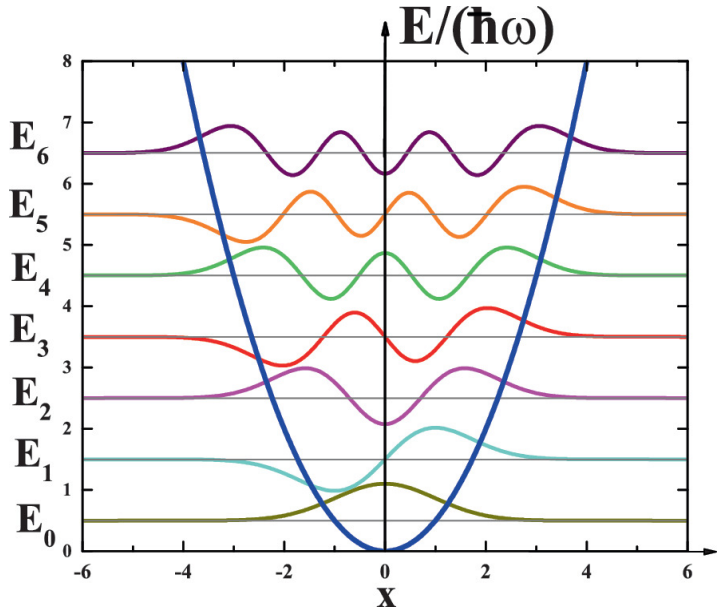

Fig. 7.11 Illustration of the oscillator wave functions and the associated energy levels

$$H_2(x) = 4x^2 - 2$$

$$H_3(x) = 8x^3 - 12x$$

$$H_4(x) = 16x^4 - 48x^2 + 12$$

and follow the recursion relation:

$$H_{n+1}(x) = 2xH_n(x) - 2nH_{n-1}(x). \tag{7.108}$$

The orthogonality of the wavefunctions follows from the hermiticity of H

$$(\psi_n, \psi_m) = \delta_{nm}; \tag{7.109}$$

for the proof see Sect. 4.3.

Addition: The functions (7.105) also form a complete basis in the space of square-integrable functions (which we do not want to prove explicitly).

7.4.3 Three-Dimensional Case

We consider the Hamilton operator

$$H = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + \frac{m}{2}(\omega_x^2 x^2 + \omega_y^2 y^2 + \omega_z^2 z^2), \tag{7.110}$$

where in general $\omega_x \neq \omega_y \neq \omega_z$. Since H obviously decouples in the coordinates x, y, z,

$$H = H_x + H_y + H_z, \tag{7.111}$$

we can solve the eigenvalue problem of H by the **separation Ansatz**

$$\psi(\mathbf{r}) = \psi_1(x)\psi_2(y)\psi_3(z) \tag{7.112}$$

and employ the solutions for the one-dimensional case. For the energy eigenvalues of H we get:

$$E_{n_1 n_2 n_3} = \hbar\{\omega_x(n_1 + \tfrac{1}{2}) + \omega_y(n_2 + \tfrac{1}{2}) + \omega_z(n_3 + \tfrac{1}{2})\} \tag{7.113}$$

with $n_i = 0, 1, 2, ...$

The separation process above can also be carried out in the case that the potential energy has a positive-definite, quadratic form in x, y, z, also containing mixed terms in xy. By an axis transformation one can then always achieve the form (7.110) in the new coordinates.

As long as $\omega_x \neq \omega_y \neq \omega_z$ and the particle under consideration has no internal degree of freedom (like e.g. spin), the spectrum of H from (7.110) is not degenerate, if one disregards so-called random degeneracies, that may occur for certain states (i.e. certain values n_1, n_2, n_3) depending on the ratio $\omega_x : \omega_y : \omega_z$. In contrast, the three-dimensional

7.4.4 Isotropic Oscillator

has a degenerate spectrum. With

$$\omega_x = \omega_y = \omega_z \equiv \omega \tag{7.114}$$

(7.113) becomes

$$E_{n_1 n_2 n_3} = \hbar\omega(n + \tfrac{3}{2}) = E_n \tag{7.115}$$

with

$$n = n_1 + n_2 + n_3. \tag{7.116}$$

The same energy E_n can obviously be achieved in different ways. One finds for the degree of degeneracy

$$g_n = \tfrac{1}{2}(n+1)(n+2), \tag{7.117}$$

since by choosing one of the numbers from 0 to *n* for n_1, then n_2 runs between 0 and $(n - n_1)$. This gives $(n - n_1 + 1)$ possible realizations of (7.116). This leads to

$$g_n = \sum_{n_1=0}^{n}(n - n_1 + 1) = \frac{1}{2}(n + 1)(n + 2). \tag{7.118}$$

Instead of classifying the isotropic oscillator according to the quantum numbers n_1, n_2, n_3 w.r.t. cartesian coordinates, we can also use the angular momentum quantum numbers *l*, *m*, since for

$$H = \frac{1}{2\,m}p^2 + \frac{m}{2}\ \omega^2 r^2 \tag{7.119}$$

the commutation rules

$$[H, l_i] = 0;\ i = x, y, z \tag{7.120}$$

hold. We can thus choose the eigenfunctions of *H* in such a way that they – at the same time – are eigenfunctions of l^2 and l_z. To this aim (for fixed E_n) we just have to form suitable linear combinations of degenerate functions in the cartesian basis (7.112). We then get instead of $\psi_{n_1 n_2 n_3}(x, y, z)$ eigenfunctions $\psi_{\nu l m}(r, \vartheta, \varphi)$, which are determined by the quantum numbers *l*, *m* of angular momentum as well as the one resulting from the degree of freedom *r* which is denoted by the **radial quantum number** ν.

7.4.5 Good Quantum Numbers

The quantum numbers n_1, n_2, n_3 completely characterize spinless particles or ν, *l*, *m* the eigenstates of the isotropic, harmonic oscillator in the respective representation. Such quantum numbers, which belong to conserved quantities of the system and commute, are denoted by **good quantum numbers**. If the particle moving in the oscillator potential has spin 1/2, then e.g. the *z* component of the spin is also a good quantum number, since trivially

$$[H, S_z] = 0 \tag{7.121}$$

as well as

$$[l_i, S_z] = 0. \tag{7.122}$$

The degree of degeneracy g_n from (7.117) then has to be multiplied by a factor of 2 corresponding to the 2 possible eigenvalues of S_z.

In the following we will make extensive use of the concept of **good quantum numbers** by first finding the commuting conserved quantities for each problem. This already leads to a partial classification of the intrinsic states of the system under consideration.

7.5 Spatially Constant Magnetic Field

For a spatially constant magnetic field $\mathbf{B}$ the Pauli equation (with $\Phi \equiv 0$)

$$i\hbar\frac{\partial}{\partial t}\ \Psi = \frac{1}{2\,m}\left(\mathbf{p} - \frac{e}{c}\mathbf{A}\right)^2\Psi - \frac{e}{mc}\ \mathbf{S}\cdot\mathbf{B}\ \Psi \tag{7.123}$$

can be rewritten with the separation Ansatz

$$\Psi(\mathbf{r};t) = \psi(\mathbf{r};t)\chi(t) \tag{7.124}$$

with

$$\chi(t) = a(t)\ \begin{pmatrix}1\\0\end{pmatrix}\ + b(t)\ \begin{pmatrix}0\\1\end{pmatrix} \tag{7.125}$$

as

$$i\hbar\frac{\partial}{\partial t}\ \psi = \frac{1}{2\,m}\left(\mathbf{p} - \frac{e}{c}\mathbf{A}\right)^2\psi + \gamma\psi \tag{7.126}$$

and

$$i\hbar\frac{\partial}{\partial t}\ \chi(t) = -\frac{e\hbar}{2mc}\boldsymbol{\sigma}\cdot\mathbf{B}\ \chi(t) - \gamma\chi(t) \tag{7.127}$$

with an arbitrary constant γ. For the proof one multiplies (7.126) with χ and (7.127) with ψ and adds the resulting equations. The term with $\gamma\chi\psi$ then is eliminated by the addition and one gets (7.123).

The constant γ has no physical meaning and without loosing generality can be set to zero, since with the Ansatz

$$\psi = \exp\left(\frac{i}{\hbar}\gamma t\right)\tilde{\psi}, \tag{7.128}$$

$$\chi = \exp\left(-\frac{i}{\hbar}\gamma t\right)\tilde{\chi} \tag{7.129}$$

the overall wave function

$$\Psi(\mathbf{r};t) = \psi\ \chi = \tilde{\psi}\tilde{\chi} \tag{7.130}$$

does not change and γ no longer appears in the differential equations for $\tilde{\psi}, \tilde{\chi}$. In the following we will thus always use $\gamma = 0$.

We write the vector potential $\mathbf{A}$ in the form

(7.131)

$$\mathbf{A} = \tfrac{1}{2}(\mathbf{B} \times \mathbf{r}),$$

where $\mathbf{B}$ can still be time-dependent:

$$\mathbf{B} = \mathbf{B}(t). \tag{7.132}$$

The Ansatz (7.131) leads to the gauge:

$$\overrightarrow{\nabla} \cdot \mathbf{A} = 0. \tag{7.133}$$

In the following we will examine two cases that are of practical importance:
(i) the (temporally and spatially) constant magnetic field $\mathbf{B}$,
(ii) the time-periodic field $\mathbf{B}$.
According to (7.126) and (7.127) we can calculate the spatial motion (i.e. $\psi(\mathbf{r};t)$) and the time evolution of the spin (via $\chi(\mathbf{r};t)$) separately.

7.5.1 Stationary States in a Constant Magnetic Field

We fix the coordinate origin such that

$$\mathbf{A} = \begin{pmatrix} -By \\ 0 \\ 0 \end{pmatrix}. \tag{7.134}$$

This choice is of advantage for computational reasons, although it does not account for the axial symmetry of the problem given by the form of $\mathbf{B}$,

$$\mathbf{B} = \overrightarrow{\nabla} \times \mathbf{A} = \begin{pmatrix} 0 \\ 0 \\ B \end{pmatrix}. \tag{7.135}$$

With (7.134) or (7.135) equation (7.127) gets the form:

$$i\hbar \tfrac{\partial}{\partial t}\ \chi = -\tfrac{e\hbar}{2mc}\sigma_z B\chi. \tag{7.136}$$

By the Ansatz for stationary solutions

$$\chi = \exp\left(-\tfrac{i}{\hbar}\epsilon_s t\right)\chi_0 \tag{7.137}$$

with

$$\chi_0 = a_0\begin{pmatrix}1\\0\end{pmatrix} + b_0\ \begin{pmatrix}0\\1\end{pmatrix} \tag{7.138}$$

and normalization

$$|a_0|^2 + |b_0|^2 = 1 \tag{7.139}$$

(7.136) turns to the eigenvalue problem

$$\epsilon_s \chi_0 = -\frac{e\hbar}{2mc} B\sigma_z \chi_0. \tag{7.140}$$

The solutions are known from chapter 6.5:
(i) $a_0 = 1; b_0 = 0 \Rightarrow$

$$\chi_0 = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \text{with} \, \epsilon_s = -\frac{\mathrm{eB}\,\hbar}{2\,\mathrm{mc}} \tag{7.141}$$

(ii) $a_0 = 0; b_0 = 1 \Rightarrow$

$$\chi_0 = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \text{with} \;\; \epsilon_s = +\frac{\mathrm{eB}\,\hbar}{2\,\mathrm{mc}}. \tag{7.142}$$

The stationary solutions of (7.126) follow from

$$\epsilon\varphi = \frac{1}{2\,m}\left\{\left(p_x + \frac{e}{c}\;By\right)^2 + p_y^2 + p_z^2\right\}\varphi, \tag{7.143}$$

with

$$\psi(\mathbf{r};t) = \exp\left(-\frac{i}{\hbar}\epsilon t\right)\varphi(\mathbf{r}). \tag{7.144}$$

The Hamiltonian of orbital motion (righthand side of (7.143)) commutes with p_x and p_z, since it only explicitly contains the coordinate y. The eigenvalues of p_x and p_z hence are good quantum numbers, according to which we can find the solutions (7.143). These, as well as the eigenfunctions, are known from section 6.3.3. For $\varphi(\mathbf{r})$ we can employ the Ansatz:

$$\varphi(\mathbf{r}) = \exp\,(i(k_x x + k_z z))\tilde{\varphi}(y). \tag{7.145}$$

We then get from (7.143) an equation in the single variable (y) :

$$\left[\frac{p_y^2}{2\,m} + \frac{m}{2}\;\omega^2(y + y_0)^2\right]\tilde{\varphi} = \left[\epsilon - \hbar^2\frac{k_z^2}{2\,m}\right]\tilde{\varphi} \tag{7.146}$$

with the abbreviations

$$\omega = \frac{eB}{mc}; y_0 = \frac{\hbar k_x c}{eB}. \tag{7.147}$$

Apart from the displacement y_0, which is insignificant for the determination of the eigenvalues, (7.146) represents the eigenvalue problem of a linear harmonic oscillator with the frequency $\omega = \frac{eB}{mc}$ (**Larmor frequency**). We can immediately specify the eigenvalues (**Landau levels**):

$$\epsilon_{n,k_z} = \frac{\hbar^2 k_z^2}{2m} + \frac{e\hbar}{mc} B\left(n + \tfrac{1}{2}\right), \quad n = 0, 1, 2, \ldots; \tag{7.148}$$

they are ∞—fold degenerate because the eigenfunctions $\tilde{\varphi}$ belong to the same eigenvalue (7.148) regardless of the value y_0.

To interpret the solutions of (7.143) we recall the solution of the classical problem: a charged particle in the constant $\mathbf{B}$ field moves on spirals whose axis—for the choice (7.135)—points in the *z* direction and whose projections onto the $x - y$ plane are circles. The classical particle moves straight in *z*-direction; quantum mechanically this corresponds to the plane wave $\exp(ik_z z)$. The circular orbits in the $x - y$ plane we can decompose into 2 harmonic oscillations in $x-$ and $y-$ direction with the same frequency $\omega = \frac{eB}{mc}$ and a phase shift of $\pi/2$.

The quantum mechanical solution (7.145) corresponds to the *y* coordinate of the classical motion: we have bound states in the form of harmonic vibrations. With regards to the *x* coordinate, the solution (7.145) excludes a spatial localization (contrary to the classical case) because in (7.145) the momentum p_x is sharp and therefore the coordinate *x* completely undetermined due to the uncertainty relation. The solution of (7.143) corresponds to, for a fixed value of *n* (fixed energy) and fixed displacement y_0, a family of classical orbits with a fixed radius and centers $y = y_0$ (see Fig. 7.12).

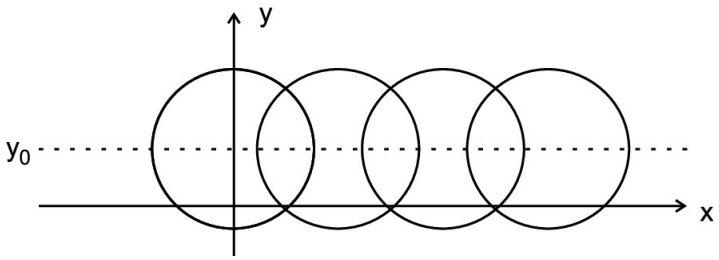

Fig. 7.12 Illustration of the solution to (7.145)

If we want to achieve a symmetric treatment of the problem with respect to *x*, *y*, we have to use (instead of (7.134))

$$\mathbf{A} = \frac{1}{2} \begin{pmatrix} -By \\ Bx \\ 0 \end{pmatrix}, \tag{7.149}$$

which also leads to (7.135) for $\mathbf{B}$. The Hamiltonian for the path motion then is:

$$H = \frac{1}{2m}(p_x^2 + p_y^2) + \frac{1}{2}\ m\Big(\frac{eB}{2mc}\Big)^2(x^2 + y^2) + \frac{p_z^2}{2m} + \frac{eB}{2mc}l_z. \tag{7.150}$$

The Hamilton operator therefore consists of a 2-dim. isotropic oscillator in the $x-y$ plane, the kinetic energy in the z direction and the energy of the orbital motion of the magnetic moment in the $\mathbf{B}$ field.

Instead of looking for the stationary solutions (7.126) and (7.127), we can also directly transfer (7.123) with the Ansatz

$$\Psi(\mathbf{r};t) = \exp\left(-\frac{i}{\hbar}Et\right)\Phi(\mathbf{r}) \tag{7.151}$$

to the time-independent Pauli equation

$$\left\{\frac{1}{2m}\left(\mathbf{p} - \frac{e}{c}\mathbf{A}\right)^2 - \frac{e}{mc}\ \mathbf{S}\cdot\mathbf{B}\right\}\Phi = E\Phi. \tag{7.152}$$

We know the solutions after the investigations above:

$$\Phi(\mathbf{r}) = \varphi(\mathbf{r})\chi_0 \tag{7.153}$$

with the eigenvalues:

$$E = \epsilon + \epsilon_s, \tag{7.154}$$

with ϵ from (7.148) and ϵ_s from (7.141) or (7.142).

7.5.2 Spin Precession

After having determined the stationary solutions of (7.123) in Sect. 7.5.1 we now turn to the time evolution of the spin. Let $\mathbf{B}$ be constant and chosen according to (7.135). We now use Ehrenfest's theorem, which for particles with spin 1/2 can be proven in the same way as for particles without spin in Sect. 5.3. If $\Psi(\mathbf{r};t)$ is a solution of the Pauli equation, then for the temporal change in the expectation value of $\mathbf{S}$ in the state Ψ we get:

$$\frac{d}{dt} < \mathbf{S} >= \frac{i}{\hbar} < [H, \mathbf{S}] > + < \frac{\partial}{\partial t}\ \mathbf{S} >= \frac{i}{\hbar} < [H, \mathbf{S}] >. \tag{7.155}$$

For the commutator $[H, \mathbf{S}]$ the following holds (for any magnetic field $\mathbf{B}$)

$$[H, \mathbf{S}] = -\frac{e}{mc}[\mathbf{S} \cdot \mathbf{B}, \mathbf{S}]; \tag{7.156}$$

this expression is simplified by specifying $\mathbf{B}$ according to (7.135),

$$[H, \mathbf{S}] = -\frac{eB}{mc}[S_z, \mathbf{S}]. \tag{7.157}$$

With (7.157) we immediately get

$$\frac{d}{dt} < S_z >= 0, \tag{7.158}$$

thus

$$< S_z >= \text{const.} \tag{7.159}$$

For the *x* and *y* components we have (6.206) and $[S_i, S_j] = i\hbar\epsilon_{ijk}S_k$:

$$\frac{d}{dt} < S_x >= \frac{eB}{mc} < S_y > \tag{7.160}$$

$$\frac{d}{dt} < S_y >= -\frac{eB}{mc} < S_x >. \tag{7.161}$$

A further differentiation with respect to *t* gives the decoupled equations:

$$\frac{d^2}{dt^2} < S_x >= -\omega^2 < S_x > \tag{7.162}$$

$$\frac{d^2}{dt^2} < S_y >= -\omega^2 < S_y > \tag{7.163}$$

with ω from (7.147). With the initial condition

$$< S_x >_{t=0}= \frac{1}{2}; \quad < S_y >_{t=0}=< S_z >_{t=0}= 0 \tag{7.164}$$

the solution to (7.162), (7.163) is:

$$< S_x >= \frac{1}{2} \cos(\omega t); < S_y >= -\frac{1}{2} \sin(\omega t); < S_z >= 0 \tag{7.165}$$

consistent with (7.160) and (7.161). The expectation value of the spin therefore leads to a **precession** around the direction of $\mathbf{B}$ with frequency ω; in the general case $< S_z >$ = const. $\neq 0$.

An important application of **spin precession** is the measurement of the magnetic moment of elementary particles, e.g. electrons, protons, etc.

7.5.3 Spin Resonance

As a second example for the time evolution of spin we consider a spatially constant, however, oscillating magnetic field of the form:

$$\mathbf{B}(\mathbf{r};t) = \begin{pmatrix} B_1 \cos(\omega_a t) \\ -B_1 \sin(\omega_a t) \\ B_0 \end{pmatrix}. \tag{7.166}$$

To solve equation (7.136) we note that the magnetic field (7.166) for an observer in a moving coordinate system, which rotates with the frequency ω_a around the z axis, appears constant in time. According to Sect. 6.4.3 the transition to a rotated coordinate system (moving by the angle $\varphi = \omega_a t$ around the z axis) is equivalent to a transformation of the wave function; this was used for the case of spinors specified in Sect. 6.5.4. The following holds for the spin component of the wave function $\Psi(\mathbf{r};t)$ for a rotation around the z axis by the angle $\varphi = \omega_a t$:

$$\chi'(t) = \exp\left(-\tfrac{i}{\hbar}\omega_a t\ S_z\right)\chi(t) = \textstyle\sum_{n=0}^{\infty} \frac{1}{n!}\left(-\tfrac{i}{\hbar}\omega_a t\ S_z\right)^n \chi(t); \tag{7.167}$$

for the time evolution of $\chi'(t)$ we expect—according to the considerations above—a differential equation which is represented by a $\mathbf{B}$ field that is constant in time.

In fact, the original differential equation

$$i\hbar\tfrac{\partial}{\partial t}\ \chi = -\tfrac{e\hbar}{2mc}\overrightarrow{\sigma}\cdot\mathbf{B}\ \chi \tag{7.168}$$

is transferred with the Ansatz

$$\chi(t) = \exp\left(+\tfrac{i}{2}\ \omega_a t\ \sigma_z\right)\chi'(t) \tag{7.169}$$

to

$$i\hbar\tfrac{\partial}{\partial t}\ \chi' = \tfrac{\hbar}{2}\{\sigma_z[\omega_a - \omega_0] + \sigma_x\omega_1\}\chi'. \tag{7.170}$$

Proof: With the abbreviation (for the 2×2 matrix)

$$U(t) = \exp\left(\tfrac{i}{2}\ \omega_a t\ \sigma_z\right) = \textstyle\sum_{n=0}^{\infty} \frac{1}{n!}\left(\tfrac{i}{2}\ \omega_a t\ \sigma_z\right)^n \tag{7.171}$$

the left side of (7.168) gives

$$i\hbar\frac{\partial}{\partial t}\{U(t)\chi'(t)\} = U(t)\Big\{i\hbar\frac{\partial}{\partial t}\ \chi' - \frac{\hbar}{2}\ \omega_a\sigma_z\chi'\Big\}. \tag{7.172}$$

To transform the right side of (7.168) we write

$$\overrightarrow{\sigma}\cdot\mathbf{B}\ U(t) = U(t)U^{-1}(t)\overrightarrow{\sigma}\cdot\mathbf{B}\hat{U}(t), \tag{7.173}$$

where the operator $U^{-1}(t)$ is the inverse to $U(t)$ and has the explicit form

$$U^{-1}(t) = \exp\ \Big(-\frac{i}{2}\ \omega_a t\ \sigma_z\Big). \tag{7.174}$$

To prove (7.173) we write

$$U(t) = \cos\ \Big(\frac{1}{2}\ \omega_a t\Big) + i\ \ \sin\ \Big(\frac{1}{2}\ \omega_a t\Big)\sigma_z, \tag{7.175}$$

(cf. (6.220)) and note that

$$\Big\{\cos\ \Big(\frac{\omega_a t}{2}\Big) + i\ \ \sin\ \Big(\frac{\omega_a t}{2}\Big)\sigma_z\Big\}\Big\{\cos\ \Big(\frac{\omega_a t}{2}\Big) - i\ \ \sin\ \Big(\frac{\omega_a t}{2}\Big)\sigma_z\Big\} \tag{7.176}$$

$$= \cos^2\ \left(\frac{\omega_a t}{2}\right) + \sin^2\ \left(\frac{\omega_a t}{2}\right) = 1.$$

We now compute

$$(\sigma_x B_x + \sigma_y B_y)U(t) = U^{-1}(t)(\sigma_x B_x + \sigma_y B_y) \tag{7.177}$$

and using (cf. (6.207))

$$\sigma_x\sigma_z = -\sigma_z\sigma_x; \tag{7.178}$$

with

$$\sigma_x\sigma_y = i\sigma_z\ \ (\text{cyclic}) \tag{7.179}$$

(cf. (6.205), (6.207)) we obtain:

$$U^{-1}(t)\{\sigma_x B_x + \sigma_y B_y\}U(t) = (\cos\ \tfrac{\varphi}{2} - i\ \sigma_z\ \sin\ \tfrac{\varphi}{2})^2(\sigma_x B_x + \sigma_y B_y) \tag{7.180}$$

$$= (\cos\ \varphi - i\ \sigma_z\ \sin\ \varphi)(\sigma_x\ \cos\ \varphi - \sigma_y\ \sin\ \varphi)B_1$$

$$= B_1\{\sigma_x(\cos^2\ \varphi + \sin^2\ \varphi) - \sigma_y(\cos\ \varphi\ \ \sin\ \varphi - \sin\ \varphi\ \ \cos\ \varphi)\} = B_1\sigma_x.$$

With the abbreviations

$$\omega_0 = \tfrac{eB_0}{mc}; \omega_1 = \tfrac{eB_1}{mc} \tag{7.181}$$

we then obtain Eq. (7.170).

For the solution of (7.170), which corresponds to the case of a time-independent $\mathbf{B}$-field as in (7.136), we introduce the 2×2 matrix

$$\tilde{\sigma} = \sigma_z \frac{(\omega_a - \omega_0)}{\Omega} + \sigma_x \frac{\omega_1}{\Omega} \tag{7.182}$$

with the abbreviation

$$\Omega = \sqrt{(\omega_a - \omega_0)^2 + \omega_1^2}. \tag{7.183}$$

The factor Ω^{-1} in (7.182) leads to the fact that—similar to σ_x, σ_z—also

$$\tilde{\sigma}^2 = 1_{2\times 2} = E_2. \tag{7.184}$$

Equation (7.170) then achieves the form

$$i\hbar \frac{\partial}{\partial t} \chi' = \frac{\hbar}{2} \Omega \tilde{\sigma} \chi' \tag{7.185}$$

and has the solution

$$\chi'(t) = \exp\left\{-\frac{i}{2} \omega t \tilde{\sigma}\right\} \chi'_0 \tag{7.186}$$

with

$$\chi'_0 = \chi'(t = 0). \tag{7.187}$$

The full solution then reads

$$\chi(t) = \exp\left\{\frac{i}{2} \omega_a t \sigma_z\right\} \exp\left\{-\frac{i}{2} \Omega t \tilde{\sigma}\right\} \chi_0 \tag{7.188}$$

with

$$\chi_0 = \chi(t = 0). \tag{7.189}$$

We now want to calculate the expectation value of σ_z within the state $\chi(t)$ as a function of time *t*. As initial condition we choose

$$\chi_0 = \chi^u, \ \text{with}\, \sigma_z \chi^u = +\chi^u \ (\text{spin} - \text{up}). \tag{7.190}$$

For the calculation of

$$< \sigma_z >= (\chi(t), \sigma_z \chi(t)) \tag{7.191}$$

we expand $\chi(t)$ in the basis of the eigenstates of σ_z

$$\chi(t) = c_u(t)\chi^u + c_d(t)\chi^d \tag{7.192}$$

and obtain—in line with the general considerations about the expectation value of observables (cf. Sect. 6.1)—(using χ_0 to be normalized to 1)

$$< \sigma_z >= E_2|c_u(t)|^2 - E_2|c_d(t)|^2 \tag{7.193}$$

with

$$c_u(t) = (\chi^u, \chi(t)); c_d(t) = (\chi^d, \chi(t)). \tag{7.194}$$

With (7.188) and (7.190) we obtain from (7.194):

$$|c_u(t)|^2 = \left|\left(\chi^u, \exp\left(-\tfrac{i}{2}\ \Omega t\tilde{\sigma}\right)\chi_0\right)\right|^2 = \left|\left(\chi^u, \left\{\cos\left(\tfrac{\Omega t}{2}\right) - i\tilde{\sigma}\sin\left(\tfrac{\Omega t}{2}\right)\right\}\chi^u\right)\right|^2 \tag{7.195}$$

$$= \left|\cos\left(\frac{\Omega t}{2}\right) - i\frac{(\omega_a - \omega_0)}{\Omega}\ \sin\left(\frac{\Omega t}{2}\right)\right|^2 = \cos^2\left(\frac{\Omega t}{2}\right) + \left[\frac{(\omega_a - \omega_0)}{\Omega}\right]^2 \sin^2\left(\frac{\Omega t}{2}\right)$$

using

$$(\chi^u, \sigma_x\chi^u) = 0. \tag{7.196}$$

In analogy we obtain

$$|c_d(t)|^2 = |(\chi^d, \exp\left\{-\tfrac{i}{2}\ \omega t\tilde{\sigma}\right\}\chi_0)|^2 \tag{7.197}$$

$$= \left|(\chi^d, \left[\cos\left(\frac{\Omega t}{2}\right) - i\tilde{\sigma}\sin\left(\frac{\Omega t}{2}\right)\right]\chi^u)\right|^2 = \left(\frac{\omega_1}{\Omega}\right)^2 \sin^2\left(\frac{\Omega t}{2}\right),$$

since

$$(\chi^d, \sigma_z\chi^u) = 0 \tag{7.198}$$

and

$$(\chi^d, \sigma_x\chi^u) = 1. \tag{7.199}$$

Together we obtain:

$$< \sigma_z >= \cos^2\left(\tfrac{\Omega t}{2}\right) + \frac{\left[(\omega_a - \omega_0)^2 - \omega_1^2\right]}{\Omega^2}\ \sin^2\left(\tfrac{\Omega t}{2}\right) \tag{7.200}$$

The expectation value $< \sigma_z >$ thus oscillates between its maximum value 1 (due to (7.190)) and its minimum value

$$< \sigma_z >_{\min} = \frac{[(\omega_a - \omega_0)^2 - \omega_1^2]}{[(\omega_a - \omega_0)^2 + \omega_1^2]}; \tag{7.201}$$

in particular we get for $\omega_a = \omega_0$:

$$< \sigma_z >_{\min} = -1 \tag{7.202}$$

The minimum value (7.201) shows a resonant behavior as a function of ω_0 (i.e. B_0) for $\omega_a = \omega_0$, where the spin is flipping periodically. In flipping the spin it absorbs the energy from the magnetic field (see (7.141) and (7.142))

$$\Delta\epsilon_s = \frac{e\hbar B_0}{mc} = \hbar\omega_0; \tag{7.203}$$

thus by measuring the energy absorption as a function of B_0 a **spin resonance** can be found experimentally.

7.6 Central Forces

7.6.1 The General Radial Equation

In this section we want to investigate the stationary states of a particle in a central potential ($r = |\mathbf{r}|$)

$$V = V(r). \tag{7.204}$$

The Hamilton operator

$$H = T + V \tag{7.205}$$

does not contain any spin-dependent terms and therefore we can forget about the spin of the particle when solving the eigenvalue problem

$$H\psi = E\psi. \tag{7.206}$$

But in the end it should be taken into account that each eigenvalue *E* is at least 2-fold degenerate due to the spin.

Since

$$[T, l_i] = 0, i = x, y, z \tag{7.207}$$

as well as

$$[V(r), l_i] = 0, \tag{7.208}$$

we get

$$[H, l_i] = 0. \tag{7.209}$$

Thus H, l^2 and l_z have a common system of eigenfunctions and the quantum numbers l, m of the angular momentum are good quantum numbers. The Hamiltonian H, furthermore, is still invariant with respect to the **parity operation**

$$\mathbf{r} \to \mathbf{r}' = -\mathbf{r}, \tag{7.210}$$

such that the parity is also a good quantum number. However, the parity is automatically determined for states with good orbital angular momentum $\mathbf{l}$ because the eigenfunctions $Y_{lm}(\vartheta, \varphi)$ of l^2, l_z (cf. (6.179)) with respect to the parity operation

$$r \to r;\ \vartheta \to \pi - \vartheta;\ \varphi \to \varphi + \pi \tag{7.211}$$

behave like

$$Y_{lm}(\vartheta, \varphi) \to Y_{lm}(\pi - \vartheta, \varphi + \pi) = (-1)^l Y_{lm}(\vartheta, \varphi). \tag{7.212}$$

This results from

$$\exp\,(im\varphi) \to \exp\,(im(\varphi + \pi)) = (-1)^m \exp\,(im\varphi), \tag{7.213}$$

$$\sin\,\vartheta \to \sin\,(\pi - \vartheta) = \sin\,\vartheta \tag{7.214}$$

and

$$\cos\,\vartheta \to \cos\,(\pi - \vartheta) = -\cos\,\vartheta, \tag{7.215}$$

such that

$$\frac{d^{l-m}}{d(\cos\vartheta)^{l-m}} \to (-1)^{l-m} \frac{d^{l-m}}{d(\cos\vartheta)^{l-m}}. \tag{7.216}$$

Now using the above symmetry considerations for the solutions from (7.206) we start with the product Ansatz:

$$\psi(\mathbf{r}) = \varphi_{lm}(r) Y_{lm}(\vartheta, \varphi). \tag{7.217}$$

This reduces the Schrödinger equation (7.206) to an ordinary differential equation in the variable *r* for the determination of $\varphi_{lm}(r)$. In order to obtain the explicit form of this radial equation we have to rewrite the kinetic energy operator in spherical coordinates (r, ϑ, φ)

$$x = r \ \sin\vartheta \ \cos\varphi;\ y = r \ \sin\vartheta \ \sin\varphi;\ z = r \ \cos\vartheta. \tag{7.218}$$

To this aim we can either use the operator

$$T = -\frac{\hbar^2}{2\,m}\Delta = -\frac{\hbar^2}{2\,m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) \tag{7.219}$$

and convert to (7.218) or use the classic expression for *T* in spherical coordinates and refer to the procedure described in chapter 5.2, which specifies the rules for the transition to quantum theory. We use the latter method and start from

$$T_{kl.} = \frac{1}{2\,m}p^2_{r\ kl.} + \frac{l^2_{kl.}}{2mr^2_{kl.}}. \tag{7.220}$$

We can directly translate to quantum theory

$$\mathbf{r}_{kl.} \rightarrow \mathbf{r};\ \mathbf{l}_{kl.} \rightarrow \hat{\mathbf{l}}; \tag{7.221}$$

however, to translate the radial component

$$p_{r\ kl.} = \frac{1}{r_{kl.}}(\mathbf{r}_{kl.} \cdot \mathbf{p}_{kl.}) \tag{7.222}$$

we have to consider Eq. (5.27) and obtain for the operator p_r in quantum theory

$$p_r = \frac{1}{2}\left\{\frac{\mathbf{r}}{r} \cdot \mathbf{p} + \mathbf{p} \cdot \frac{\mathbf{r}}{r}\right\}, \tag{7.223}$$

which can be reduced to

$$p_r = \frac{\hbar}{i}\left(\frac{\mathbf{r}}{r} \cdot \nabla + \frac{1}{r}\right) = \frac{\hbar}{i}\left(\frac{\partial}{\partial r} + \frac{1}{r}\right) \tag{7.224}$$

using

$$\frac{\partial}{\partial r} = \frac{\partial x}{\partial r}\ \frac{\partial}{\partial x} + \frac{\partial y}{\partial r}\ \frac{\partial}{\partial y} + \frac{\partial z}{\partial r}\ \frac{\partial}{\partial z} \tag{7.225}$$

$$= \frac{x}{r}\ \frac{\partial}{\partial x} + \frac{y}{r}\ \frac{\partial}{\partial y} + \frac{z}{r}\ \frac{\partial}{\partial z} = \frac{\mathbf{r}}{r} \cdot \nabla.$$

Together we get for the operator of the kinetic energy:

$$T = -\frac{\hbar^2}{2m}\left\{\frac{\partial^2}{\partial r^2} + \frac{2}{r}\ \frac{\partial}{\partial r} - \frac{\hat{l}^2}{r^2}\right\}, \tag{7.226}$$

since

$$p_r^2 = -\hbar^2\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\ \frac{\partial}{\partial r}\right). \tag{7.227}$$

This gives the **radial equation** to determine $\varphi_{lm}(r)$:

$$\left\{\frac{\partial^2}{\partial r^2} + \frac{2}{r}\ \frac{\partial}{\partial r} - \frac{l(l+1)}{r^2} + \epsilon - U(r)\right\}\varphi_l(r) = 0 \tag{7.228}$$

with

$$\epsilon = \frac{2m}{\hbar^2}E; U(r) = \frac{2m}{\hbar^2}V(r). \tag{7.229}$$

The quantum number *m* no longer appears in the radial equation and therefore is omitted for the radial function $\varphi_{lm}(r)$. The independence of the radial equation from *m* is based on the fact that the Hamilton operator does not contain a special spatial direction.

We can make the following statements (in the sense of necessary conditions)—without having to specify the form of *V*(*r*)—for the behavior of $\varphi_l(r)$ at $r = 0$ and for $r \to \infty$:

(i) The **normalization** requires that

$$\int_0^\infty r^2 dr\ |\varphi_l(r)|^2 < \infty, \tag{7.230}$$

such that $\varphi_l(r)$ must drop faster than $1/r$ for $r \to \infty$, i.e.

$$r\ \varphi_l(r) \to 0 \quad \text{for} \quad \mathrm{r} \to \infty. \tag{7.231}$$

For $r \to 0$, $r\ \varphi_l(r)$ must remain finite.

(ii) The **hermiticity** of p_r requires

$$r^2|\varphi_l(r)|^2|_0^\infty = 0. \tag{7.232}$$

Since according to (7.231) $r\ \varphi_l(r)$ for $\mathrm{r} \to \infty$ vanishes, we have to require (7.232)

$$r\ \varphi_l(r) \to 0 \quad \text{for} \quad \mathrm{r} \to 0. \tag{7.233}$$

The problem is more simplified when—instead of $\varphi_l(r)$—using

$$\chi_l(r) = r\ \varphi_l(r), \tag{7.234}$$

since due to

$$\left(\tfrac{\partial^2}{\partial r^2} + \tfrac{2}{r}\tfrac{\partial}{\partial r}\right)\tfrac{1}{r}\chi_l = \tfrac{\partial}{\partial r}\left(-\tfrac{1}{r^2}\chi_l + \tfrac{1}{r}\tfrac{\partial}{\partial r}\chi_l\right) + \tfrac{2}{r}\left(-\tfrac{1}{r^2}\chi_l + \tfrac{1}{r}\tfrac{\partial}{\partial r}\chi_l\right) \tag{7.235}$$

$$= \frac{2}{r^3}\chi_l - \frac{1}{r^2}\frac{\partial}{\partial r}\chi_l + \frac{1}{r}\frac{\partial^2}{\partial r^2}\chi_l - \frac{2}{r^3}\chi_l - \frac{1}{r^2}\frac{\partial}{\partial r}\chi_l + \frac{2}{r^2}\frac{\partial}{\partial r}\chi_l = \frac{1}{r}\frac{\partial^2}{\partial r^2}\chi_l$$

the radial Eq. (7.228) simplifies to

$$\left\{\tfrac{\partial^2}{\partial r^2} - \tfrac{l(l+1)}{r^2} + \epsilon - U(r)\right\}\chi_l(r) = 0, \tag{7.236}$$

and (7.230) translates to

$$\int_0^\infty dr\ |\chi_l(r)|^2 < \infty. \tag{7.237}$$

From (7.233) we then get

$$\chi_l(r) \to 0 \quad \text{for} \quad \mathrm{r} \to 0 \tag{7.238}$$

and from (7.231)

$$\chi_l(r) \to 0 \quad \text{for} \quad \mathrm{r} \to \infty. \tag{7.239}$$

Further statements about the solutions of the radial Eq. (7.228) or (7.236) require the knowledge about the structure of $V(r)$. Some general statements, which are based on the behavior of V for $r \to 0$ and $r \to \infty$, are stated below.

(i) If

$$\lim_{r\to 0} r^2 U(r) = 0, \tag{7.240}$$

the behavior of $\chi_l(r)$ at the origin is determined by the differential equation

$$\left\{r^2 \frac{\partial^2}{\partial r^2} - l(l+1)\right\}\tilde{\chi}_l(r) = 0. \tag{7.241}$$

Equation (7.241) has the solutions

$$\tilde{\chi}_l(r) \sim r^s \tag{7.242}$$

with

$$s(s-1) = l(l+1), \tag{7.243}$$

thus

$$s = -l \quad \text{or s} = \text{l} + 1. \tag{7.244}$$

Due to (7.238) only the case $s = l + 1$ is possible for $\chi_l(r)$, thus:

$$\chi_l(r) \sim r^{l+1} \quad \text{for r} \to 0. \tag{7.245}$$

(ii) If $U(r)$ is bounded from below,

$$U(r) \geq U_0 \quad \text{for all} \quad \text{r}, \tag{7.246}$$

or if $U(r)$ has a weaker singularity than $-1/r^2$ for $r \to 0$, the energy spectrum is limited from below. This implies that the particle does not drop into the center $r = 0$ if the conditions above are fulfilled. In the case (7.246) the claim is immediately clear, since the expectation value of the kinetic energy is non-negative; the second case is only listed here without proof.

(iii) If

$$\lim_{r\to\infty} r\ U(r) \to 0, \tag{7.247}$$

then there is a continuous spectrum for $\epsilon > 0$ and the solutions χ_l behave like the solutions of the free particle (see Sect. 7.6.4); for $\epsilon < 0$ there is a discrete spectrum and the associated eigenfunctions behave asymptotically like

$$\chi_l(r)_{r\to\infty} \sim \exp\ (-\kappa r); \kappa > 0. \tag{7.248}$$

These statements are also cited without proof. The physically important case

$$U(r) \sim \tfrac{1}{r} \tag{7.249}$$

is briefly outlined in Sect. 7.6.4 for positive energies.

7.6.2 The Isotropic Oscillator

The case

$$V(r) = \text{const.}\ \ \mathrm{r}^2 \tag{7.250}$$

we have covered already in Sect. 7.6.2, but in the cartesian representation and only mentioned the transition to the spherical representation (**angular momentum representation**). Thus some details have to be added and specified here.

For fixed energy

$$E_n = \hbar\omega\big(n + \tfrac{3}{2}\big); n = n_1 + n_2 + n_3 \tag{7.251}$$

l can take a maximum value of *n*, since the cartesian solution $\psi_{n_1 n_2 n_3}$ is a polynomial in *x*, *y*, *z* of order *n* (multiplied by a spherical Gauss function) and the angular momentum eigenfunctions are polynomials in cos ϑ, sin ϑ of order *l* (apart from the φ -dependence), since *x*, *y*, *z* by (7.218) are linked to cos ϑ, sin ϑ.

Since the eigenfunctions $\psi_{n_1 n_2 n_3}$ for even (odd) values of *n* have positive (negative) parity, for even (odd) *n* according to (7.212), only even (odd) *l* values may occur. The connection between *n* and *l* therefore must be

$$n = 2\nu + l; \nu = 0, 1, 2, \ldots, \tag{7.252}$$

with $2\nu \leq n$. Some examples are displayed in the table, where the degeneracy g_n is given by (7.117):

n	**l**	**m**	ν	g_n
0	0	0	0	1
1	1	0,± 1	0	3
2	0	0	1	6
	2	0,± 1,± 2	0	

We now can also write the energy eigenvalues within the framework of the spherical representation as

$$E_n = \hbar\omega\big(2\nu + l + \tfrac{3}{2}\big); n = 2\nu + l. \tag{7.253}$$

7.6.3 The Free Particle

For a free particle,

$$V = 0 \ \ \Rightarrow \ \ H = T, \tag{7.254}$$

we have

$$[H, \mathbf{p}] = 0 \tag{7.255}$$

as well as

$$[H, \mathbf{l}] = 0. \tag{7.256}$$

Thus we can—depending on the problem—classify an ensemble of free particles either according to energy and momentum—the eigenfunctions then are plane waves (see Sect. 6.3.3)—or according to energy and angular momentum. We want to examine the latter representation here in more detail because it is of special interest with regards to scattering problems (Chap. 8).

In this case we are looking for solutions of the radial equation

$$\left\{\frac{\partial^2}{\partial r^2} - \frac{l(l+1)}{r^2} + \epsilon\right\}\chi_l(r) = 0. \tag{7.257}$$

Since for free particles $\epsilon \geq 0$, we can assume

$$\epsilon = k^2, k \,\text{real}. \tag{7.258}$$

We then (for convenience) rewrite (7.257) in the variable

$$\rho = kr; \tag{7.259}$$

the result is:

$$\left\{\frac{d^2}{d\rho^2} - \frac{l(l+1)}{\rho^2} + 1\right\}\chi_l(\rho) = 0. \tag{7.260}$$

For $l = 0$ we find the basic solutions

$$\chi_0(\rho) = \exp\,(\pm i\rho) \tag{7.261}$$

or real:

$$\chi_0(\rho) = \sin\,(\rho);\;\; \cos\,(\rho). \tag{7.262}$$

For $l > 0$ the solutions can be constructed by recursion from (7.262) or (7.261) by introducing the following operators:

$$d_l^+ \equiv \frac{d}{d\rho} - \frac{l}{\rho}; d_l^- \equiv \frac{d}{d\rho} + \frac{l}{\rho}. \tag{7.263}$$

Then we can rewrite (7.260) as

$$\{d_l^+ d_l^- + 1\}\chi_l(\rho) = \left[\left(\frac{\partial}{\partial\rho} - \frac{l}{\rho}\right)\left(\frac{\partial}{\partial\rho} + \frac{l}{\rho}\right) + 1\right]\chi_l(\rho) = \tag{7.264}$$

$$\left[\left(\frac{\partial^2}{\partial\rho^2}-\frac{l}{\rho}\frac{\partial}{\partial\rho}-\frac{l}{\rho^2}+\frac{l}{\rho}\frac{\partial}{\partial\rho}-\frac{l^2}{\rho^2}\right)+1\right]\chi_l(\rho)=\left[\frac{\partial^2}{\partial\rho^2}-\frac{l(l+1)}{\rho^2}+1\right]\chi_l(\rho)=0$$

or equivalently

$$\{d^-_{l+1}d^+_{l+1}+1\}\chi_l(\rho)=0, \tag{7.265}$$

which is easily proven. Operating with d^+_{l+1} from the left of (7.265) we get

$$\{d^+_{l+1}d^-_{l+1}+1\}(d^+_{l+1}\chi_l(\rho))=0. \tag{7.266}$$

The function $(d^+_{l+1}\chi_l)$ therefore is a solution of Eq. (7.260) or (7.264) for angular momentum $l+1$, i.e.

$$\chi_{l+1}\sim d^+_{l+1}\chi_l. \tag{7.267}$$

Since we already know χ_0, we can recursively construct the solutions χ_l for $l>0$ with (7.267).

