Quantum Mechanics

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

Contents

Literature

G. Baym
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good, compact, modern

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entry, clear, modern structure

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beautiful introduction to quantum mechanics

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classic, emphasis on the formalism of quantum mechanics

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modern, quantum information theory, not classical quantum mechanics

Chapter 1

Introduction

1.1 Planck's Radiation Law (1900)

In the classical view, there are *particles* and *waves*. The particles define matter. They move on paths and have 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 then interfere again. Light is a wave described by the Maxwell equations. Waves and matter interact with each other. In a cavity made of matter at a temperature T, the enclosed radiation reaches a thermal equilibrium.

The free electromagnetic field satisfies the Maxwell 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

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

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[1] The alternative boundary condition $\boldsymbol{E}_{\perp} = 0$ does not lead to a solution that satisfies Gauss's law $\boldsymbol{\nabla}\cdot\boldsymbol{E} = 0$.

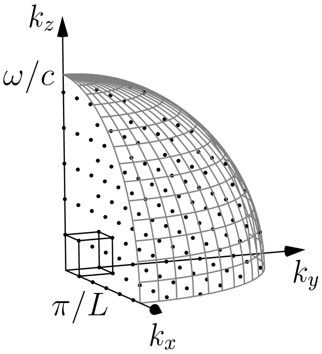

Fig. 1.1: Representation of the allowed modes: each point corresponds to a wave number allowed by the boundary condition. For large ω, the number of modes is approximately given by the volume of the octant divided by the volume $(\pi/L)^3$ of the unit cell.

The boundary conditions are satisfied if

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

On the other hand, the Maxwell equations require

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

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

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

Thus, the result of Rayleigh and Jeans for high frequencies cannot be correct.

Experiments and empirical analyses show (Wien 1896) that

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

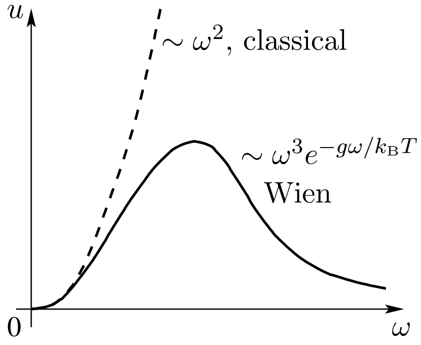

Fig. 1.2: The spectral energy density $u(\omega)$. The classically unlimited energy density (dotted) saturates in reality (solid) and exponentially decreases to zero at high energies (Wien's and Planck's radiation laws).

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

The Planck theory is able to correctly predict both limits in (1.10). The Planck 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 with frequency ω are *quantized* with $E = n\hbar\omega$, $n = 0, 1, 2, \ldots$. Thus, the average energy of the mode is given by

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

Substituting 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 the experiment provided a first indication of the *quantization* of the radiation field. The light quanta with energy $\hbar\omega$ are also called *photons.*

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

1.2 Photons (1905)

After Planck's realization that the energy of the radiation field is quantized in units of $\hbar\omega$, Einstein postulated (1905) that light consists of photons, which are indivisible and carry energy $\hbar\omega$. Considering radiation as light propagating as a plane wave with (circular) frequency ω in the 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

$$\begin{aligned}\boldsymbol{E}(\boldsymbol{r},t) = \mathrm{Re}\left(\boldsymbol{\mathcal{E}}e^{ikz-i\omega t}\right) \quad \text{with} \quad \boldsymbol{\mathcal{E}} &= E_1e^{i\phi_1}\boldsymbol{e}_1 + E_2e^{i\phi_2}\boldsymbol{e}_2 \\ &\equiv \begin{pmatrix} E_1e^{i\phi_1} \\ E_2e^{i\phi_2}\end{pmatrix} \in \mathbb{C}^2\end{aligned} \tag{1.15}$$

The vector $\boldsymbol{\mathcal{E}}$ determines the intensity of the radiation and its *polarization.* However, not every vector describes a different 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 $\theta \in \mathbb{R}$ is simply related to the shift of the time origin by $t \mapsto t - \theta/\omega$. This freedom can be used to choose $\mathcal{E}_1 \geq 0$ without loss of generality.

The following designations are used for special polarizations:

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

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

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

A general wave is called elliptically polarized.

The energy density is given by

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

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

Using

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

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 energy is quantized in units of $\hbar\omega$, we have

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

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

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

which corresponds to a photon, is called the *zero-point fluctuation* of radiation.

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

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

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

Let us now consider the following thought experiment: the radiation field is passed through a polarization filter. We assume that the polarization filter only allows radiation in the x-direction to 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 a similar calculation as above, we obtain 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 $(0 \le p \le 1)$ of photons that pass through the polarization filter.

Considering the situation with only one photon in the volume ($N = 1$), we conclude that p must be interpreted as the *probability* for the transmission of the photon. Since a photon is indivisible, it does not make sense for a fractional number p of photons to pass through the polarization filter. For the consistency of quantum theory with classical physics (*correspondence principle*), it is therefore inevitable 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 in discrete emission spectral lines. For the hydrogen atom, the empirical equation holds

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

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

Classically, the electron moves on a circular path and is therefore accelerated. Due to this circular motion, an atom should continuously emit energy and the electron should fall into the nucleus. Bohr postulates, analogous to Planck's quantization condition, that the atom can only exist in discrete states of well-defined energy E_n. The sharp spectral lines are then the consequence of transitions between these states. For example, the transition $m \mapsto n$ yields a photon with frequency

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

With this approach, one can understand the Balmer formula as 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, it is obtained 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 with mass m and charge $-e$ orbits a proton with mass $M \gg m$ and charge $e > 0$. For the discrete quantum states, Bohr postulated circular orbits with radius r, angular velocity ω, angular momentum L, and energy E. From the classical description of the central force problem, the following relationships are obtained:

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

Solving for r and E gives

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

In order for the results to match with (1.27), we need $L \propto n$. Bohr chose the quantum condition

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

This leads to

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

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

1.4 Bohr Correspondence Principle (1920)

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

As an example, we consider the Bohr atom with energies $E_n = -E_R/n^2$, see Fig. 1.3. In the classical picture, the electron orbits the proton with the angular frequency [see (1.30)]

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

Thus, we expect the atom's radiation to consist of harmonics of the fundamental frequency ω_{cl}.

Quantum mechanically, the radiation 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 relationship $n = (E_R/|E_n|)^{1/2}$.

From (1.33) we immediately obtain the correspondence

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

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

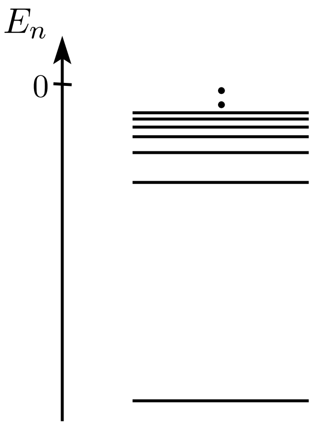

Fig. 1.3: Discrete spectrum in the Bohr atomic model. The lowest energy level is at $-E_R$. The correspondence principle can be applied to high excitation energies E_n with $n \gg 1$, where the spectrum is quasi-continuous.

1.5 Sommerfeld Quantization (1915)

The correspondence principle (or Bohr quantization) leads to discrete classical paths that are allowed in quantum mechanics. The quantization condition can be seen 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 revolution along the closed path. In fact, L is precisely the canonical momentum with respect to the angle φ in the orbital plane and it is conserved along the path. The Bohr 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. He had to assume that the problem is completely separable: that is, there are generalized coordinates q_i and momenta p_i, such that p_i depends only on the coordinate q_i (and potentially conserved quantities) but not on $q_{j\neq i}$. A bound motion is then periodic in each coordinate 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, we consider a particle moving in a 1D box potential, i.e., the motion is restricted to $x \in [0, L]$ with L being the width of the box. We consider a trajectory where the particle starts at $x = 0$ with momentum $p_0 > 0$. At $x = L$, the particle is reflected back. Conservation of energy requires that the momentum on the way back takes the value $-p_0$. Overall, the action integral is given by

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

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

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

Rigid 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 $T = \frac{1}{2}mR^2\dot{\varphi}^2$, we obtain 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 values

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

For the angular momentum $L = mR^2\omega$, we obtain analogously

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

Two-Body Problem: As shown in classical mechanics, the 2-body problem can be transformed, after separating the center-of-mass motion, into 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 $\mu = m_1m_2/(m_1+m_2)$ being the reduced mass. 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

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

making 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 square of the angular momentum

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

From (1.45), we see 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, we obtain the additional condition (for $|p_\varphi| \leq L$)[4]

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

In the final step, energy conservation provides the expression

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

Equations (1.50) and (1.51) yield the quantization of angular momentum. In general, we obtain

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

Since $|\boldsymbol{L} \cdot \boldsymbol{e}_3| \leq L$ must hold, for each l there are exactly $2l + 1$ values for $m = n_\varphi \in \{-l, -l+1, \ldots, l-1, l\}$.[5] However, the energy depends only on n_r and l due to (1.52). Therefore, each energy eigenvalue is $(2l+1)$-fold *degenerate*.

Hydrogen Atom: The hydrogen problem is a two-body problem with the reduced mass $\mu = \frac{Mm}{M+m} \approx m$ and $V(r) = -\frac{e^2}{r}$. For this specific potential, the integral (1.52) can be carried out explicitly. We obtain (for $-\frac{E_R \hbar^2}{L^2} \leq E < 0$)[6]

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

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

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

[6] For this integral, the substitution $(1 + x^2)r = r_- + r_+ x^2$ with $r_\pm$ as the turning points, which satisfy $r_+ + r_- = \frac{e^2}{|E|}$ and $r_+ r_- = \frac{L^2}{2|E|m}$, is useful.

Solving for E yields the result

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

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

In waves, it is quite 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 background. Assuming that the electron with mass m is described by a standing *matter wave* with wavelength λ_n, the wave function on the circular path with radius r_n is given by

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

The condition that the wave function transitions to itself as a standing wave under $\varphi \mapsto \varphi + 2\pi$ (see Figure 1.4) leads to $2\pi r_n = n\lambda_n$. The Bohr quantization condition is therefore equivalent to the hypothesis that matter is also waves with the de Broglie wavelength

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

which is 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 a general bound motion in a completely separable system, the integral

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

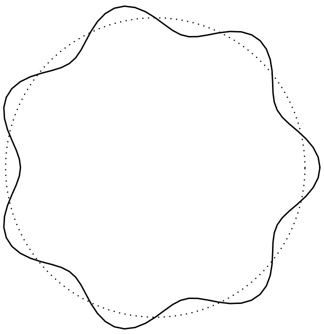

Fig. 1.4: For an allowed orbit, the wavelength λ must be chosen in such a way that a standing wave is formed. In the specific example, 7 wavelengths fit into the circumference.

corresponds exactly to the optical path length. In order for a standing matter wave to form, this integral (on a closed path) must be an integer n_i, because then exactly n_i wavelengths fit into the path.

1.7 Schrödinger Equation (1926)

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

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

suggesting a ray-optical description (note that the size of a proton is approximately $1\,\mathrm{fm} = 10^{-15}\,\mathrm{m}$). The fundamental equation of ray optics is Fermat's principle, which states that the ray minimizes the optical path length. With de Broglie [see (1.59)], this statement is equivalent to the Hamiltonian principle, which states that the classical path minimizes the action. Therefore, it remains to find a wave equation that reproduces classical mechanics in the ray-optical limit.

Schrödinger succeeded in this in 1926; the resulting Schrödinger equation[7]

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

is the fundamental equation of quantum mechanics.

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

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

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

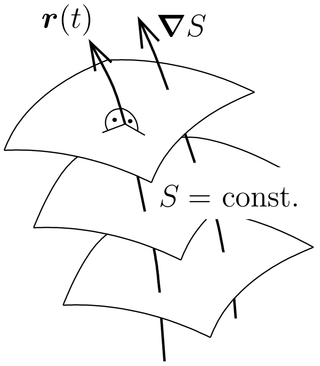

Fig. 1.5: Connection between ray optics and the Hamilton-Jacobi action: The solution $S(\boldsymbol{r},t)$ of the Hamilton-Jacobi equation corresponds to the phase of the wave function. The classical motion is along $\boldsymbol{\nabla}S$ and thus orthogonal to the surfaces of constant phase. The wavelength is given by $2\pi\hbar/|\boldsymbol{p}|$.

where A represents the amplitude and $S/\hbar$ represents 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 describes all possible classical paths and the amplitude A is a measure of 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 1.5. This means concretely that at time t, the ray at position $\boldsymbol{r}$ points in the direction of $\boldsymbol{\nabla}S$, or in formulas

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

Using

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

it is easy to calculate 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 changes only weakly over a wavelength $\propto \hbar/|\boldsymbol{\nabla}S|$. With

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

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

Inserting (1.64) into the Schrödinger equation leads, after separation of real and imaginary parts, to 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 is only valid 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 the momentum in general mechanics as $\boldsymbol{p} = \boldsymbol{\nabla} S$. The rays of wave mechanics are exactly the trajectories of the particles according to (1.63).[8] The wavelength $\lambda = 2\pi\hbar/|\boldsymbol{\nabla} S|$ corresponds to the de Broglie relationship (1.58), which explains the factor $\hbar^{-1}$ in the exponent of (1.62).

The equation (1.67) is an expression of the conservation of 'trajectories'. In fact, the density of the rays is locally described by $\rho = A^2$. In regions where many rays converge, A becomes large and an increased intensity is obtained. Multiplying equation (1.67) by A/m can be rewritten as a continuity equation

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

with the current density

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

The density expressed by the wave function results in $\rho = |\Psi|^2$. The continuity equation then yields the conservation quantity

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

As we have seen in Chapter 1.2, the wave function must be interpreted *statistically*. Due to the linearity of the Schrödinger equation, any multiple of $\Psi(\boldsymbol{r}, t)$ is also a solution. If the function $\Psi(\boldsymbol{r}, t)$ is normalized such that

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

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 located in the region $\Omega \subset \mathbb{R}^3$ at time t is given by

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

---

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

Chapter 2

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. We will see that the superposition principle plays a crucial role in the solution. We will also introduce the time-independent Schrödinger equation and observe that it leads to bound motion with a discrete spectrum, while 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 this also holds for 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 are determined by the initial condition $\Psi(\boldsymbol{r},t_0$; we will come back to this later. 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 discussed earlier,

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

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

2.2 Conservation of Probability

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

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

where in the last step we used that the additional term $\boldsymbol{\nabla}\Psi^*\cdot\boldsymbol{\nabla}\Psi = |\boldsymbol{\nabla}\Psi|^2$ is purely real. It can be seen 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*

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

being fulfilled. The probability is thus locally conserved. Integrating the continuity equation over an arbitrary region Ω, we obtain

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

The probability $p_\Omega(t)$ that the particle is located in the region Ω can only be increased or decreased by a probability current $\boldsymbol{j}$ transported through the surface $\partial\Omega$. In particular, with $\boldsymbol{j}(\boldsymbol{r},t)r^2 \to 0$ as $r\to\infty$, the surface term vanishes and the normalization of the wave function remains preserved over time, with

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

2.3 Ehrenfest's Theorem

So far, we have examined the total probability density $\rho(\boldsymbol{r},t)$. However, often we are only interested in the expectation value of the position at time t:

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

In quantum mechanics, the expectation value is conventionally denoted with square brackets, i.e., $\langle A\rangle$ is the expectation value of A.

The temporal change of the mean position of the particle can be calculated using the Schrödinger equation. We obtain for the expectation value of the velocity:

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

By performing partial integration (neglecting the boundary terms), the k-th component of the integral can be rewritten 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 therefore does not contribute to (2.10). The first term is purely imaginary due to:

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

Thus, we obtain the expression for the expectation value of the momentum:

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

By performing a similar calculation for $d\langle \boldsymbol{p} \rangle_t / dt$, we 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 moves on an inertial path 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 in the principal axis system is given by $V(\boldsymbol{r}) = \frac{m}{2} \sum_{k=1}^{3} \omega_k^2 r_k^2$. The Ehrenfest 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 the angular frequency ω_k.

In the two examples, we have seen that the mean particle position follows a classical trajectory. However, this is not always the case. In particular, the Ehrenfest theorem, due to $\langle \boldsymbol{\nabla} V(\boldsymbol{r})\rangle_t \neq \boldsymbol{\nabla} V(\langle \boldsymbol{r}\rangle_t)$, is generally not a closed equation system for the expectation value of the particle position. In order for the mean position of a particle to follow a classical trajectory, the additional assumption is needed that the wave packet is sufficiently localized.

The localization length ξ is linked to the variance (fluctuation square)

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

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

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

Thus, $\boldsymbol{r}_{\mathrm{cl}}$ satisfies the classical equation of motion up to terms of order $\xi^2\partial^3 V$. However, it is important to note that it is not sufficient to localize the particle enough at the initial time, as the probability distribution of the particle will spread 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 remains constant along the classical trajectory. In the Schrödinger equation, we can 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 a *stationary state*, since the associated density $\rho = |\Psi|^2 = |\psi|^2$ is time-independent.

The boundary condition of the eigenvalue problem determines the allowed energies E_n and the corresponding eigenfunctions ψ_n. In many cases, the set of eigenfunctions is countable with $n \in \mathbb{N}$. Furthermore, we want to assume that every (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 be written as a superposition

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

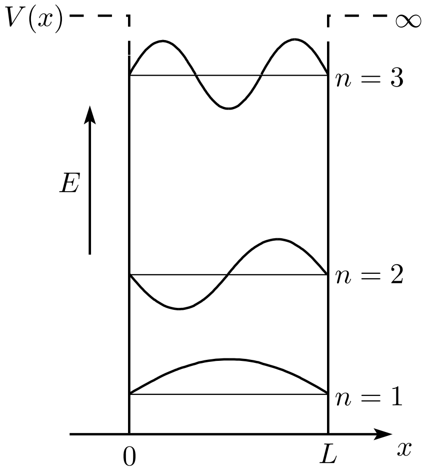

Fig. 2.1: Stationary states in the box potential.

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

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

Therefore, we have reduced the problem of finding the general solution of the Schrödinger equation (for given initial conditions) to finding eigenfunctions of the time-independent Schrödinger equation.

2.5 Bound Motion: Particle in a Box

In the following chapters, we will examine the Schrödinger equation in one dimension in a few examples. We will simply denote the spatial coordinate by $x \in \mathbb{R}$.

As a first problem, we consider the case of a particle in a box potential, which is a potential-free region surrounded by walls of infinite height, see Fig. 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 no probability of being located outside of Ω, so $\psi(x) = 0$ there. For $x \in \Omega$, the Schrödinger equation holds

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

The general solution of this differential equation has the form

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

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

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

The condition $\psi(0) = 0$ requires $A = 0$. Thus, the remaining requirement is

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

This leads to a nontrivial solution for ψ only for $\sqrt{2mE}L/\hbar = n\pi$ with $n \in \mathbb{N}$. The eigenenergies are then 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 due to the linearity of the Schrödinger equation, the eigenfunctions are only determined up to a constant B_n. In the final step, we choose the constant such that $\int dx\, |\psi_n|^2 = 1$. Thus, $\rho_n(x) = |\psi_n(x)|^2$ describes the probability of being in the stationary state with energy E_n.

Note that the energy is quantized into *discrete* values. In particular, the lowest energy is not simply $E = 0$, as classically for a stationary particle, 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*, as the particle remains in a finite region for all times. Another difference from our classical understanding 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 through superposition

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

with a_n such 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 transformation. 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 ($t > 0$)

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

The propagator satisfies the following properties:

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

The propagator can also be defined by these two properties. Since every initial value problem is solved with the propagator through (2.34), it is also called the *fundamental solution*.

It is useful to consider the condition that 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 $\Psi_0(x)$. This leads to 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 using the fundamental solution can also be generalized to other problems, as will be seen later.

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

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

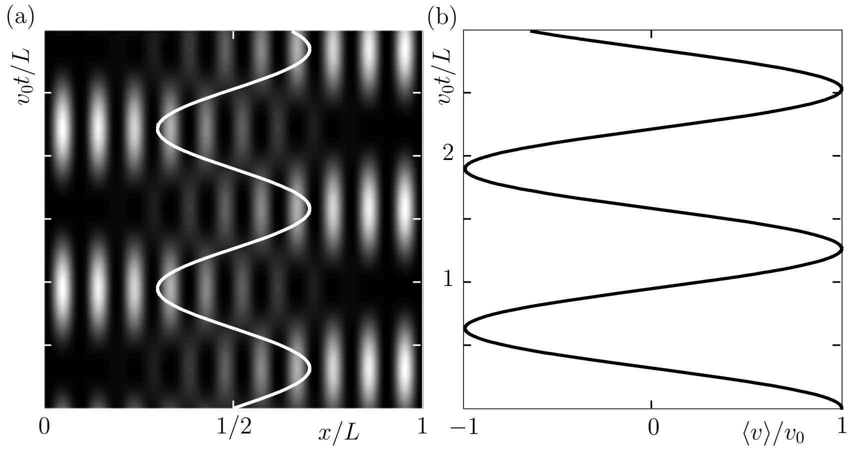

Fig. 2.2: (a) Time evolution of the probability density $\rho(x,t)$ (gray scale) of the particle for $n_0 = 10$. The white line shows the expectation value of the particle position. The particle 'moves' at least approximately with the velocity v_0 at the beginning. Unlike in the classical picture, the particle is reflected from the wall slightly earlier than at the time $L/2v_0$. (b) The expectation value of the velocity is similarly a smooth function. In classical mechanics, it would jump at each turning point between $\pm v_0$.

The probability density at time $t_0 = 0$ is given by

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

The particle has the mean position at the initial time[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 the standard deviation (square root of the variance)

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

The particle is therefore reasonably well localized in the middle of the allowed interval.

---

[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 solution of the Schrödinger equation is given by

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

The probability density follows the time dependence

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

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

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

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

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

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

with the (average) 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 version of the classical solution, see Figure 2.2: Classically, the particle moves towards the barrier at $x = L$ at the beginning. At time $L/2v_0$, the particle is then reflected at the right edge.

2.6 Unbound Motion: Free Particle

We want to apply the solution strategy from the last 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

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

---

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

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 linked to the energy through

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

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

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

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

Note that the parameter $\boldsymbol{p}$ is still related to the expectation value of the momentum. If we consider 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, every 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 much 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, from the Plancherel theorem, it follows that with $\rho(\boldsymbol{r}, t) = |\Psi(\boldsymbol{r}, t)|^2$

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

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

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

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

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

Due to probability conservation, $\Psi(\boldsymbol{r},t)$ remains normalized for all times, even though the components $\psi_{\boldsymbol{p}}$ are not normalized. For the free particle, 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

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

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

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

For fixed t, $|K(\boldsymbol{r},\boldsymbol{r}';t)| = (2\pi\hbar|t|/m)^{-3/2}$. This leads to the estimation

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

---

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

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

With this, we have seen that the solutions $\psi_{\boldsymbol{p}}$ are useful, even though they are not normalizable states. Eigenfunctions $\psi_{\boldsymbol{p}}$ of the stationary Schrödinger equation that are not normalizable are referred to as *improper* states for the eigenvalue $\boldsymbol{p}$. Such functions always occur for unbound motion with a continuous spectrum. However, it must be noted that the usefulness of the functions $\psi_{\boldsymbol{p}}$ comes from the fact that they are 'almost' normalizable. In particular, from $\psi_{\boldsymbol{p}}$ with $\boldsymbol{p}$ from a very small range, normalizable *wave packets* can be formed. It should be noted that the eigenfunctions $\exp(\boldsymbol{p}\cdot\boldsymbol{r}/\hbar)$ for $E < 0$ do not fulfill this property and therefore 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 $\psi_{p,\epsilon}$ describes a particle with momentum $\simeq p$, which is localized on a length $\xi \simeq \hbar/\epsilon$. The normalization can be easily verified 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 local wave packets from ψ_p. We will always normalize improper states in the following to

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

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

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

with the 'normalization'

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

By multiplying the improper states $\psi_q(x)$ by the phase factor $\exp(-iE_q t/\hbar)$, one obtains 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, the last term can be neglected. We then obtain the expression

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

with $v_p = p/m$ the (group) velocity. The particle thus moves with the velocity v_p, without smearing out. The contradiction to (2.58) is resolved by taking a closer look at the condition for neglecting the term. The additional phase factor has the order of magnitude $(q-p)^2t/2m\hbar \simeq \epsilon^2 t/m\hbar$. It can only be neglected 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} being the time at which the *dispersion* sets in. The approximation (2.66) is therefore only valid up to the dispersion time.

