

Chapter 1

Formal Principles of Quantum Mechanics

Here we describe concisely the formal principles of quantum mechanics as they were introduced in a previous lecture. To this end we review at first the quantization of one-particle mechanics in the representation independent Dirac notation and then explain how to obtain the corresponding coordinate representation of quantum mechanics, which is due to Schrödinger. And, finally, we summarize exemplarily the results for two paradigmatic quantum systems, namely the harmonic oscillator and the hydrogen atom.

1.1 Classical Mechanics

A nonrelativistic classical particle of mass M moving in a potential $V(\mathbf{x})$ is described by the action

$$\mathcal{A}[\mathbf{x}(\bullet)] = \int_{t_1}^{t_2} L(\mathbf{x}(t); \dot{\mathbf{x}}(t)) dt, \quad (1.1)$$

which represents a functional of the particle path $\mathbf{x}(t)$ in configuration space. The corresponding Lagrange function is given by the difference of kinetic and potential energy:

$$L(\mathbf{x}; \dot{\mathbf{x}}) = \frac{M}{2} \dot{\mathbf{x}}^2 - V(\mathbf{x}). \quad (1.2)$$

The Hamilton principle of Lagrangian mechanics states that extremizing the action (1.1) according to the functional derivative, see Appendix A

$$\frac{\delta \mathcal{A}[\mathbf{x}(\bullet)]}{\delta \mathbf{x}(t)} = 0 \quad (1.3)$$

yields the underlying equation of motion. Indeed, applying the functional derivative calculus leads to the Euler-Lagrange equation

$$\frac{\partial L}{\partial \mathbf{x}(t)} - \frac{d}{dt} \frac{\partial L}{\partial \dot{\mathbf{x}}(t)} = 0, \quad (1.4)$$

which reduces with the Lagrange function (1.2) to the Newton equations of motion:

$$M\ddot{\mathbf{x}}(t) = -\nabla V(\mathbf{x}(t)). \quad (1.5)$$

Here we have introduced the Nabla operator

$$\nabla = \frac{\partial}{\partial \mathbf{x}} = \begin{pmatrix} \frac{\partial}{\partial x} \\ \frac{\partial}{\partial y} \\ \frac{\partial}{\partial z} \end{pmatrix}. \quad (1.6)$$

The transition to the Hamilton formalism is implemented by introducing the canonically conjugated momentum

$$\mathbf{p} = \frac{\partial L}{\partial \dot{\mathbf{x}}} = M\dot{\mathbf{x}} \quad (1.7)$$

and by performing the Legendre transformation

$$H(\mathbf{p}; \mathbf{x}) = \mathbf{p}\dot{\mathbf{x}} - L(\mathbf{x}; \dot{\mathbf{x}}) \quad (1.8)$$

which yields the Hamilton function

$$H(\mathbf{p}; \mathbf{x}) = \frac{\mathbf{p}^2}{2M} + V(\mathbf{x}). \quad (1.9)$$

Correspondingly, the action (1.1) converts with the Lagrange function (1.2) to

$$\mathcal{A}[\mathbf{p}(\bullet); \mathbf{x}(\bullet)] = \int_{t_1}^{t_2} \left\{ \mathbf{p}(t)\dot{\mathbf{x}}(t) - H(\mathbf{p}(t); \mathbf{x}(t)) \right\} dt, \quad (1.10)$$

which represents a functional of a path $\mathbf{p}(t)$, $\mathbf{x}(t)$ in phase space. In Hamilton mechanics the Hamilton principle demands the extremization

$$\frac{\delta \mathcal{A}[\mathbf{p}(\bullet); \mathbf{x}(\bullet)]}{\delta \mathbf{p}(t)} = 0, \quad (1.11)$$

$$\frac{\delta \mathcal{A}[\mathbf{p}(\bullet); \mathbf{x}(\bullet)]}{\delta \mathbf{x}(t)} = 0. \quad (1.12)$$

Taking into account the functional derivative calculus, see Appendix A, this leads to the Hamilton equations

$$\dot{\mathbf{x}}(t) = \frac{\partial H}{\partial \mathbf{p}(t)} = \frac{\mathbf{p}(t)}{M}, \quad (1.13)$$

$$\dot{\mathbf{p}}(t) = -\frac{\partial H}{\partial \mathbf{x}(t)} = -\nabla V(\mathbf{x}(t)), \quad (1.14)$$

which turn out to be equivalent to the Newton equations of motion (1.5).

1.2 Quantization

The transition from classical mechanics to quantum mechanics is achieved by assigning operators to observables:

$$\mathbf{x} \rightarrow \hat{\mathbf{x}}, \quad \mathbf{p} \rightarrow \hat{\mathbf{p}}, \quad H(\mathbf{p}; \mathbf{x}) \rightarrow H(\hat{\mathbf{p}}; \hat{\mathbf{x}}). \quad (1.15)$$

In order to obey the Heisenberg uncertainty relation, one has to postulate the following canonical commutation relations for the respective components of the coordinate and the momentum vector operator:

$$[\hat{x}_j, \hat{x}_k]_- = [\hat{p}_j, \hat{p}_k]_- = 0, \quad [\hat{p}_j, \hat{x}_k]_- = \frac{\hbar}{i} \delta_{jk}, \quad (1.16)$$

where the commutator between two quantum mechanical operators \hat{A} and \hat{B} is defined by

$$[\hat{A}, \hat{B}]_- = \hat{A}\hat{B} - \hat{B}\hat{A}. \quad (1.17)$$

The time evolution of a quantum mechanical state vector $|\psi(t)\rangle$ is described by the Schrödinger equation:

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = \hat{H}|\psi(t)\rangle. \quad (1.18)$$

In order to convert this representation independent formulation of quantum mechanics, which is due to Dirac, to the coordinate representation, one chooses as a basis the eigenstates $|\mathbf{x}\rangle$ of the coordinate operator $\hat{\mathbf{x}}$. They fulfill the eigenvalue problem

$$\hat{\mathbf{x}}|\mathbf{x}\rangle = \mathbf{x}|\mathbf{x}\rangle \quad (1.19)$$

as well as the orthonormality relation

$$\langle \mathbf{x} | \mathbf{x}' \rangle = \delta(\mathbf{x} - \mathbf{x}') \quad (1.20)$$

and the completeness relation

$$\int d^3x |\mathbf{x}\rangle \langle \mathbf{x}| = 1. \quad (1.21)$$

The coordinate representation of the momentum operators $\hat{\mathbf{p}}$ is given by the Jordan rule:

$$\langle \mathbf{x} | \hat{\mathbf{p}} = \frac{\hbar}{i} \nabla \langle \mathbf{x} |, \quad (1.22)$$

Evolving the quantum mechanical state vector $|\psi(t)\rangle$ with respect to this basis yields due to the completeness relation (1.21)

$$|\psi(t)\rangle = \int d^3x \psi(\mathbf{x}, t) |\mathbf{x}\rangle, \quad (1.23)$$

where the expansion coefficients represent the wave function

$$\psi(\mathbf{x}, t) = \langle \mathbf{x} | \psi(t) \rangle. \quad (1.24)$$

Multiplying (1.18) from the left with the bra-vector $\langle \mathbf{x} |$ leads for the wave function (1.24) the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \psi(\mathbf{x}, t) = \hat{H} \psi(\mathbf{x}, t). \quad (1.25)$$

Here the coordinate representation of the Hamilton operator \hat{H} follows due to (1.15), (1.19), and (1.22) from the Hamilton function H as follows:

$$\hat{H} = H \left(\frac{\hbar}{i} \nabla; \mathbf{x} \right). \quad (1.26)$$

In case of the standard Hamilton function (1.9) we get

$$\hat{H} = -\frac{\hbar^2}{2M} \Delta + V(\mathbf{x}) \quad (1.27)$$

with the Laplace operator

$$\Delta = \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}. \quad (1.28)$$

As we have assumed here that the potential $V(\mathbf{x})$ does not explicitly depend on time, one can perform for the wave function the separation ansatz

$$\psi(\mathbf{x}, t) = \psi_E(\mathbf{x}) e^{-iEt/\hbar}. \quad (1.29)$$

This reduces the time-dependent Schrödinger equation (1.25) to the time-independent Schrödinger equation:

$$\hat{H} \psi_E(\mathbf{x}) = E \psi_E(\mathbf{x}), \quad (1.30)$$

where E denotes the energy eigenvalue and $\psi_E(\mathbf{x})$ the energy eigenfunction.

1.3 Harmonic Oscillator

The harmonic oscillator represents an ubiquitous quantum mechanical model with which it is possible to describe quite successfully, for instance, collective oscillations in molecules or in solids. The Hamilton operator of a one-dimensional harmonic oscillator with mass M and angular frequency ω reads

$$\hat{H} = \frac{\hat{p}^2}{2M} + \frac{M}{2} \omega^2 \hat{x}^2. \quad (1.31)$$

Thus, we conclude together with (1.27) and (1.30) that the corresponding time-independent Schrödinger equation for the one-dimensional harmonic oscillator is given in coordinate representation by

$$\left(-\frac{\hbar^2}{2M} \frac{d^2}{dx^2} + \frac{M}{2} \omega^2 x^2\right) \psi(x) = E\psi(x). \quad (1.32)$$

It is a standard problem in quantum mechanics to solve the eigenvalue problem (1.32) together with Dirichlet boundary conditions, i.e. the wave function $\psi(x)$ has to vanish in the limits $x \rightarrow \pm\infty$.

1.3.1 Kummer Differential Equation

At first we focus on the relevant physical dimensions. From the mass M and the angular frequency ω of the harmonic oscillator follows as a characteristic length scale

$$l = \sqrt{\frac{\hbar}{M\omega}}, \quad (1.33)$$

which is called the the oscillator length. Considering a single ^{87}Rb atom with the mass $M = 87 \times 1.66 \cdot 10^{-27}$ kg in a harmonic trap of angular frequency $\omega = 2\pi \times 100$ Hz, the oscillator length amounts to $l = 1.16 \mu\text{m}$. Furthermore, the relevant energy scale is given by $\hbar\omega$, which motivates to introduce the dimensionless energy

$$\varepsilon = \frac{E}{\hbar\omega}. \quad (1.34)$$

With this the time-independent Schrödinger equation for the harmonic oscillator (1.32) is recognized to be of the form of the Weber differential equation:

$$\left(-\frac{d^2}{dx^2} + \frac{x^2}{l^2}\right) \psi(x) = \frac{2\varepsilon}{l^2} \psi(x). \quad (1.35)$$

In the next step we introduce a dimensionless coordinate by implementing the nonlinear coordinate transformation

$$y = \frac{x^2}{l^2} \quad \Longleftrightarrow \quad x = l\sqrt{y}. \quad (1.36)$$

Consequently this implies a transformation of the wave function according to

$$\psi(x) = \varphi\left(\frac{x^2}{l^2}\right) \quad \Longleftrightarrow \quad \varphi(y) = \psi(l\sqrt{y}). \quad (1.37)$$

Taking into account the chain rule of differentiation yields then

$$\frac{d\psi}{dx} = \frac{2x}{l^2} \frac{d\varphi}{dy}, \quad (1.38)$$

$$\frac{d^2\psi}{dx^2} = \frac{2}{l^2} \left(\frac{d\varphi}{dy} + \frac{2x^2}{l^2} \frac{d^2\varphi}{dy^2}\right), \quad (1.39)$$

so the Weber differential equation (1.35) is transformed to

$$y \frac{d^2 \varphi}{dy^2} + \frac{1}{2} \frac{d\varphi}{dy} + \left(\frac{\varepsilon}{2} - \frac{y}{4} \right) \varphi = 0. \quad (1.40)$$

Afterwards, it turns out to be advantageous to split off the asymptotic solution. As the wave function of the harmonic oscillator solving the Weber differential equation (1.35) can be shown to behave asymptotically as the Gauß function

$$\psi(x) \rightarrow e^{-x^2/2l^2}, \quad x \rightarrow \pm\infty, \quad (1.41)$$

this implies due to (1.37) the following ansatz for the transformed wave function:

$$\varphi(y) = e^{-y/2} \phi(y). \quad (1.42)$$

Taking into account the product rule of differentiation this leads to

$$\frac{d\varphi}{dy} = e^{-y/2} \left(\frac{d\phi}{dy} - \frac{1}{2} \phi \right), \quad (1.43)$$

$$\frac{d^2 \varphi}{dy^2} = e^{-y/2} \left(\frac{d^2 \phi}{dy^2} - \frac{d\phi}{dy} + \frac{1}{4} \phi \right), \quad (1.44)$$

so (1.40) reduces to

$$y \frac{d^2 \phi}{dy^2} + \left(\frac{1}{2} - y \right) \frac{d\phi}{dy} + \left(\frac{\varepsilon}{2} - \frac{1}{4} \right) \phi = 0. \quad (1.45)$$

With this we have obtained the standard form of a Kummer differential equation (B.21) with the parameters

$$a = \frac{1}{4} - \frac{\varepsilon}{2}, \quad c = \frac{1}{2}. \quad (1.46)$$

As (1.45) represents a linear differential equation of second order, it has two fundamental solutions, which are derived in detail in Appendix B. From (1.46) and (B.24) we conclude that the Kummer differential equation (1.45) can be solved for each dimensionless energy ε and has the general solution

$$\phi(y) = A_1 F_1 \left(\frac{1}{4} - \frac{\varepsilon}{2}; \frac{1}{2}; y \right) + B \sqrt{y} {}_1F_1 \left(\frac{3}{4} - \frac{\varepsilon}{2}; \frac{3}{2}; y \right). \quad (1.47)$$

Here the confluent hypergeometric function ${}_1F_1(a; c; y)$ is defined by the series (B.26).

1.3.2 Quantization

The quantization of the energy eigenvalues emerges only once we implement the Dirichlet boundary condition. To this end we have to take into account the asymptotic behaviour of the confluent hypergeometric function ${}_1F_1(a; c; y)$ as determined in (B.39). Apart from some

polynomial dependency, which is irrelevant for the present argument, we notice that both fundamental solutions in (1.47) grow exponentially like e^y , which implies due to (1.42) that $\varphi(y) \sim e^{y/2}$. As this yields via (1.37) the leading asymptotic behaviour $\psi(x) \sim e^{x^2/2l^2}$, the normalization integral diverges and the Dirichlet boundary condition is not fulfilled. In order to prevent this to happen, we have to guarantee that the series (B.26) terminates at some finite order. Due to the definition of the Pochhammer symbol (B.8) this implies the quantization condition $a = -n$ with $n = 0, 1, 2, \dots$. As we have two fundamental solutions (1.47), we have to consider two cases. Taking into account (1.34) the first fundamental solution in (1.47) leads to the quantized energy eigenvalues

$$\frac{1}{4} - \frac{\varepsilon}{2} = -n \quad \Longrightarrow \quad E_n = 2\hbar\omega \left(2n + \frac{1}{2} \right), \quad n = 0, 1, 2, \dots \quad (1.48)$$

They correspond due to (1.37) and (1.42) to the energy eigenfunctions

$$\psi_n(x) = N_n {}_1F_1 \left(-n; \frac{1}{2}; \frac{x^2}{l^2} \right) e^{-x^2/2l^2}, \quad n = 0, 1, 2, \dots \quad (1.49)$$

where N_n denotes a yet to be determined normalization constant. The appearing confluent hypergeometric function is identified to be a Hermite polynomial with an even index [16, (8.953.1)]:

$$H_{2n}(\xi) = (-1)^n \frac{(2n)!}{n!} {}_1F_1 \left(-n; \frac{1}{2}; \xi^2 \right) e^{-x^2/2l^2}, \quad n = 0, 1, 2, \dots \quad (1.50)$$

Correspondingly the second fundamental solution in (1.47) implies the quantized energy eigenvalues

$$\frac{3}{4} - \frac{\varepsilon}{2} = -n \quad \Longrightarrow \quad E_n = 2\hbar\omega \left(2n + 1 + \frac{1}{2} \right), \quad n = 0, 1, 2, \dots \quad (1.51)$$

together with the energy eigenfunctions

$$\psi_n(x) = N_n {}_1F_1 \left(-n; \frac{3}{2}; \frac{x^2}{l^2} \right) e^{-x^2/2l^2}, \quad n = 0, 1, 2, \dots \quad (1.52)$$

They contain Hermite polynomials with an odd index according to [16, (8.953.2)]

$$H_{2n+1}(\xi) = (-1)^n \frac{2(2n+1)!}{n!} \xi {}_1F_1 \left(-n; \frac{3}{2}; \xi^2 \right) e^{-x^2/2l^2}, \quad n = 0, 1, 2, \dots \quad (1.53)$$

1.3.3 Results

Combining (1.48) and (1.51) yields the energy eigenvalues

$$E_n = \hbar\omega \left(n + \frac{1}{2} \right), \quad (1.54)$$

where the quantum numbers turn out to be the natural numbers including the zero:

$$n = 0, 1, 2, \dots \quad (1.55)$$

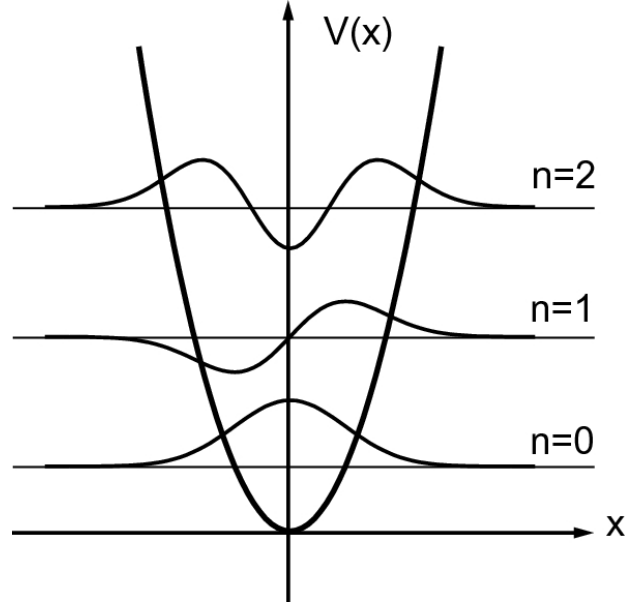


Figure 1.1: Schematic illustration of the harmonic potential $V(x) = M\omega^2 x^2/2$ together with the first three energy eigenvalues (1.54) and eigenfunctions (1.56).

Thus, the harmonic oscillator has an equidistant energy spectrum with energy spacing $\hbar\omega$ and the ground-state energy $\hbar\omega/2$ represents the zero-point energy. Furthermore, we read off from (1.49), (1.50) and (1.52), (1.53) that the energy eigenfunctions are given by

$$\psi_n(x) = N_n H_n \left(\frac{x}{l} \right) \exp \left(-\frac{x^2}{2l^2} \right). \quad (1.56)$$

Furthermore, $H_n(x)$ stands for the Hermite polynomials, whose properties are listed in Ref. [16, (8.95)]. They are defined according to

$$H_n(x) = (-1)^n e^{x^2} \frac{d^n}{dx^n} e^{-x^2}, \quad (1.57)$$

so the first five Hermite polynomials read:

$$H_0(x) = 1, \quad (1.58)$$

$$H_1(x) = 2x, \quad (1.59)$$

$$H_2(x) = 4x^2 - 2, \quad (1.60)$$

$$H_3(x) = 8x^3 - 12x, \quad (1.61)$$

$$H_4(x) = 16x^4 - 48x^2 + 12. \quad (1.62)$$

From Fig. 1.1 we read off that the quantum number (1.55) directly corresponds to the number of zeros of the energy eigenfunctions (1.56). Furthermore, the orthonormality relation of the energy eigenfunctions (1.56)

$$\int_{-\infty}^{\infty} dx \psi_n^*(x) \psi_m(x) = \delta_{nm} \quad (1.63)$$

allows to determine the normalization constant from the integral [16, (7.374)], yielding

$$N_n = \sqrt{\frac{1}{\sqrt{\pi} 2^n n!}}. \quad (1.64)$$

1.4 Hydrogen Atom

Another important quantum mechanical system is the hydrogen atom. Here one is interested in describing the possible states of an electron, which has the mass M and the charge $-e$, in the vicinity of a proton having the elementary charge $e = 1.602 \times 10^{-19}$ C. The corresponding Hamilton operator reads in SI units

$$\hat{H} = -\frac{\hbar^2}{2M} \Delta - \frac{e^2}{4\pi\epsilon_0|\mathbf{x}|} \quad (1.65)$$

with the vacuum dielectric constant $\epsilon_0 = 8.854 \times 10^{-12}$ C/Vm. Thus, from (1.27) and (1.30) follows that the corresponding time-independent Schrödinger equation for the hydrogen atom in coordinate representation is given by

$$\left(-\frac{\hbar^2}{2M} \Delta - \frac{e^2}{4\pi\epsilon_0|\mathbf{x}|} \right) \psi(\mathbf{x}) = E\psi(\mathbf{x}). \quad (1.66)$$

At first one recognizes that the underlying Coulomb potential is isotropic. Therefore, it is appropriate to rewrite (1.66) in terms of the spherical coordinates r, ϑ, φ :

$$\left[-\frac{\hbar^2}{2M} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{\hat{L}^2}{\hbar^2 r^2} \right) - \frac{e^2}{4\pi\epsilon_0 r} \right] \psi(r, \vartheta, \varphi) = E\psi(r, \vartheta, \varphi). \quad (1.67)$$

Here the angle dependences of the Laplace operator are contained in the square of the angular momentum operator

$$\hat{L}^2 = -\hbar^2 \left(\frac{\partial^2}{\partial \vartheta^2} + \frac{\cos \vartheta}{\sin \vartheta} \frac{\partial}{\partial \vartheta} + \frac{1}{\sin^2 \vartheta} \frac{\partial}{\partial \varphi^2} \right). \quad (1.68)$$

Solving (1.67) together with Dirichlet boundary conditions also represents a standard problem in quantum mechanics. At first, we recognize that (1.67) is a separable, partial differential equation which can be solved in terms of special functions. To this end we separate angular and radial dependences of the energy eigenfunctions by factorizing according to

$$\psi(r, \vartheta, \varphi) = Y(\vartheta, \varphi)R(r). \quad (1.69)$$

1.4.1 Angular Part

In the lecture Quantum Mechanics I it is worked out in detail that the angular part of the energy eigenfunction $Y(\vartheta, \varphi)$ turns out to be a common eigenfunction of the square of the angular momentum operator \hat{L}^2 and the z -component of the angular momentum operator

$$\hat{L}_z = \frac{\hbar}{i} \frac{\partial}{\partial \varphi}. \quad (1.70)$$

Thus, these so-called spherical harmonics $Y_{lm}(\vartheta, \varphi)$ fulfill

$$\hat{L}^2 Y_{lm}(\vartheta, \varphi) = \hbar^2 l(l+1) Y_{lm}(\vartheta, \varphi), \quad (1.71)$$

$$\hat{L}_z Y_{lm}(\vartheta, \varphi) = \hbar m Y_{lm}(\vartheta, \varphi) \quad (1.72)$$

and depend on the angular quantum number

$$l = 0, 1, 2, \dots \quad (1.73)$$

as well as the magnetic quantum number

$$m = -l, -l+1, \dots, l-1, l. \quad (1.74)$$

They are defined according to [12, Sect. 5.3]

$$Y_{lm}(\vartheta, \varphi) = \sqrt{\frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!}} P_l^{(m)}(\cos \vartheta) e^{im\varphi} \quad (1.75)$$

with the associated Legendre polynomials

$$P_l^{(m)}(x) = (-1)^m (1-x^2)^{m/2} \frac{d^m}{dx^m} P_l(x) \quad (1.76)$$

following from the Legendre polynomials

$$P_l(x) = \frac{1}{2^l l!} \frac{d^l}{dx^l} (x^2 - 1)^l. \quad (1.77)$$

Note that the the associated Legendre polynomials (1.76) satisfy recurrence relations [16, (8.733.2)]

$$x P_l^{(m)}(x) = \frac{l+1-m}{2l+1} P_{l+1}^{(m)}(x) + \frac{l+m}{2l+1} P_{l-1}^{(m)}(x). \quad (1.78)$$

and that the Legendre polynomials (1.77) obey the differential equation [16, (8.910)]

$$(1-x^2)P_l''(x) - 2xP_l'(x) + l(l+1)P_l(x) = 0. \quad (1.79)$$

The first Legendre polynomials read [16, (8.912)]

$$P_0(x) = 1, \quad P_1(x) = x, \quad P_2(x) = \frac{1}{2}(3x^2 - 1), \quad P_3(x) = \frac{1}{2}(5x^3 - 3x). \quad (1.80)$$

Thus, the spherical harmonics for $l = 0$ and $l = 1$ read explicitly

$$Y_{00}(\vartheta, \varphi) = \frac{1}{\sqrt{4\pi}}, \quad Y_{10}(\vartheta, \varphi) = \sqrt{\frac{3}{4\pi}} \cos \vartheta, \quad Y_{1\pm 1}(\vartheta, \varphi) = \mp \sqrt{\frac{3}{8\pi}} \sin \vartheta e^{\pm i\varphi}. \quad (1.81)$$

A graphical representation of the spherical harmonics up to $l = 3$ is provided by Fig. 1.2. Note that the spherical harmonics (1.75) are normalized according to

$$\int_0^\pi d\vartheta \sin \vartheta \int_0^{2\pi} d\varphi Y_{lm}^*(\vartheta, \varphi) Y_{l'm'}(\vartheta, \varphi) = \delta_{ll'} \delta_{mm'}. \quad (1.82)$$

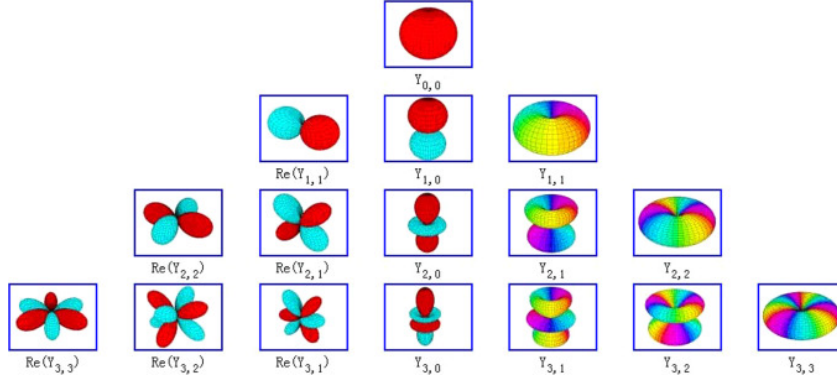


Figure 1.2: Graphical representation of the first spherical harmonics up to $l = 3$.

