

*Quantum mechanics provides the tools for a quantitative understanding of atoms and molecules. The reader is expected to be familiar at least with the main concepts. Here we want to repeat and refurbish the most important notions and methods so that we can work with them directly in the following chapters.*

## Overview

If the reader is already familiar with quantum mechanics he may just want to browse this chapter and return later if necessary. However, readers who have experienced quantum mechanics up to now only as compulsory mathematical exercise may perhaps read this chapter with advantage and find it helpful to approach the indispensable instruments without big formal hurdles. In Sects. 2.1–2.3 we summarize a minimum of formalism. Section 2.4 treats as a first example the well known particle in a box and the free electron gas which in atomic and solid state physics is an important elementary model. Section 2.5 gives an overview of how to treat angular momenta, needed in all following text, specified in Sect. 2.5.4 for the electron spin  $s = 1/2$ . Section 2.6 offers a ‘crash course’ in nonrelativistic quantum mechanics of the H atom – essential knowledge for all the following chapters. We refrain here from formal derivations in favour of a plausible, possibly somewhat hand waving introduction. Finally, Sect. 2.7 presents a first, elementary approach to interactions of atomic electrons with external fields, which will be extended and deepened in Chap. 8. Clearly, such a brief introduction into quantum mechanics cannot substitute a profound study of the formal theory. It should, however, facilitate the access to it and make the reader ‘fit’ for the following chapters.

## 2.1 Matter Waves

### 2.1.1 Limits of Classical Theory

The classical picture of a well defined trajectory with known coordinate  $x(t)$  and momentum  $p(t)$  loses its validity in quantum mechanics, as sketched in the phase

diagram Fig. 2.1: position and momentum cannot be measured simultaneously. They may only be determined with an accuracy in accordance with the uncertainty relation  $\Delta p_i \Delta x_i \geq h/2\pi$ . Quantum mechanics only makes statements about *probability amplitudes*  $\Psi(\mathbf{r}, t)$ . These may assume the form of so called *Wave-packets* which localize particles in space and time as well as the uncertainty relation allows it. One finds a particle at position  $\mathbf{r}$  and time  $t$  with the *probability*

$$w(\mathbf{r}, t) = |\Psi(\mathbf{r}, t)|^2. \quad (2.1)$$

This is the key assumption of the statistical interpretation of quantum mechanics as formulated by Max BORN (1927) in the early days of quantum mechanics, for which he received the NOBEL prize in physics in 1954. Quantum mechanics allows to describe the evolution of a wave packet quantitatively. If formed at time  $t = 0$  with widths in momentum and space,  $\Delta p_i(0)$  and  $\Delta x_i(0)$ , respectively, one finds for larger times  $t > 0$  always  $\Delta p_i(t)\Delta x_i(t) > \Delta p_i(0)\Delta x_i(0)$ : the wave packet diverges as indicated in Fig. 2.1.

### 2.1.2 Probability Amplitudes in Optics

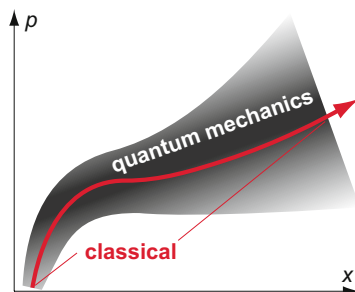
One may easily visualize the concept of a *probability amplitude* for the example of photons in a YOUNG's double slit experiment. The probability to find a photon at position  $\mathbf{r}$  and time  $t$  is proportional to the intensity  $I(\mathbf{r}, t)$  of the light, and the latter is proportional to the square of the field amplitude. Let us consider only one component of polarization, say  $E_x$ . The dependence of the intensity on position may then be written as

$$I(\mathbf{r}) \propto |E_x(\mathbf{r})|^2 = |\psi(\mathbf{r})|^2 = w(\mathbf{r}).$$

The last two equalities can help us to get used to quantum mechanical terminology: we call the quantity  $\psi(\mathbf{r})$  now the (position dependent) probability amplitude or *wave function*. In the case of light, it is simply represented by the electric field component  $E_x$ . One determines it according to the laws of optics as solution of the corresponding *wave equation*

$$\Delta\psi(\mathbf{r}) + k^2\psi(\mathbf{r}) = 0 \quad (2.2)$$

**Fig. 2.1** Classical trajectory (red line) and quantum mechanical probability (grey shaded) in phase space. Note: also at the beginning of a quantum mechanical 'trajectory', i.e. a wave-packet, its position and momentum are not precisely defined – corresponding to the uncertainty relation



(with  $\Delta = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$ ) for given boundary conditions. For optical applications a variety of approximations may be used such as HUYGENS-FRESNEL principle or the diffractions theory of KIRCHHOFF. As the wave function is derived from a linear partial differential equation (PDE), we may use the linear superposition principle to describe the interference of waves. For diffraction by two slits we thus have

$$\psi(\mathbf{r}) = \psi_1(\mathbf{r}) + \psi_2(\mathbf{r}), \quad (2.3)$$

if  $\psi_1$  and  $\psi_2$  each describe the wave from one or the other slit. With these amplitudes, the probability to find an atom at the detector positions  $\mathbf{r}$  is given by:

$$w = |\psi(\mathbf{r})|^2 = |\psi_1(\mathbf{r}) + \psi_2(\mathbf{r})|^2.$$

This expression contains interference terms  $\psi_1^* \psi_2$  and is not simply a superposition of probabilities but rather (we omit here the  $\mathbf{r}$ ):

$$w = |\psi_1|^2 + |\psi_2|^2 + 2 \operatorname{Re}(\psi_1^* \psi_2). \quad (2.4)$$

We may see this expression as a reinterpretation of the classical YOUNG double slit experiment in terms of quantum mechanical probability amplitudes.

In an actual experiment one may now reduce the light intensity such that only one single photon at a time is near the double slits and participates to the observed interference pattern. One may easily verify such a setup with a particle counter detecting single photons – one may even ‘hear the individual photons click’.<sup>1</sup> If a sufficient number of such single photon events are recorded and added up, one finds – quite counter intuitively – that the classical diffraction pattern known from optics is recovered! Thus, the *probability distribution of each individual photon* behind the double slit is determined by the wave amplitudes  $\psi = \psi_1 + \psi_2$  and it is impossible to say through which slit the particle has passed (see Fig. 1.31). One also says that *one photon always interferes only with itself*. We shall discuss this statement in some detail in Chap. 2, Vol. 2 and quantify it statistically.

### 2.1.3 Probability Amplitudes and Matter Waves

From the perspective just discussed let us have a look at the matter waves introduced in Sect. 1.7.1. We have already familiarized ourselves with the relation between momentum and wavelength as postulated by DE BROGLIE. Matter waves are

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<sup>1</sup>For the experts: One may invest a lot of thought and substantial experimental efforts to make absolutely sure that only isolated photons reach the double slit setup (for a recent review on single photon sources see EISAMAN et al. 2011). In the present context we shall be content if the average time  $t_{\text{av}}$  between each interference event (photon counted) is long compared to the coherence time of the photon source  $\tau_c = 1/\Delta\omega \ll t_{\text{av}}$ , with  $\Delta\omega$  being the bandwidth of the source (see Sect. 2.1.4, Vol. 2).

also characterized by an amplitude  $\psi(\mathbf{r})$ , determining the probability for finding a particle at position  $\mathbf{r}$  in a volume element  $d^3\mathbf{r}$ :

$$dw(\mathbf{r}) = w(\mathbf{r})d^3\mathbf{r} = |\psi(\mathbf{r})|^2 d^3\mathbf{r}. \quad (2.5)$$

And as in optics, diffraction and interference occurs, e.g. at a double slit for which (2.4) describes the experimentally observable signal of particles.

However, in contrast to electromagnetic radiation, where  $\psi$  was identified with the electric (or magnetic) field, for matter waves  $\psi(\mathbf{r})$  cannot be attributed to any directly measurable physical quantity: the observable physics is described by the probability  $w(\mathbf{r})$ . So we call  $\psi(\mathbf{r})$  simply the *probability amplitude* for finding a particle at position  $\mathbf{r}$ .

Otherwise, analogue considerations are valid for photons and particles of matter. If e.g. we try to localize them on their pathways, we loose the interference patterns! One *important general rule* holds: *interference phenomena are observed if different but indistinguishable pathways exist* on which the particles may proceed toward the detector. In contrast, no interference is observed if the two pathways may in principle be distinguished – even when no distinction is made in the actual experiment.

### Section summary

- In classical mechanics well defined trajectories in position  $\mathbf{r}(t)$  and momentum  $\mathbf{p}(t)$  space describe the motion of particles. In contrast, quantum mechanics describes probability amplitudes  $\psi(\mathbf{r})$  and probabilities  $dw(\mathbf{r}) = |\psi(\mathbf{r})|^2 d^3\mathbf{r}$  for finding a particle at a certain position  $\mathbf{r}$  in a volume element  $d^3\mathbf{r}$ .
- Diffraction and interference of matter waves can be described by concepts in analogy to those used in wave optics. The big difference is that for photons the “probability amplitude” is also a directly measurable quantity (electric or magnetic field) while for matter waves  $\psi(\mathbf{r})$  cannot be measured directly – only probabilities  $|\psi(\mathbf{r})|^2$  refer to the real world.

## 2.2 SCHRÖDINGER Equation

Wave equations for matter waves were derived independently by Erwin SCHRÖDINGER and PAUL DIRAC who in 1933 jointly received the NOBEL prize in physics for their ground breaking work. The nonrelativistic SCHRÖDINGER equation is most commonly used in AMO physics and will briefly be introduced here. As we shall see in Chap. 6, the relativistically correct DIRAC equation, valid for fermions, is significantly more complex and describes inherently also the electron spin. Its key results may, however, also be introduced as perturbations into the SCHRÖDINGER equation which then leads to sufficiently accurate results in the non relativistic energy regime.

### 2.2.1 Stationary SCHRÖDINGER Equation

In contrast to photons, particles of matter may be exposed to external forces which change their momentum and hence their wavelength. One may start from the wave equation (2.2) and try to guess, how to modify it for matter waves. Considering a particle of mass  $m$  with a total energy  $W$  moving in a conservative potential  $V(\mathbf{r})$ , we simply use the (nonrelativistic) energy conservation law of classical mechanics  $W = W_{\text{kin}} + V$  to determine its momentum from the kinetic energy  $W_{\text{kin}}$ :

$$p^2 = 2m W_{\text{kin}} = 2m(W - V(\mathbf{r})).$$

With  $W$  being a constant of motion we ‘derive’ from this and (1.118) the absolute value of the wave vector  $k = p/\hbar$  and insert it into (2.2):

$$\Delta\psi(\mathbf{r}) + \frac{p^2}{\hbar^2}\psi(\mathbf{r}) = \Delta\psi(\mathbf{r}) + \frac{2m(W - V(\mathbf{r}))}{\hbar^2}\psi(\mathbf{r}) = 0.$$

Rewritten, this is already the *stationary SCHRÖDINGER equation*

$$-\frac{\hbar^2}{2m}\Delta\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}) = W\psi(\mathbf{r}), \quad (2.6)$$

or somewhat more compact

$$\hat{H}\psi(\mathbf{r}) = W\psi(\mathbf{r}) \quad (2.7)$$

with the *eigenfunction*  $\psi(\mathbf{r})$  and the *eigenenergy*  $W$ . The HAMILTON operator  $\hat{H}$  represents the total energy (briefly just *Hamiltonian*):

$$\hat{H} = -\frac{\hbar^2}{2m}\Delta + V(\mathbf{r}). \quad (2.8)$$

In the often encountered one-dimensional case the SCHRÖDINGER equation (2.6) is further simplified:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = W\psi(x). \quad (2.9)$$

### 2.2.2 HAMILTON and Momentum Operators

We may write the HAMILTON operator (2.8) even more suggestive:

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) = \frac{\hat{\mathbf{p}}^2}{2m} + V(\mathbf{r}). \quad (2.10)$$

Here we have introduced the *momentum operator* (a vector operator)

$$\hat{\mathbf{p}} = -i\hbar\nabla = -i\hbar \begin{pmatrix} \partial/\partial x \\ \partial/\partial y \\ \partial/\partial z \end{pmatrix} \quad (2.11)$$

so that

$$\hat{\mathbf{p}}^2 = \hat{\mathbf{p}} \cdot \hat{\mathbf{p}} = -\hbar^2 \nabla^2 = -\hbar^2 \Delta = -\hbar^2 \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right). \quad (2.12)$$

Thus, (2.10) is the operator form of the *classical energy conservation law*

$$W = W_{\text{kin}} + V = \frac{p^2}{2m} + V(\mathbf{r}).$$

### 2.2.3 Time Dependent SCHRÖDINGER Equation

So far we have discussed probability amplitudes only as a function of  $\mathbf{r}$ , the particle's position in space. For many problems in [AMO](#) physics such a description of quantum systems by stationary states is fully sufficient. However, often time dependence is equally important. In respect of photons we know, that electromagnetic waves follow a time dependent wave equation, which is a 2nd order partial differential equation (PDE) in space *and* time derived from the MAXWELL equations. In contrast, for matter waves the *time dependent SCHRÖDINGER equation* holds:

$$\hat{H}\Psi(\mathbf{r}, t) = i\hbar \frac{\partial \Psi(\mathbf{r}, t)}{\partial t} \quad (2.13)$$

$$\text{or more explicitly: } -\frac{\hbar^2}{2m} \Delta \Psi(\mathbf{r}, t) + V(\mathbf{r})\Psi(\mathbf{r}, t) = i\hbar \frac{\partial \Psi(\mathbf{r}, t)}{\partial t}.$$

It cannot be derived, and we just communicate it here as it was ‘found’ by Erwin SCHRÖDINGER in the beginning of 1926 – by the way: during a winter ski holiday in the Swiss Alps. *We point out some key aspects:*

- The SCHRÖDINGER equation is a linear [PDE](#) of 2nd order in space and 1st order in time! As a consequence, time dependence of stationary states is truly complex.
- The linear superposition principle may be applied to the solutions.
- The statistical interpretation of quantum mechanics understands solutions  $\Psi(\mathbf{r}, t)$  of this [PDE](#) as probability amplitudes for finding a particle at a position  $\mathbf{r}$  in space at time  $t$  according to (2.1).
- Although the SCHRÖDINGER equation cannot be ‘derived’, it is able to describe a wealth of atomic phenomena and to predict observables quantitatively (under nonrelativistic conditions) with excellent accuracy: we emphasize that is this very fact which defines the “validity” of a physical theory.
- Equivalently, formal (algebraic) quantum mechanics can be deduced from a consistent set of axioms, which are, however, also heuristically assumed.

- Consistent alternatives of wave equations for matter waves are the DIRAC equation for fermions, a multi component spinor equation and the KLEIN-GORDON equation, a single component PDE of 2nd order in time, which turns out to be valid for bosons – both are relativistically correct.

If the *Hamiltonian itself does not depend on time*,  $\hat{H}(\mathbf{r}, t) = \hat{H}(\mathbf{r})$ , the time dependence of the wave function may be factored by a *product ansatz*:

$$\begin{aligned}\Psi(\mathbf{r}, t) &= \psi(\mathbf{r})\varphi(t) & (2.14) \\ \hat{H}\Psi(\mathbf{r}, t) &= i\hbar \frac{\partial \Psi(\mathbf{r}, t)}{\partial t} \Rightarrow \hat{H}\psi(\mathbf{r})\varphi(t) = i\hbar \frac{\partial \psi(\mathbf{r})\varphi(t)}{\partial t} \\ \frac{\hat{H}\psi(\mathbf{r})}{\psi(\mathbf{r})} &= \frac{i\hbar}{\varphi(t)} \frac{\partial \varphi(t)}{\partial t} \equiv W.\end{aligned}$$

The last identity (with the constant  $W$  which has to be determined) must hold so that the former equality can be valid for all values of  $\mathbf{r}$  and  $t$ . One thus has to solve  $i\hbar d\varphi(t)/dt = W\varphi(t)$  and  $\hat{H}\psi(\mathbf{r}) = W\psi(\mathbf{r})$ . In this case, the time dependent equation leads to the trivial solution

$$\varphi(t) \propto \exp\left(-i\frac{W}{\hbar}t\right). \quad (2.15)$$

The position dependent part is nothing but *the stationary SCHRÖDINGER equation (2.6)* and the parameter  $W$  introduced is *the total energy of the system*. The overall wave function is given by

$$\Psi(\mathbf{r}, t) = \psi(\mathbf{r}) \exp\left(-i\frac{W}{\hbar}t\right). \quad (2.16)$$

*Note:* The time dependence is truly complex and the imaginary unit  $i$  in the prefactor is needed for the solution! In the present case, however, with  $\hat{H} \neq \hat{H}(t)$  the time dependence is trivial in the sense that only

$$w(\mathbf{r}, t) = |\Psi(\mathbf{r}, t)|^2 = |\psi(\mathbf{r})|^2 \quad (2.17)$$

can be measured, which contains only information about the stationary state.

*In order to find these stationary atomic states* for a given potential  $V(\mathbf{r})$  – which are the equivalent to BOHR's stationary orbits – one has to solve the stationary SCHRÖDINGER equation (2.6) under suitably chosen boundary conditions. For bound states this typically leads to a whole *series of discrete total energies*  $W_\gamma < 0$  with a set of *quantum numbers*  $\gamma$  characterizing the states. The corresponding *series of wave functions* – for individual electrons called *orbitals* – describe the probability of finding the particles at a given position in space.

