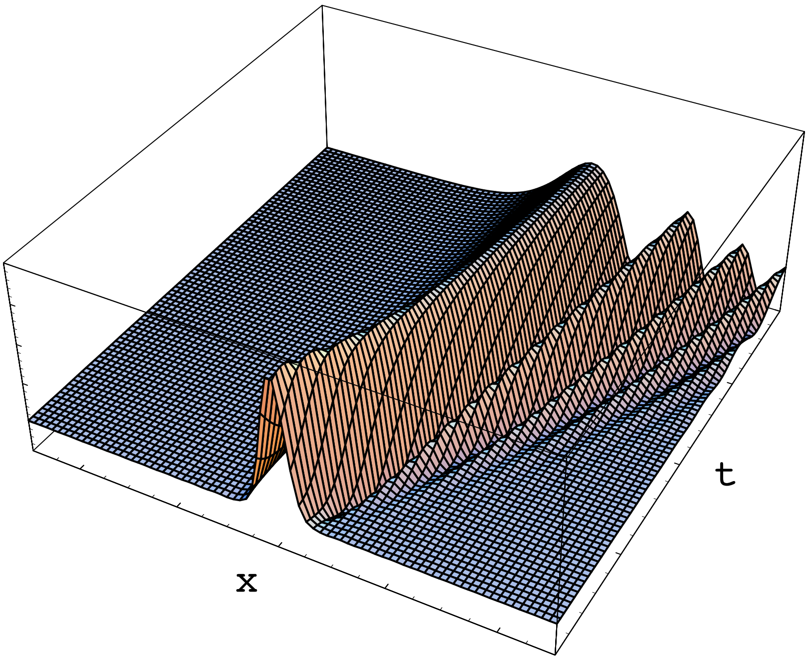
School of Mathematics and Natural Sciences
Physics Department
Bergische Universität Wuppertal

A course on

Introductory Quantum Theory



by

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Preface

I recall a physics student expressing his opinion that "real physics" begins with quantum mechanics. This opinion, to which I cannot agree, probably is due to the "strangeness" in quantum theory, which is summarized in an often cited quote by the late Richard Feynman [1] expressing his believe that "nobody really understands quantum mechanics".

These lecture notes cover introductory quantum theory to an extend that can be presented in a one semester course. The subject is approached by looking first at some of the pressing questions by the end of the 19th century, when classical physics, in the eyes of many, had come close to explaining all known physical phenomena. We will focus on a special question (e.g. the black body problem), then introduce an idea or concept to answer this question in simple terms (e.g. energy quantization), relate the quantum theoretical answer to classical theory or experiment, and finally progress deeper into the mathematical formalism if it provides a general basis for answering the next question. In this spirit we develop quantum theory by adding in a step by step procedure postulates and abstract concepts, testing the theory as we go along, i.e. we will accept abstract and maybe sometimes counter-intuitive concepts as long as they lead to verifiable predictions.

Chapter one is devoted to the early developments in quantum theory [2]; chapter two provides a formal basis for quantum mechanics treating bound state problems; chapter three deals with scattering; chapter four introduces perturbation theory together with selected numerical techniques; in chapter five we turn to many particle systems and exploit the fact that in nature there are two types of particles-fermions and bosons; the final chapter, chapter six, presents a short glimpse at the quantized radiation field and second quantization. Chapters five and six mark the departure of physics from chemistry as far as university education is concerned. Atomic or molecular systems with more than two electrons are usually reserved for students of quantum chemistry. Solids as well as advanced quantum theory, which leads to the physics of elementary particles, appear to be the domain of physics students. Here, in a limited sense of course, I attempt to satisfy both tastes. Because of this the lecture does not follow one particular text. However, in preparing these notes I have been guided by the references [5, 6, 7, 8]. Additional textbooks on quantum mechanics containing most of the material discussed here include [9, 10, 11, 12, 13].

The initial version of these notes was prepared for a course on introductory quantum mechanics during the fall/winter term 2002/2003. Subsequently these notes were used and extended during the summers of 2004, 2006, 2007, as well as during the fall/winter terms 2008/2009 and 2015/16. I owe thanks to many students during these years for their valuable comments.

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[1] Feynman, Richard Phillips, american physicist, *New York 11.5.1918, †Los Angeles 15.2.1988; he made many seminal contributions to theoretical physics including the theory of superfluid helium and, in particular, to the development of quantum electrodynamics. He introduced the Feynman diagram technique and the concept of path integration. He not only was a brilliant scientist but also famous for his way of teaching physics. In 1965 he was awarded the Nobel prize in physics together with Julian S. Schwinger and Sin-Itiro Tomonaga.

[2] The student should be aware that these lecture notes, for the most part, cover only a few years in the development of quantum theory, i.e. "early" is appropriate in a limited sense only. In 1900 Planck presented his treatment of black body radiation; Einstein's interpretation of the photoelectric effect appeared in 1905/06; Bohr's seminal work "On the constitution of atoms and molecules" was published in 1913. But after 1925/26, when a formal framework (matrix mechanics/wave mechanics) had been suggested to do calculations, the development became extremely rapid! Maybe not surprising it took only about five years and a number of textbooks on quantum mechanics had appeared (e.g, Weyl, 1930 [1]; Dirac, 1930 [2]; von Neumann, 1932 [3]). These lecture notes, as almost all texts aimed at beginners, do (partially!) cover this exciting period only. A good historical source on important steps in physics in the 19th and early 20th century leading up to the developments discussed here is A. Sommerfeld's "Atombau und Spektrallinien" [4], which first appeared in 1919!

Chapter 1

Early developments in quantum mechanics

1.1 Quantization conditions

The year 1900 marks the beginning of what we call "Quantum Theory". Until then various physicists of reputation had failed to derive a valid formula describing the frequency dependence of radiation intensity emitted from a black body. A black body can be a metal cavity with walls kept at a fixed temperature T. A small hole drilled into the walls of this oven will allow radiation to escape - the black body radiation. This may sound academic. But what makes this problem especially interesting is, that all prior calculations were based on apparently well founded theories like Maxwell's [1] equations and classical statistical mechanics. These pillars of physics, however, as we shall see below, produced nonsense. In order to obtain a correct formula describing black body radiation the physicist Max Planck [2] had to introduce a revolutionary concept. The energy of the radiation field inside the black body is not continuous. It is the sum of discrete amounts of energy of size $h\nu$ or $\hbar\omega$. Here ν is the radiation frequency ($\omega = 2\pi\nu$), and h is the now famous Planck's constant (dt.: Planckscches Wirkungsquantum)

$$h = 6.6256 \pm 0.0005 \cdot 10^{-34} Js \, .$$

Discrete entities were not new in science at that time. Chemists had long accepted the notion that matter consists of atoms. This idea was formulated by Dalton [3] in his book *A new system of chemical philosophy*, which appeared in two volumes in 1808 and 1810. Also, Thomson [4] in 1897 had discovered the electron. However, energy was firmly believed to be continuous. E.g., we all are used to changing the speed of our car and thus its kinetic energy continuously. However, like matter, which macroscopically appears continuous but microscopically must be 'chemically' discrete in order to explain chemical reactions and their mass ratios, energy also reveals its discrete nature on the microscopic scale. That classical physics had worked to everybody's satisfaction had to do with the experimental inability of that time to probe the microscopic (or atomic) scale. However, in addition to the black body problem, where a microscopic phenomenon could be measured macroscopically, scientists already knew of other troubling facts. Chemists had come up with the periodic table. But how chemical reactions really work or the nature of chemical bounds were beyond comprehension. Spectral lines of simple atoms, e.g., hydrogen (Balmer series [5]),

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[1] Maxwell, James Clerk, british physicist, *Edinburgh 13.6.1831, †Cambridge 5.11.1879; he is best known for his theory of electromagnetism, i.e. the Maxwell equations. However, he also made important contributions in other areas in physics, e.g. kinetic gas theory, and mathematics.

[2] Planck, Max, german physicist, *Kiel 23.4.1858, †Göttingen 4.10.1947; his solution to the black body problem laid the foundation to the development of quantum theory. For this work he received the Nobel prize in physics in 1918.

[3] Dalton, John, british scientist, *Eaglesfield (County Cumbria) 5. or 6.9.1766, †Manchester 27.7.1844

[4] Thomson, Sir (since 1908) Joseph John, british physicist, *Cheetham Hill (now Manchester) 18.12.1856, †Cambridge 30.8.1940; Nobel prize in physics 1906.

[5] Balmer, Johann Jakob, swiss mathematician, *Lausen (Kanton Basel-Landschaft) 1.5.1825, †Basel 12.3.1898

had been measured but could not be explained. Besides Planck other scientist were productive too. J. J. Thomson, who had discovered the electron, suggested a new model for the atom in 1904. According to him atoms are small spheres of certain mass containing a uniformly distributed positive charge as well as a corresponding number of electrons embedded into this positive background. An improved model was suggested by E. Rutherford [6] in 1911 based on his experiments in which he bombarded thin metal foils with α-particles. His model was essentially a planetary system with a tiny positive nucleus at the center circled by electrons. This immediately caused a problem. According to Maxwell's theory accelerated charges emit radiation. Therefore Rutherford's atoms should lose energy and collapse. Similar to Planck in the case of the black body Niels Bohr [7] postulated a solution to this problem. In his model of the atom the electrons are confined to discrete orbits E_1, E_2, ... They may however absorb one of Planck's radiation packages, if it supplies the proper amount of energy separating two orbits, e.g. $\hbar\omega = E_{n+1} - E_n$. This package also may be emitted, and the electron returns to its previous orbit. However, there always exists an orbit whose energy is lowest, and therefore the atom cannot collapse. These postulates were in accord with Einstein's [8] earlier explanation of the photoelectric effect. A metal surface exposed to electromagnetic radiation (e.g., visible light) emits electrons if the radiation exceeds a threshold frequency ν_0. Below ν_0 no electrons are emitted, independent of the radiation's intensity! The kinetic energy of the emitted electrons, $\frac{1}{2}m_e v^2$, is described by

$$\frac{1}{2}m_e v^2 + \phi_0 = \hbar\omega \tag{1.1}$$

with $\phi_0 = \hbar\omega_0\,(= h\nu_0)$. The constant ϕ_0 is called the work function [9].

Nevertheless, Bohr's postulates were merely postulates. To justify postulates, which were in disagreement with Maxwell's beautiful theory of electromagnetism, Bohr needed to make verifiable predictions based on his model. He needed a quantization condition. In 1924 Louis deBroglie [10] suggested the relation

$$p = \frac{h}{\lambda} \tag{1.2}$$

connecting the momentum of a particle (e.g., an electron) to a wavelength λ via Planck's constant. DeBroglie's idea that an electron may behave as a wave was proven experimentally by C. Davisson and L. Germer in 1927, who observed electron diffraction from a nickel crystal. This introduced the concept of particle-wave-dualism. DeBroglie's relation immediately allows to write down an expression for the orbital energy of the electron in the hydrogen atom, which for instance explains the Balmer series [11].

From the Kepler problem in classical mechanics we borrow the relation $-\frac{1}{2}\bar{\mathcal{U}} = \bar{\mathcal{K}}$, where $\bar{\mathcal{U}}$ and $\bar{\mathcal{K}}$ are the average potential and kinetic energy respectively [12]. For a simple circular orbit of radius a we therefore have

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[6] Rutherford, Ernest, Lord Rutherford of Nelson (since 1931), british physicist, *Brightwater (New Zealand) 30.8.1871, †Cambridge 19.10.1937; one of the most outstanding experimentalists in the 20. century, concentrating on nuclear physics. He was awarded the Nobel prize in chemistry in 1908.

[7] Bohr, Niels Henrik David, danish physicist, *Kopenhagen 7.10.1885, †Kopenhagen 18.11.1962; he was the leading (father) figure in the early development of quantum physics. His model of the atom paved the way to our understanding of the nano-world. In 1922 he was awarded the Nobel prize in physics.

[8] Einstein, Albert, german/american physicist, *Ulm 14.3.1879, †Princeton (New Jersey) 18.4.1955; perhaps the one most outstanding scientists of all times. His work had profound influence on all areas in physics and science in general, including cosmology, quantum physics, and many-body theory. He was awarded the Nobel prize in physics in 1921.

[9] The photoelectric effect can be used to measure $\hbar$.

[10] Broglie, Louis-Victor, french physicist, *Dieppe 15.8.1892, †Louveciennes (D'epartement Yvelines) 19.3.1987; 1929 Nobel prize in physics.

[11] This sounds as if Bohr had to wait until deBroglie had put forward his idea. But this is not true. We merely choose this path because relation (1.2) allows to interpret Bohr's quantization conditions via the wave-picture of particles.

[12] This is easy to show in the special case of a circular orbit. The constant kinetic energy is $\mathcal{K} = (\mu/2)(r\dot{\varphi})^2$, where μ is the (reduced) mass, r is the orbit's radius, and $\dot{\varphi}$ is the constant angular velocity. The latter may be related to the constant potential energy, $\mathcal{U} = -\alpha/r$ (with $\alpha > 0$), via Newton's second law, $\mu\ddot{\vec{r}} = -\vec{\nabla}\mathcal{U} = -\vec{e}_r \cdot \partial\mathcal{U}/\partial r = -\vec{e}_r\alpha/r^2$. Using polar coordinates, i.e. $\vec{r} = r(\cos\varphi, \sin\varphi) = r\vec{e}_r$ we obtain $\dot{\vec{r}} = r\dot{\varphi}(-\sin\varphi, \cos\varphi)$ and $\ddot{\vec{r}} = -r\dot{\varphi}^2\vec{e}_r$. We find the relation $(r\dot{\varphi})^2 = \alpha/(\mu r)$ and therefore $\mathcal{K} = -\mathcal{U}/2$. This relation, as we have mentioned, holds for general Kepler orbits if $\mathcal{K}$ and $\mathcal{U}$ are replaced by their averages over one complete orbit (cf. [14] exercise 24).

$$\frac{p^2}{2\mu} = \frac{1}{2}\frac{e^2}{a} \ , \tag{1.3}$$

where $\mu = m_e m_n/(m_e + m_n)$ is the reduced mass, and $-e$ is the electron charge [13]. Requiring that the circumference of the orbit corresponds to an integer number of deBroglie wavelengths, a standing electron wave, we find the quantization condition

$$2\pi a = n\lambda \quad (n = 1, 2, \ldots) \ . \tag{1.4}$$

Putting (1.2), (1.3) and (1.4) together we obtain

$$\frac{1}{a} = \frac{\mu e^2}{\hbar^2}\frac{1}{n^2} \ . \tag{1.5}$$

With $E = \bar{\mathcal{K}} + \bar{\mathcal{U}} = \frac{1}{2}\bar{\mathcal{U}}$ follows

$$E_n = -\frac{\mu e^4}{2\hbar^2}\frac{1}{n^2} = -13.6 \ eV \frac{1}{n^2} \tag{1.6}$$

[14]. The quantity n is called quantum number. Thus, an electromagnetic energy packet or photon emitted during the transition from an excited state $(n = m)$ to the ground state $(n = 1)$ should be given by

$$\hbar\omega_{m\to 1} = -13.6 \ eV \left(\frac{1}{m^2} - 1\right) \ . \tag{1.7}$$

This is an agreement with the experiment! [15]

But Bohr's theory must pass another test. When we increase the orbit of the electron to macroscopic dimensions in what we call a Gedankenexperiment it should obey Maxwell's equations and thus emit radiation according to this classical theory. According to classical mechanics we have $\mid \vec{L} \mid \equiv L = \mu a^2 \dot{\phi} = \mu a^2 \omega_{cl}$. Here $\vec{L}$ is the angular momentum vector, and ϕ is the angle of the position vector $\vec{r}(\mid \vec{r} \mid \equiv a)$ with a fixed axis in the two-body problem. Condition (1.4) immediately implies

$$L = n\hbar \ . \tag{1.8}$$

Combining this with the above equation as well as (1.5) we obtain for the classical orbital frequency

$$\omega_{cl} = \frac{\mu e^4}{\hbar^3 n^3} \ . \tag{1.9}$$

For large n this should be equal to ω_{qt} obtained via a transition from orbit $n + 1$ to orbit n:

$$\begin{aligned} \omega_{qt} &= -\frac{\mu e^4}{2\hbar^3}\left(\frac{1}{(n+1)^2} - \frac{1}{n^2}\right) \\ &= -\frac{\mu e^4}{2\hbar^3}\frac{1}{n^2}\left(\frac{1}{(1+\frac{1}{n})^2} - 1\right) \\ &\approx -\frac{\mu e^4}{2\hbar^3}\frac{1}{n^2}\left(1 - 2\frac{1}{n} - 1\right) \\ &= \frac{\mu e^4}{\hbar^3 n^3} \ . \end{aligned}$$

This is an example of the important correspondence principle, which describes the classical limit of quantum theory.

Here we may look at the classical limit from another angle. For large n we always require

$$\frac{\Delta E_n}{\hbar \Delta n} \to \omega_{cl} \ . \tag{1.10}$$

In the case of Eq. (1.6) for example we have

$$\frac{\Delta E_n}{\Delta n} \approx \frac{dE_n}{dn} = \frac{\mu e^4}{\hbar^2}\frac{1}{n^3} \overset{(1.9)}{=} \hbar w_{cl} \ .$$

Integrating Eq. (1.10) we obtain

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[13] Here we have omitted the factor $(4\pi\epsilon_o)^{-1}$ multiplying the potential energy, i.e. we occasionally toggle between the MKSA and the Gauß unit systems.

[14] If a charge q is accelerated due to the force $F = qE$, where E is the electric field strength, between two parallel plates of a capacitor, then the energy ΔE it gains is given by

$$\Delta E = Fd = qEd = -dq\Delta\phi/d = -q\Delta\phi \ .$$

Here d is the plate-to-plate separation and $\Delta\phi$ is the voltage drop from one plate to the other. If $q = -1.602 \cdot 10^{-19} \ C$, the charge of an electron, and $\Delta\phi = 1 \ V$, then ΔE equals 1 eV. Notice: $1 \ eV = 96.5 \ kJ/mol$.

[15] This particular series of frequencies is called Lyman-series (1906). Balmer's series corresponds to $\hbar\omega_{m\to 2} = -13.53 eV\left(\frac{1}{m^2} - \frac{1}{4}\right)$.

$$\frac{1}{h}\int_0^{E_n}\frac{dE}{\nu\,(E)}=\int_0^n dn'=n\;. \tag{1.11}$$

This equation may be cast in another useful form, i.e.

$$\oint pdq=hn\;, \tag{1.12}$$

where the loop integral covers the area in classical phase space bounded by a trajectory corresponding to the energy E [16].

We show Eq. (1.12) utilizing the classical action (dt.: Wirkung), $S=S\,(q,t)$, as a function of the (generalized) coordinate q and time t [17]. It is useful to introduce a Legendre transformation to a new function, $\tilde{S}=\tilde{S}\,(q,\mathcal{H})$, where $\mathcal{H}$ is the Hamilton function [18], via

$$\begin{aligned} d\tilde{S} &= d\,(\mathcal{H}t)+dS \\ &= td\mathcal{H}+\mathcal{H}dt+\underbrace{\frac{\partial S}{\partial q}}_{=p}dq+\underbrace{\frac{\partial S}{\partial t}}_{=-\mathcal{H}}dt \\ &= pdq+td\mathcal{H} \end{aligned}$$

Setting $\mathcal{H}=E=const$ we integrate the last equation between q and q_o to obtain

$$\tilde{S}(q,E)-\tilde{S}(q_o,E)=\int_{q_o}^q pdq'\;.$$

Now we take the derivative with respect to E:

$$\underbrace{\frac{\partial\tilde{S}(q,E)}{\partial E}}_{=t}-\underbrace{\frac{\partial\tilde{S}(q_o,E)}{\partial E}}_{=t_o}=\frac{\partial}{\partial E}\int_{q_o}^q pdq'\;.$$

Here t and t_o correspond to $q=q(t)$ and $q_o=q(t_o)$. Extending the integration over a full period of the (periodic) motion yields

$$T(E)=\frac{\partial}{\partial E}\oint pdq\;.$$

Note that $T(E)=1/\nu(E)$ is the period of the orbit corresponding to the energy E. Finally we integrate this equation from 0 to E, which yields the desired equality

$$\int_0^E T(E')dE'=\int_0^E\frac{dE'}{\nu\,(E')}=\oint pdq\;. \tag{1.13}$$

This is a result of classical mechanics. We test Eq. (1.13) using the classical harmonic oscillator, $E=p^2/(2m)+(k/2)x^2$, as an example. Because the oscillator's period is $T=2\pi\sqrt{m/k}$ we have

$$\int_0^E T(E')dE'=T\int_0^E dE'=2\pi\sqrt{\frac{m}{k}}E\;. \tag{1.14}$$

Now we evaluate the right side of Eq. (1.13), i.e.

$$\begin{aligned} \oint pdq &= 2\int_{-\sqrt{2E/k}}^{\sqrt{2E/k}}dx\sqrt{2m\left(E-\frac{k}{2}x^2\right)} \\ &= 2\sqrt{2mE}\sqrt{\frac{2E}{k}}\underbrace{\int_{-1}^1 dz\sqrt{1-z^2}}_{=\pi/2} \\ &= 2\pi\sqrt{\frac{m}{k}}E\;, \end{aligned} \tag{1.15}$$

where $\sqrt{2E/k}$ is the amplitude of the oscillator. Obviously the two results, (1.14) and (1.15), do agree.

1.2 The black body problem

At this point we want to consider the black body problem explicitly to figure out what goes wrong as well as how to correct classical theory [19].

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[16] Notice that by using $p_\phi=\mid\vec{L}\mid$ we obtain $\oint p_\phi d\phi=\oint Ld\phi=nh$. This is the generalized form of Eq. (1.8).

[17] cf. the section on Hamilton-Jacobi theory in Ref. [14].

[18] Hamilton, Sir (since 1835) William Rowan, irish mathematician and physicist, *Dublin 4.8.1805, †Dunsink (near Dublin) 2.9.1865.

[19] Historically, this system has been looked upon from two, practically identical but conceptually different, points of view: (i) The earlier one, the one we take here, views the radiation field as a collection of independent oscillators. (ii) Later, after the photon had fully established itself as an elementary particle, the radiation field was treated as a gas of Bosons. But this is a matter of statistical mechanics, which we mention only in order to prevent the reader from getting confused.

A black body cavity contains electromagnetic radiation. Its classical energy density is given by

$$W = \frac{\vec{E}^2 + \vec{H}^2}{8\pi} \tag{1.16}$$

[15] (Eq. (2.49)), where $\vec{E}$ and $\vec{H}$ are the electric and the magnetic field strengths, respectively. The total field energy E in the cavity is given by

$$E = \int_V dVW \ , \tag{1.17}$$

where V is the volume of the cavity. We may use a gauge, where $\vec{E} = -\frac{1}{c}\frac{\partial \vec{A}}{\partial t}$ and thus Eq. (1.17) becomes

$$E = \frac{1}{8\pi}\int \left[\left(\frac{1}{c}\frac{\partial \vec{A}}{\partial t} \right)^2 + \left(\vec{\nabla} \times \vec{A} \right)^2 \right] dV \tag{1.18}$$

(cf. [15] (2.18) and (2.19) as well as (2.15)). The vector potential in turn is expressed as a Fourier series

$$\begin{aligned} \vec{A}(\vec{r},t) &= \frac{1}{\sqrt{V}}\sum_{\vec{k},\alpha} \Big\{ c_{\vec{k},\alpha}\vec{u}_{\vec{k},\alpha}(\vec{r})e^{-i\omega t} \\ &\quad + c^*_{\vec{k},\alpha}\vec{u}^*_{\vec{k},\alpha}(\vec{r})e^{i\omega t} \Big\} \ , \end{aligned} \tag{1.19}$$

where $k_x = \frac{2\pi}{L}n_x$, $k_y = \frac{2\pi}{L}n_y$, $k_z = \frac{2\pi}{L}n_z$ (n_x, n_y, $n_z = \pm 1, \pm 2, \ldots$), $V = L^3$, and

$$\vec{u}_{\vec{k},\alpha}(\vec{r}) = \vec{\epsilon}^{(\alpha)}e^{i\vec{k}\cdot\vec{r}} \ . \tag{1.20}$$

Here and in the following the asterisk $*$ indicates the complex conjugate. $\vec{\epsilon}^{(\alpha)}$ is real unit vector in the α-direction of the plane perpendicular to the momentum vector $\vec{k}$. Inserting Eq. (1.19) into Eq. (1.18) we obtain [20]

$$E = \sum_{\vec{k},\alpha} \frac{w^2}{2\pi c^2} c^*_{\vec{k},\alpha}c_{\vec{k},\alpha} \tag{1.21}$$

and via

$$q_{\vec{k},\alpha} = \frac{1}{\sqrt{4\pi c}}\left(c_{\vec{k},\alpha} + c^*_{\vec{k},\alpha} \right) \tag{1.22}$$

$$p_{\vec{k},\alpha} = -\frac{i\omega}{\sqrt{4\pi c}}\left(c_{\vec{k},\alpha} - c^*_{\vec{k},\alpha} \right) \tag{1.23}$$

the final form

$$E = \sum_{\vec{k},\alpha} \frac{1}{2}\left(p^2_{\vec{k},\alpha} + \omega^2 q^2_{\vec{k},\alpha} \right) \ . \tag{1.24}$$

This means that the electromagnetic field energy inside the cavity corresponds to $\sum_{\vec{k},\alpha}$ uncoupled one-dimensional (1D) harmonic oscillators.

At this point electrodynamics has done its job, and we now turn to statistical mechanics. In statistical mechanics you will learn that the average energy contained in a system consisting of a fixed number of particles (e.g., oscillators) inside a fixed volume, which is in thermal equilibrium with its surroundings (here the cavity walls), is given by

$$\langle E \rangle = \frac{\sum_m E_m e^{-\beta E_m}}{\sum_m e^{-\beta E_m}} = -\frac{\partial}{\partial \beta}\ln \sum_m e^{-\beta E_m} \ , \tag{1.25}$$

where $\beta^{-1} = k_B T$. T is the temperature, and k_B is Boltzmann's constant. The sum $\sum_m$ is over all energy values accessible to the system (cf. [16] section 2.1).

We interrupt briefly to explain the difference between $\langle E \rangle$ as compared to E used above. Statistical mechanics considers the electromagnetic field inside the cavity as in thermal equilibrium with the cavity walls kept at fixed temperature T. In this sense energy may be exchanged between the field and the walls, i.e. the field's energy fluctuates.

In classical physics energy is continuous, and the summation in Eq. (1.25) becomes an integration. From classical mechanics we know that a harmonic oscillator at constant energy is described by a trajectory in phase space. Changing energy means moving to another trajectory. Summing over all possible energy states (microstates) of the system, with their proper statistical weight, therefore means integrating over the entire phase space. Thus, for a single oscillator we have

$$\sum_m \sim \int_{-\infty}^{\infty} dpdq \ .$$

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[20] this is a homework problem

We neglect a constant factor (the phase space density), because it drops out of the calculation of $\langle E\rangle$ which now, for a single oscillator, becomes

$$-\frac{\partial}{\partial\beta}\ln\int_{-\infty}^{\infty}dpdqe^{-\beta(p^2+\omega^2q^2)/2}=k_BT\ .$$

Because the oscillators are independent we obtain for the entire cavity

$$\langle E\rangle=k_BT\sum_{\vec{k},\alpha}1\ . \tag{1.26}$$

The problem is now reduced to counting the number of modes $\sum_{\vec{k},\alpha}$!

It is useful to transform the summation into an integration. The general prescription for this is

$$\sum_{\vec{k}}\to\rho_{\vec{k}}\int d^3k=4\pi\rho_{\vec{k}}\int_0^{\infty}dkk^2\ . \tag{1.27}$$

$\rho_{\vec{k}}$ is the density in $\vec{k}$-space given by

$$\rho_{\vec{k}}=\frac{V}{(2\pi)^3}\ . \tag{1.28}$$

This follows because the $\vec{k}$-vectors lie on a cubic grid, whose gridpoints are given by (k_x,k_y,k_z). The lattice constant of this grid is $2\pi/L$. The combination of Eqs. (1.26) and (1.28) finally gives

$$\frac{\langle E\rangle}{V}=k_BT\int_0^{\infty}d\omega\frac{\omega^2}{\pi^2c^3}=\infty\ . \tag{1.29}$$

This means that the energy density of the black body radiation field is infinity. Clearly, this result cannot be correct. And it is very disturbing that we have obtained it via correct application of electrodynamics and classical statistical mechanics!

We now make a second attempt at solving this problem - using the quantization condition (1.12)! We conclude that the energy of the radiation field written in the form of Eq. (1.24) should be quantized as follows: For a single 1D harmonic oscillator we have

$$n=\frac{1}{h}\oint pdx\overset{(1.15)}{=}\frac{E_n}{\hbar\omega} \tag{1.30}$$

$(\omega=\sqrt{k/m})$. This is exactly what Planck had assumed in 1900.

Again we consider a single 1D oscillator. This time energy is discrete, and the summation remains a summation. The right side of Eq. (1.25) now becomes

$$-\frac{\partial}{\partial\beta}\ln\sum_{n=0}^{\infty}e^{-\beta\hbar\omega n}=\frac{\hbar\omega}{e^{\beta\hbar\omega}-1}$$

[21]. For the entire cavity we obtain

$$\langle E\rangle\ =\ \sum_{\vec{k},\alpha}\frac{\hbar\omega}{e^{\beta\hbar\omega}-1} \tag{1.31}$$

and therefore

$$\begin{aligned}\frac{\langle E\rangle}{V}&\overset{(1.27)}{=}\frac{\hbar}{\pi^2c^3}\int_0^{\infty}d\omega\frac{\omega^3}{e^{\beta\hbar\omega}-1}\\&\overset{\text{(cf. [16]; Eq. (3.13))}}{=}\frac{\pi^2}{15}\frac{(k_BT)^4}{(\hbar c)^3}\ .\end{aligned}$$

This in fact is the correct result in agreement with the experiment [22]! Notice that in the (classical) limit $\hbar\to0$ the integrand becomes $\sim\omega^3(1+\beta\hbar\omega-1)^{-1}$ and we recover the classical result of Eq. (1.29).

In the next section we learn that the above equation for the energy levels of a harmonic oscillator is not quite correct. It neglects the so called zero-point energy. However, here the zero-point energy is a constant which does not contribute to the radiation detected outside the black body cavity, because photons correspond to transitions from and to excited oscillator states only [23].

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[21] Using $\sum_{n=0}^{\infty}z^n=(1-z)^{-1}$ for $z<1$.

[22] It is possible to drill a hole into one of the container walls and observe the photon current density $I(T)=c\langle E\rangle/V$. This is Stefan's law ($I(T)\propto T^4$). Notice that the T^4-dependence may be argued on classical grounds - not, however, the coefficient [18] (section 12.1).

In 1989 the cosmic background explorer or COBE-satellite measured the intensity spectrum of the cosmic background radiation over a wide range of frequencies finding perfect agreement with Planck's distribution (cf. Ref. [16]; section 3.1).

[23] This does not mean that zero-point energy is not interesting as we demonstrate in appendix C.

1.3 Building a general formalism

Using energy quantization we are able to explain the crude structure of the spectral lines of the hydrogen atom, and we have solved the black body problem. But there remains much more to explain: What happens if a second electron is added, how can we calculate intensities of spectral lines etc. Clearly, we need a general theory for electrons, atoms, molecules, radiation and their interaction.

A first step may be the following thought: Looking into our mathematical tool chest, we may ask whether quantization can be formulated in terms of eigenvalue problems either through the use of matrices or differential equations. The latter are especially appealing if we think of particles as waves - as standing waves possessing a discrete spectrum of frequencies. What we may aim for at this point is an eigenvalue differential equation for a particle (e.g., an electron) in an external potential, $\mathcal{U}$, yielding discrete energy levels like

$$E_n = -\frac{\mu e^4}{2\hbar^2}\frac{1}{n^2} \quad \text{for} \quad \mathcal{U} = -\frac{e^2}{r}$$

in the case of the Coulomb potential or

$$E_n = \hbar\omega n \quad \text{for} \quad \mathcal{U} = \frac{1}{2}kx^2$$

in the case of the harmonic oscillator. Consequently we seek an equation of the form

$$\underline{\mathcal{H}} \mid n\rangle = E_n \mid n\rangle \; , \tag{1.32}$$

where E_n are energy eigenvalues, and $\underline{\mathcal{H}}$ is an operator, the so called Hamilton operator, corresponding to the classical Hamilton function $\mathcal{H}$. But what is $\mid n\rangle$? If we think in terms of matrix theory, then $\mid n\rangle$ is an eigenvector corresponding to the eigenvalue E_n. In the following we will talk about energy eigenstates, and $\mid n\rangle$ will be called a state vector (dt.: Zustandsvektor).

Matrix mechanics:

The prescription for a quantum theory based on matrix algebra is as follows (The following ideas are due to Heisenberg, Jordan, and Born [24] [25] [26]): We seek a system of $2k$ matrices $\underline{q}_1, \ldots, \underline{q}_k, \ldots, \underline{p}_1, \ldots \underline{p}_k$, which correspond to the generalized coordinates and momenta of the mechanical analog. The key requirement is that these matrices must obey the commutator relations

$$\left[\underline{q}_m, \underline{q}_n\right] \equiv \underline{q}_m\underline{q}_n - \underline{q}_n\underline{q}_m = 0 \; , \tag{1.33}$$

$$\left[\underline{p}_m, \underline{p}_n\right] \equiv \underline{p}_m\underline{p}_n - \underline{p}_n\underline{p}_m = 0 \tag{1.34}$$

and

$$\left[\underline{p}_m, \underline{q}_n\right] \equiv \underline{p}_m\underline{q}_n - \underline{q}_n\underline{p}_m = -i\hbar\delta_{mn} \; . \tag{1.35}$$

Even though these relations seemingly appear out of the blue, we remind the reader of the close correspondence between these so called commutators and the Poisson brackets in Hamiltonian mechanics ($\{q_m, q_n\} = 0$, $\{p_m, p_n\} = 0$ and $\{p_m, q_n\} = \delta_{mn}$ [14]). Secondly the matrix $\underline{\mathcal{H}}\left(\underline{q}_1, \ldots, \underline{q}_k, \ldots, \underline{p}_1, \ldots, \underline{p}_k\right)$, which is the analog of the Hamilton function $\mathcal{H}$, becomes diagonal.

As an example we consider the 1D harmonic oscillator, i.e. $\mathcal{H} = \frac{p^2}{2m} + \frac{1}{2}m\omega^2x^2$. We make a bold guess and write down the matrices

$$\underline{x} = \sqrt{\frac{\hbar}{2m\omega}} \begin{pmatrix} 0 & 1 & 0 & 0 & \cdots \\ 1 & 0 & \sqrt{2} & 0 & \cdots \\ 0 & \sqrt{2} & 0 & \sqrt{3} & 0 \\ 0 & 0 & \sqrt{3} & 0 & \\ \vdots & \vdots & 0 & & \ddots \end{pmatrix} \tag{1.36}$$

and

$$\underline{p} = i\sqrt{\frac{\hbar m\omega}{2}} \begin{pmatrix} 0 & -1 & 0 & 0 & \cdots \\ 1 & 0 & -\sqrt{2} & 0 & \cdots \\ 0 & \sqrt{2} & 0 & -\sqrt{3} & 0 \\ 0 & 0 & \sqrt{3} & 0 & \\ \vdots & \vdots & 0 & & \ddots \end{pmatrix} \; , \tag{1.37}$$

---

[24] Heisenberg, Werner Karl, german physicist, *Würzburg 5.12.1901, †München 1.2.1976; one of the major contributors to the development of quantum theory, of which his uncertainty principle remains a central and characteristic piece. He received the Nobel prize in physics in 1932.

[25] Jordan, Ernst Pascual, german physicist, *Hannover 18.10.1902, †Hamburg 31.7.1980.

[26] Born, Max, german physicist, *Breslau 11.12.1882, †Göttingen 5.1.1970; a leading figure in quantum theory in pre-war Germany. He shared the 1954 Nobel prize in Physics with W. Bothe.

which indeed obey the relations (1.33) to (1.35). Inserting (1.36) and (1.37) into

$$\underline{\mathcal{H}} = \frac{1}{2m}\underline{p}^2 + \frac{m\omega^2}{2}\underline{x}^2 \tag{1.38}$$

yields

$$\underline{\mathcal{H}} = \hbar\omega \begin{pmatrix} \frac{1}{2} & 0 & 0 & 0 & \cdots \\ 0 & \frac{3}{2} & 0 & 0 & \cdots \\ 0 & 0 & \frac{5}{2} & 0 & \cdots \\ 0 & 0 & 0 & \frac{7}{2} & \\ \vdots & \vdots & \vdots & & \ddots \end{pmatrix} . \tag{1.39}$$

Thus, we obtain the desired eigenvalues E_n for

$$\mid n\rangle = \begin{pmatrix} \vdots \\ 0 \\ 1 \\ 0 \\ \vdots \end{pmatrix} , \tag{1.40}$$

where 1 stands for the nth element.

There is an interesting difference to our previous result, Eq. (1.30), based on the original quantization condition. The lowest attainable energy, the ground state energy, now is $\frac{1}{2}\hbar\omega$ [27]! However, the increments are still equal to $\hbar\omega$. We recall that the original quantization condition, $\oint pdq = nh$, resulted from (1.10), which is based on large n. Our new quantum mechanical theory however produces the proper ground state energy as we shall see.

Notice also that there is a basic problem inherent in the above prescription for constructing the quantum analog of a mechanical system. The classical generalized coordinates and momenta may be interchanged without altering the Hamilton function. The corresponding operators or matrices, according to (1.35), may (in general) not be interchanged without altering $\underline{\mathcal{H}}$. Fortunately we do not run into this problem often, because for $\mathcal{H} = \mathcal{K}(p_1, \ldots, p_k) + \mathcal{U}(q_1, \ldots, q_k)$ there is no such problem.

We do not want to investigate the origin of the relations (1.33) to (1.35), which is heuristic in any case, because quantum mechanics cannot be derived from mechanics. We rather want to suggest a second recipe for constructing a quantum theory. Later, however, we will return to matrix mechanics and show how it is connected to the ideas of wave mechanics which we explore next.

Wave mechanics:

We return to the notion that particles may behave as waves. A plane wave traveling in the positive x-direction may be described via

$$\psi(x,t) \sim \cos\left(2\pi\left[\frac{x}{\lambda} - \nu t\right]\right) , \tag{1.41}$$

where λ is the wavelength, and ν is the frequency. We may also write this as

$$\psi(x,t) \sim \cos(kx - \omega t) . \tag{1.42}$$

If we think about particles, we think about localized objects. However, our $\psi(x,t)$ thus far is not localized. Therefore we construct a wave packet by writing

$$\psi(x,t) = \int_0^\infty dk w(k) \cos(kx - \omega t) \tag{1.43}$$

with

$$w(k) = e^{-b^2k^2} . \tag{1.44}$$

Setting $t = 0$ for the moment we obtain for

$$\psi(x, t=0) = \sqrt{\frac{\pi}{4b^2}} e^{-x^2/4b^2} . \tag{1.45}$$

We see that by adding up a sufficient number of plane waves, putting in many more waves around $k = 0$ (long wavelengths), we obtain an object, i.e. a wave packet localized around $x = 0$. The exact form of $w(k)$ does not matter. Here we choose a Gaussian shape because it is simpler to integrate. You may try this out yourself using the *Mathematica* program shown in Fig. 1.1, e.g. you may substitute $e^{-|k|}$ instead of e^{-k^2}.

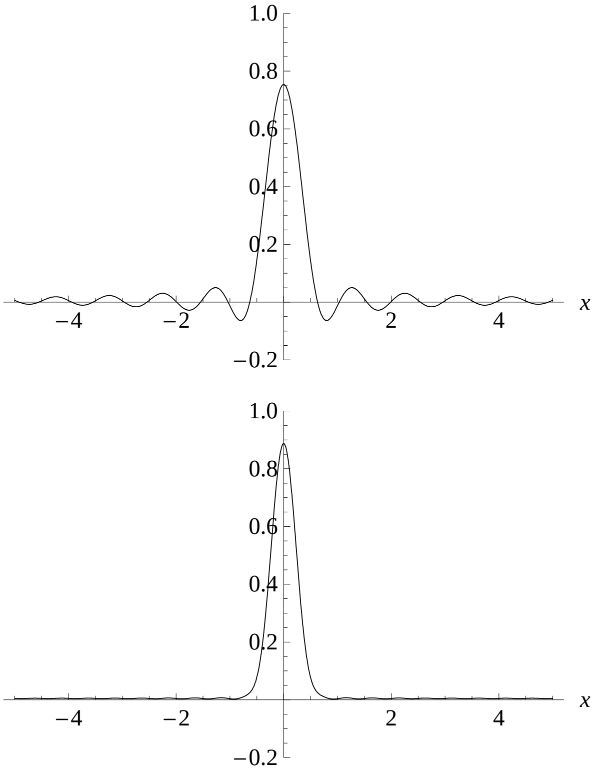
As Fig. 1.2 shows, we may put $t > 0$ and observe the wave packet travelling along x. Here we choose $\omega = c_p k$, where $c_p = 1$ is a constant velocity identical for all plane waves in the packet [28]. This representation of a free particle moving in space appears acceptable.

However we have not used the correct dispersion relation (here: $\omega \propto k$). From Eq. (1.2) we have

---

[27] This energy is also called zero-point energy.

[28] Exact solution: $\psi(x,t) = \sqrt{\frac{\pi}{4b^2}} \exp\left[-(x-t)^2/4b^2\right]$.

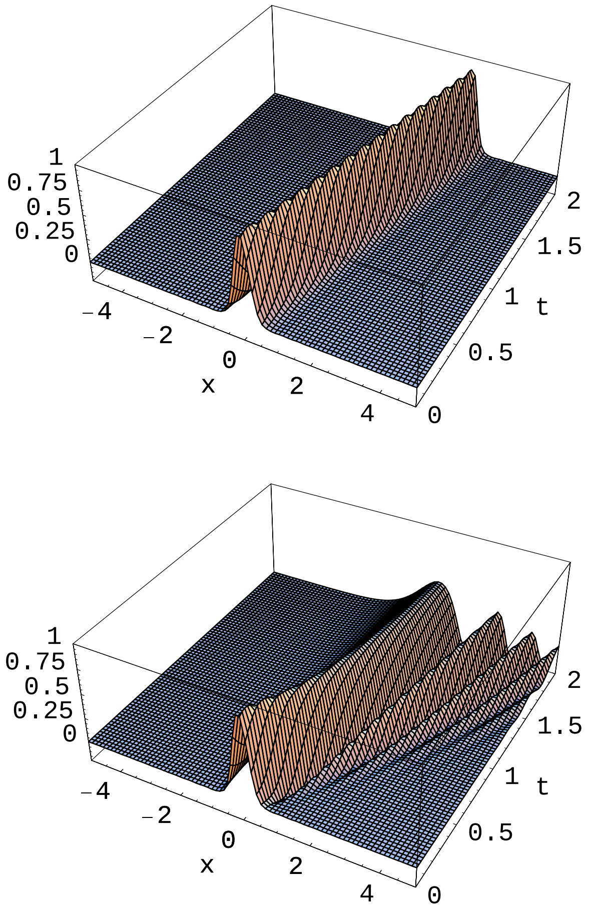


```
w[k_] := Exp[-k^2]

Plot[Sum[w[k] Cos[2 π (k x) ], {k, 0, 1, .01}] / 100,
 {x, -5, 5}, PlotRange → {-.2, 1}, AxesLabel → {x, " "},
 TextStyle → {FontSize → 12}, PlotStyle → Black]

Plot[Sum[w[k] Cos[2 π (k x) ], {k, 0, 2, .01}] / 100,
 {x, -5, 5}, PlotRange → {-.2, 1}, AxesLabel → {x, " "},
 TextStyle → {FontSize → 12}, PlotStyle → Black]
```

Figure 1.1: Top: A wave packet constructed by the superposition of cos-waves using Eq. (1.44). Because the summation over k is finite there appear secondary maxima. These secondary maxima are reduced by including additional k-values. Bottom: Text of the *Mathematica* program.
.



```
Plot3D[Sum[w[k] Cos[2 π (k (x - k t)) ],
     {k, 0, 2, .01}]/100, {x, -5, 5}, {t, 0, 2},
     PlotPoints -> 80, PlotRange -> {-.2, 1},
     AxesLabel -> {"x", "t", " "},
     TextStyle -> {FontSize -> 10}]
```

Figure 1.2: The wave packet plotted as function of time using $\omega = k$ (top) and $\omega = k^2$ (bottom). Also shown is the *Mathematica* program which generates the bottom graph.
.

$k = p/\hbar$. Together with $\hbar\omega = E$ and $E = p^2/2m$ for the classical free particle, we obtain

$$\omega = \frac{\hbar k^2}{2m} \ , \tag{1.46}$$

i.e. $\omega \propto k^2$. Fig. 1.2 illustrates what happens to the wave packet (setting $\frac{\hbar}{2m} = 1$). It loses its localization as t increases!

Nevertheless, let us proceed and write more generally

$$\psi\left(\vec{r}, t\right) = \int_{\text{all space}} d^3p w\left(\vec{p}\right) e^{i(\vec{p}\cdot\vec{r}-Et)/\hbar} \ . \tag{1.47}$$

Here we use complex waves, which is equivalent to using $\cos\left(\frac{\vec{p}\cdot\vec{r}}{\hbar} - \frac{Et}{\hbar}\right)$ as long as we apply linear operations to $\psi\left(\vec{r}, t\right)$. Next we apply the operators $\vec{\nabla}^2$ and ∂_t to Eq. (1.47):

$$\vec{\nabla}^2\psi\left(\vec{r}, t\right) = \int d^3p \left(-\frac{p^2}{\hbar^2}\right) w\left(\vec{p}\right) e^{\frac{i}{\hbar}(\vec{p}\cdot\vec{r}-Et)} \ .$$

and

$$\partial_t\psi\left(\vec{r}, t\right) = \int d^3p \left(-\frac{i}{\hbar}E\right) w\left(\vec{p}\right) e^{\frac{i}{\hbar}(\vec{p}\cdot\vec{r}-Et)} \ .$$

Multiplication of the upper relation by $-\frac{\hbar^2}{2m}$ and the lower relation by $i\hbar$ yields, if both relations are combined,

$$\left(-\frac{\hbar^2}{2m}\vec{\nabla}^2 - i\hbar\partial_t\right)\psi\left(\vec{r}, t\right) = 0 \ , \tag{1.48}$$

where we have used $E = p^2/2m$! This differential equation looks very much like a diffusion equation with a complex diffusion constant $\frac{i\hbar}{2m}$. It describes the free particle.

Notice that analogous to matrix quantum mechanics, where we have replaced the classical coordinates and momenta by $\underline{q}_m$ and $\underline{p}_m$, we now define the operators

$$E \rightarrow i\hbar\partial_t \tag{1.49}$$

and

$$\vec{p} \rightarrow -i\hbar\vec{\nabla} \ . \tag{1.50}$$

The operators $\underline{\vec{r}} \equiv \vec{r}$ and $\underline{\vec{p}} \equiv -i\hbar\vec{\nabla}$ again satisfy the commutator relations (1.33), (1.34), and (1.35), i.e.

$$\left[\underline{x}_m, \underline{x}_n\right] = 0 \tag{1.51}$$

$$\left[\underline{p}_m, \underline{p}_n\right] = 0 \tag{1.52}$$

$$\left[\underline{p}_m, \underline{x}_n\right] = -i\hbar\delta_{mn} \ . \tag{1.53}$$

More precisely

$$\begin{aligned} \left[\underline{p}_m, \underline{x}_n\right] &\equiv \left[\underline{p}_m, \underline{x}_n\right]\psi\left(\vec{r}, t\right) \\ &= -i\hbar\left(\partial_{x_m}x_n\psi - x_n\partial_{x_m}\psi\right) \\ &= -i\hbar\delta_{mn}\psi\left(\vec{r}, t\right) \ . \end{aligned} \tag{1.54}$$

Notice also that we may satisfy the classical relation $E = \frac{p^2}{2m} + \mathcal{U}\left(\vec{r}, t\right)$ (with $E = const$) by formally adding a term $\mathcal{U}\left(\vec{r}, t\right)\psi\left(\vec{r}, t\right)$ to (1.48). The result is Schrödinger's equation for a single particle moving in a potential $\mathcal{U}\left(\vec{r}, t\right)$ [29]:

$$\left(-\frac{\hbar^2}{2m}\vec{\nabla}^2 + \mathcal{U}\left(\vec{r}, t\right) - i\hbar\partial_t\right)\psi\left(\vec{r}, t\right) = 0 \ . \tag{1.55}$$

This equation, which yet has to prove itself, is the starting point for all calculations in wave mechanics.

Notice that we can insert the Ansatz

$$\psi\left(\vec{r}, t\right) = \psi\left(\vec{r}\right) e^{-\frac{i}{\hbar}Et} \tag{1.56}$$

into Eq. (1.55. This then yields the time-independent or stationary Schrödinger equation

$$\left(-\frac{\hbar^2}{2m}\vec{\nabla}^2 + \mathcal{U}\left(\vec{r}\right) - E\right)\psi\left(\vec{r}\right) = 0 \ . \tag{1.57}$$

---

[29] Schrödinger, Erwin, austrian physicist, *Vienna 12.8.1887, †Vienna 4.1.1961; he shared the 1993 Nobel prize in physics with Paul A. M. Dirac for his groundbreaking contributions to quantum theory.

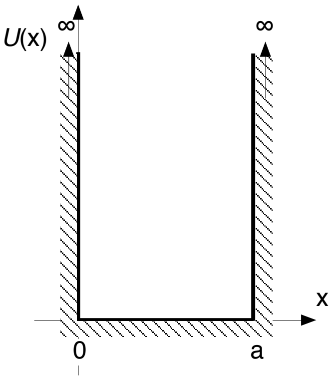


Figure 1.3: Infinite rectangular potential.

A 1D particle between infinite walls:

The first example, to which we apply our new equation in the form of (1.57), is a particle trapped between two barriers, one at $x = 0$ and the other one at $x = a$ as shown in Fig. 1.3. This is a one-dimensional (1D) problem. In this case Eq. (1.57) becomes

$$\left(-\frac{\hbar^2}{2m}{\partial_x}^2 + \mathcal{U}(x) - E\right)\psi(x) = 0 \ . \tag{1.58}$$

Before we do anything to solve this problem, we transform Eq. (1.58) into its dimensionless form. This is done by introducing the new dimensionless coordinate

$$q = x/a \tag{1.59}$$

and subsequently dividing the above equation through $\hbar^2/(2ma^2)$:

$$\left(-{\partial_q}^2 + u(q) - \epsilon\right)\psi(q) = 0 \ , \tag{1.60}$$

where

$$E = \frac{\hbar^2}{2ma^2}\epsilon \text{ and } u = \left\{\begin{array}{cc} 0 & 0 < q < 1 \\ \infty & \text{otherwise} \end{array}\right. . \tag{1.61}$$

This is not merely cosmetics. There is valuable information here. Notice that the typical energy of the problem, i.e. $\hbar^2/(2ma^2)$, is proportional to a^{-2}. Here a is the wall-to-wall separation, but generally speaking it is the linear dimension of the space to which the particle is confined. This remains true in three dimensions. In the case of an atom, a typically is one to several $10^{-10}m$. For a particle confined to the nucleus a is on the order of $10^{-14}m$. This means that typical energies of chemical reactions involving the electrons (responsible for the size of the atom) are around 8 orders of magnitude (!) less than the typical energy of nuclear reactions.

In the two regions $q \leq 0$ and $q \geq 1$ it is reasonable to assume that $\psi(q)$ must vanish in order for (1.60) to remain true. In the region $0 < q < 1$ we have

$$\left(-{\partial_q}^2 - \epsilon\right)\psi(q) = 0 \ . \tag{1.62}$$

A solution is

$$\psi(q) = \psi_o \sin(\sqrt{\epsilon} q) \ . \tag{1.63}$$

Notice that $\psi(0) = 1$ and thus this ψ ties continuously on to $\psi(q) = 0$ in region $q \leq 0$. Why we should require the two solutions to be the same at $q = 0$ is not clear at this moment, but it becomes clear below when we discuss the physical meaning of ψ. In order to also tie (1.63) continuously to $\psi(q) = 0$ in region $q \geq 1$, we must require

$$\sqrt{\epsilon} = \pi n \quad (n = 1, 2, \ldots) \ . \tag{1.64}$$

We exclude $n = 0$, because it would mean $\psi(q)$ vanishes everywhere, which should mean that there is no particle at all. Thus, the two ad hoc boundary conditions yield the discrete energy levels

$$E_n = \frac{\hbar^2}{2ma^2}\pi^2 n^2 \ . \tag{1.65}$$

available to our particle on the basis of the (stationary) Schrödinger equation.

Can we test this result? Well, our problem is somewhat artificial, but there is a resemblance of our particle to an ideal classical gas particle (or molecule). We know that the average thermal energy per particle in an ideal gas is

$$\langle E\rangle = \frac{3}{2}k_B T \ , \tag{1.66}$$

i.e. $k_B T/2$ contributed by each momentum component. In the present 1D case we therefore expect exactly this. Combination of Eqs. (1.25) and (1.65) yields

$$\langle E\rangle = k_B T_o t^2 \partial_t \ln \sum_{n=1}^{\infty} \exp[-n^2/t] \; , \qquad (1.67)$$

where $t = T/T_o$ and $T_o = (\frac{\hbar^2}{2ma^2}\pi^2)/k_B$. If we consider the limit $t \ll 1$, i.e. the limit of low temperature, it is sufficient to only keep the $n = 1$-term in the sum and our result becomes

$$\langle E\rangle_{t\ll 1} = k_B T_o \; . \qquad (1.68)$$

If we assume $t \gg 1$ instead, i.e. high temperatures, then we may write

$$\langle E\rangle_{t\gg 1} = k_B T_o t^2 \partial_t \ln \int_0^{\infty} dn e^{-n^2/t} = \frac{k_B T}{2} \qquad (1.69)$$

This is indeed the expected classical result, which follows in the limit of high temperature or, alternatively, in the limit $h \to 0$. In the low temperature limit we find that our solution deviates from the classical result and $\langle E\rangle$ approaches a finite value. The crossover from classical to quantum behavior apparently happens when T approaches T_o from above. But what is the value of T_o? If we assume that our particle is an Argon atom and that $a = 1cm$, then we find $T_o \sim 10^{-16}K$! Remark: This is the reason why in Statistical Mechanics the translational contribution to the energy of an atomic or molecular gas can always be calculated based on classical mechanics.

Even though we have shown that our solution produces the correct result in the classical limit, this does not prove that Schrödinger's equation yields correct results in cases when experiments deviate from the classical expectations. Thus, we must study more examples.

The meaning of $\psi(\vec{r}, t)$:

The second example for which we try out Eq. (1.55) or rather Eq. (1.57) is

$$\mathcal{U}(x) = \frac{1}{2} m\omega^2 x^2 \; ,$$

i.e. the 1D harmonic oscillator. Eq. (1.57) in this case becomes

$$\left(-\frac{\hbar^2}{2m}\partial_x^2 + \frac{1}{2}m\omega^2 x^2 - E\right)\psi(x) = 0 \; . \qquad (1.70)$$

The solution is

$$\begin{aligned}\psi_n(x) &= \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{n!2^n}} \qquad (1.71)\\ &\times H_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right) \exp\left[-\frac{m\omega}{2\hbar}x^2\right]\end{aligned}$$

with

$$H_n(q) = (-1)^n e^{q^2} \frac{d^n}{dq^n} e^{-q^2} \; . \qquad (1.72)$$

The $H_n(q)$ are Hermite polynomials ($H_0(q) = 1$, $H_1(q) = 2q, \ldots$) [30]. Each index n corresponds to an energy eigenvalue

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right) \qquad n = 0, 1, 2, \ldots \qquad (1.74)$$

This means that Schrödinger's equation agrees with (1.39)! Notice in particular that $E_0 = \frac{1}{2}\hbar\omega$. Notice also that the discrete eigenvalues result from the requirement $\psi_n(\pm\infty) = 0$. This is illustrated in Fig. 1.4 for the case of $n = 0$, which shows the numerical solution for three different energies, only one of which corresponds to the 'possible' energy $E_0 = \frac{1}{2}\hbar\omega$. However, what is the meaning of the so called wave function $\psi_n(x)$?

---

[30] Substitution of $x = \sqrt{\hbar/(m\omega)}q$ into Eq. (1.70) yields

$$\left(\partial_q^2 - q^2 + 2\epsilon\right)\psi(q) = 0$$

with $E = \hbar\omega\epsilon$. The Ansatz $\psi(q) = const H_n(q)\exp[-q^2/2]$ transforms this equation to its final form known in mathematics as Hermite's differential equation:

$$\left(\partial_q^2 - 2q\partial_q + 2\epsilon - 1\right) H_n(q) = 0 \qquad (1.73)$$

with $2\epsilon - 1 = 2\left(n + \frac{1}{2}\right) - 1 = 2n$ ($n = 0, 1, 2, \ldots$) [19] (Chapter 22).

We revisit the harmonic oscillator again in section 1.5. The approach discussed there will allow us to construct the solutions more easily. Thus, there is no need to discuss Hermite's differential equation in detail at this point.

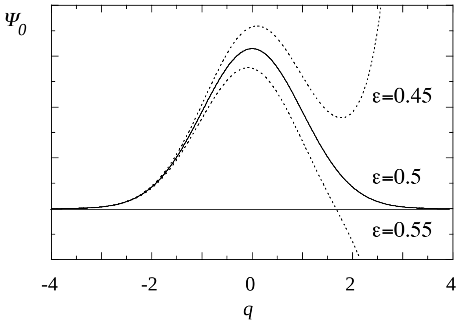


Figure 1.4: ψ_0 of the 1D harmonic oscillator computed numerically for different ϵ starting from $q = -4$ using the initial values $\psi_0 = \psi_0{}' = 0.0001$. Here $q = \sqrt{m\omega/\hbar}x$.

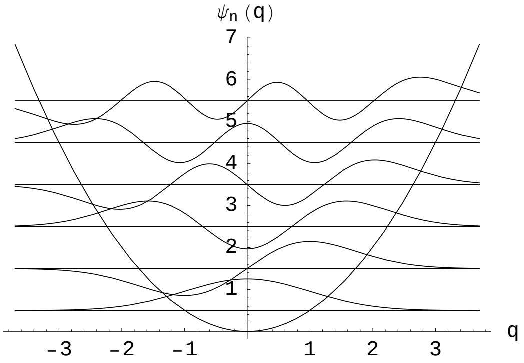


Figure 1.5: The ground state and the first five excited states of the 1D harmonic oscillator (shifted according to energy) together with the harmonic potential. Here $q = \sqrt{m\omega/\hbar}x$, whereas energy is in units of $\hbar\omega$.

Fig. 1.5 shows the wave functions $\psi_0(q)$ to $\psi_6(q)$. Guided by the original idea behind the wave packet we might try to interpret $\psi_n(q)$ as a measure of likelihood to find a particle in a harmonic potential at a certain q-value. But the $\psi_n(q)$, except for the ground state, $n = 0$, may be negative. The next best thing to try is $\psi_n(q)^2$ or even better $|\psi_n(q)|^2 = \psi_n(q)\psi_n^*(q)$, because in general the wave function may be a complex function (as we will see). Accepting this idea we must require

$$\int_{-\infty}^{\infty} dq \mid \psi_n(q) \mid^2 = 1 \,, \tag{1.75}$$

which means that the particle must be somewhere in space [31] [32]. It also means that $|\psi_n(q)|^2$ should be interpreted as a probability density.

Note also that the integration extends from $-\infty$ to ∞ and not from $-a$ to a given by the classical condition $E - \mathcal{U}(a) = 0$ [33]. As Fig. 1.5 shows, if our interpretation of $|\psi_n(q)^2|$ is correct, then the quantum particle penetrates into the classically forbidden area $E < \mathcal{U}(q)$ [34]!

Let us again consider the correspondence principle, which allows a stringent check of our interpretation of the wave function. For the classical harmonic oscillator $p_{cl}(x)\,\delta x$ is the probability for finding the oscillator in the interval δx. p_{cl} is given by

$$p_{cl}(x) = \frac{1}{\pi a}\frac{1}{\sqrt{1-\left(\frac{x}{a}\right)^2}} \,. \tag{1.76}$$

In order to compare this with $p_{qt}(x) \equiv |\psi_n(x)|^2$ we write $E = \frac{1}{2}m\omega^2 a^2$ and inserting $E = \hbar\omega\left(n+\frac{1}{2}\right)$ we obtain

$$a = \sqrt{\frac{\hbar}{m\omega}}\sqrt{2\left(n+\frac{1}{2}\right)} \,. \tag{1.77}$$

Fig. 1.6 shows the results for $n = 0$, $n = 1$, $n = 10$ and $n = 20$. We see that for large n, i.e.

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[31] This normalization already is build into Eq. (1.71).

[32] This explains the above requirement $\psi_n(\pm\infty) = 0$!

[33] Integration from $-a$ to a (requiring $\psi(\pm a) = 0$) does not yield the correct energy eigenvalues!

[34] If the potential barrier is not infinite, as in the case at hand, then there is a finite probability for the particle to penetrate this barrier, which is not possible in classical mechanics. This is called tunneling.

in the limit where the correspondence principle should hold, indeed $p_{cl}\,(x) \equiv p_{qt}\,(x)$ or better $p_{cl}\,(x)\,\delta x \equiv p_{qt}\,(x)\,\delta x$. This is a nice confirmation of the assumptions which we have made thus far.

One-dimensional rectangular well potential I:

Before we launch into the discussion of the application of Schrödinger's equation to problems like the hydrogen atom, it is wise to exercise our skills by means of another simple problem. This one is a modification of the particle trapped between infinite walls considered above.

Imagine the following, still not very realistic but nevertheless instructive, potential in one dimension:

$$\mathcal{U}\,(x) = \begin{cases} -\mathcal{U}_o & \text{for} \quad -\frac{a}{2} \leq x \leq \frac{a}{2} \\ 0 & \qquad\quad \text{otherwise} \end{cases}$$

($\mathcal{U}_o > 0$). The potential is depicted in Fig. 1.7. It is a so called rectangular well potential. There are two important differences compared to the harmonic oscillator. The potential is finite, and its shape requires the separate treatment of the three regions $x < -a/2$ (I), $-a/2 \leq x \leq a/2$ (II), and $a/2 < x$ (III).

We start from the stationary Schrödinger equation (1.57). Using the substitution

$$x = \frac{a}{2} q \,, \tag{1.78}$$

which here is slightly more convenient than $x = aq$ (cf. Eq. (1.59)) used previously, yields

$$\left(\partial_q^2 - u(q) + \epsilon\right) \psi(q) = 0 \,. \tag{1.79}$$

Notice that $u\,(q)$ is given by

$$u\,(q) = \begin{cases} -u_o & \text{for} \quad -1 \leq q \leq 1 \\ 0 & \qquad\quad \text{otherwise} \end{cases} \,,$$

where

$$u_o = \frac{ma^2}{2\hbar^2} \mathcal{U}_o \,.$$

and

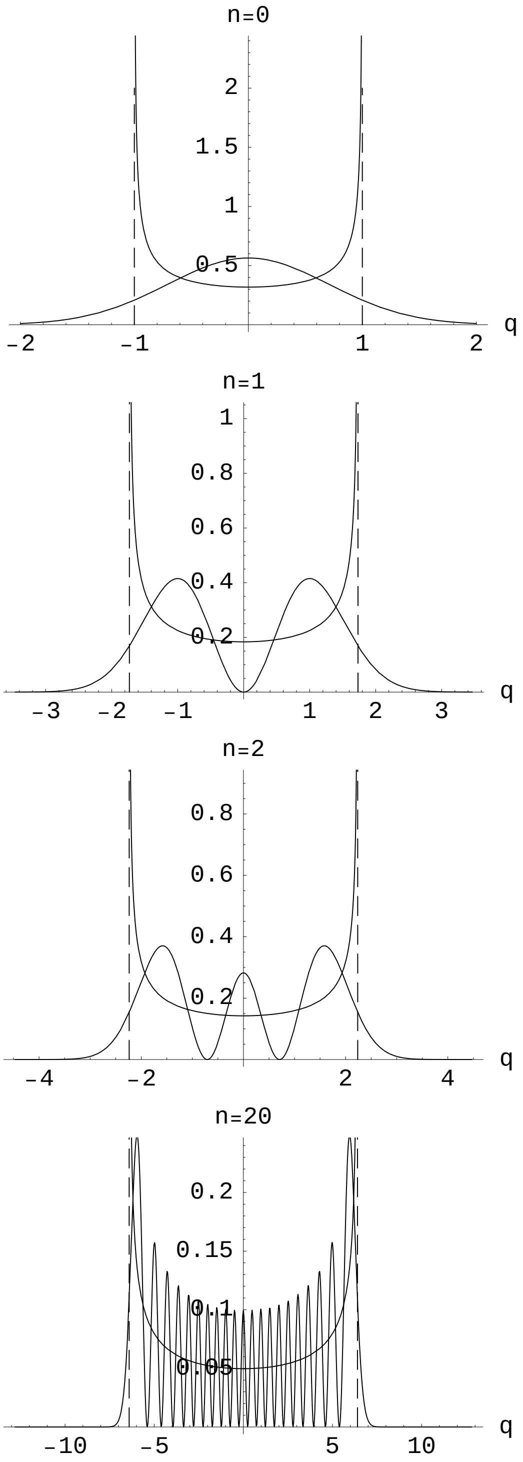

Figure 1.6: Comparison of $p_{qt}\,(x)$ with $p_{cl}\,(x)$ for $n = 0,\ 1,\ 2,$ and 20. Again the unit of length is $\sqrt{\hbar/m\omega}$. Dashed vertical lines indicate the classical turning points.

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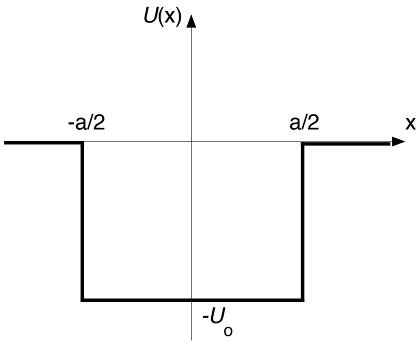


Figure 1.7: Rectangular well potential in one dimension.

$$\epsilon = \frac{ma^2}{2\hbar^2} E \,. \tag{1.80}$$

The general solutions in each of the three regions are

$$\psi_\alpha\left(q\right) = \psi^{(1)}_{\alpha,o} e^{ik_\alpha q} + \psi^{(2)}_{\alpha,o} e^{-ik_\alpha q} \,, \tag{1.81}$$

where $\psi^{(1)}_{\alpha,o}$ and $\psi^{(2)}_{\alpha,o}$ are constants and $\alpha = I, II, III$. Inserting (1.81) into (1.79) yields

$$-k_\alpha^2 - u_\alpha + \epsilon = 0 \,,$$

where $u_I = u_{III} = 0$ and $u_{II} = -u_o$, or

$$k_\alpha = \sqrt{-u_\alpha + \epsilon} \,.$$

In the following we concentrate on the so called bound states for which $\epsilon < 0$, i.e. the particle is trapped "inside" the potential well [35]. Thus

$$k_I = k_{III} = \pm i \sqrt{\mid \epsilon \mid} \qquad \text{and} \qquad k_{II} = \sqrt{u_o + \epsilon}$$

$(u_0 + \epsilon \geq 0)$ and therefore (using $k_I = k_{III} = -i\sqrt{-\epsilon}$)

$$\begin{aligned} \psi_I\left(q\right) &= \psi^{(1)}_{I,o} e^{\sqrt{-\epsilon}q} + \psi^{(2)}_{I,o} e^{-\sqrt{-\epsilon}q} \\ \psi_{III}\left(q\right) &= \psi^{(1)}_{III,o} e^{\sqrt{-\epsilon}q} + \psi^{(2)}_{III,o} e^{-\sqrt{-\epsilon}q} \,. \end{aligned}$$

In order to ensure normalizability (cf. Eq. (1.75)) we must require

$$\psi^{(2)}_{I,o} = \psi^{(1)}_{III,o} = 0 \,.$$

We are left with four unknown coefficients $\psi^{(i)}_{\alpha,o}$ and ϵ. At this point we assume the following boundary conditions

$$\begin{aligned} \psi_I\left(-1\right) &= \psi_{II}\left(-1\right) \\ \partial_q \psi_I\left(q\right)|_{q=-1} &= \partial_q \psi_{II}\left(q\right)|_{q=-1} \end{aligned}$$

(set 1) and

$$\begin{aligned} \psi_{II}\left(1\right) &= \psi_{III}\left(1\right) \\ \partial_q \psi_{II}\left(q\right)|_{q=1} &= \partial_q \psi_{III}\left(q\right)|_{q=1} \,, \end{aligned}$$

(set 2), i.e. the solution is continuous and differentiable at $q = \pm 1$ [36].