1.4.2 Radial Part

Inserting the separation ansatz (1.69) into the time-independent Schrödinger equation (1.67) and taking into account (1.71) yields a second-order ordinary differential equation for the yet undetermined radial wave function $R(r)$:

$$\left[-\frac{\hbar^2}{2M} \left(\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right) + \frac{\hbar^2 l(l+1)}{2Mr^2} - \frac{e^2}{4\pi\epsilon_0 r} \right] R(r) = ER(r). \quad (1.83)$$

One can get rid of the first derivative via the ansatz

$$R(r) = \frac{u(r)}{r}. \quad (1.84)$$

Indeed, with this we have

$$\frac{dR}{dr} = \frac{1}{r} \frac{du}{dr} - \frac{1}{r^2} u, \quad (1.85)$$

$$\frac{d^2 R}{dr^2} = \frac{1}{r} \frac{d^2 u}{dr^2} - \frac{2}{r^2} \frac{du}{dr} + \frac{2}{r^3} u, \quad (1.86)$$

so the differential equation (1.69) reduces to

$$\left[-\frac{\hbar^2}{2M} \frac{d^2}{dr^2} + \frac{\hbar^2 l(l+1)}{2Mr^2} - \frac{e^2}{4\pi\epsilon_0 r} \right] u(r) = Eu(r). \quad (1.87)$$

Thus, $u(r)$ solves a one-dimensional Schrödinger equation with an effective potential, which consists of a centrifugal barrier and the Coulomb potential. In the next step we analyze the behaviour of $u(r)$ for both small and large radii r . Considering the former case reduces (1.87) to

$$\left[\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} \right] u(r) = 0, \quad r \rightarrow 0. \quad (1.88)$$

This differential equation is solved by the ansatz $u(r) = r^\alpha$ provided that the parameter α is given by $\alpha_1 = l+1$ and $\alpha_2 = -l$. The second solution has to be neglected in order to guarantee

the normalizability of the radial wave function. Thus we conclude that $u(r)$ reads for small radii

$$u(r) \rightarrow r^{l+1}, \quad r \rightarrow 0. \quad (1.89)$$

Correspondingly, for larger radii (1.87) reduces to

$$\left(\frac{d^2}{dr^2} + \frac{2ME}{\hbar^2} \right) u(r) = 0, \quad r \rightarrow \infty. \quad (1.90)$$

As we aim for obtaining a bound energy eigenfunctions, we can assume that the energy E is negative. This suggests introducing the abbreviation

$$\kappa = \sqrt{-\frac{2ME}{\hbar^2}}, \quad E < 0, \quad (1.91)$$

so that (1.90) simplifies to

$$\left(\frac{d^2}{dr^2} - \kappa^2 \right) u(r) = 0, \quad r \rightarrow \infty. \quad (1.92)$$

From the two solutions $u_1(r) = e^{-\kappa r}$, $u_2(r) = e^{\kappa r}$ the second one has to be discarded due to the Dirichlet boundary condition, yielding finally for large radii

$$u(r) \rightarrow e^{-\kappa r} \quad r \rightarrow \infty. \quad (1.93)$$

It is now suggestive to combine the small and the large distance behaviour of $u(r)$ in (1.89) and (1.93) by the ansatz

$$u(r) = r^{l+1} e^{-\kappa r} v(r), \quad (1.94)$$

where the newly introduced function $v(r)$ covers the radial wave function for intermediate distances. Calculating the first derivative

$$\frac{du}{dr} = \left[r \frac{dv}{dr} + (l+1 - \kappa r)v \right] r^l e^{-\kappa r} \quad (1.95)$$

and the second derivative

$$\frac{d^2u}{dr^2} = \left\{ r \frac{d^2v}{dr^2} + 2(l+1 - \kappa r) \frac{dv}{dr} + \left[\frac{(l+1)l}{r} - 2\kappa(l+1) + \kappa^2 r \right] v \right\} r^l e^{-\kappa r} \quad (1.96)$$

we obtain from (1.87) by taking into account (1.91)

$$\left\{ r \frac{d^2}{dr^2} + 2(l+1 - \kappa r) \frac{d}{dr} - \left[2\kappa(l+1) - \frac{e^2 M}{2\pi\epsilon_0 \hbar^2} \right] \right\} v(r) = 0. \quad (1.97)$$

Introducing the dimensionless coordinate $y = 2\kappa r$ via

$$\phi(y) = v\left(\frac{y}{2\kappa}\right) \quad \Longleftrightarrow \quad v(r) = \phi(2\kappa r) \quad (1.98)$$

finally yields

$$\left[y \frac{d^2}{dy^2} + (2l + 2 - y) \frac{d}{dy} - \left(l + 1 - \frac{e^2 M}{4\pi\epsilon_0 \hbar^2 \kappa} \right) \right] \phi = 0. \quad (1.99)$$

With this we have obtained the standard form of a Kummer differential equation (B.21) with the parameters

$$a = l + 1 - \frac{e^2 M}{4\pi\epsilon_0 \hbar^2 \kappa}, \quad c = 2l + 2. \quad (1.100)$$

The general solution of the second-order differential equation (1.99) represents according to (B.24) a superposition of two fundamental solutions in terms of confluent hypergeometric functions (B.26):

$$\phi(y) = A {}_1F_1 \left(l + 1 - \frac{e^2 M}{4\pi\epsilon_0 \hbar^2 \kappa}; 2l + 2; y \right) + B y^{-2l-1} {}_1F_1 \left(-l - \frac{e^2 M}{4\pi\epsilon_0 \hbar^2 \kappa}; -2l; y \right). \quad (1.101)$$

Taking into account the series expansion of the confluent hypergeometric function (B.26) and the definition of the Pochhammer symbol (B.8) we conclude that $(-2l)_n$ vanishes for $n = 1 + 2l$ so that the second fundamental solution in (1.101) diverges and has to be excluded. Thus we conclude that the time-independent Schrödinger equation for the hydrogen atom (1.66) can be solved for any κ , i.e. according to (1.91) for each energy $E < 0$, yielding

$$\phi(y) = A {}_1F_1 \left(l + 1 - \frac{e^2 M}{4\pi\epsilon_0 \hbar^2 \kappa}; 2l + 2; y \right). \quad (1.102)$$

1.4.3 Energy Eigenvalues

But still we have to consider the asymptotic behaviour of the confluent hypergeometric functions in (1.102) and check whether it is compatible with the Dirichlet boundary conditions. Similar to the treatment of the harmonic oscillator in Subsection 1.3.2 we obtain from the confluent hypergeometric function in (1.102) due to the asymptotics (B.39) the quantization condition

$$l + 1 - \frac{e^2 M}{4\pi\epsilon_0 \hbar^2 \kappa} = -n_r \quad (1.103)$$

with the radial quantum number

$$n_r = 0, 1, 2, \dots \quad (1.104)$$

This leads to the following energy eigenvalues of the hydrogen atom

$$E_n = -\text{Ry} \frac{1}{n^2} \quad (1.105)$$

with the principal quantum number

$$n = n_r + l + 1. \quad (1.106)$$

Here the relevant energy scale is provided by the Rydberg energy

$$\text{Ry} = \frac{Me^4}{32\pi^2\epsilon_0^2\hbar^2}, \quad (1.107)$$

which characterizes the ionization energy of the hydrogen atom in its ground state. It can be re-expressed in terms of the rest energy Mc^2 of the electron according to

$$\text{Ry} = \frac{1}{2} Mc^2 \alpha^2 \quad (1.108)$$

by introducing the Sommerfeld fine-structure constant

$$\alpha = \frac{e^2}{4\pi\hbar\epsilon_0 c} \approx 0.0073 \approx \frac{1}{137}. \quad (1.109)$$

Note that the latter dimensionless quantity is a fundamental physical constant, which quantifies the strength of the electromagnetic interaction between elementary charged particles, and can be expressed as the ratio of two length scales via

$$\alpha = \frac{\lambda_C}{2\pi a_B}. \quad (1.110)$$

Here the Compton wavelength of the electron appears in the numerator

$$\lambda_C = \frac{2\pi\hbar}{Mc}, \quad (1.111)$$

stemming from unifying quantum mechanics with special relativity. And the denominator is given by the Bohr radius as the characteristic length scale of the hydrogen atom

$$a_B = \frac{4\pi\epsilon_0\hbar^2}{Me^2}, \quad (1.112)$$

which already appears within the Bohr model. Furthermore, we note that Rydberg energy (1.107) and Bohr radius (1.112) are related via

$$\text{Ry} = \frac{\hbar^2}{2Ma_B^2}. \quad (1.113)$$

Thus, restricting the electron to a length scale of the Bohr radius a_B yields a kinetic energy in form of the Rydberg energy Ry . With the electron mass $M = 9.109 \times 10^{-31}$ kg this leads for the Compton wavelength (1.111) and the Bohr radius (1.112) to the value $\lambda_C = 2.426 \times 10^{-12}$ m and $a_B = 5.292 \times 10^{-11}$ m, respectively. Furthermore, the rest energy Mc^2 of the electron turns out to be 0.511 MeV, yielding for the Rydberg energy (1.108) the value

$$\text{Ry} = \frac{0.511 \text{ MeV}}{2(137)^2} = 13.6 \text{ eV}. \quad (1.114)$$

Furthermore, from (1.104) and (1.106) we read off that fixing the principal quantum number to some value

$$n = 1, 2, 3, \dots \quad (1.115)$$

implies that the angular quantum number l is restricted to

$$l = 0, 1, 2, \dots, n - 1. \quad (1.116)$$

Together with the magnetic quantum number (1.74) the corresponding energy eigenfunctions of the electron $\psi_{nlm}(\mathbf{x})$ are indexed with the three quantum numbers n , l , and m . Thus, the energy eigenvalue (1.105) for some principal quantum number n has the degeneracy

$$d_n = \sum_{l=0}^{n-1} (2l + 1) = n^2. \quad (1.117)$$

Note that each degeneracy occurs, in principle, twice as the electron has in addition an internal degree of freedom called spin, which can point up- or downwards. For the time being, however, we simplify our discussion by neglecting this additional spin degree of freedom.

1.4.4 Radial Eigenfunctions

Combining (1.84), (1.94), (1.98), (1.102), and (1.103) the radial wave function of the hydrogen atom reads

$$R(r) = Ar^l e^{-\kappa r} {}_1F_1(-n_r; 2l + 2; 2\kappa r). \quad (1.118)$$

Here the confluent hypergeometric function coincides according to [16, (8.972.1)] with a Laguerre polynomial

$$L_n^{(\alpha)}(x) = \binom{n + \alpha}{n} {}_1F_1(-n; \alpha + 1; x). \quad (1.119)$$

Note the Laguerre polynomials are defined via the Rodrigues formula [16, (8.970)]

$$L_n^{(\alpha)}(x) = \frac{1}{x^\alpha n!} e^x \frac{d^n}{dx^n} (e^{-x} x^{n+\alpha}), \quad (1.120)$$

which reduces to

$$L_n^{(\alpha)}(x) = \sum_{\nu=0}^n \binom{n + \alpha}{n - \nu} \frac{(-x)^\nu}{\nu!} \quad (1.121)$$

with the binomial coefficient

$$\binom{\alpha}{n} = \frac{\alpha!}{n!(\alpha - n)!}. \quad (1.122)$$

Furthermore, we remark that the Hermite polynomials appearing for the harmonic oscillator are special cases of the Laguerre polynomials [16, (8.972.2), (8.972.3)]:

$$H_{2n}(x) = (-1)^n 2^{2n} n! L_n^{(-1/2)}(x^2), \quad (1.123)$$

$$H_{2n+1}(x) = (-1)^n 2^{2n+1} n! L_n^{(1/2)}(x^2). \quad (1.124)$$

Thus, taking into account (1.91), (1.103), (1.105), (1.106), (1.113), and (1.118) as well as normalizing the radial eigenfunction via

$$\int_0^\infty dr r^2 R_{nl}(r) R_{n'l}(r) = \delta_{nn'}, \quad (1.125)$$

the radial contribution to the energy eigenfunction (1.69) turns out to be

$$R_{nl}(r) = \frac{2}{n^2 a_B^{3/2}} \sqrt{\frac{(n-l-1)!}{(n+l)!}} \left(\frac{2r}{na_B}\right)^l L_{n-l-1}^{(2l+1)}\left(\frac{2r}{na_B}\right) \exp\left(-\frac{r}{na_B}\right). \quad (1.126)$$

Consequently, the lowest radial energy eigenfunctions read for $n = 1$

$$R_{10}(r) = \frac{2}{a_B^{3/2}} \exp\left(-\frac{r}{a_B}\right) \quad (1.127)$$

and $n = 2$

$$R_{20}(r) = \frac{1}{2\sqrt{2}a_B^{3/2}} \left(2 - \frac{r}{a_B}\right) \exp\left(-\frac{r}{2a_B}\right), \quad R_{21}(r) = \frac{1}{2\sqrt{6}a_B^{3/2}} \frac{r}{a_B} \exp\left(-\frac{r}{2a_B}\right), \quad (1.128)$$

respectively.

1.4.5 Energy Eigenfunctions

Thus, we conclude from (1.82) and (1.125) that the energy eigenfunctions (1.69) are orthonormal:

$$\int_0^\infty dr r^2 \int_0^\pi d\vartheta \sin \vartheta \int_0^{2\pi} d\varphi \psi_{n'l'm'}^*(r, \vartheta, \varphi) \psi_{nlm}(r, \vartheta, \varphi) = \delta_{nn'} \delta_{ll'} \delta_{mm'}. \quad (1.129)$$

Finally, we mention for the purpose of illustration the lowest energy eigenfunctions as they follow from (1.69), (1.81), (1.127), and (1.128). The ground-state wave functions reads

$$\psi_{100}(r, \vartheta, \varphi) = \frac{1}{\sqrt{\pi}a_B^{3/2}} \exp\left(-\frac{r}{a_B}\right) \quad (1.130)$$

and has the energy $E_1 = -1 \text{ Ry}$. The principal quantum number $n = 2$ defines the four-fold degenerate first excited state with the energy $E_2 = -\text{Rb}/4$ with the respective energy eigenfunctions

$$\psi_{200}(r, \vartheta, \varphi) = \frac{1}{4\sqrt{2\pi}a_B^{3/2}} \left(2 - \frac{r}{a_B}\right) \exp\left(-\frac{r}{2a_B}\right), \quad (1.131)$$

$$\psi_{210}(r, \vartheta, \varphi) = \frac{1}{4\sqrt{2\pi}a_B^{3/2}} \frac{r}{a_B} \exp\left(-\frac{r}{2a_B}\right) \cos \vartheta, \quad (1.132)$$

$$\psi_{21\pm 1}(r, \vartheta, \varphi) = \frac{\pm 1}{8\sqrt{\pi}a_B^{3/2}} \frac{r}{a_B} \exp\left(-\frac{2r}{2a_B}\right) \sin \vartheta e^{\pm i\varphi}. \quad (1.133)$$

Figure 1.3 shows the plots of the radial probability densities $P_{nl}(r) = r^2 R_{nl}^2(r)$ for the first three principle quantum numbers n . Also here we can read off a node rule, namely the zeros of the radial wave functions $R_{nl}(r)$ correspond to the radial quantum number $n_r = n - l - 1$. This is due to the fact that the radial quantum number n_r appears in the radial contribution to the energy eigenfunction (1.126) as the lower index of the Laguerre polynomial.

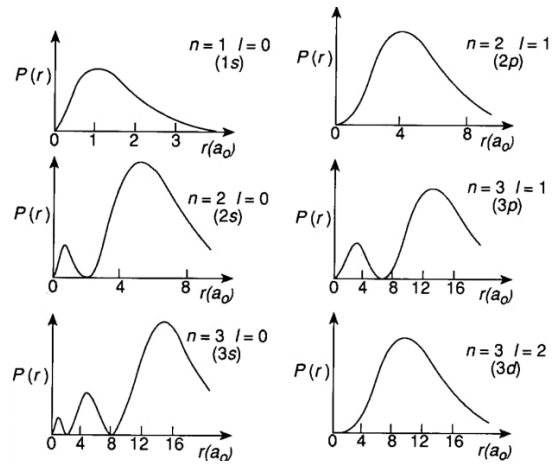


Figure 1.3: Radial probability densities $P_{nl}(r) = r^2 R_{nl}^2(r)$ for the first three principle quantum numbers n .

Chapter 2

Time-Independent Non-Degenerate Perturbation Theory

In quantum mechanics only a quite limited number of systems can be treated exactly. Among them are, for instance, a few one-dimensional problems as, for instance, diverse box problems or the harmonic oscillator. Another class of exactly solvable problems are spherically symmetric problems like the hydrogen atom as, due to symmetry reasons, they can be reduced to effective one-dimensional ones. Therefore, there is a need for approximation methods which allow to study non-exactly solvable problems at least approximately. To this end it is advantageous to provide an introduction to time-independent perturbation theory, which deals with a time-independent Hamiltonian operator \hat{H} decomposing into an unperturbed contribution \hat{H}_0 and a perturbation \hat{V} :

$$\hat{H} = \hat{H}_0 + \hat{V}. \quad (2.1)$$

Depending on whether non-degenerate or degenerate eigenvalues of the underlying unperturbed Hamilton operator \hat{H}_0 are considered, one distinguishes between non-degenerate and degenerate perturbation theory.

2.1 Schrödinger Equation

In the former case one aims at solving the Schrödinger equation

$$\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle \quad (2.2)$$

for the perturbed Hamilton operator (2.1). Here it is assumed that the eigenvalues $E_n^{(0)}$ of the unperturbed Hamilton operator \hat{H}_0 are known together with their eigenstates $|\psi_n^{(0)}\rangle$, i.e. its corresponding eigenvalue problem

$$\hat{H}_0|\psi_n^{(0)}\rangle = E_n^{(0)}|\psi_n^{(0)}\rangle \quad (2.3)$$

is already solved. It is supposed that the eigenvalues $E_n^{(0)}$ are not degenerate as well as that the eigenstates $|\psi_n^{(0)}\rangle$ are orthonormal

$$\langle \psi_n^{(0)} | \psi_m^{(0)} \rangle = \delta_{nm} \quad (2.4)$$

and represent a basis

$$\sum_n |\psi_m^{(0)}\rangle \langle \psi_n^{(0)}| = 1. \quad (2.5)$$

For the following derivation it is useful to consider the family of Hamilton operators

$$\hat{H}(\lambda) = \hat{H}_0 + \lambda \hat{V}, \quad (2.6)$$

as it is then easier to monitor the different perturbative orders. Thus, also the corresponding eigenvalues $E_n(\lambda)$ and eigenstates $|\psi_n(\lambda)\rangle$ are considered to be functions of the parameter λ , which reduce for $\lambda = 0$ and $\lambda = 1$ to the respective unperturbed and perturbed quantities. For technical reasons we consider the family parameter λ to be small, so that it is suggestive to expand both $E_n(\lambda)$ and $|\psi_n(\lambda)\rangle$ in a Taylor series with respect to the parameter λ :

$$E_n(\lambda) = \sum_{\nu=0}^{\infty} E_n^{(\nu)} \lambda^\nu = E_n^{(0)} + E_n^{(1)} \lambda + E_n^{(2)} \lambda^2 + \dots, \quad (2.7)$$

$$|\psi_n(\lambda)\rangle = \sum_{\nu=0}^{\infty} |\psi_n^{(\nu)}\rangle \lambda^\nu = |\psi_n^{(0)}\rangle + |\psi_n^{(1)}\rangle \lambda + |\psi_n^{(2)}\rangle \lambda^2 + \dots. \quad (2.8)$$

Note that the existence of the Taylor series (2.7) and (2.8) is not obvious at all and represents, in fact, a basic assumption of time-independent non-degenerate perturbation theory. For instance, the function $f(x) = e^{-1/x}$ has a vanishing Taylor series but a non-vanishing Laurent series around the expansion point $x_0 = 0$. Although a physicist might have the impression that this as a rather far-fetched mathematical counterexample, this is not the case. For instance, the Bardeen-Cooper-Schrieffer theory yields for the critical temperature of superconductivity the non-perturbative result $T_C \sim e^{-1/N(E_F)g}$, where $N(E_F)$ denotes the electronic density of states at the Fermi edge and g the electron-phonon interaction strength.

Inserting both Taylor series (2.7) and (2.8) into the eigenvalue problem

$$\hat{H}(\lambda)|\psi_n(\lambda)\rangle = E_n(\lambda)|\psi_n(\lambda)\rangle \quad (2.9)$$

of the family of Hamilton operators (2.6) we get

$$\hat{H}_0 \sum_{\nu=0}^{\infty} |\psi_n^{(\nu)}\rangle \lambda^\nu + \hat{V} \sum_{\nu=0}^{\infty} |\psi_n^{(\nu)}\rangle \lambda^{\nu+1} = \sum_{\nu=0}^{\infty} \sum_{\mu=0}^{\infty} E_n^{(\nu)} |\psi_n^{(\mu)}\rangle \lambda^{\nu+\mu}. \quad (2.10)$$

Here we shift the index ν in the second term according to $\nu'(\nu) = \nu + 1$. Furthermore, we change the index ν in the third term via $\nu'(\nu) = \nu + \mu$, see Fig. 2.1, due to the Cauchy product

$$\sum_{\nu=0}^{\infty} \sum_{\mu=0}^{\infty} a_\nu b_\mu = \sum_{\nu'=0}^{\infty} \sum_{\mu=0}^{\nu'} a_{\nu'-\mu} b_\mu. \quad (2.11)$$

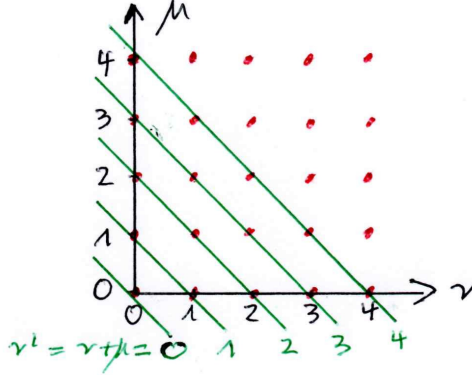


Figure 2.1: Changing the summation indices within the Cauchy product (2.11).

This converts (2.10) to

$$\hat{H}_0 \sum_{\nu=0}^{\infty} |\psi_n^{(\nu)}\rangle \lambda^\nu + \hat{V} \sum_{\nu=1}^{\infty} |\psi_n^{(\nu-1)}\rangle \lambda^\nu = \sum_{\nu=0}^{\infty} \left(\sum_{\mu=0}^{\nu} E_n^{(\nu-\mu)} |\psi_n^{(\mu)}\rangle \right) \lambda^\nu. \quad (2.12)$$

In zeroth order, i.e. $\nu = 0$, Eq. (2.12) reduces to the unperturbed eigenvalue problem (2.3), whereas the higher orders give

$$\hat{H}_0 |\psi_n^{(\nu)}\rangle + \hat{V} |\psi_n^{(\nu-1)}\rangle = \sum_{\mu=0}^{\nu} E_n^{(\nu-\mu)} |\psi_n^{(\mu)}\rangle, \quad \nu = 1, 2, \dots \quad (2.13)$$

In the following we analyze in detail the first two perturbative orders, i.e. $\nu = 1$ and $\nu = 2$, for which we have

$$\hat{H}_0 |\psi_n^{(1)}\rangle + \hat{V} |\psi_n^{(0)}\rangle = E_n^{(1)} |\psi_n^{(0)}\rangle + E_n^{(0)} |\psi_n^{(1)}\rangle, \quad (2.14)$$

$$\hat{H}_0 |\psi_n^{(2)}\rangle + \hat{V} |\psi_n^{(1)}\rangle = E_n^{(2)} |\psi_n^{(0)}\rangle + E_n^{(1)} |\psi_n^{(1)}\rangle + E_n^{(0)} |\psi_n^{(2)}\rangle. \quad (2.15)$$

2.2 Normalization

The task is now to solve both equations (2.14) and (2.15) for $E_n^{(1)}$, $|\psi_n^{(1)}\rangle$ and $E_n^{(2)}$, $|\psi_n^{(2)}\rangle$, respectively. However, a detailed investigation shows that (2.14) and (2.15) stemming from the eigenvalue problem (2.6) are not sufficient to determine the eigenstates $|\psi_n^{(1)}\rangle$, $|\psi_n^{(2)}\rangle$ and, thus, also the eigenenergies $E_n^{(1)}$, $E_n^{(2)}$. In order to solve each perturbative order one additional condition turns out to be needed. This is provided by demanding without loss of generality that also the eigenstates $|\psi_n(\lambda)\rangle$ are orthonormal for each λ :

$$\langle \psi_n(\lambda) | \psi_m(\lambda) \rangle = \delta_{n,m}. \quad (2.16)$$

Inserting the Taylor series (2.8) into (2.16) one gets

$$\sum_{\nu=0}^{\infty} \sum_{\mu=0}^{\infty} \langle \psi_n^{(\nu)} | \psi_m^{(\mu)} \rangle \lambda^{\nu+\mu} = \delta_{n,m}. \quad (2.17)$$

Taking into account again the Cauchy product (2.11) converts (2.17) to

$$\sum_{\nu=0}^{\infty} \left(\sum_{\mu=0}^{\nu} \langle \psi_n^{(\nu-\mu)} | \psi_m^{(\mu)} \rangle \right) \lambda^\nu = \delta_{n,m}. \quad (2.18)$$

In zeroth order, i.e. $\nu = 0$, Eq. (2.18) leads to the orthonormality of the unperturbed eigenstates $|\psi_m^{(0)}\rangle$:

$$\langle \psi_n^{(0)} | \psi_m^{(0)} \rangle = \delta_{n,m}, \quad (2.19)$$

whereas in each higher order $\nu > 0$ one additional condition emerges:

$$\sum_{\mu=0}^{\nu} \langle \psi_n^{(\nu-\mu)} | \psi_m^{(\mu)} \rangle = 0. \quad (2.20)$$

Concretely, they read in the first two perturbative orders, i.e. $\nu = 1$ and $\nu = 2$:

$$\langle \psi_n^{(1)} | \psi_m^{(0)} \rangle + \langle \psi_n^{(0)} | \psi_m^{(1)} \rangle = 0, \quad (2.21)$$

$$\langle \psi_n^{(2)} | \psi_m^{(0)} \rangle + \langle \psi_n^{(1)} | \psi_m^{(1)} \rangle + \langle \psi_n^{(0)} | \psi_m^{(2)} \rangle = 0. \quad (2.22)$$

Now we show that, indeed, (2.14), (2.21) and (2.15), (2.22) allow to determine $E_n^{(1)}$, $|\psi_n^{(1)}\rangle$ and $E_n^{(2)}$, $|\psi_n^{(2)}\rangle$, respectively. To this end we use the fact that the unperturbed eigenstates $|\psi_l^{(0)}\rangle$ are complete, i.e. they represent a basis for the underlying Hilbert space. Consequently each state can be expanded with respect to the basis states $|\psi_l^{(0)}\rangle$. This is valid, for instance, for both perturbative corrections $|\psi_n^{(1)}\rangle$ and $|\psi_n^{(2)}\rangle$:

$$|\psi_n^{(1)}\rangle = \sum_l c_{nl}^{(1)} |\psi_l^{(0)}\rangle, \quad (2.23)$$

$$|\psi_n^{(2)}\rangle = \sum_l c_{nl}^{(2)} |\psi_l^{(0)}\rangle. \quad (2.24)$$

2.3 First Order

Inserting (2.23) into (2.14) yields initially

$$\sum_l c_{nl}^{(1)} \hat{H}_0 |\psi_l^{(0)}\rangle + \hat{V} |\psi_n^{(0)}\rangle = E_n^{(1)} |\psi_n^{(0)}\rangle + \sum_l c_{nl}^{(1)} E_n^{(0)} |\psi_l^{(0)}\rangle. \quad (2.25)$$

Multiplying from the left with $\langle \psi_m^{(0)} |$ as well as taking into account both the eigenvalue problem (2.3) and the orthonormality (2.19) for the unperturbed system reduces (2.25) to

$$E_m^{(0)} c_{nm}^{(1)} + V_{mn} = E_n^{(1)} \delta_{nm} + E_n^{(0)} c_{nm}^{(1)}. \quad (2.26)$$

Here we have introduced as an abbreviation the matrix elements of the perturbation \hat{V} with respect to the unperturbed eigenstates:

$$V_{mn} = \langle \psi_m^{(0)} | \hat{V} | \psi_n^{(0)} \rangle. \quad (2.27)$$

In case that $n = m$ we read off from (2.26) the first-order correction for eigenenergies:

$$E_n^{(1)} = V_{nn}. \quad (2.28)$$

And in case of $n \neq m$ Eq. (2.26) can be solved for the coefficients $c_{nm}^{(1)}$, yielding

$$c_{nm}^{(1)} = \frac{V_{mn}}{E_n^{(0)} - E_m^{(0)}}, \quad n \neq m. \quad (2.29)$$

Thus, analyzing the Schrödinger equation in first order (2.14) does not allow to fix the diagonal coefficient $c_{nn}^{(1)}$. Inserting (2.29) into (2.23) we obtain as an intermediate result

$$|\psi_n^{(1)}\rangle = c_{nn}^{(1)}|\psi_n^{(0)}\rangle + \sum_{m \neq n} \frac{V_{mn}}{E_n^{(0)} - E_m^{(0)}} |\psi_m^{(0)}\rangle, \quad (2.30)$$

which contains the yet unknown coefficient $c_{nn}^{(1)}$. Therefore, it becomes relevant to study also the additional condition (2.21), which followed from the orthonormality (2.16). Inserting (2.23) into (2.21), using the sesquilinearity of the scalar product, i.e.

$$\langle c\psi_1|\psi_2\rangle = c^*\langle\psi_1|\psi_2\rangle, \quad \langle\psi_1|c\psi_2\rangle = c\langle\psi_1|\psi_2\rangle, \quad (2.31)$$

and taking into account (2.19) one gets

$$c_{nn}^{(1)} + (c_{nn}^{(1)})^* = 0. \quad (2.32)$$

Due to (2.29) we observe that (2.32) is fulfilled in case of $n \neq m$ as the hermiticity of the perturbation \hat{V} implies the hermiticity of the matrix element (2.27):

$$V_{mn} = V_{nm}^*. \quad (2.33)$$

But for $n = m$ we conclude from (2.33) that the coefficient $c_{nn}^{(1)}$ must be imaginary:

$$c_{nn}^{(1)} = i\gamma_n^{(1)}, \quad \gamma_n \in \mathbb{R}. \quad (2.34)$$

Due to (2.8), (2.30), and (2.32) the eigenstate reads up to first order in λ :

$$|\psi_n(\lambda)\rangle = (1 + i\gamma_n^{(1)}\lambda) |\psi_n^{(0)}\rangle + \lambda \sum_{m \neq n} \frac{V_{mn}}{E_n^{(0)} - E_m^{(0)}} |\psi_m^{(0)}\rangle + \dots \quad (2.35)$$

Up to first order in λ this can be rearranged to

$$|\psi_n(\lambda)\rangle = e^{i\gamma_n^{(1)}\lambda} \left(|\psi_n^{(0)}\rangle + \lambda \sum_{m \neq n} \frac{V_{mn}}{E_n^{(0)} - E_m^{(0)}} |\psi_m^{(0)}\rangle + \dots \right), \quad (2.36)$$

so that $\gamma_n^{(1)}$ describes a phase factor. As phase factors can be arbitrarily chosen in quantum mechanics, one can set without loss of generality

$$\gamma_n^{(1)} = 0. \quad (2.37)$$

With this the perturbed eigenstate reads up to first order

$$|\psi_n(\lambda)\rangle = |\psi_n^{(0)}\rangle + \lambda \sum_{m \neq n} \frac{V_{mn}}{E_n^{(0)} - E_m^{(0)}} |\psi_m^{(0)}\rangle + \dots \quad (2.38)$$

and we conclude for later purposes from (2.34)

$$c_{nn}^{(1)} = 0. \quad (2.39)$$

Thus, in first order the orthonormality condition was needed to fix the correction of the eigenstate, but it only led to an irrelevant phase factor. This changes now in second order, where the orthonormality condition turns out to contribute to a correction of the eigenstate apart from containing another irrelevant phase factor.

