Quantum Mechanics

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Please report typos and other errors to F. Hassler. The translation has been done with the help of Mistral Small 4. In case of ambiguities, it might be helpful to consult the German version.

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Chapter 1

Introduction

1.1 Planck's Radiation Law (1900)

In the classical picture there are *particles* and *waves*. The particles define matter. They move along trajectories and possess a well-defined position and a well-defined velocity. Waves cannot be localized arbitrarily precisely. They can be split, for example at a double slit, and the parts can later interfere again. Light is a wave described by Maxwell's equations. Waves and matter interact with each other. In a cavity made of matter at temperature T, the enclosed radiation attains thermal equilibrium.

The free electromagnetic field satisfies Maxwell's equations ($c = 2.998 \times 10^8$ m/s is the speed of light)

$$\left(\frac{\partial^2}{\partial t^2} - c^2\Delta\right) \boldsymbol{E}(\boldsymbol{r}, t) = 0, \qquad \boldsymbol{\nabla} \cdot \boldsymbol{E}(\boldsymbol{r}, t) = 0. \tag{1.1}$$

Consider a mirrored cavity ($V = L \times L \times L$) with the boundary conditions (n is the component along the normal vector)[1]

$$\boldsymbol{E}_\parallel = 0, \qquad \frac{\partial}{\partial n}\boldsymbol{E}_\perp = 0\,. \tag{1.2}$$

The Maxwell equations are solved by the separation ansatz

$$\boldsymbol{E}(\boldsymbol{r}, t) = \boldsymbol{E}(\boldsymbol{r}) \cos(\omega t + \phi_0) \tag{1.3}$$

with

$$\begin{aligned} E_1(\boldsymbol{r}) &= E_1 \cos(k_1 r_1) \sin(k_2 r_2) \sin(k_3 r_3), \\ E_2(\boldsymbol{r}) &= E_2 \sin(k_1 r_1) \cos(k_2 r_2) \sin(k_3 r_3), \\ E_3(\boldsymbol{r}) &= E_3 \sin(k_1 r_1) \sin(k_2 r_2) \cos(k_3 r_3). \end{aligned} \tag{1.4}$$

The boundary conditions are satisfied provided

$$k_i = \frac{\pi}{L} n_i, \qquad n_i = 0, 1, 2, \ldots\,. \tag{1.5}$$

Maxwell's equations further require

$$\omega^2 = c^2 k^2 \qquad \text{and} \qquad \boldsymbol{E} \cdot \boldsymbol{k} = 0. \tag{1.6}$$

[1] The alternative boundary condition $\boldsymbol{E}_\perp = 0$ leads to no solution that satisfies Gauss's law $\boldsymbol{\nabla} \cdot \boldsymbol{E} = 0$.

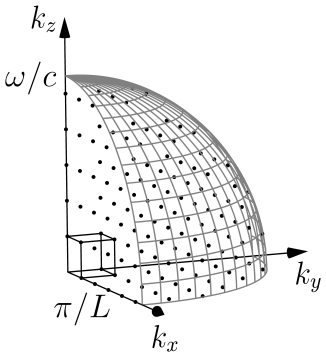


Fig. 1.1: Representation of the allowed modes: each point corresponds to a wave number permitted by the boundary condition. For large ω the number of modes is approximately given by the octant volume divided by the volume $(\pi/L)^3$ of the unit cell.

The last equation shows that for every $\boldsymbol{k}$ (defined by a triple $\boldsymbol{n}$) there are two linearly independent eigenmodes. Hence the number of eigenmodes $N(\omega)$ with frequency less than ω is, for $\omega \gg c/L$, approximately given by dividing the volume $\frac{1}{8} \times \frac{4\pi}{3}\omega^3/c^3$ of the spherical sector in the positive octant of frequency space by the volume $(\pi/L)^3$ per mode, see Figure 1.1 and (1.5). Taking into account the two polarization degrees of freedom one thereby obtains

$$N(\omega) = 2 \times \frac{\pi\omega^3}{6} \times \frac{V}{\pi^3 c^3} = \frac{V\omega^3}{3\pi^2 c^3}. \tag{1.7}$$

The classical Rayleigh-Jeans law for the spectral energy density $u(\omega)$ [energy / volume frequency] then follows from the equipartition theorem. This states that each mode carries the (average) energy $\overline{E} = k_{\mathrm{B}}T$ ($k_{\mathrm{B}} = 0.8617 \times 10^{-4}\,\mathrm{eV/K}$ denotes Boltzmann's constant). One thereby obtains the spectral energy density (Rayleigh 1900, corrected by Jeans 1905)

$$u(\omega)d\omega = \overline{E}\frac{dN}{V} = \frac{k_{\mathrm{B}}T}{\pi^2 c^3}\omega^2 d\omega. \tag{1.8}$$

The Rayleigh-Jeans law leads to the ultraviolet catastrophe with

$$\int_0^\infty d\omega\, u(\omega) = \infty. \tag{1.9}$$

Hence the result of Rayleigh and Jeans cannot be correct at high frequencies.

Experiments and empirical analyses show (Wien 1896) that

$$u(\omega) \sim \begin{cases} \omega^2, & \omega \to 0, \\ \omega^3 e^{-g\omega/k_{\mathrm{B}}T}, & \omega \to \infty, \end{cases} \tag{1.10}$$

as depicted in Figure 1.2. The prefactor ω^3 was chosen so as to reproduce the Stefan-Boltzmann law with $\int d\omega\, u(\omega) \propto T^4$. The exponential factor $\exp(-g\omega/k_{\mathrm{B}}T)$ arises from the thermodynamic consideration that, under adiabatic expansion of the cavity, the maximum of the energy density must scale proportionally to the temperature (Wien's displacement law, 1893).[2] The constant g has the dimension energy times seconds, corresponding to an action; it is determined by comparison with experiment (see below).

[2] This argument can be found, for example, in Edgar Buckingham, *'On the deduction of Wien's displacement law'*.

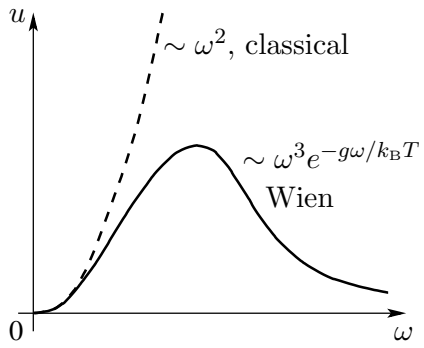


Fig. 1.2: The spectral energy density $u(\omega)$. The classically unbounded energy density (dotted) saturates in reality (solid) and falls off exponentially to zero at high energies (Wien's and Planck's radiation laws).

Planck's theory is able to predict both limits in (1.10) correctly. Planck's radiation law is based on the hypothesis that matter emits radiation only in *quanta* of $\hbar\omega$. Under this assumption the energies of a mode of frequency ω are *quantized* with $E = n\hbar\omega$, $n = 0, 1, 2, \ldots$. The mean energy of the mode is therefore

$$\begin{aligned}\overline{E} &= \frac{\sum_{n=0}^{\infty} \hbar\omega n e^{-\hbar\omega n/k_{\mathrm{B}}T}}{\sum_{n=0}^{\infty} e^{-\hbar\omega n/k_{\mathrm{B}}T}} = -\hbar\omega \frac{\partial}{\partial y} \ln\left(\sum_{n=0}^{\infty} e^{-yn}\right)\Bigg|_{y=\hbar\omega/k_{\mathrm{B}}T} \\ &= \hbar\omega \frac{\partial}{\partial y} \ln(1 - e^{-y})\Big|_{y=\hbar\omega/k_{\mathrm{B}}T} = \frac{\hbar\omega}{e^{\hbar\omega/k_{\mathrm{B}}T} - 1}\,. \end{aligned} \tag{1.11}$$

Inserting this into (1.8) yields the expression for the spectral energy density (Planck 1900)

$$u(\omega) = \frac{\omega^2}{\pi^2 c^3} \frac{\hbar\omega}{e^{\hbar\omega/k_{\mathrm{B}}T} - 1}, \tag{1.12}$$

$$\text{where} \quad \hbar = 6.582 \times 10^{-16}\,\mathrm{eV\,s} = 1.055 \times 10^{-34}\,\mathrm{J\,s} \tag{1.13}$$

is a new fundamental constant, the *Planck constant*. The successful comparison with experiment provided the first evidence for the *quantization* of the radiation field. The light quanta with energy $\hbar\omega$ are also called *photons*.

1.2 Photons (1905)

Following Planck's insight that the energy of the radiation field is quantized in units of $\hbar\omega$, Einstein (1905) postulated that light consists of photons, which are indivisible and carry energy $\hbar\omega$. As radiation we consider light propagating as a plane wave with (angular) frequency ω in z direction. The corresponding solution of (1.1) is given by

$$\boldsymbol{E}(\boldsymbol{r}, t) = E_1 \cos(kz - \omega t + \phi_1)\boldsymbol{e}_1 + E_2 \cos(kz - \omega t + \phi_2)\boldsymbol{e}_2 \tag{1.14}$$

with $\boldsymbol{B} = \boldsymbol{e}_3 \times \boldsymbol{E}$.[3]

In the following it is useful to introduce the compact notation

$$\begin{aligned}\boldsymbol{E}(\boldsymbol{r}, t) = \mathrm{Re}\left(\boldsymbol{\mathcal{E}} e^{ikz - i\omega t}\right) \quad \text{with} \quad \boldsymbol{\mathcal{E}} &= E_1 e^{i\phi_1}\boldsymbol{e}_1 + E_2 e^{i\phi_2}\boldsymbol{e}_2 \\ &\equiv \begin{pmatrix} E_1 e^{i\phi_1} \\ E_2 e^{i\phi_2} \end{pmatrix} \in \mathbb{C}^2 \end{aligned} \tag{1.15}$$

[3] We use Gaussian units for the electromagnetic fields.

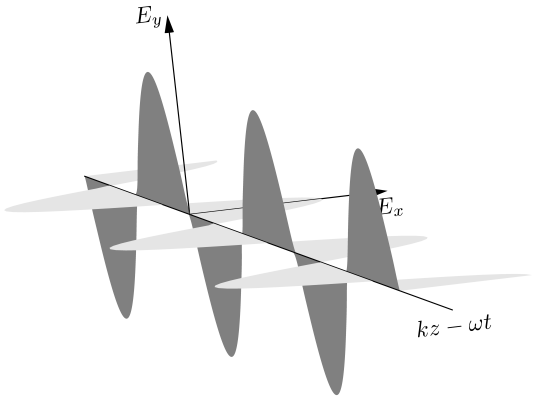


Fig. 1.3: Right-circularly polarized plane wave.

The vector $\boldsymbol{\mathcal{E}}$ determines the intensity of the radiation and its *polarization*. However, not every vector corresponds to a distinct polarization. In particular, $\boldsymbol{\mathcal{E}}_1, \boldsymbol{\mathcal{E}}_2$ with $\boldsymbol{\mathcal{E}}_1 = e^{i\theta}\boldsymbol{\mathcal{E}}_2$ describe the same wave, since the angle $\theta \in \mathbb{R}$ merely reflects a shift of the time origin by $t \mapsto t - \theta/\omega$. One may use this freedom to choose, without loss of generality, $\mathcal{E}_1 \geq 0$.

The following designations are used for special polarizations:

- $\boldsymbol{\mathcal{E}} \in \mathbb{R}^2$: linearly polarized wave (in direction $\pm\boldsymbol{\mathcal{E}}$).
- $\mathcal{E}_2 = i\mathcal{E}_1$: right-circularly polarized wave. The y-component follows the x-component by 90° out of phase with

  $$\boldsymbol{E} = E_0 \cos(kz - \omega t)\boldsymbol{e}_1 - E_0 \sin(kz - \omega t)\boldsymbol{e}_2.$$

  . The wave is called right-circular because, viewed against the direction of propagation, the electric field rotates counterclockwise.[4]
- $\mathcal{E}_2 = -i\mathcal{E}_1$: left-circularly polarized wave.

A general wave is said to be elliptically polarized.

The energy density is given by

$$\begin{aligned} u(\boldsymbol{r}, t) &= \frac{1}{8\pi}[E(\boldsymbol{r}, t)^2 + B(\boldsymbol{r}, t)^2] \\ &= \frac{1}{4\pi}[E_1^2 \cos^2(kz - \omega t + \phi_1) + E_2^2 \cos^2(kz - \omega t + \phi_2)]\,. \end{aligned} \tag{1.16}$$

With

$$\frac{1}{L}\int_0^L dx\, \cos^2(x) \overset{(L\to\infty)}{\to} \frac{1}{2}$$

we obtain the total energy

$$U = \int_V u(\boldsymbol{r}, t)\, dV = \frac{V|\boldsymbol{\mathcal{E}}|^2}{8\pi} \tag{1.17}$$

in a volume $V = L^3$ with $kL \gg 1$. From Planck's hypothesis that the energy is quantized in units of $\hbar\omega$ one finds

$$\frac{V|\boldsymbol{\mathcal{E}}|^2}{8\pi} = N\hbar\omega \tag{1.18}$$

[4]This convention corresponds to the IEEE standard. In optics textbooks the opposite convention is often used.

with $N \in \mathbb{N}$. This implies in particular that the amplitude $|\boldsymbol{\mathcal{E}}|$ cannot take arbitrary values. The value

$$|\boldsymbol{\mathcal{E}}|_{\mathrm{np}} = \sqrt{\frac{8\pi\hbar\omega}{V}}, \tag{1.19}$$

corresponding to a single photon is called the *zero-point fluctuation* of the radiation.

The momentum density of the electromagnetic field is given by $\boldsymbol{g} = \boldsymbol{S}/c^2$ with $\boldsymbol{S} = c(\boldsymbol{E} \times \boldsymbol{B})/4\pi$ the Poynting vector. For the example of the plane wave we obtain

$$\boldsymbol{g}(\boldsymbol{r}, t) = \frac{1}{4\pi c}[E_1^2 \cos^2(kz - \omega t + \phi_1) + E_2^2 \cos^2(kz - \omega t + \phi_2)]\boldsymbol{e}_3 \,. \tag{1.20}$$

The total momentum of the plane wave is therefore

$$\boldsymbol{P} = \int_V \boldsymbol{g}(\boldsymbol{r}, t)\, dV = \frac{V|\boldsymbol{\mathcal{E}}|^2 \boldsymbol{e}_3}{8\pi c} = N\hbar\boldsymbol{k}, \tag{1.21}$$

where in the last step we used (1.18). This equation can be interpreted as stating that each photon carries momentum $\boldsymbol{p} = \hbar\boldsymbol{k}$.

Consider now the following thought experiment: the radiation field is sent through a polarization filter. We assume that the filter only lets radiation in x direction pass. In particular, after the filter the radiation (1.14) is given by

$$\boldsymbol{E}(\boldsymbol{r}, t) = E_1 \cos(kz - \omega t + \phi_1)\boldsymbol{e}_1 \,. \tag{1.22}$$

From an analogous calculation as above one obtains the new total energy

$$U = \frac{VE_1^2}{8\pi} = \frac{V|\boldsymbol{e}_1 \cdot \boldsymbol{\mathcal{E}}|^2}{8\pi} = pN\hbar\omega, \tag{1.23}$$

where

$$p = \frac{|\boldsymbol{e}_1 \cdot \boldsymbol{\mathcal{E}}|^2}{|\boldsymbol{\mathcal{E}}|^2} \tag{1.24}$$

describes the fraction ($0 \leq p \leq 1$) of photons that pass the polarization filter.

If one imagines the situation with only a single photon in the volume ($N = 1$) one concludes that p must be interpreted as a *probability* for the transmission of the photon. Since a photon is indivisible, it makes no sense that a fractional number p of photons pass the filter. For consistency of quantum theory with classical physics (*correspondence principle*) it is therefore indispensable that quantum mechanics is a probabilistic theory.

1.3 Bohr's Quantization of the Atom (1913)

Atoms do not emit radiation at all frequencies $f = \omega/2\pi$, but only at discrete emission *species* lines. For the hydrogen atom the empirical relation

$$f = R\left(\frac{1}{n^2} - \frac{1}{m^2}\right), \qquad n, m \in \mathbb{N}, \quad m > n, \tag{1.25}$$

was found by Balmer in 1885 (with $n = 2$) and then extended by Rydberg in 1888. The Rydberg constant has the value $R = 3.290 \cdot 10^{15}$ Hz.

Classically the electron moves on a circular orbit and is thus accelerated. On account of this circular motion an atom should radiate energy continuously and the electron would spiral into the nucleus. Bohr postulated, analogously to Planck's quantization condition, that the atom can exist only in discrete states of well-defined energy E_n. The sharp spectral lines are then a consequence of transitions between these states. For example, the transition $m \mapsto n$ emits a photon of frequency

$$f = \frac{1}{2\pi\hbar}(E_m - E_n)\,. \tag{1.26}$$

With this ansatz one can interpret the Balmer formula as a quantization of the hydrogen states to the values

$$E_n = -\frac{2\pi\hbar R}{n^2}, \qquad n \in \mathbb{N} \tag{1.27}$$

In particular one obtains that the ground state with energy

$$-E_R = -2\pi\hbar R = -13.61\,\mathrm{eV} \tag{1.28}$$

is stable.

Bohr used the Rutherford model (1911) to describe the hydrogen atom: an electron of mass m and charge $-e$ orbits a proton of mass $M \gg m$ and charge $e > 0$. For the discrete quantum states Bohr postulated circular orbits of radius r, angular velocity ω, angular momentum L, and energy E. From the classical description of the central-force problem one obtains the relations

$$mr\omega^2 = \frac{e^2}{r^2}, \qquad L = mr^2\omega, \qquad E = \frac{L^2}{2mr^2} - \frac{e^2}{r}\,. \tag{1.29}$$

Solving for r and E yields

$$r = \frac{L^2}{me^2}, \qquad E = -\frac{me^4}{2L^2}, \qquad \omega = \frac{me^4}{L^3}\,. \tag{1.30}$$

To make the results agree with (1.27) one needs $L \propto n$. Bohr chose the quantization condition

$$L_n = \hbar n, \qquad n \in \mathbb{N}\,. \tag{1.31}$$

One thereby finds

$$r_n = a_B n^2, \qquad a_B = \frac{\hbar^2}{me^2} = 0.5292 \times 10^{-10}\,\mathrm{m} \qquad \text{(Bohr radius)}\,, \tag{1.32}$$

$$E_n = -\frac{E_R}{n^2}, \qquad E_R = \frac{me^4}{2\hbar^2} = 13.61\,\mathrm{eV} \qquad \text{(Rydberg energy)}\,. \tag{1.33}$$

1.4 Bohr's Correspondence Principle (1920)

Classical theory is correct macroscopically but fails when quantization aspects become relevant. Quantum theory, however, should reproduce the results of classical theory in the limit of large quantum numbers. Consequently there must exist a formal analogy between quantum theory and classical theory. These arguments form the basis of the correspondence principle.

As an example consider the Bohr atom with energies $E_n = -E_R/n^2$, cf. Figure 1.4. In the classical picture the electron orbits the proton with orbital frequency [see (1.30)]

$$\omega_{\mathrm{kl}} = \frac{me^4}{L^3} = \frac{2}{e^2}\left(\frac{2|E_{\mathrm{kl}}|^3}{m}\right)^{1/2}\,. \tag{1.34}$$

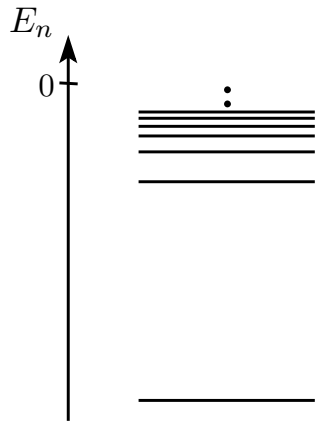


Fig. 1.4: Discrete spectrum in the Bohr atomic model. The lowest energy level is at $-E_R$. The correspondence principle applies at high excitation energies E_n with $n \gg 1$, where the spectrum is quasi-continuous.

Thus we expect the radiation of the atom to consist of harmonics of the fundamental frequency $\omega_{\rm kl}$.

Quantum mechanically the radiation emitted in the transition from $n+l$ to n with $n \gg l$ is given by

$$\omega_{n+l\to n} = \frac{E_{n+l} - E_n}{\hbar} \approx \frac{l}{\hbar}\frac{dE_n}{dn} = \frac{2lE_R}{\hbar n^3} = \frac{2l}{\hbar}\left(\frac{|E_n|^3}{E_R}\right)^{1/2}, \tag{1.35}$$

where in the last step we used the relation $n = (E_R/|E_n|)^{1/2}$.

From (1.33) one immediately obtains the correspondence

$$\omega_{n+l\to n} = l\,\omega_{\rm kl} \qquad (\text{ at energy } E_{\rm cl} = E_n = -E_R/n^2) \tag{1.36}$$

between the classical expression (1.34) and the quantum-mechanical expression (1.35). Alternatively, the correspondence principle can be used to replace the Bohr quantization condition (1.31).

1.5 Sommerfeld Quantization (1915)

The correspondence principle (or Bohr's quantization) leads to discrete classical orbits that are allowed in quantum mechanics. The quantization condition can be viewed as a condition on the reduced action integral

$$S_\varphi = \oint p_\varphi\, d\varphi = \oint L\, d\varphi = 2\pi L \tag{1.37}$$

for one circuit along the closed orbit. Indeed L is precisely the canonical momentum conjugate to the angle φ in the orbital plane and is conserved along the orbit. Bohr's quantization condition is therefore equivalent to the postulate

$$S_\varphi = 2\pi n\hbar\,. \tag{1.38}$$

Sommerfeld generalized this principle to f degrees of freedom. To do so he had to assume that the problem is completely separable: that is, there exist generalized coordinates q_i and momenta p_i such that p_i depends only on the coordinate q_i (and possibly conserved

quantities) but not on $q_{j\neq i}$. For bound motion each coordinate is periodic and the Sommerfeld quantization condition demands

$$S_i = \oint p_i(q_i)\, dq_i = 2\pi n_i \hbar, \qquad n_i \in \mathbb{N}\,. \tag{1.39}$$

Examples

Particle in a box: As a first example consider a particle moving in a 1D box potential, i.e. motion is restricted to $x \in [0, L]$ with L the width of the box. We consider a trajectory where the particle starts at position $x = 0$ with momentum $p_0 > 0$. At position $x = L$ the particle is reflected back. Energy conservation requires that on the return path the momentum takes the value $-p_0$. Altogether the action integral becomes

$$S = \oint p\, dx = p_0 \int_0^L dx - p_0 \int_L^0 dx = 2Lp_0\,. \tag{1.40}$$

According to Sommerfeld $2Lp_0 = 2\pi n\hbar$. Thus the initial momentum and the energy are quantized with

$$E_n = \frac{p_0^2}{2m} = \frac{\pi^2\hbar^2}{2mL^2} n^2\,. \tag{1.41}$$

Rotating mass point (rotor): A mass point m moves on a circle of radius R. The position is described by the generalized coordinate $q = \varphi$. From the kinetic energy $T = \frac{1}{2} mR^2\dot{\varphi}^2$ one obtains the canonical momentum $p = \partial T/\partial\dot{\varphi} = mR^2\omega$. The Sommerfeld quantization condition requires that

$$S = \oint p\, dq = 2\pi mR^2\omega = 2\pi n\hbar\,. \tag{1.42}$$

Thus the angular frequency is quantized to the values

$$\omega_n = \frac{\hbar}{mR^2} n \tag{1.43}$$

For the angular momentum $L = mR^2\omega$ one analogously finds

$$L_n = mR^2 \frac{\hbar}{mR^2} n = \hbar n\,. \tag{1.44}$$

2-body problem: As shown in classical mechanics, after separating the center-of-mass motion the 2-body problem can be brought to the form (in spherical coordinates)

$$H = \frac{1}{2\mu}\left(p_r^2 + \frac{p_\theta^2}{r^2} + \frac{p_\varphi^2}{r^2\sin^2\theta}\right) + V(r) \tag{1.45}$$

with $\mu = m_1 m_2/(m_1 + m_2)$ the reduced mass. Here the canonical momenta are given by

$$p_r = \mu\dot{r}, \qquad p_\theta = \mu r^2\dot{\theta}, \qquad p_\varphi = \mu r^2 \sin^2\theta\, \dot{\varphi}\,. \tag{1.46}$$

The 2-body problem has as conserved quantities the energy $E = H$ and the angular-momentum vector

$$\boldsymbol{L} = \mu \boldsymbol{r} \times \dot{\boldsymbol{r}} = p_\theta \boldsymbol{e}_\varphi - \frac{p_\varphi}{\sin\theta}\boldsymbol{e}_\theta\,, \tag{1.47}$$

which renders the problem integrable. Of particular interest is the z-component

$$\boldsymbol{e}_3 \cdot \boldsymbol{L} = p_\theta \underbrace{\boldsymbol{e}_3 \cdot \boldsymbol{e}_\varphi}_{=0} - \frac{p_\varphi}{\sin\theta} \underbrace{\boldsymbol{e}_3 \cdot \boldsymbol{e}_\theta}_{=-\sin\theta} = p_\varphi \tag{1.48}$$

and the absolute square

$$L^2 = \boldsymbol{L}^2 = p_\theta^2 + \frac{p_\varphi^2}{\sin^2\theta}\,. \tag{1.49}$$

From (1.45) one sees that the variable φ is cyclic. Thus p_φ is conserved and we find

$$S_\varphi = \oint p_\varphi \, d\varphi = 2\pi p_\varphi = 2\pi n_\varphi \hbar\,. \tag{1.50}$$

By solving the conservation of angular momentum (1.49) for p_θ one obtains the additional condition (for $|p_\varphi| \le L$)[5]

$$S_\theta = \oint p_\theta \, d\theta = 2\int_{p_\theta \ge 0} \sqrt{L^2 - \frac{p_\varphi^2}{\sin^2\theta}}\, d\theta = 2\pi(L - |p_\varphi|) = 2\pi n_\theta \hbar\,. \tag{1.51}$$

In the last step energy conservation yields the expression

$$S_r = \oint p_r \, dr = 2\int_{p_r \ge 0} \sqrt{2\mu[E - V(r)] - \frac{L^2}{r^2}}\, dr = 2\pi n_r \hbar\,. \tag{1.52}$$

The equations (1.50) and (1.51) give the quantization of angular momentum. In general one obtains

$$\boldsymbol{L} \cdot \boldsymbol{e}_3 = n_\varphi \hbar \qquad \text{and} \qquad L^2 = \underbrace{(n_\varphi + n_\theta)}_{=l}{}^2 \hbar^2\,. \tag{1.53}$$

Since $|\boldsymbol{L} \cdot \boldsymbol{e}_3| \le L$ must hold, for each l there are exactly $2l+1$ values for $m = n_\varphi \in \{-l, -l+1, \dots, l-1, l\}$.[6] The energy depends, however, via (1.52) only on n_r and l. Each energy eigenvalue is therefore $(2l+1)$-fold *degenerate*.

Hydrogen atom: The hydrogen problem is a 2-body problem with reduced mass $\mu = Mm/(M+m) \approx m$ and $V(r) = -e^2/r$. For this special potential the integral (1.52) can be evaluated explicitly. One obtains (for $-E_R\hbar^2/L^2 \le E < 0$)[7]

$$S_r = 2\int_{p_r \ge 0} \sqrt{2mE + \frac{2me^2}{r} - \frac{L^2}{r^2}}\, dr = 2\pi\hbar\left(\sqrt{\frac{E_R}{-E}} - l\right) = 2\pi n_r \hbar\,. \tag{1.54}$$

Solving for E yields the result

$$E_n = -\frac{E_R}{n^2}, \qquad (n = n_r + l = 1, 2, \dots) \tag{1.55}$$

[5] For the evaluation of the integral the substitution $|p_\varphi| \cot\theta = \sqrt{L^2 - p_\varphi^2}\, x$ may be helpful.

[6] Since n_φ corresponds to a rotation, negative values for the quantum number are also allowed. For fixed l the variables n_φ and n_θ take the values $(n_\varphi, n_\theta) \in \{(-l, 2l), \dots, (l, 0)\}$.

[7] For this integral the substitution $(1+x^2)r = r_- + r_+ x^2$ with $r_\pm$ the turning points satisfying $r_+ + r_- = e^2/|E|$ and $r_+ r_- = L^2/2|E|m$ is convenient.

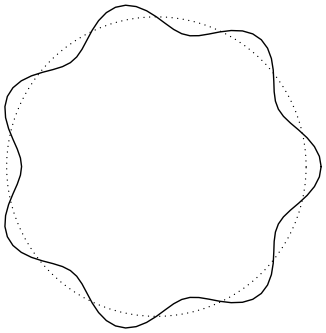


Fig. 1.5: For an allowed orbit the wavelength λ must be chosen so that a standing wave results. In the concrete example seven wavelengths fit into the circumference.

which agrees with (1.27). Note that the energy depends only on $n = n_r + n_\varphi + n_\theta$ (and not on the individual constants). The hydrogen problem is thus completely degenerate. The additional degeneracy reflects the fact that the mechanical orbits are closed. For each n there are the possible quantum numbers $(n_r, l) \in \{(n,0), \ldots, (1, n-1)\}$. The total degeneracy is therefore

$$\sum_{l=0}^{n-1} (2l+1) = n^2 \,. \tag{1.56}$$

Note that for the generic case of a non-separable system the Sommerfeld quantization condition is not applicable.

1.6 De Broglie Hypothesis (1923)

After Planck, radiation has certain particle-like properties since the energy of light is quantized in units of $\hbar\omega$. De Broglie extended the wave-particle duality to matter and postulated that matter also has a wave character.

For waves it is natural that oscillations occur only in certain eigenmodes, see (1.5). In de Broglie's picture the Bohr quantization condition $L_n = r_n p_n = \hbar n$ has a similar origin. If one assumes that the electron of mass m is described by a standing *matter wave* of wavelength λ_n, then on the circular orbit of radius r_n the wavefunction

$$\Psi(\varphi) \propto \cos(2\pi r_n \varphi / \lambda_n) \,. \tag{1.57}$$

obeys the condition that under $\varphi \mapsto \varphi + 2\pi$ it returns to itself as a standing wave (see Figure 1.5), leading to $2\pi r_n = n\lambda_n$. The Bohr quantization condition is therefore equivalent to the hypothesis that matter is also a wave with the de Broglie wavelength

$$\lambda = \frac{2\pi\hbar}{p}, \tag{1.58}$$

determined by the momentum. The n-th state then corresponds exactly to the case where n de Broglie wavelengths fit into the circumference of the n-th Bohr orbit.

With the de Broglie hypothesis one can also better understand the Sommerfeld quantization condition. For general bound motion in a completely separable system the integral

$$\oint \frac{1}{\lambda_i}\, dq_i = \frac{1}{2\pi\hbar} \oint p_i \, dq_i \tag{1.59}$$

is precisely the optical path length. For a standing matter wave to form this integral (over a closed orbit) must be an integer n_i, since then exactly n_i wavelengths fit into the orbit.

1.7 Schrödinger Equation (1926)

Based on de Broglie's hypothesis that particles in quantum mechanics should be described by matter waves, Schrödinger asked whether classical mechanics might simply be the ray-optical approximation of an underlying wave mechanics. As one knows from optics, light at small wavelengths can be described by rays that, for example, are reflected or refracted at interfaces. The de Broglie wavelength is quite small in classical situations. For a human of mass $m = 100$ kg moving at speed $v = 1\,\mathrm{m/s}$, one obtains, for instance,

$$\lambda = \frac{2\pi\hbar}{mv} = \frac{2\pi \times 1.055 \times 10^{-34}\,\mathrm{J\,s}}{100\,\mathrm{kg\,m/s}} \approx 6.6 \times 10^{-36}\,\mathrm{m}\,, \tag{1.60}$$

so that a ray-optical description is appropriate (note that the proton's size is about $1\,\mathrm{fm} = 10^{-15}$ m). The fundamental equation of ray optics is Fermat's principle, that the ray minimizes the optical path length. With de Broglie [see (1.59)], this statement is equivalent to Hamilton's principle, that the classical trajectory minimizes the action. Thus only a wave equation remains to be found that reproduces classical mechanics in the ray-optical limit.

This Schrödinger accomplished in 1926; the resulting Schrödinger equation[8]

$$\left(-\frac{\hbar^2\Delta}{2m} + V(\boldsymbol{r})\right)\Psi(\boldsymbol{r},t) = i\hbar\frac{\partial}{\partial t}\Psi(\boldsymbol{r},t) \tag{1.61}$$

is the fundamental equation of quantum mechanics.

In the ray-optical limit the wave is described by a *bundle of rays*

$$\Psi(\boldsymbol{r},t) = A(\boldsymbol{r},t)e^{iS(\boldsymbol{r},t)/\hbar}, \qquad A, S \in \mathbb{R}, \tag{1.62}$$

where A is the amplitude and $S/\hbar$ the phase. The wavelength λ is given by the distance between two surfaces on which $S/\hbar$ differs by 2π, i.e. $\lambda|\boldsymbol{\nabla}S|/\hbar = 2\pi$. The bundle represents all possible classical trajectories, and the amplitude A measures the density of the rays.

The rays $\boldsymbol{r}(t)$ are the (instantaneous) orthogonal trajectories to the surfaces $S(\boldsymbol{r},t)$ of constant phase, see Figure 1.7. Concretely, at time t the ray at position $\boldsymbol{r}$ points in the direction $\boldsymbol{\nabla}S$, or in formulas

$$\frac{d\boldsymbol{r}}{dt} \propto \boldsymbol{\nabla}S\,. \tag{1.63}$$

With

$$\boldsymbol{\nabla}(Ae^{iS/\hbar}) = \left(\boldsymbol{\nabla}A + \frac{iA}{\hbar}\boldsymbol{\nabla}S\right)e^{iS/\hbar}$$

one easily computes that

$$\Delta(Ae^{iS/\hbar}) = \left(\Delta A + \frac{iA}{\hbar}\Delta S + \frac{2i}{\hbar}\boldsymbol{\nabla}A\cdot\boldsymbol{\nabla}S - \frac{A}{\hbar^2}(\boldsymbol{\nabla}S)^2\right)e^{iS/\hbar}. \tag{1.64}$$

Ray optics is valid in regions where the amplitude varies only weakly over a wavelength $\propto \hbar/|\boldsymbol{\nabla}S|$. With

$$\left|\frac{\Delta A}{A}\right| \ll \left|\frac{\boldsymbol{\nabla}S}{\hbar}\right|^2 \tag{1.65}$$

[8] The symbol $\Delta = \boldsymbol{\nabla}\cdot\boldsymbol{\nabla} = \sum_{j=1}^{3}\frac{\partial^2}{\partial r_j^2}$ denotes the Laplace operator.

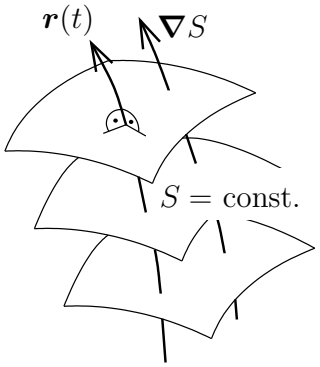


Fig. 1.6: Connection between ray optics and Hamilton-Jacobi action: The solution $S(\boldsymbol{r}, t)$ of the Hamilton-Jacobi equation corresponds to the phase of the wave function. Classical motion proceeds along $\boldsymbol{\nabla} S$ and is therefore orthogonal to the surfaces of constant phase. The wavelength is given by $2\pi\hbar/|\boldsymbol{p}|$.

one may then neglect the first term in (1.64) compared to the last.

Inserting (1.64) into the Schrödinger equation and separating real and imaginary parts yields the system of equations

$$\frac{(\boldsymbol{\nabla} S)^2}{2m} + V + \frac{\partial S}{\partial t} = 0, \tag{1.66}$$

$$A \Delta S + 2 \boldsymbol{\nabla} A \cdot \boldsymbol{\nabla} S = -2m \frac{\partial A}{\partial t}. \tag{1.67}$$

The first equation is the Hamilton-Jacobi equation of classical mechanics. It holds only in the ray-optical limit (1.65). The solution of the Hamilton-Jacobi equation divided by $\hbar$ corresponds to the phase of the wave function in the ray-optical limit.

From the action S one also obtains, by general mechanics, the momentum as $\boldsymbol{p} = \boldsymbol{\nabla} S$. The rays of wave mechanics are, by (1.63), precisely the trajectories of the particle.[9] The wavelength $\lambda = 2\pi\hbar/|\boldsymbol{\nabla} S|$ agrees with the de Broglie relation (1.58), thereby explaining the factor $\hbar^{-1}$ in the exponent of (1.62).

Equation (1.67) is an expression of the conservation of "trajectories." Indeed, the density of rays is locally given by $\rho = A^2$. Where many rays converge A becomes large, yielding an increased intensity. Multiplying (1.67) by A/m one can rewrite it as a continuity equation

$$\frac{\partial \rho}{\partial t} + \boldsymbol{\nabla} \cdot \boldsymbol{j} = 0 \tag{1.68}$$

with the probability current

$$\boldsymbol{j} = \frac{A^2}{m} \boldsymbol{\nabla} S = \rho \boldsymbol{v}\,. \tag{1.69}$$

Expressed in terms of the wave function, the density is $\rho = |\Psi|^2$. The continuity equation then supplies the conserved quantity

$$\int |\Psi(\boldsymbol{r}, t)|^2 \, dV = \text{const}\,. \tag{1.70}$$

As we saw in Chapter 1.2, the wave function must be interpreted *statistically*. Because the Schrödinger equation is linear, any multiple of $\Psi(\boldsymbol{r}, t)$ is also a solution. If one normalizes the function $\Psi(\boldsymbol{r}, t)$ so that

$$\int |\Psi(\boldsymbol{r}, t)|^2 \, dV = 1\,, \tag{1.71}$$

[9] The solution of the Hamilton-Jacobi equation describes a whole bundle of classical trajectories.

then $\rho(\boldsymbol{r},t) = |\Psi(\boldsymbol{r},t)|^2$ is a probability density, the *probability density* (Born 1926). The probability $p_\Omega(t)$ that the particle is in the region $\Omega \subset \mathbb{R}^3$ at time t is therefore given by

$$p_\Omega(t) = \int_\Omega |\Psi(\boldsymbol{r},t)|^2 \, dV \, . \tag{1.72}$$

Chapter 2

The Schrödinger Equation

To familiarize ourselves with quantum mechanics, we will solve the Schrödinger equation

$$\left(-\frac{\hbar^2\Delta}{2m}+V(\boldsymbol{r})\right)\Psi(\boldsymbol{r},t)=i\hbar\frac{\partial}{\partial t}\Psi(\boldsymbol{r},t) \tag{2.1}$$

for a few selected problems below. In doing so, we will see that the superposition principle plays a decisive role in the solution. We will also introduce the time-independent Schrödinger equation and observe that it leads to a discrete spectrum for bound motion, whereas unbound motion leads to a continuous spectrum.

2.1 Superposition Principle

The Schrödinger equation (2.1) is a linear differential equation. If Ψ_n are solutions of the Schrödinger equation, then so is the superposition

$$\Psi(\boldsymbol{r},t)=\sum_n a_n\Psi_n(\boldsymbol{r},t), \qquad a_n\in\mathbb{C}. \tag{2.2}$$

The coefficients a_n follow from the initial condition $\Psi(\boldsymbol{r},t_0)$; we will return to this later. The linearity is also used to *normalize* the wave function at the initial time t_0, so that $\int|\Psi(\boldsymbol{r},t_0)|^2\,dV=1$. With this normalization, as already discussed,

$$\rho(\boldsymbol{r},t)=|\Psi(\boldsymbol{r},t)|^2 \tag{2.3}$$

can be interpreted as a probability density in the sense of Born. For the wave function to be normalizable, it must decay for $r\to\infty$. In what follows, we will assume that the wave function decays exponentially (as is the case in most applications), so that we may always neglect boundary terms.

2.2 Probability Conservation

It is important to understand how the probability density ρ changes as Ψ evolves in time according to the Schrödinger equation. The time derivative of the probability density is

given by

$$\frac{\partial \rho}{\partial t} = \Psi^*(\partial_t \Psi) + (\partial_t \Psi)^* \Psi = 2\,\mathrm{Re}(\Psi^* \partial_t \Psi) \overset{(2.1)}{=} 2\,\mathrm{Re}\left[\Psi^*\left(-\frac{\hbar\Delta}{2im} + \frac{V}{i\hbar}\right)\Psi\right]$$
$$= \mathrm{Im}\left[\Psi^*\left(-\frac{\hbar\Delta}{m}\right)\Psi\right] = \boldsymbol{\nabla}\cdot\left[-\frac{\hbar}{m}\,\mathrm{Im}(\Psi^*\boldsymbol{\nabla}\Psi)\right], \tag{2.4}$$

where in the last step we have used that the additional term $\boldsymbol{\nabla}\Psi^* \cdot \boldsymbol{\nabla}\Psi = |\boldsymbol{\nabla}\Psi|^2$ is purely real. One sees that the density satisfies the continuity equation

$$\frac{\partial \rho}{\partial t} + \boldsymbol{\nabla}\cdot\boldsymbol{j} = 0 \tag{2.5}$$

with the *probability current density*

$$\boldsymbol{j} = \frac{\hbar}{m}\,\mathrm{Im}(\Psi^*\boldsymbol{\nabla}\Psi) = \frac{\hbar}{2im}\,(\Psi^*\boldsymbol{\nabla}\Psi - \Psi\boldsymbol{\nabla}\Psi^*) \tag{2.6}$$

Probability is thus locally conserved. Integrating the continuity equation over an arbitrary region Ω yields

$$\frac{dp_\Omega(t)}{dt} = -\int_\Omega (\boldsymbol{\nabla}\cdot\boldsymbol{j})\,dV = -\int_{\partial\Omega} \boldsymbol{j}\cdot d\boldsymbol{S}\,. \tag{2.7}$$

The probability $p_\Omega(t)$ that the particle is found in the region Ω can only increase or decrease if a probability current $\boldsymbol{j}$ is transported through the surface $\partial\Omega$. In particular, with $\boldsymbol{j}(\boldsymbol{r},t)r^2 \to 0$ for $r \to \infty$, the surface term drops out and the normalization of the wave function is preserved in time, so that

$$\frac{\partial}{\partial t}\int |\Psi(\boldsymbol{r},t)|^2\,dV = 0 \quad \Rightarrow \quad \int |\Psi(\boldsymbol{r},t)|^2\,dV = \int |\Psi(\boldsymbol{r},t_0)|^2\,dV = 1\,. \tag{2.8}$$

2.3 Ehrenfest's Theorem

So far we have examined the entire probability density $\rho(\boldsymbol{r},t)$. Often, however, one is interested only in the expectation value of the position

$$\langle \boldsymbol{r}\rangle_t = \int \boldsymbol{r}\rho(\boldsymbol{r},t)\,dV \tag{2.9}$$

at time t. Conventionally, the expectation value in quantum mechanics is denoted by angle brackets, i.e., $\langle A\rangle$ is the expectation value of A.

One can again compute the time evolution of the mean position of the particle using the Schrödinger equation. For the expectation value of the velocity we obtain

$$\langle \boldsymbol{v}\rangle_t = \frac{d}{dt}\langle \boldsymbol{r}\rangle_t = \int \boldsymbol{r}\,\partial_t\rho\,dV \overset{(2.4)}{=} -\frac{\hbar}{m}\,\mathrm{Im}\left(\int \boldsymbol{r}\,\Psi^*\Delta\Psi\,dV\right). \tag{2.10}$$

By partial integration (neglecting boundary terms) one can rewrite the k-th component of the integral as

$$\int r_k\Psi^*\Delta\Psi\,dV = -\int(\boldsymbol{\nabla}r_k\Psi^*)\cdot(\boldsymbol{\nabla}\Psi)\,dV = -\int\Psi^*\frac{\partial\Psi}{\partial r_k}\,dV - \int r_k|\boldsymbol{\nabla}\Psi|^2\,dV\,. \tag{2.11}$$

The second term is real and thus makes no contribution to (2.10). The first term is purely imaginary because of

$$\left(\int \Psi^* \boldsymbol{\nabla} \Psi \, dV\right)^* = \int \Psi \boldsymbol{\nabla} \Psi^* \, dV \overset{\text{(PI)}}{=} - \int \Psi^* \boldsymbol{\nabla} \Psi \, dV \tag{2.12}$$

We therefore obtain for the expectation value of the momentum the expression

$$\langle \boldsymbol{p} \rangle_t = m \langle \boldsymbol{v} \rangle_t = \int \Psi^* (-i\hbar \boldsymbol{\nabla}) \Psi \, dV. \tag{2.13}$$

With an analogous calculation for $d\langle \boldsymbol{p} \rangle_t / dt$ one can derive the *Ehrenfest's theorem*

$$m \frac{d^2}{dt^2} \langle \boldsymbol{r} \rangle_t = \frac{d}{dt} \langle \boldsymbol{p} \rangle_t = - \langle \boldsymbol{\nabla} V(\boldsymbol{r}) \rangle_t \tag{2.14}$$

Examples

Free particle: For a free particle with $V(\boldsymbol{r}) = 0$ the expectation value of the position satisfies the differential equation $d^2 \langle \boldsymbol{r} \rangle_t / dt^2 = 0$. On average, the particle thus moves along an inertial trajectory with $\langle \boldsymbol{r} \rangle_t = \boldsymbol{v}_0 t + \boldsymbol{r}_0$ and $\boldsymbol{v}_0 = \langle \boldsymbol{p} \rangle_t / m$.