From set 1 follows

$$\begin{aligned} \psi^{(1)}_{I,o} e^{-\sqrt{-\epsilon}} &= \psi^{(1)}_{II,o} e^{-ik_{II}} + \psi^{(2)}_{II,o} e^{ik_{II}} \\ \sqrt{-\epsilon}\psi^{(1)}_{I,o} e^{-\sqrt{-\epsilon}} &= ik_{II}\left(\psi^{(1)}_{II,o} e^{-ik_{II}} - \psi^{(2)}_{II,o} e^{ik_{II}}\right) \end{aligned}$$

and therefore

$$\sqrt{-\epsilon} = -ik_{II} \frac{\psi^{(2)}_{II,o} e^{ik_{II}} - \psi^{(1)}_{II,o} e^{-ik_{II}}}{\psi^{(2)}_{II,o} e^{ik_{II}} + \psi^{(1)}_{II,o} e^{-ik_{II}}} \,. \tag{1.82}$$

From set 2 follows

$$\begin{aligned} \psi^{(2)}_{III,o} e^{-\sqrt{-\epsilon}} &= \psi^{(1)}_{II,o} e^{ik_{II}} + \psi^{(2)}_{II,o} e^{-ik_{II}} \\ \sqrt{-\epsilon}\psi^{(2)}_{III,o} e^{-\sqrt{-\epsilon}} &= \frac{k_{II}}{i}\left(\psi^{(1)}_{II,o} e^{ik_{II}} - \psi^{(2)}_{II,o} e^{-ik_{II}}\right) \end{aligned}$$

and therefore

---

[35] The situation $\epsilon > 0$ we discuss in the next section starting on page 24.

[36] We discuss these assumptions at the end of this section.

$$\sqrt{-\epsilon} = -ik_{II}\frac{\psi^{(1)}_{II,o}e^{ik_{II}} - \psi^{(2)}_{II,o}e^{-ik_{II}}}{\psi^{(1)}_{II,o}e^{ik_{II}} + \psi^{(2)}_{II,o}e^{-ik_{II}}} \ . \qquad (1.83)$$

Eqs. (1.82) and (1.83) may be fulfilled simultaneously by setting

$$\underbrace{\psi^{(1)}_{II,o} = \psi^{(2)}_{II,o}}_{(+)}$$

or

$$\underbrace{\psi^{(1)}_{II,o} = -\psi^{(2)}_{II,o}}_{(-)} \ .$$

The condition (+) yields

$$\sqrt{-\epsilon} = \sqrt{u_o+\epsilon}\tan\sqrt{u_o+\epsilon} \ , \qquad (1.84)$$

whereas the condition (−) yields

$$\sqrt{-\epsilon} = -\sqrt{u_o+\epsilon}\cot\sqrt{u_o+\epsilon} \ . \qquad (1.85)$$

Using the substitution $z = \sqrt{u_o+\epsilon}$ we have

$$\sqrt{\frac{u_o - z^2}{z^2}} = \tan z \quad (+)$$

and

$$\sqrt{\frac{u_o - z^2}{z^2}} = -\cot z \quad (-)$$

Fig. 1.8 illustrates the graphical solution of these equations.

The z-values at which the long-dashed curve intersects $\tan z$ and $-\cot z$, respectively, correspond to discrete energy levels

$$-\epsilon_{2n-1} = u_o - z^2_{2n-1} \quad (+) \ , \qquad (1.86)$$

and

$$-\epsilon_{2n} = u_o - z^2_{2n} \quad (-) \ , \qquad (1.87)$$

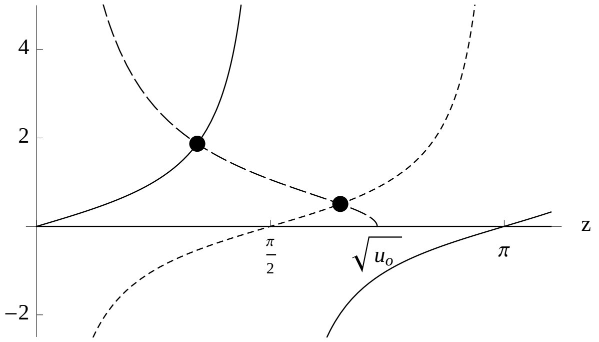


Figure 1.8: Example graphical solutions for $u_o = 5\pi/3$ indicated by the solid circles. Solid lines: $\tan z$; short-dashed line: $-\cot z$; long-dashed line: $\sqrt{(u_o - z^2)/z^2}$.

where $n = 1, 2, \ldots, n_{max}$. Obviously there is a highest energy level for a given finite u_o. On the other hand the smallest possible number of energy levels is one when $\sqrt{u_o}$ becomes less than $\pi/2$.

If we use (1.86) and (1.87) to write down corresponding solutions in region II we find

$$\psi_{II,2n-1}(q) = c_{II,2n-1}\cos\left(\sqrt{u_o+\epsilon_{2n-1}}q\right)$$

and

$$\psi_{II,2n}(q) = c_{II,2n}\sin\left(\sqrt{u_o+\epsilon_{2n}}q\right) \ ,$$

where $c_{II,2n-1}$ and $c_{II,2n}$ are constants. The complete solution can be constructed by tying these functions to the solutions for $q < -1$ and $q > 1$:

$$\psi_{I/III,2n-1}(q) = c_{I/III,2n-1}\exp\left(\pm\sqrt{-\epsilon_{2n-1}}q\right)$$

and

$$\psi_{I/III,2n}(q) = c_{I/III,2n}\exp\left(\pm\sqrt{-\epsilon_{2n}}q\right) \ .$$

The coefficients are determined by the required continuity together with the overall normalization

$$\int_{-\infty}^{\infty} dq \mid \psi(q) \mid^2 = 1 \ .$$

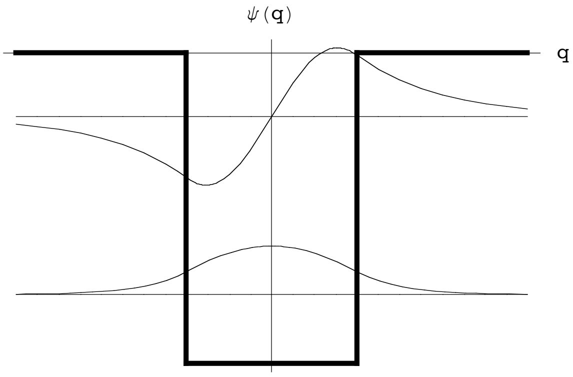


Figure 1.9: Ground state and one excited state corresponding to the graphical solutions in Fig. 1.8. The horizontal lines indicate the energy eigenvalues relative to the potential.

Fig. 1.9 shows the two possible solutions for $u_o = 5\pi/3$ (cf. Fig. 1.8). As in the case of the harmonic oscillator there is a finite probability to find the particle in the classically forbidden regions I and III. This probability obviously is larger for the energy level higher up in the potential well.

An interesting limit is $u_o \to \infty$, i.e. the rectangular well becomes an infinite rectangular well, which we had discussed on page 11. In this case the function $\sqrt{(u_o - z^2)/z^2}$ depicted in Fig. 1.8 approximates a horizontal straight line. The corresponding energy levels are

$$-\epsilon^{(\infty)}_{2n-1} = u_o + \epsilon_{2n-1} = \left(\frac{\pi}{2}(2n-1)\right)^2 \quad (+) \quad (1.88)$$

and

$$-\epsilon^{(\infty)}_{2n} = u_o + \epsilon_{2n} = \left(\frac{\pi}{2}(2n)\right)^2 \quad (-) \; . \quad (1.89)$$

Notice that $-\epsilon^{(\infty)}$ measures a level's energy from the bottom of the potential well on an energy scale for which the bottom is at zero energy. Notice also that due to the difference between the substitution (1.78) vs. the one defined via Eq. (1.59) the above ϵ-values deviate from ϵ in Eq. (1.64) by a factor of four. However, the final values for E_n are identical of course.

The normalized solutions are particularly simple:

$$\psi^{(\infty)}_{II,2n-1}(q) = \cos\left(\frac{\pi}{2}(2n-1)\,q\right)$$

and

$$\psi^{(\infty)}_{II,2n}(q) = \sin\left(\frac{\pi}{2}2nq\right)$$

with $n = 1, 2, \ldots, \infty$. Outside region II, i.e. outside the well, the solutions vanish due to the exponential factors

$$e^{-\sqrt{-\epsilon_{2n-1}}|q|} \quad \text{and} \quad e^{-\sqrt{-\epsilon_{2n}}|q|} \; .$$

Note that both $-\epsilon_{2n-1}$ and $-\epsilon_{2n}$ are infinitely large for every finite n.

Before we move on to the next section, we briefly return to the assumptions regarding the continuity and differentiability of the wave functions on page 15. Let us approximate the rectangular well potential shown in Fig. 1.9 using the following function:

$$u(q) = -\frac{5\pi}{3}\exp[-q^m] \; . \quad (1.90)$$

The results for $m = 2$, 10, and 40 are shown in Fig. 1.10. Obviously, we obtain the rectangular well in the limit of large m. We use the same numerical method as in Fig. 1.4 to compute eigenfunctions and energy eigenvalues for this potential. Selected examples, i.e. two ground state wave functions, are shown in Fig. 1.11. The result for $m = 40$ is not included, because it basically cannot be distinguished from the corresponding result obtained above for the true rectangular well (shown here as dashed curve). The eigenvalues are listed in the following table:

m	ϵ_1
2	$-3.3243\ldots$
10	$-3.9485\ldots$
40	$-4.0457\ldots$
∞	$-4.0706\ldots$

Apparently we are able to obtain the rectangular well results via a continuous deformation of a smooth potential function thereby avoiding the "sharp edges" which bring about the boundary conditions introduced on page 15. In this sense the above is a "numerical justification" of the boundary conditions - at least in this special case.

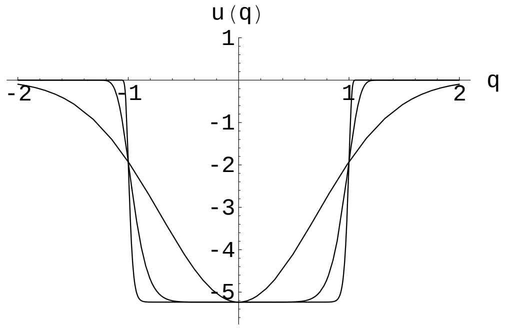
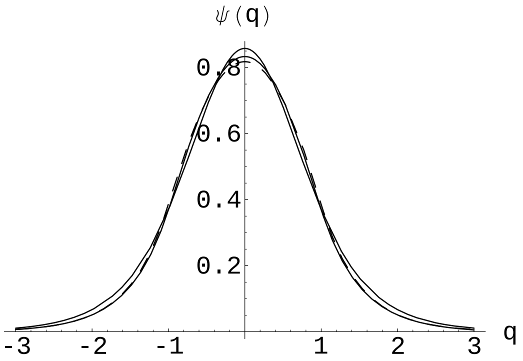


Figure 1.10: Approximations to the rectangular well potential in Fig. 1.9 via Eq. (1.90) with $m = 2$, 10, and 40.



```
f = NDSolve[{ψ''[q] - 3.32432 ψ[q] ==
    - (5 π / 3) Exp[-q^2] ψ[q],
   ψ[-6] == 0.000001, ψ'[-6] == 0.00},
  ψ, {q, -4, 4}];
Ψ[q_] := ψ[q] /. f[[1]];
norm = NIntegrate[Ψ[q]^2, {q, -4, 4}];
Plot[ Ψ[q] / Sqrt[norm], {q, -3, 3}]
```

Figure 1.11: Top: Numerical ground state wave functions for the potential (1.90) with $m = 2$ and 10. The dashed curve is the previous result for the rectangular well. Bottom: *Mathematica*-code for computing and plotting the ground state wave function in the case $m = 2$.

1.4 The hydrogen atom

The obvious problem to tackle next is the hydrogen atom. This is the first major project, to which we apply wave mechanics. It also is a two-body problem. We proceed by writing $\underline{\mathcal{H}}$ in terms of the cartesian coordinates of the electron $\vec{r}_e$ and the nucleus $\vec{r}_n$:

$$\underline{\mathcal{H}} = -\frac{\hbar^2}{2m_e}\vec{\nabla}_e^2 - \frac{\hbar^2}{2m_n}\vec{\nabla}_n^2 + \mathcal{U}\left(\mid \vec{r}_e - \vec{r}_n \mid\right) \ . \qquad (1.91)$$

Next we introduce the new coordinates

$$\vec{r} = \vec{r}_e - \vec{r}_n \qquad \vec{R} = \frac{m_e\vec{r}_e + m_n\vec{r}_n}{m_e + m_n}$$

(in analogy to the Kepler problem in classical mechanics; cf. section 5.2 in [14]), which yield

$$\underline{\mathcal{H}} = -\frac{\hbar^2}{2\mu}\vec{\nabla}_r^2 - \frac{\hbar^2}{2m}\vec{\nabla}_R^2 + \mathcal{U}(r) \ , \qquad (1.92)$$

where $\mu = m_e m_n / (m_e + m_n)$ is the reduced mass, and $m = m_e + m_n$. We disregard the second term, because we are interested in the solution for the center of mass frame only. The resulting Schrödinger's equation corresponds exactly to Eq. (1.55). The potential energy obviously is $\mathcal{U}(r) = -(4\pi\epsilon_o r)^{-1} e^2$, where $-e$ is the electron charge. Using again $\psi(\vec{r}, t) = \psi(\vec{r}) e^{-\frac{i}{\hbar}Et}$ we finally have in dimensionless (!) units

$$\left(\vec{\nabla}_{\vec{\rho}}^2 + \frac{2}{\rho} + \epsilon\right)\psi(\vec{\rho}) = 0 \ , \qquad (1.93)$$

i.e. lengths now are in units of

$$a = \frac{4\pi\epsilon_o\hbar^2}{\mu e^2} \approx \frac{4\pi\epsilon_o\hbar^2}{m_e e^2} \equiv a_o \ , \qquad (1.94)$$

[37], where $a_o = 0.529177$Å is Bohr's radius or the atomic unit of length, and

$$\epsilon = \frac{2\mu a^2}{\hbar^2}E \approx 2\left(\frac{e^2}{4\pi\epsilon_o a_o}\right)^{-1} E \ .$$

Note that $\frac{e^2}{4\pi\epsilon_o a_o}$, the atomic unit of energy, is called

---

[37]
$$\mu = m_e\frac{1}{1 + \frac{m_e}{m_n}} \approx m_e\left(1 - \frac{m_e}{m_n}\right)$$

the hartree (symbol E_h) (1 hartree $= 27.2114eV = 4.35975 \cdot 10^{-18} J$) [38].

It is useful to introduce spherical coordinates, because we are dealing with a problem possessing spherical symmetry. In addition we try to simplify matters using the following separation Ansatz:

$$\psi\left(\rho, \theta, \phi\right) = \frac{u\left(\rho\right)}{\rho} Y\left(\theta, \phi\right) \ . \tag{1.95}$$

Here $u\left(\rho\right)$ solely depends on the dimensionless radial coordinate ρ, whereas $Y\left(\theta, \phi\right)$ is a function of the angles θ and ϕ. We also need the Laplace operator expressed in spherical coordinates:

$$\vec{\nabla}^2_{\vec{\rho}} = \frac{1}{\rho^2} \partial_\rho \left(\rho^2 \partial_\rho\right) + \vec{\nabla}^2_{\phi,\theta}$$

where

$$\vec{\nabla}^2_{\phi,\theta} = \frac{1}{\rho^2} \left(\frac{1}{\sin^2\theta} \partial^2_\phi + \frac{1}{\sin\theta} \partial_\theta \left(\sin\theta \partial_\theta\right) \right)$$

(cf. appendix B. 1). Inserting (1.95) into (1.93) yields

$$\begin{aligned} \frac{\rho^2}{u\left(\rho\right)} \left(\partial^2_\rho + \frac{2}{\rho} + \epsilon \right) u\left(\rho\right) & \\ = - \frac{1}{Y\left(\theta, \phi\right)} \rho^2 \vec{\nabla}^2_{\phi,\theta} Y\left(\theta, \phi\right) & \ , \end{aligned} \tag{1.96}$$

where we have used

$$\frac{1}{\rho^2} \partial_\rho \left(\rho^2 \partial_\rho\right) \frac{u\left(\rho\right)}{\rho} = \frac{1}{\rho} \partial^2_\rho u\left(\rho\right) \ .$$

Notice that the left side of Eq. (1.96) depends exclusively on ρ, whereas the right side depends on the angles θ and ϕ. In order for this equation to be generally valid, both sides must be equal to a constant c, i.e.

$$\left(\partial^2_\rho + \frac{2}{\rho} + \epsilon \right) u\left(\rho\right) = c \frac{u\left(\rho\right)}{\rho^2} \tag{1.97}$$

and

$$-\rho^2 \vec{\nabla}^2_{\phi,\theta} Y\left(\theta, \phi\right) = c Y\left(\theta, \phi\right) \ . \tag{1.98}$$

The second (eigenvalue) differential equation, Eq. (1.98), we investigate in detail in the next section. We will find that c is given by

$$c = l\left(l+1\right)$$

with

$$l = 0, 1, 2, \dots \ . \tag{1.99}$$

The corresponding solutions,

$$Y\left(\theta, \phi\right) = Y_{lm}\left(\theta, \phi\right) \tag{1.100}$$

are the so called spherical harmonics (dt.: Kugelflächenfunktionen), where

$$m = l, l-1, \dots, 0, \dots, -l+1, -l \ . \tag{1.101}$$

These values for the index m follow from a second (eigenvalue) differential equation satisfied by $Y_{lm}\left(\theta, \phi\right)$:

$$-i \partial_\phi Y_{lm}\left(\theta, \phi\right) = m Y_{lm}\left(\theta, \phi\right) \ . \tag{1.102}$$

This again is an equation which we will study in detail in the next section.

Eqs. (1.98) and (1.102) both have distinct physical meaning. If we define an angular momentum operator via

$$\underline{\vec{L}} = \underline{\vec{r}} \times \underline{\vec{p}} \, ,$$

where $\underline{\vec{p}} = -i\hbar\vec{\nabla}$, it is rather straightforward to show that

$$\underline{L}^2 = -\hbar^2 \rho^2 \vec{\nabla}^2_{\phi,\theta} \tag{1.103}$$

and

$$\underline{L}_z = -i\hbar \partial_\phi \tag{1.104}$$

---

[38] In the following we will omit the factor $4\pi\epsilon_o$.

(cf appendix B.1.). In other words, this means according to Eqs. (1.98) and (1.102)

$$\underline{L}^2 Y_{lm}(\theta,\phi) = \hbar^2 l\,(l+1)\,Y_{lm}(\theta,\phi) \tag{1.105}$$

and

$$\underline{L}_z Y_{lm}(\theta,\phi) = \hbar m Y_{lm}(\theta,\phi) \ . \tag{1.106}$$

Analogous to the energy described by the Hamilton operator $\underline{\mathcal{H}}$, we now have two additional physical quantities, the angular momentum square and the z-component of angular momentum, which are quantized! The quantization condition (1.105) must be compared to Eq. (1.92), corresponding to quasi-classical quantization. As in the case of energy quantization there is a noticeable difference for smaller integer values of l (or n). The quantization condition (1.106) is somewhat mysterious, because, at this point, it appears out of the blue [39]. It tells us that the direction of angular momentum is quantized even though we are free to choose the direction of the z-axis of our coordinate system. We will come back to this point later in the course. For the moment we want to return to the radial equation (1.97).

Using the result (1.98) the radial equation becomes

$$\left(\partial_\rho^2 \underbrace{-\frac{l\,(l+1)}{\rho^2}+\frac{2}{\rho}}_{\equiv -\mathcal{U}_{eff}} + \epsilon\right) u_l(\rho) = 0 \ . \tag{1.107}$$

Here we define $\mathcal{U}_{eff}$ merely to highlight the similarity with the classical two-body problem. At this point it is useful to investigate the limiting behavior of $u_l(\rho)$ for $\rho \to \infty$ and $\rho \to 0$. In the former case Eq. (1.107) becomes $\left(\partial_\rho^2+\epsilon\right) u_l(\rho) = 0$ and $u_l(\rho) \sim e^{-\sqrt{-\epsilon}\rho}$; in the latter case Eq. (1.107) becomes $\left(\partial_\rho^2 - \frac{l(l+1)}{\rho^2}\right) u_l(\rho) = 0$ and $u_l(\rho) \sim \rho^{(l+1)}$. Therefore it is sensible to try

$$u_l(\rho) = e^{-\sqrt{-\epsilon}\rho}\rho^{l+1}\sum_{j=0}^{\infty} c_j \rho^j \ . \tag{1.108}$$

Inserting Eq. (1.108) into Eq. (1.107) yields the recursion relation

$$\frac{c_{j+1}}{\sqrt{-\epsilon}} = \frac{2\left[l+j+1-\frac{1}{\sqrt{-\epsilon}}\right]}{(j+1)\,(j+2l+2)}\,c_j \ . \tag{1.109}$$

In order for the series to remain finite we require $[\ldots] = 0$ at $j = j_{\text{max}}$. Therefore $\frac{1}{\sqrt{-\epsilon}}$ must be an integer number $n \geq l+1$, i.e.

$$\epsilon_n = -\frac{1}{n^2} \qquad (n \geq l+1) \ . \tag{1.110}$$

We recognize that our previous solution, Eq. (1.6), has emerged. However, there is more information here. First we note that we get several solutions for each value of n. More exactly, there are $0 \leq l \leq n-1$ possible values for l, and each l has $2l+1$ possible m-values. Thus there are

$$\sum_{l=0}^{n-1}(2l+1) = n^2 \tag{1.111}$$

solutions $\psi_n(\rho,\theta,\phi)$ for each ϵ_n. This is called degeneracy. The high level of degeneracy is a special feature of the $1/r$ potential. Later we will learn that if the Coulomb potential is altered by an external field, we call this a perturbation, then the degeneracy is reduced or entirely removed.

We now turn to calculating the wave functions explicitly:

1. $n = 1$ according to (1.109) implies $0 = l + j_{\text{max}} + 1 - 1$ and therefore $j_{\text{max}} = 0$. The solution $\psi_{n,l,m}(\rho,\theta,\phi)$ is $\psi_{1,0,0}(\rho,\theta,\phi) = \frac{c_0}{\sqrt{4\pi}}e^{-\rho}$. The normalization condition

   $$\int d^3r \mid \psi \mid^2 = 1$$

   yields $c_0 = 2$, i.e.

   $$\psi_{1,0,0}(\rho,\theta,\phi) = \frac{1}{\sqrt{\pi}}e^{-\rho} \ . \tag{1.112}$$

---

[39] We can see how Eq. (1.106) (or rather Eq. (1.102)) arises, if we work out the commutator $[\underline{L}^2, \underline{L}_z] = 0$ (cf. the next section). Thus $\underline{L}^2\underline{L}_z Y_{lm} = \underline{L}_z\underline{L}^2 Y_{lm} = \hbar^2 l\,(l+1)\,\underline{L}_z Y_{lm}$. This implies that $\underline{L}_z Y_{lm} = c_z Y_{lm}$, where c_z is a constant.

2. $n = 2$ implies according to (1.109) $0 = l + j_{\max} + 1 - 2$, i.e. $j_{\max} = 1 - l$. For $l = 0$ we have $\psi_{2,0,0} = \frac{c_0}{\sqrt{4\pi}}\left(1 - \frac{\rho}{2}\right)e^{-\rho/2}$ and therefore

$$\psi_{2,0,0} = \frac{1}{\sqrt{8\pi}}\left(1 - \frac{\rho}{2}\right)e^{-\rho/2}\ ; \tag{1.113}$$

   for $l = 1$ we obtain

$$\begin{aligned}
\psi_{2,1,-1} &= \frac{1}{8\sqrt{\pi}}\sin\theta e^{-i\phi}\rho e^{-\rho/2} \qquad (1.114)\\
\psi_{2,1,0} &= \frac{1}{4\sqrt{2\pi}}\cos\theta\rho e^{-\rho/2} \qquad (1.115)\\
\psi_{2,1,1} &= -\frac{1}{8\sqrt{\pi}}\sin\theta e^{i\phi}\rho e^{-\rho/2} \qquad (1.116)
\end{aligned}$$

3. . . .

4. The general expression for $\psi_{n,l,m}(\rho,\theta,\phi)$ is

$$\psi_{n,l,m}(\rho,\theta,\phi) = R_{n,l}(\rho)\,Y_{lm}(\theta,\phi)\ , \tag{1.117}$$

   where the radial wave function is

$$\begin{aligned}
R_{n,l}(\rho) = \frac{2}{n^2}\sqrt{\frac{(n-l-1)!}{(n+l)!}}\left(\frac{2\rho}{n}\right)^l \\
\times \exp\left[-\frac{\rho}{n}\right]L_{n-l-1}^{2l+1}\left(\frac{2\rho}{n}\right)
\end{aligned} \tag{1.118}$$

   [19] (chapter 22). $L_{n-l-1}^{2l+1}\left(\frac{2\rho}{n}\right)$ are generalized Laguerre polynomials; they can be obtained via LaguerreL $\left[n-l-1, 2l+1, \frac{2\rho}{n}\right]$ in *Mathematica*.

In spectroscopy n is called the main quantum number, and the different $l = 0, 1, 2\ldots$ are denoted by small letters, i.e. $l = s, p, d, \ldots$ We will call every $\psi_{n,l,m}(\rho,\theta,\phi)$ an atomic orbital. Thus hydrogen has one s-orbital for every n, three p-orbitals for every n if $l = 1$, five d-orbitals for every n if $l = 2$ and so on [40]. Fig. 1.12 shows a schematic of the hydrogen energy levels expressed in this language. Fig. 1.13 shows the radial part of the ground state wave function as well as the radial wave functions corresponding to the first excited energy level. Fig. 1.14, finally, shows the absolute square of the angular part of the wave functions shown in the previous figure. These can be viewed as orientation distribution of the electron "cloud".

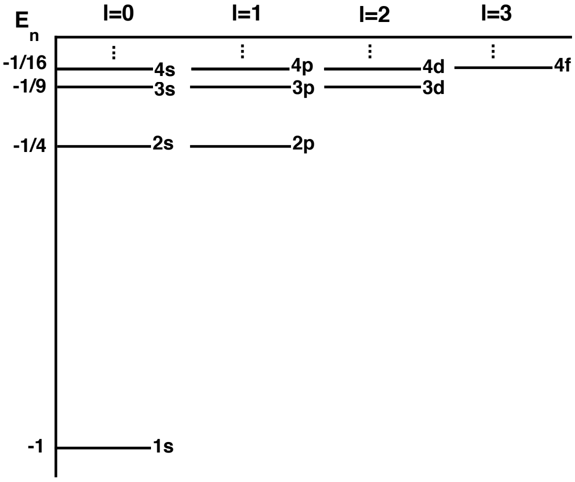


Figure 1.12: Spectroscopic terminology of the hydrogen energy levels.

It is important to note that the complete solution of Schrödinger's equation for a hydrogen atom with energy E_n in the absence of symmetry breaking fields [41] is the linear combination

$$\psi_n(\rho,\theta,\phi) = \sum_{l=0}^{n-1}\sum_{m=-l}^{l} c_{nlm}\psi_{n,l,m}(\rho,\theta,\phi) \tag{1.119}$$

where $\sum_{l=0}^{n-1}\sum_{m=-l}^{l} c_{nlm} = 1$. This follows because the spherical harmonics form a complete set of orthogonal functions (cf. the appendix).

Magnetic moment of atomic hydrogen:

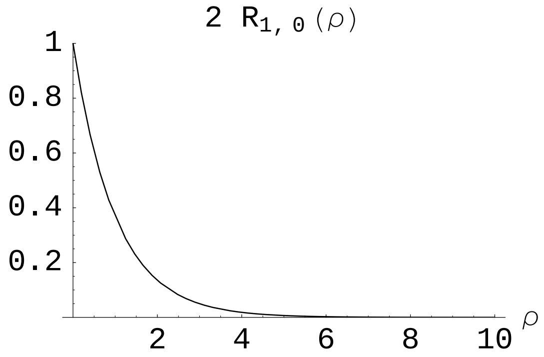
In electrodynamics we had derived the following formula for the magnetic moment produced by a current density $-e\vec{j}$:

$$\vec{m} = \frac{-e}{2c}\int \vec{r} \times \vec{j}\,(\vec{r})\,d^3r \tag{1.120}$$

---

[40] Examples for common notation: $\psi_{1,0,0} \equiv \psi_{1s}$ or $\psi_{2,1,-1} \equiv \psi_{2p_{-1}}$.

[41] The level splitting due to an electrostatic field is called Stark effect. If the applied field is a magnetic field the analogous effect is called Zeeman effect.



```
R[n_, l_, ρ_] := 2/(n^2) Sqrt[(n - l - 1)!/(n + l)!] (2ρ/n)^l
   Exp[-ρ/n] LaguerreL[n - l - 1, 2 l + 1, 2ρ/n]

R0 = Limit[R[1, 0, x], x → 0]
Plot[R[1, 0, ρ] / R0, {ρ, 0.0, 10},
 PlotRange → {0, 1}, PlotLabel → "2 R1, 0 (ρ)",
 AxesLabel → {ρ, " "}, TextStyle → {FontSize → 12}]
```

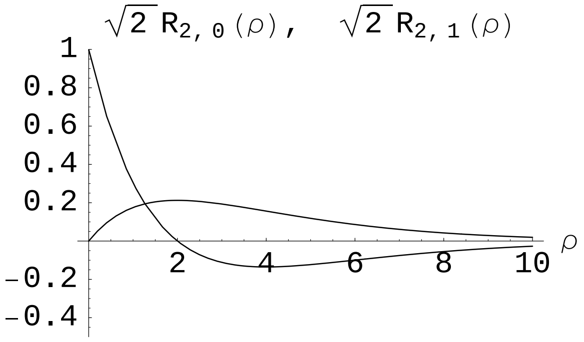
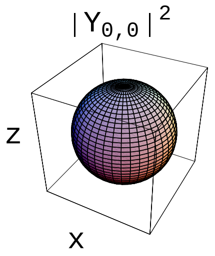


Figure 1.13: Radial wave functions for the hydrogen atom. Top: The ground state $2R_{1,0}\,(\rho)$ including the *Mathematica*-code. Bottom: $\sqrt{2}R_{2,0}\,(\rho)$ and $\sqrt{2}R_{2,1}\,(\rho)$. Note that $R_{2,1}$ becomes zero at the center.



```
<< Graphics`ParametricPlot3D`
r = 0.09; p[θ_, ϕ_] :=
 Abs[SphericalHarmonicY[0, 0, θ, ϕ]] ^ 2;
ParametricPlot3D[{p[θ, ϕ] Cos[ϕ] Sin[θ],
  p[θ, ϕ] Sin[ϕ] Sin[θ], p[θ, ϕ] Cos[θ]},
 { θ, 0, Pi}, {ϕ, 0, 2 Pi}, PlotPoints → 40,
 PlotRange → {{-r, r}, {-r, r}, {-r, r}},
 Ticks → None, AxesLabel → {x, y, z},
 PlotLabel → "|Y0,0|2", TextStyle → {FontSize → 18}]
```

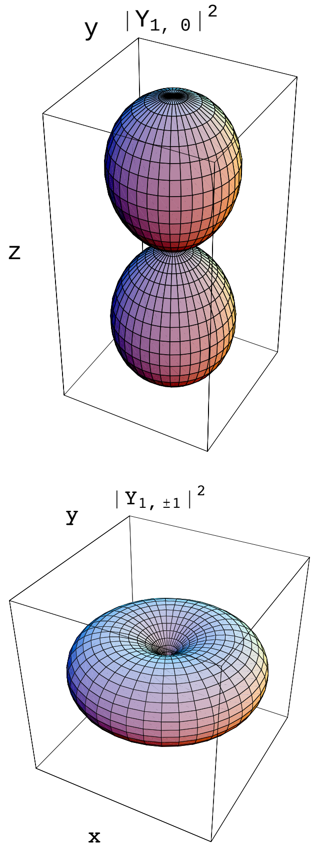


Figure 1.14: Angular charge distributions. Top: The ground state $|Y_{00}(\theta,\phi)|^2$ including the *Mathematica*-code. Bottom: $|Y_{10}(\theta,\phi)|^2$ and $|Y_{1\pm1}(\theta,\phi)|^2$.

(cf. [15]; Eq. (3.62)). Here $-e\left(=-1.602\cdot 10^{-19}C\right)$ is the electron charge, and $\vec{j}$ is a current density in units of $-e$. In the following we first derive a general expression for $\vec{j}$ in terms of the wave function. Then we write down an expression for $\vec{m}$ in the case of hydrogen in a state described by n, l, and m.

We start by adding the equations

$$\begin{aligned} \psi^*\partial_t\psi &= \frac{1}{i\hbar}\psi^*\underline{\mathcal{H}}\psi && (1.121)\\ \psi\partial_t\psi^* &= -\frac{1}{i\hbar}\psi\underline{\mathcal{H}}^*\psi^* \; . && (1.122) \end{aligned}$$

The result is

$$\partial_t\left(\psi\psi^*\right)+\frac{i\hbar}{2m}\left(\psi\vec{\nabla}^2\psi^*-\psi^*\vec{\nabla}^2\psi\right)=0\;, \quad (1.123)$$

where we have used $\underline{\mathcal{H}}=\frac{p^2}{2m}+\underline{\mathcal{U}}$ and assumed that $\underline{\mathcal{U}}$ is real and independent of velocity. The second bracket in (1.123) may be transformed, i.e.

$$\begin{aligned} (\ldots) &= \psi\vec{\nabla}^2\psi^*+\left(\vec{\nabla}\psi\right)\left(\vec{\nabla}\psi^*\right)-\left(\vec{\nabla}\psi\right)\left(\vec{\nabla}\psi^*\right)\\ &\quad -\psi^*\vec{\nabla}^2\psi\\ &= \vec{\nabla}\left(\psi\vec{\nabla}\psi^*-\psi^*\vec{\nabla}\psi\right)\; . && (1.124) \end{aligned}$$

This yields the continuity equation

$$\partial_t\rho+\vec{\nabla}\cdot\vec{j}=0 \quad (1.125)$$

with

$$\rho\equiv|\,\psi\,|^2 \quad (1.126)$$

and the probability current density

$$\vec{j}\equiv\frac{i\hbar}{2m}\left(\psi\vec{\nabla}\psi^*-\psi^*\vec{\nabla}\psi\right)\; . \quad (1.127)$$

Note that in the case of hydrogen we must replace m by μ.

We proceed by evaluating (1.127) for hydrogen using spherical coordinates, i.e.

$$\vec{\nabla}=\vec{e}_\tau\partial_\tau+\vec{e}_\phi\frac{1}{\tau\sin\theta}\partial_\phi+\vec{e}_\theta\frac{1}{\tau}\partial_\theta$$

(cf. the appendix). Because the radial part of the hydrogen wave functions is real, cf. Eq. (1.117), we immediately have

$$\vec{j}_\tau=\vec{e}_\tau i\frac{\hbar}{2\mu}\left(\psi\partial_\tau\psi^*-\psi^*\partial_\tau\psi\right)=0\;, \quad (1.128)$$

which makes sense if hydrogen is supposed to be stable. The same argument applies for the θ-part of the wave functions (cf. appendix), i.e.

$$\vec{j}_\theta=\vec{e}_\theta i\frac{\hbar}{2\mu\tau}\left(\psi\partial_\theta\psi^*-\psi^*\partial_\theta\psi\right)=0\;. \quad (1.129)$$

Thus, the only non-vanishing contribution is

$$\vec{j}_\phi=\vec{e}_\phi i\frac{\hbar}{2\mu}\frac{1}{\tau\sin\theta}\left(\psi\partial_\phi\psi^*-\psi^*\partial_\phi\psi\right)\;. \quad (1.130)$$

For the moment we concentrate on $\psi_{n,l,m}$ instead on ψ_n given by Eq. (1.119), i.e. in this special state

$$\vec{j}_{\phi,lm}=\vec{e}_\phi\underbrace{\frac{m\hbar}{\mu\tau\sin\theta}\,|\,\psi_{n,l,m}\,|^2}_{\equiv j_{\phi,lm}}\;, \quad (1.131)$$

where we have used $\partial_\phi Y_{lm}=imY_{lm}$ (cf. the appendix). This is a current density corresponding to a current circling the z-axis in counter clockwise direction. Inserting Eq. (1.131) into Eq. (1.120) yields

$$\begin{aligned} \vec{m}' &= \frac{-e}{2c}\int j_{\phi,lm}\tau\underbrace{\vec{e}_\tau\times\vec{e}_\phi}_{=-\vec{e}_\theta}d^3\tau\\ &= \frac{m\hbar e}{2\mu c}\int\frac{\vec{e}_\theta}{\sin\theta}\,|\,\psi_{n,l,m}\,|^2\,d^3\tau\\ &\overset{(*)}{=} -\frac{m\hbar e}{2\mu c}\underbrace{\int|\,\psi_{n,l,m}\,|^2\,d^3\tau}_{=1}\begin{pmatrix}0\\0\\1\end{pmatrix}\;, \end{aligned}$$

and thus

$$\vec{m}'=-\frac{m\hbar e}{2\mu c}\vec{e}_z\;. \quad (1.132)$$

The equation $(*)$ is correct because $|\,\psi_{n,l,m}\,|^2$ does not depend on ϕ. The prime in Eq. (1.132) reminds us that we have used $\psi_{n,l,m}$ only to compute $\vec{m}$.

We note that the quantity

$$m_B = \frac{\hbar e}{2 m_e c} \simeq \frac{\hbar e}{2\mu c} \tag{1.133}$$

is called Bohr's magneton. Note also that

$$0 \leq \mid \vec{m}' \mid \leq l m_B \; . \tag{1.134}$$

From the appendix we have $\underline{L}_z \psi_{n,l,m} = -i\hbar\partial_\phi \psi_{n,l,m}$, i.e.

$$\underline{L}_z \psi_{n,l,m} = \underbrace{\hbar m}_{\equiv L_z} \psi_{n,l,m} \tag{1.135}$$

(cf. Eq. (1.106)). The quantity g, defined via

$$\frac{m'_z \hbar}{L_z} = -\frac{\hbar e}{2\mu c} g \; , \tag{1.136}$$

is called gyromagnetic factor or g-factor. Here we have $g = 1$ obviously. If we insert the full linear combination (1.119) instead of just $\psi_{n,l,m}$ into Eq. (1.130) then a similar but somewhat more elaborate calculation (homework problem) yields

$$\vec{m} = 0 \; . \tag{1.137}$$

This is the result for the completely degenerate hydrogen atom in the energy eigenstate ϵ_n.

One-dimensional rectangular well potential II:

In order to better understand the meaning of the probability current density introduced above, we return to the rectangular potential well (cf. page 14). Previously we had omitted the discussion of states above the potential well ($\epsilon > 0$; cf. Fig. 1.7), i.e. the states no longer are bound states. The general solutions for $\epsilon > 0$ still are given by Eq. (1.81). In addition we employ the same boundary conditions as before (cf. set 1 and set 2 on page 15). However, there is an important difference to the $\epsilon < 0$-case when the states are bound. The overall normalization of the wave function no longer converges. All k_α are positive real numbers and the solution is oscillatory in all three regions $q < -1$, $-1 \leq q \leq 1$, and $1 < q$. In addition ϵ no longer has to assume discrete values.

In principle there are two alternatives at this point. The first one is illustrated in Fig. 1.15, where the original potential well now is a small depression embedded in the middle of a vastly larger normalization potential well with infinitely high walls.

Solving Schrödinger's equation for the box-inside-a-box problem is not difficult. Our previous bound state solutions, i.e. the solutions for $\epsilon < 0$, are not affected by the normalization well. This is because the bound state wave functions decay to zero before they begin to feel the walls of the normalization well [42]. However, the solutions for $\epsilon > 0$ now must vanish at the walls of the normalization well and beyond (cf. our discussion of the infinite potential well on page 17). The resulting wave function is normalizable, and the additional boundary condition yields discrete energies as before. The spacing ΔE of these energy values depends on the width and depths of the original well, but more strongly it is determined by the width of the normalization well. If we call this quantity a_{nw} then, as we have seen before, we have $\Delta E \propto a_{nw}^{-2}$ (cf. Eq. (1.80)). In other words, for large a_{nw} the spectrum of energy eigenvalues for $\epsilon > 0$ is almost continuous. Here, however, we want to pursue a different approach. But we will return to the method of the normalization box.

The second alternative is based on a different idea. The problem is treated as a scattering problem. The solutions (1.81) are used to construct one-dimensional probability current densities. In

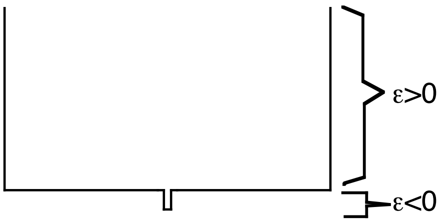


Figure 1.15: Square well potential in one dimension (small well) including normalization box.

---

[42] Unless of course for energy eigenvalues close zero, when the tails of the attending eigenfunction decay slowly.

the following j_i corresponds to a current (let's say) incident from $q = -\infty$ on the potential well. We are interested in the transmitted current density, j_t, in region III ($q > 1$) propagating to the right and in the reflected current density, j_r, propagating to the left in region I ($q < -1$). We will calculate the so called transmission coefficient $T = |j_t/j_i|$ and the reflection coefficient $R = |j_r/j_i|$ (Note: $T+R = 1$). Thus, T measures the probability of an incident particle to overcome the potential well, whereas R measures the probability that the incident particle is reflected.

Incident particles are described via

$$\psi_I\left(q\right) = \psi_{I,o}^{(1)} e^{ik_I q} \ .$$

Here k_I is a positive wave "vector". The coefficient $\psi_{I,o}^{(2)}$ vanishes, because otherwise there also would be a wave in the opposite direction with $-k_I$. Likewise we have

$$\psi_{III}\left(q\right) = \psi_{III,o}^{(1)} e^{ik_{III} q} \ .$$

for the transmitted particles. Now we can work out the current densities via Eq. (1.127). In order to simplify the computation we use the algebraic computer program *Mathematica*. The following is a list of the various program steps (in bold face) and their results.

First we express the coefficients of the solutions in the regions I to III in terms of the coefficient $\psi_{I,o}^{(1)}$ which is called A in the program:

```
"Rectangular Square Well (ε>0)";
```

```
"Wave vectors and wave functions";
k₁ = √ε ;
k₂ = √(u₀ + ε) ;
k₃ = √ε ;
ψ₁ [q_] := A Exp[I k₁ q] + c12 Exp[-I k₁ q]
ψ₂ [q_] := c21 Exp[I k₂ q] + c22 Exp[-I k₂ q]
ψ₃ [q_] := c31 Exp[I k₃ q]
```

Thus the coefficients are

Now we evaluate the current densities as well as the transmission (T) and reflection (R) coefficient. Figure 1.16 shows that for small positive ϵ reflection dominates, whereas for large positive ϵ we find $T \approx 1$. Also worth noting is the oscillatory intermittent behavior.

```
"Solving for the coefficients using the assumption that
   the wave function is continuous and differentiable
   at q=±1. Notice that A remains undetermined.";
s = Solve[{ψ₁ [-1] == ψ₂ [-1], ψ₂ [1] == ψ₃ [1],
    (D[ψ₁ [q], q] /. q → -1) == (D[ψ₂ [q], q] /. q → -1),
    (D[ψ₂ [q], q] /. q → 1) == (D[ψ₃ [q], q] /. q → 1)},
   {c12, c21, c22, c31}];
ss = FullSimplify[Flatten[s]];
c12 = c12 /. ss
c21 = c21 /. ss
c22 = c22 /. ss
c31 = c31 /. ss
```

$$\frac{\mathrm{i}\,A\,\mathrm{e}^{-2\,\mathrm{i}\left(\sqrt{\varepsilon}+\sqrt{\varepsilon+u_0}\right)}\left(-1+\mathrm{e}^{4\,\mathrm{i}\sqrt{\varepsilon+u_0}}\right)u_0}{2\left(2\,\mathrm{i}\sqrt{\varepsilon}\,\mathrm{Cos}[2\sqrt{\varepsilon+u_0}]\sqrt{\varepsilon+u_0}+\mathrm{Sin}[2\sqrt{\varepsilon+u_0}]\,(2\,\varepsilon+u_0)\right)}$$

$$\frac{\mathrm{i}\,A\,\mathrm{e}^{-\mathrm{i}\left(\sqrt{\varepsilon}+\sqrt{\varepsilon+u_0}\right)}\sqrt{\varepsilon}\left(\sqrt{\varepsilon}+\sqrt{\varepsilon+u_0}\right)}{2\,\mathrm{i}\sqrt{\varepsilon}\,\mathrm{Cos}[2\sqrt{\varepsilon+u_0}]\sqrt{\varepsilon+u_0}+\mathrm{Sin}[2\sqrt{\varepsilon+u_0}]\,(2\,\varepsilon+u_0)}$$

$$\frac{A\,\mathrm{e}^{\mathrm{i}\left(-\sqrt{\varepsilon}+\sqrt{\varepsilon+u_0}\right)}\left(-\varepsilon+\sqrt{\varepsilon}\sqrt{\varepsilon+u_0}\right)}{2\sqrt{\varepsilon}\,\mathrm{Cos}[2\sqrt{\varepsilon+u_0}]\sqrt{\varepsilon+u_0}-\mathrm{i}\,\mathrm{Sin}[2\sqrt{\varepsilon+u_0}]\,(2\,\varepsilon+u_0)}$$

$$\frac{2\,\mathrm{i}\,A\,\mathrm{e}^{-2\,\mathrm{i}\sqrt{\varepsilon}}\sqrt{\varepsilon}\sqrt{\varepsilon+u_0}}{2\,\mathrm{i}\sqrt{\varepsilon}\,\mathrm{Cos}[2\sqrt{\varepsilon+u_0}]\sqrt{\varepsilon+u_0}+\mathrm{Sin}[2\sqrt{\varepsilon+u_0}]\,(2\,\varepsilon+u_0)}$$

```
"Computing the probability current densities";

      I ħ
jᵢ = ──── (A Exp[I k₁ q] D[Simplify[
      2 m
        Conjugate[A Exp[I k₁ q]], ε > 0 && u₀ > 0 && q < 0], q] -
     Simplify[Conjugate[A Exp[I k₁ q]], ε > 0 && u₀ > 0 && q < 0]
      D[A Exp[I k₁ q], q] )
```

$$\frac{A\sqrt{\varepsilon}\,\hbar\,\mathrm{Conjugate}[A]}{m}$$

```
      I ħ
jₜ = ──── FullSimplify[ψ₃ [q]
      2 m
      D[Simplify[Conjugate[ψ₃ [q]], ε > 0 && u₀ > 0 && q > 0], q]
     Simplify[Conjugate[ψ₃ [q]], ε > 0 && u₀ > 0 && q > 0]
      D[ψ₃ [q], q], Assumptions → {ε > 0, u₀ > 0} ]
```

$$\frac{4\,A\,\varepsilon^{3/2}\,\hbar\,\mathrm{Conjugate}[A]\,(\varepsilon+u_0)}{m\left(4\,\varepsilon^2+4\,\varepsilon\,u_0+\mathrm{Sin}[2\sqrt{\varepsilon+u_0}]^2\,u_0^2\right)}$$

```
"Transmission coefficient:";
T = FullSimplify[Abs[jₜ / jᵢ], Assumptions → {ε > 0, u₀ > 0}]
```

$$\frac{4\,\varepsilon\,(\varepsilon+u_0)}{4\,\varepsilon^2+4\,\varepsilon\,u_0+\mathrm{Sin}[2\sqrt{\varepsilon+u_0}]^2\,u_0^2}$$

```
      I ħ
jᵣ = ──── FullSimplify[
      2 m
   c12 Exp[-I k₁ q] D[Simplify[Conjugate[c12 Exp[-I k₁ q]],
       ε > 0 && u₀ > 0 && q < 0], q] -
    Simplify[Conjugate[c12 Exp[-I k₁ q]], ε > 0 && u₀ > 0 && q <
     D[c12 Exp[-I k₁ q], q], Assumptions → {ε > 0, u₀ > 0} ]
```

$$-\frac{A\sqrt{\varepsilon}\,\hbar\,\mathrm{Conjugate}[A]\,\mathrm{Sin}[2\sqrt{\varepsilon+u_0}]^2\,u_0^2}{m\left(4\,\varepsilon^2+4\,\varepsilon\,u_0+\mathrm{Sin}[2\sqrt{\varepsilon+u_0}]^2\,u_0^2\right)}$$

```
"Reflection coefficient:";
R = FullSimplify[Abs[jᵣ / jᵢ], Assumptions → {ε > 0, u₀ > 0} ]
```

$$1-\frac{4\,\varepsilon\,(\varepsilon+u_0)}{4\,\varepsilon^2+4\,\varepsilon\,u_0+\mathrm{Sin}[2\sqrt{\varepsilon+u_0}]^2\,u_0^2}$$

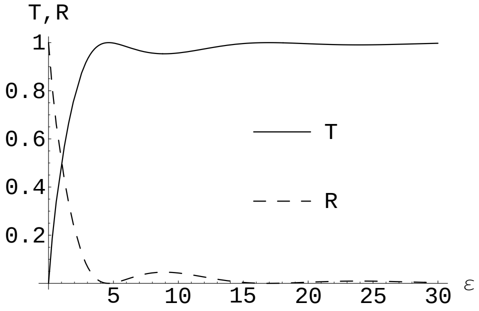


Figure 1.16: Transmission (T) and reflection (R) coefficient vs. energy, ϵ, for $u_o = 5\pi/3$ (cf. Fig. 1.9).

1.5 Angular momentum algebra

Raising and lowering operators:

In order to better understand the following discussion of angular momentum, we first introduce the key concept using the harmonic oscillator in one dimension as a simpler example.

The definitions $q = \sqrt{m\omega/\hbar}x$ and $E = \hbar\omega\epsilon$ transform the stationary Schrödinger equation (1.70) into

$$\left(-\frac{1}{2}\partial_q^2 + \frac{1}{2}q^2\right)\psi_n(q) = \epsilon_n\psi_n(q) \qquad (1.138)$$

Notice that the left side of this equation can be expressed either as

$$\left(\underline{a}^+\underline{a} + \frac{1}{2}\right)\psi_n(q) \qquad (1.139)$$

or as

$$\left(\underline{a}\underline{a}^+ - \frac{1}{2}\right)\psi_n(q) \ , \qquad (1.140)$$

where

$$\underline{a}^+ \equiv -\frac{1}{\sqrt{2}}\partial_q + \frac{1}{\sqrt{2}}q \qquad (1.141)$$

and

$$\underline{a} \equiv \frac{1}{\sqrt{2}}\partial_q + \frac{1}{\sqrt{2}}q \ . \qquad (1.142)$$

The Hamilton operator of the above dimensionless 1D harmonic oscillator thus becomes

$$\underline{\mathcal{H}} = \underline{a}^+\underline{a} + \frac{1}{2} = \underline{a}\underline{a}^+ - \frac{1}{2} \ , \qquad (1.143)$$

i.e.

$$\underline{\mathcal{H}}\psi_n(q) = \epsilon_n\psi_n(q) \ . \qquad (1.144)$$

Notice also that (1.143) implies the commutator

$$\left[\underline{a}^+, \underline{a}\right] = \underline{a}^+\underline{a} - \underline{a}\underline{a}^+ = -1 \ . \qquad (1.145)$$

(cf. the previous commutator relations (1.33), (1.34), and (1.35)).

We can use Eq. (1.145) to quickly solve the 1D harmonic oscillator. However, first we must work out the results of $\underline{\mathcal{H}}(\underline{a}^+\psi_n(q))$, i.e.

$$\begin{aligned}
\underline{\mathcal{H}}\left(\underline{a}^+\psi_n\right) &= \underline{a}^+\underline{a}\underline{a}^+\psi_n + \frac{1}{2}\underline{a}^+\psi_n \\
&\overset{(1.145)}{=} \underline{a}^+\left(\underline{a}^+\underline{a} + 1\right)\psi_n + \frac{1}{2}\underline{a}^+\psi_n \\
&= \underline{a}^+ \underbrace{\left(\underline{a}^+\underline{a} + \frac{1}{2}\right)\psi_n}_{\overset{(1.143),(1.144)}{=}\epsilon_n\psi_n} + \underline{a}^+\psi_n \\
&= \left(\epsilon_n + 1\right)\left(\underline{a}^+\psi_n\right) \ ,
\end{aligned}$$

and $\underline{\mathcal{H}}(\underline{a}\psi_n(q))$, i.e.

$$\begin{aligned}
\underline{\mathcal{H}}\left(\underline{a}\psi_n\right) &\overset{(1.143)}{=} \underline{a}\underline{a}^+\underline{a}\psi_n - \frac{1}{2}\underline{a}\psi_n \\
&= \underline{a}\left(\underline{a}^+\underline{a} - \frac{1}{2}\right)\psi_n \\
&= \left(\epsilon_n - 1\right)\left(\underline{a}\psi_n\right) \ .
\end{aligned}$$

Apparently this means

$$\underline{a}^+\psi_n \propto \psi_{n+1} \qquad (1.146)$$

and

$$\underline{a}\psi_n \propto \psi_{n-1} \ . \qquad (1.147)$$

Because of this $\underline{a}^+$ is called a raising operator, whereas $\underline{a}$ is called a lowering operator.

Now we require that if $\underline{a}$ is applied to ψ_0, where the index indicates the lowest energy eigenvalue of the oscillator, the result is zero, i.e.

$$\underline{a}\psi_0 = 0 \ . \qquad (1.148)$$

Notice that this equation in conjunction with (1.144) and (1.143) implies

$$\epsilon_0 = \frac{1}{2} \; . \tag{1.149}$$

We find $\psi_0(q)$ itself using the original definition of $\underline{a}$, i.e. Eq. (1.142), in Eq. (1.148):

$$\partial_q \psi_0(q) = -q\psi_0(q) \; . \tag{1.150}$$

Separation of variables and integration yields

$$\psi_0(q) \propto \exp[-q^2/2] \; . \tag{1.151}$$

All other $\psi_n(q)$, up to a constant, follow via successive application of $\underline{a}^+$, i.e.

$$\psi_n(q) \propto \frac{1}{2^{n/2}} \left(-\partial_q + q\right)^n \exp[-q^2/2] \tag{1.152}$$

($n = 1, 2, 3, \ldots$). The missing constants follow from the normalization condition introduced above in Eq. (1.75). Here this means

$$\int_{-\infty}^{\infty} dq \psi_n(q)^2 = 1 \tag{1.153}$$

for $n = 0, 1, 2, \ldots$.

However, there is an much quicker way to obtain the normalization constants. Notice that

$$\int_{-\infty}^{\infty} dq \, \underbrace{(\underline{a}^+\psi_n)}_{=c\psi_{n+1}}(\underline{a}^+\psi_n) = \int_{-\infty}^{\infty} dq \psi_n \underline{a}\underline{a}^+\psi_n \tag{1.154}$$

We can verify this equation by inserting the definitions (1.141) and (1.142) and subsequent integration by parts (note that we must require that all terms $|_{-\infty}^{\infty} \ldots$ vanish).

The left side of (1.154) is

$$\int_{-\infty}^{\infty} dq (c\psi_{n+1})^2 = c^2 \underbrace{\int_{-\infty}^{\infty} dq (\psi_{n+1})^2}_{=1} \; , \tag{1.155}$$

whereas the right side is

$$\int_{-\infty}^{\infty} dq \psi_n \underline{a}\underline{a}^+ \psi_n = (n+1) \underbrace{\int_{-\infty}^{\infty} dq \psi_n^2}_{=1} \; . \tag{1.156}$$

Thus

$$\psi_{n+1} = c^{-1}\underline{a}^+\psi_n = (n+1)^{-1/2}\underline{a}^+\psi_n \; , \tag{1.157}$$

i.e.

$$\underline{a}^+\psi_n = \sqrt{n+1}\psi_{n+1} \; , \tag{1.158}$$

Starting with the normalized ψ_0, i.e.

$$\psi_0(q) = \pi^{-1/4}\exp[-q^2/2] \; , \tag{1.159}$$

we now quickly generate all following normalized $\psi_n(q)$.

Notice that analogous to Eq. (1.158) for the raising operator we have

$$\underline{a}\psi_n = \sqrt{n}\psi_{n-1} \tag{1.160}$$

in the case of the lowering operator. This follows via

$$\begin{aligned} n\psi_{n-1} = \; & (\underline{\mathcal{H}} + \frac{1}{2})\psi_{n-1} \overset{(1.143)}{=} \underline{a}\underline{a}^+\psi_{n-1} \\ & \overset{(1.158)}{=} \sqrt{n}\underline{a}\psi_n \; . \end{aligned} \tag{1.161}$$

The bra...ket notation:

Often it is convenient to write ψ_n instead of $\psi_n(q)$. Operator equations like Eq. (1.148) or the operator manipulations that led to the relations (1.146) and (1.147) make perfect sense - even without q appearing in them. Only when we want to calculate $\psi_n(q)$, we need to use the explicit representations of the raising and lowering operators in terms of ∂_q and q. The bra...ket notation makes use of this observation [43]. Eq. (1.148) for instance becomes

$$\underline{a} \mid 0\rangle = 0 \; . \tag{1.162}$$

Here ψ_0 is replaced by the symbol $\mid 0\rangle$. More generally we may replace ψ_n by $\mid n\rangle$. Thus Eq. (1.144) may be expressed via

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[43] This notation was introduced by Dirac [2].

$$\underline{\mathcal{H}} \mid n\rangle = \epsilon_n \mid n\rangle \ . \tag{1.163}$$

The object $\mid n\rangle$ is a 'ket'. It is characterized by n, which here is the number of the nth Eigenvalue of the 1D oscillator. This number is all we need to know. It characterizes this particular quantum state of the oscillator. Remember that we had already used the ket-notation in the context of Eq. (1.32).

There also is a shorthand for the normalization condition (1.75), i.e.

$$\langle n \mid n\rangle = 1 \ . \tag{1.164}$$

Here $\langle n \mid$ corresponds to ψ^*. $\langle n \mid$ is a 'bra'. In the following this notation will begin to appear with increasing frequency. As we proceed, we will become familiar with its use and usefulness.

Application to angular momentum:

Prior to the solution of the hydrogen atom via Schrödinger's equation we only dealt with problems characterized by a single quantum number n associated with an energy level. Now there are two more quantum numbers. These are l and m associated with the eigenvalues of $\underline{\vec{L}}^2$ (cf. Eq. (1.105)) and $\underline{L}_z$ (cf. Eq. (1.106)). We will learn in section 2.2 that only the expectation values of commuting operators can be measured both exactly and simultaneously. The significance of this statement is that the set of quantum numbers of all (relevant) commuting operators characterize the state of the system! In the case of hydrogen these operators are $\underline{\mathcal{H}}, \underline{\vec{L}}^2$, and $\underline{L}_z$. Because we have dealt with $\underline{\mathcal{H}}$ already, we now must deal with $\underline{\vec{L}}^2$ and $\underline{L}_z$.

In the following our goal is the solution of the eigenvalue problems (1.105) and (1.106). And we use a generalization of the above notation:

$$\underline{\vec{L}}^2 \mid n_1, n_2\rangle = \lambda_{\underline{\vec{L}}^2} \mid n_1, n_2\rangle \tag{1.165}$$

and

$$\underline{L}_z \mid n_1, n_2\rangle = \lambda_{\underline{L}_z} \mid n_1, n_2\rangle \ . \tag{1.166}$$

Why we do not yet use the seemingly obvious notation $\mid l, m\rangle$ instead of $\mid n_1, n_2\rangle$ will become clear shortly.

First we point out that it is easy to confirm the following commutator relations involving the components of the angular momentum operator:

$$\begin{aligned}
\left[\underline{L}_i, \underline{r}_j\right] &= i\hbar\epsilon_{ijk}\underline{r}_k, && (1.167)\\
\left[\underline{L}_i, \underline{p}_j\right] &= i\hbar\epsilon_{ijk}\underline{p}_k, && (1.168)\\
\left[\underline{\vec{L}}, \underline{\vec{r}}^2\right] &= \left[\underline{\vec{L}}, \underline{\vec{p}}^2\right] && (1.169)\\
&= \left[\underline{\vec{L}}, \underline{\vec{r}}\cdot\underline{\vec{p}}\right] = 0 &&\\
\left[\underline{L}_i, \underline{L}_j\right] &= i\hbar\epsilon_{ijk}\underline{L}_k \ , && (1.170)
\end{aligned}$$

[44] and

$$\left[\underline{\vec{L}}^2, \underline{L}_i\right] = 0 \tag{1.171}$$

for $i = 1, 2, 3$. Here $\epsilon_{123} = \epsilon_{231} = \epsilon_{312} = 1$, $\epsilon_{132} = \epsilon_{213} = \epsilon_{321} = -1$ and $\epsilon_{ijk} = 0$ for all other ijk.

We pursue our original goal by defining raising and lowering operators via their commutators

$$\begin{aligned}
\left[\underline{a}_i, \underline{a}_j^+\right] &= \delta_{ij} && (1.172)\\
\left[\underline{a}_i, \underline{a}_j\right] &= \left[\underline{a}_i^+, \underline{a}_j^+\right] = 0 && (1.173)
\end{aligned}$$

with $i = 1, 2$. In accordance with the preceding example we have here $\left(\underline{a}_1^+\right)^{n_1}\left(\underline{a}_2^+\right)^{n_2} \mid 0, 0\rangle = \sqrt{n_1! n_2!} \mid n_1, n_2\rangle$. It is somewhat laborious but otherwise easy to show that the right hand sides of

$$\begin{aligned}
\underline{L}_x &:= \frac{\hbar}{2}\left(\underline{a}_1^+\underline{a}_2 + \underline{a}_2^+\underline{a}_1\right) && (1.174)\\
\underline{L}_y &:= i\frac{\hbar}{2}\left(\underline{a}_2^+\underline{a}_1 - \underline{a}_1^+\underline{a}_2\right) && (1.175)
\end{aligned}$$

and

$$\underline{L}_z := \frac{\hbar}{2}\left(\underline{a}_1^+\underline{a}_1 - \underline{a}_2^+\underline{a}_2\right) \tag{1.176}$$

are consistent with the above relations (1.170) and (1.171). In this sense the right hand sides of the

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[44] Again there is a strong resemblance to the Poisson brackets in classical mechanics.

above definitions are truly equivalent to the angular momentum components. The fact that the angular momentum components can be expressed in terms of raising and lowering operators is not a mere complication but can be applied quite efficiently to our original purpose!

Using the commutators (1.172) and (1.173) we obtain

$$\begin{aligned}\underline{L}^2 &= \frac{\hbar^2}{2}\left(\underline{N}_1+\underline{N}_2\right) \qquad (1.177)\\ &+\frac{\hbar^2}{4}\left(\underline{N}_1^2+\underline{N}_2^2+2\underline{N}_1\underline{N}_2\right)\ ,\end{aligned}$$

where $\underline{N}_1$ and $\underline{N}_2$ are the number operators

$$\underline{N}_i = \underline{a}_i^+\underline{a}_i \quad (i=1,2) \qquad (1.178)$$

obeying $[\underline{N}_1,\underline{N}_2]=0$. We therefore immediately obtain

$$\begin{aligned}\underline{L}^2 \mid n_1,n_2\rangle &= \hbar^2\Big(\frac{n_1+n_2}{2} \qquad (1.179)\\ &+\frac{\left(n_1+n_2\right)^2}{4}\Big)\mid n_1,n_2\rangle\end{aligned}$$

and

$$\begin{aligned}\underline{L}_z \mid n_1,n_2\rangle &= \frac{\hbar}{2}\left(\underline{N}_1-\underline{N}_2\right)\mid n_1,n_2\rangle\\ &= \hbar\frac{n_1-n_2}{2}\mid n_1,n_2\rangle\ . \qquad (1.180)\end{aligned}$$

Using the substitutions

$$l=\frac{n_1+n_2}{2} \qquad (1.181)$$

and

$$m=\frac{n_1-n_2}{2} \qquad (1.182)$$

we find

$$\underline{L}^2\mid l+m,l-m\rangle = \hbar^2 l\left(l+1\right)\mid l+m,l-m\rangle$$

and

$$\underline{L}_z\mid l+m,l-m\rangle = \hbar m\mid l+m,l-m\rangle\ .$$

With the natural replacement $\mid l+m,l-m\rangle \rightarrow\mid l,m\rangle$ we finally write

$$\underline{L}^2\mid l,m\rangle = \hbar^2 l\left(l+1\right)\mid l,m\rangle \qquad (1.183)$$

and

$$\underline{L}_z\mid l,m\rangle = \hbar m\mid l,m\rangle\ , \qquad (1.184)$$

which partially fulfills our original goal. But there is more information here. From

$$l+m=n_1\geq 0 \quad \text{and} \quad l-m=n_2\geq 0$$

follows

$$m=-l,-l+1,\ldots,l-1,l\ , \qquad (1.185)$$

which is also in agreement with our previous assumption. On the other hand we find from (1.181) that

$$l=0,\frac{1}{2},1,\frac{3}{2},\ldots \qquad (1.186)$$

Thus, in addition to the expected integer values we also get half integer values, which requires an explanation.

In the appendix we had shown $\underline{L}_z=-i\hbar\partial\phi$ in polar coordinates. In particular we may write Eq. (1.184) in a concrete representation [45], i.e. for $m=-l$ we may write

$$\underline{L}_z Y_{l,-l}\left(\theta,\phi\right) = -\hbar l Y_{l,-l}\left(\theta,\phi\right)\ ,$$

and thus

$$Y_{l,-l}\left(\theta,\phi\right)\sim e^{-il\phi}\ , \qquad (1.187)$$

where we pretend to not know that Y_{lm} are spherical harmonics. Relation (1.187) yields $Y_{lm}(\theta,0)=$

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[45] The exact meaning of 'representation' will be explained in the next chapter.

$Y_{lm}(\theta, 2\pi)$ only if $l = 0, 1, 2, \ldots$; but this is exactly what we expect in the case of angular momentum [46]!

In order to find the explicit form of $Y_{lm}(\theta, \phi)$ we need to first calculate $\underline{a}_1^+ \underline{a}_2 \mid n_1, n_2\rangle$ and $\underline{a}_2^+ \underline{a}_1 \mid n_1, n_2\rangle$. Here we go!

$$\begin{aligned}
&\underline{a}_1^+ \underline{a}_2 \mid n_1, n_2\rangle \\
&\quad = \underline{a}_1^+ \underline{a}_2 \left(\underline{a}_1^+\right)^{n_1} \left(\underline{a}_2^+\right)^{n_2} \mid 0,0\rangle \frac{1}{\sqrt{n_1! n_2!}} \\
&\quad = \left(\underline{a}_1^+\right)^{n_1+1} \underline{a}_2 \left(\underline{a}_2^+\right)^{n_2} \mid 0,0\rangle \frac{1}{\sqrt{n_1! n_2!}} \\
&\quad = \left(\underline{a}_1^+\right)^{n_1+1} \underbrace{\underline{a}_2 \underline{a}_2^+}_{=\underline{a}_2^+ \underline{a}_2 + 1} \left(\underline{a}_2^+\right)^{n_2-1} \mid 0,0\rangle \frac{1}{\sqrt{n_1! n_2!}} \\
&\quad = \left(\underline{a}_2^+ \underline{a}_2 + 1\right) \mid n_1+1, n_2-1\rangle \sqrt{\frac{n_1+1}{n_2}} \\
&\quad = \sqrt{(n_1+1)\, n_2} \mid n_1+1, n_2-1\rangle \ .
\end{aligned}$$

With $n_1 = l + m$ and $n_2 = l - m$ follows

$$\begin{aligned}
&\underline{a}_1^+ \underline{a}_2 \mid l+m, l-m\rangle \\
&\quad = \sqrt{l\,(l+1) - m\,(m+1)} \\
&\quad \times \mid l + (m+1), l - (m+1)\rangle \ .
\end{aligned}$$

Using the same replacements as above we finally have

$$\begin{aligned}
&\underline{a}_1^+ \underline{a}_2 \mid l, m\rangle \\
&\quad = \sqrt{l\,(l+1) - m\,(m+1)} \\
&\quad \times \mid l, m+1\rangle \ .
\end{aligned} \tag{1.188}$$

The operator $\underline{a}_1^+ \underline{a}_2$ acts as raising operator on m! Analogously we can show

$$\begin{aligned}
&\underline{a}_2^+ \underline{a}_1 \mid l, m\rangle \\
&\quad = \sqrt{l\,(l+1) - m\,(m-1)} \\
&\quad \times \mid l, m-1\rangle \ .
\end{aligned} \tag{1.189}$$

Therefore the operator $\underline{a}_2^+ \underline{a}_1$ acts as lowering operator on m! Now we put Eqs. (1.188) and (1.189) to work. We start considering

$$\underline{a}_2^+ \underline{a}_1 Y_{l,-l}(\theta, \phi) = 0 \ . \tag{1.190}$$

This is sensible because $-l$ is the lowest possible value for m. Using Eqs. (1.174) and (1.175) we obtain

$$\begin{aligned}
0 &= \frac{1}{\hbar}\left(\underline{L}_x - i\underline{L}_y\right) Y_{l,-l}(\theta, \phi) \\
&\overset{\text{appendix}}{=} e^{-i\phi}\left(i \cot\theta \partial_\phi - \partial_\theta\right) Y_{l,-l}(\theta, \phi) \ .
\end{aligned}$$

Inserting $Y_{l,-l}(\theta, \phi) = f(\theta)\, e^{-il\phi}$ (cf. Eq. (1.187)) we get

$$0 = e^{-i(l+1)\phi}\left(l \cot\theta - \partial_\theta\right) f(\theta)$$

and therefore

$$f(\theta) \sim \sin^l \theta$$

or

$$Y_{l,-l}(\theta, \phi) \sim \sin^l \theta e^{-il\phi} \ .$$

Because we use the normalization

$$\int Y_{lm}^* Y_{lm} d\Omega = 1 \ ,$$

we finally obtain

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

At this point we can apply Eq. (1.188), i.e.

$$\begin{aligned}
&\underline{a}_1^+ \underline{a}_2 Y_{l,-l}(\theta, \phi) \\
&\quad = \frac{1}{\hbar}\left(\underline{L}_x + i\underline{L}_y\right) Y_{l,-l}(\phi, \theta) \\
&\quad \overset{\text{appendix}}{=} e^{-i\phi}\left(i \cot\theta \partial_\phi + \partial_\theta\right) Y_{l,-l}(\theta, \phi) \\
&\quad = \sqrt{2l} Y_{l,-l+1}(\theta, \phi)
\end{aligned} \tag{1.191}$$

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[46] Remark: This expectation is based on our macroscopic point of view. In section section 5.3 we discuss the spin of the electron. This intrinsic angular momentum is different. We cannot increase the electron to macroscopic size and watch it spinning. In fact, the l of the electron is $1/2$. According to our above reasoning this means that a 360^o rotation is not sufficient. We have to rotate twice in order to return to the original orientation.

or [47]

$$\begin{aligned} Y_{lm}\left(\theta,\phi\right) = & \left((2l)!\frac{(l+m)!}{(l-m)!}\right)^{-\frac{1}{2}} \\ & \times\left[e^{-i\phi}\left(i\cot\theta\partial_\phi+\partial_\theta\right)\right]^{l+m}Y_{l,-l}\left(\theta,\phi\right)\ . \end{aligned} \tag{1.192}$$

Thus, combining the results (1.183), (1.184), and (1.192) we have derived Eqs. (1.105) and (1.106) assumed previously!