Example As an example, we consider a Gaussian wave packet with the 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

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

According to the Ehrenfest theorem for the free particle, this implies

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

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

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

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

The time evolution is obtained from (2.55)

$$
\begin{aligned}
\Psi(\boldsymbol{r},t) &= \left(\frac{\xi}{2\pi^{3/2}\hbar^2}\right)^{3/2} \int e^{i(\boldsymbol{p}\cdot\boldsymbol{r}-E_{\boldsymbol{p}}t)/\hbar} e^{-\xi^2|\boldsymbol{p}-\boldsymbol{p}_0|^2/2\hbar^2}\, d^3p \\
&\overset{(\boldsymbol{p}=\boldsymbol{q}+\boldsymbol{p}_0)}{=} \left(\frac{\xi}{2\pi^{3/2}\hbar^2}\right)^{3/2} e^{i\boldsymbol{p}_0\cdot\boldsymbol{r}/\hbar - i\boldsymbol{p}_0^2 t/2m\hbar} \int e^{i\boldsymbol{q}\cdot(\boldsymbol{r}-\boldsymbol{v}_0 t)/\hbar}\, e^{-iq^2t/2m\hbar}\, e^{-\xi^2q^2/2\hbar^2}\, d^3q \\
&= \left(\frac{\xi}{\pi^{1/2}\sigma_t}\right)^{3/2} \underbrace{e^{i\boldsymbol{p}_0\cdot\boldsymbol{r}-i\boldsymbol{p}_0^2t/2m\hbar}}_{\text{Phase}}\, e^{-|\boldsymbol{r}-\boldsymbol{v}_0t|^2/2\sigma_t}\,, \qquad (2.73)
\end{aligned}
$$

where $\sigma_t = \xi^2 + i\hbar t/m$. With the wave function (2.73), we find the variance

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

Here one can nicely see 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 out with $\Delta r \simeq \hbar t/m\xi$. The cause can be understood as follows: At the initial time, the velocity is only determined up to $\Delta v = \Delta p/m \simeq \hbar/m\xi$. The ballistic motion leads the uncertainty in velocity to an uncertainty in position $\Delta r = \Delta v\, t$, which grows linearly with time. This is different from diffusion, where the standard deviation only grows as $\Delta r \propto t^{1/2}$.

The product of the standard deviations

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

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 examine a scattering problem in one dimension using the example of a step potential with ($V_0 > 0$)

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

As always, we first look for solutions to the stationary Schrödinger equation. Since the potential does not allow for bound orbits, we expect only continuous eigenvalues with improper states to exist. In particular, we are interested in describing the scattering

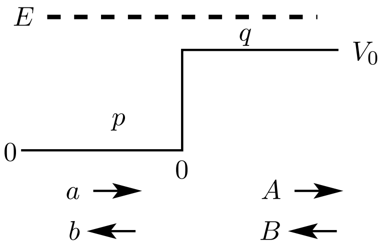

Fig. 2.3: Step potential: waves with amplitude a, A propagate to the right, while others propagate to the left.

of a particle that approaches the step from the left for $t \to -\infty$. The goal is to calculate the probability of the particle being reflected at the step.

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

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

The general solution for a fixed energy $E > 0$ is

$$\psi_p(x < 0) = a e^{ipx/\hbar} + b e^{-ipx/\hbar} \tag{2.78}$$

with $p = \sqrt{2mE}$. In the region where $x > 0$, on the other hand,

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

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

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

with $q = \sqrt{2m(E - V_0)}$. The terms with amplitudes a, A correspond to a positive momentum and therefore describe processes where the particle moves to the right, see Figure 2.3. Since we are interested in a scattering process where the particle approaches from the left, we can set $B = 0$ (the term B corresponds to a process where the particle approaches 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 derivative (with respect to position) must be continuous. These *boundary conditions* follow from the fact that the Schrödinger equation contains a second derivative. A discontinuity in the wave function or its first derivative would not satisfy the time-dependent Schrödinger equation at $x = 0$. The continuity condition of 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 the solution

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

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

$$\Psi_{p,\epsilon}(x,t) = (2\pi\hbar)^{1/2} a \underbrace{e^{ip^2t/2m\hbar}}_{\text{Phase}} \begin{cases} \overbrace{\phi_{p,\epsilon}(x-v_pt)}^{\text{incident}} + \overbrace{r\phi^*_{p,\epsilon}(x+v_pt)}^{\text{reflected}}, & x<0, \\ e^{-2imV_0x/\hbar q}\underbrace{(1+r)\phi_{p,\epsilon}[(p/q)(x-v_qt)]}_{\text{transmitted}}, & x>0, \end{cases} \tag{2.83}$$

with the wave packet of the free particle

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

which is normalized and decays on the characteristic length $\xi \simeq \hbar/\epsilon$ with $\phi(|x| \gg \xi) \approx 0$. The individual terms of $\Psi_{p,\epsilon}$ are called *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 non-zero and we obtain ($-t_{\rm disp} \ll t \ll -\xi/v_p$)

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

Since the normalization is preserved under time evolution, we can perform it at the initial time on the incident wave function with

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

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

For 'late' times (with $\xi/v_q \ll t \ll t_{\rm disp}$) the incident wave disappears and we obtain

$$\Psi_{p,\epsilon}(x,t) = e^{ip^2t/2m\hbar}\Big\{ r\phi^*_{p,\epsilon}(x+v_pt) + e^{-2imV_0x/\hbar q}(1+r)\phi_{p,\epsilon}[(p/q)(x-v_qt)]\Big\}. \tag{2.87}$$

---

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

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

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

The reflected part is located at position $-v_p t$, the transmitted part at $v_q t$ (apart from the uncertainty ξ). The overlap disappears 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 part. It is also clear here that only a probability interpretation makes sense. For long times, the point particle should either be reflected *or* transmitted. Therefore,

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

is the reflection probability and

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

is the transmission probability. Since the particle is either reflected or transmitted at late times, $R+T=1$ holds due to probability conservation.

Resistance quantum and shot noise: Scattering of electrons is microscopically the reason why materials have a finite conductivity. Consider the situation of two electrodes with a voltage difference V, connected by a quantum wire. At low temperatures, an electron has a probability T of moving from one electrode to the other. To describe the resistance, we only need one result from many-body theory: Due to the *Pauli principle*, electrode 2 injects two electrons[8] per time $2\pi\hbar/eV$. In the measurement time τ, $N = eV\tau/\pi\hbar$ electrons are injected 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 a charge of $-e$. On average, the current flows as

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

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

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

---

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

Due to the granularity of charge, the current on average over time is not constant but exhibits shot noise. The fluctuation in 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 only be transmitted without noise in a perfect quantum conductor with $T=1$. If the conductor has a finite transmission probability, there are fluctuations in the current, which are proportional to the charge of the electron.

2.8 Periodic Boundary Conditions: Particles on the Ring

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

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

where the wave function must 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 requires $e^{ip_nL/\hbar} = 1$. 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 box potential, all energies are

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

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

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

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

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 transformation

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

The general solution thus 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

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

Rotor: The mass point is a quantum mechanical rotor, meaning a particle that moves on the radius $R = L/2\pi$. Classically, the mass point has the moment of inertia

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

with the energy (L_z is the angular momentum)

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

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

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

Continuum Limit: We want to show that the free particle with periodic boundary conditions in the limit $L \to \infty$ transitions to the free particle from Chapter 2.6. The advantage of periodic boundary conditions is that there is only a discrete spectrum and thus no improper states need to be considered. Therefore, in theoretical physics, artificial periodic boundary conditions are often introduced in order to take the limit $L \to \infty$ at the end of the calculation.

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

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

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

In order for the development $\Psi_0 = \sum_n a_n\psi_n$ with (2.101) to have a finite continuum limit, we introduce the rescaled functions

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

Thus, we have

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

with the expansion coefficients (in the second step, we use the fact 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 $\tilde{a}_p$ correspond exactly to the momentum representation $\hat{\Psi}_0(p)$ and $\tilde{\psi}_p$ are the improper states with the normalization (2.61).

In general, the continuum limit corresponds 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 can introduce the periodic boundary condition in three dimensions as well 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) then applies to each coordinate direction separately.

2.9 WKB Approximation

The semiclassical or WKB approximation (Wentzel, Kramers, Brillouin 1926) allows us to approximately solve the Schrödinger equation in one dimension for large quantum numbers (which corresponds to small $\hbar$). This allows us to establish a connection between the Schrödinger equation and the old quantum theory in the Sommerfeld formulation.

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

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

Substituting into the time-independent Schrödinger equation and separating 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

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

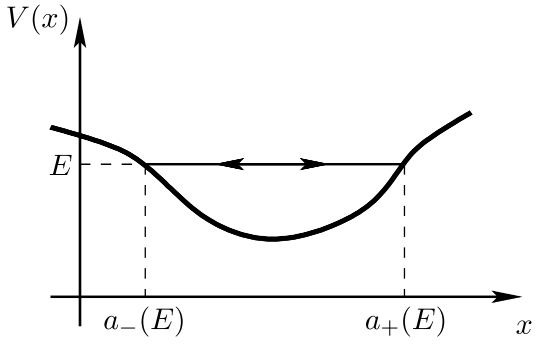

Fig. 2.4: Potential with classical turning points $a_\pm(E)$.

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

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

By integration, we obtain the solution

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

with free constants $A_\pm$.

Bound States: We are looking for eigenvalues at an energy E for which the classical trajectory is bound within the allowed range $x \in [a_-(E), a_+(E)]$, see Figure 2.4. In the allowed range, 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, we obtain 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’

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

In order for the solution to be normalizable, it must hold that $\tilde{A}_- = 0$ for $x < a_-$ and $\tilde{A}_+ = 0$ for $x > a_+$. To determine the eigenvalues E_n, we need to ‘glue together’ the solutions of the individual regions.

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 almost everywhere fulfilled, as the right-hand side becomes arbitrarily large for $\hbar \to 0$. The only exception is near the turning points. There, it holds

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

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

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

applicable. Since the approximation does not hold, especially at the turning point, it is not possible to find the correct matching condition with the WKB approximation.

We want to find the correct boundary condition at the left turning point $a = a_-$ (the other turning point follows analogously). For this, we introduce the scaled variable

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

We need the boundary condition that connects the solution for $y \ll -1$ with $y \gg 1$. In order for the wave function to be normalizable, we need the solution that decays for $y \ll -1$.

In the range $|y| \leq 1$, we need to solve the time-independent Schrödinger equation, as the condition for the WKB approximation is not satisfied. However, it is still allowed to use the linearization (2.122), since it only requires that $|V''(a)(x-a)^2| \ll |V'(a)(x-a)|$, which means

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

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

The time-dependent Schrödinger equation thus takes the form

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

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

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

This differential equation is called the Airy equation.

The solution, which 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 being any curve 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, since $e^{yz+z^3/3}$ vanishes at the endpoints and thus

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

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

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

With the parameterization $z = z_+ + it$, 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 procedure for $y \gg 1$ is analogous. The saddle points are now complex conjugate pairs $z_\pm = \pm i\sqrt{y}$ with the expansion

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

This time, 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 then 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, the result is obtained analogously

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

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[9] All these curves yield the same value due to Cauchy's theorem.

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

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

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

with $\alpha \in \mathbb{C}$. However, this is only possible if $\alpha = \pm 1$ and therefore 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: By inverting the potential in Figure 2.4, we obtain a tunneling problem. The problem is a scattering problem with the classically allowed region for $x < a_-$ and $x > a_+$. The question is about the *tunneling probability* that a particle, which approaches from the left for $t \to -\infty$, transmits to the right for $t \to +\infty$. The relevant scattering state has the form

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

The amplitudes r, t can be found again using the boundary 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 has been reduced by the value $t = \exp(-\int_{a_-}^{a_+} \tilde{p}(x)\,dx/\hbar)$. Thus, the tunneling probability is given by 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 with exponentially small probability. It is said that a particle *tunnels* through the forbidden region. The tunneling effect is important for explaining the alpha decay of atomic nuclei. Furthermore, it provides the basis for many technological 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 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 of a Hilbert space compared to a (finite-dimensional) unitary vector space is the fact that we need a concept of convergence. We require that $\mathcal{H}$ is *complete*, meaning that every convergent 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

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

The completeness is trivial.

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 $a_n \in \mathbb{C}$, $n = 1, 2, \dots$ 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 develop 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 any scalar product, then the Cauchy-Schwarz inequality holds

$$\left|\langle\phi|\psi\rangle\right|^2 \leq \|\phi\|^2 \|\psi\|^2\,. \tag{3.7}$$

3.2 Operators

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

The *adjoint operator* $A^\dagger$ is defined such that

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

for all $\phi, \psi \in \mathcal{H}$. It is naturally true that $(AB)^\dagger = B^\dagger A^\dagger$ 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 inner product with

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

Therefore, $U^\dagger = U^{-1}$.

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 apply:

- 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 different eigenvalues a_n and a_m are orthogonal with $\langle \psi_n | \psi_m \rangle = 0$. This follows from

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

Furthermore, we 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 $[B, A] = -[A, B]$. It also 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 the 'multiplication by $\boldsymbol{r}$',

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

Using the position operator, the expectation value of the particle's position in the state ψ can be written as

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

as shown in (2.9). The position operator is Hermitian, since

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

Similarly, it can be shown that $\boldsymbol{r}$ is also a Hermitian operator on $\mathcal{H}_{\text{per}}$ and $\mathcal{H}_{\text{off}}$.

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

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

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

is the correct operator. The momentum operator is Hermitian, since

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

The boundary term $\propto \phi^*\psi|_{r_j=-\infty}^{\infty}$ vanishes because the wave functions ψ, ϕ are square-integrable and therefore $\phi^*\psi$ decays rapidly enough. Similarly, it can be shown that $\boldsymbol{p}$ is Hermitian on $\mathcal{H}_{\text{per}}$ and $\mathcal{H}_{\text{off}}$.

The commutator between position and momentum operators is calculated as

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

with the Kronecker δ function

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

Furthermore, $[r_j, r_k] = [p_j, p_k] = 0$. The relations

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

are called 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 established itself as the notation for quantum mechanics. It is particularly useful for performing basis changes or writing equations independently of the basis. 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 it a 'ket'. Visually, $|\psi\rangle$ should remind us of the right part of the scalar product, see also later. 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 $|\psi\rangle$ as

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

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

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

The last expression is also called applying the operator A from the *left*.

For later, it is useful 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 the rank 1 mapping that maps the vector $|\phi\rangle$ to $|\psi\rangle$ and maps vectors in the orthogonal complement to 0. In formulae, 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 the definition step where the naturalness of Dirac notation becomes apparent. Visually, it is as if (the 'bra' vector) $\langle\phi|$ merges with $|\chi\rangle$ to form the scalar product ('bracket') $\langle\phi|\chi\rangle$. The adjoint operator to $A = |\psi\rangle\langle\phi|$ 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 Change of Basis: 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 the *identity* with $1|\psi\rangle = |\psi\rangle$. Completeness means that every state $|\psi\rangle$ can be developed in the basis. In fact, from completeness it follows

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

and thus $a_n = \langle n|\psi\rangle$ are the expansion coefficients of the state $|\psi\rangle$ in the basis $|\psi_n\rangle$. The expansion coefficients a_n are also called a *representation* of $|\psi\rangle$. For the scalar product of $|\psi\rangle$ with $|\phi\rangle = \sum_n b_n|n\rangle$ then holds

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

In general, a basis consists of both discrete states $|n\rangle$ and continuous improper states $|\alpha\rangle$, $\alpha \in \mathbb{R}^d$ with 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 the Dirac notation, the basis transformation from $\{\psi_n\}$ to $\{\phi_m\}$ can be easily understood. For the components a_n (in the basis ψ_n) of a general vector ψ, we have the transformation behavior

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

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

The Dirac notation allows us to represent transformations invariantly (i.e., independent of the basis). The relationship $|\phi\rangle = A|\psi\rangle$ 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' $\mathsf{A} = (A_{nm})$, it is simply $\boldsymbol{b} = \mathsf{A}\boldsymbol{a}$. In each basis, the components of the vectors and the elements of the matrix are different, but it always holds that $\boldsymbol{b} = \mathsf{A}\boldsymbol{a}$, which is clarified by the Dirac notation $|\phi\rangle = A|\psi\rangle$. Relationships that have been proven in one representation also hold in any other representation. Therefore, we will require a certain mental flexibility in the following and occasionally switch between the (abstract) vector $|\psi\rangle$ and its components $\langle n|\psi\rangle$ in a specific basis.

Position/Momentum Representation: We consider the Hilbert space $\mathcal{H} = L^2(\mathbb{R}^3)$. To establish the connection between an (abstract) vector $|\psi\rangle$ and 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 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

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

For the transition 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 is indeed

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

as desired by the Fourier transformation (2.52). For the inverse transformation, one obtains accordingly

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

This shows 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. A comparison with the action of the position operator $\boldsymbol{r}$ in (3.14) shows that the position vectors $|\boldsymbol{r}'\rangle$ are the improper states with eigenvalue $\boldsymbol{r}' \in \mathbb{R}^3$ given by

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

Similarly, $|\boldsymbol{p}\rangle$ is the improper state of the momentum operator $\boldsymbol{p}$ with eigenvalue $\boldsymbol{p}'$ given by

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

The position representation of the momentum operator is calculated as

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

which agrees with our previous result (3.17). A similar calculation can determine the momentum representation of the position operator

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

It should be noted 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 equivalence, a *state* of the system given by

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

One also calls a state a *ray* in the 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. The fact 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 $|n\rangle$ which uniquely correspond to the measurement values $m_n \in \mathbb{R}$. These states form an orthogonal basis and we require that any state $|\psi\rangle$ can be developed into the eigenstates $|n\rangle$ with

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

The normalization of the state implies

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

Thus, the quantity $|a_n|^2$ can be interpreted, according to Born, as the *probability* of measuring the value m_n. If we register the measurement value m_n, we know that the system is in the state $|n\rangle$ after the measurement.

In general, a measurement quantity M (*Observable*) is a Hermitian operator $M = M^\dagger$, whose eigenstates $|n\rangle$ correspond to the eigenvalues m_n and non-eigenstates $|\alpha\rangle$ correspond to the eigenvalues $m(\alpha)$ form a complete basis according to (3.34). For a measurement quantity, we need the completeness of the eigenbasis so that the probabilities add up to 1. We assume initially that M only has discrete eigenstates and that there is no degeneracy. Then the measurement of M on the state $|\psi\rangle$ is described by the *Born's rule*:

- The probability of finding the measurement value 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 value m_n is measured, the state after the measurement is $|n\rangle$.

If there is degeneracy, the rule must be generalized. We denote the eigenvectors corresponding to the eigenvalue m_n as $|n, r\rangle$, where r describes the degeneracy ($r = 1, 2, \ldots, d_n$ with d_n being the degree of degeneracy). The *generalized Born's rule* requires:

- The probability of finding the measurement value 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 value m_n is obtained, the state after the measurement (the state under the condition that m_n was measured) 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 of conditional probability in classical probability theory.

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 $\rho(\alpha)$ allow for a probability interpretation. On one hand, they are positive since they are defined by an absolute value. On the other hand, the completeness relation (generalized Plancherel relationship) yields

$$1 = \langle\psi|\psi\rangle = \langle\psi|\Big(\sum_n |n\rangle\langle n| + \int d^d\alpha\, |\alpha\rangle\langle\alpha|\Big)|\psi\rangle = \sum_n p_n + \int \rho(\alpha)\, d^d\alpha\,. \tag{3.60}$$

This means that the individual probabilities sum up to 1.

Spectral representation: An observable can be written in the spectral representation due to the completeness relation 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 has a *spectral representation*.

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

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

This is shown 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: Similarly, the momentum operator $\boldsymbol{p}$ on $L^2(\mathbb{R}^3)$ is an observable (see momentum representation). The same applies to the momentum operator $p = -i\hbar\partial/\partial x$ on $\mathcal{H}_{\text{per}}$. However, it should be noted 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, we have

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

with the general solution

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

However, the boundary conditions $\psi(0) = \psi(L) = 0$ cannot be satisfied for any choice of integration constants $A \in \mathbb{C}$. Therefore, the operator p 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

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

or

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

in the position representation. It can be easily shown 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 only yields 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, any function $f(M)$ is also an observable. We define $f(M)$ through 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-Space: As another example, we consider the Hilbert space

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

of a particle on the half-space. This Hilbert space is relevant, for example, in the case where we have a potential barrier at $x = 0$ with $V(x < 0) = \infty$. The momentum operator $p = -i\hbar\partial/\partial x$ is Hermitian. However, it is not an observable because there are no eigenfunctions: note that the plane wave

$\exp(ipx/\hbar)$ does not satisfy the boundary condition. This does not mean, of course, that one cannot measure the momentum of a particle on the half-space. It is just that there is no measurement apparatus that measures the operator p 'exactly'. Such a measurement is unphysical, as a projection onto the state $\exp(ipx/\hbar)$ requires 'infinite' energy, since the particle would then have a finite probability of being in the forbidden region with $V = \infty$.

Overall, measurement theory is still an active field of research. In the specific case, one could study a particular measurement setup in more detail to determine a more realistic momentum operator. Here, we will stick to an idealized description. We consider a detector located in the region $\Omega = [x_0, x_0 + \xi]$ (meaning the detector only has access to the wave function $|\psi_\Omega\rangle$). It can be shown 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 in $L^2(\Omega)$. It is natural to assign the momentum p_n to the state $|n\rangle$. Therefore, we 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, as we have already written it in the spectral representation. If the particle is outside the region Ω of the detector, the measurement of p_{HR} yields zero. If the particle is at Ω, the measurement results p_n are possible. The measurement accuracy is given by $p_{n+1} - p_n = 2\pi\hbar/\xi$. For an accurate momentum measurement, a long detector is required (ξ large). Furthermore, the measurement of p_{HR} is only a momentum measurement under the condition that the particle is in Ω. The relevant conditional wave function is given by (3.69).

Heisenberg Uncertainty Principle: We define the *variance* 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 therefore $\Delta M = 0$. An eigenstate is thus exactly the state in which the observable M takes the value m_n with certainty.

Two observables M and N usually do not have a common eigenstate, so it is not possible for M and N to be simultaneously (sharply) determined. In fact, for two observables M, N in the state ψ, the *Heisenberg Uncertainty Principle* holds

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

The inequality follows from the relationship

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

for two arbitrary Hermitian operators A, B. Therefore,

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

and we 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 used the Cauchy-Schwarz inequality. With $A = M - \langle M\rangle$, $B = N - \langle N\rangle$ and $[A,B] = [M,N]$, this leads to the Heisenberg Uncertainty Principle.

The name 'uncertainty relation' is inappropriate in that it does not describe an inaccuracy of the measuring apparatus. Rather, there is no state of the system such that the product of the standard deviations $\Delta M\,\Delta N$ of the measurements of M and N falls below the threshold of (3.75).

On $\mathcal{H} = L^2(\mathbb{R}^3)$, we have

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

for the commutator of the position and momentum operators, see (3.19). This implies the uncertainty relation [cf. (2.75)]

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

Therefore, the position and momentum cannot be simultaneously precisely determined (in the same direction).

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

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

Observables M and N can be *simultaneously diagonalized* if and only if $[M,N] = 0$. Therefore, two observables are compatible if they can be simultaneously diagonalized.

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

For the reverse 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 developed in the eigenspaces of M as,

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

with $M|\psi_j\rangle = m_j|\psi_j\rangle$ and m_j different.[2] 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. Therefore, the individual summands satisfy

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

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 common system of eigenfunctions is non-degenerate. The simultaneous measurements of $M_1, \cdots, M_n$ therefore uniquely determine the state $|m_1, \ldots, m_n\rangle$ by specifying the measurement values $m_1, \cdots, m_n$.

3.5 Hamiltonian Operator

The Schrödinger equation generally has 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 *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 then require that H is an observable with real eigenvalues, which correspond to the energy of the stationary state. The completeness of the eigenbasis allows the development of any initial state, see (2.21).

Examples

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

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

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

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

N-Particles: The wave function of N particles 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 of finding the particles at positions $\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N$. The Hamiltonian operator in this case is

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

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

One can consider the 2-particle system as a *tensor product* with

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

This implies $L^2(\mathbb{R}^6) = L^2(\mathbb{R}^3) \otimes L^2(\mathbb{R}^3)$. 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) from $\psi_1 \in \mathcal{H}_1$ and $\psi_2 \in \mathcal{H}_2$ as $|\psi_1, \psi_2\rangle = |\psi_1\rangle \otimes |\psi_2\rangle$. 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 similarly for the second argument. The space $\mathcal{H}$ is a Hilbert space with the scalar product $\langle \phi_1, \phi_2 | \psi_1, \psi_2 \rangle = \langle \phi_1 | \psi_1 \rangle \, \langle \phi_2 | \psi_2 \rangle$. An operator O acts on the tensor product as $O = A \otimes B$ 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 single-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 thus the tensor space $\mathcal{H}^{(N)} = \otimes^N L^2(\mathbb{R}^3)$ with N factors.

