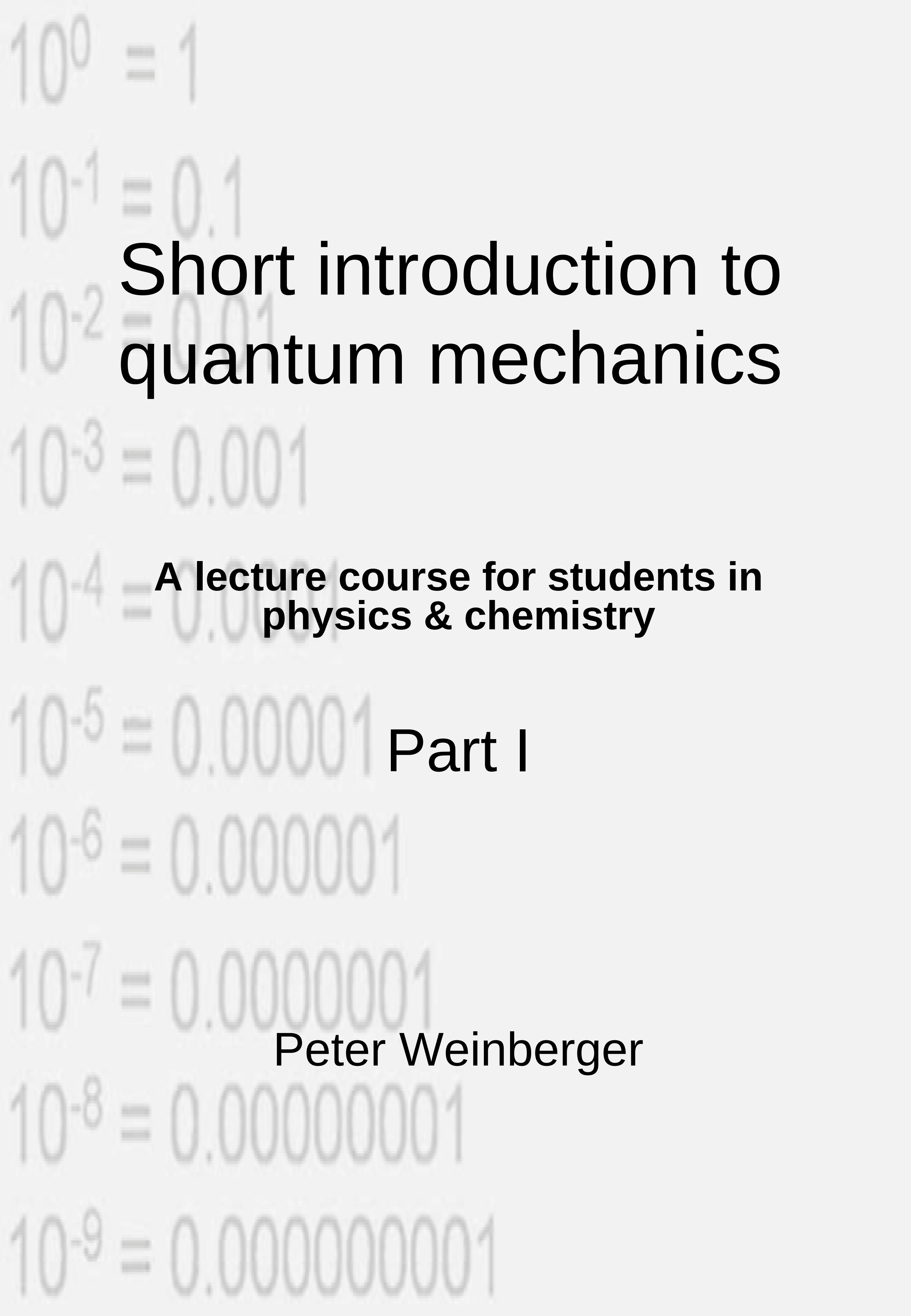

Short introduction to quantum mechanics

A lecture course for students in physics & chemistry

Part I

Peter Weinberger

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1 Introduction

"Physics (al-'ilm-al-tabi'i) investigates bodies that exist by nature, not human will, such as the various species of minerals, plants, and animals. Physics investigates all these and whatever exists in them, I mean, all their accidents, properties, and causes, as well as all that in which they exist by necessity, like time, space, and motion"

"Guide to the Perplexed", Moses Maimonides (1138-1204)

Physical phenomena are related to the number of particles participating in the corresponding processes. Just as well of course one could say that physical phenomena are a question of dimensions or of the scale under consideration.

Measurements of macroscopical properties are determined by macroscopical dimensions, those of microscopical properties by the dimensions in the microcosmos:

	MACROCOSMOS	MICROCOSMOS
# of particles	$\sim\ 10^{23}$	$\sim\ 10^{n},\ n \leq 5$
length	$[cm]$	$10^{-8}\ [cm]$
mass	$[g]$	$10^{-28}\ [g]$
time	$[s]$	$10^{-10}\ [s]$

Macroscopical properties can be related to microscopical properties by means of statistical methods, they never can never be used to interpret microscopical quantities, since statistically averaged quantities do not permit to single out a "single event" ("single case").

MACROCOSMOS		MICROCOSMOS
Classical Mechanics		*Quantum Mechanics*
$\uparrow$		$\downarrow$
$\longleftarrow$	*Statistical Mechanics*	$\longleftarrow$

CLASSICAL MECHANICS:

> "The coordinates of space[0] (x, y, z) and momentum (p_x, p_y, p_z) of a body in motion can be determined simultaneously exact."

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[0] By space the so-called configuration space is meant, ie.e, the set of (cartesian) position coordinates of an object.

"The energy E of a body in motion is always a continuous function of its space and momentum coordinates."

"The laws of classical mechanics are equations of motion for **"classical particles"**:

$$\Delta p_x \Delta x = \Delta p_y \Delta y = \Delta p_z \Delta z = 0 \quad , \tag{0}$$

where

$$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} \qquad , \qquad \Delta p_x = \sqrt{\langle p_x^2 \rangle - \langle p_x \rangle^2} \qquad , \tag{1}$$

i.e., where Δx is the statistical fluctuation of the measured value of x around the averaged value of x, $\langle x \rangle$, etc.

QUANTUM MECHANICS

"Space and momentum coordinates of a body in motion can not be determined simultaneously exact."

"The energy of a body in motion is not a continuous function of its space and momentum coordinates."

The uncertainty for a simultaneous measurement of space and momentum coordinates or of the energy and time is a universal constant, namely *Planck's* constant:

$$h = \; 6.62517.10^{-34} \; Js$$

The laws of quantum mechanics are equations of motion for **"non-classical particles"**:

$$\Delta p_x \Delta x \geq \hbar, \quad \Delta p_y \Delta y \geq \hbar, \quad \Delta p_z \Delta z \geq \hbar, \tag{2}$$

$$\Delta E \Delta t = \geq \hbar, \qquad \hbar = h/2\pi \quad . \tag{3}$$

The uncertainty relations in (2) and (3) are usually called *Heisenberg Uncertainty Principle.*

References

[1] W.Pauli, Letter to M.Born (31.4.1954), in: *"A.Einstein - M.Born, Briefwechsel"*, Ullstein Verlag, 1986

[2] W.Pauli, *"Die allgemeinen Prinzipien der Wellenmechanik"*, Handbuch der Physik, Bd. VVIV, 1933

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2 The postulates of quantum mechanics

2.1 *Postulate 1*

"The states of a physical system are completely described by in general complex functions $\Psi(q_1, q_2, q_3, ..., q_n; t)$."

A physical (microscopical) system can be an atom, a molecule or a solid [1]. By completely is implied that the function $\Psi(q_1, q_2, q_3, ..., q_n; t)$ contains all information obtainable by experiments. The q_i, $i = 1, .., n$, are called characteristic variables such as space coordinates, t is the time dependence. The functions Ψ are called **state functions** or **wavefunctions**. These functions have to satisfy the following conditions:

(1) The wavefunctions have to be continuous functions of their independent variables.

(2) They have to have continuous derivatives with respect to their independent variables.

(3) They have to be square integrable, i.e., the integral

$$N = \int .. \int \Psi^*(q_1, q_2, q_3, ..., q_n; t)\Psi(q_1, q_2, q_3, ..., q_n; t)dq_1 dq_2..dq_n \tag{1}$$

has to exist and has to be finite. N is called the **norm of the wavefunction** and $d\tau = dq_1 dq_2..dq_n$ the **volume element**.

(4) They are only unique with respect to a complex phase factor

$$\Psi' = e^{i\alpha}\Psi, \ (\Psi')^* = e^{-i\alpha}\Psi^* \ , \tag{2}$$

since

$$N = \int (\Psi')^*\Psi' d\tau = \int \underbrace{e^{-i\alpha}e^{i\alpha}}_{=1}\Psi^*\Psi d\tau = \int \Psi^*\Psi d\tau \quad . \tag{3}$$

2.2 *Postulate 2*

"To each dynamical variable (observable) a linear (Hermitian) operator can be assigned, which acts on the state function Ψ."

An operator is a formal description (operation) by which from one function another one is generated. Let $\widehat{O}$ be such an operation then

$$\widehat{O}\Psi = \Psi' \ . \tag{4}$$

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[1] A careful reader will immediately guess that in the end still Democrit's view of matter is the underlying principle.

In other words $\widehat{O}$ is an operation by which Ψ is mapped onto Ψ'.

The differential operator $\frac{d}{dx}$ is defined for functions, for which the independent variable is x such as for the following function $f(x)$

$$f(x) = \exp\left(-\frac{1}{2}x^2\right) \quad , \tag{5}$$

$$\frac{d}{dx}f(x) = (-\frac{1}{2}2x)\exp\left(-\frac{1}{2}x^2\right) = -x\exp\left(-\frac{1}{2}x^2\right) \quad . \tag{6}$$

As one can see from this example $\frac{d}{dx}$ maps the function $\exp\left(-\frac{1}{2}x^2\right)$ onto the function $-x\exp\left(-\frac{1}{2}x^2\right)$.

2.3 *Linear operators:*

Consider two operators $\widehat{O}_1$ and $\widehat{O}_2$. They are called linear if and only if

$$\widehat{O}_i(\Psi + \Phi) = \widehat{O}_i\Psi + \widehat{O}_i\Phi \ , \quad i = 1,2 \quad , \tag{7}$$

$$(\widehat{O}_1 + \widehat{O}_2)\Psi = \widehat{O}_1\Psi + \widehat{O}_2\Psi \quad , \tag{8}$$

$$\widehat{O}_i(c\Psi) = c\widehat{O}_i\Psi \ , \ i = 1,2, \ c \in Z \ , \tag{9}$$

where Z is the field of complex numbers.

2.4 *Hermitian operators:*

An operator $\widehat{O}$ is called Hermitian[2] if and only if $\widehat{O}$ is a (real) linear operator and

$$\int \Phi_i^* \underbrace{\widehat{O}\ \Phi_j}_{=\phi_k} d\tau \ = \int \Phi_i \underbrace{(\widehat{O}\ \Phi_j)^*}_{=\phi_k^*} d\tau \ \equiv \int \Phi_i \widehat{O} \Phi_j^* d\tau \quad , \tag{10}$$

i.e.,

$$\int \Phi_i^* \Phi_k d\tau \ - \int \Phi_i \Phi_k^* d\tau \ = \ 0 \quad . \tag{11}$$

---

[2] For a more formal definition see chapter 14

2.5 *Correspondence principle*

The operators that describe physical observables can be obtained from the corresponding quantities in classical mechanics using the following assignment for the three basic quantities space, momentum and energy ($\hbar = h/2\pi$):

	classical observable	*QM − operator*
space	$x,\ q$ $\mathbf{r} = (x, y, z)$	$\widehat{x}\ ,\ \widehat{q}$ $\widehat{r} = (\widehat{x}, \widehat{y}, \widehat{z})$
momentum	p_x $\mathbf{p} = (p_x, p_y, p_z)$	$\widehat{p}_x = -i\hbar\frac{\partial}{\partial x} = -i\hbar\nabla_x$ $\widehat{\mathbf{p}} = (\widehat{p}_x, \widehat{p}_y, \widehat{p}_z) = -i\hbar\boldsymbol{\nabla}$
energy	E	$\widehat{E} = i\hbar\frac{\partial}{\partial t}$

With the help of these three basic ”correspondences” most other operators can be composed:

	classical observable	*QM − operator*
potential energy	$V = V(\mathbf{r})$	$\widehat{V} = V(\mathbf{r})$
kinetic energy	$T = \frac{p^2}{2m} =$ $= \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2)$	$\widehat{T} = \frac{\widehat{p}^2}{2m} = -\frac{\hbar^2}{2m}\left[\boldsymbol{\nabla} \cdot \boldsymbol{\nabla}\right] =$ $= -\frac{\hbar^2}{2m}\Delta$
energy	$H(\mathbf{p}, \mathbf{r}) = T(\mathbf{p}) + V(\mathbf{r})$	$\widehat{H} = \widehat{T} + \widehat{V} =$ $= -\frac{\hbar^2}{2m}\Delta + V(\mathbf{r})$

$H(\mathbf{p}, \mathbf{r})$ is the (classical) **Hamilton function**, $\widehat{H}$ is therefore consequently called the **Hamilton operator**. The correspondence principle is sometimes also called **Bohr's principle**. The operator $\Delta = \nabla \cdot \nabla = \nabla^2$ carries a famous name. It is the **Laplace operator**, ∇ is sometimes also called **Nabla operator**.

2.6 *Postulate 3*

”If the state function $\Psi_i(q_1, q_2, q_3, ..., q_n; t)$ is an eigenfunction of an operator $\widehat{O}$ that corresponds to the observable Ω then the measured

value of Ω assumes exactly one particular value λ_i:

$$\widehat{O}\Psi_i(q_1, q_2, q_3, ..., q_n; t) = \lambda_{\mathbf{i}}\Psi_i(q_1, q_2, q_3, ..., q_n; t)\ . \tag{12}$$

$\Psi_i(q_1, q_2, q_3, ..., q_n; t)$ is then called **eigenfunction** of the operator $\widehat{O}$ corresponding to the **eigenvalue** $\lambda_{\mathbf{i}}$.

> Suppose the operator $\widehat{O}$ is given by $\frac{d^2}{d\phi^2}$ and Ψ_i by $\cos(4\phi)$,
>
> $$\frac{d^2}{d\phi^2}\left(\cos(4\phi)\right) = -16\cos(4\phi)\ . \tag{13}$$
>
> The function $\cos(4\phi)$ is therefore an eigenfunction of $\frac{d^2}{d\phi^2}$ corresponding to the eigenvalue -16. Quite clearly also $\sin(4\phi)$ is an eigenfunction of $\frac{d^2}{d\phi^2}$ to the eigenvalue -16, and so is any linear combination of $\cos(4\phi)$ and $\sin(4\phi)$, $\alpha\cos(4\phi) + \beta\sin(4\phi)$, α, $\beta \in Z$.

2.7 *Schrödinger equation*

For a physical system for which the classical Hamilton function is not explicitly time-dependent an eigenvalue equation applies for the Hamilton operator $\widehat{H}$, the so-called **stationary** or **time-independent Schrödinger** equation,

$$\widehat{H}\Psi_n(\mathbf{q}) = E_n\Psi_n(\mathbf{q})\ , \quad \mathbf{q} = (q_1, q_2, .., q_n) \tag{14}$$

where the $\Psi_n(\mathbf{q})$ are the eigenfunctions and the E_n the possible energy (eigen-) values of $\widehat{H}$. If the Hamilton function is explicitly time-dependent then the state function describes the time evolution of the system. Using the correspondence principle in order to identify $\widehat{H}$ with the energy operator $\widehat{E}$, one gets the so-called **time-dependent Schrödinger equation**:

$$\widehat{H}\Psi(\mathbf{q}, t) = \widehat{H}\Psi(\mathbf{q}, t) = i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{q}, t) \tag{15}$$

The time-dependent Schrödinger equation applies in general also to the case of a time-independent classical Hamilton function. In this particular case the wave function $\Psi(\mathbf{q}, t)$ can be separated with respect to space and time using the following product of functions:

$$\Psi(\mathbf{q}, t) = \psi_n(\mathbf{q})F(t)\ . \tag{16}$$

With the above ansatz in the time-dependent Schrödinger equation, one gets:

$$\widehat{H}\Psi(\mathbf{q},t) = \widehat{H}\{\psi_n(\mathbf{q})F(t)\} = \{\widehat{H}\psi_n(\mathbf{q})\}F(t) =$$

$$= i\hbar\frac{\partial}{\partial t}\{\psi_n(\mathbf{q})F(t)\} = \psi_n(\mathbf{q})\{i\hbar\frac{\partial}{\partial t}F(t)\} \ . \tag{17}$$

Dividing by $\psi_n(\mathbf{q})F(t)$,

$$\frac{\widehat{H}\psi_n(\mathbf{q})}{\psi_n(\mathbf{q})} = \frac{i\hbar\frac{\partial}{\partial t}F(t)}{F(t)} \ , \tag{18}$$

it is evident that the left hand side (lhs) is only space dependent, whereas the right hand side (rhs) is only time dependent. The equality implies that the lhs and the rhs equals a constant, say E_n,

$$\frac{\widehat{H}\psi_n(\mathbf{q})}{\psi_n(\mathbf{q})} = E_n \ , \tag{19}$$

$$\frac{i\hbar\frac{\partial}{\partial t}F(t)}{F(t)} = E_n \ , \tag{20}$$

E_n being a so-called **Lagrange parameter**.

The first equation is nothing but the time-independent Schrödinger equation, the second equation,

$$i\hbar\frac{\partial}{\partial t}F(t) = E_nF(t) \ , \tag{21}$$

is easy to solve using as solution $F(t) = \exp(-iE_nt/\hbar)$. If therefore the Hamilton operator $\widehat{H}$ is not explicitly time-dependent, the wavefunction $\Psi(\mathbf{q},t)$ is given by

$$\Psi(\mathbf{q},t) = \Psi(\mathbf{q})\exp(-iE_nt/\hbar) \quad . \tag{22}$$

2.8 *Postulate 4*

If the state function $\psi(q,t)$ is not an eigenfunction of the operator $\widehat{O}$ corresponding to the observable Ω, then the measured value of Ω can be any of the possible eigenvalues of $\widehat{O}$. The average over a series of measurements, however, is identical to the so-called expectation value of $\widehat{O}$:

$$< \widehat{O} > \ = \frac{\int \psi^*(\mathbf{q},t)\widehat{O}\psi(\mathbf{q},t)d\mathbf{q}dt}{\int \psi^*(\mathbf{q},t)\psi(\mathbf{q},t)d\mathbf{q}dt} \ . \tag{23}$$

Once the state function is known, by means of this postulate for all well-defined observables the corresponding expectation values can be obtained. In particular also an interpretation of the state functions can be given. In a single particle system the probability dW to find the particle at a particular time t in the vicinity $d\tau = dxdydz$ of the position $\mathbf{r} =(x, y, z)$ is given by

$$dW = \frac{\Psi^*(\mathbf{r}, t)\Psi(\mathbf{r}, t)d\tau}{\int \Psi^*(\mathbf{r}, t)\Psi(\mathbf{r}, t)d\tau} = \frac{|\Psi(\mathbf{r}, t)|^2 \, d\tau}{\int |\Psi(\mathbf{r}, t)|^2 \, d\tau} \quad . \tag{24}$$

In a many particle system the expression

$$dW = \frac{|\Psi(\mathbf{q}_1, \mathbf{q}_2, .., \mathbf{q}_n, t)|^2 \, d\mathbf{q}_1 d\mathbf{q}_2..d\mathbf{q}_n}{\int .. \int |\Psi(\mathbf{q}_1, \mathbf{q}_2, .., \mathbf{q}_n, t)|^2 \, d\mathbf{q}_1 d\mathbf{q}_2..d\mathbf{q}_n} \quad , \tag{25}$$

defines the probability to find at a given time t simultaneously particle 1 in $d\mathbf{q}_1 = (dx_1 dy_1 dz_1)$, particle 2 in $d\mathbf{q}_2 = (dx_2 dy_2 dz_2)$ etc.

In general $\rho(\mathbf{q}_1, \mathbf{q}_2, .., \mathbf{q}_n, t)$,

$$\rho(\mathbf{q}_1, \mathbf{q}_2, .., \mathbf{q}_n, t) = \frac{dW}{d\mathbf{q}_1 d\mathbf{q}_2..d\mathbf{q}_n} =$$

$$= \frac{|\Psi(\mathbf{q}_1, \mathbf{q}_2, .., \mathbf{q}_n, t)|^2}{\int .. \int |\Psi(\mathbf{q}_1, \mathbf{q}_2, .., \mathbf{q}_n, t)|^2 \, d\mathbf{q}_1 d\mathbf{q}_2..d\mathbf{q}_n} \quad , \tag{26}$$

is called **probability density** or (less appropriate particle density or charge density). As one can see from (24) and (25) only the square of the state function is physically meaningful, the state function itself (see also (2)) has no meaning at all.

2.9 Consequences

2.9.1 Norm of a one-dimensional wavefunction

Suppose the wavefunction $\Psi_i(x)$ is defined within the interval [a,b]. The norm of this wavefunction is then a positive number N:

$$\int_a^b \Psi_i^*(x)\Psi_i(x)dx = N \quad . \tag{27}$$

Suppose that Ψ_i is given by $\cos\theta$ and the interval by $[0, 2\pi]$ then

$$N = \int_0^{2\pi} \cos^2\theta d\theta = \left| \frac{\sin\theta\cos\theta}{2} + \frac{\theta}{2} \right|_0^{2\pi} = \pi \quad . \tag{28}$$

Is the norm of a wavefunction identically unity, then the wavefunction is called **normalized**. An unnormalized wavefunction has to be normalized by the square root of the norm. Suppose $\Psi_i(x)$ is the unnormalized wavefunction and $\Psi_i'(x)$ the corresponding normalized wavefunction,

$$\Psi_i'(x) = \frac{1}{\sqrt{N}} \Psi_i(x) \ , \tag{29}$$

then

$$\int\limits_a^b \left(\Psi_i'(x)\right)^* \Psi_i^{'}(x) dx = \int\limits_a^b \left(\frac{1}{\sqrt{N}} \Psi_i^*(x)\right) \left(\frac{1}{\sqrt{N}} \Psi_i(x)\right) dx =$$

$$= \frac{1}{N} \int\limits_a^b \Psi_i^*(x) \Psi_i(x) dx = 1 \ . \tag{30}$$

2.10 Properties of a Hermitian operator

2.10.1 Eigenvalues

> **The eigenvalues of a Hermitian operator are always real numbers and correspond therefore to real measured values of the corresponding observable.**

Suppose the eigenvalue equation of a Hermitian operator $\widehat{O}$ is given by

$$\widehat{O} \phi_n = \lambda_n \phi_n \ . \tag{31}$$

$$(\widehat{O} \phi_n)^* = \lambda_n^* \phi_n^* \ , \tag{32}$$

and that the eigenfunction ϕ_n is square integrable

$$\int \phi_n^* \phi_n d\tau = N \ , \ N \ > \ 0 \ . \tag{33}$$

Multiplying from the left (31) with ϕ_n^* and (32) with ϕ_n , one gets

$$\phi_n^* \widehat{O} \phi_n = \lambda_n \phi_n^* \phi_n \ , \tag{34}$$

$$\phi_n (\widehat{O} \phi_n)^* = \lambda_n^* \phi_n \phi_n^* \ . \tag{35}$$

Integrating now the above two equations over the volume element $d\tau$ (see (33)) one gets

$$\int \phi_n^* \widehat{O} \phi_n d\tau = \lambda_n \int \phi_n^* \phi_n d\tau \ , \tag{36}$$

$$\int \phi_n (\widehat{O} \phi_n)^* d\tau = \lambda_n^* \int \phi_n \phi_n^* d\tau \ . \tag{37}$$

By taking the difference of these two equations

$$\underbrace{\int \phi_n^* \widehat{O} \phi_n d\tau \ - \ \int \phi_n \widehat{O} \phi_n^* d\tau}_{=\,0} = N(\lambda_n \ - \ \lambda_n^*) \ , \tag{38}$$

one easily can see that if the operator is indeed Hermitian the lhs is zero (see (10)), this in turn implies for the rhs that either the norm of the eigenfunction is zero, which was excluded, or that the eigenvalue λ_n is real.

2.10.2 Orthogonality relations

Suppose ϕ_i and ϕ_j are two functions defined over the same range corresponding to the volume element $d\tau$. These two functions are called **orthogonal**, if and only if

$$\int \phi_i^* \phi_j d\tau = \int \phi_j^* \phi_i d\tau = 0 \ . \tag{39}$$

Eigenfunctions $\phi_i, i = 1, 2, .., \infty$, **of a Hermitian operator** $\widehat{O}$ **that belong to different eigenvalues are orthogonal to each other**.

Let ϕ_i and ϕ_j be two functions belonging to different eigenvalues of $\widehat{O}$:

$$\widehat{O}\phi_i = \lambda_i \phi_i \quad , \tag{40}$$

$$\widehat{O}\phi_j = \lambda_j \phi_j \quad . \tag{41}$$

If one multiplies from the left the first equation with ϕ_j^* and the second with ϕ_i^* one simply gets:

$$\phi_j^* \widehat{O}\phi_i = \lambda_i \phi_j^* \phi_i \quad , \tag{42}$$

$$\phi_i^* \widehat{O}\phi_j = \lambda_j \phi_i^* \phi_j \quad . \tag{43}$$

Integrating now both equations over $d\tau$ and subtracting the first equation from the second yields

$$\underbrace{\int \phi_i^* \widehat{O} \phi_j d\tau \ - \int \phi_j^* \widehat{O} \phi_i d\tau}_{=\,0} \ = (\lambda_j - \lambda_i) \int \phi_i^* \phi_j d\tau \quad . \tag{44}$$

Now it is easy to see that either $\lambda_i = \lambda_j$, which was excluded, or $\int \phi_i^* \phi_j d\tau = 0$.

Orthogonal and normalized ("**orthonormalized**") eigenfunctions ϕ_i of a Hermitian operator can therefore be characterized compactly by

$$\int \phi_i^* \phi_j d\tau = \int \phi_j^* \phi_i d\tau = \delta_{ij} \quad , \tag{45}$$

where δ_{ij} is the so-called **Kronecker** symbol,

$$\delta_{ij} = \{ \begin{array}{cc} 1 & , \; i = j \\ & \\ 0 & , \; i \neq j \end{array} \quad . \tag{46}$$

If not only one eigenfunction ϕ_i belongs to a particular eigenvalue λ_i, but a set of functions $\Phi_{ij}, j = 1, 2.., m$, then this eigenvalue is said to be **m-fold degenerated** (see also Example 2). The set of eigenfunctions belonging to one and the same eigenvalue forms a linear manifold.

2.10.3 Completeness relation

> **The set of eigenfunctions of a Hermitian operator is not only a set of orthogonal functions, but is also complete**[3].

In order to illustrate this statement one can make use of the properties of Postulate 4, namely of expectation values. Suppose one expands the state function $\Psi(\mathbf{q})$ in terms of the normalized eigenfunctions $\phi_n(\mathbf{q})$ of the operator $\widehat{O}$ corresponding to the observable Ω,

$$\Psi(\mathbf{q}) = \sum_n c_n \phi_n(\mathbf{q}) \quad , \tag{47}$$

$$\Psi^*(\mathbf{q}) = \sum_m c_m^* \phi_m^*(\mathbf{q}) \quad ; \quad c_n, c_m \in Z \quad , \tag{48}$$

$$\widehat{O} \phi_n(\mathbf{q}) = \lambda_n \phi_n(\mathbf{q}) \quad . \tag{49}$$

Forming now the expectation value of $\widehat{O}$, one gets:

$$< \widehat{O} > = \int \Psi^*(\mathbf{q}) \widehat{O} \Psi(\mathbf{q}) d\tau =$$

$$= \sum_{n,m} c_m^* c_n \int \phi_m^*(\mathbf{q}) \underbrace{\widehat{O} \phi_n}_{=\lambda_n \phi_n(\mathbf{q})} (\mathbf{q}) d\tau = \sum_{n,m} c_m^* c_n \lambda_n \int \phi_m^*(\mathbf{q}) \phi_n(\mathbf{q}) d\tau =$$

$$= \sum_{n,m} c_m^* c_n \lambda_n \delta_{nm} = \sum_n c_n^* c_n \lambda_n = \sum_n |c_n|^2 \lambda_n = \sum_n W_n \lambda_n \qquad . \tag{50}$$

Quite clearly $|c_n|^2$ is a real number and therefore W_n is the probability that Ω takes on the eigenvalue λ_n of the corresponding operator $\widehat{O}$. In particular

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[3] For a more formal definition see chapter 14

consider now that the operator $\widehat{O}$ is the identity operator $\widehat{I}$, $\widehat{I}\Psi(\mathbf{q}) = \Psi(\mathbf{q})$, and recall *Postulate 1*:

$$\int \Psi^*(\mathbf{q})\widehat{I}\Psi(\mathbf{q})d\tau = \sum_n |c_n|^2 = 1 \qquad . \tag{51}$$

This last equation is nothing but the statement that the set of eigenfunctions of a Hermitian operator is complete, formulated in terms of *Postulate 4*.