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[47] Using (1.188) to obtain the correct normalization.

Chapter 2

Formal quantum mechanics

The above examples have inspired some confidence in the newly developed quantum mechanics. Now it is time to explore the formal aspects of this theory.

We begin by introducing the notation

$$\psi\,(\vec{r},t) \equiv \langle \vec{r} \mid \psi\,(t)\rangle \tag{2.1}$$

for the wave function. If we Fourier transform Eq. (2.1), we obtain the wave function in $\vec{k}$-space, i.e.

$$\psi\,(\vec{r},t) \overset{\text{F. T.}}{\longrightarrow} \tilde{\psi}(\vec{k},t) \equiv \langle \vec{k} \mid \psi\,(t)\rangle\ . \tag{2.2}$$

We recognize that instead of $\psi(\vec{r},t)$ or $\tilde{\psi}(\vec{k},t)$, which describe the wave function in $\vec{r}$- or $\vec{k}$-representation, we may view $\mid \psi\,(t)\rangle$ as an abstract or non-specific representation of the wave function. In order to tie $\psi\,(\vec{r},t)$ to $\tilde{\psi}(\vec{k},t)$ using the new notation we introduce the "complete sets"

$$1 = \int d^3r \mid \vec{r}\rangle\langle\vec{r} \mid \tag{2.3}$$

and

$$1 = \int d^3k \mid \vec{k}\rangle\langle\vec{k} \mid\ \ . \tag{2.4}$$

The meaning of (2.3) and (2.4) becomes clear if we multiply both sides of (2.4) by $\langle \vec{r} \mid$ from the left and by $\mid \psi\,(t)\rangle$ from the right. The result is

$$\begin{aligned} \psi\,(\vec{r},t) &= \langle \vec{r} \mid \psi\,(t)\rangle \\ &= \int d^3k \langle \vec{r} \mid \vec{k}\rangle \underbrace{\langle \vec{k} \mid \psi\,(t)\rangle}_{=\tilde{\psi}(\vec{k},t)}\ , \end{aligned} \tag{2.5}$$

and we obtain

$$\langle \vec{r} \mid \vec{k}\rangle = \frac{1}{(2\pi)^{3/2}} e^{i\vec{k}\cdot\vec{r}}\ . \tag{2.6}$$

Similarly we have

$$\langle \vec{k} \mid \vec{r}\rangle = \frac{1}{(2\pi)^{3/2}} e^{-i\vec{k}\cdot\vec{r}}\ , \tag{2.7}$$

i.e. $\langle \vec{r} \mid \vec{k}\rangle$ is the complex conjugate of $\langle \vec{k} \mid \vec{r}\rangle$. Of course, what we have so far is not limited to Fourier transformation. It applies to every complete set of functions, which can be used to expand the wave function.

Note also that using

$$\vec{p} = \hbar\vec{k} \tag{2.8}$$

the relations (2.6) and (2.7) may be written as

$$\langle \vec{r} \mid \vec{p}\rangle = \frac{1}{(2\pi\hbar)^{3/2}} e^{i\vec{p}\cdot\vec{r}/\hbar} \tag{2.9}$$

and

$$\langle \vec{p} \mid \vec{r}\rangle = \frac{1}{(2\pi\hbar)^{3/2}} e^{-i\vec{p}\cdot\vec{r}/\hbar}\ . \tag{2.10}$$

Hilbert space:

We have already discussed the necessity and the physical meaning of the existence of

$$\langle \psi \mid \psi \rangle = \int_{\text{a.s.}} \mid \psi \mid^2 dV = \text{finite} \qquad (2.11)$$

for the wave function ψ (a.s.: all space). The set of all functions for which the above integral exists span the Hilbert space $\mathbf{H}$. In addition to (2.11) there are other properties the wave functions must have:

1. Linearity: ψ_1, $\psi_2 \in \mathbf{H} \Rightarrow c_1\psi_1 + c_2\psi_2 \in \mathbf{H}$ for $c_1, c_2 \in$ complex numbers.
2. Scalar product: The relation $\langle \psi_1 \mid \psi_2 \rangle = \int_{\text{a.s.}} \psi_1^* \psi_2 dV$ defines a scalar product with the following properties. (i) $\langle \psi_1 \mid \psi_2 \rangle = \langle \psi_2 \mid \psi_1 \rangle^*$, (ii) $\langle \phi \mid c_1\psi_1 + c_2\psi_2 \rangle = c_1\langle \phi \mid \psi_1 \rangle + c_2\langle \phi \mid \psi_2 \rangle$, and $\langle \psi \mid \psi \rangle \geq 0$. (i) through (iii) yield the Schwarz inequality:

$$\mid \langle \psi_1 \mid \psi_2 \rangle \mid \leq \sqrt{\langle \psi_1 \mid \psi_1 \rangle \langle \psi_2 \mid \psi_2 \rangle} \; . \qquad (2.12)$$

Hermitian Operators:

We interpret the quantity $\mid \psi(\vec{r}, t) \mid^2 d^3r$ as the probability of finding the particle in a volume element d^3r at position $\vec{r}$. Therefore it is sensible to require

$$\frac{\partial}{\partial t} \int_{\text{a.s.}} \psi^*(\vec{r}, t)\, \psi(\vec{r}, t)\, d^3r = 0 \; , \qquad (2.13)$$

i.e. probability conservation. Using $\partial_t \psi = \frac{1}{i\hbar} \underline{\mathcal{H}} \psi$ and $(\partial_t \psi)^* = -\frac{1}{i\hbar} (\underline{\mathcal{H}} \psi)^*$ respectively, we do obtain

$$\frac{1}{i\hbar} \int_{\text{a.s.}} \left(\psi^* (\underline{\mathcal{H}} \psi) - \psi (\underline{\mathcal{H}} \psi)^* \right) d^3r = 0 \qquad (2.14)$$

or

$$\int_{\text{a.s.}} d^3r \psi^* (\underline{\mathcal{H}} \psi) = \int_{\text{a.s.}} d^3r \psi (\underline{\mathcal{H}} \psi)^* \; . \qquad (2.15)$$

Every operator $\underline{\Lambda}$ obeying Eq. (2.15) for arbitrary $\psi(\vec{r}, t)$ is called hermitian.

Eq. (2.15) may be generalized to

$$\int_{\text{a.s.}} d^3r \psi_1^* (\underline{\Lambda} \psi_2) = \int_{\text{a.s.}} d^3r (\underline{\Lambda} \psi_1)^* \psi_2 \; . \qquad (2.16)$$

In order to prove this, we insert $\psi = \psi_1 + \psi_2$ into Eq. (2.15), where we replace $\underline{\mathcal{H}}$ with $\underline{\Lambda}$. The argument of the integral on the left side becomes

$$\begin{aligned} \psi^* (\underline{\Lambda} \psi) &= (\psi_1 + \psi_2)^* (\underline{\Lambda} (\psi_1 + \psi_2)) \\ &= \psi_1^* (\underline{\Lambda} \psi_1) + \psi_2^* (\underline{\Lambda} \psi_2) \\ &\quad + \psi_1^* (\underline{\Lambda} \psi_2) + \psi_2^* (\underline{\Lambda} \psi_1) \; . \end{aligned}$$

Notice that we assume that $\underline{\Lambda}$ is a linear operator [1]. Analogously we obtain on the right side

$$\begin{aligned} (\underline{\Lambda} \psi)^* \psi &= (\underline{\Lambda} \psi_1)^* \psi_1 + (\underline{\Lambda} \psi_2)^* \psi_2 \\ &\quad + (\underline{\Lambda} \psi_1)^* \psi_2 + (\underline{\Lambda} \psi_2)^* \psi_1 \; . \end{aligned}$$

Combining these two equations and using the definition (2.15) for hermitian operators we obtain

$$\begin{aligned} &\int_{\text{a.s.}} d^3r \Big(\psi_1^* (\underline{\Lambda} \psi_2) + \psi_2^* (\underline{\Lambda} \psi_1) \Big) \\ &= \int_{\text{a.s.}} d^3r \Big((\underline{\Lambda} \psi_1)^* \psi_2 + (\underline{\Lambda} \psi_2)^* \psi_1 \Big) \end{aligned}$$

or

$$\begin{aligned} &\int_{\text{a.s.}} d^3r \underbrace{\Big(\psi_1^* (\underline{\Lambda} \psi_2) - (\underline{\Lambda} \psi_2)^* \psi_1 \Big)}_{=2\mathrm{Im}\left(\psi_1^* (\underline{\Lambda} \psi_2)\right)} \\ &= \int_{\text{a.s.}} d^3r \underbrace{\Big((\underline{\Lambda} \psi_1)^* \psi_2 - \psi_2^* (\underline{\Lambda} \psi_1) \Big)}_{=2\mathrm{Im}\left((\underline{\Lambda} \psi_1)^* \psi_2\right)} \; . \end{aligned}$$

Therefore

$$\begin{aligned} &\mathrm{Im} \int_{\text{a.s.}} d^3r \psi_1^* (\underline{\Lambda} \psi_2) \\ &\quad = \mathrm{Im} \int_{\text{a.s.}} d^3r (\underline{\Lambda} \psi_1)^* \psi_2 \; . \qquad (2.17) \end{aligned}$$

Now we repeat this calculation using a different $\psi(\vec{r}, t)$, i.e. $\psi = \psi_1 + i\psi_2$. The result is

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[1] That is $\underline{\Lambda}(c_1\psi_1 + c_2\psi_2) = c_1\underline{\Lambda}\psi_1 + c_2\underline{\Lambda}\psi_2$, where c_1, c_2 are constants.

$$\begin{aligned}&\mathrm{Re}\int_{\text{a.s.}} d^3r\psi_1^*\left(\underline{\Lambda}\psi_2\right)\\ &\quad= \mathrm{Re}\int_{\text{a.s.}} d^3r\left(\underline{\Lambda}\psi_1\right)^*\psi_2\ . \qquad (2.18)\end{aligned}$$

Eqs. (2.17) and (2.18) together show that Eq. (2.16) is indeed correct.

Let us consider an example, i.e. we want to show that $\underline{p}_x = -i\hbar\partial_x$ is hermitian. We write

$$\begin{aligned}&\int_{\text{a.s.}} d^3r\psi^*\left(-i\hbar\frac{\partial}{\partial x}\psi\right)\\ &\overset{\text{p. i.}}{=} -i\hbar\Big|_{-\infty}^{\infty}\int_{-\infty}^{\infty} dydz\psi^*\psi\\ &+i\hbar\int_{\text{a.s.}} d^3r\left(\frac{\partial}{\partial x}\psi^*\right)\psi\\ &=\int_{\text{a.s.}} d^3r\left(-i\hbar\frac{\partial}{\partial x}\psi\right)^*\psi\ .\end{aligned}$$

Here p. i. stands for partial integration. The $|_{-\infty}^{\infty}\dots$–term vanishes, because of the normalizability of the wave function, and we find that $\underline{p}_x$ obeys Eq. (2.15). Notice that $i\underline{p}_x$ on the other hand does not.

Finally we want to translate the condition for hermiticity to our new bra...ket notation. Using $\psi(\vec{r},t) = \langle\vec{r}\mid\psi(t)\rangle$ and $\psi^*(\vec{r},t) = \langle\psi(t)\mid\vec{r}\rangle$, i.e. Eq. (2.5), we may write the left hand side of Eq. (2.16) as

$$\begin{aligned}&\int_{\text{a.s.}} d^3r\psi_1(\vec{r},t)^*\left(\underline{\Lambda}\psi_2(\vec{r},t)\right)\\ &\quad=\int_{\text{a.s.}} d^3r\langle\psi_1(t)\mid\vec{r}\rangle\langle\vec{r}\mid\phi_2(t)\rangle\ ,\end{aligned}$$

where $\mid\phi_2(t)\rangle \equiv \underline{\Lambda}\mid\psi_2(t)\rangle$. Inserting "1", i.e. Eq. (2.3), between $\underline{\Lambda}$ and $\mid\psi_2(t)\rangle$ we obtain

$$\begin{aligned}&\int_{\text{a.s.}} d^3r\psi_1(\vec{r},t)^*\left(\underline{\Lambda}\psi_2(\vec{r},t)\right)\\ &\quad=\int_{\text{a. s.}} d^3rd^3r'\langle\psi_1(t)\mid\vec{r}\rangle\langle\vec{r}\mid\underline{\Lambda}\mid\vec{r}'\rangle\langle\vec{r}'\mid\psi_2(t)\rangle\\ &\quad=\langle\psi_1(t)\mid\underline{\Lambda}\mid\psi_2(t)\rangle\ .\end{aligned}$$

Now we consider the right hand side of Eq. (2.16), i.e.

$$\begin{aligned}&\int_{\text{a.s.}} d^3r\left(\underline{\Lambda}\psi_1(\vec{r},t)\right)^*\psi_2(\vec{r},t)\\ &\quad=\int_{\text{a. s.}} d^3r\langle\phi_1(t)\mid\vec{r}\rangle\langle\vec{r}\mid\psi_2(t)\rangle\\ &\quad=\int_{\text{a. s.}} d^3rd^3r'\left(\langle\vec{r}\mid\underline{\Lambda}\mid\vec{r}'\rangle^*\langle\vec{r}'\mid\psi_1\rangle^*\right)\langle\vec{r}\mid\psi_2(t)\rangle\ ,\end{aligned}$$

where $\langle\phi_1(t)\mid\vec{r}\rangle \equiv \langle\vec{r}\mid\phi_1(t)\rangle^* = \langle\vec{r}\mid\underline{\Lambda}\mid\psi_1(t)\rangle^*$. Therefore

$$\begin{aligned}&\int_{\text{a.s.}} d^3r\left(\underline{\Lambda}\psi_1(\vec{r},t)\right)^*\psi_2(\vec{r},t)\\ &\quad=\int_{\text{a. s.}} d^3rd^3r'\langle\psi_2(t)\mid\vec{r}\rangle^*\langle\vec{r}\mid\underline{\Lambda}\mid\vec{r}'\rangle^*\langle\vec{r}'\mid\psi_1(t)\rangle^*\\ &\quad=\langle\psi_2(t)\mid\underline{\Lambda}\mid\psi_1(t)\rangle^*\ .\end{aligned}$$

Using the definition

$$\langle\psi_2(t)\mid\underline{\Lambda}\mid\psi_1(t)\rangle^* \equiv \langle\psi_1(t)\mid\underline{\Lambda}^+\mid\psi_2(t)\rangle \qquad (2.19)$$

Eq. (2.16) becomes

$$\langle\psi_1(t)\mid\underline{\Lambda}\mid\psi_2(t)\rangle = \langle\psi_1(t)\mid\underline{\Lambda}^+\mid\psi_2(t)\rangle\ . \qquad (2.20)$$

Because Eq. (2.20) must hold for arbitrary states $\mid\psi_1(t)\rangle$ and $\mid\psi_2(t)\rangle$ we conclude from

$$\langle\psi_1(t)\mid\underline{\Lambda}-\underline{\Lambda}^+\mid\psi_2(t)\rangle = 0$$

that

$$\underline{\Lambda} = \underline{\Lambda}^+ \qquad (2.21)$$

for hermitian operators.

Expansion of states in eigenstates:

We return to the general eigenvalue equation

$$\underline{\Lambda}\mid\psi_n\rangle = \lambda_n\mid\psi_n\rangle\ . \qquad (2.22)$$

Here the λ_1, λ_2, ... form a discrete eigenvalue spectrum of the hermitian operator $\underline{\Lambda}$. The $\mid\psi_n\rangle$ are the so called eigenstates of Λ.

1. The eigenvalues are real [2].
2. Two eigenfunctions belonging to two different eigenvalues are orthogonal [3] and thus linearly independent.
3. If λ is n-fold degenerate, it is still possible to construct n eigenfunctions to λ which are orthonormal (e.g., via the procedure according to Schmidt). Therefore each eigenvalue is associated with a series of orthonormal eigenfunctions which consists of either one element (no degeneracy), a finite number of elements (finite degeneracy) or an infinite number of elements (infinite degeneracy).
4. We postulate that the set of eigenstates $\mid \psi_n \rangle$ of any hermitian operator $\underline{\Lambda}$ that represents a physical quantity form a complete set. Using the notation introduced in (2.3) and (2.4) this can be expressed as

$$\begin{aligned} \mid \psi \rangle &= \sum_n \mid \psi_n \rangle \langle \psi_n \mid \psi \rangle \\ &= \sum_n c_n \mid \psi_n \rangle \; . \end{aligned} \qquad (2.23)$$

Therefore

$$\underline{P}_n \equiv \mid \psi_n \rangle \langle \psi_n \mid \qquad (2.24)$$

can be view as a projection operator, which, if it is applied to $\mid \psi \rangle$, singles out a certain component of the "state vector":

$$\underline{P}_n \mid \psi \rangle = c_n \mid \psi_n \rangle \qquad (2.25)$$

A simple analogy may serve as illustration. Consider a vector $\vec{a}$ expressed in terms of its components via

$$\vec{a} = \sum_{n=1}^{3} \vec{e}_n \left(\vec{e}_n \cdot \vec{a} \right) \; ,$$

where the $\vec{e}_n$ are unit vectors along the axes of the coordinate system. Here $\vec{e}_n \left(\vec{e}_n \cdot \right)$ is analogous to P_n.

Intuitively all of this makes perfect sense, because we are used to expressing even complicated boundary conditions, which appear in the context of eigenvalue differential equations, in terms of linear combinations of the eigenfunctions. Completeness of the eigenfunctions can be proved in 1D and in certain multidimensional cases, but must be postulated for most multidimensional systems. For details see [3, 20, 21].

Much of this is very formal, and the usefulness of the new notation may not be apparent at this stage. But it will be!

2.1 Operator averages

We have noted that the quantity $\mid \psi(\vec{r}) \mid^2 d^3r$ corresponds to the probability of finding a particle inside the volume element d^3r. In this spirit we define the following average of the position 'operator'

$$\langle \underline{\vec{r}} \rangle = \int_{\text{a.s.}} d^3r \psi^* \left(\vec{r}, t \right) \vec{r} \psi \left(\vec{r}, t \right) \; . \qquad (2.26)$$

Using the new notation this reads

$$\langle \underline{\vec{r}} \rangle = \langle \psi(t) \mid \underline{\vec{r}} \mid \psi(t) \rangle \; . \qquad (2.27)$$

Here we use $\underline{\vec{r}}$ to remind us that $\vec{r}$ really is an operator. To show the connection between Eq. (2.27) and Eq. (2.26) we again insert 1, i.e. (2.3), on both sides of $\underline{\vec{r}}$ in Eq. (2.27):

$$\begin{aligned} \langle \underline{\vec{r}} \rangle &= \int d^3r d^3r\,' \langle \psi(t) \mid \vec{r} \rangle \\ &\quad \times \langle \vec{r} \mid \underline{\vec{r}} \mid \vec{r}\,' \rangle \langle \vec{r}\,' \mid \psi(t) \rangle \; . \end{aligned} \qquad (2.28)$$

Comparison with Eq. (2.26) implies

$$\begin{aligned} \langle \vec{r} \mid \underline{\vec{r}} \mid \vec{r}\,' \rangle &= \vec{r} \langle \vec{r} \mid \vec{r}\,' \rangle &(2.29) \\ &= \vec{r} \delta(\vec{r} - \vec{r}\,') \; . &(2.30) \end{aligned}$$

The last equality we prove via

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[2] This is evident from Eq. (2.15), when $\underline{\Lambda}$ replaces $\underline{\mathcal{H}}$

[3] This is evident from Eq. (2.16). In bra...ket notation the prove is $\langle \psi_2 \mid \underline{\Lambda} \mid \psi_1 \rangle - \langle \psi_1 \mid \underline{\Lambda^+} \mid \psi_2 \rangle^* = \langle \psi_2 \mid \underline{\Lambda} \mid \psi_1 \rangle - \langle \psi_1 \mid \underline{\Lambda} \mid \psi_2 \rangle^* = (\lambda_1 - \lambda_2) \langle \psi_2 \mid \psi_1 \rangle = 0$.

$$\begin{aligned}\langle\vec r\mid\vec r\,'\rangle &\overset{(2.4)}{=} \int d^3k\langle\vec r\mid\vec k\rangle\langle\vec k\mid\vec r\,'\rangle\\ &\overset{(2.6,2.7)}{=} \frac{1}{(2\pi)^3}\int d^3k e^{i\vec k\cdot(\vec r-\vec r\,')}\\ &= \delta(\vec r-\vec r\,')\ .\end{aligned}$$

Next we want to look at the time derivative of $\langle\underline{\vec r}\rangle$, i.e.

$$\frac{d}{dt}\langle\underline{\vec r}\rangle = \langle\dot\psi\,(t)\mid\underline{\vec r}\mid\psi\,(t)\rangle + \langle\psi\,(t)\mid\underline{\vec r}\mid\dot\psi\,(t)\rangle\ .$$

Using Schrödinger's equation in representation free notation,

$$i\hbar\mid\dot\psi\,(t)\rangle \;=\; \underline{\mathcal{H}}\mid\psi\,(t)\rangle$$

and

$$-i\hbar\langle\dot\psi\,(t)\mid \;=\; \langle\psi\,(t)\mid\underline{\mathcal{H}}\ ,$$

we may write

$$\frac{d}{dt}\langle\underline{\vec r}\rangle = \frac{i}{\hbar}\langle\psi\,(t)\mid[\underline{\mathcal{H}},\underline{\vec r}]\mid\psi\,(t)\rangle\ . \tag{2.31}$$

Inserting $\underline{\mathcal{H}} = \frac{\underline{p}^2}{2m} + \mathcal{U}\,(\underline{\vec r})$ we obtain (using (1.51)).

$$\begin{aligned}\frac{d}{dt}\langle\underline{\vec r}\rangle &= \frac{i}{2m\hbar}\langle\psi\,(t)\mid\left[\underline{\vec p}^2,\underline{\vec r}\right]\mid\psi\,(t)\rangle\\ &= \frac{1}{m}\langle\underline{\vec p}\rangle \qquad (2.32)\end{aligned}$$

[4]. Notice the analogy between (2.32) and the classical momentum-velocity-relation $\vec p = m\vec v$.

To make this analogy even more apparent we consider

$$\begin{aligned}\frac{d^2}{dt^2}\langle\underline{\vec r}\rangle &= \frac{1}{m}\frac{d}{dt}\langle\underline{\vec p}\rangle\\ &= \frac{i}{m\hbar}\langle\psi\,(t)\mid\left[\underline{\mathcal{H}},\underline{\vec p}\right]\mid\psi\,(t)\rangle\\ &= \frac{i}{m\hbar}\langle\psi\,(t)\mid\left[\underline{\mathcal{U}},\underline{\vec p}\right]\mid\psi\,(t)\rangle\ . \qquad (2.34)\end{aligned}$$

The last equality results from relation (Eq. (1.52)). In a homework problem we will prove that for every analytic function $F\,(x)$ we have $[\underline{A},\underline{F}\,(\underline{B})] = [\underline{A},\underline{B}]\,F\,'\,(\underline{B})$, where $F\,'\,(x)$ denotes the derivative of $F\,(x)$ [5]. Assuming that $\mathcal{U}\,(\vec r)$ is analytic we find

$$\left[\underline{\mathcal{U}},\underline{\vec p}\right] = \begin{pmatrix}[\underline{\mathcal{U}},\underline{p}_x]\\ [\underline{\mathcal{U}},\underline{p}_y]\\ [\underline{\mathcal{U}},\underline{p}_z]\end{pmatrix} = \begin{pmatrix}[\underline{x},\underline{p}_x]\frac{d\underline{\mathcal{U}}}{dx}\\ [\underline{y},\underline{p}_y]\frac{d\underline{\mathcal{U}}}{dy}\\ [\underline{z},\underline{p}_z]\frac{d\underline{\mathcal{U}}}{dz}\end{pmatrix} = i\hbar\vec\nabla\underline{\mathcal{U}}$$

and thus

$$\begin{aligned}m\frac{d^2}{dt^2}\langle\underline{\vec r}\rangle &= \langle\psi\,(t)\mid-\vec\nabla\underline{\mathcal{U}}\mid\psi\,(t)\rangle\\ &= \langle-\vec\nabla\underline{\mathcal{U}}\rangle\ . \qquad (2.35)\end{aligned}$$

i.e. we obtain Newton's second law for the quantum mechanical averages. Relations (2.32) and (2.35) are known as Ehrenfest's theorem [6].

We note that in Eq. (2.31) instead of $\underline{\vec r}$ we could have inserted other operators. Replacing $\underline{\vec r}$ by $\underline{\Lambda}(t)$ we obtain

$$\frac{d}{dt}\langle\underline{\Lambda}\rangle = \frac{i}{\hbar}\langle\psi\,(t)\mid[\underline{\mathcal{H}},\underline{\Lambda}]\mid\psi\,(t)\rangle + \langle\frac{\partial\underline{\Lambda}(t)}{\partial t}\rangle\ . \tag{2.36}$$

For a $\underline{\Lambda}$ which does not depend on time explicitly, we find that $\frac{d}{dt}\langle\underline{\Lambda}\rangle = 0$ if $\underline{\Lambda}$ commutes with $\underline{\mathcal{H}}$. Because $\underline{\mathcal{H}}$ commutes with itself, we find that in a closed quantum mechanical system energy is conserved. From Eqs. (2.34) and (2.35) we also find $\frac{d}{dt}\langle\underline{\vec p}\rangle = 0$ in the absence of external forces. Thus we

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[4] $\left[\underline{\vec p}^2,\underline{\vec r}\right] = \begin{pmatrix}[\underline{p}_x^2+\underline{p}_y^2+\underline{p}_z^2,\underline{x}]\\ [\ldots,\underline{y}]\\ [\ldots,\underline{z}]\end{pmatrix} = \begin{pmatrix}[\underline{p}_x{}^2,\underline{x}]\\ [\underline{p}_y{}^2,\underline{y}]\\ [\underline{p}_z{}^2,\underline{z}]\end{pmatrix} = 2(-i\hbar)\begin{pmatrix}\underline{p}_x\\ \underline{p}_y\\ \underline{p}_z\end{pmatrix} = 2(-i\hbar)\underline{\vec p}$. Here we have used

$$[\underline{A}\underline{B},\underline{C}] = \underline{A}\,[\underline{B},\underline{C}] + [\underline{A},\underline{C}]\,\underline{B}\ , \tag{2.33}$$

which we prove by expanding both sides of the equation, and the commutator (1.53).

[5] provided that the operators $\underline{A}$ and $\underline{B}$ commute with their commutator, i.e. $[\underline{B},[\underline{A},\underline{B}]] = [\underline{A},[\underline{A},\underline{B}]] = 0$.

[6] Ehrenfest, Paul, austrian physicist, *Wien 18.1.1880, †Amsterdam 25.9.1933; made significant contributions to the new quantum theory as well as to statistical mechanics.

obtain momentum conservation. Finally, for centrosymmetric force systems we have $[\underline{\mathcal{H}}, \underline{L}^2] = 0$ and $[\underline{\mathcal{H}}, \underline{L}_z] = 0$, which is the conservation of angular momentum.

2.2 The uncertainty principle

The relations (2.32) and (2.35) may be pleasing in the sense that they relate quantum and classical mechanics. But now we compute the root mean square of operators, and the result will be entirely new and unique to quantum theory.

We are going to work out the right side of the inequality

$$0 \leq \langle \psi(t) \mid (\alpha\delta\underline{A} - i\delta\underline{B})^{+} (\alpha\delta\underline{A} - i\delta\underline{B}) \mid \psi(t)\rangle$$

Here $\delta\underline{A} = \underline{A} - \langle\underline{A}\rangle$ and $\delta\underline{B} = \underline{B} - \langle\underline{B}\rangle$. We assume that $\underline{A}$ and $\underline{B}$ are hermitian operators, i.e. $\underline{A} = \underline{A}^{+}$ and $\underline{B} = \underline{B}^{+}$. α finally is a real parameter. Expanding the right side of the above inequality yields

$$\begin{aligned} 0 &\leq \langle\psi(t) \mid \Big(\alpha^2\delta\underline{A}^2 + \delta\underline{B}^2 \\ &\quad -\alpha\, \underbrace{i\,[\delta\underline{A}, \delta\underline{B}]}_{=-\underline{C}}\Big) \mid \psi(t)\rangle \\ &= \langle\delta\underline{A}^2\rangle \left(\alpha^2 + \alpha\frac{\langle\underline{C}\rangle}{\langle\delta\underline{A}^2\rangle}\right) + \langle\delta\underline{B}^2\rangle \\ &= \langle\delta\underline{A}^2\rangle \left(\alpha + \frac{1}{2}\frac{\langle\underline{C}\rangle}{\langle\delta\underline{A}^2\rangle}\right)^2 - \frac{1}{4}\frac{\langle\underline{C}\rangle^2}{\langle\delta\underline{A}^2\rangle} + \langle\delta\underline{B}^2\rangle\,. \end{aligned}$$

Because α is a parameter, we may chose α such that $(\ldots)^2 = 0$ (provided $\langle\underline{C}\rangle$ is real), i.e.

$$\langle\delta\underline{A}^2\rangle\langle\delta\underline{B}^2\rangle \geq \frac{1}{4}\langle\underline{C}\rangle^2$$

or

$$\Delta A \Delta B \geq \frac{1}{2} \mid \langle\underline{C}\rangle \mid , \tag{2.37}$$

where $\Delta A = \sqrt{\langle\delta\underline{A}^2\rangle}$ and $\Delta B = \sqrt{\langle\delta\underline{B}^2\rangle}$.

In order to understand the meaning of the inequality (2.37) we consider the two operators we know best - $\underline{\vec{r}}$ and $\underline{\vec{p}}$. They do not commute and thus

$$\Delta x \Delta p_x \geq \frac{1}{2}\hbar\,. \tag{2.38}$$

In the units, which we used to discuss the wave packet idea (cf. Eq. (1.43)), this reads

$$\Delta x \Delta k \geq \frac{1}{2}\,. \tag{2.39}$$

A simple example may serve to illustrate this inequality. First we note that for any operator $\underline{A}$ we may write

$$\begin{aligned} \Delta A^2 &= \langle(\underline{A} - \langle\underline{A}\rangle)^2\rangle \\ &= \langle\underline{A}^2 - 2\underline{A}\langle\underline{A}\rangle + \langle\underline{A}\rangle^2\rangle \\ &= \langle\underline{A}^2\rangle - \langle\underline{A}\rangle^2\,. \end{aligned} \tag{2.40}$$

In the case of Δx we have

$$\Delta x^2 = \langle\underline{x}^2\rangle - \langle\underline{x}\rangle^2\,,$$

where

$$\langle\underline{x}\rangle = \int_{-\infty}^{\infty} \psi(x,t)^* x \psi(x,t) dx \tag{2.41}$$

and

$$\langle\underline{x}^2\rangle = \int_{-\infty}^{\infty} \psi(x,t)^* x^2 \psi(x,t) dx\,. \tag{2.42}$$

In section 1.3 (cf. Eq. (1.45)) we had constructed a wave package for which

$$\psi(x, t = 0) = c\exp[-x^2/(4b^2)]\,,$$

where c is a constant. Inserting this expression into the above integrals yields

$$\langle\underline{x}\rangle_{t=0} = c^* c \int_{-\infty}^{\infty} x\exp[-x^2/(2b^2)]dx$$

and

$$\langle \underline{x}^2\rangle_{t=0} = c^* c \int_{-\infty}^{\infty} x^2 \exp[-x^2/(2b^2)]dx \; .$$

Because the corresponding argument under the integral is an odd function we have

$$\langle \underline{x}\rangle_{t=0} = 0 \; .$$

In the case of $\langle \underline{x}^2\rangle_{t=0}$ we express c^*c in terms of the normalization, i.e.

$$\begin{aligned}
\langle \underline{x}^2\rangle_{t=0} &= \frac{\int_{-\infty}^{\infty} x^2 \exp[-x^2/(2b^2)]dx}{\int_{-\infty}^{\infty} \exp[-x^2/(2b^2)]dx} \\
&= \frac{d}{d\left(-\frac{1}{2b^2}\right)} \ln\left[\int_{-\infty}^{\infty} \exp[-\frac{x^2}{2b^2}]dx\right] \\
&\overset{z=\sqrt{\frac{1}{2b^2}}x}{=} \frac{d}{d\left(\frac{1}{2b^2}\right)} \ln\left[\sqrt{\frac{1}{2b^2}} \int_{-\infty}^{\infty} e^{-z^2} dz\right] \\
&= b^2 \; .
\end{aligned}$$

Therefore we have

$$\Delta x_{t=0} = b \; . \tag{2.43}$$

Now we must compute Δp_x, i.e.

$$\Delta {p_x}^2 = \langle {\underline{p}_x}^2\rangle - \langle \underline{p}_x\rangle^2 \; .$$

This time we have

$$\begin{aligned}
\langle \underline{p_x}\rangle_{t=0} &= -i\hbar c^* c \int_{-\infty}^{\infty} \exp[-\frac{x^2}{4b^2}] \\
\times & \quad \frac{d}{dx} \exp[-\frac{x^2}{4b^2}]dx
\end{aligned}$$

and

$$\begin{aligned}
\langle {\underline{p}_x}^2\rangle_{t=0} = -\hbar^2 c^* c &\int_{-\infty}^{\infty} \exp[-\frac{x^2}{4b^2}] \\
&\times \frac{d^2}{dx^2} \exp[-\frac{x^2}{4b^2}]dx \; .
\end{aligned}$$

The argument under the first integral is again odd and therefore

$$\langle \underline{p}_x\rangle_{t=0} = 0 \; .$$

The second integral is simplified by applying partial integration once which yields

$$\begin{aligned}
\langle {\underline{p}_x}^2\rangle_{t=0} &= \hbar^2 c^* c \int_{-\infty}^{\infty} \left(\frac{d}{dx} \exp[-\frac{x^2}{4b^2}]\right)^2 dx \\
&= \frac{\hbar^2}{(2b^2)^2} c^* c \int_{-\infty}^{\infty} x^2 \exp[-\frac{x^2}{2b^2}]dx \\
&= \frac{\hbar^2}{(2b^2)^2} \langle \underline{x}^2\rangle_{t=0} \\
&= \frac{\hbar^2}{4b^2} \; .
\end{aligned}$$

And thus

$$\Delta p_{x\,t=0} = \frac{\hbar}{2b} \; . \tag{2.44}$$

Combining Eqs. (2.43) and (2.44) we find for the special case of our wave packet (at $t = 0$) in section 1.3

$$\Delta x \Delta p_x \big|_{t=0} = \frac{\hbar}{2}$$

in agreement with (2.38).

If we localize a particle by reducing its Δx then we must allow for a larger Δp_x. Position and momentum along the same coordinate direction cannot both be defined or measured with arbitrary precision! This was first noted by W. Heisenberg 1928 and is called uncertainty principle. The inequality (2.37) is a general expression of the uncertainty principle. If, on the other hand, the state of a physical system like the hydrogen atom is determined by a complete set of quantum numbers, e.g. n, l, and m, then the associated operators must commute. In the case of hydrogen these operators are $\underline{\mathcal{H}}$, $\underline{L}^2$ and $\underline{L}_z$.

Remark: We may wonder whether in analogy to $\Delta x \Delta p_x \geq \frac{\hbar}{2}$ we may write

$$\Delta t \Delta E \geq \frac{\hbar}{2} \; . \tag{2.45}$$

(cf. (1.49)). However, contrary to the spatial coordinates time is merely a parameter in quantum mechanics. It is therefore not straightforward to give an interpretation of relation (2.45). Below we will address this question in detail.

2.3 From wave mechanics to matrix mechanics

Looking at the definition (2.27) we may wonder whether the expression on the right is meaningful if we chose different state functions, i.e. if we define

$$\Lambda_{mn} \equiv \langle \psi_m \mid \underline{\Lambda} \mid \psi_n \rangle \ . \tag{2.46}$$

Here $\underline{\Lambda}$ is an arbitrary hermitian operator.

Let us try to evaluate (2.46) for the 1D harmonic oscillator with $\underline{\Lambda} = \underline{q}$, i.e.

$$\begin{aligned} q_{mn} &\equiv \langle \psi_m \mid \underline{q} \mid \psi_n \rangle & (2.47) \\ &= \int \langle \psi_m \mid q \rangle \langle q \mid \underline{q} \mid q\,' \rangle \langle q\,' \mid \psi_n \rangle dq dq\,' \ . \end{aligned}$$

Using again (2.30) we obtain

$$q_{mn} = \int \psi_m^* \left(q \right) q \psi_n \left(q \right) dq \ . \tag{2.48}$$

With the aid of (1.72) and (1.73) it is easy to show that

$$qH_n \left(q \right) = \frac{1}{2} H_{n+1} \left(q \right) + nH_{n-1} \left(q \right) \ . \tag{2.49}$$

Now we employ the useful theorem for hermitian operators introduced above: Two eigenfunctions belonging to two different eigenvalues are orthogonal. Therefore

$$\begin{aligned} q_{mn} &= \frac{1}{\sqrt{\pi}} \Bigg[\sqrt{\frac{n+1}{2}} \frac{1}{(n+1)!2^{n+1}} \\ &\quad \times \int_{-\infty}^{\infty} dq e^{-q} H_{n+1}^2 \left(q \right) \delta_{m,n+1} \\ &\quad + \sqrt{\frac{n}{2}} \frac{1}{(n-1)!2^{n-1}} \\ &\quad \times \int_{-\infty}^{\infty} dq e^{-q} H_{n-1}^2 \left(q \right) \delta_{m,n-1} \Bigg] \\ &= \sqrt{\frac{n+1}{2}} \delta_{m,n+1} + \sqrt{\frac{n}{2}} \delta_{m,n-1} & (2.50) \end{aligned}$$

(note that $m, n \geq 0$) or if we write $\underline{q}$ in matrixform,

$$\underline{q} = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 & 0 & \cdots \\ 1 & 0 & \sqrt{2} & 0 & \cdots \\ 0 & \sqrt{2} & 0 & \sqrt{3} & \cdots \\ \vdots & \vdots & \vdots & & \ddots \end{pmatrix} \ . \tag{2.51}$$

We note that (2.51) agrees exactly with Eq. (1.36) if we take $\sqrt{\hbar/(m\omega)}$ as the unit of length, i.e. we have discovered the bridge between matrix and wave mechanics! The recipe is easy. Solve Schrödinger's equation for a given potential function and calculate (2.46) for $\underline{\Lambda} = \vec{\underline{r}}$ and $\underline{\Lambda} = \vec{\underline{p}}$.

Because in our example we have used the eigenfunctions of the Hamiltonian to evaluate the matrix elements in (2.46) the right side of this equation is called the energy representation of $\underline{\Lambda}$. Thus (2.51) is the energy representation of $\underline{q}$.

Let us consider a another example dealing with a different representation of the position operator $\vec{\underline{r}}$. Eq. (2.26) we now call $\vec{r}$-space representation of $\vec{\underline{r}}$. Inserting Eq. (2.4) twice into Eq. (2.30) we can easily work out the $\vec{p}$-representation of $\vec{\underline{r}}$:

$$\begin{aligned} \vec{r}\delta(\vec{r} - \vec{r}\,') &= \langle \vec{r} \mid \vec{\underline{r}} \mid \vec{r}\,' \rangle \\ &= \int d^3k d^3k\,' \langle \vec{r} \mid \vec{k} \rangle \langle \vec{k} \mid \vec{\underline{r}} \mid \vec{k}\,' \rangle \langle \vec{k}\,' \mid \vec{r}\,' \rangle \\ &\overset{(*)}{=} \frac{1}{(2\pi)^3} \int d^3k d^3k\,' e^{i\vec{k}\cdot\vec{r}} \langle \vec{k} \mid \vec{\underline{r}} \mid \vec{k}\,' \rangle e^{-i\vec{k}\,'\cdot\vec{r}\,'} \end{aligned}$$

In order to satisfy $(*)$ we must have

$$\langle \vec{k} \mid \vec{\underline{r}} \mid \vec{k}\,' \rangle = i\delta(\vec{k} - \vec{k}\,') \vec{\nabla}_{k\,'} \tag{2.52}$$

or

$$\langle \vec{p} \mid \vec{\underline{r}} \mid \vec{p}\,' \rangle = i\hbar\delta(\vec{p} - \vec{p}\,') \vec{\nabla}_{p\,'} \ . \tag{2.53}$$

In $\vec{p}$-space the position operator $\vec{\underline{r}}$ therefore is given by $i\hbar\vec{\nabla}_{\vec{p}}$!

We can show also that the $\vec{p}$-representation of $\vec{\underline{p}}$ is

$$\langle \vec{p} \mid \underline{\vec{p}} \mid \vec{p}\,'\rangle = \vec{p}\delta(\vec{p}-\vec{p}\,') \ . \tag{2.54}$$

Inserting Eq. (2.4) twice into

$$\langle \underline{\vec{p}} \rangle = \langle \psi \mid \underline{\vec{p}} \mid \psi \rangle \tag{2.55}$$

yields

$$\langle \underline{\vec{p}} \rangle = \int d^3p d^3p\,' \tilde{\psi}^*(\vec{p}) \langle \vec{p} \mid \underline{\vec{p}} \mid \vec{p}\,'\rangle \tilde{\psi}(\vec{p}\,') \ . \tag{2.56}$$

Here $\tilde{\psi}(\vec{p})$ is the Fourier transform of $\psi(\vec{r})$ given by

$$\tilde{\psi}(\vec{p}) = \frac{1}{(2\pi\hbar)^{3/2}} \int d^3r \psi(\vec{r}) e^{-(i/\hbar)\vec{p}\cdot\vec{r}} \ . \tag{2.57}$$

Inserting $\tilde{\psi}(\vec{p})$ into the previous equation gives

$$\begin{aligned}\langle \underline{\vec{p}} \rangle = \frac{1}{(2\pi\hbar)^3} \int d^3r d^3r\,' \int d^3p d^3p\,' \\ \psi^*(\vec{r}) \langle \vec{p} \mid \underline{\vec{p}} \mid \vec{p}\,'\rangle \psi(\vec{r}\,') e^{(i/\hbar)(\vec{p}\cdot\vec{r}-\vec{p}\,'\cdot\vec{r}\,')} \ .\end{aligned} \tag{2.58}$$

Now, assuming that Eq. (2.54) is indeed correct, we can first integrate over $\vec{p}\,'$ and subsequently we replace $\vec{p}$ in the integrand by a derivative with respect to $\vec{r}$, i.e.

$$\begin{aligned}\langle \underline{\vec{p}} \rangle = \frac{1}{(2\pi\hbar)^3} \int d^3r d^3r\,' \int d^3p \\ \psi^*(\vec{r})(-i\hbar\vec{\nabla}_{\vec{r}}) \psi(\vec{r}\,') e^{(i/\hbar)\vec{p}\cdot(\vec{r}-\vec{r}\,')} \ .\end{aligned} \tag{2.59}$$

Finally we integrate over $\vec{p}$, which produces a δ-function, i.e.

$$\langle \underline{\vec{p}} \rangle = \int d^3r d^3r\,' \psi^*(\vec{r})(-i\hbar\vec{\nabla}_{\vec{r}}) \psi(\vec{r}\,') \delta(\vec{r}-\vec{r}\,') \tag{2.60}$$

After a last integration over $\vec{r}\,'$ we obtain the $\vec{r}$-represention of the momentum operator, which is $-i\hbar\vec{\nabla}_{\vec{r}}$. Because we know this already, we have shown that Eq. (2.54) is correct.

In summary:

operator	$\vec{r}$-space	$\vec{p}$-space
$\underline{\vec{r}}$	$\vec{r}$	$i\hbar\vec{\nabla}_{\vec{p}}$
$\underline{\vec{p}}$	$-i\hbar\vec{\nabla}_{\vec{r}}$	$\vec{p}$

As a closing remark we point out that matrix elements like (2.46) also have a physical interpretation. They describe transitions from a state characterized by $\mid \psi_n\rangle$ to a state characterized by $\mid \psi_m\rangle$ under the influence of a physical perturbation described in terms of $\underline{\Lambda}$. The right side of (2.46) is sometimes called transition matrix element.

2.4 The time evolution operator

A system may be in a state described by $\mid \psi\,(t)\rangle$ at time t. We may express this formally as

$$\mid \psi\,(t)\rangle = \underline{S}\,(t) \mid \psi\,(0)\rangle \ . \tag{2.61}$$

To find out what the operator $\underline{S}\,(t)$ stands for we insert (2.61) into Schrödinger's equation, i.e.

$$\begin{aligned} 0 &= (i\hbar\partial_t - \underline{\mathcal{H}}) \mid \psi\,(t)\rangle \\ &= (i\hbar\partial_t \underline{S}\,(t) - \underline{\mathcal{H}}\underline{S}\,(t)) \mid \psi\,(0)\rangle \ . \end{aligned} \tag{2.62}$$

Assuming that $\underline{\mathcal{H}}$ is independent of t we obtain

$$\underline{S} = e^{-\frac{i}{\hbar}\underline{\mathcal{H}}t} \equiv \sum_{\nu} \frac{1}{\nu!} \left(-\frac{i}{\hbar}\underline{\mathcal{H}}t\right)^{\nu} \tag{2.63}$$

[7]. Using $\underline{\mathcal{H}} = \underline{\mathcal{H}}^+$ we see that

---

[7] Here me make use of the energy representation of $\underline{S}\,(t)$, i.e. $\langle \phi_m \mid \underline{S}\,(t) \mid \phi_n\rangle$. The $\mid \phi_n\rangle$ are Eigenkets of $\underline{\mathcal{H}}$. By multiplication of Schrödinger's equation from the left with $\langle \phi_m \mid$ and by inserting $1 = \sum_n \mid \phi_n\rangle\langle\phi_n \mid$ we obtain

$$\begin{aligned}\sum_n \Big(i\hbar\partial_t \langle \phi_m \mid \underline{S}\,(t) \mid \phi_n\rangle \\ - \sum_{n\,'} \langle \phi_m \mid \underline{\mathcal{H}} \mid \phi_{n\,'}\rangle\langle \phi_{n\,'} \mid \underline{S}\,(t) \mid \phi_n\rangle \Big) \langle \phi_n \mid \psi\,(0)\rangle = 0 \ .\end{aligned}$$

Using $\langle \phi_m \mid \underline{\mathcal{H}} \mid \phi_{n\,'}\rangle = E_m \langle \phi_m \mid \phi_{n\,'}\rangle = E_m \delta_{mn\,'}$ this simplifies to

$$\sum_n \Big(i\hbar\partial_t \langle \phi_m \mid \underline{S}\,(t) \mid \phi_n\rangle$$

$$\underline{S}^{+}\underline{S} = \underline{S}\underline{S}^{+} = 1 \; . \tag{2.64}$$

Operators with this property are called unitary.

Thus far we always had assumed time-independent operators and time-dependent state - or wave functions. This is called the Schrödinger picture. However, using $\underline{S}\,(t)$ we may transform the Schrödinger picture into the Heisenberg picture, where the state functions do not depend on time but the operators do, i.e.

$$\mid \psi\rangle_{H} = \underline{S}^{+}\,(t) \mid \psi\,(t)\rangle_{S} \tag{2.65}$$

and

$$\underline{\Lambda}_{H}\,(t) = \underline{S}^{+}\,(t)\,\underline{\Lambda}_{S}\underline{S}\,(t) \;\; , \tag{2.66}$$

where the index H stands for Heisenberg and the index S for Schrödinger. Both pictures are completely equivalent.

Both pictures may be used simultaneously. We divide the Hamilton operator according to

$$\underline{\mathcal{H}}\,(t) = \underline{\mathcal{H}}_{0} + \underline{\mathcal{H}}_{1}\,(t) \;\; , \tag{2.67}$$

where $\underline{\mathcal{H}}_{1}\,(t)$ is a small and time-dependent interaction term. In this case we write

$$\mid \psi\,(t)\rangle_{I} = \underline{S}^{(0)+} \mid \psi\,(t)\rangle_{S} \tag{2.68}$$

and

$$\underline{\Lambda}_{I}\,(t) = \underline{S}^{(0)+}\underline{\Lambda}_{S}\underline{S}^{(0)} \tag{2.69}$$

where

$$\underline{S}^{(0)}\,(t) = e^{-\frac{i}{\hbar}\underline{\mathcal{H}}_{0}t} \; . \tag{2.70}$$

This is the interaction picture (Index I). But why is the interaction picture useful? To see this we insert $\underline{S} = \underline{S}^{(0)}\underline{S}^{(1)}$ into (2.62) and multiply from the left with $\underline{S}^{(0)}{}^{+}$:

$$i\hbar\partial_{t}\underline{S}^{(1)} = \underline{S}^{(0)}{}^{+}\left(\underline{H}\underline{S}^{(0)} - i\hbar\partial_{t}\underline{S}^{(0)}\right)\underline{S}^{(1)} \; . \tag{2.71}$$

If $(\ldots)$ is close to zero, then Eq. (2.71) is more suitable for an approximation schema than the original Eq. (2.62), because $\underline{S}^{(1)}$ varies slowly with time. In particular (2.71) can be written as

$$i\hbar\partial_{t}\underline{S}^{(1)} = \underline{H}_{I}^{(1)}\underline{S}^{(1)} \; .$$

In section 4.2 this equation will be discussed in detail.

Uncertainty principle revisited:

Consider a time-independent Hamiltonian and assume that the spectrum is nondegenerate. The state $\mid \psi\,(t_0)\rangle$ may be written as

$$\mid \psi\,(t_0)\rangle = \sum_{n} \mid \phi_n(t_0)\rangle\langle\phi_n(t_0) \mid \psi\,(t_0)\rangle \; . \tag{2.72}$$

The $\mid \phi_n(t_0)\rangle$ are eigenstates of the Hamiltonian at time t_0. For the following it is convenient to consider a continuous spectrum so that the above sum becomes an integral

$$\mid \psi\,(t_0)\rangle = \int \alpha\,(E) \mid \phi_E(t_0)\rangle dE \; , \tag{2.73}$$

where $\langle\phi_n(t_0) \mid \psi\,(t_0)\rangle = \alpha\,(E)\,\Delta E$. The absolute square of $\alpha\,(E)$ is sketched in figure 2.1. This means that the state $\mid \psi\,(t_0)\rangle$ is composed mainly of energy eigenstates $\mid \phi_E(t_0)\rangle$ belonging to energies close to E_o. Application of Eq. (2.61) to $\mid \psi\,(t_0)\rangle$ yields its time evolution

$$\mid \psi\,(t)\rangle = \int \alpha\,(E)\,e^{-iE(t-t_0)/\hbar} \mid \phi_E(t_0)\rangle dE \; . \tag{2.74}$$

We now want to know how long it takes for $\mid \psi\,(t_0)\rangle$ to change significantly. In order to estimate the time interval during which the system evolves to an appreciable extent, we calculate the probability of finding the system in a different state $\mid \chi(t)\rangle$ at time t. This probability is defined via

$$P_{\chi}\,(t) := \mid \langle\chi(t) \mid \psi\,(t)\rangle \mid^{2} \;\; . \tag{2.75}$$

This interpretation more or less follows if we expand the normalized scalar product $\langle\psi \mid \psi\rangle$ in

---

$$-E_m\langle\phi_m \mid \underline{S}\,(t) \mid \phi_n\rangle\Big)\langle\phi_n \mid \psi\,(0)\rangle = 0 \; .$$

This equation holds for arbitrary $\mid \psi\,(0)\rangle$ and therefore $(\ldots) = 0$. The solution therefore is

$$\langle\phi_m \mid \underline{S}\,(t) \mid \phi_n\rangle = \exp\left[-iE_m t/\hbar\right]\delta_{mn} \; .$$

Here δ_{mn} results from $\underline{S}\,(0) = 1$.

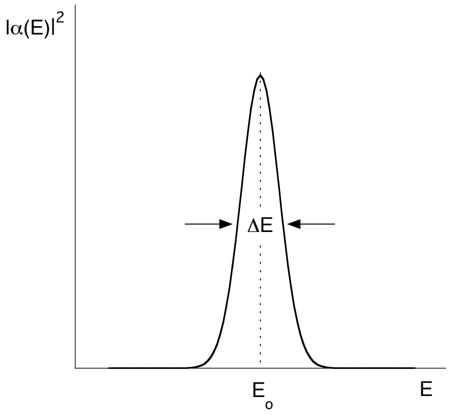

Figure 2.1: $| \alpha(E) |^2$ vs. E

eigenstates of some hermitian operator (cf. Eq. (2.23)), i.e.

$$
\begin{aligned}
1 &= \langle \psi \mid \psi \rangle \\
&= \sum_{\nu} \langle \psi \mid \varphi_\nu \rangle \langle \varphi_\nu \mid \psi \rangle \\
&= \sum_{\nu} \mid \langle \varphi_\nu \mid \psi \rangle \mid^2 .
\end{aligned}
$$

Each Term $\mid \langle \varphi_\nu \mid \psi \rangle \mid^2$ is the contribution of the respective projection to the total probability.

Inserting Eq. (2.74) into (2.75) we have

$$
\begin{aligned}
P_\chi(t) &= \mid \langle \chi(t) \mid \psi(t) \rangle \mid^2 \\
&= \left| \int \alpha(E)\, e^{-iE(t-t_0)/\hbar} \langle \chi(t) \mid \phi_E(t_0) \rangle dE \right|^2 .
\end{aligned}
$$

Let us assume that the width of $\mid \alpha(E) \mid^2$ is small compared to the energy variation of $\mid \langle \chi(t) \mid \phi_E(t_0) \rangle \mid^2$. With this assumption we may approximate $P_\chi(t)$ as

$$
\begin{aligned}
P_\chi(t) &\cong \mid \langle \chi(t) \mid \phi_{E_o}(t_0) \rangle \mid^2 \\
&\quad \times \left| \int \alpha(E)\, e^{-iE(t-t_0)/\hbar} dE \right|^2 .
\end{aligned}
$$

For the sake of concreteness we may further assume that the E-dependence of $\alpha(E)$ is Lorentzian [8], i.e.

$$
\alpha(E) \sim \frac{(\Delta E/2)^2}{(E-E_o)^2 + (\Delta E/2)^2} . \tag{2.76}
$$

This yields

$$
\int_{-\infty}^{\infty} \alpha(E)\, e^{-iE(t-t_0)/\hbar} dE \sim \exp\left[-\frac{\Delta E \mid t - t_0 \mid}{2\hbar} \right]
$$

[9] and therefore

$$
P_\chi(t) \sim \exp\left[-\frac{\Delta E \mid t - t_0 \mid}{\hbar} \right] , \tag{2.77}
$$

still under the assumption that the factor $\langle \chi(t) \mid \phi_{E_o}(t_0) \rangle \mid^2$ varies slowly by comparison. We may therefore use the relation

$$
\Delta t \Delta E \approx \hbar \tag{2.78}
$$

to define the time interval $\Delta t = \mid t - t_0 \mid$ beyond which the state $\mid \psi(t_0) \rangle$ has changed significantly, i.e. Δt is a measure of the "lifetime" of $\mid \psi(t_0) \rangle$. The lifetime is short if ΔE is large and long if ΔE is small.

2.5 The density operator

Again we consider an operator average, i.e.

$$
\langle \underline{\Lambda} \rangle = \langle \psi(t) \mid \underline{\Lambda} \mid \psi(t) \rangle . \tag{2.79}
$$

We expand the state vector $\mid \psi(t) \rangle$ in orthonormal eigenstates of $\underline{\Lambda}$, i.e.

$$
\begin{aligned}
\mid \psi(t) \rangle &= \sum_{\nu} \mid \varphi_\nu(t) \rangle \langle \varphi_\nu(t) \mid \psi(t) \rangle \\
&= \sum_{\nu} c_\nu \mid \varphi_\nu(t) \rangle .
\end{aligned}
$$

In the following we define $p_\nu \equiv |c_\nu|^2$, which is the probability for finding the system described by $\mid \psi(t) \rangle$ in the state $\mid \varphi_\nu(t) \rangle$. Thus, $\langle \underline{\Lambda} \rangle$ may be written as

---

[8] This is not an essential assumption, e.g. we may use a Gaussian instead.

[9] $\int_{-\infty}^{\infty} dx \frac{e^{-ipx}}{a^2+x^2} = \frac{\pi}{a} \exp[- \mid ap \mid]$

$$\begin{aligned}\langle\underline{\Lambda}\rangle &= \sum_{\nu} p_{\nu}\langle\varphi_{\nu}(t) \mid \underline{\Lambda} \mid \varphi_{\nu}(t)\rangle \\ &= \sum_{\nu,n} p_{\nu}\langle\varphi_{\nu}(t) \mid \varphi_{n}(t)\rangle\langle\varphi_{n}(t) \mid \underline{\Lambda} \mid \varphi_{\nu}(t)\rangle \\ &= \sum_{\nu}\langle\varphi_{\nu}(t) \mid \\ &\quad \times\sum_{n} \mid \varphi_{n}(t)\rangle p_{n}\langle\varphi_{n}(t) \mid \underline{\Lambda} \mid \varphi_{\nu}(t)\rangle \\ &= \sum_{\nu}\langle\varphi_{\nu}(t) \mid \underline{\rho}\underline{\Lambda} \mid \varphi_{\nu}(t)\rangle \\ \langle\underline{\Lambda}\rangle &= Tr\left(\underline{\rho}\underline{\Lambda}\right) \ . \end{aligned} \tag{2.80}$$

The operator $\underline{\rho}$ defined via

$$\underline{\rho} \equiv \sum_{n} \mid \varphi_{n}(t)\rangle p_{n}\langle\varphi_{n}(t) \mid \ . \tag{2.81}$$

is called density operator [10]. The operation Tr is defined via

$$Tr\left(\ldots\right) \equiv \sum_{\nu}\langle\varphi_{\nu}(t) \mid \ldots \mid \varphi_{\nu}(t)\rangle \ ; \tag{2.82}$$

it is called trace (dt.: Spur). Eq. (2.80) may be generalized to an arbitrary function of $\underline{\Lambda}$, i.e.

$$\langle F(\underline{\Lambda})\rangle = Tr\left(\underline{\rho}F(\underline{\Lambda})\right) \ . \tag{2.83}$$

An important property of the trace is that it is invariant under cyclic permutation of operators:

$$Tr\left(\underline{ABC}\right) = Tr\left(\underline{BCA}\right) = Tr\left(\underline{CAB}\right) \ . \tag{2.84}$$

Proof:

$$\begin{aligned} Tr\left(\underline{ABC}\right) &= \sum_{\nu,a,b,c}\langle\nu \mid a\rangle a\langle a \mid b\rangle b\langle b \mid c\rangle c\langle c \mid \nu\rangle \\ &= \sum_{a,b,c} a\langle a \mid b\rangle b\langle b \mid c\rangle c\langle c \mid a\rangle \\ &= \sum_{\nu,a,b,c} a\langle a \mid \nu\rangle\langle\nu \mid b\rangle b\langle b \mid c\rangle c\langle c \mid a\rangle \\ &= \sum_{\nu,a,b,c}\langle\nu \mid b\rangle b\langle b \mid c\rangle c\langle c \mid a\rangle a\langle a \mid \nu\rangle \\ &= Tr\left(\underline{BCA}\right) \ . \end{aligned} \tag{2.85}$$

Notice in particular that $Tr\left(\underline{\Lambda}\right)$ is invariant under a unitary transformation of $\underline{\Lambda}$, i.e.

$$Tr\left(\underline{\Lambda}\right) = Tr\big(\underbrace{\underline{SS^{+}}}_{=1}\underline{\Lambda}\big) = Tr\left(\underline{S^{+}\Lambda S}\right) \ .$$

The significance of this is that the trace remains unaltered when the representation is changed. E.g., we may write

$$\begin{aligned} &\sum_{n}\langle\phi_{n} \mid \underline{\Lambda} \mid \phi_{n}\rangle \\ &\quad = \sum_{n,\nu,\nu'}\langle\phi_{n} \mid \varphi_{\nu}\rangle\langle\varphi_{\nu} \mid \underline{\Lambda} \mid \varphi_{\nu'}\rangle\langle\varphi_{\nu'} \mid \phi_{n}\rangle \\ &\quad = \sum_{\nu,\nu'}\langle\varphi_{\nu} \mid \underline{\Lambda} \mid \varphi_{\nu'}\rangle\underbrace{\sum_{n}\langle\varphi_{\nu'} \mid \phi_{n}\rangle\langle\phi_{n} \mid \varphi_{\nu}\rangle}_{=\delta_{\nu\nu'}} \\ &\quad = \sum_{\nu}\langle\varphi_{\nu} \mid \underline{\Lambda} \mid \varphi_{\nu}\rangle \end{aligned}$$

Here the $\mid \varphi_{\nu}\rangle$ are (normalized) eigenkets of $\underline{\Lambda}$, whereas for the $\mid \phi_{n}\rangle$ this may not be the case!

A system is considered to be in a pure state if we can write $\underline{\rho}$ as

$$\underline{\rho} = \mid \psi_{pure}\rangle\langle\psi_{pure} \mid \ . \tag{2.86}$$

Otherwise it is a mixed state.

The density operator is very useful in the context of many particle systems. A gas, for instance, contained in a fixed volume in thermal equilibrium with its walls at temperature T, is described via

$$\langle\phi_{n} \mid \underline{\rho} \mid \phi_{n}\rangle = \frac{1}{Q}e^{-\beta E_{n}} \ , \tag{2.87}$$

where the $\mid \phi_{n}\rangle$ are eigenkets of $\underline{\mathcal{H}}$. Here Q is the canonical partition function. We may obtain Q via $1 = \sum_{n}\langle\phi_{n} \mid \underline{\rho} \mid \phi_{n}\rangle$, i.e.

$$1 = \frac{1}{Q}\sum_{n} e^{-\beta E_{n}} = \frac{1}{Q}Tr\left(e^{-\beta\underline{\mathcal{H}}}\right) \ , \tag{2.88}$$

and therefore

$$Q = Tr\left(e^{-\beta\underline{\mathcal{H}}}\right) = \sum_{n}\langle\phi_{n} \mid e^{-\beta\underline{\mathcal{H}}} \mid \phi_{n}\rangle \ . \tag{2.89}$$

---

[10] In this example the $|\varphi_{n}\rangle$ are orthogonal but this is not essential for the definition of the density operator.

The partition function can be used to derive all quantities of interest for many particle systems, provided of course that we can diagonalize the system's Hamilton operator (for details see Ref. [16]).

Notice that in this example we consider a system, a gas confined in a container, which only is a small portion of the universe. However, we do not need the state function of the universe; the state function of the gas is sufficient for the construction of $\underline{\rho}$.

Finally we want to again consider the time derivative

$$\frac{d}{dt}\langle\underline{\Lambda}\rangle = \frac{d}{dt}\sum_{\nu} p_{\nu}\langle\varphi_{\nu}(t) \mid \underline{\Lambda} \mid \varphi_{\nu}(t)\rangle \; . \tag{2.90}$$

Here the statistical weights p_{ν} are assumed to be independent of time [11]. According to Eq. (2.36) we may write

$$\begin{aligned}\frac{d}{dt}\langle\underline{\Lambda}\rangle &= \sum_{\nu} p_{\nu}\frac{d}{dt}\langle\varphi_{\nu}(t) \mid \underline{\Lambda} \mid \varphi_{\nu}(t)\rangle \\ &= \sum_{\nu} p_{\nu}\frac{i}{\hbar}\langle\varphi_{\nu}(t) \mid \; [\underline{\mathcal{H}},\underline{\Lambda}] \mid \varphi_{\nu}(t)\rangle \\ &\quad +\langle\frac{\partial\underline{\Lambda}}{\partial t}\rangle \; .\end{aligned}$$

Inserting $1=\sum_n \mid \varphi_n\rangle\langle\varphi_n \mid$ we obtain

$$\begin{aligned}\frac{d}{dt}\langle\underline{\Lambda}\rangle &= \sum_{\nu,n}\frac{i}{\hbar}\langle\varphi_{\nu} \mid \varphi_n\rangle p_n\langle\varphi_n \mid \Big[\underline{\mathcal{H}},\underline{\Lambda}\Big] \mid \varphi_{\nu}\rangle \\ &\quad +\langle\frac{\partial\underline{\Lambda}}{\partial t}\rangle \\ &= \frac{i}{\hbar}Tr\left(\underline{\rho}\Big[\underline{\mathcal{H}},\underline{\Lambda}\Big]\right)+\langle\frac{\partial\underline{\Lambda}}{\partial t}\rangle \\ &= \frac{i}{\hbar}Tr\left(\Big[\underline{\rho},\underline{\mathcal{H}}\Big]\underline{\Lambda}\right)+\langle\frac{\partial\underline{\Lambda}}{\partial t}\rangle \\ &= Tr\left(\dot{\underline{\rho}}\underline{\Lambda}\right)+\langle\frac{\partial\underline{\Lambda}}{\partial t}\rangle \; ,\end{aligned} \tag{2.91}$$

where $\dot{\underline{\rho}}$ is given by

$$\dot{\underline{\rho}} = \frac{i}{\hbar}\Big[\sum_n \mid \varphi_n\rangle p_n\langle\varphi_n \mid, \underline{\mathcal{H}}\Big] \equiv \frac{i}{\hbar}\left[\underline{\rho},\underline{\mathcal{H}}\right] \; . \tag{2.92}$$

Eq. (2.92) follows from

$$\begin{aligned}\frac{d}{dt}\underline{\rho} &\overset{(2.63)}{=} \sum_n \frac{d}{dt}\left(\underline{S} \mid \varphi_n(0)\rangle p_n\langle\varphi_n(0) \mid \underline{S}^{+}\right) \\ &= -\frac{i}{\hbar}\underline{\mathcal{H}}\underline{\rho}+\frac{i}{\hbar}\underline{\rho}\underline{\mathcal{H}} \; .\end{aligned}$$

If we assume that the $\mid \varphi_n(t)\rangle$ in Eq. (2.92) are stationary, i.e.

$$\mid \varphi_n(t)\rangle = e^{-\frac{i}{\hbar}E_n t} \mid \varphi_n(0)\rangle \; , \tag{2.93}$$

it follows that

$$\dot{\underline{\rho}} = 0 \; . \tag{2.94}$$

2.6 Path integration and the density operator

In classical mechanics the path followed by a particle in space and time can be derived from a least action principle, $\delta S = 0$, where the action is $S=\int_{t_1}^{t_2}\mathcal{L}(q,\dot{q},t)dt$, and $\mathcal{L}$ is the Lagrangian depending on the coordinates q, velocities $\dot{q}$, and time t [12]. We may ask whether the action does play any related role in quantum mechanics. It is this question we want to address here.

Notice that the density operator $\underline{\rho}$, given by Eq. (2.87), may be written as

$$\underline{\rho}(\beta) = \frac{e^{-\beta\underline{\mathcal{H}}}}{Tr\left(e^{-\beta\underline{\mathcal{H}}}\right)} \tag{2.95}$$

($\beta^{-1}=k_B T$) [13]. However, in the following we want to use the unnormalized $\underline{\rho}$ defined by

$$\underline{\rho}_u(\beta) = e^{-\beta\underline{\mathcal{H}}} \; . \tag{2.96}$$

In order to avoid the additional index u we just omit it from here on throughout the remainder of this chapter unless noted otherwise.

First note that $\underline{\rho}(\beta)$ obeys the differential equation

---

[11] This refers to a condition called equilibrium later in Statistical Mechanics. In particular Eq. (2.87) holds in equilibrium.

[12] Do not confuse the action in this section with the time evolution operator.

[13] Note: $\underline{\rho}=\sum_{n,n'} \mid \phi_n\rangle\langle\phi_n \mid \underline{\rho} \mid \phi_n{}'\rangle\langle\phi_n{}' \mid$ and $\langle\phi_n \mid \underline{\rho} \mid \phi_n{}'\rangle = (Tr(\exp[-\beta\underline{\mathcal{H}}]))^{-1}\exp[-\beta E_n]\delta_{nn'}$.

$$-\partial_\beta \underline{\rho} = \underline{\mathcal{H}}\underline{\rho}\ . \tag{2.97}$$

We can see this by writing $\underline{\rho}$ in energy representation as

$$\rho_{nm} = \delta_{nm} e^{-\beta E_n} \tag{2.98}$$

(cf. page 41). Differentiating this equation we have

$$-\partial_\beta \rho_{nm} = \delta_{nm} E_n e^{-\beta E_n} = E_n \rho_{nm}\ ,$$

which is the energy representation of Eq. (2.97).