A compact relationship between χ_l and χ_0 we get by noting

$$d^+_l\equiv\rho^l\tfrac{d}{d\rho}\ \rho^{-l}=\rho^l\left(\rho^{-l}\tfrac{d}{d\rho}-\tfrac{l}{\rho^{l+1}}\right)=\tfrac{d}{d\rho}-\tfrac{l}{\rho}. \tag{7.268}$$

Then after recursion (7.267) reads

$$\chi_l\sim\rho^l\tfrac{d}{d\rho}\ \rho^{-l}\cdots\cdots\rho\ \tfrac{d}{d\rho}\ \rho^{-1}\chi_0 \tag{7.269}$$

or

$$\tfrac{1}{\rho}\ \chi_l(\rho)\sim\rho^l(\tfrac{1}{\rho}\ \tfrac{d}{d\rho})^l(\tfrac{1}{\rho}\ \chi_0(\rho)). \tag{7.270}$$

Depending on the choice of χ_0 we get the following solutions:

$\chi_0(\rho)$	$(-1)^l/\rho\ \chi_l(\rho)$	**label**
sin ρ	Spherical Bessel functions	$j_l(\rho)$
cos ρ	Spherical Neumann functions	$n_l(\rho)$
exp $(\pm i\rho)$	spherical Hankel functions	$h^\pm_l(\rho)$

Apart from the oscillating parts the solutions to the angular momentum *l* contain powers in $1/\rho$ up to the maximum power $1/\rho^{l+1}$. Due to the condition (7.233) only spherical Bessel functions $j_l(\rho)$ are solutions for the free particle, since only these are regular at the origin $r = 0$, where they are (cf. (7.245)) $\sim \rho^l$. The eigenfunctions of the free particle in the **angular momentum representation** are (except for possible normalization factors)

$$\psi_{klm}(r) = j_l(kr)Y_{lm}(\vartheta, \varphi); \tag{7.271}$$

they are orthogonal with respect to the quantum numbers *k*, *l*, *m*, but—like plane waves—not normalizable, since

$$\int_0^\infty \; j_l^2(kr)r^2 dr \to \infty. \tag{7.272}$$

With regards to the following chapter the asymptotic behavior of the solutions of (7.257) are of interest for scattering problems. For $\rho \to \infty$ we only need to take into account the slowest decreasing term, i.e. the powers ρ^0 in $\chi_l(\rho)$. If we start e.g. from $h_0^\pm(\rho)$, the only interesting term in $h_1^\pm(\rho)$ (arising from the differentiation of (7.270) is $\sim \mp i \;\; \exp\,(\pm i\rho) = \exp\,(\pm i[\rho - \pi/2])$; in general:

$$h_l^\pm(\rho)_{\rho\to\infty} \sim \tfrac{1}{\rho}(\mp i)^l \exp\,(\pm i\rho) = \tfrac{1}{\rho} \;\; \exp\,\left(\pm i\left[\rho - \tfrac{l\pi}{2}\right]\right). \tag{7.273}$$

Accordingly one finds:

$$j_l(\rho)_{\rho\to\infty} \sim \tfrac{1}{\rho} \;\; \sin\,\left(\rho - \tfrac{l\pi}{2}\right) \tag{7.274}$$

and

$$n_l(\rho)_{\rho\to\infty} \sim \tfrac{1}{\rho} \;\; \cos\,\left(\rho - \tfrac{l\pi}{2}\right). \tag{7.275}$$

7.6.4 Coulomb Potential for Positive Energies

Instead of (7.257) we now consider the differential equation

$$\left\{\tfrac{\partial^2}{\partial r^2} - \tfrac{l(l+1)}{r^2} + k^2 - \tfrac{2\gamma k}{r}\right\}\chi_l = 0 \tag{7.276}$$

with the Coulomb parameter

$$\gamma = \pm Z_1 Z_2 e^2 \frac{m}{\hbar^2 k} \tag{7.277}$$

for the case of the Coulomb potential $V(r) = \pm Z_1 Z_2 e^2/r$. We only want to focus here on the asymptotics of the Coulomb solutions $\chi_l(r)$, which is important for scattering problems.

For large values of *r* we neglect the centrifugal term ($\sim 1/r^2$) versus the Coulomb term ($\sim 1/r$) in (7.276) and find as an asymptotic solution

$$\chi_l(\rho)_{r\to\infty} \sim \frac{1}{\rho} \quad \exp\left(\pm i[kr - \gamma \quad \ln\left(2kr\right)]\right), \tag{7.278}$$

as can be confirmed by insertion into (7.276); consequently all terms $\sim 1/r^2$ have to be neglected. In (7.278) we have—as in (7.273)—another *l*-dependent phase free. Since we are interested in the deviation from the case of the free particle, we introduce the phase as follows:

$$\chi_l(\rho)_{r\to\infty} \sim \frac{1}{\rho} \quad \exp\left(\pm i\left[kr - l\frac{\pi}{2} - \gamma \quad \ln\left(2kr\right) + \sigma_l\right]\right). \tag{7.279}$$

It is worth noting that this asymptotic behavior (which is confirmed by the exact solution of (7.276)) has the additional phase $\sim \gamma \ln\left(2kr\right)$, which shows that even for $r \to \infty$ the Coulomb potential is still effective. We will come back to this point when dealing with scattering problems (in Sect. 8.3).

7.6.5 Bound States of the Hydrogen Atom

In the *H* atom an electron moves in an electrostatic Coulomb field (potential energy)

$$V(r) = -\frac{e^2}{r} \tag{7.280}$$

with energy *E* (or ϵ) < 0. In contrast to (7.258), $\epsilon = k^2$ cannot be fulfilled for real *k*, but only for purely imaginary values. We thus define

$$\kappa = \frac{2}{\hbar}\sqrt{2\,m(-E)}, \tag{7.281}$$

or $\epsilon = -\kappa^2/4$ with an additional factor 2 with regards to the normalization of wave functions to be discussed later. In analogy to (7.259) we define a dimensionless variable by

(7.282)

$$\xi = \kappa\ r,$$

such that the radial Eq. (7.236)

$$\left\{\frac{d^2}{dr^2} + \left[\frac{2\,me^2}{\hbar^2 r} - \frac{l(l+1)}{r^2}\right] - \frac{\kappa^2}{4}\right\}\chi_l(r) = 0 \tag{7.283}$$

(after division by κ^2) turns to the dimensionless form

$$\left\{\frac{d^2}{d\xi^2} + \left[\frac{\eta}{\xi} - \frac{l(l+1)}{\xi^2}\right] - \frac{1}{4}\right\}\chi_l(\xi) = 0 \tag{7.284}$$

with the **Sommerfeld parameter**

$$\eta = \frac{e^2}{\hbar}\sqrt{\frac{m}{2|E|}} = \eta(E). \tag{7.285}$$

As an alternative to (7.285), the Sommerfeld parameter $\eta(E)$, which includes the information about the energy of the electron, can also be written as

$$\eta(E) = \frac{e^2}{\hbar c}\sqrt{\frac{mc^2}{2|E|}} = \alpha\sqrt{\frac{mc^2}{2|E|}} \tag{7.286}$$

with the **fine structure constant**

$$\alpha = \frac{e^2}{\hbar c} \approx \frac{1}{137}, \tag{7.287}$$

which is characteristic of all electromagnetic forces.

To solve (7.284) we first consider the asymptotic behavior for $\xi \to \infty\ \ (r \to \infty)$, which is determined by the differential equation

$$\left\{\frac{\partial^2}{\partial\xi^2} - \frac{1}{4}\right\}\chi_l(\xi) = 0\ \ (\text{for}\ \ \xi \to \infty) \tag{7.288}$$

with the fundamental solutions $\exp\,(-\xi/2)$ and $\exp\,(\xi/2)$. Due to the requirement for normalization of the wave function the solution $\sim\exp\,(\xi/2)$ is omitted. The asymptotics for $\xi \to 0\ \ (r \to 0)$ on the other hand is determined by the differential equation

(7.289)

$$\left\{\frac{\partial^2}{\partial\xi^2} - \frac{l(l+1)}{\xi^2}\right\}\chi_l(\xi) = 0$$

which in analogy to (7.241) is solved with the Ansatz ξ^s with

$$s(s-1) = l(l+1) \tag{7.290}$$

(cf. (7.243)). The solution with $s = -l$ has to be excluded in accordance with the considerations in Sect. 7.6.1 such that only the case $s = l+1$ has to be considered. We therefore write

$$\chi_l(\xi) = \xi^{l+1}\,\exp\left(-\frac{\xi}{2}\right)g_l(\xi), \tag{7.291}$$

and (7.284) turns to

$$\left\{\xi\,\frac{d^2}{d\xi^2} + (2l+2-\xi)\,\frac{d}{d\xi} + (\eta(E) - l - 1)\right\}g_l(\xi) = 0. \tag{7.292}$$

For the solution of the differential equation (7.292) we now employ the power series

$$g_l(\xi) = \textstyle\sum_{n=0}^{\infty} a_n^l \xi^n. \tag{7.293}$$

By insertion into (7.292) and renaming the summation indices appropriately in the series for $dg/d\xi, \xi\ d^2g/d\xi^2$ we get

$$\sum_{m=0}^{\infty}\left\{m(m-1)a_m^l\xi^{m-1} + \left[(2l+2)ma_m^l\xi^{m-1} - ma_m^l\xi^m\right] + (\eta - l - 1)a_m^l\xi^m\right\}$$

$$= \textstyle\sum_{n=0}^{\infty}\left\{n(n+1)a_{n+1}^l + \left[(2l+2)(n+1)a_{n+1}^l - na_n^l\right] + (\eta - l - 1)a_n^l\right\}\xi^n = 0 \tag{7.294}$$

$$= \sum_{n=0}^{\infty}\left\{[n + (2l+2)(n+1)]a_{n+1}^l - [n + l + 1 - \eta]a_n^l\right\}\xi^n,$$

from which we obtain the **recursion formula** for the expansion coefficients a_n^l:

$$a_{n+1}^l = \frac{n+l+1-\eta(E)}{(n+2l+2)(n+1)}a_n^l. \tag{7.295}$$

The start value a_0^l will be calculated later by normalizing the wave function. For large n (7.295) becomes

(7.296)

$$\frac{a^l_{n+1}}{a^l_n} \to \frac{1}{n+1} \ (\text{for n} \to \infty),$$

i.e. the power series (7.293) contains a subseries

$$a^l_0 \sum_{n=0}^{\infty} \frac{\xi^n}{n!} = a^l_0 \exp(\xi), \tag{7.297}$$

if it does not stop in finite order. Inserting this subseries in (7.291), the solution $\chi_l(\xi)$ diverges like $\exp(\xi/2)$, i.e. $\chi_l(\xi)$ will not be normalizable. Thus (as in case of the oscillator) the power series must be of finite order: at a finite *n* then the numerator according to (7.295) is

$$n + l + 1 - \eta(E) = 0 \leftrightarrow \eta(E) = n + l + 1. \tag{7.298}$$

Since $l \geq 0$ is an integer,

$$N = n + l + 1 \tag{7.299}$$

is also an integer ≥ 1. Equation (7.298) then implies:

$$\eta(E) = N;\ N = 1, 2, 3, \ldots \tag{7.300}$$

or

$$\frac{\alpha^2 mc^2}{2|E|} = \frac{e^4 mc^2}{2|E|\hbar^2 c^2} = N^2. \tag{7.301}$$

This implies that the energy eigenvalues of the *H* atom are

$$E = E_N = -\frac{1}{2N^2}\ \alpha^2 mc^2 = -\frac{1}{2N^2}\ \frac{e^4 mc^2}{\hbar^2 c^2} = -\frac{1}{2N^2}\frac{e^2}{a} \approx \frac{-13.6\ \text{eV}}{N^2}, \tag{7.302}$$

where the length *a*, the **Bohr radius** is given by,

$$a = \frac{\hbar^2}{me^2} \approx 0.529 \cdot 10^{-10}\ \text{m}. \tag{7.303}$$

Quantum mechanics thus naturally explains the spectral lines of the *H* atom found empirically (Lyman, Balmer, Paschen, Bracket, Pfund series), which follow the $1/N^2$ law (7.302) very precisely.

N is called the **principal quantum number**. According to (7.299) there are *N* different possible *l* values for a given *N*

$$l = 0, 1, 2, \ldots, N - 1, \tag{7.304}$$

i.e. the angular momentum is limited from above for a given energy eigenvalue. On the other hand, these l values arise because the radial Eq. (7.292)—apart from l—also explicitly depends on N and there are N different radial wave functions—except for $N = 1$, where only $l = 0$ is possible. For a certain eigenvalue $E = E_N$ there are not only $2l + 1$ different functions $Y_{lm}(\vartheta, \varphi)$, but also N independent radial components. The **degree of degeneracy** for the eigenvalue E_N thus is not $2l + 1$, but

$$\sum_{l=0}^{N-1}(2l+1) = 1 + (2 \cdot 1 + 1) + \cdots + (2[N-1]+1) = N^2. \tag{7.305}$$

This additional degeneracy is characteristic for the $1/r$ potential and not present for other spherically symmetric potentials.

We now turn to the calculation of the hydrogen eigenfunctions. For each eigenvalue E_N we have a certain κ according to (7.281) and (7.302),

$$\kappa = \kappa_N = \frac{2}{\hbar}\sqrt{2\,m|E_N|} = \frac{2}{\hbar N}\sqrt{\frac{me^2}{a}} = \frac{2}{N}\sqrt{\frac{me^2}{a\hbar^2}} = \frac{2}{aN} \tag{7.306}$$

with (7.303). The polynomials of n-th degree, which arize from the termination condition (7.298) in the series (7.294), with

$$n = N - l - 1 = N - 1, N - 2, \ldots, 0 \tag{7.307}$$

are called—with conventional normalization:

Laguerre polynomials

$$L_n^{2l+1}(\xi) = g_{N,l}(\xi) = L_{N-l-1}^{2l+1}(\xi) \tag{7.308}$$

with $\xi = \kappa_N r$. The normalization can be calculated using the **generating function**

$$U_p(\xi, s) \equiv \frac{1}{(1-s)^{p+1}}\ \exp\left[-\xi\frac{s}{1-s}\right] = \sum_{n=0}^{\infty} L_n^p(\xi)\frac{s^n}{(n+p)!}. \tag{7.309}$$

Some results are e.g.

$$l = 0, \hat{n} = 0 : L_0^1(\xi) = 1 \tag{7.310}$$

$$l = 0,\ \ n = 1 :\ \ L_1^1(\xi) = 2(2 - \xi)$$

$$l = 1,\ \ n = 0 :\ \ L_0^3(\ xi) = 6$$

$$L_n^p(\xi) = \frac{\exp\,(\xi)\xi^{-p}}{n!}\ \frac{d^n}{d\xi^n}\left(\exp\,(-\xi)\xi^{n+p}\right).$$

The complete radial function then is

$$\chi_{N,l}(r) = C_{N,l}\left[\tfrac{2r}{aN}\right]^{l+1}\exp\,\left(-\tfrac{r}{aN}\right)L_{N-l-1}^{2l+1}\left(\tfrac{2r}{aN}\right), \tag{7.311}$$

where the normalization constant $C_{N,l}$ is to be determined from

$$\int_0^\infty |\chi_{N,l}(r)|^2 dr = 1. \tag{7.312}$$

The total wave function

$$\psi_{N,l,m}(r,\vartheta,\varphi) = \tfrac{1}{r}\ \chi_{N,l}(r)Y_{lm}(\vartheta,\varphi) \tag{7.313}$$

then is uniquely characterized by the 3 discrete quantum numbers *N*, *l*, *m*.

For the ground state of the *H* atom with $N = 1$ (only $l = m = 0$ is possible). we get from (7.312) $C_{1,0} = 1/\sqrt{a}$ and with $Y_{00} = 1/\sqrt{4\pi}$ the **ground state eigenfunction**

$$\psi_{1,0,0}(r,\vartheta,\varphi) = \sqrt{\tfrac{1}{a^3\pi}}\ \exp\,\left(-\tfrac{r}{a}\right). \tag{7.314}$$

For the expectation value $< r >$ in the ground state we obtain (by partial integration)

$$< r >_{1,0,0} = \int |\psi_{1,0,0}|^2 r\ d^3r = \tfrac{4}{a^3}\int_0^\infty \exp\,\left(-\tfrac{2r}{a}\right)r^3\ dr = \tfrac{3}{2}a. \tag{7.315}$$

Up to a factor of 3/2 the length *a* is the average distance of the electron from the proton in the ground state. This statistical statement replaces the classic idea of the lowest Bohr orbit of radius *a*.

In summarizing this chapter we have discussed the quantum mechanics of a single particle in an external potential and classified the possible solutions. As examples we have calculated the wave functions for an infinite and a finite well and for potentials that are periodic in space. Furthermore, the harmonic oscillator problem has been examined in detail as well as the motion of a charged particle (and its spin) in a magnetic field. Moreover, the bound states and energy levels of the hydrogen atom have been calculated.

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8. Basic Concepts of Scattering Theory

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In this chapter we will introduce to the scattering theory of a single particle with an interaction potential and investigate the continuum states of the effective single-particle problem in case of two-body scattering.

In a scattering experiment a beam of particles with given properties (energy, momentum, polarization) hits a target; the influence of the target on the incident particle beam is measured in the form of the angular distribution, excitation function, the scattered radiation etc. (Fig. 8.1).

With such scattering experiments one essentially pursues two goals:

(i) In scattering experiments with elementary particles an information is obtained about the forces between the particles involved. For example, we know that the interaction between two nucleons at small distances (~ 0.25 fm) is strongly repulsive.

(ii) If one scatters e.g. electrons on atoms (or molecules) one can get information about possible excited states of the atom (molecule) because the interaction electron—atom (molecule) is known (electromagnetic interaction). An example of such an (inelastic) scattering experiment is the **Franck-Hertz experiment** (cf. Chap. 2).

For the practical evaluation of scattering experiments we want to formulate the following **requirements**:

(1) The intensity of the primary beam is so low that one can neglect the interaction between the particles of the incident beam.

(2) The distances between the scattering centers of the target are large compared to the wavelength of the incident particles, such that interference effects between the scattering waves from different scattering centers are negligible; each scattering center then acts as a single one. –This requirement is not fulfilled in diffraction experiments on crystals.–

(3) The target is so thin that multiple scattering does not occur.

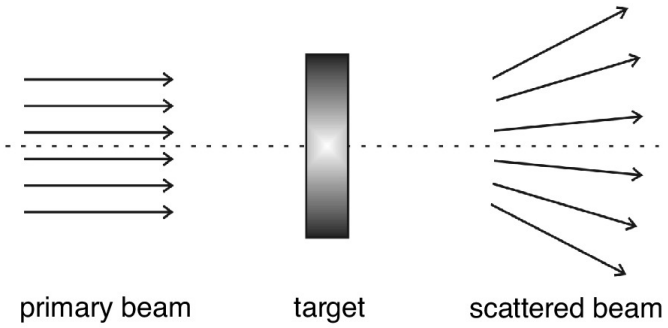

Fig. 8.1 Illustration of a scattering process

If the primary beam is well defined in terms of energy, direction, polarization etc., then with the assumptions (1)–(3) a scattering experiment is equivalent to an **ensemble** of scattering systems, which consist of a **single** incident particle and a **single** (resting) particle of the target.

In the following we will restrict to elastic scattering processes (unless stated otherwise).

8.1 Basic Definitions

8.1.1 Scattering Cross Section

If j_0 is the incident current density in *z*- direction and ΔN the number of scattered particles per unit time measured in the solid angle $\Delta\Omega$, we define (within the assumptions (1)–(3)) the **differential scattering cross section** $\sigma = \sigma(\Omega)$—as the quantity characterizing the scattering process—by:

$$\lim_{\Delta\Omega\to 0} \frac{\Delta N}{\Delta\Omega} = n \; j_0 \; \sigma(\Omega); \tag{8.1}$$

here $\Omega = (\vartheta, \varphi)$ indicates the direction in which the scattered particles are observed relative to the primary beam, and *n* is the number of scattering centers contained in the target. σ has the dimension of an area. In order to measure the quantity ΔN in (8.1) the detector must be placed outside the area of the incident wave; thus one cannot measure $\sigma(\Omega)$ in the forward direction $(\vartheta = 0)$. Since by increasing the distance between detector and target—for a given size of the primary beam—one can reach smaller angles Ω, this restriction is practically not important.

The **total scattering cross section** σ then is defined as

$$\sigma = \int d\Omega \; \sigma(\Omega) = \int d\Omega \; \frac{d\sigma}{d\Omega}; \tag{8.2}$$

it gives the total number of scattered particles (from the primary beam) per unit of time relative to the incident current density j_0 and the number of scattering centers *n* in the target.

8.1.2 Scattering Amplitude

As stated above, a scattering experiment can be viewed as an ensemble of two-particle scattering systems. Such a two-particle problem can be reduced in classical physics to a single-particle problem by introducing center of mass and relative coordinates; the center of mass of

the two particles moves—in the absence of external forces—like a free mass point with the mass $M = m_1 + m_2$, and the relative motion of the particles is characterized by the reduced mass $\mu = m_1 m_2/(m_1 + m_2)$ and the potential $V(r)$, where r is the relative coordinate. We will show later that the separation in center of mass and relative coordinates is also possible in quantum theory; this reduces our task to the scattering of a particle of mass μ at the potential $V(r)$.

There are two methods for the quantum mechanical treatment of potential scattering: In the

(1) **method of stationary states** it is assumed that the primary beam is switched on long before the measurement and is switched off again only long after the measurement such that the state of the system during the measurement can be described as stationary.

(2) **The time-dependent theory of scattering** processes considers the scattering of the incident particles at the target as a (time-dependent) perturbation which transforms the incident particles from an initial state (before the collision) in a final state (after the collision). One then calculates the probability for this transition and from that directly the scattering cross section.

In the following we will use the (1) method and only later examine method (2) more closely.

For spinless particles the method of stationary states is to find solutions of the Schrödinger equation

$$(T + V)\psi = E\psi; E = \frac{\hbar^2 k^2}{2\mu} \tag{8.3}$$

at given energy E in the center of mass system (determined by the energy of the primary beam in the laboratory system) and to look for solutions, which asymptotically have the form:

$$\psi(r)_{r\to\infty} \sim \exp(ikz) + f(\Omega)\frac{\exp(ikr)}{r}, \tag{8.4}$$

if the potential $V(r)$ drops asymptotically faster than $1/r$. In the case of the Coulomb potential (8.4) must be modified due to the logarithmic phase $\sim \ln(2kr)$ (7.279) (see Chap. 8.3). According to (8.4) the asymptotic form of $\psi(r)$ contains both the possibility that the particle is deflected in Ω-direction (direction-modulated spherical wave), as well as the case that no scattering takes place (plane wave in z-direction).

We now want to show how to connect the **scattering amplitude** $f(\Omega)$ with the differential scattering cross section $\sigma(\Omega)$. To this aim we use Eq. (8.1); the current density j_0 from (3.23) for the plane wave $\exp(ikz)$ is

$$j_0 = \frac{\hbar k}{\mu}. \tag{8.5}$$

On the left side of (8.1) the radial component of the current density of scattered particles appears. Taking into account (7.225) it follows that

$$j_{scat} = \frac{\hbar}{2i\mu}|f(\Omega)|^2 \left\{ \frac{\exp(-ikr)}{r} \frac{1}{r} \frac{\partial}{\partial r} \exp(ikr) - \frac{\exp(ikr)}{r} \frac{1}{r} \frac{\partial}{\partial r} \exp(-ikr) \right\} \tag{8.6}$$

$$= \frac{\hbar k}{\mu} \frac{|f(\Omega)|^2}{r^2}.$$

Then we get

$$\sigma(\Omega) = |f(\Omega)|^2, \tag{8.7}$$

if we consider that j_{scat} is related to the area $\Delta f = r^2 \Delta\Omega$. The aim of the following considerations is the practical calculation of the scattering amplitude $f(\Omega)$ from the Schrödinger equation (8.3) with the boundary condition (8.4).

Before we look at methods for calculating $f(\Omega)$ let's briefly state the requirements, for which the method of stationary states, as developed above, is applicable. To the requirements (1)–(3) we have to add:

(4) The incident wave is considered as a stationary state in form of a plane wave, which has a sharp momentum $\hbar\mathbf{k}$ and sharp energy *E*. In practice, however, we are dealing with wave packets of finite spatial and temporal extent, which necessarily (see Sect. 6.3.7) have a width with respect to *E* and $\mathbf{k}$. If our idealization should be a useful approximation, then must hold

$$kd \gg 1; kl \gg 1, \tag{8.8}$$

if *k* is the wave number, *l* and *d* are the longitudinal and transversal extensions of the wave packet, respectively. In order to avoid the melting of the in- and out- wave packets, also the following must apply,

$$d \gg \sqrt{\tfrac{R}{k}}; l \gg \sqrt{\tfrac{R}{k}}, \tag{8.9}$$

if *R* denotes the distance between target and detector.

(5) The area in which the interaction between an incident particle and a target particle takes place must be within distances $r \leq r_0$ from the scattering center and

$$d \gg r_0; l \gg r_0. \tag{8.10}$$

(6) When calculating j_{scat} the interference between the plane wave and the spherical wave is neglected—as in (8.6)-, thus we must require

$$d \ll R \ \sin\vartheta. \tag{8.11}$$

Within the assumptions above one can show that Eq. (8.7) remains valid also for wave packets.

8.1.3 Reactions, Inelastic Scattering

The previous considerations relate to elastic scattering processes,

$$A_1 + A_2 \to A_1 + A_2. \tag{8.12}$$

In addition, inelastic processes are also of interest such as

$$A_1 + A_2 \to A_1 + A_2^*, \tag{8.13}$$

where A_2^* denotes an excited state of the target particles, or reactions

$$A_1 + A_2 \to B_1 + B_2, \tag{8.14}$$

e.g. transfer of a particle C :

$$B_1 = A_1 + C;\ B_2 = A_2 - C. \tag{8.15}$$

To deal with such problems, we can no longer consider the particles A_1 and A_2—involved in the process—as structureless mass points; in addition to the wave function of the relative motion the internal state of the scattering partners has to be described by a wave function. Then we have to deal with a multi-particle problem which we will describe later.

For a general reaction (8.12)–(8.14) we have to differentiate

(i) the **input channel** $A_1 + A_2$, specified by the type and state of the reaction partners and their relative motion before the start of the reaction, and

(ii) the possible **output channels** $A_1 + A_2$, $A_1 + A_2^*$, $B_1 + B_2$, with the corresponding specification as in (i).

In general, a reaction channel is characterized by a certain fragmentation, specification of the internal state of the fragments as well as kinematic data (e.g. energy or angular momentum of the relative motion). A distinction is made between **open** and **closed** channels depending on whether the reaction in question is energetically possible or not.

8.2 The Integral Equation Method

8.2.1 The Lippmann-Schwinger Equation

Conceptually, the following method for the calculation of scattering problems is of importance: The Schrödinger equation (8.3) is transformed into an integral equation such that the solutions automatically satisfy the boundary conditions (8.4). For this purpose we write (8.3) formally as an inhomogeneous differential equation

$$(\Delta + k^2)\psi(\mathbf{r}) = U(\mathbf{r})\psi(\mathbf{r}), \tag{8.16}$$

with (as in (7.3)), (7.6)

$$U(\mathbf{r}) = \tfrac{2\mu}{\hbar^2} V(\mathbf{r});\ k^2 = \tfrac{2\mu}{\hbar^2} E. \tag{8.17}$$

The general solution of (8.16) then is:

$$\psi_k(\mathbf{r}) = \varphi_k(\mathbf{r}) + \int\ G_k(\mathbf{r}, \mathbf{r}')U(\mathbf{r}')\psi_k(\mathbf{r}')d^3r', \tag{8.18}$$

where φ_k is an arbitrary solution of the homogeneous equation

$$(\Delta + k^2)\varphi_k(\mathbf{r}) = 0 \tag{8.19}$$

and $G_k(\mathbf{r}, \mathbf{r}')$ the corresponding **Green's function** defined by,

$$(\Delta + k^2) G_k(\mathbf{r}, \mathbf{r}') = \delta^3(\mathbf{r} - \mathbf{r}'). \tag{8.20}$$

For the proof one applies the operator $(\Delta + k^2)$ to (8.18) and uses (8.19) and (8.20).

To explain the definition (8.20) of the Green's function, let us multiply (8.20) from the right by an arbitrary function $\chi(\mathbf{r}')$ and integrate the resulting equation over $\mathbf{r}'$. We then get

$$\int d^3r' (\Delta + k^2) G_k(\mathbf{r}, \mathbf{r}') \chi(\mathbf{r}') = \chi(\mathbf{r}) \tag{8.21}$$

or

$$(\Delta_r + k^2) G_r \chi(\mathbf{r}) = \chi(\mathbf{r}) \tag{8.22}$$

with the abbreviation

$$G_r \chi(\mathbf{r}) \equiv \int d^3r' \; G_k(\mathbf{r}, \mathbf{r}') \chi(\mathbf{r}'). \tag{8.23}$$

According to (8.22) G_r can be interpreted as the inverse operator to $(\Delta_r + k^2)$; as we will see, it is not uniquely defined.

In the integral equation (8.18), which is equivalent to the Schrödinger equation, we can now incorporate the boundary condition (8.4) as follows: Instead of the general solution $\varphi_k(\mathbf{r})$ of the homogeneous equation (8.19) we choose the special solution

$$\varphi_k(\mathbf{r}) = \exp\,(ikz). \tag{8.24}$$

Then the 2nd term in (8.18) for $r \to \infty$ must convert into a directionally modulated outgoing spherical wave. To investigate this question we need the explicit form of the solutions of (8.20).

Since (8.20) is invariant with respect to translations,

$$\mathbf{r} \to \mathbf{r} + \mathbf{a}; \; \mathbf{r}' \to \mathbf{r}' + \mathbf{a}, \tag{8.25}$$

$G_k(\mathbf{r}, \mathbf{r}')$ depends only on $(\mathbf{r} - \mathbf{r}')$. We therefore write $G_k(\mathbf{r}, \mathbf{r}') \equiv G_k(\mathbf{r} - \mathbf{r}')$ as a Fourier integral of the form

$$G_k(\mathbf{r} - \mathbf{r}') = \frac{1}{(2\pi)^3} \int d^3q \; g_k(\mathbf{q}) \exp\,(i\mathbf{q} \cdot (\mathbf{r} - \mathbf{r}')). \tag{8.26}$$

Inserting (8.26) into (8.20) and using

$$\frac{1}{(2\pi)^3} \int d^3q \;\; \exp\,(i\mathbf{q} \cdot (\mathbf{r} - \mathbf{r}')) = \delta^3(\mathbf{r} - r'), \tag{8.27}$$

we get for $g_k(\mathbf{q})$ the equation

$$(k^2 - q^2) g_k(\mathbf{q}) = 1 \tag{8.28}$$

and thus

$$g_k(\mathbf{q}) = (k^2 - q^2)^{-1}. \tag{8.29}$$

The integrand in (8.26) has poles of 1st order for $\mathbf{q} = \pm\mathbf{k}$. We therefore must clarify—by means of an additional rule - how the integral (8.26) has to be taken; depending on the choice of this rule, we get different Green's functions that have a different asymptotic behavior of the desired solution (8.18).

With respect to the position of the poles at $\mathbf{q} = \pm\mathbf{k}$ it is useful to introduce polar coordinates in $\mathbf{q}$-space, i.e.

$$G_k(\rho) = \frac{1}{(2\pi)^3} \int q^2 dq \; d\Omega_q \; \frac{\exp(iq\rho \cos\vartheta_q)}{k^2 - q^2} \tag{8.30}$$

with

$$\rho \equiv |\mathbf{r} - \mathbf{r}'|. \tag{8.31}$$

Since the singularities of the integrand only effect the q-integration, we can integrate over the possible directions of $\mathbf{q}$ and obtain

$$G_k(\rho) = \frac{1}{4i\pi^2\rho} \int_0^\infty q \; dq \; \frac{\exp(iq\rho) - \exp(-iq\rho)}{(k-q)(k+q)}. \tag{8.32}$$

The integrand in (8.32) is an even function in q and we can—instead of (8.32)—also write

$$G_k(\rho) = \frac{1}{4i\pi^2\rho} \int_{-\infty}^\infty q \; dq \; \frac{\exp(iq\rho)}{(k+q)(k-q)}. \tag{8.33}$$

We now carry out the q integration in (8.33) in the following way: We substitute

$$k \to k + i\epsilon; \; \epsilon\text{real} > 0, \tag{8.34}$$

such that the pole at $q = k \;\; (-k)$ is moved from the real axis into the upper (lower) half-plane of the complex q-plane (see Fig. 8.2).

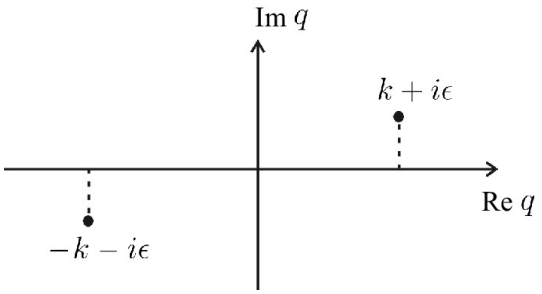

Fig. 8.2 Location of the poles in the complex q plane

We then define as Green's function

$$G_k^{(+)}(\rho) = \lim_{\epsilon\to 0} \frac{1}{4i\pi^2\rho} \int_{-\infty}^\infty dq \; q \; \frac{\exp(iq\rho)}{\{(k+i\epsilon-q)(k+i\epsilon+q)\}}, \tag{8.35}$$

where the $\lim_{\epsilon \to 0}$ has to be taken only after the q integration.

For positive $\epsilon > 0$ the integral in (8.35) can be calculated as follows: Since $\rho > 0$, for $\Im q > 0$ the argument of $\exp\,(..)$ is negative and $\exp\,(-\Im q \rho)$ disappears for $|q| \to \infty$. Then the integration path in the upper half plane of the complex q plane can be closed by a semicircle with a radius pushed to infinity.

The integral in (8.35) over the contour C then has the form:

$$\tfrac{1}{2} \int_C dq \;\; \exp\,(iq\rho) \Big[\tfrac{1}{k+i\epsilon-q} - \tfrac{1}{k+i\epsilon+q} \Big], \tag{8.36}$$

using

$$\tfrac{q}{(k-q)(k+q)} = \tfrac{1}{2} \Big[\tfrac{1}{k-q} - \tfrac{1}{k+q} \Big]. \tag{8.37}$$

According to the **residue theorem** the value of the integral (8.36) is $2\pi i$—times the sum of the residues of the poles enclosed by the integration path. For the case considered, only the pole at $k + i\epsilon$ is within the integration path; its residue is

$$-\tfrac{1}{2} \;\; \exp\,(i(k+i\epsilon)\rho). \tag{8.38}$$

Thus we get for $\epsilon \to 0$

$$G_k^{(+)}(\rho) = -\tfrac{1}{4\pi} \tfrac{\exp(+ik\rho)}{\rho}, \tag{8.39}$$

which is the solution we are looking for, since the 2nd term in (8.18) asymptotically describes a direction-modulated outgoing spherical wave.

There are alternative rules for calculating the integral (8.32): choosing $\epsilon < 0$ in (8.34) an analogous consideration (as above) gives

$$G_k^{(-)}(\rho) = -\tfrac{1}{4\pi} \tfrac{\exp(-ik\rho)}{\rho}, \tag{8.40}$$

i.e. the asymptotics of (8.18) is an incoming spherical wave. Finally, the q integration in (8.32) can be done in the sense of a principle value; one then arrives at a standing spherical wave

$$G_k^{(0)}(\rho) = -\tfrac{1}{4\pi} \tfrac{\cos(k\rho)}{\rho}. \tag{8.41}$$

The integral equation (**Lippmann-Schwinger equation**), which is equivalent to the Schrödinger equation (8.16) with the boundary condition (8.4), then reads:

$$\begin{aligned} \psi_k^{(+)}(\mathbf{r}) =& \exp\,(ikz) + \int \;\; G_k^{(+)}(\mathbf{r},\mathbf{r}') U(\mathbf{r}') \psi_k^{(+)}(\mathbf{r}') d^3r' \\ =& \exp\,(ikz) - \frac{1}{4\pi} \int \;\; \frac{\exp\,(ik|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|} U(\mathbf{r}') \psi_k^{(+)}(\mathbf{r}') d^3r'. \end{aligned} \tag{8.42}$$

Equation (8.42) represents a **formal solution** of the scattering problem, which in a practical calculation of the scattering solution $\psi_k^+(\mathbf{r})$ can be solved by an iteration process. Before addressing this issue in more detail we first will specify a formula for the scattering amplitude $f(\Omega)$ with the help of (8.42).

8.2.2 Scattering Amplitude

For distances *r* from the scattering center, that are large compared to the range r_0 of the potential *V*,

$$r = |\mathbf{r}| \gg r_0, \tag{8.43}$$

we can approximate the Green's function in (8.42) by

$$\frac{\exp(ik|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|} \approx \frac{\exp(ikr)}{r} \quad \exp\,(-i\mathbf{k}\cdot\mathbf{r}') \tag{8.44}$$

with

$$\mathbf{k} \equiv k\frac{\mathbf{r}}{r}. \tag{8.45}$$

Here we have used

$$|\mathbf{r}-\mathbf{r}'| \approx r - \frac{\mathbf{r}}{r}\cdot\mathbf{r}' \ldots \text{for r} \gg \text{r}'. \tag{8.46}$$

The factor $\exp\,(ikr)/r$ in the integral in (8.42) now can be written in front of the integral and by comparison with (8.4) we find

$$f(\Omega) = -\frac{1}{4\pi}\int \quad \exp\,(-i\mathbf{k}\cdot\mathbf{r}')U(\mathbf{r}')\psi_k^{(+)}(\mathbf{r}') \; d^3r' = -\frac{1}{4\pi}(\varphi_k, U\psi_k^{(+)}) \tag{8.47}$$

with $\varphi_k(\mathbf{r}') = \exp\,(i\mathbf{k}\cdot\mathbf{r}')$. The expression (8.47) for $f(\Omega)$ is exact for $\psi_k^{(+)}$ from (8.42); if $V = V(r)$ is a central potential then $f(\Omega)$ simplifies to $f(\vartheta)$ since the scattering amplitude does not depend on the angle φ.

For the practical evaluation of (8.47) one needs the exact solution of the Lippmann-Schwinger equation (8.42). We want to show in the following how to get an approximate solution to the scattering problem by means of an **iteration method**.

8.2.3 The Born Series

The starting solution for an iteration process for $\psi_0^{(+)}(\mathbf{r})$ on the right of (8.42) (index *k* furtheron suppressed) is:

$$\psi_0^{(+)}(\mathbf{r}) = \exp\,(ikz), \tag{8.48}$$

which gives

$$\psi_1^{(+)}(\mathbf{r}) = \exp\,(ikz) + \int d^3r' \; G^{(+)}(\mathbf{r},\mathbf{r}')U(\mathbf{r}')\,\exp\,(ikz'). \tag{8.49}$$

This procedure ultimately gives (assuming convergence) the exact solution in the form of the **Born series**

$$\psi^{(+)} = \exp(ikz) + \sum_{n=1}^{\infty} \int K_n(\mathbf{r}, \mathbf{r}') \psi_0^{(+)}(\mathbf{r}') \, d^3r' \tag{8.50}$$

with

$$K_n(\mathbf{r}, \mathbf{r}') = \int K_1(\mathbf{r}, \mathbf{r}'') K_{n-1}(\mathbf{r}'', \mathbf{r}') \, d^3r'', n > 1 \tag{8.51}$$

$$K_1(\mathbf{r}, \mathbf{r}') = G^{(+)}(\mathbf{r}, \mathbf{r}') U(\mathbf{r}').$$

The question of the convergence of the series (8.50) cannot be addressed here in detail; for local potentials, which for $r \to 0$ become singular less than $1/r^2$ and for $r \to \infty$ drop stronger than $1/r$, the convergence is given in any case (without proof).

8.2.4 The First Born Approximation

In the best case scenario one can hope to get a meaningful solution to (8.42) by the first term in the series (8.50):

$$\psi^{(+)}(\mathbf{r}) \approx \exp(ikz) + \int d^3r' \; G^{(+)}(\mathbf{r}, \mathbf{r}') U(\mathbf{r}') \exp(ikz'). \tag{8.52}$$

Then we get for the scattering amplitude (see (8.47))

$$f(\Omega) \approx -\tfrac{1}{4\pi} \int d^3r' \; \exp(-i\mathbf{k} \cdot \mathbf{r}') U(\mathbf{r}') \exp(ikz'), \tag{8.53}$$

and especially for central forces

$$f(\vartheta) \approx -\tfrac{1}{4\pi} \int d^3r' \; \exp(-i\mathbf{k} \cdot \mathbf{r}') U(r') \exp(ikz'), \tag{8.54}$$

where the angular integration can be carried out explicitly. With

$$\mathbf{k}_0 = (0, 0, k) \tag{8.55}$$

Equation (8.54) becomes

$$f(\vartheta) \approx -\tfrac{1}{4\pi} \int d^3r' \; \exp(i(\mathbf{k}_0 - \mathbf{k}) \cdot \mathbf{r}') \; U(\mathbf{r}'). \tag{8.56}$$

Equation (8.56) suggests to introduce the momentum change during the collision

(8.57)

$$\mathbf{K} = \mathbf{k}_0 - \mathbf{k},$$

such that

$$f(\vartheta) \approx -\tfrac{1}{4\pi} \int \; d^3r' \;\; \exp\,(i\mathbf{K}\cdot\mathbf{r}')\; U(\mathbf{r}'). \tag{8.58}$$

We now place the z' axis for the $\mathbf{r}'$ integration such that

$$\exp\,(i\mathbf{K}\cdot\mathbf{r}') = \exp\,(iKr'\,\cos\,\vartheta') \tag{8.59}$$

and

$$\int d^3r' \ldots = \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} d\varphi' \;\; \sin\,\vartheta' d\vartheta' \;\; r'^2 dr' \ldots \tag{8.60}$$

After integration over the angles ϑ', φ' we then obtain in **1. Born's approximation**

$$f(\vartheta) \approx -\tfrac{1}{K}\int_0^{\infty} r'U(r')\,\sin\,(Kr')\;\,dr', \tag{8.61}$$

where the ϑ -dependence is contained in *K* (see Fig. 8.3):

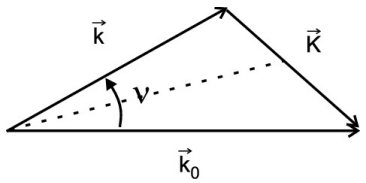

Fig. 8.3 Illustration of the momentum transfer $\mathbf{K}$

$$K = 2k \;\; \sin\,\tfrac{\vartheta}{2}. \tag{8.62}$$

For a short-range potential *U* we can find a criterion for the quality of the first Born approximation. The main contribution to $f(\vartheta)$ then comes from small *r* values. For $r \approx 0$ we get from (8.52):

$$\psi^{(+)}(\mathbf{r}) \approx \exp\,(ikz) - \int_0^{\infty} \tfrac{\exp(ikr')}{r'} U(r') \tfrac{\sin(kr')}{kr'} r'^2 \;\, dr'. \tag{8.63}$$

Since the first Born approximation can only be useful, if the modification of the plane wave by the potential *U* is small, we get the condition:

$$\tfrac{1}{k}\left|\int_0^{\infty} \exp\,(ikr')U(r')\,\sin\,(kr')\;\,dr'\right|^2 \ll 1; \tag{8.64}$$

this condition can be satisfied for high energies (large *k* values).

As an example, in which (8.61) can be evaluated exactly, we consider a **Yukawa potential** (or meson exchange potential) of the form

(8.65)

$$U = U_0 \ \frac{\exp(-\gamma r)}{r}, \ \gamma > 0.$$

The elementary integration gives:

$$f(\vartheta) = -U_0 \frac{1}{4\ k^2 \sin^2\frac{\vartheta}{2} + \gamma^2} = -\frac{U_0}{K^2+\gamma^2}, \tag{8.66}$$

thus

$$\sigma(\vartheta) = \frac{U_0^2}{\left(4\ k^2 \sin^2\frac{\vartheta}{2} + \gamma^2\right)^2} = \frac{U_0^2}{(K^2+\gamma^2)^2} \tag{8.67}$$

as the result in first order Born approximation. For $\gamma \to 0$ we obtain the

Rutherford formula

$$\sigma(\vartheta) = \left\{\frac{Z_1 Z_2 e^2}{4E}\right\}^2 \frac{1}{\sin^4\frac{\vartheta}{2}} \tag{8.68}$$

for

$$U_0 = \pm Z_1 Z_2 e^2 \mathbf{2} \frac{\mu}{\hbar^2}. \tag{8.69}$$

which is classically and quantum mechanically exact (inspite of the comments on the validity of the first Born approximation).

8.2.5 The Electric Form Factor

For the elastic scattering of electrons on atoms one can start (in lowest order approximation) with the assumption, that the atom can be described by an electrostatic potential $V(r)$, which contains the nuclear charge Z and the charge distribution of the electrons $\rho(\mathbf{r})$ in the form

$$\Delta V(\mathbf{r}) = 4\pi\ e^2[Z\delta^3(\mathbf{r}) - \rho(\mathbf{r})] \tag{8.70}$$

with

$$Z = \int d^3r\ \rho(\mathbf{r}) \tag{8.71}$$

due to the charge neutrality of the atom. If $v(\mathbf{q})$ and $F(\mathbf{q})$ are the Fourier—transforms of $V(\mathbf{r})$ and $\rho(\mathbf{r})$,

$$v(\mathbf{q}) = \int d^3r\ \ \exp\left(-i\mathbf{q}\cdot\mathbf{r}\right)V(\mathbf{r}); \quad F(\mathbf{q}) = \int d^3r\ \ \exp\left(-i\mathbf{q}\cdot\mathbf{r}\right)\rho(\mathbf{r}), \tag{8.72}$$

then after Fourier transformation follows from (8.70),

$$q^2 v(\mathbf{q}) = -4\pi\ e^2 (Z - F(\mathbf{q})). \tag{8.73}$$

Now $\sigma(\Omega)$ in first order Born approximation (according to (8.58)) is:

$$\sigma(\Omega) = |f(\Omega)|^2 = \frac{4\mu^2}{16\pi^2\hbar^4} |v(\mathbf{K})|^2, \tag{8.74}$$

and with (8.73) follows:

$$\sigma(\Omega) = \frac{4\mu^2 e^4}{\hbar^4 K^4} (Z - F(\mathbf{K}))^2. \tag{8.75}$$

For a spherical charge distribution

$$\rho = \rho(r) \tag{8.76}$$

the formfactor becomes

$$F = F(q) = \frac{4\pi}{q} \int_0^\infty \sin\,(qr)\rho(r) r\ dr. \tag{8.77}$$

This implies for the **form factor** $F(q)$:
(i)

$$F(0) = Z \tag{8.78}$$

and for small values of K
(ii)

$$F(K) \approx Z - \frac{1}{6}\ K^2 R_0^2 \ldots \tag{8.79}$$

with the abbreviation

$$R_0^2 = 4\pi \int_0^\infty r^2 \rho(r) r^2 dr. \tag{8.80}$$

Here R_0^2 is the mean square radius of the charge distribution of the electrons of the atoms, which can be determined from the scattering of electrons on atoms.