### 2.2.4 Freely Moving Particle – The Most Simple Example

As the most simple example we consider now a freely moving particle with mass  $m$ , (kinetic) energy  $W$  and momentum  $\mathbf{p}$ . The relevant stationary SCHRÖDINGER equation (2.6) reads

$$-\frac{\hbar^2}{2m}\Delta\psi(\mathbf{r}) = W\psi(\mathbf{r}) \quad \text{and has solutions} \quad \psi(\mathbf{r}) = C \cdot \exp(i\mathbf{k}\mathbf{r}). \quad (2.18)$$

As one verifies by inserting the solution with wave vector  $\mathbf{k} = \mathbf{p}/\hbar$  into the equation, the total energy is given by  $W = \hbar^2 k^2/(2m) = p^2/(2m) = W_{\text{kin}}$ . With the time dependence (2.16) the whole probability amplitude for this free particle is simply a plane wave:

$$\begin{aligned} \Psi(\mathbf{r}, t) &= C \cdot \exp[-i(\omega t - \mathbf{k}\mathbf{r})] = C \cdot \exp\left[-i\left(\frac{\hbar k^2}{2m}t - \mathbf{k}\mathbf{r}\right)\right] \\ &= C \cdot \exp\left[-i\left(\frac{W}{\hbar}t - \frac{\mathbf{p}\mathbf{r}}{\hbar}\right)\right]. \end{aligned} \quad (2.19)$$

With this we obtain the important *dispersion relation for free matter waves*:

$$\omega = \frac{W}{\hbar} = \frac{p^2}{2m\hbar} = \frac{\hbar k^2}{2m} = \omega(k) \quad \text{or} \quad W = \frac{\hbar^2}{2m}k^2. \quad (2.20)$$

*Note:* The probability to find this particle,  $w(\mathbf{r}, t) = |\Psi(\mathbf{r}, t)|^2 = |C|^2$ , is independent of position and time – as expected for an infinitely extended plane wave. In other words, a particle with well defined momentum may not be localized at all – as expected according to the uncertainty relation (1.123).

#### Section summary

- The stationary SCHRÖDINGER equation (2.6) may be gleaned from the classical wave equation combined with a free interpretation of the DE BROGLIE wavelength in a conservative potential. It is validated by the excellent agreement of its predictions with experimentally observed data in the sub-microscopic world at nonrelativistic energies.
- In its most compact form it reads  $\hat{H}\psi = W\psi$ , where the HAMILTON operator (2.10), also called Hamiltonian, is constructed in full analogy to its classical counterpart, just replacing the momentum by the quantum mechanical momentum operator  $\hat{\mathbf{p}} = -i\hbar\nabla$ .
- The time dependence of the wave function is described by the time dependent SCHRÖDINGER equation (2.13). In the case that the Hamiltonian itself is not time dependent, the (stationary) solutions are given by the product of the solutions  $\psi(\mathbf{r})$  of the stationary equation (2.6) and a simple exponential function  $\propto \exp(-i(W/\hbar)t)$ .
- The most simple solution of the time dependent SCHRÖDINGER equation is a plane wave  $\exp[-i((W/\hbar)t - \mathbf{k}\mathbf{r})]$ , with the energy  $W = \hbar^2 k^2/(2m)$ .



## 2.3 Basics and Definitions of Quantum Mechanics

### 2.3.1 Axioms, Terminology and Rules

Here we summarize briefly the fundamental axioms of quantum mechanics and recall some terminology and rules which we shall use later on:

#### Quantum States and Wave Functions

*States of quantum systems* (in the world, in atomic physics ...) are described by *state vectors* for which we introduce here the “*bra*” and “*ket*” notation of DIRAC,  $\langle\psi|$  and  $|\psi\rangle$ , respectively. Typically, states may be expressed in terms of *basis states*, or basis vectors, say  $|f_1\rangle, |f_2\rangle, |f_3\rangle, \dots, |f_n\rangle, \dots$ . We speak about a *complete basis set*, if each state of a system can be written as *ket vector*

$$|\psi\rangle = \sum_{i=1}^{\infty} c_i |f_i\rangle, \quad \text{alternatively as } \textit{bra vector} \quad \langle\psi| = \sum_{i=1}^{\infty} c_i^* \langle f_i|. \quad (2.21)$$

*Note:* the sum includes all bound (discrete) and free (continuum) states.

One calls a *basis orthonormal* if

$$\langle f_k | f_i \rangle = \delta_{ki}, \quad (2.22)$$

where  $\langle\phi|\psi\rangle$  is the *scalar product* of two state vectors  $|\psi\rangle$  and  $|\phi\rangle$ . With this, the projection of the state  $|\psi\rangle$  onto the basis vector  $|f_k\rangle$  is

$$\langle f_k | \psi \rangle = \sum_{i=1}^{\infty} c_i \langle f_i | f_k \rangle = c_k. \quad (2.23)$$

Wave functions, the most commonly used representation of states, are formally obtained by expanding  $|\psi\rangle$  in a continuous “position basis”  $\{|\mathbf{r}\rangle\}$  where  $\mathbf{r}$  extends over all points in 3D position space. We write (2.21) as *ket*

$$|\psi\rangle = \iiint d^3\mathbf{r}' \psi(\mathbf{r}') |\mathbf{r}'\rangle \quad \text{or as } \textit{bra} \quad \langle\psi| = \iiint d^3\mathbf{r}' \psi^*(\mathbf{r}') \langle\mathbf{r}'|. \quad (2.24)$$

Per definition we have, in analogy to (2.22),

$$\langle\mathbf{r}|\mathbf{r}'\rangle = \delta(\mathbf{r} - \mathbf{r}'), \quad (2.25)$$

and obtain from (2.24) the *definition of a wave function in position space*,

$$\langle\mathbf{r}|\psi\rangle = \langle\psi|\mathbf{r}\rangle^* = \iiint d^3\mathbf{r}' \psi(\mathbf{r}') \langle\mathbf{r}|\mathbf{r}'\rangle = \psi(\mathbf{r}), \quad (2.26)$$

and  $\psi^*(\mathbf{r}) = \langle \psi | \mathbf{r} \rangle$ . In practice, wave functions are determined by solving the stationary SCHRÖDINGER equation. With (2.24) and (2.25) we derive (after one 3D integration) the *scalar product in terms of wave functions*:<sup>2</sup>

$$\langle \psi | \phi \rangle = \iiint \psi^*(\mathbf{r}) \phi(\mathbf{r}) d^3\mathbf{r} = \langle \phi | \psi \rangle^*. \quad (2.27)$$

For the eigenstates  $|\psi_k\rangle$  of the SCHRÖDINGER equation the *orthonormality relation* (2.22) thus reads:

$$\langle \psi_i | \psi_k \rangle = \iiint \psi_i^*(\mathbf{r}) \psi_k(\mathbf{r}) d^3\mathbf{r} = \delta_{ik}. \quad (2.28)$$

We finally note that, equivalent to the state expansion in position space, one may define wave functions  $\psi(\mathbf{p})$  in momentum space by

$$\begin{aligned} |\psi\rangle &= \iiint d^3\mathbf{p}' \psi(\mathbf{p}') |\mathbf{p}'\rangle \quad \text{and} \\ \langle \mathbf{p} | \psi \rangle &= \iiint d^3\mathbf{p}' \psi(\mathbf{p}') \langle \mathbf{p} | \mathbf{p}' \rangle = \psi(\mathbf{p}). \end{aligned}$$

## Operators

Linear operators play a key role in quantum mechanics: in general an operator changes an object onto which it acts (e.g. a state vector, a wave function, another operator) into something different. Let us call the operator  $\hat{A}$  and let it act on a ket vector  $|\psi\rangle$ :

$$\hat{A}|\psi\rangle = |\tilde{\psi}\rangle.$$

Linearity implies that for a superposition of states  $|\psi\rangle = c_1|\psi_1\rangle + c_2|\psi_2\rangle + \dots$

$$\hat{A}(c_1|\psi_1\rangle + c_2|\psi_2\rangle + \dots) = c_1\hat{A}|\psi_1\rangle + c_2\hat{A}|\psi_2\rangle + \dots.$$

The product of two operators  $\hat{A}\hat{B}$  is defined by

$$(\hat{A}\hat{B})|\psi\rangle = \hat{A}(\hat{B}|\psi\rangle). \quad (2.29)$$

Operator multiplication is distributive, i.e.  $\hat{A}\hat{B}\hat{C} = (\hat{A}\hat{B})\hat{C} = \hat{A}(\hat{B}\hat{C})$  but not necessarily commutative. In general  $\hat{A}\hat{B} \neq \hat{B}\hat{A}$  and one defines a *commutator*

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} \quad (2.30)$$

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<sup>2</sup>We shall use the  $\langle \text{bra} |$  and  $| \text{ket} \rangle$  symbols rather loosely. In particular, we shall often write wave functions simply as  $|\psi\rangle$ ,  $|\psi_k\rangle$ , etc.

which only in special cases may vanish (see Sect. 2.3.3). With  $|\psi\rangle$  and  $|\phi\rangle$  being two state vectors or wave functions one defines as *matrix element of  $\hat{A}$*  between states  $|\phi\rangle$  and  $|\psi\rangle$  (which may or may not be basis states of an operator  $\hat{A}$ ):

$$A_{\psi\phi} = \langle\psi|\hat{A}\phi\rangle = \int \psi^*(\hat{A}\phi) d^3\mathbf{r}. \quad (2.31)$$

Without going into details we define the so called *adjoint* (or *Hermitian conjugate*) operator  $\hat{A}^\dagger$  by

$$\langle\hat{A}^\dagger\psi|\phi\rangle = \langle\psi|\hat{A}\phi\rangle \quad \text{or} \quad \langle\phi|\hat{A}^\dagger\psi\rangle = \langle\psi|\hat{A}\phi\rangle^* \quad (2.32)$$

$$\text{or} \quad \int (\hat{A}^\dagger\psi)^*\phi d^3\mathbf{r} = \int \psi^*(\hat{A}\phi) d^3\mathbf{r}. \quad (2.33)$$

Of particular importance are the so called *Hermitian operators*, let us call them  $\hat{O}$ . They are *self-adjoint*:

$$\hat{O}^\dagger \equiv \hat{O}. \quad (2.34)$$

By this definition and with (2.31)–(2.33) the matrix elements

$$\langle\hat{O}\psi|\phi\rangle = \langle\psi|\hat{O}\phi\rangle = \int (\hat{O}\psi)^*\phi d^3\mathbf{r} = \int \psi^*(\hat{O}\phi) d^3\mathbf{r} \quad (2.35)$$

$$= \langle\psi|\hat{O}\phi\rangle = \langle\phi|\hat{O}\psi\rangle^* \quad (2.36)$$

are all equivalent for Hermitian operators.<sup>3</sup>

## Observables

*Observables* are all physical quantities which can in principle be measured (observed). Every quantity which is observable in classical physics is *represented quantum mechanically by a linear Hermitian operator*, let us call it  $\hat{O}$ . A quantum system can be characterized by a set of eigenstates (eigenvectors)  $|f_k\rangle$  of an observable  $\hat{O}$  which it may in principle assume. From the eigenvalue equation

$$\hat{O}|f_k\rangle = \omega_k|f_k\rangle \quad (2.37)$$

one determines the *eigenvalues*  $\omega_k$  of the *observable*  $\hat{O}$  for the *eigenvectors*  $|f_k\rangle$ . In any individual physical measurement of the observable  $\hat{O}$  *only one of its eigenvalues  $\omega_k$  can be observed*.

From (2.37) and the orthonormality of the  $|f_k\rangle$  basis one sees that the *matrix elements of  $\hat{O}$  in the basis of its eigenstates* between  $|f_i\rangle$  and  $|f_k\rangle$  are

$$O_{ik} = \langle f_i|\hat{O}|f_k\rangle = \omega_k\delta_{ik}, \quad (2.38)$$

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<sup>3</sup>To verify these relations one simply expands  $|\psi\rangle$  and  $|\phi\rangle$  in a basis of eigenvectors (eigenfunctions) of  $\hat{O}$ .

i.e. the matrix  $\widehat{O}_{ik}$  is diagonal and because of (2.36) the eigenvalues  $\omega_k$  must be real – as one has to demand for measurable quantities!

### Superposition and Expectation Values

In general, a quantum systems to be investigated may be found in a *state*  $|\psi\rangle$  which is not an eigenstate of the operator  $\widehat{O}$ . Let the state  $|\psi\rangle$  be a linear superposition of eigenstates  $|f_i\rangle$  of the operator  $\widehat{O}$  with eigenvalues  $\omega_i$  according to (2.37):

$$|\psi\rangle = \sum_i c_i |f_i\rangle \quad \text{with the expansion coefficients} \quad c_i = \langle f_i | \psi \rangle. \quad (2.39)$$

The latter relation follows directly with (2.22). If we measure now the observable  $\widehat{O}$  many times (as one does in a real experiment), the result of each individual measurement is one of the eigenvalues  $\omega_i$  of  $\widehat{O}$ . The probability to detect this particular eigenvalue  $\omega_i$  is determined by the probability amplitude  $c_i$ :

$$\widehat{O}|\psi\rangle = \widehat{O} \sum c_i |f_i\rangle = \sum c_i \omega_i |f_i\rangle. \quad (2.40)$$

The average value measured for this observable, i.e. the result of many individual measurements applied to the same state  $|\psi\rangle$ , is called *expectation value of the observable*:

$$\langle \widehat{O} \rangle \equiv \sum |c_i|^2 \omega_i = \langle \psi | \widehat{O} | \psi \rangle. \quad (2.41)$$

The latter identity follows from

$$\begin{aligned} \langle \psi | \widehat{O} | \psi \rangle &= \left\langle \sum_i c_i f_i \left| \widehat{O} \sum_k c_k f_k \right. \right\rangle = \left\langle \sum_i c_i f_i \left| \sum_k c_k \widehat{O} f_k \right. \right\rangle \\ &= \sum_i \sum_k \omega_k c_i^* c_k \langle f_i | f_k \rangle = \sum_i \sum_k \omega_k c_i^* c_k \delta_{ik} = \sum_i \omega_i |c_i|^2. \end{aligned}$$

Somewhat more general, if the state of the system is  $|\psi\rangle = \sum_i c_i^{(\psi)} |g_i\rangle$ , i.e. it is given in an arbitrary basis  $\{|g_i\rangle\}$  and  $|g_i\rangle$  are not eigenstates of  $\widehat{O}$ , its expectation value is

$$\langle \widehat{O} \rangle = \langle \psi | \widehat{O} | \psi \rangle = \sum_i c_i^{*(\psi)} \langle g_i | \widehat{O} | \sum_k c_k^{(\psi)} |g_k\rangle = \sum_{ik} c_i^{*(\psi)} \langle g_i | \widehat{O} | g_k \rangle c_k^{(\psi)}. \quad (2.42)$$

### Unit Operator

We note in passing a nice mathematical trick by rewriting (2.39) as

$$|\psi\rangle = \sum_i |f_i\rangle c_i = \sum_i |f_i\rangle \langle f_i | \psi \rangle = \left( \sum_i |f_i\rangle \langle f_i| \right) |\psi\rangle.$$

From this we deduce the often very useful fact that the *quantum mechanical unit operator*<sup>4</sup> (which does not change the operand) may be written as

$$\hat{\mathbf{1}} = \sum_i |f_i\rangle\langle f_i|, \quad (2.43)$$

as long as the states  $|f_i\rangle$  represent a complete orthogonal basis and the summation goes over all states of this basis.

### Quantization

Experimentally, when an observable  $\hat{O}$  is determined in an individual measurement one always finds one of its *eigenvalues*. With the measurement one prepares also the corresponding *eigenfunction* (*eigenstate*, *eigenvector*) of the observable  $\hat{O}$ . One may say that by a measurement one projects the eigenvector out of the state  $|\psi\rangle$  under investigation.

### Example: HAMILTON Operator

The eigenvalues of the HAMILTON operator  $\hat{H}$  are the eigenenergies  $W_n$  of a system. Thus, the Hamiltonian is a particularly important example of an observable. Its eigenvectors  $|\psi_n\rangle$  and eigenenergies are determined by solving the SCHRÖDINGER equation (2.7). We may also write it in algebraic form:

$$\hat{H}|\psi_n\rangle = W_n|\psi_n\rangle.$$

### Example: Spin Projection onto the z-Axis

As a further example we mention the projection of the spin of a particle onto a given axis in 3D space. Typically, but not necessarily, one measures the  $\hat{S}_z$  component of the spin. We have already discussed such a measurement in Sect. 1.10, the STERN-GERLACH experiment. The eigenvalues are here  $m_s\hbar$  and we write the eigenstates quite formally as  $|sm_s\rangle$ . The eigenvalue equation is then

$$\hat{S}_z|sm_s\rangle = m_s\hbar|sm_s\rangle.$$

## 2.3.2 Representations

We have already made use of different ways to describe quantum systems and their changes. The standard terminology speaks about *representations* of states and operators.