As an example application of (2.97) we calculate the $\vec{r}$-representation of $\underline{\rho}$, $\underline{\rho}(x, x'; \beta) = \langle x \mid \underline{\rho} \mid x'\rangle$, for a 1D free particle with $\underline{\mathcal{H}} = \frac{p^2}{2m}$, i.e.

$$-\partial_\beta \rho\,(x, x'; \beta) = -\frac{\hbar^2}{2m}\partial_x^2 \rho\,(x, x'; \beta)\ . \tag{2.99}$$

Eq. (2.99) is a 1D diffusion equation which has the solution [14]

$$\rho\,(x, x'; \beta) = \sqrt{\frac{m}{2\pi\hbar^2\beta}}\, e^{-\frac{m}{2\hbar^2\beta}(x-x')^2} \tag{2.100}$$

for the initial condition $\rho\,(x, x'; 0) = \delta\,(x - x')$. Notice that β here assumes the role of time.

Now assume that we are interested in $\langle\underline{\mathcal{H}}\rangle$ [15], which according to Eq. (2.80) is given by

$$\begin{aligned} \langle\underline{\mathcal{H}}\rangle &\overset{(*)}{=} Tr\left(\underline{\rho}\underline{\mathcal{H}}\right) \\ &\overset{(2.89)}{=} -\partial_\beta \ln Q \end{aligned} \tag{2.101}$$

($*$: Note that $\underline{\rho}$ in this formula is the full $\underline{\rho}$ not $\underline{\rho}_u$!). If Q is evaluated in $\vec{r}$-representation [16] instead of in energy representation as in Eq. (2.89) we have

$$\begin{aligned} \langle\underline{\mathcal{H}}\rangle &= -\partial_\beta \ln \int \rho\,(x, x; \beta)\, dx \\ &= -\frac{\int \partial_\beta \rho\,(x, x; \beta)\, dx}{\int \rho\,(x, x; \beta)\, dx} \\ &= \frac{1}{2} k_B T\ . \end{aligned}$$

This means that the average thermal energy of a 1D free particle is $\frac{1}{2}k_B T$ as promised.

After this brief excursion into Statistical Mechanics we now turn to the idea of path integration. At this point you should have noticed the resemblance of Eq. (2.97) to the Schrödinger equation, when β is replaced by $\frac{i}{\hbar}t$. Thus, instead of (2.96) we now consider

$$\underline{\rho}\,(t) = e^{-\frac{i}{\hbar}\underline{\mathcal{H}}t} \tag{2.102}$$

[17], which can be broken up into n time slices according to

$$\begin{aligned} \underline{\rho}\,(t) &= e^{-\frac{i}{\hbar}\underline{\mathcal{H}}\epsilon} e^{-\frac{i}{\hbar}\underline{\mathcal{H}}\epsilon} \ldots e^{-\frac{i}{\hbar}\underline{\mathcal{H}}\epsilon} \\ &= \underline{\rho}\,(\epsilon)\,\underline{\rho}\,(\epsilon) \ldots \underline{\rho}\,(\epsilon) \quad \text{(n factors)}\ . \end{aligned} \tag{2.103}$$

In x-representation this becomes

$$\begin{aligned} \rho\,(x, x'; t) &= \int \ldots \int \rho\,(x, x_{n-1}; \epsilon) \\ &\quad \times \rho\,(x_{n-1}, x_{n-2}; \epsilon) \ldots \rho\,(x_1, x'; \epsilon) \\ &\quad \times dx_1 \ldots dx_{n-1}\ . \end{aligned} \tag{2.104}$$

Figure 2.2 illustrates how to interpret this equation. The 1D particle travels from x' through a series of intermediate steps, x_1, x_2, …, x_{n-1}, which define a 'path'. The total $\rho\,(x, x'; t)$ for the particle starting at x' and finishing at x is given by a sum over all possible paths, i.e. for all possible intermediate positions x_i. As the time increment ϵ approaches zero, the number of integrations over the intermediate variables becomes infinite and the last equation can be written symbolically as

---

[14] See any book on partial differential equations in physics!

[15] Clearly, we know that the energy of an ideal gas consisting of N point-like particles is $\langle\underline{\mathcal{H}}\rangle = \frac{3}{2}N k_B T$, where each of the $3N$ degrees of freedom contributes $\frac{1}{2}k_B T$. This is what we want to show here!

[16] $Q = \sum_n \int dx dx' \langle\phi_n \mid x\rangle\langle x \mid \exp[-\beta\underline{\mathcal{H}}] \mid x'\rangle\langle x' \mid \phi_n\rangle = \int dx dx' \langle x \mid \exp[-\beta\underline{\mathcal{H}}] \mid x'\rangle\delta(x - x')$.

[17] Notice that our $\underline{\rho}(t)$ is nothing else but the time evolution operator $\underline{S}(t)$ introduced above - and for the remainder of this section $\underline{\rho}(t)$ should not be confused with density operator $\underline{\rho}(\beta)$! The main reason for using such a dangerous notation is the conceptual closeness of $\underline{\rho}(\beta)$ in equilibrium Statistical Mechanics -referring to the summation over 'paths'- to the time evolution operator.

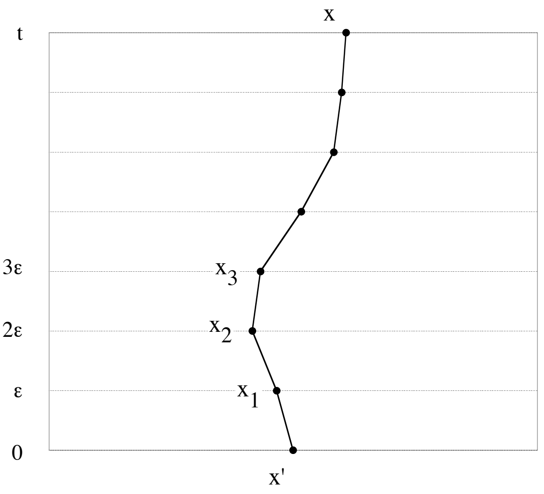

Figure 2.2: A particle travelling from x' to x along a path x_1, x_2 etc.

$$\rho\left(x,x';t\right)=\int\Phi\left[x\left(t'\right)\right]\mathcal{D}x\left(t'\right)\ ,\qquad(2.105)$$

where

$$\begin{aligned}\Phi\left[x\left(t'\right)\right]&=\lim_{\epsilon\to0,n\epsilon\to t}\rho\left(x,x_{n-1};\epsilon\right)\\&\quad\times\rho\left(x_{n-1},x_{n-2};\epsilon\right)\ldots\rho\left(x_1,x';\epsilon\right)\end{aligned}\qquad(2.106)$$

and

$$\mathcal{D}x\left(t'\right)=\lim_{n\to\infty}dx_1dx_2\ldots dx_{n-1}\ .$$

To better understand the meaning of Eq. (2.105) we again consider the 1D free particle, i.e. we must solve Eq. (2.99), where now β is replaced by $i\frac{t}{\hbar}$. From (2.100) we see that

$$\rho\left(x,x';\epsilon\right)=\sqrt{\frac{m}{2\pi i\hbar\epsilon}}e^{-\frac{m}{2\hbar i\epsilon}\left(x-x'\right)^2}\ .\qquad(2.107)$$

According to (2.106) we may write [18]

$$\begin{aligned}&\rho\left(x,x';t\right)\qquad(2.108)\\&=\lim_{\epsilon\to0}\int\ldots\int\exp\Bigg[-\frac{m\epsilon}{2i\hbar}\Bigg\{\left(\frac{x-x_{n-1}}{\epsilon}\right)^2\\&+\left(\frac{x_{n-1}-x_{n-2}}{\epsilon}\right)^2+\ldots\\&\ldots+\left(\frac{x_1-x'}{\epsilon}\right)^2\Bigg\}\Bigg]\\&\times\frac{dx_1}{\sqrt{2\pi i\hbar\epsilon/m}}\ldots\frac{dx_{n-1}}{\sqrt{2\pi i\hbar\epsilon/m}}\ .\end{aligned}$$

Now we let ϵ approach zero:

$$\frac{x_k-x_{k-1}}{\epsilon}\to\left.\frac{dx\left(t'\right)}{dt'}\right|_{t'=k\epsilon}\equiv\left.\dot{x}\left(t'\right)\right|_{t'=k\epsilon}\ .$$

Therefore the integrand in (2.108) becomes

$$\exp\left[\ldots\right]=\exp\left[\frac{i}{\hbar}\int_0^t\frac{m}{2}\dot{x}\left(t'\right)^2dt'\right]\ .\qquad(2.109)$$

Eq. (2.105) in the case of the free particle now reads

$$\begin{aligned}&\rho\left(x,x';t\right)\qquad(2.110)\\&=\int\exp\left[\frac{i}{\hbar}\int_0^t\frac{m}{2}\dot{x}\left(t'\right)^2dt'\right]\mathcal{D}x\left(t'\right)\ ,\end{aligned}$$

where $\mathcal{D}x\left(t'\right)$ is given by

$$\mathcal{D}x\left(t'\right)=\lim_{\epsilon\to0}\prod_{i=1}^{n-1}\frac{dx_i}{\sqrt{2\pi\hbar i\epsilon/m}}\ .$$

The argument of the exponent in Eq. (2.110) begins to look interesting. The integral we identify as the action (dt.: Wirkung) introduced in classical mechanics, i.e. $S=\int_{t_1}^{t_2}\mathcal{L}\left(x,\dot{x},t\right)dt$. To complete this analogy we must subject our 1D free particle to a potential $\mathcal{U}\left(x\right)$. In this case the equation for $\rho(x,x';t)$ is

$$\begin{aligned}&i\hbar\partial_t\rho\left(x,x';t\right)=\qquad(2.111)\\&-\frac{\hbar^2}{2m}\partial_x^2\rho\left(x,x';t\right)+\mathcal{U}\left(x\right)\rho\left(x,x';t\right)\ .\end{aligned}$$

It can be shown (cf. below) that Eq. (2.109) becomes

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[18] We show this explicitly in a homework problem.

$$\exp[\ldots] = \exp\left[\frac{i}{\hbar}\int_0^t \mathcal{L}\left(t,\dot{x}(t'),x(t')\right)dt'\right] \qquad (2.112)$$

or

$$\begin{aligned}\rho\left(x,x';t\right) & \qquad (2.113)\\ = \int \exp\left[\frac{i}{\hbar}\int_0^t \mathcal{L}\left(t,\dot{x}(t'),x(t')\right)dt'\right]\mathcal{D}x\left(t'\right) \ ,\end{aligned}$$

where

$$\mathcal{L}\left(t,\dot{x}(t'),x(t')\right) = \frac{m}{2}\dot{x}^2(t') - \mathcal{U}\left(x(t')\right) \qquad (2.114)$$

is the Lagrangian.

Remark: In order to show that Eq. (2.113) is indeed true, we want to take a different route than the one above and 'restart' by considering a single 'slice', e.g. $\rho(x_{n-1},x_{n-2};\epsilon) = \langle x_{n-1}|\exp[-(i/\hbar)\underline{\mathcal{H}}\epsilon]|x_{n-2}\rangle$, in Eq. (2.104), where $\underline{\mathcal{H}} = \underline{p}^2/(2m) + \mathcal{U}(\underline{x})$.

In the following it will be convenient to use the approximation

$$e^{-\frac{i}{\hbar}\underline{\mathcal{H}}\epsilon} \approx e^{-\frac{i}{\hbar}\mathcal{U}(\underline{x})\frac{\epsilon}{2}} e^{-\frac{i}{\hbar}\frac{\underline{p}^2}{2m}\epsilon} e^{-\frac{i}{\hbar}\mathcal{U}(\underline{x})\frac{\epsilon}{2}} \ . \qquad (2.115)$$

The validity of this formula including the linear order in ϵ is easily shown be straightforward expansion of the two sides in ϵ. Higher order terms are not interesting, because they will disappear in the final limit when $\epsilon \to 0$. Using this approximation we can write

$$\begin{aligned}\rho(x_{n-1},x_{n-2};\epsilon) \approx & \qquad (2.116)\\ e^{-\frac{i}{\hbar}\mathcal{U}(x_{n-1})\frac{\epsilon}{2}}\langle x_{n-1}|e^{-\frac{i}{\hbar}\frac{\underline{p}^2}{2m}\epsilon}|x_{n-2}\rangle e^{-\frac{i}{\hbar}\mathcal{U}(x_{n-2})\frac{\epsilon}{2}} &\\ = \langle x_{n-1}|e^{-\frac{i}{\hbar}\frac{\underline{p}^2}{2m}\epsilon}|x_{n-2}\rangle e^{-\frac{i}{\hbar}\frac{\mathcal{U}(x_{n-1})+\mathcal{U}(x_{n-2})}{2}\epsilon} \ . &\end{aligned}$$

Corrections in the exponents are of $\mathcal{O}(\epsilon^2)$ or higher. Inserting $1 = \int dk|k\rangle\langle k|$ into the matrix element yields

$$\langle x_{n-1}|e^{-\frac{i}{\hbar}\frac{\underline{p}^2}{2m}\epsilon}|x_{n-2}\rangle = \qquad (2.117)$$

$$\begin{aligned}& \int dkdk'\langle x_{n-1}|k\rangle\langle k|e^{-i\hbar\frac{\underline{k}^2}{2m}\epsilon}|k'\rangle\langle k'|x_{n-2}\rangle\\ &= \int dkdk'\langle x_{n-1}|k\rangle e^{-i\hbar\frac{k^2}{2m}\epsilon}\delta(k-k')\rangle\langle k'|x_{n-2}\rangle\\ &= \frac{1}{2\pi}\int_{-\infty}^{\infty} dk\, e^{-i\hbar\frac{k^2}{2m}\epsilon}e^{ik(x_{n-1}-x_{n-2})}\\ &= \sqrt{\frac{m}{2\pi i\hbar\epsilon}}e^{\frac{i}{\hbar}\frac{m}{2\epsilon}(x_{n-1}-x_{n-2})^2}\end{aligned}$$

[19], confirming (2.108). If we now use the new formula for $\rho(x_{n-1},x_{n-2};\epsilon)$, i.e. the formula which we obtain by inserting the last line in (2.117) into (2.116, in Eq. (2.108), we immediately see that (2.113) is indeed correct.

Let us now apply the above to the computation of the probability for finding a system (or particle) in a state $\langle\chi\left(t\right)\mid$ at time t, when it was in a state $\mid\psi\left(0\right)\rangle$ at time zero (cf. page 42).

This probability was $\mid\langle\chi\left(t\right)\mid\psi\left(t\right)\rangle\mid^2$, which we may express via

$$\begin{aligned}\left|\langle\chi\left(t\right)\mid\psi\left(t\right)\rangle\right|^2 & \qquad (2.118)\\ = \left|\langle\chi\left(t\right)\mid\underline{\rho}\mid\psi\left(0\right)\rangle\right|^2 &\\ = \left|\int d^3rd^3r'\langle\chi\left(t\right)\mid\vec{r}\rangle\langle\vec{r}\mid\underline{\rho}\mid\vec{r}\,'\rangle\langle\vec{r}\,'\mid\psi\left(0\right)\rangle\right|^2 &\\ = \left|\int d^3rd^3r'\chi^*\left(\vec{r},t\right)\rho(\vec{r},\vec{r}\,';t)\psi(\vec{r}\,',0)\right|^2 . &\end{aligned}$$

The quantity inside $\mid\ldots\mid^2$ is called transition amplitude. Thus, for any two fixed points $\vec{r}$ and $\vec{r}\,'$ the 'propagator' $\rho(\vec{r},\vec{r}\,';t)$ sums up all possible paths, which the system does follow in getting from $\vec{r}\,'$ to $\vec{r}$.

Whereas in classical mechanics there is only one path defined via $\delta S = 0$, there are infinitely many paths followed simultaneously by the quantum mechanical system. However, we would expect that paths close to the classical path are more important than those deviating from it. One may understand this as follows. A system may be well described by the classical least action path $\delta S = 0$. For every deviation Δx from the path the quantity $\Delta S/\hbar$ is large, and the corresponding phase angle $\phi = \Delta S/\hbar$ varies strongly with Δx. This results in

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[19] $\int_{-\infty}^{\infty} dk\, e^{-i(ak^2-bk)} = \sqrt{\frac{\pi}{ia}}e^{ib^2/(4a)}$

cancellations among the many possible phase factors $\exp[iS/\hbar]$ - except for the contributions from the classical path!

Clearly, Eq. (2.118) describes a key quantity in quantum theory. Therefore it is highly desirable to compute $\rho(\vec{r},\vec{r}\,';t)$ or in the 1D case $\rho(x,x\,';t)$. However, the path integrals, $\int\dots\mathcal{D}x\,(t\,')$, are difficult, and this is not the place to discuss the various solution techniques. The interested reader is referred to R. P. Feynman and A. R. Hibbs (1965) Quantum mechanics and path integrals. Mc Graw-Hill or to H. Kleinert (1993) Pfadintegrale. B. Wissenschaftsverlag (again, this is advanced reading!) [20].

Remark: This remark is intended to show the equivalence of the path integration approach to Schrödinger's equation. We follow R. P. Feynman and A. R. Hibbs (1965) Quantum mechanics and path integrals. Mc Graw-Hill (section 4-1).

Let us assume the following is valid:

$$\begin{aligned}\langle x|\psi(t+\epsilon)\rangle = \\ \int_{-\infty}^{\infty}\frac{dx\,'}{A}e^{(i/\hbar)\epsilon\mathcal{L}(\dots)}\langle x\,'|\psi(t)\rangle\end{aligned} \tag{2.119}$$

[21], where A is a constant and

$$\begin{aligned}\mathcal{L}\left(\frac{x-x\,'}{\epsilon},\frac{x+x\,'}{2}\right) \\ = \frac{m}{2}\left(\frac{x-x\,'}{\epsilon}\right)^2-\mathcal{U}\left(\frac{x+x\,'}{2}\right)\ .\end{aligned} \tag{2.120}$$

This means that we consider one (very thin) time slice in Fig. 2.2. Note that in the case $\mathcal{U}=0$, the integrand in (2.119) is given by Eq. (2.107), i.e. the x-representation of the time evolution operator for this time slice. In particular $A^{-1}=\sqrt{m/(2\pi i\hbar\epsilon)}$.

Now we expand both sides of Eq. (2.119) in the small quantity ϵ. The left side becomes

$$\langle x|\psi(t+\epsilon)\rangle = \psi(x,t)+\dot{\psi}(x,t)\epsilon+\mathcal{O}(\epsilon^2)\ . \tag{2.121}$$

where the dot indicates the time derivative.

Inside the integrand on the right we define the new quantity η via $x\,'=x+\eta$ and expand $\langle x\,'|\psi(t)\rangle$ in powers of η around x, i.e.

$$\begin{aligned}\langle x\,'|\psi(t)\rangle = \psi(x,t)+ \\ \psi\,'(x,t)\eta+\frac{1}{2}\psi''(x,t)\eta^2+\mathcal{O}(\eta^3)\ .\end{aligned} \tag{2.122}$$

Here the prime indicates the derivative with respect to x. Notice that η is not necessarily small, because the integral over $x\,'$, i.e. $\int_{-\infty}^{\infty}dx\,'$, is replaced by the integral $\int_{-\infty}^{\infty}d\eta$. However, the overwhelming contribution to this integral is due to small η-values - as we shall see. This makes physical sense, because if the time the particle travels is short, i.e. ϵ is very small, so should be the distance traveled. Applying the same idea to the potential, i.e. $\mathcal{U}(x+\eta/2)=\mathcal{U}(x)+\mathcal{O}(\eta)$, we have

$$e^{(i/\hbar)\epsilon\mathcal{L}(\dots)} = e^{\frac{im}{2\hbar\epsilon}\eta^2}\left(1-\frac{i}{\hbar}\epsilon\mathcal{U}(x)+\mathcal{O}(\epsilon\,\eta)\right) \tag{2.123}$$

After insertion of the expansions (2.122) and (2.123) into (2.119) we carry out the integration $\int_{-\infty}^{\infty}dx\,'=\int_{-\infty}^{\infty}d\eta$, where we make use of

$$\int_{-\infty}^{\infty}d\eta e^{(-b+ia)\eta^2}=\sqrt{\frac{\pi}{b-ia}}\overset{b\to 0}{\to}\sqrt{i\frac{\pi}{a}}\ , \tag{2.124}$$

where $b\geq 0$,

$$\int_{-\infty}^{\infty}d\eta\eta e^{(-b+ia)\eta^2}=0 \tag{2.125}$$

and

$$\begin{aligned}\int_{-\infty}^{\infty}d\eta\eta^2 e^{(-b+ia)\eta^2} \\ = \frac{\sqrt{\pi}}{2(b-ia)^{3/2}}\overset{b\to 0}{\to}\sqrt{i\frac{\pi}{a}}\frac{i}{2a}\end{aligned} \tag{2.126}$$

with $a=m/(2\hbar\epsilon)$. This is sufficient, because we only keep the terms up to first order in ϵ. Thus,

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[20] The origin of the procedure discussed in this section is a remark of Dirac ([2]; section 32, p. 125 "The action principle"; the book was first published in 1930!) developed by Feynman (R.P. Feynman (1949) Phys. Rev. **76**, 769; (1950) **80**, 440).

[21] Actually, this formula is the basis of Eq. (2.118), i.e. it is the part of this equation which describes the time development of the wave function $\langle\vec{r}|\psi(0)\rangle$. Here we apply $\rho\,(x,x\,';\epsilon)$ according to Eq. (2.113), where t is replaced by single time slice ϵ.

$$\int_{-\infty}^{\infty} \frac{dx\,'}{A} e^{(i/\hbar)\epsilon\mathcal{L}(\dots)} \langle x\,'|\psi(t)\rangle = \psi(x,t) \qquad (2.127)$$
$$+\frac{i\hbar}{2m}\psi''(x,t)\epsilon - \frac{i}{\hbar}\mathcal{U}(x)\psi(x,t)\epsilon + \mathcal{O}(\epsilon^2)\ .$$

Comparison of this result to the expansion (2.121) yields Schrödinger's equation:

$$i\hbar\dot{\psi}(x,t) = -\frac{\hbar^2}{2m}\psi''(x,t) + \mathcal{U}(x)\psi(x,t) \quad (2.128)$$

(in the limit $\epsilon \to 0$). This proves in particular that the time-development according to Eq. (2.119) agrees with the solution of Schrödinger's equation.

We close with a quote from Feynman's book: "In this book we shall give the laws to compute the probability amplitude for nonrelativistic problems in a manner which is somewhat unconventional. In some ways, particularly in developing a conceptual understanding of quantum mechanics, it may be preferred, but in others, e.g., in making computations for simpler problems and for understanding the literature, it is disadvantageous." It is the 'conceptual understanding' of puzzling experiments, like for instance the double slit experiment, which provide ample motivation for this section.

Chapter 3

Scattering theory

3.1 The Lippmann-Schwinger equation

Scattering experiments are among the most important to verify quantum theory. The central quantity is the scattering cross section (dt.: Streuquerschnitt). We imagine a homogeneous (particle) current density $\vec{j}_{in}$ directed at a target at "infinite" distance. Infinite means that the interaction between target and current can be neglected at this distance. In the same sense we place a suitable detector at an "infinite" distance behind the target.

In classical mechanics we had defined the differential scattering cross section via

$$d\sigma = \frac{dN}{n} \tag{3.1}$$

(cf. [14]; section 5.3)). Here dN is the number of particles detected in an angular interval $(\theta, \theta + d\theta)$, where θ is the scattering angle, and n is the area density measured perpendicular to the incoming current. More generally, however, dN is given by the number of particles detected to hit an area $r^2 d\Omega = r^2 d\varphi \sin\theta d\theta$, where φ is the angle in the plane perpendicular to the incoming current density $\vec{j}_{in}$. Thus,

$$d\sigma = \frac{j_{scat} r^2 d\Omega}{j_{in}} \; , \tag{3.2}$$

where $\vec{j}_{scat}$ is the scattered current density. Notice that we consider r always to be large in the above sense!

In order to calculate j_{scat} we need to find the solution of

$$(\underline{\mathcal{H}}_0 + \underline{\mathcal{H}}_1) \mid \psi\rangle = E \mid \psi\rangle \; , \tag{3.3}$$

or

$$(E - \underline{\mathcal{H}}_0) \mid \psi\rangle = \underline{\mathcal{H}}_1 \mid \psi\rangle \; , \tag{3.4}$$

i.e. we treat the scattering problem as a stationary problem. This is sensible if E is the eigenvalue of a time-independent operator [1]. Here $\underline{\mathcal{H}}_0 = \frac{\hbar^2 \vec{\underline{k}}^2}{2\mu}$ describes the free particle in the center of mass frame, where μ is the reduced mass of target and beam particle. $\underline{\mathcal{H}}_1$ on the other hand is the interaction Hamilton operator. We may solve (3.4) in a formal sense by writing

$$\mid \psi\rangle = \mid \Phi\rangle + \frac{1}{E - \underline{\mathcal{H}}_0} \underline{\mathcal{H}}_1 \mid \psi\rangle \tag{3.5}$$

[2], where $\mid \Phi\rangle$ satisfies

$$(\underline{\mathcal{H}}_0 - E) \mid \Phi\rangle = 0 \; . \tag{3.6}$$

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[1] In particular we consider the beam-target interaction to be elastic!

[2] The operator $(E - \underline{\mathcal{H}}_0)^{-1}$ we do understand as the power series expansion of $(1-x)^{-1}$, i.e.

$$\frac{1}{E} \left(\frac{1}{1 - E^{-1} \underline{\mathcal{H}}_0} \right) = \frac{1}{E} \left(1 + \frac{\underline{\mathcal{H}}_0}{E} + \left(\frac{\underline{\mathcal{H}}_0}{E} \right)^2 + \dots \right) \; .$$

We note that multiplication with $E - \underline{\mathcal{H}}_0$ yields

$$\begin{aligned} &(E - \underline{\mathcal{H}}_0) \frac{1}{E - \underline{\mathcal{H}}_0} \\ &= E \cdot \frac{1}{E} \left(1 - \frac{\underline{\mathcal{H}}_0}{E} \right) \left(1 + \frac{\underline{\mathcal{H}}_0}{E} + \left(\frac{\underline{\mathcal{H}}_0}{E} \right)^2 + \dots \right) \\ &= \left[1 + \frac{\underline{\mathcal{H}}_0}{E} + \left(\frac{\underline{\mathcal{H}}_0}{E} \right)^2 + \dots - \frac{\underline{\mathcal{H}}_0}{E} - \left(\frac{\underline{\mathcal{H}}_0}{E} \right)^2 - \dots \right] \\ &= 1 \; . \end{aligned}$$

The first term on the right in Eq. (3.5) corresponds to particles passing the target area without interaction. The second term, however, will yield j_{scat}. For reasons which will be discussed below we rewrite Eq. (3.5) as

$$\mid \psi^{(+)}\rangle = \mid \Phi\rangle + \frac{1}{E-\underline{\mathcal{H}}_0+i\epsilon}\underline{\mathcal{H}}_1 \mid \psi^{(+)}\rangle \ . \tag{3.7}$$

ϵ is a small positive number, and in the limit $\epsilon \to +0$ we recover Eq. (3.5). Eq. (3.7) is called the Lippmann-Schwinger equation [3].

In order to obtain j_{scat} we need the $\vec{r}$-representation of (3.7), i.e.

$$\begin{aligned}\langle \vec r \mid \psi^{(+)}\rangle &= \langle \vec r \mid \Phi\rangle + \int d^3r\,' d^3k d^3k\,' \langle \vec r \mid \vec k\rangle \\ &\quad \times \langle \vec k \mid \frac{1}{E-\underline{\mathcal{H}}_0+i\epsilon} \mid \vec k\,'\rangle\langle \vec k\,' \mid \vec r\,'\rangle \\ &\quad \times \langle \vec r\,' \mid \underline{\mathcal{H}}_1 \mid \psi^{(+)}\rangle \ . \end{aligned}\tag{3.8}$$

We have inserted the $\vec k$-states, because in $\vec k$-representation $(E-\underline{\mathcal{H}}_0+i\epsilon)^{-1}$ is diagonal [4], and we obtain

$$\begin{aligned}\langle \vec r \mid \psi^{(+)}\rangle &= \langle \vec r \mid \Phi\rangle + \frac{2\mu}{\hbar^2}\int d^3r\,' d^3k \frac{e^{i\vec k\cdot\vec r}}{(2\pi)^{3/2}} \\ &\times \frac{e^{-i\vec k\cdot\vec r\,'}}{(2\pi)^{3/2}}\frac{1}{k_0^2-k^2+i\eta}\langle \vec r\,' \mid \underline{\mathcal{H}}_1 \mid \psi^{(+)}\rangle \ , \end{aligned}\tag{3.9}$$

where $E=\frac{\hbar^2 k_0^2}{2\mu}$ and $\epsilon = \frac{\hbar^2}{2\mu}\eta$. Introducing the definition

$$G_0^{(+)}(\vec r-\vec r\,') = \frac{1}{(2\pi)^3}\int d^3k \frac{e^{i\vec k\cdot(\vec r-\vec r\,')}}{k_0^2-k^2+i\eta} \tag{3.10}$$

we have

$$\begin{aligned}\langle \vec r \mid \psi^{(+)}\rangle &= \langle \vec r \mid \Phi\rangle \\ &+\frac{2\mu}{\hbar^2}\int d^3r\,' G_0^{(+)}(\vec r-\vec r\,')\langle \vec r\,' \mid \underline{\mathcal{H}}_1 \mid \psi^{(+)}\rangle \ . \end{aligned}\tag{3.11}$$

$G_0^{(+)}(\vec r-\vec r\,')$ is the so called Green function of the free particle.

When we do the integral in Eq. (3.10) (cf. below), we will find that $G_0^{(+)}(\vec r-\vec r\,')$ is such that Eq. (3.11) may be written as

$$\begin{aligned}\langle \vec r \mid \psi^{(+)}\rangle &= \langle \vec r \mid \Phi\rangle - \frac{2\mu}{\hbar^2}\frac{e^{ik_0 r}}{4\pi r} \\ &\times \underbrace{\int d^3r\,' (2\pi)^{3/2}\langle \vec k\,' \mid \vec r\,'\rangle\langle \vec r\,' \mid \underline{\mathcal{H}}_1 \mid \psi^{(+)}\rangle}_{=(2\pi)^{3/2}\langle \vec k\,'\mid\underline{\mathcal{H}}_1\mid\psi^{(+)}\rangle}\end{aligned}$$

or

$$\langle \vec r \mid \psi^{(+)}\rangle = \langle \vec r \mid \Phi\rangle + \frac{A}{(2\pi)^{3/2}}\frac{e^{ik_0 r}}{r} \ , \tag{3.12}$$

where

$$A = -\left(\frac{2\pi}{\hbar}\right)^2 \mu\langle \vec k\,' \mid \underline{\mathcal{H}}_1 \mid \psi^{(+)}\rangle \tag{3.13}$$

is the scattering amplitude.

Using Eq. (1.127) we obtain

$$\begin{aligned}\vec{j}_{scat} &= \frac{\hbar}{2i\mu}\frac{\mid A\mid^2}{(2\pi)^3}\Big[\frac{e^{-ik_0 r}}{r}\partial_r\frac{e^{ik_0 r}}{r} \\ &-\frac{e^{ik_0 r}}{r}\partial_r\frac{e^{-ik_0 r}}{r}\Big]\vec e_r = \frac{\hbar k_0}{\mu r^2}\frac{\mid A\mid^2}{(2\pi)^3}\vec e_r \ . \end{aligned}\tag{3.14}$$

And what about j_{in}? We do require that the incoming particles possess sharply defined momentum $\vec k_0$. Thus $\mid \Phi\rangle = \mid \vec k_0\rangle$. The corresponding current density, which we obtain by inserting $\langle \vec r \mid \vec k_0\rangle$ into Eq. (1.127) is

$$\vec{j}_{in} = \frac{\hbar}{\mu}\frac{\vec k_0}{(2\pi)^3} \ . \tag{3.15}$$

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[3] Schwinger, Julian Seymour, american physicist, *New York 12.2.1918, †Los Angeles (Kalifornien) 16.7.1994; one of the main contributors to quantum electrodynamics (QED)arbeitete; shared the 1965 Nobel prize in physics with R. P. Feynman und S.Tomonaga.

[4] Notice that we understand $\left(E-\underline{\mathcal{H}}_0+i\epsilon\right)^{-1}$ in terms of an expansion in powers of $E^{-1}(\underline{\mathcal{H}}_0-i\epsilon)$. We further note that our previous result (cf. (2.54)), $\langle \vec k \mid \underline{\vec k} \mid \vec k\,'\rangle = \vec k\delta(\vec k-\vec k\,')$, may be generalized to

$$\langle \vec k \mid \underline{k}_x^{2l}\underline{k}_y^{2m}\underline{k}_z^{2n} \mid \vec k\,'\rangle = k_x^{2l}k_y^{2m}k_z^{2n}\delta(\vec k-\vec k\,') \ ,$$

where $l,m,n=0,1,2,\ldots$.

Inserting Eqs. (3.14) and (3.15) into (3.2) yields

$$d\sigma =\mid A\mid^2 d\Omega \; . \tag{3.16}$$

At this point we want to interrupt for a moment and compute $G_0^{(+)}(\vec{r}-\vec{r}\,')$ in Eq. (3.10) explicitly. We use polar coordinates defining te z-axis along $\vec{r}-\vec{r}\,'$, i.e.

$$\begin{aligned} \int d^3k &= \int_0^\infty dk k^2 \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin\theta \\ &= \int_0^\infty dk k^2 \int_0^{2\pi} d\phi \int_{-1}^1 dy \; , \end{aligned} \tag{3.17}$$

where $y=\cos\theta$. This yields

$$\begin{aligned} G_0^{(+)}(\vec{r}-\vec{r}\,') &= \frac{1}{(2\pi)^2 i \mid \vec{r}-\vec{r}\,'\mid} \\ &\times \int_0^\infty dk \frac{k\left(e^{ik|\vec{r}-\vec{r}\,'|}-e^{-ik|\vec{r}-\vec{r}\,'|}\right)}{k_0^2-k^2+i\eta} \\ &= \frac{1}{(2\pi)^2 i \mid \vec{r}-\vec{r}\,'\mid} \int_{-\infty}^\infty dk \frac{k e^{ik|\vec{r}-\vec{r}\,'|}}{k_0^2-k^2+i\eta} \end{aligned}$$

We evaluate the integral by the residue method [5] along the path in the upper half plane shown in figure 3.1. Note that the loop does not contribute to the integral, because for $ik=i\rho e^{i\varphi}=i\rho\cos\varphi-\rho\sin\varphi$ the resulting factor $e^{-\rho\sin\varphi}$ suppresses this contribution in the limit $\rho\to\infty$ for $0\le\varphi\le\pi$. Thus only the contribution from the real axis remains. But according to the residue theorem we may write

$$\begin{aligned} G_0^{(+)}(\vec{r}-\vec{r}\,') &= \frac{1}{4\pi^2 i \mid \vec{r}-\vec{r}\,'\mid} \\ &\times \lim_{\rho\to\infty} \oint dk \frac{k e^{ik|\vec{r}-\vec{r}\,'|}}{k_0^2-k^2+i\eta} \\ &= \frac{2\pi i}{4\pi^2 i \mid \vec{r}-\vec{r}\,'\mid} \sum \text{all residues of} \frac{k e^{ik|\vec{r}-\vec{r}\,'|}}{k_0^2-k^2+i\eta} \end{aligned}$$

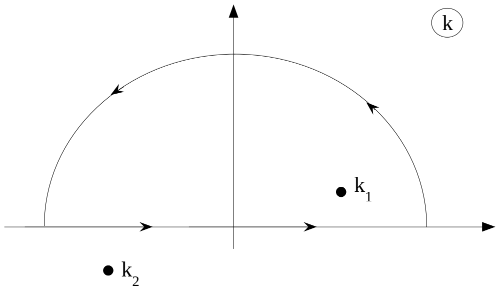

Figure 3.1: Integration path in the upper complex plane. The poles are indicated by $k_1\approx k_0+i\eta/(2k_0)$ and $k_2=-k_1$.
.

at all poles inside the integration loop. The poles occur at $k_{1,2}=\pm\sqrt{k_0^2+i\eta}$. But only the one with the positive sign lies within the integration loop. We therefore have

$$\begin{aligned} & Res \frac{k e^{ik|\vec{r}-\vec{r}\,'|}}{k_0^2-k^2+i\eta}\Big|_{k_1} \\ &= Res \frac{k e^{ik|\vec{r}-\vec{r}\,'|}}{\left(\sqrt{k_0^2+i\eta}-k\right)\left(\sqrt{\ldots}+k\right)} \\ &= \lim_{k\to k_1} \frac{(k-k_1)\, k e^{ik|\vec{r}-\vec{r}\,'|}}{\left(\sqrt{\ldots}-k\right)\left(\sqrt{\ldots}+k\right)} \\ &= -\frac{e^{ik_1|\vec{r}-\vec{r}\,'|}}{2} \; . \end{aligned}$$

Letting $\eta\to 0$ we obtain finally

$$G_0^{(+)}(\vec{r}-\vec{r}\,') = -\frac{e^{i|\vec{k}_0||\vec{r}-\vec{r}\,'|}}{4\pi|\vec{r}-\vec{r}\,'|} \; . \tag{3.20}$$

Now we consider the case when $\mid\vec{r}\mid\gg\mid\vec{r}\,'\mid$. We obtain

$$\begin{aligned} (\vec{r}-\vec{r}\,')^2 &= r^2+r\,'^2-2rr\,'\cos(\vec{r},\vec{r}\,') \\ &= r^2\left(1-\frac{2r\,'}{r}\cos(\vec{r},\vec{r}\,')+\left(\frac{r\,'}{r}\right)^2\right) \end{aligned}$$

---

[5] The residue theorem: Let $f(z)$ be single valued and analytic on a simple close curve C except at the singularities a_{-1}, b_{-1}, ... Then the residue theorem states that

$$\oint_C f(z)dz = 2\pi i\,(a_{-1}+b_{-1}+\ldots) \; . \tag{3.18}$$

Calculation of residues: The function $f(z)$ has a pole of order k at $z=a$. a_{-1} is given by

$$a_{-1} = \lim_{z\to a} \frac{1}{(k-1)!}\frac{d^{k-1}}{dz^{k-1}}\left[(z-a)^k f(z)\right] \tag{3.19}$$

(cf. [22]).

from which we have

$$\mid \vec r - \vec r\,' \mid = r\left(1 - \frac{r\,'}{r}\cos(\vec r, \vec r\,') + \ldots\right) \; .$$

Therefore

$$G_0^{(+)}(\vec r - \vec r\,') \to -\frac{e^{ik_0 r}}{r}\frac{1}{4\pi}e^{-ik_0 r\,'\cos(\vec r,\vec r\,')} + \ldots \tag{3.21}$$

If we now introduce $\vec k\,'$ according to

$$\vec k\,' = k_0\frac{\vec r}{r}$$

we get

$$\begin{aligned} e^{-ik_0 r\,'\cos(\vec r,\vec r\,')} &= e^{-i\vec k\,'\cdot\vec r\,'} &(3.22)\\ &= (2\pi)^{3/2}\langle\vec k\,' \mid \vec r\,'\rangle \; . \end{aligned}$$

Combining Eqs. (3.21) and (3.22) we now see that Eq. (??) was indeed justified.

3.2 The 1st Born approximation

The simplest approach to solving the Lippmann-Schwinger equation is iteration. Replacing $\mid \psi^{(+)}\rangle$ on the right side by $\mid \Phi\rangle$ we obtain the first Born approximation to the scattering amplitude:

$$A^{(1)} = -\frac{4\pi^2\mu}{\hbar^2}\langle\vec k\,' \mid \underline{\mathcal{H}}_1 \mid \Phi\rangle \; . \tag{3.23}$$

Setting $\mid \Phi\rangle = \mid \vec k\rangle$ yields the scattering amplitude to lowest order in terms of the $\vec k$-representation of $\underline{\mathcal{H}}_1$.

We now consider the special case of a spherically symmetric potential:

$$\underline{\mathcal{H}}_1 = \mathcal{U}\left(\underline{r}\right) \; . \tag{3.24}$$

We now obtain

$$\begin{aligned} A^{(1)} &= -\frac{4\pi^2\mu}{\hbar^2}\int\langle\vec k\,' \mid \vec r\rangle d^3r\,\mathcal{U}\left(\underline{r}\right)\langle\vec r \mid \vec k\rangle \\ &= -\frac{\mu}{2\pi\hbar^2}\int d^3r\,\mathcal{U}\left(r\right)e^{i\vec r\cdot(\vec k - \vec k\,')} \\ &= -\frac{2\mu}{\hbar^2 q}\int_0^\infty dr\,r\,\mathcal{U}\left(r\right)\sin\left(rq\right) \; . &(3.25) \end{aligned}$$

The quantity

$$\begin{aligned} q &= \mid \vec k - \vec k\,' \mid = \sqrt{k^2 + k\,'^2 - 2kk\,'\cos\theta} \\ &\overset{(k=k\,')}{=} \sqrt{2k^2\left(1-\cos\theta\right)} \\ &= 2k\sin(\theta/2) &(3.26) \end{aligned}$$

is called momentum transfer [6].

If we insert the so called Yukawa potential

$$\mathcal{U}\left(r\right) = \frac{\alpha e^{-\kappa r}}{r} \; , \tag{3.27}$$

where κ^{-1} is a measure for the range of the interaction, we obtain [7]

$$A^{(1)} = -\frac{2\mu\alpha}{\hbar^2}\frac{1}{q^2+\kappa^2} \; . \tag{3.28}$$

Setting $\kappa = 0$ (infinite range) yields the scattering cross section for the Coulomb potential:

$$\begin{aligned} d\sigma &= \frac{4\mu^2\alpha^2}{\hbar^4}\frac{1}{q^4}d\Omega \\ &= \frac{\mu^2\alpha^2}{4\hbar^4 k^4\sin^4\left(\theta/2\right)}d\Omega \; . &(3.29) \end{aligned}$$

Because $\frac{\hbar^2k^2}{2\mu} = \frac{1}{2}\mu v_\infty^2$ is the kinetic energy in the center of mass system, where v_∞ is the relative velocity for large distances, this can be written as

$$d\sigma = \frac{\alpha^2}{4\mu^2 v_\infty^4\sin^4\left(\theta/2\right)}d\Omega \; . \tag{3.30}$$

This expression is known as the Rutherford scattering from classical mechanics (cf. [14]; section

---

[6] This particular θ, which is the scattering angle, should not be confused with other θs in this text.

[7] Notice that the resulting integral is the Laplace transform of $\sin\left(qr\right)$.

5.3)! The agreement must be considered accidental, however. The limit $\kappa \to 0$ collides with our previous assumption, that at large distances between beam particles and target the interaction should not be felt. If higher approximations are included this leads to problems with divergencies (for a more detailed discussion see Ref. [5]). Thus (3.30) is a computational example of the first Born approximation, and not so much an important result.

We close this discussion with a remark regarding $\mid \psi^{(+)}\rangle$. The same calculation could have been carried out with $\mid \psi^{(-)}\rangle$, which leads to an integration in the lower complex half plane. The result is an unscattered plane wave plus an incoming spherical wave instead of an outgoing spherical wave.

3.3 Partial wave expansion

In the following we look at scattering from a different angle. Consider a low energy quantum particle approaching a target. The range of the particle-target interaction is small compared to the de-Broglie wavelength of the particle, which is large because of the low energy. In this situation the structure of the target is not resolved very well and it is sensible to expand the angular dependence of the scattering amplitude. Increasing the order of this expansion basically corresponds to including more structural information.

Before we do this, we must take a step back and once again study Schrödinger's equation when the interaction potential has spherical symmetry, i.e.

$$\left(-\frac{\hbar^2}{2\mu}\vec{\nabla}^2_{\vec{r}} + \mathcal{U}(r) - E\right)\psi(\vec{r}) = 0\ . \tag{3.31}$$

Setting $E = \hbar^2 k^2/(2\mu)$, $z = kr$ and $u(z) = 2\mu U(r)/(\hbar^2 k^2)$, we obtain

$$\left(\frac{\partial_z(z^2\partial_z)}{z^2} - \frac{l(l+1)}{z^2} - u(z) + 1\right)\chi(z) = 0 \tag{3.32}$$

This equation is basically the radial equation, which we already discussed in the context of the hydrogen atom in section 1.4 [8]. Its solutions for $u(z) = 0$ are linear combinations of the spherical Bessel functions of the first and second kind, i.e.

$$j_l(z) = z^l\left(-\frac{1}{z}\frac{d}{dz}\right)^l \frac{\sin z}{z} \tag{3.33}$$

and

$$y_l(z) = -z^l\left(-\frac{1}{z}\frac{d}{dz}\right)^l \frac{\cos z}{z} \tag{3.34}$$

$(l = 0, 1, 2, \ldots)$ (see [19] (section10.1)).

In the following, since we are dealing with scattering, we are interested in the behavior of the solution at large distances from the target. The leading terms in the limit of large r (or large z), i.e. the ones vanishing most slowly, are

$$j_l(z) \overset{z\to\infty}{\to} (-1)^l \frac{1}{z}\frac{d^l}{dz^l}\sin z = \frac{1}{z}\sin\left(z - \frac{\pi}{2}l\right)$$

(check this!). Similarly

$$y_l(z) \overset{z\to\infty}{\to} -(-1)^l \frac{1}{z}\frac{d^l}{dz^l}\cos z = -\frac{1}{z}\cos\left(z - \frac{\pi}{2}l\right)\ .$$

A linear combination of these two solutions can be written as

$$\chi_{l,\infty}(z) = c_l \frac{1}{z}\sin\left(z - \frac{\pi}{2}l + \delta_l\right)\ , \tag{3.35}$$

where the δ_l are phase shifts. The index ∞ is just a reminder that this is the radial part of the solution at large distances from the target. However, even though we arrive at this form of the solution by setting $u(z) = 0$, the phase shifts do contain information about $u(z) \neq 0$. This is because the phase shifts are determined by smoothly tying the asymptotic solution to the solution in the target area. We will not do this here. Instead we focus on the basic relation of the δ_l to the scattering cross section.

At this point we can express the previous result for the scattered wave function in Eq. (3.12) in terms of the above (partial wave) expansion. Here this means that the scattering angle-dependent structure far from the target is described in terms of Legendre polynomials $P_l(\cos\theta)$:

---

[8] Here however $u(z)$ in not the same as $u_l(\rho)$ in section 1.4

$$\langle r,\theta \mid \psi^{(+)}\rangle = \sum_{l=0}^{\infty} c_l \frac{1}{kr} \sin\left(kr - \frac{\pi}{2} l + \delta_l\right) P_l\left(\cos\theta\right) \ . \tag{3.36}$$

Applying the same expansion on the other side of Eq. (3.12) yields

$$\langle \vec{r} \mid \Phi\rangle = \langle \vec{r} \mid \vec{k}\rangle = \frac{e^{i\vec{k}\vec{r}}}{(2\pi)^{3/2}} = \frac{e^{ikr\cos\theta}}{(2\pi)^{3/2}} = \overset{(*)}{=} \frac{1}{(2\pi)^{3/2}} \sum_{l=0}^{\infty} i^l \left(2l+1\right) j_l\left(kr\right) P_l\left(\cos\theta\right) \tag{3.37}$$

as well as

$$A\left(\theta\right) = \sum_{l=0}^{\infty} \left(2l+1\right) A_l P_l\left(\cos\theta\right) \ . \tag{3.38}$$

Notice that in the case of Eq. (3.37) we have made use of a result (*) from the literature (cf. [17] (section 16.8)). The coefficients c_l and in particular the A_l can be determined by equating terms on the two sides of Eq. (3.12). Notice also that $j_l\left(kr\right)$ in Eq. (3.37) must be replaced by its limiting expression for large r. Following this prescription we obtain

$$c_l = \frac{2l+1}{(2\pi)^{3/2}} i^l e^{i\delta_l} \tag{3.39}$$

and

$$A_l = \frac{1}{2ik}\left(e^{2i\delta_l} - 1\right) \ . \tag{3.40}$$

Thus, the differential cross section is given by

$$\frac{d\sigma}{d\Omega} = \frac{1}{k^2} \left| \sum_{l=0}^{\infty} \left(2l+1\right) e^{i\delta_l} \sin\delta_l P_l\left(\cos\theta\right) \right|^2 \tag{3.41}$$

and the total cross section becomes

$$\begin{aligned} \sigma &= 2\pi \int_0^{\pi} \left| A\left(\theta\right) \right|^2 \sin\theta d\theta \\ &= \frac{4\pi}{k^2} \sum_{l=0}^{\infty} \left(2l+1\right) \sin^2\delta_l \end{aligned} \tag{3.42}$$

[9]. Inserting (3.40) into (3.38) and comparing the result to (3.42) yields [10]

$$\sigma = \frac{4\pi}{k} \mathrm{Im} A\left(0\right) \ . \tag{3.43}$$

This is the optical theorem.

Remark: The limit

$$\sigma_{k\to 0} = 4\pi a^2 \ . \tag{3.44}$$

defines the so called scattering length a. Applying this limit in the case of Eq. (3.42) we find

$$\left.\frac{\delta_o}{k}\right|_{k\to 0} = -a \ , \tag{3.45}$$

where the sign is by convention. The scattering length can be both positive or negative. Here we have made use of the plausible assumption that the so called s-wave scattering ($l = 0$) dominates. An in depth discussion of the scattering of slow particles can be found in Ref. [8] (§132).

3.4 Some remarks on formal scattering theory

The Lippmann-Schwinger equation

$$\mid \psi^{(+)}\rangle = \mid \vec{k}\rangle + \underline{G}_0^{(+)} \underline{\mathcal{H}}_1 \mid \psi^{(+)}\rangle \tag{3.46}$$

with

$$\underline{G}_0^{(+)} = \left(E - \underline{\mathcal{H}}_0 + i\epsilon\right)^{-1} \ , \tag{3.47}$$

where $G_0^{(+)}$ is also called the free propagator, can be solved formally by multiplication with the inverse of $\underline{G}_0^{(+)}$ from the left and using $\underline{\mathcal{H}} = \underline{\mathcal{H}}_0 + \underline{\mathcal{H}}_1$. The result is

$$\begin{aligned} &\left(E - \underline{\mathcal{H}} + i\epsilon\right) \mid \psi^{(+)}\rangle \\ &\quad = \left(E - \underline{\mathcal{H}} + i\epsilon\right) \mid \vec{k}\rangle + \underline{\mathcal{H}}_1 \mid \vec{k}\rangle \end{aligned}$$

---

[9] with $\int_{-1}^{1} P_l(x) P_{l'}(x) dx = 2/(2l+1)$ for $l = l'$ and zero otherwise

[10] with $P_l\left(1\right) = 1$

or

$$\mid \psi^{(+)}\rangle = \left(1+\underline{G}^{(+)}\underline{\mathcal{H}}_1\right) \mid \vec{k}\rangle \ , \tag{3.48}$$

where

$$\underline{G}^{(+)} = \left(E-\underline{\mathcal{H}}+i\epsilon\right)^{-1} \ . \tag{3.49}$$

Inserting Eq. (3.48) into Eq. (3.13) yields

$$\begin{aligned} A &= -\left(\frac{2\pi}{\hbar}\right)^2 \mu\langle \vec{k}\,' \mid \underline{\mathcal{H}}_1 \left(1+\underline{G}^{(+)}\underline{\mathcal{H}}_1\right) \mid \vec{k}\rangle \\ &\equiv -\left(\frac{2\pi}{\hbar}\right)^2 \mu\langle \vec{k}\,' \mid \underline{T} \mid \vec{k}\rangle \ , \end{aligned} \tag{3.50}$$

where

$$\underline{T} = \underline{\mathcal{H}}_1 \left(1+\underline{G}^{(+)}\underline{\mathcal{H}}_1\right) \ . \tag{3.51}$$

Multiplication of Eq. (3.46) by $\underline{\mathcal{H}}_1$ and using $\underline{\mathcal{H}}_1 \mid \psi^{(+)}\rangle = \underline{T} \mid \vec{k}\rangle$ yields another more useful operator equation for $\underline{T}$, i.e.

$$\underline{T} = \underline{\mathcal{H}}_1 \left(1+\underline{G}_0^{(+)}\underline{T}\right) \ . \tag{3.52}$$

Obviously (3.52) may be iterated,

$$\begin{aligned} \underline{T} &= \underline{\mathcal{H}}_1 \left(1+\underline{G}_0^{(+)}\underline{\mathcal{H}}_1 \left(1+\underline{G}_0^{(+)}\underline{T}\right)\right) \\ &= \underline{\mathcal{H}}_1 \Big(1+\underline{G}_0^{(+)}\underline{\mathcal{H}}_1 \\ &\quad \times \left(1+\underline{G}_0^{(+)}\underline{\mathcal{H}}_1 \left(1+\underline{G}_0^{(+)}\underline{T}\right)\right)\Big) \\ &= \ldots \end{aligned} \tag{3.53}$$

[11], which allows to obtain the higher order corrections to the 1st Born approximation!

The operator $\underline{T}$ is also useful in scattering problems involving crystals. To be specific, in practical calculations of electron beams scattered off crystal surfaces [12]. The target crystal is assumed to be an ordered lattice of non-overlapping spherically symmetric atomic potentials $\underline{u}\left(\vec{r}-\vec{r}_i\right)$ centered around nuclear positions $\vec{r}_i$. Therefore $\underline{\mathcal{H}}_1\left(\vec{r}\right)$ becomes

$$\underline{\mathcal{H}}_1\left(\vec{r}\right) = \sum_i \underline{u}\left(\vec{r}-\vec{r}_i\right)$$

and Eq. (3.53) yields

$$\begin{aligned} \underline{T} = \sum_i \underline{u}_i &+ \sum_{ij} \underline{u}_i \underline{G}_0^{(+)} \underline{u}_j \\ &+ \sum_{i,j,k} \underline{u}_i \underline{G}_0^{(+)} \underline{u}_j \underline{G}_0^{(+)} \underline{u}_k + \ldots \ . \end{aligned} \tag{3.54}$$

We note that $\underline{G}_0^{(+)}$ indeed describes the free propagation of the "electron waves" between the scattering potentials $\underline{u}_i$!

Remark: Inserting the first term of $\underline{T}$ in Eq. (3.54) into Eq. (3.50) we obtain

$$\begin{aligned} A &\approx -\left(\frac{2\pi}{\hbar}\right)^2 \mu\langle \vec{k}\,' \mid \sum_i \underline{u}_i \mid \vec{k}\rangle \\ &= -\frac{\mu}{2\pi\hbar^2}\sum_i \int d^3r u_i(\vec{r}) e^{i\vec{r}\cdot\vec{q}} \ . \end{aligned} \tag{3.55}$$

Here $\vec{q}=\vec{k}-\vec{k}\,'$ is called momentum transfer. If atom i is located at $\vec{r}_i$ and $\vec{\tau}$ is a vector extending from the center of the atom to a volume element $d^3\tau$ in which the scattering occurs, i.e. $\vec{r}=\vec{r}_i+\vec{\tau}$, then we have

$$A \approx -\frac{\mu}{2\pi\hbar^2}\sum_i f_i(\vec{q}) e^{i\vec{r}_i\cdot\vec{q}} \ , \tag{3.56}$$

where

$$f_i(\vec{q}) = \int d^3\tau u_i(\vec{\tau}) e^{i\vec{\tau}\cdot\vec{q}} \tag{3.57}$$

is the so called form factor of the atom. Eq. (3.56) or the attendant expression for $|A|^2$, i.e.

$$|A|^2 \approx \left(\frac{\mu}{2\pi\hbar^2}\right)^2 \sum_{i,j} f_i(\vec{q}) f_j^*(\vec{q}) e^{i\vec{r}_{ij}\cdot\vec{q}} \tag{3.58}$$

($\vec{r}_{ij}=\vec{r}_i-\vec{r}_j$), are the usual starting points of texts discussing X-ray scattering, where the leading term in Eq. (3.54) dominates.

---

[11] Note that formally this geometric series may be summed up to yield $\underline{T}=\underline{\mathcal{H}}_1(1-\underline{G}_0^{(+)}\underline{\mathcal{H}}_1)^{-1}$.

[12] This technique is used to investigate the surface structure of metal surfaces, because electrons of typically 100 eV do not penetrate more than a few atomic layers into the surface. The technique is called LEED (Low Energy Electron Diffraction). Literature: M. A. van Hove and S. Y. Tong (1979) Surface Crystallography by LEED. Springer

Chapter 4

Solution methods in quantum mechanics

In most practical cases the Schrödinger equation cannot be solved analytically. Therefore it is necessary to develop suitable approximation methods. Here we discuss four such methods.

The first two assume that the Hamiltonian may be split into two parts, the first of which can be solved exactly. The second part is a small perturbation, which may be either time-independent or time-dependent. In both cases the corrections to the unperturbed eigenvalues and eigenstates are written as power series in terms of the perturbation. The first approach will tell us something about the fine structure of spectral lines. The second approach is more general and encompasses the calculation of transition probabilities as well as problems in many particle quantum theory or even in relativistic quantum field theory.

The above decomposition of the Hamiltonian is not always possible. Here we look at two approximation schemes, which are useful in such cases. The first, the variation method, is particularly useful for the computation of eigenvalues and eigenfunctions of larger atoms or molecules. The second method is the WKB-method, a generalization of the approach that led to Eq. (1.12).

4.1 Time-independent perturbations

We start by writing $\underline{\mathcal{H}}$ as

$$\underline{\mathcal{H}} = \underline{\mathcal{H}}_0 + \underline{\mathcal{H}}_1 \,. \tag{4.1}$$

$\underline{\mathcal{H}}_0$ can be diagonalized exactly, i.e.

$$\langle k \mid \underline{\mathcal{H}}_0 \mid l \rangle = E_{k,0}\delta_{kl} \,, \tag{4.2}$$

with $\langle k \mid l \rangle = \delta_{kl}$ and $1 = \sum_{k=1}^{n} \mid k\rangle\langle k \mid$. Momentarily we assume that all $E_{k,0}$ are distinct, and that all matrix elements of $\underline{\mathcal{H}}_1$ in this representation are small. We express this fact via

$$\underline{\mathcal{H}}_1 = \lambda \underline{\mathcal{W}} \,, \tag{4.3}$$

where λ is small. Thus, we expand the eigenvalue E_k and the eigenstate $\mid \psi_k \rangle$ of $\underline{\mathcal{H}}$ in powers of λ

$$E_k = E_{k,0} + \lambda E_{k,1} + \lambda^2 E_{k,2} + \ldots \tag{4.4}$$

and

$$\mid \psi_k \rangle = \underbrace{\mid \psi_{k,0} \rangle}_{=\mid k \rangle} + \lambda \mid \psi_{k,1} \rangle + \lambda^2 \mid \psi_{k,2} \rangle + \ldots \,. \tag{4.5}$$

Inserting this into $\underline{\mathcal{H}} \mid \psi_k \rangle = E_k \mid \psi_k \rangle$ yields

$$\begin{aligned} &(\underline{\mathcal{H}}_0 + \lambda \underline{\mathcal{W}}) \big(\mid \psi_{k,0} \rangle + \lambda \mid \psi_{k,1} \rangle + \lambda^2 \mid \psi_{k,2} \rangle + \ldots \big) \\ &\quad = (E_{k,0} + \lambda E_{k,1} + \ldots) \left(\mid \psi_{k,0} \rangle + \lambda \mid \psi_{k,1} \rangle + \ldots \right) \end{aligned}$$

and therefore

$$\begin{aligned} &\underline{\mathcal{H}}_0 \mid \psi_{k,0} \rangle \\ &\qquad + \lambda \big(\underline{\mathcal{W}} \mid \psi_{k,0} \rangle + \underline{\mathcal{H}}_0 \mid \psi_{k,1} \rangle \big) \end{aligned}$$

$$
\begin{aligned}
&\quad +\lambda^2\big(\underline{\mathcal{W}} \mid \psi_{k,1}\rangle + \underline{\mathcal{H}}_0 \mid \psi_{k,2}\rangle\big) + \dots \quad (4.6)\\
= &\quad E_{k,0} \mid \psi_{k,0}\rangle\\
&\quad +\lambda\big(E_{k,1} \mid \psi_{k,0}\rangle + E_{k,0} \mid \psi_{k,1}\rangle\big)\\
&\quad +\lambda^2\big(E_{k,2} \mid \psi_{k,0}\rangle + E_{k,1} \mid \psi_{k,1}\rangle\\
&\quad +E_{k,0} \mid \psi_{k,2}\rangle\big) + \dots \,.
\end{aligned}
$$

Comparison of coefficients yields

$$\underline{\mathcal{H}}_0 \mid \psi_{k,0}\rangle = E_{k,0} \mid \psi_{k,0}\rangle$$

and the recursion relation

$$
\begin{aligned}
&\underline{\mathcal{W}} \mid \psi_{k,m-1}\rangle + \underline{\mathcal{H}}_0 \mid \psi_{k,m}\rangle \qquad (4.7)\\
&\quad = E_{k,m} \mid \psi_{k,0}\rangle + E_{k,m-1} \mid \psi_{k,1}\rangle + \dots\\
&\quad +E_{k,0} \mid \psi_{k,m}\rangle
\end{aligned}
$$

with $m = 1, 2, \dots$. The solution of the first equation is $\mid k\rangle$, as we already know. In order to solve the second equation for $m = 1$ we expand $\mid \psi_{k,1}\rangle$ in terms of the basis of the unperturbed system:

$$\mid \psi_{k,1}\rangle = \sum_{r=1}^{n} \mid r\rangle\langle r \mid \psi_{k,1}\rangle \,.$$

This yields

$$\langle l \mid \underline{\mathcal{W}} \mid k\rangle + E_{l,0}\langle l \mid \psi_{k,1}\rangle = E_{k,1}\delta_{lk} + E_{k,0}\langle l \mid \psi_{k,1}\rangle \,,$$

and for $l = k$ we obtain the first correction to the eigenvalue

$$E_{k,1} = \langle k \mid \underline{\mathcal{W}} \mid k\rangle \,. \qquad (4.8)$$

The first correction to the eigenvector follows for $l \neq k$:

$$\langle l \mid \psi_{k,1}\rangle = \frac{\langle l \mid \underline{\mathcal{W}} \mid k\rangle}{E_{k,0} - E_{l,0}} \,. \qquad (4.9)$$

This, however, does not yet determine the amplitude, because we still must normalize $\mid \psi_k\rangle$, i.e. $1 = \langle \psi_k \mid \psi_k\rangle$. Insertion of the expansion (4.5) yields

$$
\begin{aligned}
1 &= \langle \psi_{k,0} \mid \psi_{k,0}\rangle\\
&+ \lambda\Big(\langle \psi_{k,0} \mid \psi_{k,1}\rangle + \langle \psi_{k,1} \mid \psi_{k,0}\rangle\Big)\\
&+ \lambda^2\Big(\langle \psi_{k,0} \mid \psi_{k,2}\rangle + \langle \psi_{k,1} \mid \psi_{k,1}\rangle\\
&\quad +\langle \psi_{k,2} \mid \psi_{k,0}\rangle\Big) + \dots \,.
\end{aligned}
$$

Because λ is an arbitrary number, the terms in brackets must vanish, i.e.

$$
\begin{aligned}
&\langle \psi_{k,0} \mid \psi_{k,1}\rangle + \langle \psi_{k,1} \mid \psi_{k,0}\rangle = 0\\
&\langle \psi_{k,0} \mid \psi_{k,2}\rangle + \langle \psi_{k,1} \mid \psi_{k,1}\rangle + \langle \psi_{k,2} \mid \psi_{k,0}\rangle = 0\\
&\text{etc.}
\end{aligned}
$$

Therefore

$$\langle k \mid \psi_{k,1}\rangle = i\gamma \,,$$

where γ is real. To first order we find

$$\mid \psi_k\rangle = (1 + i\lambda\gamma) \mid k\rangle + \sum_{r\neq k} \mid r\rangle \frac{\lambda\langle r \mid \underline{\mathcal{W}} \mid k\rangle}{E_{k,0} - E_{r,0}} + \dots$$

To this level of approximation we may also write $1 + i\lambda\gamma \approx e^{i\lambda\gamma}$.

The second order approximation may be found by setting $m = 2$ in the recursion relation (4.7). By proceeding in the same fashion as before and using the first order results we now find

$$
\begin{aligned}
E_k &= E_{k,0} + \langle k \mid \underline{\mathcal{H}}_1 \mid k\rangle \qquad (4.10)\\
&+ \sum_{l(\neq k)} \frac{\langle k \mid \underline{\mathcal{H}}_1 \mid l\rangle\langle l \mid \underline{\mathcal{H}}_1 \mid k\rangle}{E_{k,0} - E_{l,0}} + \dots
\end{aligned}
$$

and

$$\mid \psi_k\rangle = \mid k\rangle T_k + \sum_{l(\neq k)} \mid l\rangle R_{lk} \qquad (4.11)$$

with

$$T_k = 1 - \frac{1}{2} \sum_{m(\neq k)} \frac{\langle k \mid \underline{\mathcal{H}}_1 \mid m\rangle\langle m \mid \underline{\mathcal{H}}_1 \mid k\rangle}{\left(E_{k,0} - E_{m,0}\right)^2} + \dots (4.12)$$

and

$$\begin{aligned} R_{lk} &= \frac{\langle l \mid \underline{\mathcal{H}}_1 \mid k\rangle}{E_{k,0}-E_{l,0}} \\ &+ \sum_{m(\neq k)} \Big[\frac{\langle l \mid \underline{\mathcal{H}}_1 \mid m\rangle\langle m \mid \underline{\mathcal{H}}_1 \mid k\rangle}{(E_{k,0}-E_{l,0})\,(E_{k,0}-E_{m,0})} \\ &\quad - \frac{\langle l \mid \underline{\mathcal{H}}_1 \mid k\rangle\langle k \mid \underline{\mathcal{H}}_1 \mid k\rangle}{(E_{k,0}-E_{l,0})^2} \Big] \ . \qquad (4.13) \end{aligned}$$

In principle we may continue like this, but the degree of complexity quickly increases.

Example – anharmonic oscillator:

As an example we consider the anharmonic oscillator in 1D of problem 8, i.e.

$$\underline{\mathcal{H}} = \hbar\omega\big(-\frac{1}{2}\partial_q^2 + \frac{1}{2}\underline{q}^2 + \frac{\lambda}{4}\underline{q}^4 \big) \ ,$$

where $q = \sqrt{m\omega/\hbar}x$ and $\lambda = (2\hbar/m\omega)^2\chi$ is a parameter.

The first order energy correction due to the perturbation $\frac{\lambda}{4}\underline{q}^4$ is given by

$$\frac{\lambda}{4}\langle k \mid \underline{q}^4 \mid k\rangle \ .$$

Instead of working in an explicit representation we choose to express $\underline{q}^4$ in terms of the raising and lowering operators introduced on page 27, i.e.

$$\underline{q} = \frac{1}{\sqrt{2}}\left(\underline{a} + \underline{a}^+\right) \ .$$

Using the commutator (1.145) it is somewhat laborious but straightforward to work out the following expression for $4\underline{q}^4$:

$$\begin{aligned} 4\underline{q}^4 &= 3(2\underline{N}^2 + 2\underline{N} + 1) + \underline{a}^4 + (\underline{a}^+)^4 \\ &\quad +(2\underline{N}+1)\left(\underline{a}^2 + (\underline{a}^+)^2\right) \\ &\quad + \left(\underline{a}^2 + (\underline{a}^+)^2\right)(2\underline{N}+1) \ . \qquad (4.14) \end{aligned}$$

Here $\underline{N} = \underline{a}^+\underline{a}$ is the number operator (cf. Eq. (1.178). We notice that due to the othogonality of different energy states we may write

$$\begin{aligned} \langle k \mid \underline{q}^4 \mid k\rangle &= \langle k \mid 3(2\underline{N}^2 + 2\underline{N} + 1) \mid k\rangle \\ &= 3(2k^2 + 2k + 1) \ . \end{aligned}$$

To first order in λ we therefore obtain

$$E_k \approx \hbar\omega\left(k + \frac{1}{2} + \frac{3}{8}(k^2 + k + \frac{1}{2})\lambda\right) \ .$$

The second order correction may be computed based on the other terms in Eq. (4.14). For the ground state we obtain $E_0 \approx \hbar\omega\left(1/2 + (3/16)\lambda - (21/128)\lambda^2\right)$ (exercise!).

At the beginning of the above calculation we had ruled out degeneracy between the $E_{k,0}$. But what happens, if there are degenerate eigenvalues? Obviously, Eq. (4.10) no longer applies. Let us assume that an eigenvalue is m-fold degenerate. We then try to construct m new eigenfunctions from linear combinations of the m original eigenfunctions. Our goal hereby is to construct the new eigenfunction in a way that the matrix elements of $\underline{\mathcal{H}}_1$ between the new eigenfunctions become zero. This procedure corresponds to a unitary transformation in the subspace of the degenerate eigenfunctions. The resulting representation of $\underline{\mathcal{H}}_1$ can be treated with the above formalism. In general this leads to the removal of the degeneracy, and the eigenvalues of the perturbed problem are distinct.