2.4 Second Order

In second order the insertion of (2.23), (2.24) into (2.15) leads to

$$\sum_l c_{nl}^{(2)} \hat{H}_0 |\psi_l^{(0)}\rangle + \sum_l c_{nl}^{(1)} \hat{V} |\psi_l^{(0)}\rangle = E_n^{(2)} |\psi_n^{(0)}\rangle + \sum_l E_n^{(1)} c_{nl}^{(1)} |\psi_l^{(0)}\rangle + \sum_l E_n^{(0)} c_{nl}^{(2)} |\psi_l^{(0)}\rangle. \quad (2.40)$$

Again multiplying from the left with $\langle \psi_m^{(0)} |$, taking into account both the eigenvalue problem (2.3) and the orthonormality (2.19) for the unperturbed system as well as using the matrix element (2.27) leads to

$$E_m^{(0)} c_{nm}^{(2)} + \sum_l V_{ml} c_{nl}^{(1)} = E_n^{(2)} \delta_{nm} + E_n^{(1)} c_{nm}^{(1)} + E_n^{(0)} c_{nm}^{(2)}. \quad (2.41)$$

Evaluating (2.41) for $n = m$ determines the energy correction $E_n^{(2)}$ in the form

$$E_n^{(2)} = \sum_l V_{nl} c_{nl}^{(1)} - E_n^{(1)} c_{nn}^{(1)}. \quad (2.42)$$

Taking into account (2.28), (2.29), (2.33), and (2.39) this reduces to the final expression:

$$E_n^{(2)} = \sum_{l \neq n} \frac{|V_{nl}|^2}{E_n^{(0)} - E_l^{(0)}}, \quad (2.43)$$

Furthermore, in case of $n \neq m$ Eq. (2.41) can be solved for the coefficient $c_{nm}^{(2)}$:

$$c_{nm}^{(2)} = \sum_l \frac{V_{ml}}{E_n^{(0)} - E_m^{(0)}} c_{nl}^{(1)} - \frac{E_n^{(1)}}{E_n^{(0)} - E_m^{(0)}} c_{nm}^{(1)}, \quad n \neq m. \quad (2.44)$$

Inserting therein (2.28), (2.29), and (2.39) one finally gets

$$c_{nm}^{(2)} = \sum_{l \neq n} \frac{V_{ml} V_{ln}}{(E_n^{(0)} - E_m^{(0)}) (E_n^{(0)} - E_l^{(0)})} - \frac{V_{nn} V_{mn}}{(E_n^{(0)} - E_m^{(0)})^2}, \quad n \neq m. \quad (2.45)$$

Thus, also in second-order the diagonal coefficient $c_{nn}^{(2)}$ is not determined from the Schrödinger equation, leading with (2.24) and (2.45) to the following intermediate result for the perturbed eigenstate

$$|\psi_n(\lambda)\rangle = (1 + c_{nn}^{(2)}\lambda^2) |\psi_n^{(0)}\rangle + \sum_{m \neq n} \left\{ \lambda \frac{V_{mn}}{E_n^{(0)} - E_m^{(0)}} \right. \quad (2.46)$$

$$\left. + \lambda^2 \left[\sum_{l \neq n} \frac{V_{ml}V_{ln}}{(E_n^{(0)} - E_m^{(0)})(E_n^{(0)} - E_l^{(0)})} - \frac{V_{nn}V_{mn}}{(E_n^{(0)} - E_m^{(0)})^2} \right] \right\} |\psi_m^{(0)}\rangle + \dots$$

Therefore, also the second order of the orthonormality condition (2.22) has to be considered. Inserting therein (2.24) and using (2.31) one gets

$$c_{nm}^{(2)} + \sum_l \left(c_{nl}^{(1)} \right)^* c_{ml}^{(1)} + (c_{nm}^{(2)})^* = 0. \quad (2.47)$$

In case of $n \neq m$ one obtains together with (2.29), (2.33), and (2.45)

$$\sum_{l \neq n, m} V_{nl}V_{lm} \left[\frac{1}{(E_m^{(0)} - E_n^{(0)})(E_m^{(0)} - E_l^{(0)})} \right. \quad (2.48)$$

$$\left. + \frac{1}{(E_n^{(0)} - E_m^{(0)})(E_n^{(0)} - E_l^{(0)})} + \frac{1}{(E_n^{(0)} - E_l^{(0)})(E_m^{(0)} - E_l^{(0)})} \right] = 0, \quad n \neq m,$$

which is, indeed valid due to the identity

$$\frac{1}{x-y} \frac{1}{x-z} + \frac{1}{y-x} \frac{1}{y-z} + \frac{1}{z-x} \frac{1}{z-y} = 0, \quad x \neq y \neq z \neq x. \quad (2.49)$$

On the other hand, setting $n = m$ in Eq. (2.47) yields due to (2.39)

$$c_{nn}^{(2)} + \sum_{l \neq n} \left(c_{nl}^{(1)} \right)^* c_{nl}^{(1)} + (c_{nn}^{(2)})^* = 0. \quad (2.50)$$

This can be solved for the yet unknown second-order diagonal coefficient $c_{nn}^{(2)}$, yielding together with (2.29)

$$c_{nn}^{(2)} = -\frac{1}{2} \sum_{l \neq n} \frac{|V_{ln}|^2}{(E_n^{(0)} - E_l^{(0)})^2} + i\gamma_n^{(2)}, \quad (2.51)$$

where $i\gamma_n^{(2)}$ denotes a second-order arbitrary imaginary contribution. Inserting the finding (2.51) into the perturbed eigenstate (2.46), we get up to second order in λ

$$|\psi_n(\lambda)\rangle = e^{i\gamma_n^{(2)}\lambda^2} \left(\left[1 - \frac{1}{2} \sum_{l \neq n} \frac{|V_{ln}|^2}{(E_n^{(0)} - E_l^{(0)})^2} \lambda^2 \right] |\psi_n^{(0)}\rangle + \sum_{m \neq n} \left\{ \lambda \frac{V_{mn}}{E_n^{(0)} - E_m^{(0)}} \right. \quad (2.52)$$

$$\left. + \lambda^2 \left[\sum_{l \neq n} \frac{V_{ml}V_{ln}}{(E_n^{(0)} - E_m^{(0)})(E_n^{(0)} - E_l^{(0)})} - \frac{V_{nn}V_{mn}}{(E_n^{(0)} - E_m^{(0)})^2} \right] \right\} |\psi_m^{(0)}\rangle + \dots \right).$$

As in first order we can also argue in second order that the phase factor can be chosen arbitrarily, so we demand without loss of generality

$$\gamma_n^{(2)} = 0. \quad (2.53)$$

2.5 Second-Order Result

Inserting (2.53) into (2.52) and setting $\lambda = 1$ we obtain the following second-order result for the eigenstates:

$$\begin{aligned} |\psi_n\rangle = & \left[1 - \frac{1}{2} \sum_{l \neq n} \frac{|V_{ln}|^2}{(E_n^{(0)} - E_l^{(0)})^2} \right] |\psi_n^{(0)}\rangle \\ & + \sum_{m \neq n} \left[\frac{V_{mn}}{E_n^{(0)} - E_m^{(0)}} + \sum_{l \neq n} \frac{V_{ml}V_{ln}}{(E_n^{(0)} - E_m^{(0)})(E_n^{(0)} - E_l^{(0)})} - \frac{V_{nn}V_{mn}}{(E_n^{(0)} - E_m^{(0)})^2} \right] |\psi_m^{(0)}\rangle + \dots \end{aligned} \quad (2.54)$$

Here the first line reveals that the diagonal corrections are of second order, whereas the off-diagonal corrections in the second line are at least of first order. By construction these eigenstates are orthonormal with respect to each other. Furthermore, the corresponding second-order result for the eigenenergies follows from (2.7), (2.28), and (2.43) as well as setting $\lambda = 1$:

$$E_n = E_n^{(0)} + V_{nn} + \sum_{m \neq n} \frac{|V_{nm}|^2}{E_n^{(0)} - E_m^{(0)}} + \dots \quad (2.55)$$

Note that the second-order term always leads to a decrease of the ground-state energy with quantum number n_0 as $E_{n_0} < E_m^{(0)}$ holds for all quantum numbers $m > n_0$. Finally we discuss the validity range of this perturbative result. To this end we argue a posteriori that such a perturbative result can only be reasonable provided that a correction term in one order is smaller than the previous order, yielding the condition

$$\left| \frac{V_{nm}}{E_n^{(0)} - E_m^{(0)}} \right| \ll 1, \quad n \neq m. \quad (2.56)$$

Provided that this condition is violated, one can not expect convergence of the perturbative series.

2.6 Anharmonic Oscillator

One of the most studied perturbative problems is the anharmonic oscillator. It appears wherever a particle can explore a potential landscape farther away from a local minimum. This occurs, for instance, in solid-state physics provided that the thermal energy allows larger

elongations for the atoms, yielding anharmonic interactions for the phonons. The Hamilton operator of the anharmonic oscillator

$$\hat{H} = \frac{\hat{p}^2}{2M} + \frac{M}{2}\omega^2\hat{x}^2 + g\hat{x}^4 \quad (2.57)$$

is of the form (2.1) and contains as the unperturbed system the harmonic oscillator (1.31), whereas the anharmonicity represents the perturbation

$$\hat{V} = g\hat{x}^4. \quad (2.58)$$

Let us determine the first-order correction to the unperturbed energy eigenvalues (1.54) in the coordinate representation. According to (2.27) and (2.28) this amounts to evaluating the integral

$$E_n^{(1)} = g \int_{-\infty}^{\infty} dx x^4 |\psi_n^{(0)}(x)|^2. \quad (2.59)$$

Inserting therein (1.56) and introducing the dimensionless coordinate $\xi = x/l$ with the oscillator length (1.33) then yields

$$E_n^{(1)} = \frac{g}{\sqrt{\pi}2^n n!} \left(\frac{\hbar}{M\omega} \right)^2 \int_{-\infty}^{\infty} d\xi \xi^4 [H_n(\xi)]^2 e^{-\xi^2}. \quad (2.60)$$

In order to solve the integral a recursion relation of the Hermite polynomials is of use [16, (8.952.2)]

$$\xi H_n(\xi) = \frac{1}{2}H_{n+1}(\xi) + nH_{n-1}(\xi), \quad (2.61)$$

which directly follows from the definition of the Hermite polynomials (1.57). Successively iterating (2.61) yields at first

$$\xi^2 H_n(\xi) = \frac{1}{4}H_{n+2}(\xi) + \left(n + \frac{1}{2} \right) H_n(\xi) + n(n-1)H_{n-2}(\xi), \quad (2.62)$$

$$\xi^3 H_n(\xi) = \frac{1}{8}H_{n+3}(\xi) + \frac{3(n+1)}{4}H_{n+1}(\xi) + \frac{3}{2}n^2 H_{n-1}(\xi) + n(n-1)(n-2)H_{n-3}, \quad (2.63)$$

and then finally

$$\begin{aligned} \xi^4 H_n(\xi) &= \frac{1}{16}H_{n+4}(\xi) + \frac{2n+3}{4}H_{n+2}(\xi) + \frac{3(2n^2+2n+1)}{4}H_n(\xi) \\ &\quad + \frac{2n^3-3n^2+1}{2}H_{n-2}(\xi) + n(n-1)(n-2)(n-3)H_{n-4}(\xi). \end{aligned} \quad (2.64)$$

Multiplying this expression with $H_n(\xi)$ and integrating over the whole real axis, only the term in (2.64) contributes due to the orthonormality relation (1.63) of the energy eigenfunctions (1.56). With this the first-order energy correction of the anharmonic oscillator reads

$$E_n^{(1)} = g \left(\frac{\hbar}{M\omega} \right)^2 \frac{3(2n^2+2n+1)}{4}. \quad (2.65)$$

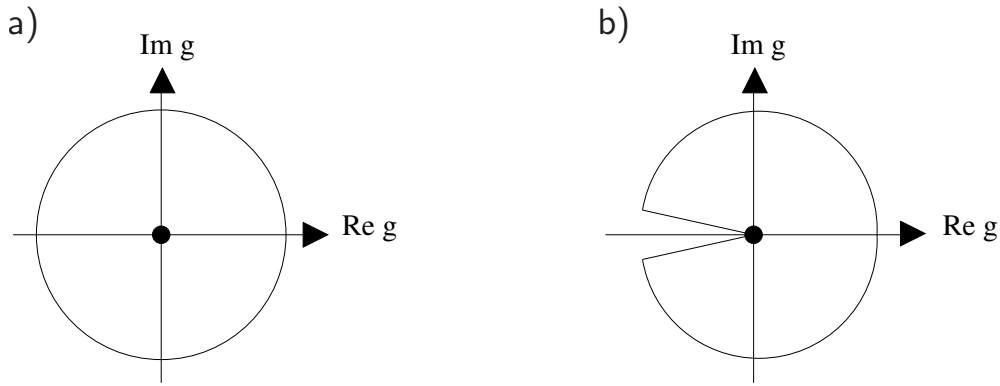


Figure 2.2: Comparing schematically analytic properties of convergent a) and asymptotic b) series.

2.7 General Remarks

Let us finalize this chapter by making some general remarks concerning perturbation theory. Indeed, this is a useful method in order to gain approximate information of real physical systems. Perturbation expansions are based on the fact that quite often a physical quantity f can be exactly calculated for a special value g_0 of a coupling constant g . The whole function $f(g)$ is then determined perturbatively in the deviation $g - g_0$ from this special value g_0 . For the following generic discussion we assume without loss of generality that $g_0 = 0$ and that the respective weak-coupling coefficients f_n are known up to some order N :

$$f_N(g) = \sum_{n=0}^N f_n g^n. \quad (2.66)$$

A prominent example for such a weak-coupling series is the anomalous magnetic moment of the electron g_e , the so-called Landé factor, which is expanded in powers of the Sommerfeld fine-structure constant (1.109). Theoretical calculations have been performed up to the order $N = 3$ [19] and yield a numerical value which coincides within the error bars with the experimental value $g_e = 2.0023193043(74)$ [20]. According to a comparison of Richard Feynman, this precision corresponds to a resolution, where the thickness of a single hair is resolvable by looking from the West to the East Coast of the United States of America or vice versa [21]. It is this impressive agreement which has established quantum electrodynamics as the prototype for relativistic quantum field theories. Furthermore, one should be aware that this theory-experiment agreement for the anomalous magnetic moment of the electron is the most accurate precise one in all natural sciences.

However, already in 1952, Freeman Dyson pointed out that the quality of this agreement depends crucially on the smallness of the Sommerfeld fine-structure constant (1.109) [22]. He discovered that physical quantities in quantum electrodynamics have a vanishing convergence radius with respect to the Sommerfeld fine-structure constant α . Thus an expansion in powers of α can never converge for any positive value of α however small it may be. In fact it turns out that

the expansion of the anomalous magnetic moment of the electron g_e in powers of the Sommerfeld fine-structure constant α is not an example for a convergent but for an asymptotic series, see Figure 2.2. Whereas a convergent series is expanded around a regular point $g_0 = 0$ in the complex g -plane and has a finite convergence radius, an asymptotic series is expanded around a singular point $g_0 = 0$. In the latter case, typically the negative $\text{Re } g$ -axis does not belong to the convergence region. Convergence occurs only in the sector of a circle, so the convergence radius vanishes per definition. For practical purposes, both convergent and asymptotic series have in common that they lead to good approximations as long as they are evaluated for small coupling constants g . The difference between a convergent and an asymptotic series reveals itself, if one investigates their properties for an increase of the order N . For a fixed value of the coupling constant g , an increase in N leads to an improved approximation for a convergent series as its weak-coupling coefficients f_n tend to zero or are bounded in the large-order limit $n \rightarrow \infty$. For an asymptotic series one observes, however, that the approximation is improved for small N but diverges for larger N . The reason for this peculiar behavior is the large-order behavior of the weak-coupling coefficients f_n . They turn out to increase factorially with n in the limit $n \rightarrow \infty$, yielding ultimately the vanishing convergence radius of the weak-coupling series.

At this stage of the general discussion the question arises whether it might not be possible to obtain more reliable results from an asymptotic series by performing a certain resummation, which amounts to a non-perturbative approach. The crudest method to approximate $f(g)$ is via Padé approximants. These are rational functions with the same power series expansions as $f(g)$. The Padé method approximates the left-hand cut of the function $f(g)$ in the complex g -plane by a string of poles. A better approximation can be found by using, in addition, the knowledge of the large-order behavior of the weak-coupling coefficients f_n . This is done by a so-called Borel transformation, which eliminates in combination with the Padé method the factorial growth of the coefficients f_n [23]. And an even more advanced method is provided by variational perturbation theory, which systematically allows to convert weak-coupling into strong-coupling expansions and is applicable to both quantum systems [4] and critical phenomena [24].

It turns out that also the expansion of the ground-state energy of the anharmonic oscillator (2.57) in powers of the anharmonicity strength g is a prime example for an asymptotic series. This particular problem allows to go systematically beyond low-order results due to a recursive solution method for the underlying Schrödinger equation, which was developed implemented efficiently on a computer by Bender and Wu [25]. Furthermore, this recursive method was used to determine the large-order behavior for the weak-coupling coefficients of the ground-state energy and to prove that the perturbative expansion is, indeed, asymptotic [26]. And in Ref. [27] this calculation was even extended to the 250th perturbative order, so that the exponential convergence of the corresponding resummation with the help of variational perturbation theory could be proven [28].

Chapter 3

Time-Independent Degenerate Perturbation Theory

The second-order result of Eqs. (2.54) and (2.55) reveals why it was essential to assume that the unperturbed eigenenergies are non-degenerate. Namely, in case of a degeneracy one of the denominators could vanish, so that the corresponding perturbative result for the energy eigenfunction or the energy eigenvalues diverges. Therefore, the degenerate perturbation theory has to be worked out from the scratch.

3.1 Motivation

To this end we consider again a decomposition of the underlying Hamilton operator according to (2.1) but this time we assume that the unperturbed Hamilton operator \hat{H}_0 has several eigenstates with the same energy eigenvalue $E_n^{(0)}$:

$$\hat{H}_0|\psi_{n\alpha_n}^{(0)}\rangle = E_n^{(0)}|\psi_{n\alpha_n}^{(0)}\rangle. \quad (3.1)$$

Here α_n denotes the degeneracy index. It runs from 1 to d_n , i.e. the d_n eigenstates

$$|\psi_{n1}^{(0)}\rangle, |\psi_{n2}^{(0)}\rangle, \dots, |\psi_{nd_n}^{(0)}\rangle \quad (3.2)$$

belong to the same energy eigenvalue $E_n^{(0)}$. According to the basic laws of quantum mechanics, eigenstates to different eigenenergies are always orthonormal. Furthermore, degenerate eigenstates can always be chosen orthonormal due to the Schmidt orthonormalization procedure [12]. Thus, we have

$$\langle\psi_{n\alpha_n}^{(0)}|\psi_{m\beta_m}^{(0)}\rangle = \delta_{nm}\delta_{\alpha_n\beta_m}. \quad (3.3)$$

Solving the eigenvalue problem of the family of Hamilton operators (2.6)

$$\hat{H}(\lambda)|\tilde{\psi}_{n\alpha_n}(\lambda)\rangle = E_{n\alpha_n}(\lambda)|\tilde{\psi}_{n\alpha_n}(\lambda)\rangle, \quad (3.4)$$

it turns out generically that the degeneracy is lifted completely or at least partially, i.e. also the energy eigenvalues $E_{n\alpha_n}(\lambda)$ turn out to depend from the degeneracy index α_n . Provided that the perturbation is switched off, i.e. one considers the limit $\lambda \rightarrow 0$, the energy eigenvalues $E_{n\alpha_n}(\lambda)$ converge to the unperturbed energy eigenvalues $E_n^{(0)}$, i.e. we have $E_{n\alpha_n}(\lambda) \rightarrow E_n^{(0)}$. Thus, for small λ we expect a series

$$E_{n\alpha_n}(\lambda) = E_n^{(0)} + E_{n\alpha_n}^{(1)} \lambda + \dots, \quad (3.5)$$

which is similar to the perturbation theory without degeneracies. The crucial difference of the perturbation theory with degeneracy is, however, that a corresponding expansion does not exist for the eigenstates:

$$|\tilde{\psi}_{n\alpha_n}(\lambda)\rangle \neq |\psi_{n\alpha_n}^{(0)}\rangle + |\psi_{n\alpha_n}^{(1)}\rangle\lambda + \dots \quad (3.6)$$

This follows already from the fact that one could have chosen for the considered degenerate subspace instead of the basis states (3.2) also any linear combination

$$\sum_{\beta_n=1}^{d_n} c_{n\alpha_n\beta_n}^{(0)} |\psi_{n\beta_n}^{(0)}\rangle. \quad (3.7)$$

In contrast to that the eigenstates $|\tilde{\psi}_{n\alpha_n}(\lambda)\rangle$ of the eigenvalue problem (2.6) are in general fixed provided that the degeneracy is completely lifted. Thus, in the limit $\lambda \rightarrow 0$ one obtains unique zeroth-order eigenstates

$$|\tilde{\psi}_{n\alpha_n}(\lambda \rightarrow 0)\rangle = |\tilde{\psi}_{n\alpha_n}^{(0)}\rangle, \quad (3.8)$$

which generically differ from the original unperturbed eigenstates $|\psi_{n\alpha_n}^{(0)}\rangle$. But as they lie within the considered degenerate subspace spanned the basis states (3.2), they must be represented by a suitable linear combination of the basis states (3.2):

$$|\tilde{\psi}_{n\alpha_n}^{(0)}\rangle = \sum_{\beta_n=1}^{d_n} c_{n\alpha_n\beta_n}^{(0)} |\psi_{n\beta_n}^{(0)}\rangle. \quad (3.9)$$

In the following we will show that the states (3.8) turn out to be eigenstates of the perturbation \hat{V} . Once they are found the eigenstates $|\tilde{\psi}_{n\alpha_n}(\lambda)\rangle$ of the family of Hamilton operators (2.6) can be represented by the Taylor series

$$|\tilde{\psi}_{n\alpha_n}(\lambda)\rangle = |\tilde{\psi}_{n\alpha_n}^{(0)}\rangle + |\tilde{\psi}_{n\alpha_n}^{(1)}\rangle\lambda + \dots \quad (3.10)$$

3.2 Derivation

Inserting the Taylor series for both the energy eigenvalues (3.5) and the eigenstates (3.10) into the eigenvalue problem (2.6) we obtain at first

$$\begin{aligned} & \hat{H}_0 |\tilde{\psi}_{n\alpha_n}^{(0)}\rangle + \lambda \hat{V} |\tilde{\psi}_{n\alpha_n}^{(0)}\rangle + \lambda \hat{H}_0 |\tilde{\psi}_{n\alpha_n}^{(1)}\rangle + \dots \\ & = E_n^{(0)} |\tilde{\psi}_{n\alpha_n}^{(0)}\rangle + \lambda E_{n\alpha_n}^{(1)} |\tilde{\psi}_{n\alpha_n}^{(0)}\rangle + \lambda E_n^{(0)} |\tilde{\psi}_{n\alpha_n}^{(1)}\rangle + \dots \end{aligned} \quad (3.11)$$

As the yet to be determined eigenstates $|\tilde{\psi}_{n\alpha_n}^{(0)}\rangle$ represent a linear combination of the original unperturbed eigenstates $|\psi_{n\alpha_n}^{(0)}\rangle$ according to (3.9), we conclude from (3.1) that the zeroth-order terms on the left- and the right-hand side of Eq. (3.11) cancel each other. What remains in lowest order are the first-order terms in (3.11):

$$\hat{V}|\tilde{\psi}_{n\alpha_n}^{(0)}\rangle + \hat{H}_0|\tilde{\psi}_{n\alpha_n}^{(1)}\rangle = E_{n\alpha_n}^{(1)}|\tilde{\psi}_{n\alpha_n}^{(0)}\rangle + E_n^{(0)}|\tilde{\psi}_{n\alpha_n}^{(1)}\rangle. \quad (3.12)$$

A further simplification arises from multiplying (3.12) from the left with $\langle\psi_{n\gamma_n}^{(0)}|$, yielding

$$\langle\psi_{n\gamma_n}^{(0)}|\hat{V}|\tilde{\psi}_{n\alpha_n}^{(0)}\rangle + \langle\psi_{n\gamma_n}^{(0)}|\hat{H}_0|\tilde{\psi}_{n\alpha_n}^{(1)}\rangle = E_{n\alpha_n}^{(1)}\langle\psi_{n\gamma_n}^{(0)}|\tilde{\psi}_{n\alpha_n}^{(0)}\rangle + E_n^{(0)}\langle\psi_{n\gamma_n}^{(0)}|\tilde{\psi}_{n\alpha_n}^{(1)}\rangle. \quad (3.13)$$

Indeed, taking into account again (3.1) and (3.9) we recognize that the second terms on the left- and the right-hand side of Eq. (3.13) are equal and, thus, can be dropped:

$$\langle\psi_{n\gamma_n}^{(0)}|\hat{V}|\tilde{\psi}_{n\alpha_n}^{(0)}\rangle = E_{n\alpha_n}^{(1)}\langle\psi_{n\gamma_n}^{(0)}|\tilde{\psi}_{n\alpha_n}^{(0)}\rangle. \quad (3.14)$$

This equation allows to determine both the eigenstates $|\tilde{\psi}_{n\alpha_n}^{(0)}\rangle$ and the energy corrections $E_{n\alpha_n}^{(1)}$. To this end we insert the linear combination (3.9) and take into account the definition of the matrix elements (2.27). Furthermore, in order to simplify the notation we drop the quantum number n , which characterizes the degenerate subspace under investigation, and obtain

$$\sum_{\beta=1}^d c_{\alpha\beta}^{(0)} (V_{\gamma\beta} - E_{\alpha}^{(1)}\delta_{\gamma\beta}) = 0. \quad (3.15)$$

Thus, considering α to be fixed, we have d linear equations for the d coefficients $c_{\alpha\beta}$, as γ runs from 1 to d . This linear system of equations reads explicitly

$$\begin{pmatrix} V_{11} - E_{\alpha}^{(1)} & V_{12} & \dots & V_{1d} \\ V_{21} & V_{22} - E_{\alpha}^{(1)} & \dots & V_{2d} \\ \vdots & \vdots & \vdots & \vdots \\ V_{d1} & V_{d2} & \vdots & V_{dd} - E_{\alpha}^{(1)} \end{pmatrix} \begin{pmatrix} c_{\alpha 1}^{(0)} \\ c_{\alpha 2}^{(0)} \\ \vdots \\ c_{\alpha d}^{(0)} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \vdots \\ 0 \end{pmatrix}. \quad (3.16)$$

It determines d linear independent eigenvectors

$$c_{1\beta}^{(0)}, c_{2\beta}^{(0)}, \dots, c_{d\beta}^{(0)} \quad (3.17)$$

and d eigenvalues

$$E_1^{(1)}, E_2^{(1)}, \dots, E_d^{(1)}. \quad (3.18)$$

Non-vanishing eigenvectors (3.17) follow from (3.16) only provided that the following condition is fulfilled

$$\text{Det} (V_{\gamma\beta} - E_{\alpha}^{(1)}\delta_{\gamma\beta}) = 0. \quad (3.19)$$

This so-called secular equation reads in detail

$$\begin{vmatrix} V_{11} - E_\alpha^{(1)} & V_{12} & \dots & V_{1d} \\ V_{21} & V_{22} - E_\alpha^{(1)} & \dots & V_{2d} \\ \vdots & \vdots & \vdots & \vdots \\ V_{d1} & V_{d2} & \vdots & V_{dd} - E_\alpha^{(1)} \end{vmatrix} = 0, \quad (3.20)$$

which represents a polynomial of degree d in the energy correction $E_\alpha^{(1)}$. Thus, the energy eigenvalues (3.18) are the eigenvalues of the matrix $V_{\gamma\beta}$. In case that some roots (3.18) of (3.20) coincide, the degeneracy is only partially lifted. Inserting the energy corrections (3.18) one by one into Eqs. (3.16), one obtains linear homogeneous systems of equations determining the corresponding eigenvectors (3.17). Due to the hermiticity (2.33) of the matrix $V_{\gamma\beta}$ eigenvectors (3.17) to different energy eigenvalues (3.18) are orthogonal:

$$\sum_{\gamma=1}^d (c_{\alpha\gamma}^{(0)})^* c_{\alpha'\gamma}^{(0)} = 0, \quad E_\alpha^{(1)} \neq E_{\alpha'}^{(1)}. \quad (3.21)$$

Provided that some energy eigenvalues (3.18) coincide, the corresponding eigenvectors (3.17) can be chosen to be orthogonal without loss of generality. Together with a proper normalization we, thus, conclude that the eigenvectors (3.17) can be assumed to be orthonormal:

$$\sum_{\gamma=1}^d (c_{\alpha\gamma}^{(0)})^* c_{\alpha'\gamma}^{(0)} = \delta_{\alpha\alpha'}. \quad (3.22)$$

From this and the orthonormality (3.3) of the original basis follows then directly that also the adapted eigenstates (3.9) turn out to be orthonormal:

$$\langle \tilde{\psi}_{n\alpha_n}^{(0)} | \tilde{\psi}_{m\beta_m}^{(0)} \rangle = \delta_{nm} \delta_{\alpha_n\beta_m}. \quad (3.23)$$

In case that we would have started originally with the adapted eigenvectors $|\tilde{\psi}_{m\beta_n}^{(0)}\rangle$ instead of the original eigenvectors $|\psi_{m\beta_n}^{(0)}\rangle$, then the matrix $V_{\gamma\beta}$ would be diagonal and the determination of its eigenvalues would be trivial. Note that the special case of a double degeneracy is treated in Ref. [1, Chap. 69].

Here we will not discuss in detail higher orders of the degenerate perturbation theory. Is the degeneracy completely lifted, then higher perturbative orders follow along quite similar lines as in non-degenerate perturbation theory. However, in case that the degeneracy will be lifted completely only in some higher perturbative order, the calculations turn out to be more involved.

3.3 Stark Effect of Hydrogen Atom

In this section we assume that the hydrogen atom as the unperturbed quantum system is treated non-relativistically as discussed in Section 1.4. According to Eq. (1.105), the energy

eigenvalues then only depend on the principal quantum number n , so they are degenerate with respect to the angular quantum number l and the magnetic quantum number m . Note that relativistic corrections, which would lead to a partial lifting of that degeneracy in form of a fine-structure splitting, are not considered. Their discussion is relegated to a later stage of the lecture.