Harmonic oscillator: The potential of a harmonic oscillator is given in principal axes by $V(\boldsymbol{r}) = \frac{m}{2} \sum_{k=1}^{3} \omega_k^2 r_k^2$. Ehrenfest's theorem requires that

$$\frac{d^2}{dt^2} \langle r_k \rangle_t = - \omega_k^2 \langle r_k \rangle_t, \qquad k = 1, 2, 3 \,. \tag{2.15}$$

The general solution is given by

$$\langle r_k \rangle_t = a_k \cos(\omega_k t + \varphi_k) \tag{2.16}$$

with $a_k, \varphi_k \in \mathbb{R}$. The k-th component of the mean particle position thus oscillates with angular frequency ω_k.

In the two examples we have seen that the mean particle position follows a classical trajectory. This is, however, not always the case. In particular, Ehrenfest's theorem, because of $\langle \boldsymbol{\nabla} V(\boldsymbol{r}) \rangle_t \neq \boldsymbol{\nabla} V(\langle \boldsymbol{r} \rangle_t)$, is in general not a closed system of equations for the expectation value of the particle position. For the mean position of a particle to follow a classical trajectory, one needs the additional assumption that the wave packet is sufficiently localized.

The localization length ξ is related to the variance

$$\xi^2 \simeq (\Delta \boldsymbol{r})^2 = \sum_k \left\langle (r_k - \langle r_k \rangle)^2 \right\rangle = \langle \boldsymbol{r}^2 \rangle - |\langle \boldsymbol{r} \rangle|^2 \,. \tag{2.17}$$

If the localization length is sufficiently small, one can expand $V(\boldsymbol{r})$ about $\boldsymbol{r}_{\mathrm{kl}}(t) = \langle \boldsymbol{r} \rangle_t$. In this case we obtain

$$\langle \boldsymbol{\nabla} V(\boldsymbol{r}) \rangle_t = \boldsymbol{\nabla} V(\boldsymbol{r}_{\mathrm{kl}}) + \sum_{k,l} \frac{\partial^2 V(\boldsymbol{r}_{\mathrm{kl}})}{\partial r_k \partial r_l} \underbrace{\left\langle r_l - \langle r_l \rangle_t \right\rangle_t}_{=0} \boldsymbol{e}_k + O\big(\xi^2 \partial^3 V\big) \,. \tag{2.18}$$

Thus $\boldsymbol{r}_{\mathrm{kl}}$ satisfies the classical equation of motion up to terms of order $\xi^2 \partial^3 V$. Note, however, that it is not sufficient to localize the particle sufficiently at the initial time, since the probability distribution of the particle spreads out under time evolution, as we will see later.

2.4 Time-Independent Schrödinger Equation

Since the potential $V(\boldsymbol{r})$ does not depend on time, the energy E is conserved along the classical trajectory. In the Schrödinger equation we may choose the separation ansatz

$$\Psi(\boldsymbol{r},t) = e^{-iEt/\hbar}\psi(\boldsymbol{r}) \tag{2.19}$$

Inserting this into (2.1) yields the time-independent (stationary) Schrödinger equation

$$\left(-\frac{\hbar^2}{2m}\Delta + V(\boldsymbol{r})\right)\psi(\boldsymbol{r}) = E\psi(\boldsymbol{r})\,. \tag{2.20}$$

It is an eigenvalue equation, and a solution $\Psi(\boldsymbol{r},t) = e^{-iEt/\hbar}\psi(\boldsymbol{r})$ is called an *stationary state*, since the associated density $\rho = |\Psi|^2 = |\psi|^2$ is time-independent.

The boundary conditions of the eigenvalue problem determine the allowed energies E_n and the corresponding eigenfunctions ψ_n. In many cases the set of eigenfunctions is countable with $n \in \mathbb{N}$. We further assume that any (physically reasonable) wave function can be written as a linear combination of the eigenfunctions ψ_n. In particular, the wave function Ψ_0 at the initial time t_0 can then be written as the superposition

$$\Psi_0(\boldsymbol{r}) = \Psi(\boldsymbol{r},t_0) = \sum_{n=1}^{\infty} a_n\psi_n(\boldsymbol{r}) \tag{2.21}$$

The solution of the time-dependent Schrödinger equation is then given by

$$\Psi(\boldsymbol{r},t) = \sum_{n=1}^{\infty} a_n\psi_n(\boldsymbol{r})e^{-iE_n(t-t_0)/\hbar}\,. \tag{2.22}$$

We have thus reduced the problem of finding the general solution of the Schrödinger equation (for given initial conditions) to that of finding eigenfunctions of the time-independent Schrödinger equation.

2.5 Bound Motion: Particle in a Box

In the following chapters we will consider the Schrödinger equation in one dimension in a few examples. In doing so, we will denote the position coordinate simply by $x \in \mathbb{R}$.

As a first problem we consider the case of a particle in a box potential, that is, a potential-free region surrounded by walls of height ∞, cf. Figure 2.1. The potential has the form

$$V(x) = \begin{cases} 0, & x \in [0,L], \\ \infty, & \text{otherwise.} \end{cases} \tag{2.23}$$

The particle can move freely in the interval $\Omega = [0,L]$ but has zero probability of being found for $x \notin \Omega$, so that $\psi(x) = 0$ there. For $x \in \Omega$ the Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x)\,. \tag{2.24}$$

holds. The general solution of this differential equation has the form

$$\psi(x) = A\cos(\sqrt{2mE}\,x/\hbar) + B\sin(\sqrt{2mE}\,x/\hbar) \tag{2.25}$$

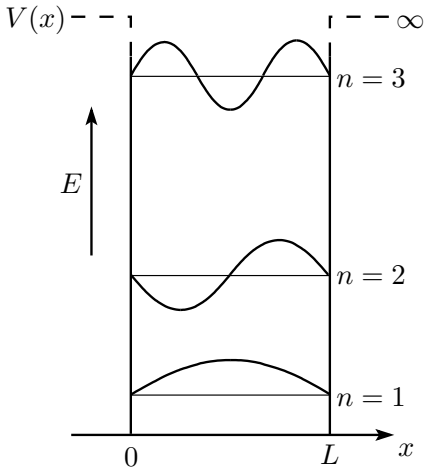


Fig. 2.1: Stationary states in the box potential.

with A, B free parameters. Note that the time-independent Schrödinger equation is not an initial value problem but an eigenvalue problem. In particular, we seek eigenvalues E_n such that the solutions of (2.24) satisfy the boundary conditions. In the present case the probability density must vanish at the boundary, so that

$$\psi(0) = \psi(L) = 0\,. \tag{2.26}$$

The condition $\psi(0) = 0$ requires that $A = 0$. This leaves the requirement

$$0 = \psi(L) = B\sin(\sqrt{2mE}\,L/\hbar)\,. \tag{2.27}$$

One thus obtains a nontrivial solution for $\sqrt{2mE}L/\hbar = n\pi$ with $n \in \mathbb{N}$ only if ψ. The eigenvalues are therefore given by [cf. (1.41)]

$$E_n = \frac{\pi^2\hbar^2}{2mL^2}n^2 = E_{\mathrm{np}}n^2 \tag{2.28}$$

with the eigenfunctions

$$\psi_n(x) = B_n\sin(n\pi x/L) = \sqrt{\frac{2}{L}}\sin(n\pi x/L)\,. \tag{2.29}$$

Note that the eigenfunctions are determined by the linearity of the Schrödinger equation only up to a constant B_n. In the last step we have chosen the constant so that $\int dx\,|\psi_n|^2 = 1$. Thus $\rho_n(x) = |\psi_n(x)|^2$ describes the probability of finding the particle in the stationary state with energy E_n.

Note that the energy is quantized to *discrete* values. In particular, the lowest energy is not simply $E = 0$, as would be the case classically for a particle at rest, but $E_{\mathrm{np}} > 0$. We will see later that this is an expression of the *zero-point motion*, which follows from the Heisenberg uncertainty principle. The states corresponding to the discrete energies are called *bound states*, since the particle remains within a finite region for all time. Another difference from our classical intuition is the fact that the expectation value of the momentum (2.13) vanishes in every stationary state, since

$$\langle p\rangle = \int \psi_n^*(-i\hbar\partial_x)\psi_n\,dx \propto \int_0^L \sin(n\pi x/L)\cos(n\pi x/L)\,dx = 0. \tag{2.30}$$

A general solution $\Psi(x,t)$ is obtained by superposition

$$\Psi(x,t) = \sum_n a_n \psi_n(x) e^{-iE_n(t-t_0)/\hbar} \tag{2.31}$$

with a_n, so that $\Psi_0 = \sum_n a_n \psi_n$. Since ψ_n is proportional to a sine function, the expansion coefficients are given by the Fourier transform. In particular, we have

$$a_n = \int_\Omega \psi_n^*(y)\Psi_0(y)\,dy = \sqrt{\frac{2}{L}} \int_0^L \sin(n\pi y/L)\Psi(y,t_0)\,dy\,. \tag{2.32}$$

Thus the general solution of the Schrödinger equation (2.1) is given by

$$\Psi(x,t) = \int K(x,y;t-t_0)\Psi(y,t_0)\,dy \tag{2.33}$$

with the propagator ($t > 0$)

$$K(x,y;t) = \sum_n \psi_n(x)\psi_n^*(y)e^{-iE_n t/\hbar} = \frac{2}{L}\sum_{n=1}^{\infty} \sin(n\pi x/L)\sin(n\pi y/L)e^{-iE_{\mathrm{n}\mathrm{p}}n^2 t/\hbar}. \tag{2.34}$$

The propagator satisfies the following properties:

- As a function of (x,t) for $t > 0$ it solves the Schrödinger equation, since each term $\psi_n(x)e^{-iE_n t/\hbar}$ does.
- In the limit $t \to 0^+$ we have $K(x,y;t) \to \delta(x-y)$. This ensures that $\Psi(x,t)$ tends to $\Psi_0(x) = \Psi(x,t_0)$ as $t \to t_0$.

One can also define the propagator by these two properties. Since the propagator solves every initial value problem via (2.34), it is also called the *fundamental solution*.

It is useful to consider what condition the probability conservation (2.8) imposes on the propagator. We require

$$\begin{aligned}\int |\Psi(x,t)|^2\,dx &= \int \left[\int K^*(x,y';t-t_0)K(x,y;t-t_0)dx\right] \Psi_0^*(y')\Psi_0(y)dy\,dy' \\ &= \int |\Psi_0(y)|^2\,dy\end{aligned} \tag{2.35}$$

for all initial conditions $\Psi_0(x)$. From this follows the *unitarity condition*

$$\int K^*(x,y';t-t_0)K(x,y;t-t_0)\,dx = \delta(y'-y) \tag{2.36}$$

for the propagator K. The solution strategy via the fundamental solution can be generalized to other problems, as we will see later.

Example To gain a better understanding of quantum mechanics in this simple system, we discuss an example: We choose as initial condition the normalized wave function

$$\Psi_0(x) = \frac{1}{\sqrt{2}}\Big[\psi_{n_0}(x) - i\psi_{n_0+1}(x)\Big], \qquad \text{with } n_0 \in \mathbb{N} \text{ fixed.} \tag{2.37}$$

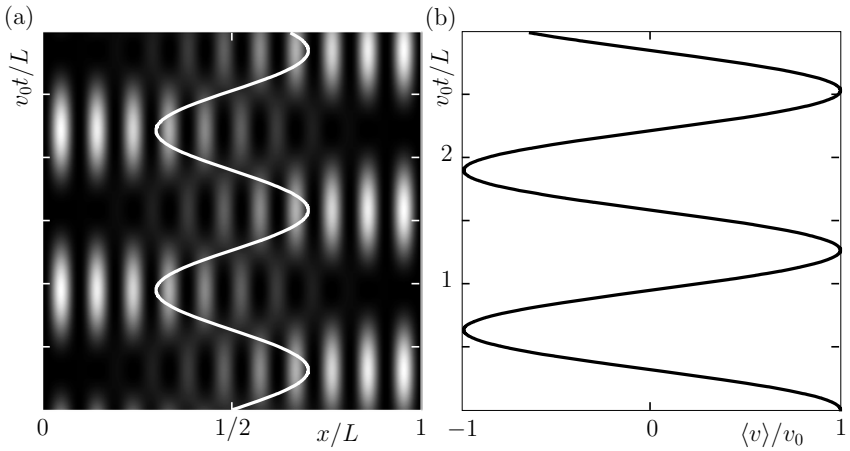


Fig. 2.2: (a) Time evolution of the probability of finding the particle $\rho(x,t)$ (gray scale) for $n_0 = 10$. The white line shows the expectation value of the particle position. The particle "moves" at least initially with approximately the velocity v_0. Unlike in the classical picture, the particle is reflected from the wall somewhat earlier than at time $L/2v_0$. (b) The expectation value of the velocity is likewise a smooth function. In classical mechanics it would jump at every turning point between $\pm v_0$.

The probability of finding the particle at time $t_0 = 0$ is given by

$$\begin{aligned}\rho_0(x) = |\Psi_0(x)|^2 &= \frac{1}{2}\Big[\psi_{n_0}(x)^2 + \psi_{n_0+1}(x)^2\Big] \\ &= \frac{1}{L} - \frac{1}{2L}\Big[\cos(2n_0\pi x/L) + \cos(2(n_0+1)\pi x/L)\Big]\,. \end{aligned} \tag{2.38}$$

At the initial time the particle has mean position[1]

$$x_0 = \langle x\rangle = \int_0^L \rho_0(x)\, x\, dx = \frac{1}{L}\int_0^L x\, dx = \frac{L}{2} \tag{2.39}$$

with standard deviation (square root of the variance)

$$\Delta x = \langle (x-x_0)^2\rangle^{1/2} \leq^{2} \left[\frac{1}{L}\int_0^L (x-x_0)^2\, dx\right]^{1/2} = \frac{L}{2\sqrt{3}} \approx 0.3L\,. \tag{2.40}$$

The particle is thus fairly well localized in the middle of the allowed interval.

The solution of the Schrödinger equation is given by

$$\begin{aligned}\Psi(x,t) &= \frac{1}{\sqrt{2}}\left[\psi_{n_0}(x)e^{-iE_{n_0}t/\hbar} - i\psi_{n_0+1}(x)e^{-iE_{n_0+1}t/\hbar}\right] \\ &= \frac{e^{-iE_{n_0}t/\hbar}}{\sqrt{2}}\left[\psi_{n_0}(x) - i\psi_{n_0+1}(x)e^{-iE_{\rm np}(2n_0+1)t/\hbar}\right]. \end{aligned} \tag{2.41}$$

[1] One uses that $\int_0^L \cos(2n_0\pi x/L)x\, dx = -(L/2n_0\pi)\int_0^L \sin(2n_0\pi x/L)\, dx = 0$.
[2] It holds that $\int_0^L \cos(2n_0\pi x/L)(x-x_0)^2\, dx = \int_0^L \cos(2n_0\pi x/L)x^2\, dx = L^3/2\pi^2 n_0^2 \geq 0$.

The probability of finding the particle thus evolves in time as

$$\rho(x,t) = \rho_0(x) - \psi_{n_0}(x)\psi_{n_0+1}(x)\sin[E_{\rm np}(2n_0+1)t/\hbar], \tag{2.42}$$

see Figure 2.2. The expectation value of the particle position (relative to x_0)[3],

$$\begin{aligned}\langle x\rangle_t - x_0 &= -\sin[E_{\rm np}(2n_0+1)t/\hbar]\int_0^L \psi_{n_0}(x)\psi_{n_0+1}(x)\,x\,dx \\ &= -\frac{\sin[E_{\rm np}(2n_0+1)t/\hbar]}{L}\int_0^L\Big[\cos(\pi x/L) - \cos((2n_0+1)\pi x/L)\Big]x\,dx \\ &= \frac{2L\sin[E_{\rm np}(2n_0+1)t/\hbar]}{\pi^2}\left[1 - \frac{1}{(2n_0+1)^2}\right],\end{aligned} \tag{2.43}$$

oscillates with frequency $E_{\rm np}(2n_0+1)/\hbar$, which corresponds to the energy difference between the stationary states with quantum numbers n_0 and n_0+1.

From (2.10) we can compute the expectation value of the particle's velocity. We obtain

$$\langle v\rangle_t = \frac{d}{dt}\langle x\rangle_t = v_0\cos[E_{\rm np}(2n_0+1)t/\hbar] \tag{2.44}$$

with the (mean) initial velocity

$$v_0 = \left[1 - \frac{1}{(2n_0+1)^2}\right]\frac{(2n_0+1)\hbar}{mL} > 0\,. \tag{2.45}$$

The quantum mechanical "motion" is thus a smeared-out version of the classical solution, see Figure 2.2: Classically, the particle initially moves toward the barrier at $x = L$. At time $L/2v_0$ the particle is then reflected at the right boundary.

2.6 Unbound Motion: Free Particle

We now apply the solution strategy of the previous chapter to the problem of the free particle with $V(\boldsymbol{r}) = 0$. To find a solution $\Psi(\boldsymbol{r},t)$ of the Schrödinger equation, we first solve the time-independent problem

$$-\frac{\hbar^2}{2m}\Delta\psi(\boldsymbol{r}) = E\psi(\boldsymbol{r}) \tag{2.46}$$

The solutions (for $E \geq 0$) are given by *plane waves*

$$\psi_{\boldsymbol{p}}(\boldsymbol{r}) = \frac{B_{\boldsymbol{p}}}{(2\pi\hbar)^{3/2}}e^{i\boldsymbol{p}\cdot\boldsymbol{r}/\hbar} = B_{\boldsymbol{p}}\prod_{j=1}^{3}\psi_{p_j}(r_j), \qquad \psi_p(x) = \frac{1}{(2\pi\hbar)^{1/2}}e^{ipx/\hbar} \tag{2.47}$$

with a free normalization constant $B_{\boldsymbol{p}} \in \mathbb{C}$. The function $\psi_{\boldsymbol{p}}$ is indexed by the wave vector $\boldsymbol{p}/\hbar$, which is related to the energy by

$$E_{\boldsymbol{p}} = \frac{\boldsymbol{p}^2}{2m} \tag{2.48}$$

[3] It holds that $\int_0^L \cos[(2n_0+1)\pi x/L]\,x\,dx = -[L/(2n_0+1)\pi]\int_0^L \sin[(2n_0+1)\pi x/L]\,dx = -2L^2/[\pi^2(2n_0+1)^2]$.

There is, however, a problem: The functions $\psi_{\boldsymbol{p}}$ are *not* stationary states. It holds that

$$\int |\psi_{\boldsymbol{p}}|^2 \, dV = \frac{|B_{\boldsymbol{p}}|^2}{(2\pi\hbar)^3} \int dV \to \infty \,. \tag{2.49}$$

independent of $B_{\boldsymbol{p}}$. The wave functions $\psi_{\boldsymbol{p}}$ thus cannot be normalized and they do not correspond to a probability distribution. This is connected with the fact that the classical motion is unbound. Quantum mechanically, all energies are allowed and there are no discrete energy eigenvalues. One speaks of a *continuous* spectrum.

Note that the parameter $\boldsymbol{p}$ is nevertheless related to the expectation value of the momentum. Considering for a moment a finite spatial region $\Omega \subset \mathbb{R}^3$, then $\psi_{\boldsymbol{p}}$ can be normalized with $B_{\boldsymbol{p}} = (2\pi\hbar)^{3/2}/|\Omega|^{1/2}$ and we obtain

$$\langle \boldsymbol{p} \rangle = \int_\Omega \psi^*_{\boldsymbol{p}}(\boldsymbol{r})(-i\hbar\boldsymbol{\nabla})\psi_{\boldsymbol{p}}(\boldsymbol{r}) \, dV = \frac{\boldsymbol{p}}{|\Omega|} \int_\Omega dV = \boldsymbol{p} \tag{2.50}$$

independent of the region Ω.

Although plane waves are not states, any initial state $\Psi_0(\boldsymbol{r}) = \Psi(\boldsymbol{r}, t_0)$ can be written as a superposition

$$\Psi_0(\boldsymbol{r}) = (2\pi\hbar)^{-3/2} \int e^{i\boldsymbol{p}\cdot\boldsymbol{r}/\hbar} \hat{\Psi}_0(\boldsymbol{p}) \, d^3p = \int \psi_{\boldsymbol{p}}(\boldsymbol{r}) \hat{\Psi}_0(\boldsymbol{p}) d^3p, \tag{2.51}$$

of plane waves, where we have chosen $B_{\boldsymbol{p}} = 1$ to maintain the analogy with (2.21) as closely as possible. The Fourier transform

$$\hat{\Psi}_0(\boldsymbol{p}) = (\mathcal{F}\Psi_0)(\boldsymbol{p}) = (2\pi\hbar)^{-3/2} \int e^{-i\boldsymbol{p}\cdot\boldsymbol{r}/\hbar} \Psi_0(\boldsymbol{r}) \, dV = \int \psi^*_{\boldsymbol{p}}(\boldsymbol{r}) \Psi_0(\boldsymbol{r}) \, dV, \tag{2.52}$$

is also called the *momentum representation* of $\Psi_0(\boldsymbol{r})$. In particular, it follows from Plancherel's theorem that if $\rho(\boldsymbol{r}, t) = |\Psi(\boldsymbol{r}, t)|^2$ then

$$\tilde{\rho}(\boldsymbol{p}, t) = |\hat{\Psi}(\boldsymbol{p}, t)|^2 = |(\mathcal{F}\Psi)(\boldsymbol{p}, t)|^2 \tag{2.53}$$

is also a probability density. From the relation $\mathcal{F}(-i\hbar\boldsymbol{\nabla}\Psi) = \boldsymbol{p}\hat{\Psi}$ one further obtains that the expectation value of the momentum is given by

$$\begin{aligned} \langle \boldsymbol{p} \rangle_t &= \int \Psi^*(\boldsymbol{r}, t)(-i\hbar\boldsymbol{\nabla})\Psi(\boldsymbol{r}, t) \, dV \overset{\text{(Plancherel)}}{=} \int \hat{\Psi}^*(\boldsymbol{p}, t)\mathcal{F}(-i\hbar\boldsymbol{\nabla}\Psi)(\boldsymbol{p}, t) \, d^3p \\ &= \int \boldsymbol{p} \, \tilde{\rho}(\boldsymbol{p}, t) \, d^3p \end{aligned} \tag{2.54}$$

Thus one can interpret $\tilde{\rho}(\boldsymbol{p}, t)$ as the probability density that the particle has momentum $\boldsymbol{p}$.

For a free particle the *energy-momentum* relation (2.48) holds. Because the integrand in (2.51) is a solution of the time-independent Schrödinger equation with energy $E_{\boldsymbol{p}}$, it evolves in time with $\exp(-iE_{\boldsymbol{p}}t/\hbar)$. The general solution of the Schrödinger equation is thus given by

$$\Psi(\boldsymbol{r}, t) = (2\pi\hbar)^{-3/2} \int e^{i\boldsymbol{p}\cdot\boldsymbol{r}/\hbar} \underbrace{\hat{\Psi}_0(\boldsymbol{p}) e^{-iE_{\boldsymbol{p}}t/\hbar}}_{=\hat{\Psi}(\boldsymbol{p},t)} \, d^3p \,. \tag{2.55}$$

Because of probability conservation $\Psi(\boldsymbol{r}, t)$ remains normalized for all time, although the components $\psi_{\boldsymbol{p}}$ are not normalized. For the free particle the momentum is conserved and thus the momentum distribution is time-independent with $\tilde{\rho}(\boldsymbol{p}, t) = |\hat{\Psi}(\boldsymbol{p}, t)|^2 = |\hat{\Psi}_0(\boldsymbol{p})|^2$.

Inserting (2.52) yields the propagator

$$K(\boldsymbol{r},\boldsymbol{r}';t) = \int \psi_{\boldsymbol{p}}(\boldsymbol{r})\psi^*_{\boldsymbol{p}}(\boldsymbol{r}')e^{-iE_{\boldsymbol{p}}t/\hbar}\,d^3p = \prod_{j=1}^{3}\left[(2\pi\hbar)^{-1}\int e^{ip_j(r_j-r'_j)/\hbar - ip_j^2 t/2m\hbar}\,dp_j\right]$$
$$= \Big(\frac{m}{2\pi\hbar it}\Big)^{3/2}\exp\left(\frac{im|\boldsymbol{r}-\boldsymbol{r}'|^2}{2\hbar t}\right) \tag{2.56}$$

of the free particle. Here we have used that[4]

$$\int e^{ip(r-r')/\hbar - ip^2 t/2m\hbar}\,dp = e^{im(r-r')^2/2\hbar t}\int \exp\left[-\frac{it}{2\hbar m}\left(p-\frac{m(r-r')}{t}\right)^2\right]dp$$
$$= \sqrt{\frac{2\pi\hbar m}{it}}\,e^{im(r-r')^2/2\hbar t}\,. \tag{2.57}$$

For fixed t we have $|K(\boldsymbol{r},\boldsymbol{r}';t)| = (2\pi\hbar|t|/m)^{-3/2}$. Thus we obtain the estimate

$$|\Psi(\boldsymbol{r},t)| \le \left(\frac{m}{2\pi\hbar|t|}\right)^{3/2}\int |\Psi_0(\boldsymbol{r}')|\,d^3r' = \frac{\text{const}}{|t|^{3/2}} \tag{2.58}$$

if $|\Psi_0|$ is integrable. We can thus conclude that the solution disperses for large times. This is a consequence of the fact that the motion is unbound and no stationary states exist.

We have thus seen that the solutions $\psi_{\boldsymbol{p}}$ are useful, even though they are not normalizable states. One refers to eigenfunctions $\psi_{\boldsymbol{p}}$ of the stationary Schrödinger equation that are not normalizable as *improper* states with eigenvalue $\boldsymbol{p}$. Such functions always arise for unbound motion with a continuous spectrum. One must note, however, that the usefulness of the functions $\psi_{\boldsymbol{p}}$ stems from the fact that they are "almost" normalizable. In particular, one can form normalizable *wave packets* from $\psi_{\boldsymbol{p}}$ with $\boldsymbol{p}$ from an arbitrarily small region. Note that the eigenfunctions $\exp(\boldsymbol{p}\cdot\boldsymbol{r}/\hbar)$ for $E<0$ do not have this property and thus are not improper states.

To better understand this property, we introduce the normalized, one-dimensional wave packets ($\epsilon > 0$)

$$\psi_{p,\epsilon}(x) = \frac{1}{\epsilon^{1/2}}\int_{p-\epsilon/2}^{p+\epsilon/2}\psi_q(x)\,dq \tag{2.59}$$

The wave function $\psi_{p,\epsilon}$ then describes a particle with momentum $\simeq p$, localized on the length $\xi \simeq \hbar/\epsilon$. One can easily verify the normalization with

$$\int |\psi_{p,\epsilon}(x)|^2\,dx = \frac{1}{\epsilon}\iint_{p-\epsilon/2}^{p+\epsilon/2}\underbrace{\left[\int \psi^*_{q'}(x)\psi_q(x)\,dx\right]}_{=\delta(q'-q)}dq\,dq' = 1\,. \tag{2.60}$$

In this sense one can form localized wave packets from ψ_p. In what follows we will always "normalize" improper states on

$$\int \psi^*_{p'}(x)\psi_p(x)\,dx = \delta(p'-p) \tag{2.61}$$

[4]The Gaussian integral $\int e^{-\alpha x^2}\,dx = \sqrt{\pi/\alpha}$ holds for $\operatorname{Re}\alpha \ge 0$.

which is equivalent to saying that $\psi_{p,\epsilon}$ are normalized wave packets. In the three-dimensional case we analogously obtain

$$\psi_{\boldsymbol{p},\boldsymbol{\epsilon}}(\boldsymbol{r}) = \prod_{j=1}^{3} \psi_{p_j,\epsilon_j}(r_j) \tag{2.62}$$

with the "normalization"

$$\int \psi^*_{\boldsymbol{p}'}(\boldsymbol{r})\psi_{\boldsymbol{p}}(\boldsymbol{r})\, dV = \delta^{(3)}(\boldsymbol{p}' - \boldsymbol{p}) = \prod_{j=1}^{3} \delta(p'_j - p_j). \tag{2.63}$$

Multiplying the improper states $\psi_q(x)$ by the phase factor $\exp(-iE_q t/\hbar)$ yields a solution

$$\Psi_{p,\epsilon}(x,t) = \frac{1}{\epsilon^{1/2}} \int_{p-\epsilon/2}^{p+\epsilon/2} \psi_q(x) e^{-iE_q t/\hbar}\, dq \tag{2.64}$$

of the Schrödinger equation. We write

$$E_q = -\frac{p^2}{2m} + \frac{pq}{m} + \frac{(q-p)^2}{2m}\,. \tag{2.65}$$

For small ϵ one can neglect the last term. We then obtain the expression

$$\Psi_{p,\epsilon}(x,t) = \frac{e^{ip^2 t/2m\hbar}}{(2\pi\hbar\epsilon)^{1/2}} \int_{p-\epsilon/2}^{p+\epsilon/2} e^{iq(x-v_p t)/\hbar}\, dq = \underbrace{e^{ip^2 t/2m\hbar}}_{\text{Phase}} \psi_{p,\epsilon}(x - v_p t) \tag{2.66}$$

with $v_p = p/m$ the (group) *velocity*. The particle thus moves with velocity v_p without spreading. The contradiction with (2.58) is resolved by noting that the condition for neglecting the term is more subtle. The additional phase factor has order of magnitude $(q-p)^2 t/2m\hbar \simeq \epsilon^2 t/m\hbar$. One may neglect it only if it is much smaller than 1. This is equivalent to

$$|t| \ll t_{\text{disp}} = \frac{m\hbar}{\epsilon^2} \tag{2.67}$$

with t_{disp} the time at which *dispersion* sets in. The approximation (2.66) is thus valid only up to the dispersion time.

Example As an example we consider a Gaussian wave packet with wave function

$$\Psi_0(\boldsymbol{r}) = \left(\pi^{1/2}\xi\right)^{-3/2} e^{i\boldsymbol{p}_0\cdot\boldsymbol{r}/\hbar - \boldsymbol{r}^2/2\xi^2}\,, \tag{2.68}$$

consisting of a carrier $\exp(i\boldsymbol{p}_0\cdot\boldsymbol{r}/\hbar)$, an envelope $\exp(-\boldsymbol{r}^2/2\xi^2)$, and a normalization factor. The expectation value of the position is $\langle\boldsymbol{r}\rangle = 0$ at the initial time $t_0 = 0$. In the momentum representation the wave function also has a Gaussian form

$$\hat{\Psi}_0(\boldsymbol{p}) = (\mathcal{F}\Psi_0)(\boldsymbol{p}) = \int \psi^*_{\boldsymbol{p}}(\boldsymbol{r})\Psi_0(\boldsymbol{r})\, dV = \left(\frac{\xi}{\pi^{1/2}\hbar}\right)^{3/2} e^{-\xi^2|\boldsymbol{p}-\boldsymbol{p}_0|^2/2\hbar^2}. \tag{2.69}$$

The expectation value of the momentum is given by

$$\langle\boldsymbol{p}\rangle = \int \boldsymbol{p}\, |\hat{\Psi}_0(\boldsymbol{p})|^2\, d^3p \overset{(\boldsymbol{p}=\boldsymbol{p}_0+\boldsymbol{q})}{=} \boldsymbol{p}_0 + \left(\frac{\xi}{\pi^{1/2}\hbar}\right)^3 \int \boldsymbol{q}\, e^{-\xi^2\boldsymbol{q}^2/\hbar^2}\, d^3q = \boldsymbol{p}_0\,. \tag{2.70}$$

By Ehrenfest's theorem for the free particle we have

$$\langle \boldsymbol{p} \rangle_t = \boldsymbol{p}_0 \text{ and } \langle \boldsymbol{r} \rangle_t = \boldsymbol{v}_0 t \tag{2.71}$$

with $m\boldsymbol{v}_0 = \boldsymbol{p}_0$. The momentum is not sharply determined but has variance

$$(\Delta p_j)^2 = \int (p_j - p_{0,j})^2 |\hat{\Psi}_0(\boldsymbol{p})|^2 \, d^3p = \frac{\hbar^2}{2\xi^2} \tag{2.72}$$

Here we have used that a Gaussian distribution with probability density $\propto \exp(-ax^2)$ has variance $(\Delta x)^2 = 1/2a$.

The time evolution is obtained from (2.55)

$$\begin{aligned}
\Psi(\boldsymbol{r},t) &= \left(\frac{\xi}{2\pi^{3/2}\hbar^2}\right)^{3/2} \int e^{i(\boldsymbol{p}\cdot\boldsymbol{r} - E_{\boldsymbol{p}}t)/\hbar} e^{-\xi^2|\boldsymbol{p}-\boldsymbol{p}_0|^2/2\hbar^2} \, d^3p \\
&\overset{(\boldsymbol{p}=\boldsymbol{q}+\boldsymbol{p}_0)}{=} \left(\frac{\xi}{2\pi^{3/2}\hbar^2}\right)^{3/2} e^{i\boldsymbol{p}_0\cdot\boldsymbol{r}/\hbar - i\boldsymbol{p}_0^2 t/2m\hbar} \int e^{i\boldsymbol{q}\cdot(\boldsymbol{r}-\boldsymbol{v}_0 t)/\hbar} \, e^{-iq^2 t/2m\hbar} \, e^{-\xi^2 q^2/2\hbar^2} \, d^3q \\
&= \left(\frac{\xi}{\pi^{1/2}\sigma_t}\right)^{3/2} \underbrace{e^{i\boldsymbol{p}_0\cdot\boldsymbol{r} - i\boldsymbol{p}_0^2 t/2m\hbar}}_{\text{Phase}} \, e^{-|\boldsymbol{r}-\boldsymbol{v}_0 t|^2/2\sigma_t} \,,
\end{aligned} \tag{2.73}$$

where $\sigma_t = \xi^2 + i\hbar t/m$. With the wave function (2.73) one finds the mean square fluctuation

$$\begin{aligned}
(\Delta r_j)^2 = \langle (r_j - v_{0,j}t)^2 \rangle_t &= \int (r_j - v_{0,j}t)^2 |\Psi(\boldsymbol{r},t)|^2 \, dV = \left(\frac{1}{\sigma_t} + \frac{1}{\sigma_t^*}\right)^{-1} \\
&= \frac{\xi^2}{2}\left(1 + \frac{\hbar^2 t^2}{m^2\xi^4}\right).
\end{aligned} \tag{2.74}$$

Here one clearly sees the influence of the characteristic time $t_{\text{disp}} \simeq m\xi^2/\hbar$. For small times ($\ll t_{\text{disp}}$) the width of the wave packet remains constant, see (2.66). Only for large times ($\gg t_{\text{disp}}$) does the wave packet spread with $\Delta r \simeq \hbar t/m\xi$. One can understand the origin as follows: At the initial time the velocity is determined only up to $\Delta v = \Delta p/m \simeq \hbar/m\xi$ of accuracy. The ballistic motion converts the uncertainty in the velocity into an uncertainty in position $\Delta r = \Delta v \, t$ which grows linearly in time. This is different from diffusion, where the standard deviation grows only like $\Delta r \propto t^{1/2}$.

The product of the standard deviations

$$\Delta r_j \, \Delta p_j = \frac{\hbar}{2}\sqrt{1 + \frac{\hbar^2 t^2}{m^2\xi^4}} \;\geq\; \frac{\hbar}{2}. \tag{2.75}$$

increases with time. The lower bound is the *Heisenberg uncertainty principle*, which must always be satisfied, as we will prove later.

2.7 Scattering problem: step potential

Next we study a one-dimensional scattering problem using the example of the step potential with ($V_0 > 0$)

$$V(x) = \begin{cases} 0, & x \leq 0, \\ V_0, & x > 0. \end{cases} \tag{2.76}$$

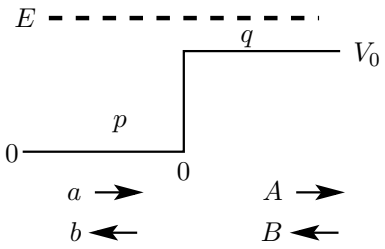


Fig. 2.3: Step potential: the waves with amplitude a, A travel to the right, the others to the left.

As usual, we first seek solutions of the stationary Schrödinger equation. Since the potential admits no bound orbits, we expect that only continuous eigenvalues with improper states exist. We are particularly interested in describing the scattering of a particle that, for $t \to -\infty$, is incident from the left onto the step. Our goal is to compute the probability with which the particle is reflected at the step.

For $x < 0$ the particle is free. The Schrödinger equation requires

$$-\frac{\hbar^2}{2m}\psi''(x) = E\psi(x)\,. \tag{2.77}$$

The general solution at fixed energy $E > 0$ is

$$\psi_p(x < 0) = ae^{ipx/\hbar} + be^{-ipx/\hbar} \tag{2.78}$$

with $p = \sqrt{2mE}$. In the region with $x > 0$ one has instead

$$-\frac{\hbar^2}{2m}\psi''(x) = (E - V_0)\psi(x)\,. \tag{2.79}$$

The solution is given by $(E > V_0)$

$$\psi_p(x > 0) = Ae^{iqx/\hbar} + Be^{-iqx/\hbar}, \tag{2.80}$$

with $q = \sqrt{2m(E - V_0)}$. The terms with amplitude a, A correspond to a positive momentum and therefore describe processes in which the particle moves to the right, see Figure 2.3. Since we are interested in a scattering process in which the particle is incident from the left, we may set $B = 0$ (the term B would describe a process in which the particle is incident from the right).

The functions (2.78) and (2.80) for the different regions do not satisfy the Schrödinger equation for all constants. In particular, at $x = 0$ the wave function and its first spatial derivative must be continuous. These *matching conditions* follow from the fact that the Schrödinger equation contains a second spatial derivative. A discontinuity in the wave function or its first derivative would therefore not solve the time-dependent Schrödinger equation at $x = 0$. The continuity requirement on ψ_p and $\partial_x\psi_p$ leads to the system of equations

$$a + b = A, \qquad (a - b)p = Aq\,, \tag{2.81}$$

with solution

$$b = \underbrace{\frac{p - q}{p + q}}_{=r} a, \qquad A = \underbrace{\frac{2p}{p + q}}_{=1+r} a\,. \tag{2.82}$$

To determine the reflection and transmission probabilities we must form a wave packet from the improper states. For normalization we use the following trick. We consider the wave packet at a time $|t| \ll t_{\text{disp}}$ before dispersion sets in. The wave function then has the form [cf. (2.66)][5]

$$\Psi_{p,\epsilon}(x,t) = (2\pi\hbar)^{1/2} a \underbrace{e^{ip^2 t/2m\hbar}}_{\text{Phase}} \begin{cases} \overbrace{\phi_{p,\epsilon}(x-v_p t)}^{\text{incident}} + \overbrace{r\phi^*_{p,\epsilon}(x+v_p t)}^{\text{reflected}}, & x<0, \\ e^{-2imV_0 x/\hbar q} \underbrace{(1+r)\phi_{p,\epsilon}[(p/q)(x-v_q t)]}_{\text{transmitted}}, & x>0, \end{cases} \tag{2.83}$$

with the free-particle wave packet

$$\phi_{p,\epsilon}(x) = \frac{1}{(2\pi\hbar\epsilon)^{1/2}} \int_{p-\epsilon/2}^{p+\epsilon/2} e^{ikx/\hbar}\, dk = \left(\frac{2\hbar}{\pi\epsilon}\right)^{1/2} \frac{e^{ipx/\hbar} \sin(\epsilon x/2\hbar)}{x}, \tag{2.84}$$

which is normalized and decays on the characteristic length $\xi \simeq \hbar/\epsilon$ with $\phi(|x| \gg \xi) \approx 0$. One calls the individual terms of $\Psi_{p,\epsilon}$ the *incident*, *reflected* and *transmitted* waves.

We consider the wave packet $\Psi_{p,\epsilon}(x,t)$ at "early" times ($t \ll -\xi/v_p$) before the wave packet reaches the step.[6] In this limit only the incident wave is nonzero and we obtain ($-t_{\text{disp}} \ll t \ll -\xi/v_p$)

$$\Psi_{p,\epsilon}(x,t) = (2\pi\hbar)^{1/2} a e^{ip^2 t/2m\hbar} \phi_{p,\epsilon}(x-v_p t). \tag{2.85}$$

Because normalization is preserved under time evolution, we may perform it at the initial time on the incident wave function via

$$\int |\Psi_{p,\epsilon}|^2\, dx = (2\pi\hbar)|a|^2 \underbrace{\int |\phi_{p,\epsilon}(x-v_p t)|^2\, dx}_{=1} = 1 \tag{2.86}$$

Thus we have shown that $a = (2\pi\hbar)^{-1/2}$ gives the correct normalization of the improper states.[7] In particular, (2.61) also holds for the scattering states.

For "late" times (with $\xi/v_q \ll t \ll t_{\text{disp}}$) the incident wave vanishes and we obtain

$$\Psi_{p,\epsilon}(x,t) = e^{ip^2 t/2m\hbar} \Big\{ r\phi^*_{p,\epsilon}(x+v_p t) + e^{-2imV_0 x/\hbar q}(1+r)\phi_{p,\epsilon}[(p/q)(x-v_q t)] \Big\}. \tag{2.87}$$

The reflected part is located at position $-v_p t$, the transmitted part at $v_q t$ (up to the uncertainty ξ). The overlap vanishes and we obtain the probability density

$$\rho(x,t) = r^2 \big|\phi_{p,\epsilon}(x+v_p t)\big|^2 + (1+r)^2 \big|\phi_{p,\epsilon}[(p/q)(x-v_q t)]\big|^2. \tag{2.88}$$

The first term describes the reflected particle, the second term corresponds to the transmitted contribution. One sees clearly again that only a probabilistic interpretation makes sense. For long times the point particle must be either reflected *or* transmitted. Hence

$$R = r^2 \underbrace{\int \big|\phi_{p,\epsilon}(x+v_p t)\big|^2\, dx}_{=1} = \frac{(p-q)^2}{(p+q)^2} \tag{2.89}$$

[5] For the transmitted part one uses the expansion $\sqrt{k^2 - 2mV_0} = q + (p/q)(k-p) + O(k-p)^2 = -2mV_0/q + (p/q)k + O(k-p)^2$.

[6] Since $t_{\text{disp}} \propto \epsilon^{-2}$ both conditions can be met simultaneously for sufficiently small ϵ.

[7] The argument is valid for all scattering potentials and $a = (2\pi\hbar)^{-1/2}$ is therefore always the correct normalization.

is the reflection probability and

$$T = \underbrace{(1+r)^2}_{=4p^2/(p+q)^2} \int \left|\phi_{p,\epsilon}[(p/q)(x-v_q t)]\right|^2 \, dx = \frac{4pq}{(p+q)^2} \underbrace{\int \left|\phi_{p,\epsilon}(y-v_p t)\right|^2 dy}_{=1} \tag{2.90}$$

the transmission probability. Since the particle at late times is either reflected or transmitted, one has $R + T = 1$ by probability conservation.

Resistance quantum and shot noise: Electron scattering is microscopically the reason materials possess a finite conductance. Consider two electrodes with voltage difference V connected by a quantum wire. At low temperatures an electron has probability T to travel from one electrode to the other. To describe the resistance we need only one result from many-body theory: By the *Pauli principle* electrode 2 injects 2 electrons[8] per time $2\pi\hbar/eV$. In the measurement time τ one thus injects $N = eV\tau/\pi\hbar$ electrons into the quantum wire. Each electron is then transmitted with probability T and reflected with probability R. The probability that n electrons are transmitted follows the binomial distribution

$$P_n = \binom{N}{n} T^n R^{N-n}, \tag{2.91}$$

where each electron carries charge $-e$. On average the current is therefore

$$\langle I \rangle = \frac{\langle Q \rangle}{\tau} = \frac{e}{\tau} \sum_{n=0}^{N} n P_n = \frac{eTN}{\tau} = \frac{e^2}{\pi\hbar} TV \,. \tag{2.92}$$

A perfect quantum conductor (with $T = 1$) thus has the finite resistance (von-Klitzing constant)

$$R_K = \frac{\pi\hbar}{e^2} = 25.8\,\mathrm{k\Omega} \,. \tag{2.93}$$

Because of the granularity of charge the current is not constant in time but exhibits shot noise. The fluctuation in the current is given by

$$\frac{\langle Q^2 \rangle - \langle Q \rangle^2}{\tau} = \frac{e^2}{\tau} \sum_{n=0}^{N} (n - TN)^2 P_n = \frac{e^2 RTN}{\tau} = e(1-T)\langle I \rangle \,. \tag{2.94}$$

Charge can therefore be transmitted without noise only in a perfect quantum conductor with $T = 1$. If the conductor has a finite transmission probability, there are current fluctuations proportional to the electron's charge.