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

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

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 operator changes with $H' \neq H$. 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

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

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

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

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

with the initial condition $|\Psi_{t_0}\rangle = |\Psi_0\rangle$. The propagator $U(t) = e^{-iHt/\hbar}$ forms a 1-parameter group of unitary operators. Unitarity follows from the Hermiticity $H = H^\dagger$ because

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

Thus, the scalar product remains conserved 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 time evolution provides

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

with [cf. (2.56)]

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

3.6 Pictures

The task of quantum mechanics is to predict the expectation value (measurement 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 any observable M at time t. The observable and states are only determined up to a *unitary equivalence*. This means that one can choose any unitary mapping $V_t\colon \mathcal{H}\to\mathcal{H}$ at time t and transform the states and observables with $|\Psi_t\rangle \mapsto |\tilde\Psi_t\rangle = V_t|\Psi_t\rangle$, $M \mapsto \tilde M_t = V_tMV_t^\dagger$, without changing measurement quantities. The Hamiltonian operator 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

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

there is also the *Heisenberg picture*

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

to mention, where the observables

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

evolve in time and the states are static. The observables change according to the *Heisenberg equation*[3]

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

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

3.7 Mixed States

According to Born's rule, a state $|\psi\rangle$ describes the probabilities that certain measurement results 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 a probability of 0 on the other hand. Probabilities p with $0 < p < 1$ 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. For example, consider the case where a colleague in her quantum lab can prepare two orthogonal states $|\psi_1\rangle$ and $|\psi_2\rangle$. She informs us that she will prepare the state $|\psi_1\rangle$ with probability p_1 and the state $|\psi_2\rangle$ with probability $p_2 = 1 - p_1$. In this case, the description of the system cannot be achieved by a pure state. A similar situation occurs during measurement when our colleague tells us that she has measured an observable, but does not (unfortunately) inform us of the measurement result. In both cases, we only have 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:

---

[3] We use that $[H, V_t] = 0$ and $\dot{V}_t = iHV_t/\hbar$.

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

Due to Hermiticity, the density matrix can be diagonalized with an orthonormal basis $|\psi_j\rangle$ with eigenvalues $p_j \in \mathbb{R}$. Furthermore, we have $p_j \geq 0$ (due to point 2) and $\sum_j p_j = 1$ (due to 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 exactly the cases where ρ is a projector with $\rho^2 = \rho$ (thus there exists a j such that $p_j = 1$ 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 operator H according to the Schrödinger equation is given by $e^{-iHt/\hbar}|\psi_j\rangle$. Thus, 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 thus follows the *von Neumann equation*

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

Note the different sign compared to (3.105).

3.8 Harmonic Oscillator

The harmonic oscillator is a 'Drosophila' of quantum mechanics. Many problems can be mapped to the (shifted) harmonic oscillator and are therefore exactly solvable (phonons in the crystal lattice, electrons in a magnetic field, electromagnetic radiation field, ...). The 1-dimensional Hamiltonian operator 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 look for stationary states $|\psi\rangle \in \mathcal{H}$ with $H|\psi\rangle = E|\psi\rangle$. We switch 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 operator

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

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 is calculated as

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

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 operator 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 do this, 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.

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

However, the states $a^\dagger|n\rangle$ and $a|n\rangle$ are not yet normalized. We find

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

Therefore, 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 results from the truncation 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 arbitrarily lowered by applying a, and the ladder $|n\rangle \overset{a}{\mapsto} |n-1\rangle \overset{a}{\mapsto} \cdots$ must terminate. This is only possible if a state is mapped to the 0-vector by a. 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 an energy of $E_{n=0} = \frac{1}{2}\hbar\omega > 0$, which corresponds to the zero-point fluctuation.

The further 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 as

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

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

In position representation, the states are represented by wave functions. The determination equation (3.127) for the vacuum state then has the form

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

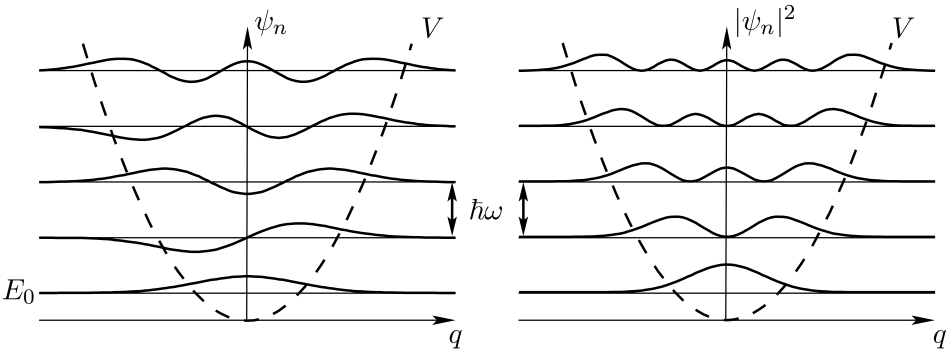

Fig. 3.1: Eigenfunctions of the harmonic oscillator, left the amplitudes ψ_n, right the probabilities $|\psi_n|^2$ for $n = 0, \ldots, 4$.

with the normalized and unique solution

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

The equation (3.128) provides 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, as 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

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

Coherent States: We know from the Ehrenfest theorem that the expectation values $\langle x\rangle_t$ and $\langle p\rangle_t$ for the harmonic oscillator move along classical paths. The question is therefore about wave packets that minimize the standard deviations Δx and Δp, so that the states are described as accurately as possible by the expectation values. The Heisenberg uncertainty relation $\Delta x\, \Delta p \geq \frac{1}{2}\hbar$ represents a lower bound. In fact, the vacuum state $|0\rangle$ saturates the lower bound, since

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

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

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

meaning the shifted 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 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 calculation, one can show that $a|\alpha\rangle = \alpha|\alpha\rangle$ holds. The time evolution of 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 expectations values follow 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 onto itself. The transformation can be imagined as passive (changing the reference system) or active (transforming the particle). An important example is the *spatial 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 observables do not transform under the symmetry (otherwise we would have a trivial unitary equivalence).

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

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

Due to complex conjugation, A cannot be a linear operator. In fact, A is an *antilinear* operator with

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

The adjoint operator is defined as [compare with (3.26) for a linear operator]

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

Thus, 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 refers to S as a *symmetry of the system* described by the Hamiltonian operator 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 helpful when one knows the eigenspaces of S. Since S and H commute, they are simultaneously diagonalizable. Therefore, one can consider H restricted to the eigenspaces of S to simplify the problem.

For any observable M, one finds the symmetry transformation of any expectation value

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

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

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

under the symmetry transformation. If S is a symmetry of the system, the Hamiltonian operator remains invariant under S. This is because from $HS = SH$ it follows

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

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

Spatial Reflection: As a simple example, we consider spatial reflection (parity) $(P\psi)(\boldsymbol{r}) = \psi(-\boldsymbol{r})$. Spatial reflection is a Hermitian operator $P = P^\dagger$, which maps $L^2(\mathbb{R}^3)$ onto itself. It satisfies $P^2 = 1$. Thus, P is an involution with eigenvalues ±1. One can examine its action on the position operator

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

This leads to the relationships

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

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

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

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

A parity-invariant system with a non-degenerate 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, an observable M is called

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

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

Examples of observables that are even under parity are $\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p}$ and $\boldsymbol{p}^2$. On the other hand, observables that are odd under parity include $\boldsymbol{r}, \boldsymbol{p}, \boldsymbol{L} \cdot \boldsymbol{r}$.

Now, let's consider two eigenstates $|\phi\rangle$ and $|\psi\rangle$ with parities p_ϕ and p_ψ, and an observable with parity p_M. A simple calculation then yields

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

For such matrix elements, the *selection rule* is

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

Time reversal: For time reversal T, the following conditions 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, we have

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

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

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

From the antilinearity, we obtain

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

and thus

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

The Schrödinger equation transforms under time reversal as

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

with the time-reversed state and Hamiltonian operator

$$\tilde{\Psi}(\boldsymbol{r},t) = T^\dagger \Psi(\boldsymbol{r},-t), \qquad\qquad \tilde{H} = T^\dagger H T\,. \tag{4.22}$$

If the system is time-reversal invariant ($\tilde{H} = H$), 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 exactly when $\Psi(\boldsymbol{r},t)$ does.

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[1] This is not necessarily the case for the state, as it cannot be measured. Such a representation is called *projective*.

For a particle with Hilbert space $L^2(\mathbb{R}^3)$, the time reversal is given by complex conjugation (in position representation)

$$(T\psi)(\boldsymbol{r}) = \psi(\boldsymbol{r})^* \tag{4.23}$$

with $T^2 = 1$. The Hamiltonian operator

$$H = \frac{\boldsymbol{p}^2}{2m} + V(\boldsymbol{r}) = -\frac{\hbar^2}{2m}\Delta + V(\boldsymbol{r}) \tag{4.24}$$

is time reversal invariant, since

$$T^\dagger V(\boldsymbol{r}) T = V(\boldsymbol{r}) \qquad \text{and} \qquad T^\dagger \boldsymbol{p}^2 T = \boldsymbol{p}^2\,, \tag{4.25}$$

due to (4.16). The stationary states can therefore be chosen as real with $T\psi = \psi$.

For a particle in a static electromagnetic field, we have

$$T^\dagger \left\{ \frac{1}{2m}\left[\boldsymbol{p} - \frac{q}{c}\boldsymbol{A}(\boldsymbol{r})\right]^2 + q\varphi(\boldsymbol{r}) \right\} T = \frac{1}{2m}\left[\boldsymbol{p} + \frac{q}{c}\boldsymbol{A}(\boldsymbol{r})\right]^2 + q\varphi(\boldsymbol{r})\,. \tag{4.26}$$

The system is only time reversal invariant if no external magnetic field is applied, $\boldsymbol{A} = 0$. Since time reversal is an antiunitary operator, it does not provide selection rules analogous to (4.15).

Kramers degeneracy: An antiunitary symmetry T of the system with $T^2 = -1$ leads to a degeneracy of all eigenenergies. Let ψ be an eigenstate with energy $E \in \mathbb{R}$. The state $\phi = T\psi$ is also a state with the same energy, since

$$H\phi = HT\psi \overset{[T,H]=0}{=} TH\psi = E\phi\,. \tag{4.27}$$

Due to the following argument, ϕ cannot be the same state as ψ: from $T^\dagger = -T$ it follows that

$$\langle\psi|\phi\rangle = \langle\psi|T\psi\rangle = \langle\psi|T^\dagger\psi\rangle = -\langle\psi|T\psi\rangle = -\langle\psi|\phi\rangle\,. \tag{4.28}$$

Thus, the states ψ and ϕ are orthogonal to each other. The two states $\phi = T\psi$ and ψ are also called ‘complex-conjugate’ states.

Lattice translations: We consider a particle in the Hilbert space $L^2(\mathbb{R})$. The potential has a discrete translational symmetry $V(x + L) = V(x)$. This is a model for the electron motion in the ionic background of a solid. The Hamiltonian operator $H = p^2/2m + V(x)$ 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 given by $e^{i\lambda}$ with $\lambda \in [-\pi, \pi]$. Since τ is a symmetry of the system, the Hamiltonian operator can be individually diagonalized in the eigenspaces for fixed λ. In the eigenspaces, we have

$$(\tau\psi)(x) = \psi(x+L) = e^{i\lambda}\psi(x)\,. \tag{4.31}$$

It is conventional to parameterize the eigenvalue with $\lambda = kL$. Writing the wave function as $\psi(x) = e^{ikx}u_k(x)$, we have $e^{i\lambda+ikx}u_k(x+L) = \psi(x+L) \overset{(4.31)}{=} e^{i\lambda}\psi(x) = e^{i\lambda+ikx}u_k(x)$.

Thus, the *Bloch Theorem* holds: eigenfunctions of the Hamiltonian operator H can be chosen such that

$$\psi(x) = e^{ikx}u_k(x) \qquad \text{with} \qquad u_k(x+L) = u_k(x) \quad \text{(periodic)}. \tag{4.32}$$

This reduces the problem to a problem in $\mathcal{H}_{\text{per}}$. In particular, one only needs to solve the eigenvalue problem (also called the $\boldsymbol{k}\cdot\boldsymbol{p}$ problem)

$$\begin{aligned} Eu(x) = e^{-ikx}H\psi(x) &= \frac{1}{2m}e^{-ikx}\left(-i\hbar\frac{d}{dx}\right)^2 e^{ikx}u_k(x) + V(x)u_k(x) \\ &= \frac{1}{2m}\underbrace{\left(\hbar k - i\hbar\frac{d}{dx}\right)^2}_{(\hbar k+p)^2} u_k(x) + V(x)u_k(x), \qquad u_k \in \mathcal{H}_{\text{per}} \end{aligned} \tag{4.33}$$

to solve for $u_k(x)$. The crystal momentum of the particle is denoted by $\hbar k$.

4.2 Continuous Symmetries

Just like in classical physics, continuous symmetries in quantum mechanics are related to conserved observables. In quantum mechanics, a continuous symmetry is a 1-parameter group of unitary transformations[2] with

$$U(\alpha)U(\beta) = U(\alpha+\beta), \qquad U(0) = 1. \tag{4.34}$$

Due to unitarity, we have $U^\dagger(\alpha) \equiv U(\alpha)^\dagger = U(\alpha)^{-1} = U(-\alpha)$. As before, symmetries act either on the state with $\psi \mapsto U\psi$ or on observables with $M \mapsto U^\dagger M U$ (but not both). The group is a continuous symmetry of the system if

$$U^\dagger(\alpha)HU(\alpha) = H, \qquad \text{for all } \alpha. \tag{4.35}$$

A continuous symmetry satisfies the differential equation

$$\frac{dU(\alpha)}{d\alpha} = \frac{dU(\alpha+\beta)}{d\beta}\Big|_{\beta=0} = i\left[-iU'(0)\right]U(\alpha) = \frac{iG}{\hbar}U(\alpha) \tag{4.36}$$

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[2] Continuous symmetries are always unitary, since every $U(a) = U(a/2)^2$ is the square of a symmetry.

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 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, properties are typically shown for an infinitesimal transformation (Lie algebra). Due to the uniqueness of the solution of the differential equation (4.37), it can be extended to finite transformations (Lie group).

From the unitarity of U, it follows that the generator G is a Hermitian operator. Because

$$0 = \frac{d}{d\alpha}(U^\dagger U)\Big|_{\alpha=0} = U^\dagger(0)U'(0) + U^{\dagger\prime}(0)U(0) = \frac{i}{\hbar}(G - G^\dagger)\,. \tag{4.38}$$

Any observable M is mapped by the symmetry group to the family $M(\alpha) = U^\dagger(\alpha)MU(\alpha)$. For an infinitesimal transformation, we have

$$\frac{d}{d\alpha}M(\alpha)\Big|_{\alpha=0} = U^\dagger(0)MU'(0) + U^{\dagger\prime}(0)MU(0) = \frac{i}{\hbar}(MG - GM) = \frac{i}{\hbar}[M, G]\,. \tag{4.39}$$

If $U(\alpha)$ is a symmetry of the system, then

$$0 = [H, G]\,. \tag{4.40}$$

Therefore, the observable[3] G commutes with the Hamiltonian operator and can be simultaneously diagonalized. In the Heisenberg picture, it is also clear that

$$\frac{d}{dt}G_H = \frac{i}{\hbar}[H, G]_H = 0\,. \tag{4.41}$$

This means that the quantity G remains constant under time evolution.

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

$$(G_{\boldsymbol{e}}\psi)(\boldsymbol{r}) = -i\hbar\frac{d}{d\alpha}\psi(\boldsymbol{r} + \alpha\boldsymbol{e})\Big|_{\alpha=0} = -i\hbar\boldsymbol{e}\cdot\boldsymbol{\nabla}\psi(\boldsymbol{r}) = (\boldsymbol{e}\cdot\boldsymbol{p})\psi(\boldsymbol{r})\,. \tag{4.43}$$

This corresponds exactly to the momentum operator in the direction of $\boldsymbol{e}$. The momentum operator is therefore conserved under time evolution if the system is translationally invariant. In this case, energy eigenstates with well-defined momentum can be found.

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[3] In this chapter, we neglect the subtle distinction and refer to all Hermitian operators as ‘observables’.

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 the translational invariance $\boldsymbol{r}_k \mapsto \boldsymbol{r}_k + \alpha \boldsymbol{e}$ of the Hamiltonian operator that the total momentum $\boldsymbol{P} = \sum_k \boldsymbol{p}_k$ is conserved.

4.3 Angular Momentum

The angular momentum is an important continuous symmetry. Especially because most particles in quantum mechanics have an internal degree of freedom, the *spin*, which behaves like an angular momentum. The rotation $R_{\boldsymbol{e}}(\alpha)$ around the axis $\boldsymbol{e}$ ($|\boldsymbol{e}| = 1$) with the rotation angle α is generated by the continuous symmetry[4]

$$(U_{\boldsymbol{e}}(\alpha)\psi)(\boldsymbol{r}) = \psi(R_{\boldsymbol{e}}(\alpha)\boldsymbol{r})\,. \tag{4.45}$$

For $R \in \mathsf{SO}(3)$, we know from mechanics that

$$\frac{d}{d\alpha} R_{\boldsymbol{e}}(\alpha)\boldsymbol{r}\Big|_{\alpha=0} = \boldsymbol{e} \times \boldsymbol{r}\,. \tag{4.46}$$

For an infinitesimal transformation, we therefore have

$$(G_{\boldsymbol{e}}\psi)(\boldsymbol{r}) = -i\hbar \frac{d}{d\alpha}\psi(R_{\boldsymbol{e}}(\alpha)\boldsymbol{r})\Big|_{\alpha=0} = -i\hbar(\boldsymbol{e} \times \boldsymbol{r}) \cdot \boldsymbol{\nabla}\psi(\boldsymbol{r}) = -i\hbar \boldsymbol{e} \cdot (\boldsymbol{r} \times \boldsymbol{\nabla})\psi(\boldsymbol{r})\,. \tag{4.47}$$

We find the generator

$$G_{\boldsymbol{e}} = \boldsymbol{e}\cdot(\boldsymbol{r}\times\boldsymbol{p}) = \boldsymbol{e}\cdot\boldsymbol{L}, \quad \text{(angular momentum component in the direction of the axis of rotation).} \tag{4.48}$$

For the expectation value of the rotated position operator $\boldsymbol{r}(\alpha)$ in any state ψ, we have

$$\langle\psi|\boldsymbol{r}(\alpha)|\psi\rangle = \langle U\psi|\boldsymbol{r}|U\psi\rangle = \int \psi(R\boldsymbol{r})^* \boldsymbol{r} \psi(R\boldsymbol{r})\, d^3r = \int \psi(\boldsymbol{r})^* (R^{-1}\boldsymbol{r}) \psi(\boldsymbol{r})\, d^3r \tag{4.49}$$

This implies $\boldsymbol{r}(\alpha) = U_{\boldsymbol{e}}^\dagger(\alpha)\boldsymbol{r}U_{\boldsymbol{e}}(\alpha) = R_{\boldsymbol{e}}^{-1}(\alpha)\boldsymbol{r}$ and the observables are transformed exactly opposite to the states. This makes sense, because the untransformed operator

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[4] In this script, we consider symmetry transformations from a passive standpoint. This is a different convention than most texts on representation theory. A concatenation of two rotations then leads to $(U_{\boldsymbol{e}_2}(\alpha_2)U_{\boldsymbol{e}_1}(\alpha_1)\psi)(\boldsymbol{r}) = \psi(R_{\boldsymbol{e}_1}(\alpha_1)R_{\boldsymbol{e}_2}(\alpha_2)\boldsymbol{r})$. Similarly, for a vector operator $U_{\boldsymbol{e}_1}^\dagger(\alpha_1)U_{\boldsymbol{e}_2}^\dagger(\alpha_2)\boldsymbol{v}U_{\boldsymbol{e}_2}(\alpha_2)U_{\boldsymbol{e}_1}(\alpha_1) = R_{\boldsymbol{e}_1}(\alpha_1)^{-1}R_{\boldsymbol{e}_2}(\alpha_2)^{-1}\boldsymbol{v} = [R_{\boldsymbol{e}_2}(\alpha_2)R_{\boldsymbol{e}_1}(\alpha_1)]^{-1}\boldsymbol{v}$, see (4.51). The vector operators $\boldsymbol{v}$ thus rotate in the 'reverse' direction compared to the coordinates $\boldsymbol{r}$ in the wave function $\psi(\boldsymbol{r})$ and $U_{\boldsymbol{e}}^\dagger(\alpha)$ is a representation of the rotation group.

$\boldsymbol{r}$ applied to the transformed state $\psi(R\boldsymbol{r})$ gives the same result as the transformed operator $R^{-1}\boldsymbol{r}$ applied to the untransformed state $\psi(\boldsymbol{r})$.

For an infinitesimal rotation, we obtain the commutator [see Eq. (4.46)]

$$\frac{i}{\hbar}[\boldsymbol{r}, \boldsymbol{e}\cdot\boldsymbol{L}] = \frac{d}{d\alpha}\boldsymbol{r}(\alpha)\Big|_{\alpha=0} = \frac{d}{d\alpha}R_{\boldsymbol{e}}^{-1}(\alpha)\boldsymbol{r}\Big|_{\alpha=0} = -\boldsymbol{e}\times\boldsymbol{r}\,. \tag{4.50}$$

Scalar and Vector Operators: A vector $\boldsymbol{v} = (v_1, v_2, v_3)$ consisting of three operators v_j is called a *vector operator* if its three components transform under rotations like the position operator; that is, $\boldsymbol{v}$ is a vector operator if

$$\begin{aligned} U_{\boldsymbol{e}}^{\dagger}(\alpha)\boldsymbol{v}U_{\boldsymbol{e}}(\alpha) = R_{\boldsymbol{e}}^{-1}(\alpha)\boldsymbol{v} \quad &\overset{(4.50)}{\Leftrightarrow} \quad [\boldsymbol{v}, \boldsymbol{e}\cdot\boldsymbol{L}] = i\hbar\,\boldsymbol{e}\times\boldsymbol{v} \\ &\overset{\boldsymbol{f}\cdot}{\Leftrightarrow} \quad [\boldsymbol{f}\cdot\boldsymbol{v}, \boldsymbol{e}\cdot\boldsymbol{L}] = i\hbar\,(\boldsymbol{f}\times\boldsymbol{e})\cdot\boldsymbol{v}\,. \end{aligned} \tag{4.51}$$

This equation means that measuring the rotated components $R^{-1}\boldsymbol{v}$ of $\boldsymbol{v}$ yields the same result as measuring $\boldsymbol{v}$ in the rotated state $(U\psi)(\boldsymbol{r}) = \psi(R\boldsymbol{r})$.

An operator A is called 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 also examines a well-defined transformation behavior under parity. Scalars that behave oddly under parity are called *pseudoscalars*. Depending on their symmetry under parity, vectors are called *polar* (odd under parity) or *axial* (even under parity).

Examples

Position Operator: As shown before, the position operator $\boldsymbol{r}$ is a (polar) vector operator.

Momentum Operator: From the canonical commutation relation $[r_j, p_k] = i\hbar\delta_{jk}$, we have

$$[p_j, \boldsymbol{e}\cdot\boldsymbol{L}] = [p_j, \boldsymbol{r}\cdot(\boldsymbol{p}\times\boldsymbol{e})] = \sum_k [p_j, r_k](\boldsymbol{p}\times\boldsymbol{e})_k = -i\hbar(\boldsymbol{p}\times\boldsymbol{e})_j \tag{4.53}$$

and thus $\boldsymbol{p}$ 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, the following holds for the cross product (either rotating the initial vectors or equivalently their product)

$$(R^{-1}\boldsymbol{v})\times(R^{-1}\boldsymbol{w}) = R^{-1}(\boldsymbol{v}\times\boldsymbol{w})\,. \tag{4.55}$$

From the fact that $\boldsymbol{v}$ and $\boldsymbol{w}$ are vector operators, it immediately follows for any rotation

$$U^\dagger(\boldsymbol{v}\times\boldsymbol{w})U \overset{(UU^\dagger=1)}{=} (U^\dagger\boldsymbol{v}U)\times(U^\dagger\boldsymbol{w}U) = (R^{-1}\boldsymbol{v})\times(R^{-1}\boldsymbol{w}) = R^{-1}(\boldsymbol{v}\times\boldsymbol{w})\,. \tag{4.56}$$

Thus, $\boldsymbol{v}\times\boldsymbol{w}$ 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 therefore an axial vector and satisfies the *angular momentum algebra*

$$[\boldsymbol{L},\boldsymbol{e}\cdot\boldsymbol{L}] = i\hbar\,\boldsymbol{e}\times\boldsymbol{L} \qquad \overset{\boldsymbol{f}\cdot}{\Leftrightarrow} \qquad [\boldsymbol{f}\cdot\boldsymbol{L},\boldsymbol{e}\cdot\boldsymbol{L}] = i\hbar\,(\boldsymbol{f}\times\boldsymbol{e})\cdot\boldsymbol{L}\,. \tag{4.57}$$

Dot Product: For the dot product of two vectors $\boldsymbol{v}$ and $\boldsymbol{w}$, we have

$$(R^{-1}\boldsymbol{v})\cdot(R^{-1}\boldsymbol{w}) = \boldsymbol{v}\cdot\boldsymbol{w}\,. \tag{4.58}$$

For two vector operators, this immediately implies

$$U^\dagger(\boldsymbol{v}\cdot\boldsymbol{w})U = (U^\dagger\boldsymbol{v}U)\cdot(U^\dagger\boldsymbol{w}U) = (R^{-1}\boldsymbol{v})\cdot(R^{-1}\boldsymbol{w}) = \boldsymbol{v}\cdot\boldsymbol{w}\,. \tag{4.59}$$

The dot product $\boldsymbol{v}\cdot\boldsymbol{w}$ of two vector operators is a scalar operator. The parity ('true' scalar or pseudoscalar) again follows 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 dot product of two axial vectors. Therefore, $\boldsymbol{L}^2$ is a scalar operator with

$$[\boldsymbol{L}^2,\boldsymbol{L}] = 0\,. \tag{4.60}$$

The angular momentum squared commutes with all components of the angular momentum operator. Similarly, $\boldsymbol{p}^2$ 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. However, it holds that

$$\boldsymbol{r}\cdot\boldsymbol{L} = \boldsymbol{r}\cdot(\boldsymbol{r}\times\boldsymbol{p}) = (\boldsymbol{r}\times\boldsymbol{r})\cdot\boldsymbol{p} = 0\,. \tag{4.62}$$

Thus, the angular momentum is 'perpendicular' to the position vector. Similarly, it can be shown 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 operator $H=\boldsymbol{p}^2/2m+V(\boldsymbol{r})$ is conserved only when $V(\boldsymbol{r})$ is rotationally symmetric around the axis of rotation $\boldsymbol{e}$. In a completely rotationally symmetric system with $V(\boldsymbol{r}) = V(r)$, all angular momentum components $\boldsymbol{L}$ are conserved. However, L_1, L_2, L_3 are not compatible observables, as shown in equation (4.57).