A paradigmatic example for degenerate perturbation theory is provided by the Stark effect of the hydrogen atom. Thus, we investigate how the energy eigenvalues of the hydrogen atom (1.105) are perturbatively affected by an electric field $\mathbf{E}(\mathbf{x}) = \mathcal{E}\mathbf{e}_z$, which is spatiotemporally constant and points without loss of generality in z -direction. Due to the fact that the electric field $\mathbf{E}(\mathbf{x})$ is related in electrostatics to the scalar potential $\Phi(\mathbf{x})$ via

$$\mathbf{E}(\mathbf{x}) = -\nabla\Phi(\mathbf{x}), \quad (3.24)$$

the latter is given by

$$\Phi(\mathbf{x}) = -\mathcal{E}z. \quad (3.25)$$

The corresponding potential energy $V(\mathbf{x}) = q\Phi(\mathbf{x})$ reduces then due to the charge $q = -e$ of the electron to

$$V(\mathbf{x}) = e\mathcal{E}z. \quad (3.26)$$

Thus, the potential energy (3.26) represents a correction of the hydrogen Hamiltonian operator (1.65). An estimate for the atomic electric field strength is provided by

$$\mathcal{E}_{\text{atom}} = \frac{e}{4\pi\epsilon_0 a_{\text{B}}^2} \quad (3.27)$$

and turns out to be of the order $\mathcal{E}_{\text{atom}} = 5.8 \times 10^{11} \text{ V/m}$. As this is large in comparison with experimentally realizable electric field strengths, the correction (3.26) can really be treated as a perturbation.

As a preparation for the following perturbative calculations we need to know which matrix elements

$$z_{fi} = \int d^3x \psi_{n_f l_f m_f}^*(\mathbf{x}) z \psi_{n_i l_i m_i}(\mathbf{x}) \quad (3.28)$$

vanish or do not vanish. This kind of information is called selection rules. Here the wave function $\psi_{nlm}(\mathbf{x})$ of the electron in the hydrogen atom with the main quantum number n , the angular quantum number l , and the magnetic quantum number m as introduced in Section 1.4. In Appendix C we prove that the matrix elements (3.28) are different from zero only provided that the selection rules

$$\Delta l = l_f - l_i = \pm 1, \quad \Delta m = m_f - m_i = 0 \quad (3.29)$$

are fulfilled. As we will see below, these selection rules have the consequence that the leading correction for the energy eigenvalues due to the perturbation (3.26) depends linearly (quadratically) on the electric field strength for the first excited state (ground state) of the hydrogen atom. This effect is named after the German physicist Johannes Stark, who discovered it in 1913 and for which he was awarded with the Nobel Prize in Physics in the year 1919.

3.3.1 Linear Stark Effect

At first we deal with the first excited state, i.e. $n = 2$, which has according to (1.117) a fourfold degeneracy. Thus, we aim at determining the corresponding energy splitting $E_\alpha^{(1)}$ for these degenerate states with the quantum numbers $\alpha \in \{(2, 0, 0), (2, 1, 0), (2, 1, \pm 1)\}$. According to degenerate perturbation theory as well as Eqs. (2.27) and (3.15) this amounts to determine the involved matrix elements

$$V_{\alpha\beta} = \int d^3x \psi_\alpha^*(\mathbf{x}) e\mathcal{E}z \psi_\beta(\mathbf{x}) \quad (3.30)$$

for all four energy eigenfunctions (1.131)–(1.133). In view of a systematic evaluation of these $4 \times 4 = 16$ matrix elements we sort the energy eigenfunctions in the following order:

$$\psi_1(\mathbf{x}) = \psi_{200}(\mathbf{x}), \quad \psi_2(\mathbf{x}) = \psi_{210}(\mathbf{x}), \quad \psi_3(\mathbf{x}) = \psi_{211}(\mathbf{x}), \quad \psi_4(\mathbf{x}) = \psi_{21-1}(\mathbf{x}). \quad (3.31)$$

Thus, the matrix elements are of the form

$$(V_{\alpha\beta}) = \begin{pmatrix} V_{200,200} & V_{200,210} & V_{200,211} & V_{200,21-1} \\ V_{210,200} & V_{210,210} & V_{210,211} & V_{210,21-1} \\ V_{211,200} & V_{211,210} & V_{211,211} & V_{211,21-1} \\ V_{21-1,200} & V_{21-1,210} & V_{21-1,211} & V_{21-1,21-1} \end{pmatrix}. \quad (3.32)$$

Here we can conclude from the selection rules (3.29) that the majority of matrix elements vanishes

$$(V_{\alpha\beta}) = \begin{pmatrix} 0 & V_{200,210} & 0 & 0 \\ V_{210,200} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \quad (3.33)$$

and that the only non-vanishing matrix elements is given by

$$V = V_{200,210} = V_{210,200} = e\mathcal{E} \int d^3x \psi_{200}(\mathbf{x})\psi_{210}(\mathbf{x})z. \quad (3.34)$$

Taking into account (1.69) and (1.81) this reduces to

$$V = \frac{\sqrt{3}e\mathcal{E}}{4\pi} \int d^3x \frac{R_{20}(r)R_{21}(r)}{r} z^2. \quad (3.35)$$

Applying again symmetry reasons we conclude

$$\int d^3x f(r)z^2 = \frac{1}{3} \int d^3x f(r) (x^2 + y^2 + z^2) = \frac{1}{3} \int d^3x f(r)r^2 = \frac{4\pi}{3} \int_0^\infty dr f(r)r^4, \quad (3.36)$$

so that the matrix element (3.35) leads to

$$V = \frac{e\mathcal{E}}{\sqrt{3}} \int_0^\infty dr R_{20}(r)R_{21}(r)r^3. \quad (3.37)$$

Inserting therein the radial energy eigenfunctions (1.128) we get

$$V = \frac{e\mathcal{E}a_B}{24} \int_0^\infty d\rho (2\rho^4 - \rho^5)e^{-\rho}. \quad (3.38)$$

The remaining two integrals are of the form

$$\int_0^\infty d\rho \rho^k e^{-\rho} = k!, \quad (3.39)$$

so the final result for the non-vanishing matrix element reads

$$V = -3e\mathcal{E}a_B. \quad (3.40)$$

With this the secular equation (3.20) for the considered Stark effect is given by

$$\begin{vmatrix} -E^{(1)} & -3e\mathcal{E}a_B & 0 & 0 \\ -3e\mathcal{E}a_B & -E^{(1)} & 0 & 0 \\ 0 & 0 & -E^{(1)} & 0 \\ 0 & 0 & 0 & -E^{(1)} \end{vmatrix} = (E^{(1)})^2 \left[(E^{(1)})^2 - (3e\mathcal{E}a_B) \right] = 0. \quad (3.41)$$

The corresponding solutions result in

$$E_1^{(1)} = -3e\mathcal{E}a_B < 0, \quad E_2^{(1)} = E_3^{(1)} = 0, \quad E_4^{(1)} = 3e\mathcal{E}a_B > 0. \quad (3.42)$$

where we have taken into account $e > 0$. Determining the corresponding eigenvectors of the 4×4 matrix we obtain the result that the fourfold degenerate energy level $n = 2$ splits into three terms:

$$E_1 = E_2^{(0)} + 3e\mathcal{E}a_B, \quad \tilde{\psi}_1^{(0)}(\mathbf{x}) = \frac{1}{\sqrt{2}} \left[\psi_{200}^{(0)}(\mathbf{x}) - \psi_{210}^{(0)}(\mathbf{x}) \right], \quad (3.43)$$

$$E_2 = E_2^{(0)}, \quad \tilde{\psi}_2^{(0)}(\mathbf{x}) = \psi_{211}^{(0)}(\mathbf{x}), \quad (3.44)$$

$$E_3 = E_2^{(0)}, \quad \tilde{\psi}_3^{(0)}(\mathbf{x}) = \psi_{21-1}^{(0)}(\mathbf{x}), \quad (3.45)$$

$$E_4 = E_2^{(0)} - 3e\mathcal{E}a_B, \quad \tilde{\psi}_4^{(0)}(\mathbf{x}) = \frac{1}{\sqrt{2}} \left[\psi_{200}^{(0)}(\mathbf{x}) + \psi_{210}^{(0)}(\mathbf{x}) \right]. \quad (3.46)$$

Thus, the energy levels $m = \pm 1$ are not shifted as the corresponding energy eigenfunctions $\psi_{21\pm 1}(\mathbf{x})$ are mirror symmetric with respect to the plane $z = 0$, as can be read off from (1.133) and is illustrated in Fig. 1.2. And the new eigenfunctions in (3.43) and (3.46) follow from (1.131) and (1.132):

$$\tilde{\psi}_{1,4}(\mathbf{x}) = \frac{1}{8\sqrt{\pi}a_B^{3/2}} \left(2 - \frac{r}{a_B} \mp \frac{z}{\sqrt{3}a_B} \right) \exp\left(-\frac{r}{2a_B}\right). \quad (3.47)$$

They reveal that $\tilde{\psi}_1(\mathbf{x})$ ($\tilde{\psi}_4(\mathbf{x})$) amounts to an electron distribution, which is shifted in positive (negative) z -direction, yielding an energy increase (decrease), respectively, in accordance with the potential energy (3.26). This partial lifting of the degeneracy for the first excited state of the hydrogen atom is schematically illustrated in Fig. 3.1.

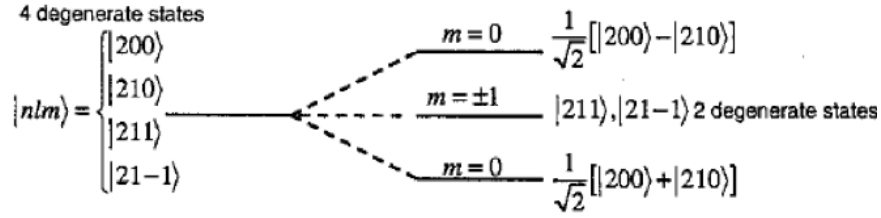


Figure 3.1: Partial lift of the degeneracy for the first excited state of the hydrogen atom in a homogeneous electric field.

3.3.2 Quadratic Stark Effect

Let us consider now also the ground state of the hydrogen atom, which is the only non-degenerate energy level. Thus, its shift due to the presence of the electric field can be treated within non-degenerate perturbation theory. In first order the energy correction reads according to (2.27) and (2.28):

$$E_1^{(1)} = \int d^3x \psi_{100}^*(\mathbf{x}) V(\mathbf{x}) \psi_{100}(\mathbf{x}). \quad (3.48)$$

Inserting therein the ground-state wave function (1.130) and the potential energy (3.26), we recognize that the integral (3.48) vanishes due to symmetry reasons:

$$E_1^{(1)} = 0. \quad (3.49)$$

Indeed, this result also follows immediately from the selection rules (3.29). Thus, the ground-state energy is not shifted linearly with the electric field. Instead the leading contribution for the ground state turns out to be quadratic in the electric field, which is therefore called the quadratic Stark effect. Note that this quadratic Stark effect shifts the ground-state energy to smaller values according to the general remark below Eq. (2.55). In order to determine this negative shift one would naively expect to have to evaluate the series

$$E_1^{(2)} = \sum_{n=2}^{\infty} \sum_{l=0}^{n-1} \sum_{m=-l}^l \frac{|V_{100,nlm}|^2}{E_1^{(0)} - E_n^{(0)}}, \quad (3.50)$$

which reduces due to the selection rules (3.29) to

$$E_1^{(2)} = \sum_{n=2}^{\infty} \frac{|V_{100,n10}|^2}{E_1^{(0)} - E_n^{(0)}}. \quad (3.51)$$

However, this naive expectation is physically wrong. Namely, apart from the discrete spectrum, which gives rise to the sum in (3.51), one also has to consider the continuum states of the hydrogen atom, which correspond to scattering states and will be discussed later, see Fig. 3.2. Therefore, an additional integral over the continuum states has to be added. In such a case of an unperturbed quantum system having both discrete and continuous eigenstates the second-order

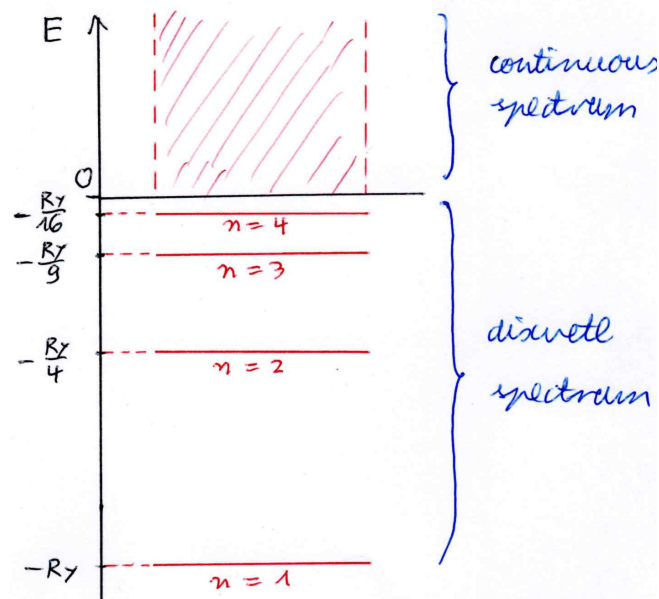


Figure 3.2: The hydrogen spectrum consists of both a discrete and a continuous part.

correction (2.43) of non-degenerate perturbation theory should read more precisely

$$E_n^{(2)} = \sum_{m \neq n}^f \frac{|V_{nm}|^2}{E_n^{(0)} - E_m^{(0)}}. \quad (3.52)$$

Here we have used a modified notation, which emphasizes that a summation (integration) has to be performed over all discrete (continuous) quantum numbers [3]. Therefore, directly evaluating such a second-order perturbative result for the hydrogen atom is extremely complicated.

However, intriguingly, it is possible to circumvent the direct evaluation of (3.52) with the help of a sum rule, which is derived in Appendix D. It amounts to the result that (3.52) coincides with

$$E_n^{(2)} = \frac{2M}{\hbar^2} [(VW)_{nn} - V_{nn}W_{nn}], \quad (3.53)$$

which only involves diagonal matrix elements with respect to the state with the quantum number n , for which the second-order perturbation has to be determined. In coordinate representation $V(\mathbf{x})$ denotes the perturbation of the Hamilton operator and $W(\mathbf{x})$ represents one solution of the differential equation

$$\Delta W(\mathbf{x})\psi_n^{(0)}(\mathbf{x}) + 2\nabla W(\mathbf{x}) \cdot \nabla \psi_n^{(0)}(\mathbf{x}) = V(\mathbf{x})\psi_n^{(0)}(\mathbf{x}). \quad (3.54)$$

In view of the quadratic Stark effect for the ground state of the hydrogen atom, the differential equation (3.54) has to be specialized for the spherically symmetric ground-state wave function (1.130) and the cylinder-symmetric perturbation (3.26). Thus, due to symmetry reasons, we expect that also the solution of (3.54) is cylinder-symmetric, which justifies in spherical coordinates the ansatz

$$W(r, \vartheta, \varphi) = \sum_{l=0}^{\infty} W_l(r) P_l(\cos \vartheta) \quad (3.55)$$

with the Legendre polynomials $P_l(x)$. Thus, also the Laplace and the nabla operator should be used in spherical coordinates:

$$\Delta = \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \left(\frac{\partial^2}{\partial \vartheta^2} + \frac{\cos \vartheta}{\sin \vartheta} \frac{\partial}{\partial \vartheta} + \frac{1}{\sin^2 \vartheta} \frac{\partial^2}{\partial \varphi^2} \right), \quad (3.56)$$

$$\nabla = \frac{\partial}{\partial r} \mathbf{e}_r + \frac{1}{r} \frac{\partial}{\partial \vartheta} \mathbf{e}_\vartheta + \frac{1}{r \sin \vartheta} \frac{\partial}{\partial \varphi} \mathbf{e}_\varphi. \quad (3.57)$$

Taking into account the differential equation for the Legendre polynomials (1.77) and the property of the ground-state wave function (1.130)

$$\frac{\partial \psi_{100}^{(0)}(r, \vartheta, \varphi)}{\partial r} = -\frac{1}{a_B} \psi_{100}^{(0)}(r, \vartheta, \varphi), \quad (3.58)$$

the insertion of (3.55)–(3.57) into the differential equation (3.54) yields due to $P_1(x) = x$, compare with Eq. (1.80):

$$W_l''(r) + 2 \left(\frac{1}{r} - \frac{1}{a_B} \right) W_l'(r) - \frac{l(l+1)}{r^2} W_l(r) = eEr \delta_{l,1}. \quad (3.59)$$

These inhomogeneous differential equations are solved, for instance, by

$$W_l(r) = -\frac{1}{4} e\mathcal{E} a_B (r + 2a_B) r \delta_{l,1}, \quad (3.60)$$

so that we obtain from (3.55) and (3.60) the result

$$W(r, \vartheta, \varphi) = -\frac{1}{4} e\mathcal{E} a_B (r + 2a_B) r \cos \vartheta. \quad (3.61)$$

Using (1.130), (3.26), (3.61) and $z = r \cos \vartheta$ we read off from the selection rules (3.29) that both matrix elements in the second term of the sum rule (3.53) vanish for the ground state of the hydrogen atom:

$$V_{100,100} = e\mathcal{E} \int d^3x z \left| \psi_{100}^{(0)}(r) \right|^2 = 0, \quad (3.62)$$

$$W_{100,100} = -\frac{1}{4} e\mathcal{E} a_B \int d^3x (r + 2a_B) z \left| \psi_{100}^{(0)}(r) \right|^2 = 0. \quad (3.63)$$

In contrast to that the matrix element in the first term of the sum rule (3.53) reads

$$(VW)_{100,100} = -\frac{1}{4} e^2 \mathcal{E}^2 a_B \int d^3x (r + 2a_B) z^2 \left| \psi_{100}^{(0)}(r) \right|^2, \quad (3.64)$$

which reduces due to the symmetry result (3.36) to

$$(VW)_{100,100} = -\frac{1}{12} e^2 \mathcal{E}^2 a_B \int d^3x (r + 2a_B) r^2 \left| \psi_{100}^{(0)}(r) \right|^2, \quad (3.65)$$

Thus, together with (1.130) it remains to solve the radial integral

$$(VW)_{100,100} = -\frac{e^2 \mathcal{E}^2}{3a_B} \int d^3x \left(\frac{r}{a_B} + 2 \right) r^2 e^{-2r/a_B}, \quad (3.66)$$

yielding, ultimately, due to (3.39) from the sum rule (3.53) the second-order correction of the ground-state energy in the presence of a homogeneous electric field:

$$E_1^{(2)} = -\frac{9Me^2}{4\hbar^2} \mathcal{E}^2 a_B^4. \quad (3.67)$$

We can further interpret this result physically as follows. In the absence of the electric field both the wave function and the probability density of the electron in the ground state of the hydrogen atom are spherical symmetric. Therefore, negative and positive center of charge coincide and the resulting electric dipole moment vanishes. In an external electric field \mathbf{E} , however, the center of charges are separated, which leads to an induced electric dipole moment $\mathbf{p} \sim \mathbf{E}$ in the direction of the electric field. The proportionality coefficient defines the electric polarizability α_P :

$$\mathbf{p} = \varepsilon_0 \alpha_P \mathbf{E}. \quad (3.68)$$

The energy of the induced electric dipole in an external electric field follows from

$$E = - \int_0^{\mathbf{E}} \mathbf{p} \cdot d\mathbf{E}, \quad (3.69)$$

yielding

$$E = -\frac{1}{2} \alpha_P \varepsilon_0 \mathbf{E}^2. \quad (3.70)$$

Note that a permanent electric dipole moment would have instead the energy $E = -\mathbf{p} \cdot \mathbf{E}$. Equating (3.67) and (3.70) as well as taking into account the Bohr radius (1.112) yields for the polarizability of the hydrogen atom in its ground state

$$\alpha_P = 18\pi a_B^3 \quad (\text{SI units}). \quad (3.71)$$

This result in SI units is converted in a corresponding result in cgs units by applying the formal substitution rule $\varepsilon_0 \rightarrow 1/(4\pi)$. Thus, due to factor ε in the definition of the atomic polarizability (3.68) we then get

$$\alpha_P = \frac{9}{2} a_B^3 \quad (\text{cgs units}) \quad (3.72)$$

in accordance with [10, 11, 12].

Chapter 4

Brillouin-Wigner Perturbation Theory

So far we have worked out separately the time-independent perturbation theory for non-degenerate and degenerate quantum systems. In this chapter we show that both perturbative approaches of the previous two chapters can formally be united into a single formalism. This framework is the Brillouin-Wigner perturbation theory [32], which we work out by following the concise summary provided in Appendix A of Ref. [33]. As a side result it turns out to be straight-forward to extend non-degenerate perturbation theory to higher orders as we demonstrate exemplarily for the fourth order.

4.1 General Formalism

The main idea underlying the Brillouin-Wigner perturbation theory is to derive an effective Hamilton operator for an arbitrarily chosen Hilbert subspace, which is characterized by a projection operator \hat{P} . This is accomplished by formally eliminating the complementary Hilbert subspace with the help of also introducing a complementary projection operator

$$\hat{Q} = 1 - \hat{P}. \quad (4.1)$$

As any projection operator also \hat{P} has to fulfill the idempotent property

$$\hat{P}^2 = \hat{P}. \quad (4.2)$$

From this we conclude that also (4.2) obeys the idempotent property

$$\hat{Q}^2 = \hat{Q} \quad (4.3)$$

and that \hat{P} and \hat{Q} project into disjunct subspaces $\hat{P}\mathcal{H}$ and $\hat{Q}\mathcal{H}$ of the Hilbert space \mathcal{H} , see Fig. 4.1:

$$\hat{Q}\hat{P} = 0 = \hat{P}\hat{Q}. \quad (4.4)$$

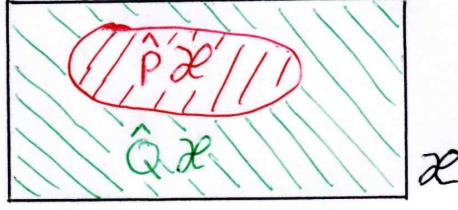


Figure 4.1: The projection operators \hat{P} and \hat{Q} decompose the Hilbert space \mathcal{H} of a quantum system into into disjunct subspaces $\hat{P}\mathcal{H}$ and $\hat{Q}\mathcal{H}$.

Since we have now two projection operators \hat{P} and \hat{Q} , we need two conditions to define the respective Hilbert subspaces. So, we start by reformulating the full time-independent Schrödinger equation

$$\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle. \quad (4.5)$$

with the help of the projection operators. To this end we insert the unity operator according to (4.1) and get

$$\hat{H}\hat{P}|\psi_n\rangle + \hat{H}\hat{Q}|\psi_n\rangle = E_n\hat{P}|\psi_n\rangle + E_n\hat{Q}|\psi_n\rangle. \quad (4.6)$$

Multiplying by \hat{P} the left side of (4.6) and considering the projector operator relations (4.2) and (4.4) results in

$$\hat{P}\hat{H}\hat{P}|\psi_n\rangle + \hat{P}\hat{H}\hat{Q}|\psi_n\rangle = E_n\hat{P}|\psi_n\rangle. \quad (4.7)$$

Conversely, multiplying by \hat{Q} the left side of (4.6) and using correspondingly (4.3) and (4.4), we also have

$$\hat{Q}\hat{H}\hat{P}|\psi_n\rangle + \hat{Q}\hat{H}\hat{Q}|\psi_n\rangle = E_n\hat{Q}|\psi_n\rangle. \quad (4.8)$$

The next step is to try to find a single equation for $\hat{P}|\psi_n\rangle$ in a shape similar to a time-independent Schrödinger equation. In order to eliminate $\hat{Q}|\psi_n\rangle$ from (4.7) we use (4.8) and take into account again (4.3)

$$\hat{Q}\hat{H}\hat{P}|\psi_n\rangle + \hat{Q}\hat{H}\hat{Q}^2|\psi_n\rangle = E_n\hat{Q}|\psi_n\rangle. \quad (4.9)$$

From rearranging and factorizing out follows straight-forwardly

$$\hat{Q}\hat{H}\hat{P}|\psi_n\rangle = \left(E_n - \hat{Q}\hat{H}\hat{Q}\right)\hat{Q}|\psi_n\rangle. \quad (4.10)$$

Thus, a formal solution with respect to $\hat{Q}|\psi_n\rangle$ yields

$$\hat{Q}|\psi_n\rangle = \left(E_n - \hat{Q}\hat{H}\hat{Q}\right)^{-1}\hat{Q}\hat{H}\hat{P}|\psi_n\rangle. \quad (4.11)$$

A further action of \hat{Q} results due to (4.3) in

$$\hat{Q}|\psi_n\rangle = \hat{Q}\left(E_n - \hat{Q}\hat{H}\hat{Q}\right)^{-1}\hat{Q}\hat{H}\hat{P}|\psi_n\rangle. \quad (4.12)$$

Inserting (4.12) in (4.7) we get a single equation for $\hat{P}|\psi_n\rangle$:

$$\left[\hat{P}\hat{H}\hat{P} + \hat{P}\hat{H}\hat{Q} \left(E_n - \hat{Q}\hat{H}\hat{Q} \right)^{-1} \hat{Q}\hat{H}\hat{P} \right] |\psi_n\rangle = E_n \hat{P}|\psi_n\rangle. \quad (4.13)$$

Splitting the Hamilton operator \hat{H} into an unperturbed and a perturbed contribution \hat{H}_0 and $\lambda\hat{V}$, respectively, i.e.

$$\hat{H} = \hat{H}_0 + \lambda\hat{V} \quad (4.14)$$

allows one to rewrite (4.13) according to

$$\hat{P}\hat{H}\hat{P} + \hat{P} \left(\hat{H}_0 + \lambda\hat{V} \right) \hat{Q} \left(E_n - \hat{Q}\hat{H}\hat{Q} \right)^{-1} \hat{Q} \left(\hat{H}_0 + \lambda\hat{V} \right) \hat{P}|\psi_n\rangle = E_n \hat{P}|\psi_n\rangle. \quad (4.15)$$

4.2 Specialization

So far we considered the projection operator \hat{P} to be independent from the unperturbed Hamilton operator \hat{H}_0 . Now we assume in addition that the projection operator \hat{P} and the unperturbed Hamilton operator \hat{H}_0 commute:

$$\left[\hat{P}, \hat{H}_0 \right]_- = 0. \quad (4.16)$$

This means physically that applying \hat{H}_0 to a state within the subspace characterized by \hat{P} does not yield a state outside of that subspace. Furthermore, this has the consequence that there are states, which are eigenstates of both the projection operator \hat{P} and the unperturbed Hamilton operator \hat{H}_0 . This justifies to assume that a projection operator \hat{P} with the property (4.16) is of the form

$$\hat{P} = \sum_{k \in N} |\psi_n^0\rangle \langle \psi_n^0| \quad (4.17)$$

with $|\psi_n^0\rangle$ solving the unperturbed eigenvalue problem

$$\hat{H}_0|\psi_n^0\rangle = E_n^{(0)}|\psi_n^0\rangle \quad (4.18)$$

and N representing some set of quantum numbers n . Indeed, it turns out that (4.17) fulfills the idempotent property (4.2) as the projection operator for some unperturbed energy state

$$\hat{P}_n = |\psi_n^0\rangle \langle \psi_n^0| \quad (4.19)$$

obeys the identity

$$\hat{P}_n \hat{P}_{n'} = \delta_{nn'} \hat{P}_n \quad (4.20)$$

due to the orthonormality of the unperturbed eigenstates

$$\langle \psi_n^{(0)} | \psi_m^{(0)} \rangle = \delta_{n,m}. \quad (4.21)$$

Furthermore, we obtain for the complementary projection operator (4.1) the representation

$$\hat{Q} = \sum_{k \in \bar{N}} |\psi_k^0\rangle \langle \psi_k^0| \quad (4.22)$$

with \bar{N} denoting the complement of N .

After this specialization we conclude from (4.16) by taking into account (4.4)

$$\hat{Q}\hat{H}_0\hat{P} = \hat{P}\hat{H}_0\hat{Q} = 0, \quad (4.23)$$

Inserting (4.23) into (4.15) we finally obtain a single equation for $\hat{P}|\psi_n\rangle$:

$$\hat{P} \left[\hat{H} + \lambda \hat{V} \hat{Q} \left(E_n - \hat{Q} \hat{H} \hat{Q} \right)^{-1} \hat{Q} \lambda \hat{V} \right] \hat{P} |\psi_n\rangle = E_n \hat{P} |\psi_n\rangle. \quad (4.24)$$

It represents the basis of the Brillouin-Wigner perturbation theory. The resulting equation (4.24) is of the form of a time-independent Schrödinger equation

$$\hat{P} \hat{H}_{\text{eff}} \hat{P} |\psi_n\rangle = E_n \hat{P} |\psi_n\rangle, \quad (4.25)$$

where we have introduced the effective Hamilton operator

$$\hat{H}_{\text{eff}} = \hat{H} + \lambda^2 \hat{V} \hat{Q} \left(E_n - \hat{Q} \hat{H} \hat{Q} \right)^{-1} \hat{Q} \hat{V}. \quad (4.26)$$

Since \hat{H}_{eff} is sandwiched by \hat{P} in (4.25), everything that goes in or out of \hat{H}_{eff} must involve the Hilbert subspace \hat{P} projects into. However, \hat{H}_{eff} contains according to (4.26) also the projection operator \hat{Q} , so one has to go beyond the Hilbert subspace \hat{P} projects into.