2.8 Periodic boundary condition: particle on a ring

As a further example we consider a free particle of mass m moving on a ring of circumference L. The particle's position is described by the coordinate $x \in [0, L]$, where $x = 0$ and $x = L$ denote the same location. The time-independent Schrödinger equation is therefore

$$-\frac{\hbar^2}{2m} \psi''(x) = E\psi(x), \tag{2.95}$$

[8] Here 2 is the spin-degeneracy factor for a spin-$\frac{1}{2}$ particle, see later.

with the wave function required to satisfy the *periodic boundary condition*

$$\psi(L) = \psi(0) \tag{2.96}$$

The Schrödinger equation is solved by the eigenfunction

$$\psi_n(x) = A_n e^{ip_n x/\hbar} \tag{2.97}$$

with $p_n = \sqrt{2mE_n}$. The periodic boundary condition demands $e^{ip_n L/\hbar} = 1$. The momenta are therefore quantized to the values

$$p_n = \frac{2\pi\hbar}{L} n, \qquad n \in \mathbb{Z}, \tag{2.98}$$

Unlike in the particle-in-a-box, all energies

$$E_n = \frac{(2\pi\hbar)^2}{2mL^2} n^2 = E_{\rm np} n^2 \tag{2.99}$$

with $n \neq 0$ are *doubly degenerate*, since $E_n = E_{-n}$.

The parameter A_n is fixed (up to a phase) by the normalization of the wave function

$$\int_0^L |\psi_n(x)|^2 \, dx = |A_n|^2 L \qquad \text{on} \qquad A_n = \frac{1}{\sqrt{L}} \tag{2.100}$$

The general solution $\Psi(x,t)$ is obtained by superposing the eigenfunctions, $\Psi = \sum_n a_n \psi_n e^{-iE_n(t-t_0)/\hbar}$. The expansion coefficients a_n are determined by the Fourier transform

$$a_n = \int_0^L \psi_n^*(x) \Psi_0(x) \, dx \tag{2.101}$$

The general solution therefore has the form

$$\Psi(x,t) = \int_0^L K(x,y;t-t_0) \Psi(y,t_0) \, dy \tag{2.102}$$

with the propagator

$$K(x,y;t) = \sum_n \psi_n(x) \psi_n^*(y) e^{-iE_n t/\hbar} = \frac{1}{L} \sum_n e^{2\pi i n(x-y)/L - iE_{\rm np} n^2 t/\hbar} \, . \tag{2.103}$$

Rotor: The mass point is a quantum-mechanical rotor, i.e. a particle moving on a circle of radius $R = L/2\pi$. Classically the mass point has moment of inertia

$$\theta = mR^2 = \frac{mL^2}{(2\pi)^2} \tag{2.104}$$

with energy (L_z is the angular momentum)

$$E = \frac{L_z^2}{2\theta} \, . \tag{2.105}$$

Comparison with (2.99) shows that energy quantization fixes the angular momentum to [cf. (1.44)]

$$L_z = n\hbar \tag{2.106}$$

Continuum limit: We wish to show that the free particle with periodic boundary conditions in the limit $L \to \infty$ reduces to the free particle treated in Chapter 2.6. The advantage of periodic boundary conditions is that there is only a discrete spectrum and no improper states need be considered. For this reason periodic boundary conditions are often introduced artificially in theoretical physics in order to take the limit $L \to \infty$ at the end of the calculation.

For $L \to \infty$ all values of $p_n = 2\pi\hbar n/L$ are allowed. We therefore replace p_n by the continuous parameter p. The propagator becomes a Riemann sum

$$K(x,y;t) = \frac{1}{2\pi\hbar}\frac{2\pi\hbar}{L}\sum_n e^{2\pi i n(x-y)/L - iE_n t/\hbar} \to \frac{1}{2\pi\hbar}\int dp\, e^{ip(x-y)/\hbar - E_p t/\hbar} \tag{2.107}$$

with spacing $\delta = 2\pi\hbar/L$ between the nodes. Thus in the limit $L \to \infty$ we obtain the propagator (2.56) of the free particle in one dimension.

To ensure that the expansion $\Psi_0 = \sum_n a_n \psi_n$ with (2.101) has a finite continuum limit, we introduce the rescaled functions

$$\tilde{a}_n = \delta^{-1/2} a_n \qquad \text{and} \qquad \tilde{\psi}_n = \delta^{-1/2}\psi_n = \frac{1}{(2\pi\hbar)^{1/2}} e^{ip_n x/\hbar} \tag{2.108}$$

Hence

$$\Psi_0 = \sum_n a_n \psi_n = \delta \sum_n \tilde{a}_n \tilde{\psi}_n \to \int dp\, \tilde{a}_p \tilde{\psi}_p \tag{2.109}$$

with expansion coefficients (in the second step we use that Ψ_0 and ψ_n are periodic)

$$\tilde{a}_n = \delta^{-1/2}\int_0^L \psi_n^* \Psi_0\, dx = \int_{-L/2}^{L/2} \tilde{\psi}_n^* \Psi_0\, dx \to \tilde{a}_p = \int \tilde{\psi}_p^*(x)\Psi_0(x)\, dx\,. \tag{2.110}$$

The coefficients $\tilde{a}_p$ therefore coincide exactly with the momentum representation $\hat{\Psi}_0(p)$ and $\tilde{\psi}_p$ are the improper states with normalization (2.61).

The continuum limit therefore corresponds in general to the substitution

$$p_n \mapsto p, \qquad a_n \mapsto \delta^{1/2}\tilde{a}_p, \qquad \psi_n \mapsto \delta^{1/2}\tilde{\psi}_p, \qquad \delta\sum_n \mapsto \int dp\,. \tag{2.111}$$

One may of course also introduce periodic boundary conditions in three dimensions with $\psi(r_1 + L, r_2, r_3) = \psi(r_1, r_2 + L, r_3) = \psi(r_1, r_2, r_3 + L) = \psi(r_1, r_2, r_3)$. The continuum limit (2.111) is then taken separately in each coordinate direction.

2.9 WKB approximation

The quasi-classical or WKB approximation (Wentzel, Kramers, Brillouin 1926) allows one to solve the one-dimensional Schrödinger equation approximately for large quantum numbers (i.e. $\hbar$ small). We can thereby establish a connection between the Schrödinger equation and the old quantum theory in the Sommerfeld formulation.

We seek solutions of the time-independent Schrödinger equation (2.20) with the ansatz ($A, S \in \mathbb{R}$)

$$\psi(x) = A(x)\, \exp\left[\frac{i}{\hbar}\, S(x)\right]. \tag{2.112}$$

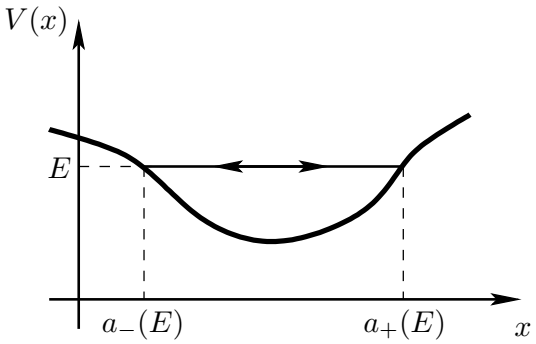


Fig. 2.4: Potential with classical turning points $a_\pm(E)$.

Insertion into the time-independent Schrödinger equation and separation into real and imaginary parts leads to [cf. (1.66) and (1.67)]

$$S'^2 - 2m(E-V) = \hbar^2 \frac{A''}{A}, \tag{2.113}$$

$$\frac{d}{dx}(A^2 S') = 0. \tag{2.114}$$

The WKB approximation requires that

$$\hbar^2 \left| \frac{A''}{A} \right| \ll 2m|E-V|, \tag{2.115}$$

which is the ray-optical condition (1.65). Hence the first equation simplifies to $S' = \pm p(x)$ with the classical momentum

$$p(x) = \sqrt{2m[E-V(x)]}\,. \tag{2.116}$$

Integrating gives the solution

$$S(x) = \pm \int^x p(x')\,dx', \qquad A(x)^2 = \frac{A_\pm^2}{p(x)} \tag{2.117}$$

with free constants $A_\pm$.

Bound states: We seek eigenvalues at energy E for which the classical orbit is bound with the allowed region $x \in [a_-(E), a_+(E)]$, see Figure 2.4. In the allowed region we obtain the WKB approximation

$$\psi(x) = \frac{1}{\sqrt{p(x)}} \left(A_+ e^{i\int^x p(x')\,dx'/\hbar} + A_- e^{-i\int^x p(x')\,dx'/\hbar} \right). \tag{2.118}$$

In the forbidden region one finds analogously

$$\psi(x) = \frac{1}{\sqrt{\tilde{p}(x)}} \left(\tilde{A}_+ e^{\int^x \tilde{p}(x')\,dx'} + \tilde{A}_- e^{-\int^x \tilde{p}(x')\,dx'} \right) \tag{2.119}$$

with the "imaginary momentum"

$$\tilde{p}(x) = ip(x) = \sqrt{2m[V(x)-E]}\,. \tag{2.120}$$

For the solution to be normalizable one must have $\tilde{A}_- = 0$ for $x < a_-$ and $\tilde{A}_+ = 0$ for $x > a_+$. To determine the eigenvalues E_n one must "glue" the solutions from the separate regions together.

For small $\hbar$ the WKB condition

$$\frac{A''}{A} = \frac{5}{16}\left(\frac{V'}{E-V}\right)^2 + \frac{1}{4}\frac{V''}{E-V} \ll \frac{2m(E-V)}{\hbar^2} \tag{2.121}$$

is satisfied almost everywhere, since the right-hand side becomes arbitrarily large for $\hbar \to 0$. The only exception is near the turning points. There one has

$$E - V(x) \approx -V'(a_\pm)(x - a_\pm)\,. \tag{2.122}$$

Hence near a turning point the first term on the left-hand side of (2.121) is more singular than the second. The WKB approximation is therefore applicable only for

$$|x - a_\pm| \gg \left|\frac{\hbar^2}{2mV'(a_\pm)}\right|^{1/3} = \varepsilon \tag{2.123}$$

Since the approximation fails in particular at the turning point, it is not possible to find the correct matching condition within the WKB approximation.

We now wish to derive the correct matching condition at the left turning point $a = a_-$ (the other turning point follows analogously). To this end we introduce the scaled variable

$$y = \frac{x - a}{\varepsilon} \tag{2.124}$$

We need the matching condition that links the solution of $y \ll -1$ with $y \gg 1$. For the wave function to be normalizable we require the solution that decays for $y \ll -1$.

In the region $|y| \leq 1$ we must solve the time-independent Schrödinger equation, since the condition for the WKB approximation is not satisfied. However it remains permissible to use the linearization (2.122), since this only requires $|V''(a)(x-a)^2| \ll |V'(a)(x-a)|$, i.e.

$$|y| \ll \varepsilon^{-1}\left|\frac{V'(a)}{V''(a)}\right|\,. \tag{2.125}$$

Because $\varepsilon \propto \hbar^{2/3}$ becomes small for $\hbar \to 0$, one can always find a $\hbar$ such that the linearization can even be used in the region $|y| \gg 1$ (where the WKB approximation holds).

The time-dependent Schrödinger equation therefore has the form

$$-\frac{\hbar^2}{2m}\psi''(x) - |V'(a)|(x-a)\psi(x) = 0\,. \tag{2.126}$$

After changing variables from x to y with $dx/dy = \epsilon^{-1}$ we obtain equivalently

$$\frac{d^2}{dy^2}\psi(y) + y\,\psi(y) = 0\,. \tag{2.127}$$

This differential equation is called the Airy equation.

The solution that decays for $y \ll -1$ is given by

$$\psi(y) = \frac{1}{2\pi^{1/2}i}\int_C e^{yz+\frac{1}{3}z^3}\,dz \tag{2.128}$$

with C an arbitrary path that starts at $z_a = e^{-i\pi/3}\infty$ and ends at $z_e = e^{i\pi/3}\infty$.[9] The function $\psi(y)$ solves the Airy equation because $e^{yz+z^3/3}$ vanishes at the endpoints and hence

$$\begin{aligned}\frac{d^2}{dy^2}\psi(y) &= \frac{1}{2\pi^{1/2}i}\int_C \underbrace{z^2}_{=\frac{d}{dz}(yz+\frac{1}{3}z^3)-y} e^{yz+\frac{1}{3}z^3}\,dz = \frac{e^{yz+\frac{1}{3}z^3}}{2\pi^{1/2}i}\bigg|_{z=z_a}^{z_e} - \frac{1}{2\pi^{1/2}i}\int_C y e^{yz+\frac{1}{3}z^3}\,dz \\ &= -y\psi(y)\,. \end{aligned} \tag{2.129}$$

For $y \ll -1$ the integral has saddle points at $z_\pm = \pm\sqrt{|y|}$. We deform the contour so that it passes through the saddle point at z_+. Near the saddle point one has

$$yz + \frac{1}{3}z^3 = -\frac{2|y|^{3/2}}{3} + \sqrt{|y|}(z-z_+)^2 + O(z-z_+)^3\,. \tag{2.130}$$

With the parametrization $z = z_+ + it$ the value of $\psi(y)$ is dominated by the saddle point and we obtain

$$\psi(y) \sim \frac{1}{2\pi^{1/2}} e^{-\frac{2}{3}|y|^{3/2}} \int e^{-\sqrt{|y|}t^2}\,dt = \frac{1}{2|y|^{1/4}} e^{-\frac{2}{3}|y|^{3/2}}\,. \tag{2.131}$$

This corresponds, as desired, to a decaying solution.

The treatment for $y \gg 1$ is analogous. The saddle points are now complex-conjugate pairs $z_\pm = \pm i\sqrt{y}$ with the expansion

$$yz + \frac{1}{3}z^3 \approx \pm\left[\frac{2}{3}iy^{3/2} + i\sqrt{y}(z-z_\pm)^2\right]\,. \tag{2.132}$$

We deform the contour locally along $z = z_\pm + e^{\pm i\pi/4}t$. For $y \gg 1$ the contributions of the saddle points are well separated. The solution $\psi(y)$ is therefore the sum of the two contributions

$$\begin{aligned}\psi(y) &\sim \frac{1}{2\pi^{1/2}} e^{\frac{2}{3}iy^{3/2}-i\pi/4}\int e^{-\sqrt{y}t^2}\,dt + (i \leftrightarrow -i) = \frac{1}{2y^{1/4}} e^{\frac{2}{3}iy^{3/2}-i\pi/4} + (i \leftrightarrow -i) \\ &= \frac{1}{y^{1/4}}\cos\left(\frac{2}{3}y^{3/2} - \frac{\pi}{4}\right)\,. \end{aligned} \tag{2.133}$$

Thus we have found the matching condition

$$\frac{1}{2|y|^{1/4}} e^{-\frac{2}{3}|y|^{3/2}} \quad (y \ll -1) \qquad \Rightarrow \qquad \frac{1}{y^{1/4}}\cos\left(\frac{2}{3}y^{3/2} - \frac{\pi}{4}\right) \quad (y \gg 1) \tag{2.134}$$

In the original variables one obtains analogously the result

$$\frac{1}{2\sqrt{\tilde{p}(x)}}\exp\left[-\frac{1}{\hbar}\int_x^{a_-}\tilde{p}(x')\,dx'\right] \quad \Rightarrow \quad \frac{1}{\sqrt{p(x)}}\cos\left[\frac{1}{\hbar}\int_{a_-}^{x} p(x')\,dx' - \frac{\pi}{4}\right]\,. \tag{2.135}$$

The matching condition at the second turning point is obtained with $x \mapsto -x$ and $a_- \mapsto a_+$.

A stationary solution that is normalizable must decay exponentially in both directions. The condition for this is that the solution in the allowed region at the left turning point matches the solution at the right turning point; i.e.

$$\cos\left[\frac{1}{\hbar}\int_{a_-}^{x} p(x')\,dx' - \frac{\pi}{4}\right] = \alpha\cos\left[\frac{1}{\hbar}\int_x^{a^+} p(x')\,dx' - \frac{\pi}{4}\right] \tag{2.136}$$

[9] All such paths give the same value by Cauchy's theorem.

with $\alpha \in \mathbb{C}$. This is possible only if $\alpha = \pm 1$ and hence also

$$\frac{1}{\hbar}\int_{a_-}^{a_+} p(x)\,dx - \frac{\pi}{2} = \begin{cases} 2m\pi, & \alpha = +1, \\ (2m+1)\pi, & \alpha = -1. \end{cases} \tag{2.137}$$

With $n = 2m, 2m+1$ one can summarize the condition as

$$\oint p(x)\,dx = 2\int_{a_-}^{a_+} p(x)\,dx = 2\pi\left(n + \tfrac{1}{2}\right)\hbar, \qquad n = 0, 1, 2, \ldots\,. \tag{2.138}$$

This corresponds to the Sommerfeld quantization condition with $n \mapsto n + \frac{1}{2}$.

Tunneling problem: Inverting the potential in Figure 2.4 yields a tunneling problem. The problem is a scattering problem with the classically allowed regions for $x < a_-$ and $x > a_+$. The question is the *tunneling probability* that a particle incident from the left at $t \to -\infty$ is transmitted to the right at $t \to +\infty$. The relevant scattering state has the form

$$\psi_p(x) = \frac{1}{(2\pi\hbar)^{1/2}} \begin{cases} e^{ipx/\hbar} + re^{-ipx/\hbar}, & x < a_-, \\ te^{ipx/\hbar}, & x > a_+\,. \end{cases} \tag{2.139}$$

One may again find the amplitudes r, t using the matching condition (2.135). The plane wave in the region $x < a_-$ leads to an exponentially decaying solution for $a_- < x < a_+$. At the point $x = a_+$ the amplitude is reduced by the factor $t = \exp(-\int_{a_-}^{a_+} \tilde{p}(x)\,dx/\hbar)$. One thus obtains as tunneling probability the result

$$T = |t|^2 = \exp\left(-\frac{2}{\hbar}\int_{a_-}^{a_+} \tilde{p}(x)\,dx\right) = \exp\left(-\frac{2}{\hbar}\int_{a_-}^{a_+} \sqrt{2m[V(x) - E]}\,dx\right). \tag{2.140}$$

Unlike in classical physics, particles can move through "forbidden" regions with $V > E$. However such processes occur only with exponentially small probability. One says that a particle *tunnels* through the forbidden region. Tunneling is important to explain alpha decay of nuclei. Moreover it underlies many technical applications such as the tunnel diode or the Josephson junction.

Chapter 3

Formalism

3.1 Hilbert space

The validity of the superposition principle requires as a mathematical foundation for the description of quantum mechanics a *Hilbert space*, a vector space $\mathcal{H}$ over $\mathbb{C}$ with a scalar product $\langle\phi|\psi\rangle$ for the normalization with $\phi, \psi \in \mathcal{H}$. The scalar product satisfies the following properties:

- $\langle\phi|\psi\rangle = \langle\psi|\phi\rangle^*$ (Hermitian)
- $\langle\phi|a\psi_1 + b\psi_2\rangle = a\langle\phi|\psi_1\rangle + b\langle\phi|\psi_2\rangle$ (linear in the second argument)
- $\|\psi\|^2 = \langle\psi|\psi\rangle \geq 0$ (positive)
- $\|\psi\| = 0 \Rightarrow \psi = 0$ (definite)

The essential difference between a Hilbert space and a (finite-dimensional) unitary vector space is the fact that we need a notion of convergence. We require that $\mathcal{H}$ be *complete*, that is, every Cauchy sequence ψ_n converges to $\psi \in \mathcal{H}$. The Hilbert spaces relevant in physics have a countable basis and are therefore separable.

Examples

Unitary space: The space $\mathbb{C}^N$ is a Hilbert space with scalar product

$$\langle\phi|\psi\rangle = \sum_{n=1}^{N} \phi_n^* \psi_n \,. \tag{3.1}$$

Completeness is trivial in this case.

Square-integrable functions: In Chapter 2 we worked with the Hilbert space $L^2(\mathbb{R}^3)$ of square-integrable functions ($\|\psi\|^2 < \infty$) with the scalar product

$$\langle\phi|\psi\rangle = \int_{\mathbb{R}^3} \phi(\boldsymbol{r})^* \psi(\boldsymbol{r})\, dV \tag{3.2}$$

Periodic boundary conditions: In Chapter 2.8 we worked with the Hilbert space

$$\mathcal{H}_{\text{per}} = \{\psi \in L^2([0, L]) : \psi(0) = \psi(L)\} \tag{3.3}$$

with the scalar product

$$\langle\phi|\psi\rangle = \int_0^L \phi(x)^*\psi(x)\,dx \tag{3.4}$$

Open boundary conditions: Analogously, there is the Hilbert space

$$\mathcal{H}_{\text{off}} = \{\psi \in L^2([0,L]) : \psi(0) = \psi(L) = 0\} \tag{3.5}$$

with the same scalar product, which is relevant for Chapter 2.5.

Sequence space: Another Hilbert space is the sequence space ℓ^2. An element $a \in \ell^2$ is given by the sequence $a_n \in \mathbb{C}$, $n = 1, 2, \ldots$ with $\|a\|^2 < \infty$. The scalar product has the form

$$\langle a|b\rangle = \sum_{n=1}^{\infty} a_n^* b_n\,. \tag{3.6}$$

The sequence space is important because we often expand a general vector ψ in a countable, orthonormal basis with $\psi = \sum_n a_n\psi_n$.

Cauchy-Schwarz inequality: Let $\langle\cdot|\cdot\rangle$ be an arbitrary scalar product, then the Cauchy-Schwarz inequality

$$\big|\langle\phi|\psi\rangle\big|^2 \le \|\phi\|^2\|\psi\|^2\,. \tag{3.7}$$

As a proof we use only the axioms of the scalar product. We have ($\lambda = \langle\psi|\phi\rangle/\|\psi\|^2$, $\|\psi\| \neq 0$ w.l.o.g.)

$$\begin{aligned} 0 \le \langle\phi - \lambda\psi|\phi - \lambda\psi\rangle &= \langle\phi|\phi\rangle - \lambda\langle\phi|\psi\rangle - \lambda^*\langle\psi|\phi\rangle + |\lambda|^2\langle\psi|\psi\rangle \\ &= \|\phi\|^2 - \frac{|\langle\phi|\psi\rangle|^2}{\|\psi\|^2} - \frac{|\langle\phi|\psi\rangle|^2}{\|\psi\|^2} + \frac{|\langle\phi|\psi\rangle|^2}{\|\psi\|^2} = \frac{\|\phi\|^2\|\psi\|^2 - |\langle\phi|\psi\rangle|^2}{\|\psi\|^2}\,. \end{aligned}$$

From definiteness it also follows that $\big|\langle\phi|\psi\rangle\big|^2 = \|\phi\|^2\|\psi\|^2$ only if $\phi = c\psi$ with $c \in \mathbb{C}$.

3.2 Operators

An operator A on $\mathcal{H}$ is a linear map from $A\colon \mathcal{D} \subset \mathcal{H} \to \mathcal{H}$, where $\mathcal{D}$ is in general only a dense subspace of $\mathcal{H}$.

The *adjoint operator* $A^\dagger$ is defined by the requirement that

$$\langle\phi|A^\dagger\psi\rangle = \langle A\phi|\psi\rangle \tag{3.8}$$

for all $\phi, \psi \in \mathcal{H}$. Naturally, $(AB)^\dagger = B^\dagger A^\dagger$ holds for the composition of two operators AB, $(\alpha A)^\dagger = \alpha^* A^\dagger$ and $(A^\dagger)^\dagger = A$. An operator U is *unitary* if it is invertible and preserves the scalar product via

$$\langle U\phi|U\psi\rangle = \langle\phi|\psi\rangle, \qquad \phi, \psi \in \mathcal{H}\,. \tag{3.9}$$

Hence $U^\dagger = U^{-1}$.

An operator H is *Hermitian* if $H^\dagger = H$. For the eigenvalues a_n and eigenvectors ψ_n of Hermitian operators the following important properties hold:

- The spectrum is real with $a_n \in \mathbb{R}$. This follows from

$$a_n\|\psi_n\|^2 = \langle\psi_n|H\psi_n\rangle = \langle H\psi_n|\psi_n\rangle = a_n^*\|\psi_n\|^2\,. \tag{3.10}$$

- The eigenstates ψ_n and ψ_m corresponding to distinct eigenvalues a_n and a_m are orthogonal with $\langle\psi_n|\psi_m\rangle = 0$. This follows from

$$0 = \langle\psi_n|H\psi_m\rangle - \langle H\psi_n|\psi_m\rangle = (a_m - a_n)\langle\psi_n|\psi_m\rangle\,. \tag{3.11}$$

We further define the *commutator* of A and B as

$$[A, B] = AB - BA\,. \tag{3.12}$$

Like the cross product, the commutator is linear $[A+B, C] = [A, C]+[B, C]$ and antisymmetric $[B, A] = -[A, B]$. Moreover, it satisfies the Leibniz rule[1]

$$[A, BC] = [A, B]C + B[A, C]. \tag{3.13}$$

Examples

Position operator: The position operator $\boldsymbol{r}$ on $L^2(\mathbb{R}^3)$ is defined by "multiplication by $\boldsymbol{r}$",

$$(\boldsymbol{r}\,\psi)(\boldsymbol{r}) \mapsto \boldsymbol{r}\psi(\boldsymbol{r})\,. \tag{3.14}$$

With the position operator one writes the expectation value of the particle's position in the state ψ as

$$\langle\boldsymbol{r}\rangle = \langle\psi|\boldsymbol{r}\psi\rangle = \int \boldsymbol{r}\,|\psi(\boldsymbol{r})|^2\,dV \tag{3.15}$$

see (2.9). The position operator is Hermitian because

$$\langle\phi|\boldsymbol{r}\psi\rangle = \int \boldsymbol{r}\,\phi^*(\boldsymbol{r})\psi(\boldsymbol{r})\,dV = \langle\boldsymbol{r}\phi|\psi\rangle\,. \tag{3.16}$$

Analogously one can show that $\boldsymbol{r}$ is also a Hermitian operator on $\mathcal{H}_{\text{per}}$ and $\mathcal{H}_{\text{off}}$.

Momentum operator: We wish to define the momentum operator $\boldsymbol{p}$ on $L^2(\mathbb{R}^3)$ so that the expectation value is given by (3.15) with $\boldsymbol{r} \mapsto \boldsymbol{p}$. Comparing with (2.50) shows that

$$\boldsymbol{p} = -i\hbar\boldsymbol{\nabla} \tag{3.17}$$

is the correct operator. The momentum operator is Hermitian because

$$\begin{aligned}\langle\phi|p_j\psi\rangle &= \int \phi^*(\boldsymbol{r})(-i\hbar)\frac{\partial\psi(\boldsymbol{r})}{\partial r_j}\,dV \overset{\text{(PI)}}{=} \int\left[i\hbar\frac{\partial\phi^*(\boldsymbol{r})}{\partial r_j}\right]\psi(\boldsymbol{r})\,dV \\ &= \int\left[-i\hbar\frac{\partial\phi(\boldsymbol{r})}{\partial r_j}\right]^*\psi(\boldsymbol{r})\,dV = \langle p_j\phi|\psi\rangle\,.\end{aligned} \tag{3.18}$$

The boundary term $\propto \phi^*\psi|_{r_j=-\infty}^{\infty}$ vanishes because the wavefunctions ψ, ϕ are square-integrable and hence $\phi^*\psi$ decay sufficiently fast. Analogously one can show that $\boldsymbol{p}$ is also Hermitian on $\mathcal{H}_{\text{per}}$ and $\mathcal{H}_{\text{off}}$.

The commutator between position and momentum operator evaluates to

$$[r_j, p_k]\psi(\boldsymbol{r}) = r_j(-i\hbar)\frac{\partial\psi}{\partial_k} + i\hbar\underbrace{\frac{\partial}{\partial_k}r_j\psi}_{=\delta_{kj}\psi + r_j\partial\psi/\partial_k} = i\hbar\delta_{jk}\psi(\boldsymbol{r}) \tag{3.19}$$

[1] The rule is called the Leibniz rule because it is analogous to the product rule $(fg)' = f'g + fg'$ for the derivative (derivation) $[A, \cdot]$ is.

with the Kronecker δ-function

$$\delta_{jk} = \begin{cases} 1, & j = k, \\ 0, & \text{otherwise.} \end{cases} \tag{3.20}$$

Moreover, $[r_j, r_k] = [p_j, p_k] = 0$. One calls the relations

$$[r_j, p_k] = i\hbar\,\delta_{jk}, \qquad [r_j, r_k] = 0, \qquad [p_j, p_k] = 0 \tag{3.21}$$

the *canonical commutation relations* between position and momentum. They follow from the fundamental Poisson brackets of classical mechanics by the replacement

$$\{A, B\}_{\text{Poisson}} \mapsto -\frac{i}{\hbar}[A, B]\,. \tag{3.22}$$

This replacement is called the *canonical quantization*.

3.3 Dirac notation

The Dirac notation has become the standard notation for quantum mechanics. It is especially useful for performing basis changes or writing equations in a basis-independent way. For vectors $\psi_n \in \mathcal{H}$ one writes in Dirac notation

$$|\psi_n\rangle = |n\rangle \ \in \mathcal{H}, \tag{3.23}$$

and calls them "kets." Visually, $|\psi\rangle$ should remind us of the right-hand side of the scalar product, see below. The "kets" form a vector space with

$$|\psi\rangle = |a\psi_1 + b\psi_2\rangle = a|\psi_1\rangle + b|\psi_2\rangle\,. \tag{3.24}$$

An operator A acts on the state $|\psi\rangle$ via

$$|A\psi\rangle = A|\psi\rangle \ = aA|\psi_1\rangle + bA|\psi_2\rangle. \tag{3.25}$$

For the scalar product between $|\phi\rangle$ and $|\psi\rangle$ we write $\langle\phi|\psi\rangle$, as usual. For the adjoint operator we then have

$$\langle\phi|A|\psi\rangle = \langle\phi|A\psi\rangle = \langle A^\dagger\phi|\psi\rangle\,. \tag{3.26}$$

One also refers to the last expression as applying the operator A to the *left*.

For later use it is convenient to introduce a special class of operators. The operator

$$A = |\psi\rangle\langle\phi|, \qquad A\colon \mathcal{H} \to \mathcal{H} \tag{3.27}$$

describes a rank-1 map that sends the vector $|\phi\rangle$ to $|\psi\rangle$ and all vectors in the orthogonal complement to 0. In formulas, for an arbitrary vector $|\chi\rangle$

$$A|\chi\rangle = (|\psi\rangle\langle\phi|)|\chi\rangle \overset{\text{(def)}}{=} |\psi\rangle \underbrace{\langle\phi|\chi\rangle}_{\in\mathbb{C}} = \langle\phi|\chi\rangle|\psi\rangle\,. \tag{3.28}$$

It is in the definition where the naturalness of Dirac notation becomes apparent. Visually, it is as if the "bra" vector $\langle\phi|$ merges with $|\chi\rangle$ into the scalar product ("bracket") $\langle\phi|\chi\rangle$. The adjoint of $A = |\psi\rangle\langle\phi|$ is given by

$$A^\dagger = (|\psi\rangle\langle\phi|)^\dagger = |\phi\rangle\langle\psi|, \tag{3.29}$$

since $\langle\chi_1|A\chi_2\rangle = \langle\chi_1|\psi\rangle\,\langle\phi|\chi_2\rangle = \big(\langle\chi_2|\phi\rangle\,\langle\psi|\chi_1\rangle\big)^* = \langle\chi_2|A^\dagger\chi_1\rangle^* = \langle A^\dagger\chi_1|\chi_2\rangle$.

Basis and basis changes: A *basis* is a set of states $\{|\psi_n\rangle = |n\rangle\}$ which are orthonormal,

$$\langle n|m\rangle = \delta_{nm} \tag{3.30}$$

and complete

$$\sum_n |n\rangle\langle n| = 1 \tag{3.31}$$

The operator 1 is then the *identity* with $1|\psi\rangle = |\psi\rangle$. Completeness means that every state $|\psi\rangle$ can be expanded in the basis. Indeed, from completeness it follows that

$$|\psi\rangle = 1|\psi\rangle = \sum_n |n\rangle\langle n|\psi\rangle = \sum_n a_n|n\rangle, \tag{3.32}$$

and hence $a_n = \langle n|\psi\rangle$ are the expansion coefficients of the state $|\psi\rangle$ in the basis $|\psi_n\rangle$. One also calls the expansion coefficients a_n a *representation* of $|\psi\rangle$. For the scalar product of $|\psi\rangle$ with $|\phi\rangle = \sum_n b_n|n\rangle$ one then has

$$\langle\phi|\psi\rangle = \sum_{m,n} b_m^* a_n \langle m|n\rangle = \sum_n b_n^* a_n = \langle b|a\rangle_{\ell_2}\,. \tag{3.33}$$

In general, a basis may consist of both discrete states $|n\rangle$ and continuous, improper states $|\alpha\rangle$, $\alpha \in \mathbb{R}^d$ with the normalization $\langle\alpha|\beta\rangle = \delta^{(d)}(\alpha - \beta)$, see (2.61). The completeness relation then takes the form

$$\sum_n |n\rangle\langle n| + \int d^d\alpha\, |\alpha\rangle\langle\alpha| = 1\,. \tag{3.34}$$

A general vector thus has the representation

$$|\psi\rangle = \sum_n a_n|n\rangle + \int d^d\alpha\, \psi(\alpha)|\alpha\rangle \tag{3.35}$$

with the "wave function"

$$\psi(\alpha) = \langle\alpha|\psi\rangle\,. \tag{3.36}$$

With Dirac notation, the basis transformation from $\{\psi_n\}$ to $\{\phi_m\}$ becomes easy to understand. For the components a_n (in the basis ψ_n) of a general vector ψ the transformation law

$$a_n = \langle\psi_n|\psi\rangle = \langle\psi_n|\left(\sum_m |\phi_m\rangle\langle\phi_m|\right)|\psi\rangle = \sum_m \langle\psi_n|\phi_m\rangle \underbrace{a'_m}_{=\langle\phi_m|\psi\rangle}\,. \tag{3.37}$$

holds. The transformation matrix is therefore given by the overlap of the basis states $\langle\psi_n|\phi_m\rangle$ (direction cosines).

Dirac notation allows us to write transformations in an invariant (i.e. basis-independent) manner. The relation $|\phi\rangle = A|\psi\rangle$ is represented in the basis $\{\psi_n\}$ by

$$b_n = \langle n|\phi\rangle = \sum_m \langle n|A|m\rangle\langle m|\psi\rangle = \sum_m A_{nm}a_m, \qquad A_{nm} = \langle n|A|m\rangle\,. \tag{3.38}$$

With the "vectors" $\boldsymbol{a} = (a_n)$, $\boldsymbol{b} = (b_n)$ and the "matrix" $\mathsf{A} = (A_{nm})$ one simply has $\boldsymbol{b} = \mathsf{A}\boldsymbol{a}$. In every basis the components of the vectors and the elements of the matrix differ, but $\boldsymbol{b} = \mathsf{A}\boldsymbol{a}$ always holds, which is made clear by the Dirac notation $|\phi\rangle = A|\psi\rangle$. Relations that have been proved in one representation therefore also hold in every other representation. Henceforth we will require a certain mental flexibility and will occasionally switch between the (abstract) vector $|\psi\rangle$ and its components $\langle n|\psi\rangle$ in a given basis.

Position/momentum representation: We consider the Hilbert space $\mathcal{H} = L^2(\mathbb{R}^3)$. To relate an (abstract) vector $|\psi\rangle$ to the wave function $\psi(\boldsymbol{r})$, we introduce the improper position vectors $|\boldsymbol{r}\rangle$ with $\boldsymbol{r} \in \mathbb{R}^3$ as basis vectors. We thereby define the state in the *position representation* as

$$\psi(\boldsymbol{r}) = \langle \boldsymbol{r}|\psi\rangle \,. \tag{3.39}$$

The completeness relation then simply guarantees the correct representation of the scalar product with

$$\langle\phi|\psi\rangle = \langle\phi|\left(\int d^3r |\boldsymbol{r}\rangle\langle\boldsymbol{r}|\right)|\psi\rangle = \int d^3r \underbrace{\langle\phi|\boldsymbol{r}\rangle}_{=\langle\boldsymbol{r}|\phi\rangle^*}\langle\boldsymbol{r}|\psi\rangle = \int \phi(\boldsymbol{r})^*\psi(\boldsymbol{r})\,dV \,. \tag{3.40}$$

To go over to the *momentum representation* $\hat{\psi}(\boldsymbol{p}) = \langle\boldsymbol{p}|\psi\rangle$ we need the overlap [cf. (2.47)]

$$\psi_{\boldsymbol{p}}(\boldsymbol{r}) = \langle\boldsymbol{r}|\boldsymbol{p}\rangle = \frac{1}{(2\pi\hbar)^{3/2}} e^{i\boldsymbol{p}\cdot\boldsymbol{r}/\hbar} \,. \tag{3.41}$$

Thus the basis transformation

$$\hat{\psi}(\boldsymbol{p}) = \langle\boldsymbol{p}|\psi\rangle = \int d^3r \underbrace{\langle\boldsymbol{p}|\boldsymbol{r}\rangle}_{=\langle\boldsymbol{r}|\boldsymbol{p}\rangle^*}\langle\boldsymbol{r}|\psi\rangle = \frac{1}{(2\pi\hbar)^{3/2}} \int d^3r\, e^{-i\boldsymbol{p}\cdot\boldsymbol{r}/\hbar}\psi(\boldsymbol{r}) \tag{3.42}$$

is indeed implemented by the Fourier transform (2.52). For the inverse transformation one correspondingly obtains

$$\psi(\boldsymbol{r}) = \langle\boldsymbol{r}|\psi\rangle = \frac{1}{(2\pi\hbar)^{3/2}} \int d^3p\, e^{i\boldsymbol{p}\cdot\boldsymbol{r}/\hbar}\hat{\psi}(\boldsymbol{p}) = \int d^3p\, \langle\boldsymbol{r}|\boldsymbol{p}\rangle\langle\boldsymbol{p}|\psi\rangle \,. \tag{3.43}$$

We have thereby shown that the momentum basis $|\boldsymbol{p}\rangle$ is complete with

$$\int d^3p\, |\boldsymbol{p}\rangle\langle\boldsymbol{p}| = 1 \,. \tag{3.44}$$

The action of an operator A on the state $|\psi\rangle$ is given by

$$(A\psi)(\boldsymbol{r}) = \langle\boldsymbol{r}|A|\psi\rangle = \int d^3r'\, \langle\boldsymbol{r}|A|\boldsymbol{r}'\rangle\langle\boldsymbol{r}'|\psi\rangle = \int d^3r'\, A(\boldsymbol{r},\boldsymbol{r}')\psi(\boldsymbol{r}') \tag{3.45}$$

with the position representation

$$A(\boldsymbol{r},\boldsymbol{r}') = \langle\boldsymbol{r}|A|\boldsymbol{r}'\rangle \tag{3.46}$$

of the operator A. Comparing with the action of the position operator $\boldsymbol{r}$ in (3.14) shows that the position vectors $|\boldsymbol{r}'\rangle$ are the improper eigenstates of the position operator with eigenvalue $\boldsymbol{r}' \in \mathbb{R}^3$, satisfying

$$\boldsymbol{r}|\boldsymbol{r}'\rangle = \boldsymbol{r}'|\boldsymbol{r}'\rangle \,. \tag{3.47}$$

Analogously, $|\boldsymbol{p}\rangle$ is the improper eigenstate of the momentum operator $\boldsymbol{p}$ with eigenvalue $\boldsymbol{p}'$, satisfying

$$\boldsymbol{p}|\boldsymbol{p}'\rangle = \boldsymbol{p}'|\boldsymbol{p}'\rangle \,. \tag{3.48}$$

The position representation of the momentum operator evaluates to

$$(\boldsymbol{p}\psi)(\boldsymbol{r}) = \langle \boldsymbol{r}|\boldsymbol{p}|\psi\rangle = \int d^3p' \underbrace{\langle \boldsymbol{r}|\boldsymbol{p}|\boldsymbol{p}'\rangle}_{=\boldsymbol{p}'\langle \boldsymbol{r}|\boldsymbol{p}'\rangle} \underbrace{\langle \boldsymbol{p}'|\psi\rangle}_{=\hat{\psi}(\boldsymbol{p}')} = \frac{1}{(2\pi\hbar)^{3/2}} \int d^3p' \underbrace{\boldsymbol{p}' e^{i\boldsymbol{p}'\cdot\boldsymbol{r}/\hbar}}_{=-i\hbar\boldsymbol{\nabla} e^{i\boldsymbol{p}'\cdot\boldsymbol{r}/\hbar}} \hat{\psi}(\boldsymbol{p}')$$
$$= -i\hbar\boldsymbol{\nabla}\psi(\boldsymbol{r}) \tag{3.49}$$

which agrees with our earlier result (3.17). With an analogous calculation one can determine the momentum representation of the position operator

$$(\boldsymbol{r}\hat{\psi})(\boldsymbol{p}) = i\hbar\boldsymbol{\nabla}\hat{\psi}(\boldsymbol{p}) \tag{3.50}$$

Note that the canonical commutation relations are representation-independent and hold in both the position and momentum representations.

3.4 Observables and measurement

A normalized vector $|\psi\rangle \in \mathcal{H}$ with $\|\psi\| = \langle\psi|\psi\rangle = 1$ represents, up to the equivalence

$$|\psi\rangle \equiv e^{i\varphi}|\psi\rangle, \qquad \varphi \in \mathbb{R} \tag{3.51}$$

a *state* of the system. One also calls a state a *ray* in Hilbert space. The orthogonal *projection operator*

$$P_\psi = |\psi\rangle\langle\psi| \tag{3.52}$$

onto the state $|\psi\rangle$ is uniquely determined, i.e., it does not depend on the phase φ. That P_ψ is a projector follows from $P_\psi^\dagger = P_\psi$ and

$$P_\psi^2 = |\psi\rangle \underbrace{\langle\psi|\psi\rangle}_{1}\langle\psi| = P_\psi\,. \tag{3.53}$$

To describe a measurement M we assume that there are states $|n\rangle$ that correspond uniquely to the measurement outcomes $m_n \in \mathbb{R}$. These states form an orthogonal basis and we require that an arbitrary state $|\psi\rangle$ can be expanded in the eigenstates $|n\rangle$ with

$$|\psi\rangle = \sum_n a_n|n\rangle\,. \tag{3.54}$$

The normalization of the state implies

$$1 = \langle\psi|\psi\rangle = \sum_{m,n} a_m^* a_n \underbrace{\langle m|n\rangle}_{=\delta_{mn}} = \sum_n |a_n|^2\,. \tag{3.55}$$

One can therefore interpret the quantity $|a_n|^2$, following Born, as the *probability* of measuring the value m_n. If we register the measurement outcome m_n, we know that after the measurement the system is in the state $|n\rangle$.

In general, a measurable quantity M (*observable*) is a Hermitian operator $M = M^\dagger$ whose eigenstates $|n\rangle$ corresponding to the eigenvalues m_n and improper eigenstates $|\alpha\rangle$ corresponding to the eigenvalues $m(\alpha)$ form a complete basis according to (3.34). [2] For a measurable quantity we need the completeness of the eigenbasis so that the probabilities sum to 1. We first assume that M has only discrete eigenstates and that there is no degeneracy. Then the measurement M of the state $|\psi\rangle$ is described by the *Born rule*:

[2] In the mathematical literature observables are referred to as *self-adjoint* operators. Hermitian operators are then often called *symmetric*.

- The probability of finding the measurement outcome m_n is given by
$$p_n = |\langle n|\psi\rangle|^2 = \langle\psi|P_n|\psi\rangle \tag{3.56}$$
with $P_n = |n\rangle\langle n|$ the projector onto the n-th state.
- If the measurement outcome m_n is obtained, the state after the measurement is $|n\rangle$.

If there are degeneracies, the rule must be generalized. We then label the eigenvectors corresponding to the eigenvalue m_n by $|n, r\rangle$, where r describes the degeneracy ($r = 1, 2, \ldots, d_n$ with d_n the degree of degeneracy). The *generalized Born rule* requires:

- The probability of finding the measurement outcome m_n is given by
$$p_n = \langle\psi|P_n|\psi\rangle \tag{3.57}$$
with the projector $P_n = \sum_r |n, r\rangle\langle n, r|$ onto the eigenspace corresponding to the eigenvalue m_n.
- If the measurement outcome m_n is obtained, the state after the measurement (the state conditioned on having measured m_n) is given by
$$\frac{1}{\sqrt{p_n}} P_n|\psi\rangle\,. \tag{3.58}$$
The prefactor ensures that the state is correctly normalized. The new normalization is analogous to the expression for conditional probability in classical probability theory.

The fact that quantum mechanics predicts only certain probabilities for the measurement of the observable M in the state $|\psi\rangle$ implies that to test the theory an experiment must be performed repeatedly. One thereby prepares N systems, all in the same state $|\psi\rangle$. The theory then predicts that upon measuring the observable M only the measurement outcomes m_n (N_n times) will occur. Moreover, one must have $N_n/N \to p_n$ for $N \to \infty$.

If the observable also has a continuous spectrum, the probability of measuring the value $m(\alpha)$ is given by
$$\rho(\alpha)\, d^d\alpha = |\langle\alpha|\psi\rangle|^2\, d^d\alpha\,. \tag{3.59}$$
It is easy to see that p_n and $\rho(\alpha)$ admit a probabilistic interpretation. On the one hand they are positive, since they are defined via an absolute value. On the other hand the completeness relation (generalized Plancherel relation)
$$1 = \langle\psi|\psi\rangle = \langle\psi|\Big(\sum_n |n\rangle\langle n| + \int d^d\alpha\, |\alpha\rangle\langle\alpha|\Big)|\psi\rangle = \sum_n p_n + \int \rho(\alpha)\, d^d\alpha\,. \tag{3.60}$$
ensures that the individual probabilities sum to 1.