In analogy, by electron scattering at sufficiently high energy one can measure the charge distribution in atomic nuclei or even within hadrons (nucleons, mesons, etc.).

8.3 The Partial Wave Method

8.3.1 Scattering in the Central Field

For a central potential

$$V = V(r) \tag{8.81}$$

the Schrödinger equation can be calculated using the separation Ansatz (see Sect. 7.6.1)

$$\psi_{lm}(\mathbf{r}) = \frac{1}{r}\ \chi_l(r) Y_{lm}(\vartheta, \varphi) \tag{8.82}$$

leading to

$$\left\{ \frac{\partial^2}{\partial r^2} - \frac{l(l+1)}{r^2} + k^2 - U(r) \right\} \chi_l(r) = 0, \tag{8.83}$$

with

$$U(r) = \frac{2\mu}{\hbar^2} V(r) \tag{8.84}$$

and

$$k^2 = \frac{2\mu}{\hbar^2} E > 0 \tag{8.85}$$

in case of a scattering problem. Due to the boundary conditions specified experimentally (incident plane wave in z-direction, directionally modulated outgoing spherical wave) the scattering solution cannot be an eigenfunction of l^2. However, it has axial symmetry around the z-axis because of (8.81) and the axial symmetry of the incident particle beam; the scattering solution then has the general form

$$\boxed{\psi(\mathbf{r}) = \sum_{l=0}^{\infty} \frac{1}{r}\ \chi_l(r) Y_{l0}(\vartheta, \varphi),} \tag{8.86}$$

where the φ -dependence can be omitted due to the special geometry. The remaining Legendre polynomials are

$$Y_{l0}(\vartheta) = \sqrt{(2l+1)/(4\pi)} P_l(\cos\vartheta).$$

If

$$\lim_{r\to\infty} rV(r) \to 0, \tag{8.87}$$

the solutions for (8.86) asymptotically merge with the solutions of the free particle (cf. 7.6). We can therefore (by combining (7.274) and (7.275)) write for the asymptotics of $\chi_l(r)$

$$\boxed{\chi_l(r)_{r\to\infty} = A_l \sin\left(kr - \frac{l\pi}{2} + \delta_l\right).} \tag{8.88}$$

The separation of the phase in (8.88) into two parts ($l\pi/2$ and δ_l) is useful because for $V \equiv 0$ (7.271)

$$\chi_l = kr\ j_l(kr), \tag{8.89}$$

such that asymptotically (cf. (7.274))

$$\chi_l(r)_{r\to\infty} \sim \sin\left(kr - \tfrac{l\pi}{2}\right). \tag{8.90}$$

Thus the phases δ_l are **phase shifts** of the individual partial waves (for the respective angular momentum *l*) caused by the potential *V*. The **scattering phases** δ_l of course not only depend on *V*(*r*), but also on *E* or *k*, i.e.

$$\delta_l = \delta_l(k). \tag{8.91}$$

8.3.2 Convergence of the Partial Wave Expansion

The expansion (8.86) is only of practical use if one focuses on a few *l* values; this is the case if *V* is short-range or if the energy is low.

Instead of a mathematical investigation of convergence, we limit ourselves to the following physical argument: In the scattering of a classical particle at a central potential the possible trajectories are characterized by the impact parameter *b*. The latter depends on the angular momentum and the momentum of the particle by:

$$l_{kl.} = b\ p_{kl.}. \tag{8.92}$$

For a potential of finite range r_0,

$$V(r) = 0 \,\text{for r} > \text{r}_0, \tag{8.93}$$

a classical particle is only deflected if

$$b \le r_0 \tag{8.94}$$

or because of (8.92)

$$l_{kl.} \le r_0\ p_{kl.}. \tag{8.95}$$

Accordingly, we expect that in (8.86) only the *l* values have to be taken into account with

$$l \le r_0\ k, \tag{8.96}$$

if *k* is the wave number associated with $p_{kl.}$. For low energy $E = \hbar^2 k^2/(2\mu)$ therefore only a few *l* values in (8.86) should be sufficient.

The following consideration leads to the same estimate: For fixed energy *E* the minimum distance $r_{\min}$ of the particle from the scattering center is determined by the condition

$$E \ge V(r)_{kl.} + \frac{l_{kl.}^2}{2\mu r_{kl.}^2}. \tag{8.97}$$

With increasing angular momentum l_{kl} the closest distance $r_{\min}$ becomes larger since the centrifugal barrier becomes more and more repulsive until finally no more deflection can take place for $r_{\min} > r_0$ by the potential *V*.

The classical estimates above are confirmed qualitatively by the quantum theory.

8.3.3 Scattering Phases and Scattering Amplitude

We now try to connect the scattering phases δ_l with the scattering amplitude $f(\vartheta)$, which in turn gives the differential cross section $\sigma(\vartheta)$ by its magnitude squared.

To this aim we expand the asymptotic form

$$\psi(\mathbf{r})_{r\to\infty} = \exp\,(ikz) + f(\vartheta)\frac{\exp(ikr)}{r} \tag{8.98}$$

by partial waves. According to section 7.6.3 the plane wave—as the solution of the Schrödinger equation for the free particle—can be represented as (7.271)

$$\exp\,(ikz) = \sum_{l=0}^{\infty}\; a_l\; j_l(kr)Y_{l0}(\vartheta). \tag{8.99}$$

The expansion coefficients a_l are obtained according to Sect. 7.6.3 and read

$$a_l = i^l(2l+1)\sqrt{\tfrac{4\pi}{2l+1}}. \tag{8.100}$$

In the 2nd term of (8.98) we expand

$$f(\vartheta) = \sum_l f_l\; Y_{l0}(\vartheta) \tag{8.101}$$

and get

$$\exp\,(ikz) + f(\vartheta)\tfrac{\exp(ikr)}{r} = \sum_l\Big\{a_l\; j_l(kr) + f_l\tfrac{\exp(ikr)}{r}\Big\}Y_{l0}(\vartheta). \tag{8.102}$$

With the asymptotics of the j_l from (7.274) we obtain

$$\psi(\mathbf{r})_{r\to\infty} = \sum_l \tfrac{1}{r}\; Y_{l0}(\vartheta)\Big\{\Big[f_l + \tfrac{(-i)^l}{2ik}a_l\Big]\,\exp\,(ikr) - \tfrac{(+i)^l}{2ik}a_l\,\exp\,(-ikr)\Big\}. \tag{8.103}$$

On the other hand, according to (8.86) and (8.88)

$$\psi(\mathbf{r})_{r\to\infty} = \sum_l \tfrac{1}{r}\; Y_{l0}(\vartheta)A_l\,\sin\,\big(kr - \tfrac{l\pi}{2} + \delta_l\big) \tag{8.104}$$

$$= \sum_l \frac{1}{r}\; Y_{l0}(\vartheta)A_l\frac{1}{2i}\left[\exp\,\left(i(kr - \frac{l\pi}{2} + \delta_l)\right) - \exp\,\left(-i(kr - \frac{l\pi}{2} + \delta_l)\right)\right].$$

By a comparison of the coefficients (with $i^l = \exp\,(il\pi/2)$) we get

$$A_l = i^l\tfrac{\sqrt{4\pi(2l+1)}}{k}\;\;\exp\,(i\delta_l) \tag{8.105}$$

and

$$f_l = \tfrac{\sqrt{4\pi(2l+1)}}{k}\;\;\exp\,(i\delta_l)\,\sin\,(\delta_l). \tag{8.106}$$

Then we obtain for $f(\vartheta)$

$$f(\vartheta) = \tfrac{1}{k}\sum_l \sqrt{4\pi(2l+1)}\,\exp\,(i\delta_l)\,\sin\,(\delta_l)Y_{l0}(\vartheta) \tag{8.107}$$

$$= \frac{1}{k} \sum_l (2l+1) \exp(i\delta_l) \sin(\delta_l) P_l(\cos\vartheta),$$

and for the differential scattering cross section

$$\sigma(\vartheta) = \tfrac{1}{k^2} \textstyle\sum_{l,l'} (2l+1)(2l'+1) \exp(i(\delta_l - \delta_{l'})) \sin(\delta_l) \sin(\delta_{l'}) P_l(\cos\vartheta) P_{l'}(\cos\vartheta). \quad (8.108)$$

After integration over the angles we finally obtain for the total scattering cross section

$$\sigma = \tfrac{4\pi}{k^2} \textstyle\sum_{l=0}^{\infty} (2l+1) \sin^2 \delta_l, \quad (8.109)$$

taking into account the orthogonality of the $P_l(\cos\vartheta)$.
Comparing (8.107) and (8.109) we obtain the

8.3.4 Optical Theorem

$$\sigma = \tfrac{4\pi}{k} \Im(f(0)), \quad (8.110)$$

since $P_l(\cos\vartheta = 1) = 1$. Equation (8.110) is the quantitative expression for the fact, that the scattering of particles is necessarily linked to a weakening of the particle beam in the forward direction ($\vartheta = 0$).

Since (8.110) is important for an understanding of the scattering process we will prove (8.110) still in another way, that allows for an easier physical interpretation. Since *V*(*r*) was assumed to be real, the continuity Eq. (3.21) holds. Due to the stationarity of the states Eq. (3.21) simplifies to

$$\nabla \cdot \mathbf{j} = 0. \quad (8.111)$$

We integrate (8.111) over a sphere centered around the origin $r = 0$ with the radius *R* chosen so large that the asymptotic form (8.4) can be used:

$$\int d^3r \ \nabla \cdot \mathbf{j} = R^2 \int d\Omega \ j_R = 0, \quad (8.112)$$

where $j_R = j_R(\Omega)$ is the radial component of $\mathbf{j}$ on the surface of the sphere at a distance *R* from the scattering center. The radial component at distance *r* (sufficiently large)

$$j_r = \tfrac{\hbar}{2i\mu} \left\{ \psi^* \tfrac{\partial}{\partial r} \psi - \psi \tfrac{\partial}{\partial r} \psi^* \right\} \quad (8.113)$$

gives three parts when inserting ψ according to (8.4):

$$j_{r,0} = \tfrac{\hbar k}{\mu} \ \cos\vartheta, \quad (8.114)$$

which arizes from the plane wave $\exp\,(ikz) = \exp\,(ikr\ \ \cos\vartheta)$;

$$j_{r,scat} = \frac{\hbar k}{\mu}\,\frac{|f(\Omega)|^2}{r^2} \tag{8.115}$$

from the spherical wave and the interference term

$$j_{r,int} = \frac{\hbar k}{\mu}\,\frac{1+\cos\vartheta}{2r}\{f(\vartheta)\,\exp\,(ik(r-z)) + f^*(\vartheta)\,\exp\,(-ik(r-z))\}, \tag{8.116}$$

when considering only the leading term in $1/r$.

The term (8.114) gives no contribution to (8.112) since

$$\int d\Omega\ \ \cos\vartheta = 2\pi\int_{-1}^{1} d\cos\vartheta\ \ \cos\vartheta = 0. \tag{8.117}$$

From (8.115) we get the contribution

$$\frac{\hbar k}{\mu}\ \sigma \tag{8.118}$$

according to (8.2) and (8.7). For the validity of (8.112) to hold, (8.118) must be compensated by the contribution of (8.116). Since we know the exact result, equation (8.110), the following heuristic considerations are sufficient: Due to the rapidly oscillating terms in (8.116) for $kr \gg 1$ contributions to the integral (8.112) arize only for values $\vartheta \approx 0$. We therefore get:

$$R^2\int\ j_{R,int}\ d\Omega$$

$$\approx \frac{\hbar k}{\mu}\ R\ 2\pi\big\{f(0)\int dx\ \ \exp\,(ikR(1-x)) + f^*(0)\int dx\ \ \exp\,(-ikR(1-x))\big\}, \tag{8.119}$$

provided that $f(\vartheta)$ changes slowly. After performing the *x* integration a contribution proportional to $\Im(f(0)) = 1/2(f(0) + f^*(0))$ remains in accordance with the exact result (8.110).

8.3.5 Calculation of the Scattering Phases δ_l

We consider again the radial equation

$$\Big\{\frac{\partial^2}{\partial r^2} - \frac{l(l+1)}{r^2} + k^2 - U(r)\Big\}\chi_l(r) = 0 \tag{8.120}$$

and assume that the (real) solutions are normalized in such a way that

$$\chi_l(r)_{r\to\infty} \sim \sin\,\big(kr - \tfrac{l\pi}{2} + \delta_l\big). \tag{8.121}$$

We now compare the solutions χ_l (or the phases δ_l) with the solutions χ_l^0 (or phases δ_l^0) to the potential $U^0(r)$ at the same energy. To this aim we use the Wronski theorem (cf. Sect. 7.1.2):

$$W(\chi_l,\chi_l^0)|_a^b = \chi_l\chi_l^{0\prime} - \chi_l^0\chi_l'\big|_a^b = -\int_a^b \chi_l^0(U-U^0)\chi_l\ dr. \tag{8.122}$$

Choosing specifically the integration limits $a = 0$ and $b = \infty$, we get

$$W(\chi_l, \chi_l^0)|_0^\infty = k \ \ \sin(\delta_l - \delta_l^0), \tag{8.123}$$

since according to Sect. 7.6.1

$$\chi_l(0) = 0 = \chi_l^0(0). \tag{8.124}$$

Thus

$$\sin(\delta_l - \delta_l^0) = -\tfrac{1}{k} \int_0^\infty \chi_l^0 (U - U^0) \chi_l \ dr. \tag{8.125}$$

Equation (8.125) is exact. We can get two important results from (8.125):
(i) For $U^0 \equiv 0$ we have $\delta_l^0 \equiv 0$ and

$$\chi_l^0 = kr \ j_l(kr), \tag{8.126}$$

such that

$$\sin(\delta_l) = -\int_0^\infty j_l(kr) U(r) \chi_l(r) r \ dr. \tag{8.127}$$

Equation (8.127) can be used to calculate the phases iteratively in the same way as in Sect. 8.2.3. In the **first Born approximation** we obtain:

$$\sin(\delta_l) \approx -k \int_0^\infty U(r) j_l^2(kr) r^2 dr. \tag{8.128}$$

Now the Bessel functions behave for small values of the argument $\rho \equiv kr$ like (cf. Sect. 7.6.1),

$$j_l(kr) \sim (kr)^l. \tag{8.129}$$

For a potential of finite range r_0 follows from (8.127) or (8.128) that the phases δ_l for fixed energy *E* (fixed *k* value) decrease with increasing *l*. For $k \approx 0$ one expects only contributions to the scattering cross section for small *l* values; especially for $k \to 0$ we only expect contributions for $l = 0$, i.e. isotropic scattering (***s*-wave scattering**).

In this limiting case the scattering cross section σ (8.109) is given by

$$\sigma(k = 0) = \lim_{k \to 0} \tfrac{4\pi}{k^2} \ \sin^2 \ \delta_0(k) \tag{8.130}$$

and in first order Born's approximation (with (8.128) and (8.129)) we get explicitly,

$$\sigma(k = 0) = 4\pi \ a^2, \tag{8.131}$$

with the **scattering length**

(8.132)

$$a = \lim_{k\to 0} \frac{1}{k} \int_0^\infty U(r) j_0(kr) \chi_0(kr) r \; dr.$$

With increasing *k*, except for $l = 0$, also *l* = 1 (*p*-wave scattering), $l = 2$ (*d*-wave scattering) etc. become important which is reflected in the experimental angular distribution. The results of the classical discussion in Sect. 8.3.2 thus are confirmed.

(ii) If $\Delta U \equiv U - U^0$ is small, in general - with the exception of resonance scattering - the phase difference $\Delta\delta_l \equiv \delta_l - \delta_l^0$ will be small and (8.125) turns to:

$$\Delta\delta_l = -\frac{1}{k} \int_0^\infty \Delta U \; \chi_l^2 \; dr; \tag{8.133}$$

the difference between χ_l^0 and χ_l on the right side of (8.125) has been neglected here. Thus if $\Delta U > 0 \;\; (< 0)$ for all *r* then $\Delta\delta_l < 0 \;\; (> 0)$; in particular for a repulsive potential everywhere the phase δ_l is negative, for an attractive potential everywhere the phase δ_l is positive. Thus from the sign of δ_l (or a change in sign for a certain energy) we can extract general properties of the potential *V*.

8.3.6 Coulomb Scattering

Due to the requirement (8.87) the Coulomb potential needs a special treatment. The crucial point is that for the Coulomb potential for the asymptotics of χ_l Eq. (8.88) no longer holds, but has to be replaced by (7.279). The phases σ_l are the scattering phases of the Coulomb potential in analogy to the phases δ_l used above; the Coulomb phases σ_l can be calculated exactly.

8.3.7 Inelastic Scattering

For elastic scattering we can rewrite the asymptotics of ψ (8.104) as follows:

$$\psi(\mathbf{r})_{r\to\infty} = \sum_l (2l+1) i^l \exp(i\delta_l) \frac{\sin\left(kr - \frac{l\pi}{2} + \delta_l\right)}{kr} P_l(\cos\vartheta) \tag{8.134}$$

$$= \frac{i}{2kr} \sum_l (2l+1) [(-1)^l \exp(-ikr) - S_l \exp(ikr)] P_l(\cos\vartheta)$$

with

$$S_l = \exp(2i\delta_l). \tag{8.135}$$

As long as δ_l is real, S_l is a pure phase factor, such that ψ contains incoming and outgoing spherical waves with the same weight. This characterizes elastic scattering, for which the continuity Eq. (8.111) or (8.112) holds.

For inelastic processes the outgoing spherical wave - in the elastic channel - must be weakened compared to the incoming one because part of the current flows into the inelastic channels. We can formally take this into account by replacing the real phases δ_l with complex phases

$$\eta_l = \delta_l + i\gamma_l; \gamma_l > 0, \tag{8.136}$$

such that the magnitude of S_l will be

$$|S_l| < 1, \tag{8.137}$$

while for elastic scattering we always have

$$|S_l| = 1. \tag{8.138}$$

The scattering amplitude in the elastic channel then (in analogy to (8.107)) is

$$f(\vartheta) = \frac{1}{k} \sum_l (2l+1) \exp(i\eta_l) \sin(\eta_l) P_l(\cos\vartheta) \tag{8.139}$$

or expressed by S_l

$$f(\vartheta) = \frac{1}{2ik} \sum_l (2l+1)[S_l - 1] P_l(\cos\vartheta). \tag{8.140}$$

Using (8.140) one can characterize two limiting cases: for a given partial wave *l* then $S_l = 1$ means no scattering and $S_l = 0$ total absorption.

For the scattering cross section of elastic scattering follows from (8.140):

$$\sigma_{el.} = \frac{\pi}{k^2} \sum_l (2l+1) |S_l - 1|^2. \tag{8.141}$$

By S_l also the **reaction cross section** σ_r—with respect to all inelastic channels—and the **total scattering cross section**

$$\sigma_t \equiv \sigma_{el.} + \sigma_r \tag{8.142}$$

can be expressed. For σ_t again the optical theorem (expressed via the continuity Eq. (8.111) or (8.112)) must hold:

$$\sigma_t = \frac{4\pi}{k} \Im(f(0)) = \frac{2\pi}{k^2} \sum_l (2l+1)[1 - \Re(S_l)] \tag{8.143}$$

using (8.140). Note that the imaginary part of the forward scattering amplitude for the elastic channel enters (8.143), since this weakens the incident particle beam! From (8.142) and (8.143) we then obtain

$$\sigma_r = \frac{\pi}{k^2} \sum_l (2l+1)[1 - |S_l|^2]. \tag{8.144}$$

For purely real potentials inelastic scattering, of course, does not happen since the current is conserved alone as shown in Sect. 8.3.4. Without discussing the mechanism, which causes inelasticity, we can formally describe inelastic scattering by introducing a complex potential. The scattering phases—calculated for such a complex potential—are then the complex phases η_l introduced ad hoc above. From the scattering phases η_l we then can calculate σ_{el}, σ_r and σ_t.

Remark: Inelastic scattering,

$$|S_l| < 1, \;\; \sigma_r \neq 0, \tag{8.145}$$

is necessarily accompanied by elastic scattering,

$$\sigma_{el} \neq 0, \tag{8.146}$$

since with (8.145)

$$|S_l - 1| \neq 0. \tag{8.147}$$

This is clear, since inelastic channels imply a loss of current in the elastic channel such that the plane wave cannot remain undisturbed.

8.3.8 Gamov States Resonance Scattering

We have seen in Sect. 7.1.1 that for positive energy—apart from pure scattering states (classically: open trajectories)—also **Gamov states** may occur. In the following we only want to make (qualitatively) clear that the phases δ_l and the scattering cross section σ in the two cases behaves differently. In the first case (Sect. 7.1.1, type $2+3$) we expect that δ_l and σ vary monotonically with energy (a); in the second case (Sect. 7.1.1, type 4) we note that quasi-bound states in the inner region of the potential (Gamov states) can exist, which due to tunneling decay in time. In a scattering experiment for a (type 4) potential then δ_l and σ will depend sensitively on whether the energy is close to that of a Gamov state or not. In the latter case, the incident plane wave only weakly penetrates into the potential wall; the potential behaves in analogy to a hard sphere, for which the scattering consists of reflection and diffraction. In the other case, however, a sizeable fraction of the incident wave can penetrate the interior area, where **quasi-bound states** exist for a time τ, which strengthen the scattering wave after decay. Such Gamov states thus will induce a pronounced variation of δ_l and σ with the energy (see Fig. 8.4).

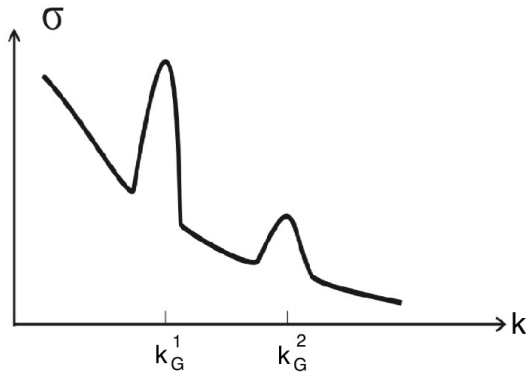

Fig. 8.4 Illustration of 'hard sphere' and 'resonant' scattering

In this case we are dealing with **resonance scattering**. The maxima in Fig. 8.4 at k_G^1 and k_G^2 correspond to the center position (in energy) of the Gamov states.

We now will briefly indicate the quantitative treatment of the Gamov states. We consider the finite-range potential

$$V(r) = v(r) \,\text{for}\, \mathrm{r} \leq \mathrm{r}_0, \tag{8.148}$$

which vanishes for $r > r_0$, and restrict ourselves to the case $l = 0$:

$$\left\{-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2} + V(r) - E\right\}\chi(r) = 0. \tag{8.149}$$

The Gamov solutions $\chi_m(r)$ from (8.149) can decay by tunneling; for $r > r_0$ therefore only outgoing waves exist,

$$\chi_m(r) = A_m \exp\left(ik_m r\right) \text{for } \mathrm{r} > \mathrm{r}_0. \tag{8.150}$$

where

$$E_m = \frac{\hbar^2 k_m^2}{2\mu} \tag{8.151}$$

is the energy of the Gamov state χ_m. The solutions χ_m must be connected continuous and with a continuous derivative to the outside area $r > r_0$. This is given by the condition:

$$\left(\frac{\partial\chi_m}{\partial r}\frac{1}{\chi_m}\right)_{r=r_0} = ik_m, \tag{8.152}$$

which is independent from the normalization constant introduced in (8.150).

The condition (8.152) leads to solutions of (8.149), for which the Hamiltonian (more precisely: the kinetic energy) is not hermitian, such that the energies E_m, which have to be calculated, become complex

$$E_m = \epsilon_m - \frac{i}{2\Gamma_m}. \tag{8.153}$$

The time-dependent solutions—corresponding to the χ_m—then have a time factor

$$\exp\left(-\frac{i}{\hbar}E_m t\right) = \exp\left(-\frac{i}{\hbar}\epsilon_m t\right)\exp\left(-\frac{\Gamma_m}{2\hbar}t\right), \tag{8.154}$$

which for $\Gamma_m > 0$ corresponds to an exponential decay with the decay constant Γ_m. In simple cases (e.g. for box-shaped potentials) an analytical solution of (8.149) with the boundary condition (8.152) can be carried out.

Since for a negative imaginary part of E_m (i.e. $\Gamma_m > 0$) also k_m—according to (8.151)—has a negative imaginary part, we get from (8.150) that a solution diverges exponentially in the outer space. This defect, however, is not a problem in practice, since we are interested in the decay constant Γ_m, which is determined by the wave function χ_m in the range $r \leq r_0$. To show this, we'll use again the Wronsky theorem:

$$-\frac{\hbar^2}{2\mu}(\chi_m^*\chi_m' - \chi_m\chi_m^{*\prime})|_0^{r_0} = (E_m - E_m^*)\int_0^{r_0}|\chi_m|^2 dr. \tag{8.155}$$

Due to

$$\chi_m(0) = 0 \tag{8.156}$$

and (8.150) we get from (8.155)

$$\Gamma_m = \frac{\hbar^2 k_m}{\mu} \frac{|\chi_m(r_0)|^2}{\int_0^{r_0} |\chi_m|^2 \, dr}. \tag{8.157}$$

Thus the decay constant Γ_m is actually determined by χ_m in the range $r \leq r_0$; it is proportional to the probability to find the fragments (e.g. α particles or the residual nucleus) at the distance r_0 from each other, relative to the probability to find the entire system inside the sphere with radius r_0 around the origin $r = 0$.

Formula (8.157) shows that the decay model outlined above only applies for very slowly decaying Gamov states: while Γ_m is defined as real by (8.153), the right-hand side of (8.157) is complex since k_m is complex. For very slowly decaying states ($\Gamma_m \ll |\epsilon_m - \epsilon_{m+1}|$) we can neglect $\Im(k_m)$ in (8.157) and obtain

$$\Gamma_m = \hbar v_m \frac{|\chi_m(r_0)|^2}{\int_0^{r_0} |\chi_m|^2 \, dr} \tag{8.158}$$

with

$$v_m = \hbar \frac{\Re(k_m)}{\mu} \tag{8.159}$$

as the relative velocity of the (separated) fragments.

Finally, we want to examine the case of resonance scattering on a simple, idealized example. For $l = 0$ we can solve the radial equation in the outer space $r > r_0$ and write as

$$\chi_k(r) = \frac{1}{2ik}(S_0 \exp{(ikr)} - \exp{(-ikr)}) \tag{8.160}$$

with

$$S_0 = \exp{(2i\delta_0)}; \tag{8.161}$$

cf. (8.134) and (8.135). We use the logarithmic derivative of χ at the point $r = r_0$ as an auxiliary variable:

$$R = \frac{\partial \chi}{\partial r} \frac{1}{\chi(r)}|_{r=r_0}. \tag{8.162}$$

Then we get as a connection condition between innner and outer space

$$R = ik \frac{S_0 \exp(ikr_0) + \exp(-ikr_0)}{S_0 \exp(ikr_0) - \exp(-ikr_0)}, \tag{8.163}$$

or solving for S_0

$$S_0 = \frac{R+ik}{R-ik} \exp{(-2ikr_0)}. \tag{8.164}$$

For the scattering cross section follows from (8.164) with (8.109) or (8.141):

$$\sigma_0 = \tfrac{\pi}{k^2}|S_0 - 1|^2 \equiv \tfrac{\pi}{k^2}|f_{res} + f_{pot}|^2, \tag{8.165}$$

where

$$f_{res} = \tfrac{2ik}{R - ik} \tag{8.166}$$

$$f_{pot} = 1 - \exp\,(2ikr_0). \tag{8.167}$$

The significance of the contribution of f_{pot} becomes immediately clear when considering the scattering on a hard sphere:

$$V(r) = \infty \,\text{for}\;\; \mathrm{r} \leq \mathrm{r}_0 \tag{8.168}$$

and $= 0$ else. Since $\chi(r_0) = 0$ for the potential (8.168), $R \to \infty$ and $f_{res} \to 0$. For the hard sphere then we get

$$\sigma_0 = 4\pi\;\, r_0^2 \left\{ \tfrac{\sin(kr_0)}{kr_0} \right\}^2. \tag{8.169}$$

We now consider the other extreme case, where f_{pot} can be neglected versus f_{res}. This happens if one (or more) Gamov states exist in the potential and the scattering energy $E = \hbar^2 k^2/(2\mu)$ is close to the energy ϵ_m of the Gamov state χ_m. Then we can approximate, if other Gamov states are energetically far away from χ_m, the wave function $\chi(r)$ in the interior region $r \leq r_0$ by

$$\chi(r) \approx \chi_m(r) \,\text{for}\, \mathrm{r} \leq \mathrm{r}_0. \tag{8.170}$$

Then according to (8.152)

$$R \approx ik_m, \tag{8.171}$$

thus

$$f_{res} \approx \tfrac{2k}{k_m - k}. \tag{8.172}$$

For $k = \Re(k_m)$, f_{res} has a maximum, which is narrow if the width of the Gamov state considered is small. Accordingly, one expects a strong change for $\sigma = \sigma(k)$: **resonance scattering** in the neighborhood of $k = \Re(k_m)$.

In summary, we have formulated the scattering theory for a single particle with an interaction $V(r)$, investigated the continuum states in different representations and derived the scattering amplitude as well as the differential cross section. Furthermore, the partial wave expansion for the scattering amplitude has been presented and the scattering phase shifts $\delta_l(k)$

been computed in lowest order. The discussion of resonance scattering has completed this chapter.

Part III
Mathematical Foundations of Quantum Mechanics

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9. Hilbert Space

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In this chapter we introduce to the concept of abstract states in a **Hilbert space** $\mathscr{H}$ and specify the formal requirements. Furthermore, we will introduce the Dirac notation which is particularly suited for many-body problems.

The central quantity in the quantum mechanics of a particle without spin is the spatial wave function $\psi(\mathbf{r})$, which describes the state of an ensemble of particles. However, this

(i) **spatial representation**

of a quantum mechanical state is not the only possible one. We have seen in Sect. 6.3 that the knowledge of the Fourier amplitudes $\tilde{\psi}(\mathbf{k};t)$ of the wave function $\psi(\mathbf{r};t)$ are also suitable for describing the state under consideration. We then have a

(ii) **momentum representation**

In general, we can expand a spatial wave function $\psi(\mathbf{r};t)$—describing a quantum mechanical state—according to any complete, orthonormalized set of functions $\varphi_\mu(\mathbf{r})$ and use the expansion coefficients

$$c_\mu(t) = \int d^3r \ \varphi_\mu^*(\mathbf{r})\psi(\mathbf{r};t) = (\varphi_\mu, \psi) \tag{9.1}$$

to characterize the state under consideration. In this

(iii) *C* **-representation**

the state is represented by a column vector

$$\mathbf{C}(t) = \begin{pmatrix} c_1(t) \\ c_2(t) \\ c_3(t) \\ \vdots \end{pmatrix} .$$

This kind of representation also includes the description of the spin of fermions using column vectors of dimension 2 (Sect. 6.5).

The same picture emerges for the operators to which we assign observables. In the spatial representation, $\mathbf{r}$ and $-i\hbar\nabla_r$ are the basic operators from which we built all other operators such as orbital angular momentum or potentials (see Chap. 5). In the momentum representation, the roles of position and momentum are just exchanged: the basic operators are $\mathbf{p} = \hbar\mathbf{k}$ and $i\hbar\nabla_p$. Starting from an observable in the spatial representation $F = F(\mathbf{r}, \mathbf{p})$, by forming the integrals

$$\int d^3r \ \varphi_\mu^* \ F \ \varphi_\nu = (\varphi_\mu, F \ \varphi_\nu) \equiv F_{\mu\nu} \tag{9.2}$$

in a complete basis $\{\varphi_\mu\}$, one arrives at the *C*-representation of *F* in the form of ∞-dimensional matrices. We recall that the Pauli spin matrices form a *C*-representation of the spin operators for fermions, even if they are not defined via an integral like (9.2).

The independence of quantum mechanical statements from the specific representation is shown explicitly by the fact, that e.g. the eigenvalues of the harmonic oscillator or the angular momentum can be determined solely on the basis of formal commutation rules of the operators describing the problem. It will be shown that quantum mechanical states can be described by **vectors in Hilbert space**.

9.1 Definition of Hilbert Space

A Hilbert space $\mathscr{H}$ is a set of elements $f, g, h \cdots$ (**vectors**) for which the following axioms are fulfilled:

(1) Linearity.

In $\mathscr{H}$ there is a connection of the elements (**addition**), with respect to which $\mathscr{H}$ forms an additive, abelian group. This implies in detail:

(1.1) For all $f, g \ \epsilon \ \mathscr{H}$ also $f + g = g + f \ \epsilon \ \mathscr{H}$;

(1.2) Associativity: $f + (g + h) = (f + g) + h$,

(1.3) Neutral element: there is an element $0 \in \mathscr{H}$ with $f + 0 = f$ for all $f \in \mathscr{H}$.

(1.4) Inverse element: for every $f \in \mathscr{H}$ there is an inverse element $(-f)$ such that $f + (-f) = 0$. Instead of $g + (-f)$ we write in short: $g - f$.

Furthermore, a multiplication with complex numbers is defined as follows: for complex numbers *a*, *b*, *c*.. the following holds

(1.5) If $f \in \mathscr{H}$, then also $af \in \mathscr{H}$.

(1.6) Distributivity: $a(f + g) = af + ag$; $(a + b)f = af + bf$.

(1.7) Associativity: $a(bf) = (ab)f$.

(1.8) $1\ f = f$ for all $f \in \mathscr{H}$.

(2) Metric:

In $\mathscr{H}$ an **inner product** is defined as follows: To each pair of vectors *f*, *g* we assign a complex number, denoted by $(f, g) \in \mathbb{C}$, with the properties:

(2.1) $(f, g) = (g, f)^*$

(2.2) $(f, ag) = a(f, g)$ for any complex numbers *a*,

(2.3) $(f, g_1 + g_2) = (f, g_1) + (f, g_2)$

(2.4) $(f, f) \geq 0$ for all $f \in \mathscr{H}$, where

(2.5) $(f, f) = 0$ only holds for the neutral element.

Because of (2.1) (f, f) is real.

The following properties directly follow from the definition of the inner product:

(i) **Orthogonal vectors**

Two vectors f, g are called **orthogonal** if

$$(f, g) = 0; \tag{9.3}$$

in particular the neutral element (zero vector) is orthogonal to every $f \in \mathscr{H}$.

(ii) **Parallel vectors**

Two vectors $f, g \in \mathscr{H}$ are called **parallel** if $f = ag$ with $a \in \mathbb{C}$.

(iii) **Length of a vector**

We define the length of a vector as

$$\|f\| = \sqrt{(f, f)}. \tag{9.4}$$

Before we complete the definition of the Hilbert space, we want to point out that axioms (1) and (2) guarantee the superposition principle (see Sect. 3.3) and the probability interpretation (Chap. 4).

(3) Completeness

As an auxiliary term we introduce the **strong convergence** of vectors: A sequence of vectors $f_n \in \mathscr{H}$ is called to converge to a vector $f \in \mathscr{H}$,

$$\lim_{n\to\infty} f_n = f, \tag{9.5}$$

if

$$\lim_{n\to\infty} \|f_n - f\| = 0. \tag{9.6}$$

From (9.6) follows by the triangle inequality

$$\lim_{n,m\to\infty} \|f_m - f_n\| = 0, \tag{9.7}$$

since

$$\|f_m - f_n\| \leq \|f_m - f\| + \|f_n - f\|. \tag{9.8}$$

A sequence of vectors f_n with the property (9.7) is called **Cauchy sequence**. The limit (9.7) is a necessary but not sufficient condition for (9.6); e.g. $(1+1/n)^n$ as a Cauchy sequence has no limit in the space of rational numbers. We therefore require that in $\mathscr{H}$ for every Cauchy sequence of vectors f_n there exists a limit element $f \in \mathscr{H}$: **completeness axiom**.

(4) Separability
In contrast to the usual definition of a Hilbert space in mathematics, in physics the additional requirement of separability is requested: In $\mathscr{H}$ there is a finite set $\{N\}$ of vectors f_ν with the property, that for every vector $f \in \mathscr{H}$ and any $\epsilon > 0$ there exists a vector $f_{\nu_0} \epsilon \{N\}$ that satisfies the inequality

$$\|f - f_{\nu_0}\| < \epsilon. \tag{9.9}$$

This completes the definition of the Hilbert space $\mathscr{H}$ as required in quantum theory.

The implications of axioms (3) and (4) become clear when we compare the Hilbert space $\mathscr{H}$ with a finite-dimensional, linear unitary vector space $\mathscr{L}_N$. Axioms (1) and (2) hold for both spaces; for $\mathscr{L}_N$ it follows that any vector $\gamma \in \mathscr{L}_N$ can be represented as

$$\gamma = \sum_{i=1}^{N} c_i \ \varphi_i \tag{9.10}$$

with

$$c_i = (\varphi_i, \gamma), \tag{9.11}$$

where the vectors φ_i, $i = 1, 2, \ldots, N$, are orthonormalized. For an ∞-dimensional vector space one must add axioms 3 and 4 such that each vector

g of the space can be represented by a finite set of orthogonal vectors f_i of the same space as

$$g = \sum_{i=1}^{\infty} d_i f_i \tag{9.12}$$

with

$$d_i = (f_i, g). \tag{9.13}$$

The (=)sign in (9.12) is to be understood in the sense of equation (9.6) as

$$\lim_{n\to\infty} \|g - \sum_{i=1}^{n} d_i f_i\| = 0. \tag{9.14}$$

Equation (9.14) is equivalent to the **completeness relation**

$$\|g\|^2 = \sum_{i=1}^{\infty} |d_i|^2. \tag{9.15}$$

While axiom (4) ensures that every vector $g \in \mathscr{H}$ can be expanded according to (9.12), (9.14), axiom (3) guarantees that the sequence $g_n \equiv \sum_{i<n} d_i f_i$ does not lead out of $\mathscr{H}$.

Axioms (3) and (4) guarantee the **probability interpretation** of **expectation values** (Chap. 6). The concept of convergence used in (9.6) is precisely tailored to the requirements of quantum theory, since all measurable quantities have been introduced as scalar products.

9.2 Schwarz's Inequality

For $f, g, h \in \mathscr{H}$ we have

$$|(f, g)| \leq \|f\| \cdot \|g\|. \tag{9.16}$$

Proof

(1) If f or g or both are the neutral element, then (9.16) is correct: the $(=)$ sign then holds.

(2) If $f \neq 0$, $g \neq 0$, we decompose $(h \in \mathscr{H})$

$$f = \frac{(g,f)}{(g,g)} g + h. \tag{9.17}$$

Then obviously

$$(g,h)=0, \tag{9.18}$$

i.e.

$$(f,f)=\left(\frac{(g,f)}{(g,g)}g+h,\frac{(g,f)}{(g,g)}g+h\right)=\frac{|(f,g)|^2}{(g,g)^2}(g,g)+(h,h), \tag{9.19}$$

such that

$$(f,f)\geq\frac{|(f,g)|^2}{(g,g)},\text{q. e. d.} \tag{9.20}$$

Schwarz's inequality (9.16) becomes an equality if and only if (in the proof) $h=0$, i.e. $f=ag$ (parallel vectors).

The **triangle inequality** follows from Schwarz's inequality:

$$\|f+g\|\leq\|f\|+\|g\|. \tag{9.21}$$

Proof

(1) If $\|f+g\|=0$ the statement is correct.

(2) Let $\|f+g\|\neq 0$. Then

$$\begin{aligned}\|f+g\|^2 &= (f+g,f+g)=(f+g,f)+(f+g,g)\\ &\leq\|f+g\|\cdot\|f\|+\|f+g\|\cdot\|g\|;\end{aligned} \tag{9.22}$$

the statement follows after division by $\|f+g\|$.

9.3 Realizations of $\mathscr{H}$

The abstract Hilbert space $\mathscr{H}$ can be realized in various ways. We give two examples that are important for quantum theory.

(i) The set of all column vectors

(9.23)

$$c =: \mathbf{C} = \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \end{pmatrix}$$

with ∞-many complex numbers c_i as components, for which

$$\sum_{i=1}^{\infty} |c_i|^2 < \infty. \tag{9.24}$$

The addition of two column vectors c, d is defined as

$$c + d = \begin{pmatrix} c_1 + d_1 \\ c_2 + d_2 \\ c_3 + d_3 \\ \vdots \end{pmatrix} \tag{9.25}$$

and the multiplication of a column vector with a complex number α as

$$\alpha c =: \begin{pmatrix} \alpha c_1 \\ \alpha c_2 \\ \alpha c_3 \\ \vdots \end{pmatrix}. \tag{9.26}$$

Finally, the scalar product is defined by

$$(c, d) = \sum_{i=1}^{\infty} c_i^* d_i. \tag{9.27}$$

The space thus formed is indeed a Hilbert space: Axiom 1.1 is fulfilled, because for two complex numbers c_i, d_i the following holds

$$|c_i + d_i|^2 \leq (|c_i| + |d_i|)^2 \leq (|c_i| + |d_i|)^2 + (|c_i| - |d_i|)^2 = 2|c_i|^2 + 2|d_i|^2, \tag{9.28}$$

such that with (9.24)

(9.29)

$$\sum_{i=1}^{\infty} |c_i + d_i|^2 < \infty,$$

i.e. the sum $c + d$ (defined by (9.25)) is an element of the space under consideration. The remaining requirements 1.2–1.8 are fulfilled trivially. From (9.27) together with (9.24) it follows that (c, d) is a complex number:

$$|c_i^* d_i| = |c_i||d_i| \leq \tfrac{1}{2}(|c_i|^2 + |d_i|^2); \tag{9.30}$$

due to (9.24)

$$\sum_{i=1}^{\infty} |c_i^* d_i| < \infty \tag{9.31}$$

and thus

$$\sum_{i=1}^{\infty} c_i^* d_i < \infty. \tag{9.32}$$

The axioms 2.1–2.5 then are satisfied trivially. Furthermore, the infinitely many vectors

$$\begin{pmatrix} 1 \\ 0 \\ 0 \\ \vdots \end{pmatrix}, \quad \begin{pmatrix} 0 \\ 1 \\ 0 \\ \vdots \end{pmatrix}, \quad \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \\ \vdots \end{pmatrix}, \ldots, \tag{9.33}$$

whose components all vanish except for a single one (which is chosen as 1), form a complete, orthonormal basis such that axioms 3. and 4. are fulfilled.

(ii) The set of all complex-valued functions $f(\mathbf{r})$, that are integrable in the sense of **Lebesgue**, for which holds:

$$\int d^3r \ |f(\mathbf{r})|^2 < \infty \tag{9.34}$$

form a Hilbert space, if we define addition and multiplication with complex numbers in the usual way and introduce the scalar product by

$$(f, g) := \int d^3r \ f^*(\mathbf{r}) \ g(\mathbf{r}). \tag{9.35}$$

The scalar product defined in (9.35) exists because of (9.34); the proof is as in example (i). Axioms 1.1–1.8 and 2.1–2.4 are obviously fulfilled. In contrast, 2.5 only holds, if we consider functions to be equivalent that differ only on a set of points of measure 0. For the proofs of axioms 3. and 4. we refer to the mathematical literature.

Remark: Axioms 3. and 4. with the scalar product (9.35) do not hold for merely continuous functions!

In the space $\mathscr{L}_2(-\infty, \infty)$ defined above, there are countably infinite, orthonormal systems of functions $\varphi_i(\mathbf{r})$; an example are the eigenfunctions of the harmonic oscillator. We can therefore expand any function $f(\mathbf{r})$ from $\mathscr{L}_2(-\infty, \infty)$ as

$$f(\mathbf{r}) = \sum_{i=1}^{\infty} c_i \ \varphi_i(\mathbf{r}). \tag{9.36}$$

The $(=)$ sign in (9.36) implies **no pointwise** convergence, but **convergence in the mean**,

$$\lim_{n\to\infty} \int d^3r \ \left| f(\mathbf{r}) - \sum_{i=1}^{n} c_i \ \varphi_i(\mathbf{r}) \right|^2 = 0. \tag{9.37}$$

The function $f(\mathbf{r})$ and its expansion (9.36) can therefore still differ on a set of points with measure 0.

The realization of the Hilbert space $\mathscr{H}$ by the space $\mathscr{L}_2(-\infty, \infty)$ just gives the spatial representation for a particle without spin. If we want to describe a particle with spin 1/2 or several particles, we need the concept of the **product space**. To simplify the notation we use the

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9.4 Dirac Notation

We denote a Hilbert vector, that describes a quantum mechanical state, by

$$|\Psi\rangle : \qquad \text{'ket vector'}. \tag{9.38}$$

We assign a 'bra vector' $\langle\Psi|$ uniquely to each 'ket vector' $|\Psi\rangle$ by specifying that

(i) the 'ket vector' $a|\Psi\rangle (a \ \epsilon \ \mathbb{C})$ is assigned to the 'bra vector' $a^*\langle\Psi|$, and

(ii) the sum $|\Psi_1\rangle + |\Psi_2\rangle$ to the 'bra vector' $\langle\Psi_1| + \langle\Psi_2|$.

By (i) and (ii) an **antilinear mapping** is defined, i.e. for an antilinear operator *O* the following holds:

$$O(a|\psi_1\rangle + b|\psi_2\rangle) = a^* O|\psi_1\rangle + b^* O|\psi_2\rangle.$$

Between a ket vector $|\Psi_1\rangle$ and a bra vector $\langle\Psi_2|$ a scalar product is introduced by

(iii) $\langle\Psi_2|\Psi_1\rangle = (\Psi_2, \Psi_1)$.