Therefore, the task is to determine the maximum number of commuting observables from $\boldsymbol{L}$. In this specific case, it turns out that two compatible observables can be obtained from $\boldsymbol{L}$. Usually, one 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, in addition to the position $\boldsymbol{r}$, an internal degree of freedom (spin) that behaves like angular momentum. In quantum mechanics, the spin is described by the wave function becoming a vector-valued wave function on $L^2(\mathbb{R}^3) \otimes \mathbb{C}^n$ with

$$\boldsymbol{\psi}(\boldsymbol{r}) = \begin{pmatrix} \psi_1(\boldsymbol{r}) \\ \vdots \\ \psi_n(\boldsymbol{r}) \end{pmatrix}, \qquad \langle \boldsymbol{r}, m | \boldsymbol{\psi} \rangle = \psi_m(\boldsymbol{r}) \,. \tag{4.63}$$

Naturally, we choose the scalar product to be

$$\langle \boldsymbol{\phi} | \boldsymbol{\psi} \rangle = \int \boldsymbol{\phi}(\boldsymbol{r})^* \cdot \boldsymbol{\psi}(\boldsymbol{r}) \, d^3r = \sum_m \int \phi_m(\boldsymbol{r})^* \cdot \psi_m(\boldsymbol{r}) \, d^3r \,. \tag{4.64}$$

It is useful at the beginning to consider the internal n-dimensional degree of freedom separately; that is, we fix a location $\boldsymbol{r}_0$ and only consider the spin wave function in the following

$$\boldsymbol{\chi} = \boldsymbol{\psi}(\boldsymbol{r}_0), \qquad \boldsymbol{\chi} \in \mathbb{C}^n \,. \tag{4.65}$$

Alternatively, there are many problems in which spin and orbit do not interact with each other, so we can separate the wave function as

$$\boldsymbol{\psi}(\boldsymbol{r}) = \psi(\boldsymbol{r}) \otimes \boldsymbol{\chi} \,, \tag{4.66}$$

where $\boldsymbol{\chi}$ is the spin wave function and $\psi(\boldsymbol{r})$ is called the orbit wave function. The alternative notation $\chi(m) = \langle m | \chi \rangle = \chi_m$ is also used for the m-th component of the spin wave function.

The internal degree of freedom is used to model an internal angular momentum, the *spin* $\boldsymbol{S}$. The spin 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 exclusively on the spin space with [cf. (4.51)]

$$U_{\boldsymbol{e}}(\alpha) \boldsymbol{S} U_{\boldsymbol{e}}^\dagger(\alpha) = R_{\boldsymbol{e}}(\alpha) \boldsymbol{S} \,. \tag{4.67}$$

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 $\boldsymbol{e} \cdot \boldsymbol{S}$ being the generator of rotation around the axis $\boldsymbol{e}$. A rotation on the entire Hilbert space (spin and orbit) 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 then 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. The *irreducible representations* are important, which cannot be decomposed into a direct sum of smaller representations by a clever choice of basis.

Representations of the Angular Momentum Algebra: It turns out that for each n there is 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 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 last chapter, it immediately follows that $\boldsymbol{S}^2$ is a scalar operator with $[\boldsymbol{S}^2, S_3] = 0$. This means that $\boldsymbol{S}^2$ and S_3 can be simultaneously measured precisely.

We start with an arbitrary eigenstate χ_z of S_3 with eigenvalue $\hbar z$. We introduce the creation operator S_+ and the annihilation operator S_- as

$$S_\pm = S_1 \pm i S_2 \,. \tag{4.70}$$

From the angular momentum algebra (4.68), it follows[5]

$$[S_3, S_\pm] = \pm\hbar S_\pm \qquad \text{and} \qquad [S_+, S_-] = 2\hbar S_3 \,. \tag{4.71}$$

Therefore, $\hbar(z \pm 1)$ is also an eigenvalue of S_3,

$$S_3 S_\pm \chi_z = S_\pm S_3 \chi_z + [S_3, S_\pm]\chi_z = \hbar(z \pm 1) S_\pm \chi_z, \tag{4.72}$$

if $\chi_{z\pm1} = S_\pm \chi_z \neq 0$. Since the Hilbert space $\mathcal{H} = \mathbb{C}^n$ is finite, S_+ cannot be applied arbitrarily many times to generate further eigenstates. In particular, there is a maximum eigenvalue $\hbar s$ such that

$$S_3 \chi_s = \hbar s \chi_s \qquad \text{and} \qquad S_+ \chi_s = 0 \,. \tag{4.73}$$

Starting from χ_s, one can recursively apply S_- ($S_- \chi_s = \chi_{s-1}, \dots$). This sequence must also terminate. Therefore, there exists a $k \in \mathbb{N}$ such that

$$\chi_{s-k} \neq 0, \qquad \chi_{s-k-1} = S_- \chi_{s-k} = 0 \,. \tag{4.74}$$

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[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 $[S_3, S_2] = -i\hbar S_1$.

Thus, we have generated a basis $\{\chi_s, \ldots, \chi_{s-k}\}$, which is a candidate for an irreducible representation of the angular momentum algebra. The elements χ_m transform among themselves under the action of the annihilation operator S_-. It is important that the application of S_+ also remains in the subspace and does not generate new states. Initially,

$$S_+\chi_m = \hbar^2 c_m \chi_{m+1} \tag{4.75}$$

for $m = s$ with $c_s = 0$. We want to recursively show that $S_+\chi_m$ is always proportional to χ_{m+1} up to a factor of $\hbar^2 c_m$. For this purpose, we examine (m arbitrary)

$$S_+\chi_{m-1} = S_+S_-\chi_m = \underbrace{[S_+, S_-]}_{=2\hbar S_3}\chi_m + S_-\underbrace{S_+\chi_m}_{=\hbar^2 c_m\chi_{m+1}} = \hbar^2(2m + c_m)\chi_m\,. \tag{4.76}$$

Thus, (4.75) holds with $c_{m-1} = 2m + c_m$. It follows inductively 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) with (4.74) implies that $c_{s-k-1} = 0$. Thus, we obtain $2s = k$ [from the second factor in (4.77)] and there are only representations with

$$s = 0, \tfrac{1}{2}, 1, \tfrac{3}{2}, \ldots\,. \tag{4.78}$$

We denote these representations as $\mathcal{D}_s$. In each representation, there are $(2s+1)$ 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 $\boldsymbol{S}^2$ on the representation is 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 $\mathbb{C}^{2s+1}$. For this purpose, one defines the vectors $|s,m\rangle \propto \chi_m$, $m = -s, \ldots, s$ as the orthonormal basis vectors. The vectors are simultaneously 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, $S_+|s,m\rangle = \hbar\sqrt{c_m}|s,m+1\rangle$.

The representation of the spin operators in the basis $|s,m\rangle$ of $\mathcal{D}_s$ is defined by (4.80) and

$$S_\pm|s,m\rangle = \hbar\sqrt{s(s+1)-m(m\pm 1)}|s,m\pm 1\rangle = \hbar\mu^\pm_{s,m}|s,m\pm 1\rangle \tag{4.82}$$

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[6] It holds $\boldsymbol{S}^2 = S_1^2 + S_2^2 + S_3^2 = (S_1 - iS_2)(S_1 + iS_2) - i[S_1, S_2] + S_3^2 = S_-S_+ + S_3(S_3 + \hbar)$.

It is called the representation $\mathcal{D}_s$ also *Spin-s*.

Since $\boldsymbol{S}$ commutes with $\boldsymbol{S}^2$, a spin-s transforms under a rotation by an angle α about $\boldsymbol{e}$ as

$$U_{\boldsymbol{e}}(\alpha)|s,m\rangle = \sum_{m'=-s}^{s} \underbrace{\langle s,m'|e^{i\alpha\boldsymbol{e}\cdot\boldsymbol{S}/\hbar}|s,m\rangle}_{=u^{(s)}_{\boldsymbol{e};m',m}(\alpha)} |s,m'\rangle\,. \tag{4.83}$$

The matrices $u^{(s)}_{\boldsymbol{e}}(\alpha)$ are called the spin-s representation of the rotation group.

Examples

Spin-0: The 1-dimensional representation $\mathcal{D}_0$ is trivial. The wave functions 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 are two basis functions $|s=\frac{1}{2},\pm\frac{1}{2}\rangle$. These are also referred to as $|0\rangle = |+\rangle = |\uparrow\rangle$ and $|1\rangle = |-\rangle = |\downarrow\rangle$. From (4.82), the relationships are obtained as

$$S_+|\downarrow\rangle = \hbar|\uparrow\rangle, \quad S_+|\uparrow\rangle = 0, \quad S_-|\downarrow\rangle = 0, \quad S_-|\uparrow\rangle = \hbar|\downarrow\rangle\,. \tag{4.84}$$

Furthermore, according to (4.80), $S_3|\pm\rangle = \pm\frac{\hbar}{2}|\pm\rangle$. The matrices in the basis $\{|\uparrow\rangle, |\downarrow\rangle\}$ are 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 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 the general considerations, we know that $\boldsymbol{S}^2 = \hbar^2 s(s+1) = \frac{3}{4}\hbar^2$. Therefore,

$$\boldsymbol{\sigma}^2 = \frac{4\boldsymbol{S}^2}{\hbar^2} = \sigma_1^2 + \sigma_2^2 + \sigma_3^2 = 3\,. \tag{4.88}$$

Furthermore, $\boldsymbol{S} = \frac{\hbar}{2}\boldsymbol{\sigma}$ generates rotations on $\mathcal{D}_{\frac{1}{2}}$ with $u^{(\frac{1}{2})}_{\boldsymbol{e}}(\alpha) = e^{i\alpha\boldsymbol{e}\cdot\boldsymbol{\sigma}/2}$. 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 also 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 $\boldsymbol{v}, \boldsymbol{w} \in \mathbb{R}^3$. This implies

$$(\boldsymbol{v}\cdot\boldsymbol{\sigma})^2 = \boldsymbol{v}^2 = |\boldsymbol{v}|^2 \tag{4.91}$$

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 of 2π with $u_{\boldsymbol{e}}^{(\frac{1}{2})}(2\pi) = e^{i\pi\boldsymbol{e}\cdot\boldsymbol{\sigma}} = -1$, it is recognized 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, as ψ and $-\psi$ represent the same state. The representation with the Pauli matrices is rather a representation of $\mathsf{SU}(2)$. This is a double 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, the representations of angular momentum algebra for half-integer spin always belong to the group $\mathsf{SU}(2)$, which is twice as large.

The time reversal operator T must reverse the spin $\boldsymbol{S}$

$$T^\dagger \boldsymbol{S} T = -\boldsymbol{S}\,. \tag{4.93}$$

It can be easily verified that

$$T\boldsymbol{\chi} = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}\boldsymbol{\chi}^* \tag{4.94}$$

takes on this task. Because $T^2 = -1$ holds for a spin-$\frac{1}{2}$ (as for any half-integer spin), the Kramers degeneracy applies.

The electron is a particle with spin-$\frac{1}{2}$. The simplest Hamiltonian operator 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 factor $g = 2$. For a homogeneous magnetic field $\boldsymbol{B}$, we have $\boldsymbol{A} = \frac{1}{2}\boldsymbol{B}\times\boldsymbol{r}$ and thus (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 the orthonormal basis $|1,1\rangle, |1,0\rangle, |1,-1\rangle$. The relation (4.82) for $s = 1$ written as a matrix means

$$S_+ = \sqrt{2}\,\hbar\begin{pmatrix}0 & 1 & 0\\ 0 & 0 & 1\\ 0 & 0 & 0\end{pmatrix}, \qquad S_- = S_+^\dagger, \qquad S_3 = \hbar\begin{pmatrix}1 & 0 & 0\\ 0 & 0 & 0\\ 0 & 0 & -1\end{pmatrix}. \tag{4.99}$$

Thus follows

$$S_1 = \frac{1}{2}(S_+ + S_-) = \frac{\hbar}{\sqrt{2}}\begin{pmatrix}0 & 1 & 0\\ 1 & 0 & 1\\ 0 & 1 & 0\end{pmatrix}, \quad S_2 = \frac{1}{2i}(S_+ - S_-) = \frac{\hbar}{\sqrt{2}}\begin{pmatrix}0 & -i & 0\\ i & 0 & -i\\ 0 & i & 0\end{pmatrix}.$$

From the general considerations we can conclude again that $S_1^2 + S_2^2 + S_3^2 = 2\hbar^2$ and, of course, that (4.67) also holds.

4.5 Angular Momentum Addition

For the treatment of selection rules arising from rotational symmetry, and for determining the total angular momentum $\boldsymbol{J}$ of a composite system, it is important to know how to add angular momenta. To do this, we consider the following question. Given two systems that transform under rotation with spins 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 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 about a new basis $|j, m\rangle$, such that the vectors transform like irreducible representations $\mathcal{D}_j$.

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[7] We compactly write $\boldsymbol{S}_1 \equiv \boldsymbol{S}\otimes 1$ and $\boldsymbol{S}_2 \equiv 1\otimes\boldsymbol{S}$. The operators $\boldsymbol{J}$ naturally satisfy the angular momentum algebra.

Two Spin-$\frac{1}{2}$: Let's consider a simple example of two Spin-$\frac{1}{2}$. We solve the problem using 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 therefore 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 the maximum eigenvalue of $\hbar$. Therefore, the representation $\mathcal{D}_1$ is contained in $\mathcal{H}$. In particular, $|+,+\rangle$ must be equal to the state $|j=1,m=1\rangle$.[8] We obtain the remaining states by applying J_-. In particular, we have

$$\frac{J_-}{\hbar}|+,+\rangle = |-,+\rangle + |+,-\rangle, \qquad \frac{J_-^2}{\hbar^2}|+,+\rangle = \frac{J_-}{\hbar}\big(|-,+\rangle + |+,-\rangle\big) = 2|-,-\rangle\,. \tag{4.102}$$

Therefore, we have found (up to normalization) all states for $j=1$. In the Hilbert space $\mathcal{H}$, the state $|+,-\rangle - |-,+\rangle$ remains as the only state orthogonal to the states in $\mathcal{D}_1$. This state must correspond to the representation $\mathcal{D}_0$. After normalization, we obtain

$$\left.\begin{array}{ll} \text{Singlet:} & \left.|0,0\rangle = \frac{1}{\sqrt{2}}\big(|+,-\rangle - |-,+\rangle\big)\right\}\ \mathcal{D}_0 \\[2ex] \text{Triplet:} & \left.\begin{array}{ll} |1,1\rangle & = |+,+\rangle \\ |1,0\rangle & = \frac{1}{\sqrt{2}}\big(|+,-\rangle + |-,+\rangle\big) \\ |1,-1\rangle & = |-,-\rangle \end{array}\right\}\ \mathcal{D}_1 \end{array}\right\} \mathcal{D}_{\frac{1}{2}} \otimes \mathcal{D}_{\frac{1}{2}}\,. \tag{4.103}$$

We have thus 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 be simultaneously 'diagonalized' into even smaller block matrices.

Interessingly, $|j,m\rangle$ are eigenstates of $\boldsymbol{S}_1 \cdot \boldsymbol{S}_2$. 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 an eigenvalue of 0 and thus $\boldsymbol{S}_1 \cdot \boldsymbol{S}_2|0,0\rangle = -\frac{3\hbar^2}{4}|0,0\rangle$. Similarly, for

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[8] There is, of course, the possibility of a phase. However, we use the Condon-Shortley phase convention with $\langle s_1, s_1; s_2, j-s_1|jj\rangle > 0$.

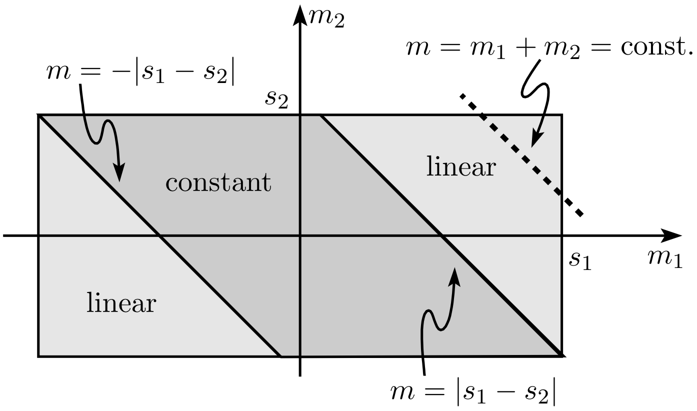

Fig. 4.1: Scheme for counting the eigenstates $|j, m\rangle$ for the total angular momentum j of two particles with angular momenta s_1 and s_2.

$j = 1$ the result is $\boldsymbol{S}_1 \cdot \boldsymbol{S}_2 |1, m\rangle = \frac{\hbar^2}{4} |1, m\rangle$. This allows us to 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 are looking for allowed j values such that $|j, m\rangle$ spans the same Hilbert space with irreducible representations with respect to the total angular momentum $\boldsymbol{J}$. First, we want to 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 thus 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 as follows, see Fig. 4.1:

- one state with $m = s_1 + s_2 =$ (maximum),
- two states with $m = s_1 + s_2 - 1$: $\begin{cases} m_1 = s_1, m_2 = s_2 - 1, \\ m_1 = s_1 - 1, m_2 = s_2, \end{cases}$

⋮

- $s_1 + s_2 - m + 1$ states for $m \geq |s_1 - s_2|$, (the number of ways to construct an $m = m_1 + m_2 \geq |s_1 - s_2|$ from m_1 and m_2)
- $s_1 + s_2 - |s_1 - s_2| + 1 = \text{const.}$ 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 maximum $m = s_1 + s_2$ must belong to the representation $\mathcal{D}_{j = s_1 + s_2}$. Together with it, a total of $(2j + 1)$ states belong 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 maximum m from the representation with $j = s_1 + s_2 - 1$. We can continue this reasoning recursively. As long as $m \geq |s_1 - s_2|$, one state is still not included 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,

$$\sum_{j=|s_1-s_2|}^{s_1+s_2} (2j+1) \quad = (2s_1+1)(2s_2+1) \tag{4.109}$$

so that we have considered all states in the Hilbert space $\mathcal{H}$.

Clebsch-Gordan coefficients: The transition from $|s_1, m_1; s_2, m_2\rangle$ to $|j, m\rangle$ is a change of basis 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 show shortly that these can indeed be chosen to be 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 first apply $J_\pm$ to the left side of (4.110),

$$J_\pm|j, m\rangle = \hbar\mu^\pm_{j,m}|j, m \pm 1\rangle = \hbar\mu^\pm_{j,m} \sum_{m_1,m_2} \langle s_1, m_1; s_2, m_2|j, m \pm 1\rangle|s_1, m_1; s_2, m_2\rangle \,. \tag{4.112}$$

On the other hand, applying it to the right side yields

$$\hbar \sum_{m_1,m_2} \langle s_1, m_1; s_2, m_2|j, m\rangle \big(\mu^\pm_{s_1,m_1}|s_1, m_1 \pm 1; s_2, m_2\rangle + \mu^\pm_{s_2,m_2}|s_1, m_1; s_2, m_2 \pm 1\rangle\big) \tag{4.113}$$

$$= \hbar \sum_{m_1,m_2} \big(\mu^\pm_{s_1,m_1\mp 1}\langle s_1, m_1 \mp 1; s_2, m_2|j, m\rangle + \mu^\pm_{s_2,m_2\mp 1}\langle s_1, m_1; s_2, m_2 \mp 1|j, m\rangle\big)|s_1, m_1; s_2, m_2\rangle \,.$$

Setting (4.112) equal to (4.113) leads to the recursion relation (Racah 1941)

$$\begin{aligned}&\mu^{\pm}_{j,m}\langle s_1,m_1;s_2,m_2|j,m\pm 1\rangle\\ &\quad=\mu^{\pm}_{s_1,m_1\mp 1}\langle s_1,m_1\mp 1;s_2,m_2|j,m\rangle+\mu^{\pm}_{s_2,m_2\mp 1}\langle s_1,m_1;s_2,m_2\mp 1|j,m\rangle\,. \end{aligned}\qquad(4.114)$$

One finds the Clebsch-Gordan coefficients by first choosing $m=j$ and '+'. The left 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 using 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 at `https://en.wikipedia.org/wiki/Table_of_Clebsch-Gordan_coefficients`. It is of course $\langle s_1,m_1;s_2,m_2|j,m\rangle=0$ except for $m=m_1+m_2$ *and* $|s_1-s_2|\le j\le s_1+s_2$.

With the Clebsch-Gordan coefficients, one obtains for the representations of rotations $u^{(j)}_{m',m}=\langle j,m'|e^{i\alpha\boldsymbol{e}\cdot\boldsymbol{J}/\hbar}|j,m\rangle$ for spin-j the *addition theorem*

$$\begin{aligned}u^{(s_1)}_{\boldsymbol{e};m_1',m_1}(\alpha)\,u^{(s_2)}_{\boldsymbol{e};m_2',m_2}(\alpha)&=\langle s_1,m_1';s_2,m_2'|e^{i\alpha\boldsymbol{e}\cdot\boldsymbol{J}/\hbar}|s_1,m_1;s_2,m_2\rangle\\ &=\sum_{\substack{j',j\\ m',m}}\langle s_1,m_1';s_2,m_2'|j',m'\rangle\langle j,m|s_1,m_1;s_2,m_2\rangle\overbrace{\langle j',m'|e^{i\alpha\boldsymbol{e}\cdot\boldsymbol{J}/\hbar}|j,m\rangle}^{\propto\delta_{jj'}}\\ &=\sum_{j,m,m'}\langle s_1,m_1';s_2,m_2'|j,m'\rangle\langle s_1,m_1;s_2,m_2|j,m\rangle u^{(j)}_{\boldsymbol{e};m',m}(\alpha).\end{aligned}\qquad(4.115)$$

Tensor Operators and Selection Rules: We consider a Hilbert space $\mathcal{H}$ on which rotations R around $\boldsymbol{e}$ act with the unitary transformation

$$U_{\boldsymbol{e}}(\alpha)=e^{i\alpha\boldsymbol{e}\cdot\boldsymbol{J}/\hbar}\qquad(4.116)$$

The generators $\boldsymbol{J}$ satisfy the angular momentum algebra. Important examples are the position Hilbert space [with $\mathcal{H}=L^2(\mathbb{R}^3)$ and $\boldsymbol{J}=\boldsymbol{L}=\boldsymbol{r}\times\boldsymbol{p}$], the spin-$s$ [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 $\boldsymbol{J}=\boldsymbol{L}\otimes 1+1\otimes\boldsymbol{S}$].