4.3 Resolvent

Inserting (4.14) into the effective Hamilton operator (4.26) yields

$$\hat{H}_{\text{eff}} = \hat{H}_0 + \lambda \hat{V} + \lambda^2 \hat{V} \hat{Q} \hat{R}(E_n) \hat{Q} \hat{V}, \quad (4.27)$$

where we have introduced the resolvent

$$\hat{R}(E_n) = \left[E_n - \hat{Q} \left(\hat{H}_0 + \lambda \hat{V} \right) \hat{Q} \right]^{-1} \hat{Q} \hat{V}. \quad (4.28)$$

Using the general property $(\hat{A}\hat{B})^{-1} = \hat{B}^{-1}\hat{A}^{-1}$ the resolvent (4.28) can be expanded in a series with respect to λ :

$$\hat{R}(E_n) = \left(E_n - \hat{Q} \hat{H}_0 \hat{Q} \right)^{-1} \hat{Q} \sum_{s=0}^{\infty} \left[\lambda \hat{Q} \hat{V} \hat{Q} \left(E_n - \hat{Q} \hat{H}_0 \hat{Q} \right)^{-1} \right]^s. \quad (4.29)$$

In the case that λ approaches zero the effective Hamilton operator (4.27) reduces to the unperturbed Hamilton operator \hat{H}_0 . Furthermore, the first perturbative order $\lambda \hat{V}$ in (4.27) is not

contained in the resolvent $\hat{R}(E_n)$ but directly emanates from the perturbed Hamiltonina (4.14). In contrast to that, all higher orders in (4.27) originate from the resolvent term. In particular, $s = 0$ gives the second perturbative order, $s = 1$ goes up to the third perturbative order, and so on. This fundamental difference of origin of perturbative orders is already evident in (4.6), where the term $\hat{H}\hat{P}$ gives rise to the zeroth and the first perturbative order, and the term $\hat{H}\hat{Q}$ gives rise to all higher orders. In other words, the zeroth and the first perturbative order are within the Hilbert space \hat{P} projects into, while for all higher orders the Hilbert subspace \hat{Q} projects into must be taken into account.

For later applications we calculate explicitly all correction terms of the effective Hamiltonian up to the order λ^4 . To do so, we have to take the sum over s in the resolvent (4.29) up to $s = 2$ and obtain with (4.27)

$$\begin{aligned} \hat{H}_{\text{eff}} &= \hat{H}_0 + \lambda\hat{V} + \lambda^2\hat{V}\hat{Q}\hat{R}^{(0)}(E_n)\hat{Q}\hat{V} + \lambda^3\hat{V}\hat{Q}\hat{R}^{(0)}(E_n)\hat{Q}\hat{V}\hat{Q}\hat{R}^{(0)}(E_n)\hat{Q}\hat{V} \\ &\quad + \lambda^4\hat{V}\hat{Q}\hat{R}^{(0)}(E_n)\hat{Q}\hat{V}\hat{Q}\hat{R}^{(0)}(E_n)\hat{Q}\hat{V}\hat{Q}\hat{R}^{(0)}(E_n)\hat{Q}\hat{V} + \dots \end{aligned} \quad (4.30)$$

Here we have used as an abbreviation

$$\hat{R}^{(0)}(E_n) = \left(E_n - \hat{Q}\hat{H}_0\hat{Q} \right)^{-1}. \quad (4.31)$$

Now we use (4.17), (4.19), and (4.22) in order to obtain the matrix element of the resolvent (4.31) as

$$\langle \psi_l^{(0)} | \hat{R}^{(0)}(E_n) | \psi_l^{(0)} \rangle = \frac{1}{E_n - E_l^{(0)}}, \quad n \in N, l \in \bar{N}. \quad (4.32)$$

Indeed, expanding formally the left-hand side of (4.32) into a geometric series, using the idempotent property (4.3), and taking into account $n \in N, l \in \bar{N}$ leads straight-forwardly to the right-hand side. Inserting (4.32) in (4.30) yields, finally, the effective Hamiltonian

$$\begin{aligned} \hat{H}_{\text{eff}} &= \hat{H}_0 + \lambda\hat{V} + \lambda^2 \sum_{l \in \bar{N}} \frac{\hat{V}|\psi_l^{(0)}\rangle\langle\psi_l^{(0)}|\hat{V}}{E_n - E_l^{(0)}} + \lambda^3 \sum_{l, l' \in \bar{N}} \frac{\hat{V}|\psi_l^{(0)}\rangle\langle\psi_l^{(0)}|\hat{V}|\psi_{l'}^{(0)}\rangle\langle\psi_{l'}^{(0)}|\hat{V}}{\left(E_n - E_l^{(0)}\right)\left(E_n - E_{l'}^{(0)}\right)} \\ &\quad + \lambda^4 \sum_{l, l', l'' \in \bar{N}} \frac{\hat{V}|\psi_l^{(0)}\rangle\langle\psi_l^{(0)}|\hat{V}|\psi_{l'}^{(0)}\rangle\langle\psi_{l'}^{(0)}|\hat{V}|\psi_{l''}^{(0)}\rangle\langle\psi_{l''}^{(0)}|\hat{V}}{\left(E_n - E_l^{(0)}\right)\left(E_n - E_{l'}^{(0)}\right)\left(E_n - E_{l''}^{(0)}\right)} + \dots \end{aligned} \quad (4.33)$$

This representation of the effective Hamiltonian \hat{H}_{eff} has no operators anymore in the denominators and, thus, can be used as a starting point for further calculations. And we recognize that each perturbative order consists of one term.

Now we determine an equation for the perturbed eigenenergy E_m . To this end we choose $n, n' \in N$ and formulate (4.25) with the help of the projection operator (4.17):

$$\sum_{n, n' \in N} |\psi_n^{(0)}\rangle\langle\psi_n^{(0)}| \hat{H}_{\text{eff}} |\psi_{n'}^{(0)}\rangle\langle\psi_{n'}^{(0)}| \psi_m \rangle = E_m \sum_{n' \in N} |\psi_{n'}^{(0)}\rangle\langle\psi_{n'}^{(0)}| \psi_m \rangle. \quad (4.34)$$

Then we multiply the left-hand side by $\langle \psi_{n''}^{(0)} |$, yielding with the help of the orthonormality (4.21)

$$\langle \psi_n^{(0)} | \psi_m \rangle \sum_{n' \in N} \left(\langle \psi_n^{(0)} | \hat{H}_{\text{eff}} | \psi_{n'}^{(0)} \rangle - E_m \delta_{n,n'} \right). \quad (4.35)$$

In order to obtain a non-trivial solution $\psi_{n'}^{(0)} | \psi_m \rangle \neq 0$ from (4.35), we have to demand

$$\text{Det} \left(\langle \psi_n^{(0)} | \hat{H}_{\text{eff}} | \psi_{n'}^{(0)} \rangle - E_m \delta_{n,n'} \right) = 0. \quad (4.36)$$

where the determinant has to be performed with respect to $n, n' \in N$. Note that (4.36) defines E_m as a zero of a polynomial of finite order. Furthermore, we recognize that the effective Hamiltonian (4.36) contains explicitly the perturbed eigenenergy E_m being determined from (4.36). Thus, Eq. (4.36) represents a self-consistency equation for E_m .

4.4 Specific Cases

Now we specialize (4.36) to the specific cases, which often appear in concrete applications. To this end we assume that the projection operator (4.17) consists of one or two states, respectively.

4.4.1 One-State Approach

At first we consider the special case that the projection operator \hat{P} contains only one state, namely

$$\hat{P} = \hat{P}_n \quad (4.37)$$

In this case, where $n = n' = m$, Eq. (4.36) simplifies to

$$E_n = \langle \psi_n^{(0)} | \hat{H}_{\text{eff}} | \psi_n^{(0)} \rangle. \quad (4.38)$$

Inserting the effective Hamilton operator (4.33) into (4.38) we get

$$\begin{aligned} E_n &= E_n^{(0)} + \lambda V_{nn} + \lambda^2 \sum_{l \neq n} \frac{V_{nl} V_{ln}}{E_n - E_l^{(0)}} + \lambda^3 \sum_{l, l' \neq n} \frac{V_{nl} V_{ll'} V_{l'n}}{(E_n - E_l^{(0)}) (E_n - E_{l'}^{(0)})} \\ &+ \lambda^4 \sum_{l, l', l'' \neq n} \frac{V_{nl} V_{ll'} V_{l'l''} V_{l''n}}{(E_n - E_l^{(0)}) (E_n - E_{l'}^{(0)}) (E_n - E_{l''}^{(0)})} + \dots \end{aligned} \quad (4.39)$$

Note that, due to the nonlinear appearance of E_n , Eq. (4.39) represents a self-consistency equation for the perturbed energy eigenvalue E_n . Inserting on the right-hand side of Eq. (4.39) a Taylor expansion ansatz

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \lambda^3 E_n^{(3)} + \lambda^4 E_n^{(4)} + \dots, \quad (4.40)$$

a systematic expansion with respect to λ yields straight-forwardly the result of non-degenerate perturbation theory up to fourth order:

$$\begin{aligned}
E_n = & E_n^{(0)} + \lambda V_{nn} + \lambda^2 \sum_{l \neq n} \frac{V_{nl} V_{ln}}{E_n^{(0)} - E_l^{(0)}} + \lambda^3 \left[\sum_{l, l' \neq n} \frac{V_{nl} V_{ll'} V_{l'n}}{(E_n^{(0)} - E_l^{(0)}) (E_n^{(0)} - E_{l'}^{(0)})} - V_{nn} \sum_{l \neq n} \frac{V_{nl} V_{ln}}{(E_n^{(0)} - E_l^{(0)})^2} \right] \\
& + \lambda^4 \left[\sum_{l, l', l'' \neq n} \frac{V_{nl} V_{ll'} V_{l'l''} V_{l''n}}{(E_n^{(0)} - E_l^{(0)}) (E_n^{(0)} - E_{l'}^{(0)}) (E_n^{(0)} - E_{l''}^{(0)})} - 2V_{nn} \sum_{l, l' \neq n} \frac{V_{nl} V_{ll'} V_{l'n}}{(E_n^{(0)} - E_l^{(0)})^2 (E_n^{(0)} - E_{l'}^{(0)})} \right. \\
& \left. + \sum_{l \neq n} \frac{V_{nl} V_{ln}}{E_n^{(0)} - E_l^{(0)}} \sum_{l' \neq n} \frac{V_{nl'} V_{l'n}}{(E_n^{(0)} - E_{l'}^{(0)})^2} + V_{nn}^2 \sum_{l \neq n} \frac{V_{nl} V_{ln}}{(E_n^{(0)} - E_l^{(0)})^3} + \dots \right]. \tag{4.41}
\end{aligned}$$

Thus, starting with the third order more than one term appears in the respective order. Furthermore, since we have $n \neq l, l', l''$, the denominator is never zero, so that no divergence occurs in this perturbative representation for the perturbed energy eigenvalue E_n .

4.4.2 Two-State Approach

Now we consider the situation that the projection operator \hat{P} consists of two states:

$$\hat{P} = \hat{P}_n + \hat{P}_{n'}. \tag{4.42}$$

Thus, we read off from Eq. (4.36)

$$\text{Det} \begin{pmatrix} \langle \psi_n^{(0)} | \hat{H}_{\text{eff}} | \psi_n^{(0)} \rangle - E_m & \langle \psi_n^{(0)} | \hat{H}_{\text{eff}} | \psi_{n'}^{(0)} \rangle \\ \langle \psi_{n'}^{(0)} | \hat{H}_{\text{eff}} | \psi_n^{(0)} \rangle & \langle \psi_{n'}^{(0)} | \hat{H}_{\text{eff}} | \psi_{n'}^{(0)} \rangle - E_m \end{pmatrix} = 0, \tag{4.43}$$

It turns out that the two-state approach contains degenerate perturbation theory as a special case. In order to illustrate this connection, we restrict the effective Hamilton operator (4.33) in (4.43) up to first order:

$$\text{Det} \begin{pmatrix} \langle \psi_n^{(0)} | \hat{H}_0 + \lambda \hat{V} | \psi_n^{(0)} \rangle - E_m & \langle \psi_n^{(0)} | \hat{H}_0 + \lambda \hat{V} | \psi_{n'}^{(0)} \rangle \\ \langle \psi_{n'}^{(0)} | \hat{H}_0 + \lambda \hat{V} | \psi_n^{(0)} \rangle & \langle \psi_{n'}^{(0)} | \hat{H}_0 + \lambda \hat{V} | \psi_{n'}^{(0)} \rangle - E_m \end{pmatrix} = 0. \tag{4.44}$$

And we specialize to a twofold degeneracy of the unperturbed Hamilton operator \hat{H}_0 with $E_n^{(0)} = E_{n'}^{(0)}$, so we have

$$E_m = E_n^{(0)} + \lambda E_{n\alpha n}^{(1)} + \dots \tag{4.45}$$

In the diagonal of the matrix in (4.44) we then get due to (4.18) and the normalization of the unperturbed energy states (4.21)

$$\langle \psi_n^{(0)} | \hat{H}_0 | \psi_n^{(0)} \rangle = E_n^{(0)} = \langle \psi_{n'}^{(0)} | \hat{H}_0 | \psi_{n'}^{(0)} \rangle. \tag{4.46}$$

Correspondingly, the non-diagonal elements of the matrix in (4.44) simplifies due to (4.18) and the orthogonality of the unperturbed energy states (4.21):

$$\langle \psi_n^{(0)} | \hat{H}_0 | \psi_{n'}^{(0)} \rangle = 0 = \langle \psi_{n'}^{(0)} | \hat{H}_0 | \psi_n^{(0)} \rangle. \tag{4.47}$$

Thus, we conclude that (4.44)–(4.47) yields the secular equation (3.20).

Chapter 5

Time-Dependent Perturbation Theory

This chapter contrasts the previous time-independent perturbative theories with a corresponding time-dependent perturbative calculation. After exploring the general properties of time-dependent perturbation theory in first-order, we will apply it to deal with the intricate interaction between light and matter. To this end we model the individual atoms quantum mechanically, but treat light still classically. Thus, we neglect here the corpuscular character of the electromagnetic field, which is dealt with in a quantum optics lecture and leads to new intriguing phenomena. For instance, treating light classically we find that the probability for an atomic transition does not depend upon whether the initial or the final atomic state is energetically higher or lower. This symmetry is only broken by considering the light quantum mechanically, which leads, ultimately, to the three elementary processes for the interaction of light and matter as discovered by Albert Einstein in 1916 within his rederivation of the black-body radiation formula of Max Planck. In particular, a full quantum mechanical treatment of the light field yields the fundamental result that absorption and induced emission happen to be identical as a consequence of an incident electromagnetic wave, but the spontaneous emission can even occur randomly in the absence of any photons and, thus, is exclusively of quantum mechanical origin. Note that these perturbative results are only valid provided that the population transfer between the initial and the final state is small.

5.1 General Theory

Let us assume that the considered quantum mechanical system is described by a time-dependent Hamilton operator $\hat{H}(t)$. Then an immediate consequence of the time dependence is that there are now no stationary solutions, i.e. the time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = \hat{H}(t)|\psi(t)\rangle \quad (5.1)$$

can not be solved via

$$|\psi(t)\rangle = e^{-iE_n t/\hbar} |\psi_n\rangle \quad (5.2)$$

with an eigenvalue E_n and an eigenstate $|\psi_n\rangle$ of $\hat{H}(t)$. In general it is not even possible to find an analytical solution of (5.1). In order to obtain at least an approximative solution of (5.1) we have to specialize to the case that $\hat{H}(t)$ decomposes into an unperturbed time-independent Hamilton operator \hat{H}_0 and a time-dependent perturbation $\hat{V}(t)$ according to

$$\hat{H}(t) = \hat{H}_0 + \hat{V}(t). \quad (5.3)$$

For a small enough perturbation we expect physically the following scenario. Once the quantum system is initially at time $t = 0$ in an eigenstate $|\psi_n^{(0)}\rangle$ of \hat{H}_0 , then $\hat{V}(t)$ initiates for $t > 0$ a transition from that eigenstate $|\psi_n^{(0)}\rangle$ to another eigenstate $|\psi_m^{(0)}\rangle$. In order to investigate such a transition in more detail, we assume that the eigenvalue problem (2.3) of the unperturbed Hamilton operator \hat{H}_0 is solved and that the eigenstates $|\psi_n^{(0)}\rangle$ represent an orthonormal basis. Due to the completeness relation (2.5) the solution of the time-dependent Schrödinger equation (5.1) can then be expanded as follows

$$|\psi(t)\rangle = \sum_n c_n(t) e^{-iE_n^{(0)}t/\hbar} |\psi_n^{(0)}\rangle, \quad (5.4)$$

where $c_n(t)$ denote some time-dependent expansion coefficients. Note that it is a matter of taste whether the exponential factor $e^{-iE_n^{(0)}t/\hbar}$ is explicitly used as in Eq. (5.4) or whether it is implicitly included within the expansion coefficients $c_n(t)$. In the former (latter) case the differential equation for $c_n(t)$ will turn out to become a little bit simpler (more involved). Furthermore, due to normalization reasons, the time-dependent expansion coefficients $c_n(t)$ satisfy the condition

$$\sum_n |c_n(t)|^2 = 1. \quad (5.5)$$

Inserting the ansatz (5.4) into the time-dependent Schrödinger equation (5.1) yields

$$\sum_n i\hbar \frac{\partial c_n(t)}{\partial t} e^{-iE_n^{(0)}t/\hbar} |\psi_n^{(0)}\rangle = \sum_n c_n(t) e^{-iE_n^{(0)}t/\hbar} \hat{V}(t) |\psi_n^{(0)}\rangle. \quad (5.6)$$

Multiplying from the left with $\langle\psi_m^{(0)}|$ and taking into account the orthonormality (2.4) of the stationary states $|\psi_n^{(0)}\rangle$ then leads to coupled first-order ordinary differential equations for the time-dependent expansion coefficients

$$i\hbar \frac{\partial c_n(t)}{\partial t} = \sum_m e^{i\omega_{nm}^{(0)}t} V_{nm}(t) c_m(t) \quad (5.7)$$

with the matrix elements

$$V_{nm}(t) = \langle\psi_n^{(0)}|\hat{V}(t)|\psi_m^{(0)}\rangle \quad (5.8)$$

and the transition frequencies

$$\omega_{nm} = \frac{E_n^{(0)} - E_m^{(0)}}{\hbar}. \quad (5.9)$$

As an initial condition respecting the normalization condition (5.5) we require that only the initial state with the quantum number i is occupied:

$$c_i(0) = 1; \quad c_n(0) = 0, \text{ for } n \neq i. \quad (5.10)$$

As time progresses, the state i becomes less occupied, while the occupation of a previously unoccupied state f increases. The probability for a transition of the atom from state i to state f at time $t > 0$ is given by

$$P_{i \rightarrow f}(t) = |c_f(t)|^2. \quad (5.11)$$

So far we have not implemented any approximation. The intermediate result (5.7) is a representation of the underlying time-dependent Schrödinger equation (5.1) in the eigenbasis of the unperturbed Hamilton operator \hat{H}_0 . Mathematically Eq. (5.7) is an infinitely large coupled system of first-order differential equations, which can only be solved analytically in exceptional cases. Therefore, numerical or analytical approximative solution methods are generically used.

5.2 Iterative Solution

In the case of time-dependent perturbation theory, it is assumed that the perturbation $\hat{V}(t)$ is small, so (5.7) can be solved iteratively. To this end we expand the time-dependent expansion coefficients perturbatively

$$c_n(t) = c_n^{(0)}(t) + c_n^{(1)}(t) + c_n^{(2)}(t) + \dots, \quad (5.12)$$

where $c_n^{(k)}(t)$ is supposed to be of k th order in $\hat{V}(t)$. With this Eq. (5.7) yields up to second order

$$\frac{\partial c_n^{(0)}(t)}{\partial t} = 0, \quad (5.13)$$

$$\frac{\partial c_n^{(1)}(t)}{\partial t} = -\frac{i}{\hbar} \sum_m e^{i\omega_{nm}t} V_{nm}(t) c_m^{(0)}(t), \quad (5.14)$$

$$\frac{\partial c_n^{(2)}(t)}{\partial t} = -\frac{i}{\hbar} \sum_m e^{i\omega_{nm}t} V_{nm}(t) c_m^{(1)}(t), \quad (5.15)$$

which can, indeed, be solved iteratively. In zeroth order we get in accordance with the normalization condition (5.5)

$$c_n^{(0)}(t) = c_n^{(0)}(t_0) = \delta_{ni}, \quad (5.16)$$

while the first order results in

$$c_n^{(1)}(t) = -\frac{i}{\hbar} \int_{t_0}^t dt' e^{i\omega_{ni}t'} V_{ni}(t'). \quad (5.17)$$

Correspondingly follows for the second order

$$c_n^{(2)}(t) = \left(-\frac{i}{\hbar}\right)^2 \int_{t_0}^t dt' \int_{t_0}^{t'} dt'' \sum_m e^{i\omega_{nm}t'} V_{nm}(t') e^{i\omega_{mi}t''} V_{mi}(t''). \quad (5.18)$$

The total probability (5.11) for a transition from the initial state i to the final state $f \neq i$ is determined from these expansion coefficients as follows:

$$P_{i \rightarrow f}(t) = \left| c_f^{(0)}(t) + c_f^{(1)}(t) + c_f^{(2)}(t) + \dots \right|^2. \quad (5.19)$$

In case that the final state f differs from the initial state i , we have $c_f^{(0)}(t) = 0$ due to (5.16), so the transition probability (5.19) reduces to

$$P_{i \rightarrow f}(t) = \left| c_f^{(1)}(t) + c_f^{(2)}(t) + \dots \right|^2. \quad (5.20)$$

This means that $P_{i \rightarrow f}(t)$ depends in lowest order quadratically from the perturbation $\hat{V}(t)$.

5.3 Short Perturbation

Let us consider as an initial application a perturbation $\hat{V}(t)$, which acts only shortly, i.e. $\hat{V}(t)$ is only non-vanishing during a finite time interval $0 \leq t \leq T$. Physical examples are provided, for instance, by the disturbance, which is caused by the recoil of an emitted photon or by a particle flying by. Inserting in such a case (5.17) into (5.20), the transition probability reads then

$$P_{i \rightarrow f}(T) = \frac{1}{\hbar^2} \left| \int_0^T dt e^{i\omega_{fi}t} V_{fi}(t) + \dots \right|^2. \quad (5.21)$$

As the Fourier transformed of the time-dependent matrix element is given by

$$V_{fi}(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} V_{fi}(t) = \int_0^T dt e^{i\omega t} V_{fi}(t) + \dots, \quad (5.22)$$

the transition probability (5.21) results in lowest order in [1, Chap. 84]

$$P_{i \rightarrow f}(T) = \frac{|V_{fi}(\omega_{fi})|^2}{\hbar^2}. \quad (5.23)$$

5.4 Quench of Perturbation

Another application is provided by a quench, where the perturbation operator $\hat{V}(t)$ is suddenly switched on at time $t_0 = 0$. In addition, we assume that this happens monochromatically, i.e. the perturbation must be of the generic form

$$\hat{V}(t) = \hat{A} e^{-i\omega t} + \hat{A}^\dagger e^{i\omega t}, \quad (5.24)$$

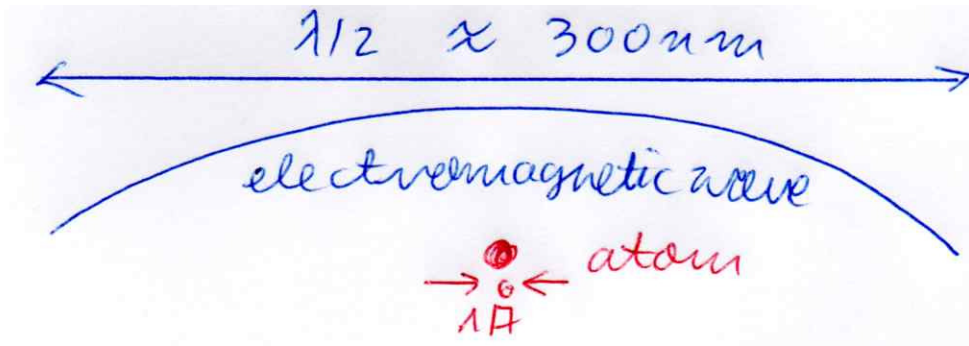


Figure 5.1: Comparison of length scales: electromagnetic wavelength versus extension of an atom.

where \hat{A} is some general time-independent operator. A prominent example for such a case occurs once a hydrogen atom is affected by an electromagnetic plane wave, where the major contribution stems from the interaction with the electric field, so the interaction with the magnetic field is approximately negligible. Provided that the hydrogen atom is located without loss of generality at the origin $\mathbf{x}_0 = \mathbf{0}$, its interaction with the electric plane wave is given by

$$\hat{V}(t) = -\mathbf{d} \cdot \mathbf{E}(t). \quad (5.25)$$

Here the electric dipole moment of the electron in the hydrogen atom reads

$$\mathbf{d} = -e\mathbf{x} \quad (5.26)$$

and the electric field is described by

$$\mathbf{E}(t) = \frac{\mathbf{E}_0}{2} e^{i(\mathbf{k} \cdot \mathbf{x} - \omega t)} + \text{c.c.}, \quad (5.27)$$

where the amplitude vector $\mathbf{E}_0 = \mathcal{E}\mathbf{e}$ contains both the amplitude \mathcal{E} and the polarization vector \mathbf{e} . Thus, Eqs. (5.25)–(5.27) are of the form (5.24) with identifying

$$\hat{A} = -\frac{1}{2} \mathbf{E}_0 \cdot \mathbf{d} e^{i\mathbf{k} \cdot \mathbf{x}}. \quad (5.28)$$

Let us consider more closely the absolute value of the wave vector \mathbf{k} , i.e. $|\mathbf{k}| = 2\pi/\lambda$, which is determined by the wavelength λ . In the optical range the wavelength varies between 400 nm and 700 nm, so we obtain the following estimate for an atom with an extension in the range of an Angström, see Fig. 5.1:

$$\mathbf{k} \cdot \mathbf{x} \approx |\mathbf{k}| \cdot |\mathbf{x}| \approx \frac{2\pi}{600 \text{ nm}} \cdot 1 \text{ \AA} \approx 10^{-3} \ll 1. \quad (5.29)$$

This means that the electric plane wave (5.27) does not change over the extension of an atom and is, therefore, approximately homogeneous. This leads to the so-called dipole approximation, where we can approximately neglect the spatial dependence in (5.28), so we get

$$\hat{A} = -\frac{1}{2} \mathbf{E}_0 \cdot \mathbf{d}. \quad (5.30)$$

The electric dipole moment (5.26) and, thus, due to (5.30) the perturbed Hamilton operator (5.24) have odd parity, so that the diagonal matrix elements (5.8) vanish:

$$V_{nn}(t) = 0. \quad (5.31)$$

Therefore, the first-order correction (5.17) for the initial state i vanishes

$$c_i^{(1)}(t) = -\frac{i}{\hbar} \int_0^t dt' V_{ii}(t') = 0 \quad (5.32)$$

and results in $c_i(t) = c_i^{(0)}(t) = 1$ up to the first order. For the final state $f \neq i$, on the other hand, we get

$$c_f^{(1)}(t) = -\frac{i}{\hbar} \int_0^t dt' e^{i\omega_{fi}t'} V_{fi}(t'). \quad (5.33)$$

With the perturbed Hamilton operator (5.24) and (5.30) follows then

$$c_f^{(1)}(t) = \frac{i}{2\hbar} \int_0^t dt' \left[(\mathbf{d}_{if} \cdot \mathbf{E}_0)^* e^{i(\omega_{fi}+\omega)t'} + \mathbf{d}_{fi} \cdot \mathbf{E}_0 e^{i(\omega_{fi}-\omega)t'} \right], \quad (5.34)$$

where the evaluation of the elementary integral yields

$$c_f^{(1)}(t) = \frac{1}{2\hbar} \left[(\mathbf{d}_{if} \cdot \mathbf{E}_0)^* \frac{e^{i(\omega_{fi}+\omega)t} - 1}{\omega_{fi} + \omega} + \mathbf{d}_{fi} \cdot \mathbf{E}_0 \frac{e^{i(\omega_{fi}-\omega)t} - 1}{\omega_{fi} - \omega} \right]. \quad (5.35)$$

Due to (5.26) here the dipole matrix element

$$\mathbf{d}_{nm} = -e \mathbf{x}_{nm} \quad (5.36)$$

depend the matrix elements of the coordinates

$$\mathbf{x}_{nm} = \langle \psi_n^{(0)} | \hat{\mathbf{x}} | \psi_m^{(0)} \rangle. \quad (5.37)$$

Thus, in case that the electric amplitude vector \mathbf{E}_0 of the plane wave points along the z -axis, the selection rules from Appendix C can be used to find out, which matrix elements (5.36) are non-vanishing for the hydrogen atom. In the case $\omega_{fi} > 0$ the second term in (5.35) dominates, as it is resonant. Thus, one can neglect the first term, as it is anti-resonant. This yields the so-called rotating wave approximation, which is ubiquitous in quantum optics:

$$c_f^{(1)}(t) = \frac{1}{2\hbar} \mathbf{d}_{fi} \cdot \mathbf{E}_0 \frac{e^{i(\omega_{fi}-\omega)t} - 1}{\omega_{fi} - \omega}. \quad (5.38)$$

Due to the initial condition $c_f^{(0)}(t) = 0$ we conclude that $c_f(t) = c_f^{(1)}(t)$ holds up to the first order and that the transition probability (5.19) is given in lowest order according to

$$P_{i \rightarrow f}(t) = \left| c_f^{(1)}(t) \right|^2 = \frac{|\mathbf{d}_{fi} \cdot \mathbf{E}_0|^2}{\hbar^2} \frac{\sin^2(\Delta t/2)}{\Delta^2}. \quad (5.39)$$

Here the detuning Δ is defined by the difference between the frequency ω of the electromagnetic

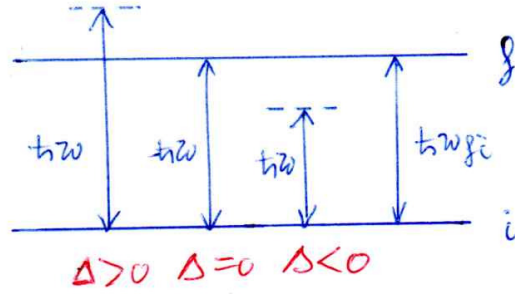


Figure 5.2: Definition of the detuning Δ between the light field frequency ω and the atomic transition frequency ω_{fi} according to (5.40).