If the vectors $|\varphi_\nu\rangle$, $\nu = 1, 2, \ldots$, form a complete, orthonormalized basis in the Hilbert space, then the expansion of an arbitrary vector $|\Psi\rangle$ in this basis is:

$$|\Psi\rangle = \sum_{\nu=1}^{\infty} |\varphi_\nu\rangle\langle\varphi_\nu|\Psi\rangle \tag{9.39}$$

with the expansion coefficients

$$\langle\varphi_\nu|\Psi\rangle = (\varphi_\nu, \Psi). \tag{9.40}$$

Equation (9.39) suggests, that

$$\sum_{\nu=1}^{\infty} |\varphi_\nu\rangle\langle\varphi_\nu| = E_{\mathscr{H}} \equiv 1_{\mathscr{H}} \tag{9.41}$$

can be interpreted as the **identity operator** in Hilbert space. This is possible indeed: the mathematical background (keyword: dual spaces $\mathscr{H}^\dagger$; $|\Psi\rangle \epsilon\ \mathscr{H}$, $\langle\Psi| \epsilon\ \mathscr{H}^\dagger$; $\mathscr{H}^\dagger \equiv \mathscr{H}$ in the case of Hilbert spaces) will not be discussed here explicitly.

9.5 Product Spaces

Let the vectors $|\chi_i^1\rangle;\ i = 1, 2, \ldots$, form a complete, orthonormal basis in a Hibert space $\mathscr{H}_1$, $|\varphi_j^2\rangle$ a similar basis in another Hilbert space $\mathscr{H}_2$. We now consider the set of products

$$|\Psi_k^{1,2}\rangle =: |\chi_i^1\rangle|\varphi_j^2\rangle; k =: (i, j), \tag{9.42}$$

which should have the following properties:

(1) The multiplication (9.42) is commutative

(9.43)

$$|\chi_i^1\rangle|\varphi_j^2\rangle = |\varphi_j^2\rangle|\chi_i^1\rangle.$$

(2) The multiplication (9.42) is distributive with respect to the addition in $\mathscr{H}_1$ or $\mathscr{H}_2$, if

$$|\chi_i^1\rangle = \lambda|\chi_n^1\rangle + \lambda'|\chi_{n'}^1\rangle, \tag{9.44}$$

then

$$|\chi_i^1\rangle|\varphi_j^2\rangle = \lambda|\chi_n^1\rangle|\varphi_j^2\rangle + \lambda'|\chi_{n'}^1\rangle|\varphi_j^2\rangle. \tag{9.45}$$

If one declares a scalar product in the space of vectors $|\Psi_k^{1,2}\rangle$ by ($k = (i,j)$, $k' = (i',j')$)

$$\langle\Psi_k^{1,2}|\Psi_{k'}^{1,2}\rangle =: \langle\chi_i^1|\chi_{i'}^1\rangle\langle\varphi_j^2|\varphi_{j'}^2\rangle, \tag{9.46}$$

then the **product space** spanned by the vectors $|\Psi_k^{1,2}\rangle$, which we denote by

$$\mathscr{H}_1 \otimes \mathscr{H}_2, \tag{9.47}$$

is also a Hilbert space in which the vectors $|\Psi_k^{1,2}\rangle$ form a complete, orthonormal basis.

Examples:

(i) **2 particles without spin**

Particle 1 is described in a Hilbert space $\mathscr{H}_1$, realized by spatial wave functions $\chi_i(\mathbf{r}_1)$, which form a **complete orthonormal system** in $\mathscr{H}_1$. $\varphi_j(\mathbf{r}_2)$ is also a complete orthonormal system in the Hilbert space $\mathscr{H}_2$ belonging to particle 2. The product functions

$$\psi_k(\mathbf{r}_1,\mathbf{r}_2) =: \chi_i(\mathbf{r}_1)\varphi_j(\mathbf{r}_2); k =: (i,j), \tag{9.48}$$

form a complete basis in $\mathscr{H}_1 \otimes \mathscr{H}_2$ in which every wave function of the two-particle system can be expanded as:

$$\Psi(\mathbf{r}_1,\mathbf{r}_2) = \sum_{k=1}^{\infty} c_k\ \psi_k(\mathbf{r}_1,\mathbf{r}_2). \tag{9.49}$$

(ii) Separation Ansatz
The Ansatz

$$\psi(\mathbf{r}) = \psi_1(x)\psi_2(y)\psi_3(z) \tag{9.50}$$

leads to a decomposition of the Hilbert space $\mathscr{H}$, to which the vectors $\psi(\mathbf{r})$ belong, i.e.

$$\mathscr{H} = \mathscr{H}_x \otimes \mathscr{H}_y \otimes \mathscr{H}_z. \tag{9.51}$$

(iii) Particles with spin 1/2
The Hilbert space of the spinors introduced in Chap. 6.5

$$\Psi(\mathbf{r};t) = \Psi_u(\mathbf{r};t)\begin{pmatrix}1\\0\end{pmatrix} + \Psi_d(\mathbf{r};t)\begin{pmatrix}0\\1\end{pmatrix} \tag{9.52}$$

can be understood as a product space of the Hilbert space of the pure spatial functions $\Psi_{u/d}(\mathbf{r};t)$ and the space of the pure spin states, built up from the two unit vectors

$$\begin{pmatrix}1\\0\end{pmatrix}, \qquad \begin{pmatrix}0\\1\end{pmatrix}. \tag{9.53}$$

9.6 Improper Hilbert Vectors

In Sect. 6.3 we have seen that the momentum operator has a continuous spectrum and the eigenfunctions are plane waves:

$$\mathbf{p} \;\; \exp\,(i\mathbf{k}\cdot\mathbf{r}) = \hbar\mathbf{k} \;\; \exp\,(i\mathbf{k}\cdot\mathbf{r}). \tag{9.54}$$

The plane waves are orthogonal for different $\mathbf{k}$, but not normalizable. They are nevertheless useful because of their completeness: according to **Fourier's integral theorem**, every square-integrable function $\psi(x;t)$ can be represented as

$$\psi(x;t) = \lim_{a\to\infty} \frac{1}{\sqrt{(2\pi}} \int_{-a}^{a} \exp\,(ikx)\tilde{\psi}(k;t)\;\, dk, \tag{9.55}$$

(cf. Sect. 6.3). After extension to the 3-dimensional case, we write for (9.55) in Dirac notation briefly (including the formation of the limit) as

$$|\psi\rangle = \int d^3k \ |\mathbf{k}\rangle\langle\mathbf{k}|\psi\rangle, \tag{9.56}$$

where the improper vector $|\mathbf{k}\rangle$ corresponds to the plane wave $(2\pi)^{-3/2} \exp(i\mathbf{k}\cdot\mathbf{r}) \equiv \langle\mathbf{r}|\mathbf{k}\rangle$ and

$$\langle\mathbf{k}|\psi\rangle = \tilde{\psi}(\mathbf{k}) \tag{9.57}$$

is the Fourier transform of the spatial wave function $\psi(\mathbf{r})$, which describes the abstract Hilbert vector $|\psi\rangle$ in spatial representation. We write the completeness relation in analogy to (9.41) as

$$\int d^3k \ |\mathbf{k}\rangle\langle\mathbf{k}| = 1_{\mathscr{H}}. \tag{9.58}$$

The '**normalization**' of the improper vectors $|\mathbf{k}\rangle$ is

$$\langle\mathbf{k}|\mathbf{k}'\rangle = \delta^3(\mathbf{k}-\mathbf{k}'). \tag{9.59}$$

Similar to the momentum, but mathematically a little more subtle, is the eigenvalue problem of the position operator. The '**eigenfunctions**' of the operator $\hat{\mathbf{r}}$ for the eigenvalue $\mathbf{r}'$ are δ**-distributions**

$$\hat{\mathbf{r}} \ \delta^3(\mathbf{r}-\mathbf{r}') = \mathbf{r}' \ \delta^3(\mathbf{r}-\mathbf{r}'). \tag{9.60}$$

This system of δ-distributions is complete, since every wave function $\psi(\mathbf{r})$ has the integral representation

$$\psi(\mathbf{r}) = \int d^3r' \ \delta^3(\mathbf{r}-\mathbf{r}')\psi(\mathbf{r}') \tag{9.61}$$

according to the definition of the δ- distribution. If $|\mathbf{r}'\rangle$ is the improper vector, which is assigned to the distribution $\delta^3(\mathbf{r}-\mathbf{r}')$ with a fixed $\mathbf{r}$ in Dirac notation, then (9.61) is written in Dirac notation as

(9.62)

$$|\psi\rangle = \int d^3r' \ |\mathbf{r}'\rangle\langle\mathbf{r}'|\psi\rangle = \int d^3r' \ |\mathbf{r}'\rangle\psi(\mathbf{r}').$$

Since

$$\langle\mathbf{r}|\mathbf{r}'\rangle = \int d^3r'' \ \delta^3(\mathbf{r}-\mathbf{r}'')\delta^3(\mathbf{r}'-\mathbf{r}'') = \delta^3(\mathbf{r}-\mathbf{r}'), \tag{9.63}$$

(9.61) follows from (9.62) after forming $\langle\mathbf{r}|\psi\rangle$. We can therefore identify

$$\langle\mathbf{r}|\psi\rangle \equiv \psi(\mathbf{r}). \tag{9.64}$$

Spatial wave functions $\psi(\mathbf{r})$ or their Fourier transforms $\tilde{\psi}(\mathbf{k})$ are thus expansion coefficients of a state vector $|\psi\rangle$ in the basis of the position eigenvectors $|\mathbf{r}\rangle$ or the momentum eigenvectors $|\mathbf{k}\rangle$.

If one wants to avoid the use of distributions, one must give up the sharp localization in momentum or position space inherent in the improper vectors $|\mathbf{k}\rangle$ or $|\mathbf{r}\rangle$. Instead of plane waves one uses **wave packets**; the use of the plane waves in the asymptotics of scattering states always has to be understood in this sense. From the δ-distribution, e.g. a Gauss function of small but finite width is obtained. An alternative is to restrict the position space (or momentum space) to a very large but finite **normalization volume** and to introduce suitable boundary conditions (e.g. periodic). This provides a discrete spectrum and normalizable functions.

In summarizing this chapter we have introduced the concept of abstract states in a **Hilbert space** $\mathscr{H}$ and specified the formal requirements. Furthermore, we have introduced the Dirac notation, which is particularly suited for many-body problems, and specified the eigen-vectors for momentum and position in $\mathscr{H}$.

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10. Operators in Hilbert Space

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In this chapter we introduce linear operators in $\mathscr{H}$ and their respective domains. Physical observables will be identified with matrix-elements of self-adjoint operators in $\mathscr{H}$ and their spectra and eigenstates will be investigated. This concept will be extended to operators in product spaces. As an example we will calculate the coupling of angular momenta in $\mathscr{H}$ and the separation of the center of mass and relative motion. Furthermore, the exchange symmetry for identical particles will be studied and lead to a separation of symmetric and anti-symmetric many-body states, i.e. Bose and Fermi systems.

10.1 Heuristic Introduction

In the context of the quantum theory of a particle we have assigned **operators** to classical observables using a quantization rule. In the case of spin, which has no analogue in classical physics, we have introduced **spin operators** in the form of 2 $\times$ 2 matrices with characteristic commutation rules based on the orbital angular momentum.

In order to be able to interpret the expectation values of such operators as statistical averages, these operators had to be hermitean (i.e. only have real eigenvalues, which represent the possible measured values) and have a complete set of eigenfunctions. The discussion of the hermiticity of momentum and orbital angular momentum has shown that for the complete determination of an operator, its **domain of definition** and its **domain of image** are also important. We will clarify these concepts again using the operators x and p_x. In the space $\mathscr{L}_2(-\infty, \infty)$ of square-integrable functions, x is applicable to every element $\psi(x)$ of the space (domain of definition); the image functions $x\psi(x)$ (domain of image), however, do not always belong to $\mathscr{L}_2(-\infty, \infty)$, e.g. functions $\psi(x)$, which drop asymptotically as $1/x$. On the other hand, p_x is only applicable to differentiable functions $\epsilon\ \mathscr{L}_2(-\infty, \infty)$; the image functions $-i\hbar\partial/\partial x\ \ \psi(x)$ also do not always belong to $\mathscr{L}_2(-\infty, \infty)$. This problem of the domain of definition and the domain of image

has already been discussed in connection with the uncertainty relation (see Sect. 6.4).

10.2 Basic Concepts

An operator (mapping) in Hilbert space $\mathscr{H}$ is defined by a mapping rule A, a domain $D_A \subseteq \mathscr{H}$ and an image domain $B_A \subseteq \mathscr{H}$, which consists of all elements

$$f' = Af \tag{10.1}$$

if f runs through the entire domain D_A, i.e. $\forall f \epsilon D_A$.

In quantum theory, due to the superposition principle, only the class of **linear operators** is of interest, which is defined by the fact that D_A is a linear manifold and for any $f_1, f_2 \epsilon D_A$ and any complex numbers a_1, a_2 the following holds:

$$A(a_1 f_1 + a_2 f_2) = a_1 A f_1 + a_2 A f_2. \tag{10.2}$$

10.3 Calculation Rules

1. **Equality**: 2 operators A and B are called to be equal if

$$A = B \tag{10.3}$$

and

$$D_A = D_B. \tag{10.4}$$

2. **Products**: Let two operators be defined by A, D_A, B_A and by B, D_B, B_B. Then we can execute the mapping AB in the order AB(= first B, then A) one after the other, if B_B and D_A have common elements. The domain of the product with the mapping AB is thus the set of all $f \epsilon D_B$ for which $Bf \epsilon D_A$.

This somewhat complex definition already shows that operators do not commute in general. The definition of the commutator of operators is only simple, if the domain of both operators is the entire Hilbert space $\mathscr{H}$. Commutability then means

$$AB = BA. \tag{10.5}$$

In contrast, operator multiplication is always associative.

Example: Operators that can be represented by (∞-dimensional) matrices in general do not commute, since the matrix multiplication is not commutative; however, it is always associative.

3. **Addition**: *a*, *b* are arbitrary complex numbers; D_A, D_B are the domains of the operators *A*, *B*. Then it is declared

$$(aA + bB)f = aAf + bBf \tag{10.6}$$

for all *f* from the intersection $D_A \bigcap D_B$. The addition is commutative and associative.

10.4 Linear Operators in Product Spaces

In $\mathscr{H}_1$ a linear operator is defined by the rule A_1 and the domain $D_{A_1} = \mathscr{H}_1$,

$$A_1|\chi_i^1\rangle = |\chi_i'^1\rangle;\ |\chi_i^1\rangle \ \text{ and } \ |\chi_i'^1\rangle \epsilon\ \mathscr{H}_1; \tag{10.7}$$

likewise in $\mathscr{H}_2$:

$$B_2|\varphi_j^2\rangle = |\varphi_j'^2\rangle;\ |\varphi_j^2\rangle \ \text{ and } \ |\varphi_j'^2\rangle \epsilon\ \mathscr{H}_2. \tag{10.8}$$

The application of A_1 to elements of the product space $\mathscr{H}_1 \otimes \ \mathscr{H}_2$ should then imply:

$$A_1|\chi_i^1\rangle|\varphi_j^2\rangle = |\chi_i'^1\rangle|\varphi_j^2\rangle \tag{10.9}$$

and correspondingly

$$B_2|\chi_i^1\rangle|\varphi_j^2\rangle = |\chi_i^1\rangle|\varphi_j'^2\rangle. \tag{10.10}$$

From (10.9) and (10.10) it follows that—when forming a product—the order of the operators is unimportant: **operators from different Hilbert spaces commute**.

In (10.9) and (10.10) we have defined the operation of the operators A_1 and B_2 in the product space **operational**, as explained in $\mathscr{H}_1$ and $\mathscr{H}_2$. In principle, one must extend the operators—declared in $\mathscr{H}_1$, $\mathscr{H}_2$—to operators in the product space $\mathscr{H}_1 \otimes \mathscr{H}_2$, defined by the commutative **direct product** (Kronecker product)

$$A_1 \otimes E_2; \qquad E_1 \otimes B_2, \tag{10.11}$$

where E_1, E_2 are the unit operators in $\mathscr{H}_1$ and $\mathscr{H}_2$.

Example: In Sect. 6.5 the position operator in the space of spinors was described by

$$\mathbf{r} \otimes E_2 = \begin{pmatrix} \mathbf{r} & 0 \\ 0 & \mathbf{r} \end{pmatrix}. \tag{10.12}$$

10.5 The Inverse Operator

We have introduced the concept of the inverse operator in Sect. 8.2 using the example of the Green's function. We now define in general:

The **inverse operator** of an operator A, D_A, B_A is defined by the domain $D_{A^{-1}} = B_A$ and the rule $A^{-1}(Af) = f$ for all $f \in D_A$.

The inverse operator exists if and only if different images $Af \in B_A$ belong to different $f \in D_A$; if it exists, it is unique.

As an example we consider $A_z := H - z$ defined in $\mathscr{H}$, where H is the Hamiltonian of a particle without spin. A_z has an inverse for all z with the exception of values for which

$$H\psi = z\psi, \qquad \psi \in \mathscr{H}, \tag{10.13}$$

i.e. with the exception of the (discrete and (or) continuous) eigenvalues of H. In particular, for z with $\Im(z) \neq 0$, A_z always has an inverse.

The following statements are important for practical calculations:

1. If A is defined in $D_A = \mathscr{H}$ and if A^{-1} exists, then

$$A^{-1}Af = f \qquad \forall f \in D_A = \mathscr{H}, \tag{10.14}$$

thus

$$A^{-1}A = E_{\mathscr{H}}, \tag{10.15}$$

where $E_{\mathscr{H}}$ is the unit operator in $\mathscr{H}$. From (10.14) we do not directly get

$$AA^{-1} = E_{\mathscr{H}}. \tag{10.16}$$

Only if $D_A = B_A = \mathscr{H}$ we obtain that

$$AA^{-1} = A^{-1}A = E_{\mathscr{H}}. \tag{10.17}$$

2. If inverse operators for two operators A, B with domains D_A, D_B and AB are defined, then the product also has an inverse and is

$$(AB)^{-1} = B^{-1}A^{-1}. \tag{10.18}$$

10.6 The Adjoint Operator

For a (linear) operator A with domain D_A—for the image domain, in the following it is only necessary that $B_A \subseteq \mathscr{H}$—where D_A is dense in $\mathscr{H}$ (see definition (10.23)), we define an adjoint operator $A^\dagger$ with domain $D_{A^\dagger}$ as follows:

The domain $D_{A^\dagger}$ is given by the set of all $g \in \mathscr{H}$ for which a $\tilde{g} \in \mathscr{H}$ exists such that

$$(g, Af) = (\tilde{g}, f) \qquad \forall f \in D_A. \tag{10.19}$$

The mapping rule should be

$$A^\dagger g = \tilde{g}. \tag{10.20}$$

Thus for any $f \in D_A, g \in D_{A^\dagger}$ the relationship holds

$$(g, Af) = (A^\dagger g, f) = (f, A^\dagger g)^* \tag{10.21}$$

or in Dirac notation

$$\langle g|A|f\rangle = \langle f|A^\dagger|g\rangle^*. \tag{10.22}$$

Due to property 2. of the scalar product in $\mathscr{H}$ and the linearity of A on D_A, it follows that $A^\dagger$ on $D_{A^\dagger}$ is linear. Since D_A was assumed to be dense in $\mathscr{H}$, i.e. D_A dense in $\mathscr{H}$ $<=>$ $\forall g \in \mathscr{H}$ there is a sequence $f_n \in D_A$ with

$$\lim_{n\to\infty} \|g - f_n\| = 0, \tag{10.23}$$

$A^\dagger$ is uniquely defined on $D_{A^\dagger}$.

Proof If for a fixed $g \in \mathscr{H}$ two elements $\tilde{g}, \tilde{g}' \in \mathscr{H}$ exist with the properties (10.19) and (10.20), then

$$(\tilde{g}, f) = (\tilde{g}', f) \tag{10.24}$$

and for $\Delta\tilde{g} = \tilde{g} - \tilde{g}'$ we get

$$(\Delta\tilde{g}, f) = 0 \tag{10.25}$$

for all $f \in D_A$. But this cannot be the case, since D_A was assumed to be dense in $\mathscr{H}$!

The domains of all operators in quantum theory are dense in $\mathscr{H}$, such that no difficulties arise in defining adjoint operators.

10.7 Self-Adjoint Operators

Are particularly important for quantum theory, since **observables** are represented in quantum theory by **self-adjoint operators**.

We call an operator **self-adjoint** if

$$D_A = D_{A^\dagger} \tag{10.26}$$

and

$$Af = A^\dagger f \qquad \forall f \in D_A. \tag{10.27}$$

Then follows

$$(g, Af) = (Ag, f) \qquad \forall f, g \in D_A \tag{10.28}$$

or in Dirac notation

$$\langle g|A|f\rangle = \langle f|A|g\rangle^*. \tag{10.29}$$

Operators with the property (10.28) we have denoted by hermitian in Chap. 5 without regards to their domain of definition. According to the definition above, self-adjoint operators have the essential additional requirement that their domain of definition is dense in $\mathscr{H}$. This additional requirement guarantees that the (real) spectrum of self-adjoint operators is complete (without proof). We can therefore

represent physical observables by self-adjoint operators, since this class of operators has the properties necessary for the statistical interpretation of expectation values.

We now turn to the eigenvalue problem of self-adjoint operators A,

$$A|\varphi\rangle = a|\varphi\rangle, \tag{10.30}$$

and first consider the case of a purely discrete spectrum with eigenvalues a_i and eigenvectors $|\varphi_i\rangle$. As in Chap. 6, one proves that the eigenvalues a_i are real and eigenvectors are orthogonal for different eigenvalues. The completeness of $|\varphi_i\rangle$—which are assumed to be orthonormalized in the following—can be expressed (cf. (9.41)) in Dirac notation as

$$\sum_i |\varphi_i\rangle\langle\varphi_i| = E_{\mathscr{H}}. \tag{10.31}$$

We can also give a representation for A in analogy to (10.31). The expectation value of A in an arbitrary state $|\psi\rangle$,

$$\langle A\rangle =: \langle\psi|A|\psi\rangle, \tag{10.32}$$

we insert the unit operator $E_{\mathscr{H}}$ before and after A in the form (10.31)

$$\langle\psi|A|\psi\rangle = \sum_i \sum_j \langle\psi|\varphi_i\rangle\langle\varphi_i|A|\varphi_j\rangle\langle\varphi_j|\psi\rangle \tag{10.33}$$

$$= \sum_i \langle\psi|\varphi_i\rangle a_i \langle\varphi_i|\psi\rangle = \sum_i a_i \ |\langle\varphi_i|\psi\rangle|^2$$

due to the orthonormalization $\langle\varphi_i|\varphi_j\rangle = \delta_{ij}$ and $\langle\varphi_i|\psi\rangle = \langle\psi|\varphi_i\rangle^*$ according to the definition of the scalar product. From (10.33) we can read off the

spectral representation of A:

$$A = \sum_i a_i \ |\varphi_i\rangle\langle\varphi_i|. \tag{10.34}$$

A corresponding spectral representation is also possible if the spectrum is continuous or partly discrete and partly continuous. In (10.34) the summation then has to be replaced (in whole or in part) by an integration. For the general case we obtain

$$\sum_i |\varphi_i\rangle\langle\varphi_i| + \int d\nu \ |\varphi_\nu\rangle\langle\varphi_\nu| = E_{\mathscr{H}} \tag{10.35}$$

$$\sum_i a_i \ |\varphi_i\rangle\langle\varphi_i| + \int d\nu \ a(\nu) \ |\varphi_\nu\rangle\langle\varphi_\nu| = A. \tag{10.36}$$

Examples:
1. The z component of the spin:
We form the dyadic products (with eigenvalues $\pm\hbar/1$):

$$\tfrac{\hbar}{2}\begin{pmatrix}1\\0\end{pmatrix}(1\ 0) - \tfrac{\hbar}{2}\begin{pmatrix}0\\1\end{pmatrix}(0\ 1) = S_z \tag{10.37}$$

$$= \frac{\hbar}{2}\left[\begin{pmatrix}1&0\\0&0\end{pmatrix} - \begin{pmatrix}0&0\\0&1\end{pmatrix}\right] = \frac{\hbar}{2}\begin{pmatrix}1&0\\0&-1\end{pmatrix}.$$

2. The momentum operator:
The spectral representation of the momentum operator

$$\mathbf{p} = \int d^3k \ \hbar\mathbf{k} \ |\mathbf{k}\rangle\langle\mathbf{k}| \tag{10.38}$$

yields as expectation value in an arbitrary (normalizable) state $|\psi\rangle$

$$\langle\mathbf{p}\rangle = \int d^3k \ \hbar\mathbf{k}\langle\psi|\mathbf{k}\rangle\langle\mathbf{k}|\psi\rangle = \int d^3k \ \hbar\mathbf{k} \ \tilde{\psi}^*(\mathbf{k})\tilde{\psi}(\mathbf{k}), \tag{10.39}$$

as we already know from Sect. 6.3. (Note again that according to Axiom 2.1 $\langle\psi|\mathbf{k}\rangle = \langle\mathbf{k}|\psi\rangle^*$.)

10.8 Projection Operators

An important class of self-adjoint operators in Hilbert space $\mathscr{H}$ are the projection operators ($\equiv$ **projectors**). We consider a subspace $\mathscr{H}_r \subset \mathscr{H}$ spanned by the orthonormal vectors $\varphi_i, i = 1, 2, \ldots, r$; then we define the projector, which projects vectors from $\mathscr{H}$ onto the subspace $\mathscr{H}_r$, by

$$P_r f = \sum_{i=1}^r \varphi_i \ (\varphi_i, f) \qquad \forall f \ \epsilon \ \mathscr{H} \tag{10.40}$$

or in Dirac notation

$$P_r|f\rangle = \sum_{i=1}^r |\varphi_i\rangle\langle\varphi_i|f\rangle \qquad \forall f \ \epsilon \ \mathscr{H}; \tag{10.41}$$

i.e. in short:

$$P_r = \sum_{i=1}^r |\varphi_i\rangle\langle\varphi_i|. \tag{10.42}$$

The definition above might give the impression that the definition of P_r depends on the choice of the basis of φ_i. But this is not the case: if χ_m, $m = 1, \ldots, r$ is another orthonormal basis in $\mathscr{H}_r$, then we can use the expansion

$$|\varphi_i\rangle = \sum_{m=1}^{r} |\chi_m\rangle\langle\chi_m|\varphi_i\rangle \tag{10.43}$$

to express P_r in terms of $|\chi_m\rangle$

$$P_r = \sum_{i,m}^{r} \sum_{m'=1}^{r} |\chi_{m'}\rangle\langle\chi_{m'}|\varphi_i\rangle\langle\varphi_i|\chi_m\rangle\langle\chi_m|. \tag{10.44}$$

If we consider the inverse of (10.43)

$$|\chi_m\rangle = \sum_{i=1}^{r} |\varphi_i\rangle\langle\varphi_i|\chi_m\rangle, \tag{10.45}$$

then the orthonormalization of $|\chi_m\rangle$

$$\sum_{i=1}^{r} \langle\chi_{m'}|\varphi_i\rangle\langle\varphi_i|\chi_m\rangle = \delta_{mm'} \tag{10.46}$$

provides the independence from the basis, i.e.

$$P_r = \sum_{m=1}^{r} |\chi_m\rangle\langle\chi_m|. \tag{10.47}$$

It was already mentioned above that the projectors are also self-adjoint operators. To prove this, since the P_r are defined in the entire Hilbert space $\mathscr{H}$, we only need to check whether

$$\langle f|P_r|g\rangle = \langle g|P_r|f\rangle^* \tag{10.48}$$

for all $f, g \in \mathscr{H}$. This is indeed the case since

$$\sum_{i=1}^{r} \langle f|\varphi_i\rangle\langle\varphi_i|g\rangle = \sum_{i=1}^{r} \langle\varphi_i|f\rangle^*\langle g|\varphi_i\rangle^* = \sum_{i=1}^{r} \left(\langle g|\varphi_i\rangle\langle\varphi_i|f\rangle\right)^*. \tag{10.49}$$

We thus have

$$P_r = P_r^\dagger. \tag{10.50}$$

The eigenvalue spectrum of P_r is particularly simple. We first prove the **idempotence**

(10.51)

$$P_r^2 = P_r.$$

For any vector $|f\rangle \epsilon\ \mathscr{H}$ the following holds

$$P_r^2|f\rangle = P_{r_i} \sum_{i=1}^{r} |\varphi_i\rangle\langle\varphi_i|f\rangle = \sum_{i=1}^{r} \sum_{j=1}^{r} |\varphi_j\rangle\langle\varphi_j|\varphi_i\rangle\langle\varphi_i|f\rangle \tag{10.52}$$

$$= \sum_{i=1}^{r} |\varphi_i\rangle\langle\varphi_i|f\rangle = P_r|f\rangle,$$

since $\langle\varphi_j|\varphi_i\rangle = \delta_{ij}$ by assumption. With (10.51) it follows from the eigenvalue equation

$$P_r|f\rangle = P_r^2|f\rangle = e_r|f\rangle, \tag{10.53}$$

since for the eigenvalues e_r we have

$$e_r^2 = e_r \ \ => \ \ e_r = 0, 1. \tag{10.54}$$

Every operator *P* defined in the entire Hilbert space $\mathscr{H}$ with the properties (10.50) and (10.51) is a projector, and can therefore be written in the form (10.42). Such an operator *P* decomposes the entire Hilbert space $\mathscr{H}$ into two mutually orthogonal subspaces. To prove it, we use the identity:

$$|f\rangle \equiv P|f\rangle + (E_{\mathscr{H}} - P)|f\rangle \tag{10.55}$$

for any vector $|f\rangle \epsilon\ \mathscr{H}$. With the notation

$$P|f\rangle = |f_1\rangle; \qquad (E_{\mathscr{H}} - P)|f\rangle = |f_0\rangle, \tag{10.56}$$

we obtain with (10.50) and (10.51)

$$\langle f_1|f_0\rangle = \langle f_1|P(E_{\mathscr{H}} - P)|f_0\rangle = 0. \tag{10.57}$$

Mathematical addition: If two projectors P_1, P_2 are given in $\mathscr{H}$, the question arises if the sum $P_1 + P_2$ and the product P_1P_2 are also projectors. The result is:

(i) P_1P_2 is a projector if and only if

$$P_1P_2 = P_2P_1, \tag{10.58}$$

since with (10.58)

$$(P_1P_2)^2 = P_1^2P_2^2 = P_1P_2, \tag{10.59}$$

such that (10.51) is satisfied, and from

$$(P_1P_2)^\dagger = P_2^\dagger P_1^\dagger = P_2P_1 = P_1P_2 \tag{10.60}$$

also (10.50) follows (whereby we exploit the fact that P_1, P_2 are defined on the whole $\mathscr{H}$). The condition (10.58) is also necessary; the proof is trivial. If P_1P_2 is a projector, then it obviously projects onto the intersection $\mathscr{H}_{P_1} \bigcap \mathscr{H}_{P_2}$; $P_1P_2 = 0$ then implies orthogonality of $\mathscr{H}_{P_1}$ and $\mathscr{H}_{P_2}$.

(ii) $P_1 + P_2$ is a projector if and only if $P_1P_2 = 0$;

it projects onto the direct sum $\mathscr{H}_{P_1} \oplus \mathscr{H}_{P_2}$.

The physical meaning of projectors is explained by two examples:

1. We want to analyze the state $|\psi\rangle$ of a particle according to the orbital angular momentum *l*, i.e. ask the question whether or with which probability a certain orbital angular momentum *l* is contained in $|\psi\rangle$. This question is answered by the projector

$$P_l = \sum_{m=-l}^{l} \sum_{\alpha(l)} |\alpha lm\rangle\langle\alpha lm|, \tag{10.61}$$

where $|\alpha lm\rangle$ are eigenvectors of l^2, l_z with eigenvalues *l*, *m*, while α is the radial quantum number. The sum is taken over all *m*, α that are possible for a given *l*. The expectation value of P_l in the state $|\psi\rangle$

$$\langle\psi|P_l|\psi\rangle = \sum_{m=-l}^{l} \sum_{\alpha(l)} |\langle\psi|\alpha lm\rangle|^2 \tag{10.62}$$

has exactly the form of a measurement probability. The measured values are 0 or 1 and state, that in each individual experiment the answer to the question posed above is 'no' or 'yes'.

2. We consider two particles 1, 2 described by a wave function $\Psi(1,2)$, where 1, 2 stands for all the degrees of freedom (position, spin, possibly isospin, color ...) of the particles 1, 2. If they are identical particles (bosons or fermions), then the wave function must not change (**bosons**) or only in sign (**fermions**) with respect to particle exchange P_{12},

$$P_{12}\Psi(1,2) = \Psi(2,1) = \pm\Psi(1,2), \tag{10.63}$$

since double exchange reproduces the original state,

$$P_{12}^2 = E_{\mathscr{H}_2}. \tag{10.64}$$

For the case of independent particles, eigenfunctions for the Hamiltonian operator $H(1,2) = H(1) + H(2)$ are now product functions, $\varphi(1)\chi(2)$. Such a product function will, however, generally not have the property (10.63), but it can be decomposed into a **symmetric** and an **antisymmetric** part by projectors $\mathscr{S}$ and $\mathscr{A}$ with the properties:

$$\mathscr{S}\ \varphi(1)\chi(2) =: \tfrac{1}{\sqrt{2}}\{\varphi(1)\chi(2) + \varphi(2)\chi(1)\}; \tag{10.65}$$

$$\mathscr{A}\ \varphi(1)\chi(2) = \frac{1}{\sqrt{2}}\{\varphi(1)\chi(2) - \varphi(2)\chi(1)\}.$$

Examples 1 and 2 show that projectors **measure properties** of quantum systems, e.g. the property of having a certain angular momentum or a certain symmetry with respect to the exchange of identical particles.

10.9 Unitary Operators

An operator *U* in Hilbert space $\mathscr{H}$ is called **unitary**, if its domain and its image domain is the whole Hilbert space $\mathscr{H}$,

$$D_U = \mathscr{H} = B_U, \tag{10.66}$$

and if the mapping rule *U* is:

$$(Uf, Ug) = (f, g) \qquad \forall f, g \,\epsilon\, \mathscr{H}. \tag{10.67}$$

Unitary operators are linear, as follows immediately from the properties of the scalar product with (10.67). They also always have an inverse

$$U^{-1} = U^{\dagger}, \tag{10.68}$$

since U is defined in the whole $\mathscr{H}$, one gets

$$(Uf, Ug) = (U^\dagger U f, g) = (f, g) \qquad \forall f, g \in \mathscr{H}, \tag{10.69}$$

since

$$U^\dagger U = E_{\mathscr{H}} = U U^\dagger, \tag{10.70}$$

which directly gives (10.68).

Two **examples** of unitary operators are translations,

$$\tau(\mathbf{a}) = \exp\left\{-\tfrac{i}{\hbar}\mathbf{a}\cdot\mathbf{p}\right\} \tag{10.71}$$

and rotations

$$R(\boldsymbol{\varphi}) = \exp\left\{-\tfrac{i}{\hbar}\boldsymbol{\varphi}\cdot\mathbf{j}\right\} \tag{10.72}$$

with $\mathbf{j} = \mathbf{l} + \mathbf{s}$. The domains of definition of $\mathbf{p}$ and $\mathbf{j}$ do not cover the entire Hilbert space, but are dense in $\mathscr{H}$. This is enough to achieve a **continuation** of the definitions (10.71) and (10.72) for the entire Hilbert space $\mathscr{H}$. The rotations and translations are linear and norm-preserving, such that (10.67) is satisfied. We will see later that the time translation operator is also unitary. Ultimately, every transition from one representation to an equivalent one is described by a unitary mapping.

Example: The transition from the spatial representation to the momentum representation by Fourier transformation is a unitary mapping; likewise the half-side Fourier transformation from the spatial representation or momentum representation to the phase-space representation (**Wigner transformation**)

$$f(\mathbf{r},\mathbf{p};t) = (2\pi\hbar)^{-3/2}\int d^3 s \;\; \exp\left(-\tfrac{i}{\hbar}\mathbf{p}\cdot\mathbf{s}\right)\; \psi(\mathbf{r}+\tfrac{\mathbf{s}}{2};t)\psi^*(\mathbf{r}-\tfrac{\mathbf{s}}{2};t) \tag{10.73}$$

or

$$f(\mathbf{r},\mathbf{p};t) = (2\pi\hbar)^{-3/2}\int d^3 q \;\; \exp\left(\tfrac{i}{\hbar}\mathbf{q}\cdot\mathbf{r}\right)\; \tilde{\psi}(\mathbf{p}+\tfrac{\mathbf{q}}{2};t)\tilde{\psi}^*(\mathbf{p}-\tfrac{\mathbf{q}}{2};t) \tag{10.74}$$

for square-integrable wave functions $\psi(\mathbf{r};t) = \langle \mathbf{r}|\psi\rangle$, which allows for a simple transition to the classical limit.

The measurable properties of an observable *A* must be independent on the specific representation or the choice of a specific coordinate system. This requires a special transformation behavior of observables with respect to unitary mappings. To this aim we transform the expectation value of an observable *A* in an arbitrary state $|\psi\rangle$, taking into account (10.70) as follows:

$$\langle\psi|A|\psi\rangle = \langle\psi|U^{\dagger}U\ A\ U^{\dagger}U|\psi\rangle = \langle\psi'|U\ A\ U^{\dagger}|\psi'\rangle = \langle\psi'|A'|\psi'\rangle. \qquad (10.75)$$

From (10.75) we get

$$A' = U\ A\ U^{\dagger}. \qquad (10.76)$$

It is easy to check that *A* and A' have the same spectrum.

10.10 Realizations of Linear Operators in $\mathscr{H}$

In line with the vectors of the abstract Hilbert space the linear operators can also be realized (**represented**) in different ways. Important examples are:

(1) In the *C*-**representation**, linear operators are represented by ∞-dimensional matrices. They act on the column vectors introduced in (9.23) in the same way as finite matrices on finite column vectors. If one represents $g\ \epsilon\ D_A$ by the column vector

$$g = \begin{pmatrix} g_1 \\ g_2 \\ g_3 \\ . \\ . \end{pmatrix}, \qquad (10.77)$$

correspondingly $f\ \epsilon\ B_A$ by

(10.78)

$$f = \begin{pmatrix} f_1 \\ f_2 \\ f_3 \\ . \\ . \end{pmatrix},$$

the mapping

$$f = Ag \tag{10.79}$$

in matrix representation is

$$f_i = \sum_{j=1}^{\infty} A_{ij} g_j \qquad\qquad i = 1, 2, \ldots . \tag{10.80}$$

If the operator in question is defined in the **entire** Hilbert space $\mathscr{H}$, then all the calculation rules apply as defined for finite matrices. If, on the other hand, the domain of definition is **not** the entire Hilbert space $\mathscr{H}$, then one must be cautious! To illustrate this, we consider the commutator

$$xp - px = i\hbar E_{\mathscr{H}}, \tag{10.81}$$

which in matrix representation is:

$$\sum_{k=1}^{\infty} (x_{jk}\ p_{kl} - p_{jk}\ x_{kl}) = i\hbar\delta_{jl}. \tag{10.82}$$

Now, for **finite** matrices the trace of a product is invariant with respect to cyclic permutations of the factors. According to this rule, after formation of the trace in (10.82) the left side of the resulting equation should disappear, whereas the right side obviously diverges!

For an operator *A* with domain $D_A = \mathscr{H}$, a matrix representation can always be obtained: we choose a complete, orthonormalized system of vectors $|\varphi_i\rangle, i = 1, 2, \ldots$ in $\mathscr{H}$ and form

$$\langle \varphi_i | A | \varphi_j \rangle =: A_{ij}. \tag{10.83}$$

If $D_A \neq \mathscr{H}$, caution is again necessary! For the physically interesting operators, however, no difficulties arise, since D_A is always dense in $\mathscr{H}$.

Examples: The domains of *x*, *p* do not enclose the entire Hilbert space $\mathscr{H}$, but are dense in $\mathscr{H}$. If one chooses the eigenvectors of the harmonic oscillator as the

basis, then this complete system of vectors is contained in the domains of *x*, *p*. One can therefore represent *x*, *p* by the following matrices:

$$x \equiv \left(\frac{\hbar}{2\,m\omega}\right)^{1/2} \begin{pmatrix} 0 & \sqrt{1} & 0 & 0 & 0 & . \\ \sqrt{1} & 0 & \sqrt{2} & 0 & 0 & . \\ 0 & \sqrt{2} & 0 & \sqrt{3} & 0 & . \\ 0 & 0 & \sqrt{3} & 0 & \sqrt{4} & . \\ 0 & 0 & 0 & \sqrt{4} & 0 & . \\ . & . & . & . & . & . \end{pmatrix} \tag{10.84}$$

and

$$p \equiv i\left(\frac{m\omega\hbar}{2}\right)^{1/2} \begin{pmatrix} 0 & -\sqrt{1} & 0 & 0 & 0 & . \\ \sqrt{1} & 0 & -\sqrt{2} & 0 & 0 & . \\ 0 & \sqrt{2} & 0 & -\sqrt{3} & 0 & . \\ 0 & 0 & \sqrt{3} & 0 & -\sqrt{4} & . \\ 0 & 0 & 0 & \sqrt{4} & 0 & . \\ . & . & . & . & . & . \end{pmatrix} \tag{10.85}$$

as can be easily verified with

$$x = \left(\frac{\hbar}{2m\omega}\right)^{1/2}\left(a + a^{\dagger}\right) \text{ and } p = i\left(\frac{m\omega\hbar}{2}\right)^{1/2}\left(a^{\dagger} - a\right).$$

The eigenvalue problem (10.30) is equivalent to diagonalizing the matrix A_{ij} using a unitary transformation. The matrix U_{kl} has to be determined, for which

$$\sum_{i,j} U_{ki} A_{ij} U_{jl}^{\dagger} = a_l \delta_{kl}. \tag{10.86}$$

We will present a practical approximation method in the form of a diagonalization of A_{ij} in a finite-dimensional subspace elsewhere.

(2) **Spatial representation**

We obtain the spatial representation of an operator *A* defined in all $\mathscr{H}$ by considering the scalar product

$$\langle \mathbf{r}|A|\psi\rangle, \tag{10.87}$$

where $|\mathbf{r}\rangle$ is the improper position eigenvector and $|\psi\rangle$ is an arbitrary normalized Hilbert vector. If we write the identity in the form

$$E_{\mathscr{H}} = \int d^3r' \ |\mathbf{r}'\rangle\langle\mathbf{r}'| \tag{10.88}$$

in (10.87), then

$$\int d^3r' \langle \mathbf{r}|A|\mathbf{r}'\rangle\langle\mathbf{r}'|\psi\rangle =: \int d^3r' \ A(\mathbf{r},\mathbf{r}') \ \psi(\mathbf{r}'). \tag{10.89}$$

Thus A in general is represented in position space by a **nonlocal** operator

$$\int d^3r' \ A(\mathbf{r},\mathbf{r}'). \tag{10.90}$$

The local potentials $V(\mathbf{r})$ introduced in Chap. 4 are a practical exception. Equivalent to this is a position- and momentum-dependent operator, which we obtain from (10.89) by using

$$\psi(\mathbf{r}') = \exp\left(\tfrac{i}{\hbar}(\mathbf{r}-\mathbf{r}')\cdot\mathbf{p}\right)\psi(\mathbf{r}). \tag{10.91}$$

Then

$$\int d^3r' \ A(\mathbf{r},\mathbf{r}')\psi(\mathbf{r}') = \tilde{A}(\mathbf{r},\mathbf{p}) \ \psi(\mathbf{r}), \tag{10.92}$$

and $\tilde{A}(\mathbf{r},\mathbf{p})$ is the position- and momentum-dependent operator we are looking for.

Special cases are $\mathbf{r}$ and $\mathbf{p}$ themselves; e.g. for the position operator $\mathbf{r}_{Op.}$ follows from (10.89)

$$\langle \mathbf{r}|\mathbf{r}_{Op.}|\Psi\rangle = \int d^3r' \langle \mathbf{r}|\mathbf{r}_{Op.}|\mathbf{r}'\rangle\langle\mathbf{r}'|\psi\rangle = \int d^3r' \ \mathbf{r}' \ \delta^3(\mathbf{r}-\mathbf{r}')\psi(\mathbf{r}') = \mathbf{r} \ \psi(\mathbf{r}). \tag{10.93}$$

In the spatial representation, the position operator simply means 'multiplication by $\mathbf{r}$'. The momentum operator, according to the derivation of (10.91), has the well-known form

$$\mathbf{p} = -i\hbar\nabla_r.$$

(3) **Momentum representation**

In analogy to (2) we form

$$\langle \mathbf{k}|A|\psi\rangle = \int d^3k' \ \langle \mathbf{k}|A|\mathbf{k}'\rangle\langle\mathbf{k}'|\psi\rangle = \int d^3k' \ \tilde{A}(\mathbf{k},\mathbf{k}')\tilde{\psi}(\mathbf{k}') \tag{10.94}$$

and obtain with

$$\int d^3k' \;\; \tilde{A}(\mathbf{k},\mathbf{k}') \tag{10.95}$$

the momentum representation of the operator *A*. Here the momentum operator has the simple form 'multiplication by $\mathbf{p} = \hbar\mathbf{k}$', while the position operator has the form

$$i\hbar\nabla_p \equiv i\nabla_k, \tag{10.96}$$

as is easily confirmed by Fourier transformation.

(4) **General uncertainty relation**

Let *A* on D_A and *B* on D_B be two self-adjoint operators. Then *AB* is defined on $D_A \bigcap B_B =: D_{AB}$. On $D_{AB} \bigcap D_{BA}$ the commutator

$$[A,B] = iC \tag{10.97}$$

is defined and *C* is a self-adjoint operator, too. We now want to prove that for all $\psi \;\epsilon\; D_C$ the following holds:

$$\Delta A \;\; \Delta B \geq \tfrac{1}{2}|\langle\psi|C|\psi\rangle|, \tag{10.98}$$

where ΔA and ΔB are the mean square fluctuations of *A* and *B* in the state ψ, respectively.

To prove (10.98) we introduce

$$A' = A - \langle A\rangle; \qquad\qquad B' = B - \langle B\rangle, \tag{10.99}$$

such that

$$\langle A'^2\rangle = \Delta A^2; \qquad\qquad \langle B'^2\rangle = \Delta B^2; \qquad\qquad [A',B'] = [A,B]. \tag{10.100}$$

For any real number β we then have

$$\begin{aligned} 0 \;\; &\leq \|(A' + i\beta B')\psi\|^2 = \|A'\psi\|^2 + \beta^2\|B'\psi\|^2 \\ &+i\beta\{(A'\psi, B'\psi) - (B'\psi, A'\psi)\}. \end{aligned} \tag{10.101}$$

If we use the self-adjointness of *A*, *B* in the brackets $\{\ldots\}$, then we obtain with (10.100):

(10.102)

$$0 \leq \Delta A^2 + \beta^2 \Delta B^2 + i\beta \langle \psi | [A, B] | \psi \rangle .$$

The right-hand side in (10.102) cannot have two real zeros in β. The discriminant condition

$$\Delta A^2 \Delta B^2 - \left\{ \tfrac{i}{2} \langle \Psi | [A, B] | \psi \rangle \right\}^2 = \Delta A^2 \Delta B^2 - \left\{ \tfrac{1}{2} \langle \Psi | C | \psi \rangle \right\}^2 \geq 0 \quad (10.103)$$

proofs the claim (10.98).