2.11 Products of operators, commutators and constants of motion

Very often one has to deal with products of operators. The operator of the kinetic energy for example can be viewed as such product, $\widehat{T} = \frac{1}{2m}\widehat{\mathbf{p}}\cdot\widehat{\mathbf{p}} = \frac{1}{2m}\widehat{p}^2$, namely as a scalar product.

Let $\widehat{O}_1$ and $\widehat{O}_2$ be two operators acting in turn on the function ϕ ,

$$\widehat{O}_1\widehat{O}_2\phi = \widehat{O}_1(\underbrace{\widehat{O}_2\phi}_{=\phi'}) = \widehat{O}_1\phi' = \phi'' \qquad , \tag{52}$$

then in general

$$\widehat{O}_1\widehat{O}_2\phi \neq \widehat{O}_2\widehat{O}_1\phi; \quad \left(\widehat{O}_1\widehat{O}_2 - \widehat{O}_2\widehat{O}_1\right)\phi = [\widehat{O}_1, \widehat{O}_2]_-\phi \neq 0 \qquad . \tag{53}$$

However, if $[\widehat{O}_1, \widehat{O}_2]_- = \widehat{0}$ (zero operator), then these two operators are said to **commute .** The expression $[\widehat{O}_1, \widehat{O}_2]_-$ is called the **commutator** of the operators $\widehat{O}_1$ and $\widehat{O}_2$.

If two operators commute then they share the same set of eigenfunctions.

Suppose that the operators $\widehat{A}$ and $\widehat{B}$ commute, $[\widehat{A}, \widehat{B}]_- = \widehat{0}$, and that they belong to the following two eigenvalue problems:

$$\widehat{A}\psi_i = \alpha_i\psi_i \quad , \tag{54}$$

$$\widehat{B}\phi_j = \beta_j\phi_j \quad .$$

Formally therefore one can write

$$(\widehat{A}\widehat{B})\psi_i = (\widehat{B}\widehat{A})\psi_i = \widehat{B}(\widehat{A}\psi_i) = \widehat{B}(\alpha_i\psi_i) = \alpha_i(\widehat{B}\psi_i) \quad . \tag{55}$$

However, since

$$(\widehat{A}\widehat{B})\psi_i = \widehat{A}(\widehat{B}\psi_i) = \alpha_i(\widehat{B}\psi_i) \quad , \tag{56}$$

quite obviously the functions $\widehat{B}\psi_i$ are also eigenfunctions of the operator $\widehat{A}$! If one assumes for matter of simplicity that the functions ψ_i are not degenerated then

$$\widehat{B}\psi_i = c\psi_i \quad , \quad c \in Z \quad , \tag{57}$$

i.e., the action of $\widehat{B}$ on ψ_i can only generate a (complex) multiple of ψ_i, which in turn means that ψ_i is also an eigenfunction of the operator $\widehat{B}$ belonging to the eigenvalue c! In particular if one of the operators in a vanishing commutator is the Hamilton operator the other operator is called a **constant of motion**.

2.12 Coordinate transformations, invariance transformations

> **If the Hamilton operator $\widehat{H} = \widehat{H}(\mathbf{r})$ is invariant under a coordinate transformation $\widetilde{P}$** ($\widetilde{P}^{-1}\widetilde{P} = \widetilde{P}\widetilde{P}^{-1} = \widetilde{I}$, $\widetilde{I}$ identity transformation), **then the (function space) operator $\widehat{P}$ of this transformation commutes with $\widehat{H}$** , i.e. $[\widehat{H}, \widehat{P}]_- = 0$.

Suppose the coordinates of the function $f(x)$ are transformed by $\widetilde{P}$ and $\widehat{P}$ is the corresponding function space operator, then

$$\widehat{P}f(x) = f'(x) = f(\widehat{P}^{-1}x) = f(x') \quad . \tag{58}$$

Since equation (58) looks awfully abstract the following example shall be considered.

> Let $f(x)$ be a parabola and the coordinate transformation a translation $\widetilde{T}$ by a constant a :
>
> $$\widetilde{T}x = x + a \ , \quad \widetilde{T}^{-1}x = x - a \quad , \tag{59}$$
>
> $$\widetilde{T}^{-1}\widetilde{T}x = \widetilde{T}^{-1}(x+a) = x + a - a = x = \widetilde{I}x = \widetilde{T}\widetilde{T}^{-1}x \quad . \tag{60}$$
>
> Consider now each step from *Fig. 1*:
>
> $$y = f(x) = x^2 \underset{x'=x+a}{\longmapsto} f'(x') = (x'-a)^2 = y' \quad , \tag{61}$$
>
> $$f'(x') = (x'-a)^2 = (x+a-a)^2 = x^2 = f(x) \quad . \tag{62}$$

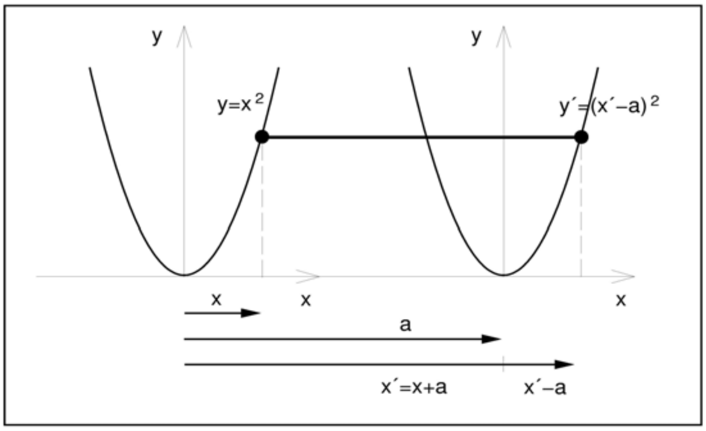

Figure 1: Translation of a parabola

Converting the figural aspects into an operator language, one gets:

$$\widehat{T}f = f' \quad , \quad \widetilde{T}x = x' \quad , \tag{63}$$

$$f'(x') = \widehat{T}f(\widetilde{T}x) = f(x) \quad . \tag{64}$$

Substituting now x by $\widetilde{T}^{-1}q$

$$f'(x') = \widehat{T}f(\widetilde{T}x) = \widehat{T}f(\widetilde{T}\widetilde{T}^{-1}q) = \widehat{T}f(q) \quad , \tag{65}$$

$$f(x) = f(\widetilde{T}^{-1}q) \quad , \tag{66}$$

and combing the rhs's of (65) and (66), one indeed regains (58)

$$\widehat{T}f(q) = f(\widetilde{T}^{-1}q) \quad . \tag{67}$$

Suppose finally that the Hamilton operator is given by $\widehat{H}(\mathbf{r})$ [4],

$$\widehat{H}(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r}) \quad , \tag{68}$$

and $\widetilde{R}$, $\widetilde{R}\widetilde{R}^{-1} = \widetilde{R}^{-1}\widetilde{R} = \widetilde{I}$, leaves $\widehat{H}(\mathbf{r})$ invariant, i.e.,

$$\widehat{R}\widehat{H}(\mathbf{r}) = \widehat{H}(\widetilde{R}^{-1}\mathbf{r}) = \widehat{H}(\mathbf{r}) \quad , \tag{69}$$

then transforming equation (68) with $\widetilde{R}$ yields immediately that

$$\widehat{R}\{\widehat{H}(\mathbf{r})\psi(\mathbf{r})\} = \{\widehat{R}\widehat{H}(\mathbf{r})\}\{\widehat{R}\psi(\mathbf{r})\} = E\{\widehat{R}\psi(\mathbf{r})\} \quad , \tag{70}$$

$$\{\widehat{H}(\widetilde{R}^{-1}\mathbf{r})\}\{\widehat{R}\psi(\mathbf{r})\} = \widehat{H}(\mathbf{r})\{\widehat{R}\psi(\mathbf{r})\} = E\{\widehat{R}\psi(\mathbf{r})\} \quad , \tag{71}$$

namely that **the transformed functions $\widehat{R}\psi(\mathbf{r})$ are also eigenfunctions of** $\widehat{H}(\mathbf{r})$, i.e., $\left[\widehat{H},\widehat{R}\right]_{-} = 0$, (see equations (56) and (57)).

---

[4] Note that a product of functions is transformed by transforming each of the factors.

2.13 Compatible and complementary variables

Let $\widehat{O}_1$ and $\widehat{O}_2$ be two operators that correspond to the dynamical variables Ω_1 and Ω_2. If $\psi(\mathbf{q};t)$, $\mathbf{q} = (q_1, q_2, \ldots, q_n)$ denotes the state function then the root mean square of these operators is defined by

$$\Delta\widehat{O}_i = \sqrt{\left(\widehat{O}_i - \langle\widehat{O}_i\rangle\right)^2} \quad , \quad i = 1,2 \quad , \tag{72}$$

and the following uncertainty relation holds true:

$$\Delta\widehat{O}_1\Delta\widehat{O}_2 \geq \frac{1}{2}\hbar \mid \langle\widehat{O}_3\rangle \mid \quad , \tag{73}$$

where

$$\widehat{O}_3 = -\frac{i}{\hbar}[\widehat{O}_1, \widehat{O}_2]_- \quad . \tag{74}$$

If $\widehat{O}_1$ and $\widehat{O}_2$ commute then the dynamical variables Ω_1 and Ω_2 are called compatible variables, **otherwise they are called complementary variables**.

As can be read off from the table summarizing the correspondence principle, the momentum and position coordinates, p_k and q_k, are such complementary variables, i.e.,

$$[q_k, p_k]_- = i\hbar \quad . \tag{75}$$

The Heisenberg uncertainty principle,

$$\Delta q_k \Delta p_k \geq \frac{1}{2}\hbar \quad , \tag{76}$$

is therefore a special case of (74).

It should be noted that the energy-time uncertainty principle[5] ,

$$\Delta E \Delta t \geq \frac{1}{2}\hbar \quad , \tag{77}$$

does have a different meaning, since at any given time t the energy E can have a well-defined value. ΔE is the difference between two values for the energy E, say E_1 and E_2, measured at $t = t_1$ and $t = t_2$ ($\Delta t = t_2 - t_1$). The uncertainty relation for complementary variables states that **at a given time** t, these variables cannot be measured simultaneously exact.

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[5] see also chapter 1

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3 The importance of boundary conditions

In this chapter three very important concepts shall be discussed, namely **boundary conditions**, **symmetry operators** and the **separability of differential equations**. These concepts are introduced using simple quantum mechanical models. The basis of all discussions is of course the time-independent or the time-dependent Schrödinger equation.

3.1 Free particles - matter waves

A free particle is classically characterized by the fact that its motion is independent of the coordinates of its potential energy ("**Galilei** motion"). As energy zero one can choose therefore the potential energy to be zero. The Hamilton operator for a "one-dimensional" free motion is then simply given by

$$\widehat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \quad , \tag{1}$$

and the corresponding time-dependent Schrödinger equation by

$$i\hbar\frac{\partial}{\partial t}\psi(x,t) = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x,t) \quad . \tag{2}$$

If one uses the separation of space and time variables as discussed in the previous chapter, namely,

$$\psi(x,t) = \phi(x)\exp(-iEt/\hbar) \quad , \tag{3}$$

then the time-independent Schrödinger equation is of the following form

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\phi(x) = E\phi(x),\ -\infty < x < +\infty \quad . \tag{4}$$

This is nothing but a second order linear differential equation with a constant coefficient, the solution of which is immediately found using the ansatz $\phi(x) = \exp(\pm ikx)$:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\exp(\pm ikx) = \frac{\hbar^2}{2m}k^2\exp(\pm ikx) \quad . \tag{5}$$

The time-dependent solution, obviously a periodic function in space and time,

$$\begin{aligned} \psi(x,t) = \exp(\pm ikx)\exp(-iEt/\hbar) = \exp(\pm ikx - iEt/\hbar) = \\ = \exp\left(\frac{i}{\hbar}(\pm p_x x - Et)\right) \quad . \end{aligned} \tag{6}$$

is called a "**matter wave**". The energy $E = E(k)$ can assume all possible values in the interval $(-\infty, \infty)$. Although $\psi(x,t)$ formally is a solution of the Schrödinger equation, it is not an acceptable wavefunction, since its norm diverges for x tending to $+\infty$,

$$\int\limits_{-\infty}^{\infty} \psi^*(x,t)\psi(x,t)dx =$$

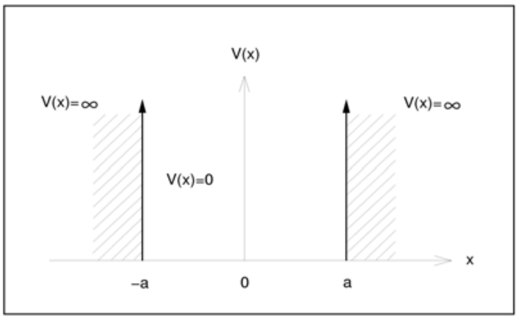

Figure 2: Particle in a box

$$= \int_{-\infty}^{\infty} \exp\left(\frac{i}{\hbar}(\pm p_x x - Et)\right) \exp\left(-\frac{i}{\hbar}(\pm p_x x - Et)\right) dx \tag{7}$$

3.2 Particle in a box

”Physically useful” solutions of a differential equation such as in (4) are only obtained if boundary conditions for a particular problem are defined . For (4) the following boundary condition shall be considered by confining the particle to a ”one-dimensional box” with infinite barriers (see Fig. 2):

$$\Psi\left(|x| \ \geq \ a\right) = 0 \quad , \tag{8}$$

The differential equation is still the same, namely,

$$\frac{d^2}{dx^2}\psi(x) + \frac{2mE}{\hbar^2}\psi(x) = 0 \quad , \tag{9}$$

which formally is of the form

$$\psi'' + C\psi = 0 \quad , \quad C = \frac{2mE}{\hbar^2} \quad . \tag{10}$$

The general solution of such a differential equation is given by

$$\psi(x) = A\exp(i\sqrt{C}x) + B\exp(-i\sqrt{C}x) \quad , \tag{11}$$

i.e., $\psi(x)$ is a superposition of two ”**plane waves**”, with opposite directions of propagation and amplitudes A and B. Using now the boundary condition (8),

$$\psi(-a) = 0 \ \rightarrow \quad A\exp(-i\sqrt{C}a) + B\exp(+i\sqrt{C}a) = 0 \quad , \tag{12}$$

$$\psi(+a) = 0 \ \rightarrow \quad A\exp(+i\sqrt{C}a) + B\exp(-i\sqrt{C}a) = 0 \quad , \tag{13}$$

one gets

$$\psi(-a)=0\ \rightarrow\quad A=-B\exp(2i\sqrt{C}a)\quad , \tag{14}$$

$$\psi(+a)=0\ \rightarrow\quad A=-B\exp(-2i\sqrt{C}a)\quad . \tag{15}$$

If one divides the first condition by the second, one obtains

$$1=\frac{\exp(2i\sqrt{C}a)}{\exp(-2i\sqrt{C}a)}=\exp(4i\sqrt{C}a)=\exp(2i\sqrt{C}a)\exp(2i\sqrt{C}a)\quad . \tag{16}$$

The squareroot of this equation,

$$\exp(2i\sqrt{C}a)=\pm 1\quad , \tag{17}$$

directly leads to a "quantization" of the energy, since

$$\exp(i\alpha)=1\qquad \text{only if the phase}\quad \alpha=n\pi\ ,\quad n\text{: even}\quad ,$$

$$\exp(i\alpha)=-1\quad \text{only if the phase}\quad \alpha=n\pi\ ,\quad n\text{: odd}\quad ,$$

i.e.,

$$2\sqrt{C}a=n\pi\quad ,\quad \sqrt{C}=\sqrt{\frac{2mE}{\hbar^2}}\quad , \tag{18}$$

$$E=E_n=\frac{\hbar^2\pi^2}{8ma^2}n^2\quad ;\quad n=1,2,....\quad . \tag{19}$$

Quite obviously the value $n=0$ has to be excluded, since then $\psi(x)$ would be identically zero for all values of x ($\forall x$; see also (11)and (12)) and consequently its norm would be identically zero. Equation (19) clearly shows that the particle in the box can have only discrete energies, i.e., the **energy is quantized because of the chosen boundary conditions**! n is therefore called a **quantum number**.

Using now the result from (18), namely $\sqrt{C}=n\pi/2a$ in the boundary conditions

$$\psi(-a)=0\rightarrow\quad A=-B\exp(in\pi)\quad , \tag{20}$$

$$\psi(+a)=0\rightarrow\quad A=-B\exp(-in\pi)\quad , \tag{21}$$

one can immediately see that

$$A=-B;\quad n\text{: even}\quad , \tag{22}$$

$$A=B;\quad n\text{: odd}\quad . \tag{23}$$

The wavefunction, i.e., the general solution in (11) can now be formulated in terms of the quantum number n

$$\psi_n(x)=A\left[\exp(i\sqrt{C}x)+(-1)^{n+1}\exp(-i\sqrt{C}x)\right]\quad . \tag{24}$$

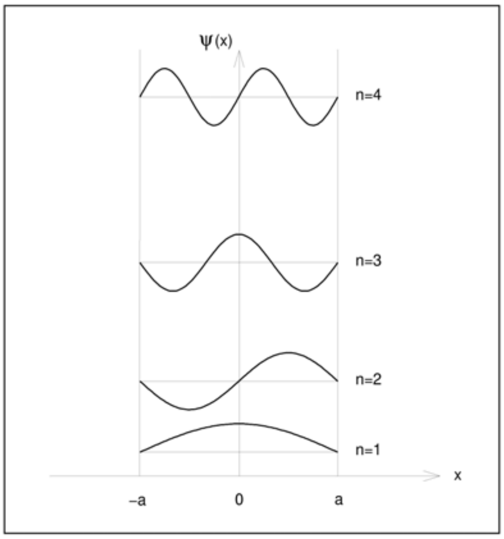

Figure 3: Wavefunctions for a particle in a box

However, since $\exp(\pm i\alpha) = \cos\alpha \pm i\sin\alpha$, one gets

$$\psi_n(x) = \{ \begin{array}{lcl} 2A\cos(\sqrt{C}x) & , & n: \text{ odd } , \\ 2Ai\sin(\sqrt{C}x) & , & n: \text{ even } . \end{array} \tag{25}$$

As a final step the wavefunctions have to be normalized (see also example 3)

$$n: \text{ odd } \quad \rightarrow \quad 4A^2 \int\limits_{-a}^{a} \Big[\cos(\sqrt{C}x)\Big]^2 dx = 4A^2 a \ , \ \rightarrow A = \frac{1}{2\sqrt{a}} \quad , \tag{26}$$

$$n: \text{ even } \quad \rightarrow \quad -4A^2 \int\limits_{-a}^{a} \Big[\sin(\sqrt{C}x)\Big]^2 dx = -4A^2 a \ , \rightarrow \ A = \frac{-i}{2\sqrt{a}} \quad , \tag{27}$$

$$\psi_n(x) = \{ \begin{array}{lcl} \frac{1}{\sqrt{a}}\cos(\frac{n\pi}{2a}x) & , & n: \text{ odd } , \\ \frac{1}{\sqrt{a}}\sin(\frac{n\pi}{2a}x) & , & n: \text{ even } . \end{array} \tag{28}$$

For the first few values of n the shape of the wavefunctions is shown in Figure 3.

Suppose now $\widetilde{P}$ is the inversion operator, $\widetilde{P}x = -x$, then

$$\widehat{P}\psi_n(x) = \{ \begin{array}{lll} \frac{1}{\sqrt{a}}\cos(-\frac{n\pi}{2a}x) = & \frac{1}{\sqrt{a}}\cos(\frac{n\pi}{2a}x) & n: \text{ odd } , \\ \frac{1}{\sqrt{a}}\sin(-\frac{n\pi}{2a}x) = & -\frac{1}{\sqrt{a}}\sin(\frac{n\pi}{2a}x) & n: \text{ even } . \end{array} \tag{29}$$

Quite clearly these results can be summarized as follows

$$\widehat{P}\psi_n(x) = (-1)^{n+1}\psi_n(x) \quad , \tag{30}$$

which only means that the wavefunction $\psi_n(x)$ is also an eigenfunction of $\widehat{P}$ with respect to the eigenvalue $(-1)^{n+1}$and therefore that the commutator $\left[\widehat{H}, \widehat{P}\right]_- = 0$.

From Figure 3-1, the starting point of the present discussion, one can see that the Hamilton operator is given by

$$\widehat{H} \equiv H(x) = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x) \quad , \tag{31}$$

$$V(|x| < a) = 0, \quad V(|x| \geq a) = \infty \quad . \tag{32}$$

Since both the kinetic energy term $-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$ and $V(x)$ are invariant under $\widehat{P}$,

$$\widehat{P}H(x) = H(\widetilde{P}^{-1}x) = H(x) \quad . \tag{33}$$

Not only the Hamilton operator is invariant under the inversion, but also the boundary conditions

$$\widehat{P}\psi_n(a) = \psi_n(-a) = \psi_n(a) = 0 \quad . \tag{34}$$

An operator that leaves the Hamilton operator *and* the boundary conditions invariant is called a symmetry operator. Since then $\widehat{P}$ commutes with $\widehat{H}$, $\widehat{P}$ is also a constant of motion.

3.3 Cyclic boundary conditions

In order to convince how important boundary conditions are for the quantization of the energy, in the following the same Schrödinger equation as in (9)

$$\frac{d^2}{dx^2}\psi(x) + \frac{2mE}{\hbar^2}\psi(x) = 0 \quad ,$$

and therefore the same general solution as in (11)

$$\psi(x) = A\exp(i\sqrt{C}x) + B\exp(-i\sqrt{C}x) \quad , \quad C = \frac{2mE}{\hbar^2} \quad ,$$

shall be considered, however, with different boundary conditions:

$$\psi(x) = \psi(x + L) \quad , \tag{35}$$

$$\psi'(x) = \psi'(x + L) \ , \quad \psi'(x) = \frac{d}{dx}\psi(x) \quad . \tag{36}$$

Boundary conditions of this type are called **cyclic or periodic boundary conditions**, since after a certain length L (”period”) the wavefunction is continuously repeated. Using these boundary conditions in the general solution for the wavefunction, i.e. repeating the same procedure as before in the case of a particle in a box, one gets

$$\begin{aligned} & A\exp(i\sqrt{C}x) + B\exp(-i\sqrt{C}x) = \qquad (37) \\ & = A\exp(i\sqrt{C}(x+L)) + B\exp(-i\sqrt{C}(x+L)) \quad . \end{aligned}$$

By collecting the terms with A on one side and those with B on the other side and taking out the phase $\exp(i\sqrt{C}x)$ one obtains

$$\begin{aligned} & A\exp(i\sqrt{C}x)\left(1-\exp(i\sqrt{C}L)\right) = \qquad (38) \\ & -B\exp(-i\sqrt{C}x)\left(1-\exp(-i\sqrt{C}L)\right) \ . \end{aligned}$$

However, since the number one on the rhs can be also be interpreted as $\exp(-i\sqrt{C}L)\exp(i\sqrt{C}L)$ the last equation can be formulated as

$$\begin{aligned} & A\exp(i\sqrt{C}x)\left(1-\exp(i\sqrt{C}L)\right) = \qquad (39) \\ & B\exp(-i\sqrt{C}x)\exp(-i\sqrt{C}L)\left(1-\exp(i\sqrt{C}L)\right) \ . \end{aligned}$$

Extracting now the common factor $\left(1-\exp(i\sqrt{C}L)\right)$ one gets

$$\begin{aligned} & \left(1-\exp(i\sqrt{C}L)\right) \times \\ & \times \left(A\exp(i\sqrt{C}x) \ - B\exp(-i\sqrt{C}x)\exp(-i\sqrt{C}L)\right) = 0 \qquad (40) \end{aligned}$$

Since for $\forall x$ the second factor on the lhs of this equation is not vanishing the first factor has to be zero

$$1-\exp(i\sqrt{C}L) = 0 \quad , \qquad (41)$$

which only can be the case if

$$\sqrt{C}L = 2\pi n \quad . \qquad (42)$$

Resubstituting this result into $C = 2mE/\hbar^2$, the discrete values of the energy are given by

$$E_n = \frac{\hbar^2\pi^2}{2mL^2}(2n)^2 \ , \quad n = 0, \pm1, \pm2, \ldots \ . \qquad (43)$$

Contrary to the particle in a box the quantum number $n = 0$ is allowed, since then for $\forall x$ $\exp(i\sqrt{C}x) = 1$ and the corresponding wavefunction is a constant

$$\psi_{(n=0)}(x) = A + B \quad , \frac{d}{dx}\psi_{(n=0)}(x) = 0 \ , \forall x \quad , \qquad (44)$$

and therefore normalizable.

The wavefunctions themselves are easy to obtain, since

$$\frac{d^2}{dx^2}\cos(\sqrt{C}x) = -C\cos(\sqrt{C}x) \quad , \tag{45}$$

$$\frac{d^2}{dx^2}\sin(\sqrt{C}x) = -C\sin(\sqrt{C}x) \quad , \tag{46}$$

where $C = 2mE/\hbar^2$. The inversion $\widehat{P}$ is a symmetry operator also in this case, since

$$\widehat{P}\psi_n(x) = \psi_n(-x) = (\pm 1)\,\psi_n(x) \quad , \tag{47}$$

which of course also applies for $x = L$. Obviously there are two kinds of eigenfunctions of the Hamilton operator $\widehat{H}$, namely those belonging to the eigenvalue $+1$ of $\widehat{P}$ and the other ones belonging to the eigenvalue -1 of $\widehat{P}$. The "sin"-solutions belong to the eigenvalue -1 of $\widehat{P}$, the "cos"-solutions to the eigenvalue $+1$. For $n > 0$ the eigenvalues are pairwise degenerated, i.e., for each eigenvalue E_n there are two solutions.

