Contents

1

PARTICLES IN ELECTRIC AND MAGNETIC FIELDS

1.1 Classical Treatment

The motion of a classical particle with charge q moving in an electromagnetic field $\mathbf{E}(\mathbf{x}, t)$, $\mathbf{B}(\mathbf{x}, t)$ is determined by 'Newtons law:

$$m\ddot{\mathbf{x}} = q\mathbf{E}(\mathbf{x}, t) + q[\dot{\mathbf{x}} \times \mathbf{B}(\mathbf{x}, t)] \tag{1.1}$$

The forces are the electric force and the Lorentz force.

In order to consider the quantum mechanical treatment of this problem we introduce the Hamilton description. Then we proceed to the quantum mechanical formulation using Jordan's rules discussed previously.

The electromagnetic field is governed by Maxwell's equations:

$$\nabla \cdot \mathbf{E} = \frac{\rho}{\epsilon_0}$$
$$\nabla \cdot \mathbf{B} = 0$$
$$\nabla \times \mathbf{E} = -\frac{\partial}{\partial t}\mathbf{B}$$
$$\nabla \times \mathbf{B} = \mu_0\mathbf{j} + \epsilon_0\mu_0\frac{\partial}{\partial t}\mathbf{E} \tag{1.2}$$

The electric and magnetic fields can be derived from the vector potential $\mathbf{A}(\mathbf{x}, t)$ and the scalar potential φ.

$$\mathbf{B} = \nabla \times \mathbf{A}$$
$$\mathbf{E} = -\nabla\Phi - \frac{\partial}{\partial t}\mathbf{A} \tag{1.3}$$

The potentials are defined only up to a *gauge transformation*. The transformed potentials with arbitrary function $Q(\mathbf{x}, t)$

$$\mathbf{A} = \mathbf{A}' + \nabla Q$$
$$\Phi = \Phi' - \dot{Q} \tag{1.4}$$

lead to the same fields $\mathbf{B}$, $\mathbf{E}$.

Newton's law can be rewritten in terms of the potentials

$$m\ddot{\mathbf{x}}(t) = -q\nabla\Phi(\mathbf{x}(t),t) - q[\frac{\partial}{\partial t}\mathbf{A}(\mathbf{x},t)]_{\mathbf{x}=\mathbf{x}(t)}$$
$$+ q[\dot{\mathbf{x}}(t) \times [\nabla \times \mathbf{A}(\mathbf{x}(t),t)]] \tag{1.5}$$

In the following we shall show how this equation can be obtained within the framework of Hamilton's theory. The Hamilton function will be needed for the formulation of Schrödinger's equation describing the quantum mechanical behaviour of a charged particle in an electromagnetic field.

1.1.1 Hamilton's Equation

Hamilton's canonical equations read

$$\dot{x}_i = \frac{\partial}{\partial p_i}H[\mathbf{p},\mathbf{x}]$$
$$\dot{p}_i = -\frac{\partial}{\partial p_i}H[\mathbf{p},\mathbf{x}] \tag{1.6}$$

The following Hamilton function leads to Newton's equation (1.5) for a particle moving in an electromagnetic field:

$$H = \frac{(\mathbf{p} - q\mathbf{A})^2}{2m} + q\Phi \tag{1.7}$$

This can be seen by direct evaluation of the canonical equations (1.6)

$$\dot{x}_i = \frac{\partial}{\partial p_i}H = p_i - qA_i$$
$$\dot{p}_i = -q\frac{\partial}{\partial x_i}\Phi + \sum_j q(p_j - qA_j) \cdot \frac{\partial}{\partial x_i}A_j \tag{1.8}$$

It is straightforward to combine both equations to formulate Newton's law:

$$\ddot{x}_i = \dot{p}_i - q\dot{A}_i = -q\frac{\partial}{\partial x_i}\Phi - q\frac{d}{dt}A_i + \sum_j q\dot{x}_j \cdot \frac{\partial}{\partial x_i}A_j \tag{1.9}$$

We have to take into account that the potential $\mathbf{A}(\mathbf{x}(t),t)$ depends explicitly as well as implicitly, i.e. via $\mathbf{x}(t)$, on time. Consequently,

$$\frac{d}{dt}A_i = \frac{\partial}{\partial t}A_i + \sum_k \dot{x}_k\frac{\partial}{\partial x_l}A_i \tag{1.10}$$

and we are led to Newton's law by comparing with eq. (1.5):

$$m\ddot{x}_i = -q\frac{\partial}{\partial x_i}\Phi - q\frac{\partial}{\partial t}A_i + \sum_j q\left[\dot{x}_j \cdot \frac{\partial}{\partial x_i}A_j - \dot{x}_j \cdot \frac{\partial}{\partial x_j}A_i\right] \qquad (1.11)$$

The last term can be rewritten as follows:

$$[\dot{\mathbf{x}}(t) \times [\nabla \times \mathbf{A}(\mathbf{x}(t),t)]]_i = \sum_j [\dot{x}(t)_j\frac{\partial}{\partial x_i}\mathbf{A}(\mathbf{x},t) - \dot{x}_j(t)\frac{\partial}{\partial x_j}A_i(\mathbf{x},t)]_{\mathbf{x}=\mathbf{x}(t)}$$

$$(1.12)$$

and the equation of motion explicitly is equivalent to Newton's law:

$$m\ddot{\mathbf{x}} = q\mathbf{E} + q[\dot{\mathbf{x}} \times \mathbf{B}] \qquad (1.13)$$

We have shown that the canonical equations (1.6) corresponding to the Hamilton function (1.7) is equivalent to Newton's law for a particle moving in an electromagnetic field.

1.2 Quantum Mechanical Treatment

We shall now proceed to the quantum mechanical treatment. To this end we introduce the wave function $\psi(\mathbf{x},t)$, specify the Hamilton operator, and formulate the Schrödinger equation.

1.2.1 Schrödinger Equation

As usual, we obtain the Hamilton operator from the Hamilton function by Jordan's rule, i.e. by the formal substitution of the momentum by the momentum operator

$$\mathbf{p} = \frac{\hbar}{i}\nabla \qquad (1.14)$$

The Hamilton operator reads

$$H = \frac{1}{2m}[\frac{\hbar}{i}\nabla - qA]^2 + q\Phi \qquad (1.15)$$

1.2.2 Operator Ordering

The quantization using Jordan's rule faces the so-called ordering problem: Whereas in classical mechanics the two expressions

$$F(p)G(x) = G(x)F(p) \qquad (1.16)$$

are equivalent, the corresponding operator products differ due to the fact that position and momentum operators $\hat{x}$, $\hat{p}$ do not commute.

Up to now, we have only considered a Hamiltonian operator additively consisting of the kinetic energy of the form $T = \frac{\mathbf{p}^2}{2m}$ and the potential energy

$U(x)$ and no question with respect to the ordering of operators shows up. Apparently, this changes now.

In classical mechanics, we could also have used the Hamilton function in the form

$$H = \frac{1}{2m}[\mathbf{p}^2 - 2q\mathbf{p} \cdot \mathbf{A} + q^2\mathbf{A}^2] + q\Phi \qquad (1.17)$$

Applying Jordan's rule to this form at first glance leads to different Hamiltonians.

Explicitly, the Hamiltonian takes the form

$$H = -\frac{\hbar^2}{2m}\Delta + \frac{1}{2m}\left[-q\mathbf{A} \cdot \frac{\hbar}{i}\nabla - q\frac{\hbar}{i}\nabla \cdot \mathbf{A}\right] + \frac{q^2}{2m}\mathbf{A}^2 + q\Phi \qquad (1.18)$$

However, we remind the reader that there is gauge freedom and we can choose the so-called *Coulomb gauge*

$$\nabla \cdot \mathbf{A} = 0 \qquad (1.19)$$

In this gauge,

$$\mathbf{p} \cdot \mathbf{A} = \mathbf{A} \cdot \mathbf{p} \qquad (1.20)$$

and there is no ambiguity in the formulation of the Hamilton-operator:

$$H = -\frac{\hbar^2}{2m}\Delta - \frac{q}{m}\mathbf{A} \cdot \frac{\hbar}{i}\nabla + \frac{q^2}{2m}\mathbf{A}^2 + q\Phi \qquad (1.21)$$

1.2.3 Gauge Transformation

The potentials $\mathbf{A}$ and Φ are not uniquely defined. The gauge transformation

$$\mathbf{A}' = \mathbf{A} + \nabla Q$$
$$\varphi' = \varphi - \frac{\partial}{\partial t}Q \qquad (1.22)$$

leads to a transformation of the wave funtion by a phase factor

$$\psi'(x, y, z, t) = e^{iQ(x,y,z,t)}\psi(x, y, z, t) \qquad (1.23)$$

This gauge transformation, thus, does not affect the probability density

$$|\psi'(x, y, z, t)|^2 = |\psi(x, y, z, t)|^2 \qquad (1.24)$$

The proof is as follows:

$$\dot{\psi}'(x, y, z, t) = e^{iQ}[\frac{\partial}{\partial t} + i\dot{Q}]\psi(x, y, z, t)$$
$$(-i\hbar\nabla - q\mathbf{A})e^{iQ}\psi = e^{iQ}(-i\hbar\nabla - q\mathbf{A} + \hbar\nabla Q]$$
$$(-i\hbar\nabla - qA)^2 e^{iQ}\psi = (-i\hbar\nabla - qA)e^{iQ}e^{-iQ}(-i\hbar\nabla - qA)e^{iQ}\psi$$
$$= e^{iQ}(-i\hbar\nabla - q\mathbf{A} + \hbar\nabla Q)^2 \qquad (1.25)$$

The time dependent Schrödinger equation takes the form

$$i\hbar\frac{\partial}{\partial t}\psi = \left[\frac{(\mathbf{p} - q\mathbf{A} + \hbar\nabla Q)^2}{2m} + q\Phi + \hbar\dot{Q}\right]\psi \qquad (1.26)$$

As a consequence the gauge transformation is

$$\mathbf{A}' = \mathbf{A} - \frac{\hbar}{q}\nabla Q$$

$$\Phi' = \Phi + \frac{\hbar}{q}\dot{Q} \qquad (1.27)$$

1.3 Hydrogen Atom in a Magnetic Field

We consider now the motion of an electron of charge $q = -e$ in the central field in the presence of an external magnetic field:

$$V(r) = -\frac{\gamma}{r} \qquad \gamma = \frac{e^2}{4\pi\epsilon_0} \qquad (1.28)$$

The Hamiltonian takes the following form

$$H = \frac{(\mathbf{p} + e\mathbf{A})^2}{2m} - \frac{\gamma}{r} \qquad (1.29)$$

Again, we calculate

$$(\mathbf{p} + e\mathbf{A})^2 = \mathbf{p}^2 + 2e\mathbf{A}\cdot\mathbf{p} + \mathbf{A}^2 \qquad (1.30)$$

where we have used the Coulomb gauge

$$\nabla \cdot \mathbf{A} = 0 \qquad (1.31)$$

Now, we consider a constant magnetic field oriented in z-direction

$$\mathbf{A} = \frac{B}{2}[-y, x, 0] \qquad (1.32)$$

Explicitly, we obtain the magnetic field

$$B_x = \partial_y A_z - \partial_z A_x = 0$$
$$B_y = \partial_z A_x - \partial_x A_z = 0$$
$$B_z = \partial_x A_y - \partial_y A_x = B \qquad (1.33)$$

We can summarize:

$$H = -\frac{\hbar^2}{2m}\Delta + \frac{Be}{2m}[xp_y - yp_x] + \frac{e^2B^2}{2m}(x^2 + y^2) - \frac{\gamma}{r} \qquad (1.34)$$

Using the definition of the z-component of the angular momentum,

$$L_z = xp_y - yp_x \qquad (1.35)$$

we obtain the following representation of the Hamilton operator

$$H = -\frac{\hbar^2}{2m}\Delta + \frac{Be}{2m}L_z + \frac{e^2B^2}{2m}(x^2 + y^2) - \frac{\gamma}{r} \qquad (1.36)$$

Physical Interpretation

The energy of a magnetic dipol μ in a magnetic field $\mathbf{B}$ is

$$U = -\mu \cdot \mathbf{B} \tag{1.37}$$

A circular current $\mathbf{j} = q\mathbf{v}$ generates a magnetic moment

$$\mu = IA\mathbf{e}_z = \frac{1}{2}\left[\mathbf{r} \times \mathbf{j}\right] = \frac{q}{2m_0}\mathbf{r} \times \mathbf{p} \tag{1.38}$$

Now we consider a negative charge, $q = -e$ and relate the magnetic moment to the angular momentum

$$\mu = -\frac{e}{2m_0}\mathbf{L} = -\frac{\mu_B}{\hbar}\mathbf{L} \tag{1.39}$$

The Hamilton operator reads:

$$H = -\frac{\hbar^2}{2m_0}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{\mathbf{L}^2}{2m_0r^2} - \frac{\gamma}{r} + \frac{\mu_B}{\hbar}\mathbf{B} \cdot \mathbf{L} \tag{1.40}$$

We reproduce the term linear in the magnetic field B. The term quadratic in B can be shown to be rather small, i.e. the energy shifts caused by this term is small compared to the shift caused by the linear terms. However, the second term is important in astrophysics.