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<sup>4</sup>In matrix representation this corresponds to the identity matrix

$$\hat{\mathbf{1}} = \begin{pmatrix} 1 & 0 & \cdots & 0 \\ 0 & 1 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & 1 \end{pmatrix}.$$

### SCHRÖDINGER Representation

In the SCHRÖDINGER *representation (or picture)* the operators are *differential operators*. The states are represented by *wave functions*. The scalar product is an integral according to (2.27) and the orthogonality of basis states is defined by (2.28). The *matrix elements* of an operator  $\hat{A}$  in respect of an arbitrary basis set  $|f_k\rangle, |f_i\rangle, \dots$  (in general not eigenfunctions of  $\hat{A}$ ) are

$$A_{ik} \equiv \langle f_i | \hat{A} f_k \rangle = \int f_i^*(\mathbf{r}) \hat{A} f_k(\mathbf{r}) d^3\mathbf{r} = \langle f_k | \hat{A}^\dagger f_i \rangle^* = A_{ki}^{\dagger*}, \quad (2.44)$$

where we have used the definition of adjoint operators (2.32). If the operator is Hermitian, i.e. represents and observable, this relation reads

$$O_{ik} \equiv \langle f_i | \hat{O} f_k \rangle = \int f_i^*(\mathbf{r}) (\hat{O} f_k(\mathbf{r})) d^3\mathbf{r} \quad (2.45)$$

$$= \left[ \int (\hat{O} f_k^*(\mathbf{r}))^* f_i(\mathbf{r}) d^3\mathbf{r} \right]^* = \langle f_k | \hat{O} f_i \rangle^* = O_{ki}^*. \quad (2.46)$$

### HEISENBERG Representation

In the HEISENBERG *representation (or picture)* the operators (we mention in this context the NOBEL prize for HEISENBERG 1932)  $\hat{A}$  are matrices, which are determined by their matrix elements  $A_{ik}$ . The states, say  $|\psi\rangle$  or  $|\phi\rangle$ , are *vectors in HILBERT space*<sup>5</sup> which we write

$$|\psi\rangle = \boldsymbol{\psi} = b_1 \mathbf{f}_1 + b_2 \mathbf{f}_2 + b_3 \mathbf{f}_3 + \dots$$

$$|\phi\rangle = \boldsymbol{\phi} = c_1 \mathbf{f}_1 + c_2 \mathbf{f}_2 + c_3 \mathbf{f}_3 + \dots$$

with their components  $b_i \mathbf{f}_i$  or  $c_i \mathbf{f}_i$ , respectively. The scalar product is here

$$\langle \psi | \phi \rangle = \sum b_i^* c_i. \quad (2.47)$$

*Both representations are physically as well as mathematically fully equivalent.*

### 2.3.3 Simultaneous Measurement of Two Observables

The following is a generalization of the HEISENBERG uncertainty relation which states that two canonically conjugate coordinates, such as position and momentum, cannot be measured simultaneously.

*Two observables  $\hat{A}$  and  $\hat{B}$  can be measured simultaneously if and only if the eigenstates of  $\hat{A}$  are also eigenstates of  $\hat{B}$ , i.e. if the following holds:*

$$\hat{A}|\varphi_i\rangle = \alpha_i |\varphi_i\rangle \quad \text{and} \quad \hat{B}|\varphi_i\rangle = \beta_i |\varphi_i\rangle.$$

<sup>5</sup>A HILBERT space is an extension of the 3D vector space to an arbitrary or infinite number of dimensions – in quantum mechanics to an infinite dimensional function space.

Thus, also the following relations must be valid for *simultaneous measurability* of the operators  $\hat{A}$  and  $\hat{B}$ :

$$\hat{A}\hat{B}|\varphi_i\rangle = \hat{A}\beta_i|\varphi_i\rangle = \beta_i\hat{A}|\varphi_i\rangle = \beta_i\alpha_i|\varphi_i\rangle = \hat{B}\hat{A}|\varphi_i\rangle.$$

Hence, the operators must commute,  $\hat{A}\hat{B} \stackrel{!}{=} \hat{B}\hat{A}$ . Equivalently:

*Simultaneous measurement of two observables  $\hat{A}$  and  $\hat{B}$  is possible if and only if their commutator vanishes:*

$$\hat{A}\hat{B} - \hat{B}\hat{A} = [\hat{A}, \hat{B}] = 0. \quad (2.48)$$

### 2.3.4 Operators for Space, Momentum and Energy

From the above follow some simple recipes of how to translate classical quantities into quantum mechanical operators. One simply has to substitute:

$$\begin{aligned} \mathbf{r} &\longrightarrow \mathbf{r} \quad \text{and} \quad p_i \longrightarrow -i\hbar \frac{\partial}{\partial x_i} = \hat{p}_i \\ \text{or} \quad \mathbf{p} &\longrightarrow \left( -i\hbar \frac{\partial}{\partial x}, -i\hbar \frac{\partial}{\partial y}, -i\hbar \frac{\partial}{\partial z} \right) = -i\hbar \nabla = \hat{\mathbf{p}}. \end{aligned} \quad (2.49)$$

All other substitutions are derived from these rules. In particular, the classical Hamiltonian total energy

$$H_{\text{class}} = \frac{p^2}{2m} + V(\mathbf{r}) = W_{\text{kin}} + V \quad \text{with } p^2 = \mathbf{p} \cdot \mathbf{p}$$

becomes the HAMILTON operator:

$$\hat{H} = \frac{1}{2m} (-i\hbar \nabla) \cdot (-i\hbar \nabla) + V(\mathbf{r}) = -\frac{\hbar^2}{2m} \Delta + V(\mathbf{r}).$$

Position in space  $x$  and its canonically conjugate momentum  $\hat{p}_x$  are the prime example for *non-commuting observables*. As seen from comparing

$$\begin{aligned} \hat{p}_x x \varphi(x) &= -i\hbar \frac{\partial}{\partial x} (x \varphi(x)) = -i\hbar \left( x \frac{\partial}{\partial x} \varphi(x) + \varphi(x) \right) \\ \text{with } x \hat{p}_x \varphi(x) &= -i\hbar x \frac{\partial}{\partial x} \varphi(x) \end{aligned}$$

the commuted operators  $\hat{p}_x x$  and  $x \hat{p}_x$  generate completely different results – and hence, the observables  $x$  and  $\hat{p}_x$  cannot be measured simultaneously. This is, so to say, a formal endorsement of the HEISENBERG uncertainty relation.

### 2.3.5 Eigenfunctions of the Momentum Operator $\hat{p}$

We shall now find the eigenfunctions and eigenvalues of the momentum in the SCHRÖDINGER picture, starting with the one dimensional case:

$$\hat{p}_x \varphi(x) = p_x \varphi(x) \quad \Rightarrow \quad -i\hbar \frac{d\varphi(x)}{dx} = p_x \varphi(x).$$

One easily verifies that  $\varphi(x) = \exp(ip_x x/\hbar) = \exp(ik_x x)$  are solutions of this eigenvalue problem. Each value of  $p_x$  (with  $-\infty < p_x < \infty$ ) is an eigenvalue of the momentum operator  $\hat{p}_x$  in  $x$ -direction: the eigenfunction is thus a plane wave with a continuum of eigenvalues.

This is easily extended into 3D space. The eigenvalue equation

$$\hat{\mathbf{p}}\varphi(\mathbf{r}) = -i\hbar\nabla\varphi(\mathbf{r}) = \hbar\mathbf{k}\varphi(\mathbf{r}) \quad \text{is solved by}$$

a plane wave  $\varphi(\mathbf{r}) = C \exp(i\hbar\mathbf{k} \cdot \mathbf{r}).$

The unit directional vector for an arbitrary direction in space is  $\mathbf{e} = a_x \mathbf{e}_x + a_y \mathbf{e}_y + a_z \mathbf{e}_z$  with  $a_x^2 + a_y^2 + a_z^2 = 1$ . If we are interested in the magnitude of the momentum  $\mathbf{p}$  in any given direction  $\mathbf{e}$ , the operator providing this information is:

$$\hat{p}_e = \mathbf{e} \cdot \hat{\mathbf{p}} = a_x \hat{p}_x + a_y \hat{p}_y + a_z \hat{p}_z = -i\hbar \left( a_x \frac{\partial}{\partial x} + a_y \frac{\partial}{\partial y} + a_z \frac{\partial}{\partial z} \right). \quad (2.50)$$

Any plane wave  $\exp(i\mathbf{k} \cdot \mathbf{r})$  in arbitrary direction  $\mathbf{k}$  and with arbitrary magnitude  $k$  is an eigenfunction of  $\hat{p}_e$ , with eigenvalue  $p \cos \gamma$ , as one easily verifies

$$\begin{aligned} \hat{p}_e \exp(i\mathbf{k} \cdot \mathbf{r}) &= \hbar(a_x k_x + a_y k_y + a_z k_z) \exp(i\mathbf{k} \cdot \mathbf{r}) = \mathbf{e} \cdot \hbar\mathbf{k} \exp(i\mathbf{k} \cdot \mathbf{r}) \\ &= \hbar k \cos \gamma \exp(i\mathbf{k} \cdot \mathbf{r}) = p \cos \gamma \exp(i\mathbf{k} \cdot \mathbf{r}), \end{aligned} \quad (2.51)$$

with  $p = \hbar k$  and the angle  $\gamma$  between  $\mathbf{e}$  and  $\mathbf{k}$  – just as one would guess.

#### Section summary

- In the SCHRÖDINGER picture, states (bra  $|\psi\rangle$  and ket  $\langle\phi|$ ) of quantum systems are represented by wave functions  $\psi(\mathbf{r})$  and  $\psi^*(\mathbf{r})$ , respectively. The HEISENBERG picture uses state vectors in HILBERT space.
- Quantum states may be expressed as a linear superposition of states (2.21) from a complete, orthonormal basis – with  $\langle f_i | f_k \rangle = \delta_{ik}$ . The unit operator may be written  $\sum_i |f_i\rangle\langle f_i|$ .
- The SCHRÖDINGER representation uses differential operators. Classical theory is translated by replacing  $\mathbf{r} \rightarrow \mathbf{r}$  and  $\mathbf{p} \rightarrow \hat{\mathbf{p}} = -i\hbar\nabla$ .
- Matrix elements of an operator  $\hat{A}$  are  $A_{ik} \equiv \langle f_i | \hat{A} f_k \rangle = \int f_i^*(\mathbf{r}) \hat{A} f_k(\mathbf{r}) d^3\mathbf{r}$  in the SCHRÖDINGER picture. In the Heisenberg representation operators are defined by the corresponding matrices.
- The adjoint  $\hat{A}^\dagger$  of an operator  $\hat{A}$  is defined by  $\langle \hat{A}^\dagger \psi | \phi \rangle = \langle \psi | \hat{A} \phi \rangle$ . Hermitian operators are self-adjoint  $\hat{A}^\dagger = \hat{A}$ , and  $\hat{A}_{ik} = \hat{A}_{ki}^*$  holds.



- Observables are represented by Hermitian operators. With  $\hat{O}|f_k\rangle = \omega_k|f_k\rangle$  their eigenvalues  $\omega_k$  are the only values of that observable which can be observed experimentally.
- Such an experiment projects the eigenstate  $|f_k\rangle$  of the observable out of a state  $|\psi\rangle$  under investigation. If the operators for two observables,  $\hat{A}$  and  $\hat{B}$ , commute (commutator  $[\hat{A}\hat{B}] = 0$ ) they can be measured simultaneously.
- The average value of an observable in a state  $|\psi\rangle$  is called its *expectation value*:  $\langle\hat{O}\rangle = \langle\psi|\hat{O}|\psi\rangle = \int \psi^*(\hat{O}\psi)d^3\mathbf{r}$ .
- Eigenstates of the momentum operator  $\hat{\mathbf{p}}$  are plane waves  $\exp(i\hbar\mathbf{k} \cdot \mathbf{r})$ , with  $\mathbf{p} = \hbar\mathbf{k}$ .

## 2.4 Particles in a Box – And the Free Electron Gas

### 2.4.1 One Dimensional Potential Box

We first consider the one dimensional problem of a particle in a potential box, i.e. between two infinitely high walls at a distance  $L$ . In between the walls, the 1D SCHRÖDINGER equation (2.9) simply reads

$$-\frac{\hbar^2}{2m} \frac{d^2\psi_n(x)}{dx^2} = W_n\psi_n(x).$$

Solutions can in principle be  $\psi(x) = \sin(kx)$  or  $\cos(kx)$ . However, since the wave function cannot penetrate into the wall, it must vanish on the walls which at  $x = 0$  is only possible for the  $\sin(kx)$  solution. For continuity on the other wall  $\sin(kL) = 0$  and thus  $k = n\pi/L$  must hold, with  $n = 1, 2, 3, \dots$ . In summary, the solutions (eigenfunctions) are standing waves with nodes on both walls of the box. The eigenenergies assume discrete values  $W_n$ :

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \quad \text{with } W_n = \frac{\hbar^2 k^2}{2m} = \frac{h^2 n^2}{8mL^2}. \quad (2.52)$$

The expectation value of the momentum  $\hat{p}_x$  is derived from

$$\begin{aligned} \langle\hat{p}_x\rangle &= \langle\psi_n|\hat{p}_x|\psi_n\rangle = \int \psi_n^*(x)\hat{p}_x\psi_n(x)dx \\ &= \frac{2}{L} \int_0^L \sin \frac{n\pi x}{L} \left(-i\hbar \frac{d \sin \frac{n\pi x}{L}}{dx}\right) dx \\ &= \frac{-i\hbar 2n\pi}{L^2} \int_0^L \sin \frac{n\pi x}{L} \cos \frac{n\pi x}{L} dx \equiv 0. \end{aligned}$$

This corresponds to the fact that the particle in the box moves with equal probability back and forth. In contrast, the square of the momentum,

$$\langle\hat{p}_x^2\rangle = \langle\psi_n|\hat{p}_x^2|\psi_n\rangle = \int \psi_n^*\hat{p}_x^2\psi_n dx = \frac{2}{L} \int_0^L \sin \frac{n\pi x}{L} \left(\hbar^2 \frac{d^2 \sin \frac{n\pi x}{L}}{dx^2}\right) dx$$

$$= \frac{2(n\pi\hbar)^2}{L^3} \int_0^L \sin^2 \frac{n\pi x}{L} dx = \frac{1}{4} \frac{\hbar^2}{L^2} n^2,$$

is not zero. With this and  $\langle \hat{H} \rangle = \langle \hat{p}_x^2 \rangle / 2m$  we verify  $W_n$  in (2.52).

### 2.4.2 Three Dimensional Potential Box

A next step towards reality is the extension into the 3D space. The movement of a particle is now restricted to a large but finite 3-dimensional box, with rigid walls beyond which the probability to find a particle is zero. For simplicity we assume the box to be a cube with edge length  $L$  as illustrated in Fig. 2.2(a). Inside the box particles move freely. Stationary solutions are plane waves (2.18) which we write in the box as real functions – now as product in three dimensions:

$$\psi(x, y, z) = \sin(k_x x) \sin(k_y y) \sin(k_z z). \quad (2.53)$$

To be continuous, the wave function must vanish on the walls of the cube:

$$\sin(k_j L) = 0 \quad \Rightarrow \quad k_j = n_j \frac{\pi}{L} \quad \text{for } j = x, y, z. \quad (2.54)$$

With these boundary conditions, and in analogy to the 1D case (2.52),

*the energy of the particle in a box becomes*

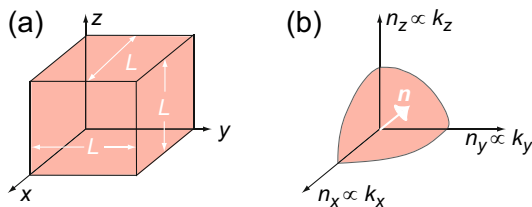
$$W = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2) = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 \pi^2}{2m L^2} n^2, \quad (2.55)$$

now with three integer quantum numbers  $n_x, n_y, n_z$  and  $n^2 = n_x^2 + n_y^2 + n_z^2$ .

One may view this in  $\mathbf{k}$  or  $\mathbf{n}$  space as indicated in Fig. 2.2(b). Equation (2.54) says that precisely one solution exists for each lattice point with integer  $n_x, n_y$  and  $n_z$ . Thus, one reads from the figure that the total number of states with quantum numbers 1 to  $n_x$ , 1 to  $n_y$  and 1 to  $n_z$ , i.e. the number of states with  $n \leq \sqrt{n_x^2 + n_y^2 + n_z^2}$  is given by  $\mathcal{N}_Z(n) = 1/8 \times 4\pi/3 n^3$ . Expressing  $n$  by the energy  $W$ , the total number of states with energies  $\leq W$  is

$$\mathcal{N}_Z(W) = \frac{1}{6\pi^2} \frac{(2mW)^{3/2}}{\hbar^3} L^3.$$

**Fig. 2.2** Boundary condition for a particle in a potential box (cube of edge length  $L$ ); (a) the nodes of the wave function are on the walls of the box in 3D position space; (b) one counts the number of states  $n$  in the  $\mathbf{n}$  or  $\mathbf{k}$  space



If the particle has a spin  $s$ , we also have to account for the energy degenerate  $g_e = 2s + 1$  possible orientations in space. Dividing by the volume of the box  $L^3$ , we obtain the total number of available states per unit volume:

$$N_Z(W) = \frac{g_e}{6\pi^2} \frac{(2mW)^{3/2}}{\hbar^3}. \quad (2.56)$$

From this we derive the number of states in an energy interval from  $W$  to  $W + dW$ , called *density of states* (DOS), here per unit volume:

$$g(W) = \frac{dN_Z(W)}{dW} = \frac{g_e}{4\pi^2} \frac{(2m)^{3/2}}{\hbar^3} \sqrt{W} = g_e \frac{4\sqrt{2}\pi m^{3/2}}{\hbar^3} \sqrt{W}. \quad (2.57)$$

We note in passing, that assuming the *phase space to be quantized in unit cells of size  $h^3$*  leads to exactly the same result.<sup>6</sup> For later use we also give the density of states in respect of a specific element of solid angle  $d\Omega$  and express the energy by  $k$ , the magnitude of the wave vector:

$$dg = \frac{d^2 N_Z(W)}{dW} \frac{d\Omega}{4\pi} = \frac{g_e m k}{(2\pi)^3 \hbar^2} d\Omega. \quad (2.58)$$

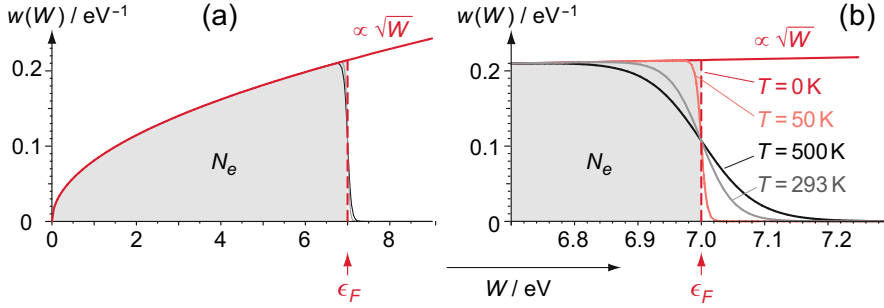
### 2.4.3 The Free Electron Gas

An important application are *electrons* (mass  $m_e$ ,  $s = 1/2$ ,  $g_e = 2$ ). In the context of the photoelectric effect (Sect. 1.4.1) we have already introduced the *free electron gas model*, where one assumes the electrons in a metal to move freely in an ‘electron sea’. Now, as a 1st order approximation, we describe this situation quantitatively by electrons in a 3D box. It turns out that such a model serves well in many areas of physics, as a first step e.g. when introducing electron bands in solid state physics, but also in atomic physics for statistical models of electrons in a large atom (see Sect. 10.1.5).