Based on the considerations above about the domains of definition of *A*, *B* and *C* it is clear that (10.98) does not apply universally to arbitrary Hilbert vectors ψ. Typical examples have already been discussed in Sect. 6.4. The proof above is valid for position and momentum, since with ψ, $x\psi$ is also differentiable again and belongs to D_p if $\psi \ \epsilon \ D_p$ and vice versa the asymptotic drop required by the elements of D_x is not weakened by differentiation. It is therefore

$$D_{xp} = D_{px} = D_x \bigcap D_p . \quad (10.104)$$

A counterexample is the false relation $\Delta l_z \Delta \varphi \geq \hbar/2$. The angular momentum operator l_z is only self-adjoint in the space of periodic functions

$$\psi(r, \vartheta, \varphi) = \psi(r, \vartheta, \varphi + 2\pi). \quad (10.105)$$

Then $\varphi \ \psi(r, \vartheta, \varphi)$ does not belong to the domain D_{l_z} on which l_z is self-adjoint.

10.11 Coupling of Angular Momenta

The problem of the coupling of angular momenta can occur in two forms:

1. Coupling of the angular momenta of two different particles, e.g. two atomic electrons outside closed shells. In order to calculate the total angular momentum of the electron shell, the angular momenta of the two electrons must be 'added' (in Hilbert space).

2. Coupling of the spin and the orbital angular momentum of a single particle for the case of a strong spin-orbit interaction (which follows naturally from the relativistic theory of electrons).

We can treat both cases in a unified manner, since the rules for angular momentum coupling depend only on the angular momentum commutation rules.

Since the angular momenta $\mathbf{j}_1, \mathbf{j}_2$—to be coupled—commute,

$$[\mathbf{j}_1, \mathbf{j}_2] = 0, \quad (10.106)$$

we can find the product states,

$$|\alpha\ j_1\ m_1;j_2\ m_2\rangle = |\alpha\rangle|j_1 m_1\rangle|j_2 m_2\rangle, \tag{10.107}$$

which are simultaneous eigenstates of j_1^2, j_{1z} with eigenvalues j_1, m_1 and of j_2^2, j_{2z} with eigenvalues j_2, m_2, where α stands for the remaining quantum numbers characterizing the product state. We are looking for the eigenstates

$$|\alpha\ j\ m\rangle \tag{10.108}$$

of the total angular momentum

$$\mathbf{j} = \mathbf{j}_1 + \mathbf{j}_2. \tag{10.109}$$

From the commutation rules for the components of $\mathbf{j}_1$ and $\mathbf{j}_2$ it follows directly that $\mathbf{j}$ also satisfies the usual angular momentum commutation rules. Since

$$[j^2, j_1^2] = [j^2, j_2^2] = 0, \tag{10.110}$$

the states $|\alpha\ j\ m\rangle$ can be represented as linear combinations of the product states $|\alpha j_1 m_1 j_2 m_2\rangle$ for fixed j_1, j_2, i.e.

$$|\alpha\ j\ m\rangle = \sum_{m_1,m_2} |\alpha j_1 m_1 j_2 m_2\rangle\langle j_1 m_1 j_2 m_2|jm\rangle. \tag{10.111}$$

The expansion coefficients (**Clebsch-Gordon coefficients**) do not depend on the index α. We now have to find out which values *j*, *m* are possible for a given j_1, j_2 and how the coefficients $\langle j_1 m_1 j_2 m_2|jm\rangle$ can be calculated.

We first note that $|\alpha j_1 m_1 j_2 m_2\rangle$ automatically is an eigenstate for j_z with eigenvalue $m = m_1 + m_2$:

$$\begin{aligned} j_z|\alpha j_1 m_1 j_2 m_2\rangle &= (j_{1z} + j_{2z})|\alpha j_1 m_1 j_2 m_2\rangle \\ &= (m_1 + m_2)|\alpha j_1 m_1 j_2 m_2\rangle = m|\alpha j_1 m_1 j_2 m_2\rangle. \end{aligned} \tag{10.112}$$

The following table lists the possible *m* values and their degeneracy N_m:

(10.113)

m	N_m
$j_1 + j_2$	1
$j_1 + j_2 - 1$	2
$j_1 + j_2 - 2$	3
.	.
$j_1 - j_2$	$2j_2 + 1$
.	.
$-(j_1 - j_2)$	$2j_2 + 1$
.	.
$-j_1 - j_2$	3
$-j_1 - j_2 + 1$	2
$-j_1 - j_2$	1

From Chap. 9 we know that the eigenvalues of j^2 have the form $j(j+1)$ with $j = 0, 1/2, 1, 3/2, 2, 5/2, \ldots$ as possible values for *j*; for every *j*-value there are $(2j+1)$ values for *m*. We now show that eigenstates for j^2 can be constructed from the states $|\alpha j_1 m_1 j_2 m_2\rangle$. To this aim we first show that $|\alpha j_1 j_1 j_2 j_2\rangle$ is an eigenstate of j^2 and write

$$j^2 = j_1^2 + j_2^2 + 2\mathbf{j}_1 \cdot \mathbf{j}_2 = j_1^2 + j_2^2 + (j_1^+ j_2^- + j_2^+ j_1^-) + 2 j_{1z} j_{2z} \qquad (10.114)$$

with

$$j_1^{\pm} = j_{1x} \pm i\ j_{1y} \qquad j_2^{\pm} = j_{2x} \pm i\ j_{2y} \qquad (10.115)$$

and note

$$j_1^+ |\alpha j_1 j_1 j_2 m_2\rangle = 0 \qquad (10.116)$$

and

$$j_2^+ |\alpha j_1 m_1 j_2 j_2\rangle = 0. \qquad (10.117)$$

Then

(10.118)

$$\begin{aligned} j^2|\alpha j_1 j_1 j_2 j_2\rangle &= [j_1(j_1+1)+j_2(j_2+1)+2j_1 j_2]|\alpha j_1 j_1 j_2 j_2\rangle \\ &= (j_1+j_2)(j_1+j_2+1)|\alpha j_1 j_1 j_2 j_2\rangle. \end{aligned}$$

We thus have found one of the *j*-values that actually occurs to be j_1+j_2; according to (10.113), there are no other *j*-values for $m=j_1+j_2$. The states $|\alpha\ j=(j_1+j_2)\ m=(j_1+j_2)\rangle$ and $|\alpha j_1 j_1 j_2 j_2\rangle$ therefore are the same (except for a phase). Using the usual phase convention, we set

$$|\alpha\ j=(j_1+j_2)\ m=(j_1+j_2)\rangle = |\alpha j_1 j_1 j_2 j_2\rangle. \tag{10.119}$$

Next, we consider $m=j_1+j_2-1$ (see (10.113)); there the possible product states are

$$|\alpha j_1(j_1-1)j_2 j_2\rangle \quad \text{and} \quad |\alpha j_1 j_1 j_2(j_2-1)\rangle. \tag{10.120}$$

We now are looking for the linear combination of the states (10.120), that are also eigenstates of j^2. One of them can be found by applying $j^-=j_1^-+j_2^-$:

$$|\alpha\ j=(j_1+j_2)\ m=(j_1+j_2-1)\rangle = \frac{j^-}{\sqrt{2}\sqrt{(j_1+j_2)}}|\alpha(j_1+j_2)(j_1+j_2)\rangle \tag{10.121}$$

$$= \frac{[j_1^-+j_2^-]}{\sqrt{2}\sqrt{j_1+j_2}}|\alpha(j_1+j_2)(j_1+j_2)\rangle$$

$$= \sqrt{\frac{j_1}{j_1+j_2}}|\alpha j_1(j_1-1)j_2 j_2\rangle + \sqrt{\frac{j_2}{j_1+j_2}}|\alpha j_1 j_1 j_2(j_2-1)\rangle.$$

Apart from this eigenstate for $j=j_1+j_2$ and $m=j_1+j_2-1$, according to table (10.113) there is exactly one further eigenstate with $j=j_1+j_2-1$ for the same value *m*; it must be orthogonal to (10.121). The only linear combination, which can be formed from (10.120) and is orthogonal to (10.121), can be specified directly (except for a phase factor):

$$|\alpha\ j=(j_1+j_2-1)\ m=(j_1+j_2-1)\rangle \tag{10.122}$$

$$= -\sqrt{\frac{j_2}{j_1+j_2}}|\alpha j_1(j_1-1)j_2 j_2\rangle + \sqrt{\frac{j_1}{j_1+j_2}}|\alpha j_1 j_1 j_2(j_2-1)\rangle.$$

In the next step we have three product states for $m = j_1 + j_2 - 2$

$$|\alpha j_1(j_1-2)j_2 j_2\rangle; |\alpha j_1 j_1 j_2(j_2-2)\rangle \quad \text{and} \quad |\alpha j_1(j_1-1)j_2(j_2-1)\rangle, \tag{10.123}$$

from which exactly 3 orthogonal eigenstates of j^2, j_z can be formed. Two of them are obtained by applying j^- to (10.121) or (10.122), the third by constructing the orthogonal state. This procedure is continued until it terminates, which occurs when either $m_1 = -j_1$ or $m_2 = -j_2$. The positive of the two numbers $j_1 + j_2 - 2j_1$ and $j_1 + j_2 - 2j_2$ gives the smallest value of *j* that can be reached. For given values j_1, j_2, *j* runs through the values

$$|j_1 - j_2| \leq j \leq j_1 + j_2. \tag{10.124}$$

For each j_1, j_2 there are $(2j_1+1)(2j_2+1)$ product states; on the other hand, the number of possible eigenstates for the total angular momentum j^2 and the component j_z :

$$\sum_{j=|j_1-j_2|}^{j_1+j_2}(2j+1) = (2j_1+1)(2j_2+1) \tag{10.125}$$

as expected.

Since by the transformation (10.111) orthonormalized vectors $|\alpha j_1 m_1 j_2 m_2\rangle$ are mapped to the same number of orthonormalized vectors $|\alpha\ j\ m\rangle$, the transformation coefficients $\langle j_1 m_1 j_2 m_2 | jm\rangle$ define a unitary matrix. For the usual phase convention all coefficients are real by construction, such that the unitarity condition is:

$$\sum_{m_1,m_2}\langle j'm'|j_1 m_1 j_2 m_2\rangle\langle j_1 m_1 j_2 m_2|jm\rangle = \delta_{jj'}\ \delta_{mm'} \tag{10.126}$$

or vice versa

(10.127)

$$\sum_{j,m}\langle j_1 m_1' j_2 m_2' | jm\rangle\langle jm | j_1 m_1 j_2 m_2\rangle = \delta_{m_1 m_1'}\ \delta_{m_2 m_2'}.$$

According to (10.112) and (10.111) only those coefficients $\langle j_1 m_1 j_2 m_2 | jm\rangle$ are different from zero for which

$$m = m_1 + m_2 \tag{10.128}$$

and the 'triangle inequality'

$$|j_1 - j_2| \leq j \leq j_1 + j_2 \tag{10.129}$$

are satisfied.

The **Clebsch-Gordon coefficients** calculated by the method above can be read off from tables; when using the tables (or source codes) one should always pay attention to the respective phase convention!

10.12 Center of Mass and Relative Motion

We first consider a system of 2 particles, described by the Hamiltonian operator

$$H = \frac{\mathbf{p}_1^2}{2m_1} + \frac{\mathbf{p}_2^2}{2m_2} + V(\mathbf{r}) \tag{10.130}$$

with the relative coordinate of the two particles

$$\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2. \tag{10.131}$$

The 2-particle problem can then be reduced (as in classical physics) to an equivalent single-particle problem by reducing the kinetic energy to the relative coordinate

$$\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2 \tag{10.132}$$

and the center of mass coordinate

$$\mathbf{R} = \frac{m_1\mathbf{r}_1 + m_2\mathbf{r}_2}{m_1 + m_2} = \frac{m_1\mathbf{r}_1 + m_2\mathbf{r}_2}{M}, \tag{10.133}$$

or

$$\mathbf{r}_1 = \mathbf{R} + \frac{m_2}{M}\mathbf{r}, \qquad \mathbf{r}_2 = \mathbf{R} - \frac{m_1}{M}\mathbf{r} \tag{10.134}$$

to the corresponding momenta

$$\mathbf{P} = \frac{\hbar}{i}\nabla_R, \qquad \mathbf{p} = \frac{\hbar}{i}\nabla_r. \tag{10.135}$$

The result is

$$H = \frac{P^2}{2M} + \frac{p^2}{2\mu} + V(\mathbf{r}) \tag{10.136}$$

with

$$M = m_1 + m_2 \qquad \text{and} \qquad \mu = \frac{m_1 m_2}{m_1 + m_2}. \tag{10.137}$$

The separation Ansatz

$$\Psi = \psi_s(\mathbf{R})\ \psi_r(\mathbf{r}) \tag{10.138}$$

converts the Schrödinger equation

$$H\ \Psi = E\Psi \tag{10.139}$$

into

$$H_s\psi_s = E_s\psi_s \qquad \text{and} \qquad H_r\psi_r(\mathbf{r}) = E_r\psi_r(\mathbf{r}) \tag{10.140}$$

with

$$E = E_s + E_r. \tag{10.141}$$

The solution for the center of mass motion is trivial:

$$\psi_s(\mathbf{R}) = \exp\left(i\mathbf{K}\cdot\mathbf{R}\right) \tag{10.142}$$

with

$$E_s = \frac{\hbar^2 K^2}{2M}. \tag{10.143}$$

This leaves

(10.144)

$$\left[\frac{p^2}{2\mu} + V(\mathbf{r})\right]\ \psi_r(\mathbf{r}) = E_r \psi_r(\mathbf{r})$$

as the **equivalent single-particle problem.**

For *N* particles the separation of center of mass and relative motion is performed in analogy to the procedure above by introducing **Jacobi coordinates**:

$$\boldsymbol{\rho}_n = \frac{\sum_{i=1}^{n} m_i \mathbf{r}_i}{\sum_{i=1}^{n} m_i} - \mathbf{r}_{n+1} \qquad n = 1, 2, \ldots, N-1 \tag{10.145}$$

and

$$\boldsymbol{\rho}_N = \mathbf{R} = \frac{\sum_{i=1}^{N} m_i \mathbf{r}_i}{\sum_{i=1}^{N} m_i}. \tag{10.146}$$

If we consider the corresponding momenta

$$\boldsymbol{\pi}_n = \frac{\hbar}{i} \nabla_{\rho_n}$$

and $\boldsymbol{\pi}_N \equiv \mathbf{P} = -i\hbar\nabla_R$, then the Hamiltonian reads

$$H = \frac{P^2}{2M} + H_r(\boldsymbol{\rho}_n, \boldsymbol{\pi}_n). \tag{10.147}$$

Mixed terms between $\mathbf{P}$ and the $\boldsymbol{\pi}_n$ ($n = 1 \cdots N-1$) do not occur since such terms would lead to the violation of Gallilei invariance.

An illustration of the Jacobi coordinates for 4 particles is given in Fig. 10.1.

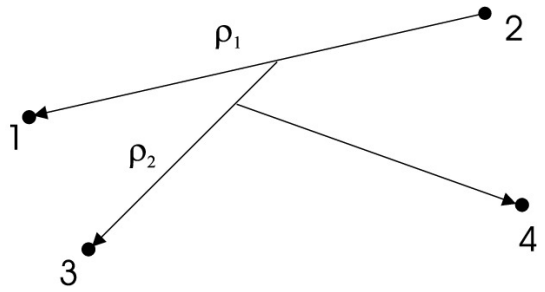

Fig. 10.1 Illustration of Jacobi coordinates for 4 particles

10.13 Pauli Principle for *N* Identical Particles

In analogy to the case of two particles we require for *N* **identical particles**, that only such states are possible for which, for any chosen particle pair (i, j), either

$$\Pi_{ij}\Psi(\xi_1, \ldots, \xi_N) = +\Psi(\xi_1, \ldots, \xi_N) \tag{10.148}$$

or

$$\Pi_{ij}\Psi(\xi_1, \ldots, \xi_N) = -\Psi(\xi_1, \ldots, \xi_N) \tag{10.149}$$

when applying the particle exchange operator Π_{ij}.

This requirement is consistent: if $+(-)$ holds for any particle pair (i, j), then it also holds for any other particle pair of the system. If for (1, 2)

$$\Pi_{12}\Psi = \pm\Psi \tag{10.150}$$

then

$$\Pi_{ij} = \Pi_{1j}\Pi_{2i}\Pi_{12}\Pi_{1j}\Pi_{2i}, \tag{10.151}$$

since

$$\Pi_{ij}\Psi = \Pi_{12}\Psi = \pm\Psi \tag{10.152}$$

regardless of whether Π_{1j} and Π_{2i} (in the state Ψ) have the eigenvalue $+1$ or -1, since these operators appear twice in (10.151).

10.14 Composite Particles

All elementary particles known to date can be classified as **bosons** or **fermions**. Without exception, bosons have integer spin, fermions have half-integer spin. **Examples**: Fermions are e.g. electrons, muons, protons, neutrons, quarks, neutrinos -spin $1/2$ -particles -, whereas photons, pions, kaons, phonons ($\equiv$ lattice vibrations in crystals) or gluons are bosons.

Atomic nuclei are bosons, if the number of nucleons is even, and fermions if the number of nucleons is odd, provided that the 'nuclei' can be treated as particles. This is the case in molecular and solid-state physics. To prove the property of atomic nuclei claimed above, we consider two identical nuclei, each with Z protons and N neutrons, a total of $2Z + 2N = 2A$ particles. Exchanging the two nuclei

then implies exchanging the nucleons of one nucleus with those of the other, this gives a total of A exchanges. Since the wave function Ψ changes sign with every single exchange of two fermions,

$$\tilde{\Pi}_{12}\Psi = (-)^{A}\Psi, \tag{10.153}$$

if $\tilde{\Pi}_{12}$ is the operator for the exchange of two identical nuclei of mass A. The extension to more than two identical nuclei is trivial; nuclei with an even number of nucleons behave like bosons (e.g. ^{4}He). These properties of composite particles are essential when calculating the specific heat of an ideal gas of diatomic molecules (see **quantum statistics**).

In summarizing this chapter we have introduced linear operators in $\mathscr{H}$ and their respective domains. Physical observables have been identified with matrix-elements of self-adjoint operators in $\mathscr{H}$ and their spectra and eigenstates have been investigated. This concept has been extended to operators in product spaces, which is mandatory for a quantum description of many-body problems. As an example we have calculated the coupling of angular momenta in $\mathscr{H}$ and the separation of the center of mass and relative motion. Furthermore, the exchange symmetry for identical particles has been studied and lead to a separation of symmetric and anti-symmetric many-body states, i.e. Bose and Fermi systems.

Part IV
Quantum Mechanics of Many-Body Systems

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11. The Time-Evolution Operator

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In order to describe the time evolution of a quantum system different 'pictures' may be employed, which in principle all are equivalent, but in practice are used in different expansion schemes. We will start with the

11.1 Schrödinger Picture

Here the starting point is the time-dependent Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle = H|\Psi(t)\rangle, \tag{11.1}$$

which describes the dynamical evolution of the system by the (*N*-body) Hamiltonian *H*. If the vector $|\Psi(t_0)\rangle$, which describes the state of the system at time t_0, is known then Eq. (11.1) uniquely defines $|\Psi(t)\rangle$ for any other time $t \neq t_0$. Accordingly, there must be a unique transformation

$$|\Psi(t)\rangle = U(t,t_0)|\Psi(t_0)\rangle \tag{11.2}$$

with a linear operator $U(t,t_0)$ due to the linearity of Eq. (11.1). Since the Hamiltonian *H* must be self-adjoint we get:

$$\frac{d}{dt}\langle\Psi(t)|\Psi(t)\rangle = 0, \tag{11.3}$$

or

$$\langle\Psi(t)|\Psi(t)\rangle = \langle\Psi(t_0)|\Psi(t_0)\rangle = \langle\Psi(t_0)|U^\dagger(t,t_0)U(t,t_0)|\Psi(t_0)\rangle. \tag{11.4}$$

Accordingly, $U(t,t_0)$ is a unitary operator, i.e.

$$U^\dagger(t,t_0)U(t,t_0) = 1_{\mathscr{H}}, \tag{11.5}$$

where $1_{\mathscr{H}}$ denotes the identity in the Hilbert space $\mathscr{H}$. $U(t,t_0)$ is denoted as **time-evolution operator** and as in case of rotations or spatial translations defines a group with

$$U^{-1}(t,t_0) = U^{\dagger}(t,t_0). \tag{11.6}$$

As in case of spatial translations this group is abelian contrary to rotations.
Inserting (11.2) in (11.1) we get:

$$i\hbar \frac{\partial}{\partial t} U(t,t_0)|\Psi(t_0)\rangle = H\ U(t,t_0)|\Psi(t_0)\rangle. \tag{11.7}$$

Since the time t_0 is arbitrary one obtains the **operator equation**

$$i\hbar \frac{\partial}{\partial t}\ U(t,t_0) = H\ U(t,t_0). \tag{11.8}$$

It is useful to consider two cases separately:
(i) If *H* does not depend on time *t* the solution is simply given by

$$U(t,t_0) = \exp\ (-\tfrac{i}{\hbar} H(t-t_0)), \tag{11.9}$$

as one finds out by differentiation of (11.9) with respect to *t*. In case of an eigenvector $|\Psi_E(t_0)\rangle$ of *H* with energy *E* we have

$$U(t,t_0)|\Psi_E(t_0)\rangle = \exp\ (-\tfrac{i}{\hbar} E(t-t_0))|\Psi_E(t_0)\rangle, \tag{11.10}$$

i.e. the time-evolution is described by a phase shift.
(ii) If *H* depends on *t*, i.e. $H = H(t)$, it is useful to consider the integral equation,

$$U(t,t_0) = 1_{\mathscr{H}} - \tfrac{i}{\hbar} \int_{t_0}^{t} dt'\ H(t')\ U(t',t_0), \tag{11.11}$$

where the boundary condition $U(t_0,t_0) = 1_{\mathscr{H}}$ is employed explicitly. Equation (11.11) practically can be solved by iteration. A formal solution is given by

$$U(t,t_0) = T\Big(\exp\ [-\tfrac{i}{\hbar} \int_{t_0}^{t} dt'\ H(t')]\Big) = \sum_{n=0}^{\infty} \tfrac{1}{n!} T[-\tfrac{i}{\hbar} \int_{t_0}^{t} dt'\ H(t')]^n, \tag{11.12}$$

where *T* denotes the time-ordering operator which places all operators at lower times to the right.

Instead of time-dependent Hilbert vectors in the Schrödinger picture the

---

11.2 Heisenberg Picture

employs time-independent Hilbert vectors, however, explicitly **time-dependent operators**. The equations of motion for the operators then replace Eq. (11.1). To obtain the latter equations of motion we consider the expectation value of an operator *A* in the state $|\Psi(t)\rangle$,

$$\langle\Psi(t)|A(t)|\Psi(t)\rangle = \langle\Psi(t_0)|U^{\dagger}(t,t_0)A(t)U(t,t_0)|\Psi(t_0)\rangle. \tag{11.13}$$

In this case the operator $A(t)$ may also explicitly depend on time t, which is useful for unclosed systems, i.e. for systems in contact with some time-dependent environment. In the **Heisenberg picture** one uses the Hilbert vector

$$|\Psi_h\rangle =: |\Psi(t_0)\rangle, \tag{11.14}$$

which fixes the system at some time t_0, and represents the observable by the time-dependent operator

$$A_h(t) =: U^\dagger(t,t_0)A(t)U(t,t_0). \tag{11.15}$$

The expectation value of A in time then reads

$$\langle A\rangle_t = \langle\Psi_h|A_h(t)|\Psi_h\rangle. \tag{11.16}$$

The time evolution of $A_h(t)$ is obtained from (11.15) and (11.8):

$$\begin{aligned} i\hbar\tfrac{\partial}{\partial t}\ A_h(t) &= i\hbar U^\dagger(t,t_0)\big(\tfrac{\partial}{\partial t}\ A(t)\big)U(t,t_0) + U^\dagger(t,t_0)[A(t)H - HA(t)]U(t,t_0) \\ &= [A_h(t),H_h] + i\hbar\left(\frac{\partial}{\partial t}\ A(t)\right)_h, \end{aligned} \tag{11.17}$$

with

$$H_h =: U^\dagger(t,t_0)H\ U(t,t_0) \tag{11.18}$$

and

$$\big(\tfrac{\partial}{\partial t}\ A(t)\big)_h =: U^\dagger(t,t_0)\big(\tfrac{\partial}{\partial t}\ A(t)\big)U(t,t_0). \tag{11.19}$$

If the observable C does not explicitly depend on time t, i.e. $C \neq C(t)$, it represents a conserved quantity if

$$[C_h,H_h] = 0, \tag{11.20}$$

which is equivalent to

$$[C,H] = 0 \tag{11.21}$$

in the Schrödinger picture.

11.3 Interaction or Dirac Picture

For practical calculations it is useful to change to the **Dirac picture**. To this aim one rewrites the Hamiltonian as

$$H = H_0 + H'(t), \tag{11.22}$$

with a time independent H_0 and known system of eigenvectors. In this case the state

$$|\Psi_D(t)\rangle = \exp\left(\tfrac{i}{\hbar} H_0\ t\right)|\Psi(t)\rangle \tag{11.23}$$

allows to separate the time evolution of the state $|\Psi(t)\rangle$ determined by H_0 such that the time evolution of $|\Psi(t)\rangle$ is essentially determined by $H'(t)$. Inserting (11.23) in (11.1) we get:

$$i\hbar \tfrac{\partial}{\partial t}|\Psi_D(t)\rangle = -H_0|\Psi_D(t)\rangle + i\hbar \exp\left(\tfrac{i}{\hbar} H_0 t\right)\ \tfrac{\partial}{\partial t}|\Psi(t)\rangle \tag{11.24}$$

$$= -H_0|\Psi_D(t)\rangle + \exp\left(\frac{i}{\hbar} H_0 t\right)\ [H_0 + H']|\Psi(t)\rangle$$

$$= \exp\left(\frac{i}{\hbar} H_0 t\right)\ H'(t)\ \ \exp\left(-\frac{i}{\hbar} H_0 t\right)|\Psi_D(t)\rangle$$

or

$$i\hbar \tfrac{\partial}{\partial t}|\Psi_D(t)\rangle = H'_D(t)|\Psi_D(t)\rangle \tag{11.25}$$

with

$$H'_D(t) = \exp\left(\tfrac{i}{\hbar} H_0 t\right)\ H'(t)\ \ \exp\left(-\tfrac{i}{\hbar} H_0 t\right). \tag{11.26}$$

Equation (11.25) differs from (11.1) in the respect that only the interaction $H'_D(t)$ appears and not the full Hamiltonian $H(t)$ as in (11.1); the exponential terms in (11.26) are known phase factors in the basis of eigenvectors of H_0.

In order to obtain an iterative solution of Eq. (11.25) we introduce the **time-evolution operator in the Dirac picture** by

$$|\Psi_D(t)\rangle = U_D(t, t_0)|\Psi_D(t_0)\rangle \tag{11.27}$$

and obtain from (11.25)

$$i\hbar \frac{\partial}{\partial t}\ U_D(t,t_0) = H'_D(t) U_D(t,t_0) \tag{11.28}$$

with the boundary condition $U_D(t_0,t_0) = 1_{\mathscr{H}}$. The corresponding integral equation for $U_D(t,t_0)$ reads:

$$U_D(t,t_0) = 1_{\mathscr{H}} - \frac{i}{\hbar}\int_{t_0}^{t} dt'\ H'_D(t') U_D(t',t_0) \tag{11.29}$$

and contrary to (11.11) only contains the interaction operator $H'_D(t)$. Accordingly, an iterative solution of (11.29) should converge fast if H_0 already provides some reasonable approximation to the system. The formal result of such an iteration (with $U_D(t,t_0) = 1_{\mathscr{H}}$ in 0'th order) is the **Dyson series**

$$U_D(t,t_0) = 1_{\mathscr{H}} - \frac{i}{\hbar}\int_{t_0}^{t} dt'\ H'_D(t') - \frac{1}{\hbar^2}\int_{t_0}^{t} dt_2 \int_{t_0}^{t_2} dt_1\ H'_D(t_2) H'_D(t_1) \cdots \tag{11.30}$$

$$= 1_{\mathscr{H}} + \sum_{n=1} \left(-\frac{i}{\hbar}\right)^n \int_{t_0}^{t} dt_n \int_{t_0}^{t_n} dt_{n-1} \int_{t_0}^{t_{n-1}} dt_{n-2} \cdots \int_{t_0}^{t_2} dt_1\ H'_D(t_n) H'_D(t_{n-1}) \cdots H'_D(t_1)$$

with

$$t \geq t_n \geq \ldots\ldots \geq t_1 \geq t_0. \tag{11.31}$$

One has to take care about the sequence of the operators $H'_D(t_n)\ H'_D(t_{n-1}) \cdots H'_D(t_1)$ etc., since for $t_1 \neq t_2$

$$[H'_D(t_1), H'_D(t_2)] \neq 0, \tag{11.32}$$

except for the trivial case $[H_0, H'] = 0$ und $H' \neq H'(t)$.

In summary: we have introduced the Schrödinger picture, the Heisenberg picture and the Dirac picture in order to describe the time evolution of a quantum system. These different 'pictures' in principle all are equivalent, but in practice are used in different situations and expansion schemes.

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12. Particle Number Representation for Fermions

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In this chapter we will introduce the particle number representation for fermions, which allows for a transparent formulation of many-body problems and takes care about the antisymmetry of the fermion wave function by simple (anti)-commutation relations. Furthermore, we give explicit expressions for one-body and two-body operators in particle number representation and calculate some characteristic examples.

12.1 Representation in Configuration Space

The state of a system of *N* identical fermions with coordinates ξ_i (position, spin, isospin, etc.); $i = 1, \ldots, N$, can be described by a wave function in configuration space

$$\Psi(\xi_1, \ldots, \xi_N; t). \tag{12.1}$$

For the calculation of Ψ from the Schrödinger equation of the *N*—particle system

$$i\hbar \frac{\partial}{\partial t} \ \Psi(\xi_1, \ldots, \xi_N; t) = H \ \Psi(\xi_1, \ldots, \xi_N; t) \tag{12.2}$$

one generally has to rely on approximate methods. The most frequently used approximation methods are ultimately all based on splitting the Hamiltonian *H*,

$$H := H_0 + H_R, \tag{12.3}$$

where

$$H_0(\xi_1, \ldots, \xi_N) = \sum_{i=1}^{N} h(\xi_i) = \sum_{i=1}^{N} [t_i + U(\xi_i)] \tag{12.4}$$

describes a system of independent particles in an average potential $U(\xi)$ and H_R captures the remaining **residual interaction** between the particles.

Example: For the electrons of an atom one could use a shielded Coulomb potential as $U(\xi)$, which captures the nucleus-electron interaction exactly and the electron-electron interaction approximately in the sense of an average potential. The approach (12.3) then forms, together with the Pauli principle, the basis of the **shell model of atomic physics**.

The Schrödinger equation for H_0 can be solved strictly (for 'reasonable' potentials *U*), since the task is reduced to a **single-particle problem**

$$h\ \varphi_k(\xi) = \epsilon_k\ \varphi_k(\xi). \tag{12.5}$$

The eigenfunctions for H_0 then are product functions (ignoring the Pauli principle, i.e. the symmetry of the states with respect to particle exchange):

$$\Phi_\mu(\xi_1 \cdots \xi_N) = \varphi_{i_1}(\xi_1) \cdot \cdots \cdot \varphi_{i_N}(\xi_N), \tag{12.6}$$

where μ characterizes the single-particle states $\{i_1 \cdots i_N\} \equiv \mu$. If the eigenfunctions for *h* form a complete system (which we will always assume to be orthonormalized in the following), then the product functions Φ_μ form a complete basis in configuration space.

The general *N* particle wave function $\Psi(\xi_1, \ldots, \xi_N; t)$, furthermore, can be constructed as a linear combination of the product functions Φ_μ.

$$\Psi = \sum_\mu C_\mu(t)\ \Phi_\mu. \tag{12.7}$$

The coefficients $C_\mu(t)$ have to be determined from the Schrödinger equation (12.2). If we want e.g. calculate the stationary solutions of (12.2), one method is to determine the coefficients C_μ by diagonalizing H_R in the basis Φ_μ: we take a finite number of states (usually the *k* most energetically favorable states) from the basis of Φ_μ and diagonalize the finite-dimensional ($k \times k$) matrix

$$\langle \Phi_\mu | H_R | \Phi_{\mu'} \rangle, \tag{12.8}$$

which ensures the diagonalization of *H* according to the construction of Φ_μ; by adding further product functions ($k \to \infty$) this approximation method can be improved systematically.

Since we are considering systems of identical particles, the resulting *N*-particle wave function Ψ—in every step of an approximation method—must satisfy the Pauli principle. This is not automatically the case in the method outlined above, since the matrix (12.8) does not 'know' whether we are considering bosons or fermions. It is therefore appropriate to carry out the required antisymmetrization directly on the basis functions Φ_μ in the expansion of Ψ (12.7).

In analogy to the case of two identical particles we form antisymmetrized product functions in the form of **Slater determinants**

$$\Phi_\mu^a = \frac{1}{\sqrt{N!}} \sum_p (-)^p P[\varphi_{i_1}(\xi_1) \cdot \cdots \cdot \varphi_{i_N}(\xi_N)]; \tag{12.9}$$

here *P* runs through all possible permutations and $(-)^p$ is the signature of the permutation. According to the rules for determinants, Φ_μ^a is totally antisymmetric with respect to particle exchange ($\equiv$ exchange of two columns or rows). In particular, $\Phi_\mu^a = 0$ as soon as any two functions φ_i from the set $\{\mu\}$ are the same. This implies that the Pauli principle for a system of independent fermions can also be formulated in such a way that **each single-particle state can only be occupied once**. However, this formulation of the Pauli principle assumes independent fermions ($H_R \equiv 0$) and is therefore only a special case of (10.149)! The expansion of Ψ in the basis (12.9) guarantees that the solutions in every step of an approximation procedure satisfy

the Pauli principle; it is of practical advantage since the expansion of Ψ in the basis Φ_μ^a contains fewer expansion coefficients, that have to be calculated, than the expansion (12.7). As a general approach, we therefore choose

$$\Psi(\xi_1,\ldots,\xi_N;t) = \sum_\mu C_\mu^a(t)\ \ \Phi_\mu^a(\xi_1,\ldots,\xi_N). \tag{12.10}$$

By an optimal choice of $U(\xi)$ one can try to keep H_R so 'small' that the system in good approximation is described by H_0, such that the particles behave approximately independent. This is a good approximation for many questions in atomic physics; (example: structure of the periodic system of elements). The ground state of the system is then approximated by the ground state of H_0, in which the lowest *N* single-particle states φ_i are occupied.

This state is not always uniquely defined: If degenerate single-particle states are present (which is always the case in central potentials), then—depending on the number of particles in the system—the lowest eigenstate of H_0 can be degenerate, e.g. if two or more energetically equal levels are available for the last particle.

Excited states of the *N*-particle system are obtained – in the approximation of independent particles!—by 'raising' one or more particles to levels that are unoccupied in the ground state (**particle-hole excitations**).

12.2 Structure of the Fock Space

The following **particle number representation** (discussed below) has two main advantages relative to the configuration space representation:

1. While the wave functions $\Psi(\xi_1,\ldots,\xi_N;t)$ describe systems with a **fixed** particle number *N*, the particle number representation allows for the description of systems whose particle number is **not sharp**. This is the case e.g. for superconducting or superfluid systems (see Chap. 17).

2. The antisymmetrization can be incorporated in the particle number representation in the form of a few, simple commutation relations for particle **creation**—or **annihilation**—operators. This generates a calculus that is easier and safer to handle than dealing with Slater determinants in the context of the configuration space representation.

In the following, we consider a system of fermions whose particle number is not fixed. We describe such a system in the so-called **Fock space**, which is constructed from all Hilbert spaces $\mathscr{H}_N$ with a fixed particle number *N* as follows:

$\mathscr{H}_1$ is the Hilbert space of a 1-fermion system, spanned by vectors $|i\rangle$, whose representation in configuration space are the wave functions $\varphi_i(\xi)$,

$$\langle\xi|i\rangle \equiv \varphi_i(\xi), \tag{12.11}$$

where *i* includes a complete set of quantum numbers for a particle.

$\mathscr{H}_2$ is the Hilbert space of a 2-fermion system, spanned by vectors $|i_1 i_2\rangle$. Such a vector $|i_1 i_2\rangle$ describes a state in which the single-particle states i_1, i_2 are occupied; the configuration space representation of these states $|i_1 i_2\rangle$ are 2×2 Slater determinants, formed with the wave functions $\varphi_{i_1}, \varphi_{i_2}$,

$$\langle \xi_2 \xi_1 | i_1 i_2 \rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_{i_1}(\xi_1) & \varphi_{i_1}(\xi_2) \\ \varphi_{i_2}(\xi_1) & \varphi_{i_2}(\xi_2) \end{vmatrix}. \tag{12.12}$$

General case: Let $\mathscr{H}_N$ be the Hilbert space of an *N*-fermion system, spanned by vectors $|i_1 \cdots i_N\rangle$. The notation $|i_1 \cdots i_N\rangle$ implies that the single-particle states $i_1, i_2, \ldots, i_N$ each are singly occupied according to the Pauli principle. In the configuration space, the vectors $|i_1 \cdots i_N\rangle$ are represented by *N*-particle Slater determinants, formed from the single-particle functions $\varphi_{i_1}, \ldots, \varphi_{i_N}$:

$$\langle \xi_N \cdots \xi_1 | i_1 \cdots i_N \rangle = \frac{1}{\sqrt{N!}} \sum_p (-)^p P[\varphi_{i_1}(\xi_1) \cdots \varphi_{i_N}(\xi_N)]. \tag{12.13}$$

Phase definition:

In order to define the sign in the determinant (12.13) unambiguously, the functions φ_i must be numbered in an arbitrary but fixed way (exchanging two indices means exchanging rows, i.e. changing the sign!). We can e.g. sort the functions φ_i in the order of increasing particle energy ϵ_i. If several φ_i are degenerate, then for a fixed energy e.g. we order according to increasing angular momentum *j* and component m_j, always starting at $-m_j$. In this way we generate a **standard ordering**

$$i_1 < i_2 < \cdots < i_N, \tag{12.14}$$

which is arbitrary, but must be maintained consistently within a calculation. This also implies that the index order in the state $|i_1 \cdots i_N\rangle$ is fixed!

In every Hilbert space $\mathscr{H}_N$ the vectors $|i_1 \cdots i_N\rangle$ are orthonormalized due to the correspondence with Slater determinants,

$$\langle i_1 \cdots i_N | j_1 \cdots j_N \rangle = \delta_{i_1 j_1} \cdots \delta_{i_N j_N}, \tag{12.15}$$

if the single-particle functions φ_i are orthonormalized.

Proof We write

$$\Phi_a\{i\} = \sqrt{N!}\ \mathscr{A}[\varphi_{i_1}(\xi_1) \cdot \cdots \cdot \varphi_{i_N}(\xi_N)] \tag{12.16}$$

where the operator

$$\mathscr{A} := \frac{1}{N!} \sum_p (-)^p P \tag{12.17}$$

is a projector onto the space of antisymmetrized *N*-particle functions. As a projection operator it has the characteristic properties

$$\mathscr{A} = \mathscr{A}^\dagger, \qquad \mathscr{A}^2 = \mathscr{A}, \tag{12.18}$$

as can be explicitly proven using (12.17) (cf. for example A. Messiah, Quantum Mechanics II, *p.* 97). We now form:

$$\langle \Phi_a\{i\}|\Phi_a\{j\}\rangle = N!\langle \mathscr{A}\ \Phi\{i\}|\mathscr{A}\ \Phi\{j\}\rangle \tag{12.19}$$

where $\Phi\{i\} = \varphi_{i_1}(\xi_1)\cdot\ldots\cdot\varphi_{i_N}(\xi_N)$, $\Phi\{j\} = \varphi_{j_1}(\xi_1)\cdot\ldots\cdot\varphi_{j_N}(\xi_N)$ are the pure product functions. With (12.18)

$$\langle \Phi_a\{i\}|\Phi_a\{j\}\rangle = N!\langle \Phi\{i\}|\mathscr{A}^2\ \Phi\{j\}\rangle = N!\langle \Phi\{i\}|\mathscr{A}\ \Phi\{j\}\rangle. \tag{12.20}$$

If we expand $\mathscr{A}\ \Phi\{j\}$ according to (12.17), then:

$$N!\langle \Phi\{i\}|\mathscr{A}\ \Phi\{j\}\rangle = \det\left(\langle \varphi_{i_n}|\varphi_{j_m}\rangle\right). \tag{12.21}$$

This expression is only $\neq 0$ if the sequences $\{i_1\cdots i_N\}$ and $\{j_1\cdots j_N\}$ agree, since otherwise in every product term of the expansion of $\det\left(\langle \varphi_{i_n}|\varphi_{j_m}\rangle\right)$ at least 1 factor $= 0$. The normalization of the φ_i then guarantees that

$$\langle i_1\cdots i_N|i_1\cdots i_N\rangle = 1. \tag{12.22}$$

By adding the space $\mathscr{H}_0$ for the particle **vacuum** with the only state $|0\rangle$, we now sum up the spaces $\mathscr{H}_0, \mathscr{H}_1, \ldots, \mathscr{H}_N$ as a direct sum to form the **Fock space** $\mathscr{H}$,

$$\mathscr{H} = \mathscr{H}_0 \oplus \mathscr{H}_1 \oplus \mathscr{H}_2 \oplus \cdots \oplus \mathscr{H}_N \oplus \cdots \tag{12.23}$$

We supplement the scalar product—already defined in the individual spaces $\mathscr{H}_i$—with

$$\langle i_1\cdots i_N|j_1\cdots j_M\rangle = 0 \quad \text{if } N \neq M. \tag{12.24}$$

This introduces a scalar product in the entire Fock space; the choice in (12.24) is free, since a scalar product between Slater determinants $\Phi_a\{\mu\}$ with different particle numbers is not defined. Thus, in contrast to (12.15), in Eq. (12.24) we are not bound by the correspondence to the configuration space.

The choice made in (12.24), i.e. the direct summation of the subspaces, implies that we have composed the subspaces $\mathscr{H}_i$ in an orthogonal manner. This choice is also the only suitable one with regards to operators preserving the particle number, e.g. the particle number operator $\hat{N}$ itself. This operator is diagonal by definition in every subspace $\mathscr{H}_i$,

$$\hat{N}|i_1\cdots i_N\rangle = N|i_1\cdots i_N\rangle. \tag{12.25}$$

In order to keep the property (12.25) in the Fock space $\mathscr{H}$, we must require (12.24), which gives

$$\langle i_1\cdots i_N|\hat{N}|j_1\cdots j_M\rangle = N\langle i_1\cdots i_N|j_1\cdots j_M\rangle = M\langle i_1\cdots i_N|j_1\cdots j_M\rangle \tag{12.26}$$

for $N \neq M$. This implies that all basis vectors in $\mathscr{H}$ are orthonormalized if one also adds

$$\langle 0|0\rangle = 1, \tag{12.27}$$

since the correspondence between the vectors $|i_1 \cdots i_N\rangle$ and the Slater determinants does not provide any information about the scalar product $\langle 0|0\rangle$. (**Caution**: do not confuse the vacuum state $|0\rangle$ with the zero vector!)

12.3 Creation and Annihilation Operators

We now introduce linear operators in the Fock space $\mathscr{H}$. The two basic types, from which all others can be constructed, are **creation and annihilation operators** for particles. Creation operators connect the subspaces $\mathscr{H}_N$ for different values *N* in the following way:

$$a_m^\dagger |i_1 \cdots i_N\rangle = 0 \quad \text{if} \quad m \ \text{ occupied in } \ |i_1 \cdots i_N\rangle \tag{12.28}$$

$$a_m^\dagger |i_1 \cdots i_N\rangle = |m i_1 \cdots i_N\rangle = (-)^k |i_1 \cdots i_k m \cdots i_N\rangle \quad \text{else.}$$

Here *k* denotes the number of states occupied in $|i_1 \cdots i_N\rangle$ that precede the state *m* in the **standard ordering**. The factor $(-)^k$ in (12.28) therefore comes from the fact that when two particles, i.e. two occupied states, are exchanged, the vector $|i_1 \cdots i_N\rangle$ changes its sign due to the antisymmetry.

The interpretation of (12.28) is obvious: The operator $a_m^\dagger$ creates a particle in the state *m*, if this is not occupied in $|i_1 \cdots i_N\rangle$; the operators $a_m^\dagger$ for different *m* values thus lead from $\mathscr{H}_N$ to $\mathscr{H}_{N+1}$. If *m* is occupied in $|i_1 \cdots i_N\rangle$, we cannot create a second particle in *m* due to the Pauli principle. The following therefore holds in general:

$$\left(a_m^\dagger\right)^2 = 0 \qquad \forall m \tag{12.29}$$

due to the Pauli principle.