1.3.1 Zeeman-Effect: Splitting of Energy Levels in a Magnetic Field

We take the magnetic field along the z-axis:

$$\mathbf{B} = B\mathbf{e}_z \tag{1.41}$$

We obtain

$$H = H_0 + \frac{\mu_B}{\hbar}BL_z = H_0 + \frac{e}{2m}BL_z \tag{1.42}$$

It is possible to find a solution for the eigenfunctions and the corresponding eigenvalues. To this end we use the fact that the operators H_0, L^2, and L_z commute and, therefore, have common eigenfunctions:

$$H_0\psi_{nlm}(x, y, z) = E_{nl}^0\psi_{nlm}(x, y, z)$$
$$L_z\psi_{nlm} = \hbar m\psi_{nlm} \tag{1.43}$$

where the eigenfunctions of the Hamiltonian without magnetic field are denoted by

$$\psi_{nlm}(\mathbf{x}) = R_{nl}(r)Y_lm(\theta, \varphi) \tag{1.44}$$

As a consequence, the eigenvalue problem

Zeeman – Splitting
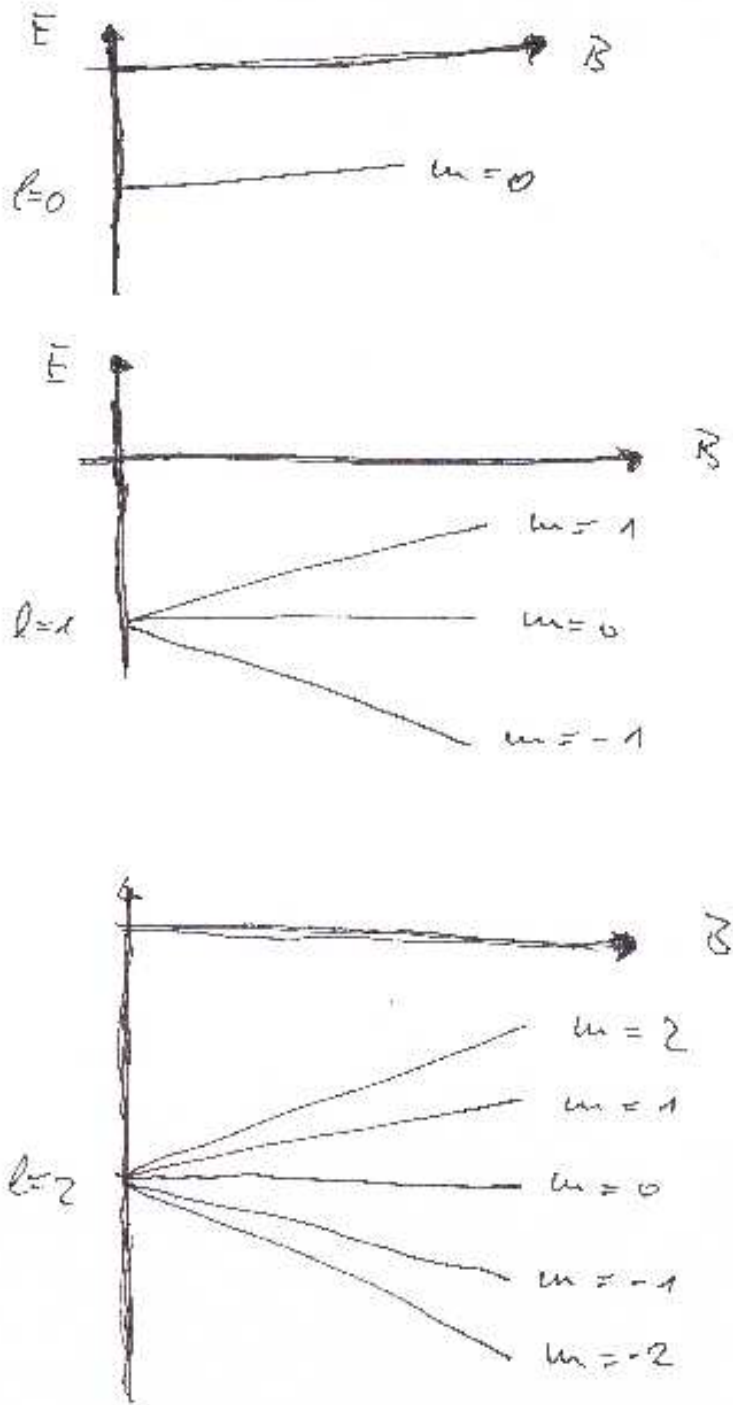
Zeeman-splitting of energy levels with l=0, l=1, l=2.

$$[H_0 + \frac{\mu_B}{\hbar}BL_z]\psi(x,y,z) = E\psi(x,y,z) \qquad (1.45)$$

has the same eigenfunctions (1.44). However, the corresponding energies change according to

$$[H_0 + \frac{e}{2\mu}BL_z]\psi_{nlm}(x,y,z) = [E_{nl}^0 + \frac{em}{2\mu}B]\psi_{nlm}(x,y,z)$$
$$= E_{nlm}\psi_{nlm}(x,y,z) \qquad (1.46)$$

A magnetic field induces a splitting of the degeneracy of the energy levels with respect to the magnetic quantum number m:

$$E_{nlm} = E_{nl}^0 + m\mu_B B = E_{nl}^0 + m\frac{e\hbar}{2m_0}B \qquad (1.47)$$

Here, we have introduced the so-called *Bohr's magneton*

$$\mu_B = \frac{e\hbar}{2m_0} \qquad (1.48)$$

We can establish the following relationship between the magnetic dipol moment μ_d and the angular momentum:

$$\mathbf{\mu_d} = -g\frac{\mu_B}{\hbar}\mathbf{L} \qquad (1.49)$$

The factor g is the g-factor of the electron,

$$g = 1 \qquad (1.50)$$

1.4 Landau: Charged Particle in a Constant Magnetic Field

Classical Treatment

Newton's equation for the motion of a particle of charge q in a magnetic field B oriented in z-direction reads:

$$\ddot{x} = \frac{qB}{m}\dot{y}$$
$$\ddot{y} = -\frac{qB}{m}\dot{x} \qquad (1.51)$$

In generality, we can assume $qB > 0$. Introducing the complex coordinate $z = x + iy$ we obtain

$$\ddot{z} = -i\omega\dot{z} \qquad (1.52)$$

where we have defined

$$\omega = \frac{qB}{m} \tag{1.53}$$

The solution of this ordinary differential equation reads

$$z(t) = z_0(0) + z_B t + z_1 e^{-i\omega t} \tag{1.54}$$

where the quantities $z_0(0)$, z_1 are specified by the initial conditions. The solution in x-y space reads

$$x(t) = x_0 + A\sin(\omega t + \varphi)$$
$$y(t) = y_0 + A\cos(\omega t + \varphi) \tag{1.55}$$

Thus, the motion of $x(t)$ can be viewed as the motion of a harmonic oscillator with frequency ω. It can be expected that in the quantum mechanical treatment, the frequency of this motion is quantized.

Quantum Mechanical Treatment

We consider now the motion of a charged particle in a constant magnetic field. Now we choose the magnetic field oriented along the z-axis. As a consequence,

$$\mathbf{A} = [0, Bx, 0] \tag{1.56}$$

It is evident that we use the Coulomb gauge. The Hamiltonian explicitly reads:

$$H = -\frac{\hbar^2}{2m}\Delta - \frac{q}{m}Bxp_y + \frac{q^2}{2m}B^2 x^2 \tag{1.57}$$

For the solution of the time independent Schrödinger equation we perform the separation ansatz:

$$\Psi(x, y, z) = e^{ik_z z}e^{iky}\varphi(x) \tag{1.58}$$

This leads to the following eigenvalue problem

$$[E - \frac{\hbar^2 k_z^2}{2m}]\varphi(x) = -\frac{\hbar^2}{2m}[\frac{\partial^2}{\partial x^2} + \frac{q^2 B^2}{2m}(x - \frac{\hbar k}{qB})^2]\varphi(x) \tag{1.59}$$

However, this the eigenvalue problem of the harmonic oscillator with mass m and (cyclotron) frequency (in the shifted variable $y = x - \frac{\hbar k}{qb}$.

$$\omega = \frac{qB}{m} \tag{1.60}$$

The corresponding energy eigenvalues take the form

$$E_{n,k,k_z} = \hbar\frac{qB}{m}[n + \frac{1}{2}] + \frac{\hbar^2 k_z^2}{2m} \tag{1.61}$$

They are denoted as Landau-levels. Experimentally, they can be observed as a phenomena, which is called Landau diamagnetism.

The complete time dependent solution reads:

$$\Psi(x, y, z, t) = \int dk_z \int dk \sum_{n=0}^{\infty} C_n(k_z, k)e^{ik_z z + iky}\psi_n(x - \frac{\hbar k}{qB})e^{i\frac{\hbar k_z^2}{2m}t + i(n+1/2)\omega t} \tag{1.62}$$

1.5 Aharonov-Bohm Effect

The Aharonov-Bohm effect demonstrates that the electromagnetic potentials have an influence on the behaviour of quantum particles also in regions where the corresponding classical electromagnetic fields vanish.

The magnetic Aharonov-Bohm effect can be seen in the following experiment. An electron beam crosses a region which contains a magnetic field. This field is confined to a tiny region, such that the electrons travel exclusivle in regions with $\mathbf{B} = 0$. However, since

$$\mathbf{B} = \nabla \times \mathbf{A} = B\mathbf{e}_z\delta(\mathbf{x}) \tag{1.63}$$

the vector potential has the form

$$\mathbf{A} = \frac{\Phi_B}{2\pi r}\mathbf{e}_\varphi \qquad \Phi_B = BF \tag{1.64}$$

The Schrödinger equation reads

$$i\hbar\frac{\partial}{\partial t}\Psi = -\frac{\hbar^2}{2m}(\nabla - q\frac{i}{\hbar}\frac{\Phi_B}{2\pi r}\mathbf{e}_\varphi)^2\Psi \tag{1.65}$$

1.5.1 Particle on a Ring

We consider a particle on a ring, moving in a region without magnetic field B.

Under the consideration of

$$\nabla = \mathbf{e}_\varphi\frac{1}{R}\frac{\partial}{\partial \varphi} \tag{1.66}$$

the Schrödinger equation reads

$$i\hbar\dot{\psi}(\varphi, t) = \frac{1}{2m_0}(\frac{\hbar}{i}\frac{1}{R}\frac{\partial}{\partial \varphi} - q\frac{\Phi_B}{2\pi R})^2\psi(\varphi, t) \tag{1.67}$$

We perform the ansatz

$$\psi(\varphi, t) = e^{-i\frac{E}{\hbar}t}\psi_E(\varphi) \tag{1.68}$$

and obtain

$$E\psi_E(\varphi) = \frac{1}{2m_0}(\frac{m\hbar}{R} - q\frac{\Phi_B}{2\pi R})^2\psi_E(\varphi) \tag{1.69}$$

Thereby, the quantum number m can achieve positive and negative quantities. Whereas for $B = 0$ the energy value is twofold degenerate, this degeneracy is lifted by the presence of the vector potential A. We obtain

$$E_\pm = \frac{\hbar^2}{2m_0R^2}(m \pm q\frac{\Phi_B}{h})^2 \tag{1.70}$$

This is a manifestation of the Aharonov-Bohm effect: Although the quantum particle moves in a region with $B = 0$ it experiences the influence of the vector potential A.
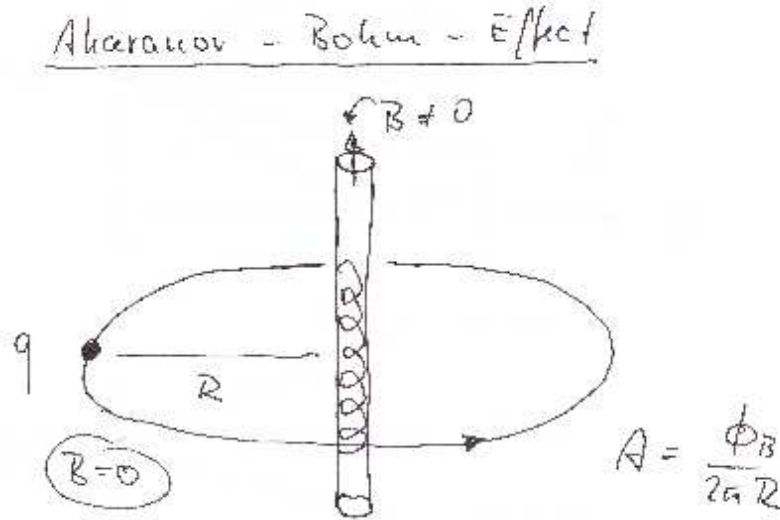
Aharonov-Bohm effect: The energy levels of a
particle encircling a coil split.