Due to the high particle density  $N_e$  (electrons per unit volume), FERMI-DIRAC statistics of electrons in the bulk is quite different from that in gases treated in Sect. 1.3.4. We estimate  $N_e = \nu \times N_A \rho / M_r \text{ g mol}^{-1}$ , with  $\nu$  the number of valence electrons per atom,  $N_A$  the AVOGADRO number,  $\rho$  the (mass) density of the material and  $M_r$  the relative atomic mass. It is typically on the order of  $10^{28} - 10^{29} \text{ m}^{-3}$ . In contrast to the situation treated in gases, the *chemical-potential*  $\mu$  is now positive and  $\mu \gg k_B T$ . At absolute zero temperature,  $T = 0$  (or rather at very low values of  $T$ ), each available state (with any given spatial wave function according to Eqs. (2.53) and (2.54)) will be filled by two electrons (with spin up and spin down,  $g_e = 2$ ). The potential box will thus be ‘filled’ up to an energy  $\epsilon_F$ . With (2.56) the

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<sup>6</sup>The size of phase space with momenta up to  $p$  is  $(4\pi/3)p^3 L^3$ . Expressing  $p$  in terms of kinetic energy  $W$ , and dividing by  $h^3$  and  $L^3$  gives the number of phase space cells per unit volume:  $N_Z = (4\pi/3)(2mW)^{3/2}/h^3$ . Differentiation in respect of  $W$  yields (2.57).



**Fig. 2.3** FERMI-DIRAC probability distribution according to (2.61) as a function of energy for electrons in a metal with a FERMI energy  $\epsilon_F = 7 \text{ eV}$  at different temperatures  $T$ : **(a)** energy range from 0 eV to 9 eV, **(b)** expanded scale around  $\epsilon_F$ ; at  $T = 0$  the electron density  $N_e$  extends up to  $\epsilon_F$  (grey shading up to the dashed vertical red line); the full red line indicates the density of states  $\propto \sqrt{W}$

total number of electrons per volume with kinetic energies between 0 and  $\epsilon_F$  is thus

$$N_e = 2N_Z(\epsilon_F) = \frac{1}{3\pi^2} \left( \frac{2m_e \epsilon_F}{\hbar^2} \right)^{3/2}. \quad (2.59)$$

We may invert this to obtain the so called FERMI energy  $\epsilon_F$ . At absolute zero temperature  $\epsilon_F$  is identical to the chemical-potential  $\mu$  introduced in Sect. 1.3.4, and corresponds to the maximum electron energy. One state after the other is filled, each by two of electrons, up to the FERMI energy:

$$\epsilon_F = \frac{\hbar^2}{2m_e} (3\pi^2 N_e)^{2/3}. \quad (2.60)$$

Typical FERMI energies for metals range from  $\simeq 1.6 \text{ eV}$  (Cs) to  $14.3 \text{ eV}$  (Be).

Expressing the prefactor  $A$  given by (1.64) with  $g_e = 2$  in terms of the FERMI energy  $\epsilon_F$  one may write the probability distribution for finding a given energy  $W$  in the electron gas in a box:

$$w(W)dw = \frac{dN_e}{N_e} = \frac{3}{2} \left( \frac{1}{\epsilon_F} \right)^{3/2} \frac{\sqrt{W}}{\exp[(W - \mu)/(k_B T)] + 1} dW \quad (2.61)$$

with  $\mu_F \simeq \epsilon_F$  as long as  $k_B T \ll \epsilon_F$ .

This is illustrated in Fig. 2.3 for a characteristic example with  $\epsilon_F = 7 \text{ eV}$  (about the value for Cu). The full red line indicates the density of states  $\propto \sqrt{W}$  according (2.57). The grey shaded area under this curve indicates for  $T = 0 \text{ K}$  the filling with electrons up to  $\epsilon_F$  (dashed vertical red line). For temperatures  $T > 0 \text{ K}$  the states will be occupied according to the FERMI-DIRAC statistics (1.66). As clearly seen on an enlarged energy scale in Fig. 2.3(b) the boundary between occupied and

unoccupied states broadens as temperature increases (width  $\simeq 2k_B T$ ) – the reduction of the probability for  $W < \epsilon_F$  is approximately compensated by the increase at  $W > \epsilon_F$ , and the FERMI distribution remains normalized, i.e.  $\int_0^\infty w(W)dw \simeq 1$ . For metals at room temperature one typically finds  $k_B T/\epsilon_F < 1/100$  and the normalization condition holds very well.

However, at higher temperatures,  $k_B T/\epsilon_F \gtrsim 0.1$ , or for different densities of states (e.g. in semiconductors), the **chemical-potential**  $\mu$  must be readjusted in order to maintain the normalization of  $w(W)$ . In solid state physics it is often called *FERMI level*  $W_F = \mu$ , which, strictly speaking, *is identical to the FERMI energy  $\epsilon_F$  only at  $T = 0$* .

### Section summary

- The *particle in a box* model allows a most simple description of electrons moving freely in a metal. The wave functions (2.53) in the 3D box (volume  $L^3$ ) have nodes at the boundaries of the box. The energies are  $W = \hbar^2 \pi^2 n^2 / (2m L^2)$  with  $n = \sqrt{n_x^2 + n_y^2 + n_z^2}$  and  $n_i$  representing positive values in 3D integer number space.
- From this the **DOS** (2.57) is derived, which according to (2.57) is  $\propto g_e m^{3/2} \sqrt{W}$ , where  $m$  is the particle's mass and  $g_e = 2s + 1$  the degeneracy due to its spin.
- In the case of electrons (Fermions) each state can be filled with up to 2 electrons. Then, at  $T = 0$  K the highest energy with occupied states is the FERMI energy  $\epsilon_F = \hbar^2 (3\pi^2 N_e)^{2/3} / (2m_e)$ .
- At temperatures  $T > 0$  the boundary between occupied and unoccupied states smears out according to (2.61). The width of the boundary layer is on the order of  $k_B T$ .

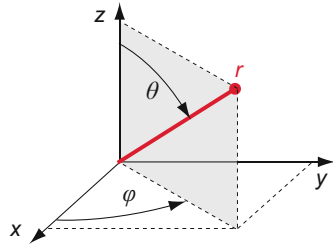
## 2.5 Angular Momentum

Angular momenta play a central role in atomic and molecular physics and Appendix B gives a summary on the essentials: their abstract definitions, properties, combinations and the relevant algebra. Here we introduce the SCHRÖDINGER picture of *orbital angular momenta* as used in the quantum mechanics of the H atom. The orbital picture emerging from this concept is directly accessible to physical imagination and visualization. At the end of this section we shall generalize the basic concepts, including electron spin.

### 2.5.1 Polar Coordinates

Quantum mechanical problems may be treated with advantage in *polar* rather than in *Cartesian coordinates* if they have a symmetry centre, e.g. if the potential depends only on the distance  $r$  from origin  $V(\mathbf{r}) = V(r)$  as in the COULOMB case. The

**Fig. 2.4** Cartesian  $(x, y, z)$  and polar coordinates  $(r, \theta, \varphi)$



transformations between Cartesian  $(x, y, z)$  and polar coordinates  $(r, \theta, \varphi)$  are read from Fig. 2.4,

$$\begin{aligned} x &= r \sin \theta \cos \varphi \\ y &= r \sin \theta \sin \varphi \\ z &= r \cos \theta, \end{aligned} \quad (2.62)$$

and the volume element transforms as

$$dx dy dz \rightarrow r^2 \sin \theta d\theta d\varphi dr. \quad (2.63)$$

Conversion of the relevant observables such as the kinetic energy

$$\frac{\hat{\mathbf{p}}^2}{2m} = -\frac{\hbar^2}{2m} \nabla^2 = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)$$

requires some – in principle trivial – partial differentiations and mathematical rearrangements which we shall not explicate here. The result is

$$\frac{\hat{\mathbf{p}}^2}{2m} = -\frac{\hbar^2}{2m} \nabla^2 = -\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{\hat{\mathbf{L}}^2}{2mr^2} \quad \text{with} \quad (2.64)$$

$$\hat{\mathbf{L}}^2 = -\hbar^2 \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right]. \quad (2.65)$$

In full analogy to classical mechanics, the form of (2.64) suggests two components of kinetic energy:

$$\text{radial energy} \quad \hat{H}_r = -\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) \quad \text{and} \quad (2.66)$$

$$\text{rotational energy} \quad \hat{H}_{\text{rot}} = \frac{\hat{\mathbf{L}}^2}{2mr^2}. \quad (2.67)$$

This suggestive way of writing the energy already implies that  $\hat{\mathbf{L}}^2$  might be the quantum mechanical equivalent to the classical angular momentum. In the following, a more formal approach to derive an expression for the angular momentum will be sketched.

### 2.5.2 Definition of Orbital Angular Momentum

In classical mechanics angular momentum is defined as  $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ . The quantum mechanical equivalent is the *orbital<sup>7</sup> angular momentum operator*  $\hat{\mathbf{L}}$  which according to the recipe (2.49) is obtained by substituting  $\mathbf{p} \rightarrow \hat{\mathbf{p}}$ :

$$\hat{\mathbf{L}} = \mathbf{r} \times \hat{\mathbf{p}}. \quad (2.68)$$

This has to be expressed in polar coordinates. We just show this for one coordinate by way of example:

$$\hat{L}_z = -i\hbar \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right). \quad (2.69)$$

With (2.62) one transforms the expression in brackets into polar coordinates:

$$\begin{aligned} \frac{\partial}{\partial \varphi} &= \frac{\partial x}{\partial \varphi} \frac{\partial}{\partial x} + \frac{\partial y}{\partial \varphi} \frac{\partial}{\partial y} + \frac{\partial z}{\partial \varphi} \frac{\partial}{\partial z} = -r \sin \theta \sin \varphi \frac{\partial}{\partial x} + r \sin \theta \cos \varphi \frac{\partial}{\partial y} + 0 \\ &= -y \frac{\partial}{\partial x} + x \frac{\partial}{\partial y} = x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x}. \end{aligned}$$

Thus, the operator for the  $z$  component of orbital angular momentum is

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \varphi}. \quad (2.70)$$

Obviously this is constructed in complete analogy to the linear momentum  $\hat{p}_x = -i\hbar \partial/\partial x$ , with the pair of canonically conjugate coordinates  $(\hat{p}_x, x)$  replaced by  $(\hat{L}_z, \varphi)$ .

The transformation of  $\hat{L}_x$  and  $\hat{L}_y$  is slightly more complicated. In summary one finds, here without proof, that the *operator of the squared orbital angular momentum*  $\hat{\mathbf{L}}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$  is indeed given by (2.65). Some details are explained in Appendix B.

### 2.5.3 Eigenvalues and Eigenfunctions

We are now ready to discuss eigenvalues and eigenstates of angular momentum operators. They will be used in more or less all of the following chapters. In the spirit of this textbook, again we only sketch the basic concepts, present a collection of necessary tools, and refer the reader to the standard textbooks on quantum mechanics and angular momentum algebra for details.

<sup>7</sup>“Orbital” to distinguish it e.g. from the spin angular momentum.

### Component $\hat{L}_z$ of the Orbital Angular Momentum

In polar coordinates the  $z$ -axis represents a preferred direction, since the polar angle  $\theta$  is defined in respect of it. With (2.70), the eigenvalue equation of  $\hat{L}_z$  is an ODE of 1st order

$$\begin{aligned}\hat{L}_z \Phi(\varphi) &= \ell_z \Phi(\varphi) \\ -i\hbar \frac{\partial}{\partial \varphi} \Phi &= \ell_z \Phi(\varphi)\end{aligned}\tag{2.71}$$

and may be integrated directly. The solution is

$$\Phi = C \exp\left(i \frac{\ell_z}{\hbar} \varphi\right)$$

with a normalization constant  $C$ . We now have to *apply some physics*: which values of  $\ell_z$  are really meaningful? Obviously  $\Phi(\varphi)$  has to be unique:

$$\Phi(0) \stackrel{!}{=} \Phi(2\pi) \quad \text{or equivalently} \quad \exp(0) \stackrel{!}{=} \exp\left(i \frac{\ell_z}{\hbar} 2\pi\right).\tag{2.72}$$

This is only possible for integer values of  $\ell_z/\hbar = m$  with  $m = 0, \pm 1, \pm 2, \dots$ . Then

$$\exp\left(i \frac{\ell_z}{\hbar} 2\pi\right) = \exp(im2\pi) = 1,$$

and  $\Phi_m(\varphi) = C_m \exp(im\varphi)$  are the eigenfunctions solving (2.71). We call  $m$  the *projection quantum number* (in the literature often also – somewhat misleadingly – called *magnetic quantum number*). These wave functions are *orthonormal*:

$$\delta_{mm'} \stackrel{!}{=} \langle \Phi_m | \Phi_{m'} \rangle = C_m^* C_{m'} \int_0^{2\pi} \exp(-im\varphi) \exp(im'\varphi) d\varphi \tag{2.73}$$

$$\text{with } C_m = 1/\sqrt{2\pi}.$$

The standard *phase convention* uses real normalization constants  $C_m$ . In summary, for the projection of the angular momentum onto the  $z$ -axis

$$\text{the eigenvalue equation is} \quad \hat{L}_z \Phi_m = m\hbar \Phi_m,$$

$$\text{with eigenfunctions} \quad \Phi_m = \frac{1}{\sqrt{2\pi}} \exp(im\varphi), \tag{2.74}$$

$$\text{and eigenvalues} \quad \hbar m \quad \text{where } m = 0, \pm 1, \pm 2, \dots$$

### Components in $x$ - and $y$ -Direction

For the  $\hat{L}_x$  and  $\hat{L}_y$  components the calculation is more complicated but in principle trivial. We communicate without proof:  $\hat{L}_x$ ,  $\hat{L}_y$ , and  $\hat{L}_z$  cannot be measured simultaneously. Each pair of them does not commute. On the contrary, one may show that the following *commutation rules for angular momenta* hold:



$$\begin{aligned}
[\widehat{L}_x, \widehat{L}_y] &= \widehat{L}_x \widehat{L}_y - \widehat{L}_y \widehat{L}_x = i\hbar \widehat{L}_z, \\
[\widehat{L}_y, \widehat{L}_z] &= i\hbar \widehat{L}_x \quad \text{and} \quad [\widehat{L}_z, \widehat{L}_x] = i\hbar \widehat{L}_y.
\end{aligned}
\tag{2.75}$$

Corresponding to this all components  $\widehat{L}_i$  are represented by different functions of  $\varphi$  and  $\theta$  (not shown here).

### Square of the Orbital Angular Momentum

With (2.65) we write the eigenvalue equation for  $\widehat{L}^2$  as

$$\widehat{L}^2 Y(\theta, \varphi) = \mathcal{L}^2 Y(\theta, \varphi) \tag{2.76}$$

with the eigenvalue  $\mathcal{L}^2$  and use a the product *ansatz* towards its solution:

$$Y(\theta, \varphi) = \Theta(\theta) \Phi(\varphi). \tag{2.77}$$

As azimuthal part we try the eigenfunctions (2.74) of  $\widehat{L}_z$  and substitute  $\Theta(\theta) \Phi_m(\varphi)$  into (2.65). This leads to

$$\begin{aligned}
& -\hbar^2 \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Theta(\theta)}{\partial \theta} \right) \Phi_m(\varphi) + \frac{1}{\sin^2 \theta} \Theta(\theta) \frac{\partial^2}{\partial \varphi^2} \Phi_m(\varphi) \right] \\
& = \mathcal{L}^2 \Theta(\theta) \Phi_m(\varphi) = \mathcal{L}^2 Y(\theta, \varphi) \\
\Rightarrow & -\hbar^2 \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Theta}{\partial \theta} \right) - \frac{m^2}{\sin^2 \theta} \Theta \right] = \mathcal{L}^2 \Theta.
\end{aligned}
\tag{2.78}$$

Thus, only one ODE remains to be solved. Several procedures lead to the correct solutions. One may directly use the *associated LEGENDRE polynomials*, known from the mathematics of ODEs, or (perhaps more elegantly) by exploiting the properties of the angular momentum operators to find appropriate *recursion formulas*. In any case, one has to demand physically reasonable boundary conditions. In analogy to (2.72) for the  $z$ -component, the wave functions must be finite and unique for  $0 \leq \theta \leq \pi$ . *Without proof* we communicate here that such physically meaningful solutions exist for which the following relations hold (for completeness we include again the  $z$ -component):

$$\text{eigenvalue equation for } \widehat{L}^2 \quad \widehat{L}^2 Y_{\ell m}(\theta, \varphi) = \ell(\ell + 1) \hbar^2 Y_{\ell m}(\theta, \varphi) \tag{2.79}$$

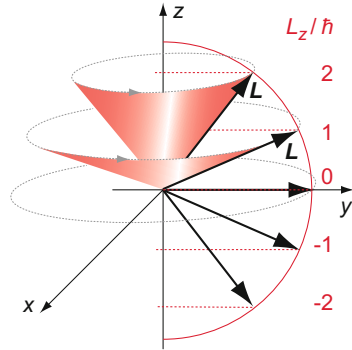
$$\text{eigenvalues of } \widehat{L}^2 \quad \mathcal{L}^2 = \ell(\ell + 1) \hbar^2 \tag{2.80}$$

$$\text{eigenvalue equation for } \widehat{L}_z \quad \widehat{L}_z Y_{\ell m}(\theta, \varphi) = m \hbar Y_{\ell m}(\theta, \varphi) \tag{2.81}$$

$$\text{quantum numbers} \quad \ell = 0, 1, 2, \dots \quad \text{and} \quad m = 0, \pm 1, \dots, \pm \ell \tag{2.82}$$

$$\text{degeneracy} \quad 2\ell + 1 \tag{2.83}$$

**Fig. 2.5** Vector diagram illustrating the  $2\ell + 1$  possible orientations of the angular momentum in space (shown for  $\ell = 2$  as an example)



The validity of (2.81) follows directly from (2.74) and (2.77), since  $\hat{L}_z$  only acts onto the  $\varphi$  component of  $Y_{\ell m}(\theta, \varphi)$ . This implies

$$\hat{L}^2 \hat{L}_z = \hat{L}_z \hat{L}^2 \quad \text{or} \quad [\hat{L}^2, \hat{L}_z] = 0. \quad (2.84)$$

Equivalently:  $\hat{L}^2$  and  $\hat{L}_z$  can be measured simultaneously. This also holds for  $\hat{L}^2$  and  $\hat{L}_x$  as well as for  $\hat{L}^2$  and  $\hat{L}_y$  – not, however, for the components  $\hat{L}_x$ ,  $\hat{L}_y$  and  $\hat{L}_z$  which according to (2.75) do not commute with each other.