In order to obtain selection rules, we need operators that transform like the states. A *tensor operator* for spin-l is a list of $(2l+1)$ operators $T^{(l)}_m$, $m=-l,\dots,l$, which behave under a rotation R as [cf. (4.83)]

$$U_{\boldsymbol{e}}(\alpha)T^{(l)}_m U^{\dagger}_{\boldsymbol{e}}(\alpha)=\sum_{m'=-l}^{l}\langle l,m'|e^{i\alpha\boldsymbol{e}\cdot\boldsymbol{S}/\hbar}|l,m\rangle T^{(l)}_{m'}=\sum_{m'=-l}^{l}u^{(l)}_{\boldsymbol{e};m',m}(\alpha)\,T^{(l)}_{m'}\qquad(4.117)$$

where $u^{(l)}$ is the rotation matrix for spin-l. Here, l is always an integer, since a rotation by 2π maps the tensors onto themselves, $U_{\boldsymbol{e}}(2\pi)T_m^{(l)}U_{\boldsymbol{e}}^\dagger(2\pi) = (\pm 1)T_m^{(l)}(\pm 1) = T_m^{(l)}$. For an infinitesimal rotation, the equivalent condition is obtained

$$[\boldsymbol{e}\cdot\boldsymbol{J}, T_m^{(l)}] = \sum_{m'=-l}^{l} \langle l, m'|\boldsymbol{e}\cdot\boldsymbol{S}|l, m\rangle\, T_{m'}^{(l)}\,. \tag{4.118}$$

Since the matrix elements of S_3 and $S_\pm$ from (4.80) and (4.82) are known, we rewrite (4.118) and define a tensor operator for spin-l through the algebra

$$[J_3, T_m^{(l)}] = \hbar m\, T_m^{(l)}, \qquad [J_\pm, T_m^{(l)}] = \sum_{m'} \langle l, m'|S_\pm|l, m\rangle\, T_{m'}^{(l)} = \hbar\mu_{l,m}^{\pm}\, T_{m\pm 1}^{(l)} \tag{4.119}$$

with $\mu_{l,m}^{\pm} = \sqrt{l(l+1) - m(m\pm 1)} = \sqrt{(l\mp m)(l+1\pm m)}$.

Examples

Scalar operator: A scalar operator (for example $\boldsymbol{p}^2, \boldsymbol{L}^2$) remains invariant under rotations. A scalar operator is therefore a tensor operator for spin-0.

Vector operator: A vector operator $\boldsymbol{v}$ transforms under rotations (with $\boldsymbol{J} = \boldsymbol{L}$) as

$$[\boldsymbol{v}, \boldsymbol{e}\cdot\boldsymbol{J}] = i\hbar\, \boldsymbol{e}\times\boldsymbol{v} \qquad \overset{\boldsymbol{f}\cdot}{\Leftrightarrow} \qquad [\boldsymbol{e}\cdot\boldsymbol{J}, \boldsymbol{f}\cdot\boldsymbol{v}] = i\hbar(\boldsymbol{e}\times\boldsymbol{f})\cdot\boldsymbol{v}\,. \tag{4.120}$$

Since all components of $\boldsymbol{v}$ transform into each other, one suspects that a vector operator is irreducible and therefore belongs to spin-1. It can be shown by simple calculation that

$$v_0^{(1)} = v_3, \qquad v_{\pm 1}^{(1)} = \mp\frac{1}{\sqrt{2}}(v_1 \pm i v_2) \tag{4.121}$$

is indeed a tensor operator for spin-1. It is also said 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 linked by (4.121).

From the position operator, we obtain the tensor operator for example

$$r_0^{(1)} = r_3, \qquad r_{\pm 1}^{(1)} = \mp\frac{1}{\sqrt{2}}(r_1 \pm i r_2), \tag{4.122}$$

for spin-1.

Selection Rule: We can now derive the selection rules for tensor operators. For a Hamiltonian with rotational symmetry $\boldsymbol{J}$, the eigenstates $|\nu, j, m\rangle$ can be characterized by the eigenvalues of the operators $\boldsymbol{J}^2$, J_3 (with possible additional quantum numbers ν). Let $T^{(l)}$ be a tensor operator for spin-l, then the *Wigner-Eckart theorem* (the factor $\sqrt{2j_1+1}$ is arbitrary but conventional) holds

$$\langle \nu_2, j_2, m_2 | T^{(l)}_m | \nu_1, j_1, m_1 \rangle = \frac{\langle \nu_2, j_2 \| T^{(l)} \| \nu_1, j_1 \rangle}{\sqrt{2j_1+1}} \langle l, m; j_1, m_1 | j_2, m_2 \rangle \,. \tag{4.123}$$

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 holds

$$\langle \nu_2, j_2, m_2 | T^{(l)}_m | \nu_1, j_1, m_1 \rangle = 0, \quad \text{except for } m_2 = m_1 + m \text{ and } |j_1 - l| \leq j_2 \leq j_1 + l \,. \tag{4.124}$$

The Wigner-Eckart theorem follows from the statement that the states

$$|\tilde{\nu}, k, q\rangle = \sum_{m,m_1} \langle l, m; j_1, m_1 | k, q \rangle \, T^{(l)}_m | \nu_1, j_1, m_1 \rangle, \tag{4.125}$$

which are obtained by 'adding' the angular momenta l (from $T^{(l)}$) and j_1 (from $|j_1, m_1\rangle$), really transform like spin-k states (one should note that the tensor operator $T^{(l)}$ generally changes the state $\nu_1 \mapsto \tilde{\nu}$). In fact, with (4.119)

$$J_3 |\tilde{\nu}, k, q\rangle = \sum_{m,m_1} \langle l, m; j_1, m_1 | k, q \rangle \underbrace{J_3 T^{(l)}_m}_{T^{(l)}_m J_3 + \hbar m T^{(l)}_m} | \nu_1, j_1, m_1 \rangle = \hbar (m_1 + m) |\tilde{\nu}, k, q\rangle \,. \tag{4.126}$$

Furthermore, we obtain

$$J_\pm |\tilde{\nu}, k, q\rangle = \sum_{m,m_1} \langle l, m; j_1, m_1 | k, q \rangle \overbrace{J_\pm T^{(l)}_m}^{= T^{(l)}_m J_\pm + \hbar \mu^\pm_{l,m} T^{(l)}_{m\pm 1}} | \nu_1, j_1, m_1 \rangle \tag{4.127}$$

$$= \hbar \sum_{m,m_1} \Big[\mu^\pm_{l,m} \langle l, m; j_1, m_1 | k, q \rangle T^{(l)}_{m\pm 1} | \nu_1, j_1, m_1 \rangle + \mu^\pm_{j_1,m_1} \langle l, m; j_1, m_1 | k, q \rangle T^{(l)}_m | \nu_1, j_1, m_1 \pm 1 \rangle \Big]$$

$$= \hbar \sum_{m,m_1} \Big[\mu^\pm_{l,m\mp 1} \langle l, m \mp 1; j_1, m_1 | k, q \rangle + \mu^\pm_{j_1,m_1\mp 1} \langle l, m; j_1, m_1 \mp 1 | k, q \rangle \Big] T^{(l)}_m | \nu_1, j_1, m_1 \rangle$$

$$\overset{(4.114)}{=} \hbar \mu^\pm_{l,q} \sum_{m,m_1} \langle l, m; j_1, m_1 | k, q \pm 1 \rangle \, T^{(l)}_m | \nu_1, j_1, m_1 \rangle = \hbar \mu^\pm_{l,q} \, |\tilde{\nu}, k, q + 1\rangle \,. \tag{4.128}$$

A comparison with (4.80) and (4.82) shows that the states $|\tilde{\nu}, k, q\rangle$ (for fixed $\tilde{\nu}, k$) transform like an irreducible representation $\mathcal{D}_k$ for spin-k. States belonging to different representations are orthogonal, so $\langle \nu_2, j_2, m_2 | \tilde{\nu}, k, q \rangle = 0$ except for $k = j_2$ and $q = m_2$.[9]

---

[9] This follows from $\boldsymbol{J}^2 |\tilde{\nu}, k, q\rangle = \hbar^2 k(k+1) |\tilde{\nu}, k, q\rangle$ and $\boldsymbol{J}^2 |\nu_2, j_2, m_2\rangle = \hbar^2 j_2(j_2+1) |\nu_2, j_2, m_2\rangle$ from $0 = \langle \nu_2, j_2, m_2 | \boldsymbol{J}^2 | \tilde{\nu}, k, q \rangle - \langle \tilde{\nu}, k, q | \boldsymbol{J}^2 | \nu_2, j_2, m_2 \rangle^* = (k - j_2)(k + j_2 + 1) \langle \nu_2, j_2, m_2 | \tilde{\nu}, k, q \rangle$. The second selection rule is obtained from $0 = \langle \nu_2, j_2, m_2 | J_3 | \tilde{\nu}, k, q \rangle - \langle \tilde{\nu}, k, q | J_3 | \nu_2, j_2, m_2 \rangle^* = \hbar (q - m_2) \langle \nu_2, j_2, m_2 | \tilde{\nu}, k, q \rangle$.

Since the representation $\mathcal{D}_k$ appears only once in the reduction of $\mathcal{D}_l \otimes \mathcal{D}_{j_1}$, we can reverse the transformation (4.125) with

$$T^{(l)}_m |\nu_1, j_1, m_1\rangle = \sum_{k,q} \langle l, m; j_1, m_1 | k, q\rangle \, |\tilde{\nu}, k, q\rangle \, . \tag{4.129}$$

For the proof of the theorem, we only need to show that

$$\langle \nu_2, j_2, m_2 | \tilde{\nu}, j_2, m_2\rangle = c \tag{4.130}$$

with a constant c independent of m_2. This follows recursively (starting from $m_2 = j_2$) from

$$\begin{aligned} \hbar\mu^+_{j_2,m_2-1} \langle \nu_2, j_2, m_2 | \tilde{\nu}, j_2, m_2\rangle &= \langle \tilde{\nu}, j_2, m_2 | J_+ | \nu_2, j_2, m_2 - 1\rangle^* = \langle \nu_2, j_2, m_2 - 1 | J_- | \tilde{\nu}, j_2, m_2\rangle \\ &= \hbar\mu^-_{j_2,m_2} \langle \nu_2, j_2, m_2 - 1 | \tilde{\nu}, j_2, m_2 - 1\rangle \, , \end{aligned} \tag{4.131}$$

since $\mu^-_{j_2,m_2} = \mu^+_{j_2,m_2-1} \neq 0$ for $j_2 \geq m_2 > -j_2$.

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)

$$V_{\text{int}} = e\,\boldsymbol{r} \cdot \boldsymbol{\mathcal{E}} \, . \tag{4.132}$$

Therefore, the absorption and emission of light depend on the matrix elements of the dipole operator $\boldsymbol{d} = -e\boldsymbol{r}$. The dipole operator is a polar vector, making $\boldsymbol{d}$ a tensor operator for spin-1. This gives us the optical selection rules for transitions with $\Delta m = m' - m$, $\Delta l = l' - l$

$$\langle l', m' | \boldsymbol{d} | l, m\rangle = 0, \qquad \text{except for } \Delta m = 0, \pm 1 \text{ and } \Delta l = 0, \pm 1. \tag{4.133}$$

Additionally, the matrix element with $l = l' = 0$ vanishes. We will see later that the states $|l, m\rangle$ have parity $(-1)^l$. This implies that $\Delta l = 0$ is forbidden.

4.6 Central Force Problem

Next, we examine stationary states in a central potential $V(\boldsymbol{r}) = V(r)$ with radius $r = |\boldsymbol{r}|$. The Hamiltonian operator on $\mathcal{H} = L^2(\mathbb{R}^3)$ is given by

$$H = \frac{\boldsymbol{p}^2}{2m} + V(r) = -\frac{\hbar^2}{2m}\Delta + V(r) \, . \tag{4.134}$$

The rotation is generated by the angular momentum operator $\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p} = -i\hbar\boldsymbol{r} \times \boldsymbol{\nabla}$. Due to the rotational symmetry of the problem, the operators $\boldsymbol{L}^2, L_3$ commute with the Hamiltonian operator. The eigenvalue problem $H\psi(\boldsymbol{r}) = E\psi(\boldsymbol{r})$ can thus be reduced to the eigenspaces $|l, m\rangle$ of the operators $\boldsymbol{L}^2, L_3$. Therefore, we will first examine the eigenvalue problem of the angular momentum operator on $\mathcal{H}$.

The angular momentum squared 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. Therefore, one must maintain the order of the operators and instead obtain (with $[p_k r_k, p_j] = p_k[r_k, p_j] = i\hbar\delta_{jk}p_j$)

$$\boldsymbol{L}^2 = (\boldsymbol{r}\times\boldsymbol{p})\cdot(\boldsymbol{r}\times\boldsymbol{p}) = \sum_{j,k}\Big[r_j \overbrace{p_k r_j}^{=r_j p_k - i\hbar\delta_{kj}} p_k - r_j \overbrace{p_k r_k p_j}^{=p_j r_k p_k - i\hbar(1-\delta_{jk})p_j}\Big] = \boldsymbol{r}^2\boldsymbol{p}^2 - i\hbar(\boldsymbol{r}\cdot\boldsymbol{p}) - (\boldsymbol{r}\cdot\boldsymbol{p})^2 + 2i\hbar(\boldsymbol{r}\cdot\boldsymbol{p})\,.$$

In polar coordinates, $\boldsymbol{r} \cdot \boldsymbol{p} = -i\hbar\,\boldsymbol{r} \cdot \boldsymbol{\nabla} = -i\hbar\, r\partial/\partial r$. Thus, we have

$$\frac{\boldsymbol{L}^2}{\hbar^2} = -r^2\Delta + \left(r\frac{\partial}{\partial r}\right)^2 + r\frac{\partial}{\partial r} = -r^2\Delta + r\frac{\partial^2}{\partial r^2}r \tag{4.135}$$

or equivalently

$$\boldsymbol{p}^2 = -\hbar^2\Delta = -\frac{\hbar^2}{r}\frac{\partial^2}{\partial r^2}r + \frac{\boldsymbol{L}^2}{r^2}\,. \tag{4.136}$$

The second term corresponds to the angular momentum barrier in mechanics.

Spherical Harmonics: We switch to *spherical coordinates* so that we can directly exploit the rotational symmetry. Spherical coordinates (r, θ, φ) are given by

$$\boldsymbol{r} = r\,\boldsymbol{e}_r\,, \quad \text{with} \quad \boldsymbol{e}_r = \sin\theta\cos\varphi\,\boldsymbol{e}_1 + \sin\theta\sin\varphi\,\boldsymbol{e}_2 + \cos\theta\,\boldsymbol{e}_3\,, \tag{4.137}$$

where $r > 0$ and $(\theta, \varphi) \in \Omega = S^2$ with $d\Omega = d(\cos\theta)d\varphi$.

Drehungen lassen r invariant, deshalb wirkt $\boldsymbol{L}$ nur auf $L^2(\Omega)$. Die Drehung um die z-Achse wird erzeugt durch L_3. In Kugelkoordinaten hat diese Erzeugende die Form

$$(L_3\psi)(\theta, \varphi) = -i\hbar\frac{d}{d\alpha}\psi(\theta, \varphi + \alpha)\Big|_{\alpha=0} = -i\hbar\frac{\partial}{\partial\varphi}\psi(\theta, \varphi)\,. \tag{4.138}$$

Eine (infinitesimale) Drehung um die x-Achse ändert die Ortskoordinate (mit $r = 1$) wie [vgl. (4.46)]

$$\boldsymbol{e}_r(\alpha) = \boldsymbol{e}_r + \alpha\,\boldsymbol{e}_1 \times \boldsymbol{e}_r + O(\alpha^2) = \boldsymbol{e}_r - \alpha\cos\theta\,\boldsymbol{e}_2 + \alpha\sin\theta\sin\varphi\,\boldsymbol{e}_3 + O(\alpha^2)\,. \tag{4.139}$$

In Kugelkoordinaten ist dies[10]

$$\theta(\alpha) = \theta - \alpha\sin\varphi + O(\alpha^2), \qquad \varphi(\alpha) = \varphi - \alpha\cot\theta\cos\varphi + O(\alpha^2)\,. \tag{4.140}$$

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[10] Aus (4.139) erhält man $\cos[\theta(\alpha)] = \cos\theta + \alpha\sin\theta\sin\varphi + O(\alpha^2)$ und $\tan[\varphi(\alpha)] = \tan\varphi - \alpha\cot\theta/\cos\varphi + O(\alpha^2)$. Die Gleichung (4.140) ergibt sich durch Linearisierung.

Damit ist die x-Komponente des Drehimpulsoperators gegeben durch

$$(L_1\psi)(\theta,\varphi) = -i\hbar\frac{d}{d\alpha}\psi(\theta(\alpha),\varphi(\alpha))\Big|_{\alpha=0} = i\hbar\left(\sin\varphi\frac{\partial}{\partial\theta} + \cot\theta\cos\varphi\frac{\partial}{\partial\varphi}\right)\psi(\theta,\varphi)\,. \tag{4.141}$$

Die y-Komponente erhält man aus dem Kommutator (4.57)

$$\begin{aligned}L_2 = \frac{i}{\hbar}[L_1,L_3] &= i\hbar[\sin\varphi\,\partial_\theta + \cot\theta\cos\varphi\,\partial_\varphi,\partial_\varphi] = i\hbar[\sin\varphi,\partial_\varphi]\partial_\theta + i\hbar[\cos\varphi,\partial_\varphi]\cot\theta\,\partial_\varphi\\ &= i\hbar\left(-\cos\varphi\frac{\partial}{\partial\theta} + \cot\theta\sin\varphi\frac{\partial}{\partial\varphi}\right)\,. \end{aligned}\tag{4.142}$$

Für die weitere Rechnung sind die Erzeugungs- und Vernichtungsoperatoren

$$L_\pm = L_1 \pm iL_2 = e^{\pm i\varphi}\left(\pm\hbar\frac{\partial}{\partial\theta} - \cot\theta\,L_3\right) \tag{4.143}$$

wichtig.

We are looking for *spherical harmonics* $Y_{l,m}(\theta,\varphi)$, which transform under the representation $\mathcal{D}_l$ of $\boldsymbol{L}$. For this to hold [see (4.80) and (4.82)], the following conditions must be satisfied:

$$\begin{aligned}L_3Y_{l,m} &= -i\hbar\frac{\partial}{\partial\varphi}Y_{l,m} = \hbar mY_{l,m}, \\ L_\pm Y_{l,m} &= e^{\pm i\varphi}\left(\pm\hbar\frac{\partial}{\partial\theta} - \cot\theta\,L_3\right)Y_{l,m} = \hbar\mu^\pm_{l,m}Y_{l,m\pm1}\,.\end{aligned}\tag{4.144}$$

The equation (4.144) is solved by

$$Y_{l,m}(\theta,\varphi) = e^{im\varphi}f_{l,m}(\theta)\,. \tag{4.145}$$

To determine $f_{l,m}(\theta)$, we first use $L_+Y_{l,l} = 0$,

$$e^{i\varphi}\left(\hbar\frac{\partial}{\partial\theta} - \cot\theta\,L_3\right)Y_{l,l} = 0 \qquad \Rightarrow \qquad \left(\frac{\partial}{\partial\theta} - l\cot\theta\right)f_{l,l} = 0, \tag{4.146}$$

with the solution $f_{l,l}(\theta) = \sin^l\theta$. In order for f to be analytic at $\theta = 0$, we need $l = 0,1,2,\ldots$. Only integer representations are allowed. After normalization to Ω, we obtain the spherical harmonic function[11]

$$Y_{l,l}(\theta,\varphi) = \frac{(-1)^l}{2^l\,l!}\sqrt{\frac{(2l+1)}{4\pi}(2l)!}\,\sin^l\theta\,e^{il\varphi}\,. \tag{4.147}$$

The remaining spherical harmonic functions are obtained simply by successively applying L_- with the result[12]

$$Y_{l,m}(\theta,\varphi) = \frac{(-1)^l}{2^l\,l!}\sqrt{\frac{(2l+1)}{4\pi}\frac{(l+m)!}{(l-m)!}}\,\frac{e^{im\varphi}}{\sin^m\theta}\left(\frac{d}{d\cos\theta}\right)^{l-m}\sin^{2l}\theta\,. \tag{4.148}$$

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[11] The factor $(-1)^l$ comes from the Condon-Shortley phase convention.

[12] This uses the fact that the factor $e^{-i\varphi}$ (in L_-) lowers L_3 by $\hbar$. Additionally, $\sin^{m-1}\theta\,\partial_{\cos\theta}(\sin^m\theta\,f) = -(\partial_\theta + m\cot\theta)f$; meaning $L^-/(\hbar e^{-i\varphi}) = \sin^{m-1}\theta\,\partial_{\cos\theta}\sin^m\theta$.

$Y_{0,0} = \frac{1}{\sqrt{4\pi}}$	
$Y_{1,0} = \sqrt{\frac{3}{4\pi}} r_3 = \sqrt{\frac{3}{4\pi}} \cos\theta$	$Y_{1,\pm 1} = \mp\sqrt{\frac{3}{8\pi}} (r_1 \pm i r_2) = \mp\sqrt{\frac{3}{8\pi}} e^{\pm i\varphi} \sin\theta$
$Y_{2,0} = \sqrt{\frac{5}{16\pi}} \left(2r_3^2 - r_1^2 - r_2^2\right)$	$Y_{2,\pm 1} = \mp\sqrt{\frac{15}{8\pi}} (r_1 \pm i r_2) r_3 = \mp\sqrt{\frac{15}{8\pi}} e^{\pm i\varphi} \sin\theta\cos\theta$
$= \sqrt{\frac{5}{16\pi}} \left(3\cos^2\theta - 1\right)$	$Y_{2,\pm 2} = \sqrt{\frac{15}{32\pi}} (r_1 \pm i r_2)^2 = \sqrt{\frac{15}{32\pi}} e^{\pm 2i\varphi} \sin^2\theta$

Table 4.1: Spherical harmonics $Y_{l,m}$ for $l = 0, 1, 2$

From the general consideration (4.79), we know that $\boldsymbol{L}^2 Y_{l,m} = \hbar^2 l(l+1) Y_{l,m}$.

One can also interpret the spherical harmonics $Y_{l,m}(\theta,\varphi)$ as (homogeneous) polynomials of 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 $r_1^2 + r_2^2 + r_3^3 = 1$, see (4.122). Therefore, we have

$$\begin{aligned} Y_{l,m\geq 0}(\boldsymbol{r}) &= \frac{(-1)^l}{2^l\, l!} \sqrt{\frac{(2l+1)}{4\pi} \frac{(l+m)!}{(l-m)!}} \frac{\left(r_1 + i r_2\right)^m}{(r^2 - z^2)^m} \left(\frac{d}{dz}\right)^{l-m} (r^2 - z^2)^l \Big|_{\substack{z = r_3 \\ r^2 = r_1^2 + r_2^2 + r_3^2}} , \\ Y_{l,m<0}(\boldsymbol{r}) &= (-1)^m Y_{l,|m|}(\boldsymbol{r})^* . \end{aligned} \tag{4.149}$$

From the general considerations (4.83), we know that a spherical harmonic function $Y_{l,m}$ transforms like a spin-l under rotations, i.e.

$$Y_{l,m}(R_{\boldsymbol{e}}(\alpha)\boldsymbol{r}) = (e^{i\alpha\boldsymbol{e}\cdot\boldsymbol{L}/\hbar} Y_{l,m})(\boldsymbol{r}) \overset{(4.144)}{=} \sum_{m'} u^{(l)}_{\boldsymbol{e};m',m}(\alpha) Y_{l,m'}(\boldsymbol{r}) . \tag{4.150}$$

This allows us to use the spherical harmonics to form tensor operators from a vector operator $\boldsymbol{v}$. In fact, [see (4.117)]

$$U_{\boldsymbol{e}}(\alpha) Y_{l,m}(\boldsymbol{v}) U^\dagger_{\boldsymbol{e}}(\alpha) \overset{(U^\dagger U = 1)}{=} Y_{l,m}\left[U_{\boldsymbol{e}}(\alpha)\boldsymbol{v}U^\dagger_{\boldsymbol{e}}(\alpha)\right] \overset{(4.51)}{=} Y_{l,m}(R_{\boldsymbol{e}}(\alpha)\boldsymbol{v}) = \sum_{m'} u^{(l)}_{\boldsymbol{e};m',m}(\alpha) Y_{l,m'}(\boldsymbol{v}) .$$

Thus, $Y_l(\boldsymbol{v})$ is a tensor operator of spin-l. For the position vector $\boldsymbol{r}$, $Y_l(\boldsymbol{r})$ is also called *multipole moments.*

Examples of the simplest spherical harmonics are given in Table 4.1. This gives us the dipole moment (Spin-1)

$$Y_{1,0}(\boldsymbol{r}) = \sqrt{\frac{3}{4\pi}}\, r_3, \quad Y_{1,\pm}(\boldsymbol{r}) = \mp\sqrt{\frac{3}{8\pi}}\, (r_1 \pm i r_2) . \tag{4.151}$$

The spherical harmonics have a well-defined parity. The parity operation $P\colon \boldsymbol{r} \mapsto -\boldsymbol{r}$ is equivalent to $\theta \mapsto \pi - \theta$, $\varphi \mapsto \varphi + \pi$, thus transforming $e^{im\varphi} \mapsto (-1)^m e^{im\varphi}$, $\sin\theta \mapsto \sin\theta$, $\cos\theta \mapsto -\cos\theta$ and we obtain [cf. (4.148)]

$$P\, Y_{l,m}(\theta,\varphi) = (-1)^l Y_{l,m}(\theta,\varphi), \qquad \begin{cases} l \text{ even:} & \text{even under } P, \\ l \text{ odd:} & \text{odd under } P. \end{cases} \tag{4.152}$$

It can be shown that every integer spin occurs exactly once in $L^2(\Omega)$. The $Y_{l,m}$ are thus complete in $L^2(\Omega)$ and orthonormal,

$$\sum_{l=0}^{\infty}\sum_{m=-l}^{l} Y_{l,m}(\theta,\varphi)Y_{l,m}^*(\theta',\varphi') = \delta(\cos\theta-\cos\theta')\delta(\varphi-\varphi'), \tag{4.153}$$

$$\int Y_{l,m}^*(\theta,\varphi)Y_{l',m'}(\theta,\varphi)\,d\Omega = \delta_{ll'}\delta_{mm'}. \tag{4.154}$$

Radial Wave Equation: With these considerations, we are ready to solve the stationary Schrödinger equation

$$\left[\frac{\boldsymbol{p}^2}{2m}+V(r)\right]\psi(\boldsymbol{r}) = E\psi(\boldsymbol{r}) \quad \overset{(4.136)}{\Rightarrow} \quad \left[-\frac{\hbar^2}{2mr}\frac{\partial^2}{\partial r^2}r+\frac{\boldsymbol{L}^2}{2mr^2}+V(r)\right]\psi(\boldsymbol{r}) = E\psi(\boldsymbol{r})$$

to solve a central force problem. Due to the rotational symmetry, we switch to spherical coordinates and choose the separation ansatz

$$\psi(\boldsymbol{r}) = \frac{u(r)}{r}\,Y_{l,m}(\theta,\varphi), \qquad \boldsymbol{L}^2\,Y_{l,m} = \hbar^2\,l(l+1)\,Y_{l,m}\,. \tag{4.155}$$

The *radial wave function* $u(r)$ is defined for $r>0$. It satisfies the normalization condition

$$\langle\psi|\psi\rangle = \int_0^\infty dr\int_\Omega d\Omega\, r^2|\psi(\boldsymbol{r})|^2 = \int_0^\infty dr\,|u(r)|^2\underbrace{\int_\Omega d\Omega\,|Y_{l,m}(\theta,\varphi)|^2}_{=1} = \int_0^\infty |u(r)|^2\,dr \tag{4.156}$$

and thus $u\in L^2([0,\infty[)$. It also holds that $u(0)=0$ (and therefore $u\in\mathcal{H}_{\mathrm{HR}}$), as otherwise $\psi\propto r^{-1}$ for small r and $-\Delta\psi = 4\pi\delta^{(3)}(\boldsymbol{r})$.