Spectral representation: An observable can, thanks to the completeness relation, be written in spectral representation as
$$\begin{aligned} M &= M\Big(\sum_n |n\rangle\langle n| + \int d^d\alpha\, |\alpha\rangle\langle\alpha|\Big) = \sum_n \overbrace{M|n\rangle}^{=m_n|n\rangle}\langle n| + \int d^d\alpha\, \overbrace{M|\alpha\rangle}^{=m(\alpha)|\alpha\rangle}\langle\alpha| \\ &= \sum_n m_n|n\rangle\langle n| + \int d^d\alpha\, m(\alpha)|\alpha\rangle\langle\alpha| \end{aligned} \tag{3.61}$$
with $\langle n|m\rangle = \delta_{nm}$, $\langle n|\alpha\rangle = 0$ and $\langle\alpha|\beta\rangle = \delta^{(d)}(\alpha - \beta)$. An observable is thus a Hermitian operator that admits a *spectral representation*.

Expectation value: The expectation value of an observable M in the state $|\psi\rangle$ has the symmetric form

$$\langle M\rangle = \sum_n p_n m_n + \int \rho(\alpha) m(\alpha)\, d^d\alpha = \langle\psi|M|\psi\rangle\,. \tag{3.62}$$

One shows this by introducing the spectral representation for M on the right-hand side.

Examples

Position operator: The position operator $\boldsymbol{r}$ on $\mathcal{H} = L^2(\mathbb{R}^3)$ is an observable. We have already shown that it is Hermitian. It has the improper basis $|\boldsymbol{r}\rangle$. Completeness follows from the position representation with

$$\int d^3r\, |\boldsymbol{r}\rangle\langle\boldsymbol{r}| = 1\,. \tag{3.63}$$

Momentum operator: Analogously, the momentum operator $\boldsymbol{p}$ on $L^2(\mathbb{R}^3)$ is an observable (see momentum representation). The same holds for the momentum operator $p = -i\hbar\partial/\partial x$ on $\mathcal{H}_{\text{per}}$. Note, however, that the momentum operator on the Hilbert space $\mathcal{H}_{\text{off}}$ is not an observable. In fact, for an eigenstate $\psi(x)$ with eigenvalue λ one has

$$p\psi(x) = -i\hbar\psi'(x) = \lambda\psi(x) \tag{3.64}$$

with the general solution

$$\psi(x) = Ae^{i\lambda x/\hbar}\,. \tag{3.65}$$

The boundary conditions $\psi(0) = \psi(L) = 0$ cannot, however, be satisfied for any choice of the integration constants $A \in \mathbb{C}$. The operator p therefore has no eigenstates and p is not an observable on $\mathcal{H}_{\text{off}}$.

Projector: As an instructive example consider a particle in one dimension with $\mathcal{H} = L^2(\mathbb{R})$. We consider the measurement P of finding the particle in the region $\Omega \subset \mathbb{R}$, described by the projector

$$P_\Omega = \int_\Omega |x\rangle\langle x|\, dx \tag{3.66}$$

respectively

$$(P_\Omega\psi)(x) = \begin{cases} \psi(x), & x \in \Omega, \\ 0, & \text{otherwise} \end{cases} \tag{3.67}$$

in the position representation. One can easily show that $P_\Omega = P_\Omega^2 = P_\Omega^\dagger$ holds.

A projector has only two possible eigenvalues $0, 1$. The measurement of P_Ω therefore yields only the results $p = 1$ (the particle is in the region) and $p = 0$ (the particle is not in the region). The probability that $p = 1$ is given by [cf. (1.72)]

$$p_\Omega = \langle\psi|P_\Omega|\psi\rangle = \int_\Omega |\psi(x)|^2\, dx\,. \tag{3.68}$$

If the measurement indicates that the particle is in the region Ω, the state after the measurement is given by

$$|\psi_\Omega\rangle = |\psi; \text{particle in region } \Omega\rangle = \frac{1}{\sqrt{p_\Omega}}\, P_\Omega\psi \tag{3.69}$$

Function of an observable: With M also an arbitrary function $f(M)$ is an observable. We define $f(M)$ via the spectral representation (3.61) as

$$f(M) = \sum_n f(m_n)|n\rangle\langle n| + \int d^d\alpha\, f[m(\alpha)]\,|\alpha\rangle\langle\alpha|\,. \tag{3.70}$$

Momentum operator on half-line: As a further example consider the Hilbert space

$$\mathcal{H}_{\mathrm{HR}} = \{\psi(x) \in L^2([0,\infty[) : \psi(0) = 0\} \tag{3.71}$$

of a particle on the half-line. This Hilbert space is, for example, relevant for the case where we have a potential wall at $x = 0$ with $V(x < 0) = \infty$. The momentum operator $p = -i\hbar\partial/\partial x$ is Hermitian. It is not, however, an observable, since there are no eigenfunctions: note that the plane wave $\exp(ipx/\hbar)$ does not satisfy the boundary condition. This does not, of course, mean that one cannot measure the momentum of a particle on the half-line. It simply means that there is no measurement apparatus that "exactly" measures the operator p. Such a measurement would be unphysical, since it would require projecting onto the state $\exp(ipx/\hbar)$ "infinitely" much energy, because the particle would then have a finite probability of being found in the forbidden region with $V = \infty$.

Overall, measurement theory is still an active field of research. In a concrete case one could study a specific measurement setup in more detail to determine a more realistic momentum operator. Here we content ourselves with an idealized description. We consider a detector located in the region $\Omega = [x_0, x_0 + \xi]$ (i.e., the detector only has access to the wave function $|\psi_\Omega\rangle$). One can show that the wave packets

$$\psi_n(x) = \langle x|n\rangle = \begin{cases} e^{ip_n x/\hbar}, & x \in \Omega, \\ 0, & \text{otherwise}, \end{cases} \qquad p_n = \frac{2\pi\hbar n}{\xi}, \tag{3.72}$$

form a complete and orthonormal basis on $L^2(\Omega)$. It is natural to associate the momentum p_n with the state $|n\rangle$. We therefore define the momentum operator at Ω as

$$p_{\mathrm{HR}} = \sum_n p_n|n\rangle\langle n| + 0\int_{x\notin\Omega} dx\,|x\rangle\langle x| = \sum_n p_n|n\rangle\langle n|\,. \tag{3.73}$$

The operator is an observable since we have already written it in spectral representation. If the particle is outside the region Ω of the detector, measuring p_{HR} yields zero. If the particle is at Ω, the possible measurement outcomes are p_n. The measurement accuracy is given by $p_{n+1} - p_n = 2\pi\hbar/\xi$. For an accurate momentum measurement one therefore needs a long detector (ξ large). Moreover, measuring p_{HR} is, of course, only meaningful under the condition that the particle is in Ω. The relevant conditional wave function is given by (3.69).

Heisenberg Uncertainty Relation: We define the *variance* (fluctuation squared) of an observable M in the state $|\psi\rangle$ as

$$(\Delta M)^2 = \|(M - \langle M\rangle)\psi\|^2 = \langle (M - \langle M\rangle)^2\rangle = \langle M^2\rangle - \langle M\rangle^2\,. \tag{3.74}$$

For an eigenstate $|n\rangle$ with eigenvalue m_n of M we have $M|n\rangle = m_n|n\rangle$ with $m_n = \langle M\rangle$ and hence $\Delta M = 0$. An eigenstate is therefore precisely the state in which the observable M takes the value m_n with certainty. One says that M is *sharp* in the state $|n\rangle$.

Two observables M and N generally do not possess a common eigenstate. Hence it is not possible for M and N to be simultaneously (sharp) determined. Here the (historical) term "simultaneously" does not refer to a measurement at the same time, but rather to a measurement in the same state.

In fact, for two observables M, N in the state $|\psi\rangle$ the *Heisenberg uncertainty relation*

$$\Delta M \, \Delta N \geq \frac{1}{2} \big| \langle [M, N] \rangle \big| \,. \tag{3.75}$$

holds. The inequality follows from the relation

$$\langle AB \rangle^* = \langle AB\psi | \psi \rangle = \langle \psi | (AB)^\dagger \psi \rangle = \langle \psi | BA\psi \rangle = \langle BA \rangle \tag{3.76}$$

for any two Hermitian operators A, B. Thus we have

$$\mathrm{Im} \langle AB \rangle = \frac{1}{2i} \big(\langle AB \rangle - \langle AB \rangle^* \big) = \frac{1}{2i} \langle [A, B] \rangle \tag{3.77}$$

and obtain

$$\frac{1}{4} \big| \langle [A, B] \rangle \big|^2 = \big| \mathrm{Im} \langle AB \rangle \big|^2 \leq \big| \langle AB \rangle \big|^2 = \big| \langle A\psi | B\psi \rangle \big|^2 \leq \|A\psi\|^2 \|B\psi\|^2, \tag{3.78}$$

where in the last step we have used the Cauchy-Schwarz inequality. With $A = M - \langle M \rangle$, $B = N - \langle N \rangle$ and $[A, B] = [M, N]$ one thereby deduces the Heisenberg uncertainty relation.

The name "uncertainty relation" is inapt insofar as it does not describe an inaccuracy of the measuring apparatus. Rather, there simply does not exist a state of the system such that the product of the standard deviations $\Delta M \, \Delta N$ of measurements of M and N falls below the bound in (3.75).

On $\mathcal{H} = L^2(\mathbb{R}^3)$ one has

$$[r_j, p_k] = i\hbar \delta_{jk} \tag{3.79}$$

for the commutator of the position and momentum operator, see (3.19). Hence the uncertainty relation follows [cf. (2.75)]

$$\Delta r_j \, \Delta p_k \geq \frac{\hbar}{2} \delta_{jk} \,. \tag{3.80}$$

Thus position and momentum cannot simultaneously be sharply determined (in the same direction).

Compatible Observables: Two observables M and N are called *compatible* if they can be simultaneously sharply determined (with $\Delta M = \Delta N = 0$). It holds

$$M \text{ and } N \text{ are compatible} \quad \Longleftrightarrow \quad [M, N] = 0 \,. \tag{3.81}$$

Observables M and N can be *simultaneously diagonalized* precisely when $[M, N] = 0$ holds. Hence two observables are compatible if they can be simultaneously diagonalized.

Proof: If the observables M and N can be simultaneously diagonalized, then $[M, N] = 0$ follows.

For the converse direction we consider two observables M and N with $NM = MN$. Let $|\psi\rangle$ be an arbitrary eigenvector of N with eigenvalue n. This vector can be expanded in the eigenspaces of M,

$$|\psi\rangle = \sum_j |\psi_j\rangle \tag{3.82}$$

with $M|\psi_j\rangle = m_j|\psi_j\rangle$ and m_j distinct.[3] Since M and N commute we have

$$M(N-n)|\psi_j\rangle = (N-n)M|\psi_j\rangle = m_j(N-n)|\psi_j\rangle\,. \tag{3.83}$$

Thus $(N-n)|\psi_j\rangle$ is an eigenvector of M with eigenvalue m_j. Hence the individual summands

$$0 = (N-n)|\psi\rangle = \sum_j (N-n)|\psi_j\rangle \tag{3.84}$$

are linearly independent (in fact even orthogonal). It follows that the vectors $|\psi_j\rangle$ are also eigenvectors of N with eigenvalue n.

State preparation: A state can be prepared by the simultaneous measurement of a complete set of commuting observables (CSCO). These are observables $M_1, \ldots, M_n$ that pairwise commute ($[M_j, M_k] = 0$) and whose joint system of eigenfunctions is non-degenerate. The simultaneous measurement of $M_1, \cdots, M_n$ thereby uniquely determines the state $|m_1, \ldots, m_n\rangle$ through the specification of the measured values $m_1, \cdots, m_n$.

3.5 Hamiltonian Operator

The Schrödinger equation has in general the form

$$i\hbar \frac{d}{dt}|\Psi_t\rangle = H|\Psi_t\rangle\,. \tag{3.85}$$

It is an ordinary differential equation for the function $t \mapsto |\Psi_t\rangle \in \mathcal{H}$. The operator H is called the *Hamiltonian operator*. For an *autonomous* system the Hamiltonian operator does not depend on time. The eigenvalue equation of the Hamiltonian operator then corresponds to the time-independent Schrödinger equation $H|\psi\rangle = E|\psi\rangle$. We require that H be an observable with real eigenvalues, which correspond to the energy of the stationary state. The completeness of the eigenbasis allows the expansion of any initial state, see (2.21).

Examples

Particle in a potential: A particle in the potential $V(\boldsymbol{r})$ is described by the Hamiltonian

$$H = \frac{\boldsymbol{p}^2}{2m} + V(\boldsymbol{r}) = \sum_{j=1}^{3} \frac{p_j^2}{2m} + V(\boldsymbol{r}) \tag{3.86}$$

on $\mathcal{H} = L^2(\mathbb{R}^3)$. The resulting Schrödinger equation corresponds to the equation (2.1), which we studied in Chapter 2.

N-particle: The wave function of N-particle systems is described by $\psi \in \mathcal{H}^{(N)} = L^2(\mathbb{R}^{3N})$. Here $|\psi(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N)|^2$ determines the probability density for finding the particles at positions $\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N$. In this case the Hamiltonian is

$$H = \sum_{k=1}^{N} \frac{(\boldsymbol{p}_k)^2}{2m} + V(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N) \tag{3.87}$$

with $\boldsymbol{p}_k = -i\hbar\boldsymbol{\nabla}_k$.

[3] Here the vector $|\psi_j\rangle$ is simply the orthogonal projection of $|\psi\rangle$ onto the respective eigenspace of M.

One may interpret the 2-particle system as a *tensor product* with

$$(\psi_1 \otimes \psi_2)(\boldsymbol{r}_1, \boldsymbol{r}_2) = \psi_1(\boldsymbol{r}_1)\psi_2(\boldsymbol{r}_2)\,. \tag{3.88}$$

Thus $L^2(\mathbb{R}^6) = L^2(\mathbb{R}^3) \otimes L^2(\mathbb{R}^3)$ holds. In general, the composite system of two Hilbert spaces $\mathcal{H}_1$ and $\mathcal{H}_2$ is described by the tensor product space $\mathcal{H} = \mathcal{H}_1 \otimes \mathcal{H}_2$. We denote the product state (3.88) of $\psi_1 \in \mathcal{H}_1$ and $\psi_2 \in \mathcal{H}_2$ by $|\psi_1, \psi_2\rangle = |\psi_1\rangle \otimes |\psi_2\rangle$. The tensor product is linear in both arguments with $|a\psi_1 + b\phi_1, \psi_2\rangle = a|\psi_1, \psi_2\rangle + b|\phi_1, \psi_2\rangle$; and analogously for the second argument. The space $\mathcal{H}$ is a Hilbert space with the scalar product $\langle \phi_1, \phi_2 | \psi_1, \psi_2\rangle = \langle \phi_1 | \psi_1\rangle \, \langle \phi_2 | \psi_2\rangle$. On the tensor product an operator $O = A \otimes B$ acts with $O(|\psi_1\rangle \otimes |\psi_2\rangle) = A|\psi_1\rangle \otimes B|\psi_2\rangle$. As in (3.87) for momentum and position, we introduce in general one-particle operators A_k, with

$$A_1 = A \otimes 1, \qquad A_2 = 1 \otimes A, \tag{3.89}$$

so that A acts only on the k-th system. The space of N-particles is therefore the tensor space $\mathcal{H}^{(N)} = \otimes^N L^2(\mathbb{R}^3)$ with N factors.

Particle in an electromagnetic field: A particle with charge q has the Hamiltonian

$$H = \frac{1}{2m}\Big[\boldsymbol{p} - \frac{q}{c}\boldsymbol{A}(\boldsymbol{r}, t)\Big]^2 + q\varphi(\boldsymbol{r}, t) \tag{3.90}$$

on $L^2(\mathbb{R}^3)$. A *gauge transformation*

$$\varphi \mapsto \varphi' = \varphi - \frac{1}{c}\frac{\partial \chi}{\partial t}, \qquad \boldsymbol{A} \mapsto \boldsymbol{A}' = \boldsymbol{A} + \boldsymbol{\nabla}\chi, \tag{3.91}$$

with $\chi(\boldsymbol{r}, t)$ an arbitrary function leaves the electromagnetic fields unchanged.

The Hamiltonian changes by $H' \neq H$. However, the transformed wave function

$$\Psi(\boldsymbol{r}, t) \mapsto \Psi'(\boldsymbol{r}, t) = \exp\Big(\frac{iq}{\hbar c}\chi\Big)\Psi(\boldsymbol{r}, t) \tag{3.92}$$

satisfies the new Schrödinger equation $(i\hbar\partial_t - H')|\Psi'_t\rangle = 0$. This follows from

$$\begin{aligned} e^{-iq\chi/\hbar c}\Big(i\hbar\frac{\partial}{\partial t} - q\varphi'\Big)e^{iq\chi/\hbar c} &= i\hbar\frac{\partial}{\partial t} - q\varphi, \\ e^{-iq\chi/\hbar c}\Big(\boldsymbol{p} - \frac{q}{c}\boldsymbol{A}'\Big)e^{iq\chi/\hbar c} &= \boldsymbol{p} - \frac{q}{c}\boldsymbol{A}\,. \end{aligned} \tag{3.93}$$

Hence the relevant combinations $i\hbar\partial_t - q\varphi$ and $\boldsymbol{p} - (q/c)\boldsymbol{A}$ remain gauge invariant.

Propagator: For an autonomous system, in which the Hamiltonian H does not depend on time, we can solve (3.85) with

$$|\Psi_t\rangle = \exp\big[-iH(t - t_0)/\hbar\big]|\Psi_0\rangle = U(t - t_0)|\Psi_0\rangle \tag{3.94}$$

for the initial condition $|\Psi_{t_0}\rangle = |\Psi_0\rangle$. The propagator $U(t) = e^{-iHt/\hbar}$ forms a one-parameter group of unitary operators. Unitarity follows from the Hermiticity $H = H^\dagger$ since

$$\frac{d}{dt}\langle \Phi_t | \Psi_t\rangle = \frac{i}{\hbar}\big[\langle H\Phi_t | \Psi_t\rangle - \langle \Phi_t | H\Psi_t\rangle\big] = 0\,. \tag{3.95}$$

Thus the scalar product is preserved under time evolution,

$$\langle U(t)\Phi_0|U(t)\Psi_0\rangle = \langle\Phi_t|\Psi_t\rangle = \langle\Phi_0|\Psi_0\rangle\,. \tag{3.96}$$

The position representation of the time evolution yields

$$K(\boldsymbol{r},\boldsymbol{r}';t) = \langle\boldsymbol{r}|U(t)|\boldsymbol{r}'\rangle \tag{3.97}$$

with [cf. (2.56)]

$$\begin{aligned}\Psi(\boldsymbol{r},t) = \langle\boldsymbol{r}|\Psi_t\rangle &= \langle\boldsymbol{r}|U(t-t_0)\left(\int d^3r'|\boldsymbol{r}'\rangle\langle\boldsymbol{r}'|\right)|\Psi_0\rangle \\ &= \int d^3r' K(\boldsymbol{r},\boldsymbol{r}';t-t_0)\Psi_0(\boldsymbol{r}')\,.\end{aligned} \tag{3.98}$$

3.6 Representations

The task of quantum mechanics is to predict the expectation value (measured quantity)

$$\langle M\rangle_t = \langle\Psi_t|M|\Psi_t\rangle = \langle V_t\Psi_t|V_tMV_t^\dagger|V_t\Psi_t\rangle \tag{3.99}$$

of an arbitrary observable M at time t. The observables and states are thereby fixed only up to an *unitary equivalence*. That is, one may choose an arbitrary unitary map $V_t\colon \mathcal{H}\to\mathcal{H}$ at time t and transform the states and observables by $|\Psi_t\rangle \mapsto |\tilde\Psi_t\rangle = V_t|\Psi_t\rangle$, $M\mapsto \tilde M_t = V_tMV_t^\dagger$ without changing measured quantities. The Hamiltonian in the new picture has the form

$$\tilde H = V_tHV_t^\dagger + i\hbar\dot V_tV_t^\dagger, \tag{3.100}$$

since

$$i\hbar\frac{d}{dt}|\tilde\Psi_t\rangle = V_t\underbrace{i\hbar\frac{d}{dt}|\Psi_t\rangle}_{=H|\Psi_t\rangle} + i\hbar\dot V_t|\Psi_t\rangle = (V_tHV_t^\dagger + i\hbar\dot V_tV_t^\dagger)|\tilde\Psi_t\rangle\,. \tag{3.101}$$

In particular, in addition to the Schrödinger picture, with

$$\langle M\rangle_t = \langle\Psi_t|M|\Psi_t\rangle = \langle e^{-iH(t-t_0)/\hbar}\Psi_0|M|e^{-iH(t-t_0)/\hbar}\Psi_0\rangle, \tag{3.102}$$

one must also mention the *Heisenberg picture*

$$\langle M\rangle_t = \langle\Psi_0|M_H(t)|\Psi_0\rangle \tag{3.103}$$

in which the observables

$$M_H(t) = V_tMV_t^\dagger, \qquad V_t = e^{iH(t-t_0)/\hbar}, \tag{3.104}$$

evolve in time while the states remain static. The observables then change according to the *Heisenberg equation*[4]

$$\frac{d}{dt}M_H(t) = \frac{i}{\hbar}[H,M_H(t)] = \frac{i}{\hbar}[H,M]_H(t)\,. \tag{3.105}$$

In particular $\dot H_H = (i/\hbar)[H,H]_H = 0$ holds and the energy does not change under time evolution in an autonomous system. The Heisenberg equation corresponds, via canonical quantization (3.22), to the Hamilton equation $\dot M = \{M,H\}$ in classical mechanics.

[4] We use that $[H,V_t]=0$ and $\dot V_t = iHV_t/\hbar$.

3.7 Mixed States

According to the Born rule, a state $|\psi\rangle$ describes the probabilities that certain measurement outcomes occur. The "wave function" $|\psi\rangle$ is thus an expression of our knowledge about the system. If an event occurs with probability 1, we are certain of it. If we are certain that an event is impossible, we assign it probability 0 on the other hand. Probabilities p with $0 < p < 1$ therefore correspond to different degrees of "certainty."

It turns out that the states $|\psi\rangle$ (also called *pure states*) cannot describe all possible assessments of the system. Consider, for example, the case in which a colleague in her quantum laboratory can prepare two orthogonal states $|\psi_1\rangle$ and $|\psi_2\rangle$. She tells us that with probability p_1 she will prepare the state $|\psi_1\rangle$ and with probability $p_2 = 1 - p_1$ the state $|\psi_2\rangle$. In this case the description of the system cannot be achieved by a pure state. A similar situation arises upon measurement when our colleague informs us that she has measured an observable but (alas) does not communicate the measurement result. In both cases we possess only incomplete information about the state of the system.

The expectation value of an observable is then given by

$$\langle M\rangle = p_1\langle\psi_1|M|\psi_1\rangle + p_2\langle\psi_2|M|\psi_2\rangle = \mathrm{Tr}(\rho M), \tag{3.106}$$

where

$$\rho = p_1 P_{\psi_1} + p_2 P_{\psi_2} = p_1|\psi_1\rangle\langle\psi_1| + p_2|\psi_2\rangle\langle\psi_2| \tag{3.107}$$

is the *density matrix* of the *mixed* state. In general a density matrix ρ is a linear map $\rho\colon \mathcal{H} \to \mathcal{H}$ with the properties:

- $\rho = \rho^\dagger$ (Hermitian),
- $\rho \geq 0$, i.e. $\langle\psi|\rho|\psi\rangle \geq 0$ for all $|\psi\rangle$ (positive semidefinite),
- $\mathrm{Tr}\,\rho = 1$ (trace 1).

Because of Hermiticity the density matrix can be diagonalized in an orthonormal basis $|\psi_j\rangle$ with eigenvalues $p_j \in \mathbb{R}$. Moreover $p_j \geq 0$ (by point 2) and $\sum_j p_j = 1$ (by point 3). Thus for any density matrix we have the representation

$$\rho = \sum_j p_j P_{\psi_j} = \sum_j p_j|\psi_j\rangle\langle\psi_j|\,, \tag{3.108}$$

where p_j is the probability that the state is given by $|\psi_j\rangle$. Pure states are precisely the cases in which ρ is a projector with $\rho^2 = \rho$ (so there exists a j with $p_j = 1$ and $p_{k\neq j} = 0$).

The expectation value of the observable M in the state ρ is then given by

$$\langle M\rangle = \mathrm{Tr}(\rho M)\,. \tag{3.109}$$

Starting from the state ρ_0 at time $t = 0$ the time evolution of the individual wave functions in (3.108) under the Hamiltonian H according to the Schrödinger equation is given by $e^{-iHt/\hbar}|\psi_j\rangle$. Hence at time t the state is

$$\rho_t = \sum_j p_j e^{-iHt/\hbar} P_{\psi_j} e^{iHt/\hbar} = e^{-iHt/\hbar}\rho_0 e^{iHt/\hbar}\,. \tag{3.110}$$

The density matrix therefore obeys the *von Neumann equation*

$$\frac{d\rho_t}{dt} = -\frac{i}{\hbar}[H, \rho_t]\,. \tag{3.111}$$

Note the different sign compared with (3.105).

3.8 The Harmonic Oscillator

The harmonic oscillator is a "Drosophila" of quantum mechanics. Many problems can be reduced to a (shifted) harmonic oscillator and thereby become exactly solvable (phonons in a crystal lattice, e^- in a magnetic field, the electromagnetic radiation field, ...). The one-dimensional Hamiltonian on the Hilbert space $\mathcal{H} = L^2(\mathbb{R})$ is given by

$$H = \frac{p^2}{2m} + \frac{f}{2}x^2 \tag{3.112}$$

with the canonical commutation relation $[x, p] = i\hbar$ and the spring constant f. Classically the solutions are periodic with the oscillator frequency $\omega = \sqrt{f/m}$.

We seek stationary states $|\psi\rangle \in \mathcal{H}$ with $H|\psi\rangle = E|\psi\rangle$. We pass to the dimensionless position

$$q = \sqrt{\frac{m\omega}{\hbar}}\, x\,. \tag{3.113}$$

With the substitution

$$x = \sqrt{\frac{\hbar}{m\omega}}\, q, \qquad\qquad p = -i\hbar\frac{d}{dx} = -i\,\sqrt{\hbar m\omega}\,\frac{d}{dq} \tag{3.114}$$

we obtain the Hamiltonian

$$H = \frac{\hbar\omega}{2}\left(-\frac{d^2}{dq^2} + q^2\right). \tag{3.115}$$

We introduce the adjoint pair of operators a (*annihilation operator*) and $a^\dagger$ (*creation operator*) with

$$a = \frac{1}{\sqrt{2}}\left(q + \frac{d}{dq}\right), \qquad\qquad a^\dagger = \frac{1}{\sqrt{2}}\left(q - \frac{d}{dq}\right). \tag{3.116}$$

Conversely, the position and momentum operators are given by

$$x = \sqrt{\frac{\hbar}{2m\omega}}(a + a^\dagger), \qquad\qquad p = i\sqrt{\frac{\hbar m\omega}{2}}(a^\dagger - a)\,. \tag{3.117}$$

The commutator evaluates to

$$[a, a^\dagger] = \frac{1}{2}[q + \partial_q, q - \partial_q] = \frac{1}{2}\big([\partial_q, q] - [q, \partial_q]\big) = [\partial_q, q] = 1\,. \tag{3.118}$$

With the *number operator*

$$N = a^\dagger a = \frac{1}{2}\left(q^2 - \frac{d^2}{dq^2} - \left[\frac{d}{dq}, q\right]\right) = \frac{1}{2}\left(q^2 - \frac{d^2}{dq^2} - 1\right) \tag{3.119}$$

we can rewrite the Hamiltonian as

$$H = \hbar\omega\Big(N + \frac{1}{2}\Big). \tag{3.120}$$

The eigenvalue problem $H|\psi\rangle = E|\psi\rangle$ reduces to

$$N|n\rangle = n|n\rangle \tag{3.121}$$

with $E = \hbar\omega(n + \frac{1}{2})$, where we still need to determine the allowed eigenvalues n.

To this end we examine the action of the operators $a^\dagger$ and a on a normalized eigenstate $|n\rangle$ of N. We determine the commutators of N with $a^\dagger$ and with a,

$$[N, a^\dagger] = [a^\dagger a, a^\dagger] = a^\dagger[a, a^\dagger] + [a^\dagger, a^\dagger]a = a^\dagger, \tag{3.122}$$

$$[N, a] = [a^\dagger a, a] = a^\dagger[a, a] + [a^\dagger, a]a = -a. \tag{3.123}$$

The states $a^\dagger|n\rangle, a|n\rangle$ thus define new eigenvectors of N with eigenvalues $n+1$ and $n-1$, i.e.

$$\begin{aligned} Na^\dagger|n\rangle &= (a^\dagger N + [N, a^\dagger])|n\rangle \;= a^\dagger n|n\rangle + a^\dagger|n\rangle = (n+1)a^\dagger|n\rangle, \\ Na|n\rangle &= (aN + [N, a])|n\rangle = an|n\rangle - a|n\rangle = (n-1)a|n\rangle. \end{aligned} \tag{3.124}$$

The states $a^\dagger|n\rangle$ and $a|n\rangle$ are, however, still not normalized. We find

$$\langle n|a^\dagger a|n\rangle = \langle n|N|n\rangle = n \qquad \text{and} \qquad \langle n|aa^\dagger|n\rangle = \langle n|N + [a, a^\dagger]|n\rangle = n + 1\,.$$

Hence the normalized eigenvectors are given by

$$|n-1\rangle = \frac{1}{\sqrt{n}}\, a|n\rangle, \qquad\qquad |n+1\rangle = \frac{1}{\sqrt{n+1}}\, a^\dagger|n\rangle. \tag{3.125}$$

The spectrum follows from the termination condition. We have

$$n = \langle n|N|n\rangle = \langle an|an\rangle = \|an\|^2 \geq 0\,. \tag{3.126}$$

Thus the eigenvalue n cannot be lowered arbitrarily by applying a, and the ladder $|n\rangle \overset{a}{\mapsto} |n-1\rangle \overset{a}{\mapsto} \cdots$ must terminate. This is possible only if some state is mapped by a to the 0 vector. We define this state $|0\rangle$ as the *vacuum* with

$$a|0\rangle = 0, \qquad \langle 0|0\rangle = 1\,. \tag{3.127}$$

The vacuum is an eigenstate of the number operator with eigenvalue $n = 0$ and corresponds to the ground state of the harmonic oscillator. It has energy $E_{n=0} = \frac{1}{2}\hbar\omega > 0$, which equals the zero-point fluctuation.

The remaining eigenstates $|n\rangle$ are obtained by applying $a^\dagger$,

$$|n\rangle = \frac{(a^\dagger)^n}{\sqrt{n!}}|0\rangle, \qquad n = 0, 1, 2, \ldots\,. \tag{3.128}$$

The eigenvalue n determines the energy E_n of the stationary state with

$$H|n\rangle = E_n|n\rangle, \qquad E_n = \hbar\omega\Big(n + \frac{1}{2}\Big). \tag{3.129}$$

Thus n counts the existing energy quanta of energy $\hbar\omega$. Applying $a^\dagger$ creates an additional energy quantum, which increases the oscillation amplitude of the oscillator.

In the position representation, states are described by wavefunctions. The defining equation (3.127) for the vacuum state then takes the form

$$a\,\psi_0(q) = \frac{1}{\sqrt{2}}\left(q + \frac{d}{dq}\right)\psi_0(q) = 0 \tag{3.130}$$

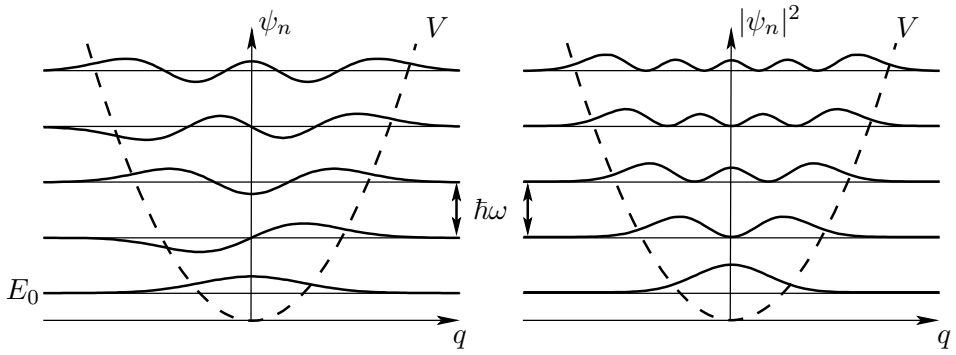


Fig. 3.1: Eigenfunctions of the harmonic oscillator, on the left the amplitudes ψ_n, on the right the probabilities $|\psi_n|^2$ for $n = 0, \ldots, 4$.

with the normalized and unique solution

$$\psi_0(q) = \pi^{-1/4} \exp\left(-\frac{q^2}{2}\right) . \tag{3.131}$$

Equation (3.128) yields the excited states (Hermite functions)

$$\psi_n(q) = \frac{\pi^{-1/4}}{\sqrt{2^n n!}} \left(q - \frac{d}{dq}\right)^n e^{-q^2/2} = \frac{\pi^{-1/4}}{\sqrt{2^n n!}} H_n(q) e^{-q^2/2}, \tag{3.132}$$

see Figure 3.1. The states $\psi_n(q)$ are orthogonal since they are eigenfunctions of the Hermitian operator N. They are also complete with

$$\delta(q - q') = \langle q|q'\rangle = \sum_n \langle q|n\rangle\langle n|q'\rangle = \sum_{n=0}^{\infty} \psi_n(q)\psi_n^*(q') . \tag{3.133}$$

The $H_n(q)$ are polynomials (*Hermite polynomials*) with leading term $(2q)^n$ defined by

$$H_n(q) = e^{q^2/2} \underbrace{\left(q - \frac{d}{dq}\right)^n e^{-q^2/2}}_{= -e^{q^2/2} \frac{d}{dq} e^{-q^2/2}} = e^{q^2} \left(-\frac{d}{dq}\right)^n e^{-q^2} . \tag{3.134}$$

Coherent states: From Ehrenfest's theorem we know that the expectation values $\langle x\rangle_t$ and $\langle p\rangle_t$ for the harmonic oscillator move along classical trajectories. The question is therefore after wave packets that minimize the standard deviations Δx and Δp so that the states are described as accurately as possible by the expectation values. Here the Heisenberg uncertainty relation $\Delta x\, \Delta p \geq \frac{1}{2}\hbar$ provides a lower bound. Indeed, the vacuum state $|0\rangle$ saturates this lower bound, since

$$\begin{aligned} \langle 0|x^2|0\rangle &= \frac{\hbar}{2m\omega} \langle 0| \overbrace{(a + a^\dagger)^2}^{= a^2 + a^{\dagger 2} + aa^\dagger + a^\dagger a} |0\rangle = \frac{\hbar}{2m\omega} \langle 0| \Big(\sqrt{2}|2\rangle + |0\rangle\Big) = \frac{\hbar}{2m\omega}, \\ \langle 0|p^2|0\rangle &= -\frac{\hbar m\omega}{2} \langle 0|(a^\dagger - a)^2|0\rangle = \frac{\hbar m\omega}{2} . \end{aligned} \tag{3.135}$$

The other states with minimal standard deviation are obtained by a displacement $a \mapsto a - \alpha$. The defining equation of the vacuum (3.130) thereby takes the form

$$(a-\alpha)|\alpha\rangle = 0 \qquad \Leftrightarrow \qquad a|\alpha\rangle = \alpha|\alpha\rangle; \tag{3.136}$$

that is, the displaced state $|\alpha\rangle$ is an eigenstate of the annihilation operator with eigenvalue $\alpha \in \mathbb{C}$. The parameter α parametrizes the expectation value of position x and momentum p in the state $|\alpha\rangle$,

$$\alpha = \langle\alpha| \overbrace{a}^{=\sqrt{\frac{m\omega}{2\hbar}}x + i\sqrt{\frac{1}{2\hbar m\omega}}p} |\alpha\rangle = \sqrt{\frac{m\omega}{2\hbar}}\langle\alpha|x|\alpha\rangle + i\frac{1}{\sqrt{2\hbar m\omega}}\langle\alpha|p|\alpha\rangle; \tag{3.137}$$

$$\langle\alpha|x|\alpha\rangle = \sqrt{\frac{2\hbar}{m\omega}}\,\mathrm{Re}\,\alpha, \qquad \langle\alpha|p|\alpha\rangle = \sqrt{2\hbar m\omega}\,\mathrm{Im}\,\alpha. \tag{3.138}$$

The eigenstates are given in the occupation-number basis by

$$|\alpha\rangle = e^{-|\alpha|^2/2}\sum_{n=0}^{\infty}\frac{\alpha^n}{\sqrt{n!}}|n\rangle\,. \tag{3.139}$$

By direct computation one can show that $a|\alpha\rangle = \alpha|\alpha\rangle$ holds. The time evolution of the coherent states has the form ($e^{-iHt/\hbar}|n\rangle = e^{-i\omega(n+\frac{1}{2})t}|n\rangle$)

$$|\alpha_t\rangle = e^{-iHt/\hbar}|\alpha\rangle = e^{-i\omega t/2}|\alpha(t)\rangle \qquad \text{with} \qquad \alpha(t) = \alpha e^{-i\omega t}. \tag{3.140}$$

The expectation values follow the classical motion with

$$\langle x\rangle_t = \langle\alpha_t|x|\alpha_t\rangle = \langle\alpha(t)|x|\alpha(t)\rangle = \sqrt{\frac{2\hbar}{m\omega}}\,\mathrm{Re}(\alpha e^{-i\omega t})\,, \tag{3.141}$$

see (2.16).

Chapter 4

Symmetries

Analogous to classical mechanics, in quantum mechanics a symmetry S is an invertible mapping of states in Hilbert space to itself. One may think of the transformation either passively (the reference frame is changed) or actively (the particle is transformed). An important example is the *space reflection* (parity) P with $(P\psi)(\boldsymbol{r}) = \psi(-\boldsymbol{r})$. For a symmetry it is essential that the probabilities do not change. In particular we require that

$$|\langle S\phi|S\psi\rangle|^2 = |\langle\phi|\psi\rangle|^2, \qquad \text{for all } \phi, \psi \in \mathcal{H}. \tag{4.1}$$

Note that the observables do not transform under the symmetry (otherwise we would have a trivial unitary equivalence).

One can show (*Wigner's theorem*) that S is either a unitary or an antiunitary operator. An *antiunitary* operator A is a mapping that satisfies

$$\langle A\phi|A\psi\rangle = \langle\psi|\phi\rangle = \langle\phi|\psi\rangle^* \tag{4.2}$$

Because of the complex conjugation A cannot be a linear operator. In fact A is an *antilinear* operator with

$$A\big(\alpha|\psi_1\rangle + \beta|\psi_2\rangle\big) = \alpha^* A|\psi_1\rangle + \beta^* A|\psi_2\rangle\,. \tag{4.3}$$

One defines the adjoint operator by [cf. with (3.26) for a linear operator]

$$\langle\phi|A\psi\rangle = \langle\psi|A^\dagger\phi\rangle = \langle A^\dagger\phi|\psi\rangle^*\,. \tag{4.4}$$

Hence for an antiunitary operator $A^{-1} = A^\dagger$. Note that the square of an antiunitary operator is again a unitary operator.

4.1 Discrete symmetries

We first consider a single (discrete) symmetry S. One calls S a *symmetry of the system* described by the Hamiltonian H if S commutes with H,

$$[S, H] = 0, \qquad \Leftrightarrow \qquad S \text{ is a symmetry of the system}\,. \tag{4.5}$$

A unitary symmetry of the system is then useful when one knows the eigenspaces of S. Since S and H commute they are simultaneously diagonalizable. One may therefore consider H restricted to the eigenspaces of S to simplify the problem.

For an arbitrary observable M one finds the symmetry transformation of an arbitrary expectation value

$$\langle\psi|M|\psi\rangle \overset{S}{\mapsto} \langle S\psi|M|S\psi\rangle = \langle\psi|S^\dagger MS|\psi\rangle. \tag{4.6}$$

It is therefore possible to act on the observables instead of the states with

$$M \overset{S}{\mapsto} S^\dagger MS \tag{4.7}$$

under the symmetry transformation. If S is a symmetry of the system, the Hamiltonian remains invariant under S. From $HS = SH$ it follows namely

$$S^\dagger HS = H \tag{4.8}$$

by applying $S^\dagger = S^{-1}$ from the left.

Space reflection: As a simple example we consider space reflection (parity) $(P\psi)(\boldsymbol{r}) = \psi(-\boldsymbol{r})$. Space reflection is a Hermitian operator $P = P^\dagger$ that maps $L^2(\mathbb{R}^3)$ to itself. It satisfies $P^2 = 1$. Hence P is an involution with eigenvalues ± 1. One may examine the action on the position operator

$$P\boldsymbol{r}P\psi(\boldsymbol{r}) = P\big[\boldsymbol{r}\psi(-\boldsymbol{r})\big] = -\boldsymbol{r}\psi(\boldsymbol{r})\,. \tag{4.9}$$

Thus we obtain the relations

$$P\boldsymbol{r}P = -\boldsymbol{r} \qquad \text{and} \qquad P\boldsymbol{p}P = -\boldsymbol{p}\,. \tag{4.10}$$

The harmonic oscillator is parity symmetric. Indeed the Hermite functions are eigenstates with respect to P. In this case $P\psi_n(x) = \psi_n(-x) = (-1)^n\psi_n(x)\,.$

Selection rule: For an eigenstate $|\pm\rangle$ of P with parity ± 1 the selection rule

$$\langle\pm|\boldsymbol{r}|\pm\rangle = \langle P\pm|\boldsymbol{r}|P\pm\rangle = \langle\pm|P\boldsymbol{r}P|\pm\rangle = -\langle\pm|\boldsymbol{r}|\pm\rangle = 0\,. \tag{4.11}$$

holds. A parity-invariant system with a nondegenerate ground state $|g\rangle$ cannot have a permanent dipole moment. The reason is that $|g\rangle$ has a well-defined parity with $\langle\boldsymbol{r}\rangle = \langle g|\boldsymbol{r}|g\rangle = 0$.

In general one calls an observable M with

$$PMP = +M, \qquad \text{even under parity} \qquad (p_M = +1), \tag{4.12}$$

$$PMP = -M, \qquad \text{odd under parity} \qquad (p_M = -1). \tag{4.13}$$

Even under parity are for example $\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p}$ and $\boldsymbol{p}^2$. Odd under parity are on the other hand the observables $\boldsymbol{r}, \boldsymbol{p}, \boldsymbol{L} \cdot \boldsymbol{r}$.

We now consider two eigenstates $|\phi\rangle$ and $|\psi\rangle$ with parity p_ϕ and p_ψ and an observable with parity p_M. A simple calculation yields then

$$\langle\phi|M|\psi\rangle = \langle P^2\phi|M|P^2\psi\rangle = \langle P\phi|PMP|P\psi\rangle = p_\phi p_M p_\psi\langle\phi|M|\psi\rangle\,. \tag{4.14}$$

For such matrix elements the *selection rule*

$$\langle\phi|M|\psi\rangle = 0, \qquad \text{holds if} \quad p_\phi p_M p_\psi \neq 1. \tag{4.15}$$

Time reversal: For time reversal T it must hold

$$T^\dagger \boldsymbol{r} T = \boldsymbol{r} \qquad \text{and} \qquad T^\dagger \boldsymbol{p} T = -\boldsymbol{p}\,. \tag{4.16}$$

For the commutator it follows

$$T^\dagger i\hbar T = T^\dagger [r_j, p_j] T = [T^\dagger r_j T, T^\dagger p_j T] = -[r_j, p_j] = -i\hbar\,. \tag{4.17}$$

This relation can only be satisfied if T is an antiunitary operator. Applying T twice, all observables M should remain invariant[1]

$$M = (T^\dagger)^2 M T^2 \qquad \Rightarrow \qquad T^2 = e^{i\varphi}\,. \tag{4.18}$$

From antilinearity we obtain

$$e^{i\varphi} T = T^3 = T T^2 = T e^{i\varphi} = e^{-i\varphi} T \tag{4.19}$$

and hence

$$T^2 = \pm 1 \qquad (\Leftrightarrow T^{-1} = T^\dagger = \pm T)\,. \tag{4.20}$$

The Schrödinger equation transforms under time reversal as

$$\begin{aligned} 0 = \left(H - i\hbar\frac{\partial}{\partial t}\right)\Psi(\boldsymbol{r},t) \quad \xrightarrow{T^\dagger\cdot} \quad 0 &= T^\dagger \left(H - i\hbar\frac{\partial}{\partial t}\right) \overbrace{T T^\dagger}^{=1} \Psi(\boldsymbol{r},t) = \left(\tilde{H} + i\hbar\frac{\partial}{\partial t}\right) T^\dagger \Psi(\boldsymbol{r},t) \\ &= \left(\tilde{H} - i\hbar\frac{\partial}{\partial t}\right)\tilde{\Psi}(\boldsymbol{r},t) \end{aligned} \tag{4.21}$$

with the time-reversed state and Hamiltonian

$$\tilde{\Psi}(\boldsymbol{r},t) = T^\dagger \Psi(\boldsymbol{r},-t), \qquad \tilde{H} = T^\dagger H T\,. \tag{4.22}$$

If the system is time-reversal invariant ($\tilde{H} = H$) then the time-reversed state $\tilde{\Psi}(\boldsymbol{r},t) = T^\dagger\Psi(\boldsymbol{r},-t) = \pm T\Psi(\boldsymbol{r},-t)$ solves the Schrödinger equation if and only if $\Psi(\boldsymbol{r},t)$ does so.