The norm of the wavefunctions can be obtained in a similar manner as in the case of the particle in the box. It is $1/\sqrt{L}$. In the following table the results for the particle in the box and for the cyclic boundary conditions are summarized. It should be noted that in both cases the Hamilton operator is the same and that only the boundary conditions are responsible for the different energy spectra.

model	*box*	*cyclic*
Hamilton operator $\widehat{H}$	$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$	$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$
boundary condition	$\psi(\lvert x\rvert \geq a) = 0$	$\psi(x) = \psi(x + L)$
potential energy	$V(x) = 0;\ \lvert x\rvert < a$ $V(x) = \infty; \lvert x\rvert \geq a$	$V(x) = 0; \forall x$
energy E_n	$\frac{\hbar^2\pi^2}{8ma^2}n^2$	$\frac{\hbar^2\pi^2}{2mL^2}(2n)^2$
quantum numbers n	$1, 2, 3, 4, ...$	$0, \pm 1, \pm 2, \pm 3, ...$
wave functions	$\frac{1}{\sqrt{a}}\cos(\frac{n\pi}{2a}x);\ n$: odd $\frac{1}{\sqrt{a}}\sin(\frac{n\pi}{2a}x);\ n$: even	$\frac{1}{\sqrt{L}};\ n = 0$ $\frac{2}{\sqrt{L}}\cos(\frac{2\pi n}{L}x);\ \forall n > 0$ $\frac{2}{\sqrt{L}}\sin(\frac{2\pi n}{L}x);\ \forall n > 0$
degeneracy	$one - fold$	$two - fold$

3.4 Separation of variables

If for a particular system the Hamilton operator is given as a sum of operators, whereby each of this operators depends only on one variable, then the wavefunction is a product of eigenfunctions of these operators, which in turn depend only on one variable, and the energy eigenvalue of the system is the sum of the eigenvalues belonging to the eigenfunctions of the product.

$$\widehat{H}(x_1, x_2, \ldots, x_n)\psi(x_1, x_2, \ldots, x_n) = E\psi(x_1, x_2, \ldots, x_n) \quad , \tag{48}$$

$$\widehat{H}(x_1, x_2, \ldots, x_n) = \widehat{h}_1(x_1) + \widehat{h}_2(x_x) + \ldots + \widehat{h}_n(x_n) = \sum_{i=1}^{n} \widehat{h}_i(x_i) \quad , \tag{49}$$

$$\widehat{h}_i(x_i)\phi_i(x_i) = \epsilon_i \phi_i(x_i) \quad , \tag{50}$$

$$\psi(x_1, x_2, \ldots, x_n) = \phi_1(x_1)\phi_2(x2) \cdots \phi_n(x_n) = \prod_{i=1}^{n} \phi_i(x_i) \quad , \tag{51}$$

$$E = \epsilon_1 + \epsilon_2 + \ldots + \epsilon_n = \sum_{i=1}^{n} \epsilon_i \quad . \tag{52}$$

The eigenvalue problem in (48)

$$\begin{aligned} \left\{\widehat{h}_1(x_1) + \widehat{h}_2(x_x) + \ldots + \widehat{h}_n(x_n)\right\} \psi(x_1, x_2, ..x_n) = \\ = \{\epsilon_1 + \epsilon_2 + \ldots + \epsilon_n\} \psi(x_1, x_2, ..x_n) \quad , \end{aligned} \tag{53}$$

is then a system of n independent eigenvalue equations

$$\begin{aligned} \widehat{h}_1(x_1)\phi_1(x_1) &= \epsilon_1\phi_1(x_1) \ , \\ \widehat{h}_2(x_2)\phi_2(x_2) &= \epsilon_2\phi_2(x_2) \ , \\ &\vdots \\ \widehat{h}_n(x_n)\phi_n(x_n) &= \epsilon_n\phi_n(x_n) \ . \end{aligned} \tag{54}$$

The eigenvalues ϵ_i, $i = 1, .., n$, are usually called Lagrange parameters.

3.5 Particle in a three-dimensional box

In order to exemplify the above important theorem in the following the problem of a particle in a three-dimensional box with infinite barriers shall be considered. The Schrödinger equation for this case is given by

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) = -\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right]\psi(\mathbf{r}) = E\psi(\mathbf{r}) \quad , \tag{55}$$

where $\mathbf{r} = (x, y, z)$. If one uses the following ansatz for the wavefunction $\psi(\mathbf{r})$,

$$\psi(\mathbf{r}) = \psi(x, y, z) = X(x)Y(y)Z(z) \quad , \tag{56}$$

the Schrödinger equation can be rewritten as

$$Y(y)Z(z)\frac{d^2}{dx^2}X(x) + X(x)Z(z)\frac{d^2}{dy^2}Y(x) + X(x)Y(y)\frac{d^2}{dz^2}Z(z) = \tag{57}$$

$$-\frac{2mE}{\hbar^2}X(x)Y(y)Z(z) \quad .$$

Dividing now both sides by $X(x)Y(y)Z(z)$ one gets

$$\frac{1}{X(x)}\frac{d^2}{dx^2}X(x) + \frac{1}{Y(y)}\frac{d^2}{dy^2}Y(y) + \frac{1}{Z(z)}\frac{d^2}{dx^2}Z(z) = -\frac{2mE}{\hbar^2} \quad . \tag{58}$$

Now one clearly can see that this last equation can be viewed as a sum of three equations

$$\frac{1}{X(x)}\frac{d^2}{dx^2}X(x) = -k_x^2 \quad , \tag{59}$$

$$\frac{1}{Y(y)}\frac{d^2}{dy^2}Y(y) = -k_y^2 \quad , \tag{60}$$

$$\frac{1}{Z(z)}\frac{d^2}{dx^2}Z(z) = -k_z^2 \quad , \tag{61}$$

with

$$k^2 = k_x^2 + k_y^2 + k_z^2 = \frac{2mE}{\hbar^2} \quad . \tag{62}$$

The solutions for the differential equations (59) - (61) are already well-known. By choosing for example the following boundary conditions

$$V(x,y,z) = \{ \begin{array}{lll} = 0 & , & |x| < a, |y| < b, |z| < c \\ = \infty & , & |x| \geq a, |y| \geq b, |z| \geq c \end{array} \quad , \tag{63}$$

i.e.,

$$\begin{array}{lll} X(x) = 0 & , & |x| \geq a \quad , \\ Y(y) = 0 & , & |y| \geq b \quad , \\ Z(z) = 0 & , & |z| \geq c \quad , \end{array} \tag{64}$$

these solutions are given by

$$X(x) = \{ \begin{array}{ll} \frac{1}{\sqrt{a}}\cos(\frac{n_x\pi}{2a}x) & , \; n_x : \text{ odd} \\ \frac{1}{\sqrt{a}}\sin(\frac{n_x\pi}{2a}x) & , \; n_x : \text{ even} \end{array} \quad , \; k_x = \frac{n_x\pi}{2a}, \; etc. \tag{65}$$

The wavefunction is therefore a combination of "cos"- and "sin"-functions, depending whether the quantum numbers n_x, n_y and n_z are even or odd. For example for only odd quantum numbers the wavefunction is given by

$$\psi_{n_x,n_y,n_z}(x,y,z) = \frac{1}{\sqrt{abc}} \cos(\frac{n_x\pi}{2a}x) \cos(\frac{n_y\pi}{2b}y) \cos(\frac{n_z\pi}{2c}z) \quad . \tag{66}$$

The energy of the system depends now clearly on three quantum numbers and is the sum of the eigenvalues of the individual eigenvalue equations

$$\begin{aligned} E = E_{n_x,n_y,n_z} &= \frac{\hbar^2}{2m}k^2 = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right) = \\ &= \frac{\pi^2\hbar^2}{8m}\left\{\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right\} \quad . \end{aligned} \tag{67}$$

Consider finally that the box is a cube, i.e., $a = b = c$, then the energy E,

$$E_{n_x,n_y,n_z} = \frac{\pi^2\hbar^2}{8ma^2}\left\{n_x^2 + n_y^2 + n_z^2\right\} \quad , \tag{68}$$

quite clearly is invariant under permutations of the quantum numbers, but not the wavefunctions! For example it is easy to check that

$$E_{2,1,1} = E_{1,2,1} = E_{1,1,2} \quad ,$$

but in general

$$\psi_{2,1,1} \neq \psi_{1,2,1} \neq \psi_{1,1,2} \quad .$$

If only $a = b \neq c$, then these degeneracies of the energies are (partially) lifted.

References

[1] L.D.Landau and E.M.Lifschitz, *"Lehrbuch der Theoretischen Physik"*, Volume III, *"Quantenmechanik"*, Akademie Verlag, 1979

[2] L.I.Schiff, *"Quantum Mechanics"*, McGraw Hill Inc., 1968

4 The hydrogen atom

The hydrogen atom not only is historically the most important system in quantum mechanics, but also the concepts connected with this system still are the most influential ones in the language of physicists and chemists. Perhaps even more important than the hydrogen atom itself is the outcome of the discussion of angular momentum operators for the predominantly atomistic picture of matter currently used in all natural sciences. It is therefore quite appropriate to reserve a what at the beginning might seem like a lengthy discussion to these two topics. Since the context of the angular momentum operators with the hydrogen atom needs to be stressed right from the beginning, the conceptual flow in this chapter is somewhat crooked: it starts with the hydrogen atom, diverts to angular momentum operators and then comes back to the hydrogen atom.

4.1 The Schrödinger equation for the hydrogen atom

4.1.1 Separation of the motion of the nucleus

The Hamilton operator for the motion of a hydrogen atom or more generally for the motion of a single electron around a (charged) nucleus in motion, is given by

$$\widehat{H} = \frac{\mathbf{p}_n^2}{2m_n} + \frac{\mathbf{p}_e^2}{2m_e} - \frac{Ze^2}{|\mathbf{r}_e - \mathbf{r}_n|} \quad , \tag{1}$$

namely by the kinetic energy of the nucleus (first term), the kinetic energy of the electron (second term) and the Coulomb energy (third term), resulting from the Coulomb interaction between the electron and the nucleus. In (1) $\mathbf{p}_n$ is the momentum of a nucleus of mass m_n and charge Ze at position $\mathbf{r}_n$, $\mathbf{p}_e$ the momentum of an electron with mass m_e and charge $-e$ at position $\mathbf{r}_e$, where e is the elementary charge (-1.602 $\cdot 10^{-19}$As). Z is the so-called atomic number of this nucleus (number of positrons). For the hydrogen atom $Z = 1$. The Hamilton operator in (1) applies also for example to He^+, Li^{++}, etc. , so-called **hydrogen-like atoms**.

The motion of the nucleus can be separated by placing the origin of the coordinate system in the center of mass (see Fig. 4), i.e. by using the following transformation

$$\mathbf{r}_e = \mathbf{R} + \mathbf{r}\frac{m_n}{M} \quad , \tag{2}$$

$$\mathbf{r}_n = \mathbf{R} - \mathbf{r}\frac{m_e}{M} \quad , \tag{3}$$

$$M = m_n + m_e \quad , \tag{4}$$

where $\mathbf{R}$ is now the position vector of the center of gravity and $\mathbf{r}$ the position vector of the reduced mass with respect to this center . Abbreviating the reduced mass by μ,

$$\mu = \frac{m_n m_e}{M} \quad , \tag{5}$$

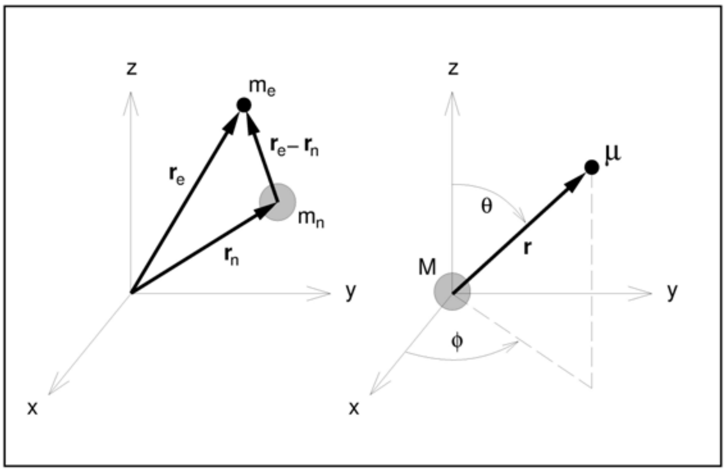

Figure 4: Coordinate systems for the hydrogen atom

the Hamilton operator in (1) can be reformulated as

$$\widehat{H} = -\frac{\hbar^2}{2M}\nabla_R^2 - \frac{\hbar^2}{2\mu}\nabla_r^2 - \frac{Ze^2}{r} \quad , \tag{6}$$

$$\nabla_R = \left(\frac{\partial}{\partial R_x}, \frac{\partial}{\partial R_y}, \frac{\partial}{\partial R_z}\right) \quad , \tag{7}$$

$$\nabla_r = \left(\frac{\partial}{\partial x}, \frac{\partial}{dy}, \frac{\partial}{\partial z}\right) \quad , \tag{8}$$

where the first term is the kinetic energy of the motion of the center of gravity and the second one the kinetic energy of a particle with mass μ moving around the center of gravity. The stationary Schrödinger equation corresponding to the Hamilton operator in (6), which now is the sum of two independent operators (see the section on separation of variables in the last chapter), is therefore simply given by

$$\widehat{H}\Psi(\mathbf{r},\mathbf{R}) = E_T\Psi(\mathbf{r},\mathbf{R}) \quad , \tag{9}$$

$$\Psi(\mathbf{r},\mathbf{R}) = \psi(\mathbf{r})\chi(\mathbf{R}) \quad , \tag{10}$$

$$E_T = E + \epsilon \quad , \tag{11}$$

where E and ϵ are the energy parameters (**Lagrange** parameters) in following the two eigenvalue equations

$$\left(-\frac{\hbar^2}{2\mu}\nabla_r^2 - \frac{Ze^2}{r}\right)\psi(\mathbf{r}) = E\psi(\mathbf{r}) \quad , \tag{12}$$

$$\left(-\frac{\hbar^2}{2M}\nabla_R^2\right)\chi(\mathbf{R}) = \epsilon\chi(\mathbf{R}) \quad . \tag{13}$$

The first of these equations describes the motion of a particle in a **central field** (the value of the Coulomb energy depends only on the distance $r = |\mathbf{r}|$ from the origin), whereas the second is nothing but the Schrödinger equation for a "free particle" of mass $M = m_e + m_n$, i.e., the second equation corresponds to the Galilei motion, which was discussed in detail in the previous chapter. One can restrict therefore the following discussion to (12), namely to the Schrödinger equation for a central field (note: $\nabla_r \equiv \nabla$)

$$\nabla^2\psi(\mathbf{r}) + \frac{2\mu}{\hbar^2}\left(E - V(r)\right)\psi(\mathbf{r}) = 0 \quad , \tag{14}$$

$$V(r) = -\frac{Ze^2}{r} \quad , \tag{15}$$

where $V(r)$ is usually called the **potential**. Since $V(r)$ only depends on the distance $r = |\mathbf{r}|$, $V(r)$ is called a **spherically symmetric potential**. It should be noted that this description applies only to hydrogen-like atoms or one-particle systems in a central field.

4.2 Polar coordinates, separation with respect to independent variables

From Figure 4-1 and as indicated there it seems almost imperative to use spherical (polar) coordinates instead of Cartesian coordinates,

$$x = r\sin\theta\cos\phi \quad , \tag{16}$$

$$y = r\sin\theta\sin\phi \quad , \tag{17}$$

$$z = r\cos\theta \quad . \tag{18}$$

In terms of the above polar coordinates the **Laplace** operator is given by [1]

$$\begin{aligned}\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left\{r^2\frac{\partial}{\partial r}\right\} + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left\{\sin\theta\frac{\partial}{\partial\theta}\right\} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2} = \\ = \frac{1}{r^2}\frac{\partial}{\partial r}\left\{r^2\frac{\partial}{\partial r}\right\} + \frac{1}{r^2}\widehat{\mathcal{L}}^2 \quad ,\end{aligned} \tag{19}$$

from which one immediately can see that this operator is a sum of two operators, namely one that depends only on the independent variable r and the other one on θ and ϕ . So once again one can separate two motions: a "**radial**" motion and an "**angular**" motion. Consequently the wavefunction $\psi(\mathbf{r})$ is a product of two functions, one in the independent variable r and the other one in θ and ϕ ,

$$\psi(\mathbf{r}) = R(r)Y(\theta,\phi) \quad . \tag{20}$$

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[1] Since it is not really relevant for the present purposes, no attempt is made to derive the Laplace operator in spherical coordinates. Interested readers should consult for example the book by Jackson (see bibliography).

The Schrödinger equation is therefore of the following form

$$Y(\theta,\phi)\left\{-\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}R(r)\right\}+R(r)\left\{-\frac{1}{r^2}\widehat{\mathcal{L}}^2Y(\theta,\phi)\right\}$$

$$+\frac{2\mu}{\hbar^2}\left(-E+V(r)\right)R(r)Y(\theta,\phi)=0 \quad , \tag{21}$$

which multiplied with $-r^2/R(r)Y(\theta,\phi)$ leads to the corresponding equations for the "radial" and the "angular" motion,

$$\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr}R(r)+\frac{2\mu}{\hbar^2}\left(E-V(r)\right)R(r)=\frac{c}{r^2}R(r) \quad , \tag{22}$$

$$\widehat{\mathcal{L}}^2Y(\theta,\phi)=-cY(\theta,\phi) \quad , \tag{23}$$

where (23) is an eigenvalue equation of the type discussed now already several times and c is the so-called separation constant (*Lagrange* parameter). As will turn out in the next section (23) is of the form of the eigenvalue equation for the square of the angular momentum operator. However, before proceeding to this section, it is worthwhile to repeat what was done "en route". Up to now all derivations served solely the aim to separate as many independent motions as possible, namely (1) to separate the motion of the nucleus from that of the electron and (2) to separate according to the independent variables r, θ and ϕ , respectively.

4.3 Angular momentum operators

Classically the angular momentum of a particle is defined by the following vector product

$$\mathbf{L}=(L_x,L_y,L_z)=\mathbf{r}\times\mathbf{p} \quad , \tag{24}$$

$$\mathbf{r}=(x,y,z) \quad ,\mathbf{p}=(p_x,p_y,p_z) \quad . \tag{25}$$

By using the determinant of the following matrix, where $\mathbf{e}_x$,$\mathbf{e}_y$ and $\mathbf{e}_z$ denote the unit vectors of $\mathbf{L}$,

$$\begin{vmatrix} \mathbf{e}_x & \mathbf{e}_y & \mathbf{e}_z \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix} = -\begin{vmatrix} \mathbf{e}_y & \mathbf{e}_x & \mathbf{e}_z \\ y & x & z \\ p_y & p_x & p_z \end{vmatrix} \quad etc. \quad , \tag{26}$$

the components of $\mathbf{L}$ can easily be read off

$$L_x=yp_z-zp_y \quad , \tag{27}$$

$$L_y=zp_x-xp_z \quad , \tag{28}$$

$$L_z=xp_y-yp_x \quad . \tag{29}$$

The quantum mechanical anlage, $\widehat{L}_x$, $\widehat{L}_y$ and $\widehat{L}_z$, follow directly from the correspondence principle (see chapter 2):

$$\mathbf{r}\rightarrow\widehat{\mathbf{r}}\equiv\mathbf{r}=(x,y,z) \quad , \tag{30}$$

$$\mathbf{p} \to \widehat{\mathbf{p}} = -i\hbar \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right) \equiv (\widehat{p}_x, \widehat{p}_y, \widehat{p}_z) \quad , \tag{31}$$

$$\widehat{L}_x = i\hbar \left(z\frac{\partial}{dy} - y\frac{\partial}{\partial z} \right) \quad , \tag{32}$$

$$\widehat{L}_y = i\hbar \left(x\frac{\partial}{dz} - z\frac{\partial}{\partial x} \right) \quad , \tag{33}$$

$$\widehat{L}_z = i\hbar \left(y\frac{\partial}{dx} - x\frac{\partial}{\partial y} \right) \quad . \tag{34}$$

Using now the Heisenberg uncertainty relation[2] in terms of commutators for the components of $\mathbf{r}$ and $\mathbf{p}$,

$$\begin{aligned} &[x, \widehat{p}_y]_- = [x, \widehat{p}_z]_- = [y, \widehat{p}_z]_- = [y, \widehat{p}_x]_- = \\ &\quad = [z, \widehat{p}_x]_- = [z, \widehat{p}_y]_- = 0 \quad , \end{aligned} \tag{35}$$

$$[\widehat{p}_x, \widehat{p}_y]_- = [\widehat{p}_x, \widehat{p}_z]_- = [\widehat{p}_y, \widehat{p}_z]_- = 0 \quad , \tag{36}$$

$$[x, \widehat{p}_x]_- = [y, \widehat{p}_y]_- = [z, \widehat{p}_z]_- = i\hbar \quad , \tag{37}$$

it is rather easy to derive similar commutator relations for the components of the angular momentum operator $\widehat{\mathbf{L}} = (\widehat{L}_x, \widehat{L}_y, \widehat{L}_z)$. For example for $\left[\widehat{L}_x, \widehat{L}_y\right]_-$ one can work out in detail that

$$\begin{aligned} \left[\widehat{L}_x, \widehat{L}_y\right]_- &= (y\widehat{p}_z - z\widehat{p}_y)(z\widehat{p}_x - x\widehat{p}_z) - (z\widehat{p}_x - x\widehat{p}_z)(y\widehat{p}_z - z\widehat{p}_y) = \\ &= [y\widehat{p}_z, z\widehat{p}_x]_- - [z\widehat{p}_y, z\widehat{p}_x]_- - [y\widehat{p}_z, x\widehat{p}_z]_- + [z\widehat{p}_y, x\widehat{p}_z]_- = \\ &= y\widehat{p}_x [\widehat{p}_z, z]_- + p_y x [z, \widehat{p}_z]_- = -i\hbar y\widehat{p}_x + i\hbar x\widehat{p}_y = i\hbar\widehat{L}_z \quad . \end{aligned} \tag{38}$$

For the three components of $\widehat{\mathbf{L}}$ one gets then the following system of commutators

$$\left[\widehat{L}_x, \widehat{L}_y\right]_- = i\hbar\widehat{L}_z \quad , \tag{39}$$

$$\left[\widehat{L}_z, \widehat{L}_x\right]_- = i\hbar\widehat{L}_y \quad , \tag{40}$$

$$\left[\widehat{L}_y, \widehat{L}_z\right]_- = i\hbar\widehat{L}_x \quad . \tag{41}$$

In analogy to classical mechanics the square of $\widehat{\mathbf{L}}$ is simply given by

$$\widehat{\mathbf{L}}^2 = \widehat{L}_x^2 + \widehat{L}_y^2 + \widehat{L}_z^2 \quad , \tag{42}$$

for which by the way the following commutator relations apply

$$\boxed{\left[\widehat{\mathbf{L}}^2, \widehat{L}_x^2\right]_- = \left[\widehat{\mathbf{L}}^2, \widehat{L}_y^2\right]_- = \left[\widehat{\mathbf{L}}^2, \widehat{L}_z^2\right]_- = 0} \quad , \tag{43}$$

$$\boxed{\left[\widehat{\mathbf{L}}^2, \widehat{L}_x\right]_- = \left[\widehat{\mathbf{L}}^2, \widehat{L}_y\right]_- = \left[\widehat{\mathbf{L}}^2, \widehat{L}_z\right]_- = 0} \quad , \tag{44}$$

as is very illustrative to derive in detail along the lines of (38).

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[2] see also chapter 1

4.4 Polar coordinates again and yet even more commutators

Going now back to (16) - (18) it seems reasonable to assume that polar coordinates once again will be of help. In terms of the partial derivatives in polar coordinates as given for example for $\frac{\partial}{\partial x}$ by

$$\frac{\partial}{\partial x} = \sin\theta\cos\phi\frac{\partial}{\partial r} + \frac{1}{r}\cos\theta\cos\phi\frac{\partial}{\partial\theta} - \frac{1}{r}\frac{\sin\phi}{\sin\theta}\frac{\partial}{\partial\phi} \quad , \tag{45}$$

$\widehat{\mathbf{L}}^2$ and its components are of the following form

$$\widehat{\mathbf{L}}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta}) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] \quad , \tag{46}$$

$$\widehat{L}_x = i\hbar(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}) \quad , \tag{47}$$

$$\widehat{L}_y = -i\hbar(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}) \quad , \tag{48}$$

$$\widehat{L}_z = -i\hbar\frac{\partial}{\partial\phi} \quad . \tag{49}$$

If one compares now the expression for the square of the angular momentum operator in (45) with the expression which was obtained when the "radial" motion was separated from the "angular" motion (see in particular (46)) then one discovers that $\widehat{\mathbf{L}}^2$ **is proportional to the operator for the "angular" motion**

$$\widehat{\mathbf{L}}^2 = -\hbar^2\widehat{\mathcal{L}}^2 \quad , \tag{50}$$

which in turn implies that instead of (23) it is sufficient to discuss the eigenvalue equation for $\widehat{\mathbf{L}}^2$,

$$\widehat{\mathbf{L}}^2 Y(\theta,\phi) = \hbar^2 c Y(\theta,\phi) \quad . \tag{51}$$

The form of the z-component of the angular momentum operator in (49) looks already quite easy, those for the x- and y-component (48) - (49) are less satisfying. However, by forming the following sums

$$\widehat{L}_+ = \widehat{L}_x + i\widehat{L}_y = \hbar\exp(i\phi)\left(\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}\right) \quad , \tag{52}$$

$$\widehat{L}_- = \widehat{L}_x - \ i\widehat{L}_y = -\hbar\exp(-i\phi)\left(\frac{\partial}{\partial\theta} - i\cot\theta\frac{\partial}{\partial\phi}\right) \quad , \tag{53}$$

one can derive two very useful commutator relations, namely

$$\left[\widehat{L}_+, \widehat{L}_-\right]_- = 2\hbar\widehat{L}_z \quad , \tag{54}$$

$$\left[\widehat{L}_+, \widehat{L}_z\right]_- = -\widehat{L}_z\left(\widehat{L}_x + i\widehat{L}_y\right) + \left(\widehat{L}_x + i\widehat{L}_y\right)\widehat{L}_z = -\hbar\widehat{L}_+ \quad . \tag{55}$$

Furthermore the following sum of products of $\widehat{L}_+$ and $\widehat{L}_-$,

$$\widehat{L}_+\widehat{L}_- + \widehat{L}_-\widehat{L}_+ = \left[\widehat{L}_+, \widehat{L}_-\right]_+ \quad , \tag{56}$$

the so-called **anticommutator** of $\widehat{L}_+$ and $\widehat{L}_-$, $\left[\widehat{L}_+, \widehat{L}_-\right]_+$, has the property that

$$\left[\widehat{L}_+, \widehat{L}_-\right]_+ = 2\left(\widehat{L}_x^2 + \widehat{L}_y^2\right) \quad . \tag{57}$$

Finally combining equations (55) to (57) one gets the amusing relations:

$$\widehat{\mathbf{L}}^2 = \widehat{L}_x^2 + \widehat{L}_y^2 + \widehat{L}_z^2 = \frac{1}{2}\left[\widehat{L}_+, \widehat{L}_-\right]_+ + \widehat{L}_z^2 \quad , \tag{58}$$

$$\widehat{L}_x^2 + \widehat{L}_y^2 = \widehat{L}_-\widehat{L}_+ + \hbar\widehat{L}_z = \widehat{L}_+\widehat{L}_- - \hbar\widehat{L}_z \quad . \tag{59}$$

4.5 Eigenvalues of $\widehat{\mathbf{L}}^2$ and $\widehat{L}_z$

Now its about time to make use of all the relations for the angular momentum operators discussed up to now. **Since $\widehat{L}^2$ commutes with all components of $\widehat{L}$, they have to have the same eigenfunctions.** Using $\widehat{L}_z$ for example, because its corresponding expression in polar coordinates is the most easy one, this implies that the eigenfunctions in the eigenvalue equation for $\widehat{\mathbf{L}}^{\mathbf{2}}$ (see (51)) can be labelled by the eigenvalues m in the eigenvalue equation for $\widehat{L}_z$,

$$\widehat{\mathbf{L}}^{\mathbf{2}} Y^m(\theta,\phi) = c\hbar^2 Y^m(\theta,\phi) \quad , \tag{60}$$

$$\widehat{L}_z Y^m(\theta,\phi) = \hbar m Y^m(\theta,\phi) \quad . \tag{61}$$

By using the label m for $Y^m(\theta,\phi)$ it is indicated that these functions are those eigenfunctions $Y(\theta,\phi)$ of $\widehat{\mathbf{L}}^{\mathbf{2}}$ which belong to the m-th eigenvalue of $\widehat{L}_z$. Since $\widehat{L}_z$ does not commute with $\widehat{L}_x$ or $\widehat{L}_y$, the functions $Y^m(\theta,\phi)$ are not eigenfunctions of $\widehat{L}_x$ and $\widehat{L}_y$. They are, however, eigenfunctions of $\widehat{L}_+$ and $\widehat{L}_-$. In order to proof this rather important fact the following manipulations are carried out in detail. Multiplying (61) from the left with $\widehat{L}_+$, one gets

$$\widehat{L}_+\left(\widehat{L}_z Y^m(\theta,\phi)\right) = \left(\widehat{L}_+\widehat{L}_z\right) Y^m(\theta,\phi) = \quad ;(lhs)$$

$$= \widehat{L}_+\left(\hbar m Y^m(\theta,\phi)\right) = \hbar m\left(\widehat{L}_+ Y^m(\theta,\phi)\right) \quad ;(rhs) \quad . \tag{62}$$

Reworking the lhs of this equation one can make use of (55), namely

$$\hbar\widehat{L}_+ = \widehat{L}_z\widehat{L}_x - \widehat{L}_x\widehat{L}_z + i\widehat{L}_z\widehat{L}_y - i\widehat{L}_y\widehat{L}_z \quad , \tag{63}$$

and the fact that

$$\widehat{L}_z\widehat{L}_+ = \widehat{L}_z\widehat{L}_x + i\widehat{L}_z\widehat{L}_y \quad . \tag{64}$$

Subtracting now the first of the last two equations from the second yields exactly what is needed for the lhs of (62)

$$\widehat{L}_z\widehat{L}_+ - \hbar\widehat{L}_+ = \widehat{L}_+\widehat{L}_z \quad , \tag{65}$$

$$\begin{aligned}\left(\widehat{L}_+\widehat{L}_z\right)Y^m(\theta,\phi) &= \left(\widehat{L}_z\widehat{L}_+ - \hbar\widehat{L}_+\right)Y^m(\theta,\phi) = \\ &= \widehat{L}_z\left(\widehat{L}_+Y^m(\theta,\phi)\right) - \hbar\left(\widehat{L}_+Y^m(\theta,\phi)\right) = \quad ;(lhs) \\ &= \hbar m\left(\widehat{L}_+Y^m(\theta,\phi)\right) \quad ;(rhs) \quad .\end{aligned} \tag{66}$$

Thus one ends up with the remarkable result that

$$\widehat{L}_z\left(\widehat{L}_+Y^m(\theta,\phi)\right) = \hbar(m+1)\left(\widehat{L}_+Y^m(\theta,\phi)\right) \quad , \tag{67}$$

namely that $\widehat{L}_+Y^m(\theta,\phi)$ **is an eigenfunction of** $\widehat{L}_z$ **, however, corresponding to the eigenvalue** $m+1$. **Since** $\widehat{L}_z$ **and** $\widehat{\mathbf{L}}^2$ **commute** (see (43)) $\widehat{L}_+Y^m(\theta,\phi)$ **has to be also an eigenfunction of** $\widehat{\mathbf{L}}^2$

$$\widehat{\mathbf{L}}^2\left(\widehat{L}_+Y^m(\theta,\phi)\right) = \hbar^2 c\left(\widehat{L}_+Y^m(\theta,\phi)\right) \quad . \tag{68}$$

The operator $\widehat{L}_+$ therefore has the property that acting on an eigenfunction of $\widehat{\mathbf{L}}^2$ an eigenfunction of $\widehat{L}_z$ is created corresponding to an eigenvalue increased by one. Because of this property $\widehat{L}_+$ sometimes is called a **creation operator** or **step-up operator**. In a similar way one can show that

$$\widehat{L}_z\left(\widehat{L}_-Y^m(\theta,\phi)\right) = \hbar(m-1)\left(\widehat{L}_-Y^m(\theta,\phi)\right) \quad , \tag{69}$$

which means that $\widehat{L}_-$ acts like an **annihilation operator** or **step-down operator**, since an eigenfunction of $\widehat{L}_z$ for an eigenvalue $(m-1)$ is generated.