This leaves us with the *Radial Problem* to solve

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2}+\underbrace{\frac{\hbar^2 l(l+1)}{2m\,r^2}+V(r)}_{V_{\mathrm{eff}}(r)}\right]u(r) = E\,u(r) \tag{4.157}$$

of a particle in one dimension in the effective potential V_{eff}. Only for $l=0$ is $V_{\mathrm{eff}}(r)=V(r)$. Otherwise, in addition to $V(r)$, the repulsive angular momentum barrier acts on the particle, see Figure 4.2.

4.7 Hydrogen Atom

The hydrogen atom can be reduced to the form with reduced mass and $V(r)=-e^2/r$ as in equation (4.157).

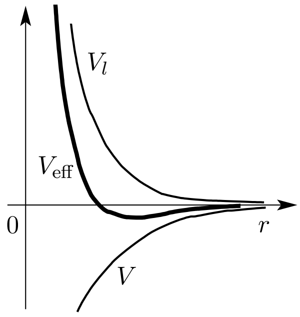

Fig. 4.2: The angular momentum creates the potential barrier $V_l = \hbar^2 l(l+1)/2mr^2$ and displaces the wave function from the vicinity of the origin. The potential $V(r)$ combines with $V_l(r)$ to form the effective potential $V_{\text{eff}}(r)$.

Two-Body Problem: First, we repeat the separation of the center of mass: Let the Hamiltonian operator for two interacting particles with masses $m_{1,2}$ be defined on $L^2(\mathbb{R}^6) = L^2(\mathbb{R}^3) \otimes L^2(\mathbb{R}^3)$ as

$$H = \frac{\boldsymbol{p}_1^2}{2m_1} + \frac{\boldsymbol{p}_2^2}{2m_2} + V(|\boldsymbol{r}_1 - \boldsymbol{r}_2|). \tag{4.158}$$

We switch to center of mass and relative coordinates $\boldsymbol{R}$ and $\boldsymbol{r}$,

$$\boldsymbol{r} = \boldsymbol{r}_1 - \boldsymbol{r}_2, \qquad \boldsymbol{R} = \frac{m_1\boldsymbol{r}_1 + m_2\boldsymbol{r}_2}{m_1 + m_2}; \tag{4.159}$$

similarly for the (conjugate) momenta

$$\boldsymbol{p} = \frac{m_2\boldsymbol{p}_1 - m_1\boldsymbol{p}_2}{m_1 + m_2}, \qquad \boldsymbol{P} = \boldsymbol{p}_1 + \boldsymbol{p}_2. \tag{4.160}$$

We define the reduced and total mass

$$\mu = \frac{m_1 m_2}{m_1 + m_2}, \qquad M = m_1 + m_2. \tag{4.161}$$

The chain rule states

$$\boldsymbol{\nabla}_{\boldsymbol{r}_1} = \frac{m_1}{M}\boldsymbol{\nabla}_{\boldsymbol{R}} + \boldsymbol{\nabla}_{\boldsymbol{r}}, \qquad \boldsymbol{\nabla}_{\boldsymbol{r}_2} = \frac{m_2}{M}\boldsymbol{\nabla}_{\boldsymbol{R}} - \boldsymbol{\nabla}_{\boldsymbol{r}}\,. \tag{4.162}$$

We obtain

$$\boldsymbol{p} = -\frac{i\hbar}{M}\left(m_2\boldsymbol{\nabla}_{\boldsymbol{r}_1} - m_1\boldsymbol{\nabla}_{\boldsymbol{r}_2}\right) = -i\hbar\boldsymbol{\nabla}_{\boldsymbol{r}}, \qquad \boldsymbol{P} = -i\hbar(\boldsymbol{\nabla}_{\boldsymbol{r}_1} + \boldsymbol{\nabla}_{\boldsymbol{r}_2}) = -i\hbar\boldsymbol{\nabla}_{\boldsymbol{R}}\,. \tag{4.163}$$

As desired, $\boldsymbol{P}$ and $\boldsymbol{p}$ are the conjugate momenta to $\boldsymbol{R}$ and $\boldsymbol{r}$. The Hamiltonian operator has the form in relative and center of mass coordinates

$$H = \frac{\boldsymbol{P}^2}{2M} + \frac{\boldsymbol{p}^2}{2\mu} + V(r)\,. \tag{4.164}$$

The Hamiltonian operator H allows for separation

$$\psi(\boldsymbol{R}, \boldsymbol{r}) = \phi(\boldsymbol{R}) \otimes \psi(\boldsymbol{r}) \tag{4.165}$$

into center of mass and relative motion. This leads to two independent Schrödinger equations

$$\frac{\boldsymbol{P}^2}{2M}\phi(\boldsymbol{R}) = E_S\phi(\boldsymbol{R}) \quad \text{and} \quad \left[\frac{\boldsymbol{p}^2}{2\mu} + V(r)\right]\psi(\boldsymbol{r}) = E\psi(\boldsymbol{r}) \tag{4.166}$$

with total energy $E_S + E$. The first equation describes the free motion of the center of mass (cf. Chapter 2.6), the second describes the relative motion. We have already examined 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 spherically symmetric problem with the Coulomb potential $V(r) = -Ze^2/r$. Here, $Z = 1$ is the nuclear charge. The radial problem for fixed angular momentum $\hbar l$ is given by (*Hydrogen problem*)

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \frac{\hbar^2 l(l+1)}{2mr^2} - \frac{Ze^2}{r}\right]u(r) = Eu(r). \tag{4.167}$$

It is useful 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

$$E = -\frac{Z^2 E_R}{n^2} = -\frac{Z^2 m e^4}{2\hbar^2 n^2}, \qquad r = \frac{n a_B}{2Z}x = \frac{n\hbar^2 x}{2Zme^2}, \tag{4.168}$$

where x describes the (dimensionless) position and n the (dimensionless) energy. So far, we have not imposed any quantization condition and thus all energies $n \geq 0$ are allowed. Later, we will see that n must be a natural number.

We write the radial wave function (in the Hilbert space $\mathcal{H}_{\mathrm{HR}}$) as

$$u(r) = \sqrt{\frac{2Z}{n a_B}}\, f(x), \tag{4.169}$$

where the prefactor ensures that $f(x)$ is normalized to 1 if $u(r)$ is also normalized. With the new variables, equation (4.167) becomes

$$\underbrace{\left[-x\frac{d^2}{dx^2} + \frac{l(l+1)}{x} + \frac{x}{4}\right]}_{=N} f(x) = nf(x)\,. \tag{4.170}$$

The hydrogen problem is equivalent to finding the eigenstates $f_n(x)$ and eigenvalues n of the operator N. Note that N is not Hermitian due to the transformation from u to f; see also footnote 14.

We will proceed analogously to the harmonic oscillator and introduce the operators N_+ (creation operator) and N_- (annihilation operator) with

$$N_\pm = \pm x\frac{d}{dx} - \frac{x}{2} + N\,. \tag{4.171}$$

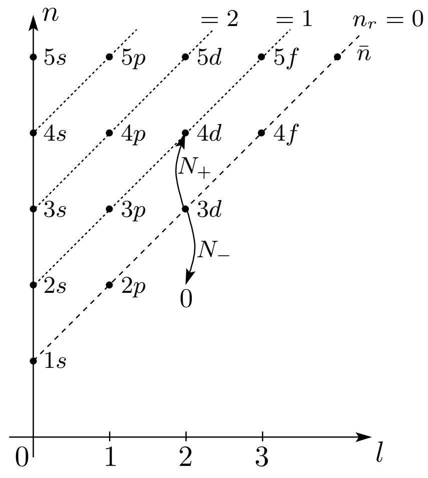

Fig. 4.3: Quantum numbers (n, l) of the hydrogen problem. The angular momenta for $l = 0, 1, 2, 3$ are conventionally denoted by s, p, d, f. The operator N_+ (N_-) raises (lowers) n for a fixed l. The absolute ground state is at $(1, 0)$. The degeneracy is n^2.

The relevant commutators for us are [cf. (3.122) and (3.123)]

$$[N, N_\pm] = \pm \underbrace{[N, x\partial_x]}_{=-\frac{x}{2}+N} - \underbrace{[N, \tfrac{1}{2}x]}_{=-x\partial_x} = \pm N_\pm \,. \tag{4.172}$$

Starting from an eigenstate $|n\rangle$ of N with eigenvalue n, we have

$$NN_+|n\rangle = \big([N, N_+] + N_+N\big)|n\rangle = N_+|n\rangle + N_+N|n\rangle = (n+1)N_+|n\rangle \,. \tag{4.173}$$

This means $N_+|n\rangle \propto |n+1\rangle$. 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.[13] Denoting the eigenvalue of the last state as $\bar{n}$, this means

$$0 = N_- f_{\bar{n}}(x) = \left[-x\frac{d}{dx} - \frac{x}{2} + N\right] f_{\bar{n}}(x) = \left[-x\frac{d}{dx} - \frac{x}{2} + \bar{n}\right] f_{\bar{n}}(x) \tag{4.174}$$

with the general solution (c is the normalization constant)

$$f_{\bar{n}}(x) = c\, g_{\bar{n}}(x), \quad g_{\bar{n}}(x) = x^{\bar{n}} e^{-x/2} \,. \tag{4.175}$$

In the following, we will denote the unnormalized eigenstates as 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

$$Ng_{\bar{n}} = \left[-x\frac{d^2}{dx^2} + \frac{l(l+1)}{x} + \frac{x}{4}\right] g_{\bar{n}} = \bar{n} g_{\bar{n}} + \frac{l(l+1) - \bar{n}(\bar{n}-1)}{x} g_{\bar{n}} \,. \tag{4.176}$$

For an eigenstate, the last term must vanish. Therefore, we have $\bar{n} = l + 1$. The second solution with $\bar{n} = -l$ must be discarded, as it is not normalizable.

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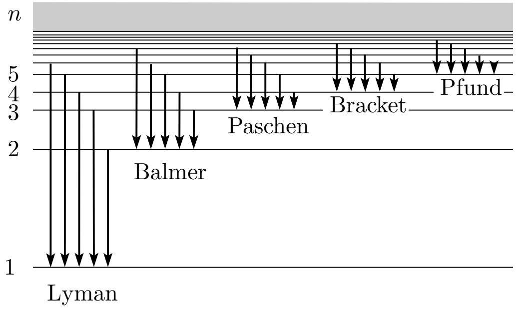
[13] For a formal proof, one simply shows that $(f, Nf) \geq 0$ with f arbitrary.



Final level n	Name	Energy range
$n = 1$	Lyman	UV
$n = 2$	Balmer	visible
$n = 3$	Paschen	IR
$n = 4$	Bracket	IR
$n = 5$	Pfund	IR

Fig. 4.4: Transitions in the hydrogen atom: Lyman, Balmer, Paschen, Bracket, and Pfund series. The Lyman series is in the ultraviolet (UV) range with energies greater than 10 eV; the Balmer series is in the visible range with energies greater than 1.9 eV (red, cyan, violet); the Paschen series is in the infrared (IR) range with energies greater than 0.65 eV.

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_-) increases (decreases) n at fixed l. The absolute ground state is at $(1, 0)$. The degeneracy is n^2.

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 $-Z^2E_R/(l+1)^2$. The absolute ground state is the state with $(n, l) = (1, 0)$. Starting from the states g_{l+1} with quantum numbers $(n, l) = (l+1, l)$, one can obtain the rest of the spectrum by applying N_+, see Figure 4.3. Here, N_+ increases the quantum number n by 1 each time. The spectrum, given by

$$E_{n,l} = E_n = -\frac{Z^2 E_R}{n^2}, \qquad n = 1, 2, 3, \dots \quad \text{(principal quantum number)}, \tag{4.177}$$

thus does not depend on l.

The eigenvalues E_n occur with the degeneracies

$$D_n = \sum_{l=0}^{n-1} \underbrace{(2l+1)}_{\sum_m} = n^2 \tag{4.178}$$

The quantum numbers n, l, m are called principal quantum number n, azimuthal or orbital angular momentum 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 considered, the degeneracy doubles to $D_n = 2n^2$. The optical selection rules require that $\Delta l = 1$ for the transitions. They belong to one of the series in Fig. 4.4.

For the state $g_{n,l}$ $(n \geq l+1)$, N_+ must be applied to g_{l+1} a total of n_r times ($n_r = n - l - 1$ is the radial quantum number). The unnormalized eigenstates for the eigenvalue n are therefore given by

$$g_{n,l}(x) = N_+^{n_r}(x^{l+1}e^{-x/2}), \qquad \text{with } N g_{n,l}(x) = n g_{n,l}(x)\,. \tag{4.179}$$

The state $g_{l+1}(x) = x^{l+1}e^{-x/2}$ corresponds to the state with the highest angular momentum at fixed $n = l+1$. The wave function has its maximum at $\bar{x} = 2n$. With

$$\ln g_{n,n-1}(x) = \ln g_{l+1}(x) = \ln g_{l+1}(\bar{x}) - \frac{(x-\bar{x})^2}{8n} + O(x-\bar{x})^3 \tag{4.180}$$

we obtain that the typical extension ξ is given by $\xi = 2n^{1/2}$. For large l, the particle is therefore relatively sharply positioned ($\xi \ll \bar{x}$). In the state $g_{n,n-1}$, the particle therefore follows an 'orbit' with radius $\bar{r} \simeq n a_B \bar{x}/Z \simeq n^2 a_B/Z$, see (1.32).

So far, we have determined the spectrum and obtained the eigenfunctions up to normalization. In the following calculation, we will determine the normalization using the result (4.187). We will calculate as before with fixed l and therefore suppress the index l. We need the relations

$$N_-N_+ = N(N+1) - l(l+1) \qquad \text{and} \qquad x = 2N - N_+ - N_-\,. \tag{4.181}$$

The natural scalar product of the problem is

$$(f,g) = \int_0^\infty \frac{f^*(x)g(x)}{x}\,dx, \qquad \langle f|g\rangle = (f,xg), \qquad \text{with } f,g \in \mathcal{H}_{\text{HR}}\,. \tag{4.182}$$

With respect to this scalar product, N_- and N_+ are adjoint operators to each other with $(N_+f,g) = (f,N_-g)$. Furthermore, N is Hermitian with respect to $(\cdot,\cdot)$, so the eigenfunctions g_n are orthogonal with $(g_n,g_m) = 0$, $n \neq m$.[14]

We first calculate the normalization of g_n with respect to $(\cdot,\cdot)$. We find the recursion relation

$$(g_{n+1},g_{n+1}) = (N_+g_n,N_+g_n) = (g_n,N_-N_+g_n) = \underbrace{[n(n+1)-l(l+1)]}_{=(n-l)(n+l+1)=c_n}(g_n,g_n)\,. \tag{4.183}$$

For $n_r = 0$, we have $g_{\bar{n}}(x) = x^{l+1}e^{-x/2}$ ($\bar{n} = l+1$) with the normalization

$$(g_{\bar{n}},g_{\bar{n}}) = \int_0^\infty x^{2l+1}e^{-x}\,dx = (2l+1)!\,. \tag{4.184}$$

This implies

$$(g_n,g_n) = c_{n-1}\,(g_{n-1},g_{n-1}) = c_{n-1}\cdots c_{\bar{n}}\,(2l+1)! = n_r!\,(n+l)!\,. \tag{4.185}$$

---

[14] The states f_n (and g_n) are *not* orthogonal with respect to $\langle\cdot|\cdot\rangle$. This is the reason why normalization is so tricky. The states $u(r)$, however, are again orthogonal with $\langle u_m|u_n\rangle = 0$, $m \neq n$. It holds that $\langle f_m|f_n\rangle \neq \langle u_m|u_n\rangle$, because the transformation $x \mapsto r$ depends on n!

The normalization with respect to the standard inner product is then given by

$$\begin{aligned}\langle g_n|g_n\rangle &= (g_n, xg_n) = 2(g_n, Ng_n) - \underbrace{(g_n, \overbrace{N_+ g_n}^{=g_{n+1}})}_{=0} - \underbrace{(g_n, N_- g_n)}_{=(N_+ g_n, g_n)=0} = 2n(g_n, g_n) \\ &= 2n\, n_r!\,(n+l)!\,. \end{aligned} \tag{4.186}$$

Therefore, we have shown that the normalized radial functions of the hydrogen atom are given by

$$f_{n,l}(x) = \frac{1}{\sqrt{2n\, n_r!\,(n+l)!}} g_{n,l}(x) = \sqrt{\frac{(n-l-1)!}{2n(n+l)!}}\, x^{l+1} L^{(2l+1)}_{n-l-1}(x)\, e^{-x/2} \tag{4.187}$$

with

$$L^{(2l+1)}_{n_r}(x) = \frac{1}{n_r!} x^{-(l+1)} e^{x/2} N_+^{n_r} (x^{l+1} e^{-x/2}) \tag{4.188}$$

the associated Laguerre polynomials of degree n_r.

We thus obtain the (normalized) eigenstates of the hydrogen problem

$$\psi_{n,l,m}(\boldsymbol{r}) = \sqrt{\frac{2Z}{na_B}}\, \frac{f_{n,l}(2Zr/na_B)}{r} Y_{l,m}(\theta, \varphi) \tag{4.189}$$

with the eigenvalues

$$E_n = -\frac{Z^2 E_R}{n^2}\,. \tag{4.190}$$

Chapter 5

Approximation Methods

Few problems are exactly solvable and we have to resort to approximate solution methods. The following approaches are available:

1) Approximating the problem by an exactly solvable problem.

2) Numerical solution via computer - this strategy provides accurate numbers, but often does not help with understanding.

3) Variational approach: Search for the best solution within a family of solutions - this requires an understanding of the solution (for the approach).

4) Perturbation theory: Systematic improvement of the solution.

We have presented some exact solutions in the previous chapters. Many problems can be reduced to the harmonic oscillator. Point 2) is covered in other lectures. We start with the variational approach. Perturbation theory will be discussed in Chapter 5.2. Note that the WKB approximation from Chapter 2.9 also provides very good results for large quantum numbers.

5.1 Variational Principle

The calculus of variations is based on the Rayleigh-Ritz *variational principle*. Let ψ be an arbitrary state ($\|\psi\| = 1$), H be a Hamiltonian operator 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'. For the proof, we introduce the complete eigenbasis ψ_n for 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 for the ground state energy. The Rayleigh-Ritz principle also allows for estimating excited states. If the ground state ψ_1 is known, then the smallest expectation value of the energy in the state $\psi^\perp$ with $\langle\psi_1|\psi^\perp\rangle = 0$ gives the first excited state. For non-degenerate 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 always assuming $\|\psi\| = 1$.

Furthermore, 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 $\boldsymbol{L}^2 = \hbar^2 l(l+1)$ gives a bound for the smallest energy with angular momentum $\hbar^2 l(l+1)$.

We can also obtain *lower* bounds, but this is generally 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

$$E_n \geq E_n^{(0)}, \qquad n = 1, 2, \dots \tag{5.4}$$

Example: Helium Atom The helium atom consists of a nucleus with two electrons, whose interaction we consider as a perturbation. We only consider the electronic degrees of freedom and describe the two-particle problem of the electrons in the field of the nucleus ($Z = 2$). The Hamiltonian operator $H = H^{(0)} + H^{(1)}$ 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 operator H commutes with the exchange symmetry

$$V\colon \psi(\boldsymbol{r}_1,\boldsymbol{r}_2) \mapsto \psi(\boldsymbol{r}_2,\boldsymbol{r}_1)\,. \tag{5.6}$$

---

[1] For simplicity, we assume that H has a discrete spectrum.

[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.

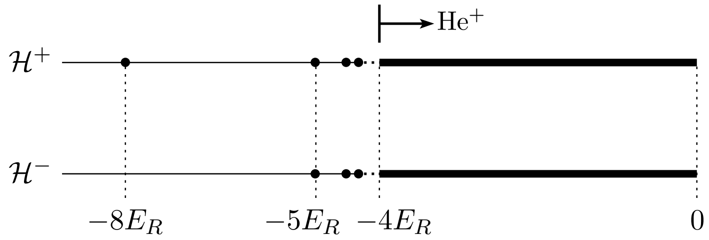


Fig. 5.1: Spectrum of the helium atom without interaction. The ground state is in the sector $\mathcal{H}^+$ at the energy $-8E_R$. The ionization threshold is at $-4E_R$.

Therefore, we can 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" the 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 (4.189) ($Z = 2$ for the He^{++} ion). We only consider states below the continuum at $-4E_R$, where one electron is free and the helium is ionized to He$^+$.

We will later learn about 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 $\mathcal{H}^+$ come with the singlet wave function ($s = 0$) (*Parahelium*), while states from $\mathcal{H}^-$ (*Orthohelium*) are threefold spin degenerate and appear with the triplet wave function ($s = 1$).

The ground state of the helium atom thus 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 upwards. However, the ionization limit $-4E_R$ (second ionization energy) remains unchanged, as the ground state of He$^+$ is unaffected by the repulsion of the electrons.

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 ground state of the helium atom, 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 need to calculate the expectation value $\langle \psi^+ | H | \psi^+ \rangle$. We obtain

$$\begin{aligned} \langle \Delta_1 \rangle = \langle \Delta_2 \rangle &= -\int (\boldsymbol{\nabla} f)^2 \, dV = -4\pi \int_0^\infty r^2 |f'(r)|^2 \, dr = -\frac{\alpha^2}{a_B^2}, \\ \langle r_1^{-1} \rangle = \langle r_2^{-1} \rangle &= 4\pi \int_0^\infty r |f(r)|^2 \, dr = \frac{\alpha}{a_B}, \end{aligned} \tag{5.13}$$

$$\begin{aligned} \left\langle \frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \right\rangle &= 2 \int d^3 r_1 \, f(r_1)^2 \int_{r_2 \leq r_1} d^3 r_2 \, \frac{f(r_2)^2}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} = 2 \int d^3 r_1 \, \frac{4\pi f(r_1)^2}{r_1} \int_0^{r_1} dr_2 \, r_2^2 f(r_2)^2 \\ &= \frac{\alpha}{a_B} \int_0^\infty dx \, x \, e^{-x} \int_0^x dy \, y^2 \, e^{-y} = \frac{5\alpha}{8 a_B} \,. \end{aligned} \tag{5.14}$$

For the calculation of the interaction energy, we used in the first line that the Coulomb potential of a spherically symmetric charge distribution outside is as if the entire charge were located at the center.

We thus 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 $\alpha = \frac{27}{16}$. This results in the following upper bound

$$E_1 \leq -2E_R \left(\frac{27}{16} \right)^2 \approx -5.695 E_R \,. \tag{5.16}$$

for the ground state energy. This result is very close to the measured value $E_1 \approx -5.807 E_R$.