For a particle with Hilbert space $L^2(\mathbb{R}^3)$ time reversal is given by complex conjugation (in the position representation)

$$(T\psi)(\boldsymbol{r}) = \psi(\boldsymbol{r})^* \tag{4.23}$$

with $T^2 = 1$. The Hamiltonian

$$H = \frac{\boldsymbol{p}^2}{2m} + V(\boldsymbol{r}) = -\frac{\hbar^2}{2m}\Delta + V(\boldsymbol{r}) \tag{4.24}$$

is time-reversal invariant, since

$$T^\dagger V(\boldsymbol{r}) T = V(\boldsymbol{r}) \qquad \text{and} \qquad T^\dagger \boldsymbol{p}^2 T = \boldsymbol{p}^2\,, \tag{4.25}$$

owing to (4.16). The stationary states can therefore be chosen real with $T\psi = \psi$.

For a particle in a static electromagnetic field it holds

$$T^\dagger \left\{ \frac{1}{2m}\left[\boldsymbol{p} - \frac{q}{c}\boldsymbol{A}(\boldsymbol{r})\right]^2 + q\varphi(\boldsymbol{r}) \right\} T = \frac{1}{2m}\left[\boldsymbol{p} + \frac{q}{c}\boldsymbol{A}(\boldsymbol{r})\right]^2 + q\varphi(\boldsymbol{r})\,. \tag{4.26}$$

The system is time-reversal invariant only if no external magnetic field is applied, $\boldsymbol{A} = 0$. Since time reversal is an antiunitary operator, it does not yield selection rules analogous to (4.15).

[1] For the state this is not necessarily the case, since it cannot be measured. One calls such a representation *projective*.

Kramers degeneracy: An antiunitary symmetry T of the system with $T^2 = -1$ leads to a degeneracy of all energy eigenvalues. Let ψ be an eigenstate with energy $E \in \mathbb{R}$. The state $\phi = T\psi$ is of course also a state at the same energy, since

$$H\phi = HT\psi \overset{[T,H]=0}{=} TH\psi = E\phi\,. \tag{4.27}$$

By the following argument ϕ cannot be the same state as ψ: from $T^\dagger = -T$ it follows namely

$$\langle\psi|\phi\rangle = \langle\psi|T\psi\rangle = \langle\psi|T^\dagger\psi\rangle = -\langle\psi|T\psi\rangle = -\langle\psi|\phi\rangle\,. \tag{4.28}$$

Thus the states ψ and ϕ are orthogonal to each other. One calls the two states $\phi = T\psi$ and ψ also "complex-conjugate" states.

Lattice translations: We consider a particle in Hilbert space $L^2(\mathbb{R})$. The potential has a discrete translation symmetry $V(x+L) = V(x)$. This is a model for the electron motion in the ionic background of a solid. The Hamiltonian $H = p^2/2m + V(x)$ is invariant under the discrete translation

$$(\tau\psi)(x) = \psi(x+L), \qquad \text{with} \qquad [H,\tau] = 0\,. \tag{4.29}$$

The operator τ is unitary, since

$$\langle\tau\phi|\tau\psi\rangle = \int \phi^*(x+L)\psi(x+L)\,dx = \int \phi^*(x)\psi(x)\,dx = \langle\phi|\psi\rangle\,. \tag{4.30}$$

The eigenvalues are therefore given by $e^{i\lambda}$ with $\lambda \in [-\pi,\pi]$. Since τ is a symmetry of the system, the Hamiltonian can be diagonalized separately in the eigenspaces of fixed λ. In the eigenspaces it holds

$$(\tau\psi)(x) = \psi(x+L) = e^{i\lambda}\psi(x)\,. \tag{4.31}$$

It is conventional to parametrize the eigenvalue with $\lambda = kL$. Writing for the wave function $\psi(x) = e^{ikx}u_k(x)$ it holds $e^{i\lambda+ikx}u_k(x+L) = \psi(x+L) \overset{(4.31)}{=} e^{i\lambda}\psi(x) = e^{i\lambda+ikx}u_k(x)$.
Hence the *Bloch theorem* holds: eigenfunctions of the Hamiltonian H can be chosen such that

$$\psi(x) = e^{ikx}u_k(x) \qquad \text{with} \qquad u_k(x+L) = u_k(x) \quad \text{(periodic)}. \tag{4.32}$$

The problem is thereby reduced to a problem in $\mathcal{H}_{\text{per}}$ The eigenvalue problem (also called $\boldsymbol{k}\cdot\boldsymbol{p}$ problem) must then be solved

$$\begin{aligned} Eu(x) &= e^{-ikx}H\psi(x) = \frac{1}{2m}e^{-ikx}\left(-i\hbar\frac{d}{dx}\right)^2 e^{ikx}u_k(x) + V(x)u_k(x) \\ &= \frac{1}{2m}\underbrace{\left(\hbar k - i\hbar\frac{d}{dx}\right)^2}_{(\hbar k+p)^2} u_k(x) + V(x)u_k(x), \qquad u_k \in \mathcal{H}_{\text{per}} \end{aligned} \tag{4.33}$$

for $u_k(x)$. One calls $\hbar k$ the crystal momentum of the particle.

4.2 Continuous symmetries

As in classical physics, continuous symmetries in quantum mechanics are associated with conserved observables. A continuous symmetry in quantum mechanics is a one-parameter group of unitary transformations[2] with

$$U(\alpha)U(\beta) = U(\alpha+\beta), \qquad U(0) = 1. \tag{4.34}$$

By unitarity it holds $U^\dagger(\alpha) \equiv U(\alpha)^\dagger = U(\alpha)^{-1} = U(-\alpha)$. As before the symmetries act either on the state with $\psi \mapsto U\psi$ or on the observables with $M \mapsto U^\dagger M U$ (but of course not on both). The group is a continuous symmetry of the system if

$$U^\dagger(\alpha) H U(\alpha) = H, \qquad \text{for all } \alpha. \tag{4.35}$$

A continuous symmetry satisfies the differential equation

$$\frac{dU(\alpha)}{d\alpha} = \frac{dU(\beta+\alpha)}{d\beta}\Big|_{\beta=0} = U'(0)U(\alpha) = -\frac{iG}{\hbar}U(\alpha) \tag{4.36}$$

where $G = i\hbar U'(0)$ is the *generator of the symmetry*. The differential equation is solved by

$$U(\alpha) = e^{-i\alpha G/\hbar}\,. \tag{4.37}$$

The symmetry group is thereby uniquely determined by the generator. It is the equivalence between (4.36) (Lie algebra) and (4.37) (Lie group) that simplifies the study of continuous symmetries. In fact one typically shows properties for an infinitesimal transformation (Lie algebra). Owing to the uniqueness of the solution of the differential equation (4.37), one can extend these to finite transformations (Lie group).

From the unitarity of U it follows that the generator G is a Hermitian operator. For

$$0 = \frac{d}{d\alpha}(U^\dagger U)\Big|_{\alpha=0} = U^{\dagger\prime}(0)U(0) + U^\dagger(0)U'(0) = \frac{i}{\hbar}(G^\dagger - G)\,. \tag{4.38}$$

An arbitrary observable M is mapped by the symmetry group to the family $M(\alpha) = U^\dagger(\alpha)MU(\alpha)$. For an infinitesimal transformation it holds

$$\frac{d}{d\alpha}M(\alpha)\Big|_{\alpha=0} = U^{\dagger\prime}(0)MU(0) + U^\dagger(0)MU'(0) = \frac{i}{\hbar}(GM - MG) = \frac{i}{\hbar}[G,M]\,. \tag{4.39}$$

If $U(\alpha)$ is a symmetry of the system, then

$$0 = [G,H]\,. \tag{4.40}$$

Hence the observable[3] G commutes with the Hamiltonian and can be simultaneously diagonalized. In the Heisenberg picture one also sees nicely that

$$\frac{d}{dt}G_H = \frac{i}{\hbar}[G,H]_H = 0\,. \tag{4.41}$$

Hence the quantity G is conserved under time evolution.

[2] Continuous symmetries are always unitary, since every $U(a) = U(a/2)^2$ is the square of a symmetry.
[3] In this chapter we neglect the subtle distinction and call all Hermitian operators "observables."

Examples

Translation: An important continuous symmetry is translation by α along $\boldsymbol{e}$ with

$$\big[U_{\boldsymbol{e}}(\alpha)\psi\big](\boldsymbol{r}) = \psi(\boldsymbol{r} - \alpha\boldsymbol{e})\,. \tag{4.42}$$

The generator is given by

$$(G_{\boldsymbol{e}}\psi)(\boldsymbol{r}) = i\hbar\frac{d}{d\alpha}\psi(\boldsymbol{r} - \alpha\boldsymbol{e})\Big|_{\alpha=0} = -i\hbar\boldsymbol{e}\cdot\boldsymbol{\nabla}\psi(\boldsymbol{r}) = (\boldsymbol{e}\cdot\boldsymbol{p})\psi(\boldsymbol{r})\,. \tag{4.43}$$

It therefore corresponds exactly to the momentum operator in the direction $\boldsymbol{e}$. The momentum operator is thus conserved under time evolution if the system is translation invariant. In this case one can find energy eigenstates with sharp momentum.

N-particles: In an N-particle system with pairwise interactions

$$H = \sum_{k=1}^{N}\frac{(\boldsymbol{p}_k)^2}{2m} + \sum_{j<k}V(|\boldsymbol{r}_k - \boldsymbol{r}_j|) \tag{4.44}$$

it follows analogously from translation invariance $\boldsymbol{r}_k \mapsto \boldsymbol{r}_k - \alpha\boldsymbol{e}$ of the Hamiltonian that the total momentum $\boldsymbol{P} = \sum_k \boldsymbol{p}_k$ is conserved.

4.3 Angular momentum

Angular momentum is an important continuous symmetry. In particular because most particles in quantum mechanics possess an internal degree of freedom, the *spin*, which behaves like angular momentum. The rotation $R_{\boldsymbol{e}}(\alpha)$ about the axis $\boldsymbol{e}$ ($|\boldsymbol{e}| = 1$) by the rotation angle α is generated by the continuous symmetry[4]

$$(U_{\boldsymbol{e}}(\alpha)\psi)(\boldsymbol{r}) = \psi(R_{\boldsymbol{e}}^{-1}(\alpha)\boldsymbol{r})\,. \tag{4.45}$$

For $R \in \mathsf{SO}(3)$ we know from mechanics that

$$\frac{d}{d\alpha}R_{\boldsymbol{e}}(\alpha)\boldsymbol{r}\Big|_{\alpha=0} = \boldsymbol{e}\times\boldsymbol{r}\,, \qquad \text{or} \qquad \frac{d}{d\alpha}R_{\boldsymbol{e}}^{-1}(\alpha)\boldsymbol{r}\Big|_{\alpha=0} = -\boldsymbol{e}\times\boldsymbol{r}\,. \tag{4.46}$$

For an infinitesimal transformation it therefore holds

$$\begin{aligned}(G_{\boldsymbol{e}}\psi)(\boldsymbol{r}) &= i\hbar\frac{d}{d\alpha}\psi(R_{\boldsymbol{e}}^{-1}(\alpha)\boldsymbol{r})\Big|_{\alpha=0} = -i\hbar(\boldsymbol{e}\times\boldsymbol{r})\cdot\boldsymbol{\nabla}\psi(\boldsymbol{r})\\ &= -i\hbar\boldsymbol{e}\cdot(\boldsymbol{r}\times\boldsymbol{\nabla})\psi(\boldsymbol{r})\,.\end{aligned} \tag{4.47}$$

We find the generator

$$G_{\boldsymbol{e}} = \boldsymbol{e}\cdot(\boldsymbol{r}\times\boldsymbol{p}) = \boldsymbol{e}\cdot\boldsymbol{L}, \quad \text{(angular momentum component along the rotation axis).} \tag{4.48}$$

For the expectation value of the rotated position operator $\boldsymbol{r}(\alpha)$ in an arbitrary state ψ it holds (we use the abbreviations $R = R_{\boldsymbol{e}}(\alpha)$ and $U = U_{\boldsymbol{e}}(\alpha)$)

$$\langle\psi|\boldsymbol{r}(\alpha)|\psi\rangle = \langle U\psi|\boldsymbol{r}|U\psi\rangle = \int\psi(R^{-1}\boldsymbol{r})^*\boldsymbol{r}\psi(R^{-1}\boldsymbol{r})\,d^3r = \int\psi(\boldsymbol{r})^*(R\boldsymbol{r})\psi(\boldsymbol{r})\,d^3r \tag{4.49}$$

[4]The definition is such that a concatenation of two rotations yields $(U_{\boldsymbol{e}_2}(\alpha_2)U_{\boldsymbol{e}_1}(\alpha_1)\psi)(\boldsymbol{r}) = \psi(R_{\boldsymbol{e}_1}(\alpha_1)^{-1}R_{\boldsymbol{e}_2}(\alpha_2)^{-1}\boldsymbol{r}) = \psi([R_{\boldsymbol{e}_2}(\alpha_2)R_{\boldsymbol{e}_1}(\alpha_1)]^{-1}\boldsymbol{r})$. Hence $U_{\boldsymbol{e}}(\alpha)$ is a representation of the rotation group.

Hence it follows $\boldsymbol{r}(\alpha) = U_{\boldsymbol{e}}^\dagger(\alpha)\boldsymbol{r}U_{\boldsymbol{e}}(\alpha) = R_{\boldsymbol{e}}(\alpha)\boldsymbol{r}$ and the observables are transformed exactly opposite to the states. This makes sense, since the untransformed operator $\boldsymbol{r}$ applied to the transformed state $\psi(R^{-1}\boldsymbol{r})$ gives the same result as the transformed operator $R\boldsymbol{r}$ applied to the untransformed state $\psi(\boldsymbol{r})$.

For an infinitesimal rotation we obtain the commutator [cf. (4.46)]

$$-\frac{i}{\hbar}[\boldsymbol{r}, \boldsymbol{e}\cdot\boldsymbol{L}] = \frac{d}{d\alpha}\boldsymbol{r}(\alpha)\Big|_{\alpha=0} = \frac{d}{d\alpha}R_{\boldsymbol{e}}(\alpha)\boldsymbol{r}\Big|_{\alpha=0} = \boldsymbol{e}\times\boldsymbol{r}\,. \tag{4.50}$$

Scalar and vector operators: One calls a vector $\boldsymbol{v} = (v_1, v_2, v_3)$ of three operators v_j an *vector operator* if the three components transform like the position operator under rotations; that is $\boldsymbol{v}$ is a vector operator if

$$\begin{aligned} U_{\boldsymbol{e}}^\dagger(\alpha)\boldsymbol{v}U_{\boldsymbol{e}}(\alpha) = R_{\boldsymbol{e}}(\alpha)\boldsymbol{v} \quad &\overset{(4.50)}{\Leftrightarrow} \quad [\boldsymbol{v}, \boldsymbol{e}\cdot\boldsymbol{L}] = i\hbar\,\boldsymbol{e}\times\boldsymbol{v} \\ &\overset{\boldsymbol{f}:}{\Leftrightarrow} \quad [\boldsymbol{f}\cdot\boldsymbol{v}, \boldsymbol{e}\cdot\boldsymbol{L}] = i\hbar\,(\boldsymbol{f}\times\boldsymbol{e})\cdot\boldsymbol{v}\,. \end{aligned} \tag{4.51}$$

The equation means that measuring the rotated components $R\boldsymbol{v}$ of $\boldsymbol{v}$ yields the same result as measuring $\boldsymbol{v}$ in the rotated state $(U\psi)(\boldsymbol{r}) = \psi(R^{-1}\boldsymbol{r})$.

One calls an operator A a *scalar operator* if it does not transform under rotations with

$$U_{\boldsymbol{e}}^\dagger(\alpha)AU_{\boldsymbol{e}}(\alpha) = A \qquad \Leftrightarrow \qquad [A, \boldsymbol{L}] = 0\,. \tag{4.52}$$

Often one additionally studies a well-defined transformation behavior under parity. One calls scalars that behave odd under parity *pseudoscalars*. Depending on the symmetry under parity vectors are called *polar* (odd under parity) or *axial* (even under parity).

Examples

Position operator: As shown earlier, the position operator $\boldsymbol{r}$ is a (polar) vector operator.

Momentum operator: From the canonical commutation relation $[r_j, p_k] = i\hbar\delta_{jk}$ it follows

$$[p_j, \boldsymbol{e}\cdot\boldsymbol{L}] = [p_j, \boldsymbol{r}\cdot(\boldsymbol{p}\times\boldsymbol{e})] = \sum_k [p_j, r_k](\boldsymbol{p}\times\boldsymbol{e})_k = -i\hbar(\boldsymbol{p}\times\boldsymbol{e})_j \tag{4.53}$$

and hence $\boldsymbol{p}$ is a (polar) vector operator with

$$[\boldsymbol{p}, \boldsymbol{e}\cdot\boldsymbol{L}] = i\hbar\,\boldsymbol{e}\times\boldsymbol{p}\,. \tag{4.54}$$

Cross product: The cross product $\boldsymbol{v}\times\boldsymbol{w}$ of two vector operators $\boldsymbol{v}, \boldsymbol{w}$ is again a vector operator. From vector geometry we know that under a rotation R for the cross product it holds (one may either rotate the original vectors or equivalently their product)

$$(R\boldsymbol{v})\times(R\boldsymbol{w}) = R(\boldsymbol{v}\times\boldsymbol{w})\,. \tag{4.55}$$

From the fact that $\boldsymbol{v}$ and $\boldsymbol{w}$ are vector operators, it follows immediately for an arbitrary rotation

$$U^\dagger(\boldsymbol{v}\times\boldsymbol{w})U \overset{(UU^\dagger=1)}{=} (U^\dagger\boldsymbol{v}U)\times(U^\dagger\boldsymbol{w}U) = (R\boldsymbol{v})\times(R\boldsymbol{w}) = R(\boldsymbol{v}\times\boldsymbol{w})\,. \tag{4.56}$$

Hence $\boldsymbol{v}\times\boldsymbol{w}$ is a vector operator. Since parity behaves multiplicatively, the product of two polar vectors is for example an axial vector.

Angular momentum: The angular momentum $\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p}$ is a cross product of two polar vectors. It is thus an axial vector and satisfies the *angular momentum algebra*

$$[\boldsymbol{L}, \boldsymbol{e} \cdot \boldsymbol{L}] = i\hbar\, \boldsymbol{e} \times \boldsymbol{L} \qquad \overset{f.}{\Leftrightarrow} \qquad [\boldsymbol{f} \cdot \boldsymbol{L}, \boldsymbol{e} \cdot \boldsymbol{L}] = i\hbar\, (\boldsymbol{f} \times \boldsymbol{e}) \cdot \boldsymbol{L}\,. \tag{4.57}$$

Scalar product: For the scalar product of two vectors $\boldsymbol{v}$ and $\boldsymbol{w}$ it holds

$$(R\boldsymbol{v}) \cdot (R\boldsymbol{w}) = \boldsymbol{v} \cdot \boldsymbol{w}\,. \tag{4.58}$$

For two vector operators it follows immediately

$$U^\dagger (\boldsymbol{v} \cdot \boldsymbol{w}) U = (U^\dagger \boldsymbol{v} U) \cdot (U^\dagger \boldsymbol{w} U) = (R\boldsymbol{v}) \cdot (R\boldsymbol{w}) = \boldsymbol{v} \cdot \boldsymbol{w}\,. \tag{4.59}$$

The scalar product $\boldsymbol{v} \cdot \boldsymbol{w}$ of two vector operators is a scalar operator. The parity ("true" scalar or pseudoscalar) follows again from the multiplication of the parities of $\boldsymbol{v}$ and $\boldsymbol{w}$.

Angular momentum squared: The angular momentum squared $\boldsymbol{L}^2 = \boldsymbol{L} \cdot \boldsymbol{L}$ is the scalar product of two axial vectors. Hence $\boldsymbol{L}^2$ is a scalar operator with

$$[\boldsymbol{L}^2, \boldsymbol{L}] = 0\,. \tag{4.60}$$

The angular momentum squared therefore commutes with all components of the angular momentum operator. Analogously $\boldsymbol{p}^2$ and $\boldsymbol{r}^2$ are scalar operators with

$$[\boldsymbol{p}^2, \boldsymbol{L}] = 0, \qquad [\boldsymbol{r}^2, \boldsymbol{L}] = 0\,. \tag{4.61}$$

The operator $\boldsymbol{r} \cdot \boldsymbol{L}$: The operator $\boldsymbol{r} \cdot \boldsymbol{L}$ is a pseudoscalar. It holds however

$$\boldsymbol{r} \cdot \boldsymbol{L} = \boldsymbol{r} \cdot (\boldsymbol{r} \times \boldsymbol{p}) = (\boldsymbol{r} \times \boldsymbol{r}) \cdot \boldsymbol{p} = 0\,. \tag{4.62}$$

Hence the angular momentum "stands perpendicular" to the position vector. Analogously one can show that $\boldsymbol{p} \cdot \boldsymbol{L} = 0$.

Since the operator $\boldsymbol{p}^2$ is a scalar, the angular momentum component $\boldsymbol{e} \cdot \boldsymbol{L}$ for the Hamiltonian $H = \boldsymbol{p}^2/2m + V(\boldsymbol{r})$ is conserved if and only if $V(\boldsymbol{r})$ is rotationally symmetric about the rotation axis $\boldsymbol{e}$. For a fully rotationally symmetric system with $V(\boldsymbol{r}) = V(r)$ all components of angular momentum $\boldsymbol{L}$ are thus conserved. However, L_1, L_2, L_3 are not compatible observables, see (4.57).

It is therefore the task to determine a maximal number of commuting observables from $\boldsymbol{L}$. In the concrete case it turns out that from $\boldsymbol{L}$ one can obtain two compatible observables. One usually chooses L_3 (angular momentum along the z axis) and $\boldsymbol{L}^2 = L_1^2 + L_2^2 + L_3^2$ (square of the angular momentum).

4.4 Spin

Many particles in nature have besides the position $\boldsymbol{r}$ an internal degree of freedom (spin), which behaves like angular momentum. In quantum mechanics spin is described by making the wave function a vector-valued function on $L^2(\mathbb{R}^3) \otimes \mathbb{C}^n$ with

$$\boldsymbol{\psi}(\boldsymbol{r}) = \begin{pmatrix} \psi_1(\boldsymbol{r}) \\ \vdots \\ \psi_n(\boldsymbol{r}) \end{pmatrix}, \qquad \langle \boldsymbol{r}, m | \boldsymbol{\psi} \rangle = \psi_m(\boldsymbol{r})\,. \tag{4.63}$$

As scalar product we naturally choose

$$\langle \boldsymbol{\phi} | \boldsymbol{\psi} \rangle = \int \boldsymbol{\phi}(\boldsymbol{r})^* \cdot \boldsymbol{\psi}(\boldsymbol{r})\, d^3r = \sum_m \int \phi_m(\boldsymbol{r})^* \psi_m(\boldsymbol{r})\, d^3r\,. \tag{4.64}$$

It is useful at the beginning to consider the internal n-dimensional degree of freedom separately; that is, we fix a position $\boldsymbol{r}_0$ and in the following consider only the spin wave function

$$\boldsymbol{\chi} = \boldsymbol{\psi}(\boldsymbol{r}_0), \qquad \boldsymbol{\chi} \in \mathbb{C}^n\,. \tag{4.65}$$

Alternatively there are many problems in which spin and orbital motion do not interact, so that we can separate the wave function with

$$\boldsymbol{\psi}(\boldsymbol{r}) = \psi(\boldsymbol{r}) \otimes \boldsymbol{\chi}\,, \tag{4.66}$$

where $\boldsymbol{\chi}$ is the spin wave function and $\psi(\boldsymbol{r})$ the orbital wave function. One also uses the alternative notation $\chi(m) = \langle m|\chi\rangle = \chi_m$ for the m-th component of the spin wave function.

The internal degree of freedom serves to model an internal angular momentum, the *spin* $\boldsymbol{S}$, which should transform under rotations (generated by $S_j \in \mathbb{C}^{n\times n}$) like an (axial) vector. In particular for the unitary transformation $U_{\boldsymbol{e}}(\alpha) = e^{-i\alpha \boldsymbol{e}\cdot\boldsymbol{S}/\hbar} \in \mathbb{C}^{n\times n}$, which acts solely on the spin space, it holds [cf. (4.51)]

$$U_{\boldsymbol{e}}^\dagger(\alpha)\boldsymbol{S}U_{\boldsymbol{e}}(\alpha) = R_{\boldsymbol{e}}(\alpha)\boldsymbol{S}\,. \tag{4.67}$$

For an infinitesimal rotation this means that (*angular momentum algebra*)

$$[\boldsymbol{S}, \boldsymbol{e}\cdot\boldsymbol{S}] = i\hbar\, \boldsymbol{e}\times\boldsymbol{S} \qquad \overset{\boldsymbol{f}\cdot}{\Leftrightarrow} \qquad [\boldsymbol{f}\cdot\boldsymbol{S}, \boldsymbol{e}\cdot\boldsymbol{S}] = i\hbar\,(\boldsymbol{f}\times\boldsymbol{e})\cdot\boldsymbol{S} \tag{4.68}$$

with $\boldsymbol{e}\cdot\boldsymbol{S}$ the generator of the rotation about the axis $\boldsymbol{e}$. On the full Hilbert space (spin and orbital) a rotation is then given by $U_{\boldsymbol{e}}(\alpha) = e^{-i\alpha\boldsymbol{e}\cdot\boldsymbol{J}/\hbar}$ and is generated by the *total angular momentum*

$$\boldsymbol{J} = \boldsymbol{L}\otimes 1 + 1\otimes\boldsymbol{S} \tag{4.69}$$

The question of the possible dimensions n of the internal degree of freedom is thereby reduced to finding the possible *representations* of $\boldsymbol{S}$ as complex $n\times n$ matrices such that the angular momentum algebra (4.68) is satisfied. Important are the *irreducible representations*, which cannot be decomposed by a clever choice of basis into a direct sum of smaller representations.

Representations of the angular momentum algebra: It turns out that for every n there exists exactly one irreducible representation of the angular momentum algebra and that these representations are also unitary (i.e., $\boldsymbol{S}$ are Hermitian operators and U is thus unitary). We will construct these in the following.

We start with the analysis of (4.57). Since this algebra is isomorphic to the angular momentum algebra $\boldsymbol{L}$ from the previous chapter, it follows immediately that $\boldsymbol{S}^2$ is a scalar operator with $[\boldsymbol{S}^2, S_3] = 0$. Hence $\boldsymbol{S}^2$ and S_3 can be simultaneously measured sharply.

We begin with an arbitrary eigenstate χ_z of S_3 for the eigenvalue $\hbar z$. We introduce the raising S_+ and lowering operator S_- with

$$S_\pm = S_1 \pm iS_2\,. \tag{4.70}$$

From the angular momentum algebra (4.68) it follows[5]

$$[S_3, S_\pm] = \pm\hbar S_\pm \qquad \text{and} \qquad [S_+, S_-] = 2\hbar S_3\,. \tag{4.71}$$

Hence $\hbar(z \pm 1)$ is also an eigenvalue of S_3,

$$S_3 S_\pm \chi_z = S_\pm S_3 \chi_z + [S_3, S_\pm]\chi_z = \hbar(z \pm 1) S_\pm \chi_z, \tag{4.72}$$

provided $\chi_{z\pm1} = S_\pm \chi_z \neq 0$. Because the Hilbert space $\mathcal{H} = \mathbb{C}^n$ is finite, one cannot apply S_+ arbitrarily often to generate ever new eigenstates. In particular there exists a maximal eigenvalue $\hbar s$ with

$$S_3\chi_s = \hbar s \chi_s \qquad \text{and} \qquad S_+\chi_s = 0\,. \tag{4.73}$$

Starting from χ_s one may apply S_- recursively ($S_-\chi_s = \chi_{s-1}, \ldots$). This sequence must also terminate. There therefore exists an $k \in \mathbb{N}$ such that

$$\chi_{s-k} \neq 0, \qquad \chi_{s-k-1} = S_-\chi_{s-k} = 0\,. \tag{4.74}$$

We have thereby generated a basis $\{\chi_s, \ldots, \chi_{s-k}\}$ that is a candidate for an irreducible representation of the angular-momentum algebra. The elements χ_m transform among themselves under application of the lowering operator S_-. It is, however, important that applying S_+ also remains within the subspace and does not generate new states. First we have

$$S_+\chi_m = \hbar^2 c_m \chi_{m+1} \tag{4.75}$$

for $m = s$ with $c_s = 0$. We wish to show recursively that $S_+\chi_m$ is always —up to a factor $\hbar^2 c_m$—proportional to χ_{m+1}. To this end we examine (m arbitrary)

$$S_+\chi_{m-1} = S_+S_-\chi_m = \underbrace{[S_+, S_-]}_{=2\hbar S_3}\chi_m + S_-\underbrace{S_+\chi_m}_{=\hbar^2 c_m \chi_{m+1}} = \hbar^2(2m + c_m)\chi_m\,. \tag{4.76}$$

Hence (4.75) holds with $c_{m-1} = 2m + c_m$. It follows by induction that

$$c_m = 2(m+1) + 2(m+2) + \cdots + 2s = s(s+1) - m(m+1) = (s-m)(s+1+m)\,. \tag{4.77}$$

For $m = s - k - 1$ (4.75) together with (4.74) implies $c_{s-k-1} = 0$. Thus we obtain $2s = k$ [from the second factor in (4.77)] and there exist only representations with

$$s = 0, \tfrac{1}{2}, 1, \tfrac{3}{2}, \ldots\,. \tag{4.78}$$

We call these representations $\mathcal{D}_s$. In every representation there are the $(2s+1)$-basis vectors $\chi_{-s}, \ldots, \chi_s$, with $m = -s, \ldots, s-1, s$. The representations are characterized by the fact that the spin-squared operator $\boldsymbol{S}^2$ acts on the representation as a multiple of the identity,

$$\boldsymbol{S}^2\chi = \hbar^2 s(s+1)\chi, \qquad \chi \in \mathcal{D}_s\,. \tag{4.79}$$

This follows from[6] $\boldsymbol{S}^2\chi_s = \hbar^2 s(s+1)\chi_s$ and the fact that $\boldsymbol{S}^2$ commutes with S_-.

The (irreducible) representations $\mathcal{D}_s$ of the angular-momentum algebra can be realized in the Hilbert space $\mathbb{C}^{2s+1}$. To this end one defines the vectors $|s, m\rangle \propto \chi_m$, $m = -s, \ldots, s$ as

[5] $[S_3, S_\pm] = [S_3, S_1] \pm i[S_3, S_2] = i\hbar S_2 \pm \hbar S_1$, since $[S_3, S_1] = i\hbar S_2$ and $[S_3, S_2] = -i\hbar S_1$.
[6] It holds $\boldsymbol{S}^2 = S_1^2 + S_2^2 + S_3^2 = (S_1 - iS_2)(S_1 + iS_2) - i[S_1, S_2] + S_3^2 = S_-S_+ + S_3(S_3 + \hbar)$.

the orthonormal basis vectors. The vectors are simultaneous eigenvectors of the (Hermitian) operators S_3 and $\boldsymbol{S}^2$ with

$$S_3|s,m\rangle = \hbar m|s,m\rangle, \qquad \boldsymbol{S}^2|s,m\rangle = \hbar^2 s(s+1)|s,m\rangle\,. \tag{4.80}$$

From (4.71) it follows that $S_\pm$ are adjoint operators to each other. We obtain from (4.75) the normalization factor of $\chi = S_+|s,m\rangle$,

$$\langle\chi|\chi\rangle = \langle s,m|S_-S_+|s,m\rangle = \hbar^2 c_m\,. \tag{4.81}$$

Thus $S_+|s,m\rangle = \hbar\sqrt{c_m}|s,m+1\rangle$ holds.

The representation of the spin operators in the basis $|s,m\rangle$ of $\mathcal{D}_s$ is defined by (4.80) and

$$S_\pm|s,m\rangle = \hbar\sqrt{s(s+1)-m(m\pm1)}|s,m\pm1\rangle = \hbar\mu^\pm_{s,m}|s,m\pm1\rangle \tag{4.82}$$

One calls the representation $\mathcal{D}_s$ also *spin-s*.

Since $\boldsymbol{S}$ commutes with $\boldsymbol{S}^2$, a spin-s transforms under a rotation by the angle α about $\boldsymbol{e}$ as

$$U_{\boldsymbol{e}}(\alpha)|s,m\rangle = \sum_{m'=-s}^{s} \underbrace{\langle s,m'|e^{-i\alpha\boldsymbol{e}\cdot\boldsymbol{S}/\hbar}|s,m\rangle}_{=u^{(s)}_{\boldsymbol{e};m',m}(\alpha)}|s,m'\rangle\,. \tag{4.83}$$

One calls the matrices $u^{(s)}_{\boldsymbol{e}}(\alpha)$ the spin-s representation of the rotation group.

Examples

Spin-0: The 1-dimensional representation $\mathcal{D}_0$ is trivial. The wavefunctions are simply $\psi(\boldsymbol{r})$ (without internal degrees of freedom). It holds $\chi = |0,0\rangle = 1$ and $S_j = 0$.

Spin-$\frac{1}{2}$: For spin-$\frac{1}{2}$ there exist the two basis functions $|s=\frac{1}{2},\pm\frac{1}{2}\rangle$. One also denotes these as $|0\rangle = |+\rangle = |\uparrow\rangle$ and $|1\rangle = |-\rangle = |\downarrow\rangle$. From (4.82) one obtains the relations

$$S_+|\downarrow\rangle = \hbar|\uparrow\rangle, \quad S_+|\uparrow\rangle = 0, \quad S_-|\downarrow\rangle = 0, \quad S_-|\uparrow\rangle = \hbar|\downarrow\rangle\,. \tag{4.84}$$

Furthermore, by (4.80) $S_3|\pm\rangle = \pm\frac{\hbar}{2}|\pm\rangle$ holds. The matrices in the basis $\{|\uparrow\rangle,|\downarrow\rangle\}$ are thus represented by

$$S_j = \frac{\hbar}{2}\sigma_j, \qquad j = 1,2,3,+,-\,, \tag{4.85}$$

with the *Pauli matrices*

$$\sigma_3 = \begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}, \qquad \sigma_+ = \begin{pmatrix}0 & 2\\ 0 & 0\end{pmatrix}, \qquad \sigma_- = \begin{pmatrix}0 & 0\\ 2 & 0\end{pmatrix}. \tag{4.86}$$

From $\sigma_\pm$ one can of course also determine

$$\sigma_1 = \frac{1}{2}(\sigma_+ + \sigma_-) = \begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix} \quad \text{and} \quad \sigma_2 = \frac{1}{2i}(\sigma_+ - \sigma_-) = \begin{pmatrix}0 & -i\\ i & 0\end{pmatrix} \tag{4.87}$$

From general considerations we know that $\boldsymbol{S}^2 = \hbar^2 s(s+1) = \frac{3}{4}\hbar^2$. Hence

$$\boldsymbol{\sigma}^2 = \frac{4\boldsymbol{S}^2}{\hbar^2} = \sigma_1^2 + \sigma_2^2 + \sigma_3^2 = 3\,. \tag{4.88}$$

Moreover, $\boldsymbol{S} = \frac{\hbar}{2}\boldsymbol{\sigma}$ generates on $\mathcal{D}_{\frac{1}{2}}$ rotations with $u_{\boldsymbol{e}}^{(\frac{1}{2})}(\alpha) = e^{-i\alpha\boldsymbol{e}\cdot\boldsymbol{\sigma}/2}$. From (4.67) it follows that

$$e^{i\alpha\boldsymbol{e}\cdot\boldsymbol{\sigma}/2}\boldsymbol{\sigma}e^{-i\alpha\boldsymbol{e}\cdot\boldsymbol{\sigma}/2} = R_{\boldsymbol{e}}(\alpha)\boldsymbol{\sigma}\,. \tag{4.89}$$

The Pauli matrices additionally satisfy the important property

$$(\boldsymbol{v}\cdot\boldsymbol{\sigma})(\boldsymbol{w}\cdot\boldsymbol{\sigma}) = \boldsymbol{v}\cdot\boldsymbol{w} + i(\boldsymbol{v}\times\boldsymbol{w})\cdot\boldsymbol{\sigma} \tag{4.90}$$

for arbitrary vectors $\boldsymbol{v}, \boldsymbol{w} \in \mathbb{R}^3$. From this it follows that

$$(\boldsymbol{v}\cdot\boldsymbol{\sigma})^2 = \boldsymbol{v}^2 = |\boldsymbol{v}|^2 \tag{4.91}$$

and we obtain

$$\begin{aligned} u_{\boldsymbol{e}}^{(\frac{1}{2})}(\alpha) = e^{-i\alpha\boldsymbol{e}\cdot\boldsymbol{\sigma}/2} &= \sum_{k=0}^{\infty}\frac{(-i\alpha/2)^{2k}\overbrace{(\boldsymbol{e}\cdot\boldsymbol{\sigma})^{2k}}^{=1}}{(2k)!} + \sum_{k=0}^{\infty}\frac{(-i\alpha/2)^{2k+1}\overbrace{(\boldsymbol{e}\cdot\boldsymbol{\sigma})^{2k+1}}^{=\boldsymbol{e}\cdot\boldsymbol{\sigma}}}{(2k+1)!} \\ &= \cos(\alpha/2) - i\sin(\alpha/2)\boldsymbol{e}\cdot\boldsymbol{\sigma}\,. \end{aligned} \tag{4.92}$$

In particular, for a complete rotation by 2π with $u_{\boldsymbol{e}}^{(\frac{1}{2})}(2\pi) = e^{-i\pi\boldsymbol{e}\cdot\boldsymbol{\sigma}} = -1$ one sees that the representation $u_{\boldsymbol{e}}^{(\frac{1}{2})}(\alpha)$ of spin-$\frac{1}{2}$ is not a representation of the rotation group $\mathsf{SO}(3)$. In quantum mechanics this is not a problem, since ψ and $-\psi$ describe the same state. The representation with the Pauli matrices is rather a representation of $\mathsf{SU}(2)$. This is a twofold covering of $\mathsf{SO}(3)$ and two rotations $\pm u_{\boldsymbol{e}}^{(\frac{1}{2})}(\alpha) \in \mathsf{SU}(2)$ correspond to the same rotation $R_{\boldsymbol{e}}(\alpha) \in \mathsf{SO}(3)$. More generally, it is the case that the representations of the angular-momentum algebra for half-integer spin always belong to the twice as large group $\mathsf{SU}(2)$.

The time-reversal operator T must reverse the spin $\boldsymbol{S}$

$$T^\dagger\boldsymbol{S}T = -\boldsymbol{S}\,. \tag{4.93}$$

One can easily verify that

$$T\boldsymbol{\chi} = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}\boldsymbol{\chi}^* \tag{4.94}$$

accomplishes this task. Because $T^2 = -1$, for a spin-$\frac{1}{2}$ (as for any half-integer spin) Kramers degeneracy holds.

The electron is a particle with spin-$\frac{1}{2}$. The simplest Hamiltonian for an electron with charge $-e$ is the Pauli operator

$$H = \frac{1}{2m}\left(\boldsymbol{p} + \frac{e}{c}\boldsymbol{A}\right)^2 + V(\boldsymbol{r}) + g\frac{e}{2mc}\boldsymbol{B}\cdot\boldsymbol{S} \tag{4.95}$$

with the external potential $V(\boldsymbol{r})$ and the gyromagnetic ratio $g = 2$. For a homogeneous magnetic field $\boldsymbol{B}$ $\boldsymbol{A} = \frac{1}{2}\boldsymbol{B}\times\boldsymbol{r}$ and hence (we assume that B is small)

$$\left(\boldsymbol{p} + \frac{e}{c}\boldsymbol{A}\right)^2 \approx \boldsymbol{p}^2 + \frac{2e}{c}\boldsymbol{A}\cdot\boldsymbol{p} = \boldsymbol{p}^2 + \frac{e}{c}\boldsymbol{B}\cdot(\boldsymbol{r}\times\boldsymbol{p})\,. \tag{4.96}$$

Thus the Pauli operator for weak magnetic fields can be written as

$$H = \frac{\boldsymbol{p}^2}{2m} + V(\boldsymbol{r}) + \frac{\mu_B}{\hbar}\boldsymbol{B}\cdot(\boldsymbol{L} + g\boldsymbol{S})\,. \tag{4.97}$$

with the *Bohr magneton* (10^4 G corresponds to 1 T)

$$\mu_B = \frac{e\hbar}{2mc} \approx 5.788 \times 10^{-9}\,\mathrm{eV/G}\,. \tag{4.98}$$

Spin-1: For the representation $\mathcal{D}_1$ the Hilbert space is $\mathbb{C}^3$. We choose as an orthonormal basis $\{|1,1\rangle, |1,0\rangle, |1,-1\rangle\}$. The relation (4.82) for $s=1$ written as a matrix means

$$S_+ = \sqrt{2}\,\hbar \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{pmatrix}, \qquad S_- = S_+^\dagger, \qquad S_3 = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}. \tag{4.99}$$

Hence it follows that

$$S_1 = \frac{1}{2}(S_+ + S_-) = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \quad S_2 = \frac{1}{2i}(S_+ - S_-) = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix}.$$

From the general considerations we can again conclude that $S_1^2 + S_2^2 + S_3^2 = 2\hbar^2$ and, naturally, that (4.67) holds.

4.5 Angular-momentum addition

For the treatment of selection rules arising from rotational symmetry and for the determination of the total angular momentum $\boldsymbol{J}$ of a composite system it is important to know how to add angular momenta. To this end we pose the following question. Given two systems that transform under rotations with spin s_1 and s_2. What is the angular momentum $\boldsymbol{J} = \boldsymbol{S} \otimes 1 + 1 \otimes \boldsymbol{S} = \boldsymbol{S}_1 + \boldsymbol{S}_2$ of the total system $\mathcal{D}_{s_1} \otimes \mathcal{D}_{s_2}$.[7] Physically, the total angular momentum describes the *simultaneous* rotation of both subsystems with

$$U_{\boldsymbol{e}}(\alpha) = e^{-i\alpha \boldsymbol{e}\cdot\boldsymbol{J}/\hbar} = e^{-i\boldsymbol{e}\cdot\boldsymbol{S}/\hbar} \otimes e^{-i\boldsymbol{e}\cdot\boldsymbol{S}/\hbar} = e^{-i\boldsymbol{e}\cdot\boldsymbol{S}_1/\hbar} e^{-i\boldsymbol{e}\cdot\boldsymbol{S}_2/\hbar}\,. \tag{4.100}$$

The basis of the Hilbert space $\mathcal{D}_{s_1} \otimes \mathcal{D}_{s_2}$ is then given by $|s_1, m_1; s_2, m_2\rangle = |s_1, m_1\rangle \otimes |s_2, m_2\rangle$, with $m_1 = -s_1, \ldots, s_1$ and $m_2 = -s_2, \ldots, s_2$. The question is therefore after a new basis $|j, m\rangle$ such that the vectors transform as irreducible representations $\mathcal{D}_j$.

Two spin-$\frac{1}{2}$: Consider as a simple example two spin-$\frac{1}{2}$. We solve the problem by means of some simple considerations. The space $\mathcal{H} = \mathcal{D}_{\frac{1}{2}} \otimes \mathcal{D}_{\frac{1}{2}}$ is spanned by $|\pm,\pm\rangle$ and is thus 4-dimensional. The states $|\pm,\pm\rangle$ are already eigenstates of J_3 with

$$J_3 |m_1, m_2\rangle = \hbar(m_1 + m_2)|m_1, m_2\rangle\,. \tag{4.101}$$

The state $|+,+\rangle$ has in this case the maximal eigenvalue $\hbar$. Thus the representation $\mathcal{D}_1$ is contained in $\mathcal{H}$. In particular, it must be that $|+,+\rangle$ equals the state $|j=1, m=1\rangle$.[8] We obtain the remaining states by applying J_-. In particular,

$$\frac{J_-}{\hbar}|+,+\rangle = |-,+\rangle + |+,-\rangle, \qquad \frac{J_-^2}{\hbar^2}|+,+\rangle = \frac{J_-}{\hbar}\big(|-,+\rangle + |+,-\rangle\big) = 2|-,-\rangle\,. \tag{4.102}$$

[7] We write compactly $\boldsymbol{S}_1 \equiv \boldsymbol{S} \otimes 1$ and $\boldsymbol{S}_2 \equiv 1 \otimes \boldsymbol{S}$. The operators $\boldsymbol{J}$ of course satisfy the angular-momentum algebra.

[8] There is of course the possibility of a phase. We use, however, the Condon-Shortley phase convention with $\langle s_1, s_1; s_2, j - s_1 | jj\rangle > 0$.