1.5.2 Interference Effects

The ansatz

$$\psi(\mathbf{x}, t) = e^{iq\frac{\Phi_b}{2\pi\hbar}\varphi}\chi(\mathbf{x}, t) \tag{1.71}$$

solves the Schrödinger equation (1.67) provided $\chi(\mathbf{x}, t)$ solves the Schrödinger
equation

$$i\hbar\dot{\chi}(\mathbf{x}, t) = -\frac{\hbar^2}{2m}\Delta\chi(\mathbf{x}, t) \tag{1.72}$$

We consider a situation where a beam of charged particles is split into
two beams crossing a coil enclosing a magnetic field B on two sides. After
traversing the coil, the wave functions of the two beams are

$$\psi = e^{\pm iq\frac{\Phi_b}{2\pi\hbar}\varphi}\chi(\mathbf{x}, t) \tag{1.73}$$

since each beam gains a different phase by traversing the coil. The wave func-
tion of the recombined beam has the form

$$\psi(\mathbf{x}, t) = [e^{iq\frac{\Phi_B}{2\hbar}} + e^{-iq\frac{\Phi_B}{2\hbar}}]\chi(\mathbf{x}, t) \tag{1.74}$$

The probability density takes the form

$$|\psi(\mathbf{x},t)|^2 = 2|\chi(\mathbf{x},t)|^2[1 + 1cos\frac{q\Phi_B}{\hbar}] \qquad (1.75)$$

and one obtains an interference pattern. The experiment has been performed by R. G. Chambers, Phys. Rev. Lett. **5**,3 (1960).
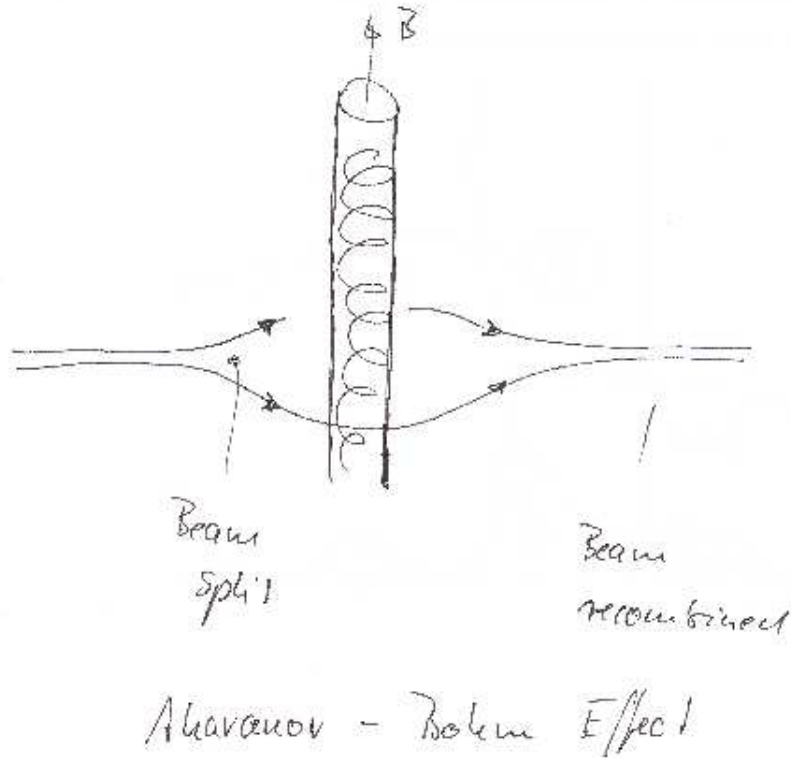
Experimental verification of the Aharonov-Bohm effect: Two beams traversing a coil at two different sides gain a relative phase of $\Phi_B/\hbar$. An interference pattern of a double slit experiment is shifted.

2

SPIN

A massiv, classical particle can rotate around an axis and therefore possesses angular momentum. If it has a charge, it also has a magnetic moment. The quantum mechanical counterpart is the spin.

2.1 Experimental Results

2.1.1 Stern-Gerlach Experiment

A beam of silver atoms traveling through an inhomogeneous magnetic field splits into two separate beams. This has been demonstrated experimentally by Stern and Gerlach (1921). They received the Nobel prize in 1943.

2.1.2 Atomic Spectra

The energy levels of atoms like the Hydrogen atom or the Alkali atoms split into several levels in the presence of a constant magnetic field. This is denoted as anomalous Zeeman effect. For instance, the levels with l=0 (s-orbitals) are found to split into two levels. This fact can not be explained by the presence of a magnetic moment due to orbital angular momentum of the electron and has prompted Uhlenbeck und Goudsmit to postulate the existence of a spin (1925).

2.1.3 Einstein-deHaas-effect

A reversal of the magnetic field changes the angular momentum of a metal with N electrons by a factor $N\hbar$.

2.2 Pauli-Equation

The Pauli equation describes the behaviour of a particle with Spin in a potential.

2.2.1 Reminder: Algebra of Angular Momentum

The algebra auf angular momentum id defined by the commutator relations

$$[L_i, L_j] = i\hbar\epsilon_{ijk}L_k \qquad i, j = 1, 2, 3 \tag{2.1}$$

The operators L_i are selfadjoint and all operators commute with the operator $\mathbf{L}^2$:

$$[\mathbf{L}^2, L_i] = 0 \tag{2.2}$$

The eigenvalue problem

We take the pair of operators $\mathbf{L}^2$ and L_z. Selfadjoint operators, which mutually commute, have the same eigenvectors. We denote the common eigenvectors of $\mathbf{L}^2$ and L_z by $|l, m>$. The eigenvectors are distinguished by the numbers l and m related to the eigenvalues of the eigenvalue problems:

$$\mathbf{L}^2|l, m> = \hbar l(l+1)|l, m>$$
$$L_z|l, m> = \hbar m|l, m> \tag{2.3}$$

Ladder Operators and Useful Commutators

It is convenient to define the following ladder operators:

$$L_{\pm} = L_1 \pm iL_2 \tag{2.4}$$

On the basis of (2.1) it is straightforward to calculate the following comutators

$$[L_{\pm}, L_3] = \mp\hbar L_{\pm} \tag{2.5}$$

Furthermore, we obtain

$$\mathbf{L}^2 = L_{\pm}L_{\mp} + L_z^2 \mp \hbar L_z \tag{2.6}$$

Proof of eq. (2.5):

$$[L_{\pm}, L_3] = [L_1, L_3] \pm i[L_2, L_3] = -i\hbar L_2 \mp \hbar L_1$$
$$= \mp\hbar L_{\pm} \tag{2.7}$$

Proof of eq. (??):
We start by calculating the operator product $L_{\pm}L_{\mp}$:

$$L_{\pm}L_{\mp} = (L_1 \pm iL_2)(L_1 \mp iL_2) = L_1^2 + L_2^2 \mp i(L_1L_2 - L_2L_1)$$
$$= L_1^2 + L_2^2 \pm \hbar L_z \tag{2.8}$$

Adding the operator L_z^2 immediately yields eq. (2.6).

We can now proof that the values l and m have to obey the following inequality:

$$l(l+1) \geq m(m+1) \qquad (2.9)$$

This relationship is obtained from the observation that due to eq. (2.6)

$$L_+L_-|lm> = \hbar^2[l(l+1) - m^2 + m]|lm> \qquad (2.10)$$

so that

$$<lm|L_+L_-|lm> = <L_-lm|L_-lm> = \hbar^2[l(l+1) - m^2 + m] \geq 0 \qquad (2.11)$$

We have used that fact that L_+ and L_- are adjoint operators.

The Ladder

We are interested in the vectors

$$L_\pm|l, m> \qquad (2.12)$$

To this end we consider the eigenvalue problem of the operator L_z. Applying the operators $L_\pm$ we obtain under consideration of the commutator, eq. (2.5),

$$\begin{aligned} L_\pm L_3|l, m> &= L_\pm \hbar m|l, m> \\ &= L_3 L_\pm|l, m> + [L_\pm, L_3]|l, m> \\ &= L_3 L_\pm|l, m> \mp \hbar L_\pm|lm> \end{aligned} \qquad (2.13)$$

This relation can be summarized as

$$L_3 L_\pm|l, m> = \hbar(m \pm 1)L_\pm|l, m> \qquad (2.14)$$

This indicates: If $|l, m>$ is an eigenvector to the operator L_3, then $C_m L_\pm|l, m>$ is an eigenvector with eigenvalue $m \pm 1$:

$$|l, m \pm 1> = C_m L_\pm|l, m> \qquad (2.15)$$

We shall now determine the factor C_m from the condition that the eigenvector $|l, m \pm 1>$ is normalized:

$$<l, m \pm 1|l, m \pm 1> = |C_m^\pm|^2 <l, m|L_\mp L_\pm|l, m> = 1 \qquad (2.16)$$

Here, we have used the fact that the operators L_+ and L_- are adjoint operators:

$$(L_\pm)^\dagger = L_\mp \qquad (2.17)$$

In order to determine the normalization constant $C_m^\pm$ it is necessary to express the operator product $L_\mp L_\pm$ by the operators $\mathbf{L}^2$ and L_z since their action on the eigenvectors $|lm>$ are known. To this end we us the identity

$$\mathbf{L}^2 = L_{\pm}L_{\mp} + L_z^2 \mp \hbar L_z \qquad (2.18)$$

and obtain

$$1 = |C_m^{\pm}|^2 [l(l+1) - m^2 \pm m]\hbar^2 \qquad (2.19)$$

Taking the numbers $C_m^{\pm}$ to be real we summarize the action of the ladder operators $L_{\pm}$ onto the eigenvectors $|lm>$

$$|l, m \pm 1> = \frac{1}{\hbar\sqrt{l(l+1) - m(m \pm 1)}} L_{\pm}|lm> \qquad (2.20)$$

It is possible to draw the following conclusions.

- a) We can take

$$l \geq 0 \qquad (2.21)$$

- b) We take the largest possible value of m, m_{max}. Then

$$L_+|l, m_{max}> = \hbar\sqrt{l(l+1) - m_{max}(m_{max}+1)}|lm_{max}+1> = 0 \quad (2.22)$$

We immediately obtain

$$m_{max} = l \qquad (2.23)$$

- c) Similarly, we take the smallest possible value of m, m_{min}. Then

$$L_-|l, m_{min}> = \hbar\sqrt{l(l+1) - m_{min}(m_{min}-1)}|lm_{min}-1> = 0 \quad (2.24)$$

We immediately obtain

$$m_{min} = -l \qquad (2.25)$$

- d) Starting from the eigenvector $|l, l>$ we can obtain $|l, -l>$ by subsequently applying the operator L_-. This takes an integer number of N steps.

$N = 0$	$l = 0$	
$N = 1$	$l = \frac{1}{2}$	$m = \frac{1}{2}, -\frac{1}{2}$
$N = 2$	$l = 1$	$m = 1, 0, -1$
$N = 3$	$l = \frac{3}{2}$	$m = \frac{3}{2}, \frac{1}{2}, \frac{-1}{2}, \frac{-3}{2}$
$N = 4$	$l = 2$	$m = 2, -1, 0, 1, -2$

We can summarize: The number l can take the values

$$-l \leq m \leq l \qquad (2.26)$$

L can either be an integer

$$l = 0, 1, 2, ... \qquad (2.27)$$

or odd multiples of 1/2

The latter values can be assigned to the spin.