### Vector Diagram

With (2.79) one may write the magnitude of the angular momentum as:

$$|\hat{L}| = \sqrt{\ell(\ell + 1)}\hbar. \quad (2.85)$$

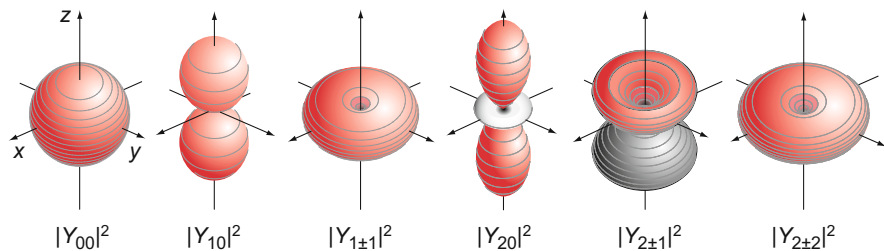
For a given set of quantum numbers  $\ell m$  the exact direction of the total angular momentum is undefined. Precisely defined is only the magnitude and component  $L_z = m\hbar$  in respect of the  $z$ -axis. One visualizes these relations with the help of a *vector diagram* shown in Fig. 2.5. of the electron spin (see Fig. 1.43). Figure 2.5 illustrates the example  $\ell = 2$ ,  $|\hat{L}|/\hbar = \sqrt{6} \simeq 2.45$  with  $\hat{L}_z/\hbar = m = -2, -1, 0, 1, 2$ . One may consider the vector arrows statistically distributed around the  $z$ -axis, i.e. on cones of height  $m\hbar$  with a side length  $\sqrt{\ell(\ell + 1)}\hbar$ .

### Spherical Harmonics

The eigenfunctions of  $\hat{L}^2$  and  $\hat{L}_z$  are called *spherical harmonics*  $Y_{\ell m}(\theta, \varphi)$ . General formulas and properties are summarized in Appendix B.1.2, and specific expressions up to  $\ell = 3$  are tabulated in Table B.1. A graphical illustration of the angular dependence is shown in Fig. 2.6.

The  $Y_{\ell m}(\theta, \varphi)$  are *orthonormalized*:

$$\int_0^{2\pi} d\varphi \int_0^\pi Y_{\ell m}^*(\theta, \varphi) Y_{\ell' m'}(\theta, \varphi) \sin \theta d\theta = \delta_{\ell' \ell} \delta_{m' m}. \quad (2.86)$$



**Fig. 2.6** 3D-plot of the  $s$ ,  $p$  and  $d$  spherical harmonics; plotted are the squared moduli as a function of angles, the shading colours indicate the sign of  $Y_{\ell m}(\theta, 0)$ . For an alternative representation in the real basis see Appendix D.3 and in particular Fig. D.1

The complex conjugate is given by

$$Y_{\ell m}^*(\theta, \varphi) = (-1)^m Y_{\ell -m}(\theta, \varphi), \quad (2.87)$$

and inversion at the origin ( $\mathbf{r} \rightarrow -\mathbf{r}$ ) leads to

$$Y_{\ell m}(\pi - \theta, \pi + \varphi) = (-1)^\ell Y_{\ell -m}(\theta, \varphi), \quad (2.88)$$

which describes (see detailed discussion in Appendix D) so called *positive or negative parity* depending on whether  $\ell$  is *even or odd*, respectively.

At this point, we introduce an important, commonly used notation:

orbital angular momenta  $\ell = 0, 1, 2, 3, 4, \dots$  are labelled  $s, p, d, f, g, \dots$

In the following text we shall, for compactness, usually write the spherical harmonics in “*bra*” and “*ket*” form, substituting

$$Y_{\ell m}(\theta, \varphi) \rightarrow |\ell m\rangle \quad \text{and} \quad Y_{\ell m}^*(\theta, \varphi) \rightarrow \langle \ell m|. \quad (2.89)$$

In this notion, the orthogonality relations (2.86) and the matrix elements of an operator  $\hat{A}$  are written as

$$\langle \ell m | \ell' m' \rangle = \delta_{\ell \ell'} \delta_{m m'} \quad \text{and} \quad A_{\ell m, \ell' m'} = \langle \ell m | \hat{A} | \ell' m' \rangle. \quad (2.90)$$

Several useful relations are summarized in Appendixes B and C.

It has to be pointed out, that the *complex form of the spherical harmonics*  $Y_{\ell m}(\theta, \varphi)$  illustrated in Fig. 2.6 is well adapted for many problems in atomic physics – but it is by no means the only possible representation of the angular part of atomic orbitals. An alternative frequently used in molecular physics (see Chaps. 3 and 4, Vol. 2) and always in chemistry, are real combinations of spherical harmonics. They are described in some detail in Appendix D.

### 2.5.4 Electron Spin

As shown by the STERN-GERLACH experiment, the electron has in addition to mass and charge one further property which we have identified in Sect. 1.10 as an intrinsic angular momentum, called *spin*. The spin is characterized by the spin quantum number  $s = 1/2$ . Its magnitude is  $|\mathbf{S}| = \sqrt{s(s+1)}\hbar$ , and two orientations with angular momentum components  $\hbar/2$  and  $-\hbar/2$  are possible. Closely related to the spin, the electron has also a magnetic moment with a  $g$  factor – as defined by (1.162) – close to  $g_e \simeq 2$ .

One simply transfers the formal rules which we have introduced in Sects. 2.5.2–2.5.3 onto the properties of the spin. Clearly, the spin may not be imaged in position space. However, we may define quite formally in analogy to the orbital angular momentum  $\hat{\mathbf{L}}$  a new vector operator  $\hat{\mathbf{S}}$  with a square magnitude operator  $\hat{\mathbf{S}}^2$  and a component  $\hat{S}_z$  in  $z$ -direction for which the general commutation rules for angular momenta (2.75) and (2.84) are valid:

$$[\hat{S}_x, \hat{S}_y] = i\hbar\hat{S}_z, \quad [\hat{S}_y, \hat{S}_z] = i\hbar\hat{S}_x, \quad [\hat{S}_z, \hat{S}_x] = i\hbar\hat{S}_y, \quad [\hat{\mathbf{S}}^2, \hat{S}_z] = 0. \quad (2.91)$$

They imply, as in the general case, that the *components of the spin* cannot be measured simultaneously. However, it is possible to determine its magnitude together with one of its components is (e.g. the  $z$ -component  $\hat{S}_z$ ).

We now introduce *spin states*  $|sm_s\rangle$ . In analogy to (2.79)–(2.83) (for the orbital angular momentum)

$$\hat{\mathbf{S}}^2 |sm_s\rangle = s(s+1)\hbar^2 |sm_s\rangle \quad \text{and} \quad \hat{S}_z |sm_s\rangle = m_s\hbar |sm_s\rangle \quad (2.92)$$

with  $m_s = -s, -s+1, \dots, s$  holds. Specifically, for the electron spin with  $s = 1/2$  and  $m_s = \pm 1/2$  only two basis states exist,

$$|\frac{1}{2} \frac{1}{2}\rangle = |\alpha\rangle = |+\rangle \quad \text{and} \quad |\frac{1}{2} -\frac{1}{2}\rangle = |\beta\rangle = |-\rangle, \quad (2.93)$$

for which the spin points into  $+z$ - and  $-z$ -direction, respectively. We have introduced here three equivalent notations which are commonly used for compactness. One also finds in the literature the notation *spin function*  $\alpha$  and  $\beta$  without *bra* or *ket*. Alternatively, one speaks about “spin up” ( $\uparrow$ ) and “spin down” ( $\downarrow$ ) states. In any case, the relations

$$\begin{aligned} \hat{\mathbf{S}}^2 |\alpha\rangle &= \frac{3}{4}\hbar^2 |\alpha\rangle & \hat{\mathbf{S}}^2 |\beta\rangle &= \frac{3}{4}\hbar^2 |\beta\rangle \\ \hat{S}_z |\alpha\rangle &= \frac{\hbar}{2} |\alpha\rangle & \hat{S}_z |\beta\rangle &= -\frac{\hbar}{2} |\beta\rangle \end{aligned} \quad (2.94)$$

hold, together with the orthonormality relations

$$\langle\alpha|\beta\rangle = \langle\beta|\alpha\rangle = 0 \quad \text{and} \quad \langle\alpha|\alpha\rangle = \langle\beta|\beta\rangle = 1. \quad (2.95)$$

From the commutation rules (2.91) one may derive how the other components of  $\widehat{\mathbf{S}}$  act onto the basis (here without proof):

$$\widehat{S}_x|\alpha\rangle = \frac{\hbar}{2}|\beta\rangle \quad \widehat{S}_x|\beta\rangle = \frac{\hbar}{2}|\alpha\rangle \quad \widehat{S}_y|\alpha\rangle = \frac{i\hbar}{2}|\beta\rangle \quad \widehat{S}_y|\beta\rangle = -\frac{i\hbar}{2}|\alpha\rangle. \quad (2.96)$$

In this basis each arbitrary spin state of an electron may be expressed as

$$|\chi\rangle = \chi_+|\alpha\rangle + \chi_-|\beta\rangle, \quad (2.97)$$

with the *probability amplitudes*  $\chi_+$  and  $\chi_-$  normalized to unity:  $\langle\chi|\chi\rangle = |\chi_+|^2 + |\chi_-|^2 = 1$ . The *probabilities* for finding in this state the  $\alpha$  and  $\beta$  component (or spin up  $\uparrow$  and spin down  $\downarrow$ ) is given by  $|\chi_+|^2$  and  $|\chi_-|^2$ , respectively. The *expectation values of the spin components*  $\widehat{S}_k$  (with  $k = x, y$  or  $z$ ) in the spin state (2.97) are readily obtained from  $\langle\widehat{S}_k\rangle = \langle\chi|\widehat{S}_k|\chi\rangle$  using (2.94) and (2.96).

*Note that although the three components of the spin cannot be measured simultaneously, magnitude and phase of the (complex) amplitudes  $\chi_+$  and  $\chi_-$  determine the orientation of the spin in three dimensional space uniquely.* Assume we start with a pure basis state – say  $|\alpha\rangle$  prepared with an ideal STERN-GERLACH experiment, pointing into an arbitrary direction of space. In a given coordinate system with  $x$ -,  $y$ -, and  $z$ -direction (differing from that STERN-GERLACH coordinate frame) this state  $|\alpha\rangle$  will again be a superposition of the type (2.97). The mathematics to do such a coordinate rotation in general is summarized in Appendix E. Experimentally one may determine the expectation values  $\langle\widehat{S}_k\rangle$  in respect of the  $x$ -,  $y$ -, and  $z$ -coordinates by using a second, rotatable STERN-GERLACH setup. With this one may perform experiments in each of the corresponding directions – and repeat them many times to obtain expectation values. From these (one needs at least two of them) the probability amplitudes  $\chi_+$  and  $\chi_-$  in the new system may easily be derived.

It is convenient to write these amplitudes with (E.16) and  $\gamma = 0$  as

$$\chi_+ = \cos \frac{\theta}{2} \exp\left(-i\frac{\varphi}{2}\right) \quad \text{and} \quad \chi_- = \sin \frac{\theta}{2} \exp\left(i\frac{\varphi}{2}\right), \quad (2.98)$$

which are normalized by definition. As an exercise, the reader may show with the aid of (2.94) and (2.96), that the *parameters  $\theta$  and  $\varphi$  give the polar and azimuthal angles, respectively*, at which the so defined spin state is *oriented in space*.

The above provides a toolbox which is fully sufficient to describe the properties of the spin states. Nevertheless one often writes – perhaps for historical reasons or better visualization – operators in the form of matrices and eigenstates as vectors, the so called *spinors*

$$\chi = \begin{pmatrix} \chi_+ \\ \chi_- \end{pmatrix} \quad \text{and} \quad \chi^\dagger = (\chi_+^* \quad \chi_-^*) \quad (2.99)$$

$$\text{with the basis } \alpha = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad \beta = \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

The matrix elements of the operators  $\widehat{S}_x$ ,  $\widehat{S}_y$  and  $\widehat{S}_z$  are obtained from (2.96). They may be summarized as spin operators in matrix form,

$$\widehat{\mathbf{S}} = \frac{\hbar}{2} \widehat{\boldsymbol{\sigma}}, \quad (2.100)$$

with  $\widehat{\boldsymbol{\sigma}}$  being a vector operator, the so called PAULI *vector*, which is built from the PAULI *matrices*:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \text{and} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (2.101)$$

$$\widehat{\mathbf{S}}^2 = \widehat{S}_x^2 + \widehat{S}_y^2 + \widehat{S}_z^2 = \frac{3}{4} \hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \quad (2.102)$$

For later use we note here that the PAULI matrices anti-commutate

$$\sigma_i \sigma_j + \sigma_j \sigma_i = 2\delta_{ij}, \quad (2.103)$$

and thus

$$\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = \widehat{\mathbf{1}} \quad \text{and} \quad \sigma_x \sigma_y = -\sigma_y \sigma_x = i\sigma_z. \quad (2.104)$$

Another useful relation is obtained by applying (2.103):

$$3(\widehat{\mathbf{S}} \cdot \mathbf{r})^2 = \frac{3}{4} \hbar^2 (\sigma_x x + \sigma_y y + \sigma_z z)^2 = \frac{3}{4} \hbar^2 r^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = r^2 \widehat{\mathbf{S}}^2. \quad (2.105)$$

---

### Section summary

- Orbital angular momentum operators may be derived from  $\widehat{\mathbf{L}} = \mathbf{r} \times \widehat{\mathbf{p}}$ , with  $\widehat{\mathbf{p}} = -i\hbar\nabla$ , or be constructed from the commutation rules (2.75).
- From the spatial representations of the operators  $\widehat{L}^2$  and  $\widehat{L}_z$  according to (2.65) and (2.70), respectively, one obtains eigenvalues and wave functions as summarized in (2.79)–(2.83), and schematically illustrated in the vector diagram Fig. 2.5.
- The shape of the orbitals with lowest angular momentum – *s*, *p* and *d* – shown in Fig. 2.6 should be memorized. General formulas and properties are summarized in Appendix B.1.2, specific expressions are tabulated in Table B.1.
- The electron spin obeys the same commutation rules as orbital angular momenta. Its intrinsic angular momentum, the spin, is however  $s = 1/2$  and the projection quantum number  $m_s = \pm 1/2$ . A frequently used representation of the spin operators are the PAULI matrices (2.101) and (2.102) which act on the so called spinors – two component representations of the spin eigenfunctions.

## 2.6 One Electron Systems and the Hydrogen Atom

We are now fully prepared to treat a particle in a centrosymmetric potential  $V(r)$ , specifically the one electron problem. Much of the following will be based on what we have learned about angular momenta in Sect. 2.5. We keep the discussion general as long as possible and specialize to the H atom, i.e. to the pure, attractive COULOMB potential  $V(r) < 0$  in Sect. 2.6.5.