In particular $\widehat{L}_+$ can be applied consecutively several times, say r times

$$\begin{aligned}\widehat{L}_z\left(\widehat{L}_+^rY^m(\theta,\phi)\right) &= \widehat{L}_z\left(\underbrace{[\widehat{L}_+\cdots\ \widehat{L}_+]}_{r-times}Y^m(\theta,\phi)\right) = \\ &= \hbar(m+r)\left(\widehat{L}_+^rY^m(\theta,\phi)\right) \quad ,\end{aligned} \tag{70}$$

$$\widehat{\mathbf{L}}^2\left(\widehat{L}_+^rY^m(\theta,\phi)\right) = \hbar^2 c\left(\widehat{L}_+^rY^m(\theta,\phi)\right) \quad . \tag{71}$$

The number of times $\widehat{L}_+$ can be applied, however, is restricted for the following reasons. Since $\widehat{L}_x$, $\widehat{L}_y$, $\widehat{L}_z$ and $\widehat{\mathbf{L}}^2$ are Hermitian operators (real eigenvalues !) the expectations values of $\widehat{L}_x^2$ and $\widehat{L}_y^2$ have to be positive, i.e.

$$<\widehat{L}_x^2> \ \geq \ 0 \quad ,<\widehat{L}_y^2> \ \geq \ 0 \quad . \tag{72}$$

On the other hand the sum of $\widehat{L}_x^2$ and $\widehat{L}_y^2$ has a well-defined eigenvalue

$$\begin{aligned}\left(\widehat{L}_x^2 + \widehat{L}_y^2\right) Y^m(\theta,\phi) \; &= \left(\widehat{\mathbf{L}}^2 - \widehat{L}_z^2\right) Y^m(\theta,\phi) = \\ &= \hbar^2(c - m^2) Y^m(\theta,\phi) \quad ,\end{aligned} \tag{73}$$

which in turn can only imply that

$$c - m^2 \geq 0 \quad or \quad c \geq m^2 \quad . \tag{74}$$

For a given separation constant c therefore there has to be a minimal eigenvalue $-l_2\hbar$ and a maximal eigenvalue $l_1\hbar$ of $\widehat{L}_z$ with $l_1, l_2 > 0$ such that

$$\widehat{L}_+ Y^{l_1}(\theta,\phi) = 0 \quad , \tag{75}$$

$$\widehat{L}_- Y^{-l_2}(\theta,\phi) = 0 \quad . \tag{76}$$

Obviously between $-l_2$ and l_1 there has to be a positive integer number of eigenstates such that

$$\widehat{L}_+^n Y^{-l_2}(\theta,\phi) = N Y^{l_1}(\theta,\phi) \quad , \tag{77}$$

i.e., where $n = l_1 - (-l_2) = l_1 + l_2$ and N is some normalization constant. Using now (59) to evaluate the eigenvalues of $\widehat{\mathbf{L}}^2$ corresponding to the eigenfunctions $Y^{l_1}(\theta,\phi)$ and $Y^{-l_2}(\theta,\phi)$,

$$\begin{aligned}\widehat{\mathbf{L}}^2 Y^{l_1}(\theta,\phi) &= \left(\widehat{L}_-\widehat{L}_+ + \hbar\widehat{L}_z + \widehat{L}_z^2\right) Y^{l_1}(\theta,\phi) = \\ = \widehat{L}_- &\underbrace{\widehat{L}_+ Y^{l_1}(\theta,\phi)}_{=0} + \; \hbar\widehat{L}_z Y^{l_1}(\theta,\phi) + \widehat{L}_z^2 Y^{l_1}(\theta,\phi) = \\ &= \hbar^2(l_1 + l_1^2) Y^{l_1}(\theta,\phi) \quad ,\end{aligned} \tag{78}$$

$$\begin{aligned}\widehat{\mathbf{L}}^2 Y^{-l_2}(\theta,\phi) &= \left(\widehat{L}_+\widehat{L}_- - \hbar\widehat{L}_z + \widehat{L}_z^2\right) Y^{-l_2}(\theta,\phi) = \\ = \widehat{L}_+ &\underbrace{\widehat{L}_- Y^{-l_2}(\theta,\phi)}_{=0} - \; \hbar\widehat{L}_z Y^{-l_2}(\theta,\phi) + \widehat{L}_z^2 Y^{-l_2}(\theta,\phi) = \\ &= \hbar^2(l_2 + l_2^2) Y^{-l_2}(\theta,\phi) \quad ,\end{aligned} \tag{79}$$

one can see that these eigenvalues are given by

$$\hbar^2 c = \hbar^2(l_1 + l_1^2) = \hbar^2(l_2 + l_2^2) \quad . \tag{80}$$

Since l_1 and l_2 were chosen to be positive, this only can be the case if $l_1 = l_2 \equiv l$. The separation constant c in equations (22) and (23) is therefore uniquely determined by the integer number l, $c = l(l+1)$, which implies that the eigenvalues of $\widehat{L}_z$ vary from $-l$ to $+l$, namely $m = -l, -l+1, -l+2, \ldots, l-2, l-1, l$. In order to classify those functions $Y^m(\theta,\phi)$ that belong to the eigenvalue $l(l+1)$ of $\widehat{\mathbf{L}}^2$ they are augmented by the index l .

Without having actually solved any differential equations, the algebra of angular momentum operators allowed to arrive at the following most important eigenvalue equations,

$$\boxed{\widehat{\mathbf{L}}^2 Y_l^m(\theta,\phi) = \hbar^2 l(l+1) Y_l^m(\theta,\phi)} \tag{81}$$

$$\boxed{\widehat{L}_z Y_l^m(\theta,\phi) = \hbar m Y_l^m(\theta,\phi)} \tag{82}$$

with

$$\boxed{m = -l, -l+1, ..., l-1, l \quad ; \quad l \geq 0} \tag{83}$$

4.6 Eigenfunctions of $\widehat{\mathbf{L}}^2$ and $\widehat{L}_z$

In order to obtain now the eigenfunctions $Y_l^m(\theta,\phi)$ one can again make use of the properties of $\widehat{L}_+$ and $\widehat{L}_-$ (75) - (76), namely that in terms of the polar coordinates for these two operators (52) - (53)

$$\widehat{L}_+ Y_l^l(\theta,\phi) = \underbrace{\hbar \exp(i\phi)}_{\neq\, 0} \left(\frac{\partial}{\partial\theta} + i\cot\theta \frac{\partial}{\partial\phi} \right) Y_l^l(\theta,\phi) = 0 \quad . \tag{84}$$

Since as indicated the prefactor is not vanishing, one is left with the following differential equation:

$$\left(\frac{\partial}{\partial\theta} + i\cot\theta \frac{\partial}{\partial\phi} \right) Y_l^l(\theta,\phi) = 0 \quad , \tag{85}$$

which once more is nothing but a sum of two operators, this time in the independent variables θ and ϕ, and therefore $Y_l^l(\theta,\phi)$ is a product of functions in θ and ϕ, respectively

$$Y_l^l(\theta,\phi) = P(\theta)\Phi(\phi) \quad . \tag{86}$$

Using this ansatz in (85) one has to face yet another a separation constant, say k,

$$\frac{1}{\cot\theta P(\theta)} \frac{\partial}{\partial\theta} P(\theta) = -\frac{i}{\Phi(\phi)} \frac{\partial}{\partial\phi} \Phi(\phi) \equiv k \quad , \tag{87}$$

appearing in the corresponding differential equations with respect to θ and ϕ,

$$\frac{\partial}{\partial\theta} P(\theta) = k \cot\theta P(\theta) \quad , \tag{88}$$

$$\frac{\partial}{\partial\phi} \Phi(\phi) = ik\Phi(\phi) \quad . \tag{89}$$

The solutions of these two equations are now almost obvious, namely

$$P(\theta) = (\sin\theta)^k \quad , \tag{90}$$

$$\Phi(\phi) = \exp(ik\phi) \quad . \tag{91}$$

The function $Y_l^l(\theta,\phi)$ is therefore given by

$$Y_l^l(\theta,\phi) = c_l^l (\sin\theta)^k \exp(ik\phi) \quad , \tag{92}$$

where c_l^l is a normalization constant yet to be determined. In order to evaluate the separation constant k one can calculate the eigenvalues of $\widehat{L}_z$ and $\widehat{\mathbf{L}}^2$, respectively, to which the eigenfunction $Y_l^l(\theta,\phi)$ belongs. For example for $\widehat{L}_z$ one gets

$$\begin{aligned}\widehat{L}_z Y_l^l(\theta,\phi) = -i\hbar\frac{\partial}{\partial\phi}Y_l^l(\theta,\phi) = -i\hbar\frac{\partial}{\partial\phi}(\sin\theta)^k\exp(ik\phi) = \\ = \hbar k Y_l^l(\theta,\phi) \equiv \hbar l Y_l^l(\theta,\phi) \quad ,\end{aligned} \tag{93}$$

i.e., one can easily show - and the same result can be obtained with $\widehat{\mathbf{L}}^2$ - that $k = l$. For the highest eigenvalue of $\widehat{L}_z$ the corresponding eigenfunction is therefore given by

$$Y_l^l(\theta,\phi) = c_l^l (\sin\theta)^l \exp(il\phi) \quad . \tag{94}$$

According to the philosophy up to now, the eigenfunctions corresponding to eigenvalues of $\widehat{L}_z$ less than l can be generated by consecutive application of $\widehat{L}_-$. Applying $\widehat{L}_-$ once, one gets

$$\begin{aligned}Y_l^{l-1}(\theta,\phi) = \frac{c_l^{l-1}}{\hbar c_l^l}\widehat{L}_- Y_l^l(\theta,\phi) = \\ = -c_l^{l-1}\exp(-i\phi)(\frac{\partial}{\partial\theta} - i\cot\theta\frac{\partial}{\partial\phi})(\sin\theta)^l\exp(il\phi) = \\ = -c_l^{l-1}\exp[i(l-1)\phi](\frac{\partial}{\partial\theta} + l\cot\theta)(\sin\theta)^l \quad .\end{aligned} \tag{95}$$

Furthermore using the identity:

$$\frac{\partial}{\partial\theta} + l\cot\theta = \frac{1}{(\sin\theta)^l}\frac{\partial}{\partial\theta}(\sin\theta)^l \tag{96}$$

$Y_l^{l-1}(\theta,\phi)$ is readily found

$$Y_l^{l-1}(\theta,\phi) = -c_l^{l-1}\exp\left(i(l-1)\phi\right)\frac{1}{(\sin\theta)^l}\frac{\partial}{\partial\theta}(\sin\theta)^{2l} \quad . \tag{97}$$

Applying now $\widehat{L}_-$ s-times, one gets the following function

$$\begin{aligned}Y_l^{l-s}(\theta,\phi) = \left(\frac{1}{\hbar}\right)^s\left(\frac{c_l^{l-s}}{c_l^l}\right)\widehat{L}_-^s Y_l^l(\theta,\phi) = \\ = (-1)^s c_l^{l-s}\exp\left(i(l-s)\phi\right)\frac{1}{(\sin\theta)^l}(\frac{\partial}{\partial\theta})^s(\sin\theta)^{2l} \quad ,\end{aligned} \tag{98}$$

which by using the actual eigenvalue of $\widehat{L}_z$, $m = l - s$, can be written as

$$Y_l^m(\theta, \phi) = (-1)^m c_l^m P_l^m(\cos\boldsymbol{\theta}) \exp(im\phi) \quad . \tag{99}$$

The functions $P_l^m(\cos\theta)$ are the so-called **associated Legendre polynomials**

$$P_l^m(\cos\theta) = \frac{(-1)^l}{2^l l!} (\sin\theta)^m \left(\frac{d}{d\cos\theta}\right)^{l-m} (\sin\theta)^{2l} \quad , \tag{100}$$

$$P_l^{-m}(\cos\theta) = (-1)^m P_l^m(\cos\theta) \quad , \tag{101}$$

which for small values of l are of very simple form as shown below:

l	m	$P_l^m(\cos\theta)$
0	0	1
1	0	$\cos\theta$
1	1	$\sin\theta$
2	0	$\frac{1}{2}(3\cos^2\theta - 1)$
2	1	$3\sin\theta\cos\theta$
2	2	$3\sin^2\theta$

Finally the normalization constants c_l^m can also be obtained in a closed form (which again can be checked by using the relations with $\widehat{L}_+$ and $\widehat{L}_-$)

$$c_l^m = \frac{1}{2^l l!}\sqrt{\frac{2l+1}{4\pi}}\sqrt{\frac{(l-m)!}{(l+m)!}} \quad . \tag{102}$$

The normalized eigenfunctions of $\widehat{L}_z$ and $\widehat{\mathbf{L}}^2$ are therefore of the following final form (the so-called **Condon-Shortley convention**, see also the bibliography)

$$\begin{aligned} Y_l^m(\theta, \phi) = {} & \frac{(-1)^{l+m}}{2^l l!}\sqrt{\frac{2l+1}{4\pi}}\sqrt{\frac{(l-m)!}{(l+m)!}} \exp(im\phi) \times \\ & \times (\sin\theta)^m \left(\frac{d}{d\cos\theta}\right)^{l+m} (1 - \cos^2\theta)^l = \\ = {} & (-1)^m \sqrt{\frac{1}{2\pi}} P_l^m(\cos\theta) \exp(im\phi) \quad , \end{aligned} \tag{103}$$

$$\left(Y_l^m(\theta, \phi)\right)^* = (-1)^m Y_l^{-m}(\theta, \phi) \quad . \tag{104}$$

They carry a very famous name. They are called **spherical harmonics**. For the first few values of l and m their analytical forms are listed below:

l	m	$Y_l^m(\theta,\phi)$
0	0	$\frac{1}{\sqrt{4\pi}}$
1	0	$\sqrt{\frac{3}{4\pi}}\cos\theta$
1	± 1	$\mp\sqrt{\frac{3}{8\pi}}\sin\theta\exp(\pm i\phi)$
2	0	$\sqrt{\frac{5}{16\pi}}(3\cos^2\theta-1)$
2	± 1	$\mp\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta\exp(\pm i\phi)$
2	± 2	$\sqrt{\frac{15}{32\pi}}\sin^2\theta\exp(\pm 2i\phi)$

In order to summarize the sections on the eigenvalues and eigenfunctions of $\widehat{L}_z$ and $\widehat{\mathbf{L}}^2$ in the boxes below are the most important properties:

$$\boxed{\widehat{L}_z\, Y_l^m(\theta,\phi) = \hbar m Y_l^m(\theta,\phi)} \tag{105}$$

$$\boxed{\widehat{\mathbf{L}}^2 Y_l^m(\theta,\phi) = \hbar^2 l(l+1) Y_l^m(\theta,\phi)} \tag{106}$$

$$\boxed{\int Y_l^m(\theta,\phi)^* Y_{l'}^{m'}(\theta,\phi)\, d\Omega = \delta_{ll'}\delta_{mm'}} \tag{107}$$

$$\boxed{-l \le m \le l\ ,\ l = 0, 1, 2,\ ...} \tag{108}$$

$$0 < \theta \le \pi \quad ,\ 0 \le \phi \le 2\pi \quad ,\ d\Omega = \sin\theta\, d\theta\, d\phi \quad . \tag{109}$$

It should be noted that (107) states nothing but the fact that (normalized) eigenfunctions of $\widehat{\mathbf{L}}^2$ and $\widehat{L}_z$ are orthogonal!

4.7 Back to the hydrogen atom

After this rather lengthy excursion to the world of angular momentum operators, the remaining thing to do is to tackle the equation for the "radial motion" (22), which is rewritten below, knowing of course that the separation constant c is given in terms of the eigenvalues of $\widehat{\mathbf{L}}^2$,

$$\frac{d^2R(r)}{dr^2} + \frac{2}{r}\frac{dR(r)}{dr} + \left\{\frac{2\mu E}{\hbar^2} + \frac{2\mu Z e^2}{\hbar^2 r} - \frac{l(l+1)}{r^2}\right\} R(r) = 0 \quad , \tag{110}$$

where the central field $V(r) = -Ze^2/r$.

4.7.1 Analytical solutions

Suppose that for $E < 0$ a parameter λ is introduced via the following relation

$$E = -\frac{\mu Z^2 e^4}{2\hbar^2 \lambda^2} \quad , \tag{111}$$

such that a substitution of the form

$$x = \frac{\lambda \hbar^2}{2\mu Z e^2} r \quad , \tag{112}$$

reduces (110) to a differential equation very well-known in mathematics since quite some time:

$$\frac{d^2 R(x)}{dx^2} + \frac{2}{x}\frac{dR(x)}{dx} + \left\{ -\frac{1}{4} + \frac{\lambda}{x} - \frac{l(l+1)}{x^2} \right\} R(x) = 0 \quad . \tag{113}$$

If $\lambda = n$, where n is a positive integer number, then the solutions of this differential equation are of the following form

$$R_{n,l}(x) = L^{2l+1}_{n-l-1}(x) x^l \exp(-x/2) \quad , \tag{114}$$

whereby physically acceptable solutions (continuous and finite in the interval $0 \leq x \leq \infty$) are only obtained for the condition that

$$\boxed{\lambda \equiv n = 1, 2, \ldots, \infty \quad , \quad l = 0, 1, 2, \ldots, (n-1)} \tag{115}$$

The so-called **associated Laguerre** polynomials $L^k_p(x)$, $k = 2l+1, p = n-l-1$, are of the following general form

$$L^k_p(x) = (-1)^k \frac{d^k}{dx^k} L^0_{p+k}(x) \quad , \tag{116}$$

$$L^0_p(x) = \exp(x) \frac{d^p}{dx^p} \left(\exp(-x) x^p \right) \quad , \quad k, p = 0, 1, 2, \ldots, \infty \tag{117}$$

and are polynomials of degree p having p zeroes in the interval $0 \leq x \leq \infty$:

$$L^k_p(x) = \sum_{s=0}^{p} (-1)^s \frac{\left((p+k)!\right)^2}{(p-s)!(k+s)!s!} x^s \tag{118}$$

Although this last equation looks a bit disgusting, for the first few values of n and l these polynomials are of very simple form:

n	l	$L^{2l+1}_{n-l-1}(x)$	n	l	$L^{2l+1}_{n-l-1}(x)$
1	0	-1	2	0	$-4 + 2x$
2	1	-6	3	0	$-18 + 18x - 3x^2$
3	2	-120	3	1	$-96 + 24x$

Resubstituting now $\lambda = n$ (115) into the expression for the energy E (111) one gets

$$E_n = -\frac{\mu Z^2 e^4}{2\hbar^2 n^2} = -\frac{Z^2}{n^2} E_H \quad , \tag{119}$$

where E_H is the so-called groundstate energy of a hydrogen atom. The result in (119) is by the way identical to that of the so-called Bohr model and as can be seen does not depend on l and m. Replacing μ by m_e (mass of the electron), $E_H = m_e e^4/2\hbar^2$ =13.6053 eV = 1 rydberg (1 ry).

The normalization integral $N_{n,l}$ of the functions $R_{n,l}(x)$, $0 \leq x \leq \infty$, can also be obtained as a closed expression

$$N_{n,l} = \int\limits_0^\infty \exp(-x) x^{2l} \left[L_{n-l-1}^{2l+1}(x)\right]^2 x^2 dx = \frac{2n\left[(n+l)!\right]^3}{(n-l-1)!} \quad . \tag{120}$$

The radial solutions $R_{n,l}(r)$ are therefore of the following form

$$R_{n,l}(r) = \left(\frac{(n-l-1)!}{2n\left((n+l)!\right)^3}\right)^{1/2} \left(\frac{Z}{na_0}\right)^{\frac{3}{2}} \exp(-Zr/na_0) r^l L_{n-l-1}^{2l+1}\left(\frac{2Z}{na_0} r\right) \quad , \tag{121}$$

where $a_0 = \hbar^2/e^2 m_e$ has the dimension of a length and is a universal constant ($a_0 = 0.5902.10^{-8}$ cm). Since a_0 coincides with the radius of the first Bohr orbital, it is called *Bohr* radius and serves as unit of length in quantum mechanics (atomic units).

Abbreviating Zr/a_0 by a , $(Z/a_0)^{3/2}$ by A and using **real spherical harmonics** as defined by the linear combinations of eigenfunctions of $\widehat{L}_z$ belonging to the pair of eigenvalues $\pm m$,

$$Y_l^{c,m}(\theta,\phi) = \frac{1}{\sqrt{2}}\left(Y_l^m(\theta,\phi) \;+\; Y_l^{-m}(\theta,\phi)\right) \quad , \tag{122}$$

$$Y_l^{s,m}(\theta,\phi) = \frac{i}{\sqrt{2}}\left(Y_l^m(\theta,\phi) \;-\; Y_l^{-m}(\theta,\phi)\right) \quad , \tag{123}$$

where the suffix "s" stands for "sine" and "c" for "cosine" , the hydrogen atomic wavefunctions are listed for the first few values of n and l in the following table

$$\boxed{\begin{aligned}
\psi_{1,00} &= \tfrac{1}{\sqrt{\pi}} A \exp(-a) \\
\psi_{2,00} &= \tfrac{1}{4\sqrt{2\pi}} A(2-a)\exp(-a/2) \\
\psi_{2,10} &= \tfrac{1}{4\sqrt{\pi}} Aa\exp(-a/2)\cos\theta \\
\psi_{2,11}^c &= \tfrac{1}{4\sqrt{2\pi}} A\exp(-a/2)\sin\theta\cos\phi \\
\psi_{2,11}^s &= \tfrac{1}{4\sqrt{2\pi}} Aa\exp(-a/2)\sin\theta\sin\phi \\
\psi_{3,00} &= \tfrac{1}{81\sqrt{3\pi}} A(27-18a+2a^2)\exp(-a/3) \\
\psi_{3,10} &= \tfrac{\sqrt{2}}{81\sqrt{\pi}} A(6-a)a\exp(-a/3)\cos\theta
\end{aligned}}$$

$$\boxed{\begin{array}{lcl}
\psi^c_{3,11} & = & \frac{\sqrt{2}}{81\sqrt{\pi}}A(6-a)a\exp(-a/3)\sin\theta\cos\phi \\
\psi^s_{3,11} & = & \frac{\sqrt{2}}{81\sqrt{\pi}}A(6-a)a\exp(-a/3)\sin\theta\sin\phi \\
\psi_{3,20} & = & \frac{1}{81\sqrt{6\pi}}Aa^2\exp(-a/3)(3\cos\theta^2-1) \\
\psi^c_{3,21} & = & \frac{\sqrt{2}}{81\sqrt{\pi}}Aa^2\exp(-a/3)\sin\theta\cos\theta\cos\phi \\
\psi^s_{3,21} & = & \frac{\sqrt{2}}{81\sqrt{\pi}}Aa^2\exp(-a/3)\sin\theta\cos\theta\sin\phi \\
\psi^c_{3,22} & = & \frac{1}{81\sqrt{2\pi}}Aa^2\exp(-a/3)\sin^2\theta\cos 2\phi \\
\psi^s_{3,22} & = & \frac{1}{81\sqrt{2\pi}}Aa^2\exp(-a/3)\sin^2\theta\sin 2\phi
\end{array}}$$

4.8 The one-electron states of an atom

Finally now one can summarize the most important results of this chapter. The relevant part of the **Hamilton operator** is defined by

$$\boxed{\widehat{H} = H(\mathbf{r}) = -\frac{\hbar^2}{2\mu}\nabla^2 \; - \frac{Ze^2}{r}} \tag{124}$$

and has the following **constants of motion**

$$\boxed{\left[\widehat{H}, \widehat{\mathbf{L}}^2\right]_- = \left[\widehat{H}, \widehat{L}_z\right]_- = 0} \tag{125}$$

The **energy eigenvalues** E_n and **eigenfunctions** $\psi_{n,lm}(\mathbf{r})$ of a "single electron" atom are given by

$$\boxed{E_n = -\frac{1}{2}\frac{Z^2e^2}{a_0}\frac{1}{n^2} \quad , \; a_0 = \frac{\hbar^2}{e^2m_e}} \tag{126}$$

$$\boxed{\psi_{n,lm}(\mathbf{r}) = \psi_{n,lm}(r,\theta,\phi) = R_{n,l}(r)Y_l^m(\theta,\phi)} \tag{127}$$

$$\boxed{\int \psi_{n,lm}(\mathbf{r})^*\psi_{n',l'm'}(\mathbf{r})d\tau = \delta_{nn'}\delta_{ll'}\delta_{mm'}} \tag{128}$$

$$d\tau = r^2dr\sin\theta d\theta d\phi = r^2drd\Omega \quad ,$$

where $\delta_{nn'}$ refers to the orthogonality of the eigenfunctions with respect to different energy eigenvalues, $\delta_{ll'}$ with respect to different eigenvalues of $\widehat{\mathbf{L}}^2$ and $\delta_{mm'}$ with respect to different eigenvalues of $\widehat{L}_z$.

Each state is therefore characterized by three **quantum numbers**, namely by

n the **"principal" quantum number**, $n = 1, 2, 3\ \dots, \infty$
l the **"angular" momentum quantum number**, $l = 0, 1, 2,\ \dots, n-1$
m the **"magnetic" quantum number**, $-l \le m \le l$.

For the angular momentum quantum number l most frequently the following common names, originally derived from spectroscopy are used

l	0	1	2	3	4
name	s	p	d	f	g

where "s" stands for "sharp", "p" for "principal", "d" for "diffuse" and "f" for "fundamental". Since for a given quantum number n and l the energy eigenvalues are degenerated with respect to $\widehat{L}_z$ (m does not appear as such or implicitly in the equation for the radial motion, the atomic energy levels of a single electron atom can be labelled by the well-known pairs of quantum numbers,

n, l	$1,0$	$2,0$	$3,1$	$3,0$	$3,1$	$3,2$	$4,0$	$4,1$	$4,2$	$4,3$
name	$1s$	$2s$	$2p$	$3s$	$3p$	$3d$	$4s$	$4p$	$4d$	$4f$

well-known of course from their use in the periodic table of elements.