2.2.2 Spin 1/2

We denote the spin operators by S_i and l by S. In the following we shall consider the case of $S = 1/2$. There exist two eigenstates, spin up and spin down.

$$S_z|\frac{1}{2} > = \frac{\hbar}{2}|\frac{1}{2} >$$
$$s_z|-\frac{1}{2} > = -\frac{\hbar}{2}|-\frac{1}{2} > \tag{2.28}$$

Since quantum mechanical quantities are related with operators acting on state vectors of a Hilbert space, the space corresponding to the spin is two dimensional and can be spanned by the two vectors

$$|\frac{1}{2} >= \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad , \quad |-\frac{1}{2} >= \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{2.29}$$

It is straightforward to introduce the adjoint (bra) -vectors

$$< \frac{1}{2}| = (1, 0)$$
$$< -\frac{1}{2}| = (0, 1) \tag{2.30}$$

The scalar product of two vectors of the Spin-1/2 Hilbert space is defined as usual

$$< u|v >= [u_1^*, u_1^*] \cdot \begin{pmatrix} v_1 \\ v_2 \end{pmatrix} \tag{2.31}$$

Here, u_i, v_i are complex numbers.

A general state is a superposition of these states:

$$|\psi_s(t) > = c_-(t)|-\frac{1}{2} > +c_+(t)|\frac{1}{2} >$$
$$< \psi_s(t)| = c_-^*(t) < -\frac{1}{2}| + c_+^*(t) < \frac{1}{2}| \tag{2.32}$$

The amplitudes c_- and c_+ are related to the probabilities $|c_-|^2$, $|c_+|^2$ finding a spin in the state *spin down* or *spin up*, respectively. The state vectors have to be normalized according to

$$< \psi_s(t)|\psi_s(t) >= |c_-(t)|^2 + |c_+(t)|^2 = 1 \tag{2.33}$$

Let us now consider the representations of the spin operators. They are represented by 2×2 hemitian matrices. We can uniquely determine these matrices by the action of the operators upon the basis vectors.

Let us first consider the representation of $\mathbf{S}^2 = S_x^2 + S_y^2 + S_z^2$ We obtain

$$\mathbf{S}^2|\frac{1}{2}> = \frac{3}{4}\hbar^2|\frac{1}{2}>$$
$$\mathbf{S}^2|-\frac{1}{2}> = \frac{3}{4}\hbar^2|-\frac{1}{2}> \tag{2.34}$$

This uniquely defines the representation

$$\mathbf{S}^2 = \frac{3}{4}\hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \tag{2.35}$$

The action of the operator S_z upon the state vectors is

$$S_z|\frac{1}{2}> = \frac{1}{2}\hbar|\frac{1}{2}>$$
$$S_z|-\frac{1}{2}> = -\frac{1}{2}\hbar|-\frac{1}{2}> \tag{2.36}$$

In turn, S_z is uniquely represented by the matrix

$$S_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{2.37}$$

The operators $S_\pm$ obey the general relations

$$S_\pm|Sm> = \hbar\sqrt{S(S+1) - m(m\pm 1)}|S, m\pm 1> \tag{2.38}$$

Explicitly, for Spin 1/2, we obtain

$$S_+|\frac{1}{2}> = 0$$
$$S_+|-\frac{1}{2}> = \hbar|\frac{1}{2}> \tag{2.39}$$

$$S_-|\frac{1}{2}> = \hbar|\frac{1}{2}>$$
$$S_-|-\frac{1}{2}> = 0 \tag{2.40}$$

This indicates that the operators $S_\pm$ have the following representations

$$S_+ = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \tag{2.41}$$

$$S_- = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \tag{2.42}$$

The matrix representations of the spin operators S_x, S_y can be obtained from the relations

$$S_x = \frac{1}{2}(S_+ + S_-) = \hbar\frac{1}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \tag{2.43}$$

$$S_y = -i\frac{1}{2}(S_+ - S_-) = \hbar\frac{1}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \tag{2.44}$$

We want to point out that the Spin operators S_x, S_y, S_z are selfadjoint operators. Therefore, they are represented by hermitian matrices. Furthermore, we explicitly see from the representations that

$$S_+ = (S_-)^\dagger \tag{2.45}$$

2.2.3 Magnetic Moment and Spin: Landé's g-Factor

For the electron, the orbital angular momentum is connected with a magnetic moment according to

$$\mu = -\frac{\mu_B}{\hbar}\mathbf{L} \tag{2.46}$$

where Bohr's magneton μ_B is given by

$$\mu_B = \frac{e\hbar}{2m_0} \tag{2.47}$$

A similar relationship is assumed to be valid for the spin:

$$\mu = -g_s\frac{\mu_B}{\hbar}\mathbf{S} \tag{2.48}$$

The quantity g_S is denoted as *gyromagnetic factor* or *Landé's g-factor*. It can be determined by the Zeeman effect and the Einstein-de-Haas experiment. It turns out that its value is close to 2. In fact, high precision measurements yield

$$g = 2,002319304386(20) \tag{2.49}$$

The factor $g = 2$ is obtained from the relativistic quantum mechanical treatment of the electron based on Dirac equation. The corrections to g can be determined from a quantum field theoretical treatment including interactions with the electromagnetic field.

Not only electrons have a spin. Also protons, neutrons and nuclei possess a spin and interact with an external magnetic field. The spin is intimately related with a magnetic moment

$$\mu = \gamma\mathbf{S} \tag{2.50}$$

where the gyromagnetic ratio γ depends on the considered particle. For the spin of protons and neutrons, the gyromagnetic ratio is expressed in terms of the nuclear magneton, which is defined in analogy to Bohr's magneton

$$\mu_N = \frac{e\hbar}{2m_p} \tag{2.51}$$

where m_p is the mass of the proton (or neutron, respectively). For nuclei, an analogous quantity is considered.

Particle	g-factor
Electron	2.0023193043622
Proton	−5.585694713
Neutron	3.82608545
Muon	2.0023318414

We have used the definition $\mu_S = -g\frac{\mu_I}{\hbar}\mathbf{S}$, where $\mu_I = |q|\hbar/2m_I$

2.2.4 Pauli-Matrices

For the following ist is convenient to introduce the Pauli matrices σ by the relation

$$\mathbf{S} = \frac{\hbar}{2}\sigma \tag{2.52}$$

Since they are related to the spin operators they fullfill the following relations

$$[\sigma_i, \sigma_j] = 2i\epsilon_{ijk}\sigma_k \tag{2.53}$$

$$\sigma_j^2 = 1 \tag{2.54}$$

$$\sigma_j\sigma_k = \delta_{jk} + i\epsilon_{ikl}\sigma_l \tag{2.55}$$

2.2.5 Pauli-Equation

In order to include the spin of the electron in the quantum mechanical description one introduced two wave funtions $\psi_+(\mathbf{x}, t)$ and $\psi_-(\mathbf{x}, t)$ for electrons with spin up and spin down. Electrons with spin $s = \frac{1}{2}$ are described by

$$|\psi(x, y, z, t) > = \psi_+(x, y, z, t)\begin{pmatrix} 1 \\ 0 \end{pmatrix} \tag{2.56}$$

$$|\psi(x, y, z, t) > = \psi_-(x, y, z, t)\begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{2.57}$$

These two wave functions are combined into so called spinors:

$$|\psi(x, y, z, t) > = \begin{pmatrix} \psi_+(x, y, z, t) \\ \psi_-(x, y, z, t) \end{pmatrix} \tag{2.58}$$

They are elements of a Hilbert space

$$|u > = \begin{pmatrix} u_+ \\ u_- \end{pmatrix} \quad , \quad < u| = (u_+^*, u_-^*) \tag{2.59}$$

where the scalar product is defined according to

$$< u|v >= \int d^3\mathbf{x} u_+^*(\mathbf{x}, t) v_+(\mathbf{x}, t) + u_-^*(\mathbf{x}, t) v_-(\mathbf{x}, t) \qquad (2.60)$$

Operators A in this Hilbert space are represented by 2×2-matrices,

$$A = \begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} \qquad (2.61)$$

where the coefficients A_{ij} are operators. Expectation values of these operators are defined by the scalar products

$$< \psi|A|\psi > = \int^3 d\mathbf{x}[< \psi_+|A_{11}|\psi_+ > + < \psi_+|A_{12}|\psi_- >$$
$$+ < \psi_-|A_{21}|\psi_+ > + < \psi_-|A_{22}|\psi_- >] \qquad (2.62)$$

We shall now consider the Hamilton operator of an electron with spin. Without magnetic field the spin of the electrons are not influenced and the Schrödinger equation holds for each wave function $\psi_\pm(\mathbf{x}, t)$ of the state vector $|\psi >$ separately. We can combine this into the Spinor equation

$$i\hbar\frac{\partial}{\partial t} \begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix} = \begin{pmatrix} H\psi_+ \\ H\psi_- \end{pmatrix} = HI \begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix} \qquad (2.63)$$

with the Hamiltonian H. (I denotes the identity).

Including the interaction of the electron spin with an external magnetic field leads to the Hamiltonian

$$H = [\frac{(\mathbf{p} + e\mathbf{A})^2}{2m_0} - e\Phi]E + g_S\frac{\mu_B}{\hbar}\mathbf{B} \cdot \mathbf{S} \qquad (2.64)$$

Explicit: Hamilton operator of an electron in a constant magnetic field

$$H = H_0 + \frac{\mu_B}{\hbar}\mathbf{B} \cdot \mathbf{L} + g_s\frac{\mu_B}{\hbar}\mathbf{B} \cdot \mathbf{S} \qquad (2.65)$$

2.2.6 Splitting of Energy Levels in a Constant Magnetic Field

The energy levels are obtainded as the eigenvalues of the eigenvalue problem

$$[H_0 + \frac{\mu_B}{\hbar}\mathbf{B} \cdot \mathbf{L} + g_s\frac{\mu_B}{\hbar}\mathbf{B} \cdot \mathbf{S}]|\Psi >= E|\Psi > \qquad (2.66)$$

Energy eigenvalues

$$E = E_{nl}^0 + \mu_B B[m \pm 1] \qquad (2.67)$$

Since $|m| \leq l$ energy splitting for l=0 occurs only due to the existence of the spin.

2.2.7 Stern-Gerlach Experiment

As has been noticed in the experiment of Stern and Gerlach, a beam of silver particles crossing an magnetic field with a gradient splits into two components. This is a direct experimental proof of the existence of the spin of particles.

In the following we shall consider the theoretical treatment of this experiment by focusing on the most simplest case of a particle with zero charge $q = 0$, mass m_0 and spin $1/2$. The treatment will be based on the Pauli equation.

We consider the inhomogeneous magnetic field

$$\mathbf{B} = B(0, 0, z) \tag{2.68}$$

We start from the Pauli Hamiltonian in the form

$$H = \frac{\mathbf{p}^2}{2m_0} - g\frac{\mu_B}{\hbar}\mathbf{B} \cdot \mathbf{S} \tag{2.69}$$

where we have taken into account that the particles have zero charge. By a separation ansatz we can split the motions in x and y directions and obtain for the motion in z direction the Hamiltonian.

$$H = -\frac{\hbar^2}{2m_0}\frac{d^2}{dz^2} + g\frac{\mu_B}{2}B[z\sigma_z] \tag{2.70}$$

In order to solve the time dependent Pauli equation we make the ansatz

$$|\psi> = \begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix} \tag{2.71}$$

The Pauli equation can be split into equations for the two components of the spinor $|\psi>$

$$i\hbar\dot{\psi}_+ = [\frac{p_z^2}{2m_0} + \frac{g}{2}\mu_B Bz]\psi_+$$

$$i\hbar\dot{\psi}_- = [\frac{p_z^2}{2m_0} - \frac{g}{2}\mu_B Bz]\psi_- \tag{2.72}$$

However, these are the Schrödinger equations for particles moving in the potentials $U = \pm g\mu_B Bz$.