### 2.6.1 Quantum Mechanics of the One Particle System

We start by formulating the SCHRÖDINGER equation precisely. With (2.64)–(2.67) we may write the Hamiltonian (2.10) as:

$$\hat{H} = -\frac{\hat{\mathbf{p}}^2}{2m_e} + V(r) = \hat{H}_r + \frac{\hat{\mathbf{L}}^2}{2m_e r^2} + V(r) \quad (2.106)$$

$$\text{with } \hat{H}_r = -\frac{\hbar^2}{2m_e} \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right), \quad (2.107)$$

and obtain the *one particle* SCHRÖDINGER equation in polar coordinates:

$$\left[ \hat{H}_r + \frac{\hat{\mathbf{L}}^2}{2m_e r^2} + V(r) \right] \psi_{n\ell m}(r, \theta, \varphi) = W_{n\ell m} \psi_{n\ell m}(r, \theta, \varphi). \quad (2.108)$$

In Sect. 2.5.3 we have discussed in detail the eigenfunctions  $Y_{\ell m}(\theta, \varphi)$  and eigenvalues  $\hbar^2 \ell(\ell + 1)$  of  $\hat{\mathbf{L}}^2$ . To solve (2.108) we make the *separation ansatz*

$$\psi_{n\ell m}(r, \theta, \varphi) = R_n(r) Y_{\ell m}(\theta, \varphi), \quad \text{so that} \quad (2.109)$$

$$\left[ \hat{H}_r + \frac{\hat{\mathbf{L}}^2}{2m_e r^2} + V(r) \right] R_{n\ell}(r) Y_{\ell m}(\theta, \varphi) = W R_{n\ell}(r) Y_{\ell m}(\theta, \varphi).$$

Since  $\hat{H}_r$  and  $V(r)$  act only on the radial and  $\hat{\mathbf{L}}^2$  only on the angular part we obtain with (2.107) and (2.79):

$$\left[ -\frac{\hbar^2}{2m_e} \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} \right) + \frac{\hbar^2 \ell(\ell + 1)}{2m_e r^2} + V(r) \right] R_{n\ell}(r) = W R_{n\ell}(r). \quad (2.110)$$

The sum of *centrifugal potential*  $\hbar^2 \ell(\ell + 1)/(2m_e r^2)$  and COULOMB potential  $\propto -1/r$  is called *effective potential*:

$$V_{\text{eff}}(r) = V(r) + \frac{\hbar^2 \ell(\ell+1)}{2m_e r^2}. \quad (2.111)$$

With this and the substitution

$$R_{n\ell}(r) = u_{n\ell}(r)/r \quad (2.112)$$

one obtains a relatively simple, one dimensional, ordinary differential equation (ODE) which may be integrated without problems:

$$\frac{\hbar^2}{2m_e} \frac{d^2 u_{n\ell}}{dr^2} + [W_{n\ell} - V_{\text{eff}}(r)] u_{n\ell}(r) = 0. \quad (2.113)$$

*Note:* The total energy does not depend on the projection quantum number  $m$  and is thus be written  $W = W_{n\ell}$ . Zero energy is usually set for the completely unbound system, i.e. for electron and nucleus at infinite distance with no kinetic energy. Bound electrons have negative energies  $W_{n\ell} < 0$ , while free electrons have total energies  $W > 0$ . Extending (2.89) to the full electron wave function one often abbreviates

$$R_{n\ell}(r) Y_{\ell m}(\theta, \varphi) \rightarrow |n\ell m\rangle. \quad (2.114)$$

More specifically, one even writes these *atomic orbitals* shorthand as  $n\ell = 1s, 2s, 2p, 3s, 3p, 3d$ , etc. in the notation introduced in Sect. 2.5.3.

## 2.6.2 Atomic Units

We recall here the concept of atomic units (a.u.), introduced in Sect. 1.8.3:

$$\begin{aligned} \text{energy} \quad E_h &= m_e e^4 \varepsilon_0^{-2} \hbar^{-2} / 4 \\ \text{length} \quad a_0 &= \varepsilon_0 \hbar^2 e^{-2} m_e^{-1} / \pi = \hbar / \sqrt{m_e E_h} \\ \text{time} \quad t_0 &= 2\varepsilon_0^2 \hbar^3 e^{-4} m_e^{-1} / \pi. \end{aligned} \quad (2.115)$$

Numerical values of these quantities are given in Appendix A, and the most recent, accurate updates can be found at NIST (2010). We use these definitions here to rewrite the radial SCHRÖDINGER equation (2.113). We multiply (2.113) by  $m_e/\hbar^2$  and  $a_0^2$ , and apply the identity  $a_0 = \hbar/\sqrt{m_e E_h}$  to obtain in dimensionless form:

$$\frac{1}{2} \frac{d^2 u_{n\ell}}{d(r/a_0)^2} + \left[ W_{n\ell}/E_h - \frac{\ell(\ell+1)}{2(r/a_0)^2} + \frac{V(r/a_0)}{E_h} \right] u_{n\ell}(r) = 0. \quad (2.116)$$

For simplicity, one may just substitute  $r/a_0 \rightarrow r$  and  $W_{n\ell}/E_h \rightarrow W_{n\ell}$  as well as  $V(r)/E_h \rightarrow V(r)$ . This just implies that *all observables are measured in a.u.* and the radial SCHRÖDINGER equation (2.113) reads now



$$\frac{1}{2} \frac{d^2 u_{n\ell}}{dr^2} + [W_{n\ell} - V_{\text{eff}}(r)] u_{n\ell}(r) = 0 \quad (2.117)$$

$$\text{with } V_{\text{eff}}(r) = V(r) + \frac{\ell(\ell+1)}{2r^2} \text{ and for the H atom } V(r) = -Z/r.$$

Following this scheme one may rewrite all atomic equations in a dimensionless, rather clean looking form. Theoreticians, in particular, like this kind of equation very much and even give the *recipe to just set  $\hbar = e = m_e = 1$*  – which *really oversimplifies what has to be done*. The procedure has one serious disadvantage: a dimensional analysis is no longer possible – which is often highly commendable to check complex calculations. Thus, we typically try to use equations in a form indicated by (2.116), and carry the a.u.  $a_0$ ,  $E_h$ , and  $t_0$  explicitly along. Sometimes one may even be able to combine elementary constants to truly dimensionless quantities, such as the fine structure constant  $\alpha = \sqrt{E_h/m_e c^2}$  according to (1.10).

### 2.6.3 Centre of Mass Motion and Reduced Mass

Up to now we have treated the problem as if the electron would orbit around a space fixed centre. As the nuclear mass is much larger than the electron mass  $m_e$  – in the case of the H atom with a proton as nucleus  $m_p \simeq 1840m_e$  – the centre of mass is indeed very close to  $r = 0$ . For more demanding precision one has, however, to correct for the difference. As in classical mechanics (see corrections to the BOHR model described in Sect. 1.8.5), in quantum mechanics too, one transforms the two body problem into an effective one particle problem by replacing the electron mass  $m_e$  with the reduced mass  $\bar{m}_e$  (1.143) of the system. All a.u. have, in principle, to be replaced correspondingly (*kinematic correction*):

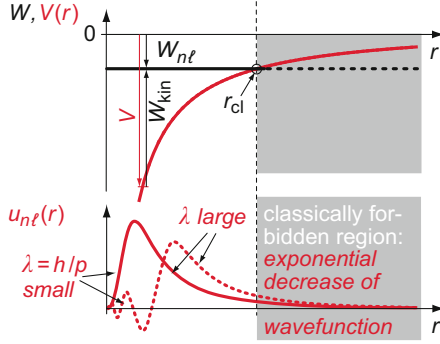
$$a_0 \rightarrow \bar{a}_0 = a_0 \frac{m_e}{\bar{m}_e}, \quad E_h \rightarrow \bar{E}_h = E_h \frac{\bar{m}_e}{m_e}, \quad \text{and} \quad t_0 \rightarrow \bar{t}_0 = t_0 \frac{\bar{m}_e}{m_e}. \quad (2.118)$$

For simplicity we shall, however, in the following text continue to use  $m_e$  and the units  $a_0$ ,  $E_h$  and  $t_0$ , and refer to the exact calculations if relevant.

### 2.6.4 Qualitative Considerations

While we know already the angular part of the hydrogenic wave functions, we are still left with the task to find physically meaningful solutions to the radial SCHRÖDINGER equation (2.117). They have to behave reasonably at  $r = 0$  (see below) and must not diverge for  $r \rightarrow \infty$ . From this follows necessarily that only a particular set of discrete total energies  $W_{n\ell} < 0$  leads to such solutions. To find these is the task at hand.

Before applying mathematics we want to obtain a qualitative picture to support our physical intuition. Figure 2.7 illustrates this for the  $\ell = 0$  case in a COULOMB potential  $V(r) = -Z/r$ . We derive the kinetic energy of the electron at different



**Fig. 2.7** Bound state radial wave functions for  $s$  states, schematic. *Top*: COULOMB potential  $V(r) \propto -1/r$  (red) and total energy  $W_{n\ell} < 0$  (black) determine the classical turning point  $r_{cl}$  (onset of the classically forbidden region). *Bottom*: The characteristic behaviour of radial wave functions  $u_{n\ell}$  is explained by changes of the kinetic energy  $W_{kin}$  in different regions of the potential (see text)

positions in the potential from  $W_{kin} = W_{n\ell} - V(r)$  and take the corresponding DE BROGLIE wavelength  $\lambda = h/p = h/(2m_e W_{kin})^{1/2}$  as an indication for changes in the radial wave function  $u_{n\ell}(r)$ . It obviously will change more rapidly for small  $r$  (large  $W_{kin}$ ) than in the neighbourhood of the classical turning point  $r_{cl}$ , where  $W_{kin} = 0$ . In the classically forbidden area with  $r > r_{cl}$  (negative kinetic energies) we expect exponential damping of the wave function, as illustrated in Fig. 2.7.

In a next step we explore *the limits for very large and very small  $r$* . For the limiting case  $r \rightarrow \infty$  we may neglect the potential altogether and (2.117) becomes a simple oscillator equation:

$$\frac{1}{2} \frac{d^2 u_{n\ell}}{dr^2} + W_{n\ell} u_{n\ell}(r) = 0.$$

The classical solution is  $u_{n\ell}(r) \propto \exp(\pm i\sqrt{2W_{n\ell}}r)$ . Since for bound states  $W_{n\ell} < 0$ , we note *for large  $r$*

$$\lim_{r \rightarrow \infty} u_{n\ell}(r) \propto r^n \exp(-\sqrt{2|W_{n\ell}|}r). \quad (2.119)$$

In the opposite limit  $r \rightarrow 0$  the centrifugal term  $\ell(\ell+1)/2r^2$  dominates the potential in (2.117) and

$$\frac{1}{2} \frac{d^2 u_{n\ell}}{dr^2} - \frac{\ell(\ell+1)}{2r^2} u_{n\ell}(r) = 0$$

has the solution  $u_{n\ell}(r) \stackrel{r \rightarrow 0}{\propto} Ar^{\ell+1}$  as one easily verifies. Thus, we note *for small  $r$*

$$\lim_{r \rightarrow 0} R_{n\ell}(r) = \lim_{r \rightarrow 0} (u_{n\ell}(r)/r) \propto r^\ell. \quad (2.120)$$

### 2.6.5 Exact Solution for the H Atom

We now specialize to the H atom. In the present chapter we neglect the size of the atomic nucleus (positively charged with  $+Ze$ ) since nuclear radii  $r_{\text{nuc}}$  are much smaller than atomic radii, typically  $r_{\text{atom}} \approx 10^5 r_{\text{nuc}}$ . Thus, we are dealing with a *pure COULOMB potential*

$$V(r) = -\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r}, \quad (2.121)$$

apart from small and very small effects which will be treated in Chaps. 6 and 9, respectively. The general solution of the radial SCHRÖDINGER equation (2.110) is found by using a power series of the type

$$R_{n\ell}(r) = \exp(-\sqrt{2|W_{n\ell}|}r) \sum_{k=\ell}^{\infty} A_k r^k,$$

which includes the limiting cases just discussed. Well known results from mathematics are used and we summarize here the results, again without proof. *For hydrogen like systems – i.e. for one electron in the COULOMB potential of a Z fold charged nucleus – the radial function is*

$$R_{n\ell}(r) = u_{n\ell}(r)/r = A_{n\ell} e^{-\rho/2} \rho^\ell L_{n+\ell}^{2\ell+1}(\rho) \quad (2.122)$$

$$\text{where } \rho = \frac{2Z}{n} r/a_0 \text{ and } A_{n\ell} = -\left(\frac{Z}{a_0}\right)^{3/2} \frac{2}{n^2} \sqrt{\frac{(n-\ell-1)!}{[(n+\ell)!]^3}}$$

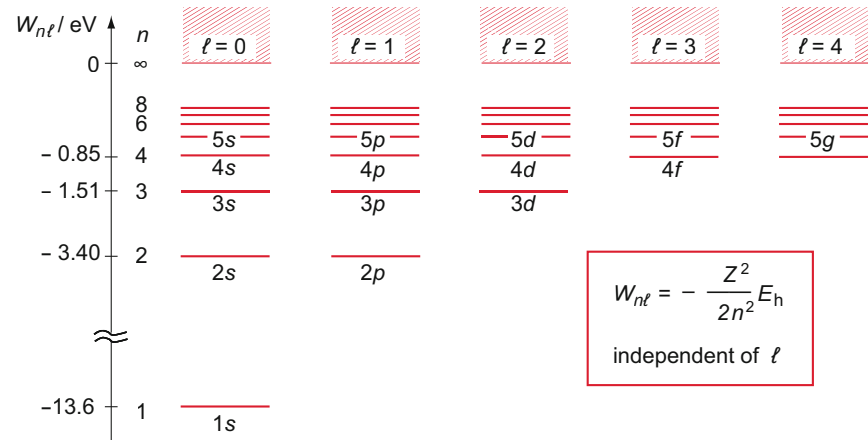
with the so called *associated LAGUERRE polynomials*:

$$L_{n+\ell}^{2\ell+1}(\rho) = \sum_{k=0}^{n-\ell-1} (-1)^{k+1} \frac{[(n+\ell)!]^2}{(n-\ell-1-k)!(2\ell+1+k)!} \frac{\rho^k}{k!}. \quad (2.123)$$

With  $A_{n\ell}$  these radial functions are orthonormalized:

$$\int_0^\infty R_{n\ell}(r) R_{n'\ell'}(r) r^2 dr = \delta_{nn'} \delta_{\ell\ell'}. \quad (2.124)$$

We introduce here finally the often used term **good quantum numbers**: They characterize the *eigenvalues of such observables that may be measured simultaneously with the HAMILTON operator*, i.e. their operators commute with the Hamiltonian. We already know  $\ell$  and  $m$  as typical examples: they are part of the set of quantum numbers characterizing the total energy of the system;  $\widehat{L}^2$  and  $\widehat{L}_z$  are simultaneously measurable with  $\widehat{H}$ .



**Fig. 2.8** Term energies of the hydrogen atom ( $Z = 1$ ) for different  $n$  and  $\ell$

**Table 2.1** The lowest atomic levels, their energies in the H atom and the degeneracy of the states (with  $E_h = 27.2$  eV)

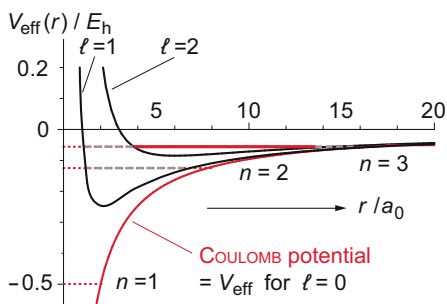
Shell	Orbital	$n$	$\ell$	$m$	$W_{n\ell}$	Degeneracy			
						Without spin sum in shell		With spin sum in shell	
K	1s	1	0	0	$-E_h/2$	1	1	2	2
L	2s	2	0	0	$-E_h/8$	1		2	
	2p	2	1	$0, \pm 1$		3	4	6	8
M	3s	3	0	0	$-E_h/18$	1		2	
	3p	3	1	$0, \pm 1$		3		6	
	3d	3	2	$0, \pm 1, \pm 2$		5	9	10	18
N	4s, p, d, f	4			$-E_h/32$		16		32

### 2.6.6 Energy Levels

These solutions of the SCHRÖDINGER equation are the quantum mechanical equivalent to BOHR’s stationary orbits. Substituting  $u_{nl}(r)$  according to (2.122) into the radial equation (2.113) one finds the *eigenenergies*  $W_{n\ell}$  for the H atom. Remarkably, they are identical to the energies (1.137) from the BOHR model.<sup>8</sup> These results are summarized in Fig. 2.8 and Table 2.1.

We recall that the states are characterized by the *principle quantum number*  $n = 1, 2, 3, \dots$ , the *angular momentum quantum number*  $\ell$  ( $0 \leq \ell \leq n - 1$ ) and the *projection quantum number*  $m$  ( $-\ell \leq m \leq \ell$ ). Each set  $n\ell m$  of quantum numbers refers to a different wave function (atomic orbital). In addition, we also have to consider the spin of the electron, with projections  $m_s = \pm 1/2$ .

<sup>8</sup>The corrections for finite mass of the atomic nucleus (Sect. 1.8.5) also apply.



**Fig. 2.9** Illustration of  $\ell$  degeneracy: Shown are the pure COULOMB potential (red line) and the effective potentials (black) for the H atom. The term energies  $W_{n\ell}$  are indicated by horizontal lines in their respective effective potentials: for  $\ell = 0$  (dotted red), for  $\ell = 1$  (dashed grey) and for  $\ell = 2$  (heavy, full red). As indicated, the COULOMB potential leads to a characteristic degeneracy of states with equal  $n$  but different  $\ell$

However, for the H atom the energies  $W_{n\ell}$  depend only on the principle quantum number  $n$ . Thus, the energy levels are degenerate, the total degeneracy in a shell  $n$  being  $g_n = 2n^2$ . This is summarized in Table 2.1 for  $n = 1$  to 4, also showing the assignment of orbitals with equal principle quantum number  $n$  (i.e. with equal energies and similar orbital radii) to specific shells (K, L, M, N ... corresponding to  $n = 1, 2, 3, 4, \dots$ ).

It is important to note that  $\ell$  degeneracy is a special property of the pure COULOMB potential, while  $m$  degeneracy occurs for all atoms if no external field is present. Figure 2.9 illustrates  $\ell$  degeneracy in the potential energy diagram, also showing the effective potentials (2.111) for  $\ell = 1$  and  $\ell = 2$  (for  $\ell = 0$  effective and COULOMB potential are identical).