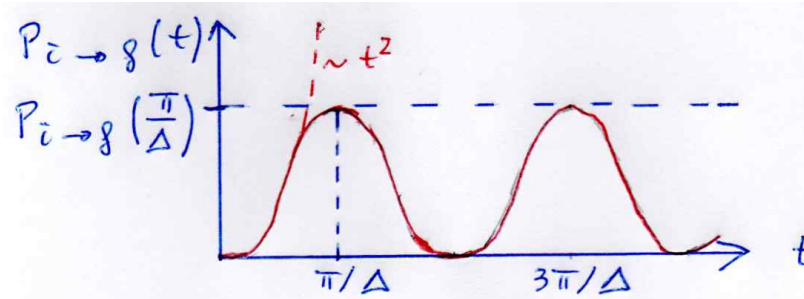


Figure 5.3: Time dependence of the transition probability (5.39).

field and the atomic frequency ω_{fi} for the transition from the initial and to the final state

$$\Delta = \omega - \omega_{fi}. \quad (5.40)$$

In the case of $\Delta > 0$ ($\Delta < 0$) one speaks of blue (red) detuning, whereas $\Delta = 0$ denotes the resonance case, see Fig. 5.2. Note that the result (5.39) depends quadratically on the detuning Δ . Thus the transition probability $P_{i \rightarrow f}(t)$ for absorption and induced emission coincide, which is an artefact of having treated the electric field classically. In order to analyze the time dependence of the transition probability $P_{i \rightarrow f}(t)$ in (5.39) further, we obtain for a non-vanishing detuning, i.e. $\Delta \neq 0$ that its maximum occurs at

$$\text{Max}_t P_{i \rightarrow f}(t) = P_{i \rightarrow f}\left(\frac{\pi}{\Delta}\right) = \frac{|\mathbf{d}_{fi} \cdot \mathbf{E}_0|^2}{\hbar^2 \Delta^2}. \quad (5.41)$$

In the resonance case $\Delta = 0$ we obtain instead that the transition probability (5.39) increases quadratically with time t :

$$P_{i \rightarrow f}(t) = \frac{|\mathbf{d}_{fi} \cdot \mathbf{E}_0|^2 t^2}{4\hbar^2}, \quad (5.42)$$

see Fig. 5.3. However, in order that this perturbative treatment remains valid, we have to demand that $P_{i \rightarrow f}(t)$ must be small. In the non-resonant case $\Delta \neq 0$ this leads due to (5.39) to a minimal value for the absolute value of the detuning Δ , namely

$$\text{Max}_t P_{i \rightarrow f}(t) \ll 1 \quad \implies \quad \frac{|\mathbf{d}_{fi} \cdot \mathbf{E}_0|}{\hbar} \ll |\Delta|, \quad (5.43)$$

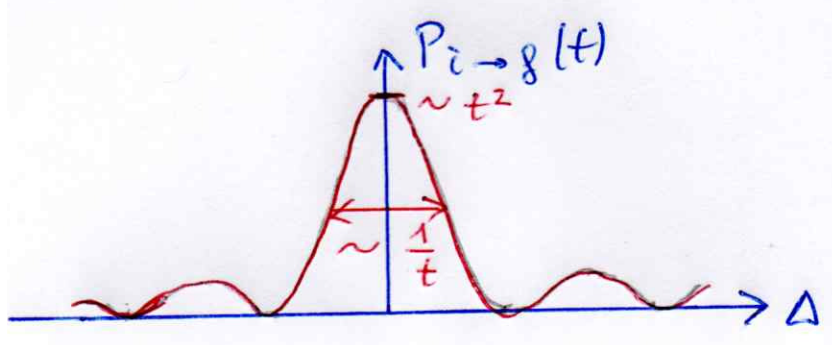


Figure 5.4: Dependence of the transition probability (5.39) as a function of the detuning Δ .

while in the resonant case $\Delta = 0$ we read off from (5.42) that one is restricted to short times:

$$P_{i \rightarrow f}(t) \ll 1 \quad \Longrightarrow \quad t \ll \frac{2\hbar}{|\mathbf{d}_{fi} \cdot \mathbf{E}_0|}. \quad (5.44)$$

Considering the transition probability (5.39) as a function of the detuning Δ , we are reminded of a slit diffraction function, see Fig. 5.4. In particular, the transition probability $P_{i \rightarrow f}(t)$ has a sharp maximum at $\Delta = 0$ with a height proportional to t^2 and a width proportional to $1/t$. Thus, the area under the curve increases linearly with t :

$$\int_{-\infty}^{\infty} d\Delta \frac{\sin^2(\Delta t/2)}{\Delta^2} = \frac{t}{2} \int_{-\infty}^{\infty} dx \frac{\sin^2 x}{x^2} = \frac{\pi t}{2}. \quad (5.45)$$

Here we applied the substitution $x(\Delta) = \Delta t/2$ and used the definite integral

$$\int_{-\infty}^{\infty} dx \frac{\sin^2 x}{x^2} = \pi, \quad (5.46)$$

which is derived in Appendix E. From Fig. 5.4 and (5.45) we then conclude the following representation of the delta function:

$$\lim_{t \rightarrow \infty} \frac{\sin^2(\Delta t/2)}{\Delta^2} = \frac{\pi t}{2} \delta(\Delta). \quad (5.47)$$

Thus, taking into account the definition of the detuning in (5.40), the transition probability (5.39) converges in the long-time limit $t \rightarrow \infty$ towards a delta function:

$$P_{i \rightarrow f}(t) \rightarrow \frac{\pi t |\mathbf{d}_{fi} \cdot \mathbf{E}_0|^2}{2\hbar^2} \delta(\omega - \omega_{fi}), \quad t \rightarrow \infty. \quad (5.48)$$

This suggests to introduce in the long-time limit $t \rightarrow \infty$ a transition rate:

$$W_{i \rightarrow f} = \lim_{t \rightarrow \infty} \frac{dP_{i \rightarrow f}(t)}{dt} \quad (5.49)$$

which yields

$$W_{i \rightarrow f} = \frac{\pi |\mathbf{d}_{fi} \cdot \mathbf{E}_0|^2}{2\hbar^2} \delta(\omega - \omega_{fi}). \quad (5.50)$$

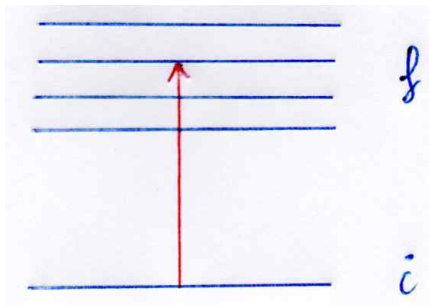


Figure 5.5: Summing the transition rates in (5.51) over all possible final states f .

In practice, however, there will be several final states f , so that the respective transition rates have to be summed up, see Fig. 5.5:

$$W_{i \rightarrow [f]} = \frac{\pi}{2} \sum_{[f]} \frac{|\mathbf{d}_{fi} \cdot \mathbf{E}_0|^2}{\hbar^2} \delta(\omega - \omega_{fi}). \quad (5.51)$$

This result is referred to in the literature as *Fermi's golden rule*. In practice, however, it can also be that the incoming light consists of different frequency components, so that the field amplitude $\mathbf{E}_0(\omega)$ becomes frequency dependent. In this case, we obtain from (5.51) for the transition rate

$$W_{i \rightarrow f} = \frac{\pi}{2\hbar^2} \int_{-\infty}^{\infty} d\omega |\mathbf{d}_{fi} \cdot \mathbf{E}_0(\omega)|^2 \delta(\omega - \omega_{fi}). \quad (5.52)$$

Provided that $\mathbf{E}_0(\omega)$ is varying slowly, the transition rate (5.52) reduces to

$$W_{i \rightarrow f} = \frac{\pi}{2\hbar^2} |\mathbf{d}_{fi} \cdot \mathbf{E}_0(\omega_{fi})|^2. \quad (5.53)$$

5.5 Adiabatic Switching on of Perturbation

Let us consider now another relevant situation. In a laboratory one generically has to switch on some potential during an experiment. In order to not disturb the set up too much, the potential switched on has to be small and the switching on of the potential has to occur adiabatically, i.e. extremely slowly. In the following we describe such an adiabatic switching on process by considering the family of potentials [9, Sect. 5.9]

$$\hat{V}^\eta(t) = e^{\eta t} \hat{V}, \quad t \leq 0, \quad \eta > 0. \quad (5.54)$$

Here the inverse of the family parameter η represents the time scale upon which the switching on process occurs. In particular we are interested in performing the limit $\eta \downarrow 0$ as this corresponds to an adiabatic switching on:

$$\lim_{\eta \downarrow 0} \hat{V}^\eta(t) = \hat{V}. \quad (5.55)$$

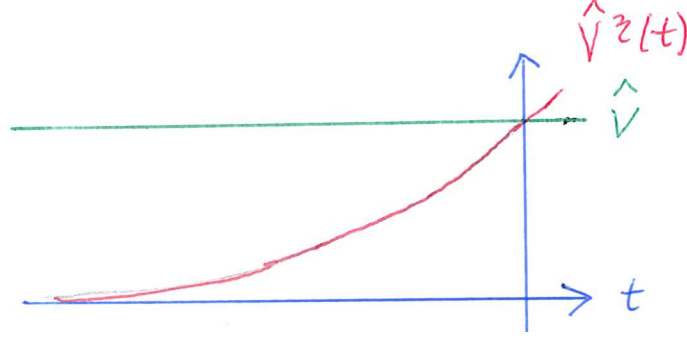


Figure 5.6: The family of potentials (5.54) connects the unperturbed system (5.56) with the perturbed system (5.57) in an adiabatic way (5.55).

Indeed, during the time evolution the family of potentials (5.54) connects the unperturbed system, where the potential is absent, in the infinitely distant past

$$\lim_{t \rightarrow -\infty} \hat{V}^\eta(t) = 0 \quad (5.56)$$

with the perturbed system, where the potential is fully switched on, at zero time

$$\lim_{t \rightarrow 0} \hat{V}^\eta(t) = \hat{V}, \quad (5.57)$$

as is illustrated in Fig. 5.6. Applying time dependent perturbation theory to this scenario necessitates to determine the matrix elements (5.8) for the family of potentials (5.54), which yields

$$V_{nm}^\eta(t) = e^{\eta t} V_{nm}, \quad V_{nm} = \langle \psi_n^{(0)} | \hat{V} | \psi_m^{(0)} \rangle. \quad (5.58)$$

In the following first-order calculations we proceed such that we consider the family parameter η as being fixed and perform the adiabatic limit $\eta \downarrow 0$ only at the very end.

5.5.1 First Case

At first we reconsider the previous situation that the final state differs from the initial state, i.e. $f \neq i$. Inserting (5.58) into (5.17) and specializing to the initial time $t_0 = -\infty$ leads to the integral

$$c_f^{(1)}(t) = -\frac{i}{\hbar} V_{fi} \int_{-\infty}^t dt' e^{(i\omega_{fi} + \eta)t'}. \quad (5.59)$$

Here we recognize that the family parameter $\eta < 0$ guarantees the convergence of the integral, which amounts to

$$c_f^{(1)}(t) = -\frac{i}{\hbar} V_{fi} \frac{e^{(i\omega_{fi} + \eta)t}}{i\omega_{fi} + \eta}. \quad (5.60)$$

Thus the probability for a transition from i to $f \neq i$ determined by (5.20) results to

$$P_{i \rightarrow f}(t) = \frac{|V_{fi}|^2}{\hbar^2} \frac{e^{2\eta t}}{\omega_{fi}^2 + \eta^2} \quad (5.61)$$

and the corresponding transition rate reads then

$$\frac{dP_{i \rightarrow f}(t)}{dt} = \frac{|V_{fi}|^2}{\hbar^2} \frac{2\eta}{\omega_{fi}^2 + \eta^2} e^{2\eta t}. \quad (5.62)$$

Now the adiabatic limit $\eta \downarrow 0$ can be evaluated, yielding a time independent transition rate

$$W_{i \rightarrow f} = \lim_{\eta \downarrow 0} \frac{dP_{i \rightarrow f}(t)}{dt}. \quad (5.63)$$

Indeed, taking into account the representation of the delta function

$$\lim_{\eta \downarrow 0} \frac{1}{\pi} \frac{\eta}{\omega_{fi}^2 + \eta^2} = \delta(\omega_{fi}), \quad (5.64)$$

the resulting transition rate is given by

$$W_{i \rightarrow f} = \frac{2\pi|V_{fi}|^2}{\hbar^2} \delta(\omega_{fi}). \quad (5.65)$$

With this we have reproduced within the adiabatic switching approach Fermi's golden rule (5.50) for a vanishing frequency $\omega = 0$. Note that (5.50) and (5.65) differ by a factor 4 due to having previously assumed that the time dependent perturbation has the generic form (5.24).

5.5.2 Second Case

Chapter 6

Different Pictures

In quantum mechanics one distinguishes different pictures for describing the underlying dynamics. To this end one has to take into account that in quantum mechanics, in the end, only the expectation values for observables are important in view of a comparison with experimental measurements. Thus, the time evolution could be distributed differently between the states and the operators as long as at each instant one and the same expectation value is determined in the respective picture. In the Schrödinger picture the states evolve in time, whereas the operators are generically time independent. Complementary to that the Heisenberg picture deals with time dependent operators and time-independent states. And the Dirac picture allows for time dependences for both operators and states, where the former (latter) ones evolve according to the unperturbed Hamilton operator (perturbation). It turns out that the Dirac picture provides an independent approach for time-dependent perturbation theory.

6.1 Schrödinger and Heisenberg Picture

We start with recapitulating the Schrödinger picture and restrict ourselves for the sake of simplicity to the case of a time-independent Hamilton operator \hat{H}_S . The corresponding equations of motion for both the time-dependent state $|\psi_S(t)\rangle$ and a time-independent operator \hat{O}_S read

$$i\hbar \frac{\partial}{\partial t} |\psi_S(t)\rangle = \hat{H}_S |\psi_S(t)\rangle, \quad (6.1)$$

$$i\hbar \frac{\partial}{\partial t} \hat{O}_S = 0. \quad (6.2)$$

The formal solution of the Schrödinger equation (6.1) is given by

$$|\psi_S(t)\rangle = e^{-i\hat{H}_S t/\hbar} |\psi_S(0)\rangle. \quad (6.3)$$

Here we identify the initial state $|\psi_S(0)\rangle$ in the Schrödinger picture with the state $|\psi_H\rangle$ in the Heisenberg picture:

$$|\psi_S(0)\rangle = |\psi_H\rangle. \quad (6.4)$$

Thus, the transformations from the Schrödinger to the Heisenberg picture and vice versa are defined according to the relations

$$|\psi_S(t)\rangle = e^{-i\hat{H}_S t/\hbar} |\psi_H\rangle \quad \Longleftrightarrow \quad |\psi_H\rangle = e^{i\hat{H}_S t/\hbar} |\psi_S(t)\rangle. \quad (6.5)$$

From (6.1) and (6.5) we then read off that the state in the Heisenberg picture $|\psi_H\rangle$ is time-independent:

$$i\hbar \frac{\partial}{\partial t} |\psi_H\rangle = -\hat{H}_S e^{i\hat{H}_S t/\hbar} |\psi_S(t)\rangle + e^{i\hat{H}_S t/\hbar} i\hbar \frac{\partial}{\partial t} |\psi_S(t)\rangle = 0. \quad (6.6)$$

In order to determine the operator $\hat{O}_H(t)$ in the Heisenberg picture, we demand that the expectation values do not change once we perform a transformation from the Schrödinger to the Heisenberg picture:

$$\langle \psi_S(t) | \hat{O}_S | \psi_S(t) \rangle = \langle \psi_H | \hat{O}_H(t) | \psi_H \rangle. \quad (6.7)$$

Inserting (6.5) into (6.7) we obtain

$$\langle e^{-i\hat{H}_S t/\hbar} \psi_H | \hat{O}_S | e^{-i\hat{H}_S t/\hbar} \psi_H \rangle = \langle \psi_H | e^{i\hat{H}_S t/\hbar} \hat{O}_S e^{-i\hat{H}_S t/\hbar} | \psi_H \rangle = \langle \psi_H | \hat{O}_H(t) | \psi_H \rangle, \quad (6.8)$$

so we determine, indeed, formally the time dependence of the operator $\hat{O}_H(t)$ in the Heisenberg picture:

$$\hat{O}_H(t) = e^{i\hat{H}_S t/\hbar} \hat{O}_S e^{-i\hat{H}_S t/\hbar}. \quad (6.9)$$

Thus, multiplying an operator in the Schrödinger picture \hat{O}_S from the left with $e^{i\hat{H}_S t/\hbar}$ and from the right with $e^{-i\hat{H}_S t/\hbar}$ yields the corresponding operator in the Heisenberg picture $\hat{O}_H(t)$. For instance, for the Hamilton operator $\hat{O}_S = \hat{H}_S$ we obtain from (6.9) the result that it does not change its form when we perform the transformation from the Schrödinger to the Heisenberg picture:

$$\hat{H}_H(t) = e^{i\hat{H}_S t/\hbar} \hat{H}_S e^{-i\hat{H}_S t/\hbar} = \hat{H}_S. \quad (6.10)$$

Furthermore, for the operator in the Heisenberg picture $\hat{O}_H(t)$ we determine from (6.2), (6.9), and (6.10) the Heisenberg equation of motion

$$i\hbar \frac{\partial}{\partial t} \hat{O}_H(t) = e^{i\hat{H}_S t/\hbar} \left[-\hat{H}_S \hat{O}_S + \hat{O}_S \hat{H}_S \right] e^{-i\hat{H}_S t/\hbar} + e^{i\hat{H}_S t/\hbar} i\hbar \frac{\partial}{\partial t} \hat{O}_S e^{-i\hat{H}_S t/\hbar}, \quad (6.11)$$

which reduces to

$$i\hbar \frac{\partial}{\partial t} \hat{O}_H(t) = \left[\hat{O}_H(t), \hat{H}_S \right]_- = \left[\hat{O}_H(t), \hat{H}_H(t) \right]_-. \quad (6.12)$$

6.2 Dirac Picture

The starting point of perturbation theory is the assumption that the Hamilton operator of the system under consideration is time-dependent and can be split into two parts in the Schrödinger picture:

$$\hat{H}_S(t) = \hat{H}_S^{(0)} + H_S^{(\text{int})}(t). \quad (6.13)$$

Here $\hat{H}_S^{(0)}$ represents the unperturbed time-independent Hamilton operator and $H_S^{(\text{int})}(t)$ denotes the perturbative part of the Hamilton operator, which is assumed to be time-dependent. In the Schrödinger picture the time-dependent state vector $|\psi_S(t)\rangle$ fulfills the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\psi_S(t)\rangle = \hat{H}_S(t) |\psi_S(t)\rangle. \quad (6.14)$$

Thus, the time dependence of $|\psi_S(t)\rangle$ is determined by the mutual influence of both the unperturbed and the perturbed Hamilton operator $\hat{H}_S^{(0)}$ and $H_S^{(\text{int})}(t)$, respectively. The idea for introducing the Dirac picture is now to take into account (6.12) and to redo the temporal evolution with the unperturbed Hamilton operator $\hat{H}_S^{(0)}$ according to

$$|\psi_D(t)\rangle = e^{i\hat{H}_S^{(0)}t/\hbar} |\psi_S(t)\rangle \iff |\psi_S(t)\rangle = e^{-i\hat{H}_S^{(0)}t/\hbar} |\psi_D(t)\rangle. \quad (6.15)$$

In order to determine the operator $\hat{O}_D(t)$ in the Dirac picture, we require that the expectation values do not change during the transition from the Schrödinger picture to the Dirac picture:

$$\langle \psi_D(t) | \hat{O}_D(t) | \psi_D(t) \rangle = \langle \psi_S(t) | \hat{O}_S | \psi_S(t) \rangle. \quad (6.16)$$

Inserting (6.15) into (6.16) then actually leads to determine the operator $\hat{O}_D(t)$ in the Dirac picture

$$\langle \psi_D(t) | e^{i\hat{H}_S^{(0)}t/\hbar} \hat{O}_S e^{-i\hat{H}_S^{(0)}t/\hbar} | \psi_D(t) \rangle = \langle \psi_D(t) | \hat{O}_D(t) | \psi_D(t) \rangle, \quad (6.17)$$

yielding finally

$$\hat{O}_D(t) = e^{i\hat{H}_S^{(0)}t/\hbar} \hat{O}_S e^{-i\hat{H}_S^{(0)}t/\hbar}. \quad (6.18)$$

For example, for the unperturbed Hamilton operator $\hat{O}_S = \hat{H}_S^{(0)}$ follows that it does not change its shape during the transition from the Schrödinger picture to the Dirac picture:

$$\hat{H}_D^{(0)}(t) = e^{i\hat{H}_S^{(0)}t/\hbar} \hat{H}_S^{(0)} e^{-i\hat{H}_S^{(0)}t/\hbar} = \hat{H}_S^{(0)}. \quad (6.19)$$

With (6.15) and (6.18) we have, thus, defined the Dirac picture both for the state vectors and the operators. It remains to investigate their respective equations of motion. Based on the equation of motion of a state vector in the Schrödinger picture (6.14) together with (6.13)

$$i\hbar \frac{\partial}{\partial t} |\psi_S(t)\rangle = \hat{H}_S(t) |\psi_S(t)\rangle = \left[\hat{H}_S^{(0)} + \hat{H}_S^{(\text{int})}(t) \right] |\psi_S(t)\rangle \quad (6.20)$$

and taking into account (6.15) we then obtain

$$i\hbar \frac{\partial}{\partial t} |\psi_{\text{D}}(t)\rangle = e^{i\hat{H}_{\text{S}}^{(0)}t/\hbar} \left[i\hbar \frac{\partial}{\partial t} |\psi_{\text{S}}(t)\rangle - \hat{H}_{\text{S}}^{(0)} |\psi_{\text{S}}(t)\rangle \right] = e^{i\hat{H}_{\text{S}}^{(0)}t/\hbar} \hat{H}_{\text{S}}^{(\text{int})}(t) |\psi_{\text{S}}(t)\rangle \quad (6.21)$$

which reduces to the equation of motion of the corresponding state vector in the Dirac picture, which is called the Tomonaga-Schwinger equation:

$$i\hbar \frac{\partial}{\partial t} |\psi_{\text{D}}(t)\rangle = \hat{H}_{\text{D}}^{(\text{int})}(t) |\psi_{\text{D}}(t)\rangle. \quad (6.22)$$

Here the interacting part of the Hamilton operator is transferred from the Schrödinger picture to the Dirac picture according to (6.18):

$$\hat{H}_{\text{D}}^{(\text{int})}(t) = e^{i\hat{H}_{\text{S}}^{(0)}t/\hbar} \hat{H}_{\text{S}}^{(\text{int})}(t) e^{-i\hat{H}_{\text{S}}^{(0)}t/\hbar}. \quad (6.23)$$

Furthermore, starting from the equation of motion of an operator in the Schrödinger picture (6.2) we use (6.18) and (6.19) in order to derive the equation of motion of the corresponding operator in the Dirac picture

$$i\hbar \frac{\partial}{\partial t} \hat{O}_{\text{D}}(t) = e^{i\hat{H}_{\text{S}}^{(0)}t/\hbar} \left[\hat{O}_{\text{S}} \hat{H}_{\text{S}}^{(0)} - \hat{H}_{\text{S}}^{(0)} \hat{O}_{\text{S}} \right] e^{-i\hat{H}_{\text{S}}^{(0)}t/\hbar}, \quad (6.24)$$

which reduces to

$$i\hbar \frac{\partial}{\partial t} \hat{O}_{\text{D}}(t) = [\hat{O}_{\text{D}}(t), \hat{H}_{\text{S}}^{(0)}]_- = [\hat{O}_{\text{D}}(t), \hat{H}_{\text{D}}^{(0)}(t)]_-. \quad (6.25)$$

While in the Dirac picture the dynamics of the state vectors is determined by the interacting part of the Hamilton operator according to (6.22), only the unperturbed Hamilton operator enters the dynamics of the operators according to (6.25).

6.3 Time Evolution Operator

In the Dirac picture the perturbation affects the dynamics of the state vectors according to (6.22). In order to investigate this in more detail we introduce the time evolution operator $\hat{U}_{\text{D}}(t_2, t_1)$, which connects the state vectors $|\psi_{\text{D}}(t_1)\rangle$ and $|\psi_{\text{D}}(t_2)\rangle$ at two consecutive times t_1 and t_2 , respectively:

$$|\psi_{\text{D}}(t_2)\rangle = \hat{U}_{\text{D}}(t_2, t_1) |\psi_{\text{D}}(t_1)\rangle. \quad (6.26)$$

A similar time evolution operator $\hat{U}_{\text{S}}(t_2, t_1)$ connects the corresponding state vectors $|\psi_{\text{S}}(t_1)\rangle$ and $|\psi_{\text{S}}(t_2)\rangle$ in the Schrödinger picture:

$$|\psi_{\text{S}}(t_2)\rangle = \hat{U}_{\text{S}}(t_2, t_1) |\psi_{\text{S}}(t_1)\rangle. \quad (6.27)$$

Thus, we conclude

$$\begin{aligned} |\psi_{\text{D}}(t_2)\rangle &= e^{i\hat{H}_{\text{S}}^{(0)}t_2/\hbar} |\psi_{\text{S}}(t_2)\rangle = e^{i\hat{H}_{\text{S}}^{(0)}t_2/\hbar} \hat{U}_{\text{S}}(t_2, t_1) |\psi_{\text{S}}(t_1)\rangle \\ &= e^{i\hat{H}_{\text{S}}^{(0)}t_2/\hbar} \hat{U}_{\text{S}}(t_2, t_1) e^{-i\hat{H}_{\text{S}}^{(0)}t_1/\hbar} |\psi_{\text{D}}(t_1)\rangle, \end{aligned} \quad (6.28)$$

and a comparison with (6.26) leads to a formal expression between the two time evolution operator $\hat{U}_D(t_2, t_1)$ and $\hat{U}_S(t_2, t_1)$:

$$\hat{U}_D(t_2, t_1) = e^{i\hat{H}_S^{(0)}t_2/\hbar} \hat{U}_S(t_2, t_1) e^{-i\hat{H}_S^{(0)}t_1/\hbar}. \quad (6.29)$$

Since $e^{i\hat{H}_S^{(0)}t_2/\hbar}$ and $\hat{U}_S(t_2, t_1)$ generally do not commute with each other, it is important to take into account the particular operator ordering in (6.29). With the help of the formal expression (6.29), various properties of the time evolution operator in the Dirac picture can be proved provided that the corresponding property is fulfilled for the time evolution operator in the Schrödinger picture. For instance, it has the initial condition

$$\hat{U}_D(t_1, t_1) = 1 \quad (6.30)$$

and fulfills the group property

$$\hat{U}_D(t_3, t_2)\hat{U}_D(t_2, t_1) = \hat{U}_D(t_3, t_1). \quad (6.31)$$

Indeed, we obtain from applying (6.29)

$$\begin{aligned} \hat{U}_D(t_3, t_2)\hat{U}_D(t_2, t_1) &= e^{i\hat{H}_S^{(0)}t_3/\hbar} \hat{U}_S(t_3, t_2) e^{-i\hat{H}_S^{(0)}t_2/\hbar} e^{i\hat{H}_S^{(0)}t_2/\hbar} \hat{U}_S(t_2, t_1) e^{-i\hat{H}_S^{(0)}t_1/\hbar} \\ &= e^{i\hat{H}_S^{(0)}t_3/\hbar} \hat{U}_S(t_3, t_1) e^{-i\hat{H}_S^{(0)}t_1/\hbar} = \hat{U}_D(t_3, t_1). \end{aligned} \quad (6.32)$$

Furthermore, we read off from evaluating (6.31) for $t_3 = t_1$ together with (6.30) the inverse time evolution operator

$$\hat{U}_D^{-1}(t_2, t_1) = \hat{U}_D(t_1, t_2). \quad (6.33)$$

And we deduce from (6.29) and (6.33) that the time evolution operator is unitary:

$$\hat{U}_D^\dagger(t_2, t_1) = e^{i\hat{H}_S^{(0)}t_1/\hbar} \hat{U}_S(t_2, t_1) e^{-i\hat{H}_S^{(0)}t_2/\hbar} = \hat{U}_D(t_1, t_2) = \hat{U}_D^{-1}(t_2, t_1). \quad (6.34)$$

Finally, we determine which differential equation the time evolution operator $\hat{U}_D(t_2, t_1)$ solves. Differentiating (6.29) with respect to t_2 and taking into account (6.13) yields

$$i\hbar \frac{\partial}{\partial t_2} \hat{U}_D(t_2, t_1) = e^{i\hat{H}_S^{(0)}t_2/\hbar} \hat{H}_S^{(\text{int})}(t) e^{-i\hat{H}_S^{(0)}t_2/\hbar} e^{i\hat{H}_S^{(0)}t_2/\hbar} \hat{U}_S(t_2, t_1) e^{-i\hat{H}_S^{(0)}t_1/\hbar}. \quad (6.35)$$

Thus, we conclude from (6.23), (6.29), and (6.35) that $\hat{U}_D(t_2, t_1)$ fulfills the differential equation

$$i\hbar \frac{\partial}{\partial t_2} \hat{U}_D(t_2, t_1) = \hat{H}_D^{(\text{int})}(t_2) \hat{U}_D(t_2, t_1). \quad (6.36)$$

The initial value problem (6.30) and (6.36) can be formally rewritten in form of an integral equation:

$$\hat{U}_D(t_2, t_1) = 1 - \frac{i}{\hbar} \int_{t_1}^{t_2} dt'_1 \hat{H}_D^{(\text{int})}(t'_1) \hat{U}_D(t'_1, t_1). \quad (6.37)$$

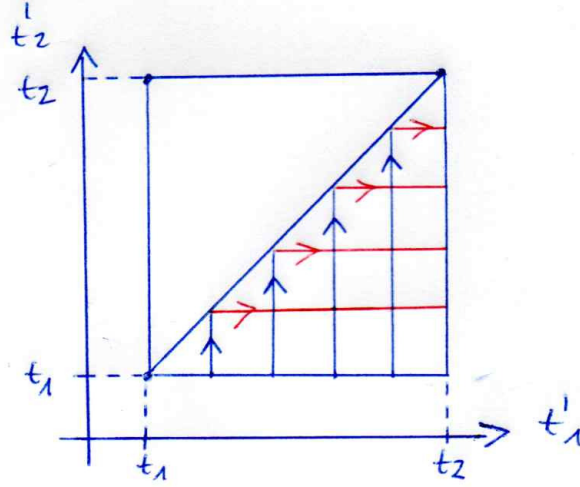


Figure 6.1: The hatched triangle can be integrated in two ways, which allows to rearrange the integral (6.39).