Degenerate case - 1st order energy correction:

We consider one particular energy level E_0 which is m-fold degenerate. The degenerate states $\mid \psi_{\nu,0}\rangle$ satisfy

$$\underline{\mathcal{H}}_0 \mid \psi_{\nu,0}\rangle = E_0 \mid \psi_{\nu,0}\rangle \qquad (4.15)$$

for $\nu = 1, \ldots, m$. Obviously, Eqs. (4.10) to (4.13) show that our previous treatment must be modified to avoid the divergencies. This modification consists in writing down the most general solution to Eq. (4.15), which is the linear combination of the $\mid \psi_{\nu,0}\rangle$, i.e.

$$\mid \tilde{\psi}_{\mu,0}\rangle = \sum_{\nu=1}^{m} c_{\mu\nu} \mid \psi_{\nu,0}\rangle \; . \tag{4.16}$$

Now we repeat the above calculation, but with this set of m unperturbed states! We write

$$\mid \psi_\mu\rangle = \mid \tilde{\psi}_{\mu,0}\rangle + \lambda \mid \psi_{\mu,1}\rangle + \lambda^2 \mid \psi_{\mu,2}\rangle + \ldots \tag{4.17}$$

for the perturbed state and

$$E_\mu = E_0 + \lambda E_{\mu,1} + \lambda^2 E_{\mu,2} + \ldots \tag{4.18}$$

for the perturbed energies. Inserting (4.17) and (4.18) into $\underline{\mathcal{H}} \mid \psi_\mu\rangle = E_\mu \mid \psi_\mu\rangle$ yields

$$\underline{\mathcal{H}}_0 \mid \tilde{\psi}_{\mu,0}\rangle = E_0 \mid \tilde{\psi}_{\mu,0}\rangle \tag{4.19}$$

and (first order only)

$$(\underline{\mathcal{H}}_0 - E_0) \mid \psi_{\mu,1}\rangle = (E_{\mu,1} - \underline{\mathcal{W}}) \mid \tilde{\psi}_{\mu,0}\rangle \; . \tag{4.20}$$

As before we write down an expansion of $\mid \psi_{\mu,1}\rangle$ in terms of the solutions of the unperturbed problem:

$$\begin{aligned} \mid \psi_{\mu,1}\rangle &= \sum_{\nu=1}^{m} \mid \psi_{\nu,0}\rangle\langle\psi_{\nu,0} \mid \psi_{\mu,1}\rangle \\ &\quad + \sum_{r=m+1}^{n} \mid r\rangle\langle r \mid \psi_{\mu,1}\rangle \; . \end{aligned} \tag{4.21}$$

The first summation includes the degenerate states, where we assume only one degenerate energy level. The second term includes all remaining states for all other energy levels. Upon inserting (4.21) into (4.20) we find

$$\begin{aligned} \sum_{r=m+1}^{n} (\underline{\mathcal{H}}_0 - E_0) \mid r\rangle\langle r \mid \psi_{\mu,1}\rangle \\ = (E_{\mu,1} - \underline{\mathcal{W}}) \mid \tilde{\psi}_{\mu,0}\rangle \; . \end{aligned} \tag{4.22}$$

Finally we multiply with $\langle\psi_{\sigma,0} \mid$ from the left to obtain

$$0 = E_{\mu,1}\langle\psi_{\sigma,0} \mid \tilde{\psi}_{\mu,0}\rangle - \langle\psi_{\sigma,0} \mid \underline{\mathcal{W}} \mid \tilde{\psi}_{\mu,0}\rangle \; , \tag{4.23}$$

where we have used $\langle\psi_{\sigma,0} \mid r\rangle = 0$ (because $\mid \psi_{\sigma,0}\rangle$ and $\mid r\rangle$ belong to distinct eigenvalues). At first glance this equation looks like Eq. (4.8), but we should not forget to insert Eq. (4.16). The result is

$$\begin{aligned} 0 &= \sum_{\nu=1}^{m} c_{\mu\nu}\{E_{\mu,1}\langle\psi_{\sigma,0} \mid \psi_{\nu,0}\rangle \\ &\quad -\langle\psi_{\sigma,0} \mid \underline{\mathcal{W}} \mid \psi_{\nu,0}\rangle\} \; , \end{aligned} \tag{4.24}$$

which is a set of linear coupled equations. The non trivial solution requires

$$\begin{aligned} 0 &= det\Big(E_{\mu,1}\langle\psi_{\sigma,0} \mid \psi_{\nu,0}\rangle \\ &\quad -\langle\psi_{\sigma,0} \mid \underline{\mathcal{W}} \mid \psi_{\nu,0}\rangle\Big) \; . \end{aligned} \tag{4.25}$$

In general we do not have $\langle\psi_{\sigma,0} \mid \psi_{\nu,0}\rangle = \delta_{\sigma\nu}$, but we can always construct such $\mid \psi_{\nu,0}\rangle$ based on a complete solution of the unperturbed problem, i.e. without loss of generality we may indeed assume $\langle\psi_{\sigma,0} \mid \psi_{\nu,0}\rangle = \delta_{\sigma\nu}$. Thus, we obtain the m first order corrections to E_0 by computing the eigenvalues of an $m \times m$ matrix with the elements $\langle\psi_{\sigma,0} \mid \underline{\mathcal{W}} \mid \psi_{\nu,0}\rangle$ in this case.

To illustrate this procedure we calculate the corrections to the eigenvalue to 1*st* order and the corresponding eigenfunctions to 0*th* order for a two-fold degenerate energy level E_0. According to Eq. (4.25) we have

$$\begin{vmatrix} \mathcal{W}_{11} - E_1 & \mathcal{W}_{12} \\ \mathcal{W}_{21} & \mathcal{W}_{22} - E_1 \end{vmatrix} = 0 \; ,$$

where $\mathcal{W}_{\sigma\nu} \equiv \langle\psi_{\sigma,0} \mid \underline{\mathcal{W}} \mid \psi_{\nu,0}\rangle$. The solution is

$$\begin{aligned} E_{\pm,1} &= \frac{1}{2}\Big[\mathcal{W}_{11} + \mathcal{W}_{22} \\ &\quad \pm\sqrt{(\mathcal{W}_{11} - \mathcal{W}_{22})^2 + 4|\mathcal{W}_{12}|^2}\Big] \; . \end{aligned}$$

The difference between these values, i.e. $\sqrt{\ldots}$, is the level splitting to 1*st* order due to the perturbation.

The (not normalized) 0*th* order eigenstate $\mid \tilde{\psi}_{\mu,0}\rangle$ is obtained via Eq. (4.16) using $m = 2$. The $c_{\mu\nu}$ are computed via (4.24) with the now known $E_{\mu,1} = E_{\pm,1}$, i.e. we solve

$$0 = \sum_{\nu=1}^{2} c_{\mu\nu}\{E_{\mu,1}\delta_{\sigma\nu} - \mathcal{W}_{\sigma\nu}\}$$

for $c_{\mu 1}$ and $c_{\mu 2}$. Including the normalization the coefficients are given by

$$\begin{aligned} c_{\mu 1} &= \sqrt{\frac{\mathcal{W}_{12}}{2 \mid \mathcal{W}_{12} \mid}\left[1 \pm \frac{\mathcal{W}_{11} - \mathcal{W}_{22}}{\sqrt{\cdots}}\right]} \\ c_{\mu 2} &= \pm\sqrt{\frac{\mathcal{W}_{21}}{2 \mid \mathcal{W}_{12} \mid}\left[1 \mp \frac{\mathcal{W}_{11} - \mathcal{W}_{22}}{\sqrt{\cdots}}\right]} \; . \end{aligned}$$

This example including how to obtain the next higher approximations can be found in reference [8] (problems 1 and 2 in §39).

The $1/r^6$-dispersion interaction:

We consider two noble gas atoms separated by a distance r. This separation refers to the nuclei of charge Ze located at 0 and r along the x-axis, each surrounded by Z electrons. The electrons bound to the nucleus at 0 have coordinates $\vec{\tau}_i$; and those bound to the nucleus at r have coordinates $\vec{\tau}_i{}'$. We assume r to be so large that there is negligible overlap between the electronic charge distributions about the two nuclei. The Hamiltonian for this two-atom system will be

$$\underline{\mathcal{H}} = \underline{\mathcal{H}}_1 + \underline{\mathcal{H}}_2 + \underline{\mathcal{U}} \; ,$$

where $\mathcal{U}$, the atom-atom interaction energy, is given by

$$\begin{aligned} \underline{\mathcal{U}} &= e^2\Big[\frac{Z^2}{r} - \sum_{i=1}^{Z}\left(\frac{Z}{\mid \vec{\tau}'_i \mid} + \frac{Z}{\mid \vec{\tau}_i - \vec{r} \mid}\right) \\ &\quad + \sum_{i,j=1}^{Z} \frac{1}{\mid \vec{\tau}_i - \vec{\tau}'_j \mid}\Big] \; . \end{aligned}$$

To second order in perturbation theory, the interaction energy between the two atoms will be

$$\Delta E = \langle 0 \mid \underline{\mathcal{U}} \mid 0 \rangle + \sum_{\nu} \frac{\mid \langle 0 \mid \underline{\mathcal{U}} \mid \nu \rangle \mid^2}{E_0 - E_\nu} \; .$$

Here $\mid 0\rangle$ is the ground state of the unperturbed two-atom system, and $\mid \nu\rangle$ are corresponding excited states.

The first term,

$$\begin{aligned} \langle 0 \mid \underline{\mathcal{U}} \mid 0 \rangle &= \frac{(eZ)^2}{r} \underbrace{\langle 0 \mid 0 \rangle}_{=1} \\ &\quad + \langle 0 \mid - \sum_{i=1}^{Z} (\ldots) + \sum_{i,j=1}^{Z} \frac{1}{\mid \vec{\tau}_i - \vec{\tau}'_j \mid} \mid 0 \rangle \; , \end{aligned}$$

expressed in $\vec{r}$-representation becomes

$$\langle 0 \mid \underline{\mathcal{U}} \mid 0 \rangle = \int d^3\tau d^3\tau' \rho_0(\tau) \frac{1}{\mid \vec{\tau} - \vec{\tau}' - \vec{r} \mid} \rho_0(\tau') \; ,$$

where ρ_0 denotes the ground state charge distribution. Note that ρ_0 includes the nuclear charge! From classical electrodynamics we know that the integral may be expressed as

$$\int d^3\tau d^3\tau' \ldots = \int d^3\tau \rho_0(\tau) \varphi_0(\tau)$$

[15] (section 3.1), where $\varphi_0(\tau)$ is the electrostatic potential at $\vec{\tau}$ due to the second atom at $\vec{r}$. A simple argument shows, however, that this term vanishes. Consider an isolated neutral and radially symmetric charge distribution ρ_0. According to Gauss's integral theorem we have $\int_{Sphere} d\vec{f} \cdot \vec{E}_0 = 0$, where ρ_0 is at the center of the sphere. By symmetry we conclude $\vec{E}_0 = 0$ everywhere outside the charge distribution. Therefore $\varphi_0 = const$, which follows from $\vec{E}_0 = -\vec{\nabla}\varphi_0$. Thus, we find that the above integral vanishes, because $\int d^3\tau \rho_0(\tau) = 0$ if there is no net charge!

This means that we are left with

$$\Delta E = \sum_{\nu} \frac{\mid \langle 0 \mid \underline{\mathcal{U}} \mid \nu \rangle \mid^2}{E_0 - E_\nu} \; . \tag{4.26}$$

This time the matrix element, i.e.

$$\langle 0 \mid \underline{\mathcal{U}} \mid \nu \rangle = \int d^3\tau d^3\tau\,' \frac{\rho_{0,\nu}\,(\vec{\tau})\,\rho_{0,\nu}(\vec{\tau}\,')}{\mid \vec{\tau} - \vec{\tau}\,' - \vec{r} \mid} \;,$$

does not vanish. Note that the function $\rho_{0,\nu}\,(\vec{\tau})$ no longer must be radially symmetric. Using the multipole expansion [15] (cf. Eq. (3.15) pp.) we find to lowest order for large r:

$$\mid \langle 0 \mid \underline{\mathcal{U}} \mid \nu \rangle \mid^2 \propto \big(\frac{1}{r^3}\big)^2$$

(dipole-dipole interaction). Notice that the numerator in Eq. (4.26) is positive, whereas the denominator is negative $\big(E_\nu > E_0!\big)$. We therefore conclude

$$\Delta E = -\frac{C}{r^6} \;, \tag{4.27}$$

where C is positive, for large r!

Eq. (4.27) is called dispersion attraction. It is build into many phenomenological atom-atom or molecule-molecule potentials. One example is the well known Lennard-Jones pair potential

$$u_{ij} = 4\epsilon \left[\big(\frac{\sigma}{r_{ij}}\big)^{12} - \big(\frac{\sigma}{r_{ij}}\big)^6 \right] \;, \tag{4.28}$$

where ϵ and σ are positive constants. Notice that the repulsive $(\sigma/r)^{12}$-term merely represents a convenient numerical form of the rather complex overlap repulsion at short distances. In contrast to the $(\sigma/r)^6$-term it is not justified by a systematic expansion.

4.2 Variation method

This method can be applied when it is not possible to split the Hamiltonian into two parts, one of which is exactly solvable whereas the remaining piece is a small perturbation. Here we discuss the method applied to the stationary case.

Application to the ground state:

First we note that the average energy in an arbitrary normalized state $\mid \psi \rangle$ of the system is always larger or equal to the smallest energy eigenvalue (ground state). Proof:

$$\begin{aligned} \langle \psi \mid \underline{\mathcal{H}} \mid \psi \rangle &= \sum_n \langle \psi \mid \underline{\mathcal{H}} \mid \psi_n \rangle \langle \psi_n \mid \psi \rangle \\ &= \sum_n E_n \mid \langle \psi \mid \psi_n \rangle \mid^2 \\ &= E_0 \underbrace{\sum_n \mid \langle \psi \mid \psi_n \rangle \mid^2}_{=1} \\ &\quad + \sum_n (E_n - E_0) \mid \langle \psi \mid \psi_n \rangle \mid^2 \geq E_0 \;. \end{aligned}$$

The idea of the method is as follows. First one decides to work in a certain representation; here we use the $\vec{r}$-space representation. Then the unknown ground state amplitude $\langle \vec{r} \mid \psi_0 \rangle$ is replaced by an Ansatz $\langle \vec{r} \mid \psi_{0,A} \rangle$, which is a function depending on one or several parameters. This function should already include the known properties of the correct solution like symmetries or asymptotic behavior. The goal is to minimize the average ground state energy by variation of the parameters, i.e.,

$$\delta \langle \psi_{0,A} \mid \underline{\mathcal{H}} \mid \psi_{0,A} \rangle = 0 \tag{4.29}$$

yields a number of coupled equations from which the variation parameters may be determined. Notice that

$$\begin{aligned} &\langle \psi \mid \underline{\mathcal{H}} \mid \psi \rangle \\ &\quad = \int \langle \psi \mid \vec{r} \rangle d^3r \langle \vec{r} \mid \underline{\mathcal{H}} \mid \psi \rangle \\ &\quad = \int d^3r \langle \psi \mid \vec{r} \rangle \left(-\frac{\hbar^2}{2m} \vec{\nabla}^2 + \mathcal{U} \right) \langle \vec{r} \mid \psi \rangle \end{aligned} \tag{4.30}$$

The idea of the above procedure is an approximation to $\langle \vec{r} \mid \psi_0 \rangle$ including the approximate ground state energy $E_{0,A}$.

Example – anharmonic oscillator:

As an example we consider again the anharmonic oscillator in 1D of problem 8, i.e.

$$\underline{\mathcal{H}} = \hbar\omega\big(-\frac{1}{2}\partial_q^2 + \frac{1}{2}\underline{q}^2 + \frac{\lambda}{4}\underline{q}^4 \big) \;,$$

where $q = \sqrt{m\omega/\hbar}x$ and $\lambda = (2\hbar/m\omega)^2\chi$ is a parameter. Our normalized Ansatz or normalized trial function (dt.: Versuchsfunktion) is

$$\psi_{0,\alpha}(q) = \left(\frac{\alpha}{\pi}\right)^{1/4} \exp\left[-\frac{\alpha}{2}q^2\right] . \qquad (4.31)$$

For $\alpha = 1$ this is the ground state of the harmonic 1D oscillator.

A not too difficult integration yields

$$\begin{aligned} \langle \underline{\mathcal{H}} \rangle_{0,\alpha} &= \int_{-\infty}^{\infty} dq \psi^*_{o,\alpha}(q) \underline{\mathcal{H}} \psi_{o,\alpha}(q) \\ &= \hbar\omega \frac{4(\alpha^3+\alpha)+3\lambda}{16\alpha^2} . \end{aligned}$$

The best estimate of $\langle \underline{\mathcal{H}} \rangle_{0,\alpha}$ based on our trail function follows via

$$\begin{aligned} 0 &= \frac{d}{d\alpha} \langle \underline{\mathcal{H}} \rangle_{0,\alpha}\big|_{\alpha_{min}} \\ &= \hbar\omega \frac{2\alpha^3 - 2\alpha - 3\lambda}{8\alpha^3}\big|_{\alpha_{min}} . \end{aligned}$$

Rather than solving this equation exactly, which of course is possible, we consider two limiting cases, i. e. $\lambda \ll 1$ and $\lambda \gg 1$. In the case $\lambda \ll 1$ we may insert $\alpha_{min} = 1 + \kappa\lambda$ into the above equation. Keeping terms linear in λ only, we obtain $\kappa = 3/4$ or $\alpha_{min} \approx 1 + (3/4)\lambda$ and thus

$$\min_\alpha \langle \underline{\mathcal{H}} \rangle_{0,\alpha} \approx \hbar\omega \left(\frac{1}{2} + \frac{3}{16}\lambda \right) .$$

[1]. In the opposite limit, $\lambda \gg 1$, we obtain via

$$0 = 2\alpha^3_{min} - 2\alpha_{min} - 3\lambda \approx 2\alpha^3_{min} - 3\lambda$$

$\alpha_{min} \approx (3\lambda/2)^{1/3}$ and therefore

$$\min_\alpha \langle \underline{\mathcal{H}} \rangle_{0,\alpha} \approx \hbar\omega \frac{3}{8} \left(\frac{3\lambda}{2} \right)^{1/3} \approx 0.4208 \hbar\omega\lambda^{1/3} .$$

We note that the numerically exact solution is $0.429\hbar\omega\lambda^{1/3}$. The attendant ground states $\langle q \mid \psi_{0,\alpha_{min}} \rangle$ are obtained via insertion of α_{min} into Eq. (4.31).

Application to excited states:

This method may also be applied to calculate approximations to the excited states. We consider the nth excited state and assume that the E_i $(i = 1, \ldots, n-1)$ and the corresponding states $\mid \psi_i \rangle$ $(i = 1, \ldots, n-1)$ are known in one particular representation (i.e., the $\vec{r}$-representation $\langle \vec{r} \mid \psi_i \rangle$). The states must be orthogonal to each other, because they belong to different eigenvalues:

$$\langle \psi_i \mid \psi_k \rangle = \int \langle \psi_i \mid \vec{r} \rangle d^3r \langle \vec{r} \mid \psi_k \rangle = 0 \quad (i \neq k) .$$

Again we construct a reasonable $\langle \vec{r} \mid \psi_{n,A} \rangle$, which depends on certain parameters. It is important that $\mid \psi_{n,A} \rangle$ is orthogonal to all other states. Now the procedure is the same as above, and we minimize $\langle \psi_{n,A} \mid \underline{\mathcal{H}} \mid \psi_{n,A} \rangle$ i.e.

$$\delta \langle \psi_{n,A} \mid \underline{\mathcal{H}} \mid \psi_{n,A} \rangle = 0 .$$

That the resulting minimal $\mid \psi_{n,A} \rangle = \mid \phi \rangle$ is reasonable we may see via

$$\begin{aligned} &\langle \phi \mid \underline{\mathcal{H}} \mid \phi \rangle \\ &= \sum_{i=0}^{n-1} \langle \phi \mid \underline{\mathcal{H}} \mid \psi_i \rangle \underbrace{\langle \psi_i \mid \phi \rangle}_{=0} \\ &\quad + \sum_{i \geq n} \langle \phi \mid \underline{\mathcal{H}} \mid \psi_i \rangle \langle \psi_i \mid \phi \rangle \\ &= \sum_{i \geq n} E_i \mid \langle \phi \mid \psi_i \rangle \mid^2 \\ &= E_n \sum_{i \geq n} \mid \langle \phi \mid \psi_i \rangle \mid^2 \\ &\quad + \sum_{i \geq n} (E_i - E_n) \mid \langle \phi \mid \psi_i \rangle \mid^2 \\ &= E_n + \sum_{i \geq n} (E_i - E_n) \mid \langle \phi \mid \psi_i \rangle \mid^2 \geq E_n . \end{aligned}$$

Notice that $1 = \langle \phi \mid \phi \rangle = \sum_{i \geq 0} \langle \phi \mid \psi_i \rangle \langle \psi_i \mid \phi \rangle = \sum_{i \geq n} \mid \langle \phi \mid \psi_i \rangle \mid^2$. A disadvantage of the variation approach is, that it is not a systematic expansion,

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[1] Including the second order in λ the bracket becomes $\left(\frac{1}{2} + \frac{3}{16}\lambda - \frac{27}{32}\lambda^2\right)$. Compare this result to the perturbation theory on page 61.

i.e. we obtain an approximation whose quality is difficult to judge. Nevertheless, with some experience it produces good results, and it is widely used also outside quantum mechanics.

4.3 The quasi classical approximation

This approximation procedure is also called WKB-approximation according to its authors Wentzel, Kramers and Brillouin, who invented it independently in 1926. The WKB-method is mainly applicable to one dimensional or radial symmetric problems. We consider both cases via

$$\langle x \mid \psi(t)\rangle = e^{-\frac{i}{\hbar}Et}\psi(\xi) \ , \tag{4.32}$$

where $\xi \equiv x$ and $\mathcal{U}(\xi) = \mathcal{U}(x)$, and

$$\langle \vec{r} \mid \psi(t)\rangle = e^{-\frac{i}{\hbar}Et}\frac{1}{r}Y_{lm}(\theta,\phi)\,\psi(\xi) \ , \tag{4.33}$$

with $\xi \equiv r$ and $\mathcal{U}(\xi) = \mathcal{U}_{eff}(\xi)$. The Schrödinger equation now has the form

$$\left(-\frac{\hbar^2}{2m}\partial_\xi^2 - E + \mathcal{U}(\xi)\right)\psi(\xi) = 0 \ . \tag{4.34}$$

The WKB-method is based on the following considerations. The solution of the Schrödinger equation for a constant potential (free particle) has the form of a plane wave $\exp\left(\pm\frac{i}{\hbar}p\xi\right)$, where $p = \sqrt{2m(E-\mathcal{U})}$. If the potential contains slight spatial variations then one might expect that this solution changes to $\exp\left(\pm\frac{i}{\hbar}\int^\xi p(\xi')\,d\xi'\right)$. 'slight variations' refers to cases when the wavelength is short compared to length scale of the changes in the potential. This corresponds to high quantum numbers (remembering for instance the harmonic oscillator). Thus, we insert the Ansatz $\psi = A_+\psi_+ + A_-\psi_-$ with

$$\psi_\pm(\xi) = \exp\left(\pm\frac{i}{\hbar}\int^\xi \pi(\xi')\,d\xi'\right) \tag{4.35}$$

into the Schrödinger equation to obtain a Riccati's differential equation:

$$\frac{(\pi(\xi))^2}{2m} - (E - \mathcal{U}(\xi)) \pm \frac{\hbar}{2im}\pi'(\xi) = 0 \ . \tag{4.36}$$

We now expand $\pi(\xi)$ in $\hbar$, i.e.

$$\pi(\xi) = \pi_0(\xi) + \hbar\pi_1(\xi) + \hbar^2\pi_2(\xi) + \dots \ . \tag{4.37}$$

Inserting this into the above equation yields

$$\begin{aligned}
\pi_0(\xi) &= \sqrt{2m(E-\mathcal{U}(\xi))} \equiv Q(\xi) \\
\pi_1(\xi) &= \pm\frac{i}{2}\frac{\pi_0'}{\pi_0} = \pm\frac{i}{2}\partial_\xi \ln Q(\xi) \\
\pi_2 &= -\frac{Q''}{4Q^2} + \frac{3(Q')^2}{8Q^3} \\
&= \frac{m}{4Q^3}\left(\mathcal{U}'' + \frac{5m}{2}\left(\frac{\mathcal{U}'}{Q}\right)^2\right) \\
&\ \ \vdots
\end{aligned}$$

Inserting this we notice that the term π_1 can be integrated and yields a factor. The final result is

$$\begin{aligned}
\psi_\pm(\xi) = \frac{1}{\sqrt{Q}}\exp\Big[\pm\frac{i}{\hbar}\int^\xi d\xi'\Big\{Q(\xi') \\
+\frac{m\hbar^2}{4Q^3}\left(\mathcal{U}'' + \frac{5m}{2}\Big(\frac{\mathcal{U}'}{Q}\Big)^2\right)\Big\} + \dots\Big]
\end{aligned} \tag{4.38}$$

This approximation is a good one if

$$\frac{m\hbar^2}{4Q^4}\left(\mathcal{U}'' + \frac{5m}{2}\left(\frac{\mathcal{U}'}{Q}\right)^2\right) \ll 1 \ . \tag{4.39}$$

If $\mathcal{U} > E$ we obtain analogously (use $\pi \to \pm i\pi$) via $\psi = B_+\varphi_+ + B_-\varphi_-$

$$\begin{aligned}
\varphi_\pm = \frac{1}{\sqrt{R}}\exp\Big[\pm\frac{1}{\hbar}\int^\xi d\xi'\Big\{R(\xi') \\
+\frac{m\hbar^2}{4R^3}\left(\mathcal{U}'' + \frac{5m}{2}\Big(\frac{\mathcal{U}'}{R}\Big)^2\right)\Big\} + \dots\Big]
\end{aligned} \tag{4.40}$$

where

$$R(\xi) = \sqrt{2m(\mathcal{U} - E)} \ .$$

Next we want to compute the energy eigenvalues. For this purpose we count the number of zeros, n, of the wave function. We consider ψ in the complex plane (not just on the real axis). If $\psi(z_0) = 0$ then the function ψ'/ψ has a simple pole with residue 1, because $\psi = A(z - z_0) + \ldots$ and $\psi' = A + \ldots$. i.e.

$$2\pi i n = \oint_C \frac{\psi'(z)}{\psi(z)} dz = \oint_C \frac{d}{dz} \ln \psi dz$$

(cf. above). Here C is a closed curve including all zeros. Note that all poles are in the range defined by $E - \mathcal{U} > 0$, because for $E - \mathcal{U} < 0$ the solution is monotonous. Inserting ψ_+ according to (4.35) (using ψ_- is analogous),

$$\begin{aligned}\psi_+(\xi) = \exp\Big[\frac{i}{\hbar}\int^{\xi} d\xi' \Big[Q(\xi') \\ + \frac{i\hbar}{2}\frac{d}{d\xi'}\ln Q(\xi') + \ldots\Big]\Big] \,,\end{aligned} \qquad (4.41)$$

we obtain

$$\frac{d \ln \psi(z)}{dz} = \frac{i}{\hbar} Q(z) - \frac{1}{2}\frac{Q'(z)}{Q(z)} + \ldots \,. \qquad (4.42)$$

The integration of the second term is easy, because $\frac{Q'}{Q}$ has simple poles of order 1 with residue 1/2 at the classical turning points. Thus

$$\oint \frac{Q'}{Q} dz = 2\pi i \,, \qquad (4.43)$$

and we obtain

$$2\pi\hbar\left(n + \frac{1}{2}\right) = \oint Q(z)\, dz + \ldots \,,$$

which yields

$$2\pi\hbar\left(n + \frac{1}{2}\right) = 2\int_{\xi_1}^{\xi_2} d\xi \sqrt{2m\left(E - \mathcal{U}(\xi)\right)} \,. \qquad (4.44)$$

Here we have used $\oint_C \to 2\int_{\xi_1}^{\xi_2}$, where ξ_1 and ξ_2 are the solutions of $E - \mathcal{U}(\xi) = 0$. Eq. (4.44) is identical with the 'enhanced' quantization condition, which we had applied to the anharmonic 1D oscillator in problem 8.

It looks as if this procedure will always yield an approximation for two special solutions of the Schrödinger equation, $\psi_\pm$, which can be combined to give a linear combination fulfilling the boundary conditions. In general, however, this is not the case, because ξ_1 and ξ_2 produce singularities. Thus, it is not possible to tie the approximations for $\mathcal{U} < E$ and $\mathcal{U} > E$ together. This difficulty may be avoided via an exact solution near the points ξ_1 and ξ_2. We do not want to do this here and refer the reader to Ref. [5] (section 41). The resulting wave functions are

$$\psi(\xi) = \frac{2B_-}{\sqrt{Q}} \cos\left(\frac{1}{\hbar}\int_{\xi}^{\xi_1} Q(\xi')\, d\xi' - \frac{\pi}{4}\right) \qquad (4.45)$$

$(\xi < \xi_1)$ and

$$\psi(\xi) = \frac{B_-}{\sqrt{R}} e^{-\frac{1}{\hbar}\int_{\xi_1}^{\xi} R(\xi') d\xi'} \qquad (4.46)$$

$(\xi > \xi_1)$ for the upper turning point, and

$$\psi(\xi) = \frac{2B'_-}{\sqrt{Q}} \cos\left(\frac{1}{\hbar}\int_{\xi_2}^{\xi} Q(\xi')\, d\xi' - \frac{\pi}{4}\right) \qquad (4.47)$$

$(\xi > \xi_2)$ and

$$\psi(\xi) = \frac{B'_-}{\sqrt{R}} e^{-\frac{1}{\hbar}\int_{\xi}^{\xi_2} R(\xi') d\xi'} \qquad (4.48)$$

$(\xi < \xi_2)$. Note that $B'_- = (-1)^n B_-$.

4.4 Time-dependent perturbation theory

This method is due to P.A.M. Dirac[2], and was invented to treat spontaneous as well as forced emission and absorption of radiation. But it is a more versatile method than that.

---

[2] Dirac, Paul Adrien Maurice, british physicist, *Bristol 8.8.1902, †Tallahassee (Florida) 20.10.1984; numerous seminal contributions to the development of quantum theory (e.g. Dirac equation); he shared the 1933 Nobel prize in physics with E. Schrödinger.

Again the Hamilton operator consists of two parts,

$$\begin{aligned}\underline{\mathcal{H}} &= \underline{\mathcal{H}}_0 + \underline{\mathcal{H}}_1(t)\\ &= \underline{\mathcal{H}}_0 + \lambda(t)\,\underline{\mathcal{W}}\ , \end{aligned}\tag{4.49}$$

where the second describes a small, time-dependent perturbation. Here we chose

$$\lambda(t) = \lambda\theta(t - t_0) = \begin{cases} \lambda & t > t_0 \\ 0 & t < t_0 \end{cases}\ , \tag{4.50}$$

i.e. $\lambda(t)$ 'switches' the perturbation on at $t = t_0$. We also use the time evolution operator introduced in section 2.4, i.e. $\mid \psi(t)\rangle = \underline{S}(t, t_0) \mid \psi(t_0)\rangle$, and we insert

$$\underline{S}(t, t_0) = \underline{S}_0(t, t_0)\,\underline{S}_1(t, t_0)\ , \tag{4.51}$$

where

$$\underline{S}_0(t, t_0) = \exp\left(-\frac{i}{\hbar}(t - t_0)\,\underline{\mathcal{H}}_0\right)\ , \tag{4.52}$$

into the differential equation for $\underline{S}$, i.e.

$$i\hbar\partial_t \underline{S}(t, t_0) = \left(\underline{\mathcal{H}}_0 + \lambda\underline{\mathcal{W}}\right)\underline{S}(t, t_0)\ . \tag{4.53}$$

After multiplication with $\underline{S}_0^{-1}$ we obtain

$$i\hbar\partial_t \underline{S}_1 = \lambda\underline{\tilde{\mathcal{W}}}\underline{S}_1\ , \tag{4.54}$$

with

$$\lambda\underline{\tilde{\mathcal{W}}} = \underline{S}_0^{-1}\lambda\underline{\mathcal{W}}\underline{S}_0\ . \tag{4.55}$$

Integration yields

$$\underline{S}_1(t, t_0) = 1 - \frac{i}{\hbar}\lambda\int_{t_0}^{t}\underline{\tilde{\mathcal{W}}}(\tau)\,\underline{S}_1(\tau, t_0)\,d\tau\ , \tag{4.56}$$

where we have included the step-function behavior of $\lambda(t)$. For small λ Eq. (4.56) may be iterated. We insert

$$\underline{S}_1(t, t_0) = \sum_{n=0}^{\infty}\lambda^n\underline{S}_{1,n}(t, t_0)$$

into (4.56), and by comparing coefficients we obtain

$$\underline{S}_{1,0} = 1 \tag{4.57}$$

and

$$\underline{S}_{1,n}(t, t_0) = -\frac{i}{\hbar}\int_{t_0}^{t} d\tau\,\underline{\tilde{\mathcal{W}}}(\tau)\,\underline{S}_{1,n-1}(\tau, t_0) \tag{4.58}$$

for $n > 0$. Combining Eq. (4.58) with Eq. (4.51) finally yields

$$\begin{aligned}\underline{S}(t, t_0) = \exp&\left(-\frac{i}{\hbar}(t - t_0)\,\underline{\mathcal{H}}_0\right)\Big[1-\\ &\frac{i}{\hbar}\int_{t_0}^{t} d\tau e^{\frac{i}{\hbar}(\tau - t_0)\underline{\mathcal{H}}_0}\underline{\mathcal{H}}_1(\tau)\,e^{-\frac{i}{\hbar}(\tau - t_0)\underline{\mathcal{H}}_0}\\ &+\left(\frac{-i}{\hbar}\right)^2\int_{t_0}^{t} d\tau'\int_{t_0}^{\tau'} d\tau e^{\frac{i}{\hbar}(\tau' - t_0)\underline{\mathcal{H}}_0}\\ &\times\underline{\mathcal{H}}_1(\tau')\,e^{-\frac{i}{\hbar}(\tau' - \tau)\underline{\mathcal{H}}_0}\underline{\mathcal{H}}_1(\tau)\\ &\times e^{-\frac{i}{\hbar}\underline{\mathcal{H}}_0(\tau - t_0)} + \ldots\Big]\ .\end{aligned}\tag{4.59}$$

Now we are able to compute the transition probabilities between eigenstates of the unperturbed system. Starting with a state $\mid i\rangle$ at t_0, i.e. $\underline{\mathcal{H}}_0 \mid i\rangle = E_i \mid i\rangle$, we look for the probability to find the system in a state $\mid f\rangle$ at time t, i.e. $\underline{\mathcal{H}}_0 \mid f\rangle = E_f \mid f\rangle$. This probability is given by

$$P_f(t) = \mid\langle f \mid \underline{S}(t, t_0) \mid i\rangle\mid^2\ , \tag{4.60}$$

(cf. Eq. (2.75)), where the transition amplitude has the form

$$\begin{aligned}\langle f \mid \underline{S}(t, t_0) \mid i\rangle = e^{-\frac{i}{\hbar}(E_f t - E_i t_0)}&\\ \times\Big[\delta_{fi} - \frac{i}{\hbar}\int_{t_0}^{t} d\tau\langle f \mid \underline{\mathcal{H}}_1(\tau) \mid i\rangle e^{\frac{i}{\hbar}(E_f - E_i)\tau}&\\ +\left(\frac{-i}{\hbar}\right)^2\int_{t_o}^{t} d\tau'\int_{t_o}^{\tau'} d\tau\sum_{\nu}\langle f \mid \underline{\mathcal{H}}_1(\tau') \mid \nu\rangle&\\ \times\langle\nu \mid \underline{\mathcal{H}}_1(\tau) \mid i\rangle&\\ \times e^{i/\hbar\left[(E_f - E_\nu)\tau' + (E_\nu - E_i)\tau\right]} + \ldots\Big]\ .&\end{aligned}\tag{4.61}$$

Remark: The derivation of Eq. (4.59) is not difficult but perhaps difficult to remember. In this case Fig. 4.1 can be of help. The line at the top describes the situation when nothing happens. The mathematical representation of the line is

$$e^{-\frac{i}{\hbar}(t-t_0)\underline{\mathcal{H}}_0} \tag{4.62}$$

with t_0 simply set to zero ($t_0 = 0$ from now on). The second line in Fig. 4.1 consists of two pieces interrupted by an perturbative 'event' happening at time τ. Its mathematical representation is

$$\frac{-i}{\hbar}\int_0^t d\tau e^{-\frac{i}{\hbar}(t-\tau)\underline{\mathcal{H}}_0}\underline{\mathcal{H}}_1(\tau)e^{-\frac{i}{\hbar}\tau\underline{\mathcal{H}}_0} \ . \tag{4.63}$$

The integral means that the event can happen at any time between 0 and t. The factor $-i/\hbar$ must be remembered - at least partially, because $1/\hbar$ is needed to make the result dimensionless. Finally, the third line in Fig. 4.1 describes two events happening at time τ and τ' ($> \tau$), respectively. Its mathematical translation is

$$\left(\frac{-i}{\hbar}\right)^2\int_0^t d\tau'\int_0^{\tau'} d\tau e^{-\frac{i}{\hbar}(t-\tau')\underline{\mathcal{H}}_0}\underline{\mathcal{H}}_1(\tau') e^{-\frac{i}{\hbar}(\tau'-\tau)\underline{\mathcal{H}}_0}\underline{\mathcal{H}}_1(\tau)e^{-\frac{i}{\hbar}\tau\underline{\mathcal{H}}_0} \ . \tag{4.64}$$

It should be clear by now how to build the third and the higher order terms from lines, i.e. factors $\underline{S}_0$, and perturbative events, i.e. factors $(-i/\hbar)\underline{\mathcal{H}}_1$.

• Special case of a time-independent perturbation: For simplicity we set $t_0 = 0$ and calculate the leading approximation only. For $i \neq f$ we obtain

$$P_f(t) = 4 \mid \mathcal{H}_{1,fi} \mid^2 \frac{\sin^2\left(\frac{\omega_{fi}t}{2}\right)}{(\hbar\omega_{fi})^2} \ .$$

where $\mathcal{H}_{1,fi} \equiv \langle f \mid \underline{\mathcal{H}}_1 \mid i\rangle$ and $\hbar\omega_{fi} = E_f - E_i$.

• Special case of an oscillating perturbation: For example an atom exposed to electromagnetic radiation in a spectrometer or in sunlight may feel such a perturbation. We assume the form

$$\underline{\mathcal{H}}_1(t) = 2\underline{\mathcal{H}}_1\cos(\omega t) \ . \tag{4.65}$$

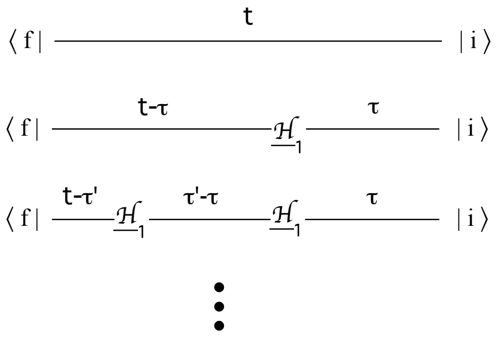

Figure 4.1: Pictorial representation of the contributions to $\underline{S}\,(t, t_0)$ including second order.

Writing $2\cos(\omega t) = \exp(i\omega t) + \exp(-i\omega t)$ and after a simple integration we find to first order

$$\begin{aligned} P_f(t) &= \frac{4}{\hbar^2} \mid \mathcal{H}_{1,fi} \mid^2 \\ &\quad\times\left| e^{i\frac{(\omega_{fi}+\omega)t}{2}} \frac{\sin(\frac{(\omega_{fi}+\omega)t}{2})}{\omega_{fi}+\omega} \right. \\ &\quad\left. + e^{i\frac{(\omega_{fi}-\omega)t}{2}} \frac{\sin(\frac{(\omega_{fi}-\omega)t}{2})}{\omega_{fi}-\omega} \right|^2 \\ &\approx \frac{4}{\hbar^2} \mid \mathcal{H}_{1,fi} \mid^2 \frac{\sin^2(\frac{(\omega_{fi}-\omega)t}{2})}{(\omega_{fi}-\omega)^2} \ . \end{aligned} \tag{4.66}$$

This approximation assumes that the frequencies are high, and the resonant behavior for $\omega \to \omega_{fi}$ dominates, i.e.

$$\lim_{\omega\to\omega_{fi}} P_f(t) = \frac{1}{\hbar^2} \mid \mathcal{H}_{1,fi} \mid^2 t^2 \ . \tag{4.67}$$

Notice that this equation cannot be valid for all t, because the probability will exceed unity. Notice also that the above resonance corresponds to absorption. We may change the sign of ω to obtain an expression valid for emission.

We may use the following limiting representation of the δ-function,

$$\pi\delta(\Delta\omega) = \lim_{t\to\infty}\frac{\sin^2(\Delta\omega t)}{\Delta\omega^2 t}, \tag{4.68}$$

to rewrite Eq. (4.66) into

$$P_f(t) \approx \frac{2\pi}{\hbar^2} \mid \mathcal{H}_{1,fi} \mid^2 t\delta(\omega_{fi} - \omega) \ . \tag{4.69}$$

This form of Eq. (4.66) is also useful for defining the lifetime τ of an excited state $\mid i\rangle$ via

$$\frac{1}{\tau} \equiv \frac{2\pi}{\hbar^2} \mid \mathcal{H}_{1,fi} \mid^2 \delta(\omega_{fi} - \omega) \ . \tag{4.70}$$

Notice that in cases when there are more than one decay channel, i.e. one final state, we must sum over all decay channels [3][4].

• Transition rates to continuum states: We may still use Eq. (4.66), but the observed transition rate is an integral over all transition probabilities to which the perturbation can drive the system. Specifically, if the density of states is written $\rho(E_f)$, where $\rho(E_f)dE_f$ is the number of states in the range E_f to $E_f + dE_f$, then the total transition probability, $P(t)$, is

$$P(t) = \int_{\text{range}} P_f(t)\rho(E_f)dE_f \ . \tag{4.71}$$

In this expression 'range' means that the integration is over all final states accessible under the influence of the perturbation.

Inserting Eq. (4.69) into Eq. (4.71) and treating $\mathcal{H}_{1,fi}$ as constant yields

$$P(t) \approx \frac{2\pi}{\hbar} \mid \mathcal{H}_{1,fi} \mid^2 \rho(E_i + E)t \tag{4.72}$$

[5]. The transition rate, which determines the intensity of spectral lines, is given by

$$\frac{dP(t)}{dt} \approx \frac{2\pi}{\hbar} \mid \mathcal{H}_{1,fi} \mid^2 \rho(E_i + E) \ . \tag{4.73}$$

This equation is known as Fermi's golden rule [6].

• Absorption coefficient: We return to the above case of an oscillating perturbation. Let us assume that electromagnetic radiation is attenuated in a sample volume containing molecules at a certain density. Macroscopically, the intensity of the radiation after it has traversed the distance x inside the sample, $I(x)$, divided by the intensity before it enters the sample, I_o, is given by the Lambert-Beer law

$$I(x)/I_o = \exp[-\alpha x] \ . \tag{4.74}$$

The quality α is the absorption coefficient in units of inverse length, which we want to calculate.

According to Eq. (4.69) the transition rate from an initial to a final state is given by

$$\frac{dP_f(t)}{dt} \approx \frac{2\pi}{\hbar^2} \mid \mathcal{H}_{1,fi} \mid^2 \delta(\omega_{fi} - \omega) \ . \tag{4.75}$$

Next we must sum over all possible initial states according to their probability ρ_i. We also sum over all final states as well. The δ-function takes care of the proper selection of final states. Thus

$$\sum_{i,f} \rho_i \frac{dP_f(t)}{dt} \approx \frac{2\pi}{\hbar^2} \sum_{i,f} \rho_i \mid \mathcal{H}_{1,fi} \mid^2 \delta(\omega_{fi} - \omega) \ .$$

By including the factor $\hbar\omega_{fi}$ we obtain the energy absorbed due to transitions from states i to states f. However, simultaneously emission processes occur. This means that the total energy absorption per time is given by the difference of the contributions due to the two types of processes:

$$\frac{dE_{abs}}{dt} \approx \tag{4.76}$$
$$\frac{2\pi}{\hbar} \sum_{i,f} (\rho_i - \rho_f)\omega_{fi} \mid \mathcal{H}_{1,fi} \mid^2 \delta(\omega_{fi} - \omega) \ .$$

Next we make use of Eq. (2.87), i.e.

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[3] In this discussion we assume that our considerations thus far remain valid for such processes involving one or few photons. The correct treatment requires the quantization of the radiation field.

[4] You should also realize the relation between τ and Δt in our discussion of Heisenberg's uncertainty principle in section 2.4.

[5] Note: $\delta(\omega_{fi} - \omega) = \hbar\delta(E_f - (E_i + E))$.

[6] Fermi, Enrico, italian physicist, *Rome 29.9.1901, †Chicago 28.11.1954; supervised the construction of the first nuclear reactor and made many important contributions to atomic and nuclear physics; received the 1938 Nobel prize in physics

$$\rho_i - \rho_f = \rho_i \left(1 - \frac{\rho_f}{\rho_i}\right) = \rho_i \left(1 - e^{-\beta\hbar\omega_{fi}}\right) . \quad (4.77)$$

We also need the flux of energy into the sample. The incoming energy per area and time is given by the magnitude of the pointing vector calculated in section 7.1 of Ref. [17] (for a nonconducting medium):

$$S = \frac{1}{2}\frac{c}{4\pi}\sqrt{\frac{\epsilon}{\mu}}\vec{E}_o^2 . \quad (4.78)$$

Here $\vec{E}_o$ is the amplitude of the oscillating electric field and the factor $1/2$ is due to the time average over the oscillation. Notice that this S is in Gaussian units. The conversion to the MKSA system requires an additional factor $(4\pi\epsilon_o)^{-1}$. Notice also that ϵ is the dielectric constant of the sample, $\mu(\approx 1)$ is its permeability, and c is the velocity of light.

We see how this has to be combined to obtain $\alpha(\omega)$ if we express the Lambert-Beer law in differential form, i.e.

$$\alpha = \frac{-\delta I(x)}{I\delta x} = \frac{-\delta E/\delta t}{E/(\delta t A)\delta V_s} . \quad (4.79)$$

Note that here $E/(\delta t A)$ is the flux of energy through the area A into the sample volume $\delta V_s = A\,\delta x$, whereas $-\delta E/\delta t$ is the energy absorbed in the same volume per time δt. Thus, the absorption coefficient is given by

$$\alpha(\omega) = \frac{dE_{abs}/dt(\omega)}{S(\omega)V_s} . \quad (4.80)$$

Note that δV_s is replaced by the total sample volume V_s because $dE_{abs}/dt(\omega)$ refers to the (integral) energy absorbed in V_s per unit time. We include the explicit dependence of the various quantities on the frequency ω of the radiation. In the case of S this dependence enters through the frequency dependence of the dielectric constant. Putting everything together we find for the absorbtion coefficient

$$\alpha(\omega) = \frac{(4\pi)^2}{\hbar c\sqrt{\epsilon(\omega)}E_o^2 V_s}\omega(1 - e^{-\beta\hbar\omega})H(\omega) \quad (4.81)$$

with

$$H(\omega) = \sum_{i,f} \rho_i \mid \mathcal{H}_{1,fi} \mid^2 \delta(\omega_{fi} - \omega) . \quad (4.82)$$

Here we have used the δ-function to extract the frequency dependent factor $\omega(1 - e^{-\beta\hbar\omega})$ from the double sum.

Next we want to gain a better understanding of $\alpha(\omega)$ and what one can learn from measuring it. For this purpose we concentrate on the rewriting of $H(\omega)$. We begin with the δ-function given via

$$\delta(\omega_{fi} - \omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{i(\omega_{fi}-\omega)t}dt , \quad (4.83)$$

(see Appendix B.4), or alternatively

$$\delta(\omega_{fi} - \omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{(i/\hbar)(E_f - E_i - \hbar\omega)t}dt . \quad (4.84)$$

Thus

$$H(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-i\omega t} \sum_{i,f} \rho_i \mid \mathcal{H}_{1,fi} \mid^2 e^{(i/\hbar)(E_f - E_i)t}dt \quad (4.85)$$

with

$$\mid \mathcal{H}_{1,fi} \mid^2 = \langle i \mid \underline{\mathcal{H}}_1^+ \mid f\rangle\langle f \mid \underline{\mathcal{H}}_1 \mid i\rangle \quad (4.86)$$

(cf. Eq. (4.65); the present $\underline{\mathcal{H}}_1$ is identical to the same quantity on the right side of this equation.). Now according to section 2.4 (The time evolution operator) we can write

$$\mid \langle f \mid \underline{\mathcal{H}}_1 \mid i\rangle e^{(i/\hbar)(E_f - E_i)t} = \langle f \mid \underline{\mathcal{H}}_1(t) \mid i\rangle , \quad (4.87)$$

whereas

$$\langle i \mid \underline{\mathcal{H}}_1^+ \mid f\rangle = \langle i \mid \underline{\mathcal{H}}_1^+(0) \mid f\rangle . \quad (4.88)$$

Notice that this allows a time dependent $\underline{H}_1$! In addition we can use $\sum_f \mid f\rangle\langle f \mid = 1$ to obtain

$$H(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-i\omega t} \underbrace{\sum_i \rho_i \langle i \mid \underline{\mathcal{H}}_1^{+}(0)\underline{\mathcal{H}}_1(t) \mid i\rangle}_{\overset{(2.80)}{=}\langle \underline{\mathcal{H}}_1^{+}(0)\underline{\mathcal{H}}_1(t)\rangle_o} dt\ . \qquad (4.89)$$

Here $\langle \ldots \rangle_o$ is the average in the unperturbed system. The final result is

$$H(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-i\omega t}\langle \underline{\mathcal{H}}_1^{+}(0)\underline{\mathcal{H}}_1(t)\rangle_o dt\ . \qquad (4.90)$$

The quantity $\langle \underline{\mathcal{H}}_1^{+}(0)\underline{\mathcal{H}}_1(t)\rangle_o$ is an autocorrelation function. It tells us on average how $\underline{\mathcal{H}}_1(t)$ changes with time provided that it had a certain value at time zero. Autocorrelations yield information on the molecular dynamics. The Fourier transform relates the characteristic times of this dynamics to attendant frequencies - here the frequency of the radiation.

As an example we consider

$$\langle \underline{\mathcal{H}}_1^{+}(0)\underline{\mathcal{H}}_1(t)\rangle_o = \cos(\omega_o t)\exp\left[-\frac{1}{2}\left(\frac{t}{\tau}\right)^2\right] \qquad (4.91)$$

depicted in Fig. 4.2. What we have in mind are molecules exhibiting periodic motion like rotations or vibrations. The oscillatory autocorrelation possesses a characteristic lifetime, τ, due to interaction of the molecules with each other. We model the functional form using a simple Gaussian. The attendant $H(\omega)$ [7] is shown in Fig. 4.3 for two different values of τ. Notice that the peak, whose position is determined by ω_o, is narrower for the larger τ (cf. our previous discussion of lifetime in the context of Eq. 2.78).

Now we focus on a more specific example. The electromagnetic field in the sample is interacting with its molecules via the interaction (energy) $-\vec{m}\cdot\vec{E} = -\vec{m}\cdot\vec{E}_o\cos(\omega t)$ i.e. $2\underline{\mathcal{H}}_1(t) = -\underline{\vec{m}}\cdot\vec{E}_o$. Here $\vec{m}$ is the electric dipole moment (cf. the following section) inside the above volume V_s. If $\vec{E}_o$ defines the x-axis of our coordinate system we obtain

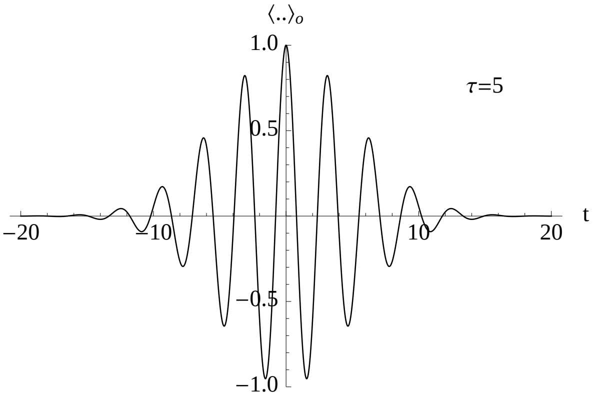

Figure 4.2: Example for an autocorrelation function ($\omega_o = 2$) possessing a characteristic lifetime $\tau = 5$.

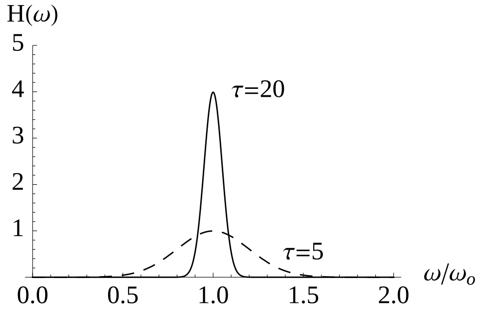

Figure 4.3: Example for $H(\omega)$ vs. ω for two different lifetimes τ.

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[7] $H(\omega) = \frac{\tau}{\sqrt{8\pi}}\left(\exp[-\frac{1}{2}(\omega+\omega_o)^2\tau^2] + \exp[-\frac{1}{2}(\omega-\omega_o)^2\tau^2]\right)$

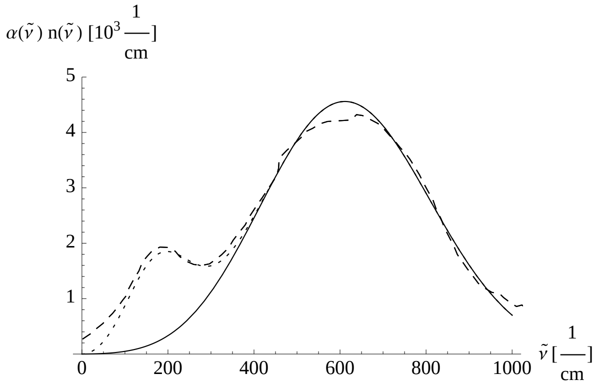

Figure 4.4: Dashed line: IR absorption spectrum of liquid water taken from Fig. 2 in P. L. Silvestrelli et al. *Chemical Physics Letters 277*, 478 (1997). Solid line: theoretical approximation to the broad peak at $\tilde{\nu}_o \approx 525$ cm^{-1}. Dotted line: theoretical approximation to the both peaks.

$$H(\omega) = \frac{E_o^2}{8\pi} \int_{-\infty}^{\infty} e^{-i\omega t} \langle \underline{m}_x(0) \underline{m}_x(t) \rangle_o dt \ . \quad (4.92)$$

If we perform all computations in an unperturbed isotropic system, in which all directions are equivalent, we can also write

$$H(\omega) = \frac{E_o^2}{24\pi} \int_{-\infty}^{\infty} e^{-i\omega t} \langle \underline{\vec{m}}(0) \cdot \underline{\vec{m}}(t) \rangle_o dt \ . \quad (4.93)$$

But what can we learn from this? For instance, a moving molecule will eventually lo se the ‘memory‘ of its orientation at time zero due to collisions with other molecules. This memory loss affects the shape of the dipole-dipole autocorrelation function. Via the Fourier transform of the latter the attendant dynamical information does enter into $\alpha(\omega)$. Thus, by analyzing $\alpha(\omega)$ we can learn something about the molecular dynamics in the sample.

The solid line in Fig. 4.4 shows an experimental IR (infrared) absorption spectrum of liquid water. The quantity $\tilde{\nu}$ is the wavenumber defined via $\omega = 2\pi c\tilde{\nu}$. Here ω is the (angular) frequency of the light in the infrared range and $n(\tilde{\nu}) = \sqrt{\epsilon(\omega)}$ is the index of refraction of the sample, i.e. water.

First we focus on the broad peak in the spectrum close to 600 cm^{-1}. Our assumption is that it is due to a some type of rotational motion of single water molecules in ’cages’ formed by their neighbours. We assume that only the projection of the dipole moment vector onto a certain plain, $\vec{m}_\perp(t)$, rotates, whereas the projection perpendicular to that plain, $\vec{m}_{||}(t)$, is constant (see Fig. 4.5) - at least during the lifetime of this mode. Thus we have

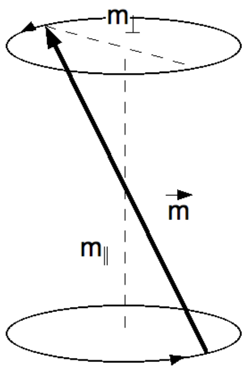

Figure 4.5: Librating dipole vector.

$$\langle \underline{\vec{m}}(0) \cdot \underline{\vec{m}}(t) \rangle_o = m_{||}^2 + m_\perp^2 \langle \cos(\omega_o t) \rangle_o \ . \quad (4.94)$$

The Fourier transform of the constant first term yields a δ-function at the origin. However, the second term is more interesting. As before we make the simple assumption

$$\langle \cos(\omega_o t) \rangle_o = \cos(\omega_o t) \exp\left[-\frac{1}{2} \left(\frac{t}{\tau} \right)^2 \right] \ . \quad (4.95)$$

There is no special justification for the exponential. We merely use it here as an intuitive description of the lifetime of this particular dynamic mode of the water molecules. A graph of Eq. (4.95) is shown in Fig. 4.6. Using Eqs. (4.94), where we omit the constant term, and (4.95), we can now calculate $H(\omega)$ and thus the absorption coefficient, which is shown in Fig. 4.4 as solid line. Again we use $\tilde{\nu}_o \approx 525$ cm^{-1} and $\tau = 0.025 \cdot 10^{-12}$ s. The ’sample’ volume is the volume of one water molecule, which is 18 ml, the molar volume of water, divided by Avogadro‘s number. In addition $m_\perp = 0.8$ Debye[8]. The resulting agreement is quite reasonable.

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[8] Note that the gas phase dipole moment of a water

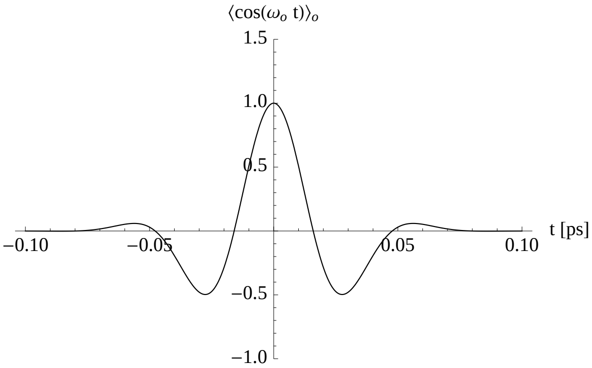

Figure 4.6: The graph shows Eq. (4.95) using $\omega_o = 2\pi c\tilde{\nu}_o$ with $\tilde{\nu}_o \approx 525$ cm^{-1} and $\tau = 0.025 \cdot 10^{-12}$ s.

Next we assume that the 'rotation' of $\vec{m}_\perp(t)$ is more complicated, e.g., $\vec{m}_\perp(0) \cdot \vec{m}_\perp(t) = m_\perp^2 \cos(\varphi(t))$ and $\cos(\varphi(t)) = \frac{1}{2}\cos(\omega_{o,1}t) + \frac{1}{2}\cos(\omega_{o,2}t)$. Here $\omega_{o,i}$ corresponds to peak $i = 1,2$ in Fig. 4.4. With $\tilde{\nu}_{o,1} \approx 525$ cm^{-1}, $\tau_1 = 0.025 \cdot 10^{-12}$ s, as before, and $\tilde{\nu}_{o,2} \approx 110$ cm^{-1}, $\tau_2 = 0.06 \cdot 10^{-12}$ s we now obtain the dotted line in Fig. 4.4. Even though this is a pretty good fit to the experimental spectrum, it does not mean that we understand the molecular dynamics of water. We have developed a simple idea, which hopefully is not too far from the truth - in this range of wavenumbers.

The interpretation of a complete absorption spectrum certainly is difficult. There are numerous features with possibly very different lifetimes due to complex dynamic modes and possibly coupling of the latter. This is not the place to dwell on these points.

However, before leaving the subject we briefly address molecular vibrations. In classical mechanics [14] we had discussed normal mode analysis. Applying this concept to the case of independent molecules, predominantly in the gas phase, we expand the molecular dipole moment in terms of its normal mode coordinates q_ν, i.e. ν is the mode index:

$$\underline{\vec{m}}(t) = \vec{m}_o(t) + \sum_\nu \frac{\partial \vec{m}}{\partial q_\nu}\Big|_0 \underline{q}_\nu(t) + \dots \,. \tag{4.96}$$

Here the index o refers to the undeformed state $q_\nu = 0$ (for all ν). Even a completely rigid molecule can have a dipole moment, which may change for instance due to rotation. This is described by $\vec{m}_o(t)$. Usually the dipole moment also changes when the molecules deforms due to normal mode vibrations - this is what the second term describes. Let us work out the dipole-dipole autocorrelation function $\langle \underline{\vec{m}}(0) \cdot \underline{\vec{m}}(t)\rangle_o$. In order to simplify matters we assume $\vec{m}_o(t) = 0$ and we neglect higher order terms as well, which also means that the different modes are independent, i.e. uncorrelated. This yields

$$\langle \underline{\vec{m}}(0) \cdot \underline{\vec{m}}(t)\rangle_o = \sum_\nu \left(\frac{\partial \vec{m}}{\partial q_\nu}\Big|_0\right)^2 \langle \underline{q}_\nu(0)\underline{q}_\nu(t)\rangle_o \tag{4.97}$$

Basically we expect $\langle \underline{q}_\nu(0)\underline{q}_\nu(t)\rangle_o$ to be similar to (4.95) with ω_o replaced by ω_ν. This is because at $t = 0$ the correlation is at its maximum and in the limit $\tau \to \infty$ the lineshape becomes a δ-function at ω_ν.

We remark that at room temperature we usually have $\beta\hbar\omega_\nu \gg 1$ for molecular vibrations. This means

$$\alpha(\omega_\nu) \propto \omega_\nu \left(\frac{\partial \vec{m}}{\partial q_\nu}\Big|_0\right)^2 , \tag{4.98}$$

where the width of the particular adsorption line at ω_ν is given by the lifetime of mode ν. In the gas phase, where the molecules interact only little with each other, the lifetime is long and the observed lines are very sharp. Because the lines are characteristic for molecules or atomic groups in molecules, we can identify these atoms and groups in the sample by measuring $\alpha(\omega)$ vs. ω over the proper range of frequencies.

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molecule is about 1.85 Debye. In the liquid state this number is increased due to polarization. Thus, the value of 0.8 Debye is sensible, because it is a fraction of the total dipole moment.

4.5 Interaction of charges with electromagnetic fields

In the following we consider a charged particle in an electromagnetic field. Because we do not know otherwise, we are going to assume that this field can be treated classically.

From electrodynamics we remember that the Lagrange function of a charged particle, its charge is e, in an electromagnetic field is given by

$$\mathcal{L} = -\frac{mc^2}{\gamma\left(v\right)} + \frac{e}{c}\vec{A}\cdot\vec{v} - e\varphi \tag{4.99}$$

([15]; Eq. (2.9)). The generalized momentum of the particle is given by

$$\vec{p} = \partial_{\vec{v}}\mathcal{L} = \gamma\left(v\right)m\vec{v} + \frac{e}{c}\vec{A}\,, \tag{4.100}$$

with $\gamma\left(v\right) = \left(1-\frac{v^2}{c^2}\right)^{-\frac{1}{2}}$. Here $\vec{v}$ is the particle's velocity, m is its rest mass, and c the velocity of light. The quantities $\vec{A}$ and φ are the vector potential and the scalar potential, respectively. Notice that Eq. (4.100) describes the relativistic momentum. In the following we use the nonrelativistic limit $v/c \to 0$, and $\vec{p}$ becomes

$$\vec{p} = m\vec{v} + \frac{e}{c}\vec{A}\,. \tag{4.101}$$

We calculate the Hamilton function via $\mathcal{H} = \vec{p}\cdot\vec{v} - \mathcal{L}$, which yields $\mathcal{H} = mc^2 + \frac{1}{2m}\left(\vec{p}-\frac{e}{c}\vec{A}\right)^2 + e\varphi$, where we have used $\gamma^{-1}\left(v\right) \approx 1 - \frac{1}{2}\frac{v^2}{c^2}$. In the following we omit the rest energy term, mc^2, because it is merely a constant. The resulting Hamilton function is

$$\mathcal{H} = \frac{1}{2m}\left(\vec{p}-\frac{e}{c}\vec{A}\left(\vec{r}\right)\right)^2 + e\varphi\left(\vec{r}\right)\,. \tag{4.102}$$

As stated above, we construct a quantum mechanical Hamiltonian by replacing $\vec{p}$ and $\vec{r}$ with their operators. Thus

$$\underline{\mathcal{H}} = \frac{1}{2m}\left(\underline{\vec{p}}-\frac{e}{c}\vec{A}\left(\underline{\vec{r}}\right)\right)^2 + e\varphi\left(\underline{\vec{r}}\right) \tag{4.103}$$

or

$$\underline{\mathcal{H}} = \frac{\underline{\vec{p}}^2}{2m} - \frac{e}{2mc}\left(\underline{\vec{p}}\cdot\vec{A}\left(\underline{\vec{r}}\right) + \vec{A}\left(\underline{\vec{r}}\right)\cdot\underline{\vec{p}}\right) + \frac{e^2}{2mc^2}\vec{A}^2\left(\underline{\vec{r}}\right) + e\varphi\left(\underline{\vec{r}}\right)\,. \tag{4.104}$$

Notice that $\underline{\vec{p}}$ and $\vec{A}\left(\underline{\vec{r}}\right)$ do not commute.

Before discussing this Hamiltonian, at least partially, we must examine its transformation properties under the gauge transformations

$$\vec{A} \to \vec{A}\,' = \vec{A} + \vec{\nabla}f \tag{4.105}$$

$$\varphi \to \varphi\,' = \varphi - \frac{1}{c}\dot{f}\,, \tag{4.106}$$

where f is a scalar function. We know (cf. [15]; Eqs. (2.18) and (2.19)) that the gauge transformations (4.105) and (4.106) do not change the electric and magnetic field strengths, i.e., they do not influence physical observations. The same should be true in quantum mechanics. And indeed, as we show in a homework problem, if $|\,\psi\left(t\right)\rangle$ is an eigenket of $\underline{\mathcal{H}}$ in (4.104) then

$$|\,\psi\,'\left(t\right)\rangle = e^{i\tilde{f}\left(\underline{\vec{r}},t\right)}\,|\,\psi\left(t\right)\rangle \tag{4.107}$$

is an eigenket of $\underline{\mathcal{H}}\,'$ with $\tilde{f} = \frac{e}{\hbar c}f$. The complex phase factor does not alter the transition probability to another state, i.e. $|\langle\chi(t)\mid\psi\,'\left(t\right)\rangle|^2 = |\langle\chi(t)\mid\psi\left(t\right)\rangle|^2$.

Induced emission and absorption:

We apply Eq. (4.104) to an atom in an electromagnetic radiation field described in terms of a linearly polarized plane wave

$$\vec{A} = A_0\vec{e}\cos\left(\vec{k}\cdot\vec{r}-wt\right) \quad \text{and} \quad \varphi = 0\,. \tag{4.108}$$

Here $\vec{e}$ is a unit vector characterizing the polarization direction. Let us insert this $\vec{A}$ into

$$\left(\underline{\vec{p}}\cdot\vec{A}+\vec{A}\cdot\underline{\vec{p}}\right) = -i\hbar\left(\vec{\nabla}\cdot\vec{A}+\vec{A}\cdot\vec{\nabla}\right) \tag{4.109}$$

in Eq. (4.104). With $\vec{\nabla}\cdot\vec{A} \propto \vec{e}\cdot\vec{k} = 0$ (Lorentz condition) we get $\underline{\mathcal{H}} = \underline{\vec{p}}^2/(2m) + \underline{\mathcal{H}}_1$, where

$$\begin{aligned} \underline{\mathcal{H}}_1 &= -\frac{e}{mc}\vec{A}\left(\underline{\vec{r}}\right)\cdot\underline{\vec{p}} \qquad (4.110)\\ &= -\frac{eA_0}{2mc}\left(e^{i\left(\vec{k}\cdot\underline{\vec{r}}-wt\right)}+e^{-i\left(\vec{k}\cdot\underline{\vec{r}}-wt\right)}\right)\left(\vec{e}\cdot\vec{p}\right) \ . \end{aligned}$$

In the following we treat $\underline{\mathcal{H}}_1$ as a time dependent perturbation. The term proportional to $\vec{A}^2$ is omitted here. It corresponds to the perturbation acting twice, a second order contribution, which we do not consider. Thus, the first order transition amplitude is

$$\begin{aligned} &\langle f \mid \underline{\mathcal{H}}_1\left(t\right) \mid i\rangle\\ &\quad = -\frac{eA_0}{2mc}\langle f \mid e^{i\left(\vec{k}\cdot\underline{\vec{r}}\right)}\left(\vec{e}\cdot\underline{\vec{p}}\right) \mid i\rangle e^{-iwt}\\ &\quad -\frac{eA_0}{2mc}\langle f \mid e^{-i\left(\vec{k}\cdot\underline{\vec{r}}\right)}\left(\vec{e}\cdot\underline{\vec{p}}\right) \mid i\rangle e^{iwt} \ . \end{aligned}$$

Now we can apply our results obtained above for a periodic perturbation. The same simple calculation yields the transition amplitude to first order for $i \neq f$ and $t_0 = 0$:

$$\begin{aligned} \langle f \mid \underline{S}\left(t,t_0\right) \mid i\rangle &= e^{-i\omega_f t}\frac{ieA_0}{2\hbar mc}\\ &\times e^{i\frac{t\Delta w}{2}}\frac{\sin\left(t\Delta w/2\right)}{\Delta w/2}\\ &\times\langle f \mid e^{\mp i\vec{k}\cdot\underline{\vec{r}}}\left(\vec{e}\cdot\underline{\vec{p}}\right) \mid i\rangle \ . \qquad (4.111) \end{aligned}$$

Note that $\omega_{fi} \pm \omega = \Delta\omega$, where the upper sign corresponds to absorption and the lower sign to emission.