Consequences from the definition (12.28):

1. Annihilation operators

The operators a_m—adjoint to the operators $a_m^\dagger$—are particle annihilation operators. To prove this, we employ the unit operator in $\mathscr{H}$ according to the completeness relation

$$\sum_{M\geq 0} \sum_{\{j_M\}} |j_1 \cdots j_M\rangle\langle j_1 \cdots j_M| = 1_{\mathscr{H}_0} \oplus 1_{\mathscr{H}_1} \oplus 1_{\mathscr{H}_2} \oplus \cdots = 1_{\mathscr{H}}. \tag{12.30}$$

Then we can write ($\{j_M\} = (j_1 \cdots j_M)$)

$$a_m |i_1 \cdots i_N\rangle = 1_{\mathscr{H}}\ a_m |i_1 \cdots i_N\rangle = \sum_{M\geq 0} \sum_{\{j_M\}} |j_1 \cdots j_M\rangle\langle j_1 \cdots j_M| a_m |i_1 \cdots i_N\rangle, \tag{12.31}$$

and for the coefficients $\langle j_1 \cdots j_M| a_m |i_1 \cdots i_N\rangle$ we get:

$$\langle j_1 \cdots j_M| a_m |i_1 \cdots i_N\rangle = \langle i_1 \cdots i_N| a_m^\dagger |j_1 \cdots j_M\rangle^* \tag{12.32}$$

according to the definition of the adjoint operator. Furthermore:

$$\langle i_1 \cdots i_N | a_m^\dagger | j_1 \cdots j_M \rangle^* = \langle i_1 \cdots i_N | m j_1 \cdots j_M \rangle^* = (-)^k \langle i_1 \cdots i_N | j_1 \cdots j_k m \cdots j_M \rangle^* . \quad (12.33)$$

Now $\langle i_1 \cdots i_N | j_1 \cdots j_k m \cdots j_M \rangle \neq 0$ only if

(a) $N = M + 1$ due to the orthogonality of the spaces $\mathscr{H}_N$ and

(b) the sequences $(i_1 \cdots i_N)$ and $(j_1 \cdots j_k m \cdots j_M)$ are the same. Thus:

$$a_m |i_1 \cdots i_N\rangle = 0 \quad \text{if} \quad m \ \text{in} \quad |i_1 \cdots i_N\rangle \ \text{empty} \quad (12.34)$$

$$a_m |i_1 \cdots i_N\rangle = (-)^k |i_1 \cdots i_k i_{k+2} \cdots i_N\rangle \quad \text{if } m \text{ occupied and } m = i_{k+1}.$$

In (12.31) only a single vector from $\mathscr{H}_{N-1}$ contributes to the double sum, i.e. the one that (except for the sign) results from the vector $|i_1 \cdots i_N\rangle$, if the state $m = i_{k+1}$ is eliminated. Thus a_m annihilates a particle in the state *m*, if *m* is occupied in $|i_1 \cdots i_N\rangle$.

12.4 Construction of *N*-Particle States

We obtain a *N*-particle state $|i_1 \cdots i_N\rangle$ by application of creation operators to the vacuum,

$$|i_1 \cdots i_N\rangle = a_{i_1}^\dagger \cdots a_{i_N}^\dagger |0\rangle = \prod_{m=i_N}^{i_1} a_m^\dagger |0\rangle. \quad (12.35)$$

The vacuum is characterized by the fact that

$$a_m |0\rangle = 0 \qquad \forall m. \quad (12.36)$$

12.5 Particle Number Operator $\hat{N}$

From (12.28) and (12.34) follows

$$a_m^\dagger a_m |i_1 \cdots i_N\rangle = 0 \quad \text{if} \quad m \ \text{in} \quad |i_1 \cdots i_N\rangle \ \text{empty} \quad (12.37)$$

$$a_m^\dagger a_m |i_1 \cdots i_N\rangle = |i_1 \cdots i_N\rangle \quad \text{if } m \text{ occupied in } |i_1 \cdots i_N\rangle \ .$$

The operator $a_m^\dagger a_m$ has the eigenstates $|i_1 \cdots i_N\rangle$ with the eigenvalues 0 and 1,

$$a_m^\dagger a_m |i_1 \cdots i_N\rangle = n_m |i_1 \cdots i_N\rangle \ \text{with} \ n_m = 0, 1; \quad (12.38)$$

i.e. $a_m^\dagger a_m$ indicates (measures) whether the state m is occupied ($n_m = 1$) or empty ($n_m = 0$).

The operator $\sum_m a_m^\dagger a_m$ therefore checks all single-particle states, whether they are occupied or not and adds up the number of occupied states; it thus determines the **particle number** of the system under consideration.

$$\hat{N} = \sum_m a_m^\dagger a_m \tag{12.39}$$

is an explicit representation of the particle number operator, whose eigenvalues for the eigenvectors $|i_1 \cdots i_N\rangle$ result in the particle number N of the system. According to (12.39), $\hat{N}$ is obviously hermitian. In any state of $\mathscr{H}$,

$$|\Psi(t)\rangle = \sum_{N\geq 0} \sum_{\{j_N\}} C_{N,\{j_N\}}(t)\ |j_1 \cdots j_N\rangle, \tag{12.40}$$

however, $\hat{N}$ is not sharp and may have fluctuations $(\Delta\hat{N})^2 \neq 0$ (see Chap. 17).

12.6 Commutation Rules

From the definition of $a_m^\dagger$ we get

$$a_m^\dagger a_n^\dagger |i_1 \cdots i_N\rangle = 0 \quad \text{if} \quad m, n \ \text{ occupied or } \ n = m \tag{12.41}$$

$$a_m^\dagger a_n^\dagger |i_1 \cdots i_N\rangle = |mni_1 \cdots i_N\rangle \ \text{ otherwise}$$

and vice versa,

$$a_n^\dagger a_m^\dagger |i_1 \cdots i_N\rangle = 0 \quad \text{if} \quad n, m \ \text{ occupied or } \ n = m \tag{12.42}$$

$$a_n^\dagger a_m^\dagger |i_1 \cdots i_N\rangle = |nmi_1 \cdots i_N\rangle = -|mni_1 \cdots i_N\rangle \ \text{ otherwise.}$$

Adding (12.41) and (12.42) gives

$$a_m^\dagger a_n^\dagger + a_n^\dagger a_m^\dagger = 0, \tag{12.43}$$

since (12.41) and (12.42) hold for any vector $|i_1 \cdots i_N\rangle$. In analogy one proves:

$$a_m a_n + a_n a_m = 0 \tag{12.44}$$

and

$$a_m^\dagger a_n + a_n a_m^\dagger = \delta_{mn}. \tag{12.45}$$

Note: The **commutation relations** (12.43), (12.44) and (12.45) become more complicated when using a non-orthogonal basis of single-particle functions.

12.7 Observables in Particle Number Representation

In order to be able to do physics in the Fock space $\mathscr{H}$, we must be able to explicitly represent operators such as the kinetic energy T, potential energy V or angular momentum $\mathbf{J}$. We want to show that operators (like those mentioned above) can be constructed from the a_i, $a_i^\dagger$.

We make use of the fact that we know the representation of the operators in the configuration space. The corresponding operators in the Fock space $\mathscr{H}$ then are to be defined in such a way, that the matrix elements of an operator in the subspaces $\mathscr{H}_N$ are the same in both representations. It is sufficient to show this for the basis vectors:

$$\int d\tau_\xi \;\Phi_a^*\{i_N\} O(\xi_1,\ldots,\xi_N)\Phi_a\{j_N\} = \langle i_1\cdots i_N|\hat{O}(a_m^\dagger, a_m)|j_1\cdots j_N\rangle. \tag{12.46}$$

Since the operators we are interested in, such as energy or angular momentum, preserve the number of particles, the following must also hold in addition to (12.46)

$$\langle i_1\cdots i_N|\hat{O}(a_m^\dagger, a_m)|j_1\cdots j_M\rangle = 0 \qquad \text{if } N \neq M. \tag{12.47}$$

The Eqs. (12.46) and (12.47) completely define the operator $\hat{O}(a_m^\dagger, a_m)$ in $\mathscr{H}$.

In the following we are interested in one- and two-particle operators and claim that any single-particle operator

$$f = \sum_{\alpha=1}^N f(\xi_\alpha) \tag{12.48}$$

and any two-particle operator

$$g = \tfrac{1}{2}\sum_{\alpha,\beta=1,\alpha\neq\beta}^N g(\xi_\alpha,\xi_\beta) \tag{12.49}$$

have the following representation in Fock space:

$$\hat{f} = \sum_{m,n}(m|f|n)\;\; a_m^\dagger a_n \tag{12.50}$$

with

$$(m|f|n) = \int d\xi\;\; \varphi_m^*(\xi)\;\; f(\xi)\;\; \varphi_n(\xi) \tag{12.51}$$

or

$$\hat{g} = \tfrac{1}{2} \sum_{n,m,p,q} (pq|g|mn)\ a_p^\dagger a_q^\dagger a_n a_m \tag{12.52}$$

with

$$(pq|g|mn) = \int\int d\xi\ d\xi'\ \varphi_p^*(\xi)\varphi_q^*(\xi')\ g(\xi,\xi')\ \varphi_m(\xi)\varphi_n(\xi'). \tag{12.53}$$

As desired, the operators $\hat{f}$ and $\hat{g}$ conserve the particle number, since $a^\dagger$ and a always occur in pairs. Therefore:

$$[\hat{f}, \hat{N}] = [\hat{g}, \hat{N}] = 0, \tag{12.54}$$

which can also be proven explicitly using the commutation relations for $a^\dagger, a$. With (12.54) we obtain

$$\langle i_1 \cdots i_N | [\hat{N}, \hat{O}] | j_1 \cdots j_M \rangle = (N - M) \langle i_1 \cdots i_N | \hat{O} | j_1 \cdots j_M \rangle = 0 \tag{12.55}$$

for $\hat{O} = \hat{f}, \hat{g}$, such that (12.47) is satisfied,

$$\langle i_1 \cdots i_N | \hat{O} | j_1 \cdots j_M \rangle = 0 \tag{12.56}$$

for $N \neq M$.

Qualitatively, the structure of $\hat{f}$ and $\hat{g}$ is immediately clear: In the configuration space each summand of $f = \Sigma_{\alpha=1}^{N} f(\xi_\alpha)$ 'acts on' only one particle and changes the state of this particle according to

$$f(\xi_\alpha)\varphi_m(\xi_\alpha) = \sum_n \varphi_n(\xi_\alpha)(n|f|m). \tag{12.57}$$

The operator $\hat{f}$ works in exactly the same way in Fock space: each summand of $\hat{f}$ in (12.50) changes the state $|i_1 \cdots i_N\rangle$ in such a way that a particle in state *n* is destroyed, but another one is created again in *m*. Correspondingly: A two-particle operator *g* acts on two particles at the same time and changes their state; $\hat{g}$ achieves the same by first destroying two particles in the states *m*, *n* and then creating two particles in the states *p*, *q*.

We want to carry out the proof for (12.50), (12.51) explicitly; for (12.52), (12.53) the proof can be carried out in analogy. Due to (12.57) the following holds when applying *f* to a product function:

$$f\ \varphi_i(\xi_1)\varphi_j(\xi_2)\cdots \tag{12.58}$$

$$= \sum_m (m|f|i)\ \varphi_m(\xi_1)\varphi_j(\xi_2) + \sum_m (m|f|j)\ \varphi_i(\xi_1)\varphi_m(\xi_2) + \cdots$$

Due to the identity of the particles the operator *f* is symmetric in all particles—otherwise the observable *f* could be used to distinguish the particles in contradiction to the assumption of

identical particles—we have

$$[f, \mathscr{A}] = 0 \tag{12.59}$$

with $\mathscr{A}$ from (12.17). Applying $\mathscr{A}$ to Eq. (12.58) then gives

$$f\ \Phi_a\{ijk\cdots\} = \sum_m (m|f|i)\ \Phi_a\{mjk\cdots\} + \sum_m (m|f|j)\ \Phi_a\{imk\cdots\} \tag{12.60}$$

$$+ \sum_m (m|f|k)\ \Phi_a\{ijm\cdots\} + \cdots$$

We compare this result with

$$\hat{f}|ijk\cdots\rangle = \sum_{m,n} (m|f|n)\ a_m^\dagger a_n |ijk\cdots\rangle \tag{12.61}$$

$$= \sum_m (m|f|i)\ |mjk\cdots\rangle + \sum_m (m|f|j)\ |imk\cdots\rangle + \sum_m (m|f|k)\ |ijm\cdots\rangle + \cdots$$

(Note the phase factors in (12.28) and (12.34)!) One can now easily verify the defining Eq. (12.46) by forming the required matrix elements in (12.60) and (12.61) and comparing them term by term.

12.8 Applications

1. Ground state and simple excitations of an *N* fermion system

We obtain the ground state by taking the *N* lowest (in energy) single-particle levels i_1, i_2, ..., i_N (Fig. 12.1):

$$|\Phi_0\rangle = a_{i_1}^\dagger \cdots a_{i_N}^\dagger |0\rangle. \tag{12.62}$$

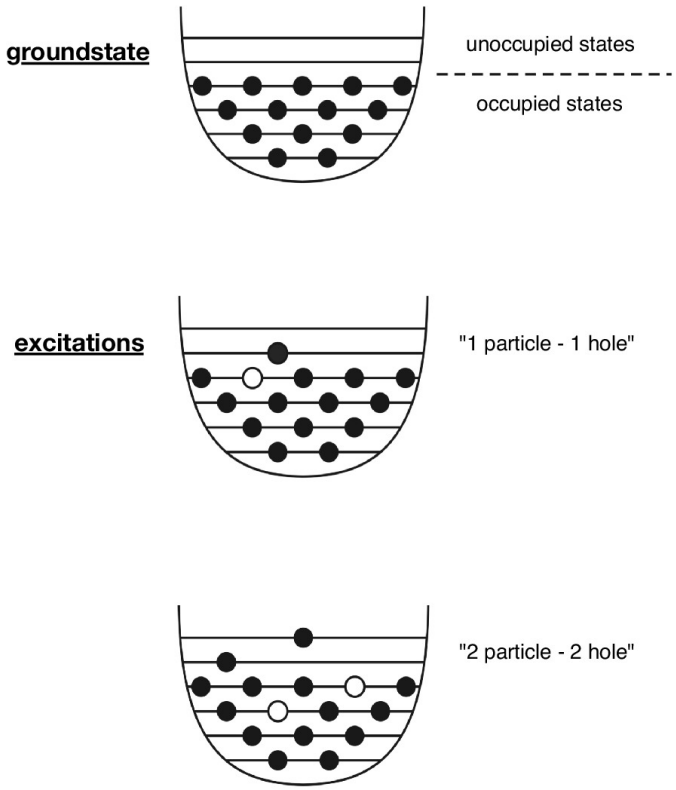

Fig. 12.1 Groundstate, 1 particle—1 hole and 2 particle—2 hole states

1-particle—1-hole excitations then have the form:

$$|\Phi_{1p-1h}\rangle = a_m^\dagger a_i |\Phi_0\rangle, \tag{12.63}$$

where *m* in $|\Phi_0\rangle$ is empty and *i* is occupied.

2. Expectation values

For the expectation value of the kinetic energy in a *N*-particle state $|i_1 \cdots i_N\rangle$ one obtains using (12.50) as well as (12.28) and (12.34):

$$\langle i_1 \cdots i_N|\hat{T}|i_1 \cdots i_N\rangle = \sum_{m,n}(m|t|n)\langle i_1 \cdots i_N|a_m^\dagger a_n|i_1 \cdots i_N\rangle = \sum_{m=i_1}^{i_N}(m|t|m), \tag{12.64}$$

since only values *n* can contribute that occur in $(i_1 \cdots i_N)$ and due to the orthogonality of different states $|i_1 \cdots i_N\rangle$ we must have $m = n$. The expectation value of the kinetic energy is therefore (as expected) the sum of the contributions of the particles present, i.e. of the occupied states; the analogous statement applies to the angular momentum, the momentum or other single-particle operators.

The case of the potential energy (in general: of a two-particle operator) is somewhat more complicated. In

$$\langle i_1 \cdots i_N|\hat{V}|i_1 \cdots i_N\rangle = \tfrac{1}{2}\sum_{m,n,p,q}(pq|V|mn)\langle i_1 \cdots i_N|a_p^\dagger a_q^\dagger a_n a_m|i_1 \cdots i_N\rangle \tag{12.65}$$

only the values $n \neq m$ contribute that are occupied in $|i_1 \cdots i_N\rangle$. Furthermore, due to the orthogonality of the basis states $|i_1 \cdots i_N\rangle$ of the Fock space, we must have either $p = m$ and

$q = n$ or $q = m$ and $p = n$. We therefore obtain:

$$\langle \hat{V} \rangle = \tfrac{1}{2} \sum_{m,n \ occupied} \{(mn|V|mn) - (mn|V|nm)\}, \tag{12.66}$$

where terms with $m = n$ automatically cancel out as **self-interactions**. The **direct** term

$$\tfrac{1}{2} \sum_{m,n \ occupied} (mn|V|mn) \tag{12.67}$$

corresponds to the **classical interaction integral**:

$$\tfrac{1}{2} \sum_{m,n \ occupied} (mn|V|mn) = \tfrac{1}{2} \sum_{m,n} \int\int d\xi \ d\xi' \ |\varphi_m(\xi)|^2 \ V(\xi,\xi') \ |\varphi_n(\xi')|^2 \tag{12.68}$$

$$= \frac{1}{2} \int\int d\xi \ d\xi' \ \rho(\xi) \ V(\xi,\xi') \ \rho(\xi').$$

Here

$$\rho(\xi) = \sum_{m=1}^{N} |\varphi_m(\xi)|^2 \tag{12.69}$$

is the probability density of finding a particle with the coordinate ξ; it is composed additively from the contributions $|\varphi_m(\xi)|^2$ of the individual particles.

Example: Coulomb energy of a charge distribution described by $\rho(\mathbf{r})$.

The second term in (12.66) is a typical quantum mechanical effect for systems of fermions (**exchange term**); it is responsible for the homopolar binding e.g. in the H_2 molecule.

Remark:

For historical reasons, the formalism developed above is often referred to as **second quantization**. However, it should be clear that the particle number representation—apart from the extension to systems with an uncertain particle number—is only a **different representation** than the configuration space representation of a system of *N* identical particles.

In summarizing this chapter we have introduced the particle number representation for fermions, which allows for a transparent formulation of many-body problems and takes care about the antisymmetry of the fermion wave function by simple (anti)-commutation relations. Furthermore, we have given explicit expressions for one-body and two-body operators in particle number representation and calculated some characteristic examples.

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13. Particle Number Representation for Bosons

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The case of bosons is analogous to that of fermions to a large extent; we will therefore restrict ourselves to a brief presentation and only work out the differences between bosons and fermions.

13.1 Representation in Configuration Space

We describe *N* independent bosons in the configuration space by completely **symmetrized** product functions:

$$\Phi^s\{i_N\} = \frac{1}{\sqrt{N!n_1!\cdots n_N!}} \sum_p P[\varphi_{i_1}(\xi_1)\cdots\varphi_{i_N}(\xi_N)]. \tag{13.1}$$

In contrast to fermions, it is possible for a single-particle state to be occupied n_j-fold; of course,

$$\sum_j n_j = N \tag{13.2}$$

for every possible state (13.1). From the basis states, the exact *N* particle states for interacting bosons (in principle) can be constructed by superposition.

13.2 Fock Space for Bosons

In the particle number representation, we assign vectors

$$|n_{i_1} n_{i_2} \cdots\rangle \tag{13.3}$$

to the symmetrized product functions (13.1), where the numbers n_{i_1}, n_{i_2} etc. indicate which single-particle states are occupied and how many times they are

occupied. Of course, the same holds for the total particle number (13.2). From the orthonormalization of the functions $\Phi^s\{i_N\}$ (as can be proven for fermions) we obtain in the particle number representation

$$\langle n_{i_1} n_{i_2} \cdots | n_{j_1} n_{j_2} \cdots \rangle = \delta_{n_{i_1} n_{j_1}} \delta_{n_{i_2} n_{j_2}} \cdots \tag{13.4}$$

The Hilbert spaces $\mathscr{H}_N$ spanned by the states (13.1) or (13.3) with the constraint (13.2) for a fixed number of bosons *N* are now combined to the Fock space $\mathscr{H}$ for bosons in analogy to Sect. 12.2:—We only differentiate quantities that refer to fermions or bosons by their designation when necessary. Of course, the Fock space $\mathscr{H}$ for bosons must be distinguished from that for fermions!—

$$\mathscr{H} = \mathscr{H}_0 \oplus \mathscr{H}_1 \oplus \mathscr{H}_2 \oplus \cdots \oplus \mathscr{H}_N \oplus \cdots \tag{13.5}$$

$\mathscr{H}_0$ adds the boson vacuum, described by the vector $|0\rangle$, which we assume to be normalized in the following,

$$\langle 0|0\rangle = 1. \tag{13.6}$$

Of course, the boson vacuum is not identical to the fermion vacuum, $|0\rangle_B \neq |0\rangle_F$. Since in Chap. 12 only fermions and here only bosons are described, we omit the indexing (for bosons or fermions).

With the same reasoning as in Sect. 12.2 we introduce the scalar product between states with different particle numbers by

$$\langle n_1 n_2 \cdots n_k .. | n'_1 n'_2 \cdots n'_k .. \rangle = 0 \tag{13.7}$$

if

$$\sum_i n_i \neq \sum_{j'} n'_j. \tag{13.8}$$

To simplify the notation, we have numbered the single-particle states with $1, 2, \ldots k$; $n'_1, n'_2 ..$ are the corresponding occupation numbers, which in the case of bosons uniquely characterize the *N* particle state. (For fermions, the occupation numbers are either 0 or 1, such that an *N* particle state is uniquely determined by the sequence of the single-particle states with occupation number 1.) In the Fock space $\mathscr{H}$, by construction, all basis states $|n_1 n_2 \cdots n_k \cdots\rangle$ are orthogonal to each other and normalized.

13.3 Creation and Annihilation Operators

We now introduce linear operators in $\mathscr{H}$ which link states from $\mathscr{H}_N$ with those from $\mathscr{H}_{N\pm1}$:

$$b_k^\dagger|\cdots n_k\cdots\rangle = \sqrt{n_k+1}|\cdots n_k+1\cdots\rangle, b_k|\cdots n_k\cdots\rangle = \sqrt{n_k}|\cdots n_k-1\cdots\rangle. \tag{13.9}$$

The operators $b_k^\dagger$ each produce a particle in the state k; b_k acts correspondingly as an annihilation operator. With the prefactors $\sqrt{n_k}$ or $\sqrt{n_k+1}$ chosen in (13.9),—as already anticipated in the notation—$b_k^\dagger$ and b_k are adjoint operators.

Proof We form

$$\langle..n_k..|b_k|\cdots n_k'..\rangle = \sqrt{n_k'}\ \delta_{n_k,n_k'-1} \tag{13.10}$$

and

$$\langle\cdots n_k'..|b_k^\dagger|..n_k..\rangle = \sqrt{n_k+1}\ \delta_{n_k',n_k+1} = \sqrt{n_k'}\ \delta_{n_k'-1,n_k} \tag{13.11}$$

Conclusions:

1. Boson vacuum

The boson vacuum is (in analogy to the fermion case) characterized by

$$b_k|0\rangle = 0 \forall k, \tag{13.12}$$

as follows directly from (13.9). Starting from the vacuum, all other states can be constructed by applying creation operators,

$$\prod_i (b_i^\dagger)^{n_i}|0\rangle = |n_1 n_2 n_3\cdots\rangle \tag{13.13}$$

with $\sum_i n_i = N$.

2. Particle number operator

From (13.9) follows

$$b_k^\dagger b_k|\cdots n_k\cdots\rangle = b_k^\dagger\sqrt{n_k}|\cdots n_k-1\cdots\rangle = n_k|\cdots n_k..\rangle; \tag{13.14}$$

the operator $b_k^\dagger b_k$ counts the particles in state *k*. The operator for the total particle number is thus

$$\hat{N} = \sum_k b_k^\dagger b_k = \sum_k \hat{N}_k. \tag{13.15}$$

Since

$$[\hat{N}, \hat{N}_k] = 0, \tag{13.16}$$

there are states in $\mathscr{H}$ in which both the total particle number *N* and the occupation numbers n_k of the single-particle states *k* are sharp.

3. Commutation relations
From the definition (13.9) we obtain

$$b_k b_k^\dagger |\cdots n_k \cdots\rangle = b_k \sqrt{n_k + 1} |\cdots n_k + 1 \cdots\rangle = (n_k + 1) |\cdots n_k \cdots\rangle \tag{13.17}$$

and

$$b_k^\dagger b_k |\cdots n_k \cdots\rangle = n_k |\cdots n_k \cdots\rangle \tag{13.18}$$

(according to (13.14)), from which—by taking the difference—we get

$$(b_k b_k^\dagger - b_k^\dagger b_k) |\cdots n_k \cdots\rangle = |\cdots n_k \cdots\rangle. \tag{13.19}$$

Since $|\cdots n_k \cdots\rangle$ was chosen arbitrarily, the operator relation results:

$$b_k b_k^\dagger - b_k^\dagger b_k = 1. \tag{13.20}$$

All other commutators vanish as can be proven in analogy. In total, we obtain the following **boson commutation rules:**

$$[b_k, b_{k'}^\dagger] = b_k b_{k'}^\dagger - b_{k'}^\dagger b_k = \delta_{kk'} \tag{13.21}$$

$$[b_k, b_{k'}] = b_k b_{k'} - b_{k'} b_k = 0$$

$$[b_k^\dagger, b_{k'}^\dagger] = b_k^\dagger b_{k'}^\dagger - b_{k'}^\dagger b_k^\dagger = 0.$$

13.4 Observables

As in Sect. 12.7 one proves that a single-particle operator f in the particle number representation has the form

$$\hat{f} = \sum_{m,n} (m|f|n)\ b_m^\dagger b_n\ ; \tag{13.22}$$

correspondingly, for a two-particle operator g in particle number representation

$$\hat{g} = \tfrac{1}{2} \sum_{p,q,m,n} (pq|g|mn)\ b_p^\dagger b_q^\dagger b_n b_m . \tag{13.23}$$

$\hat{f}$ and $\hat{g}$ have formally the same structure for bosons and fermions; the difference is only in the commutation rules for the creation and annihilation operators and the states on which $\hat{f}$, $\hat{g}$ act.

13.5 Applications

The following examples should clarify the difference between fermions and bosons.

1. Groundstate and simple excited states in boson systems of N particles.

In the groundstate of a system of N independent bosons, all N particles are in the lowest single-particle level (Fig. 13.1).

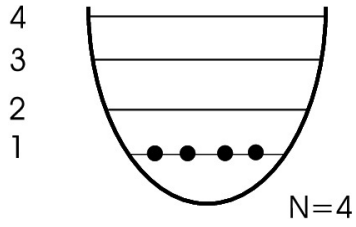

Fig. 13.1 Groundstate of a 4 particle boson system

Simple excited states are obtained by placing one (or more) particles in a higher level (Fig. 13.2).

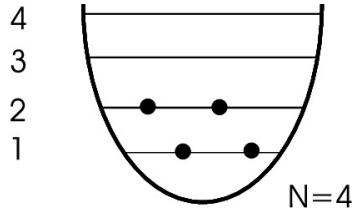

Fig. 13.2 Illustration of a $2p-2h$ excitation for a 4 particle boson system

2. Ground state expectation values
For the kinetic energy (or other single-particle operators) we obtain

$$\langle\Phi_0|\hat{T}|\Phi_0\rangle = \sum_{m,n}(m|t|n)\langle\Phi_0|b_m^\dagger b_n|\Phi_0\rangle = N\ t_0, \tag{13.24}$$

where t_0 is the kinetic energy of a particle in the lowest single-particle state $\varphi_0 = |1\rangle$.

For the potential energy (or other two-particle operators) $b_l^\dagger b_n = -\delta_{ln} + b_n b_l^\dagger$

$$\langle\Phi_0|\hat{V}|\Phi_0\rangle = \tfrac{1}{2}\sum_{m,n,k,l}(kl|V|mn)\langle\Phi_0|b_k^\dagger b_l^\dagger b_n b_m|\Phi_0\rangle = \tfrac{1}{2}N(N-1)V_0, \tag{13.25}$$

where V_0 is given by the matrix element

$$V_0 = \int\int d\xi\ d\xi'\ |\varphi_0(\xi)|^2\ V(\xi,\xi')\ |\varphi_0(\xi')|^2. \tag{13.26}$$

Addition:

The eigenvalues of $\hat{N}_k = b_k^\dagger b_k$ are real, since $\hat{N}_k$ is hermitian. They are also not negative, because

$$\langle\cdots n_k\cdots|b_k^\dagger b_k|\cdots n_k\cdots\rangle = \sum_{i'}\langle\cdots n_k\cdots|b_k^\dagger|\cdots n_i'..\rangle\langle\cdots n_i'\cdots|b_k|\cdots n_k\cdots\rangle \tag{13.27}$$

$$= \sum_{n_{i'}}|\langle\cdots n_i'\cdots|b_k|\cdots n_k\cdots\rangle|^2 \geq 0.$$

The formal properties of $\hat{N}_k$ or $\hat{N}$ are thus consistent with the physical interpretation.

In summary, we have obtained a calculus with creation and annihilation operators for bosons that differs characteristically from fermions in the commutation relations, which take care about the symmetry (or antisymmetry) of the *N*-body wave functions.

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14. Quantization of the Radiation Field: Photons

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In this chapter we describe the quantization of the electromagnetic radiation field, that in quantum mechanics can no longer be described by a classical vector field $\mathbf{A}(\mathbf{r};t)$. Furthermore, we will calculate the interaction between matter and the quantized radiation field in leading order of the coupling.

Electromagnetic radiation (**Planck's radiation formula**) plays an important role in physics. We will carry out the description of the radiation field by photons, which was implicitly used by Planck, after quantization within the framework of the particle number representation.

14.1 Energy of the Classical Radiation Field

In Coulomb gauge

$$\nabla \cdot \mathbf{A}(\mathbf{r};t) = 0 \tag{14.1}$$

the vector potential $\mathbf{A}(\mathbf{r};t)$, that has to be calculated from the wave equation

$$\Delta \mathbf{A}(\mathbf{r};t) - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\mathbf{A}(\mathbf{r};t) = 0, \tag{14.2}$$

describes the free radiation field completely. With the separation Ansatz

$$\mathbf{A}(\mathbf{r};t) = U(\mathbf{r})\mathbf{v}(t) \tag{14.3}$$

Equation (14.2) turns to

$$\Delta U + k^2 U = 0 \tag{14.4}$$

and

$$\frac{\partial^2}{\partial t^2}\mathbf{v} + \omega^2 \mathbf{v} = 0 \tag{14.5}$$

with

$$k^2 = \frac{\omega^2}{c^2}. \tag{14.6}$$

Special solutions are plane waves

$$\mathbf{A}(\mathbf{r};t) \sim \exp\{\pm i(\mathbf{k}\cdot\mathbf{r} - \omega t)\}, \tag{14.7}$$

from which the general solution can be constructed by superposition with respect to $\mathbf{k}$.

If the radiation field is enclosed in a very large—but finite normalization volume V (with periodic boundary conditions)—we obtain the general solution in the form of a Fourier series:

$$\mathbf{A}(\mathbf{r};t) = \sum_{\mu,j} \sqrt{\tfrac{4\pi c^2}{V\omega_\mu}}\; b_{\mu,j}(t)\;\mathbf{e}_{\mu,j}\;\;\exp\{i\mathbf{k}_\mu\cdot\mathbf{r}\}. \tag{14.8}$$

Here

$$\mathbf{k}_\mu = \tfrac{2\pi}{L}(\mu_1,\mu_2,\mu_3), \qquad\qquad \mu = (\mu_1,\mu_2,\mu_3), \tag{14.9}$$

where the μ_i are integers (with $V = L^3$), the wave vector (–not the four-momentum in covariant notation!–) and

$$\mathbf{e}_{\mu,j}, \qquad j = 1,2 \tag{14.10}$$

are real **polarization vectors**, which are perpendicular to each other and—due to the transversality of light—perpendicular to $\mathbf{k}_\mu$. The representation (14.8) for $\mathbf{A}$ is real if we require

$$b^*_{\mu,j} = b_{-\mu,j}. \tag{14.11}$$

We therefore write explicitly:

$$\mathbf{A}(\mathbf{r};t) = \sum_{\mu,j} \sqrt{\tfrac{2\pi c^2}{V\omega_\mu}}\;\left(b_{\mu,j}(t)\;\mathbf{e}_{\mu,j}\;\;\exp\{i\mathbf{k}_\mu\cdot\mathbf{r}\} + b^*_{\mu,j}(t)\;\mathbf{e}_{\mu,j}\;\;\exp\{-i\mathbf{k}_\mu\cdot\mathbf{r}\}\right). \tag{14.12}$$

We now want to calculate—with regards to the quantization of the radiation field—the energy of the field, starting from the well-known formula (in Gauss units)

$$H_{r,kl.} = \tfrac{1}{8\pi}\;\int d\tau\;[\mathbf{E}^2 + \mathbf{B}^2]. \tag{14.13}$$

With

$$\mathbf{B} = \nabla\times\;\;\mathbf{A}, \qquad\qquad \mathbf{E} = -\tfrac{1}{c}\tfrac{\partial\mathbf{A}}{\partial t} \tag{14.14}$$

we get

$$H_{r,kl.} = \frac{1}{8\pi} \int d\tau \, [\frac{1}{c^2}\left(\frac{\partial \mathbf{A}}{\partial t}\right)^2 + (\nabla \times \mathbf{A})^2]. \tag{14.15}$$

If we insert (14.12) we finally obtain:

$$H_{r,kl.} = \frac{1}{2} \sum_{\mu,j} \omega_\mu (b_{\mu,j} b^*_{\mu,j} + b^*_{\mu,j} b_{\mu,j}), \tag{14.16}$$

using

$$\int d\tau \;\; \exp\{i[\mathbf{k}_\mu + \mathbf{k}_{\mu'}] \cdot \mathbf{r}\} = 0 \tag{14.17}$$

except for $\mathbf{k}_\mu = -\mathbf{k}_{\mu'}$, where (14.17) just gives the volume V. As expected for a closed system, $H_{r,kl.}$ is independent of time, since the coefficients $b_{\mu,j}$ obey the differential equation

$$\frac{\partial^2}{\partial t^2} b_{\mu,j} + \omega_\mu^2 b_{\mu,j} = 0 \tag{14.18}$$

with the basic solutions

$$b_{\mu,j}(t) \sim \exp\{\pm i\omega_\mu t\}. \tag{14.19}$$

14.2 Quantization of the Radiation Field

For the quantization we note that the classical energy according to (14.16) and (14.18) is composed additively of the contributions of individual oscillators described by the amplitudes $b_{\mu,j}(t)$. The same holds for the momentum or angular momentum of the field. The quantization of the harmonic oscillator is known: we replace the classical amplitudes $b_{\mu,j}$ and $b^*_{\mu,j}$ by operators $b_{\mu,j}$ and $b^\dagger_{\mu,j}$ with the commutation rule

$$\left[b_{\mu,j}, b^\dagger_{\mu',j'}\right] = \hbar \;\; \delta_{\mu\mu'}\delta_{jj'} \tag{14.20}$$

for $t = t'$; all other commutators for $t \neq t'$ should disappear. It is convenient to substitute

$$b_{\mu,j} = \sqrt{\hbar} \;\; \tilde{b}_{\mu,j}, \tag{14.21}$$

such that the commutator (14.20) changes at equal times to

$$\left[\tilde{b}_{\mu,j}, \tilde{b}^\dagger_{\mu',j'}\right] = \delta_{\mu\mu'}\delta_{jj'}. \tag{14.22}$$

From now on we only use the operators $\tilde{b}_{\mu j}$ and $\tilde{b}^{\dagger}_{\mu j}$, but for simplicity again write $b_{\mu j} \equiv \tilde{b}_{\mu j}$. The Hamiltonian of the radiation field then is (initially)

$$H_r = \tfrac{1}{2} \sum_{\mu,j} \hbar\omega_\mu \ (b_{\mu,j} b^{\dagger}_{\mu,j} + b^{\dagger}_{\mu,j} b_{\mu,j}) = \sum_{\mu,j} \hbar\omega_\mu \ (b^{\dagger}_{\mu,j} b_{\mu,j} + \tfrac{1}{2}). \tag{14.23}$$

The radiation field can thus be treated like a system of decoupled harmonic oscillators.

If we compare (14.22) with (14.24), we can see that the degrees of freedom are bosons. These bosons—**photons**—are characterized by their momentum $\hbar\mathbf{k}_\mu$, energy $\hbar\omega_\mu$ and polarization state *j*. In (14.23)

$$\hat{N}_{\mu,j} = b^{\dagger}_{\mu,j} b_{\mu,j} \tag{14.24}$$

is the particle number operator for the oscillation type (μ, j), whose eigenvalues indicate how many photons of the type (μ, j) are present; in addition, in each oscillation type there is a zero-point energy of $1/2\hbar\omega_\mu$. The eigenstates of H_r are characterized by the number of photons of the type (μ, j) :

$$H_r |\cdots n_{\mu,j} \cdots\rangle = \sum_{\mu,j} \hbar\omega_\mu n_{\mu,j} \ |\cdots n_{\mu,j} \cdots\rangle \tag{14.25}$$

after subtracting the zero-point energy, which is divergent in (14.23). In order to avoid such divergences and to obtain a vacuum state $|0\rangle$ ($b_{\mu,j}|0\rangle = 0 \ \forall \mu, j$) of the lowest energy with $H_r|0\rangle = 0$, we introduce the **normal ordering** of the operators in field theory $b_{\mu,j}, b^{\dagger}_{\mu',j'}$, i.e. arranging all $b_{\mu,j}$ to the right of $b^{\dagger}_{\mu',j'}$. The **normal ordered Hamilton operator** then has the form

$$: H_r := \tfrac{1}{2} \sum_{\mu,j} \hbar\omega_\mu \ \ : (b_{\mu,j} b^{\dagger}_{\mu,j} + b^{\dagger}_{\mu,j} b_{\mu,j}) := \sum_{\mu,j} \hbar\omega_\mu \ (b^{\dagger}_{\mu,j} b_{\mu,j}). \tag{14.26}$$

Remarks:

1. We have intentionally written the classical energy in (14.16) symmetrically in b, b^* in order to make the transition to the Hamiltonian operator unambiguous.

2. Instead of plane waves, spherical waves could also have been used as basic solutions of (14.2). After quantization, we then would have obtained photons, which are characterized not only by energy and polarization but also by their angular momentum. The transition between the two representations is mediated by the expansion of the plane wave according to spherical harmonics (cf. Sect. 7.6.3). The situation is in close analogy to the case of free, **material** particles (i.e. rest mass $\neq 0$), where we can use the momentum (plane wave) or angular momentum (spherical wave) classification depending on the problem of interest. The angular momentum representation of photons is used in radiation problems of atoms or atomic nuclei, since atomic and nuclear states are characterized by sharp angular momentum; in solid-state physics, the momentum representation is appropriate for geometric reasons.

3. In addition to the **transversal** photons introduced above (transversal, since always $\mathbf{e}_{\mu j} \cdot \mathbf{k}_\mu = 0$), there are also **longitudinal** photons, which can be used to describe the

Coulomb interaction (analogy: explanation of nuclear forces by the exchange of mesons). They correspond to a Fourier decomposition of the scalar potential $\Phi(\mathbf{r},t)$, which describes the interaction in static charge distributions. Since we are only interested in the radiation field above, we have chosen $\Phi \equiv 0$; when describing the interaction of radiation and matter, we then must treat the Coulomb energy as a contribution to the energy of the charged particles.

14.3 Interaction of the Radiation Field and Matter

The Hamiltonian of a system of identical particles—the generalization to non-identical particles requires only the indexing of mass, charge and magnetic moment—with mass *m*, charge *e* and magnetic moment μ, in the presence of the radiation field, including the field energy (non-relativistically) is (in Gauss units)

$$H = \tfrac{1}{2m}\sum_{i=1}^{N}\left(\mathbf{p}_i - \tfrac{e}{c}\ \mathbf{A}(\mathbf{r}_i)\right)^2 + \tfrac{1}{2}\sum_{i\neq j} V_{ij} - \mu\sum_{i=1}^{N}(\vec{\sigma}_i\cdot[\nabla\times\mathbf{A}(\mathbf{r}_i)]) + H_r. \quad (14.27)$$

With regards to a perturbation series we separate the Hamiltonian in

$$H = H_p + H_r + H', \quad (14.28)$$

where H_r describes the free radiation field according to (14.26), H_p is the Hamiltonian of the particles in the absence of the **A** field (but including the Coulomb interaction)

$$H_p = \tfrac{1}{2m}\sum_i p_i^2 + \tfrac{1}{2}\sum_{i\neq j} V_{ij}, \quad (14.29)$$

and H' the interaction between particles and photons. In H', $\mathbf{A}(\mathbf{r}_i)$ is an operator:

$$\mathbf{A}(\mathbf{r}_i) = \sum_{\mu,j}\hbar c\sqrt{\tfrac{2\pi}{V\hbar\omega_\mu}}\ \mathbf{e}_{\mu,j}\ \left(b_{\mu,j}\exp\left(i\mathbf{k}_\mu\cdot\mathbf{r}_i\right) + b^\dagger_{\mu,j}\exp\left(-i\mathbf{k}_\mu\cdot\mathbf{r}_i\right)\right), \quad (14.30)$$

which contains photon creation $b^\dagger_{\mu,j}$ and annihilation $b_{\mu,j}$ operators in linear form. In detail, H' consists of 3 parts:

(i) a contribution that acts on the charge of the particles,

$$-\tfrac{e}{2mc}\sum_i(\mathbf{p}_i\cdot\mathbf{A}(\mathbf{r}_i) + \mathbf{A}(\mathbf{r}_i)\cdot\mathbf{p}_i), \quad (14.31)$$

which contains the operators $b_{\mu,j}$ and $b^\dagger_{\mu,j}$ linearly, thus enabling processes in which (in lowest order) 1 photon is created or destroyed.

(ii) a part acting on the magnetic moment μ,

(14.32)

$$-\mu \sum_i (\vec{\sigma}_i \cdot [\nabla \times \mathbf{A}(\mathbf{r}_i)]),$$

which has the same structure as i) with respect to $b_{\mu,j}$ and $b^\dagger_{\mu,j}$,
(iii) a quadratic term in $b, b^\dagger$,

$$\frac{e^2}{2mc^2} \sum_i \mathbf{A}(\mathbf{r}_i) \cdot \mathbf{A}(\mathbf{r}_i), \tag{14.33}$$

which (in lowest order) enables two-photon processes.

14.4 The 0th Approximation

We will assume in the following that the eigenfunctions are known for

$$H_0 = H_p + H_r, \tag{14.34}$$

i.e.

$$H_0 |\lambda; n_{\mu j}\rangle = \left(E_\lambda + \sum_{\mu,j} n_{\mu j}\ \hbar\omega_\mu\right) |\lambda; n_{\mu j}\rangle. \tag{14.35}$$

Here, λ characterizes the (at least approximately known) eigenstates of H_p with the energy E_λ, e.g. the eigenstates of the H atom.

Based on (14.34), (14.35) as 0th order approximation we will now try to calculate the influence of H' within the framework of a perturbation calculation.

14.5 Absorption and Emission of Photons

Photons can be created (absorbed) under the influence of H'. Due to the conservation laws for the closed system (matter + radiation field), the energy (as well as momentum, angular momentum), which is absorbed (released) by the radiation field, must be released (absorbed) by the matter (e.g. atoms, molecules). When photons are absorbed the matter goes into an excited state (Fig. 14.1), conversely, the matter can change from an excited state to a lower state (e.g. the ground state) by emitting photons (Fig. 14.2).

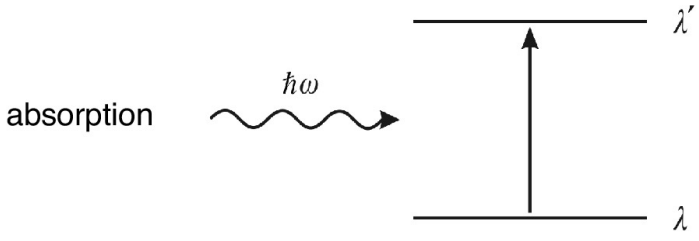

Fig. 14.1 Absorption of a photon with an excitation of the matter from state λ to state λ'

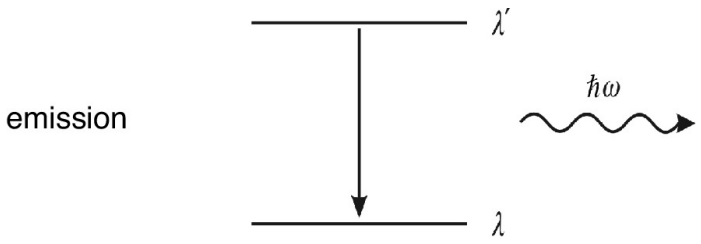

Fig. 14.2 Emission of a photon by the decay of an excited state λ' of the matter

We now have to quantitatively calculate the probability, that the non-interacting system described by H_0 changes from an initial state $|\lambda;n_{\mu j}\rangle$ to a final state $|\lambda';n'_{\mu j}\rangle$ by virtue of the interaction H'. To this aim we use the time evolution of a system in the Dirac picture (see Sect. 11.3).

At time $t = 0$ the system is in the state $|\lambda;n_{\mu j}\rangle$; the time evolution occurs in the Dirac picture according to

$$|\Psi_D(t)\rangle = U_D(t,0)|\lambda;n_{\mu j}\rangle \tag{14.36}$$

with

$$U_D(t,0) = 1 - \tfrac{i}{\hbar}\int_0^t dt' \; H'_D(t')U_D(t',0), \tag{14.37}$$

where

$$H'_D(t') = \exp\left(\tfrac{i}{\hbar}H_0t'\right) \; H' \; \exp\left(-\tfrac{i}{\hbar}H_0t'\right). \tag{14.38}$$

The operator H' in the Schrödinger picture—for the closed system under consideration—is time-independent. The amplitude, with which the final state $|\lambda';n'_{\mu j}\rangle$ is contained in $|\Psi_D(t)\rangle$, is

$$\langle\lambda';n'_{\mu j}|U_D(t,0)|\lambda;n_{\mu j}\rangle; \tag{14.39}$$

the square of its absolute value gives the probability of finding the system in $|\lambda';n'_{\mu j}\rangle$ in the final state at time *t*.

If we restrict ourselves to the most simple process—absorption or emission of 1 photon—we can use the approximation for $U_D(t,0)$

$$U_D(t,0) \approx 1 - \tfrac{i}{\hbar}\int_0^t dt' \; H'_D(t'); \tag{14.40}$$

the 1st term does not contribute to the transition probability due to the orthogonality of the states $|\lambda;n_{\mu j}\rangle$. It remains to calculate (except for the factor $-i/\hbar$)

$$\int_0^t dt' \langle \lambda'; n'_{\mu j} | H'_D(t') | \lambda; n_{\mu j} \rangle = \langle \lambda'; n'_{\mu j} | H' | \lambda; n_{\mu j} \rangle \int_0^t dt' \ \exp\left(\tfrac{i}{\hbar} t' [E' - E] \right), \tag{14.41}$$

where for H' (14.31) and (14.32) have to be inserted; furthermore, we use the abbreviation

$$E = E_\lambda + \sum_{\mu,j} n_{\mu j} \hbar \omega_\mu; \qquad E' = E_{\lambda'} + \sum_{\mu,j} n'_{\mu j} \hbar \omega_\mu. \tag{14.42}$$

The time integration in (14.41) results in

$$-i\hbar \frac{[\exp(\frac{i}{\hbar} t[E'-E]) - 1]}{E'-E} = -i \frac{\exp(2i\xi t) - 1}{2\xi} = \exp(i\xi t) \frac{\exp(i\xi t) - \exp(-i\xi t)}{2i\xi} \tag{14.43}$$

with the abbreviation

$$\xi = \tfrac{E'-E}{2\hbar}. \tag{14.44}$$

For the probability $W(t)$, that the system has passed from the initial state $|\lambda; n_{\mu j}\rangle$ to the final state $|\lambda'; n'_{\mu j}\rangle$ after time t, we obtain

$$W(t) = \tfrac{1}{\hbar^2} \left(\frac{\sin(t\xi)}{\xi} \right)^2 |\langle \lambda'; n'_{\mu j} | H' | \lambda; n_{\mu j} \rangle|^2 \tag{14.45}$$

The function $(\sin(t\xi)/\xi)^2$ has the form shown in Fig. 14.3; the main maximum at $\xi = 0$ becomes sharper with increasing t, the secondary maxima are reduced.