Thus we have found (up to normalization) all states for $j = 1$. In the Hilbert space $\mathcal{H}$ there remains $|+,-\rangle - |-,+\rangle$ as the only state that is orthogonal to the states in $\mathcal{D}_1$. This state must therefore correspond to the representation $\mathcal{D}_0$. After normalization we obtain

$$\left.\begin{array}{lll} \text{Singlet:} & |0,0\rangle = \frac{1}{\sqrt{2}}\big(|+,-\rangle - |-,+\rangle\big) & \Big\} \ \mathcal{D}_0 \\ \text{Triplet:} & \begin{array}{l} |1,1\rangle = |+,+\rangle \\ |1,0\rangle = \frac{1}{\sqrt{2}}\big(|+,-\rangle + |-,+\rangle\big) \\ |1,-1\rangle = |-,-\rangle \end{array} & \Big\} \ \mathcal{D}_1 \end{array} \right\} \mathcal{D}_{\frac{1}{2}} \otimes \mathcal{D}_{\frac{1}{2}} \,. \tag{4.103}$$

We have thereby shown the decomposition $\mathcal{D}_{\frac{1}{2}} \otimes \mathcal{D}_{\frac{1}{2}} = \mathcal{D}_0 \oplus \mathcal{D}_1$. The expression $\mathcal{D}_0 \oplus \mathcal{D}_1$ means that in the new basis $\{|0,0\rangle; |1,-1\rangle, |1,0\rangle, |1,1\rangle\}$ the spin operators $\boldsymbol{J}$ are block-diagonal. They act with the representation $\mathcal{D}_0$ on the first vector and with the representation $\mathcal{D}_1$ on the remaining 3. It holds that

$$J_j = \left(\begin{array}{c|c} 0 & 0 \\ \hline 0 & S_j \end{array}\right), \qquad \boldsymbol{J}^2 = \hbar^2 \left(\begin{array}{c|c} 0 & 0 \\ \hline 0 & 2 \end{array}\right), \tag{4.104}$$

with S_j from the spin-1 representation of (4.99). The representations $\mathcal{D}_s$ are irreducible. This means that there is no basis in which the matrices $\boldsymbol{J}$ can simultaneously be "diagonalized" into even smaller block matrices.

Interesting is also that $|j,m\rangle$ eigenstates of $\boldsymbol{S}_1 \cdot \boldsymbol{S}_2$ are. It holds

$$\boldsymbol{S}_1 \cdot \boldsymbol{S}_2 = \frac{1}{2}\Big[\big(\boldsymbol{S}_1 + \boldsymbol{S}_2\big)^2 - \underbrace{\boldsymbol{S}_1^2}_{=\hbar^2 \frac{1}{2}(\frac{1}{2}+1)} - \boldsymbol{S}_2^2\Big] = \frac{\boldsymbol{J}^2}{2} - \frac{3}{4}\hbar^2 \,. \tag{4.105}$$

For $j = 0$ $\boldsymbol{J}^2$ has the eigenvalue 0 and thus $\boldsymbol{S}_1 \cdot \boldsymbol{S}_2 |0,0\rangle = -\frac{3\hbar^2}{4}|0,0\rangle$ holds. Analogously, one obtains for $j = 1$ the result $\boldsymbol{S}_1 \cdot \boldsymbol{S}_2 |1,m\rangle = \frac{\hbar^2}{4}|1,m\rangle$. Thus we can define the projectors

$$\begin{aligned} P_t &= \frac{3}{4} + \frac{\boldsymbol{S}_1 \cdot \boldsymbol{S}_2}{\hbar^2} && \text{(onto the triplet space)}, \\ P_s &= \frac{1}{4} - \frac{\boldsymbol{S}_1 \cdot \boldsymbol{S}_2}{\hbar^2} && \text{(onto the singlet space)}, \end{aligned} \tag{4.106}$$

.

General case (Clebsch-Gordan): We now want to generalize this procedure. The Hilbert space $\mathcal{H} = \mathcal{D}_{s_1} \otimes \mathcal{D}_{s_2}$ is $(2s_1+1)(2s_2+1)$-dimensional, spanned by the product basis $|s_1, m_1; s_2, m_2\rangle$. We seek allowed j such that $|j,m\rangle$ spans the same Hilbert space with irreducible representations with respect to the total angular momentum $\boldsymbol{J}$. First we look at the eigenvalues of J_3. We obtain

$$J_3 |s_1, m_1; s_2, m_2\rangle = \hbar(m_1 + m_2)|s_1, m_1; s_2, m_2\rangle \tag{4.107}$$

and hence the states $|s_1, m_1; s_2, m_2\rangle$ are already eigenstates of J_3. The degeneracy of the eigenvalues $m = m_1 + m_2$ is determined by, cf. Figure 4.1:

- one state with $m = s_1 + s_2 =$ (maximal),
- two states with $m = s_1 + s_2 - 1$: $\begin{cases} m_1 = s_1, m_2 = s_2 - 1, \\ m_1 = s_1 - 1, m_2 = s_2, \end{cases}$

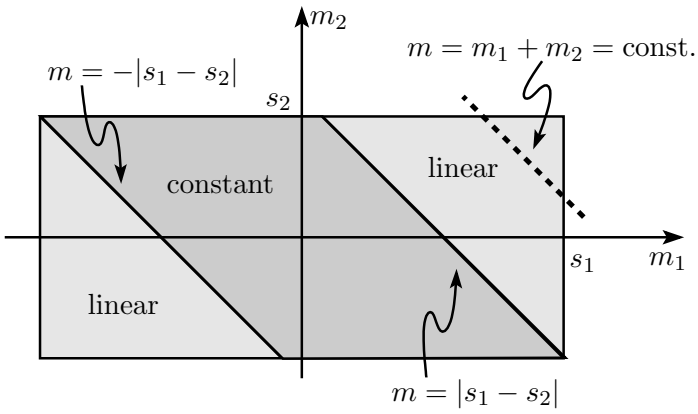


Fig. 4.1: Scheme for counting the eigenstates $|j, m\rangle$ of the total angular momentum j of two particles with angular momenta s_1 and s_2.

$\vdots$

- $s_1 + s_2 - m + 1$ states for $m \geq |s_1 - s_2|$, (the number of ways to construct a $m = m_1 + m_2 \geq |s_1 - s_2|$ from m_1 and m_2)
- $s_1 + s_2 - |s_1 - s_2| + 1 =$ constant states for $-|s_1 - s_2| < m < |s_1 - s_2|$,
- and $s_1 + s_2 - |m| + 1$ states for $m \leq -|s_1 - s_2|$.

The state with maximal $m = s_1 + s_2$ must belong to the representation $\mathcal{D}_{j=s_1+s_2}$. With it belong altogether $(2j + 1)$ states to it (one state for each m). We can generate these by applying J_-. Of the two states with $m = s_1 + s_2 - 1$, one state belongs to the representation $\mathcal{D}_{s_1+s_2}$. The orthogonal state must then naturally be the state with maximal m of the representation with $j = s_1 + s_2 - 1$. We can continue this reasoning recursively. As long as $m \geq |s_1 - s_2|$ there is always one state not yet contained in the previous representations. We thus conclude that (*Clebsch-Gordan series*)

$$\mathcal{D}_{s_1} \otimes \mathcal{D}_{s_2} = \bigoplus_{j=|s_1-s_2|}^{s_1+s_2} \mathcal{D}_j = \mathcal{D}_{s_1+s_2} \oplus \mathcal{D}_{s_1+s_2-1} \oplus \cdots \oplus \mathcal{D}_{|s_1-s_2|}\,. \tag{4.108}$$

Indeed it holds

$$\sum_{j=|s_1-s_2|}^{s_1+s_2} (2j+1) \quad = (2s_1+1)(2s_2+1) \tag{4.109}$$

so that we have accounted for all states in the Hilbert space $\mathcal{H}$.

Clebsch-Gordan coefficients: The change from $|s_1, m_1; s_2, m_2\rangle$ to $|j, m\rangle$ is a basis transformation between two orthonormal bases with

$$|j, m\rangle = \sum_{m_1,m_2} \langle s_1, m_1; s_2, m_2 | j, m\rangle \, |s_1, m_1; s_2, m_2\rangle\,. \tag{4.110}$$

The matrix elements $\langle s_1, m_1; s_2, m_2 | j, m\rangle$ of the orthogonal matrix (s_1, s_2 fixed) are called Clebsch-Gordan coefficients (we will shortly show that these can in fact be chosen real). The

inverse transformation is therefore given by

$$|s_1, m_1; s_2, m_2\rangle = \sum_{j,m} \underbrace{\langle s_1, m_1; s_2, m_2 | j, m\rangle}_{=\langle j,m|s_1,m_1;s_2,m_2\rangle} |j, m\rangle \,. \tag{4.111}$$

To determine the Clebsch-Gordan coefficients, we apply $J_\pm$ first to the left-hand side of (4.110),

$$J_\pm |j, m\rangle = \hbar \mu^\pm_{j,m} |j, m \pm 1\rangle = \hbar \mu^\pm_{j,m} \sum_{m_1,m_2} \langle s_1, m_1; s_2, m_2 | j, m \pm 1\rangle |s_1, m_1; s_2, m_2\rangle \,. \tag{4.112}$$

Applying it to the right-hand side yields on the other hand

$$\begin{aligned} &\hbar \sum_{m_1,m_2} \langle s_1, m_1; s_2, m_2 | j, m\rangle \big(\mu^\pm_{s_1,m_1} |s_1, m_1 \pm 1; s_2, m_2\rangle + \mu^\pm_{s_2,m_2} |s_1, m_1; s_2, m_2 \pm 1\rangle\big) \\ &= \hbar \sum_{m_1,m_2} \big(\mu^\pm_{s_1,m_1\mp1} \langle s_1, m_1 \mp 1; s_2, m_2 | j, m\rangle + \mu^\pm_{s_2,m_2\mp1} \langle s_1, m_1; s_2, m_2 \mp 1 | j, m\rangle\big) |s_1, m_1; s_2, m_2\rangle \,. \end{aligned} \tag{4.113}$$

Equating (4.112) and (4.113) leads to the recursion relation (Racah 1941)

$$\begin{aligned} &\mu^\pm_{j,m} \langle s_1, m_1; s_2, m_2 | j, m \pm 1\rangle \\ &\qquad = \mu^\pm_{s_1,m_1\mp1} \langle s_1, m_1 \mp 1; s_2, m_2 | j, m\rangle + \mu^\pm_{s_2,m_2\mp1} \langle s_1, m_1; s_2, m_2 \mp 1 | j, m\rangle \,. \end{aligned} \tag{4.114}$$

One finds the Clebsch-Gordan coefficients by first choosing $m = j$ and "+." The left-hand side then vanishes and one obtains all coefficients $\langle s_1, m_1; s_2, m_2 | j, j\rangle$ as multiples of $\langle s_1, s_1; s_2, j - s_1 | j, j\rangle$.

With the normalization $\sum_{m_1,m_2} \langle s_1, m_1; s_2, m_2 | j, j\rangle^2 = 1$ of $|j, j\rangle$ and the Condon-Shortley phase convention $\langle s_1, s_1; s_2, j - s_1 | jj\rangle > 0$ the coefficients $\langle s_1, m_1; s_2, m_2 | j, j\rangle$ are uniquely determined and real. By the recursion relation (4.114) with "−" one can uniquely determine the remaining Clebsch-Gordan coefficients. The general formula and a table of the most important cases can be found on Wikipedia https://en.wikipedia.org/wiki/Table_of_Clebsch-Gordan_coefficients. It holds of course $\langle s_1, m_1; s_2, m_2 | j, m\rangle = 0$ except $m = m_1 + m_2$ *and* $|s_1 - s_2| \le j \le s_1 + s_2$.

Tensor operators and selection rules: We consider a Hilbert space $\mathcal{H}$ on which rotations R by $\boldsymbol{e}$ act via the unitary transformation

$$U_{\boldsymbol{e}}(\alpha) = e^{-i\alpha \boldsymbol{e}\cdot\boldsymbol{J}/\hbar} \tag{4.115}$$

The generators $\boldsymbol{J}$ satisfy the angular-momentum algebra. Important examples are the orbital Hilbert space [with $\mathcal{H} = L^2(\mathbb{R}^3)$ and $\boldsymbol{J} = \boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p}$], the spin-$s$ space [with $\mathcal{H} = \mathbb{C}^{2s+1}$ and $\boldsymbol{J} = \boldsymbol{S}$], and the combined spin-orbit Hilbert space [with $\mathcal{H} = L^2(\mathbb{R}^3) \otimes \mathbb{C}^{2s+1}$ and $\boldsymbol{J} = \boldsymbol{L} \otimes 1 + 1 \otimes \boldsymbol{S}$].

To obtain selection rules one needs operators that transform like the states. A *tensor operator* of spin-l is a list of $(2l + 1)$ operators $T^{(l)}_m$, $m = -l, \ldots, l$, which under a rotation R behave as [cf. (4.83)]

$$U_{\boldsymbol{e}}(\alpha) T^{(l)}_m U^\dagger_{\boldsymbol{e}}(\alpha) = \sum_{m'=-l}^{l} \langle l, m' | e^{-i\alpha \boldsymbol{e}\cdot\boldsymbol{S}/\hbar} | l, m\rangle T^{(l)}_{m'} = \sum_{m'=-l}^{l} u^{(l)}_{\boldsymbol{e};m',m}(\alpha)\, T^{(l)}_{m'} \tag{4.116}$$

with $u^{(l)}$ the rotation matrix for spin-l. Here l is always an integer since a rotation by 2π maps the tensors onto themselves, $U_{\boldsymbol{e}}(2\pi)T^{(l)}_m U^\dagger_{\boldsymbol{e}}(2\pi) = (\pm 1)T^{(l)}_m(\pm 1) = T^{(l)}_m$.

For an infinitesimal rotation this implies the equivalent condition

$$[\boldsymbol{e}\cdot\boldsymbol{J}, T^{(l)}_m] = \sum_{m'=-l}^{l} \langle l, m'|\boldsymbol{e}\cdot\boldsymbol{S}|l,m\rangle\, T^{(l)}_{m'}\,. \tag{4.117}$$

Since the matrix elements of S_3 and $S_\pm$ from (4.80) and (4.82) are known, we rewrite (4.117) and define a tensor operator of spin-l via the algebra

$$[J_3, T^{(l)}_m] = \hbar m\, T^{(l)}_m, \qquad [J_\pm, T^{(l)}_m] = \sum_{m'} \langle l, m'|S_\pm|l,m\rangle\, T^{(l)}_{m'} = \hbar\mu^\pm_{l,m}\, T^{(l)}_{m\pm 1} \tag{4.118}$$

with $\mu^\pm_{l,m} = \sqrt{l(l+1) - m(m\pm 1)} = \sqrt{(l\mp m)(l+1\pm m)}$.

Examples

Scalar operator: A scalar operator (for example $\boldsymbol{p}^2, \boldsymbol{L}^2$) remains invariant under rotations. A scalar operator is thus a tensor operator of spin 0.

Vector operator: A vector operator $\boldsymbol{v}$ transforms under rotations (with $\boldsymbol{J} = \boldsymbol{L}$) as

$$[\boldsymbol{v}, \boldsymbol{e}\cdot\boldsymbol{J}] = i\hbar\, \boldsymbol{e}\times\boldsymbol{v} \qquad \overset{\boldsymbol{f}\cdot}{\Leftrightarrow} \qquad [\boldsymbol{e}\cdot\boldsymbol{J}, \boldsymbol{f}\cdot\boldsymbol{v}] = i\hbar(\boldsymbol{e}\times\boldsymbol{f})\cdot\boldsymbol{v}\,. \tag{4.119}$$

Since all components of $\boldsymbol{v}$ transform into one another, one may suspect that a vector operator is irreducible and hence belongs to spin 1. One can verify by a simple calculation that

$$v^{(1)}_0 = v_3, \qquad v^{(1)}_{\pm 1} = \mp\frac{1}{\sqrt{2}}(v_1 \pm i v_2) \tag{4.120}$$

is indeed a tensor operator of spin 1. One also says that $\boldsymbol{v}$ transforms under the defining representation $R \in \mathsf{SO}(3)$, while $v^{(1)}$ transforms like a spin 1. The two representations are related by (4.120).

From the position operator we thus obtain, for example, the tensor operator

$$r^{(1)}_0 = r_3, \qquad r^{(1)}_{\pm 1} = \mp\frac{1}{\sqrt{2}}(r_1 \pm i r_2), \tag{4.121}$$

of spin 1.

Selection rule: We can now derive the selection rules for tensor operators. For a Hamiltonian with rotational symmetry $\boldsymbol{J}$ one can characterize the eigenstates $|\nu, j, m\rangle$ by the eigenvalues of the operators $\boldsymbol{J}^2, J_3$ (with possible additional quantum numbers ν). Let $T^{(l)}$ be a tensor operator of spin-l, then the *Wigner-Eckart theorem* (the factor $\sqrt{2j_1+1}$ is conventional but arbitrary) holds:

$$\langle \nu_2, j_2, m_2|T^{(l)}_m|\nu_1, j_1, m_1\rangle = \frac{\langle \nu_2, j_2\|T^{(l)}\|\nu_1, j_1\rangle}{\sqrt{2j_1+1}}\langle l, m; j_1, m_1|j_2, m_2\rangle\,. \tag{4.122}$$

The *reduced matrix element* $\langle \nu_2, j_2\|T^{(l)}\|\nu_1, j_1\rangle$ does not depend on m_1, m_2 or m. The matrix elements within a representation are proportional to the Clebsch-Gordan coefficients $\langle l, m; j_1, m_1|j_2, m_2\rangle$. In particular the selection rule

$$\langle \nu_2, j_2, m_2|T^{(l)}_m|\nu_1, j_1, m_1\rangle = 0, \quad \text{except } m_2 = m_1 + m \text{ and } |j_1 - l| \le j_2 \le j_1 + l\,. \tag{4.123}$$

The Wigner-Eckart theorem follows from the statement that the states

$$|\tilde{\nu}, k, q\rangle = \sum_{m,m_1} \langle l, m; j_1, m_1 | k, q\rangle \, T^{(l)}_m |\nu_1, j_1, m_1\rangle, \tag{4.124}$$

obtained by "adding" the angular momenta l (of $T^{(l)}$) and j_1 (of $|j_1, m_1\rangle$) indeed transform like spin-k states (note that the tensor operator $T^{(l)}$ in general changes the state $\nu_1 \mapsto \tilde{\nu}$). Indeed, using (4.118)

$$J_3|\tilde{\nu}, k, q\rangle = \sum_{m,m_1} \langle l, m; j_1, m_1 | k, q\rangle \underbrace{J_3 T^{(l)}_m}_{T^{(l)}_m J_3 + \hbar m T^{(l)}_m} |\nu_1, j_1, m_1\rangle = \hbar(m_1 + m)|\tilde{\nu}, k, q\rangle \,. \tag{4.125}$$

Furthermore we obtain

$$J_\pm|\tilde{\nu}, k, q\rangle = \sum_{m,m_1} \langle l, m; j_1, m_1 | k, q\rangle \overbrace{J_\pm T^{(l)}_m}^{= T^{(l)}_m J_\pm + \hbar \mu^\pm_{l,m} T^{(l)}_{m\pm1}} |\nu_1, j_1, m_1\rangle \tag{4.126}$$

$$= \hbar \sum_{m,m_1} \Big[\mu^\pm_{l,m} \langle l, m; j_1, m_1 | k, q\rangle T^{(l)}_{m\pm1} |\nu_1, j_1, m_1\rangle + \mu^\pm_{j_1,m_1} \langle l, m; j_1, m_1 | k, q\rangle T^{(l)}_m |\nu_1, j_1, m_1 \pm 1\rangle \Big]$$

$$= \hbar \sum_{m,m_1} \Big[\mu^\pm_{l,m\mp1} \langle l, m \mp 1; j_1, m_1 | k, q\rangle + \mu^\pm_{j_1,m_1\mp1} \langle l, m; j_1, m_1 \mp 1 | k, q\rangle \Big] T^{(l)}_m |\nu_1, j_1, m_1\rangle$$

$$\overset{(4.114)}{=} \hbar \mu^\pm_{l,q} \sum_{m,m_1} \langle l, m; j_1, m_1 | k, q \pm 1\rangle \, T^{(l)}_m |\nu_1, j_1, m_1\rangle = \hbar \mu^\pm_{l,q} \, |\tilde{\nu}, k, q+1\rangle \,. \tag{4.127}$$

A comparison with (4.80) and (4.82) shows that the states $|\tilde{\nu}, k, q\rangle$ (at fixed $\tilde{\nu}, k$) transform as an irreducible representation $\mathcal{D}_k$ of spin-k. States belonging to different representations are orthogonal and hence $\langle \nu_2, j_2, m_2 | \tilde{\nu}, k, q\rangle = 0$ except for $k = j_2$ and $q = m_2$.[9]

Since in the reduction of $\mathcal{D}_l \otimes \mathcal{D}_{j_1}$ the representation $\mathcal{D}_k$ occurs only once,[10] we can invert the transformation (4.124) with

$$T^{(l)}_m |\nu_1, j_1, m_1\rangle = \sum_{k,q} \langle l, m; j_1, m_1 | k, q\rangle \, |\tilde{\nu}, k, q\rangle \,. \tag{4.128}$$

To prove the theorem it remains only to show that

$$\langle \nu_2, j_2, m_2 | \tilde{\nu}, j_2, m_2\rangle = c \tag{4.129}$$

differs from m_2 only by a constant c independent of . This follows recursively (starting from $m_2 = j_2$) from

$$\begin{aligned} \hbar \mu^+_{j_2,m_2-1} \langle \nu_2, j_2, m_2 | \tilde{\nu}, j_2, m_2\rangle &= \langle \tilde{\nu}, j_2, m_2 | J_+ | \nu_2, j_2, m_2 - 1\rangle^* = \langle \nu_2, j_2, m_2 - 1 | J_- | \tilde{\nu}, j_2, m_2\rangle \\ &= \hbar \mu^-_{j_2,m_2} \langle \nu_2, j_2, m_2 - 1 | \tilde{\nu}, j_2, m_2 - 1\rangle \,, \end{aligned} \tag{4.130}$$

since $\mu^-_{j_2,m_2} = \mu^+_{j_2,m_2-1} \neq 0$ for $j_2 \geq m_2 > -j_2$.

[9] This follows from $\boldsymbol{J}^2 |\tilde{\nu}, k, q\rangle = \hbar^2 k(k+1) |\tilde{\nu}, k, q\rangle$ and $\boldsymbol{J}^2 |\nu_2, j_2, m_2\rangle = \hbar^2 j_2(j_2+1) |\nu_2, j_2, m_2\rangle$ using $0 = \langle \nu_2, j_2, m_2 | \boldsymbol{J}^2 | \tilde{\nu}, k, q\rangle - \langle \tilde{\nu}, k, q | \boldsymbol{J}^2 | \nu_2, j_2, m_2\rangle^* = (k - j_2)(k + j_2 + 1) \langle \nu_2, j_2, m_2 | \tilde{\nu}, k, q\rangle$. The second selection rule is obtained from $0 = \langle \nu_2, j_2, m_2 | J_3 | \tilde{\nu}, k, q\rangle - \langle \tilde{\nu}, k, q | J_3 | \nu_2, j_2, m_2\rangle^* = \hbar(q - m_2) \langle \nu_2, j_2, m_2 | \tilde{\nu}, k, q\rangle$.

[10] The Wigner-Eckart theorem also follows directly from Schur's lemma once one has shown that $T^{(l)}_q |\nu_1, j_1, m_1\rangle$ transforms with $\mathcal{D}_l \otimes \mathcal{D}_{j_1}$. If the representation occurred multiple times, one would simply have one constant per copy of the representation.

Example

Optical selection rules: The interaction of an electron with a weak light field is described by the dipole interaction ($\boldsymbol{\mathcal{E}}$ is the electric field at the origin)

$$V_{\text{ww}} = e\,\boldsymbol{r}\cdot\boldsymbol{\mathcal{E}}\,. \tag{4.131}$$

The absorption and emission of light therefore depend on the matrix elements of the dipole operator $\boldsymbol{d} = -e\boldsymbol{r}$. The dipole operator is a polar vector. Hence $\boldsymbol{d}$ is a tensor operator of spin-1. We thereby obtain the optical selection rules for transitions with $\Delta m = m' - m$, $\Delta l = l' - l$

$$\langle l', m'|\boldsymbol{d}|l, m\rangle = 0, \qquad \text{except } \Delta m = 0, \pm 1 \text{ and } \Delta l = 0, \pm 1. \tag{4.132}$$

Moreover, the matrix element with $l = l' = 0$ vanishes. We will see later that the states $|l, m\rangle$ have parity $(-1)^l$. This further implies that $\Delta l = 0$ is forbidden.

4.6 The central-force problem

In the following we study stationary states in the central potential $V(\boldsymbol{r}) = V(r)$ with the radius $r = |\boldsymbol{r}|$. The Hamiltonian on $\mathcal{H} = L^2(\mathbb{R}^3)$ is given by

$$H = \frac{\boldsymbol{p}^2}{2m} + V(r) = -\frac{\hbar^2}{2m}\Delta + V(r)\,. \tag{4.133}$$

Rotation is generated by the angular-momentum operator $\boldsymbol{L} = \boldsymbol{r}\times\boldsymbol{p} = -i\hbar\boldsymbol{r}\times\boldsymbol{\nabla}$. By virtue of the rotational symmetry of the problem the operators $\boldsymbol{L}^2, L_3$ commute with the Hamiltonian. The eigenvalue problem $H\psi(\boldsymbol{r}) = E\psi(\boldsymbol{r})$ can therefore be reduced to the eigenspaces $|l, m\rangle$ of the operators $\boldsymbol{L}^2, L_3$. Hence we first investigate the eigenvalue problem of the angular-momentum operator on $\mathcal{H}$.

The squared angular momentum is given by $\boldsymbol{L}^2 = (\boldsymbol{r}\times\boldsymbol{p})^2$. We would like to use the vector identity $(\boldsymbol{r}\times\boldsymbol{p})^2 = \boldsymbol{r}^2\boldsymbol{p}^2 - (\boldsymbol{r}\cdot\boldsymbol{p})^2$. However, this does not hold directly because the operators do not commute. One must therefore keep the ordering of the operators and instead obtain (with $[p_k r_k, p_j] = p_k[r_k, p_j] = i\hbar\delta_{jk}p_j$)

$$\boldsymbol{L}^2 = (\boldsymbol{r}\times\boldsymbol{p})\cdot(\boldsymbol{r}\times\boldsymbol{p}) = \sum_{j,k}\big[r_j\overbrace{p_k r_j}^{=r_j p_k - i\hbar\delta_{kj}}p_k - r_j\overbrace{p_k r_k}^{=p_j r_k p_k - i\hbar(1-\delta_{jk})p_j}p_j\big] = \boldsymbol{r}^2\boldsymbol{p}^2 - i\hbar(\boldsymbol{r}\cdot\boldsymbol{p}) - (\boldsymbol{r}\cdot\boldsymbol{p})^2 + 2i\hbar(\boldsymbol{r}\cdot\boldsymbol{p})\,.$$

In spherical coordinates $\boldsymbol{r}\cdot\boldsymbol{p} = -i\hbar\,\boldsymbol{r}\cdot\boldsymbol{\nabla} = -i\hbar\, r\partial/\partial r$. Hence

$$\frac{\boldsymbol{L}^2}{\hbar^2} = -r^2\Delta + \left(r\frac{\partial}{\partial r}\right)^2 + r\frac{\partial}{\partial r} = -r^2\Delta + r\frac{\partial^2}{\partial r^2}r \tag{4.134}$$

or equivalently

$$\boldsymbol{p}^2 = -\hbar^2\Delta = -\frac{\hbar^2}{r}\frac{\partial^2}{\partial r^2}r + \frac{\boldsymbol{L}^2}{r^2}\,. \tag{4.135}$$

The second term corresponds to the centrifugal barrier in mechanics.

Spherical harmonics: We switch to *spherical coordinates* so that we can exploit the rotational symmetry directly. Spherical coordinates (r, θ, φ) are given by

$$\boldsymbol{r} = r\,\boldsymbol{e}_r, \quad \text{with} \qquad \boldsymbol{e}_r = \sin\theta\cos\varphi\,\boldsymbol{e}_1 + \sin\theta\sin\varphi\,\boldsymbol{e}_2 + \cos\theta\,\boldsymbol{e}_3\,, \tag{4.136}$$

where $r > 0$ and $(\theta, \varphi) \in \Omega = S^2$ with $d\Omega = d(\cos\theta)d\varphi$.

Rotations leave r invariant, so $\boldsymbol{L}$ acts only on $L^2(\Omega)$. A rotation about the z axis is generated by L_3. In spherical coordinates this generator takes the form

$$(L_3\psi)(\theta,\varphi) = i\hbar\frac{d}{d\alpha}\psi(\theta,\varphi-\alpha)\Big|_{\alpha=0} = -i\hbar\frac{\partial}{\partial\varphi}\psi(\theta,\varphi)\,. \tag{4.137}$$

An (infinitesimal) rotation about the x axis changes the position coordinate (with $r = 1$) as [cf. (4.46)]

$$\boldsymbol{e}_r(-\alpha) = \boldsymbol{e}_r - \alpha\,\boldsymbol{e}_1\times\boldsymbol{e}_r + O(\alpha^2) = \boldsymbol{e}_r + \alpha\cos\theta\,\boldsymbol{e}_2 - \alpha\sin\theta\sin\varphi\,\boldsymbol{e}_3 + O(\alpha^2)\,. \tag{4.138}$$

In spherical coordinates this is[11]

$$\theta(-\alpha) = \theta + \alpha\sin\varphi + O(\alpha^2), \qquad \varphi(-\alpha) = \varphi + \alpha\cot\theta\cos\varphi + O(\alpha^2)\,. \tag{4.139}$$

Thus the x component of the angular-momentum operator is given by

$$(L_1\psi)(\theta,\varphi) = i\hbar\frac{d}{d\alpha}\psi(\theta(-\alpha),\varphi(-\alpha))\Big|_{\alpha=0} = i\hbar\left(\sin\varphi\frac{\partial}{\partial\theta} + \cot\theta\cos\varphi\frac{\partial}{\partial\varphi}\right)\psi(\theta,\varphi)\,. \tag{4.140}$$

The y component is obtained from the commutator (4.57)

$$\begin{aligned} L_2 &= \frac{i}{\hbar}[L_1, L_3] = i\hbar[\sin\varphi\,\partial_\theta + \cot\theta\cos\varphi\,\partial_\varphi, \partial_\varphi] = i\hbar[\sin\varphi, \partial_\varphi]\partial_\theta + i\hbar[\cos\varphi, \partial_\varphi]\cot\theta\,\partial_\varphi \\ &= i\hbar\left(-\cos\varphi\frac{\partial}{\partial\theta} + \cot\theta\sin\varphi\frac{\partial}{\partial\varphi}\right)\,. \end{aligned} \tag{4.141}$$

For the further calculation the raising and lowering operators

$$L_\pm = L_1 \pm iL_2 = e^{\pm i\varphi}\left(\pm\hbar\frac{\partial}{\partial\theta} - \cot\theta\,L_3\right) \tag{4.142}$$

are important.

We seek *spherical harmonics* $Y_{l,m}(\theta,\varphi)$ that transform under the representation $\mathcal{D}_l$ of $\boldsymbol{L}$. This requires [see (4.80) and (4.82)]

$$\begin{aligned} L_3 Y_{l,m} &= -i\hbar\frac{\partial}{\partial\varphi}Y_{l,m} = \hbar m Y_{l,m}, \\ L_\pm Y_{l,m} &= e^{\pm i\varphi}\left(\pm\hbar\frac{\partial}{\partial\theta} - \cot\theta\,L_3\right)Y_{l,m} = \hbar\mu^\pm_{l,m}Y_{l,m\pm1}\,. \end{aligned} \tag{4.143}$$

Equation (4.143) is solved by

$$Y_{l,m}(\theta,\varphi) = e^{im\varphi}f_{l,m}(\theta)\,. \tag{4.144}$$

[11] From (4.138) one obtains $\cos[\theta(-\alpha)] = \cos\theta - \alpha\sin\theta\sin\varphi + O(\alpha^2)$ and $\tan[\varphi(-\alpha)] = \tan\varphi + \alpha\cot\theta/\cos\varphi + O(\alpha^2)$. Equation (4.139) follows by linearization.

To determine $f_{l,m}(\theta)$ we first use $L_+ Y_{l,l} = 0$,

$$e^{i\varphi}\left(\hbar\frac{\partial}{\partial\theta} - \cot\theta\, L_3\right) Y_{l,l} = 0 \qquad \Rightarrow \qquad \left(\frac{\partial}{\partial\theta} - l\cot\theta\right) f_{l,l} = 0, \tag{4.145}$$

with the solution $f_{l,l}(\theta) = \sin^l\theta$. For f to be analytic at $\theta = 0$ we need $l = 0, 1, 2, \ldots$. Hence only integer representations are allowed. After normalization to Ω we obtain the spherical harmonic[12]

$$Y_{l,l}(\theta,\varphi) = \frac{(-1)^l}{2^l\, l!}\sqrt{\frac{(2l+1)}{4\pi}(2l)!}\, \sin^l\theta\, e^{il\varphi}\,. \tag{4.146}$$

The remaining spherical harmonics are obtained simply by successive application of L_-, yielding[13]

$$Y_{l,m}(\theta,\varphi) = \frac{(-1)^l}{2^l\, l!}\sqrt{\frac{(2l+1)}{4\pi}\frac{(l+m)!}{(l-m)!}}\, \frac{e^{im\varphi}}{\sin^m\theta}\left(\frac{d}{d\cos\theta}\right)^{l-m}\sin^{2l}\theta\,. \tag{4.147}$$

From the general consideration (4.79) we know that $\boldsymbol{L}^2 Y_{l,m} = \hbar^2 l(l+1) Y_{l,m}$.

One may regard the spherical harmonics $Y_{l,m}(\theta,\varphi)$ also as (homogeneous) polynomials in the position vector $\boldsymbol{r} = r\boldsymbol{e}_r$ (at $r = 1$). In particular, on the unit sphere $r_3 = \cos\theta$, $r_1 \pm i r_2 = e^{\pm i\varphi}\sin\theta$ and $r_1^2 + r_2^2 + r_3^3 = 1$, cf. (4.121). Hence

$$\begin{aligned} Y_{l,m\geq 0}(\boldsymbol{r}) &= \frac{(-1)^l}{2^l\, l!}\sqrt{\frac{(2l+1)}{4\pi}\frac{(l+m)!}{(l-m)!}}\, \frac{(r_1+ir_2)^m}{(r^2-z^2)^m}\left(\frac{d}{dz}\right)^{l-m}(r^2-z^2)^l\Big|_{\substack{z=r_3\\ r^2=r_1^2+r_2^2+r_3^2}}\,, \\ Y_{l,m<0}(\boldsymbol{r}) &= (-1)^m Y_{l,|m|}(\boldsymbol{r})^*\,. \end{aligned} \tag{4.148}$$

From the general considerations (4.83) we know that a spherical harmonic $Y_{l,m}$ transforms like a spin-l under rotations, i.e.

$$Y_{l,m}(R_{\boldsymbol{e}}^{-1}(\alpha)\boldsymbol{r}) = (e^{-i\alpha\boldsymbol{e}\cdot\boldsymbol{L}/\hbar}Y_{l,m})(\boldsymbol{r}) \overset{(4.143)}{=} \sum_{m'} u^{(l)}_{\boldsymbol{e};m',m}(\alpha) Y_{l,m'}(\boldsymbol{r})\,. \tag{4.149}$$

Thus one can use the spherical harmonics to form tensor operators from a vector operator $\boldsymbol{v}$.[14] Indeed [cf. (4.116)]

$$U_{\boldsymbol{e}}(\alpha)Y_{l,m}(\boldsymbol{v})U_{\boldsymbol{e}}^\dagger(\alpha) \overset{(U^\dagger U=1)}{=} Y_{l,m}\big[U_{\boldsymbol{e}}(\alpha)\boldsymbol{v}U_{\boldsymbol{e}}^\dagger(\alpha)\big] \overset{(4.51)}{=} Y_{l,m}(R_{\boldsymbol{e}}^{-1}(\alpha)\boldsymbol{v}) = \sum_{m'} u^{(l)}_{\boldsymbol{e};m',m}(\alpha) Y_{l,m'}(\boldsymbol{v})\,.$$

Hence $Y_l(\boldsymbol{v})$ is a tensor operator of spin-l. For the position vector $\boldsymbol{r}$ one calls $Y_l(\boldsymbol{r})$ also *multipole moments*.

The simplest spherical harmonics are listed in Table 4.1 below. We thereby obtain the dipole moment (spin-1)

$$Y_{1,0}(\boldsymbol{r}) = \sqrt{\frac{3}{4\pi}}\, r_3, \quad Y_{1,\pm}(\boldsymbol{r}) = \mp\sqrt{\frac{3}{8\pi}}\,(r_1 \pm i r_2)\,. \tag{4.150}$$

[12] The factor $(-1)^l$ arises from the Condon-Shortley phase convention.

[13] One uses here that the factor $e^{-i\varphi}$ (in L_-) lowers L_3 by $\hbar$. Moreover $\sin^{m-1}\theta\,\partial_{\cos\theta}(\sin^m\theta\; f) = -(\partial_\theta + m\cot\theta)f$; i.e. $e^{i\varphi}L^- = \hbar\sin^{m-1}\theta\,\partial_{\cos\theta}\sin^m\theta$.

[14] We require that the individual components of $\boldsymbol{v}$ commute $[v_j, v_k] = 0$.

$Y_{0,0} = \frac{1}{\sqrt{4\pi}}$	
$Y_{1,0} = \sqrt{\frac{3}{4\pi}} r_3 = \sqrt{\frac{3}{4\pi}} \cos\theta$	$Y_{1,\pm1} = \mp\sqrt{\frac{3}{8\pi}}(r_1 \pm i r_2) = \mp\sqrt{\frac{3}{8\pi}} e^{\pm i\varphi} \sin\theta$
$Y_{2,0} = \sqrt{\frac{5}{16\pi}} (2r_3^2 - r_1^2 - r_2^2)$	$Y_{2,\pm1} = \mp\sqrt{\frac{15}{8\pi}}(r_1 \pm i r_2) r_3 = \mp\sqrt{\frac{15}{8\pi}} e^{\pm i\varphi} \sin\theta\cos\theta$
$= \sqrt{\frac{5}{16\pi}} (3\cos^2\theta - 1)$	$Y_{2,\pm2} = \sqrt{\frac{15}{32\pi}}(r_1 \pm i r_2)^2 = \sqrt{\frac{15}{32\pi}} e^{\pm 2i\varphi} \sin^2\theta$

Table 4.1: Spherical harmonics $Y_{l,m}$ for $l = 0, 1, 2$

The spherical harmonics have a well-defined parity. The parity operation $P\colon \boldsymbol{r} \mapsto -\boldsymbol{r}$ is equivalent to $\theta \mapsto \pi - \theta$, $\varphi \mapsto \varphi + \pi$, so that $e^{im\varphi} \mapsto (-1)^m e^{im\varphi}$, $\sin\theta \mapsto \sin\theta$, $\cos\theta \mapsto -\cos\theta$ and we obtain [cf. (4.147)]

$$P\, Y_{l,m}(\theta,\varphi) = (-1)^l Y_{l,m}(\theta,\varphi), \qquad \begin{cases} l \text{ even:} & \text{even under } P, \\ l \text{ odd:} & \text{odd under } P. \end{cases} \tag{4.151}$$

One can show that in $L^2(\Omega)$ every integer spin occurs exactly once. The $Y_{l,m}$ are therefore complete on $L^2(\Omega)$ and orthonormal,

$$\sum_{l=0}^{\infty} \sum_{m=-l}^{l} Y_{l,m}(\theta,\varphi) Y^*_{l,m}(\theta',\varphi') = \delta(\cos\theta - \cos\theta')\delta(\varphi - \varphi'), \tag{4.152}$$

$$\int Y^*_{l,m}(\theta,\varphi) Y_{l',m'}(\theta,\varphi)\, d\Omega = \delta_{ll'}\delta_{mm'}. \tag{4.153}$$

Radial wave equation: With these preliminaries we are ready to solve the stationary Schrödinger equation

$$\left[\frac{\boldsymbol{p}^2}{2m} + V(r)\right]\psi(\boldsymbol{r}) = E\psi(\boldsymbol{r}) \quad \overset{(4.135)}{\Rightarrow} \quad \left[-\frac{\hbar^2}{2mr}\frac{\partial^2}{\partial r^2} r + \frac{\boldsymbol{L}^2}{2mr^2} + V(r)\right]\psi(\boldsymbol{r}) = E\psi(\boldsymbol{r})$$

for a central-force problem. By rotational symmetry we switch to spherical coordinates and choose the separation ansatz

$$\psi(\boldsymbol{r}) = \frac{u(r)}{r} Y_{l,m}(\theta,\varphi), \qquad \boldsymbol{L}^2 Y_{l,m} = \hbar^2 l(l+1) Y_{l,m}\,. \tag{4.154}$$

The *radial wave function* $u(r)$ is defined for $r > 0$. It satisfies the normalization

$$\langle\psi|\psi\rangle = \int_0^\infty dr \int_\Omega d\Omega\, r^2 |\psi(\boldsymbol{r})|^2 = \int_0^\infty dr\, |u(r)|^2 \underbrace{\int_\Omega d\Omega\, |Y_{l,m}(\theta,\varphi)|^2}_{=1} = \int_0^\infty |u(r)|^2\, dr \tag{4.155}$$

and hence $u \in L^2([0,\infty[)$. Moreover $u(0) = 0$ (and thus $u \in \mathcal{H}_{\mathrm{HR}}$), since otherwise $\psi \propto r^{-1}$ for small r and $-\Delta\psi = 4\pi\delta^{(3)}(\boldsymbol{r})$.

Thus there remains the *radial problem*

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2} + \underbrace{\frac{\hbar^2 l(l+1)}{2m\, r^2} + V(r)}_{V_{\mathrm{eff}}(r)}\right] u(r) = E\, u(r) \tag{4.156}$$

of a particle in one dimension in the effective potential V_{eff} to solve. Only for $l = 0$ is $V_{\mathrm{eff}}(r) = V(r)$. Otherwise, in addition to $V(r)$ the repulsive centrifugal barrier acts on the particle, see Figure 4.2.

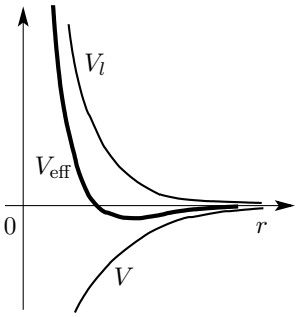


Fig. 4.2: The angular momentum generates the potential barrier $V_l = \hbar^2 l(l+1)/2mr^2$ and pushes the wave function away from the origin. The potential $V(r)$ combines with $V_l(r)$ to give the effective potential $V_{\text{eff}}(r)$.

4.7 The hydrogen atom

The hydrogen atom can be cast, with reduced mass and $V(r) = -e^2/r$, into the form (4.156).

2-body problem: We first review the separation of the center of mass: Let the Hamiltonian for two interacting particles of masses $m_{1,2}$ be given on $L^2(\mathbb{R}^6) = L^2(\mathbb{R}^3) \otimes L^2(\mathbb{R}^3)$ by

$$H = \frac{\boldsymbol{p}_1^2}{2m_1} + \frac{\boldsymbol{p}_2^2}{2m_2} + V(|\boldsymbol{r}_1 - \boldsymbol{r}_2|). \tag{4.157}$$

We switch to center-of-mass and relative coordinates $\boldsymbol{R}$ and $\boldsymbol{r}$,

$$\boldsymbol{r} = \boldsymbol{r}_1 - \boldsymbol{r}_2, \qquad \boldsymbol{R} = \frac{m_1\boldsymbol{r}_1 + m_2\boldsymbol{r}_2}{m_1 + m_2}; \tag{4.158}$$

and likewise for the (conjugate) momenta

$$\boldsymbol{p} = \frac{m_2\boldsymbol{p}_1 - m_1\boldsymbol{p}_2}{m_1 + m_2}, \qquad \boldsymbol{P} = \boldsymbol{p}_1 + \boldsymbol{p}_2. \tag{4.159}$$

We define the reduced and the total mass

$$\mu = \frac{m_1 m_2}{m_1 + m_2}, \qquad M = m_1 + m_2. \tag{4.160}$$

The chain rule states

$$\boldsymbol{\nabla}_{\boldsymbol{r}_1} = \frac{m_1}{M}\boldsymbol{\nabla}_{\boldsymbol{R}} + \boldsymbol{\nabla}_{\boldsymbol{r}}, \qquad \boldsymbol{\nabla}_{\boldsymbol{r}_2} = \frac{m_2}{M}\boldsymbol{\nabla}_{\boldsymbol{R}} - \boldsymbol{\nabla}_{\boldsymbol{r}}\,. \tag{4.161}$$

We obtain

$$\boldsymbol{p} = -\frac{i\hbar}{M}\left(m_2\boldsymbol{\nabla}_{\boldsymbol{r}_1} - m_1\boldsymbol{\nabla}_{\boldsymbol{r}_2}\right) = -i\hbar\boldsymbol{\nabla}_{\boldsymbol{r}}, \qquad \boldsymbol{P} = -i\hbar(\boldsymbol{\nabla}_{\boldsymbol{r}_1} + \boldsymbol{\nabla}_{\boldsymbol{r}_2}) = -i\hbar\boldsymbol{\nabla}_{\boldsymbol{R}}\,. \tag{4.162}$$

As desired, $\boldsymbol{P}$ and $\boldsymbol{p}$ are the conjugate momenta to $\boldsymbol{R}$ and $\boldsymbol{r}$. In relative and center-of-mass coordinates the Hamiltonian takes the form

$$H = \frac{\boldsymbol{P}^2}{2M} + \frac{\boldsymbol{p}^2}{2\mu} + V(r)\,. \tag{4.163}$$

The Hamiltonian H allows the separation

$$\psi(\boldsymbol{R}, \boldsymbol{r}) = \phi(\boldsymbol{R}) \otimes \psi(\boldsymbol{r}) \tag{4.164}$$

into center-of-mass and relative motion. This yields two independent Schrödinger equations

$$\frac{\boldsymbol{P}^2}{2M}\phi(\boldsymbol{R}) = E_S\phi(\boldsymbol{R}) \quad \text{and} \quad \left[\frac{\boldsymbol{p}^2}{2\mu} + V(r)\right]\psi(\boldsymbol{r}) = E\psi(\boldsymbol{r}) \tag{4.165}$$

with total energy $E_S + E$. The first equation describes the free motion of the center of mass (cf. Chapter 2.6), the second the relative motion. We have already studied the center-of-mass motion. The relative motion is a central-force problem in the potential $V(r)$.