Next we investigate the amplitude more closely, i.e.

$$\begin{aligned} &\langle f \mid e^{\mp i\vec{k}\cdot\underline{\vec{r}}}\left(\vec{e}\cdot\underline{\vec{p}}\right) \mid i\rangle\\ &\quad = \int\langle f \mid e^{\mp i\vec{k}\cdot\underline{\vec{r}}} \mid \vec{r}\rangle\langle\vec{r} \mid \vec{e}\cdot\underline{\vec{p}} \mid i\rangle d^3r\\ &\quad = \int\langle f \mid \vec{r}\rangle e^{\mp i\vec{k}\cdot\vec{r}}\langle\vec{r} \mid \vec{e}\cdot\underline{\vec{p}} \mid i\rangle d^3r \ . \qquad (4.112) \end{aligned}$$

Only for $r \leq a_0$ (Bohr's radius) there are be sizeable contributions (cf. above), because the wave function $\langle f \mid \vec{r}\rangle$ quickly drops off towards zero for larger r. In the case of visible light we estimate $kr < \frac{2\pi a_0}{\lambda} \approx 10^{-3}$, which means that we may expand the e-function as follows:

$$\langle f \mid e^{\mp i\vec{k}\cdot\underline{\vec{r}}}\left(\vec{e}\cdot\underline{\vec{p}}\right) \mid i\rangle \approx \langle f \mid \vec{e}\cdot\underline{\vec{p}} \mid i\rangle \ . \qquad (4.113)$$

Assuming an unperturbed Hamiltonian

$$\underline{\mathcal{H}}_0 = \frac{\underline{\vec{p}}^2}{2m} + \mathcal{U}\left(\underline{\vec{r}}\right) \ , \qquad (4.114)$$

where we have added the potential $\mathcal{U}\left(\underline{\vec{r}}\right)$, it is easy to show that

$$\underline{\vec{p}} = -\frac{m}{i\hbar}\left[\underline{\mathcal{H}}_0, \underline{\vec{r}}\right] \ . \qquad (4.115)$$

Using this relation in Eq. (4.113) we find

$$\langle f \mid \vec{e}\cdot\underline{\vec{p}} \mid i\rangle = im\omega_{fi}\langle f \mid \vec{e}\cdot\underline{\vec{r}} \mid i\rangle \ . \qquad (4.116)$$

The quantity $e\langle f \mid \underline{\vec{r}} \mid i\rangle$ is called the transition dipole moment [9], and the emitted radiation is called electrical dipole radiation. Note again that $\vec{e}$ is the polarization vector, i.e. its orientation relative to $\vec{r}$ is important! In order to calculate the emitted intensity we have to evaluate (4.116) explicitly (e.g. for hydrogen states in $\vec{r}$-representation). However, more interesting is the question whether a particular transition is at all possible. It turns out, as we will see later, that the quantum numbers, which characterize the initial and final states must obey selection rules, i.e. only certain differences between them are allowed.

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[9] Here e is the charge and not $|\vec{e}|$!

Chapter 5

Many particle systems

5.1 Two kinds of statistics

We consider an N-body system of identical particles. Identical means that the Hamiltonian operator $\underline{\mathcal{H}}$ is invariant under the exchange of any two of the particles. An N-particle state vector we might write as an ordered product

$$\begin{aligned} |\phi_\alpha\rangle &\equiv |\phi_{\alpha_1,\alpha_2,\ldots,\alpha_N}\rangle \\ &= (|\phi_{\alpha_1}\rangle|\phi_{\alpha_2}\rangle\ldots|\phi_{\alpha_N}\rangle) \ , \end{aligned} \tag{5.1}$$

where the $|\ \phi_{\alpha_i}\rangle$ denote single particle states [1]. The mathematical expression of the above invariance by definition is

$$\underline{\mathcal{H}}\underline{\sigma}_{ij} = \underline{\sigma}_{ij}\underline{\mathcal{H}} \ , \tag{5.2}$$

or

$$\underline{\sigma}_{ij}^{-1}\underline{\mathcal{H}}\underline{\sigma}_{ij} = \underline{\mathcal{H}} \ , \tag{5.3}$$

where $\underline{\sigma}_{ij}$, the permutation operator, interchanges particles i and j, i.e.

$$\underline{\sigma}_{ij}|\phi_{\ldots,\alpha_i,\ldots,\alpha_j,\ldots}\rangle = |\phi_{\ldots,\alpha_j,\ldots,\alpha_i,\ldots}\rangle \ . \tag{5.4}$$

If $|\ \phi_\alpha\rangle$ is an eigenstate of $\underline{\mathcal{H}}$ with the eigenvalue E_α, then Eq. (5.2) implies

$$\underline{\mathcal{H}}\left(\underline{\sigma}_{ij}\ |\ \phi_\alpha\rangle\right) = E_\alpha\left(\underline{\sigma}_{ij}\ |\ \phi_\alpha\rangle\right) \ . \tag{5.5}$$

This equation allows two alternative conclusions:

(a) $\underline{\sigma}_{ij}\ |\ \phi_\alpha\rangle = c\ |\ \phi_\alpha\rangle$, where c is a constant. And therefore

$$\underline{\sigma}_{ij}\ |\ \phi_\alpha\rangle = \pm\ |\ \phi_\alpha\rangle \ , \tag{5.6}$$

because $\underline{\sigma}_{ij}^2\ |\ \phi_\alpha\rangle =|\ \phi_\alpha\rangle$.

(b) $\underline{\sigma}_{ij}\ |\ \phi_\alpha\rangle$ is a linear combination of eigenstates $|\ \phi_\alpha^{(1)}\rangle,\ldots,|\ \phi_\alpha^{(s)}\rangle$, which all produce the same eigenvalue E_α. In this case the eigenvalue has an intrinsic degeneracy that cannot be removed by any perturbation $\underline{\mathcal{U}}$ consistent with our above symmetry assumption regarding $\underline{\mathcal{H}}$, i.e. $\underline{\sigma}_{ij}^{-1}\underline{\mathcal{U}}\underline{\sigma}_{ij} = \underline{\mathcal{U}}$. However, experiments thus far show that only (a) is realized in nature.

An immediate consequence of Eq. (5.6) is that state space separates into two completely disjoint spaces in the sense of the "superselection rule"

$$\langle\phi_{\alpha'}^{(+)}|\underline{\Lambda}|\phi_\alpha^{(-)}\rangle = 0 \ . \tag{5.7}$$

Proof: $\langle\phi_{\alpha'}^{(+)}|\underline{\Lambda}|\phi_\alpha^{(-)}\rangle = \langle\phi_{\alpha'}^{(+)}|\underline{\sigma}^{-1}\underline{\Lambda\sigma}|\phi_\alpha^{(-)}\rangle = \langle\phi_{\alpha'}^{(+)}|\underline{\sigma}^{+}\underline{\Lambda\sigma}|\phi_\alpha^{(-)}\rangle = -\langle\phi_{\alpha'}^{(+)}|\underline{\Lambda}|\phi_\alpha^{(-)}\rangle$. Here the indices $(+)$ and $(-)$ stand for the respective signs in Eq. (5.6), and we have used $\underline{\sigma}^{+} = \underline{\sigma}^{-1}$ [2]

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[1] Notice that here $\ldots\ |\ \phi_{\alpha_i}\rangle\ |\ \phi_{\alpha_j}\rangle\ldots$ is different from $\ldots|\ \phi_{\alpha_j}\rangle\ |\ \phi_{\alpha_i}\rangle\ldots$.

[2] Proof: Here and in the following we extend the definition of the permutation operator $\underline{\sigma}_{ij}$. The permutation operator $\underline{\sigma}$ now transforms the ordered set $\alpha_1,\alpha_2,\ldots,\alpha_N$ into the new ordered set $\sigma\alpha_1,\sigma\alpha_2,\ldots,\sigma\alpha_N$ via a succession of pair-permutations as defined before. Thus we have $\langle\phi_{\alpha'}|\underline{\sigma}|\phi_\alpha\rangle=\langle\phi_{\alpha_1{}',\alpha_2{}',\ldots,\alpha_N{}'}|\phi_{\sigma\alpha_1,\sigma\alpha_2,\ldots,\sigma\alpha_N}\rangle = \langle\phi_{\sigma^{-1}\alpha_1{}',\sigma^{-1}\alpha_2{}',\ldots,\sigma^{-1}\alpha_N{}'}|\phi_{\alpha_1,\alpha_2,\ldots,\alpha_N}\rangle$. And therefore

In addition the operator $\underline{\Lambda}$ obeys the particle exchange invariance, and only such operator makes sense in systems of indistinguishable particles. As a consequence of the above we are always dealing with physical problems, where we have $(+)$ or $(-)$-states only; one may say also 'even' or 'odd' states [3]! But what is the significance of this?

As a consequence $(-)$-states with $\alpha_i = \alpha_j$ for $i \neq j$ cannot exist! Otherwise Eq. (5.6) is incorrect. However, $(+)$-states with $\alpha_i = \alpha_j$ for $i \neq j$ can exist! Because α_i denotes the quantum numbers defining the single particle state $\mid \phi_{\alpha_i}\rangle$, this means that in $(-)$-states no two single particles may be in the same single particle state. In this case we call the particles fermions. In $(+)$-systems two or even all N particles may be in the same single particle state. These particles are bosons [4]. Thus, (5.6) introduces two ways of sorting particles into available states. If n_α is the number of particles in the single particle quantum state α, then n_α is called occupation number and we have

$$\sum_\alpha n_\alpha = N \qquad (5.8)$$

where

$$n_\alpha = \begin{cases} 0, 1, \dots, N & \text{bosons} \\ 0, 1 & \text{fermions} \end{cases} . \qquad (5.9)$$

In statistical mechanics the upper row in (5.9) yields Bose-Einstein statistics and the lower row yields Fermi-Dirac statistics.

In 1940 W. Pauli [5] (Phys. Rev. **58**, 716) showed that all particles possessing integer spin, which is an intrinsic angular momentum variable, are bosons, and all particles with half integer spin are fermions. This is the so called spin-statistics-theorem which can be proven in relativistic quantum field theory. The fact that no two fermions occupy the same state is known as Pauli principle.

5.2 Constructing N-particle wave functions

Now we want to construct the normalized N-particle states $|\phi_\alpha^{(\pm)}\rangle$ which fulfill the symmetry requirements for bosons $(+)$ and fermions $(-)$. We start from the Ansatz

$$|\phi_\alpha^{(\pm)}\rangle = K_\pm \sum_\sigma{}^{(\pm)} \delta_\sigma |\phi_{\sigma\alpha_1,\sigma\alpha_2,\dots,\sigma\alpha_N}\rangle \, . \qquad (5.10)$$

As mentioned above, $\sigma\alpha_1, \sigma\alpha_2, \dots, \sigma\alpha_N$ denotes a certain permutation of the original set $\alpha_1, \alpha_2, \dots, \alpha_N$, which is obtained via an even $(+)$ or odd $(-)$ number of pairwise particle exchanges. The respective sums, $\sum_\sigma{}^{(\pm)}$, encompass all distinct permutations for the two different cases including the identity. In addition

$$\delta_\sigma = \begin{cases} 1 & \text{bosons} \\ (-1)^P & \text{fermions} \end{cases} , \qquad (5.11)$$

$\underline{\sigma}^+ = \underline{\sigma}^{-1}$. Note that with $\underline{\sigma}^2 = \underline{\sigma}^{-1}\underline{\sigma} = 1$ we have also $\underline{\sigma}^+ = \underline{\sigma}$.

A simple example may serve to illustrate this. We compute the matrix element $\langle 1234 \mid \underline{\sigma} \mid 5678\rangle$, where the integer numbers replace $\mid \phi_{\alpha_1,\alpha_2,\dots}\rangle$. The permutation operator is defined as follows: first - interchange digit at position 3 with digit at position 4; second - interchange digit at position 3 with digit at position 1. Thus

$$\underline{\sigma} \mid 5678\rangle = \mid 8657\rangle$$

and therefore

$$\langle 1234 \mid \underline{\sigma} \mid 5678\rangle = \langle 1 \mid 8\rangle\langle 2 \mid 6\rangle\langle 3 \mid 5\rangle\langle 4 \mid 7\rangle \qquad (x) \, .$$

Now we want to check whether $\underline{\sigma}^+ = \underline{\sigma}^{-1}$. We note that

$$\langle 1234 \mid \underline{\sigma} \mid 5678\rangle = \langle 5678 \mid \underline{\sigma}^+ \mid 1234\rangle^*$$

(cf. Eq. (2.19)). First we work out $\underline{\sigma}^{-1} \mid 1234\rangle$ by reverse application of the above definition of $\underline{\sigma}$, i.e.

$$\underline{\sigma}^{-1} \mid 1234 = \mid 3241\rangle \, .$$

We therefore obtain

$$\begin{aligned} \langle 5678 \mid \underline{\sigma}^{-1} \mid 1234\rangle^* &= (\langle 5 \mid 3\rangle\langle 6 \mid 2\rangle\langle 7 \mid 4\rangle\langle 8 \mid 1\rangle)^* \\ &= \langle 3 \mid 5\rangle\langle 2 \mid 6\rangle\langle 4 \mid 7\rangle\langle 1 \mid 8\rangle \end{aligned}$$

in agreement with Eq. (x). Thus, we indeed find (in this special case) $\underline{\sigma}^{-1} = \underline{\sigma}^+$. Notice that the $\langle \dots \mid \dots\rangle$ are merely complex numbers which do commute.

[3] $(+)$-states are also referred to as symmetric; $(-)$-states are thus antisymmetric.

[4] Bose, Satyendra Nath, indian physicist, *Kolkata 1.1.1894, †Kolkata 4.2.1974

[5] Pauli, Wolfgang, swiss-american physicist, *Vienna 25.4.1900, †Zürich 15.12.1958; outstanding theoretical physicist (Pauli exclusion principle, spin-statistics theorem, prediction of the neutrino; received the 1945 Nobel prize in physics.

where P is the number of pairwise exchanges generating the set $\sigma\alpha_1, \sigma\alpha_2, \ldots, \sigma\alpha_N$ based on $\alpha_1, \alpha_2, \ldots, \alpha_N$. The normalization constant $K_\pm$ follows as usual:

$$\begin{aligned}
\delta_{\alpha\beta} &= \langle \phi_\alpha^{(\pm)} | \phi_\beta^{(\pm)} \rangle \\
&= |K_\pm|^2 \sum_{\sigma,\sigma'}{}^{(\pm)} \delta_\sigma \delta_{\sigma'} \langle \phi_{\sigma\alpha_1,\sigma\alpha_2,\ldots,\sigma\alpha_N} | \\
&\quad \times | \phi_{\sigma'\beta_1,\sigma'\beta_2,\ldots,\sigma'\beta_N} \rangle \, .
\end{aligned}$$

Fermions require $\sigma = \sigma'$, because all α_i are distinct. The remaining sum consists of $N!$ terms [6] of the form $|K_-|^2 \prod_i \langle \phi_{\sigma\alpha_i} | \phi_{\sigma\alpha_i} \rangle = |K_-|^2$. Therefore we have $K_- = \frac{1}{\sqrt{N!}}$. Bosons do not require $\sigma = \sigma'$, because this time the α_i need not be distinct. Suppose therefore n_α of the $\alpha_i (= \alpha)$ in $\alpha_1, \ldots, \alpha_N$ are identical. In this case we have

$$1 = \langle \phi_\alpha^{(+)} | \phi_\alpha^{(+)} \rangle = |K_+|^2 \, N! n_\alpha! \, .$$

The general form of this equation is

$$1 = \langle \phi_\alpha^{(+)} | \phi_\alpha^{(+)} \rangle = |K_+|^2 \, N! \prod_\alpha n_\alpha! \, ,$$

from which follows: $K_+ = (\sqrt{N! \prod_\alpha n_\alpha!})^{-1}$. Thus, we may represent both normalization constants via

$$K = K_+ = K_- = \frac{1}{\sqrt{N! \prod_\alpha n_\alpha!}} \, , \qquad (5.12)$$

where the product for fermions always is equal to unity.

Let us look at an example to see whether this really works. Here we set $N = 2$. We obtain

$$|\phi_\alpha^{(\pm)} \rangle = \frac{1}{\sqrt{2! \prod_\alpha n_\alpha!}} \left(|\phi_{\alpha_1,\alpha_2} \rangle \pm |\phi_{\alpha_2,\alpha_1} \rangle \right)$$

and therefore

$$\begin{aligned}
\langle \phi_\alpha^{(\pm)} | \phi_\alpha^{(\pm)} \rangle = \frac{1}{2 \prod_\alpha n_\alpha!} \Big(&\langle \phi_{\alpha_1,\alpha_2} | \phi_{\alpha_1,\alpha_2} \rangle \\
&\pm \langle \phi_{\alpha_1,\alpha_2} | \phi_{\alpha_2,\alpha_1} \rangle \\
&\pm \langle \phi_{\alpha_2,\alpha_1} | \phi_{\alpha_1,\alpha_2} \rangle \\
&+ \langle \phi_{\alpha_2,\alpha_1} | \phi_{\alpha_2,\alpha_1} \rangle \Big) \, .
\end{aligned}$$

For $\alpha_1 \neq \alpha_2$ follows $\prod_\alpha n_\alpha! = 1!1! = 1$ and thus

$$\begin{aligned}
\langle \phi_\alpha^{(\pm)} | \phi_\alpha^{(\pm)} \rangle &= \frac{1}{2} \Big(\underbrace{\langle \phi_{\alpha_1,\alpha_2} | \phi_{\alpha_1,\alpha_2} \rangle}_{=1} \\
&\quad + \underbrace{\langle \phi_{\alpha_2,\alpha_1} | \phi_{\alpha_2,\alpha_1} \rangle}_{=1} \Big) = 1 \, .
\end{aligned}$$

For bosons $\alpha_1 = \alpha_2$ is allowed. In this case we have $\prod_\alpha n_\alpha! = 2!0! = 2$ and thus

$$\langle \phi_\alpha^{(+)} | \phi_\alpha^{(+)} \rangle = \frac{1}{4} (1 + 1 + 1 + 1) = 1 \, .$$

In the next section we need the completeness relations for the $(\pm)$-subspaces

$$1^{(\pm)} = \frac{1}{N!} \sum_{\alpha_1,\ldots,\alpha_N} |\phi_\alpha^{(\pm)} \rangle \langle \phi_\alpha^{(\pm)} | \, , \qquad (5.13)$$

which are analogous to the completeness relations used above (cf. (2.3) and (2.4)). The proof is left as an exercise.

The ideal quantum gas:

As an application of what we have said thus far we want to work out the classical limit of the canonical partition function given by Eq. (2.89) for an ideal gas. In order to keep things simple we set $N = 2$ for the moment. We therefore have

$$\underline{\mathcal{H}} = \frac{\hbar^2}{2m} \left(\underline{\vec{k}}_1^2 + \underline{\vec{k}}_2^2 \right) \, . \qquad (5.14)$$

Here $\hbar \underline{\vec{k}}_i$ is the momentum operator corresponding to particle i. Accordingly we write for the 2-particle states

$$|\phi_k^{(\pm)} \rangle = K_\pm \left(|k_1, k_2 \rangle \pm |k_2, k_1 \rangle \right) \, . \qquad (5.15)$$

Using this we calculate the trace in Eq. (2.89), i.e.

$$\begin{aligned}
Q &= Tr \left(e^{-\beta \underline{\mathcal{H}}} \right) \\
&= \sum_n \langle \phi_n | e^{-\beta \underline{\mathcal{H}}} | \phi_n \rangle
\end{aligned}$$

---

[6] $N!$ is the number of all possible permutations of N distinct objects.

$$
\begin{aligned}
&= \sum_n \langle \phi_n | 1^{(\pm)} e^{-\beta \underline{\mathcal{H}}} | \phi_n \rangle \\
&\overset{(*)}{=} \frac{1}{2!} \sum_n \left(\frac{V}{(2\pi)^3} \right)^2 \int d^3k_1 d^3k_2 \langle \phi_n | \phi_{\vec{k}}^{(\pm)} \rangle \\
&\quad \times \langle \phi_{\vec{k}}^{(\pm)} | e^{-\beta \underline{\mathcal{H}}} | \phi_n \rangle \\
&= \frac{1}{2} \left(\frac{V}{(2\pi)^3} \right)^2 \int d^3k_1 d^3k_2 \langle \phi_{\vec{k}}^{(\pm)} | e^{-\beta \underline{\mathcal{H}}} | \phi_{\vec{k}}^{(\pm)} \rangle \\
&= \frac{1}{2} \left(\frac{V}{(2\pi)^3} \right)^2 \int d^3k_1 d^3k_2 e^{-\beta \frac{\hbar^2}{2m}(k_1^2+k_2^2)} \\
&\quad \times \langle \phi_{\vec{k}}^{(\pm)} | \phi_{\vec{k}}^{(\pm)} \rangle
\end{aligned}
$$

(*): Here we have inserted the completeness relation (5.13) as

$$
1^{(\pm)} = \frac{1}{2!} \sum_{\vec{k}_1, \vec{k}_2} |\phi_{\vec{k}}^{(\pm)} \rangle \langle \phi_{\vec{k}}^{(\pm)} | \; .
$$

The index $\vec{k}$ represents the set $\vec{k}_1, \vec{k}_2$. Using the rule (1.27) for transforming the summation into an integration we write the above relation as

$$
1^{(\pm)} = \frac{1}{2!} \left(\frac{V}{(2\pi)^3} \right)^2 \int d^3k_1 d^3k_2 \mid \phi_{\vec{k}}^{(\pm)} \rangle \langle \phi_{\vec{k}}^{(\pm)} \mid \; .
$$

Note that V is the volume to which the gas is confined.

In order to transform the integral into a more useful form we now work out the $\vec{r}$-representation of $\langle \phi_k^{(\pm)} | \phi_k^{(\pm)} \rangle$. Using the terminology developed in the last section we may write

$$
\begin{aligned}
\langle \phi_k^{(\pm)} | \phi_k^{(\pm)} \rangle &= K_\pm^2 \Big(\langle \vec{k}_1, \vec{k}_2 | \vec{k}_1, \vec{k}_2 \rangle \\
&\quad \pm \langle \vec{k}_1, \vec{k}_2 | \vec{k}_2, \vec{k}_1 \rangle \\
&\quad \pm \langle \vec{k}_2, \vec{k}_1 | \vec{k}_1, \vec{k}_2 \rangle \\
&\quad + \langle \vec{k}_2, \vec{k}_1 | \vec{k}_2, \vec{k}_1 \rangle \Big) \\
&= K_\pm^2 \int d^3r_1 d^3r_2 \Big(\langle \vec{k}_1, \vec{k}_2 | \vec{r}_1, \vec{r}_2 \rangle \\
&\quad \times \langle \vec{r}_1, \vec{r}_2 | \vec{k}_1, \vec{k}_2 \rangle \\
&\quad \pm \langle \vec{k}_1, \vec{k}_2 | \vec{r}_1, \vec{r}_2 \rangle \langle \vec{r}_1, \vec{r}_2 | \vec{k}_2, \vec{k}_1 \rangle \\
&\quad \pm \langle \vec{k}_2, \vec{k}_1 | \vec{r}_1, \vec{r}_2 \rangle \langle \vec{r}_1, \vec{r}_2 | \vec{k}_1, \vec{k}_2 \rangle \\
&\quad + \langle \vec{k}_2, \vec{k}_1 | \vec{r}_1, \vec{r}_2 \rangle \langle \vec{r}_1, \vec{r}_2 | \vec{k}_2, \vec{k}_1 \rangle \Big) \; .
\end{aligned}
$$

Here we have used the relation (2.3) twice together with $|\vec{r}_1\rangle|\vec{r}_2\rangle \equiv |\vec{r}_1, \vec{r}_2\rangle$; i.e. $\langle \vec{r}_i, \vec{r}_j | \vec{k}_{i'}, \vec{k}_{j'} \rangle = \langle \vec{r}_i | \vec{k}_{i'} \rangle \langle \vec{r}_j | \vec{k}_{j'} \rangle$. We may now be tempted to use Eq. (2.6), i.e. $\langle \vec{r}_i | \vec{k}_{i'} \rangle = \frac{1}{(2\pi)^{3/2}} e^{i \vec{k}_{i'} \cdot \vec{r}_i}$. However, this $\vec{r}$-representation of a $|\vec{k}\rangle$-state (free particle) was based on an infinite integration volume. In turn it represents a free particle state, which cannot be normalized, i.e. the free particles is not localized in a particular region in space. Our gas, however, is confined to the volume V. In order to find the proper $\langle \vec{r}_i | \vec{k}_{i'} \rangle$ in this case we write down the normalization condition for the $|\vec{k}\rangle$-states in a box of volume V using the $\vec{r}$-representation:

$$
\delta_{\vec{k}', \vec{k}} = \langle \vec{k}' | \vec{k} \rangle = \int d^3r \langle \vec{k}' \mid \vec{r} \rangle \langle \vec{r} | \vec{k} \rangle \; .
$$

From $\frac{1}{V} \int_V d^3r e^{i(\vec{k} - \vec{k}') \cdot \vec{r}} = \delta_{\vec{k}, \vec{k}'}$ (cf. problem 4) we find

$$
\langle \vec{r} | \vec{k} \rangle = \frac{1}{\sqrt{V}} e^{i \vec{k} \cdot \vec{r}} \; . \tag{5.16}
$$

Using Eq. (5.16) we obtain

$$
\begin{aligned}
\langle \phi_k^{(\pm)} | \phi_k^{(\pm)} \rangle &= K_\pm^2 \int \frac{d^3r_1}{V} \frac{d^3r_2}{V} \Big(2 \\
&\quad \pm e^{i(\vec{k}_1 - \vec{k}_2) \cdot (\vec{r}_1 - \vec{r}_2)} \\
&\quad \pm e^{-i(\vec{k}_1 - \vec{k}_2) \cdot (\vec{r}_1 - \vec{r}_2)} \Big) \; .
\end{aligned}
$$

This we substitute into the above expression for Q and obtain

$$
\begin{aligned}
Q &= \frac{K_\pm^2}{2!} 2 \int \frac{d^3r_1}{(2\pi)^3} \frac{d^3r_2}{(2\pi)^3} d^3k_1 d^3k_2 \\
&\times \; e^{-\beta \frac{\hbar^2}{2m}(k_1^2+k_2^2)} \Big(1 \pm e^{i(\vec{k}_1 - \vec{k}_2) \cdot (\vec{r}_1 - \vec{r}_2)} \Big) \\
&= \frac{1}{2!} \int \frac{d^3r_1}{(2\pi)^3} \frac{d^3r_2}{(2\pi)^3} d^3k_1 d^3k_2 \qquad (5.17) \\
&\times \; e^{-\beta \frac{\hbar^2}{2m}(k_1^2+k_2^2)} \Big[1 \pm f^2(r_{12}) \Big]
\end{aligned}
$$

with $r_{12} = |\vec{r}_1 - \vec{r}_2|$ as well as

$$
f(r_{12}) \; = \; \frac{\int d^3k \exp\left[-\frac{\beta \hbar^2 k^2}{2m} + i \vec{k} \cdot \vec{r}_{12} \right]}{\int d^3k \exp\left[-\frac{\beta \hbar^2 k^2}{2m} \right]}
$$

$$= \exp\left[-\frac{\pi r_{12}^2}{\Lambda_T^2}\right] . \tag{5.18}$$

Here $\Lambda_T = \sqrt{2\pi\beta\hbar^2/m}$ is the thermal wavelength. For $N > 2$ the calculation is analogous. The result is

$$\begin{aligned} Q &= \frac{1}{N!}\int \frac{d^3r_1 \dots d^3r_N d^3p_1 \dots d^3p_N}{(2\pi\hbar)^{3N}} \\ &\times \exp\left[-\beta\sum_{i=1}^{N}\frac{p_i^2}{2m}\right]\left[1 \pm \sum_{i<j} f^2(r_{ij})\right. \\ &\left. + \sum_{i,j,k} f(r_{ij})f(r_{ik})f(r_{kj}) \pm \dots\right] , \end{aligned} \tag{5.19}$$

where the quantum corrections are expressed in terms of an expansion involving the number of particle exchanges (cf. reference [18]). The leading correction corresponds to our result obtained above. Again $(+)$ means bosons and $(-)$ means fermions.

The classical limit of the partition function follows from $f(r) \to 0$. The quantum corrections for $f(r) > 0$ become important only if the particles are on average closer that the thermal wave length Λ_T, i.e. for

$$\Lambda_T \ll (V/N)^{1/3} \tag{5.20}$$

the classical limit is a very good approximation.

When the particles approach each other, whether they are bosons or fermions, they "feel" a statistical interaction potential, which to leading order looks like this:

$$\begin{aligned} 1 \pm \sum_{i<j} f_{ij}^2 &\approx \prod_{i<j}\left(1 \pm f_{ij}^2\right) \\ &= \exp\left(-\beta\sum_{i<j} u_{ij}\right) \end{aligned}$$

with

$$\begin{aligned} u_{ij} &\equiv -k_B T \ln\left(1 \pm f_{ij}^2\right) \\ &= -kT \ln\left[1 \pm \exp\left(-\frac{2\pi \mid \vec{r}_i - \vec{r}_j \mid^2}{\Lambda_T^2}\right)\right] \end{aligned} \tag{5.21}$$

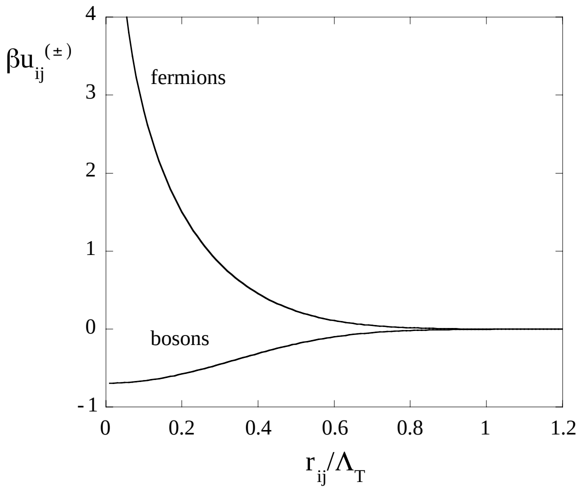

Figure 5.1: The statistical potential between bosons and fermions, respectively.

This statistical potential, which arises solely as a consequence of the symmetry of the state function, is shown in figure 5.1. We see that bosons feel an attraction, whereas fermions feel repulsion at distances below or roughly equal to the thermal wavelength. Because $\Lambda_T \propto (mT)^{-1/2}$, the potential's effect will become important especially for light particles and at low temperatures.

5.3 Electron spin

Examining the spectrum of for instance sodium (Na), one discovers that the strongest yellow line (the D line) is actually two closely spaced lines. The D line arises from a transition from a particular excited configuration to the ground state. The doublet nature of this and other lines in the Na spectrum indicates a doubling of the number of states available to the valence electron predicted by Schrödinger's equation as we know it. To explain this fine structure of atomic spectra, Uhlenbeck and Goudsmit [7] in 1925 proposed an intrinsic angular momentum, $\vec{S}$, in addition to the orbital angular momentum, $\vec{L}$. In nonrelativistic quantum mechanics, to which we are confining ourselves, electron spin must be introduced as an additional

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[7] Goudsmit, Samuel Abraham, american physicist, *Den Haag 11.7.1902, †Reno 4.12.1978; predicted the electron spin together with G.E. Uhlenbeck

hypothesis. In 1928 Dirac developed the relativistic quantum mechanics of electrons, where the electron spin arises naturally.

Analogous to the orbital angular momentum operators, $\underline{\vec{L}}^2$, $\underline{L}_x$, $\underline{L}_y$, and $\underline{L}_z$, we postulate the spin angular momentum operators $\underline{\vec{S}}^2$, $\underline{S}_x$, $\underline{S}_y$, and $\underline{S}_z$, which are assumed to be linear and hermitian. We also postulate that the spin angular momentum operators obey the same commutator relations as the orbital angular momentum operators:

$$\left[\underline{S}_i, \underline{S}_j\right] = i\hbar\epsilon_{ijk}\underline{S}_k \tag{5.22}$$

and

$$\left[\underline{\vec{S}}^2, \underline{S}_i\right] = 0 \tag{5.23}$$

for $i = 1, 2, 3$. Analogous to the angular momentum quantum numbers, l and m, we now introduce the spin quantum numbers, s and m_s. Experiment shows that for electrons $s = \frac{1}{2}$ (they are fermions) and thus $m_s = \pm\frac{1}{2}$ (cf. section 1.5). Protons and neutrons also have $s = \frac{1}{2}$. Pions have $s = 0$. Photons have $s = 1$. However, because photons are relativistic particles $m_s = \pm 1$ (but not $m_s = 0$)! These two m_s values correspond to left circularly polarized and right circularly polarized light [8].

For electrons the magnitude of the total spin angular momentum is given by

$$\left[\frac{1}{2}\left(\frac{3}{2}\right)\hbar^2\right]^{1/2} = \frac{\sqrt{3}}{2}\hbar\ . \tag{5.24}$$

The electronic spin eigenstates that correspond to the $\underline{S}_z$-eigenvalues are denoted $|\uparrow\rangle$ and $|\downarrow\rangle$:

$$\underline{S}_z\,|\uparrow\rangle = +\frac{1}{2}\hbar\,|\uparrow\rangle \tag{5.25}$$

and

$$\underline{S}_z\,|\downarrow\rangle = -\frac{1}{2}\hbar\,|\downarrow\rangle \tag{5.26}$$

[9]. Because $\underline{S}_z$ does commute with $\underline{\vec{S}}^2$ both $|\uparrow\rangle$ and $|\downarrow\rangle$ are also eigenstates of $\underline{\vec{S}}^2$:

$$\underline{\vec{S}}^2\,|\uparrow\rangle = \frac{3}{4}\hbar^2\,|\uparrow\rangle \tag{5.27}$$

and

$$\underline{\vec{S}}^2\,|\downarrow\rangle = \frac{3}{4}\hbar^2\,|\downarrow\rangle\ . \tag{5.28}$$

Notice that $\langle\uparrow|\downarrow\rangle = 0$, because $|\uparrow\rangle$ and $|\downarrow\rangle$ belong to different eigenvalues of the hermitian operator $\underline{S}_z$.

Addition of angular momenta:

In order to learn how to interpret the details of atomic and also molecular spectra we must learn how to add angular momenta [10].

Suppose we have a system with two angular momentum vectors $\underline{\vec{J}}_1$ and $\underline{\vec{J}}_2$. They might be the orbital angular momentum vector of a single electron and its spin [11], but other combinations like two spins or two orbital angular momentum vectors are also possible. We already know that the individual eigenvalues of $\underline{\vec{J}}_1^2$, $\underline{\vec{J}}_2^2$, $\underline{J}_{1,z}$, and $\underline{J}_{2,z}$ are $\hbar^2 j_1\left(j_1+1\right)$, $\hbar^2 j_2\left(j_2+1\right)$, $\hbar m_1$, and $\hbar m_2$. These quantum numbers obey the usual restrictions.

Now we define the total angular momentum

$$\underline{\vec{J}} = \underline{\vec{J}}_1 + \underline{\vec{J}}_2\ . \tag{5.29}$$

The square of $\underline{\vec{J}}$ is given by

$$\underline{\vec{J}}^2 = \underline{\vec{J}}_1^2 + \underline{\vec{J}}_2^2 + \underline{\vec{J}}_1\cdot\underline{\vec{J}}_2 + \underline{\vec{J}}_2\cdot\underline{\vec{J}}_1\ . \tag{5.30}$$

If $\underline{\vec{J}}_1$ and $\underline{\vec{J}}_2$ refer to different electrons, they will commute with each other, since each will affect only functions of the coordinates of one electron and not the other [12]. Even if $\underline{\vec{J}}_1$ and $\underline{\vec{J}}_2$ are the orbital and spin angular momenta of the same electron, they will commute, as one will affect only functions of the spatial coordinates while the other will affect

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[8] In section 6.1 we discus the photon in more detail.

[9] The terms 'spin up' and 'spin down' refer to $m_s = \pm\frac{1}{2}$.

[10] For a many electron atom, the operator for individual angular momenta of the electrons do not commute with the Hamiltonian operator, but their sum does. Hence we want to learn how to add angular momenta.

[11] the case of interest here

[12] Remember the $\vec{r}$-representation of angular momentum in terms of derivatives in appendix B.1.

functions of the 'spin coordinates'. Thus Eq. (5.30) becomes

$$\underline{\vec{J}}^2 = \underline{\vec{J}}_1^2 + \underline{\vec{J}}_2^2 + 2\underline{\vec{J}}_1 \cdot \underline{\vec{J}}_2 \, . \tag{5.31}$$

It only takes some algebra to show that $\underline{\vec{J}}$ obeys the usual angular momentum commutator relations (cf. (1.170) and (1.171)). Thus we can simultaneously quantize $\underline{\vec{J}}^2$ and one of the components of $\underline{\vec{J}}$, say $\underline{J}_z$. Since the components of the total angular momentum obey the angular momentum commutator relations, we know, based on the work in section 1.5, that the eigenvalues of $\underline{\vec{J}}^2$ are

$$\hbar^2 j\,(j+1) \qquad j = 0, \frac{1}{2}, 1, \frac{3}{2}, \ldots \, , \tag{5.32}$$

and the eigenvalues of $\underline{J}_z$ are

$$\hbar m_J \qquad m_J = -j, -j+1, \ldots, j-1, j \, . \tag{5.33}$$

What we need to find out is how the total angular momentum quantum numbers, j and m_J, are related to the quantum numbers j_1, j_2, m_1, and m_2 of the two original angular momenta.

In order to motivate this we want to briefly look at how the coupling between $\underline{\vec{L}}$ and $\underline{\vec{S}}$ gives rise to a contribution to the Hamilton operator. Such a term should be a scalar quantity, because it must be invariant under rotation and inversion. The quantities, which appear in this term should be $\underline{\vec{p}}$, the momentum of the electron, its spin, $\underline{\vec{S}}$, and the potential energy, $\mathcal{U}(\underline{\vec{r}})$. Because $\underline{\vec{p}}$ is a polar vector and $\underline{\vec{S}}$, as angular momentum, is an axial vector, we need a cross product to build up the invariant term. The simplest form is

$$\underline{\mathcal{H}}_{\underline{\vec{S}}\cdot\underline{\vec{L}}} = K\underline{\vec{S}} \cdot \left(\vec{\nabla}\mathcal{U}(\underline{\vec{r}}) \times \underline{\vec{p}}\right) \, . \tag{5.34}$$

We cannot determine the constant K, but Dirac's relativistic theory yields $K = \left(2m^2c^2\right)^{-1}$, where m is the electron mass. Using $\vec{\nabla}\mathcal{U}(\underline{\vec{r}}) = \frac{\partial \mathcal{U}(\vec{r})}{\partial r}\Big|_{r=\underline{r}} \cdot \frac{\underline{\vec{r}}}{\underline{r}}$ (radial symmetry) we find for (5.34)

$$\underline{\mathcal{H}}_{\underline{\vec{S}}\cdot\underline{\vec{L}}} = \frac{1}{2m^2c^2\underline{r}} \partial_r \mathcal{U}(\underline{\vec{r}})\,(\underline{\vec{S}} \cdot \underline{\vec{L}}) \tag{5.35}$$

[13]. Clearly, this term will lead to a level splitting, because its magnitude depends on the relative orientations of $\underline{\vec{S}}$ and $\underline{\vec{L}}$. According to Eqs. (5.31) and (5.24) the eigenvalues of $\underline{\vec{S}} \cdot \underline{\vec{L}}$ are given by

$$\frac{\hbar^2}{2}\left[j\,(j+1) - l\,(l+1) - \frac{3}{4}\right] \, . \tag{5.36}$$

Thus we are back to our question at the end of the preceding paragraph. But before we continue, here is a final remark.

If we substitute (the effective) Bohr's radius $a_0 = \frac{\hbar}{Z\alpha mc}$, where Z is the charge number and α is the fine structure constant, for $\underline{r}^{-1}$ in Eq. (5.35) we find $\langle \underline{\mathcal{H}}_{\underline{\vec{S}}\cdot\underline{\vec{L}}} \rangle \sim (Z\alpha)^2$ in units of the unperturbed

---

[13] We may also rationalize the form of $\underline{\mathcal{H}}_{\underline{\vec{S}}\cdot\underline{\vec{L}}}$ on the basis of classical electrodynamics. Remember Biot-Savart's law (cf. Ref. [15]; section 3.3):

$$\vec{H}(\vec{r}) = \frac{1}{c}\int \frac{\vec{j}(\vec{r}\,') \times (\vec{r} - \vec{r}\,')}{|\,\vec{r} - \vec{r}\,'\,|^3} d^3r\,' \, .$$

Here $\vec{H}(\vec{r})$ is the magnetic field at position $\vec{r}$ due to a stationary charge current density $\vec{j}(\vec{r}\,')$. For an observer travelling with the electron around the nucleus the latter circulates around the electron creating a magnetic field

$$\vec{H}(0) = -\frac{1}{c}\int \frac{\vec{j}(\vec{r}\,') \times \vec{r}\,'}{r\,'^3} d^3r\,'$$

at the origin (where the electron is). Using $\vec{j} = \rho_n \vec{v}_n$, the index n refers to the nucleus, we obtain for a circular orbit

$$\vec{H}(0) = -\frac{1}{c}\vec{E}_n \times \vec{v}_n \, .$$

Here $\vec{E}_n$ is the electric field of the nucleus felt by the electron. With $\vec{v}_n = -\vec{p}/m$, where $\vec{p}$ and m are momentum and mass of the electron, we have

$$\vec{H}(0) = \frac{1}{mc}\vec{E}_n \times \vec{p} = \frac{1}{mec}\vec{\nabla}\mathcal{U} \times \vec{p}$$

where $-e$ is the electron charge and $-\vec{\nabla}\mathcal{U} = -e\vec{E}_n$ is the force on the electron. Finally we use

$$\mathcal{H}_{\vec{S}\cdot\vec{L}} = -\vec{m}_e \cdot \vec{H}(0) = -\frac{1}{mec}\vec{m}_e \cdot \left(\vec{\nabla}\mathcal{U} \times \vec{p}\right) \, ,$$

where $\vec{m}_e \propto -\vec{S}$ is the magnetic moment of the electron. Notice that according to classical electrodynamics a charge, $-e$, with mass, m_e, orbiting in a circular loop produces a (loop) magnetic moment, $\vec{m}_e$, related to its angular momentum, $\vec{L}_e$, by $\vec{m}_e = \frac{-e}{2m_ec}\vec{L}_e$ (cf. Eq. (1.120)).

energy [14]. For Sodium (Na) this is $\sim 7 \cdot 10^{-3}$, which is of the same order as the above mentioned level splitting which leads to the proposal of an electron spin. This type of level spitting is small, and therefore it belongs to the so called fine structure of the quantized energy levels. Other fine structure effects are the coupling of the magnetic moment of the spin to the orbital momentum, the relativistic mass effect of the electron, and the so called Darwin term. This term arises because the path of a particle is not sharply defined, and thus it feels the potential not only at position $\vec{r}$. These corrections correspond to higher derivatives of $\mathcal{U}(\vec{r})$. Other effects are still smaller by about a factor of 10^{-3}; these are called hyperfine structure. An example is the effect due to the nuclear magnetic moment.

Again the question: How are the quantum numbers j and m_J are related to j_i and m_i $(i = 1, 2)$? First note that the angular momentum eigenfunctions for particle 1 are $\mid j_1, m_1\rangle$ and those for particle 2 are $\mid j_2, m_2\rangle$. Forming all possible products of the form $\mid j_1, m_1\rangle \mid j_2, m_2\rangle$ yields a complete set of functions for the two particles $\mid j_1, j_2, j, m_J\rangle$, because it can be shown that the four operators corresponding to these quantum numbers do commute (exercise; cf. section 4 in Ref. [9]) [15].

Each unknown eigenstate $\mid j_1, j_2, j, m_J\rangle$ can be expanded according to

$$\begin{aligned} \mid j_1, j_2, j, m_J\rangle &= \sum_{m_1, m_2} c\,(j_1, j_2, j, m_J; m_1, m_2) \\ &\quad \times \mid j_1, m_1\rangle \mid j_2, m_2\rangle, \end{aligned} \tag{5.37}$$

where the $c\,(\ldots;\ldots)$ are expansion coefficients. These are called Clebsch-Gordan or Wigner or vector addition coefficients [16]. We do not want to evaluate them here [17], but we need the form of Eq. (5.37) to answer the above question. This is because using $\underline{J}_z = \underline{J}_{1,z} + \underline{J}_{2,z}$ one can prove (homework problem) that $c\,(\ldots;\ldots) = 0$ unless

$$m_1 + m_2 = m_J\ . \tag{5.38}$$

Knowing this we need to find the possible values of the total angular momentum quantum number j. Before discussing the general case, let us consider the case with $j_1 = 1$, $j_2 = 2$. The following table lists the resulting possible values for m_1, m_2, and m_J:

$m_1 = -1$	0	+1	
−3	−2	−1	$-2 = m_2$
−2	−1	0	−1
−1	0	+1	0
0	+1	+2	+1
+1	+2	+3	+2

The number of times each value of m_J occurs is

m_J-values	3	2	1	0	−1	−2	−3
occurrence	1	2	3	3	3	2	1

The highest value of m_J is $+3$. Since m_J ranges form $-j$ to $+j$, the highest value of j must be 3. Corresponding to $j = 3$, there are seven values of m_J ranging from -3 to 3. Eliminating these seven values, we are left with

m_J-values	2	1	0	−1	−2
occurrence	1	2	2	2	1

The highest remaining value, $m_J = 2$, must correspond to $j = 2$; for $j = 2$, we have five values of m_J, which when eliminated leave

m_J-values	1	0	−1
occurrence	1	1	1

These remaining values of m_J correspond to $j = 1$. Thus, for the individual angular momentum quantum numbers $j_1 = 1$, $j_2 = 2$, the possible values of the total angular momentum quantum number j are 3, 2, and 1.

A generalization of this line of argument yields

$$j = j_1 + j_2, j_1 + j_2 - 1, \ldots, \mid j_1 - j_2 \mid \tag{5.39}$$

---

[14] Use the substitution $e^2 \to Ze^2$ in order to transform to hydrogen-like atoms.

[15] But what about the following more complete representation $\mid j_1, m_1, j_2, m_2, j, m_J\rangle$? Notice that the commutator $[\underline{J}_{i,z}, \underline{\vec{J}}^2] \neq 0$ (exercise; cf. section 4 in Ref. [9]). thus we cannot specify m_i if we specify j.

[16] Both representations, the coupled one on the left, and the uncoupled one under the sum are equivalent. We may use one or the other to describe a composite system. However, here we use the coupled representation because it is more natural in this context.

[17] see E. Merzbacher (1970) Quantum Mechanics (2nd ed.); Section 16.6. The Clebsch-Gordan coefficients are also supplied by *Mathematica*: ClebschGordan$[\{j_1, m_1\}, \{j_2, m_2\}, \{j, m_J\}]$ gives $c(\ldots;..)$ as defined in Eq. (5.37).

(cf. [23]; sec. 11.4). In particular if $j_1 = l$ and $j_2 = \frac{1}{2}$ we have $j = l + \frac{1}{2}, \mid l - \frac{1}{2} \mid$. Thus, except for $l = 0$, we find that $\underline{\mathcal{H}}_{\vec{\underline{S}}\cdot\vec{\underline{L}}}$ in Eq. (5.34) gives rise to a doublet splitting, which led Uhlenbeck and Goudsmit to propose the electron spin!

Spin magnetic moment:

Because spin itself is a relativistic phenomenon, we cannot expect that the relation (1.136), which we found in the case of orbital angular momentum, is valid if L_z is replaced by S_z. In fact, Dirac's theory yields

$$\vec{\underline{m}}_s = -g_e \frac{e}{2mc} \vec{\underline{S}} \, . \tag{5.40}$$

Here e is the magnitude of the electron charge, m is its mass, and $g_e = 2$ is the gyromagnetic factor for the electron. Theoretical and experimental work subsequent to Dirac's treatment has shown that g_e is slightly larger than 2 (see P. Kusch, Physics Today, Feb. 1966, p. 23):

$$g_e = 2\left(1 + \frac{\alpha}{2\pi} + \ldots\right) = 2.0023 \, ,$$

where $\ldots$ stands for terms containing higher powers of the fine structure constant α.

Zeeman effect:

In classical electrodynamics we have learned that in a constant magnetic field $\vec{H}$ we have $\vec{A} = \frac{1}{2}\vec{H} \times \vec{r}$ (cf. [15]; footnote 24 in section 3.3). Therefore

$$\begin{aligned} \vec{A} \cdot \vec{\underline{p}} &= \frac{1}{2}\left(\vec{H} \times \vec{\underline{r}}\right) \cdot \vec{\underline{p}} \\ &= \frac{1}{2}\vec{H} \cdot \left(\vec{\underline{r}} \times \vec{\underline{p}}\right) = \frac{1}{2}\vec{H} \cdot \vec{\underline{L}} \, . \end{aligned} \tag{5.41}$$

In addition we use Eq. (3.64) in [15] to write down the potential energy of the spin magnetic moment in the field $\vec{H}$:

$$-\vec{\underline{m}}_s \cdot \vec{H} \overset{(5.40)}{=} \frac{e}{2mc} 2\vec{\underline{S}} \cdot \vec{H} \, . \tag{5.42}$$

If we now combine Eqs. (4.104) (setting $\varphi = 0, e \to -e$ for the electron and neglecting the two last terms), (5.35), and (5.42) we obtain

$$\begin{aligned} \underline{\mathcal{H}} = \frac{\vec{\underline{p}}^2}{2m} &+ \mathcal{U}\left(\vec{\underline{r}}\right) + \frac{e}{2mc}\left(\vec{\underline{L}} + 2\vec{\underline{S}}\right) \cdot \vec{H} \\ &+ \frac{1}{2m^2c^2\underline{r}} \partial_r \mathcal{U}\left(\vec{\underline{r}}\right)\left(\vec{\underline{S}} \cdot \vec{\underline{L}}\right) \, . \end{aligned} \tag{5.43}$$

If in addition we insert $\mathcal{U}\left(\vec{\underline{r}}\right) = -Ze^2/\underline{r}$ for a hydrogen-like atom we finally get

$$\underline{\mathcal{H}} = \frac{\vec{\underline{p}}^2}{2m} - \frac{Ze^2}{\underline{r}} + \frac{Ze^2}{2m^2c^2\underline{r}^3}\vec{\underline{S}} \cdot \vec{\underline{L}} - \vec{H} \cdot \vec{\underline{\mu}}$$

with

$$\vec{\underline{\mu}} = -\frac{e}{2mc}\left(\vec{\underline{L}} + 2\vec{\underline{S}}\right) \, .$$

We now introduce an operator whose eigenvalue is the Lande factor by requiring

$$\vec{\underline{\mu}} = \underline{G}\vec{\underline{J}} \tag{5.44}$$

via multiplication with $\vec{\underline{J}}$ we find

$$\begin{aligned} \underline{G} &= \frac{-e}{2mc}\left(1 + \frac{\vec{\underline{J}} \cdot \vec{\underline{S}}}{\vec{\underline{J}}^2}\right) \\ &= \frac{-e}{2mc}\left(1 + \frac{\vec{\underline{J}}^2 + \vec{\underline{S}}^2 - \vec{\underline{L}}^2}{2\vec{\underline{J}}^2}\right) \, . \end{aligned} \tag{5.45}$$

If the magnetic field strength $\vec{H}$ in Eq. (5.43) is weak compared to the $\vec{\underline{S}} \cdot \vec{\underline{L}}$-term we may apply perturbation theory using the unperturbed states $\mid n, l, \frac{1}{2}, j, m_J\rangle$. For $\vec{H} = (0, 0, H)$ we obtain the level splitting

$$\begin{aligned} \Delta E_{nj} &= \langle n, l, \frac{1}{2}, j, m_J \mid \vec{H} \cdot \vec{\underline{\mu}} \mid n, l, \frac{1}{2}, j, m_J\rangle \\ &= \frac{e\hbar H}{2mc} g m_J \, , \end{aligned} \tag{5.46}$$

where the Lande factor is

$$g = 1 + \frac{j\,(j+1) - l\,(l+1) + 3/4}{2j\,(j+1)} \, . \tag{5.47}$$

Notice that $2j + 1$-fold degeneracy is completely gone, which is called 'anomalous' Zeeman effect.

Actually, this terminology has historical reasons, because the ordinary Zeeman effect corresponds to $g = 1$ (i.e. spin zero).

Remark: For strong magnetic fields one observes a different type of level splitting, because the $\vec{S}\cdot\vec{L}-$coupling becomes negligible and each moment interacts independently with the field (Paschen-Back effect.

5.4 Simplified theory for helium

As an application of what we have learned so far we consider the Hamiltonian

$$\begin{aligned}\underline{\mathcal{H}} &= \frac{1}{2m}\left(\underline{\vec{p}}_1^2 + \underline{\vec{p}}_2^2\right) - 2e^2\left(\frac{1}{\mid \underline{\vec{r}}_1 \mid} + \frac{1}{\mid \underline{\vec{r}}_2 \mid}\right) \\ &\quad + \frac{e^2}{\mid \underline{\vec{r}}_1 - \underline{\vec{r}}_2 \mid} \ . \end{aligned} \tag{5.48}$$

This simple model for helium is based on the Born-Oppenheimer approximation [18], which considers the position of the nuclei as fixed. The approximation is a good one, because the nuclei are so much heavier than the electrons. Secondly, spin does not appear here explicitly. Nevertheless, as we have discussed above, it enters in terms of a spin part of the total state vector, which must be anti-symmetric.

In order to find the quantum numbers characterizing the helium states we have to find the operators which commute with each other and thus have the same eigenfunctions. Here it is useful to write the permutation operator $\underline{\sigma}_{12}$ as product

$$\underline{\sigma}_{12} = \underline{R}_{12}\underline{s}_{12} \ , \tag{5.49}$$

where $\underline{s}_{12}$ acts on the spins and $\underline{R}_{12}$ on the remaining properties. We note that both, $\underline{R}_{12}$ and $\underline{s}_{12}$, commute with $\underline{\mathcal{H}}$. In addition, $\underline{s}_{12}$ does not commute with the individual spin operators $\underline{\vec{S}}_1$ and $\underline{\vec{S}}_2$, but it commutes with the total spin

$$\underline{\vec{S}} = \underline{\vec{S}}_1 + \underline{\vec{S}}_2 \ . \tag{5.50}$$

The same is true for $\underline{R}_{12}$ (or $\underline{\sigma}_{12}$) with respect to the total orbital momentum

$$\underline{\vec{L}} = \underline{\vec{L}}_1 + \underline{\vec{L}}_2 \ . \tag{5.51}$$

A system of commuting operators therefore consists of $\underline{\mathcal{H}}$, $\underline{\sigma}_{12}$, $\underline{s}_{12}$, $\underline{\vec{L}}^2$, $\underline{L}_z$, $\underline{\vec{S}}^2$, and $\underline{S}_z$. Notice that this means: the two angular momenta are coupled and the two spins are coupled; but there is no cross-coupling.

First we consider the spin part of the total state function. The single-spin states are written as $\mid s_i, m_i\rangle$, i.e. $\mid \frac{1}{2}, \frac{1}{2}\rangle \equiv\mid\uparrow\rangle$ and $\mid \frac{1}{2}, -\frac{1}{2}\rangle \equiv\mid\downarrow\rangle$. Using the terminology introduced in "Addition of angular momenta" we may write

$$\mid s, m_s\rangle \equiv\mid \frac{1}{2}, \frac{1}{2}, s, m_s\rangle \tag{5.52}$$

for the total spin state. According to the above rules for the addition of two angular momenta we thus obtain the following four orthogonal spin state functions:

$$\left.\begin{array}{l} \mid 1,1\rangle = \mid\uparrow\uparrow\rangle \\[2ex] \mid 1,0\rangle = \frac{1}{\sqrt{2}}\left(\mid\uparrow\downarrow\rangle + \mid\downarrow\uparrow\rangle\right) \\[2ex] \mid 1,-1\rangle = \mid\downarrow\downarrow\rangle \end{array}\right\} \text{symmetric}\,(+) \tag{5.53}$$

$$\mid 0,0\rangle = \frac{1}{\sqrt{2}}\left(\mid\uparrow\downarrow\rangle - \mid\downarrow\uparrow\rangle\right) \text{antisymmetric}\,(-) \tag{5.54}$$

Here we have also applied our knowledge about the symmetry properties of the state function, which must be either symmetric $(+)$ or antisymmetric $(-)$. Note that even though electrons are fermions we must also consider the symmetric spin states at this point, because it is the total state function which is $(-)$ for fermions.

Now we want to consider the remaining part of the total state function. To simplify matters we momentarily neglect the electron-electron Coulomb interaction (5.48). The dimensionless eigenvalues are then given by

$$\epsilon = -\frac{Z^2}{2}\left(\frac{1}{n_1^2} + \frac{1}{n_2^2}\right) \ , \tag{5.55}$$

---

[18] Oppenheimer, Julius Robert, american physicist, *New York 22.4.1904, †Princeton 18.2.1967; scientific head of the Manhatten project, during which the first nuclear bomb was constructed and deployed.

where $Z = 2$ in this case [19]. To build up the total state function given by

$$\mid n_1, n_2, l, m_l, s, m_s\rangle = \mid n_1, n_2, l, m_l; s\rangle \times \mid s, m_s\rangle \ , \qquad (5.56)$$

we construct the first factor, $\mid n_1, n_2, l, m_l, ; s\rangle$, from products of single particle states,

$$\mid n_1, l_1, m_{l_1}\rangle \mid n_2, l_2, m_{l_2}\rangle \ , \qquad (5.57)$$

– consistent with our approximation expressed in Eq. (5.55).

These linear combinations of products (5.57) must, however, fulfill two requirements: (a) they must be eigenstates of $\vec{\underline{L}}^2$ and $\underline{L}_z$; (b) they must obey the correct exchange symmetry. The simplest case, in which we directly see what is going on with respect to these requirements, is $n_1 = 1$, $l_1 = m_{l_1} = 0$, i.e. $l_2 = l$, $m_{l_2} = m_l$, and $n_2 \equiv n$. We then have

$$\mid n_1, n_2, l, m_l; s\rangle = \frac{1}{\sqrt{2}}\big(\mid 1, 0, 0\rangle_1 \mid n, l, m_l\rangle_2 \pm \mid 1, 0, 0\rangle_2 \mid n, l, m_l\rangle_1\big) \qquad (5.58)$$

[20]. In order for the total state to be antisymmetric we must combine the three symmetric spin states [21] with the antisymmetric $(-)$ state function in (5.58) or the antisymmetric spin state [22] with the symmetric $(+)$ state function in (5.58). Obviously the ground state, $n_1 = n_2 = 1$ and $l = m_l = 0$, only exists as singlet state, because the antisymmetric combination is zero. There are only two electrons maximum on the inner shell, which differ in the direction of their spins.

If we now include the electron-electron interaction term $\underline{\mathcal{H}}_{ee} = \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$, we see that $\underline{\mathcal{H}}_{ee}$ is diagonal in the representation which we have chosen here [23]. The expectation value of $\underline{\mathcal{H}}_{ee}$ consists of two terms:

$$\langle 1, n_2, l, m_l, s, m_s \mid \underline{\mathcal{H}}_{ee} \mid 1, n_2, l, m_l, s, m_s\rangle = D \pm A \ . \qquad (5.59)$$

D, given by

$$D = {}_1\langle 1, 0, 0 \mid {}_2\langle n, l, m_l \mid \underline{\mathcal{H}}_{ee} \mid 1, 0, 0\rangle_1 \mid n, l, m_l\rangle_2 \ ,$$

is the direct Coulomb interaction, corresponding to the screening of the Coulomb field of the nucleus by the inner electron. A, given by

$$A = {}_1\langle 1, 0, 0 \mid {}_2\langle n, l, m_l \mid \underline{\mathcal{H}}_{ee} \mid 1, 0, 0\rangle_2 \mid n, l, m_l\rangle_1 \ ,$$

is due to the exchange of the electrons. It is called exchange interaction. In general this term is positive. This is why the triplet states (ortho-helium) are found at lower energies than the corresponding singlet states (para helium). This may be understood intuitively as follows: In the triplet state the spin part of the state function is symmetric and thus the spatial part is anti-symmetric. Therefore the electrons avoid each other, and thus the Coulomb repulsion between them is reduced.

In problem 29 we had calculated the ground state energy of helium using a simple variation Ansatz. We had obtained $E \approx -2.85\frac{me^4}{\hbar^2} = -77.1eV$. Experimentally one finds $\approx 78.9eV$. Notice that even though we did not pay attention to the symmetry properties of the wave function at the time of problem 29 we obtained the correct result, because symmetry does not make a difference for the ground state.

It is also interesting to calculate the ground state energy via first order perturbation theory. In this case

$$\epsilon = -\frac{Z^2 + Z^2}{2} + D\frac{ma_0^2}{\hbar^2} \qquad (5.60)$$

In $\vec{r}$-representation D becomes $D = e^2 J_{1s1s}$ with

$$J_{1s1s} = -\frac{Z^6}{\pi^2 a_0^6}\int d^3r_1 d^3r_2 e^{-2Zr_1/a_0} \times \frac{1}{r_{12}} e^{-2Zr_2/a_0} \qquad (5.61)$$

---

[19] Notice that here ϵ is in hartree!

[20] The notation $\ldots\rangle_i$ or ${}_i\langle\ldots$ replaces the ordered product convention introduced on page 77. The index i corresponds to the position in the ordered product.

[21] One also calls them triplet states.

[22] This case is denoted as singlet state.

[23] Note that $\underline{\mathcal{H}}_{ee}$ commutes with all operators whose eigenvalues characterize the states.

This is an example of a Coulomb integral, which has the general form

$$\begin{aligned} J_{ij} &= \int d^3\tau d^3\tau\,' \mid \phi_i\left(\vec{\tau}\right) \mid^2 \\ &\quad \times \frac{1}{\mid \vec{\tau} - \vec{\tau}\,' \mid} \mid \phi_j(\vec{\tau}\,' - \vec{R}_{ij}) \mid^2 \quad .(5.62) \end{aligned}$$

Here R_{ij} is the separation of the two nuclei on which the orbital functions ϕ_i and ϕ_j are centered. In the present case $R_{ij} = 0$. For

$$\phi_i\left(\vec{\tau}\right) = \sqrt{\frac{\left(2\zeta_i\right)^{2n+1}}{4\pi\left(2n\right)!}}\tau^{n-1}e^{-\zeta_i\tau} \;, \tag{5.63}$$

the so called Slater orbitals, one obtains

$$\begin{aligned} J_{i_{ns}j_{n's}} &= \frac{1}{R_{ij}}\frac{4\zeta_i^{2n+1}\zeta_j^{2n\,'+1}}{(2n)!\,(2n\,')!} \qquad (5.64) \\ &\quad \times \frac{d^{2n-2}d^{2n\,'-2}}{d\zeta_i^{2n-2}d\zeta_j^{2n\,'-2}}\frac{1}{\zeta_i^3\zeta_j^3} \\ \times &\quad \Big[1 - \frac{\left(3\zeta_i^2 - \zeta_j^2\right)\zeta_j^4}{\left(\zeta_i - \zeta_j\right)^3\left(\zeta_i + \zeta_j\right)^3}e^{-2\zeta_j R_{ij}} \\ &\quad - \frac{\left(\zeta_i^2 - 3\zeta_j^2\right)\zeta_i^4}{\left(\zeta_i - \zeta_j\right)^3\left(\zeta_i + \zeta_j\right)^3}e^{-2\zeta_j R_{ij}} \\ &\quad - \frac{\zeta_i\zeta_j^4}{\left(\zeta_i - \zeta_j\right)^2\left(\zeta_i + \zeta_j\right)^2}R_{ij}e^{-2\zeta_i R_{ij}} \\ &\quad - \frac{\zeta_i^4\zeta_j}{\left(\zeta_i - \zeta_j\right)^2\left(\zeta_i + \zeta_j\right)^2}R_{ij}e^{-2\zeta_j R_{ij}}\Big] \;. \end{aligned}$$

In the special case $n = n\,' = 1$ we find

$$\begin{aligned} J_{i_{1s}j_{1s}} &\overset{\zeta_x = \zeta}{=} \frac{e^{-2\zeta R_{ij}}}{R_{ij}} \qquad (5.65) \\ &\quad \times \Big[e^{2\zeta R_{ij}} - 1 - \frac{11}{8}\zeta R_{ij} \\ &\quad - \frac{3}{4}\zeta^2 R_{ij}^2 - \frac{1}{6}\zeta^3 R_{ij}^3\Big] \\ &= \begin{cases} \frac{1}{R_{ij}} & (R_{ij} \to \infty) \\ \frac{5}{8}\zeta - \frac{1}{12}\zeta^3 R_{ij}^2 + \ldots & (R_{ij} \to 0) \end{cases} \end{aligned}$$

(cf. Kapitel V in R. Hentschke et al. Molekulares Modellieren mit Kraftfeldern. http://constanze.materials.uni-wuppertal.de/skripten).

Thus we obtain from (5.65) for $R_{ij} = 0$

$$D = \frac{5}{8}\frac{Z}{a_0}e^2 \tag{5.66}$$

and therefore

$$\epsilon = -Z^2 + \frac{5}{8}Z = -2.75 \;, \tag{5.67}$$

which is $E = -2.75\frac{me^4}{\hbar^2} \approx -74.4eV$. Overall the agreement is not too bad. As one might have expected, the variation approach yields the better result.

5.5 Simplified theory for the hydrogen molecule

In this section we consider an approximation of the hydrogen molecule dating essentially back to the early days of quantum mechanics (Heitler and London, 1927). The idea is as follows. We consider the nuclei, which are heavy and slow compared to the electrons, at fixed positions $\vec{R}_A$ and $\vec{R}_B$. The hydrogen molecule's Hamiltonian then becomes

$$\begin{aligned} \underline{\mathcal{H}}_{H_2} &= \frac{\vec{p}_1^{\,2}}{2m} + \frac{\vec{p}_2^{\,2}}{2m} - e^2\Big[\frac{1}{\underline{r}_{A1}} + \frac{1}{\underline{r}_{A2}} \qquad (5.68) \\ &\quad + \frac{1}{\underline{r}_{B1}} + \frac{1}{\underline{r}_{B2}} - \frac{1}{\underline{r}_{12}} - \frac{1}{R_{AB}}\Big] \end{aligned}$$

Here r_{Ai} is the distance of electron i from nucleus A (analogous for r_{Bi}), and r_{12} and R_{AB} are the electron-electron and nuclear separations, respectively.

Our goal will be the calculation of the electron distribution and the electronic energy levels. Having solved this problem, we may compute the forces between the nuclei and thus their vibrational motion (cf. below).