4.9 Atomic orbitals

In analogy to the Bohr model the one electron eigenfunctions (eigenfunctions of a single electron atom) are usually called **atomic orbitals**. Let $\psi_{n,lm}(\mathbf{r})$ be a particular atomic orbital, then $\left|\psi_{n,lm}(\mathbf{r})\right|^2 d\tau$ is the probability to find an nl-like electron in the interval $[r, r+dr]$ within the directions $[\theta, \theta+d\theta]$ and $[\phi, \phi+d\phi]$, and $\left|\psi_{n,lm}(\mathbf{r})\right|^2$ is the corresponding probability density. Its radial distribution function $D(r)$ is obtained by integrating over the angular dependence

$$D_{n,l}(r)dr = R_{n,l}^2(r)r^2dr \int_0^{2\pi}\int_0^{\pi} Y_l^m(\theta,\phi)^* Y_l^m(\theta,\phi)\sin\theta d\theta d\phi =$$
$$= R_{n,l}^2(r)r^2dr \quad . \tag{129}$$

From the table of the hydrogen atom wavefunctions one can see that they all contain an exponential factor of the form $\exp(-r)$ multiplied with a polynomial in r. It is therefore quite interesting to see what happens if r tends to zero.

4.9.1 s-orbitals

For **1s-orbitals** it is easy to see that

$$\lim_{r\to 0}\left|\psi_{1s}(r)\right|^2 = N\lim_{r\to 0}\exp(-2r/a_0) \ > \ 0 \quad , \tag{130}$$

while

$$\lim_{r\to 0} D_{1s}(r) = N\lim_{r\to 0}\left(r^2\exp(-2r/a_0)\right) = 0 \quad , \tag{131}$$

where N is the normalization constant. For $r \to 0$ the 1s-like probability density is finite, only the radial distribution goes to zero (see also *Figure 5*). Since for

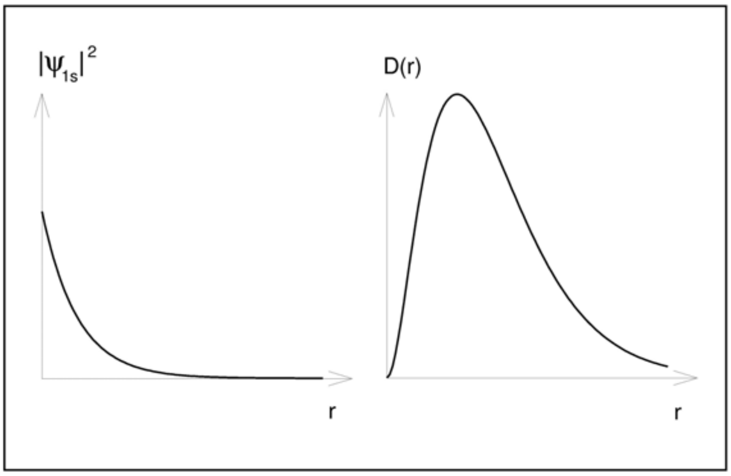

Figure 5: 1s-like probability density and radial distribution

$r \to \infty$ both the probability density as well as the radial distribution function $D_{n,l}(r) = (rR_{n,l}(r))^2$ vanish, this implies that

$$\lim_{r\to 0}(rR_{n,l}(r)) = \lim_{r\to 0}\overline{R}_{n,l}(r) = 0 \tag{132}$$

$$\lim_{r\to\infty}\left|\psi_{n,l}(r)\right|^2 = \lim_{r\to\infty} D_{n,l}(r) = 0 \quad . \tag{133}$$

This important property as stated in the last two equations, applies as easily can be checked for all the radial solutions $R_{n,l}(r)$. The function $\overline{R}_{n,l}(r)$ is said to be a **regular solution**, i.e., is **regular at the origin**. These two equations are nothing but the (radial) **boundary conditions** for the single electron atom.

For **2s-orbitals** the probability density is given by

$$|\psi_{2s}(r)|^2 = N(2 - r/a_0)^2 \exp(-r/a_0) \quad . \tag{134}$$

As can be seen in *Figure 6*, the radial distribution function $D_{2s}(r)$ has an additional zero location, usually called a **node**. In general - as can be worked out quite easily from the analytical shape of the Laguerre polynomials - the number of nodes for $l = 0$, i.e., the number of zero locations excluding the ones for $r \to 0$ and $r \to \infty$ is given by $(n - 1)$.

4.9.2 p-orbitals

For $l > 0$, the eigenfunctions $\psi_{n,l}(r)$ have an angular dependent part, namely the corresponding spherical harmonic. Using real spherical harmonics (122,123) the three 2p-like eigenfunctions are of the following form

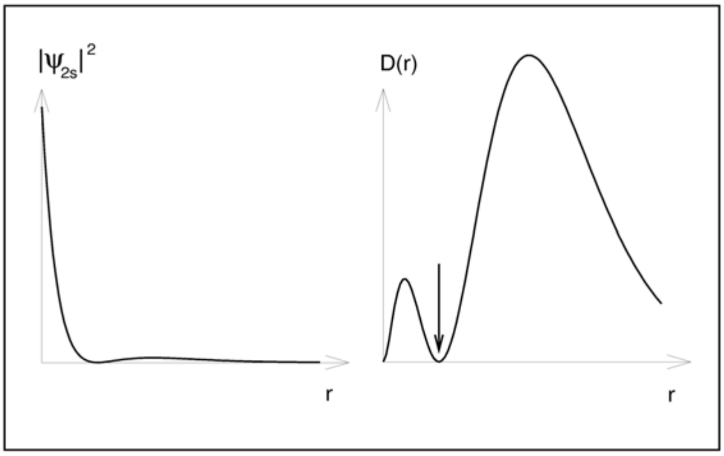

Figure 6: 2s-like probability density and radial distribution

$$\psi_{2,10}(r) \equiv \psi_{2p_z}(r) = f(r)\cos\theta \quad , \tag{135}$$

$$\psi_{2,1-1}(r) \equiv \psi_{2p_y}(r) = f(r)\sin\theta\sin\phi \quad , \tag{136}$$

$$\psi_{2,11}(r) \equiv \psi_{2p_x}(r) = f(r)\sin\theta\cos\phi \quad , \tag{137}$$

where

$$f(r) = \frac{1}{4\pi} a_0^{-5/2} r \exp(-r/2a_0) \quad . \tag{138}$$

Suppose for the sake of simplicity that for $\forall r$, $f(r)$ is a constant. The p_z-orbital is then

$$\psi_{p_z} \sim \cos\theta = \frac{z}{r} \quad , \tag{139}$$

i.e., for

$$\theta = 0 \rightarrow \frac{z}{r} = 1 \ ,$$

$$\theta = \pi/2 \rightarrow \frac{z}{r} = 0 \ ,$$

$$\theta = \pi \rightarrow \frac{z}{r} = -1 \ .$$

For a given value of r , say 1, the vector $\mathbf{r}$ ”precesses” around the z-axis, whereby the projection of $\mathbf{r}$ onto the z-axis is $\cos\theta$ (see *Figure 4-4*). The cut of this rotational figure with the yz-plane is also shown in *Figure 4-4*. Such a plot usually is called a **contour diagram**. Under the same approximations the probability density $\left|\psi_{p_z}\right|^2$ is given by

$$\left|\psi_{p_z}\right|^2 \sim \cos^2\theta \quad , \tag{140}$$

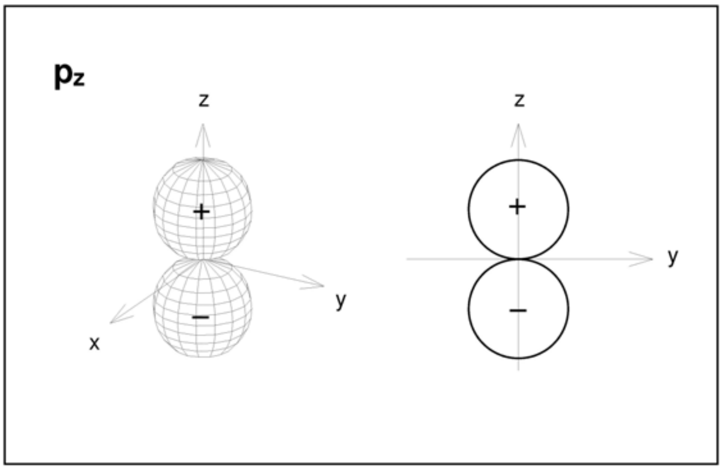

Figure 7: p_z-orbital

which of course yields a different rotational figure and cut in the yz-plane (see *Figure 7*). In the same way as for the p_z-orbital, cuts of the corresponding rotational figures for the p_x-orbital and the p_y-orbital can be generated in the xy-plane. Before commenting on these figures, the d-orbitals shall be inspected.

4.9.3 d-orbitals

There are altogether 5 d-orbitals, which in terms of real spherical harmonics are of the following form (constant $f(r)$):

$$\begin{gathered} d_1 = d_{xy} \sim xy \quad , \\ d_2 = d_{x^2-y^2} \sim (x^2 - y^2) \quad , \\ d_3 = d_{z^2} \sim \ (3z^2 - 1) \quad , \\ d_4 = d_{xz} \sim xz \quad , \\ d_5 = d_{yz} \sim yz \quad , \end{gathered} \tag{141}$$

and whose contour diagrams are shown in *Figure 9*.

Figures 7 and *9* show very famous "presentations" of p- and d-orbitals. Since these "presentations" are used in so many respects and different contexts, it is absolutely necessary to comment on their relevance: **these plots are contour diagrams of real spherical harmonics**, they only represent the angular dependence of single electron atomic wavefunctions, **they are icons of wavefunctions** and have nothing in common with probability densities. It should be recalled that the wavefunctions themselves have no physical significance, only

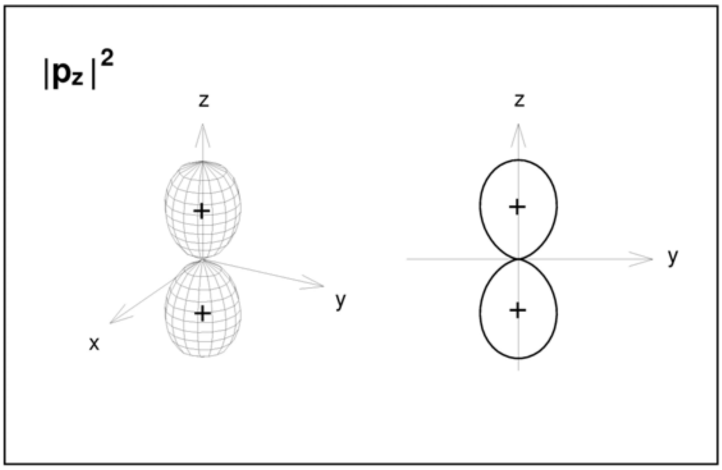

Figure 8: Contour diagram of the probability density of a p_z orbital

the probability densities. Extreme care has to be taken when using these icons: it is very easy to end up in a Micky Mouse view of reality!

4.10 Atomic selection rules

Suppose that the expectation value of the components of the electric dipole $\widehat{\mathbf{d}}$ has to be calculated,

$$\widehat{\mathbf{d}} = e\mathbf{r} \ , \ \mathbf{r} = (x, y, z) \quad , \tag{142}$$

where e is the elementary charge. Expressing the components of $\widehat{\mathbf{d}}$ in terms of polar coordinates,

$$\widehat{d_x} = e\,|\mathbf{r}| \sin\theta \cos\phi \ ,$$
$$\widehat{d_y} = e\,|\mathbf{r}| \sin\theta \sin\phi \ ,$$
$$\widehat{d_z} = e\,|\mathbf{r}| \cos\theta \quad ,$$

their expectations values in a single electron atom are given by

$$< \widehat{d_x} > = \ e \int \psi_{n,lm}(\mathbf{r})^* \, |\mathbf{r}| \sin\theta \cos\phi \psi_{n',l'm'}(\mathbf{r}) d\tau \quad , \tag{143}$$

$$< \widehat{d_y} > = \ e \int \psi_{n,lm}(\mathbf{r})^* \, |\mathbf{r}| \sin\theta \sin\phi \psi_{n',l'm'}(\mathbf{r}) d\tau \quad , \tag{144}$$

$$< \widehat{d_z} > = \ e \int \psi_{n,lm}(\mathbf{r})^* \, |\mathbf{r}| \cos\theta \psi_{n',l'm'}(\mathbf{r}) d\tau \quad , \tag{145}$$

$$d\tau = r^2 dr \sin\theta d\theta d\phi = r^2 dr d\Omega \quad .$$

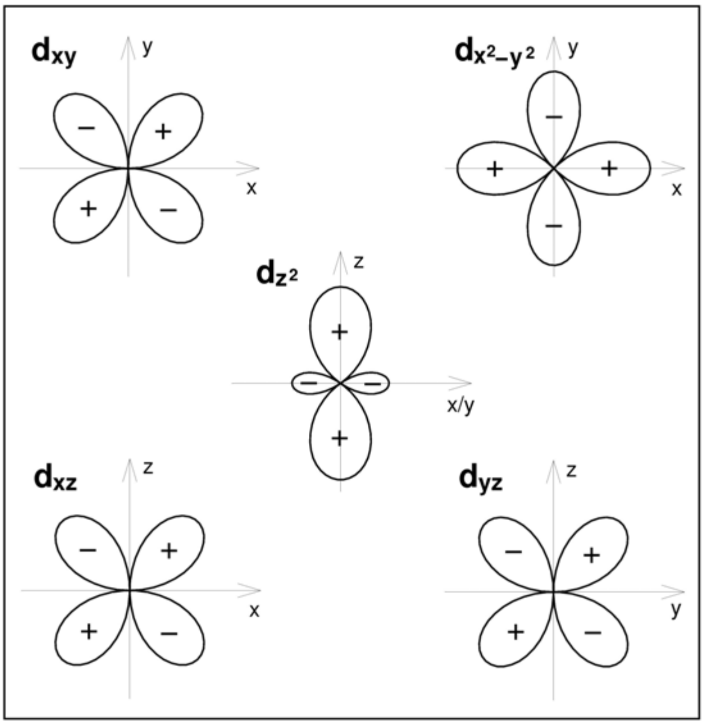

Figure 9: d-orbitals

It is easy to see that these expectation values contain a radial integral and an integral over the directions. For example for the z-component one gets

$$< \widehat{d}_z > = \; e\left[\int R_{n,l}(r)R_{n',l'}(r)r^3dr\right]\left[\int Y^l_m(\theta,\phi)^*\cos\theta Y^{l'}_{m'}(\theta,\phi)d\Omega\right] \quad . \tag{146}$$

Quite clearly this expectation value is only different from zero if and only if

$$\int Y^l_m(\theta,\phi)^*\cos\theta Y^{l'}_{m'}(\theta,\phi)d\Omega = \int Y^l_m(\theta,\phi)^* Y^1_0(\theta,\phi)Y^{l'}_{m'}(\theta,\phi)d\Omega \neq 0 \quad , \tag{147}$$

which is only the case - as can be checked very easily for the first few values of l and l' - if[3]

$$\Delta l = l - l' = \pm 1 \quad , \; \Delta m = m - m' = 0, \pm 1 \quad . \tag{148}$$

Forming now the expectation value of the square of the electric dipole,

$$< \widehat{\mathbf{d}}^2 > = < \widehat{d}^2_x > + < \widehat{d}^2_y > + < \widehat{d}^2_z > \tag{149}$$

---

[3] The so-called triangular condition is yet another very useful property of spherical harmonics. For a summary see for example appendix C of Messiah.

then this quantity once again is only not vanishing for the conditions stated in (148). These conditions are usually referred to as the **atomic (dipole) selection rules**, which viewed historically were one of the first staggering successes of quantum theory.

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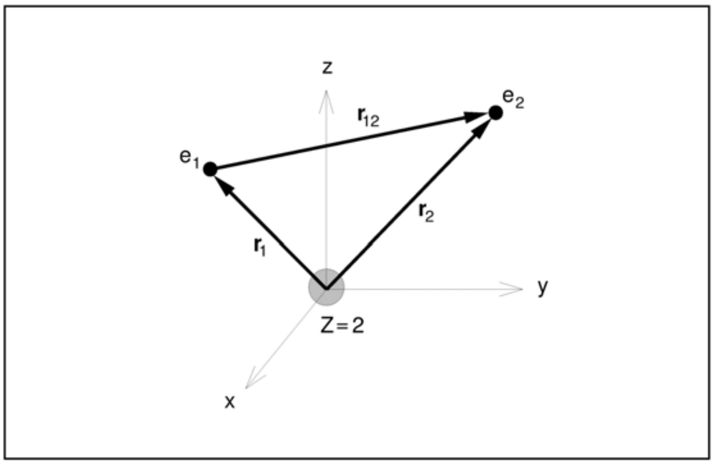

Figure 10: Coordinate system in the He atom

5 Perturbation theory, the He-atom

For systems with three or more interacting particles there are no analytical solutions for the Schrödinger equation. One has to use therefore methods of approximation. In principle, two different kinds of methods are at hand, namely the perturbation theory and the variational method, which is the subject of the next chapter. Both methods will be illustrated using the He atom as an example.

Consider the situation in the He atom (see *Figure* 10) at a given position of the nucleus (center of gravity). The motion of the nucleus can be assumed to be separated out just like in the case of the hydrogen atom. Besides the kinetic energy terms for the two electrons ($\widehat{T}_1, \widehat{T}_2$), there are two different types of Coulomb interactions, namely the interactions between the electrons and the nucleus ($\widehat{V}_1, \widehat{V}_2$) and the interaction between the two electrons ($\widehat{W}_{12}$):

$$\begin{aligned} \widehat{H} &= \widehat{T}_1 + \widehat{T}_2 + \widehat{V}_1 + \widehat{V}_2 + \widehat{W}_{12} = \\ &= -\frac{\hbar^2}{2\mu}\nabla_1^2 - \frac{\hbar^2}{2\mu}\nabla_2^2 - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}} \quad . \end{aligned} \tag{1}$$

The Schrödinger equation for the He atom,

$$\widehat{H}\psi(\mathbf{r}_1, \mathbf{r}_2) = E\psi(\mathbf{r}_1, \mathbf{r}_2) \quad , \tag{2}$$

can therefore be rewritten in form, where the Hamilton operator consists of operators that depend only on one variable and a remainder

$$\widehat{H} \equiv \widehat{H}(\mathbf{r}_1, \mathbf{r}_{2)} = \widehat{h}_1(\mathbf{r}_1) + \widehat{h}_2(\mathbf{r}_2) + \widehat{W}_{12}(\mathbf{r}_1, \mathbf{r}_{2)} \quad , \tag{3}$$

$$\widehat{h}_i(\mathbf{r}_i) = -\frac{\hbar^2}{2\mu}\nabla_i^2 \ - \frac{Ze^2}{r_i} \quad ; \quad i = 1,2 \quad , \tag{4}$$

namely as a sum of **one-particle operators** and a **two-particle operator**.

5.1 Zero order approximation

The easiest way of solving the Schrödinger equation for the He atom is of course neglecting the Coulomb interaction between the two electrons, since then one has to deal only with two independent motions:

$$\left(\widehat{h}_1(\mathbf{r}_1) + \widehat{h}_2(\mathbf{r}_2)\right)\psi(\mathbf{r}_1,\mathbf{r}_2) = E\psi(\mathbf{r}_1,\mathbf{r}_2) \quad , \tag{5}$$

$$\left(\widehat{h}_1(\mathbf{r}_1) + \widehat{h}_2(\mathbf{r}_2)\right)\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) = (E_1+E_2)\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) \quad , \tag{6}$$

$$\widehat{h}_i(\mathbf{r}_i)\phi_i(\mathbf{r}_i) = \left(-\frac{\hbar^2}{2\mu}\nabla_i^2 \ - \frac{Ze^2}{r_i}\right)\phi_i(\mathbf{r}_i) = E_i\phi_i(\mathbf{r}_i) \quad . \tag{7}$$

Furthermore, each of these motions is in principle the same as was solved for the hydrogen atom:

$$E_i = -\frac{Z^2\mu e^4}{2\hbar^2}\frac{1}{n_i^2} = \frac{Z^2 E_H}{n_i^2} \quad , \tag{8}$$

where E_H is the groundstate energy of the hydrogen atom (E_H ~-13.605 eV; eV = electron Volts). The groundstate energy for the He atom (Z=2) corresponds therefore to the single electron atomic (principal) quantum numbers $n_1 = n_2 = 1$ and is simply given by

$$E = E_1 + E_2 = 4E_H\left(\frac{1}{n_1^2} + \frac{1}{n_2^2}\right) = 8E_H \sim -108.8\ eV \quad . \tag{9}$$

Experimentally the groundstate energy of the He atom is $-78.98\ eV$, which as compared to the result in the last equation shows that the interaction between the two electrons cannot be neglected.

5.2 First order perturbation theory

Suppose that

(1) the Hamilton operator of a given system can be written as a sum of a Hamilton operator corresponding to a known and solvable problem ($\widehat{H}_0$) and a remainder ($\widehat{H}_1$),

$$\widehat{H} = \widehat{H}_0 + \widehat{H}_1 \quad , \tag{10}$$

such that for the expectation values of $\widehat{H}_0$ and $\widehat{H}_1$, $\langle\widehat{H}_0\rangle$ and $\langle\widehat{H}_1\rangle$,

$$\langle\widehat{H}_1\rangle \ \ll \ \langle\widehat{H}_0\rangle \quad , \tag{11}$$

(2) the solutions of the Schrödinger equation corresponding to $\widehat{H}_0$ are defined by

$$\widehat{H}_0\psi_i^{(0)} = E_i^{(0)}\psi_i^{(0)} \quad , \tag{12}$$

$$\int \psi_i^{(0)*}\psi_j^{(0)} d\tau = \delta_{ij} \quad , \tag{13}$$

(3) the solutions and the energy eigenvalues of $\widehat{H}$ can be approximated by

$$\psi_i = \psi_i^{(0)} + \psi_i^{(1)} \quad , \tag{14}$$

$$E_i = E_i^{(0)} + E_i^{(1)} \quad . \tag{15}$$

$\widehat{H}_0$ usually is called the **unperturbed Hamilton operator** and $\widehat{H}_1$ the **perturbation**. Using now the ansatz in (14) and (15) in the Schrödinger equation corresponding to $\widehat{H}$ and neglecting all cross terms in first order, i.e., all those terms having only the superscript 1 ,

$$\widehat{H}\psi_i = E_i\psi_i$$

$$\underbrace{\widehat{H}_0\psi_i^{(0)}}_{=E_i^{(0)}\psi_i^{(0)}} + \widehat{H}_0\psi_i^{(1)} + \widehat{H}_1\psi_i^{(0)} + \underbrace{\widehat{H}_1\psi_i^{(1)}}_{=E_i^{(1)}\psi_i^{(1)}} =$$

$$= E_i^{(0)}\psi_i^{(0)} + E_i^{(0)}\psi_i^{(1)} + E_i^{(1)}\psi_i^{(0)} + E_i^{(1)}\psi_i^{(1)} \quad , \tag{16}$$

one gets by means of (14)

$$\widehat{H}_0\psi_i^{(1)} + \widehat{H}_1\psi_i^{(0)} = E_i^{(0)}\psi_i^{(1)} + E_i^{(1)}\psi_i^{(0)} \quad . \tag{17}$$

The approximation $\widehat{H}_1\psi_i^{(1)} - E_i^{(1)}\psi_i^{(1)} = 0$ is called **first order perturbation theory**.

Since the set of eigenfunctions $\{\psi_i^{(0)}\}$ is a complete set of eigenfunctions ($\widehat{H}_0$ is a Hermitian operator!), the **perturbed wavefunctions** $\psi_i^{(1)}$ can be written as the following linear combination

$$\psi_i^{(1)} = \sum_{n=1}^{\infty} c_{ni}\psi_n^{(0)} \quad , \tag{18}$$

which in turn can be used in the previous equation

$$\sum_{n=1}^{\infty} c_{ni} \underbrace{\widehat{H}_0\psi_n^{(0)}}_{=E_n^{(0)}\psi_n^{(0)}} + \widehat{H}_1\psi_i^{(0)} = E_i^{(0)} \sum_{n=1}^{\infty} c_{ni}\psi_n^{(0)} + E_i^{(1)}\psi_i^{(0)} \quad . \tag{19}$$

By collecting now all terms with the unperturbed energies on one side, one obtains

$$\sum_{n=1}^{\infty} c_{ni}(E_n^{(0)} - E_i^{(0)})\psi_n^{(0)} = (E_i^{(1)} - \widehat{H}_1)\psi_i^{(0)} \quad . \tag{20}$$

Multiplying now with $\psi_k^{(0)*}$ from the left and integrating over $d\tau$ yields

$$\sum_{n=1}^{\infty} c_{ni}(E_n^{(0)} - E_i^{(0)}) \underbrace{\int \psi_k^{(0)*}\psi_n^{(0)} d\tau}_{=\delta_{kn}} =$$

$$= E_i^{(1)} \underbrace{\int \psi_k^{(0)*} \psi_i^{(0)} d\tau}_{=\delta_{ki}} - \int \psi_k^{(0)*} \widehat{H}_1 \psi_i^{(0)} d\tau \quad . \tag{21}$$

If one assumes that **the unperturbed system is not degenerated**, i.e. $E_1^{(0)} < E_2^{(0)} < E_3^{(0)} ....$, such that $(E_n^{(0)} - E_i^{(0)})$ never can be zero, then the last equation, rewritten below

$$\sum_{n=1}^{\infty} c_{ni}(E_n^{(0)} - E_i^{(0)})\delta_{kn} = E_i^{(1)}\delta_{ki} - \int \psi_k^{(0)*} \widehat{H}_1 \psi_i^{(0)} d\tau \quad , \tag{22}$$

results immediately in an expression for the perturbed energies $E_i^{(1)}$ as well as for the expansion coefficients c_{ni}

$$\boxed{i = k \ \rightarrow E_i^{(1)} = \ \int \psi_i^{(0)*} \widehat{H}_1 \psi_i^{(0)} d\tau} \tag{23}$$

$$\boxed{i \neq k \ \rightarrow \ c_{ki}(E_k^{(0)} - E_i^{(0)}) = -\int \psi_k^{(0)*} \widehat{H}_1 \psi_i^{(0)} d\tau} \tag{24}$$

Using these two expressions the energies of the system under consideration can be calculated

$$E_i = E_i^{(0)} + \int \psi_i^{(0)*} \widehat{H}_1 \psi_i^{(0)} d\tau \quad , \tag{25}$$

and the corresponding wavefunctions are defined by

$$\psi_i = \psi_i^{(0)} + \sum_{n \neq i}^{\infty} \left\{ \frac{\int \psi_n^{(0)*} \widehat{H}_1 \psi_i^{(0)} d\tau}{(E_i^{(0)} - E_n^{(0)})} \right\} \psi_n^{(0)} \quad . \tag{26}$$

This implies that for the **diagonal** case (23)one gets the energies and in the **off-diagonal** case (24) the coefficients for the wavefunctions. From (26) it is easy to see that for the case that the unperturbed system has a partially degenerated eigenvalue spectrum, in any application of perturbation theory the degeneracies have to be taken out.

5.3 Application to the He atom

Going now back to the situation in the He atom, namely to (3)

$$\widehat{H} \equiv \widehat{H}(\mathbf{r}_1, \mathbf{r}_{2)} = \underbrace{\widehat{h}_1(\mathbf{r}_1) + \widehat{h}_2(\mathbf{r}_2)}_{=\widehat{H}_0} + \underbrace{\widehat{W}_{12}(\mathbf{r}_1, \mathbf{r}_{2)}}_{=\widehat{H}_1} \quad , \tag{27}$$

within a first order perturbation theory the groundstate energy is given by

$$E_0 = \underbrace{E_0^{(0)}(1) + E_0^{(0)}(2)}_{E_0^{(0)}} + E_0^{(1)} =$$

$$= 8E_H \ + \int {\psi_0}^{(0)}(\mathbf{r}_1, \mathbf{r}_2)^* \left(\frac{e^2}{r_{12}}\right) {\psi_0}^{(0)}(\mathbf{r}_1, \mathbf{r}_2) d\tau \quad , \tag{28}$$

where the unperturbed wavefunction is a product of two $1s$-like hydrogen wavefunctions,

$${\psi_0}^{(0)}(\mathbf{r}_1, \mathbf{r}_2) = \phi_1(1s)\phi_2(1s) = N \exp(-2r_1/a_0) \exp(-2r_2/a_0) \quad , \tag{29}$$

N is a normalization constant and the integration volume $d\tau$ is given by

$$d\tau = r_1^2 \sin\theta_1 dr_1 d\theta_1 d\phi_1 r_2^2 \sin\theta_2 dr_2 d\theta_2 d\phi_2 \quad , \tag{30}$$

and $E_0^{(0)}(i), i = 1, 2$, is given by (8)

$$E_0^{(0)}(i) = -\frac{Z^2 \mu e^4}{2\hbar^2} \frac{1}{n_i^2} = 4E_H \quad , \tag{31}$$

since $n_i = 1$.