2.3 Spin Dynamics

2.3.1 Spin in a Constant Field

The dynamics of a spin in a constant magnetic field leads to a rotation of the expectation values of the spin vector around the axis defined by the magnetic

field. This motion, which has its classical counterpart, is denoted as Lamor precession. The Schrödinger equation reads

$$i\hbar\frac{d}{dt}|\psi> = g\frac{\mu_B}{\hbar}\mathbf{B}\cdot\mathbf{S}|\psi> \tag{2.73}$$

We represent the spin vector according to

$$|\psi> = c_+|\frac{1}{2}> + c_-|-\frac{1}{2}> \tag{2.74}$$

and obtain the two differential equations of first order

$$i\hbar\dot{c}_+ = +\frac{g\mu_B}{2}Bc_+$$
$$i\hbar\dot{c}_- = -\frac{g\mu_B}{2}Bc_- \tag{2.75}$$

The initial condition requires

$$|c_+(0)|^2 + |c_-(0)|^2 = 1 \tag{2.76}$$

The solutions of these two differential equations read

$$c_+ = e^{-i(\omega_L/2)t}c_+(0)$$
$$c_- = e^{i(\omega_L/2)t}c_-(0) \tag{2.77}$$

where we have introduced the Lamor frequency

$$\omega_L = \frac{g\mu_B B}{\hbar} \tag{2.78}$$

We are now in a position to explicitly calculate the expectation value of the Spin components

$$< S_i(t) > = |c_+|^2 < \frac{1}{2}|S_i|\frac{1}{2}> + c_-^* c_+ < -\frac{1}{2}|S_i|\frac{1}{2}>$$
$$+ c_+^* c_- < \frac{1}{2}|S_i|-\frac{1}{2}> + |c_-|^2 < -\frac{1}{2}|S_i|-\frac{1}{2}> \tag{2.79}$$

In order to calculate $< S_x >$ and $< S_y >$ we use the operators $S_\pm$.

$$< S_x > = \frac{1}{2} < S_+ + S_- > = \frac{\hbar}{2}[c_-^* c_+ + c_+^* c_-] = \hbar a\cos\omega_L t$$
$$< S_y > = \frac{1}{2i} < S_+ - S_- > = \frac{\hbar}{2}[c_-^* c_+ - c_+^* c_-] = \hbar a\sin\omega_L t \tag{2.80}$$

$$< S_z > = (|c_+|^2 - |c_-|^2)\frac{\hbar}{2} \tag{2.81}$$

2.3.2 Spin Dynamics

$$
\begin{aligned}
\mathbf{B} \cdot \mathbf{S} &= B_x S_x + B_y S_y + B_z S_z \\
&= B_x \frac{1}{2}(S_+ + S_-) + B_y \frac{1}{2i}(S_+ - S_-) + B_z S_z \\
&= \frac{1}{2}[B_- S_+ + B_+ S_-] + B_z S_z
\end{aligned} \tag{2.82}
$$

Thereby, we have defined

$$
\begin{aligned}
B_+ &= (B_x + iB_y) \\
B_- &= (B_x - iB_y)
\end{aligned} \tag{2.83}
$$

The dynamics of the amplitudes $c_\pm$ reads

$$
\begin{aligned}
i\hbar \dot{c}_+ &= g\frac{\mu_B}{2}B_z c_+ + \frac{1}{2}g\frac{\mu_B}{2}B_- c_- \\
i\hbar \dot{c}_- &= g - \frac{\mu_B}{2}B_z c_- + \frac{1}{2}g\frac{\mu_B}{2}B_+ c_+
\end{aligned} \tag{2.84}
$$

We perform the ansatz

$$
c_\pm(t) = e^{i\mp\frac{\omega_0}{2}t}d_\pm(t) \tag{2.85}
$$

and obtain

$$
\begin{aligned}
i\hbar \dot{d}_+ &= \frac{1}{2}g\frac{\mu_B}{2}B_- e^{i\omega_0 t}d_- \\
i\hbar \dot{d}_- &= \frac{1}{2}g\frac{\mu_B}{2}B_+ e^{-i\omega_0 t}d_+
\end{aligned} \tag{2.86}
$$

As an example, we take the field

$$
\begin{aligned}
B_+ &= Fe^{i\omega_L t} \\
B_- &= Fe^{-i\omega_L t}
\end{aligned} \tag{2.87}
$$

which leads us to

$$
\begin{aligned}
i\hbar \dot{d}_+ &= \frac{1}{2}g\frac{\mu_B}{2}Fd_- \\
i\hbar \dot{d}_- &= \frac{1}{2}g\frac{\mu_B}{2}Fd_+
\end{aligned} \tag{2.88}
$$

This set of equation can be further reduced.

The solution reads

$$
\begin{aligned}
d_+ &= \sin(\Omega t + \phi) \\
d_- &= i\cos(\Omega t + \phi)
\end{aligned} \tag{2.89}
$$

and we finally obtain

$$|\psi> = e^{-i(\omega_L/2)t}\sin(\Omega t + \phi)|\frac{1}{2}> + e^{i(\omega_L/2)t}i\cos(\Omega t + \phi)|-\frac{1}{2}> \quad (2.90)$$

It is straightforward to determine the expectation values

$$<S_z> = \frac{\hbar}{2}[sin^2(\Omega t) - cos^2(\Omega t)] = -\frac{\hbar}{2}cos(2\Omega t)$$

$$<S_x> = -\frac{\hbar}{2}sin(2\Omega t)sin(\omega_0 t)$$

$$<S_y> = \frac{\hbar}{2}sin(2\Omega t)cos(\omega_0 t) \quad (2.91)$$

$pi/2$-, π-Puls

2.3.3 Evolution Equations for Expectation Values of the Spin

We could have found the same result in a different way starting from the time dependent Schrödinger equation. To this end we consider the temporal derivative of the expectation values of the Spin operators:

$$i\hbar\frac{d}{dt}<\psi(t)|S_i|\psi(t)> = i\hbar<\psi(t)|S_i|\dot{\psi}(t)> = i\hbar<\dot{\psi}(t)|S_i|\psi(t)> \quad (2.92)$$

Using the Schrödinger equation in the form

$$i\hbar|\dot{\psi}> = g\frac{\mu_B}{\hbar}B_jS_j|\psi>$$

$$-i\hbar<\dot{\psi}| = g\frac{\mu_B}{\hbar}B_j<S_j\psi| \quad (2.93)$$

we obtain

$$i\hbar\frac{d}{dt}<\psi(t)|S_i|\psi(t)> = g\frac{\mu_B}{\hbar}B_j<\psi|S_iS_j|\psi> - g\frac{\mu_B}{\hbar}B_j<\psi|S_jS_i|\psi>$$

$$= g\frac{\mu_B}{\hbar}B_j<\psi|[S_i,S_j]|\psi> - \quad (2.94)$$

We have exploited the fact that the spin operators are hermitian.

Using the commutator of the spin algebra,

$$[S_i,S_j] = i\hbar\epsilon_{ijk}S_k \quad (2.95)$$

we end up with the relation

$$\frac{d}{dt}<\psi(t)|S_i|\psi(t)> = g\frac{\mu_B}{\hbar}B_j\epsilon_{ijk}<\psi(t)|S_k|\psi(t)> \quad (2.96)$$

The corresponding vector equation takes the form

$$\frac{d}{dt}<\mathbf{S}> = \frac{\mu_B}{\hbar}\mathbf{B}\times<\mathbf{S}> \quad (2.97)$$

2.3.4 Bloch's Equation

Materials with magnetic properties contain spins at spatial points $\mathbf{x}_i$. The magnetization of the material is then given by

$$\mathbf{M} = \sum_i <\mathbf{S}>^i \delta(\mathbf{x} - \mathbf{x}_i) \tag{2.98}$$

The evolution equation can be derived using the evolution equations for the individual spin $<\mathbf{S}^i$.

We calculate

$$\frac{d}{dt}\mathbf{M} = \sum_i \frac{d}{dt} <\mathbf{S}^i> \delta(\mathbf{x} - \mathbf{x}_i)$$
$$= \frac{\mu_B}{\hbar}\mathbf{B} \times \mathbf{M} \tag{2.99}$$

This equation has applications in various fields. In order to account for decay processes and pumping it has to be modified. This leads to the so-called Bloch equation, where the added terms take into account relaxation of the x, y components of the spin (relaxation time T_2) and the relaxation of the z-component (relaxation time T_1) as well as a pumping term:

$$\frac{d}{dt} <\mathbf{M}> = \frac{\mu_B}{\hbar}\mathbf{B} \times <\mathbf{M}> + \begin{pmatrix} -\frac{1}{T_2}<M_x> \\ -\frac{1}{T_2}<M_y> \\ \frac{1}{T_1}(M_0 - <M_z>) \end{pmatrix} \tag{2.100}$$

Measuring the relaxation times T_1 and T_2 yield interesting information about the material.

Bloch's equation has application in ESR (electron spin resonance) and NMR (nuclear magnetic resonance).

2.3.5 Heisenberg-Model, Landau-Lifshitz-Equation

The Landau-Lifshitz equation describes ferromagnets in terms of spins and their interaction. The idea is to consider a lattice occupied by a spin $\mathbf{S}_i$, whose expectation evolves according to

$$\frac{d}{dt}\langle \mathbf{S}_i \rangle = \gamma \mathbf{H}_i \times \langle \mathbf{S}_i \rangle \tag{2.101}$$

The magnetic field has two contributions, first an external field $\mathbf{H}_0$ and, second, a contribution from all other spin's.

In the Heisenberg-model one assumes that the contributions from the other spins result in a magnetic field, which is a linear superposition of all other spins:

$$\mathbf{H}_i = -\sum_j J_{ij}\mathbf{S}_j \tag{2.102}$$

As a result, one obtains the evolution equation for the spins lattice

$$\frac{d}{dt}\langle\mathbf{S}_i\rangle = -\gamma\sum_j J_{ij}\langle\mathbf{S}_j\rangle \times \langle\mathbf{S}_i\rangle + \gamma\mathbf{H}_0 \times \langle\mathbf{S}_i\rangle \qquad (2.103)$$

In the continuum limit, i.e. by assuming nearest neighbours interaction

$$J_{ij} = \frac{\delta_{j,i+1} + \delta_{j,i-1} - 2\delta_{ij}}{(\Delta x)^2} \qquad (2.104)$$

we end up with the so-called Landau-Lifshitz equation

$$\frac{\partial}{\partial t}\mathbf{S}(\mathbf{x},t) = \gamma\mathbf{S}(\mathbf{x},t) \times \Delta\mathbf{S}(\mathbf{x},t) \qquad (2.105)$$

This nonlinear equation can be solved in one spatial dimension and exhibits soliton solutions. In this case it is equivalent to the so-called nonlinear Schrödinger equation

The Heisenberg-model can also be formulated quantum mechanically. To this end one defines the spin operators $\mathbf{S}^i$ as well as the Hamilton operator

$$H = -\frac{1}{2}\sum_{ij}[J_{ij}^x S_x^i S_x^j + J_{ij}^y S_y^i S_y^j + J_{ij}^z S_z^i S_z^j] + \sum_i H S_z^i \qquad (2.106)$$

assuming that spin operators at different lattice points commute. For certain geometries, the spectrum of the Hamilton operator can be calculated explicitly. An example is the one-dimensional spin chain, which can be exactly solved (using the so-called Bethe ansatz).

3

Relativistiv Wave Equations

3.1 Classical Relativistic Mechanics

In an inertial coordinate system Σ the position of a particle is described by the contravariant components x^μ of the four vector $\mathbf{x}$:

$$x^\mu = [ct, x, y, z] \tag{3.1}$$

We denote the components of this four-vector of the same particle formulated with respect to an inertial system Σ', which moves with the relative velocity $\mathbf{V}$ by $x^\mu = [ct', x', y', z']$. A postulate of the theory of special relativity is that the quantity

$$c^2 dt^2 - dx^2 - dy^2 - dz^2 = c^2 dt'^2 - dx'^2 - dy'^2 - dz'^2 \tag{3.2}$$

remains invariant.

It is convenient to introduce the covariant components of the four vector $\mathbf{x}$ by

$$x_\mu = [ct, -x, -y, -z] \tag{3.3}$$

Furthermore, we define the metric tensor $g_{\mu\nu}$ by the matrix

$$g_{\mu\nu} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \tag{3.4}$$

It follows immediately that the relation between contravariant and covariant components x^μ and x_μ can be expressed by the metric $g_{\mu\nu}$ according to

$$x_\mu = g_{\mu\nu} x^\nu \tag{3.5}$$

We use the convention to sum up over dummy indices.