The electronic problem cannot be solved exactly. We, in particular, will use a simple approximation, i.e. the H_2 electronic state function is taken as

$$\begin{aligned} \mid \psi_{III/I}\rangle &= \mid s, m_s\rangle f_{III/I} \qquad (5.69) \\ &\quad \times\Big(\mid \phi_A\rangle_1 \mid \phi_B\rangle_2 \mp \mid \phi_B\rangle_1 \mid \phi_A\rangle_2\Big) \;. \end{aligned}$$

Here $\mid s, m_s\rangle$ is the spin part defined in Eq. (5.52) and written down explicitly in Eqs. (5.53) and (5.54). Notice that the $\mid \phi_A\rangle$ and $\mid \phi_B\rangle$ are simply atomic hydrogen states associated with nucleus A and B. Notice also that the $(-)$-sign corresponds to the symmetric spin triplet states (III), and the $(+)$-sign corresponds to the antisymmetric spin singlet states (I). The factor $f_{III/I}$ is obtained from the normalization condition $\langle\psi_{III/I} \mid \psi_{III/I}\rangle = 1$, i.e.

$$\begin{aligned} 1 &= \mid f_{III/I}\mid^2 \qquad (5.70)\\ &\quad\times\Big(\underbrace{{}_1\langle\phi_A \mid \phi_A\rangle_1}_{=1}\underbrace{{}_2\langle\phi_B \mid \phi_B\rangle_2}_{=1}\\ &\quad+\underbrace{{}_2\langle\phi_A \mid \phi_A\rangle_2}_{=1}\underbrace{{}_1\langle\phi_B \mid \phi_B\rangle_1}_{=1}\\ &\quad\mp{}_1\langle\phi_A \mid \phi_B\rangle_1{}_2\langle\phi_B \mid \phi_A\rangle_2\\ &\quad\mp{}_1\langle\phi_B \mid \phi_A\rangle_1{}_2\langle\phi_A \mid \phi_B\rangle_2\Big)\ . \end{aligned}$$

The ${}_i\langle\phi_A \mid \phi_B\rangle_i$ do not vanish, because the $\vec{r}$-representations of $\mid \phi_A\rangle$ and $\mid \phi_B\rangle$ are centered on different nuclei. The quantities

$$\begin{aligned} K_{AB}\left(R_{AB}\right) &\equiv {}_1\langle\phi_A \mid \phi_B\rangle_1\\ &= \int d^3r\langle\phi_A \mid \vec{r}\rangle\langle\vec{r} \mid \phi_B\rangle \qquad (5.71) \end{aligned}$$

are called overlap integrals. Consequently

$$f_{III/I} = \frac{1}{\sqrt{2\left(1\mp \mid K_{AB}\mid^2\right)}}\ . \qquad (5.72)$$

In order to clarify the notation we compute K_{AB} based on the hydrogen ground state wave functions (1.112). For simplicity we use Bohr's radius as the unit of length, i.e.

$${}_1\langle\phi_A \mid \phi_B\rangle_1 = \frac{1}{\pi}\int d^3\tau e^{-\rho_A}e^{-\rho_B}\ . \qquad (5.73)$$

The electron-to-nucleus separations ρ_A and ρ_B are shown in Fig. 5.2. The integral may be solved using elliptical coordinates μ, ν, and ϕ: $\mu = (\rho_A + \rho_B)/R_{AB}$ and $\nu = (\rho_A - \rho_B)/R$. Note that ρ_A is the separation of one particular electron (here electron 1) from nucleus A, and ρ_B is the separation of the same electron from nucleus B. ϕ is the angle of rotation around the line connecting A and B. In elliptic coordinates the volume element is $d^3\tau = (R_{AB}^3/8)(\mu^2-\nu^2)d\mu d\nu d\phi$ $(1 \leq \mu \leq \infty, -1 \leq \nu \leq 1, 0 \leq \phi \leq 2\pi)$. After a not too difficult integration we obtain

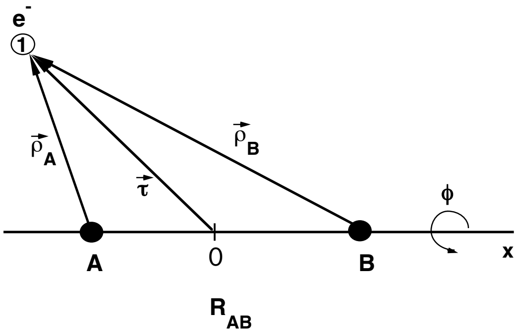

Figure 5.2: Coordinates used in the example computation of the overlap integral (5.73).

$${}_1\langle\phi_A \mid \phi_B\rangle_1 = \left(1 + R_{AB} + \frac{R_{AB}^2}{3}\right)e^{-R_{AB}}\ . \qquad (5.74)$$

At this point we may pursue different avenues. Based on $\mid \psi_{III}\rangle$ and $\mid \psi_I\rangle$ we may either do perturbation theory or, introducing again as in the case of helium an effective charge, we may take the variation approach. Here, however, we simply calculate the expectation values

$$\begin{aligned} E_I &= \langle\psi_I \mid \underline{\mathcal{H}}_{H_2} \mid \psi_I\rangle \qquad (5.75)\\ &= E_A + E_B + \frac{D + A}{1+ \mid K\mid^2} \end{aligned}$$

and

$$\begin{aligned} E_{III} &= \langle\psi_{III} \mid \underline{\mathcal{H}}_{H_2} \mid \psi_{III}\rangle \qquad (5.76)\\ &= E_A + E_B + \frac{D - A}{1- \mid K\mid^2}\ , \end{aligned}$$

where

$$\begin{aligned} D\left(R_{AB}\right) &= e^2{}_1\langle\phi_A \mid {}_2\langle\phi_B \mid \Big(\frac{1}{r_{12}} + \frac{1}{R_{AB}}\\ &- \frac{1}{r_{A2}} - \frac{1}{r_{B1}}\Big) \mid \phi_A\rangle_1 \mid \phi_B\rangle_2 \qquad (5.77) \end{aligned}$$

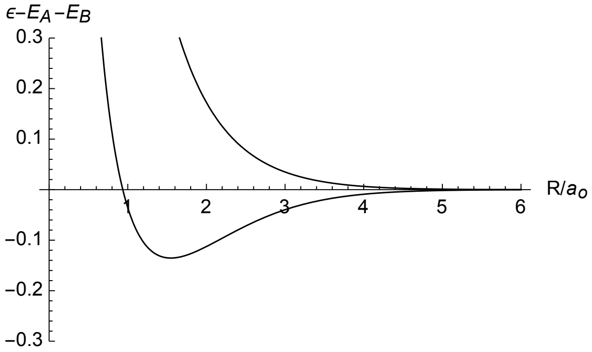

Figure 5.3: Simplified ground state theory for H_2. The bonding curve corresponds to the singlet (I) and the non-bonding curve to the triplet (III) spin state. Note that the exchange integral here was replaced by $|K|^2/a$, where $a = 2$ (cf. problem 37). Note that the binding energy of about 3.7 eV and the bond length of 0.82 Å are in fair agreement with the experimental values 4.75 eV and 0.74 Å.

is the direct Coulomb energy, and

$$\begin{aligned} A\left(R_{AB}\right) &= e^2\,{}_1\langle\phi_A\mid{}_2\langle\phi_B\mid\Big(\frac{1}{r_{12}}+\frac{1}{R_{AB}} \\ &- \frac{1}{r_{A2}}-\frac{1}{r_{B1}}\Big)\mid\phi_A\rangle_2\mid\phi_B\rangle_1 \end{aligned} \quad (5.78)$$

is an exchange interaction. Computing these expressions in $\vec{r}$-representation yields, for the ground state $(A) = (B) = (1,0,0)$, the curves shown in figure 5.3 (cf. problem 37). Notice that I corresponds to the symmetric spatial part of the wave function, whereas III corresponds to the anti-symmetric part. The latter yields a smaller probability for finding the electrons, between the nuclei. Here this leads to a larger nuclear repulsion. In the other case there is an attraction, which yields a minimum and thus a stable chemical bond.

The Hellmann-Feynman theorem:

Consider a system with a time-independent Hamiltonian $\underline{\mathcal{H}}$ that involves parameters $\lambda_i\,(i=1,\ldots)$. An example is the harmonic oscillator, where the force constant is such a parameter. It is then relatively easy to prove the generalized Hellmann-Feynman theorem:

$$\frac{\partial E_n}{\partial\lambda} = \int \psi_n^*\frac{\partial\underline{\mathcal{H}}}{\partial\lambda}\psi_n d^3r\ . \quad (5.79)$$

Here the ψ_n and E_n are eigenfunctions and eigenvalues of $\underline{\mathcal{H}}$, which in this case depends only on one parameter, λ. Notice that ψ_n also depends on λ (cf. [23]; section 14.3)!

An important application of Eq. (5.79) is the electrostatic theorem. This theorem, which is based on the Born-Oppenheimer approximation, reads:

$$\begin{aligned} \vec{\mathcal{F}}_i &= -\vec{\nabla}_i\Big[\sum_{i<j}\frac{q_iq_j}{\vec{r}_{ij}} \\ &+\int\rho_E\left(\vec{\tau};l\right)\frac{q_i}{\mid\vec{\tau}-\vec{r}_i\mid}d^3\tau\Big]\ . \end{aligned} \quad (5.80)$$

Here q_i is the charge on nucleus i, and $\rho_E\left(\vec{\tau};l\right)$ is the quantum electron density in the electronic state l. Thus, the effective force acting on a nucleus i in a molecule, $\vec{\mathcal{F}}_i$, can be calculated by simple electrostatics as the sum of the Coulombic forces exerted by other nuclei and by a hypothetical electron cloud, whose charge density, $\rho_E\left(\vec{\tau};l\right)$, is found by solving the electronic Schrödinger equation. Again, the reader is referred to [23] (section 14.4) for the details. Notice that this theorem opens up a way to do dynamic calculations at temperatures $T > 0$ (cf. R. Hentschke et al., Molekulares Modellieren mit Kraftfeldern).

5.6 Quantum mechanics in chemistry

In the late 1920s Dirac remarked: ”The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are . . . completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be solved”. In 1998 Walter Kohn and John Anthony Pople received the Nobel prize in Chemistry for their contribution to the falsification of the latter part of Dirac’s statement. Both Kohn and Pople were honored for their work on (computational) quantum chemistry made possible due to the advances in computer technology, which of course Dirac could not have foreseen.

[24] Quantum mechanics describes molecules in terms of interactions among nuclei and electrons, and molecular geometry in terms of minimum energy arrangements of nuclei. All quantum mechanical methods ultimately trace back to the Schrödinger equation, which for the special case of the hydrogen atom may be solved exactly (as we have done in section 1.4). Wave functions for the hydrogen atom are the s, p, d, … atomic orbitals, familiar to most chemists. The square of the wave function times a small volume gives the probability of finding the electron inside the volume. This is termed the total electron density (or more simply the electron density), and corresponds to the electron density measured in an X-ray diffraction experiment. It is straightforward to generalize the Schrödinger equation to a multinuclear, multielectron system:

$$\underline{\mathcal{H}}\Psi = E\Psi \tag{5.81}$$

Here, Ψ is a many-electron wave function, and $\underline{\mathcal{H}}$ is

$$\begin{aligned}\underline{\mathcal{H}} \;=\; & -\frac{\hbar^2}{2}\sum_{A}^{\text{nuclei}}\frac{1}{M_A}\vec{\nabla}_A^2 - \frac{\hbar^2}{2m}\sum_{a}^{\text{electrons}}\vec{\nabla}_a^2 \\ & -e^2\sum_{A}^{\text{nuclei}}\sum_{a}^{\text{electrons}}\frac{Z_A}{r_{Aa}} \\ & +e^2\sum_{A>B}^{\text{nuclei}}\frac{Z_A Z_B}{R_{AB}} + e^2\sum_{a>b}^{\text{electrons}}\frac{1}{r_{ab}}\end{aligned} \tag{5.82}$$

The first two terms in (5.82) describe the kinetic energy of the nuclei, A, and the electrons, a, respectively, and the last three terms describe Coulombic interactions between particles. M are nuclear masses, and R_{AB}, r_{ab} and r_{Aa} are distances separating nuclei, electrons, and nuclei and electrons, respectively.

Unfortunately, the many-electron Schrödinger equation cannot be solved exactly (or at least has not been solved) even for the simplest many-electron system. Approximations need to be introduced to provide practical methods.

Born-Oppenheimer approximation:

One way to simplify the Schrödinger equation for molecular systems is to assume that the nuclei do not move. This is termed the Born-Oppenheimer approximation, and leads to an "electronic" Schrödinger equation:

$$\underline{\mathcal{H}}^{el}\Psi^{el} = E^{el}\Psi^{el} \,, \tag{5.83}$$

where

$$\begin{aligned}\underline{\mathcal{H}}^{el} \;=\; & \frac{-\hbar^2}{2m}\sum_{a}^{\text{electrons}}\vec{\nabla}_a^2 \\ & -e^2\sum_{A}^{\text{nuclei}}\sum_{a}^{\text{electrons}}\frac{Z_A}{r_{Aa}} \\ & +e^2\sum_{a>b}^{\text{electrons}}\frac{1}{r_{ab}} \,.\end{aligned}$$

The term in (5.82) describing the nuclear kinetic energy is missing in (5.83) (it is zero), and the nuclear-nuclear Coulomb term is a constant. It needs to be added to the electronic energy, E^{el}, to yield the total energy, E, for the system.

$$E = E^{el} + e^2\sum_{A>B}^{\text{nuclei}}\frac{Z_A Z_B}{R_{AB}}$$

Note that there is no reference to (nuclear) mass in the electronic Schrödinger equation. Mass effects (isotope effects) on molecular properties and chemical reactivities are of different origin. Even with the Born-Oppenheimer approximation, the Schrödinger equation is not solvable for more than a single electron. Additional approximations need to be made.

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[24] The following section largely is taken from W.J. Hehre, J. Yu, P. E. Klunzinger, and L. Lou (1998) *A brief guide to Molecular Mechanics and Quantum Chemical calculations.* wave function, Inc. It is supposed to provide a brief outline of 'Quantum Chemistry for beginners' without going into details, which is not possible in a single course on introductory quantum theory. Nevertheless, I have added additional detail indicated by (*) – and I continue to do so as these lecture notes evolve. For the interested reader I recommend references [23] and [24]. In Wuppertal courses in quantum chemistry currently are offered by Prof. Jensen in Chemistry.

$^{(*)}$Spatial orbitals and spin orbitals:

To completely describe an electron, it is necessary to specify its spin. A complete set for describing the spin of an electron in the following consists of the two orthonormal functions $\alpha(w)$ and $\beta(w)$; i.e. spin up (↑) and spin down (↓) [25]. The wave function for an electron that describes both its spatial distribution and its spin is a spin orbital, $\chi(\vec{x})$, where $\vec{x}$ indicates both space and spin coordinates ($\vec{x}=\{\vec{r},w\}$). From each spatial orbital, $\psi(\vec{r})$, one can form two different spin orbitals, i.e.

$$\chi(\vec{x}) = \begin{cases} \psi(\vec{r})\,\alpha(w) \\ \psi(\vec{r})\,\beta(w) \end{cases}$$

Given a set of K spatial orbitals, $\{\psi_i \mid i = 1,2,\ldots,K\}$, one can thus form a set of $2K$ spin orbitals $\{\chi_i \mid i=1,2,\ldots,2K\}$ via

$$\begin{aligned} \chi_{2i-1}(\vec{x}) &= \psi_i(\vec{r})\,\alpha(w) \\ \chi_{2i}(\vec{x}) &= \psi_i(\vec{r})\,\beta(w) \end{aligned}$$

where $i=1,2,\ldots,K$.

$^{(*)}$Slater determinants:

We now consider wave functions for a collection of electrons, i.e., N-electron wave functions. We begin by defining a Hartree product:

$$\Psi^{HP}(\vec{x}_1,\vec{x}_2,\ldots,\vec{x}_N) = \chi_i(\vec{x}_1)\,\chi_j(\vec{x}_2)\ldots\chi_k(\vec{x}_N)\ .$$

Notice that Ψ^{HP} is the solution of

$$\underline{\mathcal{H}}\Psi^{HP} = E\Psi^{HP}\ ,$$

where

$$\underline{\mathcal{H}} = \sum_{i=1}^{N} \underline{h}(i)$$

and

$$E = \epsilon_i + \epsilon_j + \ldots + \epsilon_k\ .$$

Here $\underline{h}(i)$ is the Hamilton operator describing electron i.

The Hartree product does not satisfy the antisymmetry principle, however. We can obtain correctly antisymmetrical wave functions using so called Slater determinants(SD). For instance in the two electron case we may write

$$\begin{aligned} \Psi(\vec{x}_1,\vec{x}_2) &= \frac{1}{\sqrt{2}} \begin{vmatrix} \chi_i(\vec{x}_1) & \chi_j(\vec{x}_1) \\ \chi_i(\vec{x}_2) & \chi_j(\vec{x}_2) \end{vmatrix} \qquad (5.84) \\ &= \frac{1}{\sqrt{2}}\big(\chi_i(\vec{x}_1)\,\chi_j(\vec{x}_2) - \chi_i(\vec{x}_2)\,\chi_j(\vec{x}_1)\big)\ . \end{aligned}$$

The generalization to N electrons is straightforward:

$$\Psi(\vec{x}_1,\vec{x}_2,\ldots,\vec{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_i(\vec{x}_1) & \chi_j(\vec{x}_1) & \cdots & \chi_k(\vec{x}_1) \\ \chi_i(\vec{x}_2) & \chi_j(\vec{x}_2) & \cdots & \chi_k(\vec{x}_2) \\ \vdots & \vdots & & \vdots \\ \chi_i(\vec{x}_N) & \chi_j(\vec{x}_N) & \cdots & \chi_k(\vec{x}_N) \end{vmatrix}\ .$$

Interchanging the coordinates of two electrons corresponds to interchanging two rows in the SD, which changes its sign. Notice also that having two electrons occupying the same spin orbital corresponds to having two identical rows in the SD which makes it zero. Thus, the SD meets both the antisymmetry requirement and the Pauli principle.

It is convenient to introduce a short-hand notation for a normalized SD:

$$\begin{aligned} \Psi(\vec{x}_1,\vec{x}_2,\ldots,\vec{x}_N) & \qquad (5.85) \\ = \mid \chi_i(\vec{x}_1)\,\chi_j(\vec{x}_2)\cdots\chi_k(\vec{x}_N)\rangle\ . \end{aligned}$$

If we always choose the electron labels to be in the order, $\vec{x}_1,\vec{x}_2,\vec{x}_3,\ldots,\vec{x}_N$, then Eq. (5.85) can be further shortened to

$$\Psi(\vec{x}_1,\vec{x}_2,\ldots,\vec{x}_N) = \mid \chi_i\chi_j\ldots\chi_k\rangle$$

[26].

---

[25] $\alpha(w)$ and $\beta(w)$ are analogous to the $\vec{r}$-representation of the spatial wave function.

[26] This terminology, which we analyse in this chapter, is not to be confused with the multiparticle state vectors introduced previously!

$^{(*)}$Exchange correlation:

We consider the 2-electron wave function,

$$\Psi\left(\vec{x}_1, \vec{x}_2\right) = \mid \chi_1\left(\vec{x}_1\right) \chi_2\left(\vec{x}_2\right)\rangle \ ,$$

to compare two situations –
a) the two electrons have opposite spins and occupy different spatial orbitals:

$$\begin{aligned} \chi_1\left(\vec{x}_1\right) &= \psi_1\left(\vec{r}_1\right) \alpha\left(\vec{w}_1\right) \\ \chi_2\left(\vec{x}_2\right) &= \psi_2\left(\vec{r}_2\right) \beta\left(w_2\right) \ . \end{aligned} \qquad (5.86)$$

b) the two electrons have the same spin (say β) and occupy different spatial orbitals:

$$\begin{aligned} \chi_1\left(\vec{x}\right) &= \psi_1\left(\vec{r}_1\right) \beta\left(w_1\right) \\ \chi_2\left(\vec{x}\right) &= \psi_2\left(\vec{r}_2\right) \beta\left(w_2\right) \ . \end{aligned} \qquad (5.87)$$

We are interested in the quantity $P\left(\vec{r}_1, \vec{r}_2\right) d^3r_1 d^3r_2$, which is the simultaneous probability of finding electron one in the volume element d^3r_1 at $\vec{r}_1$ and electron two in the volume element d^3r_2 at $\vec{r}_2$:

$$P\left(\vec{r}_1, \vec{r}_2\right) d^3r_1 d^3r_2 = \int dw_1 dw_2 \mid \Psi \mid^2 d^3r_1 d^3r_2 \ .$$

Using Eq. (5.84) we have

$$\begin{aligned} \mid \Psi \mid^2 = \frac{1}{2}\Big| &\psi_1\left(\vec{r}_1\right) \alpha\left(w_1\right) \psi_2\left(\vec{r}_2\right) \beta\left(w_2\right) \\ &- \psi_2\left(\vec{r}_1\right) \beta\left(w_1\right) \psi_1\left(\vec{r}_2\right) \alpha\left(w_2\right) \Big|^2 \ . \end{aligned}$$

Now we apply

$$\int dw \alpha^*\left(w\right) \beta\left(w\right) = \int dw \beta^*\left(w\right) \alpha\left(w\right) = 0$$

to obtain for (a)

$$\begin{aligned} P\left(\vec{r}_1, \vec{r}_2\right) d^3r_1 d^3r_2 = \frac{1}{2}\Big[&\mid \psi_1\left(\vec{r}_1\right) \mid^2 \mid \psi_2\left(\vec{r}_2\right) \mid^2 \\ &+ \mid \psi_2\left(\vec{r}_1\right) \mid^2 \mid \psi_1\left(\vec{r}_2\right) \mid^2 \Big] d^3r_1 d^3r_2 \ . \end{aligned}$$

In particular for $\psi_1 = \psi_2$ we find

$$P\left(\vec{r}_1, \vec{r}_2\right) = \mid \psi_1\left(\vec{r}_1\right) \mid^2 \mid \psi_1\left(\vec{r}_2\right) \mid^2 \ .$$

Here $P\left(\vec{r}_1, \vec{r}_2\right) \neq 0$ even if the electrons have the same $\vec{r}$. This is completely different in case (b), which is

$$\begin{aligned} P\left(\vec{r}_1, \vec{r}_2\right) = \frac{1}{2}\Big\{ &\mid \psi_1\left(\vec{r}_1\right) \mid^2 \mid \psi_2\left(\vec{r}_2\right) \mid^2 \\ &+ \mid \psi_2\left(\vec{r}_1\right) \mid^2 \mid \psi_1\left(\vec{r}_2\right) \mid^2 \\ &- \big[\psi_1^*(\vec{r}_1)\psi_2(\vec{r}_1)\psi_2^*(\vec{r}_2)\psi_1(\vec{r}_2) \\ &+ \psi_1(\vec{r}_1)\psi_2^*(\vec{r}_1)\psi_2(\vec{r}_2)\psi_1^*(\vec{r}_2)\big]\Big\} \ . \end{aligned}$$

Notice that now $P\left(\vec{r}_1, \vec{r}_2\right) = 0$ if $\psi_1 = \psi_2$ as expected. In addition we also find $P\left(\vec{r}_1, \vec{r}_2 \rightarrow \vec{r}_1\right) \rightarrow 0$. A Fermi hole is said to exist around an electron. The electrons are correlated.

A simple example consists of two spinless non-interacting fermions in the potential well of the 1D harmonic oscillator. The ground state wave function of this system is

$$\Psi_0\left(q_1, q_2\right) = \frac{1}{\sqrt{2}}\Big(\psi_0\left(q_1\right) \psi_1\left(q_2\right) - \psi_0\left(q_2\right) \psi_1\left(q_1\right)\Big) \ ,$$

where

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

and

$$\psi_1\left(q\right) = \frac{\sqrt{2}}{\pi^{1/4}} q \exp\left[-q^2/2\right]$$

(cf. (1.71); $q = \sqrt{mw/\hbar x}$). We are interested in the probability density $P_F\left(\Delta q\right)$, that the two fermions are separated by a distance Δq, i.e.

$$\begin{aligned} P_F\left(\Delta q\right) &= \int_{-\infty}^{\infty} dq_1 dq_2 \mid \Psi_0\left(q_1, q_2\right) \mid^2 \Big|_{\Delta q = const} \\ &= \frac{1}{2}\int_{-\infty}^{\infty} dQ \Psi_0^2\left(\Delta q, Q\right) \ . \end{aligned}$$

Here $\Delta q = q_1 - q_2$ and $Q = q_1 + q_2$. Notice also that $d\Delta q dQ = 2dq_1 dq_2$. Using

$$\Psi_0(q_1,q_2)=\frac{1}{\pi^{1/2}}(q_2-q_1)\exp\left[-\frac{1}{2}\left(q_1^2+q_2^2\right)\right]$$

together with $\Delta q^2+Q^2=2\left(q_1^2+q_2^2\right)$ we find

$$P_F(\Delta q)=\frac{1}{\sqrt{2\pi}}\Delta q^2\exp\left[-\frac{1}{2}\Delta q^2\right]$$

Fig. 5.4 shows $P_F(\Delta q)$ vs. Δq. For $\Delta q\to\pm\infty$ the oscillator potential governs the behavior of $P_F(\Delta q)$. The minimum at $\Delta q=0$, however, is an effect entirely due to the exchange symmetry of fermions. The same figure shows $P_B(\Delta q)$, the analogous probability density for two non-interacting spinless bosons. Here the ground state wave function is

$$\Psi_0(q_1,q_2)=\frac{1}{2}\Big(\psi_0(q_1)\,\psi_0(q_2)+\psi_0(q_2)\,\psi_0(q_1)\Big)\ .$$

No Fermi hole is observed for the bosons.

Remark: Obviously, the basic mechanism at work in this example also causes the statistical potential in Fig. 5.1. The main difference is temperature. In this example the temperature is zero, i.e. $P_F(\Delta q=0)=0$ corresponds to an infinitely repulsive statistical potential at the origin in Fig. 5.1.

Hartree-Fock approximation:

The most obvious simplification to the Schrödinger equation involves separation of variables, that is, replacement of the many-electron wave function by a product of one-electron wave functions. The simplest acceptable replacement, termed a Hartree-Fock [27] or single-determinant wave function, involves a single determinant of products of one-electron spin orbitals. The Hartree-Fock approximation leads to a set of coupled differential equations (the Hartree-Fock equations), each involving a single electron. While they may be solved numerically, it is advantageous to first introduce one additional approximation.

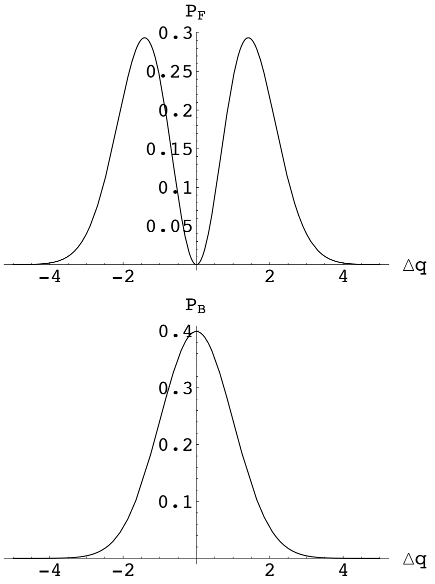


Figure 5.4: Top: Illustration of the Fermi hole for two spinless and non-interacting fermions in a 1D harmonic oscillator potential. Bottom: The analogous probability density, P_B, plotted for two spinless and non-interacting bosons.

$^{(*)}$The Hartree-Fock theory is based on the variation method which we have discussed in section 4.4. Our goal is it to find a set of spin orbitals $\{\chi_a\}$ such that the single determinant formed from these spin orbitals $\mid\psi_0\rangle=\mid\chi_1\chi_2\ldots\chi_a\chi_b\ldots\chi_N\big)$ is the best possible approximation to the ground state of the N-electron system described by the electronic Hamiltonian $\underline{\mathcal{H}}^{el}$. According to the variation principle, the "spin" orbitals are those which minimize the electronic energy

$$\begin{aligned}E_0 &= \langle\psi_0\mid\underline{\mathcal{H}}^{el}\mid\psi_0\rangle\\ &= \sum_a\langle a\mid\underline{h}\mid a\rangle+\frac{1}{2}\sum_{a,b}\{[aa\mid bb]-[ab\mid ba]\}\ ,\end{aligned}$$

where

$$[ij\mid kl]:=\int d\vec{x}_1d\vec{x}_2\chi_i^*(\vec{x}_1)\,\chi_j(\vec{x}_1)\,r_{12}^{-1}\chi_k^*(\vec{x}_2)\,\chi_l(\vec{x}_2)\ .$$

---

[27] Hartree, Douglas Rayner, british physicist and mathematician, *Cambridge 27.3.1897, †Cambridge 12.2.1958; important contributions to the quantum theory of many-electron systems (quantum chemistry).

Using the variation method we can systematically vary the spin orbitals $\{\chi_a\}$, constraining them only to the extend that they remain orthonormal,

$$\langle \chi_a \mid \chi_b \rangle = \delta_{ab}$$

until E_0 is a minimum. The resulting equation is the Hartree-Fock integro-differential equation

$$\begin{aligned} \underline{h}\,(1)\,\chi_a\,(1) + \sum_{b(\neq a)} \left[\int d\vec{x}_2 \mid \chi_b\,(2) \mid^2 r_{12}^{-1} \right] \chi_a\,(1) \\ - \sum_{b(\neq a)} \left[\int d\vec{x}_2 \chi_b^*\,(2)\, \chi_a\,(2)\, r_{12}^{-1} \right] \chi_b\,(1) \\ = \epsilon_a \chi_a\,(1) \ , \end{aligned}$$

where

$$\underline{h}\,(1) = -\frac{1}{2}\nabla_1^2 - \sum_a \frac{Z_A}{r_{1A}}$$

is the kinetic energy and potential energy for attraction to the nuclei, of a single electron chosen to be electron-one. The orbital energy of the spin orbital χ_a is ϵ_a.

LCAO approximation:

This follows from the notion that the one-electron solutions for many electron molecules will closely resemble the (one-electron) solutions for the hydrogen atom. This seems entirely reasonable. Since molecules are made up of atoms, why shouldn't molecular solutions be made up of atomic solutions? In practice, the molecular orbitals are expressed as linear combinations of a finite set (a basis set) of prescribed functions known as basis functions, ϕ:

$$\psi_i = \sum_{\mu}^{\text{basis functions}} c_{\mu i} \phi_\mu \ . \tag{5.88}$$

c are the molecular orbital coefficients, often referred to simply (and incorrectly) as the molecular orbitals. Because the ϕ are usually centered at the nuclear positions (although they do not need to be),

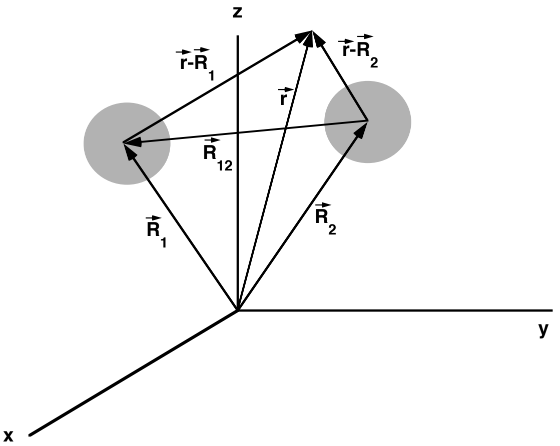


Figure 5.5: Coordinate system for minimal basis H_2.

they are referred to as atomic orbitals, and expansion (5.88) is termed Linear Combination of Atomic Orbitals or LCAO approximation.

$^{(*)}$ We illustrate the LCAO approximation using the hydrogen molecule. Each hydrogen atom has a $1s$ orbital and, as the two atoms approach, molecular orbitals (MOs) may be constructed via linear combination of the atomic orbitals (LCAO). The coordinate system is shown in Fig. (5.5). The first atomic orbital, $\phi_1 = \phi_1(\vec{r} - \vec{R}_1)$, is centered on nucleus 1 at $\vec{R}_1$. The second atomic orbital, $\phi_2 = \phi_2(\vec{r} - \vec{R}_2)$, is centered on nucleus 2 at $\vec{R}_2$. The exact $1s$ orbital of a hydrogen atom centered at $\vec{R}$ has the form

$$\phi(\vec{r} - \vec{R}) = (\zeta^3/\pi)^{1/2} \exp[-\zeta|\vec{r} - \vec{R}|]$$

(cf. Eq. (1.112)). Here ζ, the orbital exponent, has a value of 1.0. This is an example of a Slater orbital. In praxis, however, Gaussian orbitals are used, because the evaluation of the relevant integrals is computationally less demanding. The 1s Gaussian orbital has the form

$$\phi(\vec{r} - \vec{R}) = (2\alpha/\pi)^{3/4} \exp[-\alpha|\vec{r} - \vec{R}|^2] \ ,$$

where α is the Gaussian orbital exponent. Here we need not be concerned with the particular form of the $1s$ atomic orbitals. The two atomic orbitals ϕ_1

and ϕ_2 can be assumed to be normalized, but they will not be orthogonal. They will overlap, and the overlap integral is

$$K_{12} = \int d^3r \phi_1^*(\vec{r})\phi_2(\vec{r})$$

(cf. Eq. (5.71)). From the two localized atomic orbitals, ϕ_1 and ϕ_2 one can form, by linear combination, two delocalized molecular orbitals. The symmetric combination leads to a bonding MO of *gerade* symmetry,

$$\psi_1 = \frac{1}{\sqrt{2(1+K_{12})}} \left(\phi_1(\vec{r}) + \phi_2(\vec{r})\right)$$

whereas the antisymmetric combination leads to an antibonding MO of *ungerade* symmetry

$$\psi_1 = \frac{1}{\sqrt{2(1-K_{12})}} \left(\phi_1(\vec{r}) - \phi_2(\vec{r})\right) \ .$$

Using only two basis functions for H_2 is an example of a minimal basis set and an obvious choice for the two functions ϕ_1 and ϕ_2 is the 1s atomic orbitals of the atoms. The correct linear combination for this simple choice are determined by symmetry.

Given the two spatial orbitals ψ_1 and ψ_2, we can form four spin orbitals

$$\begin{aligned}
\chi_1(\vec{x}) &= \psi_1\alpha(w) \\
\chi_2(\vec{x}) &= \psi_1\beta(w) \\
\chi_3(\vec{x}) &= \psi_2\alpha(w) \\
\chi_4(\vec{x}) &= \psi_2\beta(w) \ .
\end{aligned}$$

The orbital energies associated with these spin orbitals must be obtained via explicit calculation. But, as might be expected, χ_1 and χ_2 are degenerate and have the lower energy corresponding to a bonding situation, while χ_3 and χ_4 are also degenerate having a higher energy corresponding to an antibonding situation. The Hartree-Fock ground state in this model is the single determinant

$$|\psi_o\rangle = | \chi_1\chi_2)$$

shown pictorially in Fig. 5.6.

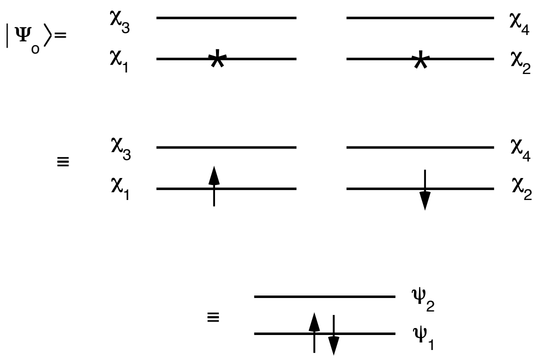


Figure 5.6: Different representations of the Hartree-Fock ground state of minimal basis H_2.

Roothaan-Hall equations:

The Hartree-Fock and LCAO approximations, taken together and applied to the electronic Schrödinger equation, lead to the Roothaan-Hall equations:

$$\sum_{\nu}^{\text{basis functions}} \left(F_{\mu\nu} - \epsilon_i K_{\mu\nu}\right) c_{\nu i} = 0 \ .$$

Here, ϵ are orbital energies, $\underline{K}$ is the overlap matrix (a measure of the extent to which basis functions "see each other"), and $\underline{F}$ is the Fock matrix, which is analogous to the Hamiltonian in the Schrödinger equation. In atomic units it is given by

$$\begin{aligned}
F_{\mu\nu} = \langle \phi_\mu \mid -\frac{1}{2}\vec{\nabla}^2 - \sum_{A}^{\text{nuclei}} \frac{Z_A}{r_A} \mid \phi_\nu \rangle + \\
\sum_{\lambda,\sigma}^{\text{basis functions}} P_{\lambda\sigma}\Big[\langle \phi_\mu\phi_\nu \mid \phi_\lambda\phi_\sigma\rangle \\
-\frac{1}{2}\langle \phi_\mu\phi_\lambda \mid \phi_\nu\phi_\sigma\rangle\Big] \ . \qquad (5.89)
\end{aligned}$$

The first term in (5.89) accounts for the kinetic and potential energies of individual electrons, while the second term accounts for interactions among electrons. $\underline{P}$ is the so-called density matrix, the elements of which involve the square of the molecular orbital coefficients summed over all occupied molecular orbitals:

$$P_{\lambda\sigma} = 2 \sum_{i}^{\text{occupied molecular orbitals}} c^*_{\lambda i} c_{\sigma i}$$

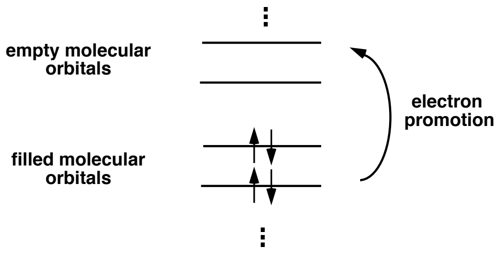
Methods resulting from solution of the Roothaan-Hall equations are termed Hartree-Fock or ab initio models. The corresponding energy for an infinite (complete) basis set is termed the Hartree-Fock energy. The Hartree-Fock energy is not equal to the experimental energy.

Correlated models:

Hartree-Fock models treat the motions individual electrons as independent of one another. Because of this, electrons "get in each others way" to a greater extent than they should. This leads to overestimation of the electron-electron repulsion energy and to too a high a total energy. Electron correlation, as it is termed, accounts for coupling of electron motions, and leads to a lessening of the electron-electron repulsion energy (and to a lowering of the overall total energy). The correlation energy is defined as the difference between the Hartree-Fock energy and the experimental energy.

Möller-Plesset models:

A number of methods have been developed to account for electron correlation. With the exception of so-called density functional methods (see discussion following), these generally involve mixing the ground state (Hartree-Fock) wave function with excited state wave functions. Operationally, this entails implicit or explicit promotion of electrons from molecular orbitals which are occupied in the Hartree-Fock wave function to molecular orbitals which are unoccupied.



Among the simplest practical schemes are Möller-Plesset models which are formulated in terms of a generalized electronic Hamiltonian, $\underline{\mathcal{H}}_\lambda$, i.e.

$$\underline{\mathcal{H}}_\lambda = \underline{\mathcal{H}}_0 + \lambda \underline{\mathcal{W}} \, . \tag{5.90}$$

$\underline{\mathcal{H}}_0$ is defined such that different states do not interact. The "perturbation" $\underline{\mathcal{W}}$ is defined according to

$$\lambda \underline{\mathcal{W}} = \lambda \left(\underline{\mathcal{H}} - \underline{\mathcal{H}}_0 \right) \, . \tag{5.91}$$

$\underline{\mathcal{H}}$ is the correct Hamiltonian and λ is a dimensionless parameter. ψ_λ and E_λ, the wave function and energy for a system described by the Hamiltonian $\underline{\mathcal{H}}_\lambda$, may then be expanded in powers of λ, i.e.

$$\psi_\lambda = \psi^{(0)} + \lambda \psi^{(1)} + \lambda^2 \psi^{(2)} + \dots \tag{5.92}$$

$$E_\lambda = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \dots \, . \tag{5.93}$$

The Möller-Plesset energy to first order is the Hartree-Fock energy. The second-order Möller-Plesset energy, $E^{(2)}$, is given by

$$E^{(2)} = \overset{\text{molecular}}{\sum\sum_{i<j}^{\text{filled}}} \; \overset{\text{orbitals}}{\sum\sum_{a<b}^{\text{empty}}} \frac{[(ij \,||\, ab)]^2}{(\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j)} \, .$$

ϵ_i, ϵ_j are energies of filled molecular orbitals, ϵ_a, ϵ_b energies of empty molecular orbitals, and integrals $(ijab)$ account for changes in electron-electron interactions as a result of promotion. Möller-Plesset theory terminated to second-order, or MP2, is perhaps the simplest model based on electron promotion which offers improvement over Hartree-Fock theory. Higher-order models (MP3, MP4, etc.) have been formulated, but in practice are limited in application to very small systems.

$^{(*)}$ Fig. 5.7 shows the interaction energy of two methane molecules as function of the distance between their nuclei. This interaction energy can be obtained experimentally from thermodynamic data on the second virial coefficient of gaseous methane. The latter can be computed using the Lennard-Jones potential (4.28). In the case of methane one obtains for the parameters $\epsilon = 1.2364 \; kJmol^{-1}$

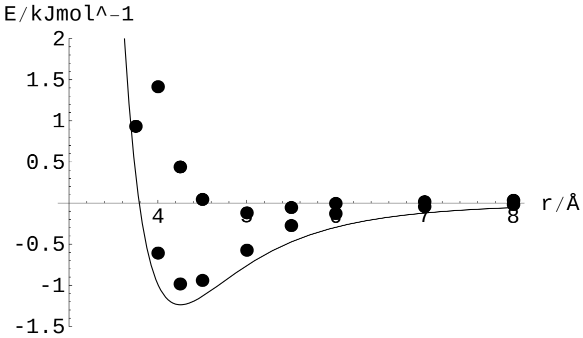


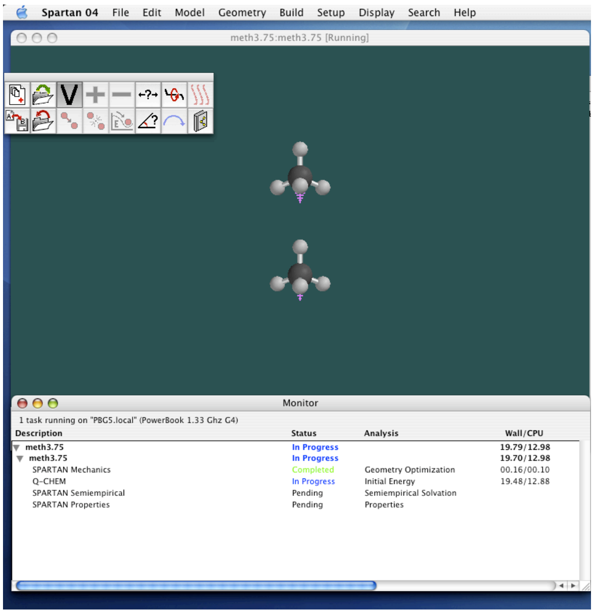
Figure 5.7: Comparison of the interaction energy of two methane molecules as function of the separation of their nuclei. Upper set of points: Hartree-Fock; lower set of points: MP2; solid curve Lennard-Jones potential.

and $\sigma = 3.79$ Å (cf. Anwendungsbeispiel III.2 in R. Hentschke et al. Molekulares Modellieren mit Kraftfeldern. http://constanze.materials.uni-wuppertal.de/skripten). Here we compare the result to a Hartree-Fock and a MP2 calculation performed with a commercial quantum chemistry package called *Spartan* (version 4; cf. Fig. 5.8). In both cased the $6-31G^*$ basis set is used. We see that MP2 already yields a significant improvement over Hartree-Fock. The results may be improved further by more extended basis sets or higher order MP-approximation. Note that the interaction energy displayed here is only about 10^{-4} of the total electronic energy of the molecules!

Density functional models:

Density functional models provide an alternative approach to the treatment of correlation in many-electron systems. They follow from a theorem, which states that the minimal energy of a collection of electrons under the influence of an external (Coulombic) field is a unique "functional" (a function of a function) of the electron density. To see how this theorem is put to practical use, first consider the energy of a many-electron system as given by Hartree-Fock theory:

$$\begin{aligned} E^{HF} &= E^{\text{nuclear}} + E^{\text{ core}} \\ &\quad + E^{\text{Coulomb}} + E^{\text{exchange}} \; . \end{aligned}$$



1 task running on "PBG5.local" (PowerBook 1.33 Ghz G4)

Description	Status	Analysis	Wall/CPU
meth3.75	In Progress		19.79/12.98
meth3.75	In Progress		19.70/12.98
SPARTAN Mechanics	Completed	Geometry Optimization	00.16/00.10
Q-CHEM	In Progress	Initial Energy	19.48/12.88
SPARTAN Semiempirical	Pending	Semiempirical Solvation	
SPARTAN Properties	Pending	Properties	

Figure 5.8: Computer screen shot showing the mathane molecules as displayed by *Spartan*.

Here, E^{nuclear} accounts for Coulombic repulsion of nuclei, E^{core} for both electron kinetic energy and Coulombic attraction between electrons and nuclei, and E^{Coulomb} for Coulombic repulsion of electrons. E^{exchange} also involves electron-electron interactions, and has the effect proceed, of reducing the size of the Coulomb term. The energy according to density functional theory includes the same nuclear, core and Coulomb terms as the Hartree-Fock energy, yet replaces the Hartree-Fock exchange energy by an exchange functional, $E^X(\rho)$, and adds a correlation functional, $E^C(\rho)$.

$$\begin{aligned} E^{DFT} &= E^{\text{nuclear}} + E^{\text{ core}} + E^{\text{Coulomb}} \\ &\quad + E^X(\rho) + E^C(\rho) \end{aligned}$$

Both of the latter are functions of the electron density, ρ. The simplest models are called local spin density or local density models, and will be referred to as SVWN (Slater, Vosko, Wilk, Nusair) models. Here, the form of the exchange and correlation functionals follows from the exact (numerical) solution of a many-electron gas of uniform density, as a function of the density, by subtracting $E^{\text{ core}}$ and $E^{\text{ Coulomb}}$ from the total energy (there is no $E^{\text{ nuclear}}$ term). The SVWN model would not be expected to be satisfactory for molecular systems where the electron density is non-uniform. The model may be improved by introducing explicit dependence on the account gradient of the electron density, in addition to the density itself. Such mirror procedures are termed gradient-corrected or non-local density model, functional models. An obvious way to do this, for the case where the density is a "slowly varying function", is in terms of a simple models power-series expansion. Unfortunately, such an approach leads to divergent behavior in the limit of large density gradients. An alternative is the so-called generalized gradient approximation those proposed by Becke and Perdew. In the Becke-Perdew (BP or BP86) model, a new potential is used in place of the local potential in the self-consistent field (SCF) procedure. This actually comprises a local part and a gradient correction. The latter needs to be recalculated at every SCF iteration. An alternative, and computationally simpler approach, is to introduce the gradient correction only after convergence based on the local potential alone has been achieved. This procedure, referred to as a perturbative Becke-Perdew model (or pBP), offers significant computational advantages over the corresponding self-consistent procedure. It yields nearly identical structures and relative energies to the full self-consistent BP model. The equations which result from both local density and self-consistent Becke-Perdew formulations may be solved iteratively by expanding the set of one-particle wave functions in terms of a set of basis functions centered on the individual nuclei. Note, however, that terms associated with the exchange and correlation functionals typically involve forms for which analytical expressions of the required integrals are either not available, or would be too complicated to deal with were they available. It is usually necessary to resort to numerical integration techniques. Because of this, calculated quantities show larger uncertainties than those from Hartree-Fock Coulomb and MP2 models. Total (and relative) energies should be accurate to 0.0002 hartrees (on the order of a tenth of a kcal/mol) and bond lengths accurate to 0.005 Å. Because density functional models take electron correlation into account in an explicit manner, resulting properties should more closely mirror those of conventional correlated models, such as the MP2 model, than those of Hartree-Fock models. That is to say, density functional results should be "better" than those from Hartree-Fock models. Because the energy is expressed as a function of a single "variable" (the electron density), the equations which result from application of density functional theory are conceptually simpler than those resulting from Hartree-Fock theory (where the "variables" are the set of one-electron wave functions). In fact, a density functional calculation scales (formally) as the cube of molecular size, compared to a (formal) fourth power dependence on size for a Hartree-Fock calculation. In practice, both density functional and Hartree-Fock calculations scale more slowly than the formal rules suggest.

Basis sets for HF and MP2 calculations:

For practical reasons, Hartree-Fock (HF) and MP2 calculations make use of basis sets of Gaussian-type functions (cf. above). These are closely related to exact solutions of the hydrogen atom, and comprise a polynomial in the Cartesian coordinates (x, y, z) followed by an exponential in r^2. Several series of Gaussian basis sets have now received widespread use and are thoroughly documented. Underlying these, are minimal (STO-3G) and split-valence (3-21G, 6-31G and 6-311G) representations. These may be supplemented by sets of polarization and/or diffuse functions.

STO-3G minimal basis set:

The simplest possible atomic orbital representation is termed a minimal basis set. This comprises only those functions required to accommodate all of the electrons of the atom, while still maintaining its overall spherical symmetry. In practice, this involves a single ($1s$) function for hydrogen and helium, and a set of five functions ($1s$, $2s$, $2p_x$, $2p_y$, $2p_z$) for lithium to neon. Note that, while $2p$ functions are not occupied in the lithium and beryllium atoms, they are required to provide proper descriptions in molecules.

Each of the basis functions in the STO-3G representation is expanded in terms of three Gaussians, where the values of the Gaussian exponents and the linear coefficients have been determined by least squares as best fits to Slater-type (exponential) functions.

There are two obvious shortcomings of a minimal basis set. The first is that all basis functions are either themselves spherical (s functions) or come in sets which, taken together, describe a sphere (p functions). As a consequence, molecules which incorporate only atoms with "spherical environments" or "nearly spherical environments" will be better described than molecules which incorporate atoms with "aspherical environments".

The second shortcoming follows from the fact that basis functions are atom centered. While this is not absolutely necessary, there are no other obvious (unambiguous) locations for the basis functions. The choice of atom-centered locations for the basis functions does, however restrict their flexibility to describe electron distributions between nuclei ("bonds").

Chapter 6

The quantized radiation field and second quantization

The following chapter contains merely a glimpse of what the title promises. Its main purpose is to take a look ahead at the next steps in the development of a quantum theory treating particles and fields on an equal footing.

6.1 Quantum theory of radiation

So far we have treated radiation fields as classical fields. Now we want to develop a quantum theoretical description. In order to find a good starting point we return to section 1.2, where we dealt with the black body problem. Notice that there is a striking similarity between Eq. (1.21), the classical field energy in the black body cavity expressed in terms of the Fourier-coefficients $c_{\vec{k},\alpha}$, and the Hamilton operator of the harmonic oscillator expressed in terms of the number operator $\underline{a}^+\underline{a}$ discussed in section 1.5! Thus, why not start by postulating that the $c_{\vec{k},\alpha}$ become operators $\underline{c}_{\vec{k},\alpha}$ obeying the commutator relations

$$\left[\underline{c}_{\vec{k},\alpha},\underline{c}^+_{\vec{k}',\alpha'}\right]=\delta_{\vec{k}\vec{k}'}\delta_{\alpha\alpha'} \tag{6.1}$$

and

$$\left[\underline{c}_{\vec{k},\alpha},\underline{c}_{\vec{k}',\alpha'}\right]=\left[\underline{c}^+_{\vec{k},\alpha},\underline{c}^+_{\vec{k}',\alpha'}\right]=0\,. \tag{6.2}$$

In order to write down the Hamilton operator describing the radiation field we do not use (1.21) directly. Instead we use the expression,

$$E=\sum_{\vec{k},\alpha}\frac{\omega^2}{4\pi c^2}\left(c^*_{\vec{k},\alpha}c_{\vec{k},\alpha}+c_{\vec{k},\alpha}c^*_{\vec{k},\alpha}\right)\,, \tag{6.3}$$

which in problem 4 was combined to obtain (1.21), because we now pay attention to (6.1). In addition we absorb a factor $\sqrt{\frac{\omega}{2\pi c^2\hbar}}$ in $\underline{c}_{\vec{k},\alpha}$ and $\underline{c}^+_{\vec{k},\alpha}$, i.e. $\sqrt{\frac{\omega}{2\pi c^2\hbar}}c_{\vec{k},\alpha}\rightarrow\underline{c}_{\vec{k},\alpha}$ and $\sqrt{\frac{\omega}{2\pi c^2\hbar}}c^*_{\vec{k},\alpha}\rightarrow\underline{c}^+_{\vec{k},\alpha}$, to obtain the Hamilton operator

$$\begin{aligned}\underline{\mathcal{H}}&=\sum_{\vec{k},\alpha}\frac{\hbar\omega}{2}\left(\underline{c}^+_{\vec{k},\alpha}\underline{c}_{\vec{k},\alpha}+\underline{c}_{\vec{k},\alpha}\underline{c}^+_{\vec{k},\alpha}\right) &(6.4)\\&\overset{(6.1)}{=}\sum_{\vec{k},\alpha}\hbar\omega\Big(\underbrace{\underline{c}^+_{\vec{k},\alpha}\underline{c}_{\vec{k},\alpha}}_{\equiv\underline{n}_{\vec{k},\alpha}}+\frac{1}{2}\Big)\,.\end{aligned}$$

Notice that $\sum_{\vec{k},\alpha}\frac{1}{2}\hbar\omega$ is the zero-point energy of the radiation field, which, as we have discussed already, is infinite. In our treatment of the black body radiation this did not matter, but there are cases when it does [1]. The quantity $\underline{n}_{\vec{k},\alpha}$ is a number operator counting the number of photons of type $(\vec{k},\alpha)$ in the volume (of the cavity) at time t. The state vector is given by

$$|\ldots,n_{\vec{k},\alpha},\ldots,n_{\vec{k}',\alpha'},\ldots\rangle\,, \tag{6.5}$$

i.e.

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[1] see appendix C

$$\begin{aligned}&\underline{c}^{+}_{\vec{k},\alpha} \mid \ldots, n_{\vec{k},\alpha}, \ldots\rangle = \\ &\sqrt{n_{\vec{k},\alpha}+1} \mid \ldots, n_{\vec{k},\alpha}+1, \ldots\rangle\end{aligned} \tag{6.6}$$

creates a photon, analogously $\underline{c}_{\vec{k},\alpha}$, annihilates a photon, whereas

$$\underline{n}_{\vec{k},\alpha} \mid \ldots, n_{\vec{k},\alpha}, \ldots\rangle = n_{\vec{k},\alpha} \mid \ldots, n_{\vec{k},\alpha}, \ldots\rangle \tag{6.7}$$

counts their number (cf. section 1.5). From Eq. (6.7) we see that the photons in this formalism are bosons, because we can generate states for $n_{\vec{k},\alpha} = 0,\ 1,\ 2,\ \ldots$.

This quantization procedure looks appealing. But does it work? As a first check we want to find the momentum operator and its eigenvalues. From classical electrodynamics we know that the Poynting-Vector, $\vec{S} = \frac{c}{4\pi}\vec{E} \times \vec{H}$, represents the radiation energy per area and time leaving a volume containing the radiation field (cf. Eq. (2.65) in reference [15]). Consequently, because $\frac{|\vec{S}|}{c}$ is a energy density and using the energy-momentum relation $E = pc$ for photons, we get

$$\vec{p} = \int_V d^3r \frac{\vec{E} \times \vec{H}}{4\pi c} \tag{6.8}$$

for the classical momentum of the electromagnetic field. Via a calculation completely analogous to the one in problem 4 and after replacing the Fourier coefficients by operators, as we have done above, we find

$$\underline{\vec{p}} = \sum_{\vec{k},\alpha} \hbar\vec{k}\,\underline{c}^{+}_{\vec{k},\alpha}\underline{c}_{\vec{k},\alpha} = \sum_{\vec{k},\alpha} \hbar\vec{k}\,\underline{n}_{\vec{k},\alpha}\ . \tag{6.9}$$

Obviously the eigenvalues of this momentum operator, which follow from

$$\begin{aligned}\underline{\vec{p}} \mid \ldots, n_{\vec{k},\alpha}, \ldots\rangle &= \sum_{\vec{k}\,',\alpha\,'} \hbar\vec{k}\,'\underline{n}_{\vec{k}\,',\alpha\,'} \mid \ldots, n_{\vec{k},\alpha}, \ldots\rangle \\ &= \sum_{\vec{k}\,',\alpha\,'} \hbar\vec{k}\,' n_{\vec{k}\,',\alpha\,'} \mid \ldots, n_{\vec{k},\alpha}, \ldots\rangle\ ,\end{aligned} \tag{6.10}$$

are $\sum_{\vec{k},\alpha} \hbar\vec{k} n_{\vec{k},\alpha}$. This is consistent with our understanding of the radiation field as a collection of photons with momentum $\hbar\vec{k}$ and polarization direction described by α.

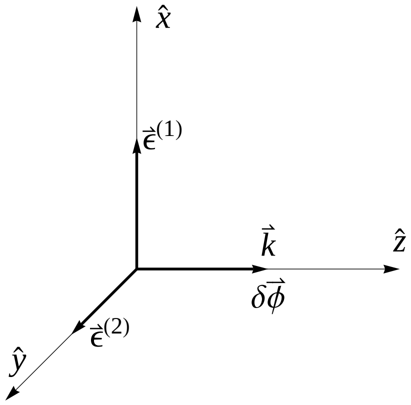

Figure 6.1: Relation between polarization basis vectors, $\vec{\epsilon}^{\,(1)} = (1, 0, 0)$ and $\vec{\epsilon}^{\,(2)} = (0, 1, 0)$, and photon momentum expressed via $\vec{k}$.

Remark 1: Notice that the relativistic energy-momentum relation (cf. [15], section 1.2) is given by

$$\begin{aligned}m^2 &= \frac{1}{c^4}\left(E^2 - \mid\vec{p}\mid^2 c^2\right) \\ &\overset{\text{photon}}{=} \frac{1}{c^4}\left((\hbar\omega)^2 - \left(\hbar \mid \vec{k} \mid c\right)^2\right) \\ &= 0\ ,\end{aligned} \tag{6.11}$$

i.e., the rest mass of the photon is zero.

Remark 2: The photon state is characterized not just by its momentum but also by the polarization basis vectors $\vec{\epsilon}^{\,(\alpha)}$ ($\alpha = 1, 2$) as depicted in Fig. 6.1. However, here we choose the complex basis

$$\vec{\epsilon}^{\,(\mp)} = \frac{1}{\sqrt{2}}\left(\vec{\epsilon}^{\,(1)} \mp i\vec{\epsilon}^{\,(2)}\right) \tag{6.12}$$

instead.

Under an infinitesimal rotation, $\delta\vec{\phi} = (0, 0, \delta\phi)$ (cf. Fig. 6.1), $\vec{\epsilon}^{\,(\mp)}$ changes according to

$$\delta\vec{\epsilon}^{\,(\mp)} = \delta\vec{\phi} \times \vec{\epsilon}^{\,(\mp)} = \pm i\delta\phi\vec{\epsilon}^{\,(\mp)}\ , \tag{6.13}$$

i.e.

$$\vec{\epsilon}^{(\mp)}(0) + \delta\vec{\epsilon}^{(\mp)} = (1 \pm i\delta\phi)\vec{\epsilon}^{(\mp)}(0)\ . \tag{6.14}$$

If we carry out n consecutive small rotations so that $\phi = n\delta\phi$, we can express the result as[2]

$$\vec{\epsilon}^{(\mp)}(\phi) = e^{\pm i\phi}\vec{\epsilon}^{(\mp)}(0)\ . \tag{6.15}$$

Let us interrupt for a moment and consider the change of a wave function ψ, likewise subject to a small rotation:

$$\begin{aligned}\delta\psi &= \delta\vec{r}\cdot\vec{\nabla}\psi = (\delta\vec{\phi}\times\vec{r})\cdot\vec{\nabla}\psi \\ &= \delta\vec{\phi}\cdot(\vec{r}\times\vec{\nabla})\psi = \frac{i}{\hbar}\delta\vec{\phi}\cdot\underline{\vec{L}}\psi\end{aligned} \tag{6.16}$$

or

$$\psi(0) + \delta\psi = (1 + \frac{i}{\hbar}\delta\vec{\phi}\cdot\underline{\vec{L}})\psi(0) \tag{6.17}$$

Notice that $\underline{\vec{L}}$ is the angular momentum operator. Again we add many infinitesimal rotations to obtain the full rotation angle ϕ, i.e.

$$\psi(\phi) = \exp[\frac{i}{\hbar}\vec{\phi}\cdot\underline{\vec{L}}]\psi(0) \tag{6.18}$$

(cf. problem 17). If the direction of the axis of rotation, defined by $\vec{\phi}$, is the along the z-axis, then

$$\psi(\phi) = \exp[\frac{i}{\hbar}\phi\underline{L}_z]\psi(0)\ , \tag{6.19}$$

i.e. the eigenvalues of $\exp[(i/\hbar)\phi\underline{L}_z]$ are

$$\exp[i\phi m]\ , \tag{6.20}$$

where m are the orientation quantum numbers of the angular momentum.

If we compare this result to Eq. (6.15), we can infer that the photon‘s intrinsic angular momentum comes in two orientations $m = \pm 1$ with respect to the quantization axis parallel to its propagation direction. Thus the photon spin is one. Notice that $m = +1$ belongs to the eigenstate $\vec{\epsilon}^{(-)}$ and $m = -1$ belongs to the eigenstate $\vec{\epsilon}^{(+)}$.

Notice also that the description of the polarization state with $\vec{\epsilon}^{(\mp)}$ as the base vectors is called circular polarization representation. We could have used $\vec{\epsilon}^{(\mp)}$ instead of $\vec{\epsilon}^{(1)}$ and $\vec{\epsilon}^{(2)}$ to expand $\vec{A}$ in problem 4. A single photon state with definite circular polarization can be constructed by applying the creation operator

$$\underline{c}^{+}_{\vec{k},\mp} = \frac{1}{\sqrt{2}}\left(\underline{c}^{+}_{\vec{k},1} \mp i\underline{c}^{+}_{\vec{k},2}\right) \tag{6.21}$$

to the vacuum state. Conversely, $\underline{c}_{\vec{k},\alpha} \mid 0\rangle$ with $\alpha = 1, 2$ and $\vec{k}$ in z-direction can be regarded as a 50/50 mixture of the $m = 1$ and $m = -1$ state.

Fluctuations and uncertainty:

It is easy to check that the quantities $\vec{A}$, $\vec{E}$, and $\vec{H}$ do not commute with $\underline{n}_{\vec{k},\alpha}$. As a consequence the number of photons and the aforementioned quantities cannot be measured simultaneously and exactly as we had shown in section 2.2. Explicitly we may take $\vec{E} = -\frac{1}{c}\frac{\partial\vec{A}}{\partial t}$ and calculate the vacuum fluctuation, i.e. no photon is present, of the electric field:

$$\langle 0 \mid \underline{\vec{E}}\cdot\underline{\vec{E}} \mid 0\rangle - \mid\langle 0 \mid \underline{\vec{E}} \mid 0\rangle\mid^2 \tag{6.22}$$

[3]. Here $\langle 0 \mid \vec{E} \mid 0\rangle$ vanishes because of $\underline{c}_{\vec{k},\alpha} \mid 0\rangle = 0$, but $\langle 0 \mid \underline{\vec{E}}\cdot\underline{\vec{E}} \mid 0\rangle$ turns out to be infinite for an unbounded volume (why? [4]). Thus, the expression (6.22) is infinite as expected from the uncertainty principle. However, it is more sensible to look at a finite volume $\Delta V = \Delta l^3$, and consider averages over this volume, $\bar{\vec{E}} = \frac{1}{\Delta V}\int_{\Delta V}\vec{E}d^3r$. One can then show that

$$\langle 0 \mid \bar{\vec{E}}\cdot\bar{\vec{E}} \mid 0\rangle \equiv \frac{\hbar c}{\Delta l^4} \tag{6.23}$$

(cf. [25]; section 2.3). We do not want to prove (6.23), but we note that the left side is an energy density, which typically should be $\frac{\hbar\omega}{\Delta l^3}$. Using

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[2] $\lim_{n\to\infty}(1 + x/n)^n = e^x$

[3] Notice that $|\vec{H}| = |\vec{E}|$ (cf. section 4.1 in Ref. [15]. Therefore we may write $\frac{1}{2}\langle 0|\vec{E}^2 + \vec{H}^2|0\rangle = \langle 0|\vec{E}^2|0\rangle$.

[4] cf. appendix C

$\omega = 2\pi\nu = 2\pi c/\Delta l$ we obtain the right side in Eq. (6.23). The significance of (6.23) is that it tells us: A classical radiation field must have an energy density much larger than $\frac{\hbar c}{\Delta l^4}$ in order for the quantum fluctuations to be unimportant. Expressing the classical energy density, $|\vec{E}|^2$ (cf. [15]; section 2.3), in terms of $\bar{n}\hbar\omega$, where $\bar{n}$ is the average number of photons in the volume Δl^3, we see that the classical description requires $\bar{n} \gg 1/\Delta l^3$.

$\boxed{\text{Emission and absorption of photons by atoms:}}$

In section 4.3 we had considered emission and absorption using classical radiation fields. The basic matrix element was $\langle f \mid \underline{\mathcal{H}}_1 \mid i\rangle$, where $\underline{\mathcal{H}}_1$, is given by Eq. (4.110). The $\langle f \mid$ and $\langle i \mid$ were atomic states.

Let us now consider the absorption of a light quantum characterized by $\vec{k}, \alpha$. An atom which is initially in a state a makes a radiative transition to state b. We assume, for simplicity, that there are only photons of type $(\vec{k}, \alpha)$ present. If there are $n_{\vec{k},\alpha}$ photons in the initial state, then there are $n_{\vec{k},\alpha}-1$ photons in the final state. Even though the vector potential $\underline{\vec{A}}$ contains both $\underline{c}_{\vec{k},\alpha}$ and $\underline{c}^{+}_{\vec{k},\alpha}$, only $\underline{c}_{\vec{k},\alpha}$ gives a non-vanishing matrix element (due to $\langle \ldots n_{\vec{k},\alpha} \pm i \ldots \mid \ldots n_{\vec{k},\alpha} \pm j \ldots\rangle = 0$ for $i \neq j$). For a similar reason the term proportional to $\underline{\vec{A}} \cdot \underline{\vec{A}}$ in the Hamiltonian (4.104), which we had neglected, also yields no contribution! It changes the total number of photons by either 0 or ± 2. Thus we have

$$\begin{aligned}
&\underbrace{\langle b; n_{\vec{k},\alpha} - 1 \mid}_{\equiv\langle f \mid} \underline{\mathcal{H}}_1 \underbrace{\mid a; n_{\vec{k},\alpha}\rangle}_{=\mid i\rangle} = \qquad (6.24)\\
&= -\frac{e}{mc\sqrt{V}} \langle b; n_{\vec{k},\alpha} - 1 \mid \underline{c}_{\vec{k},\alpha} e^{i\left(\vec{k}\cdot\underline{\vec{r}} - wt\right)} \\
&\quad \times \vec{\epsilon}^{\,(\alpha)} \cdot \underline{\vec{p}} \mid a; n_{\vec{k},\alpha}\rangle \\
&= -\frac{e}{m}\sqrt{\frac{n_{\vec{k},\alpha}}{V}} \langle b \mid e^{i\vec{k}\cdot\underline{\vec{r}}} \underline{\vec{p}} \cdot \vec{\epsilon}^{\,(\alpha)} \mid a\rangle e^{-iwt} \ .
\end{aligned}$$

At this point we are back to the semi-classical treatment of induced emission and absorption in section 4.3. The most significant difference between our old calculation and this one is that $\mid \vec{A}_0 \mid^2$ is replaced by $\frac{n_{\vec{k},\alpha}}{V}$. This corresponds to a replacement of the classical energy density, $\propto \mid \vec{E} \mid^2$, by an energy density proportional to the number of photons per volume. The analogous case of emission yields a factor $\sqrt{\frac{n_{\vec{k},\alpha}+1}{V}}$ instead of the factor $\sqrt{\frac{n_{\vec{k},\alpha}}{V}}$.

With this simple example of an application of radiation field quantization we conclude this section. The story continues in courses on advanced quantum theory/mechanics. The interested student should also consult texts like [25] or [6] ("Spezielle Kapitel").

6.2 Second quantization

The previous section has introduced a formalism where "particles" can be created as well as annihilated. Because mass is just another apparent form of energy according to Einstein's special theory of relativity, an obvious question is the following: Can this formalism be generalized to include massiv particles? Can all particles in nature be described as field quanta? Suspecting that this field has something to do with the wave function $\psi(\vec{r}, t)$ we once again start from the (non-relativistic) Schrödinger equation:

$$i\hbar\partial_t \psi(\vec{r}, t) = \underline{\mathcal{H}}\psi(\vec{r}, t) \ . \qquad (6.25)$$

Also once again we expand $\psi(\vec{r}, t)$ in eigenfunctions of $\underline{\mathcal{H}}$

$$\psi(\vec{r}, t) = \sum_n b_n(t)\, \psi_n(\vec{r}) \ . \qquad (6.26)$$

If we now use (6.26) to evaluate $\langle \underline{\mathcal{H}} \rangle$, i.e.

$$\langle \underline{\mathcal{H}} \rangle = \langle \psi \mid \underline{\mathcal{H}} \mid \psi \rangle \ ,$$

we find

$$\langle \underline{\mathcal{H}} \rangle = \sum_n E_n b_n^* b_n \ ,$$

where E_n are the energy eigenvalues. Thus, we obtain an expression which once again looks like the sum over independent harmonic oscillators.

As before we now transform the expansion coefficients into operators, $b_n^* \rightarrow \underline{b}_n^{+}$ and $b_n \rightarrow \underline{b}_n$, obeying the commutator relations

$$\left[\underline{b}_n, \underline{b}^+_{n'}\right] = \delta_{nn'} \tag{6.27}$$

and

$$\left[\underline{b}_n, \underline{b}_{n'}\right] = \left[\underline{b}^+_n, \underline{b}^+_{n'}\right] = 0\ . \tag{6.28}$$

With these definitions we obtain a new Hamiltonian

$$\underline{\mathcal{H}} = \sum_n E_n \underline{b}^+_n \underline{b}_n\ , \tag{6.29}$$

where $\underline{b}^+_n$ creates an oscillator quantum and $\underline{b}_n$ annihilates an oscillator quantum (analogous to $\underline{c}^+_{\vec{k},\alpha}$ and $\underline{c}_{\vec{k},\alpha}$ in the previous section). Because the commutator relations (6.27) and (6.28) are identical to those for photons in the previous section the "particles" created by this formalism are bosons. This immediately brings us to the question: How can we extend the method to include fermions?

It turns out that the only change consists in defining the new commutator relations

$$\{\underline{b}_n, \underline{b}^+_{n'}\} = \delta_{nn'} \tag{6.30}$$

and

$$\{\underline{b}_n, \underline{b}_{n'}\} = \{\underline{b}^+_n, \underline{b}^+_{n'}\} = 0\ , \tag{6.31}$$

where $\{..,..\}$ now means

$$\{\underline{A}, \underline{B}\} = \underline{AB} + \underline{BA}\ . \tag{6.32}$$

$\{..,..\}$ is called anti-commutator. To prove this point we first work out the relation

$$\begin{aligned}
\left(\underline{b}^+_n \underline{b}_n\right)\left(\underline{b}^+_n \underline{b}_n\right) &\overset{(6.30)}{=} \underline{b}^+_n \left(1 - \underline{b}^+_n \underline{b}_n\right) \underline{b}_n \\
&= \underline{b}^+_n \underline{b}_n - \underline{b}^+_n \underline{b}^+_n \underline{b}_n \underline{b}_n \\
&\overset{(6.31)}{=} \underline{b}^+_n \underline{b}_n + \underline{b}^+_n \underline{b}^+_n \underline{b}_n \underline{b}_n \\
&= \underline{b}^+_n \underline{b}_n\ .
\end{aligned} \tag{6.33}$$

Now we determine the eigenvalues of the number operator $\underline{N}_n = \underline{b}^+_n \underline{b}_n$:

$$\underline{N}_n \mid \lambda\rangle = \underline{b}^+_n \underline{b}_n \mid \lambda\rangle = \lambda \mid \lambda\rangle$$

and

$$\underline{N}^2_n \mid \lambda\rangle = \underline{b}^+_n \underline{b}_n \underline{b}^+_n \underline{b}_n \mid \lambda\rangle = \lambda^2 \mid \lambda\rangle \overset{(6.33)}{=} \lambda \mid \lambda\rangle\ .$$

Thus, $\lambda^2 = \lambda$ and therefore $\lambda = 0$ or $\lambda = 1$. This is exactly what we expect for fermions [5].