Without interaction, we would find the value $\alpha = 2$ (minimum of $H^{(0)}$), since the charge is $Z = 2$. However, the optimum is at $\alpha = 27/16 \leq 2$. Each electron screens the nucleus for the other electron with an effective charge of $5/16$, as shown in Figure 5.2.

5.2 Perturbation Theory

The analysis of perturbations strongly depends on the problem: we distinguish between stationary and time-dependent problems and focus on discrete spectra. In the simplest case, we have a non-degenerate spectrum – therefore, we first consider the stationary, non-degenerate case and then analyze degenerate eigenvalues. Time-dependent problems with Fermi's Golden Rule conclude the discussion.

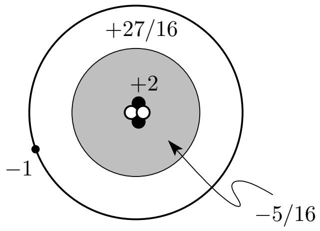


Fig. 5.2: Shielding: the second electron (charge −1) moves in the average field of the nucleus (charge +2) and the first electron (effective shielding charge −5/16); the second electron is thus subject to an effective charge of 27/16.

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 $H^{(0)}$ simple enough so that we know $|n^{(0)}\rangle$ 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 introduce the power series

$$|n\rangle = |n^{(0)}\rangle + \varepsilon|n^{(1)}\rangle + \varepsilon^2|n^{(2)}\rangle + \cdots, \quad E_n = E_n^{(0)} + \varepsilon E_n^{(1)} + \varepsilon^2 E_n^{(2)} + \ldots \tag{5.20}$$

It should be noted that such a power series may not always converge. Assuming that the series converges for small ε, we can substitute the power series into (5.17) and collect the terms according to order in ε. We obtain ($k \geq 1$)

$$\begin{aligned}
\varepsilon^0: &\quad H^{(0)}|n^{(0)}\rangle &&= E_n^{(0)}|n^{(0)}\rangle, \\
\varepsilon^1: &\quad H^{(0)}|n^{(1)}\rangle + H^{(1)}|n^{(0)}\rangle &&= E_n^{(0)}|n^{(1)}\rangle + E_n^{(1)}|n^{(0)}\rangle, \\
&&&\vdots \\
\varepsilon^k: &\quad H^{(0)}|n^{(k)}\rangle + H^{(1)}|n^{(k-1)}\rangle &&= E_n^{(0)}|n^{(k)}\rangle + E_n^{(1)}|n^{(k-1)}\rangle + \cdots + E_n^{(k)}|n^{(0)}\rangle\,.
\end{aligned} \tag{5.21}$$

It is useful to (initially) unconventionally normalize the sought wave function $|n\rangle$ as

$$\langle n^{(0)}|n\rangle = 1 \tag{5.22}$$

so that $\langle n^{(0)}|n^{(k)}\rangle = 0$ for $k \geq 1$.

Taking the scalar product of (5.21) with $|n^{(0)}\rangle$, we obtain the relationship

$$\langle n^{(0)}|H^{(1)}|n^{(k-1)}\rangle = E_n^{(k)} \tag{5.23}$$

between the wave function in the $k-1$ order and the energy in the k-th order.

We now only need to calculate the perturbation of the wave function. For this, we will need 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 $m \neq n$ follows $E_m^{(0)} \neq E_n^{(0)}$ (non-degenerate spectrum) and we recursively obtain 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 due to normalization)

$$|n^{(k)}\rangle = \sum_{m;m\neq n} \langle m^{(0)}|n^{(k)}\rangle\, |m^{(0)}\rangle\,. \tag{5.26}$$

One now iteratively solves (5.23), (5.25), and (5.26).

We explicitly state the results for $k \leq 2$, using the notation $|\mathrm{n}\rangle = |n^{(0)}\rangle$ and $\mathrm{E}_n = E_n^{(0)}$:

$$\varepsilon^0 : \begin{cases} E_n^{(0)} = \mathrm{E}_n \\ |n^{(0)}\rangle = |\mathrm{n}\rangle. \end{cases} \tag{5.27}$$

$$\varepsilon^1 : \begin{cases} E_n^{(1)} = \langle \mathrm{n}|H^{(1)}|\mathrm{n}\rangle, \\ |n^{(1)}\rangle = \displaystyle\sum_{m\neq n} \frac{\langle \mathrm{m}|H^{(1)}|\mathrm{n}\rangle}{\mathrm{E}_n - \mathrm{E}_m}|\mathrm{m}\rangle. \end{cases} \tag{5.28}$$

$$\varepsilon^2 : \begin{cases} E_n^{(2)} = \displaystyle\sum_{m\neq n} \frac{|\langle \mathrm{m}|H^{(1)}|\mathrm{n}\rangle|^2}{\mathrm{E}_n - \mathrm{E}_m}, \\ |n^{(2)}\rangle = \displaystyle\sum_{m\neq n}\left[\sum_{l\neq n} \frac{\langle \mathrm{m}|H^{(1)}|\mathrm{l}\rangle\langle \mathrm{l}|H^{(1)}|\mathrm{n}\rangle}{(\mathrm{E}_n - \mathrm{E}_m)(\mathrm{E}_n - \mathrm{E}_l)} - \frac{\langle \mathrm{m}|H^{(1)}|\mathrm{n}\rangle\langle \mathrm{n}|H^{(1)}|\mathrm{n}\rangle}{(\mathrm{E}_n - \mathrm{E}_m)^2}\right]|\mathrm{m}\rangle. \end{cases} \tag{5.29}$$

Note that the ground state energy is always lowered in 2nd order perturbation theory.

Hellmann–Feynman Theorem: Let $|\bar{n}\rangle$ be the normalized eigenstate of H with eigenvalue E_n (for the relationship between $|\bar{n}\rangle$ and $|n\rangle$, see below). The *Hellmann-Feynman Theorem* states that

$$\frac{\partial E_n}{\partial \varepsilon} = \left\langle \bar{n}\left|\frac{\partial H}{\partial \varepsilon}\right|\bar{n}\right\rangle = \langle \bar{n}|H^{(1)}|\bar{n}\rangle\,. \tag{5.30}$$

It provides a connection between the diagonal matrix elements of the perturbation operator and the derivative of the energy. It is particularly valid non-perturbatively, meaning for finite ε. For $\varepsilon = 0$, it simply corresponds to the statement (5.28) of first-order perturbation theory.

To prove this, we apply $\partial/\partial\varepsilon$ to the Schrödinger equation (5.17) with the result

$$H^{(1)}|\bar{n}\rangle + H\frac{\partial}{\partial\epsilon}|\bar{n}\rangle = \frac{\partial E_n}{\partial\varepsilon}|\bar{n}\rangle + E_n\frac{\partial}{\partial\epsilon}|\bar{n}\rangle\,. \tag{5.31}$$

Taking the scalar product with $|\bar{n}\rangle$ yields the theorem.

Normalization: The task remains to find the constant Z such that

$$|\bar{n}\rangle = Z^{1/2}|n\rangle \tag{5.32}$$

is correctly normalized with $\langle\bar{n}|\bar{n}\rangle = 1$. The factor Z is called the *renormalization of the wave function*. It is also true that $Z = |\langle n^{(0)}|\bar{n}\rangle|^2$. Thus, Z indicates the probability that a particle in the eigenstate $|\bar{n}\rangle$ of H will be measured in the unperturbed state $|n^{(0)}\rangle$ of $H^{(0)}$.

We consider $H^{(0)}$ as a function of the unperturbed energies $E_n^{(0)}$ with 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 obtain the renormalization factor[3]

$$\frac{\partial E_n}{\partial E_n^{(0)}} = \langle\bar{n}|n^{(0)}\rangle\langle n^{(0)}|\bar{n}\rangle = Z\,. \tag{5.34}$$

In 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 is seen in (5.25). The energy denominator $E_n^{(0} - E_m^{(0)}$ vanishes when $|n^{(0)}\rangle$ and $|m^{(0)}\rangle$ have the same energy. Perturbation theory is essentially

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[3] The first equality in (5.30) holds for the derivative with respect to any parameter.

a development 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 convergence radius is suppressed.

In the degenerate case, we denote the states at energy $E_n^{(0)}$ as $|n_1^{(0)}\rangle, |n_2^{(0)}\rangle, \dots, |n_k^{(0)}\rangle$ with k being the degeneracy of the energy level. The problem is that in the degenerate subspace $H^{(0)}$ does not define a distinguished basis. Therefore, we need to find linear combinations so that the problem of small energy denominators does not occur. This is the case when $H^{(1)}$ is completely diagonal.

Therefore, 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 operator $H^{(0)}$ in the subspace is proportional to the identity, V forms the leading order and determines the ‘eigen-directions’. We diagonalize the Hermitian matrix

$$V=U\,\underbrace{\mathrm{diag}(E_1^{(1)},\dots,E_k^{(1)})}_{=\tilde V}\,U^\dagger \tag{5.37}$$

with a unitary transformation U. This gives us 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 $E_j^{(1)}$ provide the corrections to the energy in order ε according to (5.28). We now carry out the perturbation theory in the basis where $|n_m^{(0)}\rangle$ is replaced by $|\tilde n_j^{(0)}\rangle$. Since $\tilde V$ is a diagonal matrix in the degenerate subspace, there are no longer issues with energy denominators, and the formulas (5.28), (5.29), and the analogous formulas for higher orders can be directly used. To do this, we simply further restrict the summations, so that $\sum_{m\neq n}\mapsto\sum_{m\neq n_1,\cdots,n_k}$ excludes all terms in the subspace with the same energy.

Examples

Stark Effect in the Hydrogen Atom: We investigate 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 $r_m^{(1)}$ for spin-1, see (4.122). From the Wigner-Eckart theorem, the selection rule is $\Delta m = 0$, $\Delta l = 0, \pm 1$. The parity selection rule requires $\Delta l = \pm 1$. Thus, the perturbation matrix has the form (we denote the states by nl_m)

$$V = \begin{array}{c} \begin{array}{cccc} 2s_0 & 2p_0 & 2p_1 & 2p_{-1} \end{array} \\ \begin{pmatrix} 0 & \delta & 0 & 0 \\ \delta^* & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \end{array} \begin{array}{c} \\ 2s_0 \\ 2p_0 \\ 2p_1 \\ 2p_{-1} \end{array} \tag{5.43}$$

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 gives

$$E_\pm^{(1)} = \pm 3 a_B e\mathcal{E} \qquad \text{with states} \qquad \psi_\pm = \frac{1}{\sqrt{2}}(\psi_{2,0,0} \mp \psi_{2,1,0})\,. \tag{5.45}$$

Thus, the 4-fold degenerate state at $-E_R/4$ splits into two non-degenerate states and one 2-fold degenerate state, see Fig. 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 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, justifying the perturbation theory.

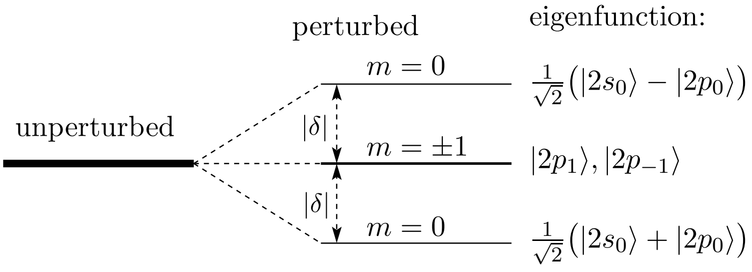

Fig. 5.3: Stark effect: the 4-fold degenerate state for $n = 2$ splits into 2 non-degenerate states and one 2-fold degenerate state.

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 operator[4]

$$H_{LS} = \frac{1}{2m^2c^2}\frac{1}{r}\frac{dV}{dr}\,\boldsymbol{L}\cdot\boldsymbol{S} = \frac{1}{2m^2c^2}\frac{e^2}{r^3}\,\boldsymbol{L}\cdot\boldsymbol{S} \tag{5.48}$$

in 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. Therefore, it is helpful to add 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

$$\Delta^l_{j,m} = \int(\boldsymbol{Y}^l_{j,m})^\dagger(\boldsymbol{L}\cdot\boldsymbol{S})\boldsymbol{Y}^l_{j,m}\,d\Omega = \frac{\hbar^2}{2}\Big[j(j+1)-l(l+1)-\frac{3}{4}\Big] = \frac{\hbar^2}{2}\begin{cases} l, & j=l+\frac{1}{2}, \\ -(l+1), & j=l-\frac{1}{2}. \end{cases}$$

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[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 due to the relativistic correction of the kinetic energy $\propto p^4/m^3c^2$.

This equation describes the *Landé interval rule*, that $E_j - E_{j-1} \propto j$ (at fixed l). In first order, the correction to the hydrogen energy levels is given by

$$\langle H_{LS}\rangle = \frac{1}{2m^2c^2}\frac{8e^2}{n^3a_B^3}\Delta^l_{j,m}\overbrace{\int\frac{f_{n,l}(x)^2}{x^3}\,dx}^{=[8l(l+\frac{1}{2})(l+1)]^{-1}} = \frac{\alpha^2E_R}{2n^3(l+\frac{1}{2})}\begin{cases}\frac{1}{l+1}, & j=l+\frac{1}{2},\\ -\frac{1}{l}, & j=l-\frac{1}{2}.\end{cases} \tag{5.51}$$

Here we have used that the typical strength of the spin-orbit interaction is given by

$$\frac{\hbar^2}{m^2c^2a_B^2}\frac{e^2}{2a_B} = \frac{e^4}{\hbar^2c^2}E_R = \alpha^2E_R \approx 725\,\mu\text{eV} \tag{5.52}$$

with the fine structure constant

$$\alpha = \frac{e^2}{\hbar c} \approx \frac{1}{137}\,. \tag{5.53}$$

From (5.51) we can see that the spin-orbit interaction lowers the energy when the spin and orbit are opposite with $j = l - \frac{1}{2}$. Otherwise, the energy is increased.

Zeeman Effect in the Hydrogen Atom: The Zeeman effect is described by the disturbance caused by 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 $\mu_B B \gtrsim \alpha^2E_R$, $B \gtrsim 10^5$ G. In this case, the Hamiltonian operator H_Z is the most important disturbance that lifts the $2n^2$-fold degeneracy in the hydrogen problem (with spin). In this case, we remain in the product representation $|l, m_l; \frac{1}{2}, m_s\rangle$ with $m_s = \pm\frac{1}{2}$ and obtain the splitting

$$\langle H_Z\rangle = \mu_B B(m_l + gm_s) \tag{5.55}$$

in first order. For example, the levels of a p state split according to 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 operator has the form

$$H(t) = H^{(0)} + H^{(1)}(t)\,, \tag{5.56}$$

where the perturbation $H^{(1)}(t)$ is now time-dependent.

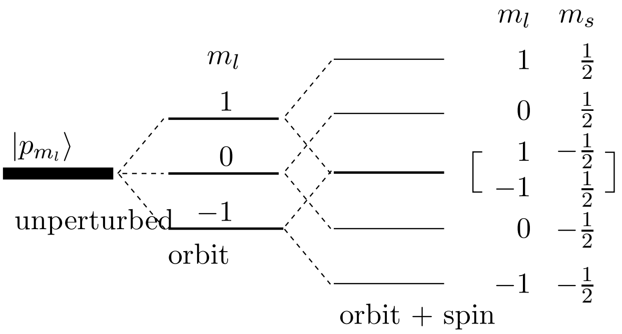

Fig. 5.4: Zeeman splitting of the $6 = 2 \times 3$-fold (spin×orbital) p state in the hydrogen atom. The orbital moment produces a triplet with doubly degenerate states (spin). The gyromagnetic factor $g = 2$ of the electron spin compensates exactly the half-integer nature of the spin angular momentum, so that orbital and spin result in the same energy splitting, resulting in a quintuplet with a doubly degenerate central state.

With the unitary transformation $V_t = e^{iH^{(0)}t/\hbar}$, we move 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 the Schrödinger equation according to (3.100)

$$i\hbar \frac{d}{dt} |\tilde{\Psi}_t\rangle = \tilde{H}^{(1)}(t) |\tilde{\Psi}_t\rangle \tag{5.58}$$

with the Hamiltonian operator

$$\tilde{H}^{(1)}(t) = H^{(0)} + \underbrace{i\hbar \dot{V}_t V_t^\dagger}_{=-H^{(0)}} + V_t H^{(1)} V_t^\dagger = e^{iH^{(0)}t/\hbar} H^{(1)}(t) e^{-iH^{(0)}t/\hbar}\,, \tag{5.59}$$

which is proportional to the perturbation.

We assume that $H^{(1)}(t) \to 0$ for $t \to -\infty$ and choose as initial state at $t = -\infty$ the stationary state $|a\rangle$ for the Hamiltonian operator $H^{(0)}$ with energy E_a. In 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

$$P_{a\to e}(t) = |\langle e|\tilde{\Psi}_t\rangle|^2 = \frac{1}{\hbar^2} \left| \int_{-\infty}^{t} dt' \, e^{i\omega_{ea}t'} \langle e|H^{(1)}(t')|a\rangle \right|^2 . \tag{5.61}$$

Thus, the probability $P_{a\to e}$ is determined by the Fourier transformation of $H^{(1)}(t)$ at the transition frequency

$$\omega_{ea} = \frac{1}{\hbar}(E_e - E_a) \tag{5.62}$$

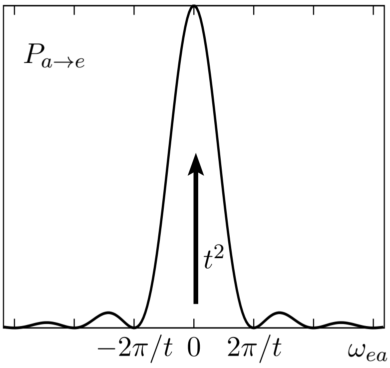

Fig. 5.5: Transition probability $P_{a\to e}(t)$ for a static perturbation. The area of the main peak grows as $t^2 \cdot (2\pi/t) \propto t$.

In order to make progress, we need to 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 $H^{(1)}(t \geq 0) = Ve^{-i\omega t} + V^\dagger e^{i\omega t}$,

where $H^{(1)}(t < 0) = 0$.

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 an energy-conserving process with $\omega_{ea} = 0$, it has the value t^2. Overall, it decays over the width $\delta\omega_{ea}$ with $\delta\omega_{ea}\, t \approx 2\pi$, see Figure 5.5. Right after turning on the perturbation, $\delta\omega_{ea} = \infty$ and transitions to any energy are possible in principle. For long times t, only nearly energy-conserving processes are allowed.

We consider the case where the final states are closely spaced with a *density of states* (states per energy) $\rho(E_e)$ at energy E_e. This gives us a typical spacing $\Delta = \rho^{-1}$ between 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 thus 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 need many states to contribute, i.e., $\delta\omega_{eg}/\Delta \gg 1$ ($t \ll 2\pi\hbar\rho$), and that the 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 frequency $\propto \omega$ and does not lead to any transitions. Thus, there are two groups of states with $\omega_+ \approx 0$ and $\omega_- \approx 0$, which contribute independently to the transition probability. We obtain the transition rate

$$\Gamma = \Gamma_{\text{em}} + \Gamma_{\text{abs}} = \frac{2\pi}{\hbar} |\langle e|V^\dagger|a\rangle|^2 \, \rho(E_e) \Big|_{E_e = E_a - \hbar\omega} + \frac{2\pi}{\hbar} |\langle e|V|a\rangle|^2 \, \rho(E_e) \Big|_{E_e = E_a + \hbar\omega} . \tag{5.67}$$

The first term with $E_e = E_a - \hbar\omega$ describes an emission process, while the second term with $E_e = E_a + \hbar\omega$ describes the absorption of energy.

Chapter 6

Identical Particles

As already discussed 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 $\mathcal{H}$ being the single-particle Hilbert space. It is natural to introduce the symmetry on this Hilbert space

$$P_{(jk)} \big(\cdots \otimes \psi_j \otimes \cdots \otimes \psi_k \otimes \cdots \big) = \cdots \otimes \psi_k \otimes \cdots \otimes \psi_j \otimes \cdots \,, \tag{6.2}$$

which describes the *exchange* of 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*

$$O^{(\text{total})} = \sum_{j=1}^{N} o_j, \qquad o_j = \underbrace{1 \otimes \cdots \otimes 1}_{(j-1 \text{ factors})} \otimes O \otimes 1 \otimes \cdots \tag{6.3}$$

which include, for example, the center of mass, the total momentum, the total spin, and the total energy.

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 $\{1, \dots, N\}$ onto itself with

$$\sigma \colon j \mapsto \sigma(j), \qquad (j = 1, \dots, N)\,. \tag{6.4}$$

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[1]

$$P_\sigma \colon \psi_1 \otimes \cdots \otimes \psi_N \quad \mapsto \quad \psi_{\sigma(1)} \otimes \cdots \otimes \psi_{\sigma(N)} = |\psi_{\sigma^{-1}(1)}, \dots, \psi_{\sigma^{-1}(N)}\rangle\,. \tag{6.5}$$

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[1] Exchanging the factors of the tensor product, as in Eq. (6.2), corresponds to exchanging the indices with the inverse permutation.

Thus, $P_\tau P_\sigma = P_{\tau\sigma}$ holds for two permutations $\sigma, \tau \in S_N$.[2] 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 due to linearity, P_σ is defined on any state.

Transpositions are exchanges of two elements $j \neq k$ and are denoted by (jk). The group with $N!$ elements is generated by transpositions. Writing a permutation σ as a product of N_t transpositions, the *signature* $\operatorname{sgn}\sigma = \pm 1$ of the permutation is precisely given by the parity $(-1)^{N_t}$.[3] It naturally holds

$$\operatorname{sgn}(\tau\sigma) = (\operatorname{sgn}\tau)(\operatorname{sgn}\sigma) \tag{6.6}$$

for the product of two permutations $\tau\sigma$.

Since the particles are identical, an N-particle state $|\Psi\rangle \in \mathcal{H}^{(N)}$ should be mapped onto itself up to a phase under a permutation P_σ. This means, we require

$$P_\sigma|\Psi\rangle = \eta(\sigma)|\Psi\rangle, \qquad |\eta(\sigma)| = 1\,. \tag{6.7}$$

Here, P_σ is a unitary transformation 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 thus $\eta(\tau\sigma) = \eta(\tau)\eta(\sigma)$ must hold.

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.[4] To do this, we consider $\eta(\sigma) = \eta(\sigma 1) = \eta(\sigma)\eta(1)$ and conclude $\eta(1) = 1$. For any transposition (jk), we have $(jk)^2 = (jk)(jk) = 1$ and therefore $\eta((jk)^2) = 1$ with the two possibilities from (6.9) as the only solution (we have $\eta((jk)) = \pm 1$ and the result follows by decomposing any permutation into transpositions)[5].

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 orbit) with the notation

$$\psi(x) = \langle x|\psi\rangle, \qquad \langle\phi|\psi\rangle = \int dx\, \phi^*(x)\psi(x) = \sum_m \int d^3r\, \phi^*(\boldsymbol{r}, m)\psi(\boldsymbol{r}, m)\,. \tag{6.10}$$

---

[2] It is said that P is a representation of S_N on $\mathcal{H}^{(N)}$.

[3] The representation as a product of transpositions is not unique, of course. However, it can be shown that the signature does not depend on the representation.

[4] In principle, there is the possibility that different states mix under P_σ. We will not consider this parastatistics.

[5] The sign of $\eta((jk)) = \pm 1$ must be chosen the same for all transpositions, since $(1j)(2k)(jk)(1j)(2k) = (12)$ and thus $\eta((jk)) = \eta((12))$.

The product states of N particles are given by $\Psi = \psi_1(x_1)\cdots\psi_N(x_N)$. A permutation σ acts on these wave functions as

$$(P_\sigma \Psi)(x_1, \ldots, x_N) = \langle x_1, \cdots, x_N | \psi_{\sigma^{-1}(1)}, \ldots, \psi_{\sigma^{-1}(N)}\rangle = \Psi(x_{\sigma(1)}, \ldots, x_{\sigma(N)})\,. \tag{6.11}$$

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-$\frac{1}{2}$ particles. We introduce the space of completely (anti-)symmetric states as

$$\mathcal{H}_s^{(N)} = \{|\Psi\rangle : P_\sigma|\Psi\rangle = |\Psi\rangle, \text{ for all } \sigma\}, \quad \mathcal{H}_a^{(N)} = \{|\Psi\rangle : P_\sigma|\Psi\rangle = \operatorname{sgn}(\sigma)|\Psi\rangle\}. \tag{6.12}$$

The total spin $\boldsymbol{S}^{(\text{total})} = \sum_j \boldsymbol{S}_j$ is invariant under the permutation operation. Therefore, 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's start with $\mathcal{H}_s^{(2)}$. The state with maximum $S_3^{(\text{total})}$ is given by $|\uparrow\uparrow\rangle$ with $(s = 1, m = 1)$. By applying $S_-^{(\text{total})}$, we then obtain 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 $|\uparrow\cdots\uparrow\rangle$ for the maximum total spin. This way, any representation $\mathcal{D}_{N/2}$ of $\mathsf{SU}(2)$ can be realized by a symmetric combination of N spin-$\frac{1}{2}$. A similar idea also works for the representations of $\mathsf{SU}(N)$ in general. However, one also 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 exactly the singlet. Thus, there is 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 exclusion principle later.