Then, the condition (**??**) can be rewritten in terms of the (indefinite) scalar product according to

$$g_{\mu\nu}dx^\mu dx^\nu = dx_\mu dx^\mu = c^2 dt^2 - dx^2 - dy^2 - dz^2 \qquad (3.6)$$

If we consider the four-vector x'^μ, evaluated in the inertial system Σ' moving with relative velocity U, then this vector can be related to the four-vector x^μ, evaluated in the inertial system Σ, via a Lorentz-transformation

$$dx'^\mu = \Lambda^\mu_{\ \nu} dx^\nu \qquad (3.7)$$

The Lorentz transformation is defined by the requirement that the scalar product is invariant

$$g_{\mu\nu}dx^\mu dx^\nu = g_{\mu\nu}dx'^\mu dx'^\nu \qquad (3.8)$$

This leads to the condition

$$g_{\mu\nu} = g_{\alpha\beta}\Lambda^\alpha_{\ \nu}\Lambda^\beta_{\ \nu} \qquad (3.9)$$

The Lorentz transformation explicitly reads

$$cdt' = \frac{1}{\sqrt{1-\beta^2}}[cdt - \beta dx]$$
$$dz' = \frac{1}{\sqrt{1-\beta^2}}[dz - \beta cdt]$$
$$dx' = dx$$
$$dy' = dy \qquad (3.10)$$

In the limit $|v| << c$ the Lorentz transform tends to the Galilei transform

$$dt' = dt$$
$$dz' = [dz - vdt]$$
$$dx' = dx$$
$$dy' = dy \qquad (3.11)$$

The Lorentz transform takes the form

$$\Lambda^\mu_{\ \nu} = \frac{1}{\sqrt{1-\beta^2}}\begin{pmatrix} 1 & 0 & 0 & -\beta \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ -\beta & 0 & 0 & 1 \end{pmatrix} \qquad (3.12)$$

We now consider a moving particle. In the coordinate system Σ its velocity is given by

$$\mathbf{v}(t) = [\dot{x}(t), \dot{y}(t), \dot{z}(t)] \qquad (3.13)$$

3.1.1 Velocity Four-Vector

It is convenient to introduce a velocity four vector u^μ, which transforms like a four-vector under Lorentz transformations

$$u'^\mu = \Lambda^\mu{}_\nu u^\nu \tag{3.14}$$

A straightforward definition is the vector

$$u^\mu = \frac{d}{d\tau} x^\mu \tag{3.15}$$

Thereby, the eigenzeit τ is defined by

$$d\tau = \sqrt{1 - (\frac{\mathbf{v}(t)}{c})^2} dt \tag{3.16}$$

The interval $d\tau$ is independent on the choosen coordinate system, due to (3.2). In the coordinate system Σ', it takes the form

$$d\tau = \sqrt{1 - \mathbf{v}'(t')/c^2} dt' \tag{3.17}$$

where $\mathbf{v}'(t')$ is the velocity of the particle with respect to time t' and the coordinates $\mathbf{x}'(t')$ of the coordinate system Σ'.

The four vector u^μ can be determined in a straight forward manner:

$$\begin{aligned}
u^\mu &= [c\frac{dt}{d\tau}, \frac{dx(t)}{d\tau}, \frac{dy(t)}{d\tau}, \frac{dz(t)}{d\tau}] \\
&= \frac{dt}{d\tau}[c\frac{dt}{dt}, \frac{dx(t)}{dt}, \frac{dy(t)}{dt}, \frac{dz(t)}{dt}] \\
&= \frac{1}{\sqrt{1 - \beta^2}}[c, \mathbf{v}(t)]
\end{aligned} \tag{3.18}$$

3.1.2 Momentum Four-Vector

It is convenient to define the momentum four-vector p^μ by the relation

$$p^\mu = mu^\mu \tag{3.19}$$

Here, m denotes the so-called *proper mass* or the *rest mass* of the particle.

The vector of four-momentum is then given by

$$p^\mu = \frac{1}{\sqrt{1 - \beta(t)^2}}[mc, m\mathbf{v}(t)] \tag{3.20}$$

Alternatively, we can defined the four momentum vector according to

$$p^\mu = [\frac{E}{c}, \mathbf{p}] \tag{3.21}$$

such that the momentum vector $\mathbf{p}$ is expressed as

$$\mathbf{p} = \frac{m}{\sqrt{1 - \beta(t)^2}} \mathbf{v}(t) \tag{3.22}$$

and the energy is defined as

$$E = \frac{m}{\sqrt{1 - \beta(t)^2}} c^2 \tag{3.23}$$

We can introduce the covariant momentum vector

$$p_\mu = [\frac{E}{c}, -p_x, -p_y, -p_z]$$
$$p^\mu = [\frac{E}{c}, p_x, p_y, p_z] \tag{3.24}$$

and determine the scalar product

$$p_\mu p^\mu = \frac{E^2}{c^2} - \mathbf{p}^2 = m^2 c^2 \tag{3.25}$$

We arrive at the relation

$$E = \sqrt{m^2 c^4 + c^2 \mathbf{p}^2} \tag{3.26}$$

We remind the reader that m is the *rest mass* of the particle and $\mathbf{p}$ is the momentum vector (3.22) defined in the inertial coordinate system Σ.

3.2 Quantization

We follow the quantization procedure

$$E = H(p, q)$$
$$E \rightarrow i\hbar \frac{\partial}{\partial t}$$
$$p \rightarrow \frac{\hbar}{i} \nabla \tag{3.27}$$

$$i\hbar \dot{\psi} = \sqrt{m^2 c^4 - c^2 \hbar^2 \Delta} \psi \tag{3.28}$$

This leads us to a nonlocal evolution equation. It is not immediately obvious, how this equation can be related to a probabilistic interpretation of the wave function.

3.3 Klein-Gordon Equation

Iteration of the equation (3.28) yields

$$-\hbar^2 \frac{\partial^2}{\partial t^2} \psi = [m^2 c^4 - c^2 \hbar^2 \Delta] \psi \qquad (3.29)$$

The Klein-Gordon equation is Lorentz-covariant. It can be rewritten as

$$[\partial_\mu \partial^\mu + (\frac{mc}{\hbar})^2] \psi = 0 \qquad (3.30)$$

where we have defined

$$x_\mu = [ct, -x, -y, -z] \qquad (3.31)$$

and

$$\partial_\mu = \frac{\partial}{\partial x_\mu} = [\frac{\partial}{\partial ct}, \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}] \qquad (3.32)$$

Using the operator

$$p_\mu = -i\hbar \partial_\mu \qquad (3.33)$$

we obtain

$$[p_\mu p^\mu - (mc)^2] | \psi >= 0 \qquad (3.34)$$

3.4 Dirac Equation

Dirac suggested to extend the wave function to a quantity consisting of several components in such a way, that each component obeys the Klein-Gordon equation:

$$|\psi >= \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix} \qquad (3.35)$$

His ansatz for the wave equation was

$$i\hbar |\dot{\psi} >= [c\frac{\hbar}{i} \sum_{i=1}^{3} \alpha_i \frac{\partial}{\partial x_i} + mc^2 \beta] | \psi > \qquad (3.36)$$

The prefactors of the matrices α_i and β are choosen in such a way that they are dimensionless.

We will now determine the shape of these matrices from the requirement that each component separately obeys a Klein-Gordon equation. To this end we iterate

$$-\hbar^2|\ddot{\psi}> = [-ic\hbar\sum_{i=1}^{3}\alpha_i\frac{\partial}{\partial x_i} + mc^2\beta]^2|\psi>$$

$$= [-\hbar^2\sum_{i=1}^{3}\sum_{j=1}^{3}\frac{\alpha_i\alpha_j + \alpha_j\alpha_i}{2}\frac{\partial}{\partial x_i}\frac{\partial}{\partial x_j}$$

$$- i\hbar mc^3\sum_{i=1}^{3}[\alpha_i\beta + \beta\alpha_i]\frac{\partial}{\partial x_i} + m^2c^4\beta^2]|\psi> \qquad (3.37)$$

Each component obeys the Klein-Gordon equation provided we require

$$\alpha_i\alpha_j + \alpha_j\alpha_i = 2\delta_{ij}$$
$$\alpha_i\beta + \beta\alpha_i = 0$$
$$\beta^2 = 1 \qquad (3.38)$$

It can be shown that the smallest dimension for which equations (3.38) can be fullfilled is the dimension N=4. In fact, all the conditions (3.38) can be verified if we choose

$$\alpha_i = \begin{pmatrix} 0 & \sigma_i \\ \sigma_i & 0 \end{pmatrix} \qquad (3.39)$$

$$\beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \qquad (3.40)$$

The 2×2-matrices are the Pauli matrices, as defined above.

This can be easily checked as follows. The representation of β is evident. The matrices $\alpha_i\beta$ are antisymmetric:

$$\sigma_i\beta = \begin{pmatrix} 0 & \alpha_i \\ \alpha_i & 0 \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \begin{pmatrix} 0 & -\alpha_i \\ \alpha_i & 0 \end{pmatrix} \qquad (3.41)$$

3.4.1 Interpretation of Wave Function: Probability Density

The probabilistic interpretation of the wave function requires the definition of a probability density ρ, which can be taken in a straightforward manner as

$$\rho = \sum_{\alpha}|\psi_\alpha|^2 \qquad (3.42)$$

Together with the probability current $\mathbf{j}$, the density ρ has to fullfill the continuity equation

$$\frac{\partial}{\partial t}\rho + \nabla \cdot \mathbf{j} = 0 \qquad (3.43)$$

The corresponding probability current turns out to be

$$j_k = c\psi^\dagger \alpha_k \psi \qquad (3.44)$$

This can be shown on the basis of the Dirac equation.

The adjoint stae vector has to be defined according to

$$\psi^\dagger = [\psi_1^*, .., \psi_4^*] \qquad (3.45)$$

and the scalar product is defined as usual:

$$\sum_{k=1}^{4} \phi_k^*(\mathbf{x}, t)\psi_k(\mathbf{x}, t) \qquad (3.46)$$

3.4.2 Dirac Equation in Lorentz Covariant Form

$$x^0 = ct \quad , \quad x^1 = x \quad , \quad x^2 = y \quad , \quad x^3 = z \qquad (3.47)$$

$$\partial_\mu = \frac{\partial}{\partial x^\mu} \qquad (3.48)$$

By multiplication with β we obtain

$$[\beta i\hbar\frac{\partial}{\partial ct} + \beta\alpha_k i\hbar\frac{\partial}{\partial x^k} - mc]|\psi> = 0 \qquad (3.49)$$

We define the matrices

$$\gamma^0 = \beta \quad , \quad \gamma^i = \beta\alpha_i \qquad (3.50)$$

The Dirac equation then takes the form

$$(i\hbar\gamma^\mu\partial_\mu - mc)|\psi> = 0 \qquad (3.51)$$

3.4.3 Minimal Coupling to the Electromagnetic Field

Coupling to electromagnetic field:

$$[\gamma^\mu(p_\mu - qA_\mu) - mc]|\psi> = 0 \qquad (3.52)$$

Four vector potential

$$A_\mu = [\frac{\Phi}{c}, A_1, A_2, A_3] \qquad (3.53)$$

Equation of motion

$$i\hbar\frac{\partial}{\partial t}|\psi> = c\sum_j \alpha_j[\frac{\hbar}{i}\frac{\partial}{\partial x_j} - qA_j] + q\Phi + mc^2\beta|\psi> \qquad (3.54)$$

3.4.4 Nonrelativistic Limit

In the following we shall consider the nonrelativistic limit.

The first step is to represent the wave vector $|\psi>$ in terms of two quantities φ, χ, each having to components, according to

$$|\psi> = \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix} = \begin{pmatrix} \varphi \\ \chi \end{pmatrix} = \begin{pmatrix} \varphi_1 \\ \varphi_2 \\ \chi_1 \\ \chi_4 \end{pmatrix} \tag{3.55}$$

It is straightforward to determine the quantities

$$\alpha_j |\psi> = \begin{pmatrix} 0 & \sigma_j \\ \sigma_j & 0 \end{pmatrix} \begin{pmatrix} \chi \\ \varphi \end{pmatrix} = \begin{pmatrix} \sigma_j \chi \\ \sigma_j \varphi \end{pmatrix} = \sigma_j \begin{pmatrix} \chi \\ \varphi \end{pmatrix} \tag{3.56}$$

As a consequence, the Dirac equation can be written as follows:

$$i\hbar \frac{\partial}{\partial t} \begin{pmatrix} \varphi \\ \chi \end{pmatrix} = c \begin{pmatrix} \sigma_i(p_i - qA_i)\chi \\ \sigma_i(p_i - qA_i) \end{pmatrix} + q\Phi \begin{pmatrix} \varphi \\ \chi \end{pmatrix} + mc^2 \begin{pmatrix} \varphi \\ -\chi \end{pmatrix} \tag{3.57}$$

We perform the separation ansatz:

$$\begin{pmatrix} \varphi \\ \chi \end{pmatrix} = e^{-imc^2 t} \begin{pmatrix} \tilde{\varphi} \\ \tilde{\chi} \end{pmatrix} \tag{3.58}$$