We also want to work out $\underline{b}^+_n \mid n_n\rangle$ and $\underline{b}_n \mid n_n\rangle$. We start by noting

$$\underline{N}_n \mid n_n\rangle = \underline{b}^+_n \underline{b}_n \mid n_n\rangle = n_n \mid n_n\rangle\ , \tag{6.36}$$

where, as we have just shown, $n_n = 0, 1$. Now we consider $\underline{b}^+_n \mid n\rangle$ by multiplication with $\underline{N}_n$, i.e.

$$\begin{aligned}
\underline{N}_n \underline{b}^+_n \mid n_n\rangle &= \underline{b}^+_n \underline{b}_n \underline{b}^+_n \mid n_n\rangle \\
&= \underline{b}^+_n \left(1 - \underline{b}^+_n \underline{b}_n\right) \mid n_n\rangle \\
&= \underline{b}^+_n \left(1 - \underline{N}_n\right) \mid n_n\rangle \\
&= \left(1 - n_n\right) \underline{b}^+_n \mid n_n\rangle\ .
\end{aligned}$$

Therefore we find $\underline{b}^+_n \mid n_n\rangle = c_n \mid 1 - n_n\rangle$, where the constant c_n follows from

$$\begin{aligned}
\mid c_n \mid^2 &= \langle n_n \mid \underline{b}_n \underline{b}^+_n \mid n_n\rangle = \langle n_n \mid 1 - \underline{b}^+_n \underline{b}_n \mid n_n\rangle \\
&= 1 - n_n\ .
\end{aligned}$$

This yields

$$\underline{b}^+_n \mid n_n\rangle = e^{i\phi_n} \sqrt{1 - n_n} \mid 1 - n_n\rangle\ . \tag{6.37}$$

Analogously we obtain

$$\underline{b}_n \mid n_n\rangle = e^{i\phi_n} \sqrt{n_n} \mid 1 - n_n\rangle\ . \tag{6.38}$$

---

[5] We also mention that both types of commutator relations (6.27), (6.28) and (6.30), (6.31), lead to the same equations of motion for $\underline{b}_n$:

$$i\hbar \frac{d\underline{b}_n}{dt} = \left[\underline{b}_n, \underline{\mathcal{H}}\right] = E_n \underline{b}_n \tag{6.34}$$

or

$$i\hbar \frac{d\underline{b}_n}{dt} = \{\underline{b}_n, \underline{\mathcal{H}}\} = E_n \underline{b}_n \tag{6.35}$$

(show this).

In summary, for …

… bosons:

$$\begin{aligned}\underline{b}_n \mid \ldots, n_n, \ldots\rangle &= \sqrt{n_n} \mid \ldots, n_n - 1, \ldots\rangle \\ \underline{b}_n^+ \mid \ldots, n_n, \ldots\rangle &= \sqrt{n_n + 1} \mid \ldots, n_n + 1, \ldots\rangle\end{aligned}$$

… fermions:

$$\begin{aligned}\underline{b}_n \mid \ldots, n_n, \ldots\rangle &= e^{i\phi_n}\sqrt{n_n} \mid \ldots, 1 - n_n, \ldots\rangle \\ \underline{b}_n^+ \mid \ldots, n_n, \ldots\rangle &= e^{i\phi_n}\sqrt{1 - n_n} \mid \ldots, 1 - n_n, \ldots\rangle \,.\end{aligned}$$

Notice the dual character of the operators $\underline{b}_n$ and $\underline{b}_n^+$ in the fermion case. Both may act as creation as well as annihilation operators depending on the value of n_n.

6.3 Interacting quantum fields:

The next logical step is to combine the quantization of the radiation field with the second quantization in terms of the number representation worked out in the previous two sections. The key quantity is the Hamiltonian

$$\begin{aligned}\underline{\mathcal{H}} &= \int d^3r \underline{\psi}^+(\vec{r}, t)\left[\frac{1}{2m}\left(\underline{\vec{p}} - \frac{e}{c}\underline{\vec{A}}\right)^2 \right.\\ &\quad \left. + \mathcal{U}(\vec{r})\right]\underline{\psi}(\vec{r}, t) \\ &+ \int d^3r \frac{1}{8\pi}\left(\underline{\vec{E}}^2 + \underline{\vec{H}}^2\right)\,, \qquad (6.39)\end{aligned}$$

where $\underline{\psi}(\vec{r}, t) = \sum_n \underline{b}_n(t)\,\psi_n(\vec{r})$. Notice that the term in square brackets corresponds to the right side of Eq. (4.103) with $\varphi(\vec{r})$ set equal to zero (using the proper gauge). Therefore the first integral (6.39) describes charged particles interacting with an electromagnetic field and with the potential $\mathcal{U}(\vec{r})$. The second integral in (6.39) describes the energy content of the electromagnetic field itself (cf. [15]; section 2.3). Notice that the electric field strength, $\vec{E}$, and the magnetic field strength, $\vec{H}$, may both be expressed in terms of the vector potential $\vec{A}$ (cf. problem 4). In our formalism they become operators, because the Fourier coefficients $c_{\vec{k},\alpha}$ are turned into operators.

Using (4.104) in conjunction with (6.4) and (6.29) we may write $\underline{\mathcal{H}}$ as

$$\begin{aligned}\underline{\mathcal{H}} = \sum_n E_n \underline{b}_n^+ \underline{b}_n + &\\ \sum_{\vec{k},\alpha} \hbar\omega_k \left(\underline{c}_{\vec{k},\alpha}^+ \underline{c}_{\vec{k},\alpha} + \frac{1}{2}\right) + \underline{\mathcal{H}}_{int}\,, &\quad (6.40)\end{aligned}$$

where

$$\underline{\mathcal{H}}_{int} = \int d^3r \underline{\psi}^+\left[i\frac{e\hbar}{mc}\underline{\vec{A}} \cdot \vec{\nabla} + \frac{e}{2mc^2}\underline{\vec{A}}^2\right]\underline{\psi} \quad (6.41)$$

describes the interaction between the particle field and the radiation field. It is not difficult but somewhat tedious to express $\underline{\mathcal{H}}_{int}$ in terms of $\underline{b}_n$, $\underline{b}_n^+$, $\underline{c}_{\vec{k},\alpha}$, and $\underline{c}_{\vec{k},\alpha}^+$. The result is a sum of terms proportional to certain products of these operators. An example is the product $\underline{b}_{n'}^+\, \underline{b}_n\, \underline{c}_{\vec{k},\alpha}$. This term corresponds to the annihilation of a photon $(\vec{k}, \alpha)$ in a process which simultaneously annihilates a particle in state $\mid n\rangle$ but creates a particle in state $\mid n'\rangle$. Another example is the product $\underline{b}_{n'}^+\, \underline{b}_n\, \underline{c}_{\vec{k},\alpha}^+$. This time the annihilation of a particle in state $\mid n\rangle$ simultaneously creates a particle in state $\mid n'\rangle$ and also creates $(\vec{k}, \alpha)$. Such 'scattering processes' can be depicted graphically by the diagrams shown in figure 6.2. There are still more processes possible here involving also two photons. However, at this point we refer the reader to the detailed account in reference [6] ("Spezielle Kapitel").

6.4 Outlook

We want to conclude these notes with a remark on what to expect from hereon. Clearly, the content of this chapter must be dealt with more carefully and in detail. This is usually done in a subsequent advanced course on quantum theory (e.g., [6, 25, 26, 27]). Nevertheless the conceptual development thus far should have familiarized the student with the 'language' used in intermediate texts on theoretical solid state physics (e.g., [28]) or statistical mechanics (e.g., [29]).

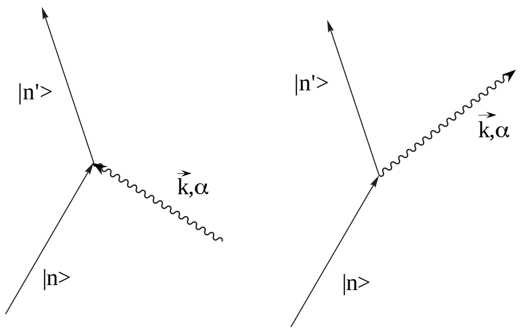


Figure 6.2: (a) Scattering of a particle from $\mid n\rangle$ to $\mid n\,'\rangle$ via the absorption of a photon $(\vec{k},\alpha)$. (b) Scattering of a particle from $\mid n\rangle$ to $\mid n\,'\rangle$ via emission of $(\vec{k},\alpha)$.

Recently McGraw-Hill has begun publishing their DeMYSTiFieD-series. With the knowledge on quantum mechanics acquired in this course I encourage students to take a look ahead into quantum field theory based on David McMahon's text *Quantum Field Theory – DeMYSTiFieD* [30].

Appendix A

Constants and units

Fundamental Physical Constants:

quantity	symbol	value	unit
speed of light	c	299792458	ms^{-1}
Planck constant	h	$6.62606876 \cdot 10^{-34}$	Js
	$\hbar = \frac{h}{2\pi}$	$1.054571596 \cdot 10^{-34}$	Js
Gravitation constant	G	$6.673 \cdot 10^{-11}$	$mkg^{-1}s^{-2}$
Planck length $\left(\hbar G/c^3\right)^{1/2}$	l_p	$1.6160 \cdot 10^{-35}$	m
Planck time l_p/c	t_p	$5.3906 \cdot 10^{-44}$	s
electric constant	ϵ_0	$8.854187817 \cdot 10^{-12}$	Fm^{-1}
elementary charge	e	$1.602176462 \cdot 10^{-19}$	C
electron mass	m_e	$9.10938188 \cdot 10^{-31}$	kg
proton mass	m_p	$1.67262158 \cdot 10^{-27}$	kg
atomic mass unit	u	$1.66053873 \cdot 10^{-27}$	kg
Boltzmann constant	k_B	$1.3806503 \cdot 10^{-23}$	JK^{-1},
Rydberg constant $\left(\alpha^2 m_e c/2h\right)$	R_∞	10973731.568	m^{-1}
inverse fine-structure constant $\left(e^2/4\pi\epsilon_0\hbar c\right)^{-1}$	α^{-1}	137.03599976	

source: http://physics.nist.gov/constants

Energy equivalents:

conversion to J		
$1kg$	$(1kg)\,c^2 =$	$8.987551787 \times 10^{16} J$
$1m^{-1}$	$\left(1m^{-1}\right) hc =$	$1.98644544\,(16) \times 10^{-25} J$
$1Hz$	$(1Hz)\,h =$	$6.62606876\,(52) \times 10^{-34} J$
$1K$	$(1K)\,k =$	$1.3806503\,(24) \times 10^{-23} J$
$1eV$	$(1eV) =$	$1.602176462\,(63) \times 10^{-19} J$
$1E_h$	$(1E_h) =$	$4.35974381\,(34) \times 10^{-18} J$

Appendix B

Mathematical appendix

B.1 Conversion to generalized coordinates

We consider $\vec{r}=\vec{r}\,(u,v,w)$, where u,v,w are generalized coordinates and define a coordinate system via

$$\begin{aligned}\vec{e}_u &= \left|\frac{\partial\vec{r}}{\partial u}\right|^{-1}\frac{\partial\vec{r}}{\partial u}\\ \vec{e}_v &= \left|\frac{\partial\vec{r}}{\partial v}\right|^{-1}\frac{\partial\vec{r}}{\partial v}\\ \vec{e}_w &= \left|\frac{\partial\vec{r}}{\partial w}\right|^{-1}\frac{\partial\vec{r}}{\partial w}\ .\end{aligned}$$

In addition the $\vec{e}_u$, $\vec{e}_v$, and $\vec{e}_w$ are required to be orthogonal. We then have

$$\begin{aligned}\vec{r} &= \vec{e}_u r_u+\vec{e}_v r_v+\vec{e}_w r_w\\ d\vec{r} &= \begin{pmatrix}dx\\ dy\\ dz\end{pmatrix}\\ &= \vec{e}_u\left|\frac{\partial\vec{r}}{\partial u}\right|du+\vec{e}_v\left|\frac{\partial\vec{r}}{\partial v}\right|dv+\vec{e}_w\left|\frac{\partial\vec{r}}{\partial w}\right|dw\\ \vec{\nabla} &= \begin{pmatrix}\partial_x\\ \partial_y\\ \partial_z\end{pmatrix}\\ &= \vec{e}_u\left|\frac{\partial\vec{r}}{\partial u}\right|^{-1}\partial_u+\vec{e}_v\left|\frac{\partial\vec{r}}{\partial v}\right|^{-1}\partial_v\\ &\quad+\vec{e}_w\left|\frac{\partial\vec{r}}{\partial w}\right|^{-1}\partial_w\end{aligned}$$

To obtain the last relation we write

$$\partial_u=\frac{\partial\vec{r}}{\partial u}\cdot\partial_{\vec{r}}\equiv\frac{\partial\vec{r}}{\partial u}\cdot\vec{\nabla}$$

i.e.

$$\left|\frac{\partial\vec{r}}{\partial u}\right|^{-1}\partial_u=\vec{e}_u\cdot\vec{\nabla}$$

for u as well as v and w. The desired result follows via

$$\vec{\nabla}=\vec{e}_u(\vec{e}_u\cdot\vec{\nabla})+\vec{e}_v(\vec{e}_v\cdot\vec{\nabla})+\vec{e}_w(\vec{e}_w\cdot\vec{\nabla})\ .$$

Special cases:

(a) Cylindrical coordinates:

$$\vec{r}=\begin{pmatrix}r\cos\phi\\ r\sin\phi\\ z\end{pmatrix}$$

$$\vec{e}_r=\begin{pmatrix}\cos\phi\\ \sin\phi\\ 0\end{pmatrix}\qquad\vec{e}_\phi=\begin{pmatrix}-\sin\phi\\ \cos\phi\\ 0\end{pmatrix}$$

$$\vec{e}_z=\begin{pmatrix}0\\ 0\\ 1\end{pmatrix}$$

$$\left|\frac{\partial\vec{r}}{\partial r}\right|=1\qquad\left|\frac{\partial\vec{r}}{\partial\phi}\right|=r\qquad\left|\frac{\partial\vec{r}}{\partial z}\right|=1$$

$$\begin{aligned}d\vec{r} &= \vec{e}_r dr+\vec{e}_\phi r d\phi+\vec{e}_z dz\\ \vec{\nabla} &= \vec{e}_r\partial_r+\vec{e}_\phi\frac{1}{r}\partial_\phi+\vec{e}_z\partial_z\\ \vec{\nabla}^2 &= \frac{1}{r}\partial_r\left(r\partial_r\right)+\frac{1}{r^2}\partial_\phi^2+\partial_z^2\end{aligned}$$

(b) Spherical coordinates

$$\vec{r} = \begin{pmatrix} r\cos\phi\sin\theta \\ r\sin\phi\sin\theta \\ r\cos\theta \end{pmatrix}$$

$$\vec{e}_r = \begin{pmatrix} \cos\phi\sin\theta \\ \sin\phi\sin\theta \\ \cos\theta \end{pmatrix} \quad \vec{e}_\phi = \begin{pmatrix} -\sin\phi \\ \cos\phi \\ 0 \end{pmatrix}$$

$$\vec{e}_\theta = \begin{pmatrix} \cos\phi\cos\theta \\ \sin\phi\cos\theta \\ -\sin\theta \end{pmatrix}$$

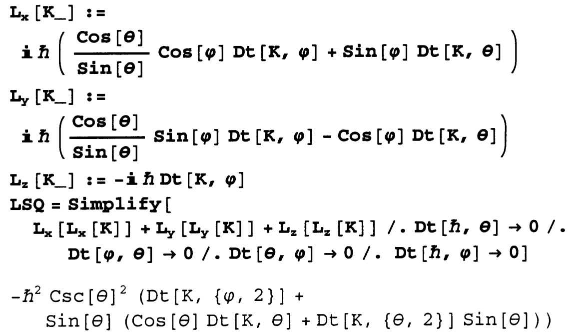
$$\left|\frac{\partial\vec{r}}{\partial r}\right| = 1 \quad \left|\frac{\partial\vec{r}}{\partial\phi}\right| = r\sin\theta \quad \left|\frac{\partial\vec{r}}{\partial\theta}\right| = r$$

$$\begin{aligned} d\vec{r} &= \vec{e}_r dr + \vec{e}_\phi r\sin\theta\partial_\phi + \vec{e}_\theta r d\theta \\ \vec{\nabla} &= \vec{e}_r\partial_r + \vec{e}_\phi\frac{1}{r\sin\theta}\partial_\phi + \vec{e}_\theta\frac{1}{r}\partial_\theta \\ \vec{\nabla}^2 &= \underbrace{\frac{1}{r^2}\partial_r\left(r^2\partial_r\right)}_{=\frac{1}{r}\partial_r^2(r\ldots)} \\ &\quad \underbrace{+\frac{1}{r^2\sin^2\theta}\partial_\phi^2 + \frac{1}{r^2\sin\theta}\partial_\theta\left(\sin\theta\partial_\theta\right)}_{\equiv\vec{\nabla}^2_{\phi,\theta}} \end{aligned}$$

Using the definition of angular momentum, $\underline{\vec{L}} = \underline{\vec{r}} \times \underline{\vec{p}}$, where $\underline{\vec{p}} = -i\hbar\vec{\nabla}$ is expressed via the above components of $\vec{\nabla}$ it is a straightforward matter to compute the following formulas:

$$\begin{aligned} \underline{L}_x &= i\hbar\left(\cos\phi\cot\theta\partial_\phi + \sin\phi\partial_\theta\right) \\ \underline{L}_y &= i\hbar\left(\sin\phi\cot\theta\partial_\phi - \cos\phi\partial_\theta\right) \\ \underline{L}_z &= -i\hbar\partial_\phi \\ \underline{L}^2 &= -\hbar^2 r^2\vec{\nabla}^2_{\phi,\theta} \end{aligned}$$

The last equation was obtained using the following *Mathematica*-code:



```
Lx[K_] :=
 iℏ (Cos[θ]/Sin[θ] Cos[φ] Dt[K, φ] + Sin[φ] Dt[K, θ])
Ly[K_] :=
 iℏ (Cos[θ]/Sin[θ] Sin[φ] Dt[K, φ] - Cos[φ] Dt[K, θ])
Lz[K_] := -iℏ Dt[K, φ]
LSQ = Simplify[
  Lx[Lx[K]] + Ly[Ly[K]] + Lz[Lz[K]] /. Dt[ℏ, θ] → 0 /.
    Dt[φ, θ] → 0 /. Dt[θ, φ] → 0 /. Dt[ℏ, φ] → 0]

-ℏ^2 Csc[θ]^2 (Dt[K, {φ, 2}] +
   Sin[θ] (Cos[θ] Dt[K, θ] + Dt[K, {θ, 2}] Sin[θ]))
```

B.2 Spherical harmonics

The spherical harmonics form a complete orthogonal system in two dimensions, i.e.

$$\int d\Omega Y^*_{lm}(\theta,\phi)\, Y_{l'm'}(\theta,\phi) = \delta_{ll'}\delta_{mm'} \ ,$$

where

$$\int d\Omega \ldots = \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\theta \ldots$$

and

$$\begin{aligned} &\sum_{l=0}^{\infty}\sum_{m=-l}^{l} Y_{lm}(\theta,\phi)\, Y^*_{lm}(\theta',\phi') \\ &= \delta(\varphi-\varphi')\delta(\cos\theta-\cos\theta') \ . \end{aligned}$$

$Y_{lm}(\theta,\phi)$ is given by

$$Y_{lm}(\theta,\phi) = \sqrt{\frac{(2l+1)(l-\mid m\mid)!}{4\pi(l+\mid m\mid)!}} e^{im\phi} P_{lm}(\cos\theta) \ ,$$

where

$$P_{lm}(\cos\theta) = \epsilon_m \sin^{|m|}\theta \left(\frac{d}{d\cos\theta}\right)^{|m|} P_l(\cos\theta)$$

with $\epsilon_m = (-1)^m$ for $m \geq 0$ and $\epsilon_m = 1$ for $m < 0$. The $P_l(x)$ are Legendre polynomials

$$P_0(x) = 1, \quad P_1(x) = x, \quad P_2(x) = \frac{1}{2}\left(3x^2-1\right), \ldots$$

$$P_l\left(x\right)=\frac{1}{2^l l!}\frac{d^l}{dx^l}\left(x^2-1\right)^l$$

obeying the differential equation

$$\left[\left(1-x^2\right)\frac{d^2}{dx^2}-2x\frac{d}{dx}+l\left(l+1\right)\right]P_l\left(x\right)=0\ .$$

Some special Y_{lm} are

$$Y_{0,0}=\frac{1}{\sqrt{4\pi}},\quad Y_{1,1}=-\sqrt{\frac{3}{8\pi}}\sin\theta e^{i\phi},$$
$$Y_{1,0}=\sqrt{\frac{3}{4\pi}}\cos\theta,\quad Y_{1,-1}=\sqrt{\frac{3}{8\pi}}\sin\theta e^{-i\phi}\ .$$

Additional $Y_{lm}\left(\theta,\phi\right)$ can be obtained via SphericalHarmonicY $[l,m,\theta,\phi]$ in *Mathematica*. For additional $P_l\left(x\right)$ use LegendreP $[l,x]$. A general reference covering the above is [19].

B.3 δ-function

The δ-function is defined via

$$\int_{-\infty}^{\infty}f\left(x\right)\delta\left(x-x_0\right)dx=f\left(x_0\right)\ .$$

Formally we may write

$$\delta\left(x-x_0\right)=\begin{cases}0 & x\neq x_0\\ +\infty & x=x_0\end{cases}$$

We summarize some of its properties:

$$\begin{aligned}\delta\left(x\right)&=\delta\left(-x\right)\\ \delta\left(ax\right)&=\frac{1}{\mid a\mid}\delta\left(x\right)\\ \delta\left(g\left(x\right)\right)&=\sum_n\frac{1}{\mid g'\left(x_n\right)\mid}\delta\left(x-x_n\right)\end{aligned}$$

(with $g\left(x_n\right)=0$ and $g'\left(x_n\right)\neq 0$)

$$\begin{aligned}x\delta\left(x\right)&=0\\ f\left(x\right)\delta\left(x-a\right)&=f\left(a\right)\delta\left(x-a\right)\\ \int\delta\left(x-y\right)\delta\left(y-a\right)dy&=\delta\left(x-a\right)\\ \delta\left(x\right)&=\frac{1}{2\pi}\int_{-\infty}^{\infty}e^{ikx}dk\quad(*)\\ \int_{-\infty}^{\infty}\delta^{(m)}\left(x\right)f\left(x\right)dx&=\left(-1\right)^m f^{(m)}\left(0\right)\quad(**)\end{aligned}$$

(*) We can show the validity of this, in the sense of the above definition of the δ-function, using the residue method (cf. page 53), i.e.

$$\begin{aligned}f(x_o)=&\int_{-\infty}^{\infty}f(x)\delta(x-x_o)dx\\ =&\frac{1}{2\pi}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}f(x)e^{ik(x-x_o)}dxdk\\ =&\lim_{K\to\infty}\frac{1}{2\pi i}\int_{-\infty}^{\infty}\frac{f(x)}{x-x_o}\\ &(e^{iK(x-x_o)}-e^{-iK(x-x_o)})dx\ .\end{aligned}$$

The final step, i.e. the application of the residue theorem, is left as an exercise to the reader.

(**) The index (m) indicates the mth derivative. Special properties of the first derivative:

$$\begin{aligned}\int_{-\infty}^{\infty}\delta'\left(x\right)f\left(x\right)dx&=-f'\left(0\right)\\ \delta'\left(x\right)&=-\delta'\left(-x\right)\\ \int\delta'\left(x-y\right)\delta\left(y-a\right)dy&=\delta'\left(x-a\right)\\ x\delta'\left(x\right)&=-\delta\left(x\right)\\ x^2\delta'\left(x\right)&=0\\ \delta'\left(x\right)&=\frac{i}{2\pi}\int_{-\infty}^{\infty}ke^{ikx}dk\ .\end{aligned}$$

Three-dimensional (3D) formulas:

$$\begin{aligned}\delta(\vec{r}-\vec{r}_0)&=\delta(x-x_0)\delta(y-y_0)\delta(z-z_0)\\ &=\frac{1}{r^2}\delta(r-r_0)\delta(\cos\theta-\cos\theta_0)\delta(\phi-\phi_0)\end{aligned}$$

$$\delta\left(\vec{r}-\vec{r}_0\right)=\frac{1}{(2\pi)^3}\int e^{i\vec{k}\cdot(\vec{r}-\vec{r}_0)}d^3k\ .$$

B.4 Fourier series and Fourier transforms

If $f(x)$ is a periodic function with a period L, then it can be expanded in a Fourier series:

$$f(x) = \sum_{n=-\infty}^{\infty} a_n e^{ik_n x} ,$$

where $k_n = 2\pi n/L$. The coefficients a_n of the series are given by

$$a_n = \frac{1}{L} \int_0^L f(x) e^{-ik_n x} dx .$$

The Fourier transform of a function $f(x)$ is

$$\tilde{f}(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x) e^{-ikx} dx .$$

The inverse transformation is given by

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \tilde{f}(k) e^{ikx} dk .$$

An important theorem is the convolution theorem: If $\tilde{f}(k)$ and $\tilde{g}(k)$ are the Fourier transforms of $f(x)$ and $g(x)$ respectively, then

$$\int_{-\infty}^{\infty} \tilde{f}(k) \tilde{g}(k) e^{-ikx} dk = \int_{-\infty}^{\infty} f(u) g(x-u) du .$$

If we define the convolution, denoted by $f * g$, of the functions f and g to be

$$f * g = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(u) g(x-u) du .$$

then the above cause written

$$f \tilde{*} g = \tilde{f}\tilde{g} .$$

This is the convolution theorem for Fourier transforms.

Identity of norms:

$$\int_{-\infty}^{\infty} | f(x) |^2 dx = \int_{-\infty}^{\infty} | \tilde{f}(k) |^2 dk .$$

Parseval's theorem:

$$\int_{-\infty}^{\infty} f(x) g^*(x) = \int_{-\infty}^{\infty} \tilde{f}(k) g^*(k) dk .$$

Appendix C

The Casimir effect

An interesting manifestation of the importance of the zero-point energy is the Casimir effect [31]. Here we illustrate the essence of the Casimir effect in a simple 1D example (cf. section 5.8 in reference [32]).

We consider again the black body cavity introduced in section 1.2. To make things simple, we reduce the 3D cavity to a 1D cavity of length L. In addition we focus on the limit $T = 0$, even though the effect discussed here also shows up at non-zero temperatures. The zero-point energy of the radiation field inside the cavity is given by

$$E_0\left(L\right) = \frac{\hbar}{2}\sum_{\omega}\omega \tag{C.1}$$

with $\omega = \pi c n/L\,(n = 1, 2, \ldots, \infty)$ [1]. This sum is infinite. But we can force it to be finite. We multiply ω by a so-called cutoff function, which suppresses the high frequency modes:

$$f\left(\omega\right) = \exp\left[-\lambda\omega\right] = \left\{\begin{array}{lll} 1 & \text{for} & \omega \to 0 \\ 0 & \text{for} & \omega \to \infty \end{array}\right. . \tag{C.2}$$

Here λ is a small real number. Now Eq. (C.1) becomes

$$E_{0,cut}\left(L\right) = \frac{\hbar}{2}\sum_{\omega}\omega f\left(\omega\right) . \tag{C.3}$$

As in the case of black body radiation we want to transform the sum into an integral. This time, however, we must be careful, because we do need not only the leading term but in addition the correction terms. A systematic transition from a sum to its integral representation is the Euler-MacLaurin summation formula:

$$\begin{aligned}
\sum_{n=1}^{m-1} F\left(n\right) &= \int_0^m F\left(n\right) dn \qquad\qquad \text{(C.4)} \\
&- \frac{1}{2}\left\{F\left(m\right) + F\left(0\right)\right\} \\
&+ \frac{1}{12}\left\{F'\left(m\right) - F'\left(0\right)\right\} \\
&- \frac{1}{720}\left\{F'''\left(m\right) - F'''\left(0\right)\right\} + \ldots \\
&+ \frac{B_{2p}}{(2p)!} \\
&\quad \times\left\{F^{(2p-1)}\left(m\right) - F^{(2p-1)}\left(0\right)\right\} + \ldots
\end{aligned}$$

[19]. The B_{2p} are the Bernoulli numbers ($B_2 = 1/6$, $B_4 = -1/30$, $B_6 = 1/42, \ldots$). Using (C.4) we obtain

$$\begin{aligned}
\frac{E_{0,cut}}{\hbar} &= \frac{1}{2}\sum_{\omega}\omega f\left(\omega\right) = \frac{\pi c}{2L}\sum_{n=1}^{\infty} n \exp\left[-\lambda\frac{\pi c n}{L}\right] \\
&= \frac{\pi c}{2L}\Big\{\underbrace{\int_0^\infty n \exp\left[-\lambda\frac{\pi c n}{L}\right] dn}_{=L^2/(\pi c\lambda)^2} \\
&\qquad -\frac{1}{12} + \frac{1}{720}\frac{3\pi^2 c^2 \lambda^2}{L^2}\ldots\Big\} \\
&= \frac{L}{2\pi c\lambda^2} - \frac{\pi c}{24L} + \frac{\pi^3 c^3}{480}\frac{\lambda^2}{L^3} + \ldots . \qquad \text{(C.5)}
\end{aligned}$$

Obviously, for $\lambda \to 0$ the result diverges! But now comes the interesting part. We insert two 1D "metal plates" into the box. Plate one is located

---

[1] Notice that $E_0(L)$ may be expressed via $E_0(L) = \frac{1}{4\pi}\int\langle 0|\vec{E}^2|0\rangle dV$ as pointed out on page 103. This means that $E_0(L)$ corresponds to the vacuum fluctuations of the electric field inside the cavity.

at $-a/2$ relative to the center of the box; plate two is located at $a/2$. Thus, the original cavity is partitioned into three compartments with lengths $L/2-a/2$, a, and $L/2-a/2$. The overall zero-point energy is described by (C.5):

$$E_{0,cut}^{total} = E_{0,cut}\left(a\right) + 2E_{0,cut}\left(\frac{L-a}{2}\right) \, . \tag{C.6}$$

Thus, according to (C.5) we obtain

$$\frac{1}{\hbar}E_{0,cut}^{total} \overset{L\to\infty}{\longrightarrow} \frac{L}{2\pi c\lambda^2} - \frac{\pi c}{24a} + \frac{\pi^3 c^3 \lambda^2}{480a^3} + \ldots \, , \tag{C.7}$$

and taking the derivative with respect to a yields

$$\frac{\partial}{\partial a}\left(\frac{1}{\hbar}E_{0,cut}^{total}\Big|_{L\to\infty}\right) = \frac{\pi c}{24a^2} - \frac{\pi^3 c^3 \lambda^2}{160a^4} \, . \tag{C.8}$$

Finally we set $\lambda = 0$ to obtain

$$-\frac{\partial E_0^{total}}{\partial a} = -\frac{\pi c\hbar}{24a^2} \, . \tag{C.9}$$

Eq. (C.9) states that the zero-point energy gives rise to an attractive force proportional to a^{-2} between the two inserted plates. A surprising result!

By inspection of Eq. (C.4) we can see easily that the result (C.9) does not depend on the form of the cutoff function as long as it obeys the limits indicated in Eq. (C.2) and as long as it is reasonably smooth (no θ-function!).

The same calculation can be carried out in 3D. The resulting force in this case is proportional to a^{-4} (cf. K. Huang or K. A. Milton) [2]. Since H. B. G. Casimir's proposal of this effect in 1948 experiments have confirmed the "Casimir force" for various geometries (e.g. plate-plate or plate-sphere).

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[2] The Casimir pressure for a plate separation of $a = 10^{-6}m$ is about $1.3 \cdot 10^{-3}Pa$.

Appendix D

Problems

Problem 1: Some integrals in quantum mechanics

Solve the following integral

$$\int_{\text{all space}} d^3r \mid \psi(\vec{r}) \mid^2$$

for

$$\begin{aligned}
\psi(\vec{r}) &= \frac{1}{\sqrt{\pi}} \exp[-r] \\
\psi(\vec{r}) &= \frac{1}{\sqrt{8\pi}} \left(1 - \frac{r}{2}\right) \exp[-r/2] \\
\psi(\vec{r}) &= \frac{1}{8\sqrt{\pi}} \sin\theta \, r \exp[-r/2 - i\phi] \, .
\end{aligned}$$

Do <u>not</u> use tables or computers! Note that $\vec{r} = r(\cos\phi \sin\theta, \sin\phi \sin\theta, \cos\theta)$.

Problem 2: Classical harmonic oscillator

Calculate the probability $p_{cl}(x)\delta x$ for finding the 1D classical harmonic oscillator within the intervall δx and plot the probability density p_{cl} in the range between $-a$ and a, where a is the amplitude.

Problem 3: Generalized coordinates

We consider $\vec{r} = \vec{r}\,(u, v, w)$, where u, v, w are generalized coordinates, and define a coordinate system via

$$\vec{e}_u = \left|\frac{\partial \vec{r}}{\partial u}\right|^{-1} \frac{\partial \vec{r}}{\partial u} \qquad \vec{e}_v = \left|\frac{\partial \vec{r}}{\partial v}\right|^{-1} \frac{\partial \vec{r}}{\partial v}$$

$$\vec{e}_w = \left|\frac{\partial \vec{r}}{\partial w}\right|^{-1} \frac{\partial \vec{r}}{\partial w} \, .$$

We assume in addition that $\vec{e}_u$, $\vec{e}_v$, and $\vec{e}_w$ are orthogonal.

(a) Show that

$$\begin{aligned}
\vec{\nabla} &= \begin{pmatrix} \partial_x \\ \partial_y \\ \partial_z \end{pmatrix} = \vec{e}_u \left|\frac{\partial \vec{r}}{\partial u}\right|^{-1} \partial_u \\
&\quad + \vec{e}_v \left|\frac{\partial \vec{r}}{\partial v}\right|^{-1} \partial_v + \vec{e}_w \left|\frac{\partial \vec{r}}{\partial w}\right|^{-1} \partial_w \, .
\end{aligned}$$

(b) Work out $\vec{\nabla}$ both in cylindrical and spherical coordinates, i.e. $\vec{r} = \vec{r}(\rho, \phi, z)$ and $\vec{r} = \vec{r}(r, \phi, \theta)$.

Problem 4: Energy density of the black body

In class we have learned that the classical field energy E contained in a black body cavity enclosing the volume V is given by

$$E = \frac{1}{8\pi} \int \left[\left| \frac{1}{c} \frac{\partial \vec{A}}{\partial t} \right|^2 + \left| \vec{\nabla} \times \vec{A} \right|^2 \right] dV \, .$$

Show that using the Fourier decomposition of the vector potential

$$\begin{aligned}
\vec{A}\,(\vec{r}, t) &= \frac{1}{\sqrt{V}} \sum_{\vec{k},\alpha} \Big\{ c_{\vec{k},\alpha} \vec{\epsilon}^{(\alpha)} e^{i(\vec{k}\cdot\vec{r} - \omega t)} \\
&\quad + c^*_{\vec{k},\alpha} \vec{\epsilon}^{(\alpha)} e^{-i(\vec{k}\cdot\vec{r} - \omega t)} \Big\} \, ,
\end{aligned}$$

where $V = L^3$, $k_x = \frac{2\pi}{L} n_x$, $k_y = \frac{2\pi}{L} n_y$, $k_z = \frac{2\pi}{L} n_z$ (n_x, n_y, $n_z = \pm1, \pm2, \ldots$), yields

$$E = \sum_{\vec{k},\alpha} \frac{w^2}{2\pi c^2} c^*_{\vec{k},\alpha} c_{\vec{k}\alpha}$$

Hints: (i) $\vec{\epsilon}^{(\alpha)}$ is a real unit vector in the α-direction of the plane perpendicular to the momentum vector $\vec{k}$ ($\alpha = 1, 2$); (ii) $\int_V d^3 r e^{i(\vec{k}-\vec{k}\,')\cdot\vec{r}} = V\delta_{\vec{k},\vec{k}\,'}$.

Problem 5: Compton effect

According to quantum theory, a monochromatic electromagnetic beam of frequency ν is regarded as a collection of particle-like photons, each possessing an energy $E = h\nu$ and a momentum $p = h\nu/c = h/\lambda$, where λ is the wavelength. Suppose that a photon moving along the x-axis collides with a particle of mass m_o. As a result of the collision, the photon is scattered at an angle θ, and its frequency is changed. Find the increase in the photon's wavelength as a function of the scattering angle. Hint: Use the relativistic energy-momentum relation, i.e. $E = \sqrt{p^2c^2 + m_o^2c^4}$.

Problem 6: Matrix-mechanics

Show that the matrices

$$\underline{x} = \sqrt{\frac{\hbar}{2m\omega}} \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & \cdots \\ 1 & 0 & \sqrt{2} & 0 & 0 & \cdots \\ 0 & \sqrt{2} & 0 & \sqrt{3} & 0 & \cdots \\ 0 & 0 & \sqrt{3} & 0 & \sqrt{4} & \cdots \\ \vdots & \vdots & 0 & \sqrt{4} & \ddots & \sqrt{5} \\ \vdots & \vdots & \vdots & 0 & \sqrt{5} & \ddots \end{pmatrix}$$

and

$$\underline{p} = i\sqrt{\frac{\hbar m\omega}{2}} \begin{pmatrix} 0 & -1 & 0 & 0 & 0 & \cdots \\ 1 & 0 & -\sqrt{2} & 0 & 0 & \cdots \\ 0 & \sqrt{2} & 0 & -\sqrt{3} & 0 & \cdots \\ 0 & 0 & \sqrt{3} & 0 & -\sqrt{4} & \cdots \\ \vdots & \vdots & 0 & \sqrt{4} & \ddots & -\sqrt{5} \\ \vdots & \vdots & \vdots & 0 & \sqrt{5} & \ddots \end{pmatrix}$$

(a) obey the commutator relation $[\underline{p}, \underline{x}] = -i\hbar$ and,

(b) if inserted in $\underline{\mathcal{H}} = \frac{1}{2m}\underline{p}^2 + \frac{m\omega^2}{2}\underline{x}^2$, yield

$$\underline{\mathcal{H}} = \hbar\omega \begin{pmatrix} \frac{1}{2} & 0 & 0 & 0 & \cdots \\ 0 & \frac{3}{2} & 0 & 0 & \cdots \\ 0 & 0 & \frac{5}{2} & 0 & \cdots \\ 0 & 0 & 0 & \frac{7}{2} & \\ \vdots & \vdots & \vdots & & \ddots \end{pmatrix} .$$

Problem 7: Phase- and group velocity

Calculate both the phase and the group velocity of a deBroglie wave for a non-relativistic particle.

Problem 8: Anharmonic 1D oscillator in the WKB-approximation

We have seen that the 'enhanced' quantization condition

$$\frac{1}{h}\oint p\,dq = n + \frac{1}{2} \qquad (n = 0, 1, 2, \ldots)$$

describes the exact energy eigenvalues of the 1D harmonic oscillator. Assuming that this formula applies approximately to other systems as well, calculate the energy eigenvalues of an anharmonic 1D oscillator, whose energy is given by

$$E = \frac{p^2}{2m} + \frac{m\omega^2}{2}x^2 + \chi x^4$$

to leading order in the small parameter χ. You may use computer algebra programs like *Mathematica* to carry out the necessary integrations and expansions. Hints: Introducing the new quantities ϵ and c via $E = \hbar\omega\epsilon$ and $c = 4\chi\hbar\epsilon/(m^2\omega^3)$ you find the simplified equation

$$\frac{2}{\pi}\epsilon \int_{-z_o}^{z_o} dz\sqrt{1 - z^2 - cz^4} = n + \frac{1}{2} ,$$

where $\pm z_o$ are the solutions of $1 - z^2 - cz^4 = 0$. Expand the integrant keeping the leading order in c only. Integrate the result. Again expand the result of the integration to leading order in c (you should find $\int_{-z_o}^{z_o} dz\sqrt{1 - z^2 - cz^4} = \pi/2 - 3\pi c/16 + \mathcal{O}(c^{3/2})$). Note that this approach fails if you try to obtain higher order corrections (why?). Insert $c = \lambda\epsilon$ and solve the quadratic equation for ϵ. Because the solution is valid only to leading order of the small parameter λ, expand one last time to obtain ϵ in terms of n and λ to leading order in λ. Your result should look like this: $\epsilon \approx n + 1/2 + \ldots (n+1/2)^2\lambda$, where $\ldots$ is a numerical coefficient.

Problem 9: Wave packet and the harmonic oscillator potential

(a) Show that whatever superposition of harmonic oscillator states is used to construct a wave packet $\psi(x,t)$, it is localized at the same place at times 0, T, $2T$, ..., where T is the classical period of the oscillator.

(b) Construct the explicit form of $\psi(x,t)$ at $x = 0$, and discuss its time behavior. Hints. $H_{2n+1}(0) = 0$ and $H_{2n}(0) = \frac{(-1)^n(2n)!}{n!}$.

Problem 10: Potential well

Consider the Schrödinger equation

$$\left(\partial_q^2 - u(q) + \epsilon\right)\psi(q) = 0$$

for the potential

$$u(q) = \left\{ \begin{array}{cc} \infty & (q \le 0) \\ -u_o & (0 < q \le 1) \\ 0 & (1 < q) \end{array} \right. ,$$

where u_o are positive.

(a) Determine the bound state eigenfunctions (you need not calculate the overall normalization constant explicitly).

(b) What is the condition the quantity u_o must fulfill in order for at least one bound state to exist. Provide an equation that allows to obtain the eigenvalues numerically.

Hint: The wave function and its derivative are continuous at $q = 1$.

Problem 11: Raising and lowering operators

(a) Prove Eq. (1.154).

(b) Show that

$$\underline{a} \mid n\rangle = \sqrt{n} \mid n-1\rangle \ .$$

Problem 12: The hydrogen atom

When we spoke in class about the hydrogen atom we left out several steps to be completed as homework problems. Here they are

(a) Show explicitly how to get from

$$\underline{\mathcal{H}} = -\frac{\hbar^2}{2m_e}\vec{\nabla}_e^2 - \frac{\hbar^2}{2m_n}\vec{\nabla}_n^2 + \mathcal{U}\left(\mid \vec{r}_e - \vec{r}_n \mid\right)$$

to

$$\underline{\mathcal{H}} = -\frac{\hbar^2}{2\mu}\vec{\nabla}_r^2 - \frac{\hbar^2}{2m}\vec{\nabla}_R^2 + \mathcal{U}\left(r\right) ,$$

where $\vec{r} = \vec{r}_e - \vec{r}_n$ and $m\vec{R} = m_e\vec{r}_e + m_n\vec{r}_n$ $(m = m_e + m_n, \mu = m_e m_n/m)$.

(b) Using $\vec{\underline{L}} = \underline{\vec{r}} \times \underline{\vec{p}}$, where $\underline{\vec{p}} = -i\hbar\vec{\nabla}$, show that

$$\begin{array}{rcl} \underline{L}_x & = & i\hbar\left(\cos\phi\cot\theta\partial_\phi + \sin\phi\partial_\theta\right) , \\ \underline{L}_y & = & i\hbar\left(\sin\phi\cot\theta\partial_\phi - \cos\phi\partial_\theta\right) , \\ \underline{L}_z & = & -i\hbar\partial_\phi \ . \end{array}$$

(c) Show also that

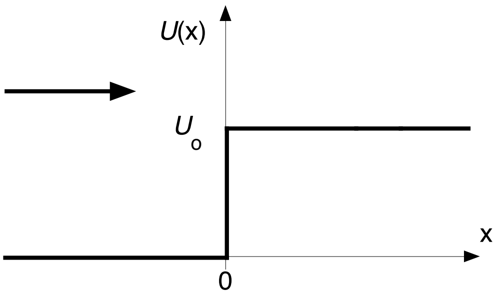
$$\underline{\vec{L}}^2 = -\hbar^2 r^2 \vec{\nabla}_{\phi,\theta}^2 \ .$$

Hint: Use $\vec{\nabla}$ in spherical coordinates. Note that $r^2\vec{\nabla}_{\phi,\theta}^2 = \sin^{-2}\theta\partial_\phi^2 + \sin^{-1}\theta\partial_\theta\left(\sin\theta\partial_\theta\right)$.

(d) Derive the recursion relation (1.109):

$$\frac{c_{j+1}}{\sqrt{-\epsilon}} = \frac{2\left[l + j + 1 - \frac{1}{\sqrt{-\epsilon}}\right]}{(j+1)(j+2l+2)}c_j \ .$$

Problem 13: Step potential



We look at the step potential

$$\mathcal{U}\,(x) = \left\{ \begin{array}{cc} \mathcal{U}_0 & x > 0 \\ 0 & x < 0 \end{array} \right. .$$

Consider a current of particles of energy $E > \mathcal{U}_0$ moving from $x = -\infty$ to the right.

(a) Write the stationary solutions for each of the regions. Express the fact that there is no current coming back from $x = +\infty$ to the left, and use the matching conditions to express the reflected and transmitted amplitudes in terms of the incident amplitude. Hint: Because the direction of the current is determined by the wave vector $\vec{k}$ (or by the sign of k in the one-dimensional case) we may express the incident part of the current, j_i, via $\psi_I(x) = A_1 \exp[ik_1 x]$, where A_1 is the incident amplitude and $\hbar k_1 = \sqrt{2mE}$. To obtain the complete $\psi_I(x)$ we must add to this the reflected contribution $(-k_1!)$ in region I. $\psi_{II}(x)$ may be constructed analogously.

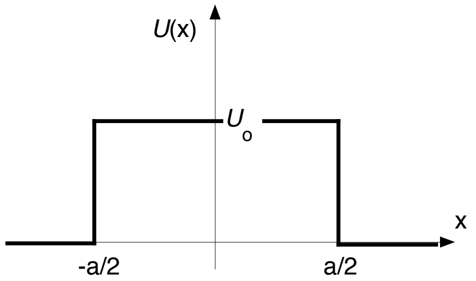
(b) Compute the probability current in the regions I and II and interpret each term.

(c) Find the reflection (r) and transmission (t) coefficients defined as $R = |j_r/j_i|$ and $T = |j_t/j_i|$.

Problem 14: Potential barrier

Consider a square potential barrier

$$\mathcal{U}\,(x) = \left\{ \begin{array}{cc} 0 & x < -a/2 \\ \mathcal{U}_0 & -a/2 \leq x \leq a/2 \\ 0 & a/2 < x \end{array} \right. .$$



(a) Assume that the incident particles of energy $E > \mathcal{U}_0$ are coming from $x = -\infty$. Find the stationary states. Apply the matching conditions at $x = -a/2$ and $x = a/2$.

(b) Find the transmission and reflection coefficients. Sketch the transmission coefficient as a function of the barrier's width a, and discuss the results.

(c) Find the stationary states describing incident particles of energy $E < \mathcal{U}_0$. Compute the transmission coefficient and discuss the results.

Remark: The effect that $R = 0$ for certain values of a in part (b) is called resonance scattering. Part (c) on the other hand is an example of the above mentioned tunnel effect.

Problem 15: Spherical infinite potential well

Consider a particle in a spherical infinite potential well:

$$\mathcal{U}(r) = \left\{ \begin{array}{cc} 0 & 0 \leq r \leq a \\ \infty & a < r \end{array} \right. .$$

Write the differential equation of the radial and angular parts, and solve the angular equation. Compute the energy levels and normalized eigenfunctions for $l = 0$.

Problem 16: The free symmetric top

A symmetric top with moments of inertia $I_x = I_y$ and I_z in the body axes frame is described by the Hamiltonian

$$\underline{H} = \frac{1}{2I_x}\left(\underline{L}_x^2 + \underline{L}_y^2\right) + \frac{1}{2I_z}\underline{L}_z^2 \; .$$

Note that moments of inertia are parameters not operators.

(a) Calculate the eigenvalues and the eigenstates of the Hamiltonian.

(b) What values are expected for a measurement of $\underline{L}_x + \underline{L}_y + \underline{L}_z$ for any state? The state of the top at time $t = 0$ is $|l = 3, m = 0\rangle$. What is the probability that for a measurement of $\underline{L}_z$ at $t = 4\pi I_x/\hbar$ we will obtain the value $\hbar$?

Problem 17: Generators of rotation and translation

(a) Using the same approach that we had applied in classical mechanics to show that angular momentum is conserved in an isotropic system, show that $\underline{U}_R(\phi)\psi(\vec{r})$, where

$$\underline{U}_R(\phi) = \exp\left[\frac{i}{\hbar}\phi\vec{e}_\phi \cdot \vec{\underline{L}}\right] \; ,$$

describes a rotation with respect to an axis oriented along the unit vector $\vec{e}_\phi$. Here ϕ is the angle of rotation, and $\vec{\underline{L}}$ is the usual angular momentum operator, which in this context is called the generator of rotation. Hint: Consider an infinitesimal rotation $\delta\vec{\phi}$ first (just replace the Lagrangian $\mathcal{L}(\vec{r}_i, \dot{\vec{r}}_i)$ by $\psi(\vec{r})$; cf. my lecture notes on Classical Mechanics), then use $\lim_{n\to\infty}\left(1 + \frac{x}{n}\right)^n = e^x$ to obtain the result for a finite rotation.

(b) Find the analogous translation operator $\underline{U}_T(\vec{a})$, where $\vec{a}$ is a displacement vector.

Problem 18: Commutator algebra

Consider the operators $\underline{A}$ and $\underline{B}$, which commute with their commutator, i.e. $[\underline{B}, [\underline{A}, \underline{B}]] = [\underline{A}, [\underline{A}, \underline{B}]] = 0$. Prove that

(a) for every analytic function $F(x)$ we have

$$[\underline{A}, F(\underline{B})] = [\underline{A}, \underline{B}]F'(\underline{B}) \; ,$$

where $F'(x)$ denotes the derivative of $F(x)$. Hint: Start by proving $[\underline{A}, \underline{B}^n] = n[\underline{A}, \underline{B}]\underline{B}^{n-1}$. Then use the fact that $F(x)$ is analytic.

(b)

$$e^{\underline{A}}e^{\underline{B}} = e^{\underline{A}+\underline{B}}e^{[\underline{A},\underline{B}]/2} \; .$$

Hint: Consider the derivative of $\underline{F}(s) = e^{\underline{A}s}e^{\underline{B}s}$ with respect to the real parameter s, and work your way towards a first order differential equation $\partial_s\underline{F}(s) = (\ldots)\underline{F}(s)$.

Problem 19: Changing representations

Consider a two-dimensional physical system. The kets $\mid \psi_1\rangle$ and $\mid \psi_2\rangle$ form an orthonormal basis of the state space. Another basis $\mid \phi_1\rangle$ and $\mid \phi_2\rangle$ is defined via

$$\begin{aligned} \mid \phi_1\rangle &= \frac{1}{\sqrt{2}}(\mid \psi_1\rangle + \mid \psi_2\rangle) \\ \mid \phi_2\rangle &= \frac{1}{\sqrt{2}}(\mid \psi_1\rangle - \mid \psi_2\rangle) \; . \end{aligned}$$

An operator $\underline{P}$ is represented in the $\mid \psi_i\rangle$-basis by the matrix

$$\begin{pmatrix} 1 & \epsilon \\ \epsilon & 1 \end{pmatrix} .$$

(a) Find the representation of $\underline{P}$ in the $\mid \phi_i\rangle$-basis, i.e. find the matrix $\langle\phi_i \mid \underline{P} \mid \phi_j\rangle$.

(b) Obtain the representation of the ket $e^{\underline{P}} \mid \psi_1\rangle$ in the $\mid \psi_i\rangle$-basis.

Problem 20: Uncertainty principle

A particle is described by the wave function

$$\psi(\vec{r}) = \frac{1}{\sqrt{\pi a^3}}\exp[-r/a] \quad (a > 0) \; .$$

Calculate Δx and Δp_x and verify the uncertainty relation for these components.

Problem 21: A simple state space

Consider a physical system with a three-dimensional state space. An orthonormal basis of the state space is chosen; in this basis the Hamiltonian is represented by the matrix

$$\underline{\mathcal{H}} = \begin{pmatrix} 2 & 1 & 0 \\ 1 & 2 & 0 \\ 0 & 0 & 3 \end{pmatrix} .$$

(a) What are the possible results when the energy of the system is measured?

(b) A particle is in the state $\mid \psi\rangle$, represented in this basis as $\frac{1}{\sqrt{3}} \begin{pmatrix} i \\ -i \\ i \end{pmatrix}$. Find $\langle \underline{\mathcal{H}} \rangle$, $\langle \underline{\mathcal{H}}^2 \rangle$, and $\Delta\mathcal{H}$.

Problem 22: Changing representations once again

The Hamiltonian of a particle in a potential $\mathcal{U}(\vec{r})$ is

$$\underline{\mathcal{H}} = \frac{1}{2m}\underline{\vec{p}}^2 + \mathcal{U}(\underline{\vec{r}}) .$$

Write the Schrödinger equation in both the $\vec{r}$- and the $\vec{p}$-representation.

Problem 23: The parity operator

The parity operator $\underline{\pi}$ is defined by

$$\underline{\pi} \mid \vec{r}\rangle = \mid -\vec{r}\rangle .$$

(a) Let $\mid \psi\rangle$ be an arbitrary ket with corresponding wave function $\psi(\vec{r})$. Find the wave function corresponding to $\underline{\pi} \mid \psi\rangle$. Show that $\underline{\pi}$ is a hermitian operator.

(b) Find the operator $\underline{\pi}^2$. What are the possible eigenvalues of $\underline{\pi}$?

(c) We define the operators

$$\underline{p}_+ = \frac{1}{2}\left(1 + \underline{\pi}\right) \qquad \underline{p}_- = \frac{1}{2}\left(1 - \underline{\pi}\right) .$$

For an arbitrary ket $\mid \psi\rangle$ we also define

$$\mid \psi_+\rangle = \underline{p}_+ \mid \psi\rangle \qquad \mid \psi_-\rangle = \underline{p}_- \mid \psi\rangle .$$

Show that $\mid \psi_+\rangle$ and $\mid \psi_-\rangle$ are eigenvectors of $\underline{\pi}$.

(d) Prove that the wave functions corresponding to $\mid \psi_+\rangle$ and $\mid \psi_-\rangle$ are even and odd functions, respectively.

Problem 24: Density matrix

(a) A system is in a pure state $|\psi\rangle$. We had said that the probability of experimentally finding it in a state $|\chi\rangle$ is given by $|\langle\chi|\psi\rangle|^2$. Show that this probability can be written as $P = \sum_n p_n |\langle\varphi_n|\chi\rangle|^2$, where $\underline{\rho} = \sum_n |\varphi_n\rangle p_n \langle\varphi_n|$.

(b) We describe polarized light using the density matrix. Consider a beam of light travelling in z-direction. The state vectors

$$\mid \varphi_1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad \mid \varphi_2\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

describe the x- and y-polarized states, respectively. Any pure state can be written as a linear combination of these two states, i.e. $\mid \psi\rangle = a \mid \varphi_1\rangle + b \mid \varphi_2\rangle$, where $|a|^2 + |b|^2 = 1$. Write down the density matrix for the pure state for the following cases: (i) x-polarized case, (ii) y-polarized case, (iii) 45^o-polarized state, and (iv) 135^o-polarized state. Show also, that the density matrices for the following two mixed states are identical: (v) mixture of 50% x-polarized and 50% y-polarized states; (vi) 50% 45^o-polarized and 50% 135^o-polarized.

Problem 25: Path integral of the free particle

Using the x-representation show that the equation

$$\underline{\rho}(t) = \underline{\rho}(\epsilon)\underline{\rho}(\epsilon)\ldots\underline{\rho}(\epsilon) \qquad (\text{n factors }; t = n\epsilon)$$

is correct for

$$\rho\left(x_k, x_{k-1}; \epsilon\right) = \sqrt{\frac{m}{2\pi\hbar i\epsilon}} \exp\left[-\frac{m}{2\hbar i\epsilon}\left(x_k - x_{k-1}\right)^2\right] .$$

Problem 26: First Born approximation

(a) A particle of mass μ and momentum $\hbar\vec{k}$ is scattered by the Yukawa potential $\mathcal{U}(r) = \mathcal{U}_o \exp[-\kappa r]/(\kappa r)$, where $\mathcal{U}_o$ is real and κ is positive. Using the first Born-approximation to calculate the scattering amplitude, i.e.

$$A^{(1)} = -\frac{4\pi^2\mu}{\hbar^2}\langle \vec{k}\,' \mid \underline{\mathcal{U}} \mid \vec{k}\rangle \ ,$$

obtain both the differential and the total scattering cross section, i.e. $d\sigma/d\Omega = |A^{(1)}|^2$ and σ.

(b) Repeat the calculation of $d\sigma/d\Omega$ in part (a) for the Gaussian potential $\mathcal{U}(r) = \frac{1}{\sqrt{4\pi}}\mathcal{U}_o \exp[-(\kappa r/2)^2]$. Compare $d\sigma/d\Omega$ graphically for the Yukawa and the Gaussian potential. Comment on the differences observed for small and large momentum transfer $q = |\vec{k} - \vec{k}\,'|$.

Problem 27: Stark effect

Consider a hydrogen atom placed in a uniform static electric field E that points along the $\hat{z}$-direction. The term that corresponds to this interaction in the Hamiltonian is

$$\underline{\mathcal{W}} = -eEz$$

Note that for the electric fields typically produced in a laboratory, the condition $\underline{\mathcal{W}} \ll \underline{\mathcal{H}}_0$ is satisfied. The appearance of the perturbation removes the degeneracy from some of the hydrogen states. This phenomenon is called the Stark effect. Calculate the Stark effect for $n = 2$ in a hydrogen atom.

Problem 28: Variation method applied to 1D harmonic oscillator

Consider a 1D harmonic oscillator:

$$\underline{\mathcal{H}} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2$$

(a) For the one-parameter family of wave functions $\psi_\alpha(x) = e^{-\alpha x^2}$ $(\alpha > 0)$, find a wave function that minimizes $\langle\underline{\mathcal{H}}\rangle$. What is the value of $\langle\underline{\mathcal{H}}\rangle_{min}$?

(b) For another one-parameter family of wave functions $\psi_\beta(x) = xe^{-\beta x^2}$ $(\beta > 0)$, find a wave function that minimizes $\langle\underline{\mathcal{H}}\rangle$ and compute the value of $\langle\underline{\mathcal{H}}\rangle_{min}$.

(c) Repeat the same procedure for

$$\psi_\gamma(x) = \frac{1}{x^2 + \gamma} \qquad (\gamma > 0) \ .$$

Problem 29: Variation method applied to helium

(a) Write the Schrödinger equation for the helium atom. What are the solutions for the ground state if one neglects the interaction between the two electrons?

(b) Assume that the electrons perform an electric screening of each other and define Z as a variational parameter. Use the variation method and find $\langle\mathcal{H}\rangle$ and the screening charge.

Problem 30: Charge in an electromagnetic field

(a) Starting from the relativistic Lagrange function $\mathcal{L} = -\frac{mc^2}{\gamma(v)} + \frac{e}{c}\vec{A}\cdot\vec{v} - e\varphi$, where $\gamma(v) = \left(1 - \frac{v^2}{c^2}\right)^{-\frac{1}{2}}$, show how one may arrive at the non-relativistic Hamilton operator

$$\begin{aligned}\underline{\mathcal{H}} \quad &= \quad \frac{\underline{\vec{p}}^2}{2m} + e\varphi(\vec{r}) - \frac{e}{mc}\vec{A}(\underline{\vec{r}})\cdot\underline{\vec{p}} \\ &\quad + \frac{i\hbar e}{2mc}\vec{\nabla}\cdot\vec{A}(\underline{\vec{r}}) + \frac{e^2}{2mc^2}\vec{A}^2(\underline{\vec{r}}) \ .\end{aligned}$$

for a charge in an electromagnetic field.

(b) In addition show that if $|\psi(t)\rangle$ is an eigenket of $\underline{\mathcal{H}}$ then $|\ \psi\,'(t)\rangle = e^{i\tilde{f}(\underline{\vec{r}},t)} \mid \psi(t)\rangle$, where $\tilde{f}(\underline{\vec{r}},t) = \frac{e}{\hbar c}f(\underline{\vec{r}},t)$, is an eigenket of $\underline{\mathcal{H}}\,'$ obtained via the gauge transformations

$$\vec{A} \ \to \vec{A}\,' = \vec{A} + \vec{\nabla}f \qquad \varphi \ \to \varphi\,' = \varphi - \frac{1}{c}\dot{f} \ ,$$

applied to $\underline{\mathcal{H}}$. Hints: (i) use $\underline{\mathcal{H}}$ in its original form (4.103); (ii) show first that $\underline{\vec{p}}|\psi\,'\rangle = e^{i\tilde{f}}(\underline{\vec{p}} + \hbar\vec{\nabla}\tilde{f})|\psi\rangle$, i.e. $(\underline{\vec{p}} - \frac{e}{c}\vec{A}\,')|\psi\,'\rangle =$

$e^{i\tilde{f}}(\underline{\vec{p}}-\frac{e}{c}\vec{A})|\psi\rangle$.

Problem 31: Time-dependent perturbation theory of a two state system

Consider a quantum system with two stationary eigenstates $\mid 1\rangle$ and $\mid 2\rangle$. The difference between their eigenvalues is given by $E_2 - E_1 = \hbar\omega_{21}$. At time $t = 0$, when the system is in state $\mid 1\rangle$, a small perturbation that does not change in time and equals $\underline{\mathcal{H}}'$ is applied. The following matrix elements are given:

$$\begin{aligned} \langle 1 \mid \underline{\mathcal{H}}' \mid 1\rangle &= 0 \\ \langle 2 \mid \underline{\mathcal{H}}' \mid 1\rangle &= \hbar\omega_0 \\ \langle 2 \mid \underline{\mathcal{H}}' \mid 2\rangle &= -\hbar\omega_{21} \end{aligned}$$

(a) Using first-order time-dependent perturbation theory, calculate the probability of finding the system at time t in state $\mid 1\rangle$, and the probability of finding it in the state $\mid 2\rangle$.

(b) Solve exactly the Schrödinger equation and find $\mid \psi(t)\rangle$.

(c) What is the probability that at time t the system is in the state $\mid 2\rangle$? When is the approximation used in part (a) a correct one? At what time (for the first order) will the system be with probability 1 in state $\mid 2\rangle$.

Problem 32: Field induced ionization of atomic hydrogen

Consider a hydrogen atom in its ground state at time $t = 0$. At the same time a uniform periodic electric field, $\vec{E} = -\frac{1}{c}\frac{\partial \vec{A}}{\partial t} - \vec{\nabla}\varphi$, is applied to the atom. Assume a simple plane wave, $\vec{A} = A_0\vec{e}\cos\left(\vec{k}\cdot\vec{r} - wt\right)$, where $\vec{e}$ is a unit vector characterizing the polarization direction. In addition with proper gauge, we may set $\varphi = 0$. Using first order time-dependent perturbation theory, find the probability of ionization per unit time. Assume that when the atom becomes ionized, its electron becomes free:

(a) Find the minimum frequency, ω_o, that the field needs in order to ionize the atom. Using the expressions discussed in sections 4.2 and 4.3 of the lecture notes write down an expression for the ionization probability $P_f(t)$ and the time-independent quantity $|\mathcal{H}_{1,fi}|^2$ in dipole approximation. Replace A_0 by $E_0 = \omega A_0/c$.

(b) Calculate the matrix element, $\langle f|\vec{e}\cdot\underline{\vec{r}}|i\rangle$ and give an expression for $|\mathcal{H}_{1,fi}|^2$. Hint: Here $\langle\vec{r}|f\rangle = \frac{1}{\sqrt{V}}\exp[i\vec{k}\cdot\vec{r}]$, where $\vec{k}$ is the wave vector of the free electron. This expression assumes that the final state corresponds to an 'almost free particle' - a particle in a large box with volume V. The confinement ensures that the state can be normalized.

(c) Write down an expression for the final density of states, $\rho(E_f)$, and use the formula

$$P(t) = \int_{\text{range}} P_f(t)\rho(E_f)dE_f d\Omega_f \ .$$

to calculate the total ionization probability. Here the integration over $d\Omega_f$ accounts for the fact that the free electron wave vector can have any direction in space. Finally express k in terms of ω and ω_o and write down an expression for the probability of ionization per unit time, $dP(t)/dt$.

Problem 33: Quasi classical approximation and Morse potential

Using the quasi classical approximation,

$$\frac{1}{\hbar}\oint p dx = 2\pi\left(n+\frac{1}{2}\right) \qquad (n = 0, 1, 2, \ldots) \ ,$$

numerically calculate the eigenvalues, $\epsilon_n = \frac{2mE_n}{\hbar^2 a^2}$, for a particle confined to a Morse potential

$$\mathcal{U}(x) = D\left(1 - \exp[-ax]\right)^2 \ ,$$

with $D = 16\frac{\hbar^2 a^2}{2m}$. You may use a computer language according to your choice. Your result should consist of a table listing all eigenvalues, a short but exact description of your algorithm, and a printout of your program.

Problem 34: Completeness relation for bosons and fermions

For the case of $N = 2$ prove the relation

$$1^{(\pm)} = \frac{1}{N!} \sum_{\alpha_1, \ldots, \alpha_N} |\phi_\alpha^{(\pm)}\rangle\langle\phi_\alpha^{(\pm)}| \,.$$

by showing

$$1^{(\pm)}|\phi_\alpha^{(\pm)}\rangle = |\phi_\alpha^{(\pm)}\rangle \,.$$

Problem 35: Pauli matrices

(a) Calculate the commutator relation $[\underline{\sigma}_i, \underline{\sigma}_j]$, where $i, j = x, y, z$ and the $\underline{\sigma}_i$, are the Pauli matrices given by

$$\begin{aligned} \underline{\sigma}_x &= \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \\ \underline{\sigma}_y &= \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \\ \underline{\sigma}_z &= \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \end{aligned}$$

The Pauli matrices are related to the spin operator via

$$\vec{\underline{S}} = \frac{\hbar}{2}\vec{\underline{\sigma}} \,.$$

Using the basis vectors of $\underline{S}_z$ eigenvectors, calculate $\underline{S}_i \mid +1/2\rangle$ and $\underline{S}_i \mid -1/2\rangle$ $(i = x, y, z)$, where $\mid +1/2\rangle$ and $\mid -1/2\rangle$ are the eigenvectors of $\underline{S}_z$ with eigenvalues $+\hbar/2$ and $-\hbar/2$, respectively.

(b) If the z-component of an electron spin is $+\hbar/2$, what is the probability that its component along a direction $z\,'$ that forms an angle θ with the z-axis equals $+\hbar/2$ or $-\hbar/2$?

(c) What is the average value of the spin along $z\,'$?

Problem 36: Clebsch-Gordan coefficients

In class we had used that the $c\,(j_1, j_2, j, m_J; m_1, m_2) = 0$ unless $m_1 + m_2 = m_J$. Show this!

Problem 37: The hydrogen molecule

In class we have discussed a simple theory for the hydrogen molecule. Our result for the electronic energy was:

$$E_{I/III} = E_A + E_B + \frac{D \pm A}{1 \pm |K|^2} \,.$$

E_A and E_B are atomic ground state energies. Formulas for the quantities $D(R)$ and $A(R)$, i.e. the direct Coulomb energy and the exchange energy, as well as $K(R)$, the overlap integral, were given in class. R is the distance between the nuclei. Evaluate $E_{I/III}$ explicitly using atomic hydrogen ground state (1s) orbitals, graph your result, and determine the bond length in units of a_0.

Hints: You will have to evaluate a number of integrals. In most cases it is useful to use elliptic coordinates μ, ν, and ϕ: $\mu = (\rho_A + \rho_B)/R$ and $\nu = (\rho_A - \rho_B)/R$. Note that ρ_A is the separation of one particular electron from nucleus A, and ρ_B is the separation of the same electron from nucleus B. ϕ is the angle of rotation around the line connecting A and B. In elliptic coordinates the volume element is $d^3r = (R^3/8)(\mu^2 - \nu^2)d\mu d\nu d\phi$ $(1 \leq \mu \leq \infty,\ -1 \leq \nu \leq 1,\ 0 \leq \phi \leq 2\pi)$. For K you should get $K = (1 + R + R^2/3)\exp[-R]$ (cf. Eq. (5.74) on page 89). *Important*: Use the equation given in class to evaluate the Coulomb integral; replace the electron-electron separation in the exchange integral by a constant a. A reasonable value for a may be obtained by applying the same approximation to the Coulomb integral. In this case you can do the integral exactly and thus obtain a formula $a = a(R)$ by the requirement that the approximation is equal to the exact solution. A reasonable value for R (e.g. 1.5) hopefully also yields a reasonable value for a.

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