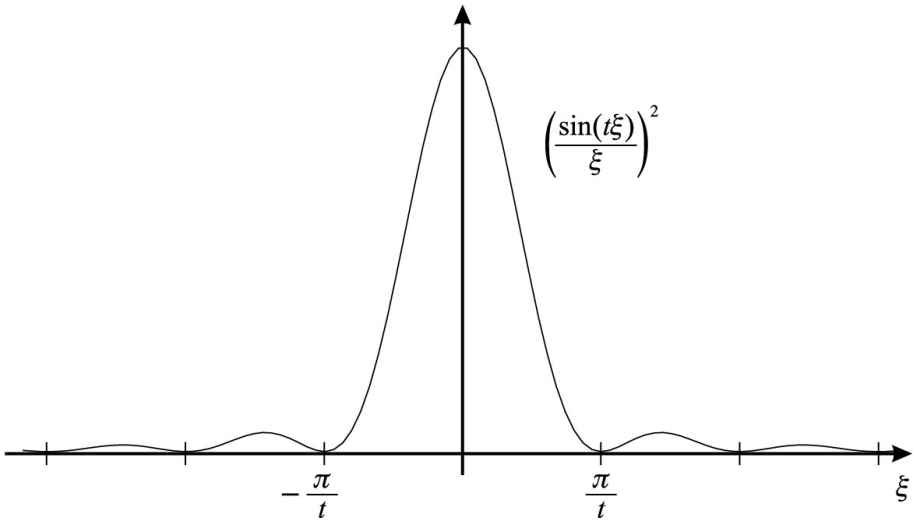

Fig. 14.3 Illustration of the function $(\sin(t\xi)/\xi)^2$ in (14.45)

Transitions are particularly likely if $\xi \approx 0$ or

$$E' \approx E. \tag{14.46}$$

The factor $(\sin\,(t\xi)/\xi)^2$ in (14.45) thus includes the conservation of energy within the framework of the energy-time uncertainty. For $t \to \infty$ the conservation of energy is strictly fulfilled, i.e. $E' = E$.

The matrix element $\langle \lambda'; n'_{\mu j}|H'|\lambda; n_{\mu j}\rangle$ from (14.45) splits into parts that only concern the matter and those that only concern the radiation. When restricting to 1 photon—processes, only the terms (14.31) and (14.32) contribute. The **electrical** transitions are determined by

$$\langle \lambda'| \sum_l \mathbf{p}_l \exp\,(\pm i\mathbf{k}\cdot\mathbf{r}_l)|\lambda\rangle, \tag{14.47}$$

and the **magnetic** transitions by

$$\langle \lambda'| \sum_i (\vec{\sigma}_i \times \mathbf{k}) \exp\,(\pm i\mathbf{k}\cdot\mathbf{r}_i)|\lambda\rangle. \tag{14.48}$$

An expansion of the plane wave according to spherical harmonics yields dipole radiation, quadrupole radiation etc. To (14.47) and (14.48) the parts concerning the radiation field have to be added

$$\langle n'_{\mu j}|b_{\mu j}|n_{\mu j}\rangle \tag{14.49}$$

or

$$\langle n'_{\mu j}|b^\dagger_{\mu j}|n_{\mu j}\rangle. \tag{14.50}$$

In the case of absorption of radiation we have

$$|\langle n_{\mu j} - 1|b_{\mu j}|n_{\mu j}\rangle|^2 = n_{\mu j}. \tag{14.51}$$

The absorption probability is thus proportional to the number of photons initially present or to the intensity of the field. The emission probability, on the other hand, is

$$\sim |\langle n_{\mu j} + 1|b^\dagger_{\mu j}|n_{\mu j}\rangle|^2 = n_{\mu j} + 1. \tag{14.52}$$

A remarkable difference to photon absorption is that photon emission also takes place if $n_{\mu j} = 0$ in the initial state, i.e. there is a **spontaneous emission** (in contrast to the **induced emission** that increases with $n_{\mu j}$). Due to this spontaneous emission all excited states of atomic systems are unstable; they have a **natural line width**.

The fact that atomic systems spontaneously pass from excited states to the ground state by emitting photons due to the electromagnetic interaction cannot be understood within the

framework of classical physics. Classically, the ground state of the free radiation field is characterized by the fact that

$$E_{kl.} \equiv 0. \tag{14.53}$$

However, if there is no electromagnetic field, then there can be no electromagnetic interaction with matter. The situation is different after quantization of the radiation field: the ground state of the free radiation field is the photon vacuum $|0\rangle$; in this state, the expectation value of the field operators **A**, $\mathbf{E}$ and $\mathbf{B}$ are zero,

$$\langle 0|\mathbf{A}|0\rangle = \langle 0|\mathbf{E}|0\rangle = \langle 0|\mathbf{B}|0\rangle = 0, \tag{14.54}$$

but there are non-zero mean-square fluctuations (**vacuum fluctuations**), e.g.

$$(\Delta\mathbf{E})^2 = (\langle 0|\mathbf{E}^2|0\rangle - \langle 0|\mathbf{E}|0\rangle^2) = \langle 0|\mathbf{E}^2|0\rangle \neq 0. \tag{14.55}$$

The formal reason for the non-vanishing expectation values of $\mathbf{E}^2$ and $\mathbf{B}^2$ is that the operators for $\mathbf{E}$ and $\mathbf{B}$ do not commute with the Hamiltonian of the radiation field and therefore cannot be measured **sharp** at the same time!

Remark: The vacuum fluctuations of gauge fields (gluons) play a decisive role for the stability of hadrons and the 'confinement' of quarks and gluons in hadrons (nucleons and mesons) (see quantum chromodynamics).

In summary, we have quantized the radiation field and evaluated the interaction between matter and the radiation field (photons) in leading order, which corresponds to the absorption (emission) of photons by matter.

Part V
Systematic Approximation Methods

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15. Formal Scattering Theory

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In Chap. 8 we have presented the scattering theory of a particle interacting with another independent particle by some potential interaction $V(\mathbf{r})$ and defined the relevant quantities such as the scattering amplitude and the differential cross section. In this chapter we will provide the formal scattering theory for many-particle systems, which will end up in the definition of the *S*-matrix, the general *T*-matrix and Born-series.

15.1 Time-Dependent Formulation of Scattering

To describe a scattering process, we write the Hamiltonian operator of the entire system—after separating the center of mass motion (see Sect. 11.2)—as

$$H = T + V + H_{int} =: H_0 + V; \tag{15.1}$$

where *T* is the kinetic energy of the relative motion (with the reduced mass) of the scattering partners, *V* is their interaction and H_{int} is the Hamiltonian operator of the remaining internal degrees of freedom.

Long before the collision, the system is described in terms of its relative motion by a force-free wave packet:

$$|\Psi_i\rangle =: \lim_{t\to-\infty} |\Psi(t)\rangle = \lim_{t\to-\infty} \sum_a \int da\ c(a)\ \exp\left(-\tfrac{i}{\hbar}E_a t\right)\ |\Phi_a\rangle, \tag{15.2}$$

where

$$H_0|\Phi_a\rangle = E_a|\Phi_a\rangle, \tag{15.3}$$

and the discrete and/or continuous index *a* stands for a complete set of quantum numbers. E_a consists of the internal energy of the collision partners and the kinetic energy of the relative motion; $c(a)$ describes the shape of the wave packet before the collision. The wave packet (15.2) then develops according to the time evolution operator $U(t, -\infty)$ belonging to the full Hamiltonian operator *H* and long after the collision it takes the shape of a force-free wave packet again:

$$|\Psi_f\rangle =: \lim_{t\to\infty} |\Psi(t)\rangle = \lim_{t\to\infty} \sum_a \int da\ \tilde{c}(a)\ \exp\left(-\tfrac{i}{\hbar}E_a t\right)\ |\Phi_a\rangle. \tag{15.4}$$

If we compare with Chap. 8, then $|\Psi_i\rangle$ corresponds to the incident plane wave and $|\Psi_f\rangle$ to the combination of a plane wave and a direction-modulated outgoing spherical wave. The indices *i* and

f stand for **initial** and **final**.

The task of the scattering theory is to calculate the unknown function $\tilde{c}(a)$, which characterizes the state of the system after the collision, from the given initial distribution $c(a)$. It is therefore suitable to introduce the

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15.2 S-Matrix

as the fundamental quantity of scattering theory, which is defined by

$$\tilde{c}(a) = \sum_{a'} \int da' \;\; S(a,a')c(a') \quad \text{with} \quad S(a,a') = \langle \Phi_a | S | \Phi_{a'} \rangle. \tag{15.5}$$

It must be unitary in order to ensure the conservation of the norm:

$$\sum_a \int da \;\; |\tilde{c}(a)|^2 \;\; = \sum_a \int da \;\; |c(a)|^2. \tag{15.6}$$

For a classification of the concept as well as the practical calculation of the *S*-matrix it is useful to consider alternative definitions to (15.5).

If we translate $|\Psi_i\rangle$ and $|\Psi_f\rangle$ into the Dirac picture,

$$|\Psi_i^D\rangle = \lim_{t\to-\infty} \exp\left(\frac{i}{\hbar} H_0 t\right) |\Psi(t)\rangle; |\Psi_f^D\rangle = \lim_{t\to\infty} \exp\left(\frac{i}{\hbar} H_0 t\right) |\Psi(t)\rangle, \tag{15.7}$$

and introducing an operator *S* by

$$|\Psi_f^D\rangle = S |\Psi_i^D\rangle, \tag{15.8}$$

then the matrix elements of *S* in the basis $|\Phi_a\rangle$ turn out to be the *S*-matrix elements introduced in (15.5). To this aim we form

$$\langle \Phi_a | \Psi_f^D \rangle = \tilde{c}(a) = \langle \Phi_a | S | \Psi_i^D \rangle = \sum_{a'} \int da' \;\; \langle \Phi_a | S | \Phi_{a'} \rangle \langle \Phi_{a'} | \Psi_i^D \rangle \tag{15.9}$$

$$= \sum_{a'} \int da' \;\; \langle \Phi_a | S | \Phi_{a'} \rangle c(a').$$

The operator *S*—introduced in (15.8)—is directly related to the time evolution operator of the Dirac picture:

$$|\Psi_f^D\rangle = U_D(\infty, -\infty) |\Psi_i^D\rangle, \tag{15.10}$$

i.e.

$$S = U_D(\infty, -\infty). \tag{15.11}$$

Mathematical details of the limit formation in $U_D(t,t_0)$ cannot be discussed here (see P. Roman, Advanced Quantum Theory, Sect. 4.3). From (15.11) we obtain the unitarity of *S*,

$$SS^\dagger = 1_{\mathscr{H}} = S^\dagger S. \tag{15.12}$$

Alternatively, *S* can be defined using the eigenstates of *H*. With (15.11), (15.9) and (15.5) we have

$$S(a,a') = \lim_{t\to\infty,t'\to-\infty} \langle\Phi_a|U_D(t,t')|\Phi_{a'}\rangle \tag{15.13}$$

$$= \lim_{t\to\infty,t'\to-\infty} \langle\Phi_a|\exp\left(\frac{i}{\hbar}E_a t\right)\ U(t,t')\ \ \exp\left(-\frac{i}{\hbar}E_{a'}t'\right)|\Phi_{a'}\rangle,$$

with

$$U(t,t') = \exp\left(-\tfrac{i}{\hbar}H(t-t')\right), \tag{15.14}$$

since *H* as the Hamiltonian of a closed system does not explicitly depend on *t*. This gives

$$S(a,a') = \langle\Psi_a^{(-)}|\Psi_{a'}^{(+)}\rangle, \tag{15.15}$$

if we introduce (see below for details of the formation of the limit)

$$|\Psi_a^{(\pm)}\rangle = \lim_{t\to\mp\infty}\exp\left(-\tfrac{i}{\hbar}(E_a - H)t\right)|\Phi_a\rangle. \tag{15.16}$$

To deal with the limits in (15.16) we note that for a function $F(t)$, whose limit exists for $t\to-\infty$, this can be written as an **abelian limit**

$$\lim_{t\to-\infty}\ F(t) = \lim_{\epsilon\to+0}\ \epsilon\int_{-\infty}^{0} dt'\ \ \exp\left(\epsilon t'\right)\ F(t')$$

$$= \lim_{\epsilon\to+0}\left(\tfrac{\epsilon}{\epsilon}\exp\left(\epsilon t\right)F(t)|_{-\infty}^{0} - \tfrac{\epsilon}{\epsilon}\int_{-\infty}^{0} dt'\ \ \exp\left(\epsilon t'\right)F'(t')\right) \equiv F(0) - \int_{-\infty}^{0} dt'\ F'(t'), \tag{15.17}$$

as can be seen immediately by partial integration. This gives

$$|\Psi_a^{(+)}\rangle = \lim_{\epsilon\to+0}\ \tfrac{\epsilon}{\hbar}\int_{-\infty}^{0} dt\ \ \exp\left[-\tfrac{i}{\hbar}(E_a - H + i\epsilon)t\right]\ \ |\Phi_a\rangle = \lim_{\epsilon\to+0}\ \tfrac{i\epsilon}{E_a - H + i\epsilon}\ \ |\Phi_a\rangle \tag{15.18}$$

after executing the *t*-integration. Since the inverse operator for $(H - E_a)$ does not exist for values E_a of the continuous spectrum (scattering states!) of *H* (Chap. 8), the transition $\epsilon\to+0$ can only be carried out after execution of the operators $i\epsilon/(E_a - H + i\epsilon)$ acting on $|\Phi_a\rangle$.

We now show that $|\Psi_a^{(+)}\rangle$ is an eigenvector of *H* with eigenvalue E_a:

$$(E_a - H)|\Psi_a^{(+)}\rangle = \lim_{\epsilon\to+0} \; (i\epsilon \tfrac{E_a - H}{E_a - H + i\epsilon}|\Phi_a\rangle) = \lim_{\epsilon\to+0} \; (i\epsilon|\Phi_a\rangle) = 0, \tag{15.19}$$

thus

$$H|\Psi_a^{(+)}\rangle = E_a|\Psi_a^{(+)}\rangle. \tag{15.20}$$

In (15.20) we have assumed that H and H_0 have the same continuous spectrum and thus only differ in the discrete spectrum. This assumption is not always fulfilled:

(i) In the case of **non-local interactions** V, bound states of H may be embedded in the continuous spectrum of H, which H_0 does not possess.

(ii) According to the above assumption, the energy of the system must not change when the interaction V is switched on; this absence of **level shifts** in the continuum is not present in quantum electrodynamics (QED).

We therefore assume in the following that V is such that the limit (15.16) exists, such that (15.3) and (15.20) are simultaneously satisfied for the scattering process.

15.3 The Lippmann-Schwinger Equation

We want to show next that $|\Psi_a^{(\pm)}\rangle$ are solutions of the scattering problem, that contain incoming and outgoing spherical waves in the spatial representation. For this we use the operator identity, which is generally important in quantum theory ($H = H_0 + V$)

$$\tfrac{1}{E_a - H + i\epsilon} = \tfrac{1}{E_a - H_0 + i\epsilon} + \tfrac{1}{E_a - H_0 + i\epsilon} V \tfrac{1}{E_a - H + i\epsilon}. \tag{15.21}$$

Proof
In the identity

$$[A + B]^{-1} = A^{-1}(1 - B[A + B]^{-1}) \tag{15.22}$$

insert $A = E_a - H_0 + i\epsilon$ and $B = -V$. Equation (15.22) is easy to show by multiplying by $(A + B)$, e.g.:

$$[A + B]^{-1}(A + B) = 1 = A^{-1}(A + B) - A^{-1}B[A + B]^{-1}(A + B) = 1 + A^{-1}B - A^{-1}B. \tag{15.23}$$

If we apply (15.21) to $|\Phi_a\rangle$, we obtain

$$\tfrac{i\epsilon}{E_a - H + i\epsilon}|\Phi_a\rangle = \tfrac{i\epsilon}{E_a - H_0 + i\epsilon}|\Phi_a\rangle + \tfrac{1}{E_a - H_0 + i\epsilon} V \; \tfrac{i\epsilon}{E_a - H + i\epsilon}|\Phi_a\rangle. \tag{15.24}$$

With (15.18) we finally get after formation of the limit $\epsilon \to 0$

$$|\Psi_a^{(+)}\rangle = |\Phi_a\rangle + G_a^{(+)} V |\Psi_a^{(+)}\rangle \tag{15.25}$$

with the **Green's operator**

$$G_a^{(+)} := \lim_{\epsilon \to +0} \frac{1}{E_a - H_0 + i\epsilon}. \tag{15.26}$$

Using the same procedure, we find

$$|\Psi_a^{(-)}\rangle = |\Phi_a\rangle + G_a^{(-)} V |\Psi_a^{(-)}\rangle \tag{15.27}$$

with

$$G_a^{(-)} := \lim_{\epsilon \to +0} \frac{1}{E_a - H_0 - i\epsilon}. \tag{15.28}$$

The spatial representation of (15.25) and (15.26) is the **Lippmann-Schwinger equation** and the Green's function from Chap. 8, if we consider the scattering of a particle at a potential V, where $H_0 \equiv T$.

We form

$$\langle \mathbf{r}|G^{(+)}|\mathbf{r}'\rangle = \int\int d^3q \; d^3q' \; \langle \mathbf{r}|\mathbf{q}\rangle \langle \mathbf{q}|G^{(+)}|\mathbf{q}'\rangle \langle \mathbf{q}'|\mathbf{r}'\rangle \tag{15.29}$$

$$= \frac{1}{(2\pi)^3} \int d^3q \;\; \exp\left(i\mathbf{q}\cdot\mathbf{r}\right) \frac{1}{E - \frac{\hbar^2\mathbf{q}^2}{2\mu} + i\epsilon} \exp\left(-i\mathbf{q}\cdot\mathbf{r}'\right)$$

$$= \frac{1}{(2\pi)^3} \frac{2\mu}{\hbar^2} \int d^3q \; \frac{\exp\left(i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')\right)}{\mathbf{k}^2 - \mathbf{q}^2 + i\epsilon} = \frac{2\mu}{\hbar^2} \; G^{(+)}(\mathbf{r},\mathbf{r}');$$

where

$$\langle \mathbf{r}|\mathbf{q}\rangle = \langle \mathbf{q}|\mathbf{r}\rangle^* = (2\pi)^{-3/2} \exp\left(i\mathbf{q}\cdot\mathbf{r}\right) \tag{15.30}$$

and

$$\langle \mathbf{q}|G^{(+)}|\mathbf{q}'\rangle = \frac{\delta^3(\mathbf{q}-\mathbf{q}')}{E - \frac{\hbar^2\mathbf{q}^2}{2\mu} + i\epsilon}. \tag{15.31}$$

Accordingly, (15.25) turns into the Lippmann-Schwinger equation.

15.4 The *T*-Matrix

We go back to

$$S(a,a') = \langle \Phi_a|S|\Phi_{a'}\rangle. \tag{15.32}$$

Since we are only interested in real scattering processes

$$\Phi_{a'} \to \Phi_a a \neq a', \tag{15.33}$$

it is useful to extract the unit-operator from *S*, which describes the trivial transition $\Phi_a \to \Phi_a$:

$$S(a,a') = \delta(a-a') - 2\pi i \ \delta(E_a - E_{a'}) T(a,a'). \tag{15.34}$$

For discrete quantum numbers a, a', the δ-function $\delta(a-a')$ has to be replaced by $\delta_{aa'}$; $\delta(E_a - E_{a'})$ takes into account energy conservation, while the factor $-2\pi i$ is split off by convention. The *T* matrix introduced in (15.34) is then responsible for real transitions.

By (15.34) the *T* matrix is defined only for transitions $\Phi_a \to \Phi_{a'}$ at $E_a = E_{a'}$, i.e. for elastic processes (**on the energy shell** *T* matrix). However, the concept of the *T* matrix can be generalized to any processes. We refer back to (15.18):

$$|\Psi_a^{(+)}\rangle = \lim_{\epsilon\to+0} \frac{i\epsilon}{E_a - H + i\epsilon}|\Phi_a\rangle = \lim_{\epsilon\to+0} \frac{i\epsilon + E_a - H_0}{E_a - H + i\epsilon}|\Phi_a\rangle \tag{15.35}$$

$$= \lim_{\epsilon\to+0} \frac{i\epsilon + E_a - H + V}{E_a - H + i\epsilon}|\Phi_a\rangle = \lim_{\epsilon\to+0} [1 + \frac{1}{E_a - H + i\epsilon} V]|\Phi_a\rangle$$

and form

$$|\Psi_a^{(-)}\rangle = \lim_{\epsilon\to+0} \frac{i\epsilon}{E_a - H - i\epsilon}|\Phi_a\rangle = \lim_{\epsilon\to+0} [1 + \frac{1}{E_a - H - i\epsilon} V]|\Phi_a\rangle$$

$$= |\Psi_a^{(+)}\rangle + \lim_{\epsilon\to+0} [\frac{1}{E_a - H - i\epsilon} - \frac{1}{E_a - H + i\epsilon}] V|\Phi_a\rangle. \tag{15.36}$$

With (15.15) we then get (the $\lim_{\epsilon\to+0}$ is suppressed in the following)

$$S(a,a') = \langle \Psi_a^{(-)} | \Psi_{a'}^{(+)} \rangle = \langle \Psi_{a'}^{(+)} | \Psi_a^{(-)} \rangle^* \tag{15.37}$$

$$= \delta_(a-a') + \langle \Psi_{a'}^{(+)} | [\frac{1}{E_a - H - i\epsilon} - \frac{1}{E_a - H + i\epsilon}] V|\Phi_a\rangle^*$$

$$= \delta_(a-a') + \langle \Phi_a | V [\frac{1}{E_a - H + i\epsilon} - \frac{1}{E_a - H - i\epsilon}] |\Psi_{a'}^{(+)}\rangle.$$

We note that $|\Psi_{a'}^{(+)}\rangle$ is an eigenvector of *H* for the energy $E_{a'}$, i.e.

$$[\frac{1}{E_a - H + i\epsilon} - \frac{1}{E_a - H - i\epsilon}] |\Psi_{a'}^{(+)}\rangle = -\frac{2i\epsilon}{(E_a - E_{a'})^2 + \epsilon^2} |\Psi_{a'}^{(+)}\rangle. \tag{15.38}$$

If we use the representation of the δ-function

$$\delta(x) =: \frac{1}{\pi} \lim_{\epsilon\to+0} \frac{\epsilon}{x^2 + \epsilon^2}, \tag{15.39}$$

we get

$$S(a,a') = \delta(a-a') - 2\pi i \ \delta(E_a - E_{a'}) \langle \Phi_a | V | \Psi_{a'}^{(+)} \rangle, \tag{15.40}$$

and with (15.34)

$$T(a,a') = \langle \Phi_a | V | \Psi_{a'}^{(+)} \rangle. \tag{15.41}$$

We now introduce an **operator** T in general by

$$T|\Phi_{a'}\rangle = V|\Psi_{a'}^{(+)}\rangle, \tag{15.42}$$

from which we obtain with (15.25)

$$T = V + V \ G^{(+)} T. \tag{15.43}$$

Since $G^{(+)} = G^{(+)}(E)$, we also write more precisely $T = T(E)$; the operator T is thus explicitly energy-dependent. Let us now form arbitrary matrix elements of T in the basis Φ_a,

$$\langle \Phi_a | T | \Phi_{a'} \rangle, \tag{15.44}$$

where in general $E_a \neq E_{a'}$, we have found the desired generalization of (15.34).
We distinguish 3 types of matrix elements of T :
1. **on energy shell**:

$$\langle \Phi_a | T | \Phi_{a'} \rangle \ \text{ for } \ E_a = E_{a'} = E.$$

They describe elastic scattering.
2. **off energy shell**:

$$\langle \Phi_a | T | \Phi_{a'} \rangle \ \text{ for } \ E_a \neq E \neq E_{a'}.$$

They occur e.g. in inelastic nucleon-nucleus scattering: $N_1 + (A + N_2) \to N_1 + N_2 + A^*$.
3. **half energy shell**:

$$\langle \Phi_a | T | \Phi_{a'} \rangle \ \text{ for } \ E_a \neq E_{a'}; E = E_a \quad \text{or} \quad E = E_{a'}.$$

Example: Proton-proton bremsstrahlung, since due to the photon in the final state $k_a^2 \neq k_{a'}^2$.
The 'on energy shell' elements are directly related to the scattering amplitude $f(\Omega)$:

$$f(\Omega) = -\tfrac{\mu}{2\pi\hbar^2} \langle \Phi_a | V | \Psi_{a'}^{(+)} \rangle = -\tfrac{\mu}{2\pi\hbar^2} T(a,a'). \tag{15.45}$$

To calculate T and thus $f(\Omega)$, it is obvious to solve (15.43) by iteration. This leads to the **Born series**, which we introduced in Sect. 8.2.3:

$$T = V + VG^{(+)}V + VG^{(+)}VG^{(+)}V + \cdots = V\frac{1}{1-G^{(+)}V}. \tag{15.46}$$

The convergence properties of (15.46) can be improved within the framework of the

15.5 Generalized Born Series (DWBA)

To this aim we separate H into

$$H = H_0' + V', \tag{15.47}$$

where now

$$H_0' = T + H_{int} + (V - V') \tag{15.48}$$

in addition to the kinetic energy of the relative motion of the collision partners also contains a part of their interaction (e.g. the Coulomb interaction). If we succeed in finding the solutions of

$$H_0'|\Phi_a'\rangle = E_a'|\Phi_a'\rangle, \tag{15.49}$$

the procedure described above can be carried out with the interaction V' instead of V and

$$G'^{(+)} = \frac{1}{E - H_0' + i\epsilon} \tag{15.50}$$

instead of $G^{(+)}$. One then obtains a better convergent series

$$T = V' + V'G'^{(+)}V' + V'G'^{(+)}V'G'^{(+)}V' + \cdots \tag{15.51}$$

An example is the scattering of protons on nuclei, where one can include the Coulomb interaction in H_0', since the Coulomb problem can be solved exactly; $V - V'$ then is the interaction solely caused by the nuclear forces. While the Coulomb waves exhibit non-vanishing scattering phases for all collision parameters (angular momentum) (Chap. 8) and thus the series (15.46) converges poorly, (15.51) is a much better convergent series due to the short range nature of the nuclear forces $(V - V')$. Since in this case the plane waves of the ordinary Born series change into Coulomb waves, the method is also called **Distorted-Wave-Born-Approximation** (**DWBA**).

15.6 S-Matrix in Angular Momentum Representation

According to the partial wave expansion (Chap. 8) we expand for $V = V(r)$

$$\Psi_{\mathbf{k}}^{(+)}(\mathbf{r}) = \sum_{l=0} i^l (2l+1) \;\; \exp\left(i\delta_l(k)\right) \;\; P_l(\cos\vartheta) \;\; \frac{\chi_{l,k}(r)}{r}. \tag{15.52}$$

While $\Psi_{\mathbf{k}}^{(+)}(\mathbf{r})$ contains an outgoing spherical wave, $\Psi_{\mathbf{k}}^{(-)}(\mathbf{r})$ contains an incoming spherical wave. Therefore,

$$\Psi_{\mathbf{k}}^{(-)}(\mathbf{r}) = \sum_{l=0} i^l (2l+1) \;\; \exp\left(-i\delta_l(k)\right) \;\; P_l(\cos\vartheta) \;\; \frac{\chi_{l,k}(r)}{r}. \tag{15.53}$$

If we denote the individual components in (15.52), (15.53) with fixed l by $\Psi_{k,l}^{(\pm)}$, then

$$S(l,k;l'k') = \langle \Psi_{l,k}^{(-)} | \Psi_{l'k'}^{(+)} \rangle = \exp\left(2i\delta_l(k)\right) \;\; \delta_{ll'} \;\; \delta(k-k'), \tag{15.54}$$

if one appropriately normalizes $\chi_{l,k}$. The S-matrix is therefore diagonal in l and k and the following holds:

$$S(l,k;l,k) = S_l(k) = \exp\left(2i\delta_l(k)\right). \tag{15.55}$$

The S matrix is thus completely described by momentum-dependent phases $\delta_l(k)$ for each partial wave l.

15.7 Energy of the Ground State

We go back to Sect. 11.3 and write the exact ground state at time $t = 0$ as

$$|\Psi_0\rangle = U_D(0,-\infty)|\Phi_0\rangle, \tag{15.56}$$

where we have separated the Hamiltonian operator in the form $H = H_0 + H'$ and the problem $(H_0 - \epsilon_n)|\Phi_n\rangle$ is considered to be known. With

$$H|\Psi_0\rangle = E_0|\Psi_0\rangle \tag{15.57}$$

we get by forming the scalar product with $\langle\Phi_0|$ and subtracting $\langle\Phi_0|H_0|\Psi_0\rangle$

$$\Delta E_0 = E_0 - \epsilon_0 = \frac{\langle\Phi_0|H'|\Psi_0\rangle}{\langle\Phi_0|\Psi_0\rangle} = \frac{\langle\Phi_0|H'U_D(0,-\infty)|\Phi_0\rangle}{\langle\Phi_0|U_D(0,-\infty)|\Phi_0\rangle}. \tag{15.58}$$

When forming (15.58) it must be ensured, however, that the states $|\Phi_0\rangle$ and $|\Psi_0\rangle$ are not orthogonal to each other. To this aim we consider the explicitly time-dependent Hamiltonian ($\eta > 0$)

(15.59)

$$H_\eta(|t|) = H_0 + \exp\,(-\eta|t|)\;\; H',$$

with

$$\lim_{|t|\to\infty} H_\eta = H_0, \lim_{\eta\to 0} H_\eta = H = H_\eta(t=0). \tag{15.60}$$

With the Ansatz (15.59) the interaction H' is switched on and off adiabatically, such that at time *t*=0 the full Hamiltonian is effective. Now in the case of (15.59) the time evolution operator U_D depends on η via $H'(t) = \exp\,(-\eta|t|)\;\; H'$ and only those quantities are meaningful for which the limit $\eta \to 0$ exists. The **theorem of Gell-Mann and Low** states: If

$$\lim_{\eta\to 0} \quad \frac{U_D(0,-\infty)|\Phi_0\rangle}{\langle\Phi_0|U_D(0,-\infty)|\Phi_0\rangle} = \frac{|\Psi_0\rangle}{\langle\Phi_0|\Psi_0\rangle} \tag{15.61}$$

exists in every order of perturbation theory, then $|\Psi_0\rangle / \langle\Phi_0|\Psi_0\rangle$ is an eigenstate of *H* and

$$\Delta E_0 = \lim_{\eta\to 0} \frac{\langle\Phi_0|H' U_D(0,-\infty)|\Phi_0\rangle}{\langle\Phi_0|U_D(0,-\infty)|\Phi_0\rangle}. \tag{15.62}$$

It should be noted that in (15.61) numerator and denominator do not necessarily exist separately!

We suppress the (lengthy) proof of the theorem and give an important transformation for ΔE_0 for applications. With

$$i\hbar \frac{\partial}{\partial t} U_D(t,t_0) = H'_D(t)\;\; U_D(t,t_0) \tag{15.63}$$

or

$$i\hbar \frac{\partial}{\partial t} \langle\Phi_0|U_D(t,t_0)|\Phi_0\rangle = \langle\Phi_0|H'_D(t)\;\; U_D(t,t_0)|\Phi_0\rangle \tag{15.64}$$

we obtain ($t_0 = -\infty$)

$$i\hbar \frac{\partial}{\partial t}\; \ln\,(\langle\Phi_0|U_D(t,-\infty)|\Phi_0\rangle) = \frac{\langle\Phi_0|H'_D(t)\;\; U_D(t,-\infty)|\Phi_0\rangle}{\langle\Phi_0|U_D(t,-\infty)|\Phi_0\rangle}. \tag{15.65}$$

This gives (for $\eta \to 0$)

$$i\hbar \lim_{\eta\to 0} \left(\frac{\partial}{\partial t}\; \ln\,(\langle\Phi_0|U_D(t,-\infty)|\Phi_0\rangle)\right)_{t=0} = \lim_{\eta\to 0} \quad \frac{\langle\Phi_0|H'_D(t)\;\; U_D(t,-\infty)|\Phi_0\rangle}{\langle\Phi_0|U_D(t,-\infty)|\Phi_0\rangle} = \Delta E_0. \tag{15.66}$$

We write (in the sense of a perturbation series)

$$\Delta E_0 = \Delta E_0^{(1)} + \Delta E_0^{(2)} + \cdots \tag{15.67}$$

and use

(15.68)

$$\ln\,(1+x) = x - \tfrac{x^2}{2} \pm \cdots$$

In **1. order approximation**:
only

$$x = \langle\Phi_0|U_D(t,-\infty) - 1|\Phi_0\rangle \approx \langle\Phi_0|-\frac{i}{\hbar}\int_{-\infty}^{t} dt_1\ H'_D(t_1)|\Phi_0\rangle$$

appears and we obtain:

$$\Delta E_0^{(1)} = i\hbar\,\lim_{\eta\to 0}\left(\tfrac{\partial}{\partial t}(\langle\Phi_0|-\tfrac{i}{\hbar}\int_{-\infty}^{t} dt_1\ H'_D(t_1)|\Phi_0\rangle)\right)_{t=0} = \tag{15.69}$$

$$\lim_{\eta\to 0}\left(\langle\Phi_0|\frac{\partial}{\partial t}\int_{-\infty}^{t} dt_1\ H'_D(t_1)|\Phi_0\rangle\right)_{t=0} =$$

$$\lim_{\eta\to 0}\left(\langle\Phi_0|\ H'_D(t)|\Phi_0\rangle\right)_{t=0} = \langle\Phi_0|H'|\Phi_0\rangle.$$

2nd order approximation:
Then $x = \langle\Phi_0|U_D(t,-\infty) - 1|\Phi_0\rangle$ in (15.68) for a series with respect to H' all contributions of 2nd order in H' must be considered. Contributions of 2nd order we obtain both from $x = \langle\Phi_0|U_D(t,-\infty) - 1|\Phi_0\rangle$ with $U_D(t,-\infty)$ in 2nd order as well as from the 2nd term in the expansion (15.68) $-x^2/2$, where *x* with $U_D(t,-\infty) - 1$ has to be considered in 1st order in H'. We thus form:
(i) $U_D(t,-\infty) - 1$ in **2nd order in** H':

$$i\hbar\tfrac{\partial}{\partial t}\left(\langle\Phi_0|(\tfrac{-i}{\hbar})^2\int_{-\infty}^{t} dt_2\ H'_D(t_2)\int_{-\infty}^{t_2} dt_1\ H'_D(t_1)|\Phi_0\rangle\right)_{t=0} = \tag{15.70}$$

$$-\frac{i}{\hbar}\left(\langle\Phi_0|H'_D(t)\int_{-\infty}^{t} dt_1\ H'_D(t_1)|\Phi_0\rangle)\right)_{t=0} =$$

$$-\frac{i}{\hbar}\langle\Phi_0|H'\int_{-\infty}^{0} dt_1\ \ \exp\,(\frac{i}{\hbar}H_0t_1)H'\exp\,(-\frac{i}{\hbar}H_0t_1)\exp\,(-\eta|t_1|)|\Phi_0\rangle =$$

$$-\frac{i}{\hbar}\sum_{n=0}^{\infty}\langle\Phi_0|H'|\Phi_n\rangle\langle\Phi_n|\int_{-\infty}^{0} dt_1\ \ \exp\,(\frac{i}{\hbar}H_0t_1)H'\exp\,(-\frac{i}{\hbar}H_0t_1)\exp\,(-\eta|t_1|)|\Phi_0\rangle =$$

$$-\frac{i}{\hbar}\sum_{n=0}^{\infty}|\langle\Phi_n|H'|\Phi_0\rangle|^2\int_{-\infty}^{0} dt_1\ \ \exp\,(-\frac{i}{\hbar}(\epsilon_0-\epsilon_n)t_1+\eta t_1) = \sum_{n=0}^{\infty}\frac{|\langle\Phi_n|H'|\Phi_0\rangle|^2}{\epsilon_0-\epsilon_n+i\eta}.$$

(ii) $(U_D(t,-\infty) - 1) \equiv x$ in 1st order in H':
With

$$\tfrac{1}{2}\tfrac{\partial}{\partial t}x^2 = x\tfrac{\partial x}{\partial t} \tag{15.71}$$

the 2nd contribution to $\Delta E_0^{(2)}$ reads:

$$-i\Big(\langle\Phi_0|-i\int_{-\infty}^{t}dt_1\ H'_D(t_1)|\Phi_0\rangle\langle\Phi_0|-i\ H'_D(t)|\Phi_0\rangle)\Big)_{t=0}= \tag{15.72}$$

$$i|\langle\Phi_0|H'|\Phi_0\rangle|^2\ \int_{-\infty}^{0}dt_1\ \ \exp\left(\eta t_1\right)=\frac{i}{\eta}\ |\langle\Phi_0|H'|\Phi_0\rangle|^2.$$

After adding contributions (i) and (ii) we get:

$$\Delta E_0^{(2)}=\lim_{\eta\to 0}\sum_{n=0}^{\infty}\ \left(\frac{|\langle\Phi_n|H'|\Phi_0\rangle|^2}{\epsilon_0-\epsilon_n+i\eta}+\frac{i}{\eta}\ |\langle\Phi_0|H'|\Phi_0\rangle|^2\right)=\sum_{n\neq 0}\ \frac{|\langle\Phi_n|H'|\Phi_0\rangle|^2}{\epsilon_0-\epsilon_n}. \tag{15.73}$$

Since $1/(i\eta)+i/\eta=0$ the limit $\eta\to 0$ exists for (15.73), while the individual contributions (i) and (ii) diverge.

15.8 Time-Independent Perturbation Theory

For the energy shift of the ground state due to the (time-independent) perturbation H' we found (15.62):

$$\Delta E_0=\langle\Phi_0|H'|\Psi_0\rangle, \tag{15.74}$$

if we normalize $|\Psi_0\rangle$ such that $\langle\Phi_0|\Psi_0\rangle=1$. Formula (15.74) only becomes meaningful, if we succeed to calculate $|\Psi_0\rangle$ at least in different ways. To this aim we introduce the projector

$$P|\Psi_0\rangle=|\Phi_0\rangle\langle\Phi_0|\Psi_0\rangle=|\Phi_0\rangle \tag{15.75}$$

and write (with the free constant $\tilde{E}$) the Schrödinger equation in the form:

$$(\tilde{E}-H_0)|\Psi_0\rangle=(\tilde{E}+H'-E_0)|\Psi_0\rangle. \tag{15.76}$$

The formal solution of (15.76) is

$$|\Psi_0\rangle=(\tilde{E}-H_0)^{-1}\ (\tilde{E}-E_0+H')|\Psi_0\rangle \tag{15.77}$$

and after multiplication with

$$Q=1-P \tag{15.78}$$

we get the equation

$$|\Psi_0\rangle=|\Phi_0\rangle+\frac{Q}{(\tilde{E}-H_0)}\ (\tilde{E}-E_0+H')|\Psi_0\rangle, \tag{15.79}$$

which is suitable for a solution by iteration:

$$|\Psi_0\rangle = |\Phi_0\rangle + \frac{Q}{(\tilde{E}-H_0)}\ (\tilde{E}-E_0+H')|\Phi_0\rangle \tag{15.80}$$

$$+\frac{Q}{(\tilde{E}-H_0)}\ (\tilde{E}-E_0+H')\ \frac{Q}{(\tilde{E}-H_0)}\ (\tilde{E}-E_0+H')|\Psi_0\rangle$$

$$= \sum_{n=0}^{\infty}\ \left(\frac{Q}{(\tilde{E}-H_0)}\ (\tilde{E}-E_0+H')\right)^n\ |\Phi_0\rangle.$$

This gives the energy shift ΔE_0 as

$$\Delta E_0 = \langle\Phi_0|H'|\Psi_0\rangle = \sum_{n=0}^{\infty}\ \langle\Phi_0|H'\Big(\frac{Q}{(\tilde{E}-H_0)}\ (\tilde{E}-E_0+H')\Big)^n\ |\Phi_0\rangle. \tag{15.81}$$

There are two obvious options for determining $\tilde{E}$. If we set $\tilde{E} = E_0$ (**Brillouin-Wigner method**), the equations

$$|\Psi_0\rangle = \sum_{n=0}^{\infty}\ \left(\frac{Q}{(E_0-H_0)}\ H'\right)^n\ |\Phi_0\rangle \tag{15.82}$$

and

$$\Delta E_0 = \sum_{n=0}^{\infty}\ \langle\Phi_0|H'\Big(\frac{Q}{(E_0-H_0)}\ H'\Big)^n\ |\Phi_0\rangle \tag{15.83}$$

have to be solved iteratively, since E_0 is unknown!
In the **Rayleigh-Schrödinger method** one sets $\tilde{E} = \epsilon_0$ and the equations become

$$|\Psi_0\rangle = \sum_{n=0}^{\infty}\ \left(\frac{Q}{(\epsilon_0-H_0)}\ (H'-\Delta E_0)\right)^n\ |\Phi_0\rangle \tag{15.84}$$

and

$$\Delta E_0 = \sum_{n=0}^{\infty}\ \langle\Phi_0|H'\Big(\frac{Q}{(\epsilon_0-H_0)}\ (H'-\Delta E_0)\Big)^n\ |\Phi_0\rangle, \tag{15.85}$$

which in turn must be solved iteratively for the unknown quantity ΔE_0!
Examples:

$$n=0 \rightarrow \Delta E_0^{(1)} = \langle\Phi_0|H'|\Phi_0\rangle \tag{15.86}$$

$$n=1 \rightarrow \Delta E_0^{(2)} = \langle\Phi_0|H'\frac{Q}{(\epsilon_0-H_0)}(H'-\Delta E_0)|\Phi_0\rangle = \tag{15.87}$$

$$\langle\Phi_0|H'\frac{Q}{(\epsilon_0-H_0)}H'|\Phi_0\rangle=\sum_n\langle\Phi_0|H'\frac{Q}{(\epsilon_0-H_0)}|\Phi_n\rangle\langle\Phi_n|H'|\Phi_0\rangle$$

$$=\sum_{n\neq 0}\frac{|\langle\Phi_0|H'|\Phi_n\rangle|^2}{\epsilon_0-\epsilon_n},$$

since $Q|\Phi_0\rangle=0$.

For $n=2$ we obtain

$$\Delta E_0^{(3)}=\langle\Phi_0|H'\tfrac{Q}{(\epsilon_0-H_0)}(H'-\Delta E_0)\tfrac{Q}{(\epsilon_0-H_0)}(H'-\Delta E_0)|\Phi_0\rangle= \tag{15.88}$$

$$=\sum_n\sum_m\langle\Phi_0|H'\frac{Q}{(\epsilon_0-H_0)}|\Phi_n\rangle\langle\Phi_n|(H'-\Delta E_0)\frac{Q}{(\epsilon_0-H_0)}|\Phi_m\rangle\langle\Phi_m|H'|\Phi_0\rangle$$

$$=\sum_{n\neq 0}\sum_{m\neq 0}\frac{\langle\Phi_0|H'|\Phi_n\rangle\langle\Phi_n|(H'-\Delta E_0)|\Phi_m\rangle\langle\Phi_m|H'|\Phi_0\rangle}{(\epsilon_0-\epsilon_n)(\epsilon_0-\epsilon_m)},$$

$$=\sum_{n\neq 0}\sum_{m\neq 0}\frac{\langle\Phi_0|H'|\Phi_n\rangle\langle\Phi_n|H'|\Phi_m\rangle\langle\Phi_m|H'|\Phi_0\rangle}{(\epsilon_0-\epsilon_n)(\epsilon_0-\epsilon_m)}-\Delta E_0\sum_{n\neq 0}\frac{|\langle\Phi_0|H'|\Phi_n\rangle|^2}{(\epsilon_0-\epsilon_n)^2},$$

where $\Delta E_0=\Delta E_0^{(1)}+\Delta E_0^{(2)}+\Delta E_0^{(3)}$ has to be set and calculated iteratively. Higher orders are obtained in analogy by inserting $\sum_\nu|\Phi_\nu\rangle\langle\Phi_\nu|$ and using the fact that Q projects onto $\sum_{\nu\neq 0}|\Phi_\nu\rangle\langle\Phi_\nu|$.

In summary, we have defined the *S*-matrix and the *T*-matrix for general scattering problems and given a generalized Born series for the *T*-matrix, that can be solved by iteration in arbitrary order.

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16. The Hartree-Fock Approximation

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In this chapter we will present the Hartree-Fock approach, which is a leading order selfconsistent approach to the many-body problem and is extensively applied in calculations of the groundstate properties of atoms, molecules and nuclei.

The Hartree-Fock theory (HF) has the task of optimally representing the groundstate of an *N* fermion system (in the sense of a variational principle) by a **single Slater determinant** (SD); i.e. the single-particle states φ_i of a Slater determinant Φ are varied until the energy

$$E = \frac{\langle\Phi|H|\Phi\rangle}{\langle\Phi|\Phi\rangle} \tag{16.1}$$

becomes minimal. The Hamiltonian *H* of the system consists in the following of a single-particle part *T* and a two-particle part *V* of the form

$$H = T + V = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + \sum_{i<j}^{N} v(ij), \tag{16.2}$$

where *v*(*ij*) describes the interaction between particles *i* and *j*. If the Slater determinant is normalized, i.e. $\langle\Phi|\Phi\rangle = 1$, the task is reduced to find the minimum of $\langle\Phi|H|\Phi\rangle$ by varying the φ_i.