### 2.6.7 Radial Functions

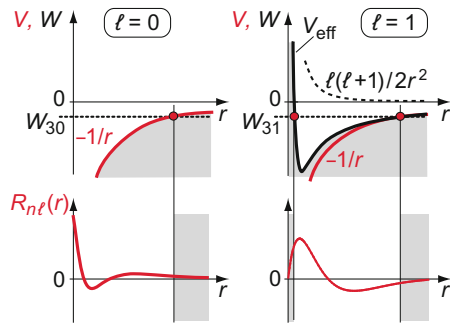
The radial wave functions have very specific shapes, which may be understood from the properties of the effective potentials. Figure 2.10 illustrates this schematically by way of example for the  $n = 3$  level and orbital angular momenta  $\ell = 0$  and 1. Shown are COULOMB potential, centrifugal potential and effective potential for  $\ell = 1$ . The classically forbidden areas ( $W_{\text{kin}} < 0$ ) are grey shaded, the classical turning points. While the radial functions for  $\ell = 0$  start with a finite value at  $r = 0$ , for  $\ell = 1$  the probability there is  $= 0$  (since  $\ell(\ell + 1)/(2r^2) \rightarrow \infty$ ). Oscillations of the radial functions are expected only in between the classically turning points.

Table 2.2 presents the radial wave functions  $R_{n\ell}(r)$  for the six energetically lowest states ( $n \leq 3$ ) of atomic hydrogen ( $Z = 1$ ) and H-like atoms ( $Z > 1$ ) in closed form.

From the radial wave functions one derives the probability distributions

$$w(r)dr = [R_{n\ell}(r)]^2 r^2 dr \quad (2.125)$$

**Fig. 2.10** Schematic illustration of the relation between potential (*top*) and corresponding wave function (*bottom*) for different  $\ell$ , exemplified for the  $n = 3$  level with  $\ell = 0$  and 1. Grey shaded is the classically forbidden region, red-black circles indicate classical turning points



**Table 2.2** Radial wave functions for the energetically lowest states of H and H-like atoms

$n$	$\ell$	$R_{n\ell}(r)$ with $\rho = 2Zr/(n\bar{a}_0)$ and $\bar{a}_0 = a_0 m_e/\bar{m}_e$
1	0	$R_{10}(r) = 2(\frac{Z}{a_0})^{3/2} e^{-\rho/2}$
2	0	$R_{20}(r) = \frac{1}{2\sqrt{2}} (\frac{Z}{a_0})^{3/2} (2 - \rho) e^{-\rho/2}$
	1	$R_{21}(r) = \frac{1}{2\sqrt{6}} (\frac{Z}{a_0})^{3/2} \rho e^{-\rho/2}$
3	0	$R_{30}(r) = \frac{1}{9\sqrt{3}} (\frac{Z}{a_0})^{3/2} (6 - 6\rho + \rho^2) e^{-\rho/2}$
	1	$R_{31}(r) = \frac{1}{9\sqrt{6}} (\frac{Z}{a_0})^{3/2} \rho(4 - \rho) e^{-\rho/2}$
	2	$R_{32}(r) = \frac{1}{9\sqrt{30}} (\frac{Z}{a_0})^{3/2} \rho^2 e^{-\rho/2}$

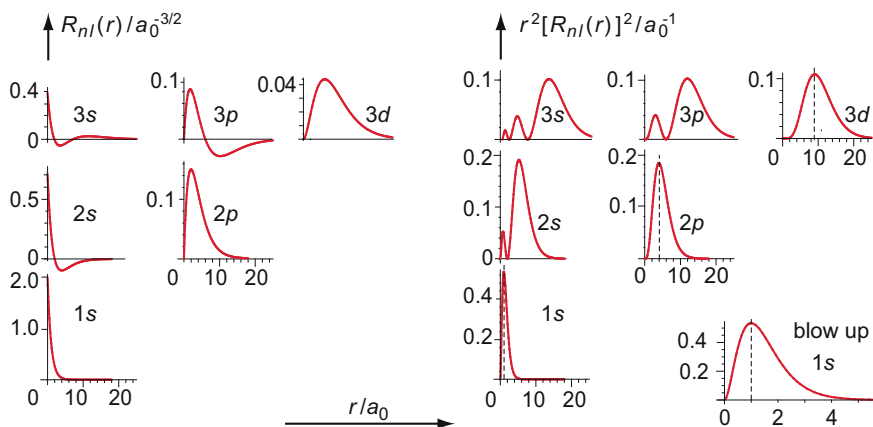
for the electron to be found between  $r$  and  $r + dr$ . For comparison with the classical picture of an orbiting electron one has to consult these probability distributions as a function of distance from the nucleus. A graphical illustration of the radial wave functions  $R_{n\ell}(r)$  and the radial probability distributions  $w(r)$  is shown in Fig. 2.11. Closer inspection of the probability distributions shows, that their maxima match exactly the radii of the respective BOHR orbits for the largest  $\ell = n - 1$  at any given  $n$ !

## 2.6.8 Density Plots

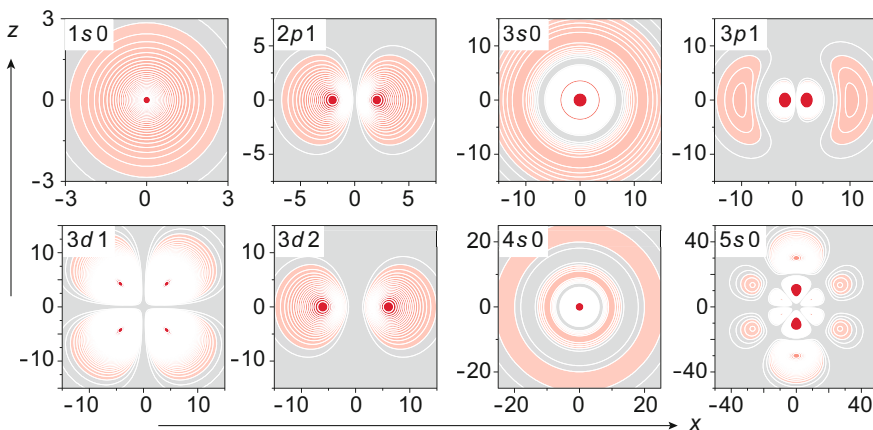
The complete solutions (atomic orbitals)  $\psi_{n\ell m}(r, \theta, \varphi)$  of the SCHRÖDINGER equation (2.108) consist of radial *and* angular part. With the spherical harmonics Sect. 2.5.3 and the just discussed radial functions the original ansatz (2.109)  $\psi_{n\ell m}(r, \theta, \varphi) = R_{n\ell}(r)Y_{\ell m}(\theta, \varphi)$  is validated. With (2.86) and (2.124) these wave functions are already orthonormalized:

$$\langle n\ell m | n'\ell' m' \rangle = \int \int \int \psi_{n\ell m}^* \psi_{n'\ell' m'} r^2 dr \sin \theta d\theta d\varphi = \delta_{nn'} \delta_{\ell\ell'} \delta_{mm'}. \quad (2.126)$$

The square of the wave function  $|\psi_{n\ell m}(r, \theta, \varphi)|^2$  represents the probability distribution for finding electrons per volume element, or equivalently the electron density within the atom as a function of position in space. Since these atomic orbitals form



**Fig. 2.11** Radial wave functions of the H atoms  $R_{n\ell}(r)$  and probability distributions  $r^2 R_{n\ell}^2(r)$  for the K, L and M shell. The dashed, vertical lines in the probability plots for the highest  $\ell$  at a given  $n$  indicate the corresponding BOHR radii. Note the drawing for the  $1s$  orbital on a blown up  $r$ -scale



**Fig. 2.12** Density plots for some characteristic H atom wave functions  $\psi_{n\ell m}$ . Plotted are equidensity lines (red high, grey low probability density). The distances are given in  $a_0$

a base for solving many key problems in atomic and molecular physics, we recommend our readers to visualize and memorize their general shape intensively. One finds a host of instructive Internet-sites, e.g. with Java applets to generate the H orbitals in a variety of displays. Thus, we present in Fig. 2.12 only a small selection of cuts through the 3D density distributions. Plotted are the contour lines of the density  $|\psi_{n\ell m}(x, y=0, z)|^2 = |R_{n\ell}(r)Y_{\ell m}(\theta, \varphi)|^2$  in the  $xz$  plane on a linear scale (in contrast to many presentations in the WWW, where one finds the density plotted on a log-scale). For clearness we have indicated the highest densities by red areas.

We finally note again, that only the  $ns$  orbitals have a finite density at the origin,  $|\psi_{ns}(0)| > 0$ , while  $\psi_{n\ell m}(0, \theta, \varphi) \equiv 0$  for  $\ell > 0$ . Specifically, from (2.122) and with  $Y_{00}(\theta, \varphi) = 1/\sqrt{4\pi}$  we record for later use:

$$|\psi_{n00}(0)|^2 = Z^3/(\pi a_0^3 n^3). \quad (2.127)$$

### 2.6.9 Spectra of the H Atom

Just as in the BOHR model, the transition energies (wavenumbers, frequencies) in atomic hydrogen are given by the RYDBERG formula (1.147)–(1.149). Traditionally, one characterizes spectral lines series for transitions  $n\ell \leftrightarrow n'\ell'$

$$\hbar\omega = h\nu = W_{n\ell} - W_{n'\ell'} = Z^2 \left( \frac{1}{n'^2} - \frac{1}{n^2} \right) \frac{E_h}{2} \frac{\bar{m}_e}{m_e} \quad (2.128)$$

according to  $n'$  (with  $n' < n$ ). Clearly, due to the  $m$  and (for the H atom)  $\ell$  degeneracy, the angular momentum quantum numbers do not influence the position of the spectral lines – as one also verifies by a glance at Fig. 2.8. This holds at least in 1st order approximation. Finer effects will be discussed in Chap. 6.

A lot of scientific detective work of the early pioneers went into discovering the connection between spectra and term energies, and the series are named after those who originally discovered them. Most prominent are the LYMAN ( $n' = 1$  in the VUV), BALMER ( $n' = 2$  in the VIS and near UV) and PASCHEN series ( $n' = 3$  in the near IR). Within the series, the BALMER lines are historically referred to as “H-alpha”, “H-beta”, “H-gamma” etc., more generally the lines of the different series are designated as Ly- $\alpha$ , and Ly- $\beta$ , Ly- $\gamma$ , ..., Ba- $\alpha$ , Ba- $\beta$ , Ba- $\gamma$ , ... and so on, with  $\alpha = n' + 2$ ,  $\beta = n' + 3$ , etc.

### 2.6.10 Expectation Values of $r^k$

One often needs to know the expectation values of the electron distance from origin  $r$  to a certain power  $k$ . In principle, they could be determined by a large number of individual measurements of this value in an suitably designed experiment. Quantum mechanics provides:

$$\langle r^k \rangle = \langle n\ell | r^k | n\ell \rangle = \int_0^\infty R_{n\ell}(r) r^k R_{n\ell}(r) r^2 dr = \int_0^\infty R_{n\ell}^2(r) r^{2+k} dr \quad (2.129)$$

with  $\int_0^\infty R_{n\ell}^2(r) r^2 dr = 1.$

These integrations are trivial but somewhat tedious. Using (2.122) and (2.123) one obtains (for later reference):<sup>9</sup>

<sup>9</sup>Here too, for high precision measurements one has to replace  $a_0 \rightarrow \bar{a}_0 = a_0 m_e / \bar{m}_e$ .



$$\begin{aligned}
\langle r \rangle_{n\ell} &= a_0 \frac{n^2}{Z} \left[ 1 + \frac{1}{2} \left( 1 - \frac{\ell(\ell+1)}{n^2} \right) \right] \\
\langle r^2 \rangle_{n\ell} &= a_0^2 \frac{n^4}{Z^2} \left\{ 1 + \frac{3}{2} \left[ 1 - \frac{\ell(\ell+1)}{n^2} - \frac{1}{3} \right] \right\} \\
\left\langle \frac{1}{r} \right\rangle_{n\ell} &= \frac{1}{a_0} \frac{Z}{n^2} \\
\left\langle \frac{1}{r^2} \right\rangle_{n\ell} &= \frac{1}{a_0^2} \frac{Z^2}{n^3 (\ell + 1/2)} \\
\left\langle \frac{1}{r^3} \right\rangle_{n\ell} &= \frac{1}{a_0^3} \frac{Z^3}{n^3 \ell (\ell + 1/2) (\ell + 1)}.
\end{aligned} \tag{2.130}$$

### 2.6.11 Comparison with the BOHR Model

One often hears the verdict that the BOHR model is basically wrong – albeit predicting the correct term energies  $W_{n\ell}$  and spectra (1.131) for the H atom in agreement with quantum mechanics – and thus should be abolished when teaching modern atomic physics. We do not adhere to such dogmatic view.

Of course, BOHR's orbits have to be replaced by atomic orbitals, i.e. by density distributions of the electrons within the atoms, and BOHR's quantization condition (1.130),  $L = n\hbar$ , has to be confronted with its quantum mechanical analogue,  $\hat{L}_z \Phi(\varphi) = m\hbar \Phi(\varphi)$ . Obviously,  $m \leq \ell \leq n - 1$  is *not equal to*  $n$  as postulated in the BOHR model – but it is a good first guess.

On the other hand, the concept of angular momentum quantization, of stationary states, and of radiation emitted upon transition between them with  $h\nu = \Delta W_{n\ell}$  was a brilliant, daring and instrumental step on the way to understand the quantum nature of microscopic phenomena – even though the fact that states without orbital angular momentum ( $\ell = 0$ ) do exist, does not fit at all into the BOHR model. However, the higher the angular momenta, the closer the atomic orbitals correspond to BOHR's orbits. And in general, the *correspondence principle* holds:

- *quantum mechanical and classical values of observables approach each other for very large quantum numbers.*

A quantitative comparison of atomic orbitals with BOHR's orbits in hydrogen like atoms shows that the maxima of the electron radial distribution (see Fig. 2.11) for  $\ell_{\max} = n - 1$  are indeed found at  $r = a_0 n^2 / Z$ , i.e. they correspond exactly to the BOHR radii according to (1.135). And more specifically, electron orbitals with  $m = \pm \ell$  may to some extent be associated with electrons moving on a circle – a notion which holds again particularly well for large  $\ell$ . Such “circular states” are actually an interesting subject studied in highly excited RYDBERG atoms.

However, the maxima of the probability distributions are of course not directly observable; rather one may compare expectation values such as  $\langle n\ell|r|n\ell\rangle = \langle r\rangle$ . For the largest angular momenta  $\ell = n - 1$  one obtains from (2.130)

$$\langle r\rangle = \lim_{n \gg 1} \left[ \frac{1}{2}n + n^2 \right] \frac{a_0}{Z} = n^2 \frac{a_0}{Z}, \quad (2.131)$$

which obviously agrees in the limit with BOHR's prediction (1.135). Conversely, for the smallest values of  $\ell = 0$ , the average radius  $\langle r\rangle$  is distinctively larger than predicted by the BOHR model, namely  $(3/2)n^2 a_0/Z$ .

In summary, we do not feel that the BOHR model should be completely forgotten. Apart from its outstanding historical impact, we shall come across a number of specific aspects in modern AMO physics for which useful, simple models or concepts have been stimulated by images of electrons moving on classical trajectories – combined with appropriate quantization rules. We may think of BORN-OPPENHEIMER approximation for molecular physics and of semiclassical trajectory calculations in atomic scattering theory, to mention just two important, and very successful examples – or, as we shall see in the following section, the derivation of the magnetic moment of an electron associated with its orbital angular momentum.

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### Section summary

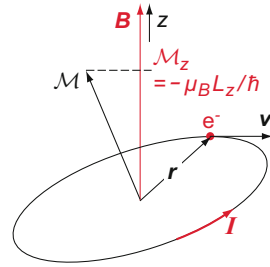
- The eigenenergies of the H atom,  $W_{n\ell} = Z^2/(2n^2)E_h$ , depend only on the principle quantum number  $n$  ... a specific consequence of the pure COULOMB potential. For precision measurements this has to be corrected by  $\bar{m}_e/m_e$  where  $\bar{m}_e$  is the reduced mass of the electron.
- Electron wave functions for the H atom can be expressed in analytical form  $\psi_{n\ell m}(r, \theta, \varphi) = R_{n\ell}(r)Y_{\ell m}(\theta, \varphi)$  with the spherical harmonics  $Y_{\ell m}(\theta, \varphi)$  and the radial function  $R_{n\ell}(r)$  being proportional to the LAGUERRE polynomials.
- The asymptotic behaviour of the wave functions should be memorized:  $\lim_{r \rightarrow \infty} R_{n\ell}(r) \propto \exp(-\sqrt{2|W_{n\ell}|}r)$  and  $\lim_{r \rightarrow 0} R_{n\ell}(r) \propto r^\ell$ .
- good quantum numbers characterize the eigenvalues of such observables that may be measured simultaneously with the HAMILTON operator.

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## 2.7 Normal ZEEMAN Effect

The so called *normal ZEEMAN effect* is actually not normal at all. It is observed only in special cases. It concerns atoms *in an external magnetic field*. The word 'normal' simply alludes to the classical interpretation of such a situation – ignoring the electron spin. We shall treat atoms in external fields in great detail in Chap. 8. Thus, the subject is touched here just briefly, and only since it confronts us for the first time with the removal of a specific energy degeneracy, the  $m$  degeneracy in this case.