The meaning of this ansatz is as follows. The energy of a particle in the nonrelativistic limit is just

$$E = mc^2 + \frac{p^2}{2m} \tag{3.59}$$

The time dependence of a wave function is

$$\psi = e^{-i\frac{E}{\hbar}t}\tilde{\psi} \tag{3.60}$$

Therefore, we split the time dependency into the contribution due to $E = mc^2$ and a remainder $\tilde{\psi}$. This separation leads us to

$$i\hbar \frac{\partial}{\partial t} \begin{pmatrix} \tilde{\varphi} \\ \tilde{\chi} \end{pmatrix} + mc^2 \begin{pmatrix} \tilde{\varphi} \\ \tilde{\chi} \end{pmatrix} = c \begin{pmatrix} \sigma_i(p_i - qA_i)\tilde{\chi} \\ c\sigma_i(p_i - qA_i)\tilde{\varphi} \end{pmatrix} + q\Phi \begin{pmatrix} \tilde{\varphi} \\ \tilde{\chi} \end{pmatrix} + mc^2 \begin{pmatrix} \tilde{\varphi} \\ -\tilde{\chi} \end{pmatrix} \tag{3.61}$$

Now we split this equation into two:

$$i\hbar \frac{\partial}{\partial t} \tilde{\varphi} = c\sigma_i(p_i - qA_i)\tilde{\chi} + q\Phi \tag{3.62}$$

$$i\hbar \frac{\partial}{\partial t} \chi + 2mc^2 \chi = c\sigma_i(p_i - qA_i)\varphi + q\Phi\chi \tag{3.63}$$

In the nonrelativistic limit we can perform the following approximation

$$\hbar|\frac{\partial}{\partial t}\tilde{\chi}| << 2mc^2|\tilde{\chi}| \tag{3.64}$$

which allows us to neglect the temporal derivative of χ

$$\tilde{\chi} = \frac{c}{+2mc^2 - q\Phi}\sigma_i(p_i - qA_i)\tilde{\varphi} \tag{3.65}$$

Furthermore, we can expand the denumerator

$$\tilde{\chi} = \frac{1}{2mc}[1 + \frac{q\Phi}{2mc^2}]\alpha_i(p_i - qA_i)\tilde{\varphi} \tag{3.66}$$

At this point, we have succeeded to eliminate the wave function $\tilde{\chi}$, since we are able to express it in terms of the wave function $\tilde{\varphi}$.

This allows us to formulate a wave equation for the two-componet quantity $\tilde{\varphi}$ in the form

$$i\hbar\frac{\partial}{\partial ct}\tilde{\varphi} = \sigma_i(p_i - qA_i)\frac{1}{2m}[1 + \frac{q\Phi}{2mc^2}]\sigma_j(p_j - qA_j)\tilde{\varphi} + q\frac{\Phi}{c}\tilde{\varphi} \tag{3.67}$$

It is evident that this equation should correspond to the Pauli equation.

In order to proof this we make use of the following relation for the Pauli matrices:

$$\sigma_i\sigma_j = \delta_{ij} + i\epsilon_{ijk}\sigma_k \tag{3.68}$$

$$i\hbar\frac{\partial}{\partial t}\tilde{\varphi} = (p_i - qA_i)\frac{1}{2m}[1 + \frac{q\Phi}{2mc^2}](p_i - qA_i)\tilde{\varphi}$$
$$+ i\epsilon_{ijk}\sigma_k(p_i - qA_i)\frac{1}{2m}[1 + \frac{q\Phi}{2mc^2}](p_j - qA_j)\tilde{\varphi}$$
$$+ q\Phi\tilde{\varphi} \tag{3.69}$$

$$i\hbar\frac{\partial}{\partial t}\tilde{\varphi} = \frac{1}{2m}(p_i - qA_i)^2\tilde{\varphi}$$
$$+ i\epsilon_{ijk}\sigma_k(p_i - qA_i)\frac{1}{2m}[1 + \frac{q\Phi}{2mc^2}](p_j - qA_j)\tilde{\varphi}$$
$$+ q\Phi\tilde{\varphi} \tag{3.70}$$

Let us first consider the term

$$i\epsilon_{ijk}\sigma_k(p_i - qA_i)\frac{1}{2m}(p_j - qA_j)\tilde{\varphi} = i\epsilon_{ijk}\sigma_k[p_ip_j + q^2A_iA_j - q(A_ip_j + A_jp_i) - q(p_iA_j)]\tilde{\varphi}$$
$$= -q\frac{\hbar}{2m}\epsilon_{ijk}\sigma_k\frac{\partial}{\partial x_i}A_j \tag{3.71}$$

However, the magnetic field is related to the vector potential $B_k = \epsilon_{kij}\frac{\partial}{\partial x_i}A_j$ such that

$$i\epsilon_{ijk}\sigma_k(p_i - qA_i)\frac{1}{2m}(p_j - qA_j)\tilde{\varphi} = -q\frac{\hbar}{2m}B_k\sigma_k = -2\frac{\mu}{\hbar}\mathbf{B}\cdot\mathbf{S} \quad (3.72)$$

As a result, we obtain the Pauli equation

$$i\hbar\frac{\partial}{\partial t}\tilde{\varphi} = (p_i - qA_i)\frac{1}{2m}(\mathbf{p} - q\mathbf{A})\tilde{\varphi} - 2\frac{\mu}{\hbar}\mathbf{B}\cdot\mathbf{S} + q\Phi\tilde{\varphi} \quad (3.73)$$

where we have defined the magneton

$$\mu = \frac{q\hbar}{2m} \quad (3.74)$$

In a similar way we can treat the term involving the potential Φ:

$$i\epsilon_{ijk}\sigma_k(p_i\frac{q\Phi}{2mc^2})p_j = -\hbar\epsilon_{ijk}\sigma_k(\frac{\partial}{\partial x_i}\frac{q\Phi}{2mc^2})p_j =$$
$$= -\frac{q\hbar}{2mc^2}[\frac{1}{r}\Phi'(r)]\sigma_k L_k \quad (3.75)$$

Resulting equation

$$i\hbar\frac{\partial}{\partial t}\varphi = \left[\frac{(\mathbf{p} - q\mathbf{A})^2}{2m} + q\Phi - 2\mu\mathbf{B}\cdot\mathbf{S} + \frac{q}{2m^2c^2}\frac{1}{r}\Phi'(r)\mathbf{S}\cdot\mathbf{L}\right]\varphi \quad (3.76)$$

The nonrelativistic limit of the Dirac equation is the Pauli equation including a term due to the so-called *spin-orbit coupling*. An implication is the value of the Landé g-factor of the electron, which turns out to be 2.

We formulate the Pauli equation for the Hydrogen atom. Here, we obtain $q = -e$, $\mu = -\mu_B = \frac{\hbar e}{2m_0}$:

$$i\hbar\frac{\partial}{\partial t}\varphi = \left[\frac{(\mathbf{p} + e\mathbf{A})^2}{2m} - \frac{\gamma}{r} + 2\mu_B\mathbf{B}\cdot\mathbf{S} + \frac{1}{2m^2c^2}\frac{\gamma}{r^3}\mathbf{S}\cdot\mathbf{L}\right]\varphi \quad (3.77)$$

3.4.5 Spin Orbit Coupling: Classical Interpretation

The origin of the spin orbit coupling has a clear physical explanation. Let us consider the Hydrogen atom. In the rest frame of the core there exist only an electric field. In the rest frame of the electron, the core is moving with a certain velocity $\mathbf{v}$ and generates a magnetic induction

$$\mathbf{B} = -\frac{1}{c}[\mathbf{v}\times\mathbf{E}] = \frac{1}{c^2}[\mathbf{r}\times\mathbf{v}]\frac{1}{r}\Phi'(r) = \frac{1}{mc^2}\frac{1}{r}\Phi'(r)\mathbf{L} \quad (3.78)$$

Thereby, we have assumed that the potential is radially symmetric, $\Phi(r)$, $\mathbf{E} = -\frac{\mathbf{r}}{r}\Phi'(r)$. The electron possesses a magnetic moment related with the spin

$$\mu = -\frac{\mu_B}{\hbar}\mathbf{S} \tag{3.79}$$

However, the energy of a magnetic moment in a field $\mathbf{B}$ is $E = -\mu \cdot \mathbf{B}$ such that the contribution to the Hamilton-operator for the electron is just

$$H_{SO} = -\frac{\mu\hbar}{mc^2}\frac{1}{r}\Phi'(r)\mathbf{L} \cdot \mathbf{S} \tag{3.80}$$

The missing factor 2, in comparision with the equation directly obtained in the nonrelativistic limit from the Dirac equation, eq. (3.77), is due to the fact that the formula (3.78) holds for a uniform velocity $\mathbf{v}$, whereas in the present case the motion is accelerated.

4

Coupling of Angular Momenta

4.1 Motivation: Spin-Orbit Coupling

As we have seen the interaction between the spin of the electron and the motion of the nucleus in the hydrogen atom leads to a contribution in the Pauli equation of the form

$$H = H_0 + a(r)\mathbf{L} \cdot \mathbf{S} \tag{4.1}$$

This contribution underlies the hyperfine splitting of the spectral lines of hydrogenlike atoms. In order to determine the energy eigenvalues it is convenient to rewrite the product $\mathbf{L} \cdot \mathbf{S}$ using the following identity:

$$\mathbf{L} \cdot \mathbf{S} = \frac{1}{2}[(\mathbf{L} + \mathbf{S})^2 - \mathbf{L}^2 - \mathbf{S}^2] \tag{4.2}$$

It is straightforward to consider the operator of the total angular momentum,

$$\mathbf{J} = \mathbf{L} + \mathbf{S} \tag{4.3}$$

As we shall discuss in the following, it is possible to show that the operator $\mathbf{J}$ obeys the following commutation rules:

$$[\mathbf{J}^2, \mathbf{L}^2] = 0 \quad , \quad [\mathbf{J}^2, \mathbf{S}^2] = 0 \quad , \quad [\mathbf{L}^2, \mathbf{S}^2] \tag{4.4}$$

Furthermore, the operator J_z commutes with $\mathbf{J}^2$, $\mathbf{L}^2$, $\mathbf{S}^2$. As a consequence there are common eigenvectors. Using these eigenvectors, the calculation of the energy eigenvalues of the time independent Pauli equation becomes possible.
    Proof:

$$[\mathbf{J}^2, J_z] = 2[\mathbf{L} \cdot \mathbf{S}, L_z + S_z] = 2[\mathbf{L}, L_z] \cdot \mathbf{S} + 2[\mathbf{S}, S_z] \cdot \mathbf{L} = 0 \tag{4.5}$$

4.2 Introductory Example: Two Spin 1/2

As a simple example we consider the coupling of two spins, described by the Hamilton operator

$$H = \gamma \mathbf{S}_1 \cdot \mathbf{S}_2 \tag{4.6}$$

Each spin can be described by a state vector in a two dimensional Hilbert space $H_{1/2}$ with basis $|+>, |->$. The Hilbert space for the two spins can be spanned by the vectors, which form a basis of the product space $H_{1/2} \times H_{1/2}$

$$|++> = |\frac{1}{2}> |\frac{1}{2}>$$
$$|+-> = |\frac{1}{2}> |-\frac{1}{2}>$$
$$|-+> = |-\frac{1}{2}> |\frac{1}{2}>$$
$$|--> = |-\frac{1}{2}> |-\frac{1}{2}> \tag{4.7}$$

The basis vectors are eigenvectors of the set of operators $\mathbf{S}_1^2$, S_{1z}, $\mathbf{S}_2^2$, S_{2z}. However, the operators S_{1z} and S_{2z} do not commute with the Hamiltonian H and we conclude that the vectors of the product basis are not all eigenvectors of the Hamilton operator.

However, the Hamiltonian commutes with the set of operators $\mathbf{S}^2$, S_z, $\mathbf{S}_1^2$, $\mathbf{S}_2^2$. We denote these eigenvectors by

$$|(S_1, S_2), S, m> = |(\frac{1}{2}, \frac{1}{2})S, m> \tag{4.8}$$

They obey the eigenvalue problems

$$S_1^2|(S_1, S_2)S, m> = \hbar^2 S_1(S_1 + 1)|(S_1, S_2)S, m>$$
$$S_2^2|(S_1, S_2)S, m> = \hbar^2 S_2(S_2 + 1)|(S_1, S_2)S, m>$$
$$S^2|(S_1, S_2)S, m> = \hbar^2 S(S + 1)|(S_1, S_2)S, m>$$
$$S_z|(S_1, S_2)S, m> = \hbar m|(S_1, S_2)S, m> \tag{4.9}$$

In the following we shall construct these eigenvectors as a superposition of the product basis

$$|(S_1, S_2), S, m> = a|++> + b|+-> + c|-+> + d|--> \tag{4.10}$$

The coefficients a,b,c,d are denoted as Clebsch-Gordon coefficients.

We know that the quantum number $m = m_1 + m_2$, so that m can take the values $m = 1, 0, -1$.