The solution Φ_0 of such a procedure can also be seen as the 0th approximation for the calculation of the exact ground state Ψ_0 in the context of a perturbation calculation. The single-particle wave functions then define an **effective mean-field potential** U_{HF}, such that the Hamiltonian operator (16.2) can be rewritten in the form

$$H = H_0 + H_R \tag{16.3}$$

with

$$H_0 = T + U_{HF}, \tag{16.4}$$

where H_0 describes the motion of independent particles. One can then consider H_R as a residual interaction and calculate the exact ground state Ψ_0 within the framework of a perturbation calculation. We then obtain

$$\Psi_0 = \Phi_0 + \sum_n C_{ph}^n \Phi_{ph}^n, \tag{16.5}$$

where Φ_{ph}^n are the *n*-particle—*n*-hole states related to Φ_0.

16.1 General Properties of the Hartree-Fock Problem

We first assume that the solution Φ_0 and the energy $E_0 = \langle\Phi_0|H|\Phi_0\rangle$ are known. For an infinitesimal change in the Slater determinant

$$\Phi_0 \to \Phi_0' = \Phi_0 + \delta\Phi_0 \tag{16.6}$$

after variation the **stationarity condition** must be fulfilled,

$$\langle \Phi_0 | H | \delta\Phi_0 \rangle = 0, \tag{16.7}$$

as can be shown by varying (16.1). The infinitesimal change of the N-particle state $\delta\Phi_0$ corresponds to an infinitesimal change of the single-particle functions

$$\varphi_i \to \varphi_i' = \varphi_i + \delta\varphi_i. \tag{16.8}$$

For the further investigations it is convenient to use the particle number representation. Instead of the Slater determinant Φ_0 we then can write

$$|\Phi_0\rangle = \prod_{i=1}^{N} a_i^\dagger |0\rangle, \tag{16.9}$$

where the creation operators $a_i^\dagger$, applied to the vacuum, create the state

$$\varphi_i(\xi) = \langle \xi | i \rangle = \langle \xi | a_i^\dagger | 0 \rangle. \tag{16.10}$$

In the **groundstate** Φ_0 all single-particle states $|i\rangle$ of lowest single-particle energy $(i = 1, \ldots, N)$ are occupied with probability 1. Then the variations φ_i' introduced in (16.8) can be represented (for $i \leq N$) by

$$\varphi_i' \equiv (a_i^\dagger + \textstyle\sum_{m>N} c_{mi} a_m^\dagger)|0\rangle, \tag{16.11}$$

i.e. by an admixture of states above the Fermi level (given by the single-particle state $|N\rangle$), since an admixture of states below the Fermi level does not change the Slater determinant. For the Φ_0' we obtain:

$$\Phi_0'(\xi_1, \ldots, \xi_N) \equiv |\Phi_0'\rangle = \prod_{i \leq N} (a_i^\dagger + \textstyle\sum_{m>N} c_{mi} a_m^\dagger)|0\rangle, \tag{16.12}$$

which can also be written more simply (proof see below) as

$$|\Phi_0'\rangle = \prod_{i \leq N} (1 + \textstyle\sum_{m>N} c_{mi} a_m^\dagger a_i)|\Phi_0\rangle, \tag{16.13}$$

if the single-particle states $|i\rangle$ are orthonormalized, such that the $a_i^\dagger$, a_i satisfy the standard commutation rules for fermions.

Proof With the relation

$$a_m^\dagger a_i a_i^\dagger |0\rangle = a_m^\dagger (1 - a_i^\dagger a_i)|0\rangle = a_m^\dagger |0\rangle \tag{16.14}$$

we first have

$$|\Phi_0'\rangle = \prod_{i \leq N} (1 + \textstyle\sum_{m>N} c_{mi} a_m^\dagger a_i) a_i^\dagger |0\rangle. \tag{16.15}$$

If we continue to use for $i \neq k$

(16.16)

$$a_i^\dagger(a_m^\dagger a_k) = -a_m^\dagger a_i^\dagger a_k = (a_m^\dagger a_k)a_i^\dagger,$$

we get (16.13) via

$$|\Phi_0'\rangle = \prod_{i\le N}(1+\sum_{m>N} c_{mi}a_m^\dagger a_i)\prod_{k\le N} a_k^\dagger|0\rangle = \prod_{i\le N}(1+\sum_{m>N} c_{mi}a_m^\dagger a_i)|\Phi_0\rangle. \tag{16.17}$$

For infinitesimal admixtures ($|c_{mi}|^2 \ll 1$) the above product can be expanded and we obtain

$$|\Phi_0'\rangle = \{1+\sum_{i\le N}\sum_{m>N} c_{mi}a_m^\dagger a_i\}|\Phi_0\rangle \equiv |\Phi_0\rangle + |\delta\Phi_0\rangle. \tag{16.18}$$

From the stationarity condition (16.7)–due to the linear independence of the vectors $a_m^\dagger a_i|\Phi_0\rangle = |\Phi_{mi}\rangle$—we obtain the **Brillouin theorem**:

$$\langle\Phi_0|H\ a_m^\dagger a_i|\Phi_0\rangle \equiv \langle\Phi_0|H|\Phi_{mi}\rangle = 0 i\le N, m>N \tag{16.19}$$

for any $1p-1h$ states $|\Phi_{mi}\rangle$.

A direct consequence of the Brillouin theorem is the stability of the HF solution against $1p-1h$ excitations, since these cannot improve the HF ground state $|\Phi_0\rangle$ because of (16.19). Only by $2p-2h$ corrections (as well as $3p-3h$ terms etc.) the ground state

$$\Psi_0 = \Phi_0 + \sum_{2p,2h}\ c_{2p2h}\Phi_{2p2h} + \cdots \tag{16.20}$$

can be improved.

Instead of the Brillouin theorem (16.19) for *N*-particle states, we now want to establish an equivalent statement for the single-particle states $|\alpha\rangle$. To this aim we need the explicit matrix elements of $\langle\Phi_0|H|\Phi_{mi}\rangle$ with the Hamiltonian operator

$$H = \sum_{\alpha\beta}(\alpha|t|\beta)a_\alpha^\dagger a_\beta + \tfrac{1}{2}\sum_{\alpha\beta\gamma\delta}(\alpha\beta|v|\gamma\delta)\ a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma. \tag{16.21}$$

For the matrix elements of $Ha_m^\dagger a_i$ with Φ_0 we then obtain in detail:

$$\langle\Phi_0|a_\alpha^\dagger a_\beta a_m^\dagger a_i|\Phi_0\rangle = \delta_{i\alpha}\delta_{m\beta}, \tag{16.22}$$

$$\langle\Phi_0|a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma a_m^\dagger a_i|\Phi_0\rangle = \langle\Phi_0|a_\alpha^\dagger a_\beta^\dagger a_\delta a_i|\Phi_0\rangle\delta_{m\gamma} - \langle\Phi_0|a_\alpha^\dagger a_\beta^\dagger a_\gamma a_i|\Phi_0\rangle\delta_{m\delta} \tag{16.23}$$

for $m>N, i\le N$. With (16.22), (16.23) the Brillouin theorem then reads

$$(i|t|m) + \tfrac{1}{2}\Big(\sum_{\beta\le N}(i\beta|v|m\beta) - \sum_{\alpha\le N}(\alpha i|v|m\alpha) - \sum_{\beta\le N}(i\beta|v|\beta m) + \sum_{\alpha\le N}(\alpha i|v|\alpha m)\Big) = 0. \tag{16.24}$$

Taking into account the symmetry

$$(\alpha\beta|v|\gamma\delta) = (\beta\alpha|v|\delta\gamma)$$

—(from (12.53) for $v(1,2)=v(2,1)$)—we finally obtain

$$(i|t|m) + \sum_{\alpha\le N}(i\alpha|v|m\alpha) - (i\alpha|v|\alpha m) = 0 \tag{16.25}$$

for $i \leq N, m > N$. To interpret (16.25) we introduce the (hermitian) operator

$$H_{HF} \equiv \sum_{\alpha\beta}\big((\alpha|t|\beta) + \sum_{n\leq N}(\alpha n|v|\beta n)_{\mathscr{A}}\big)\ a^\dagger_\alpha a_\beta = \sum_{\alpha\beta}(\alpha|h_{HF}|\beta)\ a^\dagger_\alpha a_\beta \tag{16.26}$$

with

$$(\alpha n|v|\beta n)_{\mathscr{A}} = (\alpha n|v|\beta n) - (\alpha n|v|n\beta) \tag{16.27}$$

which, as a result of the Brillouin theorem, can be diagonalized separately in the subspaces of the occupied and unoccupied states! This diagonalization process has no influence on the Slater determinant Φ_0, because

(i) Φ_0 is independent of φ_m for $m > N$ and

(ii) Φ_0 is invariant under arbitrary unitary transformations of the φ_i for $i \leq N$ among themselves.

We can thus assume, without loss of generality, that h_{HF} is diagonal in the basis of $\{\varphi_i\}$, i.e.

$$(\alpha|t|\beta) + \sum_{n\leq N}(\alpha n|v|\beta n)_{\mathscr{A}} = \epsilon_\alpha \delta_{\alpha\beta}. \tag{16.28}$$

Then H_{HF} takes the simple form

$$H_{HF} = \sum_\alpha \epsilon_\alpha a^\dagger_\alpha a_\alpha \tag{16.29}$$

with real single-particle energies ϵ_α. The Slater determinant Φ_0 then is the ground state of H_{HF} with

$$H_{HF}|\Phi_0\rangle = (T + U_{HF})|\Phi_0\rangle = \sum_{i\leq N}\epsilon_i|\Phi_0\rangle. \tag{16.30}$$

To find an explicit form for U_{HF}, we go back to (16.28). Since this equation is supposed to hold for all α, we can also write (in the **spatial representation of the Hartree-Fock equations**)

$$(t + U_H)\varphi_\beta(\xi) - \int d\xi'\ U_F(\xi,\xi')\varphi_\beta(\xi') = \epsilon_\beta\ \varphi_\beta(\xi) \tag{16.31}$$

with the **local Hartree potential**

$$U_H(\xi) = \sum_{n\leq N}\int d\xi'\ \varphi^*_n(\xi')\ v(\xi,\xi')\ \varphi_n(\xi') \tag{16.32}$$

and the **nonlocal Fock potential**

$$U_F(\xi,\xi') = \sum_{n\leq N}\ \varphi^*_n(\xi')\ v(\xi,\xi')\ \varphi_n(\xi). \tag{16.33}$$

Formally, we can also write (16.28) as a Schrödinger equation for a single particle,

$$(t + U_{HF})\varphi_\alpha = \epsilon_\alpha\varphi_\alpha, \tag{16.34}$$

where the mean-field potential $U_{HF} = U_H - U_F$ is nonlocal. This self-consistent single-particle potential U_{HF} is completely determined by the interaction $v(1, 2)$ and by the single-particle states $\varphi_i \ \ (i \leq N)$ occupied in Φ_0.

16.2 Practical Implementation of the HF Method

Equation (16.34) represents a system of N coupled integro-differential equations for $\alpha \leq N$, while for $\alpha > N$ only one integro-differential equation has to be solved. The usual procedure in practice for solving (16.34) consists in expanding the desired HF solutions φ_α according to an arbitrary (but 'close') orthonormal basis $\{\psi_\nu\}$,

$$\varphi_\alpha = \sum_\nu C_\nu^\alpha \ \psi_\nu. \tag{16.35}$$

The system of equations (16.34) then turns into a nonlinear system of equations for the expansion coefficients C_ν^α. The explicit form of this system is obtained by inserting (16.35) into (16.34), multiplying from the left by ψ_μ^* and integration over ξ:

$$\sum_\nu \Big((\psi_\mu|t|\psi_\nu) + \sum_{n\leq N} \sum_{\rho\sigma} C_\rho^{n*} (\psi_\mu \psi_\rho |v| \psi_\nu \psi_\sigma)_{\not A} C_\sigma^n \Big) \ C_\nu^\alpha = \epsilon_\alpha \ C_\mu^\alpha. \tag{16.36}$$

We can solve this system of equations iteratively by writing it formally as a linear system,

$$\sum_\nu h_{\mu\nu} C_\nu^\alpha = \epsilon_\alpha C_\mu^\alpha, \tag{16.37}$$

and note that $h_{\mu\nu} = h_{\mu\nu}(C^*, C)$.

The iteration procedure then is carried out as follows:

1st step:

A basis $\{\psi_\nu\}$ is chosen such that the matrix elements of t and v are easy to calculate (e.g. oscillator eigenfunctions or eigenfunctions of the H atom – depending on the problem). As a **starting solution** one then sets:

$$C_\mu^{\alpha(0)} = \delta_{\mu\alpha}, \tag{16.38}$$

and chooses the energetically lowest states $\psi_\nu \ \ (\nu \leq N)$.

2nd step:

Using the ψ_ν the matrix

$$h_{\mu\nu}^{(0)} = (\psi_\mu|t|\psi_\nu) + \sum_{n\leq N} (\psi_\mu \psi_n |v| \psi_\nu \psi_n) \tag{16.39}$$

is calculated. In the

3rd step:

the linear system of equations

$$\sum_\nu h_{\mu\nu}^{(0)} C_\nu^{\alpha(1)} = \epsilon_\alpha C_\mu^{\alpha(1)} \tag{16.40}$$

is diagonalized and the new states

$$\varphi_\alpha^{(1)} = \sum_\nu C_\nu^{\alpha(1)} \psi_\nu \tag{16.41}$$

are calculated. In the

4th step:

one then selects the 'occupied' states $\varphi_\alpha^{(1)}$ $(\alpha \leq N)$ and starts again with step 2, i.e. the calculation of the matrix $h_{\mu\nu}^{(1)}$ with the states $\varphi_\alpha^{(1)}$.

The procedure is continued until the **self-consistency**

$$C_\mu^{\alpha(n)} \equiv C_\mu^{\alpha(n+1)} \text{ or } h_{\mu\nu}^{(n)} \equiv h_{\mu\nu}^{(n+1)} \tag{16.42}$$

is achieved. Since the matrices $h_{\mu\nu}^{(n)}$ are Hermitian in each iteration step, the corresponding eigenvalues $\epsilon_\alpha^{(n)}$ are real and the $\varphi_\alpha^{(n)}$ orthogonal to different $\epsilon_\alpha^{(n)}$.

A practical problem, however, is that the solution does not have to be unique due to the non-linearity of the HF equations. By choosing the wrong occupied states in the $n-th$ iteration step, it can happen that instead of the absolute minimum, only a local minimum or even a maximum is found, which then corresponds to an unstable solution (see Fig. 16.1).

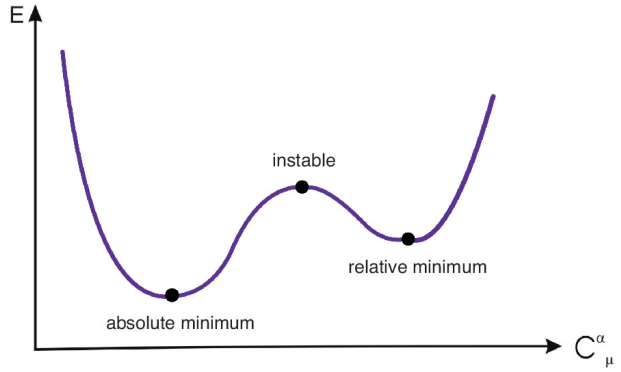

Fig. 16.1 Illustration of possible solutions to the Hartree-Fock problem

16.3 Koopman's Theorem

The ground state energy

$$\langle\Phi_0|H|\Phi_0\rangle = E_0 = \sum_{\alpha\leq N}\left((\alpha|t|\alpha) + \tfrac{1}{2}\sum_{n\leq N}(\alpha n|v|\alpha n)_{\mathscr{A}}\right) \tag{16.43}$$

differs from the expectation value of H_{HF} in the state $|\Phi_0\rangle$, since in

$$\langle\Phi_0|H_{HF}|\Phi_0\rangle = \sum_{\alpha\leq N}\left((\alpha|t|\alpha) + \sum_{n\leq N}(\alpha n|v|\alpha n)_{\mathscr{A}}\right) = \sum_{\alpha\leq N}\epsilon_\alpha \neq E_0 \tag{16.44}$$

the interaction between the particles is counted twice.

The most simple excitations of the system on top of the ground state

$$|\Phi_0\rangle = \prod_{\alpha\leq N} a_\alpha^\dagger|0\rangle \tag{16.45}$$

are $1p-1h$ states

$$|\Phi_{mi}\rangle = a_m^\dagger a_i|\Phi_0\rangle \text{with } m > N, i \leq N. \tag{16.46}$$

Its excitation energy

$$\Delta E = \epsilon_m - \epsilon_i \tag{16.47}$$

in turn is different from the difference of the expectation value of H in the states $|\Phi_0\rangle$ and $|\Phi_{mi}\rangle$,

$$\langle\Phi_{mi}|H|\Phi_{mi}\rangle - E_0 = \epsilon_m - \epsilon_i - (mi|v|mi)_{\mathscr{A}} \tag{16.48}$$

due to the double counting of the interaction in ϵ_m and ϵ_i. The question therefore arises about the physical interpretation of the single-particle energies ϵ_μ.

The **theorem of Koopman** now states that the HF single-particle energy ϵ_μ is precisely **the separation energy of a particle in the state** φ_μ. For the 'proof' we make use of the assumption, that the HF single-particle states φ_ν do not change approximately during the transition from the *N* particle system to the $(N-1)$ particle system, if *N* is sufficiently large. We then can represent a state of the $(N-1)$ particle system by annihilating a particle in the state φ_μ of the Slater determinant $|\Phi_0\rangle$ (16.45), *i.e.*

$$|\Phi_\mu\rangle = a_\mu|\Phi_0\rangle = \textstyle\prod_{\alpha\le N,\alpha\neq\mu} a_\alpha^\dagger|0\rangle. \tag{16.49}$$

The separation energy now is the difference between

$$E_\mu = \langle\Phi_\mu|H|\Phi_\mu\rangle = \textstyle\sum_{\alpha\le N,\alpha\neq\mu}\Big((\alpha|t|\alpha) + \frac{1}{2}\sum_{n\le N,n\neq\mu}(\alpha n|v|\alpha n)_{\mathscr{A}}\Big) \tag{16.50}$$

and

$$E_0 = \langle\Phi_0|H|\Phi_0\rangle = \textstyle\sum_{\alpha\le N}\big((\alpha|t|\alpha) + \frac{1}{2}\sum_{n\le N}(\alpha n|v|\alpha n)_{\mathscr{A}}\big), \tag{16.51}$$

thus

$$E_\mu - E_0 = -(\mu|t|\mu) - \textstyle\sum_{i\le N}(i\mu|v|i\mu)_{\mathscr{A}} = -\epsilon_\mu \tag{16.52}$$

as claimed. We find deviations from this statement in nuclear physics, especially in systems with a small number of particles, where the φ_ν change noticeably during the transition from the $N-$ to the $(N-1)$ particle system, or where the HF approximation itself is too poor for the exact ground state $|\Psi_0\rangle$.

Remark: In the **time-dependent Hartree-Fock theory** one restricts to the calculation of the time evolution of a Slater determinant with time-dependent single-particle wave functions $\varphi_\beta(\xi,t)$,

$$\Big(-\tfrac{\hbar^2}{2m}\nabla^2 + U_H(\xi,t)\Big)\varphi_\beta(\xi,t) - \int d\xi'\ U_F(\xi,\xi';t)\varphi_\beta(\xi',t) = i\hbar\tfrac{\partial}{\partial t}\ \varphi_\beta(\xi,t), \tag{16.53}$$

where the Hartree-Fock potential—calculated with the wave functions $\varphi_\beta(\xi,t)$—is also explicitly time-dependent. The time-dependent Hartree-Fock (TDHF) method is always applicable, if the residual interaction H_R is negligible and the time evolution of the system is dominated by the independent motion of particles in a self-consistent (time-dependent) single-particle potential. **Examples for applications** are low-energy reactions of atoms and molecules.

In summarizing this chapter we have derived the Hartree-Fock approach, which is a leading order selfconsistent approach to the many-body problem and is extensively applied in calculations of the groundstate properties of atoms, molecules and nuclei.

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17. Superconductivity in the BCS Model

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In this chapter we will introduce to the description of superconductivty, which is a generic property of fermion systems at low temperatures, if an attractive residual interaction between specific states exists.

17.1 Experimental Evidence for Cooper Pairs

In

(I) **solid state physics** pairs of electrons with antiparallel momentum and spin

$$(\mathbf{k}\ up, -\mathbf{k}\ down), \tag{17.1}$$

in

(II) **nuclear physics** pairs of nucleons with total angular momentum I=0:

$$(m_j, -m_j). \tag{17.2}$$

Below we will summarize some experimental evidence for the existence of Cooper pairs.

(1) **Odd-Even effect in nuclear physics**

The system of nuclear masses shows that

$$M_A > \tfrac{1}{2}(M_{A-1} + M_{A+1}) \tag{17.3}$$

for odd mass numbers *A*. Using the energy-mass relation

$$Am = M_A + B_A/c^2, \tag{17.4}$$

where *m* is the nucleon mass and B_A is the nuclear binding energy, we have for odd mass numbers:

$$B_A < \tfrac{1}{2}\ (B_{A-1} + B_{A+1}). \tag{17.5}$$

(2) **Energy-gap**

Single-particle excitations are systematically higher in even-even nuclei (each with an even number of protons and neutrons) than in odd-even nuclei,

$$\Delta E_{s.p.}(\text{even} - \text{even}) > \Delta E_{s.p.}(\text{odd} - \text{even}), \tag{17.6}$$

since in even-even nuclei - in contrast to odd-even nuclei - a Cooper pair must be broken up in order to enable a single-particle excitation (see below).

(3) **Superconductivity in solids**

In a normal conductor, electrical conduction occurs by quasi-free electrons; the resistance is a consequence of the collisions between the electrons and the lattice atoms. Without an external field the state of the conduction electrons is described by a Fermi sphere around the origin in momentum space

(state without current). By an external field (applied voltage *U*) the Fermi sphere is (in first order) linearly displaced in momentum space by,

$$\Delta k = \frac{\sqrt{2 e m_e U}}{\hbar}, \tag{17.7}$$

such that a non-vanishing expectation value of the current results. When switching off the external field the equilibrium state (without current) is restored by collisions between electrons and lattice atoms.

In a **superconductor** this relaxation process is strongly suppressed in the presence of Cooper pairs, as long as the energy *eU* supplied by the external field is not sufficient to break up the Cooper pairs! The current continues to flow without resistance! In a simple estimate, for

$$\frac{\hbar^2}{2m}\left((k_F + \Delta k)^2 - (k_F - \Delta k)^2\right) = \frac{\hbar^2 k_F \Delta k}{m} < P \tag{17.8}$$

a supercurrent then can flow, where in (17.8) k_F stands for the Fermi momentum, Δk for the displacement of the Fermi sphere by the external field (17.7) and *P* for the pair energy. The **critical current** j_c can be estimated via

$$\Delta k = \frac{m \Delta v}{\hbar} = \frac{m}{e\hbar n} j_c, n = \frac{k_F^3}{3\pi^2}, \tag{17.9}$$

where *n* is the electron density, which together with (17.8) leads to a critical current $j_c \sim 10^7$ Amp/cm^2.

Above a critical temperature $k_B T_c \geq P$ the Cooper pairs can be broken up 'thermally'; the superconductivity disappears again. An estimate gives $T_c < 20^o$ K for metals.

17.2 Origin of the Pair Force

In **solid state physics** the electron-phonon coupling in second order perturbation theory generates an attractive contribution to the electron-electron interaction, which under certain circumstances overcompensates the Coulomb repulsion of the electrons and leads to pair formation.

In **nuclear physics**, components of high multipolarity of the nucleon-nucleon interaction,

$$V(r_{12}) = \sum_l f_l(r_1, r_2)\ P_l(\cos(\theta_{12}))\ , \tag{17.10}$$

favor the formation of nucleon pairs with total angular momentum $I = 0$.

17.3 BCS Ground State

In the model of **B**ardeen-**C**ooper-**S**chrieffer, the ground state of the system is constructed by Cooper pairs $(k, \bar{k})$:

$$|\tilde{\Phi}_0\rangle = \prod_{k>0}\ (u_k + v_k a_k^\dagger a_{\bar{k}}^\dagger)|0\rangle, \tag{17.11}$$

where $\bar{k}$ is the time-reversed state of *k* and u_k, v_k are real expansion coefficients. The notation $k > 0$ means that only states with $m_j > 0$ in nuclear physics or only states with spin *up* in solid state physics are counted, since the time-reversed state $\bar{k}$ is already taken into account via the pair formation. Normalizing $|\tilde{\Phi}_0\rangle$ yields

$$\langle\tilde{\Phi}_0|\tilde{\Phi}_0\rangle = \prod_{k>0}(u_k^2 + v_k^2). \tag{17.12}$$

Consequently $\langle\tilde{\Phi}_0|\tilde{\Phi}_0\rangle$ is normalized to 1 if

$$u_k^2 + v_k^2 = 1 \forall\ k\ . \tag{17.13}$$

To prove (17.12) note that

$$[a_k^\dagger a_{\bar{k}}^\dagger, a_l^\dagger a_{\bar{l}}^\dagger]_+ = 0; [a_k^\dagger a_{\bar{k}}^\dagger, a_{\bar{l}} a_l]_+ = 0 \forall\ k \neq l \tag{17.14}$$

and

$$\langle 0|a_{\bar{l}} a_l a_k^\dagger a_{\bar{k}}^\dagger|0\rangle = \delta_{lk}\delta_{\bar{l}\bar{k}}. \tag{17.15}$$

In the products (with $(a_l^\dagger a_{\bar{l}}^\dagger)^\dagger = a_{\bar{l}} a_l$)

$$\langle\tilde{\Phi}_0|\tilde{\Phi}_0\rangle = \prod_{k>0}\prod_{l>0}\ \langle 0|(u_l + v_l a_{\bar{l}} a_l)(u_k + v_k a_k^\dagger a_{\bar{k}}^\dagger)|0\rangle \tag{17.16}$$

one thus can move the $a_{\bar{l}} a_l$ for $l \neq k$ past the $a_k^\dagger a_{\bar{k}}^\dagger$, such that the product for $l > 0$ only results in a factor with $l = k$:

$$\prod_{k\neq l, k>0} \langle 0|u_k u_k + u_k v_k a_k^\dagger a_{\bar{k}}^\dagger + v_k u_k a_{\bar{k}} a_k + v_k v_k a_{\bar{k}} a_k a_k^\dagger a_{\bar{k}}^\dagger|0\rangle = (u_k^2 + v_k^2)\langle\tilde{\Phi}_0|\tilde{\Phi}_0\rangle'$$

where $'$ indicates that the pair $(k, \bar{k})$ has to be omitted. Repeated application then leads to (17.12).

Remark: The shell model limiting case is contained in the approach (17.11) if we set ($u_k = 0, v_k = 1$) for states *k* below the Fermi energy and ($u_k = 1, v_k = 0$) above the Fermi energy.

As a result, one can interpret v_k^2 as the **occupation probability** of the pair state $(k, \bar{k})$. For finite $0 \leq v_k^2 \leq 1$ the sharp Fermi edge in the shell model is 'smeared' by the residual interaction. This smearing looks similar to the case of finite temperatures *T* in quantum statistics, but here the correlated ground state (17.11) (at $T = 0$) is already 'smeared' relative to the single-particle shell model!

The parameters u_k and v_k can be determined from the variational principle:

$$\delta\langle\tilde{\Phi}_0|H - \lambda\mathcal{N}|\tilde{\Phi}_0\rangle = 0, \tag{17.17}$$

where the Lagrange parameter λ has to be chosen such that the matrix element of the particle number operator $\mathcal{N}$

$$\langle\tilde{\Phi}_0|\mathcal{N}|\tilde{\Phi}_0\rangle = N \tag{17.18}$$

corresponds to the required number of particles, since the state $|\tilde{\Phi}_0\rangle$ is not sharp with respect to the number of particles (see below).

17.4 BCS Quasiparticles

Quasiparticles are defined in relation to a reference vacuum, which does not have to coincide with the physical vacuum $|0\rangle\langle 0|$. For the operators

$$\alpha_k = u_k a_k - v_k a_{\bar{k}}^\dagger; \alpha_{\bar{k}} = u_k a_{\bar{k}} + v_k a_k^\dagger \tag{17.19}$$

$$\alpha_k^\dagger = u_k a_k^\dagger - v_k a_{\bar{k}}; \alpha_{\bar{k}}^\dagger = u_k a_{\bar{k}}^\dagger + v_k a_k$$

we have

$$\alpha_k |\tilde{\Phi}_0\rangle = \alpha_{\bar{k}} |\tilde{\Phi}_0\rangle = 0 \forall \; k, \bar{k}. \tag{17.20}$$

The **proof** is done in 2 steps:
(1)

$$\alpha_l |\tilde{\Phi}_0\rangle = (u_l a_l - v_l a_{\bar{l}}^\dagger) \prod_{k>0} (u_k + v_k a_k^\dagger a_{\bar{k}}^\dagger) |0\rangle \tag{17.21}$$

$$= \left(\prod_{l \neq k, k>0} (u_k + v_k a_k^\dagger a_{\bar{k}}^\dagger) \right) (u_l a_l - v_l a_{\bar{l}}^\dagger)(u_l + v_l a_l^\dagger a_{\bar{l}}^\dagger) |0\rangle,$$

i.e. one can move $(u_l a_l - v_l a_{\bar{l}}^\dagger)$ past the operators $a_k^\dagger a_{\bar{k}}^\dagger$ for $l \neq k, \bar{k}$, since for $l \neq k, \bar{k}$ the following holds

$$[a_k^\dagger a_{\bar{k}}^\dagger, a_l]_+ = [a_k^\dagger a_{\bar{k}}^\dagger, a_l^\dagger]_+ = 0. \tag{17.22}$$

(2) Step:

$$(u_l a_l - v_l a_{\bar{l}}^\dagger)(u_l + v_l a_l^\dagger a_{\bar{l}}^\dagger) \; |0\rangle = (u_l^2 a_l + u_l v_l a_l a_l^\dagger a_{\bar{l}}^\dagger - u_l v_l a_{\bar{l}}^\dagger - v_l^2 a_{\bar{l}}^\dagger a_l^\dagger a_{\bar{l}}^\dagger) \; |0\rangle \tag{17.23}$$

$$= (u_l v_l a_l a_l^\dagger - u_l v_l) a_{\bar{l}}^\dagger |0\rangle = (u_l v_l - u_l v_l) a_{\bar{l}}^\dagger \; |0\rangle \equiv 0.$$

Consequently, $|\tilde{\Phi}_0\rangle$ can be considered as the **quasiparticle vacuum** with respect to the operators α_l.
The inverse of (17.18) is

$$a_k = u_k \alpha_k + v_k \alpha_{\bar{k}}^\dagger; a_{\bar{k}} = u_k \alpha_{\bar{k}} - v_k \alpha_k^\dagger \tag{17.24}$$

$$a_k^\dagger = u_k \alpha_k^\dagger + v_k \alpha_{\bar{k}}; a_{\bar{k}}^\dagger = u_k \alpha_{\bar{k}}^\dagger - v_k \alpha_k,$$

as can easily be calculated. In compact form:

$$a_k = u_k \alpha_k + S_k v_k \alpha_{\bar{k}}^\dagger, a_k^\dagger = u_k \alpha_k^\dagger + S_k v_k \alpha_{\bar{k}} \tag{17.25}$$

with $S_k = 1$ for $k > 0$ and $S_k = -1$ for $\bar{k} = k < 0$. From the Fermi commutation relations of the $a_k, a_k^\dagger$ also follow the Fermi commutation relations of $\alpha_k, \alpha_k^\dagger$,

$$[\alpha_k, \alpha_l^\dagger]_+ = \delta_{kl}, \quad [\alpha_k, \alpha_l]_+ = [\alpha_k^\dagger, \alpha_l^\dagger]_+ = 0. \tag{17.26}$$

The transition from particles to quasiparticles proves to be helpful for the calculation of matrix elements and as physically meaningful for the construction of excited states.

Note: The BCS quasiparticles are not to be mixed up with the Cooper pairs!

17.5 Matrix Elements in the BCS Model

The **particle number** in the BCS ground state is given by

$$\langle\tilde{\Phi}_0|\mathscr{N}|\tilde{\Phi}_0\rangle = \textstyle\sum_m \langle\tilde{\Phi}_0|a_m^\dagger a_m|\tilde{\Phi}_0\rangle \tag{17.27}$$

$$= \sum_m \langle\tilde{\Phi}_0|(u_m^2\alpha_m^\dagger\alpha_m + S_m v_m u_m \alpha_{\bar{m}}\alpha_m + u_m v_m S_m \alpha_m^\dagger \alpha_{\bar{m}} + S_m v_m S_m v_m \alpha_{\bar{m}}\alpha_{\bar{m}}^\dagger)|\tilde{\Phi}_0\rangle$$

$$= \sum_m \langle\tilde{\Phi}_0|\alpha_{\bar{m}}\alpha_{\bar{m}}^\dagger|\tilde{\Phi}_0\rangle v_m^2 = \sum_m v_m^2 = 2\sum_{m>0} v_m^2.$$

It is generally not sharp since the **particle number fluctuation**

$$(\Delta N)^2 = \langle\tilde{\Phi}_0|\mathscr{N}^2|\tilde{\Phi}_0\rangle - \langle\tilde{\Phi}_0|\mathscr{N}|\tilde{\Phi}_0\rangle^2 = 2\textstyle\sum_m u_m^2 v_m^2 \neq 0 \tag{17.28}$$

except for the shell model limit! To prove this, we form

$$\langle\tilde{\Phi}_0|\mathscr{N}^2|\tilde{\Phi}_0\rangle = \langle\tilde{\Phi}_0|\textstyle\sum_{m,n} a_m^\dagger a_m a_n^\dagger a_n|\tilde{\Phi}_0\rangle \tag{17.29}$$

$$= \langle\tilde{\Phi}_0|\sum_m a_m^\dagger a_n \delta_{nm}|\tilde{\Phi}_0\rangle - \langle\tilde{\Phi}_0|\sum_{m,n} a_m^\dagger a_n^\dagger a_m a_n|\tilde{\Phi}_0\rangle$$

$$= \sum_m v_m^2 - \sum_{m,n}\langle\tilde{\Phi}_0|\alpha_{\bar{m}}\alpha_{\bar{n}}\alpha_{\bar{m}}^\dagger\alpha_{\bar{n}}^\dagger|\tilde{\Phi}_0\rangle v_m^2 v_n^2 - \sum_{m,n}\langle\tilde{\Phi}_0|\alpha_{\bar{m}}\alpha_n^\dagger\alpha_m\alpha_{\bar{n}}^\dagger|\tilde{\Phi}_0\rangle S_n v_n S_m v_m u_n u_m$$

$$= \sum_m v_m^2 + \sum_{m\neq n} v_m^2 v_n^2 + \sum_m v_m^2 u_m^2$$

with ($v_m^2 = 1 - u_m^2$) and

$$\langle\tilde{\Phi}_0|\mathscr{N}^2|\tilde{\Phi}_0\rangle - \langle\tilde{\Phi}_0|\mathscr{N}|\tilde{\Phi}_0\rangle^2 = \textstyle\sum_m v_m^2 + \sum_{m\neq n} v_m^2 v_n^2 + \sum_m u_m^2 v_m^2 - \sum_m v_m^4 - \sum_{m\neq n} v_m^2 v_n^2 \tag{17.30}$$

$$= \sum_m v_m^2 + \sum_m u_m^2 v_m^2 - \sum_m v_m^4 = \sum_m v_m^2 + \sum_m u_m^2 v_m^2 - \sum_m v_m^2(1-u_m^2) = 2\sum_m v_m^2 u_m^2.$$

The matrix elements of the Hamiltonian operator are

$$\langle\tilde{\Phi}_0|H|\tilde{\Phi}_0\rangle = \textstyle\sum_m \big((m|t|m) + \frac{1}{2}\sum_n (mn|V|mn)_{\not\mathscr{A}}\ v_n^2\big)v_m^2 \tag{17.31}$$

$$+\sum_{m>0,n>0}(m\bar{m}|V|n\bar{n})_{\mathscr{A}}(u_nv_n)(u_mv_m),$$

where the 1st term is a sum over **modified single-particle energies** and the second term results from the pure **pair interaction**, which disappears in the shell model limit. In (17.31) t is the one-body operator for the kinetic energy and V the two-body operator for the 2-body interaction. To prove (17.31) we transform

$$\langle\tilde{\Phi}_0|H|\tilde{\Phi}_0\rangle = \sum_{m,n}(m|t|n)\langle\tilde{\Phi}_0|a_m^\dagger a_n|\tilde{\Phi}_0\rangle+\tfrac{1}{2}\sum_{k,l,m,n}(kl|V|mn)\langle\tilde{\Phi}_0|a_k^\dagger a_l^\dagger a_n a_m|\tilde{\Phi}_0\rangle \tag{17.32}$$

to quasiparticle operators. The intermediate result is

$$\langle\tilde{\Phi}_0|a_m^\dagger a_n|\tilde{\Phi}_0\rangle = \delta_{nm}v_m^2, \tag{17.33}$$

$$\langle\tilde{\Phi}_0|a_k^\dagger a_l^\dagger a_n a_m|\tilde{\Phi}_0\rangle = \langle\tilde{\Phi}_0|\alpha_{\bar{k}}\alpha_{\bar{l}}\alpha_{\bar{n}}^\dagger\alpha_{\bar{m}}^\dagger|\tilde{\Phi}_0\rangle S_kv_kS_lv_lS_nv_nS_mv_m \tag{17.34}$$

$$+\langle\tilde{\Phi}_0|\alpha_{\bar{k}}\alpha_l^\dagger\alpha_n\alpha_{\bar{m}}^\dagger|\tilde{\Phi}_0\rangle S_kv_ku_lS_mv_mu_n.$$

Non-vanishing matrix elements in the 1st term of (17.34) only exist for $k=m, l=n$ or $k=n, l=m$ and in 2. term of (17.34) only for $n=\bar{m}, l=\bar{k}$. The evaluation yields

$$\langle\tilde{\Phi}_0|H|\tilde{\Phi}_0\rangle = \sum_m\Big((m|t|m)+\tfrac{1}{2}\sum_{m,n}(mn|V|mn)_{\mathscr{A}}v_n^2\Big)v_m^2 \tag{17.35}$$

$$+\frac{1}{2}\sum_{m,n}(m\bar{m}|V|n\bar{n})S_nS_mu_nv_nu_mv_m$$

with the antisymmetrized matrix element

$$(mn|V|mn)_{\mathscr{A}} = (mn|V|mn)-(mn|V|nm). \tag{17.36}$$

Due to the time reversal invariance of the interaction and hermiticity of the kinetic energy also holds

$$(\bar{m}|t|\bar{m}) = (m|t|m)^* = (m|t|m), \tag{17.37}$$

and

$$(\bar{m}\bar{n}|V|\bar{m}\bar{n})_{\mathscr{A}} = (mn|V|mn)_{\mathscr{A}}\ , \tag{17.38}$$

$$(m\bar{n}|V|m\bar{n})_{\mathscr{A}} = (\bar{m}n|V|\bar{m}n)_{\mathscr{A}}$$

$$S_nS_m(m\bar{m}|V|n\bar{n})+S_{\bar{n}}S_m(m\bar{m}|V|\bar{n}n) = (m\bar{m}|V|n\bar{n})_{\mathscr{A}}.$$

Summing up the contributions we obtain the result (17.35).

17.6 BCS Solutions

Since $u_m^2 + v_m^2 = 1$, the variation (17.17) with respect to the parameters u_m, v_m is not independent and one takes advantage of the fact that

$$\frac{\partial}{\partial v_m}(u_m v_m) = \frac{\partial}{\partial v_m}(\sqrt{1-v_m^2}\, v_m) = -\frac{v_m^2}{u_m} + u_m = \frac{u_m^2 - v_m^2}{u_m}. \tag{17.39}$$

To calculate the remaining variation

$$\frac{\partial}{\partial v_m}\langle \tilde{\Phi}_0 | H - \lambda \mathcal{N} | \tilde{\Phi}_0 \rangle = 0 \tag{17.40}$$

we introduce (with regards to (17.27) and (17.31)) **generalized single-particle energies**,

$$\tilde{\epsilon}_m = (m|t|m) - \lambda + \sum_n (mn|V|mn)_{\mathscr{A}}\ v_n^2\ , \tag{17.41}$$

as well as an **average pair potential**

$$\Delta_m = \sum_{n>0} (m\bar{m}|V|n\bar{n})_{\mathscr{A}}\ u_n v_n\ . \tag{17.42}$$

Equation (17.40) then gives

$$2\tilde{\epsilon}_m v_m + \Delta_m \frac{u_m^2 - v_m^2}{u_m} = 0. \tag{17.43}$$

The formal solutions of (17.43) are

$$u_m^2 = \frac{1}{2}\left(1 + \frac{\tilde{\epsilon}_m}{\sqrt{\tilde{\epsilon}_m^2 + \Delta_m^2}}\right), v_m^2 = \frac{1}{2}\left(1 - \frac{\tilde{\epsilon}_m}{\sqrt{\tilde{\epsilon}_m^2 + \Delta_m^2}}\right)\ , \tag{17.44}$$

which have to be solved iteratively. One sees immediately that

$$u_m^2 v_m^2 = \frac{1}{4}\left(1 - \frac{\tilde{\epsilon}_m^2}{\tilde{\epsilon}_m^2 + \Delta_m^2}\right) = \frac{1}{4}\frac{\Delta_m^2}{\tilde{\epsilon}_m^2 + \Delta_m^2}\ . \tag{17.45}$$

As **starting values for the iteration** one chooses

(1) the Hartree-Fock values, i.e. one sets in (17.41) $v_m^2 = 1$ for energies below the Fermi energy and $v_m^2 = 0$ above.

(2) In the **gap equation** (using (17.45)),

$$\Delta_m = \frac{1}{2}\sum_{n\neq\bar{n}} (m\bar{m}|V|n\bar{n})_{\mathscr{A}} \frac{\Delta_n}{\sqrt{\tilde{\epsilon}_n^2 + \Delta_n^2}}, \tag{17.46}$$

if $\tilde{\epsilon}_n^2$ is inserted according to step (1) and Δ_n is approximated by a state-independent **gap parameter** Δ, which results from (17.46) after division by Δ,

$$1 = \frac{1}{2}\sum_{n\neq\bar{n}} (m\bar{m}|V|n\bar{n})_{\mathscr{A}} \frac{1}{\sqrt{\tilde{\epsilon}_n^2 + \Delta^2}}. \tag{17.47}$$

The meaning of λ becomes clear if one defines the **generalized Fermi level** by

$$v_F^2 = u_F^2 = \tfrac{1}{2}; \tag{17.48}$$

then

$$\tilde{\epsilon}_F = 0 \rightarrow \lambda = \epsilon_F. \tag{17.49}$$

17.7 Excitations on the BCS Ground State

In the shell model we have assumed

$$H = H_0 + H_R, H_0 = \textstyle\sum_i \epsilon_i a_i^\dagger a_i = \sum_i e_i \alpha_i^\dagger \alpha_i \tag{17.50}$$

with the quasiparticle operators α_i from (17.18) (for $v_i = 1, 0$) and

$$e_i = \epsilon_i - \epsilon_F \quad \text{if } \epsilon_i > \epsilon_F; \tag{17.51}$$

$$e_i = \epsilon_F - \epsilon_i \quad \text{if } \epsilon_i \leq \epsilon_F \ .$$

1-particle - 1 hole ($1p - 1h$) excitations then are

$$|\Phi_{mi}\rangle = a_m^\dagger a_i |\Phi_0^{SM}\rangle = \alpha_m^\dagger \alpha_i^\dagger |\Phi_0^{SM}\rangle \tag{17.52}$$

with $i \leq N$ and $m > N$; they correspond to **2-quasiparticle excitations** with the excitation energy $\epsilon_m - \epsilon_i = e_m + e_i$.

We proceed in the same way in the BCS model with the new separation

$$H = \tilde{H}_0 + \tilde{H}_R, \tilde{H}_0 = \textstyle\sum_k \tilde{e}_k \alpha_k^\dagger \alpha_k, \tag{17.53}$$

where $\tilde{H}_0$ now also contains the parts of H_R that lead to the formation of Cooper pairs. By converting H to the BCS quasiparticle operators $\alpha_i^\dagger, \alpha_i$ we find

$$\tilde{e}_k = \sqrt{\tilde{\epsilon}_k^2 + \Delta_k^2}. \tag{17.54}$$

1-quasiparticle excitations describe systems with odd mass number, e.g. (even-odd) nuclei:

$$\alpha_n^\dagger |\tilde{\Phi}_0\rangle = a_n^\dagger \ \textstyle\prod_{n \neq k, k>0} (u_k + v_k a_k^\dagger a_{\bar{k}}^\dagger) \ |0\rangle, \tag{17.55}$$

since

$$(u_n a_n^\dagger - v_n a_{\bar{n}})(u_n + v_n a_n^\dagger a_{\bar{n}}^\dagger) \ |0\rangle = (u_n^2 + v_n^2) a_n^\dagger |0\rangle; \text{and } [\alpha_n^\dagger, a_k^\dagger a_{\bar{k}}^\dagger] = 0 \forall \ k, \bar{k} \neq n \ . \tag{17.56}$$

The ground state of an odd-even system is $\alpha_n^\dagger |\tilde{\Phi}_0\rangle$ if $\tilde{\epsilon}_n$ = 0; a $1p - 1h$ excitation of the odd-even system then is described by

$$\alpha_n^\dagger \alpha_F \alpha_F^\dagger |\tilde{\Phi}_0\rangle_{ee} = \alpha_n^\dagger \alpha_F |\tilde{\Phi}_0\rangle_{eo} \tag{17.57}$$

with the energy:

$$e_n - e_F \approx \Delta(1 + \tfrac{\tilde{\epsilon}_n}{\Delta} \cdots) - \Delta \approx \tilde{\epsilon}_n \ . \tag{17.58}$$

2-quasiparticle excitations are described by

$$\alpha^\dagger_n \alpha^\dagger_{n'} |\tilde{\Phi}_0\rangle = a^\dagger_n a^\dagger_{n'} \ \prod_{n \neq k \neq n', k>0} (u_k + v_k a^\dagger_k a^\dagger_{\bar{k}}) \ |0\rangle \tag{17.59}$$

and have the excitation energy $e_n + e_{n'}$, i.e. at least $\Delta_n + \Delta_{\bar{n}} \approx 2\Delta$ for the breakup of a Cooper pair. This explains the effects in Sect. 17.1 in a 'simple' way.

In summary, we have presented a first extension of the Hartree-Fock theory by including the attractive residual interaction of Cooper pairs, which may lead to the phenomenon of superconductivity in fermion systems at low temperature (and appropriate density).

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