**Fig. 2.13** Electron circling in a magnetic field  $\mathbf{B}$  and its orbital magnetic moment  $\hat{\mathcal{M}}$



### 2.7.1 Angular Momentum in an External B-Field

As discussed in Sect. 1.9, an orbital angular momentum has a magnetic moment (1.150) which we rewrite in operator form

$$\hat{\mathcal{M}} = -\frac{e}{2m_e} \hat{\mathbf{L}} = -\mu_B \frac{\hat{\mathbf{L}}}{\hbar}, \quad (2.132)$$

with the BOHR magneton  $\mu_B$ . Its potential energy (1.153) in an external magnetic field  $\mathbf{B}$  is

$$\hat{V}_B = -\hat{\mathcal{M}} \cdot \mathbf{B} = \mu_B \frac{\hat{\mathbf{L}}}{\hbar} \cdot \mathbf{B}. \quad (2.133)$$

We choose  $z \parallel \mathbf{B}$  so that  $\hat{V}_B = +\mu_B (\hat{L}_z / \hbar B)$ , as indicated in the vector diagram Fig. 2.13. The Hamiltonian contains now an additional term  $\hat{V}_B$ ,

$$\hat{H} = \hat{H}_0 + \hat{V}_B = \hat{H}_0 + \mu_B \frac{\hat{L}_z}{\hbar} B, \quad (2.134)$$

assuming the unperturbed SCHRÖDINGER equation to be

$$\hat{H}_0 \psi_{n\ell m} = W^{(0)} \psi_{n\ell m}.$$

$\hat{H}_0$  may e.g. be the HAMILTON operator (2.106) for the H atom. Thus, in the presence of an external field the SCHRÖDINGER equation to be solved reads

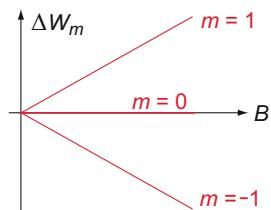
$$(\hat{H}_0 + \mu_B (\hat{L}_z / \hbar) B) |n\ell m\rangle = (W^{(0)} + \Delta W) |n\ell m\rangle, \quad (2.135)$$

with  $\Delta W$  being the change of total energy in respect of the unperturbed state. Here and in the following we use state vectors instead of wave functions  $\psi_{n\ell m} \rightarrow |n\ell m\rangle$  for compact writing.

The present problem is a particular simple case for the so called *perturbation theory* to which we shall come later in some detail. At this point we just remember that according to (2.79) and (2.81) the eigenfunctions  $\psi_{n\ell m}(r, \theta, \varphi) = R_{n\ell}(r) Y_{n\ell}(\theta, \varphi)$  of the H atom, or their eigenstates  $|n\ell m\rangle$ , respectively, are also eigenfunctions (eigenstates) of  $\hat{\mathbf{L}}^2$  and  $\hat{L}_z$  with

$$\hat{L}_z |n\ell m\rangle = m\hbar |n\ell m\rangle. \quad (2.136)$$

**Fig. 2.14** The ‘normal’ ZEEMAN effect



Thus, the eigenstates  $|n\ell m\rangle$  of the unperturbed Hamiltonian  $\hat{H}_0$  are also eigenstates of the full  $\hat{H}$  so that we may insert (2.136) into (2.135) to obtain:

$$(\hat{H}_0 + \mu_B m B)|n\ell m\rangle = (W^{(0)} + \Delta W_m)|n\ell m\rangle$$

with  $\Delta W_m = \mu_B m B$ . (2.137)

### 2.7.2 Removal of $m$ Degeneracy

The latter relation obviously implies that in a magnetic field the energy degeneracy for different  $m$  is removed. The originally identical energies of the  $2\ell + 1$  states  $|n\ell m\rangle$  which correspond to a given value of  $n$  and  $\ell$ , now split into  $2\ell + 1$  different energy sub-levels. According to (2.137) the splitting is proportional to  $m$  and  $B$ . The origin of this splitting is that *the magnetic field breaks the spherical symmetry* characteristic for the unperturbed H atom.

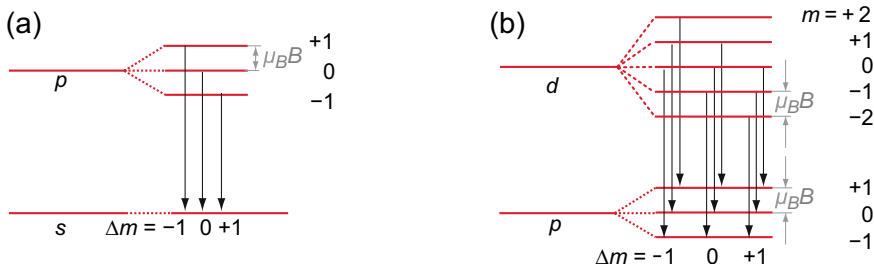
We illustrate this for the example of an  $np$  state  $|np m\rangle$  with  $\ell = 1$  and sublevels  $m = -1, 0$ , and  $1$ . Figure 2.14 shows the energy changes  $\Delta W_m$  as a function of the magnetic field  $B$ .

One may observe this splitting e.g. in optical emission spectra. Figure 2.15 compares the emerging spectra for (a) a  $p \rightarrow s$  and (b) a  $d \rightarrow p$  transition. The individual transitions are indicated by black, downward arrows. The *selection rules applied in this plot* are  $\Delta\ell = \pm 1$  and  $\Delta m = 0, \pm 1$ . They will be derived and discussed in Sect. 4.4.

As the degeneracy and hence the number of split levels is  $2\ell + 1$ , a manifold of transitions may occur if states with  $\ell > 1$  are involved. This is illustrated in Fig. 2.15(b) where the upper levels correspond to a  $d$  state. Since, however, for the normal ZEEMAN effect the splitting between neighbouring levels is always  $\mu_B B$  according to (2.137), independent of  $\ell$  and  $m$ , and since for all transitions  $\Delta m = 0, \pm 1$ , one nevertheless sees only a *line triplet* in all cases.

As mentioned at the beginning of this section: in reality this kind of ZEEMAN effect is seen only in special situations (see Sect. 8.1.2), since usually the spin of electrons plays an important role and complicates the observations.

We note here an important message from a situation which one typically encounters in quantum systems with two or more degenerate states  $|1\rangle, |2\rangle, |3\rangle$ : The *degeneracy is removed* as soon as some *additional, perturbing interaction*  $V_1$  has to be considered for which the *matrix elements*  $\langle i|V_1|j\rangle$  between some of these states *do not vanish*.



**Fig. 2.15** ‘Normal’ ZEEMAN effect for (a)  $p \rightarrow s$  and (b)  $d \rightarrow p$  transitions. In case of equal splitting in the excited and ground states one observes in each case a line triplet – in spite of the 5-fold splitting in the  $d$  state

### Section summary

- A magnetic field  $\mathbf{B}$  removes the central symmetry and hence the  $m$  degeneracy. For the so called ‘normal’ ZEEMAN effect, theory predicts a level splitting  $\Delta W_m = \mu_B m B$ .
- The selection rules for optical transitions are  $\Delta \ell = \pm 1$  and  $\Delta m = 0, \pm 1$ .

## 2.8 Dispersion Relations

We make a brief detour here, illuminating the borderline between atomic, molecular, optical and solid state physics. Traditionally, dispersion relations are used in optics and characterize an important material property: the dependence of the wavelength  $\lambda$  (or wavenumber  $k = 2\pi/\lambda$ ) of electromagnetic radiation on its frequency  $\omega$ . From a quantum mechanical point of view one may generalize this to describe the relation between the energy of a photon  $W = \hbar\omega$  (or in fact the energy of any other particle) and its wave vector  $\mathbf{k}$ .

For the massless particle photon in vacuo, with  $c = v\lambda = \omega/k$ , the dispersion relation

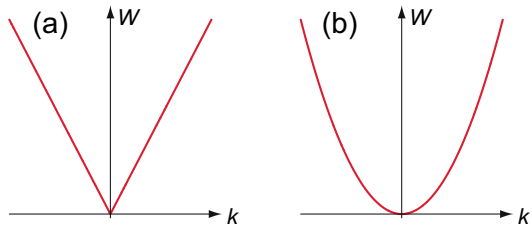
$$W = \hbar\omega = \hbar c |\mathbf{k}| \quad (2.138)$$

is obviously a linear relation between energy and wave vector. In contrast, the energy of a freely moving, nonrelativistic electron (whose mass is  $m_e$ ) is

$$W(\mathbf{k}) = W_P + \frac{m_e}{2} v^2 = W_P + \frac{p^2}{2m_e} = W_P + \frac{\hbar^2 \mathbf{k}^2}{2m_e}, \quad (2.139)$$

where we have used the DE BROGLIE relation (1.118).  $W_P$  allows for arbitrary energy calibration and may e.g. account for a potential energy or the rest mass energy. Thus, in this case the dispersion relation is quadratic. Both cases are illustrated graphically in Fig. 2.16.

**Fig. 2.16** Dispersion relations **(a)** linear for a massless particle (e.g. a photon) and **(b)** quadratic for a particle with mass (e.g. an electron), moving freely in 3D space



It should be noted that the quadratic relation (2.139) for particles with mass is in accord with the quantum mechanical calculation for a free particle in a 1D- or 3D-box according to (2.52) or (2.55). Providing the box is large enough, the energies may be considered continuous, i.e. they generally follow (2.139). However, this is only the most simple model for the *electronic band structure* in a solid. The particle in a box model does not account for the fact that the electrons in a solid do not really move freely: rather, the *electrons* move in the lattice of atomic ions and *experience a periodic potential* with strong attraction close to the ionic cores. Elsewhere the potential is partially screened by bound and other free electrons in the solid. We mention here two crucial consequences arising from this situation.

First, the dispersion relation (2.139) will have to be modified, which in principle requires a serious band structure calculation. Many phenomena may, however, be explained by the so called *parabolic approximation*. It parameterizes the band energy by introducing an *effective mass*  $m_e^*$  of the electron which may even depend on the direction into which the electron moves:

$$W(\mathbf{k}) = W_P \pm \hbar^2 \left( \frac{k_x^2}{2m_x^*} + \frac{k_y^2}{2m_y^*} + \frac{k_z^2}{2m_z^*} \right). \quad (2.140)$$

The  $\pm$  sign allows to extend the concept also to electron holes (positive charges in the lattice) and both these “quasi-particles” may have different masses. This mass enters into all further calculations on the dynamics and statistics of electrons and holes in a solid, e.g. into the FERMI-DIRAC statistics discussed in Sect. 2.4.3.

Second, one has to account for the periodicity of the motion in the lattice. The solutions for this problem are so called BLOCH waves

$$\psi(\mathbf{r}) \propto \exp(i\mathbf{k}\mathbf{r})u_{\mathbf{k}}(\mathbf{r}) \quad (2.141)$$

which are the product of a plane wave  $\exp(i\mathbf{k}\mathbf{r})$  and a periodic function  $u_{\mathbf{k}}(\mathbf{r})$ . The latter has to obey the periodic boundary condition

$$u_{\mathbf{k}}(\mathbf{r} + \mathbf{T}) = u_{\mathbf{k}}(\mathbf{r}), \quad (2.142)$$

where  $\mathbf{T}$  is any translation from one elementary cell of the lattice into another. Overall we still expect the dispersion relation (2.139) for electron energies to be more or less valid. As detailed studies show, one may have to replace the electron mass  $m_e$  by a (different) effective mass  $m_{\text{eff}}$  but the quadratic dependence of the energy  $W$

on the wave vector typically holds. The electron motion in general averages over the periodic potential. However, the energies and eigenfunctions will be influenced strongly by the lattice potential if the electrons are particularly close to the ions – or particularly far away from them. This is specifically relevant when the electron wave vector  $\mathbf{k} = \mathbf{k}_{\text{BZ}}$  is at (or close to) the BRILLOUIN zone (BZ), i.e. if the corresponding wave functions are constructively interfering (see Sect. 1.4.9). Such electrons ‘feel’ the periodic potential strongly, all others experience only an average.

We cannot go into detail of these concepts which are fundamental for the theory of band structure in solid states. We just emphasize some aspects which are also of importance in molecular physics. Thus, let us discuss the particularly simple situation of the 1D case, which e.g. describes a chain of atoms with a distance  $a$  from each other (also, with slight modifications, a ring like molecule). According to (1.95) and (1.93) the BRAGG condition for the  $n^{\text{th}}$  BZ then reads

$$k = k_{\text{BZ}} = n \frac{\pi}{a}. \quad (2.143)$$

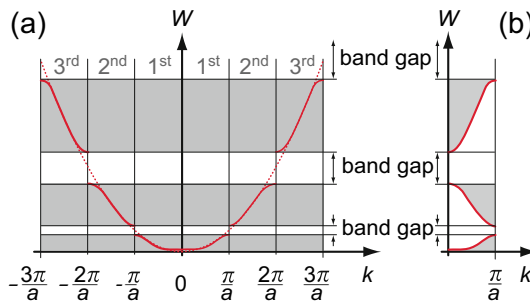
The corresponding wave functions are essentially  $\exp(ik_{\text{BZ}}x)$  and  $\exp(-ik_{\text{BZ}}x)$ , and for free travelling electrons the energy in that situation would be  $\hbar^2 k_{\text{BZ}}^2 / 2m_e$  in both cases. We have two energetically degenerate solutions. However, the most general solutions are linear superpositions of both, i.e. standing waves, with the two physically reasonable cases:

$$\psi(x) \propto \exp(ik_{\text{BZ}}x) \pm \exp(-ik_{\text{BZ}}x). \quad (2.144)$$

These correspond to  $\cos k_{\text{BZ}}x$  and  $\sin k_{\text{BZ}}x$ . The probability  $|\psi(x)|^2$  to find the electron close to the lattice ions is maximal in the first case, minimal in the latter. The *consequence* of the perturbing periodic potential is *removal of the degeneracy*, similar to ZEEMAN splitting discussed in the last section. And since the perturbing potential is highly attractive, we expect the energy to be lowered in the first case, and to be risen in the second case. In effect, at the boundary of the BZ we expect the energies to split into two, and a gap to arise between two bands of the otherwise continuous  $\hbar^2 k^2 / 2m_e$  distribution.

This is illustrated in Fig. 2.17(a). Since the periodicity of the system does not favour any particular origin in the reciprocal lattice, one projects all the possible energies onto the first BZ as shown in Fig. 2.17(b). Electrons in the system may assume all energies  $W$  in the grey shaded “energy bands”. The energy regions marked “band gap” are energetically forbidden.

In summary, in the solid state case continuous energy bands, with gaps in between them, replace the discrete energy levels which we have discussed for the atomic case (specifically for the H atom in the present chapter). One must, however, be aware of the fact that Fig. 2.17 shows only a particularly simple situation (1D case, one valence electron only). In general, the band structure of solid states is much more complicated, and depending on how many electrons are available to fill the bands, it provides the basis for such different materials as metals, isolators or semiconductors.



**Fig. 2.17** Emergence of energy bands in a periodic system (lattice constant  $a$ ) and band gaps. (a) Allowed energies (—) with distortions at the boundaries of the 1st, 2nd, and 3rd BRILLOUIN zone in comparison with the free particle (·····) as a function of  $k$ . (b) Projection onto the first BRILLOUIN zone

### Section summary

- Dispersion relations describe how the energy  $W$  of the system depends on the wave vector  $\mathbf{k}$ . The most simple cases are (a) the photon (a massless particle)  $W = \hbar c k$ , and (b) an electron (a particle with mass) moving freely  $W = \hbar^2 k^2 / (2m_e)$ .
- The influence of an average potential can be accounted for by an effective mass, replacing  $m_e$  – which even may depend on the direction of the electrons momentum.
- BLOCH waves,  $\psi(\mathbf{r}) \propto \exp(i\mathbf{k}\mathbf{r})u_{\mathbf{k}}(\mathbf{r})$ , are constructed to include the periodicity of the lattice in the function  $u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r} + \mathbf{T})$ .

## Acronyms and Terminology

AMO: ‘Atomic, molecular and optical’, physics.

a.u.: ‘atomic units’, see Sect. 2.6.2.

BZ: ‘BRILLOUIN zone’, represents all wave vectors of radiation which can be BRAGG-reflected by a crystal lattice. Important concept in solid state physics.

chemical-potential: ‘In statistical thermodynamics defined as the amount of energy or work that is necessary to change the number of particles of a system (by 1) without disturbing the equilibrium of the system’, see  $\mu$  in Sect. 1.3.4.

DOS: ‘Density of states’, number of states for a specified observable per unit of that observable. Most frequently the observable is the energy of a particle in a system. Typically it is given per unit volume of the system studied.

good quantum number: ‘Quantum number for eigenvalues of such observables that may be measured simultaneously with the HAMILTON operator (see Sect. 2.6.5)’.

IR: ‘Infrared’, spectral range of electromagnetic radiation. Wavelengths between 760 nm and 1 mm according to ISO 21348 (2007).



- NIST: ‘National institute of standards and technology’, located at Gaithersburg (MD) and Boulder (CO), USA. <http://www.nist.gov/index.html>.
- ODE: ‘Ordinary differential equation’.
- PDE: ‘Partial differential equation’.
- UV: ‘Ultraviolet’, spectral range of electromagnetic radiation. Wavelengths between 100 nm and 400 nm according to ISO 21348 (2007).
- VIS: ‘Visible’, spectral range of electromagnetic radiation. Wavelengths between 380 nm and 760 nm according to ISO 21348 (2007).
- VUV: ‘Vacuum ultraviolet’, spectral range of electromagnetic radiation. part of the [UV](#) spectral range. Wavelengths between 10 nm and 200 nm according to ISO 21348 (2007).

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Atoms, Molecules and Optical Physics 1

Atoms and Spectroscopy

Hertel, I.V.; Schulz, C.-P.

2015, XXXVII, 689 p. 285 illus., 265 illus. in color.,

Hardcover

ISBN: 978-3-642-54321-0