Successively reinserting the left-hand side of (6.37) into the right-hand side, one obtains the von Neumann series

$$\begin{aligned} \hat{U}_D(t_2, t_1) &= 1 - \frac{i}{\hbar} \int_{t_1}^{t_2} dt'_1 \hat{H}_D^{(\text{int})}(t'_1) + \left(\frac{-i}{\hbar}\right)^2 \int_{t_1}^{t_2} dt'_1 \int_{t_1}^{t'_1} dt'_2 \hat{H}_D^{(\text{int})}(t'_1) \hat{H}_D^{(\text{int})}(t'_2) + \dots \\ &+ \left(\frac{-i}{\hbar}\right)^n \int_{t_1}^{t_2} dt'_1 \int_{t_1}^{t'_1} dt'_2 \dots \int_{t_1}^{t'_{n-1}} dt'_n \hat{H}_D^{(\text{int})}(t'_1) \hat{H}_D^{(\text{int})}(t'_2) \dots \hat{H}_D^{(\text{int})}(t'_n) + \dots \end{aligned} \quad (6.38)$$

It is noticeable in the n th summand of the von Neumann series that the time arguments of the multiple integrals are ordered in decreasing order: $t'_1 > t'_2 > \dots > t'_n$. According to an idea of Freeman Dyson, all n integrals can be rewritten such that they are all performed over the same interval $[t_1, t_2]$ by using the so-called time-ordered product of operators. To this end we consider exemplarily the second term in the von Neumann series (6.38) and reorganize it as follows:

$$\int_{t_1}^{t_2} dt'_1 \int_{t_1}^{t'_1} dt'_2 \hat{H}_D^{(\text{int})}(t'_1) \hat{H}_D^{(\text{int})}(t'_2) = \int_{t_1}^{t_2} dt'_2 \int_{t'_2}^{t_2} dt'_1 \hat{H}_D^{(\text{int})}(t'_1) \hat{H}_D^{(\text{int})}(t'_2). \quad (6.39)$$

Here we use the fact that the hatched triangle in Fig. 6.1 can be integrated in two ways. Either we first integrate over t'_2 and then over t'_1 or, conversely, first over t'_1 and then over t'_2 . Exchanging both integration variables at the right-hand side of (6.39) we conclude

$$\begin{aligned} 2 \int_{t_1}^{t_2} dt'_1 \int_{t_1}^{t'_1} dt'_2 \hat{H}_D^{(\text{int})}(t'_1) \hat{H}_D^{(\text{int})}(t'_2) &= \int_{t_1}^{t_2} dt'_1 \int_{t_1}^{t'_1} dt'_2 \hat{H}_D^{(\text{int})}(t'_1) \hat{H}_D^{(\text{int})}(t'_2) \\ &+ \int_{t_1}^{t_2} dt'_1 \int_{t'_1}^{t_2} dt'_2 \hat{H}_D^{(\text{int})}(t'_2) \hat{H}_D^{(\text{int})}(t'_1) = \int_{t_1}^{t_2} dt'_1 \int_{t_1}^{t_2} dt'_2 \Theta(t'_1 - t'_2) \hat{H}_D^{(\text{int})}(t'_1) \hat{H}_D^{(\text{int})}(t'_2) \\ &+ \int_{t_1}^{t_2} dt'_1 \int_{t_1}^{t_2} dt'_2 \Theta(t'_2 - t'_1) \hat{H}_D^{(\text{int})}(t'_2) \hat{H}_D^{(\text{int})}(t'_1) = \int_{t_1}^{t_2} dt'_1 \int_{t_1}^{t_2} dt'_2 \hat{T} \left(\hat{H}_D^{(\text{int})}(t'_1) \hat{H}_D^{(\text{int})}(t'_2) \right). \end{aligned} \quad (6.40)$$

In the last step we assumed that the interacting Hamilton operator in the Dirac picture $\hat{H}_D^{(\text{int})}(t)$ is bosonic, so the time ordering was used for two bosonic operators whose time order is not yet fixed:

$$\hat{T} \left(\hat{H}_D^{(\text{int})}(t'_1) \hat{H}_D^{(\text{int})}(t'_2) \right) = \Theta(t'_1 - t'_2) \hat{H}_D^{(\text{int})}(t'_1) \hat{H}_D^{(\text{int})}(t'_2) + \Theta(t'_2 - t'_1) \hat{H}_D^{(\text{int})}(t'_2) \hat{H}_D^{(\text{int})}(t'_1). \quad (6.41)$$

Analogous to (6.40), also all other terms in the von Neumann series (6.38) can be rewritten as multiple integrals over the entire interval $[t_1, t_2]$ with the help of the time-ordered product of operators. In the case of the n th-order term, one has to take into account in total $n!$ permutations of the time arguments. Therefore the generalisation of (6.40) reads

$$\begin{aligned} & n! \int_{t_1}^{t_2} dt'_1 \int_{t_1}^{t'_1} dt'_2 \cdots \int_{t_1}^{t'_{n-1}} dt'_n \hat{H}_D^{(\text{int})}(t'_1) \hat{H}_D^{(\text{int})}(t'_2) \cdots \hat{H}_D^{(\text{int})}(t'_n) \\ &= \int_{t_1}^{t_2} dt'_1 \int_{t_1}^{t'_1} dt'_2 \cdots \int_{t_1}^{t'_2} dt'_n \hat{T} \left(\hat{H}_D^{(\text{int})}(t'_1) \hat{H}_D^{(\text{int})}(t'_2) \cdots \hat{H}_D^{(\text{int})}(t'_n) \right). \end{aligned} \quad (6.42)$$

This result can be proven by complete induction. With the help of (6.42) the von Neumann series (6.38) for the time evolution operator is finally given by the Dyson series

$$\hat{U}_D(t_2, t_1) = \sum_{n=0}^{\infty} \frac{1}{n!} \left(\frac{-i}{\hbar} \right)^n \int_{t_1}^{t_2} dt'_1 \cdots \int_{t_1}^{t'_2} dt'_n \hat{T} \left(\hat{H}_D^{(\text{int})}(t'_1) \cdots \hat{H}_D^{(\text{int})}(t'_n) \right). \quad (6.43)$$

We can explicitly verify that the Dyson series (6.43) solves the differential equation (6.36). Differentiating (6.43) with respect to t_2 we obtain due to the symmetry of the integrand with respect to the integration variables t'_1, t'_2, \dots, t'_n :

$$\begin{aligned} i\hbar \frac{\partial}{\partial t_2} \hat{U}_D(t_2, t_1) &= \sum_{n=1}^{\infty} \frac{i\hbar}{n!} \left(\frac{-i}{\hbar} \right)^n n \int_{t_1}^{t_2} dt'_1 \int_{t_1}^{t'_1} dt'_2 \cdots \int_{t_1}^{t'_2} dt'_{n-1} \\ &\quad \times \hat{T} \left(\hat{H}_D^{(\text{int})}(t'_1) \hat{H}_D^{(\text{int})}(t'_2) \cdots \hat{H}_D^{(\text{int})}(t'_{n-1}) \hat{H}_D^{(\text{int})}(t_2) \right). \end{aligned} \quad (6.44)$$

Due to the fact that the time t_2 is larger than all remaining integration variables $t'_1, t'_2, \dots, t'_{n-1}$ and using the definition (6.41) of the time-ordered product of operators, one can pull the operator $\hat{H}_D^{(\text{int})}(t_2)$ out of the time ordering and obtain together with (6.43)

$$\begin{aligned} i\hbar \frac{\partial}{\partial t_2} \hat{U}_D(t_2, t_1) &= \hat{H}_D^{(\text{int})}(t_2) \sum_{n=1}^{\infty} \frac{1}{(n-1)!} \left(\frac{-i}{\hbar} \right)^{n-1} \int_{t_1}^{t_2} dt'_1 \int_{t_1}^{t'_1} dt'_2 \cdots \int_{t_1}^{t'_2} dt'_{n-1} \\ &\quad \times \hat{T} \left(\hat{H}_D^{(\text{int})}(t'_1) \hat{H}_D^{(\text{int})}(t'_2) \cdots \hat{H}_D^{(\text{int})}(t'_{n-1}) \right) = \hat{H}_D^{(\text{int})}(t_2) \sum_{n=0}^{\infty} \frac{1}{n!} \left(\frac{-i}{\hbar} \right)^n \int_{t_1}^{t_2} dt'_1 \int_{t_1}^{t'_1} dt'_2 \cdots \int_{t_1}^{t'_2} dt'_n \\ &\quad \times \hat{T} \left(\hat{H}_D^{(\text{int})}(t'_1) \hat{H}_D^{(\text{int})}(t'_2) \cdots \hat{H}_D^{(\text{int})}(t'_n) \right) = \hat{H}_D^{(\text{int})}(t_2) \hat{U}_D(t_2, t_1). \end{aligned} \quad (6.45)$$

Formally, the Dyson series (6.43) can be summed up to a time-ordered exponential function:

$$\hat{U}_D(t_2, t_1) = \hat{T} \exp \left\{ \frac{-i}{\hbar} \int_{t_1}^{t_2} dt \hat{H}_D^{(\text{int})}(t) \right\}. \quad (6.46)$$

By taking into account that the time evolution operator (6.46) is defined by the Dyson series (6.43) one can calculate perturbatively the cross sections of scattering processes as will be worked out in the next chapter.

Appendix A

Functional Derivative

Here we provide a concise introduction into the functional derivative [14]. It generalizes the definition of a partial derivative for a finite number of variables to the case, where a continuum of variables exists. And it allows straight-forwardly to determine the Euler-Lagrange equations from the Hamilton principle of Lagrangian mechanics.

A.1 Definition

At first we consider a function x of a finite number of degrees of freedom:

$$x = x(t_1, \dots, t_N). \quad (\text{A.1})$$

The partial derivative of x with respect to the variable t_j , i.e.

$$\frac{\partial x(t_1, \dots, t_N)}{\partial t_j}, \quad (\text{A.2})$$

then denotes the change of the function (A.1) with respect to the variable t_j , where all other variables $t_1, \dots, t_{j-1}, t_{j+1}, \dots, t_N$ remain constant. The total change of the function x , i.e.

$$dx(t_1, \dots, t_N) = \sum_{j=1}^N \frac{\partial x(t_1, \dots, t_N)}{\partial t_j} dt_j, \quad (\text{A.3})$$

is then additive in all possible changes of the function, where only one variable changes and all the other variables remain constant. Specializing (A.3) to an infinitesimal change in one variable, i.e. $dt_j = \epsilon \delta_{ij}$, yields

$$x(t_1, \dots, t_i + \epsilon, \dots, t_N) - x(t_1, \dots, t_i, \dots, t_N) = dx(t_1, \dots, t_N) = \epsilon \frac{\partial x(t_1, \dots, t_N)}{\partial t_i}. \quad (\text{A.4})$$

Thus, the partial derivative follows from the limit of a difference quotient:

$$\frac{\partial x(t_1, \dots, t_N)}{\partial t_i} = \lim_{\epsilon \rightarrow 0} \frac{x(t_1, \dots, t_i + \epsilon, \dots, t_N) - x(t_1, \dots, t_i, \dots, t_N)}{\epsilon}. \quad (\text{A.5})$$

Now we generalize this concept of differentiation from a finite number to a continuum of variables. Therefore, we regard now a functional

$$F = F[x(\bullet)], \quad (\text{A.6})$$

i.e. a mapping of a function $x(t)$ to a real or a complex number. The functional derivative

$$\frac{\delta F[x(\bullet)]}{\delta x(t)} \quad (\text{A.7})$$

should then describe how the functional F changes provided that the function $x(t)$ is only changed at a single point $x(t)$. Thus, the functional derivative (A.7) becomes in this way an ordinary function, which depends on the variable t . In analogy to (A.3) the total change of the functional F is defined via

$$\delta F[x(\bullet)] = \int dt \frac{\delta F[x(\bullet)]}{\delta x(t)} \delta x(t), \quad (\text{A.8})$$

so it is additive with respect to all local changes of the function $x(t)$ at all instances t . Similar to the case of a partial derivative also the functional derivative can be determined from the limit of a difference quotient. To this end we introduce a local perturbation of the field $x(t)$ at time t' with strength ϵ according to

$$\delta x(t) = \epsilon \delta(t - t') \quad (\text{A.9})$$

and determine from (A.8) and (A.9)

$$F[x(\bullet) + \epsilon \delta(\bullet - t')] - F[x(\bullet)] = \delta F[x(\bullet)] = \int dt \frac{\delta F[x(\bullet)]}{\delta x(t)} \delta x(t) = \epsilon \frac{\delta F[x(\bullet)]}{\delta x(t')}. \quad (\text{A.10})$$

In the limit $\epsilon \rightarrow 0$ we obtain

$$\frac{\delta x[\phi(\bullet)]}{\delta x(t')} = \lim_{\epsilon \rightarrow 0} \frac{F[x(\bullet) + \epsilon \delta(\bullet - t')] - F[x(\bullet)]}{\epsilon}. \quad (\text{A.11})$$

From this definition of the functional derivative as a limit of a difference quotient follow several useful calculation rules. At first, we obtain from (A.11) the trivial functional derivative

$$\frac{\delta x(t)}{\delta x(t')} = \lim_{\epsilon \rightarrow 0} \frac{x(t) + \epsilon \delta(t - t') - x(t)}{\epsilon} = \delta(t - t'). \quad (\text{A.12})$$

Then we determine from (A.11) the product rule

$$\begin{aligned} \frac{\delta \{F[x(\bullet)]G[x(\bullet)]\}}{\delta x(t')} &= \lim_{\epsilon \rightarrow 0} \frac{F[x(\bullet) + \epsilon \delta(\bullet - t')]G[x(\bullet) + \epsilon \delta(\bullet - t')] - F[x(\bullet)]G[x(\bullet)]}{\epsilon} \\ &= \lim_{\epsilon \rightarrow 0} \left\{ \frac{F[x(\bullet) + \epsilon \delta(\bullet - t')] - F[x(\bullet)]}{\epsilon} G[x(\bullet)] + F[x(\bullet)] \frac{G[x(\bullet) + \epsilon \delta(\bullet - t')] - G[x(\bullet)]}{\epsilon} \right\} \\ &= \frac{\delta F[x(\bullet)]}{\delta x(t')} G[x(\bullet)] + F[x(\bullet)] \frac{\delta G[x(\bullet)]}{\delta x(t')}. \end{aligned} \quad (\text{A.13})$$

And, finally, combining (A.11) and (A.12) yields the chain rule:

$$\frac{\delta f(x(t))}{\delta x(t')} = \lim_{\epsilon \rightarrow 0} \frac{f(x(t) + \epsilon \delta(t - t')) - f(x(t))}{\epsilon} = \frac{\partial f(x(t))}{\partial x(t)} \delta(t - t') = \frac{\partial f(x(t))}{\partial x(t)} \frac{\delta x(t)}{\delta x(t')}. \quad (\text{A.14})$$

A.2 Application

Now we apply the concept of the functional derivative to evaluate the Hamilton principle of Lagrangian mechanics (1.3). For each component $x_i(t)$ of the particle path $\mathbf{x}(t)$ we then obtain for the functional derivative of the action (1.1) due to the chain rule

$$\frac{\delta \mathcal{A}}{\delta x_i(t)} = \sum_{i'} \int_{t_1}^{t_2} \left\{ \frac{\partial L}{\partial x_{i'}(t')} \frac{\delta x_{i'}(t')}{\delta x_i(t)} + \frac{\partial L}{\partial \dot{x}_{i'}(t')} \frac{\delta \dot{x}_{i'}(t')}{\delta x_i(t)} \right\} dt'. \quad (\text{A.15})$$

Here we use the fact that a total derivative with respect to t' and a functional derivative with respect to $x_i(t)$ can be interchanged as t and t' represent independent degrees of freedom:

$$\frac{\delta \dot{x}_{i'}(t')}{\delta x_i(t)} = \frac{\delta}{\delta x_i(t)} \frac{dx_{i'}(t')}{dt'} = \frac{d}{dt'} \frac{\delta x_{i'}(t')}{\delta x_i(t)}. \quad (\text{A.16})$$

Inserting (A.16) into (A.15) allows to perform a partial integration:

$$\frac{\delta \mathcal{A}}{\delta x_i(t)} = \sum_{i'} \left[\frac{\partial L}{\partial \dot{x}_{i'}(t')} \frac{\delta x_{i'}(t')}{\delta x_i(t)} \right]_{t_1}^{t_2} + \sum_{i'} \int_{t_1}^{t_2} \left\{ \frac{\partial L}{\partial x_{i'}(t')} - \frac{d}{dt'} \frac{\partial L}{\partial \dot{x}_{i'}(t')} \right\} \frac{\delta x_{i'}(t')}{\delta x_i(t)} dt'. \quad (\text{A.17})$$

The appearing functional derivative is defined as a straight-forward extension of (A.12):

$$\frac{\delta x_{i'}(t')}{\delta x_i(t)} = \delta_{ii'} \delta(t - t'), \quad (\text{A.18})$$

so (A.17) reduces to

$$\frac{\delta \mathcal{A}}{\delta x_i(t)} = \left[\frac{\partial L}{\partial \dot{x}_i(t')} \delta(t - t') \right]_{t_1}^{t_2} + \int_{t_1}^{t_2} \left\{ \frac{\partial L}{\partial x_i(t')} - \frac{d}{dt'} \frac{\partial L}{\partial \dot{x}_i(t')} \right\} \delta(t - t') dt'. \quad (\text{A.19})$$

The boundary terms vanish as the time t , for which we evaluate the functional derivative, is supposed to be different from the initial (final) time t_1 (t_2). And, finally, evaluating the time integral yields together with the Hamilton principle (1.3)

$$\frac{\partial L}{\partial x_i(t)} - \frac{d}{dt} \frac{\partial L}{\partial \dot{x}_i(t)} = 0, \quad (\text{A.20})$$

which coincides with the Euler-Lagrange equations (1.4).

Appendix B

Hypergeometric Functions

In mathematics, the hypergeometric function is a special function represented by a series, which includes many other special functions as specific or limiting cases. This means that many functions appearing in theoretical physics applications can be described from a unified point of view with the help of those hypergeometric functions [15].

B.1 Hypergeometric Differential Equations

The hypergeometric differential equation, which was analyzed by Leonhard Euler and Carl Friedrich Gauß, reads as follows:

$$z(1-z)\frac{d^2\phi}{dz^2} + [c - (a+b+1)z]\frac{d\phi}{dz} - ab\phi = 0. \quad (\text{B.1})$$

Thus, it represents a homogeneous linear differential equation of second order for a function $\phi(z)$. As it contains three parameters a , b , c , its solutions allow for a variety of functions. In the following we solve (B.1) with the help of a power series expansion of the form

$$\phi(z) = z^\sigma \sum_{\nu=0}^{\infty} c_\nu z^\nu, \quad (\text{B.2})$$

which contains a yet to be determined index σ . Substituting (B.2) into (B.1) yields at first

$$\begin{aligned} & z(1-z) \sum_{\nu=0}^{\infty} c_\nu (\nu + \sigma)(\nu + \sigma - 1) z^{\nu + \sigma - 2} \\ & + [c - (a+b+1)z] \sum_{\nu=0}^{\infty} c_\nu (\nu + \sigma) z^{\nu + \sigma - 1} - ab \sum_{\nu=0}^{\infty} c_\nu z^{\nu + \sigma} = 0. \end{aligned} \quad (\text{B.3})$$

Here one has to multiply out the respective factors and to reorder the summations in such a way that terms with the same power are collected. This leads to

$$c_0 \sigma(c + \sigma - 1) z^{\sigma - 1} + \sum_{\nu=0}^{\infty} [c_{\nu+1}(\nu + \sigma + c)(\nu + \sigma + 1) - c_\nu(\nu + \sigma + a)(\nu + \sigma + b)] z^{\nu + \sigma} = 0. \quad (\text{B.4})$$

The vanishing of this equation implies that all coefficients have to be zero. With this we obtain the index equation

$$\sigma(c + \sigma - 1) = 0 \quad (\text{B.5})$$

and the recurrence relation

$$c_{\nu+1} = \frac{(\nu + \sigma + a)(\nu + \sigma + b)}{(\nu + \sigma + c)(\nu + \sigma + 1)} c_{\nu}. \quad (\text{B.6})$$

The latter can be solved straight forwardly by putting without loss of generality $c_0 = 1$ and yields

$$c_{\nu} = \frac{(a + \sigma)_{\nu}(b + \sigma)_{\nu}}{(c + \sigma)_{\nu}(1 + \sigma)_{\nu}}, \quad (\text{B.7})$$

where we have introduced as a useful abbreviation the Pochhammer symbol

$$(a)_{\nu} = a(a + 1) \cdots (a + \nu - 1), \quad \nu = 1, 2, \dots, \quad (\text{B.8})$$

$$(a)_0 = 1. \quad (\text{B.9})$$

For instance, the factorial represents an example for a Pochhammer symbol

$$(1)_{\nu} = 1 \cdot 2 \cdots (\nu - 1) = \nu!. \quad (\text{B.10})$$

An alternative definition of the Pochhammer symbol is based on the Gamma function [16, (8.310.1)]

$$\Gamma(x) = \int_0^{\infty} dt t^{x-1} e^{-t}, \quad x > 0. \quad (\text{B.11})$$

Performing a partial integration we obtain the useful recursion formula

$$\Gamma(x + 1) = x \Gamma(x), \quad x > 0. \quad (\text{B.12})$$

Thus, applying (B.12) recursively, we conclude that the Gamma function interpolates between the factorials:

$$\nu! = \Gamma(\nu + 1). \quad (\text{B.13})$$

And we read off from (B.12) that the Pochhammer symbol $(a)_{\nu}$ can also be defined with the Gamma function via

$$(a)_{\nu} = \frac{\Gamma(a + \nu)}{\Gamma(a)}, \quad (\text{B.14})$$

which contains both (B.8) and (B.9) as special cases. Inserting (B.7) into (B.2) we obtain for the solution of the hypergeometric differential equation:

$$\phi(z) = z^{\sigma} \sum_{\nu=0}^{\infty} \frac{(a + \sigma)_{\nu}(b + \sigma)_{\nu}}{(c + \sigma)_{\nu}(1 + \sigma)_{\nu}} z^{\nu}. \quad (\text{B.15})$$

Furthermore, we read off from the index equation (B.5) that there are two possible values for the index σ :

- The first value amounts to $\sigma_1 = 0$, so (B.15) reduces together with (B.10) to the hypergeometric function

$$\phi_1(z) = {}_2F_1(a, b; c; z) = \sum_{\nu=0}^{\infty} \frac{(a)_\nu (b)_\nu}{(c)_\nu} \frac{z^\nu}{\nu!}. \quad (\text{B.16})$$

The indices appended to ${}_2F_1$ indicate that we have in the series (B.16) two Pochhammer symbols in the numerator and one Pochhammer symbol in the denominator. Therefore, a natural generalization of the hypergeometric function reads

$${}_pF_q(\alpha_1, \dots, \alpha_p; \beta_1, \dots, \beta_q; z) = \sum_{\nu=0}^{\infty} \frac{(\alpha_1)_\nu (\alpha_2)_\nu \cdots (\alpha_p)_\nu}{(\beta_1)_\nu (\beta_2)_\nu \cdots (\beta_q)_\nu} \frac{z^\nu}{\nu!}. \quad (\text{B.17})$$

Note that (B.16) does only exist provided that none of the factors in the denominator $(c)_\nu = c(c+1)(c+2)\cdots(c+\nu-1)$ vanishes. Thus, we have to demand $c \neq -n$ with $n = 0, 1, 2, \dots$. Conversely, in case of $a = -n$ or $b = -n$ with $n = 0, 1, 2, \dots$ the series terminates after a finite number of terms, yielding a polynomial of degree n .

- Correspondingly, the second possible value for the index reads $\sigma_2 = 1 - c$. Thus, the second solution of the hypergeometric differential equation amounts to

$$\phi_2(z) = z^{1-c} {}_2F_1(a+1-c, b+1-c; 2-c; z). \quad (\text{B.18})$$

In view of its existence we have to demand $c \neq 2, 3, \dots$

As the hypergeometric differential equation (B.1) is both linear and of second order, its general solution is given by a superposition of both solutions (B.16) and (B.18):

$$\phi(z) = A {}_2F_1(a, b; c; z) + B z^{1-c} {}_2F_1(a+1-c, b+1-c; 2-c; z). \quad (\text{B.19})$$

Note that basically all elementary functions can be represented in terms of hypergeometric functions. An exemplary selection is provided, for instance, in Ref. [16, Sect. 9.12]. Furthermore, software packages like `Mathematica`, which symbolically process for instance differential equations, are today capable of working with hypergeometric functions.

B.2 Confluent Hypergeometric Differential Equation

An important special case of the hypergeometric differential equation (B.1) follows from implementing the linear transformation $x = bz$. This substitution converts (B.1) to

$$x \left(1 - \frac{x}{b}\right) \frac{d^2\phi}{dx^2} + \left(c - x - \frac{a+1}{b}x\right) \frac{d\phi}{dx} - a\phi = 0. \quad (\text{B.20})$$

Performing here the limit $b \rightarrow \infty$ yields the Kummer differential equation, which is also called the confluent hypergeometric differential equation:

$$x \frac{d^2\phi}{dx^2} + (c - x) \frac{d\phi}{dx} - a\phi = 0. \quad (\text{B.21})$$

The derivation of (B.21) implies that its general solution follows from (B.19) according to

$$\phi(x) = \lim_{b \rightarrow \infty} \left[A {}_2F_1 \left(a, b; c; \frac{x}{b} \right) + B \left(\frac{x}{b} \right)^{1-c} {}_2F_1 \left(a+1-c, b+1-c; 2-c; \frac{x}{b} \right) \right]. \quad (\text{B.22})$$

Inserting therein the series expansion for the hypergeometric function (B.16) and taking into account the Pochhammer symbol (B.8) we recognize that the evaluation of the limit $b \rightarrow \infty$ boils down to the calculation

$$\lim_{b \rightarrow \infty} \frac{(b)_\nu}{b^\nu} = 1, \quad \lim_{b \rightarrow \infty} \frac{(b+1-c)_\nu}{b^\nu} = 1. \quad (\text{B.23})$$

Redefining the constant $B' = B/b^{1-c}$ and omitting the prime then yields for the general solution of the Kummer differential equation (B.21)

$$\phi(x) = A {}_1F_1(a; c; x) + B x^{1-c} {}_1F_1(a+1-c; 2-c; x). \quad (\text{B.24})$$

Here the series expansion of the confluent hypergeometric function

$${}_1F_1(a; c; x) = \lim_{b \rightarrow \infty} {}_2F_1 \left(a, b; c; \frac{x}{b} \right) \quad (\text{B.25})$$

turns out to be

$${}_1F_1(a; c; x) = \sum_{\nu=0}^{\infty} \frac{(a)_\nu}{(c)_\nu} \frac{x^\nu}{\nu!}, \quad (\text{B.26})$$

which is a special case of (B.17) with one Pochhammer symbol both in the numerator and in the denominator.