Hydrogen atom: The relative problem (we use that $\mu \approx m = m_e$, since $m_p \gg m_e$ for the hydrogen problem) is a centrally symmetric problem with the Coulomb potential $V(r) = -Ze^2/r$. Here $Z = 1$ is the nuclear charge number. The radial problem for fixed angular momentum $\hbar l$ is given by (*hydrogen problem*)

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \frac{\hbar^2 l(l+1)}{2mr^2} - \frac{Ze^2}{r}\right]u(r) = Eu(r). \tag{4.166}$$

It is convenient to express energy and length in terms of a_B and E_R, see (1.32) and (1.33). Since we are interested in bound states with $E < 0$, we set

$$E = -\frac{Z^2 E_R}{n^2} = -\frac{Z^2 me^4}{2\hbar^2 n^2}, \qquad r = \frac{na_B}{2Z}x = \frac{n\hbar^2 x}{2Zme^2}, \tag{4.167}$$

where x denotes the (dimensionless) position and n the (dimensionless) energy. So far we have imposed no quantization condition and hence all energies $n \geq 0$ are allowed. Later we will see that n must be a natural number.

We write the radial wave function (on the Hilbert space $\mathcal{H}_{\text{HR}}$) as

$$u(r) = \sqrt{\frac{2Z}{na_B}}\, f(x), \tag{4.168}$$

where the prefactor ensures that $f(x)$ is normalized to 1 if and only if $u(r)$ is normalized. In the new variables the equation (4.166) becomes

$$\underbrace{\left[-x\frac{d^2}{dx^2} + \frac{l(l+1)}{x} + \frac{x}{4}\right]}_{=N} f(x) = nf(x)\,. \tag{4.169}$$

The hydrogen problem is thus equivalent to finding the eigenstates $f_n(x)$ and eigenvalues n of the operator N. Note that N is not Hermitian owing to the transformation from u to f; see also footnote 16.

We proceed analogously to the harmonic oscillator and introduce the operators N_+ (creation operator) and N_- (annihilation operator) with

$$N_\pm = \pm x\frac{d}{dx} - \frac{x}{2} + N\,. \tag{4.170}$$

The relevant commutators are [cf. (3.122) and (3.123)]

$$[N, N_\pm] = \pm\underbrace{[N, x\partial_x]}_{=-\frac{x}{2}+N} - \underbrace{[N, \tfrac{1}{2}x]}_{=-x\partial_x} = \pm N_\pm\,. \tag{4.171}$$

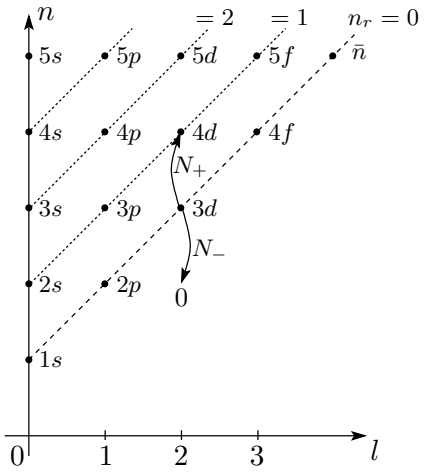


Fig. 4.3: Quantum numbers (n, l) of the hydrogen problem. The angular momenta for $l = 0, 1, 2, 3$ are conventionally denoted by s, p, d, f. The operator N_+ (N_-) raises (lowers) n at fixed l. The absolute ground state is at $(1, 0)$. The degeneracy is n^2.

Starting from an eigenstate $|n\rangle$ of N with eigenvalue n we have

$$NN_+|n\rangle = \big([N, N_+] + N_+N\big)|n\rangle = N_+|n\rangle + N_+N|n\rangle = (n+1)N_+|n\rangle\,. \tag{4.172}$$

Hence $N_+|n\rangle \propto |n+1\rangle$. Analogously one finds $N_-|n\rangle \propto |n-1\rangle$. The spectrum of N is bounded from below and the ladder $|n\rangle \overset{N_-}{\mapsto} |n-1\rangle \cdots$ must terminate.[15] Denoting the eigenvalue of the last state by $\bar{n}$, this implies

$$0 = N_- f_{\bar{n}}(x) = \left[-x\frac{d}{dx} - \frac{x}{2} + N\right] f_{\bar{n}}(x) = \left[-x\frac{d}{dx} - \frac{x}{2} + \bar{n}\right] f_{\bar{n}}(x) \tag{4.173}$$

with the general solution (c is the normalization constant)

$$f_{\bar{n}}(x) = c\, g_{\bar{n}}(x), \quad g_{\bar{n}}(x) = x^{\bar{n}} e^{-x/2}\,. \tag{4.174}$$

In the following we denote the unnormalized eigenstates by g to distinguish them from the normalized states f. We still need to ensure that $g_{\bar{n}}$ is indeed an eigenstate of N with eigenvalue $\bar{n}$. A direct calculation shows

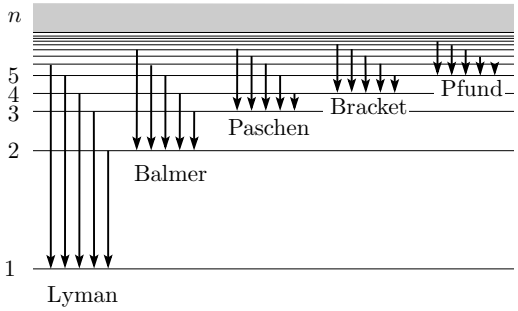
$$Ng_{\bar{n}} = \left[-x\frac{d^2}{dx^2} + \frac{l(l+1)}{x} + \frac{x}{4}\right] g_{\bar{n}} = \bar{n} g_{\bar{n}} + \frac{l(l+1) - \bar{n}(\bar{n}-1)}{x} g_{\bar{n}}\,. \tag{4.175}$$

For an eigenstate the last term must vanish. Hence $\bar{n} = l + 1$. The second solution with $\bar{n} = -l$ must be discarded because it is not normalizable.

Thus we have determined the spectrum: for a fixed angular momentum l, the ground state of the hydrogen atom is the eigenfunction g_{l+1} with energy $-Z^2 E_R/(l+1)^2$. The absolute ground state is the state with $(n, l) = (1, 0)$. Starting from the states g_{l+1} with quantum numbers $(n, l) = (l+1, l)$, the remainder of the spectrum can be obtained by applying N_+, see Figure 4.3. Here N_+ increases the quantum number n by 1 in each case. The spectrum, given by

$$E_{n,l} = E_n = -\frac{Z^2 E_R}{n^2}, \qquad n = 1, 2, 3, \ldots \quad \text{(principal quantum number)}, \tag{4.176}$$

[15] For a formal proof one simply shows that $(f, Nf) \geq 0$ with f can be made arbitrarily small.



Final level n	Name	Energy range
$n=1$	Lyman	UV
$n=2$	Balmer	visible
$n=3$	Paschen	IR
$n=4$	Brackett	IR
$n=5$	Pfund	IR

Fig. 4.4: Transitions in the hydrogen atom: Lyman, Balmer, Paschen, Brackett, and Pfund series. The Lyman series lies in the ultraviolet (UV) region with energies greater than 10 eV; the Balmer series lies in the visible region with energies in the range greater than 1.9 eV (red, cyan, violet); the Paschen series lies in the infrared (IR) region with energies greater than 0.65 eV.

, thus does not depend on l.

The eigenvalues E_n occur with the degeneracies

$$D_n = \sum_{l=0}^{n-1} \underbrace{(2l+1)}_{\sum_m} = n^2 \tag{4.177}$$

The quantum numbers n, l, m are called principal quantum number n, orbital or azimuthal quantum number l, and magnetic quantum number m. The additional degeneracy in l is a consequence of the fact that the mechanical orbits in the Coulomb potential are closed. When spin is taken into account, the degeneracy doubles to $D_n = 2n^2$. The optical selection rules require that for the transitions $\Delta l = 1$ holds. They belong to one of the series in Figure 4.4.

For the state $g_{n,l}$ ($n \geq l+1$) one must apply N_+ a total of n_r times to g_{l+1} ($n_r = n-l-1$ is the radial quantum number). The unnormalized eigenstates corresponding to the eigenvalue n are therefore given by

$$g_{n,l}(x) = N_+^{n_r}(x^{l+1}e^{-x/2}), \qquad \text{with } N g_{n,l}(x) = n g_{n,l}(x)\,. \tag{4.178}$$

The state $g_{l+1}(x) = x^{l+1}e^{-x/2}$ corresponds, at fixed $n = l+1$, to the state with the highest angular momentum. The wave function has its maximum at $\bar{x} = 2n$. With

$$\ln g_{n,n-1}(x) = \ln g_{l+1}(x) = \ln g_{l+1}(\bar{x}) - \frac{(x-\bar{x})^2}{8n} + O(x-\bar{x})^3 \tag{4.179}$$

we obtain that the typical extension ξ is given by $\xi = 2n^{1/2}$. For large l the particle is therefore relatively sharply localized ($\xi \ll \bar{x}$). In the state $g_{n,n-1}$ the particle thus executes a "circular orbit" of radius $\bar{r} \simeq n a_B \bar{x}/Z \simeq n^2 a_B/Z$, cf. (1.32).

We have so far determined the spectrum and obtained the eigenfunctions up to normalization. In the following calculation we determine the normalization with the result (4.186). As before we will work at fixed l and hence suppress the index l. We require the relations

$$N_- N_+ = N(N+1) - l(l+1) \qquad \text{and} \qquad x = 2N - N_+ - N_-\,. \tag{4.180}$$

The natural scalar product of the problem is

$$(f,g) = \int_0^\infty \frac{f^*(x)g(x)}{x}\,dx, \qquad \langle f|g\rangle = (f,xg), \qquad \text{with } f,g \in \mathcal{H}_{\rm HR}\,. \tag{4.181}$$

With respect to this scalar product N_- and N_+ are mutually adjoint operators satisfying $(N_+f,g) = (f,N_-g)$. Moreover N is Hermitian with respect to $(\cdot,\cdot)$, so that the eigenfunctions g_n are orthogonal with $(g_n,g_m) = 0$, $n \neq m$.[16]

We first compute the normalization of g_n with respect to $(\cdot,\cdot)$. We find the recursion relation

$$(g_{n+1},g_{n+1}) = (N_+g_n, N_+g_n) = (g_n, N_-N_+g_n) = \underbrace{[n(n+1) - l(l+1)]}_{=(n-l)(n+l+1)=c_n}(g_n,g_n)\,. \tag{4.182}$$

At $n_r = 0$ we have $g_{\bar n}(x) = x^{l+1}e^{-x/2}$ ($\bar n = l+1$) with the normalization

$$(g_{\bar n}, g_{\bar n}) = \int_0^\infty x^{2l+1}e^{-x}\,dx = (2l+1)!\,. \tag{4.183}$$

From this it follows that

$$(g_n,g_n) = c_{n-1}\,(g_{n-1},g_{n-1}) = c_{n-1}\cdots c_{\bar n}\,(2l+1)! = n_r!\,(n+l)!\,. \tag{4.184}$$

The normalization with respect to the standard scalar product is then obtained via

$$\begin{aligned}\langle g_n|g_n\rangle = (g_n,xg_n) &= 2(g_n,Ng_n) - \underbrace{(g_n,\overbrace{N_+g_n}^{=g_{n+1}})}_{=0} - \underbrace{(g_n,N_-g_n)}_{=(N_+g_n,g_n)=0} = 2n(g_n,g_n)\\ &= 2n\,n_r!\,(n+l)!\,.\end{aligned} \tag{4.185}$$

Thus we have shown that the normalized radial functions of the hydrogen atom are given by

$$f_{n,l}(x) = \frac{1}{\sqrt{2n\,n_r!\,(n+l)!}}g_{n,l}(x) = \sqrt{\frac{(n-l-1)!}{2n(n+l)!}}\,x^{l+1}L_{n-l-1}^{(2l+1)}(x)\,e^{-x/2} \tag{4.186}$$

with

$$L_{n_r}^{(2l+1)}(x) = \frac{1}{n_r!}x^{-(l+1)}e^{x/2}N_+^{n_r}(x^{l+1}e^{-x/2}) \tag{4.187}$$

the associated Laguerre polynomials of degree n_r.

We thereby obtain the (normalized) eigenstates of the hydrogen problem

$$\psi_{n,l,m}(\boldsymbol{r}) = \sqrt{\frac{2Z}{na_B}}\,\frac{f_{n,l}(2Zr/na_B)}{r}Y_{l,m}(\theta,\varphi) \tag{4.188}$$

corresponding to the eigenvalues

$$E_n = -\frac{Z^2E_R}{n^2}\,. \tag{4.189}$$

[16] The states f_n (and g_n) are *not* orthogonal with respect to $\langle\cdot|\cdot\rangle$. This is the reason why the normalization is so tricky. The states $u(r)$ are, however, again orthogonal with $\langle u_m|u_n\rangle = 0$, $m \neq n$. It holds $\langle f_m|f_n\rangle \neq \langle u_m|u_n\rangle$ because the transformation $x \mapsto r$ depends on n!

Chapter 5

Approximation Methods

The fewest problems are exactly solvable, and we must resort to approximative solution methods. The following approaches are available:

1) Approximating the problem by an exactly solvable one.
2) Numerical solution via computer – this strategy yields precise numbers, but often contributes little to understanding.
3) Variational approach: search within a family of solutions for the best one – this requires some understanding of the solution (for the ansatz).
4) Perturbation theory: systematic improvement of the solution.

We have presented some exact solutions in the preceding chapters. Many problems can be reduced to the harmonic oscillator. Point 2) is treated in other lectures. We begin with the variational approach. Perturbation theory is discussed in Chapter 5.2. Note that the WKB approximation from Chapter 2.9 also yields very good results for large quantum numbers.

5.1 Variational Principle

Variational calculus is based on the Rayleigh-Ritz *variational principle*. Let ψ be an arbitrary state ($\|\psi\| = 1$), H a Hamiltonian with ground-state energy E_1; then

$$\langle\psi|H|\psi\rangle \geq E_1 \,. \tag{5.1}$$

In words, "The ground-state energy is the smallest expectation value of the energy." To prove this, we introduce the complete eigenbasis ψ_n of H.[1] We obtain

$$\begin{aligned} \langle\psi|H|\psi\rangle &= \sum_n \langle\psi|n\rangle \underbrace{\langle n|H|n\rangle}_{E_n \geq E_1} \langle n|\psi\rangle \\ &\geq E_1 \,. \end{aligned} \tag{5.2}$$

This equation allows us to obtain an *upper* bound on the ground-state energy. The Rayleigh-Ritz principle also permits estimation of excited states. If the ground state ψ_1 is known,

[1] For simplicity we assume that H has a discrete spectrum.

then the smallest expectation value of the energy in a state $\psi^\perp$ orthogonal to $\langle\psi_1|\psi^\perp\rangle = 0$ gives the first excited state. For nondegenerate problems the principle can be iterated.

In general the *min-max principle* holds:

$$E_n = \min_{\dim M = n} \max_{\psi \in M} \langle\psi|H|\psi\rangle \tag{5.3}$$

where the minimum is taken over all subspaces M of dimension n and it is always assumed that $\|\psi\| = 1$.

Further, symmetries can also be exploited. Let $\mathsf{SO}(3)$ be a symmetry of H. Applying the Rayleigh-Ritz principle in the subspaces $\mathcal{H}_l$ for angular momentum $\boldsymbol{L}^2 = \hbar^2 l(l+1)$ yields a bound for the lowest energy with angular momentum $\hbar^2 l(l+1)$.

We can also obtain *lower* bounds, but this is in general much more difficult. With $H \geq H^{(0)}$ and $H^{(0)}$ solvable with the eigenenergies $E_n^{(0)}$, we obtain from the min-max principle[2] the lower bound

$$E_n \geq E_n^{(0)}, \qquad n = 1, 2, \ldots \tag{5.4}$$

Example: Helium atom The helium atom consists of a nucleus with two electrons, whose interaction we treat as a perturbation. We consider only the electronic degrees of freedom and describe the two-particle problem of the electrons in the field of the nucleus ($Z = 2$). The Hamiltonian $H = H^{(0)} + H^{(1)}$ on $\mathcal{H} = L^2(\mathbb{R}^3) \otimes L^2(\mathbb{R}^3)$ is given by

$$H^{(0)} = -\frac{\hbar^2}{2m}(\Delta_1 + \Delta_2) - 2e^2\left(\frac{1}{r_1} + \frac{1}{r_2}\right), \qquad H^{(1)} = \frac{e^2}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|}. \tag{5.5}$$

The Hamiltonian H commutes with the exchange symmetry

$$V\colon \psi(\boldsymbol{r}_1, \boldsymbol{r}_2) \mapsto \psi(\boldsymbol{r}_2, \boldsymbol{r}_1)\,. \tag{5.6}$$

We may therefore diagonalize H separately in the two eigenspaces of V

$$\begin{aligned} \mathcal{H}^+ &= \{\psi \in \mathcal{H} : V\psi = \psi\} && (\psi \text{ symmetric}), \\ \mathcal{H}^- &= \{\psi \in \mathcal{H} : V\psi = -\psi\} && (\psi \text{ antisymmetric}) \end{aligned} \tag{5.7}$$

The discrete spectrum of $H^{(0)}$ is given by ("twice" hydrogen problem, see Figure 5.1)

$$E_n^{(0)} = -4E_R\left(1 + \frac{1}{n^2}\right) \tag{5.8}$$

with the eigenfunctions

$$\begin{aligned} \psi^+_{1,0,0}(\boldsymbol{r}_1, \boldsymbol{r}_2) &= \psi_{1,0,0}(\boldsymbol{r}_1) \otimes \psi_{1,0,0}(\boldsymbol{r}_2) \\ \psi^\pm_{n,l,m}(\boldsymbol{r}_1, \boldsymbol{r}_2) &= \frac{1}{\sqrt{2}}\left[\psi_{n,l,m}(\boldsymbol{r}_1) \otimes \psi_{1,0,0}(\boldsymbol{r}_2) \pm \psi_{1,0,0}(\boldsymbol{r}_1) \otimes \psi_{n,l,m}(\boldsymbol{r}_2)\right] \end{aligned} \tag{5.9}$$

with $\psi_{n,l,m}$ from (4.188) ($Z = 2$ for the He^{++} ion). Here we consider only states below the continuum at $-4E_R$, where one electron is free and the helium is ionized to He^+.

We will later learn the Pauli principle. The symmetry of the orbital wave function ψ implies a symmetry of the spin wave function $\chi_{s,m} = |s, m\rangle$. States from $\mathcal{H}^+$ occur with the singlet

[2] The expression $A \geq B$ for two Hermitian operators A, B means that $\langle\psi|A|\psi\rangle \geq \langle\psi|B|\psi\rangle$ for all states ψ.

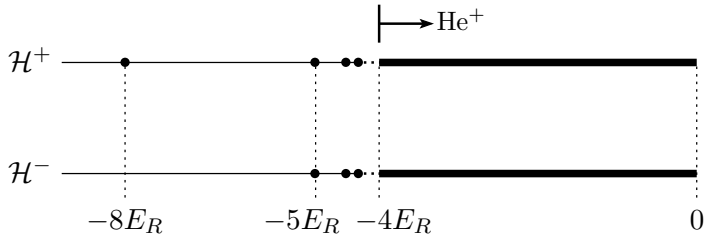


Fig. 5.1: Spectrum of the helium atom without interaction. The ground state is in the sector $\mathcal{H}^+$ at energy $-8E_R$. The ionization limit is at $-4E_R$.

wave function ($s = 0$) (*parahelium*), whereas states from $\mathcal{H}^-$ (*orthohelium*) are threefold spin-degenerate and occur with the triplet wave function ($s = 1$).

The ground state of the helium atom actually has the structure

$$\psi(\boldsymbol{r}_1, m_1; \boldsymbol{r}_2, m_2) = \psi^+_{1,0,0}(\boldsymbol{r}_1, \boldsymbol{r}_2) \otimes \chi_{0,0}(m_1, m_2), \tag{5.10}$$

where $m_j = \pm$ are the spin quantum numbers.

Under the influence of the positive perturbation $H^{(1)}$ the eigenvalues (5.8) are shifted upward. The ionization limit $-4E_R$ (second ionization energy), however, remains unchanged, since the ground state of He^+ is unaffected by the electron-electron repulsion.

The ground state in the hydrogen atom has the form

$$\psi_{1,0,0}(\boldsymbol{r}_1) = \frac{1}{\sqrt{\pi a_B^3}} e^{-r/a_B}\,. \tag{5.11}$$

For the helium ground state we make the variational ansatz

$$\psi^+(\boldsymbol{r}_1, \boldsymbol{r}_2) = f(r_1) f(r_2), \qquad f(r) = \sqrt{\frac{\alpha^3}{\pi a_B^3}} e^{-\alpha r/a_B} \tag{5.12}$$

with the variational parameter $\alpha > 0$.

We must compute the expectation value $\langle \psi^+ | H | \psi^+ \rangle$. We obtain

$$\begin{aligned} \langle \Delta_1 \rangle = \langle \Delta_2 \rangle &= -\int (\boldsymbol{\nabla} f)^2 \, dV = -4\pi \int_0^\infty r^2 |f'(r)|^2 \, dr = -\frac{\alpha^2}{a_B^2}, \\ \langle r_1^{-1} \rangle = \langle r_2^{-1} \rangle &= 4\pi \int_0^\infty r |f(r)|^2 \, dr = \frac{\alpha}{a_B}, \end{aligned} \tag{5.13}$$

$$\begin{aligned} \left\langle \frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \right\rangle &= 2 \int d^3 r_1 \, f(r_1)^2 \int_{r_2 \le r_1} d^3 r_2 \, \frac{f(r_2)^2}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} = 2 \int d^3 r_1 \, \frac{4\pi f(r_1)^2}{r_1} \int_0^{r_1} dr_2 \, r_2^2 f(r_2)^2 \\ &= \frac{\alpha}{a_B} \int_0^\infty dx \, x \, e^{-x} \int_0^x dy \, y^2 \, e^{-y} = \frac{5\alpha}{8 a_B}\,. \end{aligned} \tag{5.14}$$

For the calculation of the interaction energy we have used in the first line that the Coulomb potential of a spherically symmetric charge distribution is, outside the distribution, the same as if the entire charge were located at the center.

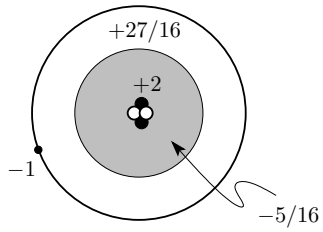


Fig. 5.2: Screening: the second electron (charge −1) moves in the average field of the nucleus (charge +2) and of the first electron (effective screening charge −5/16); hence an effective charge 27/16 acts on the second electron.

We thereby find the result ($E_R = e^2/2a_B$)

$$\langle H^{(0)}\rangle = 2E_R(\alpha^2 - 4\alpha) \qquad \text{and} \qquad \langle H^{(1)}\rangle = 2E_R\frac{5}{8}\alpha\,. \tag{5.15}$$

The total energy is minimized by $\alpha = \frac{27}{16}$. Hence we obtain the following upper bound

$$E_1 \leq -2E_R\left(\frac{27}{16}\right)^2 \approx -5.695E_R\,. \tag{5.16}$$

for the ground-state energy. This result is very close to the measured value $E_1 \approx -5.807E_R$. Without interaction we would obtain the value $\alpha = 2$ (minimum of $H^{(0)}$), since the charge $Z = 2$. The optimum, however, lies at $\alpha = 27/16 \leq 2$. Each electron screens the nucleus for the other electron with an effective charge 5/16, as illustrated in Figure 5.2.

5.2 Perturbation Theory

Perturbation analysis depends strongly on the problem: we distinguish stationary from time-dependent problems and focus on discrete spectra. In the simplest case a non-degenerate spectrum is present—we therefore treat first the stationary, non-degenerate case and then analyze degenerate eigenvalues. Time-dependent problems with Fermi's Golden Rule conclude the discussion.

Stationary, non-degenerate case

Consider the stationary Schrödinger equation

$$H|n\rangle = (H^{(0)} + \varepsilon H^{(1)})|n\rangle = E_n|n\rangle. \tag{5.17}$$

with ε a small parameter and $H^{(0)}$ sufficiently simple that one knows $|n^{(0)}\rangle$ and $E_n^{(0)}$ with

$$H^{(0)}|n^{(0)}\rangle = E_n^{(0)}|n^{(0)}\rangle \tag{5.18}$$

. For simplicity we assume that $H^{(0)}$ has only a discrete spectrum, so that the completeness relation takes the form

$$\sum_n |n^{(0)}\rangle\langle n^{(0)}| = 1 \tag{5.19}$$

For the eigenstates $|n\rangle$ and the eigenenergies E_n we insert the power series

$$|n\rangle = |n^{(0)}\rangle + \varepsilon|n^{(1)}\rangle + \varepsilon^2|n^{(2)}\rangle + \cdots\,, \qquad E_n = E_n^{(0)} + \varepsilon E_n^{(1)} + \varepsilon^2 E_n^{(2)} + \ldots \tag{5.20}$$

Note that such a power series need not always converge. Assuming that the series converges for small ε, we may substitute the power series into (5.17) and collect terms by order in ε. We obtain ($k \geq 1$)

$$\begin{aligned}
\varepsilon^0: &\quad H^{(0)}|n^{(0)}\rangle &&= E_n^{(0)}|n^{(0)}\rangle, \\
\varepsilon^1: &\quad H^{(0)}|n^{(1)}\rangle + H^{(1)}|n^{(0)}\rangle &&= E_n^{(0)}|n^{(1)}\rangle + E_n^{(1)}|n^{(0)}\rangle, \\
&\qquad\qquad\qquad\qquad \vdots \\
\varepsilon^k: &\quad H^{(0)}|n^{(k)}\rangle + H^{(1)}|n^{(k-1)}\rangle &&= E_n^{(0)}|n^{(k)}\rangle + E_n^{(1)}|n^{(k-1)}\rangle + \cdots + E_n^{(k)}|n^{(0)}\rangle\,.
\end{aligned} \tag{5.21}$$

It is convenient to normalize the desired wave function $|n\rangle$ (for the moment) unconventionally to

$$\langle n^{(0)}|n\rangle = 1 \tag{5.22}$$

so that $\langle n^{(0)}|n^{(k)}\rangle = 0$ for $k \geq 1$ holds.

We take the scalar product of (5.21) with $|n^{(0)}\rangle$ and obtain the relation

$$\langle n^{(0)}|H^{(1)}|n^{(k-1)}\rangle = E_n^{(k)} \tag{5.23}$$

between the wave function in the $k-1$ order and the energy in the k-th order.

We thus need only compute the perturbation of the wave function. To do so we will require the assumption that the spectrum is non-degenerate. We now consider the scalar product of (5.21) with $|m^{(0)}\rangle$ ($m \neq n$)

$$E_m^{(0)}\langle m^{(0)}|n^{(k)}\rangle + \langle m^{(0)}|H^{(1)}|n^{(k-1)}\rangle = E_n^{(0)}\langle m^{(0)}|n^{(k)}\rangle + \cdots + E_n^{(k-1)}\langle m^{(0)}|n^{(1)}\rangle\,. \tag{5.24}$$

From $m \neq n$ it follows $E_m^{(0)} \neq E_n^{(0)}$ (non-degenerate spectrum) and we obtain recursively the components

$$\langle m^{(0)}|n^{(k)}\rangle = \frac{1}{E_n^{(0)} - E_m^{(0)}}\left[\langle m^{(0)}|H^{(1)}|n^{(k-1)}\rangle - E_n^{(1)}\langle m^{(0)}|n^{(k-1)}\rangle - \cdots - E_n^{(k-1)}\langle m^{(0)}|n^{(1)}\rangle\right] \tag{5.25}$$

of the perturbed wave function (the term $m = n$ does not contribute because of the normalization)

$$|n^{(k)}\rangle = \sum_{m;m\neq n} \langle m^{(0)}|n^{(k)}\rangle\,|m^{(0)}\rangle\,. \tag{5.26}$$

One now solves (5.23), (5.25), and (5.26) iteratively.

We state explicitly the results for $k \leq 2$, using the notation $|\mathrm{n}\rangle = |n^{(0)}\rangle$ and $\mathrm{E}_n = E_n^{(0)}$:

$$\varepsilon^0 \colon \begin{cases} E_n^{(0)} = \mathrm{E}_n \\ |n^{(0)}\rangle = |\mathrm{n}\rangle. \end{cases} \tag{5.27}$$

$$\varepsilon^1 \colon \begin{cases} E_n^{(1)} = \langle \mathrm{n}|H^{(1)}|\mathrm{n}\rangle, \\ |n^{(1)}\rangle = \displaystyle\sum_{m\neq n} \frac{\langle \mathrm{m}|H^{(1)}|\mathrm{n}\rangle}{\mathrm{E}_n - \mathrm{E}_m}\, |\mathrm{m}\rangle. \end{cases} \tag{5.28}$$

$$\varepsilon^2 \colon \begin{cases} E_n^{(2)} = \displaystyle\sum_{m\neq n} \frac{|\langle \mathrm{m}|H^{(1)}|\mathrm{n}\rangle|^2}{\mathrm{E}_n - \mathrm{E}_m}, \\ |n^{(2)}\rangle = \displaystyle\sum_{m\neq n} \left[\sum_{l\neq n} \frac{\langle \mathrm{m}|H^{(1)}|\mathrm{l}\rangle\langle \mathrm{l}|H^{(1)}|\mathrm{n}\rangle}{(\mathrm{E}_n - \mathrm{E}_m)(\mathrm{E}_n - \mathrm{E}_l)} - \frac{\langle \mathrm{m}|H^{(1)}|\mathrm{n}\rangle\langle \mathrm{n}|H^{(1)}|\mathrm{n}\rangle}{(\mathrm{E}_n - \mathrm{E}_m)^2} \right] |\mathrm{m}\rangle. \end{cases} \tag{5.29}$$

Note that the ground-state energy in second-order perturbation theory is always lowered.

The Hellmann-Feynman Theorem: Let $|\bar{n}\rangle$ be the normalized eigenstate of H corresponding to the eigenvalue E_n (for the relation between $|\bar{n}\rangle$ and $|n\rangle$ see below). The *Hellmann-Feynman Theorem* states that

$$\frac{\partial E_n}{\partial \varepsilon} = \left\langle \bar{n} \middle| \frac{\partial H}{\partial \varepsilon} \middle| \bar{n} \right\rangle = \langle \bar{n}|H^{(1)}|\bar{n}\rangle\,. \tag{5.30}$$

It thereby provides a relation between the diagonal matrix elements of the perturbation operator and the derivative of the energy. It holds in particular nonperturbatively, i.e., for finite ε. For $\varepsilon = 0$ it simply reduces to the first-order statement (5.28) of first-order perturbation theory.

To prove this we apply $\partial/\partial\varepsilon$ to the Schrödinger equation (5.17) and obtain

$$H^{(1)}|\bar{n}\rangle + H\frac{\partial}{\partial\epsilon}|\bar{n}\rangle = \frac{\partial E_n}{\partial\varepsilon}|\bar{n}\rangle + E_n\frac{\partial}{\partial\epsilon}|\bar{n}\rangle\,. \tag{5.31}$$

Taking the scalar product with $|\bar{n}\rangle$ yields the theorem.

Renormalization: It remains to determine the constant Z by

$$|\bar{n}\rangle = Z^{1/2}|n\rangle \tag{5.32}$$

so that $\langle\bar{n}|\bar{n}\rangle = 1$ is correctly normalized. The factor Z is called the *renormalization of the wave function*. Of course one also has $Z = |\langle n^{(0)}|\bar{n}\rangle|^2$. Thus Z gives the probability that a particle, which is in the eigenstate $|\bar{n}\rangle$ of H, is measured in the unperturbed state $|n^{(0)}\rangle$ of $H^{(0)}$.

We regard $H^{(0)}$ as a function of the unperturbed energies $E_n^{(0)}$ at fixed $H^{(1)}$. Then

$$\frac{\partial H}{\partial E_n^{(0)}} = \sum_m \underbrace{\frac{\partial E_m^{(0)}}{\partial E_n^{(0)}}}_{\delta_{mn}} |m^{(0)}\rangle\langle m^{(0)}| + \epsilon \underbrace{\frac{\partial H^{(1)}}{\partial E_n^{(0)}}}_{=0} = |n^{(0)}\rangle\langle n^{(0)}| \tag{5.33}$$

is the projector onto the unperturbed state. From the Hellmann-Feynman Theorem we thereby obtain the renormalization factor[3]

$$\frac{\partial E_n}{\partial E_n^{(0)}} = \langle \bar{n}|n^{(0)}\rangle\langle n^{(0)}|\bar{n}\rangle = Z\,. \tag{5.34}$$

To second order this takes the form

$$Z = \frac{\partial\left[E_n^{(0)} + \varepsilon E_n^{(1)} + \varepsilon^2 E_n^{(2)}\right]}{\partial E_n^{(0)}} = 1 - \varepsilon^2 \sum_{m\neq n} \frac{|\langle \mathrm{m}|H^{(1)}|\mathrm{n}\rangle|^2}{(\mathrm{E}_n - \mathrm{E}_m)^2}. \tag{5.35}$$

The factor Z plays an important role in the renormalization of quantum field theory.

Stationary, Degenerate Case

The problem of degeneracy appears in (5.25). The energy denominator $E_n^{(0} - E_m^{(0)}$ vanishes when $|n^{(0)}\rangle$ and $|m^{(0)}\rangle$ share the same energy. Perturbation theory is essentially an expansion in $\varepsilon\,\langle m^{(0)}|H^{(1)}|n^{(0)}\rangle/(E_n^{(0)} - E_m^{(0)})$ for $m \neq n$. As soon as the energy denominator becomes small compared to $\langle m^{(0)}|H^{(1)}|n^{(0)}\rangle$ the radius of convergence is suppressed.

In the degenerate case we label the states at energy $E_n^{(0)}$ by $|n_1^{(0)}\rangle, |n_2^{(0)}\rangle, \ldots, |n_k^{(0)}\rangle$ with k the degree of degeneracy of the energy level. The problem is that in the degenerate subspace $H^{(0)}$ no distinguished basis is fixed. We must therefore find linear combinations so that the problem of small energy denominators does not arise. This is the case precisely when $H^{(1)}$ is fully diagonal.

Hence we project the perturbation onto the subspace and obtain the $k \times k$ matrix

$$V = \begin{pmatrix} \langle n_1^{(0)}|H^{(1)}|n_1^{(0)}\rangle & \cdots & \langle n_1^{(0)}|H^{(1)}|n_k^{(0)}\rangle \\ \vdots & \ddots & \vdots \\ \langle n_k^{(0)}|H^{(1)}|n_1^{(0)}\rangle & \cdots & \langle n_k^{(0)}|H^{(1)}|n_k^{(0)}\rangle \end{pmatrix}. \tag{5.36}$$

Since the Hamiltonian $H^{(0)}$ on the subspace is proportional to the identity, V provides the leading order and fixes the "eigen-directions." We diagonalize the Hermitian matrix

$$V = U \underbrace{\mathrm{diag}(E_1^{(1)}, \ldots, E_k^{(1)})}_{=\tilde{V}} U^\dagger \tag{5.37}$$

by a unitary transformation U. This yields the new basis

$$|\tilde{n}_j^{(0)}\rangle = \sum_{m=1}^{k} U_{mj}|n_m^{(0)}\rangle \tag{5.38}$$

in which V is diagonal. The eigenvalues $E_j^{(1)}$ give, according to (5.28), the energy corrections to order ε. We now carry out perturbation theory in the basis in which $|n_m^{(0)}\rangle$ is replaced by $|\tilde{n}_j^{(0)}\rangle$. Since $\tilde{V}$ is a diagonal matrix in the degenerate subspace, no problems with energy denominators arise, and the formulas (5.28), (5.29) and also the analogous formulas for higher orders can be used directly. To do so one simply restricts the summations further so that $\sum_{m\neq n} \mapsto \sum_{m\neq n_1,\cdots,n_k}$ excludes all terms in the subspace of equal energy.

[3]The first equality sign in (5.30) holds for the derivative with respect to an arbitrary parameter.

Examples

Stark effect in the hydrogen atom: We study the perturbation of the level $n = 2$ of the hydrogen atom with

$$H^{(0)} = \frac{\boldsymbol{p}^2}{2m} - \frac{e^2}{r} \tag{5.39}$$

by a homogeneous electric field $\boldsymbol{\mathcal{E}} = \mathcal{E}\boldsymbol{e}_3$ with the dipole interaction

$$H^{(1)} = e\,\boldsymbol{\mathcal{E}} \cdot \boldsymbol{r} = e\mathcal{E}r_3\,. \tag{5.40}$$

We are interested in weak electric fields, so $\mathcal{E}$ plays the role of the perturbation parameter ε.

The energy level $E_2 = -E_R/4$ of $H^{(0)}$ is 4-fold degenerate with the states

$$\psi_{2,l,m}(r,\theta,\varphi) = \frac{1}{\sqrt{a_B}}\frac{f_{2,l}(r/a_B)}{r}Y_{l,m}(\theta,\varphi)\,. \tag{5.41}$$

For degenerate perturbation theory we need the matrix elements

$$V_{l'm',lm} = \langle 2,l',m'|r_3|2,l,m\rangle \tag{5.42}$$

The perturbation operator r_3 is the $m = 0$ component of the tensor operator $r^{(1)}_m$ of rank 1, see (4.121). From the Wigner-Eckart theorem follows the selection rule $\Delta m = 0$, $\Delta l = 0, \pm 1$. The parity selection rule requires $\Delta l = \pm 1$. Hence the perturbation matrix takes the form (we label the states by nl_m)

$$V = \begin{array}{c} \begin{array}{cccc} 2s_0 & 2p_0 & 2p_1 & 2p_{-1} \end{array} \\ \begin{pmatrix} 0 & \delta & 0 & 0 \\ \delta^* & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \end{array} \begin{array}{l} 2s_0 \\ 2p_0 \\ 2p_1 \\ 2p_{-1} \end{array} \tag{5.43}$$

with the remaining matrix element

$$\begin{aligned} \delta = \langle 2s_0|H^{(1)}|2p_0\rangle &= a_B e E \overbrace{\int_0^\infty dx\, f_{2,0}(x) x f_{2,1}(x)}^{=-3\sqrt{3}} \overbrace{\int d\Omega\, Y_{0,0}\cos\theta\, Y_{1,0}}^{=1/\sqrt{3}} \\ &= -3a_B e\mathcal{E} \end{aligned} \tag{5.44}$$

Diagonalizing V yields

$$E^{(1)}_\pm = \pm 3a_B e\mathcal{E} \qquad \text{to the states} \qquad \psi_\pm = \frac{1}{\sqrt{2}}(\psi_{2,0,0} \mp \psi_{2,1,0})\,. \tag{5.45}$$

Thus the 4-fold degenerate state at $-E_R/4$ splits into two nondegenerate and one 2-fold degenerate state, see Figure 5.3.

The typical scale of the electric field in the atom is

$$\mathcal{E}_B = \frac{e}{a_B^2} \approx 51 \times 10^9\,\mathrm{V/cm}, \tag{5.46}$$

the field at the distance of a Bohr radius. Typical laboratory fields are much smaller than this scale. The correction

$$3a_B e\mathcal{E} = 6\frac{\mathcal{E}}{\mathcal{E}_B}E_R \tag{5.47}$$

is therefore small, which justifies perturbation theory.

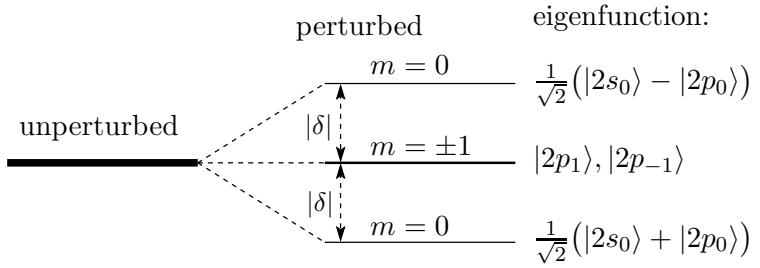


Fig. 5.3: Stark effect: the 4-fold degenerate state at $n = 2$ splits into 2 nondegenerate and one 2-fold degenerate state.

Fine structure in the hydrogen atom: Relativistic effects lead to corrections of the energy levels in the hydrogen atom. An important correction is the spin-orbit ($\boldsymbol{L}\cdot\boldsymbol{S}$) coupling with the Hamiltonian[4]

$$H_{LS} = \frac{1}{2m^2c^2}\frac{1}{r}\frac{dV}{dr}\,\boldsymbol{L}\cdot\boldsymbol{S} = \frac{1}{2m^2c^2}\frac{e^2}{r^3}\,\boldsymbol{L}\cdot\boldsymbol{S} \tag{5.48}$$

on the spin-orbit Hilbert space $\mathcal{H} = L^2(\mathbb{R}^3)\otimes\mathbb{C}^{2s+1}$ with $s = \frac{1}{2}$. This leads to the fine structure of the spectrum. The spin-orbit operator $\boldsymbol{L}\cdot\boldsymbol{S}$ is a scalar operator with respect to the total angular momentum. It is therefore helpful to couple the orbital angular momentum $\boldsymbol{L}$ and the spin $\boldsymbol{S}$ to the total angular momentum $\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$, which commutes with $\boldsymbol{L}\cdot\boldsymbol{S}$. The relevant Clebsch-Gordan coefficients are

$$\langle l, m-\tfrac{1}{2}; \tfrac{1}{2}, \tfrac{1}{2}|l\pm\tfrac{1}{2}, m\rangle = \pm\sqrt{\frac{l\pm m+\frac{1}{2}}{2l+1}}, \qquad \langle l, m+\tfrac{1}{2}; \tfrac{1}{2}, -\tfrac{1}{2}|l\pm\tfrac{1}{2}, m\rangle = \sqrt{\frac{l\mp m+\frac{1}{2}}{2l+1}}\,.$$

The combined spin-orbit wave functions are thus given by

$$\boldsymbol{\psi}_{n,l,j,m}(\boldsymbol{r}) = \sqrt{\frac{2}{na_B}}\frac{f_{n,l}(2r/na_B)}{r}\boldsymbol{Y}^l_{j=l\pm\frac{1}{2},m}(\theta,\varphi) \tag{5.49}$$

with

$$\boldsymbol{Y}^l_{j=l\pm\frac{1}{2},m}(\theta,\varphi) = \frac{1}{\sqrt{2l+1}}\begin{pmatrix}\pm\sqrt{l\pm m+\frac{1}{2}}\,Y_{l,m-1/2}(\theta,\varphi)\\ \sqrt{l\mp m+\frac{1}{2}}\,Y_{l,m+1/2}(\theta,\varphi)\end{pmatrix}. \tag{5.50}$$

From $\boldsymbol{L}\cdot\boldsymbol{S} = \frac{1}{2}(\boldsymbol{J}^2 - \boldsymbol{L}^2 - \boldsymbol{S}^2)$ it follows that

$$\Delta^l_{j,m} = \int(\boldsymbol{Y}^l_{j,m})^\dagger(\boldsymbol{L}\cdot\boldsymbol{S})\boldsymbol{Y}^l_{j,m}\,d\Omega = \frac{\hbar^2}{2}\Big[j(j+1) - l(l+1) - \frac{3}{4}\Big] = \frac{\hbar^2}{2}\begin{cases} l, & j = l+\frac{1}{2},\\ -(l+1), & j = l-\frac{1}{2}.\end{cases}$$

This equation describes the *Landé interval rule*, namely that $E_j - E_{j-1} \propto j$ (at fixed l).

To first order the correction to the hydrogen energy level is therefore given by

$$\langle H_{LS}\rangle = \frac{1}{2m^2c^2}\frac{8e^2}{n^3a_B^3}\Delta^l_{j,m}\overbrace{\int\frac{f_{n,l}(x)^2}{x^3}\,dx}^{=[8l(l+\frac{1}{2})(l+1)]^{-1}} = \frac{\alpha^2E_R}{2n^3(l+\frac{1}{2})}\begin{cases}\frac{1}{l+1}, & j = l+\frac{1}{2},\\ -\frac{1}{l}, & j = l-\frac{1}{2}.\end{cases} \tag{5.51}$$

[4]The operator $\boldsymbol{L}\cdot\boldsymbol{S}$ is of course short for $(\boldsymbol{L}\otimes 1)\cdot(1\otimes\boldsymbol{S}) = \sum_j L_j\otimes S_j$. There is an additional correction of order α^2 from the relativistic correction to the kinetic energy $\propto p^4/m^3c^2$.