Performing the integral in (28) one gets

$$E_0^{(1)} = \frac{5}{4} \frac{Ze^2}{2a_0} \equiv \frac{5}{4} \frac{m_e Z e^4}{2\hbar^2} \quad , \tag{32}$$

where m_e is the actual mass of the electron (and not the reduced mass!). Putting now the results for the He atom in a table, one can immediately see at one glimpse that the perturbation after all is not small and that obviously the deviation to the experiment suffers severely from this fact.

Groundstate energy of the He atom [eV]

zero order	first order	experimental
$E_0^{(0)}$	$E_0^{(0)} + E_0^{(1)}$	
-108.24	-74.42	-78.62

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6 The variational method

6.1 The Ritz theorem

Let $\widehat{H}$ be the Hamilton operator of given system and ϕ some compatible function that meets the boundary conditions. The expectation value of $\widehat{H}$, ϵ, is always larger than the exact ground state energy E_0

$$\epsilon = \frac{\int \phi^* \widehat{H} \phi d\tau}{\int \phi^* \phi d\tau} \geq E_0 \quad . \tag{1}$$

The function ϕ is usually called a **trial function**.

Suppose the exact eigenvalue equation is given by

$$\widehat{H}\psi_i = E_i \psi_i \quad , \quad \int \psi_i^* \psi_j d\tau = \delta_{ij} \quad . \tag{2}$$

Since the set of functions ψ_i is complete the trial function ϕ can be expanded in this set

$$\phi = \sum_n a_n \psi_n \quad , \quad \phi^* = \sum_n a_n^* \psi_n^* \quad . \tag{3}$$

In terms of this expansion the expectation value ϵ is given by

$$\epsilon = \frac{\sum\limits_m \sum\limits_n a_m^* a_n \int \psi_m^* \widehat{H} \psi_n d\tau}{\sum\limits_m \sum\limits_n a_m^* a_n \int \psi_m^* \psi_n d\tau} = \frac{\sum\limits_m \sum\limits_n a_m^* a_n E_n \delta_{nm}}{\sum\limits_m \sum\limits_n a_m^* a_n \delta_{nm}} =$$

$$= \frac{\sum\limits_n a_n^* a_n E_n}{\sum\limits_n a_n^* a_n} \quad . \tag{4}$$

If one now substracts E_0 on both sides, i.e., shifts the energy scale by E_0, one gets

$$\epsilon - E_0 = \frac{\sum\limits_n a_n^* a_n (E_n - E_0)}{\sum\limits_n a_n^* a_n} \quad . \tag{5}$$

Now one can see that since E_n is the energy of an "excited state", $E_n - E_0 \geq 0$ and since ϕ has to be normalizable, $\sum\limits_n a_n^* a_n \geq 0$. This implies that

$$\epsilon - E_0 = \frac{\sum\limits_n a_n^* a_n (E_n - E_0)}{\sum\limits_n a_n^* a_n} \geq 0 \quad . \tag{6}$$

Of course in general the exact eigenfunctions are not known (otherwise there would be hardly the need for a method of approximation). Therefore **the trial function ϕ is chosen to be dependent on parameters** $a, b, c, \ldots$ **such that ϵ is a function of these parameters,** $\epsilon \equiv \epsilon(a, b, c, \ldots)$. **The minimum of ϵ corresponds then to the condition**

$$\frac{\partial \epsilon(a,b,c,\ldots)}{\partial a} = \frac{\partial \epsilon(a,b,c,\ldots)}{\partial b} = \frac{\partial \epsilon(a,b,c,\ldots)}{\partial c} = \ldots.. = 0 \tag{7}$$

6.2 The He-atom

In order to illustrate the variational method once again the He atom is considered. In the previous chapter it was shown that within the zero order approximation of perturbation theory the wavefunction for the He atom is of the following form (see also the previous chapter)

$$\psi_0^{(0)}(\mathbf{r}_1,\mathbf{r}_2)=\phi_1(1s)\phi_2(1s)=\frac{Z^3}{\pi a_0^3}\exp(-Z(r_1+r_2)/a_0) \quad .$$

Since π and a_0 are constants the only available parameter left is the atomic number. Suppose therefore that the atomic number is treated as an adjustable parameter ξ for the trial function $\phi(\mathbf{r}_1,\mathbf{r}_2)$,

$$\phi(\mathbf{r}_1,\mathbf{r}_2)=\frac{\xi^3}{\pi a_0^3}\exp(-\xi(r_1+r_2)/a_0) \quad . \tag{8}$$

The expectation value of the Hamilton operator for the He atom is then given by

$$\begin{aligned}\epsilon &= \int \phi^*(\mathbf{r}_1,\mathbf{r}_2)\widehat{H}\phi(\mathbf{r}_1,\mathbf{r}_2)d\tau = \\ &= \int \phi^*(\mathbf{r}_1,\mathbf{r}_2)\widehat{h}_1\phi(\mathbf{r}_1,\mathbf{r}_2)d\tau + \int \phi^*(\mathbf{r}_1,\mathbf{r}_2)\widehat{h}_2\phi(\mathbf{r}_1,\mathbf{r}_2)d\tau \\ &\quad + \int \phi^*(\mathbf{r}_1,\mathbf{r}_2)\frac{e}{r_{12}}\phi(\mathbf{r}_1,\mathbf{r}_2)d\tau \quad ,\end{aligned} \tag{9}$$

namely in terms of integrals for the one-electron operators $\widehat{h}_i$ and the two-electron operator e/r_{12}. In order to make use of the fact that the integrals corresponding to the one-electron operators are of course known for $\xi = Z$, the Hamilton operator is rewritten in the following way (addition of zero!)

$$\begin{aligned}\widehat{H} &= \underbrace{-\frac{\hbar^2}{2\mu}\nabla_1^2-\frac{\xi e^2}{r_1}}_{1} \quad \underbrace{-\frac{\hbar^2}{2\mu}\nabla_2^2-\frac{\xi e^2}{r_2}}_{2}+ \\ &+ \underbrace{(\xi - Z)\{\frac{e^2}{r_1}+\frac{e^2}{r_2}\}}_{3} \quad + \quad \underbrace{\frac{e^2}{r_{12}}}_{4} \quad .\end{aligned} \tag{10}$$

With this little trick the expectation value $\epsilon(\xi)$ can be written as

$$\begin{aligned}\epsilon(\xi) &= \int \phi_1^*(1s)\underbrace{(-\frac{\hbar^2}{2\mu}\nabla_1^2-\frac{\xi e^2}{r_1}}_{1})\phi_1(1s)d\tau_1 + \\ &+ \int \phi_2^*(1s)\underbrace{(-\frac{\hbar^2}{2\mu}\nabla_2^2-\frac{\xi e^2}{r_2}}_{2})\phi_2(1s)d\tau_2 +\end{aligned}$$

$$+\int \phi^*(\mathbf{r}_1,\mathbf{r}_2)\underbrace{(\xi - Z)\{\frac{e^2}{r_1}+\frac{e^2}{r_2}}_{3}\}\phi(\mathbf{r}_1,\mathbf{r}_2)d\tau_1 d\tau_2 +$$

$$+\int \phi^*(\mathbf{r}_1,\mathbf{r}_2)\underbrace{\frac{e^2}{r_{12}}}_{4}\phi(\mathbf{r}_1,\mathbf{r}_2)d\tau_1 d\tau_2 \quad . \tag{11}$$

Integrals of type 1 and 2 correspond now to the single electron atom with atomic number ξ,

$$\int \phi_i^*(1s)\underbrace{(-\frac{\hbar^2}{2\mu}\nabla_i^2 - \frac{\xi e^2}{r_i}}_{1,2})\phi_i(1s)d\tau_i = -\xi^2 E_H \quad , \tag{12}$$

where E_H is the groundstate energy of the hydrogen atom. For the two remaining integrals one gets

$$\int \phi^*(\mathbf{r}_1,\mathbf{r}_2)\underbrace{(\xi - Z)\{\frac{e^2}{r_1}+\frac{e^2}{r_2}}_{3}\}\phi(\mathbf{r}_1,\mathbf{r}_2)d\tau_1 d\tau_2 = 4\xi(\xi - Z)E_H \quad , \tag{13}$$

$$\int \phi^*(\mathbf{r}_1,\mathbf{r}_2)\underbrace{\frac{e^2}{r_{12}}}_{4}\phi(\mathbf{r}_1,\mathbf{r}_2)d\tau_1 d\tau_2 = \frac{5}{4}\xi E_H \quad . \tag{14}$$

The expectation value $\epsilon(\xi)$ is therefore given by the following expression

$$\epsilon(\xi) = \left\{-2\xi^2 + 4\xi(\xi - Z) + \frac{5}{4}\xi\right\} E_H \quad . \tag{15}$$

The minimum of $\epsilon(\xi)$ with respect to ξ is given by the condition

$$\frac{d\epsilon(\xi)}{d\xi} = 0 = (4\xi - 4Z + \frac{5}{4}) \quad \rightarrow \quad \xi = Z - \frac{5}{16} \quad . \tag{16}$$

Using now the optimal value of ξ in (15) the minimum value of ϵ is given by

$$\epsilon = -2(Z - \frac{5}{16})^2 E_H = -76.9\ eV \quad . \tag{17}$$

In the table below the results for the He atom are summarized. As one can see this simple variational approach yields a result much closer to the experimental value than the first order perturbation theory. One also can see that $\epsilon > E_0$.

First order perturbation theory	**Variation method** with one parameter	**Experimental**
$-74.42\ eV$	$-76.9\ eV$	$-78.62\ eV$

6.3 The variational method for a linear combination of functions

The most frequently used application of the variational method in physics and chemistry is based on the expansion of trial functions as linear combinations of functions. Suppose $\chi_i, \ i = 1, ..., n$, is a set of linear independent, not necessarily orthogonal functions from which a trial function ϕ can be constructed in the following way

$$\phi = c_1\chi_1 + c_2\chi_2 + c_3\chi_3 + \cdots + c_n\chi_n = \sum_{i=1}^{n} c_i\chi_i \quad , \tag{18}$$

where the coefficients c_i are real and have to be determined minimizing the expectation value of the energy, ϵ

$$\epsilon = \frac{\sum\limits_{i,k=1}^{n} c_i c_k \int \chi_i^* \widehat{H} \chi_k d\tau}{\sum\limits_{i,k=1} c_i c_k \int \chi_i^* \chi_k d\tau} = \frac{\sum\limits_{i,k=1}^{n} c_i c_k H_{ik}}{\sum\limits_{i,k=1} c_i c_k S_{ik}} \quad , \tag{19}$$

$$\sum_{i,k=1}^{n} c_i c_k H_{ik} \ = \ \epsilon \sum_{i,k=1}^{n} c_i c_k S_{ik} \quad . \tag{20}$$

Since ϵ has to be a minimum this implies that

$$\frac{\partial \epsilon}{\partial c_j} = 0 \ , \ j = 1, ..., n \quad . \tag{21}$$

Taking the derivative of (20) with respect to a particular coefficient, say c_j , one gets

$$\begin{aligned} \frac{\partial}{\partial c_j} \left\{ \epsilon \sum_{i,k} c_i c_k S_{ik} \right\} &= \underbrace{\frac{\partial \epsilon}{\partial c_j}}_{=0} \sum_{i,k=1}^{n} c_i c_k S_{ik} \ + \epsilon \frac{\partial}{\partial c_j} \sum_{i,k=1}^{n} c_i c_k S_{ik} = \\ &= \frac{\partial}{\partial c_j} \sum_{i,k=1}^{n} c_i c_k H_{ik} \quad . \end{aligned} \tag{22}$$

In order to take the derivative of the mixed products of coefficients, the best way to handle the problem is to inspect special cases:

$$\frac{\partial}{\partial c_j} \sum_{i,k=1}^{n} c_i c_k = \{ \begin{array}{ll} 2c_j & j = i = k \\ c_k & j = i, j \neq k \\ c_i & j = k, j \neq i \\ 0 & j \neq i, j \neq k \end{array} \quad . \tag{23}$$

Because of the double sum one gets therefore

$$2\epsilon \sum_{i=1}^{n} c_i S_{ij} = 2 \sum_{i=1}^{n} c_i H_{ij} \quad . \tag{24}$$

This procedure has to be repeated for each coefficient $c_j ,\ j = 1, \ldots , n$, i.e., one gets a system n equations

$$\sum_{i=1}^{n} c_i (H_{ij} - \epsilon S_{ij}) = 0 \ ,\ j = 1, \ldots , n \quad , \tag{25}$$

which can be written in matrix form as

$$(\underline{H} - \epsilon \underline{S}) \underline{c} = 0 \quad ,$$

$$\begin{pmatrix} H_{11} - \epsilon S_{11} & H_{12} - \epsilon S_{12} & ... & H_{1n} - \epsilon S_{1n} \\ H_{21} - \epsilon S_{21} & H_{22} - \epsilon S_{22} & ... & H_{2n} - \epsilon S_{2n} \\ \vdots & \vdots & ... & \vdots \\ H_{n1} - \epsilon S_{n1} & H_{n2} - \epsilon S_{n2} & ... & H_{nn} - \epsilon S_{nn} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{pmatrix} = 0 \quad . \tag{26}$$

This system of equations has a non-trivial solution if and only if the determinant of the matrix $(\underline{H} - \epsilon \underline{S})$ vanishes

$$\det (\underline{H} - \epsilon \underline{S}) = 0 \quad . \tag{27}$$

The determinant has a very prominent name. It is called the **secular determinant**. By developing the determinant one gets a polynomial in the unknown ϵ, the n (number of basis functions χ_i) roots of which are then the approximations for the groundstate energy (E_0), the energy of the first excited state (E_1), of the second excited state (E_2) and so on, $E_0 \leq E_1 \leq E_2$ ... . If the set of basis functions is an orthonormal set of functions[1]

$$\int \chi_i^* \chi_j d\tau = \delta_{ij} \ ,\ i, j = 1, ...n \quad , \tag{28}$$

then the secular matrix

$$(\underline{H} - \epsilon \underline{1})\, \underline{c} \ = 0 \quad , \tag{29}$$

$$\begin{pmatrix} H_{11} - \epsilon S_{11} & H_{12} & ... & H_{1n} \\ H_{21} & H_{22} - \epsilon & ... & H_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ H_{n1} & H_{n2} & ... & H_{nn} - \epsilon \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{pmatrix} = 0 \quad , \tag{30}$$

is in particular easy to solve, since the problem is reduced to finding the eigenvalues and eigenvectors of an $n \times n$ matrix. In this case there exists a in general unitary matrix $\underline{U}$

$$\underline{U}^{\dagger} \underline{U} = \ \underline{U} \underline{U}^{\dagger} = \ \underline{1} \quad , \quad U_{ij}^{\dagger} = U_{ji}^{*} \quad , \tag{31}$$

---

[1] It should be noted that a set of basis functions can always be transformed into a set of orthonormal basis functions

such that by multiplying (29) from the left with $\underset{\sim}{U}$,

$$\underline{U}^{\dagger}\underline{Hc} = \underbrace{\underline{U}^{\dagger}\underline{HU}}_{\underline{\lambda}}\ \underline{U}^{\dagger}\underline{c} = \epsilon\underline{U}^{\dagger}\underline{c} \quad , \tag{32}$$

where $\underset{\sim}{\lambda}$ is a diagonal matrix

$$\underline{\lambda} = \begin{pmatrix} \lambda_1 & 0 & 0 & \\ 0 & \lambda_2 & 0 & \\ 0 & 0 & \ddots & \\ & & & \lambda_n \end{pmatrix} \quad . \tag{33}$$

It should be noted that $\underline{U}^{\dagger}\underline{c}$ is nothing but a **basis transformation**, which leaves the determinant unchanged!

References

[1] R.Courant and D.Hilbert, *"Methods of Mathematical Physics"*, John Wiley and Sons, 1989

[2] F.Constantinescu and E.Magyari, *"Problems in Quantum Mechanics"*, Pergamon Press, 1971

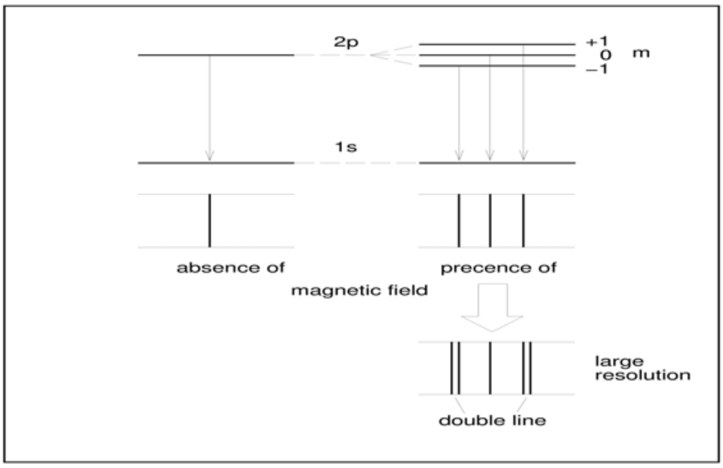

Figure 11: Spin induced splitting of atomic line spectra

7 The electronic spin, permutational symmetry and the Pauli principle

If one records the emission spectrum of an atom in the absence and in the presence of an external magnetic field one finds for example for a transition from a 2p-level to a 1s-level different patterns. In the absence of the field only one line is recorded, whereas in the presence of this field three lines can be observed (see *Figure 11*). This is totally in accordance with the very meaning of the term magnetic quantum number, namely that the degeneracy with respect to the eigenvalues of $\widehat{L}_z$ is lifted. Increasing the resolution, however, one finds that two of these lines are in fact double lines.

This doubling of lines implies that the particle (electron) must have an additional property, which up to now was not included in its formal description. This property is the (electronic) **spin** (German: ”Eigendrehimpuls”) of the electron. The reason for this formal deficiency is that the correspondence principle was only applied to problems of classical mechanics (classical Hamilton functions), which clearly does not include Einsteins theory of relativity. Strictly speaking a formal description of the spin can only be based on a theory of a relativistic motion of particles[1]. Without the use of a such relativistic theory the properties of the electronic spin can only be stated in terms of postulates, and admittingly remain slightly vague.

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[1] see for example chapter 17

7.1 Spin postulates

7.1.1 Postulate 1:

The components of the spin momentum operator $\widehat{\mathbf{S}}$ commute in the same formal way as the components of the angular momentum operator $\widehat{\mathbf{L}}$, namely

$$[\widehat{S}_x, \widehat{S}_y]_- = i\hbar\widehat{S}_z \quad , \tag{7}$$

$$[\widehat{S}_y, \widehat{S}_z]_- = i\hbar\widehat{S}_x \quad , \tag{8}$$

$$[\widehat{S}_z, \widehat{S}_x]_- = i\hbar\widehat{S}_y \quad , \tag{9}$$

and the square of $\widehat{\mathbf{S}}$ is given by

$$\widehat{S}^2 = \widehat{S}_x^2 + \widehat{S}_y^2 + \widehat{S}_z^2 \quad . \tag{10}$$

7.1.2 Postulate 2:

For an **electron** there are only two eigenfunctions of $\widehat{S}^2$ and $\widehat{S}_z$, namely α and β, corresponding to the following eigenvalue equations

$$\widehat{S}^2\alpha = \frac{1}{2}(\frac{1}{2}+1)\hbar^2\alpha \quad , \tag{11}$$

$$\widehat{S}^2\beta = \frac{1}{2}(\frac{1}{2}+1)\hbar^2\beta \quad , \tag{12}$$

$$\widehat{S}_z\alpha = \frac{1}{2}\hbar\alpha \quad , \tag{13}$$

$$\widehat{S}_z\beta = -\frac{1}{2}\hbar\beta \quad . \tag{14}$$

In analogy to the case of the angular momentum operators these eigenvalue equations are usually written as

$$\widehat{S}^2\alpha = s(s+1)\hbar^2\alpha \quad , \ \widehat{S}^2\beta = s(s+1)\hbar^2\beta \quad , \ s = \frac{1}{2} \quad , \tag{15}$$

$$\widehat{S}_z\alpha = m_s\hbar\alpha \quad , \ \widehat{S}_z\beta = m_s\hbar\beta \quad , \ m_s = \pm\frac{1}{2} \quad . \tag{16}$$

The functions α and β are so-called **spinors**,

$$\alpha = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad , \tag{17}$$

$$\beta = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad . \tag{18}$$

Traditionally the elements in these 2-vectors are labelled (in a somewhat confusing manner) by $\sigma = \frac{1}{2}$ and $\sigma = -\frac{1}{2}$, such that α and β can also be viewed as the following orthonormalized functions, usually called **spin functions**

$$\alpha(\sigma) = \{ \begin{array}{ll} 1 & ; \sigma = \frac{1}{2} \\ 0 & ; \sigma = -\frac{1}{2} \end{array} \quad , \tag{19}$$

$$\beta(\sigma) = \{ \begin{array}{ll} 0 & ;\sigma = \frac{1}{2} \\ 1 & ;\sigma = -\frac{1}{2} \end{array} \quad , \tag{20}$$

$$\sum_{\sigma=\pm\frac{1}{2}} \alpha(\sigma)^\dagger \alpha(\sigma) = \left(\begin{array}{cc} 1 & 0 \end{array} \right) \left(\begin{array}{c} 1 \\ 0 \end{array} \right) = 1 \quad , \tag{21}$$

$$\sum_{\sigma=\pm\frac{1}{2}} \beta(\sigma)^\dagger \beta(\sigma) = \left(\begin{array}{cc} 0 & 1 \end{array} \right) \left(\begin{array}{c} 0 \\ 1 \end{array} \right) = 1 \quad , \tag{22}$$

$$\sum_{\sigma=\pm\frac{1}{2}} \alpha(\sigma)^\dagger \beta(\sigma) = \left(\begin{array}{cc} 1 & 0 \end{array} \right) \left(\begin{array}{c} 0 \\ 1 \end{array} \right) = 0 \quad , \tag{23}$$

$$\sum_{\sigma=\pm\frac{1}{2}} \beta(\sigma)^\dagger \alpha(\sigma) = \left(\begin{array}{cc} 0 & 1 \end{array} \right) \left(\begin{array}{c} 1 \\ 0 \end{array} \right) = 0 \quad . \tag{24}$$

7.2 Atomic spin orbitals

In a non-relativistic description the operators $\widehat{S}_x$, $\widehat{S}_y$, $\widehat{S}_z$ and $\widehat{S}^2$ only act on the spin functions, i.e. for the Hamilton operator of the single electron atom (the hydrogen atom for example) the following commutator relations apply trivially,

$$[\widehat{H}, \widehat{S}^2]_- = [\widehat{H}, \widehat{S}_z]_- = [\widehat{H}, \widehat{L}^2]_- = [\widehat{H}, \widehat{L}_z]_- = 0 \quad , \tag{25}$$

$$[\widehat{L}^2, \widehat{S}^2]_- = [\widehat{L}_z, \widehat{S}_z]_- = 0 \quad . \tag{26}$$

Since the eigenvalue of $\widehat{S}^2$, $s(s+1)\hbar^2$ is the same for all electrons, namely $3\hbar^2/4$ only the eigenvalue $\widehat{S}_z$, $m_s\hbar$, $m_s = \pm\frac{1}{2}$, can be used for a further characterization ("symmetry") of an energy eigenvalue in the atomic single electron problem. The corresponding eigenfunctions can therefore be characterized by the four quantum numbers:

n	**principal quantum number**
l	**angular momentum quantum number**
m	**magnetic quantum number**
m_s	**spin quantum number**

The eigenfunctions are products of atomic orbitals and spin functions

$$\Psi_{n,lm,m_s}(\mathbf{r}, \sigma) = \left\{ \begin{array}{l} \psi_{n,lm}(\mathbf{r})\alpha(\sigma) \\ \psi_{n,lm}(\mathbf{r})\beta(\sigma) \end{array} \right. =$$

$$= \left\{ \begin{array}{l} R_{n,l}(r) Y_l^m(\theta, \phi)\alpha(\sigma) \\ R_{n,l}(r) Y_l^m(\theta, \phi)\beta(\sigma) \end{array} \right. \quad , \tag{27}$$

$$\widehat{S}_z \psi_{n,lm}(\mathbf{r})\alpha(\sigma) = \psi_{n,lm}(\mathbf{r})\widehat{S}_z\alpha(\sigma) = \frac{1}{2}\hbar\psi_{n,lm}(\mathbf{r})\alpha(\sigma) \quad , \tag{28}$$

$$\widehat{S}_z \psi_{n,lm}(\mathbf{r})\beta(\sigma) = \psi_{n,lm}(\mathbf{r})\widehat{S}_z\beta(\sigma) = -\frac{1}{2}\hbar\psi_{n,lm}(\mathbf{r})\beta(\sigma) \quad . \tag{29}$$

The atomic **spinorbitals** $\Psi_{n,lm,m_s}(\mathbf{r},\sigma)$ are orthonormalized wavefunctions

$$\sum_{\sigma=\pm\frac{1}{2}} \int \Psi^*_{n,lm,m_s}(\mathbf{r},\sigma)\Psi_{n,lm,m_s}(\mathbf{r},\sigma)d\tau = 1 \quad . \tag{30}$$

7.3 The Pauli principle - version 1

The Pauli principle is a principle, **independent** of the Schrödinger equation. In the context of a single electron theory of atoms it can be stated as follows:

Two electrons in an atom never can have the same set of (atomic) quantum numbers.

For the energy eigenvalues of the He atom this implies that the two electrons must have different quantum numbers. Denoting the atomic orbital of electron 1 by $\phi(1)$ and that of electron 2 by $\phi(2)$ and using the numbering for the electrons also as argument for the spin functions, the ground state wavefunction $\psi_{GS}(1,2) \equiv \psi_{GS}(\mathbf{r}_1,\mathbf{r}_2)$ of the He atom , where $\mathbf{r}_1$ and $\mathbf{r}_2$ denote the coordinates of the two electrons, obviously refers to the case that both, $\phi(1)$ and $\phi(2)$ are 1s-orbitals, formally written as $1s(1)$ and $1s(2)$. The two electrons must differ therefore in their spin functions:

$$\psi_{GS}(1,2) = \phi(1)\phi(2)\alpha(1)\beta(2) = 1s(1)1s(2)\alpha(1)\beta(2) \quad . \tag{31}$$

For the first excited state of the He atom, however, in principle two possibilities of assigning atomic orbitals to the spin-independent part of the wavefunction $\phi_{ES}(1,2)$ exist

$$\phi_{ES}(1,2) = \left\{ \begin{array}{c} 1s(1)2s(2) \\ 2s(1)1s(2) \end{array} \right. \quad , \tag{32}$$

which would imply that the two electrons are distinguishable! Since this can not be the case - just as the Hamilton operator can not dependent on the choice of the coordinate system (principle of coordinate invariance), one forms normalized linear combinations of the above two possibilities. If $\widehat{P}$ denotes an operator that permutes the indices of the electrons, one can see easily that two cases arise. The first one, denoted by an index s,

$$\phi^s_{ES}(1,2) = \frac{1}{\sqrt{2}}\left(1s(1)2s(2) + 1s(2)2s(1)\right) \quad , \tag{33}$$

is **symmetric** with respect to a **permutation** of the indices for the electrons,

$$\begin{aligned} \widehat{P}\phi^s_{ES}(1,2) = \phi^s_{ES}(2,1) = \frac{1}{\sqrt{2}}\left(1s(2)2s(1) + 1s(1)2s(2)\right) = \\ = \phi^s_{ES}(1,2) \quad , \end{aligned} \tag{34}$$

i.e. does not change the sign of the spin-independent part of the wavefunction, when permuting the numbering of the electrons. The second one, however,

$$\phi_{ES}^{as}(1,2) = \frac{1}{\sqrt{2}}\left(1s(1)2s(2) \;-\; 1s(2)2s(1)\right) \quad , \tag{35}$$

is **antisymmetric** with respect to such a permutation.

$$\widehat{P}\phi_{ES}^{as}(1,2) = \phi_{ES}^{as}(2,1) = \frac{1}{\sqrt{2}}\left(1s(2)2s(1) \;-\; 1s(1)2s(2)\right) =$$

$$= -\phi_{ES}^{as}(1,2) \quad . \tag{36}$$

Concomitantly the two electrons can not be distinguished with respect to their spin. Again the product of the corresponding spinfunctions has to be checked with respect to a permutation of indices and also with respect to the eigenvalue of $\widehat{S}_z$. For example:

$$\widehat{P}\alpha(1)\alpha(2) = \alpha(2)\alpha(1) \equiv \alpha(1)\alpha(2) \quad , \tag{37}$$

$$\widehat{S}_z\alpha(1)\alpha(2) = \alpha(2)\widehat{S}_z\alpha(1) + \alpha(1)\widehat{S}_z\alpha(2) =$$

$$= \hbar\left(m_s(1)\alpha(1)\alpha(2) + m_s(2)\alpha(1)\alpha(2)\right) = \hbar\left(m_s(1) + m_s(2)\right)\alpha(1)\alpha(2) =$$

$$= \hbar M_s\alpha(1)\alpha(2) \quad . \tag{38}$$

For the various products of the two spin functions one can construct a little table and note the occurring permutational symmetry, using as before "s" for symmetric and "as" for antisymmetric, respectively:

product	*symmetry*	M_s
$\alpha(1)\alpha(2)$	s	1
$\beta(1)\beta(2)$	s	-1
$\frac{1}{\sqrt{2}}\left(\alpha(1)\alpha(2) + \beta(1)\beta(2)\right)$	s	0
$\frac{1}{\sqrt{2}}\left(\alpha(1)\alpha(2) - \beta(1)\beta(2)\right)$	as	0

As one can see from this table, three out of four product functions are symmetric and only one is antisymmetric.