B.3 Asymptotic Properties

The hypergeometric function (B.16) represents a series with a finite radius of convergence. It can be inferred from the ratio test for convergence

$$R = \lim_{\nu \rightarrow \infty} \left| \frac{c_\nu}{c_{\nu+1}} \right|, \quad (\text{B.27})$$

which yields by taking into account the coefficients (B.7) the result $R = 1$. But the solution of the hypergeometric differential equation can also be extended beyond its region of convergence, i.e. for $|z| > 1$. A convergent series representation of ${}_2F_1(a, b; c; z)$ for $|z| > 1$ is derived in detail for instance in Ref. [17] and leads to the transformation formula [16, (9.132.2)]

$$\begin{aligned} {}_2F_1(a, b; c; z) &= \frac{\Gamma(c)\Gamma(b-a)}{\Gamma(b)\Gamma(c-a)} (-z)^a {}_2F_1 \left(a, 1-c+a; 1-b+a; \frac{1}{z} \right) \\ &+ \frac{\Gamma(c)\Gamma(a-b)}{\Gamma(a)\Gamma(c-b)} (-z)^b {}_2F_1 \left(b, 1-c+b; 1-a+b; \frac{1}{z} \right). \end{aligned} \quad (\text{B.28})$$

From this one can read off the asymptotic behaviour $|z| \rightarrow \infty$ of the hypergeometric function due to its property ${}_2F_1(a, b; c; 0) = 1$, which follows straight forwardly from its series expansion (B.28), yielding

$${}_2F_1(a, b; c; z) \longrightarrow \frac{\Gamma(c)\Gamma(b-a)}{\Gamma(b)\Gamma(c-a)} (-z)^a + \frac{\Gamma(c)\Gamma(a-b)}{\Gamma(a)\Gamma(c-b)} (-z)^b, \quad |z| \rightarrow \infty. \quad (\text{B.29})$$

Now we work out the corresponding consequences for the confluent hypergeometric functions (B.25). At first we apply the ratio test for convergence to the series (B.26) and find that the confluent hypergeometric function ${}_1F_1(a; c; x)$ has the convergence radius $R = \infty$, i.e. it converges for all real numbers x . Its asymptotic behaviour follows from combining (B.25) and (B.28):

$$\begin{aligned} {}_1F_1(a; c; x) &= \frac{\Gamma(c)}{\Gamma(c-a)} (-x)^{-a} \lim_{b \rightarrow \infty} \frac{\Gamma(b-a)}{\Gamma(b)} b^a {}_2F_1\left(a, 1-c+a; 1-b+a; \frac{b}{x}\right) \\ &\quad + \frac{\Gamma(c)}{\Gamma(a)} \lim_{b \rightarrow \infty} \frac{\Gamma(a-b)}{\Gamma(c-b)} \left(-\frac{b}{x}\right)^b {}_2F_1\left(b, 1-c+b; 1-a+b; \frac{b}{x}\right). \end{aligned} \quad (\text{B.30})$$

In order to evaluate both limits in (B.30) one needs the asymptotic representation of the Gamma function [16, (8.327)]

$$\Gamma(z) = z^{z-1/2} e^{-z} \sqrt{2\pi} \left(1 + \frac{1}{12z} + \frac{1}{288z^2} + \dots\right), \quad |z| \rightarrow \infty, \quad (\text{B.31})$$

which is also known as the Stirling formula. With this we get for the first line of (B.31)

$$\frac{\Gamma(b-a)}{\Gamma(b)} \longrightarrow b^{-a}, \quad b \rightarrow \infty, \quad (\text{B.32})$$

whereas in the second line we obtain

$$\frac{\Gamma(a-b)}{\Gamma(c-b)} \longrightarrow (-b)^{a-c}, \quad b \rightarrow \infty. \quad (\text{B.33})$$

Taking into account the series of the hypergeometric function (B.16) yields furthermore

$$\lim_{b \rightarrow \infty} \frac{b^\nu}{(1 \mp b \pm a)_\nu} = (\mp 1)^\nu. \quad (\text{B.34})$$

It turns out that (B.32) and (B.34) allow to evaluate the limit in the first line of (B.31), but the calculation of the second line needs one additional step. To this end we use one of the transformation formulas for hypergeometric functions [16, (9.131.1)]

$${}_2F_1(a, b; c; z) = (1-z)^{c-a-b} {}_2F_1(c-a, c-b; c; z). \quad (\text{B.35})$$

It mixes the parameters a , b , and c in such a favourable way that applying (B.33) and (B.34) allows to also evaluate the limit in the second line of (B.31) by taking into account the limit representation of the exponential function

$$e^x = \lim_{b \rightarrow \infty} \left(1 + \frac{x}{b}\right)^b. \quad (\text{B.36})$$

As a result we find for the confluent hypergeometric function the asymptotic expansion [18, p. 269]

$$\begin{aligned} {}_1F_1(a; c; x) &= \frac{\Gamma(c)}{\Gamma(c-a)} (-x)^{-a} {}_2F_0\left(a, 1+a-c; \frac{-1}{x}\right) \\ &\quad + \frac{\Gamma(c)}{\Gamma(a)} x^{a-c} e^x {}_2F_0\left(1-a, c-a; \frac{1}{x}\right). \end{aligned} \quad (\text{B.37})$$

Here we introduced the generalized hypergeometric function

$${}_2F_0(a, c; x) = \sum_{\nu=0}^{\infty} (a)_{\nu} (c)_{\nu} \frac{x^{\nu}}{\nu!}, \quad (\text{B.38})$$

which is a special case of (B.17) with two Pochhammer symbols in the numerator and none in the denominator. From (B.37) we read off the asymptotic behaviour of the confluent hypergeometric function due to the property ${}_2F_0(a, c; 0) = 1$ following from (B.38):

$${}_1F_1(a; c; x) \longrightarrow \frac{\Gamma(c)}{\Gamma(c-a)} (-x)^{-a} + \frac{\Gamma(c)}{\Gamma(a)} x^{a-c} e^x, \quad |x| \rightarrow \infty. \quad (\text{B.39})$$

This result is crucial for concluding from the Dirichlet boundary condition that the eigenenergies of various quantum problems are quantized. For instance, we apply (B.39) for the quantization condition of both the harmonic oscillator in Section 1.3 and the hydrogen atom in Section 1.4.

Appendix C

Selection Rules

In this Appendix we calculate the selection rules (3.29) for electric dipole transitions in the hydrogen atom. To this end we have to investigate for which quantum numbers the dipole matrix elements (3.28) do not vanish. Here the wave functions of the electron in the hydrogen atom are needed, which are given in spherical coordinates by (1.69). In the following it turns out that the selection rules are not affected by the radial wave function $R_{nl}(r)$, only the angular dependences are decisive, which are determined by the spherical harmonics $Y_{lm}(\vartheta, \varphi)$. Namely, evaluating (3.28) in spherical coordinates, this matrix element factorises according to

$$z_{fi} = I_r \cdot I_{\vartheta, \varphi} \quad (\text{C.1})$$

into the radial component

$$I_r = \int_0^\infty dr r^3 R_{n_f l_f}(r) R_{n_i l_i}(r) \quad (\text{C.2})$$

and the angular component

$$I_{\vartheta, \varphi} = \int_0^\pi d\vartheta \sin \vartheta \int_0^{2\pi} d\varphi Y_{l_f m_f}^*(\vartheta, \varphi) \cos \vartheta Y_{l_i m_i}(\vartheta, \varphi). \quad (\text{C.3})$$

Inserting (1.75) into (C.3) yields

$$I_{\vartheta, \varphi} = \int_0^\pi d\vartheta \sin \vartheta \int_0^{2\pi} d\varphi N_{l_f m_f} P_{l_f}^{(m_f)}(\cos \vartheta) e^{-im_f \varphi} \cos \vartheta N_{l_i m_i} P_{l_i}^{(m_i)}(\cos \vartheta) e^{im_i \varphi}, \quad (\text{C.4})$$

where the normalization constants are abbreviated according to

$$N_{lm} = \sqrt{\frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!}}. \quad (\text{C.5})$$

Inserting the recurrence relation the associated Legendre polynomials (1.78) into the angular integral (C.4)

$$I_{\vartheta, \varphi} = \int_0^\pi d\vartheta \sin \vartheta \int_0^{2\pi} d\varphi N_{l_f m_f} P_{l_f}^{(m_f)}(\cos \vartheta) e^{-im_f \varphi} e^{im_i \varphi} \times \left\{ \frac{l_i + 1 - m_i}{2l_i + 1} \frac{N_{l_i m_i}}{N_{l_i+1 m_i}} N_{l_i+1 m_i} P_{l_i+1}^{(m_i)}(\cos \vartheta) + \frac{l_i + m_i}{2l_i + 1} \frac{N_{l_i m_i}}{N_{l_i-1 m_i}} N_{l_i-1 m_i} P_{l_i-1}^{(m_i)}(\cos \vartheta) \right\}. \quad (\text{C.6})$$

Taking into account the normalization constants (C.5), we yield the side calculation

$$\frac{l_{i+1} - m_i}{2l_{i+1}} \frac{N_{l_i m_i}}{N_{l_{i+1} m_i}} = \sqrt{\frac{l_i + 1 + m_i}{(2l_i + 1)(2l_i + 3)(l_i + 1 - m_i)}}, \quad (\text{C.7})$$

$$\frac{l_i + m_i}{2l_i + 1} \frac{N_{l_i m_i}}{N_{l_{i-1} m_i}} = \sqrt{\frac{l_i - m_i}{(2l_i + 1)(2l_i - 1)(l_i + m_i)}}. \quad (\text{C.8})$$

With this the angular integral (C.6) goes over into

$$\begin{aligned} I_{\vartheta, \varphi} = & \int_0^\pi d\vartheta \sin(\vartheta) \int_0^{2\pi} d\varphi Y_{l_f m_f}^*(\vartheta, \varphi) \left\{ \sqrt{\frac{l_i + 1 + m_i}{(2l_i + 1)(2l_i + 3)(l_{i+1} - m_i)}} Y_{l_{i+1} m_i}(\vartheta, \varphi) \right. \\ & \left. + \sqrt{\frac{l_i - m_i}{(2l_i + 1)(2l_i - 1)(l_i + m_i)}} Y_{l_{i-1} m_i}(\vartheta, \varphi) \right\}. \end{aligned} \quad (\text{C.9})$$

Thus, the orthonormality of the spherical harmonics (1.82) leads to

$$I_{\vartheta, \varphi} = \left\{ \sqrt{\frac{l_i + 1 - m_i}{(2l_i + 1)(2l_i + 3)(l_i + 1 - m_i)}} \delta_{l_f, l_{i+1}} + \sqrt{\frac{l_i - m_i}{(2l_i + 1)(2l_i - 1)(l_i + m_i)}} \delta_{l_f, l_{i-1}} \right\} \delta_{m_f, m_i} \quad (\text{C.10})$$

so the Kronecker symbols imply the selection rules (3.29) for the matrix elements of the z -component (3.28).

Appendix D

Sum Rules

Here we derive sum rules, which represent a basic method to formally evaluate sums or integrals over discrete or continuous quantum numbers appearing in expressions of non-degenerate perturbation theory. Concerning a concrete application we have the second perturbative order (3.52) in mind, which is needed for determining the quadratic Stark effect in Subsection 3.3.2. But we follow Ref. [30] and present the derivation in such a general way that it could straight-forwardly be extended also to higher perturbative orders.

D.1 Derivation

We start with considering the unperturbed time-independent Schrödinger equations for two different energy eigenvalues $E_n^{(0)} \neq E_m^{(0)}$:

$$\left[-\frac{\hbar^2}{2M} \Delta + V_{\text{pot.}}(\mathbf{x}) \right] \psi_n^{(0)}(\mathbf{x}) = E_n^{(0)} \psi_n^{(0)}(\mathbf{x}), \quad (\text{D.1})$$

$$\left[-\frac{\hbar^2}{2M} \Delta + V_{\text{pot.}}(\mathbf{x}) \right] \psi_m^{(0)}(\mathbf{x}) = E_m^{(0)} \psi_m^{(0)}(\mathbf{x}). \quad (\text{D.2})$$

Both equations can be multiplied with a yet unspecified function $W(\mathbf{x})$. Afterwards, multiplying (D.1) and the complex conjugate of (D.2) with $[\psi_m^{(0)}(\mathbf{x})]^*$ and $\psi_n^{(0)}(\mathbf{x})$, respectively, the difference of both expressions turns out to be independent of the potential $V_{\text{pot.}}(\mathbf{x})$ and a subsequent spatial integral yields

$$\begin{aligned} & \int d^3x W(\mathbf{x}) \left\{ [\psi_m^{(0)}(\mathbf{x})]^* \Delta \psi_n^{(0)}(\mathbf{x}) - \psi_n^{(0)}(\mathbf{x}) \Delta [\psi_m^{(0)}(\mathbf{x})]^* \right\} \\ &= \frac{2M}{\hbar^2} (E_n^{(0)} - E_m^{(0)}) \int d^3x W(\mathbf{x}) [\psi_m^{(0)}(\mathbf{x})]^* \psi_n^{(0)}(\mathbf{x}). \end{aligned} \quad (\text{D.3})$$

A first partial integration with the help of the Gauß integration theorem leads together with Dirichlet boundary conditions for the energy eigenfunctions to

$$\begin{aligned}
& \int d^3x \nabla W(\mathbf{x}) \cdot \left\{ \psi_n^{(0)}(\mathbf{x}) \nabla [\psi_m^{(0)}(\mathbf{x})]^* - [\psi_m^{(0)}(\mathbf{x})]^* \nabla \psi_n^{(0)}(\mathbf{x}) \right\} \\
&= \frac{2M}{\hbar^2} (E_n^{(0)} - E_m^{(0)}) \int d^3x W(\mathbf{x}) [\psi_m^{(0)}(\mathbf{x})]^* \psi_n^{(0)}(\mathbf{x}). \tag{D.4}
\end{aligned}$$

Now we perform for the first term on the left-hand side another partial integration with the help of the Gauß integration theorem and get

$$\begin{aligned}
& \int d^3x [\psi_m^{(0)}(\mathbf{x})]^* \left\{ \psi_n^{(0)}(\mathbf{x}) \Delta W(\mathbf{x}) + 2 \nabla W(\mathbf{x}) \cdot \nabla \psi_n^{(0)}(\mathbf{x}) \right\} \\
&= \frac{2M}{\hbar^2} (E_n^{(0)} - E_m^{(0)}) \int d^3x W(\mathbf{x}) [\psi_m^{(0)}(\mathbf{x})]^* \psi_n^{(0)}(\mathbf{x}). \tag{D.5}
\end{aligned}$$

We assume that a function $W(\mathbf{x})$ could be determined from solving the differential function

$$\psi_n^{(0)}(\mathbf{x}) \Delta W(\mathbf{x}) + 2 \nabla W(\mathbf{x}) \cdot \nabla \psi_n^{(0)}(\mathbf{x}) = V(\mathbf{x}) \psi_n^{(0)}(\mathbf{x}). \tag{D.6}$$

Here $V(\mathbf{x})$ denotes a given function, which represents later on the perturbation in the Hamilton operator. Then (D.5) reduces to

$$\int d^3x [\psi_m^{(0)}(\mathbf{x})]^* V(\mathbf{x}) \psi_n^{(0)}(\mathbf{x}) = \frac{2M}{\hbar^2} (E_n^{(0)} - E_m^{(0)}) \int d^3x [\psi_m^{(0)}(\mathbf{x})]^* W(\mathbf{x}) \psi_n^{(0)}(\mathbf{x}). \tag{D.7}$$

Let us convert this result from the coordinate representation to the representation independent Dirac notation:

$$\frac{\langle \psi_m^{(0)} | \hat{V} | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} = \frac{2M}{\hbar^2} \langle \psi_m^{(0)} | \hat{W} | \psi_n^{(0)} \rangle. \tag{D.8}$$

This key formula will now be the starting point for simplifying sums or integrals over discrete or continuous quantum numbers as they appear in expressions of non-degenerate perturbation theory.

D.2 Second Order

We demonstrate the generic procedure at first for the second-order perturbative result. To this end we multiply (D.8) with $\langle \psi_n^{(0)} | \hat{V} | \psi_m^{(0)} \rangle$ and sum (integrate) over all discrete (continuous) quantum numbers:

$$\sum_{m \neq n} \frac{|\langle \psi_m^{(0)} | \hat{V} | \psi_n^{(0)} \rangle|^2}{E_n^{(0)} - E_m^{(0)}} = \frac{2M}{\hbar^2} \sum_{m \neq n} \langle \psi_n^{(0)} | \hat{V} | \psi_m^{(0)} \rangle \langle \psi_m^{(0)} | \hat{W} | \psi_n^{(0)} \rangle. \tag{D.9}$$

At the right-hand side of (D.9) we can use the completeness relation of the unperturbed energy eigenstates

$$\sum_n |\psi_m^{(0)} \rangle \langle \psi_m^{(0)}| = 1 \tag{D.10}$$

by rewriting it as follows:

$$\sum_{m \neq n}^f \int |\psi_m^{(0)}\rangle\langle\psi_m^{(0)}| = 1 - |\psi_n^{(0)}\rangle\langle\psi_n^{(0)}|. \quad (\text{D.11})$$

Taking into account the notation for the matrix elements (2.27), Eq. (D.9) reduces with the help of (D.11) to the sum rule that the second-order perturbative result (3.52) can be recast into the form (3.53), which is due to (2.28) equivalent to

$$E_n^{(2)} = \frac{2M}{\hbar^2} \left[(VW)_{nn} - E_n^{(1)} W_{nn} \right]. \quad (\text{D.12})$$

D.3 Third Order

Intriguingly this procedure is not restricted to the second perturbative order but can also be extended straight-forwardly to higher orders. To this end we use the hermiticity (2.33) of the matrix element (2.27) and derive from (D.8) the complementary result

$$\frac{\langle\psi_n^{(0)}|\hat{V}|\psi_m^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}} = \frac{2M}{\hbar^2} \langle\psi_n^{(0)}|\hat{W}|\psi_m^{(0)}\rangle. \quad (\text{D.13})$$

On the one hand, combining (D.8) and (D.13) then yields

$$\frac{\langle\psi_n^{(0)}|\hat{V}|\psi_l^{(0)}\rangle}{E_n^{(0)} - E_l^{(0)}} \langle\psi_l^{(0)}|\hat{V}|\psi_{l'}^{(0)}\rangle \frac{\langle\psi_{l'}^{(0)}|\hat{V}|\psi_n^{(0)}\rangle}{E_n^{(0)} - E_{l'}^{(0)}} = \left(\frac{2M}{\hbar^2}\right)^2 \langle\psi_n^{(0)}|\hat{W}|\psi_l^{(0)}\rangle \langle\psi_l^{(0)}|\hat{V}|\psi_{l'}^{(0)}\rangle \langle\psi_{l'}^{(0)}|\hat{W}|\psi_n^{(0)}\rangle \quad (\text{D.14})$$

Summing (integrating) over the discrete (continuous) quantum numbers l, l' gives with applying (D.11) twice

$$\begin{aligned} & \sum_{l, l' \neq n} \frac{\langle\psi_n^{(0)}|\hat{V}|\psi_l^{(0)}\rangle \langle\psi_l^{(0)}|\hat{V}|\psi_{l'}^{(0)}\rangle \langle\psi_{l'}^{(0)}|\hat{V}|\psi_n^{(0)}\rangle}{\left(E_n^{(0)} - E_l^{(0)}\right) \left(E_n^{(0)} - E_{l'}^{(0)}\right)} \\ &= \left(\frac{2M}{\hbar^2}\right)^2 \left\langle \psi_n^{(0)} \left| \hat{W} \left(1 - |\psi_n^{(0)}\rangle\langle\psi_n^{(0)}| \right) \hat{V} \left(1 - |\psi_n^{(0)}\rangle\langle\psi_n^{(0)}| \right) \hat{W} \right| \psi_n^{(0)} \right\rangle, \quad (\text{D.15}) \end{aligned}$$

which yield with taking into account the matrix element (2.27)

$$\sum_{l, l' \neq n} \frac{V_{nl} V_{l'l} V_{l'n}}{\left(E_n^{(0)} - E_l^{(0)}\right) \left(E_n^{(0)} - E_{l'}^{(0)}\right)} = \left(\frac{2M}{\hbar^2}\right)^2 \left[(VW^2)_{nn} - 2W_{nn} (VW)_{nn} + W_{nn}^2 V_{nn} \right]. \quad (\text{D.16})$$

On the other hand, another combination of (D.8) and (D.13) amounts to

$$\frac{\langle\psi_n^{(0)}|\hat{V}|\psi_l^{(0)}\rangle}{E_n^{(0)} - E_l^{(0)}} \frac{\langle\psi_l^{(0)}|\hat{V}|\psi_n^{(0)}\rangle}{E_n^{(0)} - E_l^{(0)}} = \left(\frac{2M}{\hbar^2}\right)^2 \langle\psi_n^{(0)}|\hat{W}|\psi_l^{(0)}\rangle \langle\psi_l^{(0)}|\hat{W}|\psi_n^{(0)}\rangle, \quad (\text{D.17})$$

which leads with the matrix element (2.27) and (D.11) to

$$\sum_{l \neq n} \frac{V_{nl} V_{ln}}{\left(E_n^{(0)} - E_l^{(0)}\right)^2} = \left(\frac{2M}{\hbar^2}\right)^2 \left[(W^2)_{nn} - W_{nn}^2 \right]. \quad (\text{D.18})$$

Thus, we obtain for the third-order perturbative result from (4.41)

$$E_n^{(3)} = \sum_{l,l' \neq n} \frac{V_{nl}V_{l'l}V_{l'n}}{(E_n^{(0)} - E_l^{(0)})(E_n^{(0)} - E_{l'}^{(0)})} - V_{nn} \sum_{l \neq n} \frac{V_{nl}V_{ln}}{(E_n^{(0)} - E_l^{(0)})^2} \quad (\text{D.19})$$

by combining and (D.16) and (D.18) the sum rule

$$E_n^{(3)} = \left(\frac{2M}{\hbar^2}\right)^2 \left[(VW^2)_{nn} - 2W_{nn}(VW)_{nn} - V_{nn}(W^2)_{nn} + 2W_{nn}^2 V_{nn} \right]. \quad (\text{D.20})$$

Taking into account (D.12) this amounts to

$$E_n^{(3)} = \left(\frac{2M}{\hbar^2}\right)^2 \left[(VW^2)_{nn} - 2\frac{2M}{\hbar^2} E_n^{(2)} W_{nn} - \left(\frac{2M}{\hbar^2}\right)^2 E_n^{(1)} (W^2)_{nn} \right]. \quad (\text{D.21})$$

D.4 General Perturbative Order

It is now straight-forward to derive in the same way the corresponding sum rule also for the fourth perturbative order, which is contained in (4.41). Therefore, we leave this task to the interested reader. Instead, we aim at developing another strategy to directly obtain the fourth-order sum rule. To this end we go one step back and revisit the second- and the third-order sum rule (3.53) and (D.20) with the aim to generalize it to any perturbative order. The common property of the sum rules (3.53) and (D.20) is that they all consist of expectation values of operators with respect to the unperturbed eigenstate $|\psi_n^{(0)}\rangle$ for which the respective perturbative energy correction is obtained. Furthermore, it is obvious that the k th perturbative correction of the energy eigenvalue $E_n^{(k)}$ involves the expectation value with one operator \hat{V} and $k - 1$ operators \hat{W} :

$$E_n^{(k)} \hat{=} (VW^{k-1})_{nn}. \quad (\text{D.22})$$

In the second-order sum rule (3.53) we recognize that $E_n^{(2)}$ is given by

$$E_n^{(2)} = \frac{2M}{\hbar^2} (VW)_{nn}^c, \quad (\text{D.23})$$

where we have introduced the variance

$$(VW)_{nn}^c = (VW)_{nn} - V_{nn}W_{nn}, \quad (\text{D.24})$$

which is the second cumulant. Therefore, it is suggestive to conjecture that the third-order sum rule (D.21) coincides with

$$E_n^{(3)} = \left(\frac{2M}{\hbar^2}\right)^2 (VW^2)_{nn}^c, \quad (\text{D.25})$$

where a third cumulant appears.

Note that expectation values, also called moments, and cumulants represent basic quantities in probability theory to describe the properties of probability distributions. Let us explain their respective definitions in the context of our current problem. To this end we consider a set of N operators: $\hat{O}_1, \hat{O}_2, \dots, \hat{O}_N$. Then their respective expectation values are defined by the moment generating function

$$\left(e^{z_1 O_1 + z_2 O_2 + \dots + z_N O_N} \right)_{nn} = \sum_{l_1=0}^{\infty} \sum_{l_2=0}^{\infty} \dots \sum_{l_N=0}^{\infty} \frac{z_1^{l_1}}{l_1!} \frac{z_2^{l_2}}{l_2!} \dots \frac{z_N^{l_N}}{l_N!} \left(O_1^{l_1} O_2^{l_2} \dots O_N^{l_N} \right)_{nn}, \quad (\text{D.26})$$

while the cumulants are defined by the cumulant generating function

$$\ln \left(e^{z_1 O_1 + z_2 O_2 + \dots + z_N O_N} \right)_{nn} = \sum_{l_1=0}^{\infty} \sum_{l_2=0}^{\infty} \dots \sum_{l_N=0}^{\infty} \prime \frac{z_1^{l_1}}{l_1!} \frac{z_2^{l_2}}{l_2!} \dots \frac{z_N^{l_N}}{l_N!} \left(O_1^{l_1} O_2^{l_2} \dots O_N^{l_N} \right)_{nn}^c. \quad (\text{D.27})$$

Here the prime sign denotes that the term with $l_1 = l_2 = \dots = l_N = 0$ is excluded from the summation [31]. Moments and cumulants can be expressed by cumulants and vice versa. In order to obtain their respective relations it is possible to apply a recursive procedure. To this end we start with O_1 and get its first moment, which coincides with its first cumulant:

$$(O_1 O_2 \dots O_N)_{nn} = (O_1)_{nn} (O_2 \dots O_N)_{nn} + \dots \quad (\text{D.28})$$

Then we take all possible second-order cumulants of O_1 with any other observable O_2, \dots, O_N :

$$\begin{aligned} (O_1 O_2 \dots O_N)_{nn} &= (O_1)_{nn} (O_2 \dots O_N)_{nn} \\ &+ \sum_{l_1=2}^N (O_1 O_{l_1})_{nn}^c (O_2 \dots O_{l_1-1} O_{l_1+1} \dots O_N)_{nn} + \dots \end{aligned} \quad (\text{D.29})$$

And then one has to go to all higher cumulants in the same way until, finally, the N th-order cumulant appears:

$$\begin{aligned} (O_1 O_2 \dots O_N)_{nn} &= (O_1)_{nn} (O_2 \dots O_N)_{nn} \\ &+ \sum_{l=2}^N (O_1 O_l)_{nn}^c (O_2 \dots O_{l-1} O_{l+1} \dots O_N)_{nn} + \dots + (O_1 O_2 \dots O_N)_{nn}^c. \end{aligned} \quad (\text{D.30})$$

Note that for determining the remaining moments one has to use recursively (D.30) until at the right-hand side only cumulants appear.

Let us apply this recursive procedure to our situation. At first we get

$$(VW)_{nn} = V_{nn} W_{nn} + (VW)_{nn}^c, \quad (\text{D.31})$$

which recovers the second cumulant (D.24). And then we obtain

$$(VW^2)_{nn} = V_{nn} (W_{nn}^2) + 2 (VW)_{nn}^c W_{nn} + (VW^2)_{nn}^c, \quad (\text{D.32})$$

so combining (D.21), (D.25), and (D.32) reproduces, indeed, our previous result (D.22). As this proves our conjecture (D.25) for the third-order sum rule, we extend it to any perturbative order:

$$E_n^{(k)} = \left(\frac{2M}{\hbar^2} \right)^{k-1} (VW^{k-1})_{nn}^c. \quad (\text{D.33})$$

Again we leave it to the interested reader to verify this conjecture also for the fourth order.

Appendix E

Useful Integrals

Here we deal with two integrals, which appear occasionally in theoretical physics.

E.1 First Integral

At first we determine the integral

$$\int_{-\infty}^{\infty} dx \frac{\sin x}{x}, \quad (\text{E.1})$$

where the integrand is known as the sinc-function. To this end we consider the family of auxiliary integrals

$$I(a) = \int_0^{\infty} dx \frac{\sin x}{x} e^{-ax}, \quad a > 0, \quad (\text{E.2})$$

which vanish in the limit that the family parameter a tends to infinity:

$$I(\infty) = 0. \quad (\text{E.3})$$

The partial derivative of (E.2) with respect to a then yields the elementary integral

$$\frac{\partial I(a)}{\partial a} = - \int_0^{\infty} dx \sin x e^{-ax}, \quad (\text{E.4})$$

which is straight-forwardly calculated, for instance, as follows:

$$\frac{\partial I(a)}{\partial a} = -\text{Im} \int_0^{\infty} dx e^{-(a-i)x} = -\text{Im} \frac{1}{a-i} = -\text{Im} \frac{a+i}{a^2+1} = -\frac{1}{a^2+1}. \quad (\text{E.5})$$

Integrating (E.5) with respect to a and implementing (E.3) we get $b = \pi/2$ and with this

$$I(a) = \frac{\pi}{2} - \arctan a. \quad (\text{E.6})$$

Thus, due to (E.2), evaluating (E.6) at $a = 0$ leads to the wanted integral (E.1):

$$\int_{-\infty}^{\infty} dx \frac{\sin x}{x} = 2 I(0) = \pi. \quad (\text{E.7})$$

E.2 Second Integral

Now we deal with the integral, which appears in (5.45):

$$\int_{-\infty}^{\infty} dx \frac{\sin^2 x}{x^2}, \quad (\text{E.8})$$

where the integrand is the square of the sinc-function, which occurs, for instance, also at the slit diffraction. Again we proceed by considering a family of integrals

$$J(b) = \int_{-\infty}^{\infty} dx \frac{\sin^2(bx)}{x^2}, \quad (\text{E.9})$$

which fulfill the property

$$J(0) = 0. \quad (\text{E.10})$$

Performing here the derivative with respect to the family parameter b yields

$$\frac{\partial J(b)}{\partial b} = \int_{-\infty}^{\infty} dx \frac{\sin(2bx)}{x}, \quad (\text{E.11})$$

which reduces with the substitution $z(x) = 2bx$ to the integral (E.7). Thus, we obtain a result, which turns out to be independent of b :

$$\frac{\partial J(b)}{\partial b} = \pi. \quad (\text{E.12})$$

Integrating (E.12) with respect to b and taking into account (E.10) we finally obtain

$$\int_{-\infty}^{\infty} dx \frac{\sin^2 x}{x^2} = J(1) = \pi. \quad (\text{E.13})$$

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