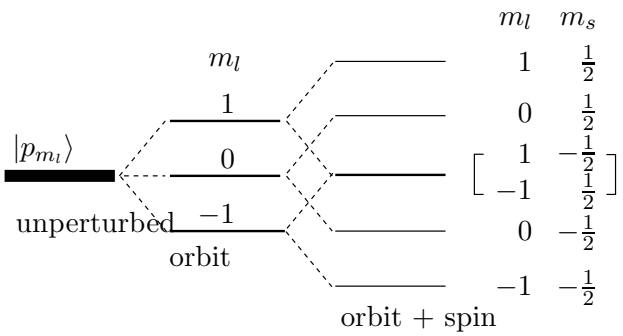


Fig. 5.4: Zeeman splitting of the $6 = 2 \times 3$-fold (spin×orbital) p state in the hydrogen atom. The orbital moment produces a triplet with two-fold degenerate states (spin). The gyromagnetic factor $g = 2$ of the electron spin exactly compensates the half-integer spin, so that orbital and spin give the same energy splitting and one obtains a quintuplet with a two-fold degenerate central state.

Here we have used that the typical strength of the spin-orbit interaction is given by

$$\frac{\hbar^2}{m^2c^2a_B^2}\frac{e^2}{2a_B} = \frac{e^4}{\hbar^2c^2}E_R = \alpha^2 E_R \approx 725\,\mu\text{eV} \tag{5.52}$$

with the fine-structure constant

$$\alpha = \frac{e^2}{\hbar c} \approx \frac{1}{137}\,. \tag{5.53}$$

From (5.51) one sees that the spin-orbit interaction lowers the energy when spin and orbit are antiparallel with $j = l - \frac{1}{2}$. Otherwise the energy is raised.

Zeeman effect in the hydrogen atom: The Zeeman effect is described by the perturbation due to the magnetic field $\boldsymbol{B} = B\boldsymbol{e}_3$

$$H_Z = \frac{\mu_B}{\hbar}B(L_3 + gS_3) \tag{5.54}$$

of the Pauli operator (4.97). We consider the case of a strong magnetic field with $\mu_B B \gtrsim \alpha^2 E_R$, $B \gtrsim 10^5$ G. Then the Hamiltonian H_Z is the dominant perturbation, which lifts the $2n^2$-fold degeneracy in the hydrogen problem (with spin). In this case one stays in the product representation $|l, m_l; \frac{1}{2}, m_s\rangle$ with $m_s = \pm\frac{1}{2}$ and obtains the splitting

$$\langle H_Z\rangle = \mu_B B(m_l + gm_s) \tag{5.55}$$

to first order. For example, the levels of a p state split as shown in Figure 5.4.

5.3 Time-dependent perturbation theory

Time-dependent perturbation theory deals with an autonomous system to which a time-dependent perturbation is applied. The Hamiltonian has the form

$$H(t) = H^{(0)} + H^{(1)}(t)\,, \tag{5.56}$$

where the perturbation $H^{(1)}(t)$ is now time dependent.

With the unitary transformation $V_t = e^{iH^{(0)}t/\hbar}$ we go over to the *interaction picture* with

$$|\tilde{\Psi}_t\rangle = V_t|\Psi_t\rangle\,. \tag{5.57}$$

The transformed state $|\tilde{\Psi}_t\rangle$ satisfies, according to (3.100), the Schrödinger equation

$$i\hbar\frac{d}{dt}|\tilde{\Psi}_t\rangle = \tilde{H}^{(1)}(t)|\tilde{\Psi}_t\rangle \tag{5.58}$$

with the Hamiltonian

$$\tilde{H}^{(1)}(t) = H^{(0)} + \underbrace{i\hbar\dot{V}_t V_t^\dagger}_{=-H^{(0)}} + V_t H^{(1)} V_t^\dagger = e^{iH^{(0)}t/\hbar}H^{(1)}(t)e^{-iH^{(0)}t/\hbar}\,, \tag{5.59}$$

which is proportional to the perturbation.

We assume that $H^{(1)}(t) \to 0$ for $t \to -\infty$ and choose as initial state at time $t = -\infty$ the stationary state $|a\rangle$ of the Hamiltonian $H^{(0)}$ at energy E_a. To first order (5.58) is solved by

$$|\tilde{\Psi}_t\rangle = |a\rangle - \frac{i}{\hbar}\int_{-\infty}^{t} dt'\,\tilde{H}^{(1)}(t')\,|a\rangle \tag{5.60}$$

The *transition probability* $P_{a\to e}(t)$ to the eigenstate $|e\rangle$, with $\langle e|a\rangle = 0$, at time t is given by

$$P_{a\to e}(t) = |\langle e|\tilde{\Psi}_t\rangle|^2 = \frac{1}{\hbar^2}\left|\int_{-\infty}^{t} dt'\,e^{i\omega_{ea}t'}\langle e|H^{(1)}(t')|a\rangle\right|^2 . \tag{5.61}$$

Hence the probability $P_{a\to e}$ is determined by the Fourier transform of $H^{(1)}(t)$ at the transition frequency

$$\omega_{ea} = \frac{1}{\hbar}(E_e - E_a) \tag{5.62}$$

Um further to proceed we must make assumptions about the time dependence of the perturbation $H^{(1)}(t)$. Typical cases are

1) static perturbation with $H^{(1)}(t \geq 0) = V$,

2) harmonic perturbation with $H^{(1)}(t \geq 0) = Ve^{-i\omega t} + V^\dagger e^{i\omega t}$,

with $H^{(1)}(t < 0) = 0$.

Static perturbation: We obtain

$$P_{a\to e}(t) = \left|\frac{e^{i\omega_{ea}t} - 1}{i\omega_{ea}}\,\frac{\langle e|V|a\rangle}{\hbar}\right|^2 = \left(\frac{\sin(\omega_{ea}t/2)}{\omega_{ea}/2}\right)^2\frac{|\langle e|V|a\rangle|^2}{\hbar^2}. \tag{5.63}$$

The prefactor of the matrix element $|\langle e|V|a\rangle|^2/\hbar^2$ describes energy conservation. In the energy-conserving process with $\omega_{ea} = 0$ it takes the value t^2. Overall it decays on the width $\delta\omega_{ea}$ with $\delta\omega_{ea}\,t \approx 2\pi$, see Figure 5.5. Directly after switching on the perturbation $\delta\omega_{ea} = \infty$ and transitions to arbitrary energies can in principle occur. For long times t only nearly energy-conserving processes are allowed.

We consider the case where the final states lie densely with a *density of states* (states per energy) $\rho(E_e)$ at the energy E_e. Thus we have a typical spacing $\Delta = \rho^{-1}$ between

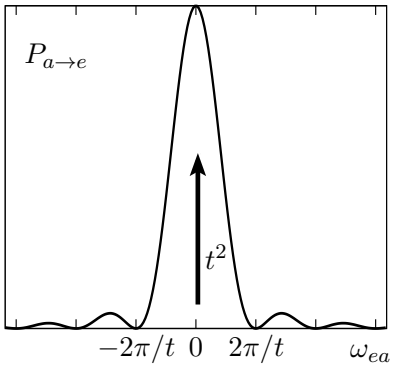


Fig. 5.5: Transition probability $P_{a\to e}(t)$ for a static perturbation. The area of the main maximum grows according to $t^2 \cdot (2\pi/t) \propto t$.

two energy levels and $\sum_e \mapsto \int dE_e\, \rho(E_e)$. We are now interested in the total probability $P(t) = \sum_e P_{a\to e}(t) = \int dE_e\, \rho(E_e) P_{a\to e}(t)$.

For times t, long enough, so that the matrix elements $|\langle e|V|a\rangle|^2$ and the density of states $\rho(E_E)$ are constant for the relevant energy states with $|E_e - E_a| < \hbar\,\delta\omega_{ea}$, we find the total transition probability

$$P(t) = \frac{|\langle e|V|a\rangle|^2}{\hbar^2}\rho(E_a) \underbrace{\int \left(\frac{\sin(\omega_{ea}t/2)}{\omega_{ea}/2}\right)^2 dE_e}_{=2\hbar t \int dx\, \sin^2(x)/x^2} = \frac{2\pi}{\hbar}|\langle e|V|a\rangle|^2 \rho(E_a)\, t\,. \tag{5.64}$$

The *transition rate* is then given by *Fermi's Golden Rule*

$$\Gamma = \frac{dP}{dt} = \frac{2\pi}{\hbar}|\langle e|V|a\rangle|^2\, \rho(E_e)\Big|_{E_e=E_a}\,. \tag{5.65}$$

For the derivation we require that many states contribute, i.e. $\delta\omega_{eg}/\Delta \gg 1$ ($t \ll 2\pi\hbar\rho$), and that perturbation theory is applicable with $\Gamma t \ll 1$.

Harmonic perturbation: For the case with $H^{(1)}(t) = Ve^{-i\omega t} + V^\dagger e^{i\omega t}$ we obtain ($\omega_\pm = \omega_{ea} \pm \omega$)

$$\begin{aligned} P_{a\to e}(t) &= \left|\frac{e^{i\omega_+ t}-1}{i\omega_+}\frac{\langle e|V^\dagger|a\rangle}{\hbar} + \frac{e^{-i\omega_- t}-1}{i\omega_-}\frac{\langle e|V|a\rangle}{\hbar}\right|^2 \\ &= \left(\frac{\sin(\omega_+ t/2)}{\omega_+/2}\right)^2 \frac{|\langle e|V^\dagger|a\rangle|^2}{\hbar^2} + \left(\frac{\sin(\omega_- t/2)}{\omega_-/2}\right)^2 \frac{|\langle e|V|a\rangle|^2}{\hbar^2} \\ &\quad + \frac{8\sin(\omega_+ t/2)\sin(\omega_- t/2)}{\omega_+\omega_-}\,\mathrm{Re}\Big[e^{i\omega t}\langle e|V|a\rangle^*\langle e|V^\dagger|a\rangle\Big]\,. \end{aligned} \tag{5.66}$$

The last term oscillates with the frequency $\propto \omega$ and leads to no transitions. Thus there are two groups of states with $\omega_+ \approx 0$ and $\omega_- \approx 0$, which independently contribute to the transition probability. We obtain the transition rate

$$\Gamma = \Gamma_{\rm em} + \Gamma_{\rm abs} = \frac{2\pi}{\hbar}|\langle e|V^\dagger|a\rangle|^2\, \rho(E_e)\Big|_{E_e=E_a-\hbar\omega} + \frac{2\pi}{\hbar}|\langle e|V|a\rangle|^2\, \rho(E_e)\Big|_{E_e=E_a+\hbar\omega}\,. \tag{5.67}$$

The first term with $E_e = E_a - \hbar\omega$ describes an emission process, the second term with $E_e = E_a + \hbar\omega$ describes the absorption of energy.

Chapter 6

Identical Particles

As already mentioned in Chapter 3, the Hilbert space of N identical *particles* is given by

$$\mathcal{H}^{(N)} = \otimes^N \mathcal{H} = \mathcal{H} \otimes \cdots \otimes \mathcal{H} \tag{6.1}$$

with $\mathcal{H}$ the single-particle Hilbert space. On this Hilbert space it is natural to introduce the symmetry

$$P_{(jk)}\big(\cdots \otimes \psi_j \otimes \cdots \otimes \psi_k \otimes \cdots\big) = \cdots \otimes \psi_k \otimes \cdots \otimes \psi_j \otimes \cdots\,, \tag{6.2}$$

which describes the *exchange* of the particles j and k. Since the particles are identical, the relevant observables are invariant under this operation. An important example is the *single-particle operators*

$$O^{(\mathrm{ges})} = \sum_{j=1}^{N} o_j, \qquad o_j = \underbrace{1 \otimes \cdots \otimes 1}_{(j-1)\text{-factors}} \otimes O \otimes 1 \otimes \cdots \tag{6.3}$$

to which, for example, the center of mass, the total momentum, the total spin, and the total energy belong.

6.1 Permutation group

In general, the exchange of identical particles is given by an element σ of the permutation group S_N. Here σ is a bijective mapping of the set $\{1, \ldots, N\}$ to itself with

$$\sigma\colon j \mapsto \sigma(j), \qquad (j = 1, \ldots, N)\,. \tag{6.4}$$

The product is simply the composition of the respective mappings, $(\tau\sigma)(j) = \tau(\sigma(j))$. The permutation acts on the N-particle Hilbert space $\mathcal{H}^{(N)}$ with

$$P_\sigma\colon \psi_1 \otimes \cdots \otimes \psi_N \quad \mapsto \quad \psi_{\sigma(1)} \otimes \cdots \otimes \psi_{\sigma(N)} = |\psi_{\sigma(1)}, \ldots, \psi_{\sigma(N)}\rangle\,. \tag{6.5}$$

Thus $P_\tau P_\sigma = P_{\tau\sigma}$ holds for two permutations $\sigma, \tau \in S_N$.[1] A general state Ψ of the Hilbert space $\mathcal{H}^{(N)}$ is of course not a product state $\psi_1 \otimes \cdots \otimes \psi_N$. However, every state can be written as a sum of product states and by linearity P_σ is thus defined on an arbitrary state.

[1] One says that P is a representation of S_N on $\mathcal{H}^{(N)}$.

Transpositions are permutations of two elements $j \neq k$ and are denoted by (jk). The group with $N!$ elements is generated by transpositions. If one writes a permutation σ as a product of N_t transpositions, the *signature* $\operatorname{sgn}\sigma = \pm 1$ of the permutation is given precisely by the parity $(-1)^{N_t}$.[2] Naturally, one has

$$\operatorname{sgn}(\tau\sigma) = (\operatorname{sgn}\tau)(\operatorname{sgn}\sigma) \tag{6.6}$$

for the product of two permutations $\tau\sigma$.

Since the particles are identical, an N-particle state $|\Psi\rangle \in \mathcal{H}^{(N)}$ under a permutation P_σ should be mapped to itself up to a phase. That is, we require

$$P_\sigma|\Psi\rangle = \eta(\sigma)|\Psi\rangle, \qquad |\eta(\sigma)| = 1\,. \tag{6.7}$$

Here P_σ is a unitary mapping with $P_\sigma^\dagger P_\sigma = 1$.

For the composition $\tau\sigma$ this implies

$$\eta(\tau\sigma)|\Psi\rangle = P_{\tau\sigma}|\Psi\rangle = P_\tau P_\sigma|\Psi\rangle = \eta(\tau)\eta(\sigma)|\Psi\rangle \tag{6.8}$$

and hence one must have $\eta(\tau\sigma) = \eta(\tau)\eta(\sigma)$.

We can now show that

$$\eta(\sigma) \equiv 1 \quad \text{(symmetric)} \qquad \text{or} \qquad \eta(\sigma) = \operatorname{sgn}(\sigma) \quad \text{(antisymmetric)} \tag{6.9}$$

are the only possibilities.[3] To this end we consider $\eta(\sigma) = \eta(\sigma 1) = \eta(\sigma)\eta(1)$ and conclude $\eta(1) = 1$. For an arbitrary transposition (jk) one has $(jk)^2 = (jk)(jk) = 1$ and hence it follows $\eta((jk)^2) = 1$ with the two possibilities of (6.9) as the only solution (we have $\eta((jk)) = \pm 1$ and the result follows by decomposing an arbitrary permutation into transpositions)[4].

Example: We consider particles with spin-s. The single-particle Hilbert space is $\mathcal{H} = L^2(\mathbb{R}^3) \otimes \mathbb{C}^{2s+1}$. We introduce the combined index $x = (\boldsymbol{r}, m)$, $\boldsymbol{r} \in \mathbb{R}^3, m = -s, \cdots, s$ (spin and orbital) with the notation

$$\psi(x) = \langle x|\psi\rangle, \qquad \langle\phi|\psi\rangle = \int dx\, \phi^*(x)\psi(x) = \sum_m \int d^3r\, \phi^*(\boldsymbol{r}, m)\psi(\boldsymbol{r}, m)\,. \tag{6.10}$$

The product states of N particles are thus given by $\Psi = \psi_1(x_1)\cdots\psi_N(x_N)$. A permutation σ acts on these wave functions with

$$(P_\sigma\Psi)(x_1, \ldots, x_N) = \langle x_1, \cdots, x_N|\psi_{\sigma(1)}, \ldots, \psi_{\sigma(N)}\rangle = \Psi(x_{\sigma^{-1}(1)}, \ldots, x_{\sigma^{-1}(N)})\,. \tag{6.11}$$

6.2 Spin-$\frac{1}{2}$

The Hilbert space $\mathcal{H}^{(N)}$ for the single-particle Hilbert space $\mathcal{H} = \mathbb{C}^2$ describes N spin-$\frac{1}{2}$ *species*. We introduce the space of completely (anti)*symmetric* states

$$\mathcal{H}_s^{(N)} = \{|\Psi\rangle : P_\sigma|\Psi\rangle = |\Psi\rangle, \text{ for all } \sigma\}, \qquad \mathcal{H}_a^{(N)} = \{|\Psi\rangle : P_\sigma|\Psi\rangle = \operatorname{sgn}(\sigma)|\Psi\rangle\}. \tag{6.12}$$

[2] The representation as a product of transpositions is of course not unique. One can however show that the signature does not depend on the representation.

[3] In principle there is the possibility that different states mix under P_σ. We do not wish to consider this parastatistics.

[4] The sign of $\eta((jk)) = \pm 1$ must be chosen the same for all transpositions, since $(1j)(2k)(jk)(1j)(2k) = (12)$ and hence $\eta((jk)) = \eta((12))$.

The total spin $\boldsymbol{S}^{(\mathrm{ges})} = \sum_j \boldsymbol{S}_j$ is invariant under the permutation operation. Hence the Hilbert spaces $\mathcal{H}_s^{(N)}, \mathcal{H}_a^{(N)}$ must contain states with well-defined total spin.

We will now determine the Hilbert spaces. Let us start with $\mathcal{H}_s^{(2)}$. The state with maximal $S_3^{(\mathrm{ges})}$ is given by $|\uparrow\uparrow\rangle$ with $(s = 1, m = 1)$. Applying $S_-^{(\mathrm{ges})}$ then yields the remaining states of the triplet, see also (4.103). Thus we have $\mathcal{H}_s^{(2)} = \mathcal{D}_1$. Analogously one can show for $\mathcal{H}_s^{(N)}$ that $\mathcal{H}_s^{(N)} = \mathcal{D}_{N/2}$. One simply starts with the state $|\uparrow \cdots \uparrow\rangle$ of maximal total spin. With this one can realize any representation $\mathcal{D}_{N/2}$ of $\mathsf{SU}(2)$ by a symmetric combination of N spin-$\frac{1}{2}$. A similar idea also works for the representations of $\mathsf{SU}(N)$ in general. For this, however, one still needs the remaining representations of S_N, which are given by the Young diagrams.

Now to the antisymmetric space $\mathcal{H}_a^{(N)}$. For $N = 2$ the antisymmetric combination of two spin-$\frac{1}{2}$ is precisely the singlet. Thus there exists a state in the space $\mathcal{H}_a^{(2)} = \mathcal{D}_0$. For $N > 2$ there is no state; see also the discussion of the Pauli principle later.

6.3 Entanglement

Often an observer ("Alice") in a Hilbert space $\mathcal{H} = \mathcal{H}_A \otimes \mathcal{H}_B$ has access only to a subspace $\mathcal{H}_A$. Such a case arises, for example, when the system consists of two spin-$\frac{1}{2}$ particles, but Alice can manipulate only one spin. The measurements M_A of a state ρ that Alice can perform on her subspace are then described solely by the *reduced density matrix*

$$\rho_A \colon \mathcal{H}_A \to \mathcal{H}_A, \qquad \rho_A = \mathrm{Tr}_B(\rho) \tag{6.13}$$

, where Tr_B denotes the trace over the Hilbert space $\mathcal{H}_B$. The expectation value of M_A

$$\langle M_A \rangle = \mathrm{Tr}(\rho M_A) = \underbrace{\mathrm{Tr}_A \mathrm{Tr}_B}_{=\mathrm{Tr}_{A\otimes B}}(\rho M_A) = \mathrm{Tr}_A(\rho_A M_A)\,. \tag{6.14}$$

is thus determined solely by ρ_A. Note that starting from a pure state ρ in general ρ_A is not a pure state.

Let us first consider the state $|\Psi_1\rangle = |s = 1, m = 1\rangle = |\uparrow\uparrow\rangle$ in the Hilbert space $\mathbb{C}^2 \otimes \mathbb{C}^2$. The corresponding density matrix is given by

$$\rho_1 = |\uparrow\uparrow\rangle\langle\uparrow\uparrow|\,. \tag{6.15}$$

For measurements on Alice's subsystem it suffices to know the reduced density matrix

$$\rho_{1,A} = \mathrm{Tr}_B(\rho_1) = \sum_{m_B = \pm} \big(1 \otimes \langle m_B|\big)\, |\uparrow\uparrow\rangle\langle\uparrow\uparrow|\, \big(1 \otimes |m_B\rangle\big) = |\uparrow\rangle\langle\uparrow|\,. \tag{6.16}$$

Note that in this case $\rho_{1,A}$ is again a pure state with $\rho_{1,A}^2 = \rho_{1,A}$.

As a second example consider the state $|\Psi_2\rangle = |s = 0, m = 0\rangle = \frac{1}{\sqrt{2}}\big(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\big)$. The density matrix is given by

$$\rho_2 = \frac{1}{2}\big(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\big)\big(\langle\uparrow\downarrow| - \langle\downarrow\uparrow|\big) = \frac{1}{2}\Big(|\uparrow\downarrow\rangle\langle\uparrow\downarrow| + |\downarrow\uparrow\rangle\langle\downarrow\uparrow| - |\uparrow\downarrow\rangle\langle\downarrow\uparrow| - |\downarrow\uparrow\rangle\langle\uparrow\downarrow|\Big)\,. \tag{6.17}$$

In this case the reduced state

$$\rho_{2,A} = \frac{1}{2}\big(|\uparrow\rangle\langle\uparrow| + |\downarrow\rangle\langle\downarrow|\big) = \frac{1}{2}\cdot 1 \tag{6.18}$$

is not a pure state. The state $\rho_{2,A}$ is in fact the *maximally mixed* state, in which $|\uparrow\rangle$ and $|\downarrow\rangle$ each occur with 50% probability.

The differing behavior of $|\Psi_1\rangle$ and $|\Psi_2\rangle$ is thus connected to the fact that $|\Psi_1\rangle = |\uparrow\rangle \otimes |\uparrow\rangle$ is a *product state*. One shows in general: let $|\Psi\rangle = |\psi_A\rangle \otimes |\psi_B\rangle$ be a product state with arbitrary $|\psi_A\rangle$ and $|\psi_B\rangle$. Then one finds that the reduced density matrix

$$\rho_A = \mathrm{Tr}_B\big(|\psi_A\rangle \otimes |\psi_B\rangle\langle\psi_A| \otimes \langle\psi_B|\big) = \big(\mathrm{Tr}_B\, |\psi_B\rangle\langle\psi_B|\big)|\psi_A\rangle\langle\psi_A| = |\psi_A\rangle\langle\psi_A| \tag{6.19}$$

corresponds to the pure state $|\psi_A\rangle$. Hence we have the following simple criterion for an arbitrary pure state $|\Psi\rangle$ on $\mathcal{H}_A \otimes \mathcal{H}_B$:

$$|\Psi\rangle \text{ can be written as a product state} \quad \Leftrightarrow \quad \rho_A \text{ is a pure state.} \tag{6.20}$$

States that cannot be written as product states are called *entangled* states. In particular, we obtain the result that the singlet state $|s = 0, m = 0\rangle$ is an entangled state and hence cannot be written as a product state. In other words, we have shown that there are no unitary operators U_A and U_B such that

$$(U_A \otimes U_B)|0, 0\rangle = |\psi_A\rangle \otimes |\psi_B\rangle \tag{6.21}$$

for arbitrary $|\psi_A\rangle$ and $|\psi_B\rangle$.

6.4 Bosons and Fermions

As we have already seen, for identical particles $P_\sigma|\Psi\rangle = \eta(\sigma)|\Psi\rangle$. Hence for any observable M the expectation value

$$\langle\Psi|M|\Psi\rangle = \underbrace{\frac{1}{N!}\sum_{\sigma\in S_N} |\eta(\sigma)|^2}_{=1} \langle\Psi|M|\Psi\rangle = \frac{1}{N!}\sum_\sigma \langle P_\sigma\Psi|M|P_\sigma\Psi\rangle = \langle\Psi|M^{(\mathrm{sym})}|\Psi\rangle\,. \tag{6.22}$$

is the same as the expectation value of the (symmetric) observable

$$M^{(\mathrm{sym})} = \frac{1}{N!}\sum_\sigma P_\sigma^\dagger M P_\sigma\,. \tag{6.23}$$

One may therefore restrict attention to symmetric observables. For example, one-particle operators are symmetric observables.

It is now easy to see that for any $\tau \in S_N$,

$$P_\tau^\dagger M^{(\mathrm{sym})} P_\tau = \frac{1}{N!}\sum_\sigma P_\tau^\dagger P_\sigma^\dagger M P_\sigma P_\tau \overset{(\mu=\sigma\tau)}{=} \frac{1}{N!}\sum_\mu P_\mu^\dagger M P_\mu = M^{(\mathrm{sym})} \tag{6.24}$$

or in other words

$$[M^{(\mathrm{sym})}, P_\tau] = 0\,. \tag{6.25}$$

Thus the particles are *in principle indistinguishable*, since no observable can distinguish the state $|\Psi\rangle$ from $P_\tau|\Psi\rangle$.

Moreover, the observables $M^{(\mathrm{sym})}$ map the subspaces $\mathcal{H}_s^{(N)}$ and $\mathcal{H}_a^{(N)}$ from (6.12) to themselves. In particular this also holds for the Hamiltonian, and hence under the map $\Psi_0 \mapsto \Psi_t = e^{-iHt/\hbar}\Psi_0$ the subspace $\mathcal{H}_s^{(N)}$ or $\mathcal{H}_a^{(N)}$, respectively, is preserved.

In the framework of relativistic quantum field theory one can prove the *spin-statistics theorem*. It states that the physical Hilbert space of N identical particles of spin s is given by

$$\mathcal{H}_s^{(N)}, \qquad \text{if } s \in \{0,1,2,\dots\}, \qquad (\text{ are bosons }), \tag{6.26}$$

$$\mathcal{H}_a^{(N)}, \qquad \text{if } s \in \{\tfrac{1}{2},\tfrac{3}{2},\dots\}, \qquad (\text{ are fermions }). \tag{6.27}$$

. In particular, under a transposition (jk) the wave functions satisfy

$$P_{(jk)}\Psi(\dots,x_j,\dots,x_k,\dots) = \Psi(\dots,x_k,\dots,x_j,\dots), \qquad (\text{ for bosons }), \tag{6.28}$$

$$P_{(jk)}\Psi(\dots,x_j,\dots,x_k,\dots) = -\Psi(\dots,x_k,\dots,x_j,\dots), \qquad (\text{ for fermions }). \tag{6.29}$$

6.5 Two-electron systems

The Hilbert space of two electrons (spin $\frac{1}{2}$) is given by $\mathcal{H}_a^{(2)}$ with $\mathcal{H} = L^2(\mathbb{R}^3)\otimes\mathbb{C}^2$. If the Hamiltonian commutes with the square $(\boldsymbol{S}^{(\text{ges})})^2$ of the total spin, one can classify states according to the total spin.

In particular we obtain as possible wave functions

$$\Psi(x_1,x_2) = \begin{cases} \Phi_s(\boldsymbol{r}_1,\boldsymbol{r}_2)\,\chi_{0,0}(m_1,m_2), & (\text{ singlet }),\\ \Phi_{t,m}(\boldsymbol{r}_1,\boldsymbol{r}_2)\,\chi_{1,m}(m_1,m_2), & (\text{ triplet }). \end{cases} \tag{6.30}$$

. We have already seen that $\chi_{0,0}(m_1,m_2) = -\chi_{0,0}(m_2,m_1)$ (the singlet is antisymmetric) and $\chi_{1,m}(m_1,m_2) = \chi_{1,m}(m_2,m_1)$ (the triplet is symmetric). In order that the total wave function Ψ lie in the space $\mathcal{H}_a^{(2)}$ we therefore need so that

$$\Phi_s(\boldsymbol{r}_1,\boldsymbol{r}_2) = \Phi_s(\boldsymbol{r}_2,\boldsymbol{r}_1) \quad \text{and} \quad \Phi_t(\boldsymbol{r}_1,\boldsymbol{r}_2) = -\Phi_t(\boldsymbol{r}_2,\boldsymbol{r}_1). \tag{6.31}$$

For the triplet state the probability

$$|\Phi_t(\boldsymbol{r}_1,\boldsymbol{r}_1)|^2 = 0, \tag{6.32}$$

of finding the electrons at the same position therefore vanishes.

Consider the simplest case of non-interacting electrons without spin-orbit coupling. The Hamiltonian is then given by

$$H = h_1 + h_2 \qquad \text{with} \qquad h_j = -\frac{\hbar^2}{2m}\Delta_j + V(\boldsymbol{r}_j)\,. \tag{6.33}$$

The one-particle problem $h|\psi_\nu\rangle = \varepsilon_\nu|\psi_\nu\rangle$ has the stationary states $|\psi_\nu\rangle$ with energies ε_ν and normalization $\langle\psi_\mu|\psi_\nu\rangle = \delta_{\mu\nu}$.

Hence we obtain the total spatial wave function

$$\Phi_{s/t}(\boldsymbol{r}_1,\boldsymbol{r}_2) = \frac{1}{\sqrt{2}}\left[\psi_\mu(\boldsymbol{r}_1)\psi_\nu(\boldsymbol{r}_2) \pm \psi_\nu(\boldsymbol{r}_1)\psi_\mu(\boldsymbol{r}_2)\right], \tag{6.34}$$

with energy $E = \varepsilon_\mu + \varepsilon_\nu$, i.e. $H\,\Phi_{s/t}(\boldsymbol{r}_1,\boldsymbol{r}_2) = E\,\Phi_{s/t}(\boldsymbol{r}_1,\boldsymbol{r}_2)$.

The probability of finding one electron at $\boldsymbol{r}_1$ and the other at $\boldsymbol{r}_2$ (in the volume dV_j) is given by

$$\rho(\boldsymbol{r}_1,\boldsymbol{r}_2)\,dV_1\,dV_2 = |\Phi_{s/t}(\boldsymbol{r}_1,\boldsymbol{r}_2)|^2\,dV_1\,dV_2 = \big[\rho_d(\boldsymbol{r}_1,\boldsymbol{r}_2) \pm \rho_a(\boldsymbol{r}_1,\boldsymbol{r}_2)\big]dV_1\,dV_2 \tag{6.35}$$

with the *direct* probability density

$$\rho_d(\boldsymbol{r}_1,\boldsymbol{r}_2) = \frac{1}{2}\Big[|\psi_\mu(\boldsymbol{r}_1)|^2|\psi_\nu(\boldsymbol{r}_2)|^2 + |\psi_\mu(\boldsymbol{r}_2)|^2|\psi_\nu(\boldsymbol{r}_1)|^2\Big] \tag{6.36}$$

and the *exchange density*

$$\rho_a(\boldsymbol{r}_1,\boldsymbol{r}_2) = \mathrm{Re}\Big[\psi^*_\nu(\boldsymbol{r}_1)\psi_\mu(\boldsymbol{r}_1)\psi^*_\mu(\boldsymbol{r}_2)\psi_\nu(\boldsymbol{r}_2)\Big]\,. \tag{6.37}$$

The exchange density is a consequence of the fermionic nature of the electrons. It is non-zero only if the overlap $\psi^*_\nu(\boldsymbol{r})\psi_\mu(\boldsymbol{r})$ does not vanish. In particular this implies that the electrons are not too far apart. The exchange density lowers (triplet) or raises (singlet) the probability of finding the two electrons at nearby positions with $\boldsymbol{r}_1 \approx \boldsymbol{r}_2$.

Example: Helium atom The states [cf. (5.9)]

$$\psi^\pm_{n,l,m}(\boldsymbol{r}_1,\boldsymbol{r}_2) = \frac{1}{\sqrt{2}}\left[\psi_{n,l,m}(\boldsymbol{r}_1)\psi_{1,0,0}(\boldsymbol{r}_2) \pm \psi_{1,0,0}(\boldsymbol{r}_1)\psi_{n,l,m}(\boldsymbol{r}_2)\right] \tag{6.38}$$

are approximate wave functions of the excited states $(1s)(nl)$ of the helium atom. The sign $+$ corresponds to a singlet state (parahelium). The state ψ^- is a triplet (orthohelium).

Without interaction the states $\psi^\pm_{n,l,m}$ have the energy [cf. (5.8)]

$$E^{(0)}_n = -4E_R\left(1+\frac{1}{n^2}\right)\,. \tag{6.39}$$

On account of the interaction $V_{12} = e^2/|\boldsymbol{r}_1-\boldsymbol{r}_2|$ this energy undergoes a shift $\Delta E_{n,l}$. Note that the shift cannot depend on m because of rotational symmetry.

The probability density is given by $\rho = \rho_d \pm \rho_a$. One thus obtains $\Delta E^\pm_{n,l} = \langle\psi^\pm_{n,l,m}|V_{12}|\psi^\pm_{n,l,m}\rangle = I_{n,l} \pm J_{n,l}$ in first-order perturbation theory. Here the direct energy

$$I_{n,l} = e^2\int dV_1\,dV_2\,\frac{\rho_d(\boldsymbol{r}_1,\boldsymbol{r}_2)}{|\boldsymbol{r}_1-\boldsymbol{r}_2|} = e^2\int dV_1\,dV_2\,\frac{|\psi_{1,0,0}(\boldsymbol{r}_1)\psi_{n,l,m}(\boldsymbol{r}_2)|^2}{|\boldsymbol{r}_1-\boldsymbol{r}_2|} > 0 \tag{6.40}$$

is of course positive. Moreover it also holds that the exchange energy

$$J_{n,l} = e^2\int dV_1\,dV_2\,\frac{\rho_a(\boldsymbol{r}_1,\boldsymbol{r}_2)}{|\boldsymbol{r}_1-\boldsymbol{r}_2|} = e^2\int dV_1\,dV_2\,\frac{\psi^*_{1,0,0}(\boldsymbol{r}_1)\psi_{n,l,m}(\boldsymbol{r}_1)\psi_{1,0,0}(\boldsymbol{r}_2)\psi^*_{n,l,m}(\boldsymbol{r}_2)}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}$$

is positive as well.[5] Hence the energy of the singlet state ψ^+ is in each case higher than that of the triplet state. Because of the Coulomb interaction between the electrons it is therefore energetically favorable for the electrons to align their spins and form a triplet. This *exchange interaction* is the basis of the magnetism of matter.

6.6 Ideal fermions and the Pauli principle

The Hamiltonian H of ideal fermions is a one-particle operator for the total energy. The one-particle problem h acts on the Hilbert space $\mathcal{H} = L^2(\mathbb{R}^3)\otimes\mathbb{C}^{2s+1}$. In the N-particle

[5] With $\rho(\boldsymbol{r}) = \psi^*_{1,0,0}(\boldsymbol{r}_1)\psi_{n,l,m}(\boldsymbol{r}_1)$ one has $\int dV_1\,dV_2\,\rho(\boldsymbol{r}_1)\rho(\boldsymbol{r}_2)^*/|\boldsymbol{r}_1-\boldsymbol{r}_2| = \int dV\,\boldsymbol{E}(\boldsymbol{r})\cdot\boldsymbol{E}(\boldsymbol{r})^*/4\pi$, where $\boldsymbol{\nabla}\cdot\boldsymbol{E} = 4\pi\rho$.

Hilbert space $\mathcal{H}^{(N)}$ (without symmetrization) the eigenvalue problem $H|\Psi\rangle = E|\Psi\rangle$ has the solution

$$\begin{aligned} &H|\nu_1,\dots,\nu_N\rangle = E|\nu_1,\dots,\nu_N\rangle, \qquad E = \varepsilon_{\nu_1}+\cdots+\varepsilon_{\nu_N}, \\ &\Psi_{\nu_1,\dots,\nu_N}(x_1,\dots,x_N) = \langle x_1,\dots,x_N|\nu_1,\dots,\nu_N\rangle = \psi_{\nu_1}(x_1)\cdots\psi_{\nu_N}(x_N)\,. \end{aligned} \tag{6.41}$$

To obtain from this the fermionic states in the correct Hilbert space $\mathcal{H}_a^{(N)}$ we antisymmetrize and obtain $\Psi_{\{\nu_1,\dots,\nu_N\}} \in \mathcal{H}_a^{(N)}$ with [6]

$$\begin{aligned} \Psi_{\{\nu_1,\dots,\nu_N\}}(x_1,\dots,x_N) &= \frac{1}{\sqrt{N!}}\sum_{\sigma\in S_N}(\operatorname{sgn}\sigma)\psi_{\nu_1}(x_{\sigma(1)})\dots\psi_{\nu_N}(x_{\sigma(N)}) \\ &= \frac{1}{\sqrt{N!}}\begin{vmatrix} \psi_{\nu_1}(x_1) & \cdots & \psi_{\nu_N}(x_1) \\ \vdots & \ddots & \vdots \\ \psi_{\nu_1}(x_N) & \cdots & \psi_{\nu_N}(x_N) \end{vmatrix} = \frac{1}{\sqrt{N!}}\det\bigl(\psi_{\nu_j}(x_l)\bigr)\,. \end{aligned} \tag{6.42}$$

One also calls this state a *Slater determinant*. The state described by the Slater determinant depends only on the set $\{\nu_1,\dots,\nu_N\}$ and not on the ordering, because a permutation of ν_j changes at most the sign of $\Psi_{\{\nu_1,\dots,\nu_N\}}$.

It also holds the *Pauli principle*: each single-particle state can occur only once. If namely $\nu_j = \nu_m$ holds for $m \neq j$, then we obtain $\Psi_{\{\nu_1,\dots,\nu_N\}} = 0$. The reason is that the two columns j and m in (6.42) then become linearly dependent.

Therefore we switch to the *occupation numbers* $n_\nu \in \{0,1\}$ and characterize the state by $n_\nu = 1$ if the state ψ_ν occurs, and $n_\nu = 0$ otherwise. Altogether we must have occupied N states so that

$$\sum_\nu n_\nu = N, \qquad \sum_\nu n_\nu\varepsilon_\nu = E\,. \tag{6.43}$$

One can also introduce occupation numbers for bosons because of the symmetry under exchange. For bosons, however, the Pauli principle does not apply and we have $n_\nu \in \{0,1,2,\dots\}$.

Shell model: With the Pauli principle one can explain the periodic table (for noninteracting electrons). In each single-particle state at most one electron can reside. One obtains the lowest energy by filling the lowest levels first. In an atom with nuclear charge Z Z electrons move in the potential $V(\boldsymbol{r}) = -Ze^2/r$. The states are $\psi_{n,l,m}$ with energy

$$\varepsilon_n = -\frac{Z^2E_R}{n^2}\,. \tag{6.44}$$

The energy level with principal quantum number n is $2n^2$-fold degenerate (the factor 2 comes from the spin $\frac{1}{2}$).

As we have already seen in the example of the helium atom, interactions lift additional degeneracies so that only the angular-momentum degeneracy remains. In particular, in an atom there are the shells (nl) with degeneracy $2(2l+1)$, i.e.

$$s\text{-shell (ent. 2)}, \qquad p\text{- (ent. 6)}, \qquad d\text{- (ent. 10)} \quad \text{and} \quad f\text{- (ent. 14)}. \tag{6.45}$$

[6] Since we sum over all permutations and $\operatorname{sgn}\sigma = \operatorname{sgn}(\sigma^{-1})$ we may permute the coordinates x_k instead of σ^- with σ.

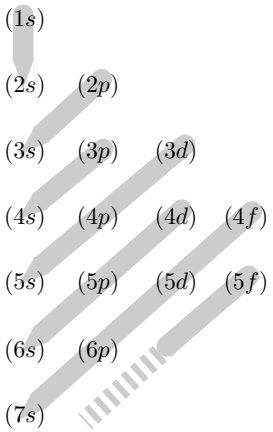


Fig. 6.1: Arrangement of the shells (nl) for the energy of the last electron in the Thomas-Fermi atom. n = principal quantum number, l = orbital angular-momentum quantum number.

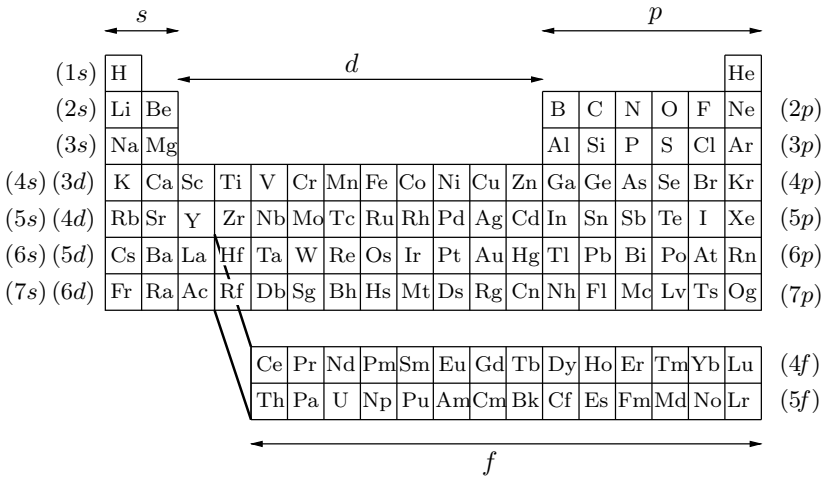


Fig. 6.2: Periodic table of the elements.

Within the Thomas-Fermi atom one finds the following ordering of the shell energies

$$(1s) < (2s) < (2p) < (3s) < (3p) < (4s) < (3d) < (4p) < (5s) < (4d) < \cdots . \tag{6.46}$$

This ordering can be memorized with the help of the schema 6.1. Correspondingly one finds the periodic table of the elements in the form 6.2.

We go through the periodic table with some comments:

- H, He: the $(1s)$ shell is filled
- Li, Be: the $(2s)$ shell, B-Ne: the $(2p)$ shell is filled. $(2s)$ and $(2p)$ have different energies; orbitals with small l lie closer to the nucleus and hence have lower energies, $\varepsilon_{2s} < \varepsilon_{2p}$.
- Na-Ar: as before, first the $(3s)$, then the $(3p)$ shell is filled.
- K-Kr: the energies of $(4s)$ are nearly equal to those of $(3d)$. This leads to the complicated filling (we list only the number of electrons in the $(4s)$ shell):

  K $(4s)^1$, Ca $(4s)^2$, $\cdots$, V $(4s)^2$, Cr $(4s)^1$, Mn $(4s)^2, \cdots$, Ni $(4s)^2$, Cu $(4s)^1$, Zn $(4s)^2$.

  With Ga-Kr the $(4p)$-shell is filled. The $(3d)$-shells are compact and therefore chemically

less important; they do, however, provide the magnetic moments that generate the ferro- or antiferromagnetism of the elements Cr-Ni.

- Rb-Xe: essentially a repetition of the K-Kr sequence. Again the s orbitals have roughly the same energy as the d orbitals of the preceding shell.

For the chemical properties of the elements the outermost electrons are relevant. Correspondingly, elements in one column of the periodic table have similar chemical properties. For example,

- the noble gases He-Rn with their filled orbitals are very inert,
- the alkali metals (H), Li-Fr with one electron, and
- the halogens F-At with one "hole" are very reactive.

Some Notations

$\boldsymbol{v}$	vector
$v_j, \quad j = 1, 2, 3$	vector component
$v = \lvert\boldsymbol{v}\rvert = \sqrt{\boldsymbol{v}^2}$	norm (length) of the vector
V	volume
$dV = d^3r$	infinitesimal volume element
$d\Omega = d(\cos\theta)\, d\varphi$	spherical surface element
$\mathcal{H}$	Hilbert space
H	Hamiltonian
E	energy or energy eigenvalue
$\boldsymbol{r}, \boldsymbol{p}$	position and momentum operator
$\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p}$	angular momentum operator
$a^\dagger, a$	creation and annihilation operator
$\Psi(\boldsymbol{r}, t)$	wave function
$\psi(\boldsymbol{r})$	stationary wave function
χ	spin wave function
$\psi_n = \lvert n\rangle$	eigenfunction (usually for energy)
E_n	eigenenergy
$l = 0, 1, \ldots$	orbital angular momentum quantum number
$s = 0, \frac{1}{2}, 1, \ldots$	spin quantum number
$T^{(l)}$	spin-l tensor operator
$u^{(s)}$	spin-s representation of the rotation group
$\boldsymbol{S}^{(s)}$	spin-s representation of the generators (spin operator)
$\boldsymbol{\nabla} = \left(\frac{\partial}{\partial r_1}, \frac{\partial}{\partial r_2}, \frac{\partial}{\partial r_3}\right)$	nabla operator
$\Delta = \boldsymbol{\nabla} \cdot \boldsymbol{\nabla}$	Laplace operator
$e > 0$	elementary charge
$\hbar$	Planck constant
$\mu_B = \frac{e\hbar}{2m_e c}$	Bohr magneton
$E_R = \frac{e^2}{2a_B} = \frac{me^4}{2\hbar^2}$	Rydberg energy
$a_B = \frac{\hbar^2}{me^2}$	Bohr radius