In the same way as M_s was obtained, also the **total spin** can be determined. For example,

$$\widehat{\mathbf{S}}^2\alpha(1)\alpha(2) = \hbar^2\left(s(1)(s(1)+1)\alpha(1)\alpha(2) + s(2)(s(2)+1)\alpha(1)\alpha(2)\right) =$$

$$= \hbar^2 S(S+1)\alpha(1)\alpha(2) \quad . \tag{39}$$

Thus, if N is the total number of electrons then the total spin S and the total spin quantum number M_s are given by:

$$S = \sum_{i=1}^{N} s(i) \quad , \quad M_s = \sum_{i=1}^{N} m_s(i) \quad . \tag{40}$$

Combining finally the spin-independent parts (orbital parts) of the wavefunction with the products of the spinfunctions, one has to remember that the product of two symmetric functions is symmetric, while the product of a symmetric function with an antisymmetric function results in an antisymmetric function. Symbolically written the following short-hand rule applies:

$$\boxed{\text{symmetric} \otimes \text{symmetric} = \text{symmetric}} \tag{41}$$

$$\boxed{\text{symmetric} \otimes \text{antisymmetric} = \text{antisymmetric}} \tag{42}$$

$$\boxed{\text{antisymmetric} \otimes \text{antisymmetric} = \text{symmetric}} \tag{43}$$

For example

$$\psi = \frac{1}{\sqrt{2}} \left(1s(1)2s(2) + 1s(2)2s(1)\right) \alpha(1)\alpha(2) \quad ,$$

is symmetric with respect to a permutation of the indices for the two electrons, while

$$\psi = \frac{1}{2} \left(1s(1)2s(2) + 1s(2)2s(1)\right) \left(\alpha(1)\beta(2) - \alpha(2)\beta(1)\right) \quad ,$$

is antisymmetric.

7.4 The Pauli principle - version 2

The wavefunction of a system of electrons has to be antisymmetric with respect to a simultaneous permutation of the coordinates and of the spins of two electrons.

The wavefunction of a system of Fermions has to be antisymmetric with respect to permutational symmetry, that of Bosons symmetric, whereby Fermions are particles with half-integer spins ($\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, ...$) like electrons, protons, neutrons etc. and Bosons particles with integer spin ($0, 1, 2, ...$) like photons, $\alpha-$particles (He nuclei) etc.

For the above example of the wavefunction for the excited state of a He atom, one gets therefore the following three (triplet) antisymmetric wavefunctions that have antisymmetric orbital parts and symmetric spin parts and which in the absence of an external magnetic field belong all to one degenerated energy eigenvalue

$$\psi^{Triplet} = \frac{1}{\sqrt{2}}\left((1s(1)2s(2) - 1s(2)2s(1)\right)\begin{cases}\alpha(1)\alpha(2) \\ \frac{1}{\sqrt{2}}\left(\alpha(1)\beta(2) + \alpha(2)\beta(1)\right) \\ \beta(1)\beta(2)\end{cases} \tag{44}$$

and one (singulet) antisymmetric wavefunction that is symmetric in its orbital part and antisymmetric in the spin part

$$\psi^{Singulet} = \frac{1}{2}\left((1s(1)2s(2) + 1s(2)2s(1)\right)\left(\alpha(1)\beta(2) - \alpha(2)\beta(1)\right) \quad . \tag{45}$$

In general the number of spin functions that in the absence of a magnetic field belong to one and the same energy eigenvalue is given by $(2S+1)$ the so-called **multiplicity**. The multiplicity and the total spin quantum number M_s are then used to characterize a particular (antisymmetric) wavefunction of a in general n-electron system

$$\psi_{M_s}^{2S+1}(1,2,3,..,n) \tag{46}$$

References

[1] W.Pauli, "Die allgemeinen Prinzipien der Wellenmechanik", Handbuch der Physik, Bd XXIV, Part 1 (1933)

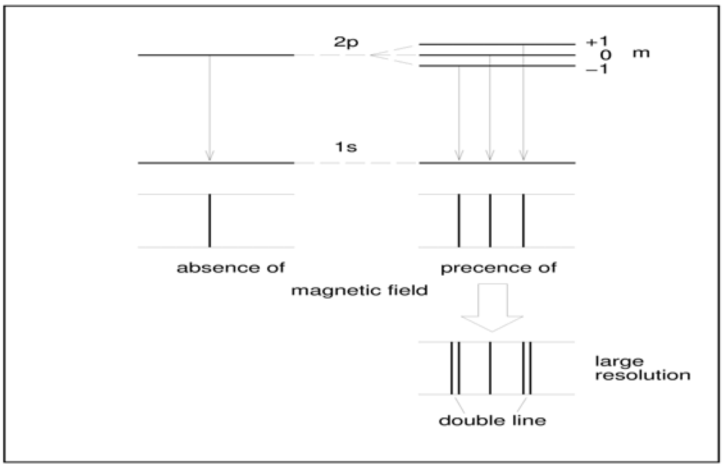

Figure 13: Spin induced splitting of atomic line spectra

8 The electronic spin, permutational symmetry and the Pauli principle

If one records the emission spectrum of an atom in the absence and in the presence of an external magnetic field one finds for example for a transition from a 2p-level to a 1s-level different patterns. In the absence of the field only one line is recorded, whereas in the presence of this field three lines can be observed (see *Figure 13*). This is totally in accordance with the very meaning of the term magnetic quantum number, namely that the degeneracy with respect to the eigenvalues of $\widehat{L}_z$ is lifted. Increasing the resolution, however, one finds that two of these lines are in fact double lines.

This doubling of lines implies that the particle (electron) must have an additional property, which up to now was not included in its formal description. This property is the (electronic) **spin** (German: ”Eigendrehimpuls”) of the electron. The reason for this formal deficiency is that the correspondence principle was only applied to problems of classical mechanics (classical Hamilton functions), which clearly does not include Einsteins theory of relativity. Strictly speaking a formal description of the spin can only be based on a theory of a relativistic motion of particles[1]. Without the use of a such relativistic theory the properties of the electronic spin can only be stated in terms of postulates, and admittingly remain slightly vague.

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[1] see for example chapter 17

8.1 Spin postulates

8.1.1 Postulate 1:

The components of the spin momentum operator $\widehat{\mathbf{S}}$ commute in the same formal way as the components of the angular momentum operator $\widehat{\mathbf{L}}$, namely

$$[\widehat{S}_x, \widehat{S}_y]_- = i\hbar \widehat{S}_z \quad , \tag{7}$$

$$[\widehat{S}_y, \widehat{S}_z]_- = i\hbar \widehat{S}_x \quad , \tag{8}$$

$$[\widehat{S}_z, \widehat{S}_x]_- = i\hbar \widehat{S}_y \quad , \tag{9}$$

and the square of $\widehat{\mathbf{S}}$ is given by

$$\widehat{S}^2 = \widehat{S}_x^2 + \widehat{S}_y^2 + \widehat{S}_z^2 \quad . \tag{10}$$

8.1.2 Postulate 2:

For an **electron** there are only two eigenfunctions of $\widehat{S}^2$ and $\widehat{S}_z$, namely α and β, corresponding to the following eigenvalue equations

$$\widehat{S}^2 \alpha = \frac{1}{2}(\frac{1}{2}+1)\hbar^2 \alpha \quad , \tag{11}$$

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$$\widehat{S}_z \alpha = \frac{1}{2}\hbar \alpha \quad , \tag{13}$$

$$\widehat{S}_z \beta = -\frac{1}{2}\hbar \beta \quad . \tag{14}$$

In analogy to the case of the angular momentum operators these eigenvalue equations are usually written as

$$\widehat{S}^2 \alpha = s(s+1)\hbar^2 \alpha \quad , \ \widehat{S}^2 \beta = s(s+1)\hbar^2 \beta \quad , \ s = \frac{1}{2} \quad , \tag{15}$$

$$\widehat{S}_z \alpha = m_s \hbar \alpha \quad , \ \widehat{S}_z \beta = m_s \hbar \beta \quad , \ m_s = \pm\frac{1}{2} \quad . \tag{16}$$

The functions α and β are so-called **spinors**,

$$\alpha = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad , \tag{17}$$

$$\beta = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad . \tag{18}$$

Traditionally the elements in these 2-vectors are labelled (in a somewhat confusing manner) by $\sigma = \frac{1}{2}$ and $\sigma = -\frac{1}{2}$, such that α and β can also be viewed as the following orthonormalized functions, usually called **spin functions**

$$\alpha(\sigma) = \{ \begin{array}{ll} 1 & ; \sigma = \frac{1}{2} \\ 0 & ; \sigma = -\frac{1}{2} \end{array} \quad , \tag{19}$$

$$\beta(\sigma) = \{ \begin{array}{ll} 0 & ;\sigma = \frac{1}{2} \\ 1 & ;\sigma = -\frac{1}{2} \end{array} \quad , \tag{20}$$

$$\sum_{\sigma=\pm\frac{1}{2}} \alpha(\sigma)^\dagger \alpha(\sigma) = \left(\begin{array}{cc} 1 & 0 \end{array} \right) \left(\begin{array}{c} 1 \\ 0 \end{array} \right) = 1 \quad , \tag{21}$$

$$\sum_{\sigma=\pm\frac{1}{2}} \beta(\sigma)^\dagger \beta(\sigma) = \left(\begin{array}{cc} 0 & 1 \end{array} \right) \left(\begin{array}{c} 0 \\ 1 \end{array} \right) = 1 \quad , \tag{22}$$

$$\sum_{\sigma=\pm\frac{1}{2}} \alpha(\sigma)^\dagger \beta(\sigma) = \left(\begin{array}{cc} 1 & 0 \end{array} \right) \left(\begin{array}{c} 0 \\ 1 \end{array} \right) = 0 \quad , \tag{23}$$

$$\sum_{\sigma=\pm\frac{1}{2}} \beta(\sigma)^\dagger \alpha(\sigma) = \left(\begin{array}{cc} 0 & 1 \end{array} \right) \left(\begin{array}{c} 1 \\ 0 \end{array} \right) = 0 \quad . \tag{24}$$

8.2 Atomic spin orbitals

In a non-relativistic description the operators $\widehat{S}_x$, $\widehat{S}_y$, $\widehat{S}_z$ and $\widehat{S}^2$ only act on the spin functions, i.e. for the Hamilton operator of the single electron atom (the hydrogen atom for example) the following commutator relations apply trivially,

$$[\widehat{H}, \widehat{S}^2]_- = [\widehat{H}, \widehat{S}_z]_- = [\widehat{H}, \widehat{L}^2]_- = [\widehat{H}, \widehat{L}_z]_- = 0 \quad , \tag{25}$$

$$[\widehat{L}^2, \widehat{S}^2]_- = [\widehat{L}_z, \widehat{S}_z]_- = 0 \quad . \tag{26}$$

Since the eigenvalue of $\widehat{S}^2$, $s(s+1)\hbar^2$ is the same for all electrons, namely $3\hbar^2/4$ only the eigenvalue $\widehat{S}_z$, $m_s\hbar$, $m_s = \pm\frac{1}{2}$, can be used for a further characterization ("symmetry") of an energy eigenvalue in the atomic single electron problem. The corresponding eigenfunctions can therefore be characterized by the four quantum numbers:

n	**principal quantum number**
l	**angular momentum quantum number**
m	**magnetic quantum number**
m_s	**spin quantum number**

The eigenfunctions are products of atomic orbitals and spin functions

$$\Psi_{n,lm,m_s}(\mathbf{r},\sigma) = \left\{ \begin{array}{l} \psi_{n,lm}(\mathbf{r})\alpha(\sigma) \\ \psi_{n,lm}(\mathbf{r})\beta(\sigma) \end{array} \right. =$$

$$= \left\{ \begin{array}{l} R_{n,l}(r)Y_l^m(\theta,\phi)\alpha(\sigma) \\ R_{n,l}(r)Y_l^m(\theta,\phi)\beta(\sigma) \end{array} \right. \quad , \tag{27}$$

$$\widehat{S}_z \psi_{n,lm}(\mathbf{r})\alpha(\sigma) = \psi_{n,lm}(\mathbf{r})\widehat{S}_z\alpha(\sigma) = \frac{1}{2}\hbar\psi_{n,lm}(\mathbf{r})\alpha(\sigma) \quad , \tag{28}$$

$$\widehat{S}_z \psi_{n,lm}(\mathbf{r})\beta(\sigma) = \psi_{n,lm}(\mathbf{r})\widehat{S}_z\beta(\sigma) = -\frac{1}{2}\hbar\psi_{n,lm}(\mathbf{r})\beta(\sigma) \quad . \tag{29}$$

The atomic **spinorbitals** $\Psi_{n,lm,m_s}(\mathbf{r},\sigma)$ are orthonormalized wavefunctions

$$\sum_{\sigma=\pm\frac{1}{2}} \int \Psi^*_{n,lm,m_s}(\mathbf{r},\sigma)\Psi_{n,lm,m_s}(\mathbf{r},\sigma)d\tau = 1 \quad . \tag{30}$$

8.3 The Pauli principle - version 1

The Pauli principle is a principle, **independent** of the Schrödinger equation. In the context of a single electron theory of atoms it can be stated as follows:

Two electrons in an atom never can have the same set of (atomic) quantum numbers.

For the energy eigenvalues of the He atom this implies that the two electrons must have different quantum numbers. Denoting the atomic orbital of electron 1 by $\phi(1)$ and that of electron 2 by $\phi(2)$ and using the numbering for the electrons also as argument for the spin functions, the ground state wavefunction $\psi_{GS}(1,2) \equiv \psi_{GS}(\mathbf{r}_1,\mathbf{r}_2)$ of the He atom , where $\mathbf{r}_1$ and $\mathbf{r}_2$ denote the coordinates of the two electrons, obviously refers to the case that both, $\phi(1)$ and $\phi(2)$ are 1s-orbitals, formally written as $1s(1)$ and $1s(2)$. The two electrons must differ therefore in their spin functions:

$$\psi_{GS}(1,2) = \phi(1)\phi(2)\alpha(1)\beta(2) = 1s(1)1s(2)\alpha(1)\beta(2) \quad . \tag{31}$$

For the first excited state of the He atom, however, in principle two possibilities of assigning atomic orbitals to the spin-independent part of the wavefunction $\phi_{ES}(1,2)$ exist

$$\phi_{ES}(1,2) = \left\{ \begin{array}{l} 1s(1)2s(2) \\ 2s(1)1s(2) \end{array} \right. \quad , \tag{32}$$

which would imply that the two electrons are distinguishable! Since this can not be the case - just as the Hamilton operator can not dependent on the choice of the coordinate system (principle of coordinate invariance), one forms normalized linear combinations of the above two possibilities. If $\widehat{P}$ denotes an operator that permutes the indices of the electrons, one can see easily that two cases arise. The first one, denoted by an index s,

$$\phi^s_{ES}(1,2) = \frac{1}{\sqrt{2}}\left(1s(1)2s(2) + 1s(2)2s(1)\right) \quad , \tag{33}$$

is **symmetric** with respect to a **permutation** of the indices for the electrons,

$$\begin{aligned} \widehat{P}\phi^s_{ES}(1,2) = \phi^s_{ES}(2,1) = \frac{1}{\sqrt{2}}\left(1s(2)2s(1) + 1s(1)2s(2)\right) = \\ = \phi^s_{ES}(1,2) \quad , \end{aligned} \tag{34}$$

i.e. does not change the sign of the spin-independent part of the wavefunction, when permuting the numbering of the electrons. The second one, however,

$$\phi^{as}_{ES}(1,2) = \frac{1}{\sqrt{2}}\left(1s(1)2s(2) \;-\; 1s(2)2s(1)\right) \quad , \tag{35}$$

is **antisymmetric** with respect to such a permutation.

$$\widehat{P}\phi^{as}_{ES}(1,2) = \phi^{as}_{ES}(2,1) = \frac{1}{\sqrt{2}}\left(1s(2)2s(1) \;-\; 1s(1)2s(2)\right) =$$
$$= -\phi^{as}_{ES}(1,2) \quad . \tag{36}$$

Concomitantly the two electrons can not be distinguished with respect to their spin. Again the product of the corresponding spinfunctions has to be checked with respect to a permutation of indices and also with respect to the eigenvalue of $\widehat{S}_z$. For example:

$$\widehat{P}\alpha(1)\alpha(2) = \alpha(2)\alpha(1) \equiv \alpha(1)\alpha(2) \quad , \tag{37}$$

$$\widehat{S}_z\alpha(1)\alpha(2) = \alpha(2)\widehat{S}_z\alpha(1) + \alpha(1)\widehat{S}_z\alpha(2) =$$
$$= \hbar\left(m_s(1)\alpha(1)\alpha(2) + m_s(2)\alpha(1)\alpha(2)\right) = \hbar\left(m_s(1) + m_s(2)\right)\alpha(1)\alpha(2) =$$
$$= \hbar M_s\alpha(1)\alpha(2) \quad . \tag{38}$$

For the various products of the two spin functions one can construct a little table and note the occurring permutational symmetry, using as before "s" for symmetric and "as" for antisymmetric, respectively:

product	*symmetry*	M_s
$\alpha(1)\alpha(2)$	s	1
$\beta(1)\beta(2)$	s	-1
$\frac{1}{\sqrt{2}}\left(\alpha(1)\alpha(2) + \beta(1)\beta(2)\right)$	s	0
$\frac{1}{\sqrt{2}}\left(\alpha(1)\alpha(2) - \beta(1)\beta(2)\right)$	as	0

As one can see from this table, three out of four product functions are symmetric and only one is antisymmetric.

In the same way as M_s was obtained, also the **total spin** can be determined. For example,

$$\widehat{\mathbf{S}}^2\alpha(1)\alpha(2) = \hbar^2\left(s(1)(s(1)+1)\alpha(1)\alpha(2) + s(2)(s(2)+1)\alpha(1)\alpha(2)\right) =$$
$$= \hbar^2 S(S+1)\alpha(1)\alpha(2) \quad . \tag{39}$$

Thus, if N is the total number of electrons then the total spin S and the total spin quantum number M_s are given by:

$$S = \sum_{i=1}^{N} s(i) \quad , \quad M_s = \sum_{i=1}^{N} m_s(i) \quad . \tag{40}$$

Combining finally the spin-independent parts (orbital parts) of the wavefunction with the products of the spinfunctions, one has to remember that the product of two symmetric functions is symmetric, while the product of a symmetric function with an antisymmetric function results in an antisymmetric function. Symbolically written the following short-hand rule applies:

$$\boxed{\text{symmetric} \otimes \text{symmetric} = \text{symmetric}} \tag{41}$$

$$\boxed{\text{symmetric} \otimes \text{antisymmetric} = \text{antisymmetric}} \tag{42}$$

$$\boxed{\text{antisymmetric} \otimes \text{antisymmetric} = \text{symmetric}} \tag{43}$$

For example

$$\psi = \frac{1}{\sqrt{2}} \left(1s(1)2s(2) + 1s(2)2s(1)\right) \alpha(1)\alpha(2) \quad ,$$

is symmetric with respect to a permutation of the indices for the two electrons, while

$$\psi = \frac{1}{2} \left(1s(1)2s(2) + 1s(2)2s(1)\right) \left(\alpha(1)\beta(2) - \alpha(2)\beta(1)\right) \quad ,$$

is antisymmetric.

8.4 The Pauli principle - version 2

The wavefunction of a system of electrons has to be antisymmetric with respect to a simultaneous permutation of the coordinates and of the spins of two electrons.

The wavefunction of a system of Fermions has to be antisymmetric with respect to permutational symmetry, that of Bosons symmetric, whereby Fermions are particles with half-integer spins ($\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, ...$) like electrons, protons, neutrons etc. and Bosons particles with integer spin ($0, 1, 2, ...$) like photons, $\alpha-$particles (He nuclei) etc.

For the above example of the wavefunction for the excited state of a He atom, one gets therefore the following three (triplet) antisymmetric wavefunctions that have antisymmetric orbital parts and symmetric spin parts and which in the absence of an external magnetic field belong all to one degenerated energy eigenvalue

$$\psi^{Triplet} = \frac{1}{\sqrt{2}}\left((1s(1)2s(2) - 1s(2)2s(1)\right)\begin{cases}\alpha(1)\alpha(2)\\ \frac{1}{\sqrt{2}}\left(\alpha(1)\beta(2) + \alpha(2)\beta(1)\right)\\ \beta(1)\beta(2)\end{cases} \tag{44}$$

and one (singulet) antisymmetric wavefunction that is symmetric in its orbital part and antisymmetric in the spin part

$$\psi^{Singulet} = \frac{1}{2}\left((1s(1)2s(2) + 1s(2)2s(1)\right)\left(\alpha(1)\beta(2) - \alpha(2)\beta(1)\right) \quad . \tag{45}$$

In general the number of spin functions that in the absence of a magnetic field belong to one and the same energy eigenvalue is given by $(2S+1)$ the so-called **multiplicity**. The multiplicity and the total spin quantum number M_s are then used to characterize a particular (antisymmetric) wavefunction of a in general n-electron system

$$\psi^{2S+1}_{M_s}(1,2,3,..,n) \tag{46}$$

References

[1] W.Pauli, "Die allgemeinen Prinzipien der Wellenmechanik", Handbuch der Physik, Bd XXIV, Part 1 (1933)

9 Determinantal wavefunctions, permutational symmetry and the H_2 molecule

The H_2 molecule - the simplest molecule, but H_2^+ - poses already a four-body problem. For given (fixed) positions of the nuclei the Hamilton operator for the H_2 molecule can be read off from *Figure 15.* In atomic units ($\hbar = m = e = 1$) this Hamilton operator is given by

$$\widehat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{r_{A1}} - \frac{1}{r_{A2}} - \frac{1}{r_{B1}} - \frac{1}{r_{B2}} + \frac{1}{r_{12}} + \frac{1}{R} \quad , \tag{1}$$

where $1/R$ describes the repulsion of the nuclei and $1/r_{12}$ the interaction between the two electrons. By rewriting this Hamilton operator in the following way,

$$\widehat{H} = \underbrace{\left\{-\frac{1}{2}\nabla_1^2 - \frac{1}{r_{A1}} - \frac{1}{r_{B1}}\right\}}_{\widehat{h}_I} + \underbrace{\left\{-\frac{1}{2}\nabla_2^2 - \frac{1}{r_{A2}} - \frac{1}{r_{B2}}\right\}}_{\widehat{h}_{II}} + \frac{1}{r_{12}} + \frac{1}{R} \quad , \tag{2}$$

one can see that the Hamilton operator is of the form

$$\widehat{H} = \widehat{H}_0 + \widehat{V} \quad , \tag{3}$$

where

$$\widehat{H}_0 = \widehat{h}_I + \widehat{h}_{II} \quad , \tag{4}$$

and

$$\widehat{V} = \frac{1}{r_{12}} \ , \tag{5}$$

if one considers $1/R$ as a constant contribution to the energy (**Born-Oppenheimer approximation**). Quite clearly $\widehat{h}_I$ as well as $\widehat{h}_{II}$ refers to the Hamilton operator of the H_2^+ molecule. Considering first the H_2 problem in terms of first order perturbation theory, the unperturbed wave function is given by

$$\psi^0(1,2) = \phi_I(1)\phi_{II}(2) \quad , \tag{6}$$

namely as the product of the wave functions for the two independent "H_2^+ - motions".

By means of the wave function for the H_2^+ molecule (see chapter 7),

$$\phi = \frac{\chi_A + \chi_B}{\sqrt{2+2S}} \ , \ \chi_\alpha = \frac{1}{\sqrt{\pi}}\exp(-r_\alpha) \ , \ \alpha = A, B \quad , \tag{7}$$

where χ_α is hydrogen 1s-atomic wavefunction centered in nucleus α and S is the overlap integral, the ground state energy for the H_2 molecule is easily obtained within first order perturbation theory using (6)

$$E(R) = 2E_{H_2^+}(R) + \iint \psi^0(1,2)^* \frac{1}{r_{12}} \psi^0(1,2) d\tau_1 d\tau_2 \quad . \tag{8}$$

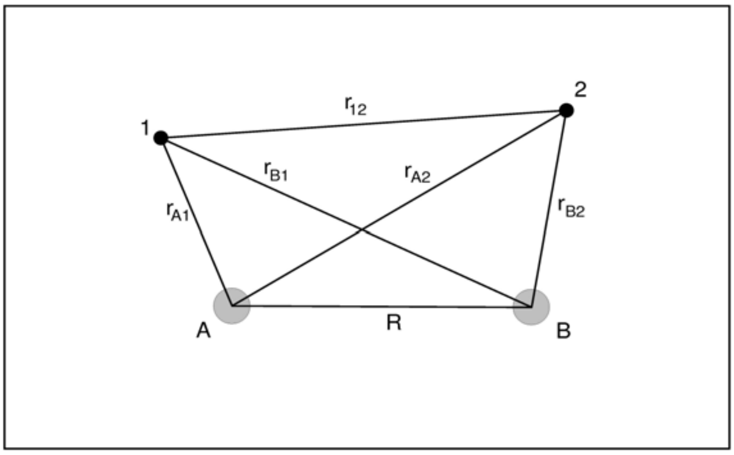

Figure 15: Coordinate system for the H_2 molecule

The result of this calculation is compared in the table below with the corresponding experimental results

	experimental	**perturbation theory**
total energy	-31.93 eV	-29.88 eV
dissociation energy	-4.75 eV	-2.67 eV
equilibrium separation	0.74 Å	0.85 Å

Again one can that obviously the perturbation is not small enough to yield a result close to experiment, which in turn implies that in the end the variational method has to be applied in order to get reasonably good agreement with experiment. In general this performed by using suitably chosen variational parameters for the spin-orbitals and minimizing the expectation value of the Hamilton operator. This in fact is the essence of the following section.