Spin-s representation of the rotation group With this insight, we now want to explicitly calculate the spin-s representation of the rotation group $u^{(s)}_{\boldsymbol{e};m',n}(\alpha)$ from (4.83). To do this, we first note that any rotation R with angle α around the axis $\boldsymbol{e}$ with Euler angles φ, θ, ψ can be decomposed as

$$R_{\boldsymbol{e}}(\alpha) = R_{\boldsymbol{e}_3}(\psi) R_{\boldsymbol{e}_2}(\theta) R_{\boldsymbol{e}_3}(\varphi) \tag{6.13}$$

We thus have

$$\begin{aligned} u^{(s)}_{\boldsymbol{e};m',m}(\alpha) &= \langle s, m'| e^{i\alpha \boldsymbol{e}\cdot\boldsymbol{S}/\hbar} |s, m\rangle = \langle s, m'| e^{i\psi S_3/\hbar} e^{i\theta S_2/\hbar} e^{i\varphi S_3/\hbar} |s, m\rangle \\ &= e^{im'\psi + im\varphi} d^{(s)}_{m',m}(\theta), \qquad d^{(s)}_{m',m}(\theta) = \langle s, m'| e^{i\theta S_2/\hbar} |s, m\rangle\,. \end{aligned} \tag{6.14}$$

Therefore, we only need to calculate the Wigner matrix $d^{(s)}_{m',m}(\theta)$.

6.3 Entanglement

Often, an observer ('Alice') in a Hilbert space $\mathcal{H} = \mathcal{H}_A \otimes \mathcal{H}_B$ only has access to a subspace $\mathcal{H}_A$. This occurs, for example, when the system consists of two spin-$\frac{1}{2}$ particles, but Alice can only manipulate one spin. The measurements M_A of a state ρ, which Alice can perform on her subspace, are then described solely by the *reduced density matrix*

$$\rho_A \colon \mathcal{H}_A \to \mathcal{H}_A, \qquad \rho_A = \mathrm{Tr}_B(\rho) \tag{6.15}$$

where Tr_B denotes the trace over the Hilbert space $\mathcal{H}_B$. The expectation value of M_A

$$\langle M_A \rangle = \mathrm{Tr}(\rho M_A) = \underbrace{\mathrm{Tr}_A \, \mathrm{Tr}_B}_{= \mathrm{Tr}_{A\otimes B}}(\rho M_A) = \mathrm{Tr}_A(\rho_A M_A) \, . \tag{6.16}$$

is thus uniquely determined by ρ_A. It should be noted 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

$$\rho_1 = |\uparrow\uparrow\rangle\langle\uparrow\uparrow| \, . \tag{6.17}$$

For measurements on the subsystem of Alice, the knowledge of the reduced density matrix is sufficient, given by

$$\rho_{1,A} = \mathrm{Tr}_B(\rho_1) = \sum_{m_B = \pm} \big(1 \otimes \langle m_B|\big) \, |\uparrow\uparrow\rangle\langle\uparrow\uparrow| \, \big(1 \otimes |m_B\rangle\big) = |\uparrow\rangle\langle\uparrow| \, . \tag{6.18}$$

It should be noted that in this case, $\rho_{1,A}$ is again a pure state with $\rho_{1,A}^2 = \rho_{1,A}$.

As a second example, let us 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

$$\rho_2 = \frac{1}{2}\big(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\big)\big(\langle\uparrow\downarrow| - \langle\downarrow\uparrow|\big) = \frac{1}{2}\Big(|\uparrow\downarrow\rangle\langle\uparrow\downarrow| + |\downarrow\uparrow\rangle\langle\downarrow\uparrow| - |\uparrow\downarrow\rangle\langle\downarrow\uparrow| - |\downarrow\uparrow\rangle\langle\uparrow\downarrow|\Big) \, . \tag{6.19}$$

In this case, the reduced state is

$$\rho_{2,A} = \frac{1}{2}\big(|\uparrow\rangle\langle\uparrow| + |\downarrow\rangle\langle\downarrow|\big) = \frac{1}{2} \cdot 1 \tag{6.20}$$

is not a pure state. The state $\rho_{2,A}$ is actually the *maximally mixed* state, where $|\uparrow\rangle$ and $|\downarrow\rangle$ each occur with 50% probability.

The different behavior of $|\Psi_1\rangle$ and $|\Psi_2\rangle$ is related to the fact that $|\Psi_1\rangle = |\uparrow\rangle \otimes |\uparrow\rangle$ is a *product state*. In general, it can be shown that if $|\Psi\rangle = |\psi_A\rangle \otimes |\psi_B\rangle$ is a product state with arbitrary $|\psi_A\rangle$ and $|\psi_B\rangle$, then the reduced density matrix

$$\rho_A = \mathrm{Tr}_B\big(|\psi_A\rangle \otimes |\psi_B\rangle\langle\psi_A| \otimes \langle\psi_B|\big) = \big(\mathrm{Tr}_B \, |\psi_B\rangle\langle\psi_B|\big)|\psi_A\rangle\langle\psi_A| = |\psi_A\rangle\langle\psi_A| \tag{6.21}$$

corresponds to the pure state $|\psi_A\rangle$. This provides a simple criterion for any pure state $|\Psi\rangle$ on $\mathcal{H}_A \otimes \mathcal{H}_B$:

$$|\Psi\rangle \text{ can be written as a product state} \quad \Leftrightarrow \quad \rho_A \text{ is a pure state.} \tag{6.22}$$

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 therefore 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

$$(U_A \otimes U_B)|0,0\rangle = |\psi_A\rangle \otimes |\psi_B\rangle \tag{6.23}$$

with arbitrary $|\psi_A\rangle$ and $|\psi_B\rangle$.

6.4 Bosons and Fermions

As we have seen, for identical particles $P_\sigma|\Psi\rangle = \eta(\sigma)|\Psi\rangle$. Therefore, for any observable M, the expectation value

$$\langle\Psi|M|\Psi\rangle = \underbrace{\frac{1}{N!}\sum_{\sigma\in S_N} |\eta(\sigma)|^2}_{=1} \langle\Psi|M|\Psi\rangle = \frac{1}{N!}\sum_\sigma \langle P_\sigma\Psi|M|P_\sigma\Psi\rangle = \langle\Psi|M^{(\mathrm{sym})}|\Psi\rangle\,. \tag{6.24}$$

is the same as the expectation value of the (symmetric) observable

$$M^{(\mathrm{sym})} = \frac{1}{N!}\sum_\sigma P_\sigma^\dagger M P_\sigma\,. \tag{6.25}$$

This allows us to focus on symmetric observables. For example, single-particle operators are symmetric observables.

It is now easy to see that for any $\tau \in S_N$,

$$P_\tau^\dagger M^{(\mathrm{sym})} P_\tau = \frac{1}{N!}\sum_\sigma P_\tau^\dagger P_\sigma^\dagger M P_\sigma P_\tau \overset{(\mu=\sigma\tau)}{=} \frac{1}{N!}\sum_\mu P_\mu^\dagger M P_\mu = M^{(\mathrm{sym})} \tag{6.26}$$

or in other words

$$[M^{(\mathrm{sym})}, P_\tau] = 0\,. \tag{6.27}$$

This means that the particles are *principally indistinguishable*, since no observable can distinguish the state $|\Psi\rangle$ from $P_\tau|\Psi\rangle$.

Furthermore, the observables $M^{(\mathrm{sym})}$ map the subspaces $\mathcal{H}_s^{(N)}$ and $\mathcal{H}_a^{(N)}$ from (6.12) onto themselves. In particular, this also applies to the Hamiltonian operator, and thus under the mapping $\Psi_0 \mapsto \Psi_t = e^{-iHt/\hbar}\Psi_0$, the subspace $\mathcal{H}_s^{(N)}$ or $\mathcal{H}_a^{(N)}$ is preserved.

In the context of relativistic quantum field theory, one can prove the *spin-statistics theorem.* This states that the physical Hilbert space of N identical particles with spin s is given by

$$\mathcal{H}_s^{(N)}, \qquad \text{if } s \in \{0, 1, 2, \dots\}, \qquad \text{(bosons)}, \tag{6.28}$$

$$\mathcal{H}_a^{(N)}, \qquad \text{if } s \in \{\tfrac{1}{2}, \tfrac{3}{2}, \dots\}, \qquad \text{(fermions)}. \tag{6.29}$$

In particular, under a transposition (jk) for the wave functions

$$P_{(jk)}\Psi(\dots, x_j, \dots, x_k, \dots) = \Psi(\dots, x_k, \dots, x_j, \dots), \qquad \text{(bosons)}, \tag{6.30}$$

$$P_{(jk)}\Psi(\dots, x_j, \dots, x_k, \dots) = -\Psi(\dots, x_k, \dots, x_j, \dots), \qquad \text{(fermions)}. \tag{6.31}$$

6.5 Two-Electron System

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 operator commutes with the square $(\boldsymbol{S}^{(\mathrm{tot})})^2$ of the total spin, states can be classified according to the total spin.

In particular, we obtain as possible wave functions

$$\Psi(x_1, x_2) = \begin{cases} \Phi_s(\boldsymbol{r}_1, \boldsymbol{r}_2)\, \chi_{0,0}(m_1, m_2), & \text{(Singlet)}, \\ \Phi_{t,m}(\boldsymbol{r}_1, \boldsymbol{r}_2)\, \chi_{1,m}(m_1, m_2), & \text{(Triplet)}. \end{cases} \tag{6.32}$$

We have already seen that $\chi_{0,0}(m_1, m_2) = -\chi_{0,0}(m_2, m_1)$ (Singlet is antisymmetric) and $\chi_{1,m}(m_1, m_2) = \chi_{1,m}(m_2, m_1)$ (Triplet is symmetric). In order for the total wave function Ψ to lie in the space $\mathcal{H}_a^{(2)}$, we need

$$\Phi_s(\boldsymbol{r}_1, \boldsymbol{r}_2) = \Phi_s(\boldsymbol{r}_2, \boldsymbol{r}_1) \quad \text{and} \quad \Phi_t(\boldsymbol{r}_1, \boldsymbol{r}_2) = -\Phi_t(\boldsymbol{r}_2, \boldsymbol{r}_1). \tag{6.33}$$

For the triplet state, the probability then vanishes

$$|\Phi_t(\boldsymbol{r}_1, \boldsymbol{r}_1)|^2 = 0, \tag{6.34}$$

to find the electrons at the same location.

Let us consider the simplest case of non-interacting electrons without spin-orbit coupling. The Hamiltonian operator is then given by

$$H = h_1 + h_2 \qquad \text{with} \qquad h_j = -\frac{\hbar^2}{2m}\Delta_j + V(\boldsymbol{r}_j)\,. \tag{6.35}$$

The single-particle problem $h|\psi_\nu\rangle = \varepsilon_\nu|\psi_\nu\rangle$ has the stationary states $|\psi_\nu\rangle$ with the energies ε_ν and the normalization $\langle\psi_\mu|\psi_\nu\rangle = \delta_{\mu\nu}$.

Thus, we obtain the total spatial wave function

$$\Phi_{s/t}(\boldsymbol{r}_1, \boldsymbol{r}_2) = \frac{1}{\sqrt{2}}\left[\psi_\mu(\boldsymbol{r}_1)\psi_\nu(\boldsymbol{r}_2) \pm \psi_\nu(\boldsymbol{r}_1)\psi_\mu(\boldsymbol{r}_2)\right], \tag{6.36}$$

with energy $E = \varepsilon_\mu + \varepsilon_\nu$, meaning $H\,\Phi_{s/t}(\boldsymbol{r}_1, \boldsymbol{r}_2) = E\,\Phi_{s/t}(\boldsymbol{r}_1, \boldsymbol{r}_2)$.

The probability of finding one electron at $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ (in the volume dV_j) is given by

$$\rho(\boldsymbol{r}_1, \boldsymbol{r}_2)\,dV_1\,dV_2 = |\Phi_{s/t}(\boldsymbol{r}_1, \boldsymbol{r}_2)|^2\,dV_1\,dV_2 = \big[\rho_d(\boldsymbol{r}_1, \boldsymbol{r}_2) \pm \rho_a(\boldsymbol{r}_1, \boldsymbol{r}_2)\big]dV_1\,dV_2 \quad (6.37)$$

with the *direct* probability density

$$\rho_d(\boldsymbol{r}_1, \boldsymbol{r}_2) = \frac{1}{2}\Big[|\psi_\mu(\boldsymbol{r}_1)|^2|\psi_\nu(\boldsymbol{r}_2)|^2 + |\psi_\mu(\boldsymbol{r}_2)|^2|\psi_\nu(\boldsymbol{r}_1)|^2\Big] \quad (6.38)$$

and the *exchange density*

$$\rho_a(\boldsymbol{r}_1, \boldsymbol{r}_2) = \mathrm{Re}\Big[\psi_\nu^*(\boldsymbol{r}_1)\psi_\mu(\boldsymbol{r}_1)\psi_\mu^*(\boldsymbol{r}_2)\psi_\nu(\boldsymbol{r}_2)\Big]\,. \quad (6.39)$$

The exchange density is a result of the fermionic nature of electrons. It is only different from zero when the overlap $\psi_\nu^*(\boldsymbol{r})\psi_\mu(\boldsymbol{r})$ does not vanish. In particular, this requires that the electrons are not too far apart. The exchange density decreases (triplet) or increases (singlet) the probability of finding both electrons at a nearby location with $\boldsymbol{r}_1 \approx \boldsymbol{r}_2$.

Example: Helium Atom The states [cf. (5.9)]

$$\psi^\pm_{n,l,m}(\boldsymbol{r}_1, \boldsymbol{r}_2) = \frac{1}{\sqrt{2}}\left[\psi_{n,l,m}(\boldsymbol{r}_1)\psi_{1,0,0}(\boldsymbol{r}_2) \pm \psi_{1,0,0}(\boldsymbol{r}_1)\psi_{n,l,m}(\boldsymbol{r}_2)\right] \quad (6.40)$$

are approximately the wave functions of the excited states $(1s)(nl)$ of the helium atom. The positive sign corresponds to a singlet state (para-helium). The state ψ^- is a triplet (ortho-helium).

The states $\psi^\pm_{n,l,m}$ without interaction have the energy [see (5.8)]

$$E_n^{(0)} = -4E_R\left(1 + \frac{1}{n^2}\right)\,. \quad (6.41)$$

Due to the interaction $V_{12} = e^2/|\boldsymbol{r}_1 - \boldsymbol{r}_2|$, this energy experiences a shift $\Delta E_{n,l}$. Note that, due to rotational symmetry, the shift cannot depend on m.

The probability density is given by $\rho = \rho_d \pm \rho_a$. This leads to $\Delta E^\pm_{n,l} = \langle \psi^\pm_{n,l,m}|V_{12}|\psi^\pm_{n,l,m}\rangle = I_{n,l} \pm J_{n,l}$ in first-order perturbation theory. The direct energy is

$$I_{n,l} = e^2 \int dV_1\,dV_2 \frac{\rho_d(\boldsymbol{r}_1, \boldsymbol{r}_2)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} = e^2 \int dV_1\,dV_2 \frac{|\psi_{1,0,0}(\boldsymbol{r}_1)\psi_{n,l,m}(\boldsymbol{r}_2)|^2}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} > 0 \quad (6.42)$$

which is naturally positive. However, 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 also positive.[6] Therefore, the energy of the singlet state ψ^+ is always higher than that of the triplet state. Due to the Coulomb interaction between the electrons, it is 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 Pauli Principle

The Hamiltonian operator H of ideal fermions is a single-particle operator for the total energy. The single-particle problem h acts on the Hilbert space $\mathcal{H} = L^2(\mathbb{R}^3) \otimes \mathbb{C}^{2s+1}$. In the N-particle Hilbert space $\mathcal{H}^{(N)}$ (without symmetrization), the eigenvalue problem $H|\Psi\rangle = E|\Psi\rangle$ has the solution

$$\begin{aligned}
&H|\nu_1, \dots, \nu_N\rangle = E|\nu_1, \dots, \nu_N\rangle, \qquad E = \varepsilon_{\nu_1} + \dots + \varepsilon_{\nu_N}, \\
&\Psi_{\nu_1,\dots,\nu_N}(x_1, \dots, x_N) = \langle x_1, \dots, x_N|\nu_1, \dots, \nu_N\rangle = \psi_{\nu_1}(x_1) \cdots \psi_{\nu_N}(x_N) \,. \qquad (6.43)
\end{aligned}$$

To obtain fermionic states from the correct Hilbert space $\mathcal{H}_a^{(N)}$, we antisymmetrize and obtain $\Psi_{\{\nu_1,\dots,\nu_N\}} \in \mathcal{H}_a^{(N)}$ with

$$\begin{aligned}
\Psi_{\{\nu_1,\dots,\nu_N\}}(x_1, \dots, x_N) &= \frac{1}{\sqrt{N!}} \sum_{\sigma \in S_N} (\operatorname{sgn}\sigma)\psi_{\nu_1}(x_{\sigma(1)}) \dots \psi_{\nu_N}(x_{\sigma(N)}) \qquad (6.44) \\
&= \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{\nu_1}(x_1) & \cdots & \psi_{\nu_N}(x_1) \\ \vdots & \ddots & \vdots \\ \psi_{\nu_1}(x_N) & \cdots & \psi_{\nu_N}(x_N) \end{vmatrix} = \frac{1}{\sqrt{N!}} \det\bigl(\psi_{\nu_j}(x_l)\bigr) \,.
\end{aligned}$$

This state is also called a *Slater determinant*. The state described by the Slater determinant depends only on the set $\{\nu_1, \dots, \nu_N\}$ and not on the arrangement, since a permutation on ν_j changes only the sign of $\Psi_{\{\nu_1,\dots,\nu_N\}}$.

It also applies the *Pauli principle*: each single-particle state can only occur once. If $\nu_j = \nu_m$ 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 (6.44) are then linearly dependent.

Therefore, we switch to the *occupation numbers* $n_\nu \in \{0, 1\}$ and characterize the state with $n_\nu = 1$ if the state ψ_ν occurs, and $n_\nu = 0$ otherwise. In total, we must have N states occupied, so that

$$\sum_\nu n_\nu = N, \qquad \sum_\nu n_\nu \varepsilon_\nu = E \,. \qquad (6.45)$$

For bosons, one can also introduce occupation numbers due to the symmetry under exchange. However, for bosons, the Pauli principle does not apply and we have $n_\nu \in \{0, 1, 2, \dots\}$.

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[6] With $\rho(\boldsymbol{r}) = \psi^*_{1,0,0}(\boldsymbol{r}_1)\psi_{n,l,m}(\boldsymbol{r}_1)$, we have $\int dV_1\, dV_2\, \rho(\boldsymbol{r}_1)\rho(\boldsymbol{r}_2)^*/|\boldsymbol{r}_1 - \boldsymbol{r}_2| = \int dV\, \boldsymbol{E}(\boldsymbol{r}) \cdot \boldsymbol{E}(\boldsymbol{r})^*/4\pi$, where $\boldsymbol{\nabla} \cdot \boldsymbol{E} = 4\pi\rho$.

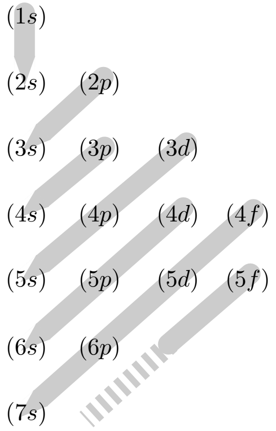

Fig. 6.1: Arrangement of the shells (nl) for the energy of the last electron in the Thomas-Fermi atom. n = principal quantum number, l = angular momentum quantum number.

Shell model: With the Pauli principle, one can explain the periodic table (for non-interacting electrons). In each single-particle state, at most one electron can be present. The lowest energy is obtained 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

$$\varepsilon_n = -\frac{Z^2 E_R}{n^2} \,. \tag{6.46}$$

The energy level with principal quantum number n is degenerate by a factor of $2n^2$ (the factor 2 comes from the spin-$\frac{1}{2}$).

As we have seen in the example of the helium atom, interaction leads to the lifting of additional degeneracy, so that only the angular momentum degeneracy remains. In particular, in an atom there are the shells (nl) with degeneracy $2(2l + 1)$, that is

$$s\text{-shell (deg. 2)}, \qquad p\text{- (deg. 6)}, \qquad d\text{- (deg. 10)} \quad \text{and} \quad f\text{- (deg. 14)}. \tag{6.47}$$

In the context of the Thomas-Fermi atom, one finds the following arrangement of the energy of the shells

$$(1s) < (2s) < (2p) < (3s) < (3p) < (4s) < (3d) < (4p) < (5s) < (4d) < \cdots \,. \tag{6.48}$$

This arrangement can be memorized using the scheme shown in Figure 6.1. Correspondingly, one finds the periodic table of elements in the form shown in Figure 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, the orbitals with small l are closer to the nucleus and therefore their energies are smaller, $\varepsilon_{2s} < \varepsilon_{2p}$.

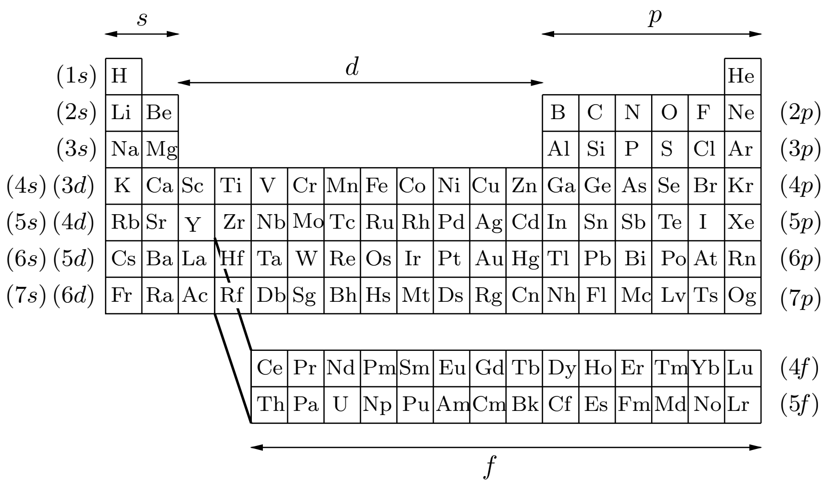

Fig. 6.2: Periodic table of elements.

- Na-Ar: as before, first the $(3s)$, then the $(3p)$ shell is filled.
- K-Kr: the energies of $(4s)$ are almost the same as those of $(3d)$. This results in a complicated filling (we only indicate the number of electrons in the $(4s)$ shell):

  $$\text{K } (4s)^1,\ \text{Ca } (4s)^2,\ \cdots,\ \text{V } (4s)^2,\ \text{Cr } (4s)^1,\ \text{Mn } (4s)^2, \cdots,\ \text{Ni } (4s)^2,\ \text{Cu } (4s)^1,\ \text{Zn } (4s)^2 \,.$$

  With Ga-Kr, the $(4p)$ shell is filled. The $(3d)$ shells are compact and therefore chemically less important; however, they provide the magnetic moments that generate the ferro- or antiferromagnetism of the elements Cr-Ni.
- Rb-Xe: essentially a repetition of the sequence K-Kr. Again, the s orbitals have approximately the same energy as the d orbitals of the previous shell.

For the chemical properties of the elements, the outermost electrons are relevant. Accordingly, elements in a column of the periodic table have similar chemical properties. For example,

- the noble gases He-Rn with their full orbitals are very inert,
- the alkali metals (H), Li-Fr with one electron, and
- the halogens F-At with a 'hole' are very reactive.

Some Designations

$\boldsymbol{v}$	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 operator
E	Energy or energy eigenvalue
$\boldsymbol{r}, \boldsymbol{p}$	Position and momentum operators
$\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p}$	Angular momentum operator
$a^\dagger, a$	Creation and annihilation operators
$\Psi(\boldsymbol{r}, t)$	Wave function
$\psi(\boldsymbol{r})$	Stationary wave function
χ	Spin wave function
$\psi_n = \lvert n\rangle$	Eigenfunction (usually related to energy)
E_n	Eigenenergy
$l = 0, 1, \ldots$	Orbital angular momentum quantum number
$s = 0, \frac{1}{2}, 1, \ldots$	Spin quantum number
$T^{(l)}$	Tensor operator for spin l
$u^{(s)}$	Representation of the rotation group for spin s
$\boldsymbol{S}^{(s)}$	Representation of the generators (spin operator) for spin s
$\boldsymbol{\nabla} = \left(\frac{\partial}{\partial r_1}, \frac{\partial}{\partial r_2}, \frac{\partial}{\partial r_3}\right)$	Nabla operator
$\Delta = \boldsymbol{\nabla} \cdot \boldsymbol{\nabla}$	Laplace operator
$e > 0$	Elementary charge
$\hbar$	Planck's constant
$\mu_B = \frac{e\hbar}{2mc}$	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