9.1 Slater determinants

According to the **Pauli principle** the unperturbed wave function has to be **antisymmetric**, i.e., by neglecting as before any interaction between the angular momentum and the spin of the electrons (non-relativistic description), the unperturbed wave function is given as the following product of **spin-orbitals**

$$\psi^0(1,2) = \mathcal{A}\left\{\phi(1)\alpha(1)\phi(2)\beta(2)\right\} \quad , \tag{9}$$

where $\phi(1)$ and $\phi(2)$ refer to the orbital parts of the wave function for electron one and two, respectively, and $\alpha(1)$ and $\beta(2)$ are their spin functions. The operator $\mathcal{A}$ is the so-called **antisymmetrizer**, that takes care of the proper permutational symmetry[1] for the indices of the electrons. As was shown by **Slater** the condition of antisymmetric behavior for the total wave function is always fulfilled if written as a **determinant**

$$\begin{aligned} \psi^0(1,2) &= \mathcal{A}\left\{\phi(1)\alpha(1)\phi(2)\beta(2)\right\} = \\ &= N \begin{vmatrix} \phi(1)\alpha(1) & \phi(1)\beta(1) \\ \phi(2)\alpha(2) & \phi(2)\beta(2) \end{vmatrix} = \\ &= N\left\{\phi(1)\alpha(1)\phi(2)\beta(2) - \phi(1)\beta(1)\phi(2)\alpha(2)\right\} \quad , \end{aligned} \tag{10}$$

where N is the normalization constant.

In general for an electronic system of $2n$ electrons the corresponding $2n$ spin-orbitals can be arranged in the following Slater determinant,

$$\psi(1,2,..,n) = \tag{11}$$

$$\begin{vmatrix} \phi_1(1)\alpha(1) & \phi_1(1)\beta(1) & \cdots & \phi_n(1)\alpha(1) & \phi_n(1)\beta(1) \\ \phi_1(2)\alpha(2) & \phi_1(2)\beta(2) & \cdots & \phi_n(2)\alpha(2) & \phi_n(2)\beta(2) \\ \vdots & \vdots & \cdots & \vdots & \vdots \\ \vdots & \vdots & \cdots & \vdots & \vdots \\ \phi_1(2n)\alpha(2n) & \cdots & \cdots & \phi_n(2n)\alpha(2n) & \phi_n(2n)\beta(2n) \end{vmatrix} \quad .$$

There are n electronic coordinates for the $2n$ electrons. Schematically the Slater determinants have $2n$ rows for the $2n$ electrons and n columns for the n orbitals, whereby each column consists of two columns, an α column and a β column,

$$\begin{array}{lccc} & \scriptstyle \textit{orbital } 1 & & \scriptstyle \textit{orbital } n \\ \text{electron 1} & \boxed{\alpha\ \beta} & \cdots\cdots & \boxed{\alpha\ \beta} \\ \text{electron 2} & \boxed{\alpha\ \beta} & \cdots\cdots & \boxed{\alpha\ \beta} \\ \vdots & \vdots & \vdots & \vdots \\ \text{electron 2n} & \boxed{\alpha\ \beta} & \cdots\cdots & \boxed{\alpha\ \beta} \end{array} \tag{12}$$

i.e., the arrangement is as follows

$$\begin{array}{ccc} & \text{n orbitals} = \text{2n spin-orbitals} & \longrightarrow \longrightarrow \\ \downarrow & \square & \square \\ \text{2n electrons} & \square & \square \\ \downarrow & \square & \square \end{array} \tag{13}$$

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[1] see also chapters 14, 15 and 18 for further discussions

9.2 The Hartree-Fock method

9.3 Two-atomic molecules

$N\ atom$			$N_2\ molecule$		$N\ atom$
$2p_x, 2p_y$	$--$			$--$	$2p_x, 2p_y$
		$1\pi_g^4$	$-- \downarrow\uparrow\downarrow\uparrow --$		
$2p_z$	$--$	$3\sigma_g^2$	$- - - \downarrow\uparrow - - -$	$--$	$2p_z$
		$2\sigma_u^2$	$- - - \downarrow\uparrow - - -$		
$2s^2$	$--$			$--$	$2s^2$
		$2\sigma_g^2$	$- - - \downarrow\uparrow - - -$		
		$1\sigma_u^2$	$- - - \downarrow\uparrow - - -$		
$1s^2$	$--$			$--$	$1s^2$
		$1\sigma_g^2$	$- - - \downarrow\uparrow - - -$		

$N\ atom : 1s^2 2s^2 2p^3$
$N_2\ molecule : 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_g^2 3\sigma_g^2 1\pi_g^4$

$O - atom$			$O_2\ molecule$		$O - atom$
		$1\pi_u^2$	$- - - \downarrow\uparrow - - -$		
$2p_x, 2p_y$	$--$			$--$	$2p_x, 2p_y$
		$1\pi_g^4$	$-- \downarrow\uparrow\downarrow\uparrow --$		
$2p_z$	$--$	$3\sigma_g^2$	$- - - \downarrow\uparrow - - -$	$--$	$2p_z$
		$2\sigma_u^2$	$- - - \downarrow\uparrow - - -$		
$2s^2$	$--$			$--$	$2s^2$
		$2\sigma_g^2$	$- - - \downarrow\uparrow - - -$		
		$1\sigma_u^2$	$- - - \downarrow\uparrow - - -$		
$1s^2$	$--$			$--$	$1s^2$
		$1\sigma_g^2$	$- - - \downarrow\uparrow - - -$		

$O\ atom : 1s^2 2s^2 2p^4$
$O_2\ molecule : 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_g^2 3\sigma_g^2 1\pi_g^4 1\pi_u^2$

$C - atom$			$CO\ molecule$		$O - atom$
				$--$	$2p_x, 2p_y$
		$1\pi^4$	$-- \downarrow\uparrow\downarrow\uparrow --$		
$2p_z$	$--$	$5\sigma^2$	$--- \downarrow\uparrow ---$	$--$	$2p_z$
		$4\sigma^2$	$--- \downarrow\uparrow ---$		
$2s^2$	$--$			$--$	$2s^2$
		$3\sigma^2$	$--- \downarrow\uparrow ---$		
		$2\sigma^2$	$--- \downarrow\uparrow ---$		
$1s^2$	$--$			$--$	$1s^2$
		$1\sigma^2$	$--- \downarrow\uparrow ---$		

$C\ atom : 1s^2 2s^2 2p^2 \qquad O\ atom : 1s^2 2s^2 2p^4$
$CO\ molecule : 1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^4$

References

[1] W.Pauli, *"Die allgemeinen Prinzipien der Wellenmechanik"*, Handbuch der Physik, Bd. XXIV, 1933

10 First order time dependent perturbation theory and the basic principles of spectroscopy

10.1 An overdue change of notation - the Dirac notation

Let $\widehat{H}(\mathbf{r})$ be the Hamilton operator in the following eigenvalue equation:

$$\widehat{H}(\mathbf{r})\psi_i(\mathbf{r}) = E_i\psi_i(\mathbf{r}) \quad , \quad i = 1, \ldots, n \quad , \tag{1}$$

where $\psi_i(\mathbf{r})$ is the eigenfunction to the i-th eigenvalue E_i. Suppose now that $\psi_i(\mathbf{r})$ is rewritten in the following way

$$\psi_i(\mathbf{r}) \equiv \langle \mathbf{r} \mid \psi_i \rangle \quad , \tag{2}$$

$$\psi_i^*(\mathbf{r}) \equiv \langle \psi_i \mid \mathbf{r} \rangle \quad , \tag{3}$$

such that the normalization integrals and orthogonality relations can be formulated using the below notation

$$\begin{aligned} \int \psi_i^*(\mathbf{r})\psi_i(\mathbf{r})d\mathbf{r} \ &\equiv \ \int \langle \psi_i \mid \mathbf{r} \rangle \langle \mathbf{r} \mid \psi_i \rangle d\mathbf{r} = \\ = \langle \psi_i \mid \underbrace{\int \mid \mathbf{r} \rangle \langle \mathbf{r} \mid d\mathbf{r}}_{=1} \mid \psi_i \rangle &\equiv \langle \psi_i \mid \psi_i \rangle \equiv \langle i \mid i \rangle = 1 \quad , \end{aligned} \tag{4}$$

$$\begin{aligned} \int \psi_i^*(\mathbf{r})\psi_j(\mathbf{r})d\mathbf{r} \ &\equiv \ \int \langle \psi_i \mid \mathbf{r} \rangle \langle \mathbf{r} \mid \psi_j \rangle d\mathbf{r} = \\ &\equiv \langle \psi_i \mid \psi_j \rangle \equiv \langle i \mid j \rangle = \delta_{ij} \quad . \end{aligned} \tag{5}$$

From the completeness relation for Hermitian operators follows then that

$$\sum_{i=1}^{n} \int \langle \mathbf{r} \mid \psi_i \rangle \langle \psi_i \mid \mathbf{r} \rangle d\mathbf{r} = \int \langle \mathbf{r} \mid \underbrace{\left(\sum_{i=1}^{n} \mid \psi_i \rangle \langle \psi_i \mid \right)}_{=\widehat{I}} \mid \mathbf{r} \rangle d\mathbf{r} = 1 \quad , \tag{6}$$

where $\widehat{I}$ is the identity operator

$$\sum_{i=1}^{n} \mid \psi_i \rangle \langle \psi_i \mid = \sum_{i=1}^{n} \mid i \rangle \langle i \mid = \widehat{I} \qquad . \tag{7}$$

This last equation is sometimes also called the "resolution of the identity". The notation, introduced in (1) - (7) is the famous **Dirac notation**. Since brackets are used to abbreviate occurring integrals, states such as $\langle \psi_i \mid \mathbf{r} \rangle, \langle \psi_i \mid, \langle i \mid$ are frequently called **"bras"** ("bra"-states) and $\langle \mathbf{r} \mid \psi_i \rangle, \mid \psi_i \rangle, \mid i \rangle$ as **"kets"** ("ket"-states). Quite clearly the Dirac notation simplifies considerably the notation in quantum mechanics.

10.2 Transition probabilities

Suppose $\widehat{H}_0$ is the time-independent Hamilton operator in the following eigenvalue equation

$$\widehat{H}_0 \mid n\rangle = E_n^0 \mid n\rangle \equiv E_n \mid n\rangle \quad , \tag{8}$$

$$\sum_n \mid n\rangle\, \langle n \mid = 1 \quad ; \qquad \langle m \mid n\rangle = \delta_{mn} \quad , \tag{9}$$

and $V(t)$ is a time-dependent perturbation of the following form,

$$\widehat{V}(t) = \{ \begin{array}{ll} \widehat{W}(t) & ;\ 0 \le t \le \tau \\ 0 & ;\ otherwise \end{array} \quad , \tag{10}$$

such that the total Hamilton operator $\widehat{H}(t)$ is time-dependent

$$\widehat{H}(t) = \widehat{H}_0 + \widehat{V}(t) \quad , \quad -\infty < t < \infty \quad . \tag{11}$$

The time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t}\psi(t) = \left(\widehat{H}_0 + \widehat{V}(t)\right)\psi(t) \quad , \tag{12}$$

has now of course no longer stationary states, however, $\psi(t)$ can be expanded in the eigenfunctions of $\widehat{H}_0$,

$$\mid \psi\rangle = \psi(t) = \sum_n a_n(t) \mid n\rangle \exp(-iE_n t/\hbar) = \sum_n a_n(t)\psi_n(t) \quad . \tag{13}$$

This expansion is usually called the **superposition principle**, since multiplying from the left with $\langle m \mid$ yields directly an interpretation of $\mid \psi\rangle$ as an "**ensemble**" of states

$$\psi_n(t) = \mid n\rangle \exp(-iE_n t/\hbar) \tag{14}$$

with the statistical weight $a_n(t)$:

$$\langle m \mid \psi\rangle = \sum_n a_n(t) \underbrace{\langle m \mid n\rangle}_{=\delta_{mn}} \exp(-iE_n t/\hbar) = a_m(t)\exp(-iE_m t/\hbar) \quad , \tag{15}$$

$$a_m^*(t) a_m(t) = \mid a_m(t) \mid^2 = \langle \psi \mid m\rangle\, \langle m \mid \psi\rangle \quad , \tag{16}$$

$$\begin{aligned} \sum_m \mid a_m(t) \mid^2 &= \sum_m \langle \psi \mid m\rangle\, \langle m \mid \psi\rangle = \\ &= \langle \psi \mid \sum_m \mid m\rangle\, \langle m \mid \psi\rangle = \langle \psi \mid \psi\rangle = 1 \quad . \end{aligned} \tag{17}$$

By using now this ensemble in the time-dependent Schrödinger equation one gets

$$\sum_n \left\{ \mid n\rangle \frac{\partial a_n(t)}{\partial t} + a_n(t) \mid n\rangle \frac{\partial}{\partial t} \right\} \exp(-iE_n t/\hbar) =$$

$$= \frac{1}{i\hbar} \sum_n \left(\widehat{H}_0 + \widehat{V}(t) \right) a_n(t) \mid n\rangle \exp(-iE_n t/\hbar) \quad . \tag{18}$$

This equation can be rearranged thus that one can read off the parts referring to the eigenvalue equation for $\widehat{H}_0$

$$\sum_n \left\{ \mid n\rangle \frac{\partial a_n(t)}{\partial t} + a_n(t) \mid n\rangle \frac{\partial}{\partial t} - \frac{\widehat{H}_0}{i\hbar} a_n(t) \mid n\rangle \right\} \exp(-iE_n t/\hbar) =$$

$$= \frac{1}{i\hbar} \sum_n a_n(t) \widehat{V}(t) \mid n\rangle \exp(-iE_n t/\hbar) \quad , \tag{19}$$

i.e., one gets

$$\sum_n \mid n\rangle \frac{\partial a_n(t)}{\partial t} \exp(-iE_n t/\hbar) = \frac{1}{i\hbar} \sum_n a_n(t) \widehat{V}(t) \mid n\rangle \exp(-iE_n t/\hbar) \quad . \tag{20}$$

Multiplying now from the left with $\psi_m^*(t) = \langle m \mid \exp(iE_m t/\hbar)$ yields an expression for the time-evolution of the expansion coefficients

$$\sum_n \underbrace{\langle m \mid n\rangle}_{=\delta_{mn}} \frac{\partial a_n(t)}{\partial t} \exp\left(i(E_m - E_n)t/\hbar\right) = \frac{\partial a_m(t)}{\partial t} =$$

$$= \frac{1}{i\hbar} \sum_n a_n(t) \; \langle m \mid \widehat{V}(t) \mid n\rangle \exp\left(i(E_m - E_n)t/\hbar\right) \quad . \tag{21}$$

In order to solve this system of partial differential equations for the expansion coefficients, the following **assumptions** (boundary conditions) shall be made:

(1) **the perturbation $\widehat{V}(t)$ is sufficiently small, such that**

$$\frac{\partial a_m(t)}{\partial t} \approx \frac{1}{i\hbar} \sum_n a_n(0) \; \langle m \mid \widehat{V}(t) \mid n\rangle \exp\left(i(E_m - E_n)t/\hbar\right) \quad , \tag{22}$$

(2) **there is a well-defined initial state at $t = 0$**

$$a_n(0) = \{ \begin{array}{ll} 1 & ; n = i \\ 0 & ; n \neq i \end{array} \quad , \tag{23}$$

(3) **for not too large time intervals τ**

$$a_m(\tau) = \frac{i}{\hbar} \int_0^\tau \langle m \mid \widehat{V}(t) \mid n\rangle \exp\left(i(E_m - E_n)t/\hbar\right) dt \quad , \tag{24}$$

whereby no explicit integration constant appears, since $a_i(0) = 1$ and $a_n(0) = 0$, $\forall n \neq i$.

If one finally uses $\mid i\rangle$ for the **initial** and $\mid f\rangle$ for the **final state** and abbreviates the difference of eigenvalues in the following way

$$\omega_{fi} = (E_f - E_i)/\hbar \quad , \tag{25}$$

one can see that the **probability** W_{fi} for the system, which was at $t = 0$ in state $\mid i\rangle$, to be after the time-lap τ in state $\mid f\rangle$ is given by

$$W_{fi} \equiv\mid a_f(\tau) \mid^2 = \frac{1}{\hbar^2} \left| \int\limits_0^\tau \langle f \mid \widehat{V}(t) \mid i\rangle \exp(i\omega_{fi} t) dt \right|^2 \quad . \tag{26}$$

10.3 Constant perturbation

The most easiest case of a time-dependent perturbation is of course a constant

$$V(t) = \{ \begin{array}{ll} W & ;\ 0 \leq t \leq \tau \\ 0 & ;\ otherwise \end{array} \quad . \tag{27}$$

For the matrix element in (26), namely for the time-integral, one obtains

$$\int\limits_0^\tau \langle f \mid W \mid i\rangle \exp(i\omega_{fi} t) dt = \langle f \mid W \mid i\rangle \int\limits_0^\tau \exp(i\omega_{fi} t) dt =$$

$$= \frac{\langle f \mid W \mid i\rangle}{i\omega_{fi}} \left(\exp(i\omega_{fi}\tau) - 1\right) \quad , \tag{28}$$

from which very easily the transition probability W_{if} can be calculated,

$$W_{if} = \frac{1}{\hbar^2} \frac{\langle f \mid W \mid i\rangle \langle i \mid W \mid f\rangle}{\omega_{fi}^2} \left(\exp(-i\omega_{fi}\tau) - 1\right)\left(\exp(i\omega_{fi}\tau) - 1\right) =$$

$$= \frac{1}{\hbar^2} \frac{|\langle f \mid W \mid i\rangle|^2}{\omega_{fi}^2} \left\{ 2 - \underbrace{\exp(-i\omega_{fi}\tau) - \exp(i\omega_{fi}\tau)}_{=-2\cos(\omega_{fi}\tau)} \right\} =$$

$$= \frac{2}{\hbar^2} |\langle f \mid W \mid i\rangle|^2 \underbrace{\frac{1}{\omega_{fi}^2} \left[1 - \cos(\omega_{fi}\tau)\right]}_{=F(E_f - E_i)} \quad . \tag{29}$$

The function $F(E_i - E_f)$, obviously the key quantity for the transition probability, can be rewritten in the following way (see (25))

$$F(E_f - E_i) = \frac{1 - \cos\left(\frac{E_f - E_i}{\hbar}\tau\right)}{(\frac{E_f - E_i}{\hbar})^2} = \hbar\tau \frac{1 - \cos\left(\frac{E_f - E_i}{\hbar}\tau\right)}{(E_f - E_i)^2 \tau/\hbar} \quad . \tag{30}$$

If one abbreviates for a moment $\tau/\hbar$ by κ , then in the limit of $\kappa \to 0$ the fraction in the last equation leads to a very famous function, the so-called **Dirac δ-function** ,

$$\lim_{\kappa \to 0} \frac{1 - \cos\left(\kappa(E_f - E_i)\right)}{\kappa(E_f - E_i)^2} = \pi\delta(E_f - E_i) \quad . \tag{31}$$

The Dirac δ-function has for example the following useful properties

$$\delta(x) = \delta(-x) \quad , \quad \delta(ax) = \frac{1}{|a|}\delta(x) \quad , \quad x\delta(x) = 0 \quad , \tag{32}$$

$$f(x)\delta(x-a) = f(a)\delta(x-a) \quad , \tag{33}$$

$$\int f(x-y)\delta(y-a)dy = f(x-a) \quad . \tag{34}$$

In terms of the Dirac δ-function the transition probability in (29) is therefore given by

$$\boxed{W_{if} = (2\pi/\hbar)\left|\langle f \mid W \mid i\rangle\right|^2 \tau\delta(E_f - E_i)} \tag{35}$$

Finally, in order to get rid of τ, which frequently is also called the **characteristic time**, one can define a transition probability per characteristic time (unit time), the so-called **transition rate**

$$\boxed{P_{if} = (2\pi/\hbar)\left|\langle f \mid W \mid i\rangle\right|^2 \delta(E_f - E_i)} \tag{36}$$

This last equation is very frequently termed **Fermi golden rule**.

10.4 Periodic perturbation

If one considers now a periodic perturbation of the following kind

$$\widehat{V}(t) = \{ \begin{array}{ll} W^{\pm}\exp(\pm i\omega t) & ; \ 0 \le t \le \tau \\ 0 & ; \ otherwise \end{array} \quad , \tag{37}$$

then the matrix element is simply given by the integral,

$$\int_0^{\tau} \langle f \mid W^{\pm} \mid i\rangle \exp\left(i(\omega_{fi} \pm \omega)t\right) dt \quad ,$$

from which exactly in the same manner as before the transition probability per unit time is obtained,

$$\boxed{P_{if}^{\pm} = (2\pi/\hbar)\left|\langle f \mid W^{\pm} \mid i\rangle\right|^2 \delta(E_f - E_i \pm \omega)} \tag{38}$$

whereby usually the Dirac δ-function $\delta(E_f - E_i \pm \omega)$ is called **energy conservation**.

10.5 Classical interaction with the electro-magnetic field

Finally the classical interaction of matter with the electro-magnetic field shall be considered. The interaction of a particle of mass μ and charge e is given (non-relativistically) by

$$W(t) = -\frac{e}{\mu c}(\mathbf{A} \cdot \mathbf{p}) + \frac{e^2}{2\mu c^2}\left|\mathbf{A}\right|^2 \quad , \tag{39}$$

where **A** is the vector potential as related to the electric field via the Maxwell equation,

$$\mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{A}}{\partial t} \quad ,$$

p is the momentum and c is the speed of light. Because of c the second term in (39) is by orders of magnitudes smaller than the first term. The interaction operator can therefore be assumed to be of the following form

$$W(t) = -\frac{e}{\mu c}(\mathbf{A} \cdot \mathbf{p}) \quad . \tag{40}$$

Furthermore the vector potential can be viewed as a plane wave in "space" and "time", i.e., can be written as

$$\mathbf{A} = A_0 \mathbf{u} \left\{ \exp(-i\mathbf{k} \cdot \mathbf{r}) \exp(i\omega t) + \exp(i\mathbf{k} \cdot \mathbf{r}) \exp(-i\omega t) \right\} \quad , \tag{41}$$

where **u** is the **polarization vector**, **k** is the **wave vector**, which determines the direction of propagation, ω is the **frequency** and A_0 is the **amplitude** of the vector potential, which usually is chosen in a standardized manner. According to the last equation the perturbation operator is of the same form as already discussed in the previous section:

$$W(t) = W \exp(i\omega t) + W^{\dagger} \exp(-i\omega t) \quad , \tag{42}$$

$$W = -\frac{e}{\mu c} A_0 (\mathbf{u} \cdot \mathbf{p}) \exp(-i\mathbf{k} \cdot \mathbf{r}) \quad , \quad \text{"}\mathbf{emission}\text{"} \quad , \tag{43}$$

$$W^{\dagger} = -\frac{e}{\mu c} A_0 (\mathbf{u} \cdot \mathbf{p}) \exp(i\mathbf{k} \cdot \mathbf{r}) \quad , \quad \text{"}\mathbf{absorption}\text{"} \quad . \tag{44}$$

The term "**emission**" refers to the case that the system "looses" energy and similarly "**absorption**" means "gaining" of energy with respect to the so-called energy conservation (see 38).

Considering now only the case of "**emission**" , the transition probability per unit time is given by the general case of a periodic perturbation, namely as

$$P_{fi} = (2\pi/\hbar) \left|\langle f \mid W \mid i \rangle\right|^2 \delta(E_f - E_i + \hbar\omega) \quad . \tag{45}$$

The only remaining part to be evaluated is now the matrix element itself,

$$\langle f \mid W \mid i \rangle = -\frac{e}{\mu c} A_0 \, \langle f \mid (\mathbf{u} \cdot \mathbf{p}) \exp(-i\mathbf{k} \cdot \mathbf{r}) \mid i \rangle \quad . \tag{46}$$

Using the well-known power series for the exponential function,

$$\exp(-i\mathbf{k}\cdot\mathbf{r}) = 1 - i(\mathbf{k}\cdot\mathbf{r}) + \frac{1}{2!}(-i\mathbf{k}\cdot\mathbf{r})^2 + ... \quad ,$$

and keeping only the first term, one ends up with the so-called **dipole approximation** ($\exp(-i\mathbf{k}\cdot\mathbf{r}) \approx 1$),

$$\langle f \mid W \mid i\rangle \approx -\frac{e}{\mu c} A_0 \, \langle f \mid (\mathbf{u}\cdot\mathbf{p}) \mid i\rangle \quad . \tag{47}$$

However, since $\mathbf{u}$ is a classical vector, one just as well can form the scalar product of this vector with the matrix element of the momentum vector $\mathbf{p}$

$$\langle f \mid W \mid i\rangle \approx -\frac{e}{\mu c} A_0 \, (\mathbf{u}\cdot\langle f \mid \mathbf{p}) \mid i\rangle) \quad . \tag{48}$$

Finally one can make use of the fact that the commutator of the unperturbed Hamilton operator $\widehat{H}_0$ and $\mathbf{r}$ is given by[1]

$$\left[\widehat{H}_0, \mathbf{r}\right]_- = \frac{i\hbar}{\mu}\mathbf{p} \quad , \tag{49}$$

from which immediately follows that

$$\begin{aligned} \frac{i\hbar}{\mu}\langle f \mid \mathbf{p} \mid i\rangle &= \underbrace{\langle f \mid \widehat{H}_0}_{=E_f\langle f|} \mathbf{r} \mid i\rangle - \langle f \mid \mathbf{r} \underbrace{\widehat{H}_0 \mid i\rangle}_{=E_i|i\rangle} = \\ &= (E_f - E_i)\langle f \mid \mathbf{r} \mid i\rangle \quad . \end{aligned} \tag{50}$$

For the matrix element in (48) this last identity therefore yields

$$\begin{aligned} \langle f \mid W \mid i\rangle &\approx -\frac{1}{ic} A_0 \frac{(E_f - E_i)}{\hbar} \left(\mathbf{u}\cdot \underbrace{\langle f \mid e\mathbf{r} \mid i\rangle}_{\mathbf{d}_{fi}} \right) = \\ &= -\frac{1}{ic} A_0 \omega_{fi} (\mathbf{u}\cdot\mathbf{d}_{fi}) \quad , \end{aligned} \tag{51}$$

where $\mathbf{d}_{if}$ is nothing but the matrix element for the electric dipole. Finally now reading off in *Figure 16* the set-up for the vectors $\mathbf{u}$ and $\mathbf{d}$ with respect to the direction of propagation of light ($\mathbf{k}$) and recalling that the polarization vector is a unit vector, one can see immediately that

$$(\mathbf{u}\cdot\mathbf{d}_{fi}) = |\mathbf{d}_{fi}| \sin\theta \quad . \tag{52}$$

If therefore the electric dipole vector is perpendicular to $\mathbf{k}$ ($\sin\theta = 1$, "**unpolarized light**"), then by omitting the constant $(2\pi/c^2\hbar)A_0^2$ in front, the transition probability per unit time is given by

$$\boxed{P_{fi} = \omega_{fi}^2 \left|\mathbf{d}_{fi}\right|^2 \delta(E_f - E_i + \hbar\omega)} \tag{53}$$

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[1] see also chapter 2

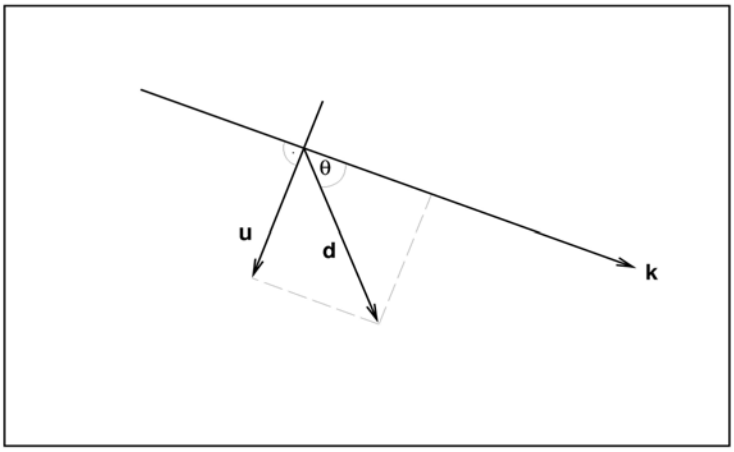

Figure 16: Propagation of light

The Dirac δ-function governs the **"energy conservation"**, whereas the square of the electric dipole matrix element governs the selection rules, such as for example discussed in chapter 4 in the case of the one electron atom. In principle this last equation determines the shape of the intensity in quite a few famous spectroscopical techniques, such as for example **photoemission** spectroscopy or **x-ray emission-** or **absorption** spectroscopy, which are widely used in all kinds of contexts.

References

[1] E.Schrödinger, Ann.Physik 81, 109-139 (1926)

[2] P.A.Dirac, *"The Principles of Quantum Mechanics"*, Oxford University Press, 1981