Furthermore, we know that $S = |m|$. Therefore, we have the two possible values $S = 0$, $S = 1$.

Let us know start to construct the normalized statevector

$$|(\frac{1}{2}, \frac{1}{2}), 1, 1> = |++> \tag{4.11}$$

The normalized state vector $|(\frac{1}{2}, \frac{1}{2}), 1, 0>$ is obtained by applying the operator S_-. Thereby, we exploit the relationship

$$S_{\pm}|(s_1, s_2), S, m> = \sqrt{S(S+1) - m(m \pm 1)}|(s_1, s_2), S, m-1> \tag{4.12}$$

This yields

$$
\begin{aligned}
S_-|(\frac{1}{2}, \frac{1}{2})1, 1> &= \sqrt{2}|(\frac{1}{2}, \frac{1}{2})1, 0> \\
&= (S_{1,-} + S_{2,-})|++> = \sqrt{\frac{3}{4} + \frac{1}{4}}(|+->+|-+>) \\
&= |-+>+|+->
\end{aligned} \tag{4.13}
$$

This yields the eigenvector

$$|(\frac{1}{2}, \frac{1}{2})1, 0> = \frac{1}{\sqrt{2}}[|-+>+|+->] \tag{4.14}$$

Furthermore,

$$
\begin{aligned}
S_-|(\frac{1}{2}, \frac{1}{2})1, 0> &= \sqrt{2}|(\frac{1}{2}, \frac{1}{2}), 1, -1> \\
&= \frac{1}{\sqrt{2}}[|-->+|-->]
\end{aligned} \tag{4.15}
$$

This leads to the eigenvector

$$|(\frac{1}{2}, \frac{1}{2})1, -1> = |--> \tag{4.16}$$

Up to now, we have constructed the three eigenfunctions with $S = 1$, $m = -1, 0, 1$. It remains to determine the fourth eigenfunction, which has the eigenvalues $S = 0, m = 0$. This eigenvector has to be orthogonal with respect to the $|(\frac{1}{2}, \frac{1}{2})1, m>$, $m = 0, \pm 1$. This leads us to

$$|(\frac{1}{2}, \frac{1}{2}), 0, 0> = \frac{1}{\sqrt{2}}[|-+> -|+->] \tag{4.17}$$

We can now summarize our new basis, which is composed of two multipletts, a triplett with $S = 1$, $-1 \le m \le 1$ and a singulett $S = 0$, $m = 0$.

$$|(\frac{1}{2}, \frac{1}{2}), S, M> = \begin{bmatrix} |(\frac{1}{2}, \frac{1}{2}), 1, 1> = |++> \\ |(\frac{1}{2}, \frac{1}{2}), 1, 0> = \frac{1}{\sqrt{2}}[|-+>+|+->] \; Triplett \\ |(\frac{1}{2}, \frac{1}{2}), 1, -1> = |--> \\ |(\frac{1}{2}, \frac{1}{2}), 0, 0> = \frac{1}{\sqrt{2}}[|-+> -|+->] \; Singulett \end{bmatrix} \tag{4.18}$$

The Triplett states are symmetric with respect to an exchange of the spins. The Singulett state is antisymmetric.

4.2.1 Clebsch-Gordon Coefficients

The new basis is found as a superposition of the product basis $|\frac{1}{2}, m_1; \frac{1}{2}, m_2 >$ with different m_1 and m_2:

$$|(\frac{1}{2}, \frac{1}{2}), S, m >= \sum_{m_1, m_2} C(\frac{1}{2}, m_1; \frac{1}{2}, m_2 | S, m) |\frac{1}{2}, m_1; \frac{1}{2}, m_2 > \qquad (4.19)$$

The so-called Clebsch-Gordon coefficients $C(\frac{1}{2}m_1, \frac{1}{2}m_2 | S, m)$ obey the selection rule

$$m = m_1 + m_2 \qquad (4.20)$$

The Clebsch-Gordan coefficients can be obtained from (4.18).

4.2.2 Energy levels of a two-Spin Hamilton Operator

Since the opertors $\mathbf{S}^2$, S_z, $\mathbf{S}_1^2$, $\mathbf{S}_2^2$ commute with the Hamilton Operator:

$$H = 2a\mathbf{S}_1 \cdot \mathbf{S}_2 = a[\mathbf{S}^2 - \mathbf{S}_1^2 - \mathbf{S}_2^2] \qquad (4.21)$$

the states $|(\frac{1}{2}, \frac{1}{2})S, M >$ are eigenstates of the Hamiltonoperator. The Triplet states all have the same energy eigenvalues, since H does not depend on S_z

$$H|1, 1 > = a\hbar^2[2 - \frac{3}{4} - \frac{3}{4}]|1, 1 >= a\hbar^2 \frac{1}{2}]|11 >$$
$$H|1, 0 > = a\hbar^2[2 - \frac{3}{4} - \frac{3}{4}]|1, 0 >= a\hbar^2 \frac{1}{2}]|11 >$$
$$H|1, -1 > = a\hbar^2[2 - \frac{3}{4} - \frac{3}{4}]|1, -1 >= a\hbar^2 \frac{1}{2}]|11 > \qquad (4.22)$$

The Singulett state has the energy eigenvalue

$$H|0, 0 >= -a\hbar^2 \frac{3}{2}|0, 0 > \qquad (4.23)$$

4.3 Orbital Angular Momentum and Spin 1/2

In this section we adress the coupling of orbital momentum and spin. This will be important for the consideration of the spin-orbit coupling of the electron in hydrogenlike atoms.

We start by representing the eigenstates of the operators L^2, S^2, J^2, J_z $|(l, \frac{1}{2}), j, m >$ using the Clebsch-Gordon coefficients $C(l, m_l; \frac{1}{2}, m_s | j, m)$ in terms of the product basis $|l, m_l >, \frac{1}{2}, m_s >$:

$$|(l, \frac{1}{2})j, m >= \sum_{m_l, m_s} C(l, m_l; \frac{1}{2}, m_s | jm) |l, m_l; \frac{1}{2}, m_s > \qquad (4.24)$$

Thereby,

$$\mathbf{J}^2|(l,\frac{1}{2})j,m> = \hbar^2 j(j+1)|(l,\frac{1}{2})j,m>$$

$$J_z|(l,\frac{1}{2})j,m> = \hbar^2 j(j+1)|(l,\frac{1}{2})j,m>$$

$$\mathbf{L}^2|(l,\frac{1}{2})j,m> = \hbar^2 l(l+1)|(l,\frac{1}{2})j,m>$$

$$\mathbf{S}^2|(l,\frac{1}{2})j,m> = \hbar^2 s(s+1)|(l,\frac{1}{2})j,m> \tag{4.25}$$

As a first step, we proof that the Clebsch-Gordon coefficients are different from zero provided

$$m = m_l + m_s \tag{4.26}$$

To this end we calculate

$$J_z|(l,\frac{1}{2})j,m> = \sum_{m_l,m_s} C(l,m_l;\frac{1}{2},m_s|jm)(L_z+S_z)|l,m_l;\frac{1}{2},m_s>$$

$$= \sum_{m_l,m_s} C(l,m_l;\frac{1}{2},m_s|jm)\hbar(m_s+m_l)|l,m_l;\frac{1}{2},m_s>$$

$$= m\hbar \sum_{m_l,m_s} C(l,m_l;\frac{1}{2},m_s|jm)(L_z+S_z)|l,m_l;\frac{1}{2},m_s> \tag{4.27}$$

We shall now construct the new basis starting with the eigenvectors $|(l,s),j_{max},m_{max}>$ with maximal value of m. Clearly, $j_{max}=m_{max}$. This maximal value is obtained for

$$m_{max} = j_{max} = m_{max,l} + m_{max,s} = l + \frac{1}{2} \tag{4.28}$$

The maximal value of j is then $j = l + \frac{1}{2}$ and the corresponding eigenfunction is

$$|(l,\frac{1}{2}),l+\frac{1}{2},l+\frac{1}{2}> = |l,m;\frac{1}{2},\frac{1}{2}> \tag{4.29}$$

The Multiplett $j = l + 1/2$

We determine now all eigenvectors of the multiplett with eigenvectors $|(l,s)l+\frac{1}{2},m>$, $-(l+\frac{1}{2} \le m \le l+\frac{1}{2}$. They can be obtained by successively applying the operator J_-:

$$J_-|(l,\frac{1}{2})l+\frac{1}{2},l+\frac{1}{2}> = \hbar\sqrt{2l+1}|(l,\frac{1}{2})l+\frac{1}{2},l-\frac{1}{2}>$$

$$= \hbar\sqrt{2l}|l,l-1;\frac{1}{2}\frac{1}{2}> + \hbar|ll;\frac{1}{2}-\frac{1}{2}> \tag{4.30}$$

This yields the eigenvector

$$|(l,\frac{1}{2})l+\frac{1}{2},l-\frac{1}{2}> = \sqrt{\frac{2l}{2l+1}}|l,l-1;\frac{1}{2}\frac{1}{2}> + \sqrt{\frac{1}{2l+1}}|ll;\frac{1}{2}-\frac{1}{2}> \tag{4.31}$$

The Mutiplett with $j = l - 1/2$

We have to determine the multiplett with $j = 1 - \frac{1}{2}$ and start by determining the eigenvector

$$|(l, 1/2), l - 1/2, l - 1/2 >= \sqrt{\frac{1}{2l+1}}|l, l-1; \frac{1}{2}, \frac{1}{2} > - \sqrt{\frac{2l}{2l+1}}|l, l, \frac{1}{2}, -\frac{1}{2} > \tag{4.32}$$

by the condition that it is orthogonal to the vector $|(l, 1/2), l + 1/2, l - 1/2 >$, and all the other eigenvectors of the multiplett with $j = l + \frac{1}{2}$.

Application of the ladder operator J_- to the eigenvectors $(l, 1/2), l + 1/2, l - 1/2 >, (l, 1/2), l - 1/2, l - 1/2 >$ yields the further eigenvectors.

By this way, we have determined

$$2(l + \frac{1}{2}) + 1 + 2(l - \frac{1}{2}) + 1 = 2(2l + 1) \tag{4.33}$$

eigenvectors. Since the product basis has also $2(2l + 1)$ eigenvectors, we have found a complete basis of eigenvectors.

The Clebsch-Gordon coefficients can be read off from the relations

Representation in terms of Spinors

$$|l + 1/2, l, 1/2, l + 1/2 >= Y_{lm} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \tag{4.34}$$

$$|l + 1/2, l, 1/2, l - 1/2 >= \sqrt{\frac{2l}{2l+1}} Y_{lm-1} \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \sqrt{\frac{1}{2l+1}} Y_{lm} \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{4.35}$$

Application of J_- yields

$$|l + 1/2, l, 1/2, 1/2, l - 1/2 > ......|l + 1/2, l, 1/2, 1/2, -l - 1/2 > \tag{4.36}$$

$$|(l, 1/2), l - 1/2, , l - 1/2 >= \sqrt{\frac{1}{2l+1}} Y_{lm} \begin{pmatrix} 1 \\ 0 \end{pmatrix} - \sqrt{\frac{2l}{2l+1}} Y_{lm-1} \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{4.37}$$

Application of J_- yields the eigenvectors

$$|(l, 1/2), l - 1/2, , l - 1/2 > ......|(l, 1/2), l - 1/2, , -l - 1/2 > \tag{4.38}$$

Nomenclature:

$$l = 0 \ {}^2S_{1/2}$$
$$l = 1 \ {}^2P_{3/2} \ \ {}^2P_{1/2}$$
$$l = 2 \ {}^2D_{5/2} \ \ {}^2D_{3/2}$$
$$l = 3 \ {}^2F_{7/2} \ \ {}^2F_{5/2}$$

General

$$n^{2S+1}P_J \tag{4.39}$$

Contribution of Spin-Orbit Coupling to Fine Structure

Energy splitting due to spin-orbit coupling:
    The energy splitting due to spin-orbit coupling is obtained through thr formula

$$H = \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{2m_0^2 c^2} \frac{1}{r^3} \mathbf{L} \cdot \mathbf{S} = \frac{a(r)}{2}[\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2] \tag{4.40}$$

    The energy splitting is given by

$$E_{SO} = \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{2m_0^2 c^2} < R_{nl}(r)|\frac{1}{r^3}|R_{nl}(r) > \frac{1}{2}[(l+\frac{1}{2})(l+\frac{3}{2} - l(l+1) - \frac{3}{4}]$$

$$= \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{2m_0^2 c^2} < R_{nl}(r)|\frac{1}{r^3}|R_{nl}(r) > \frac{1}{2}(j - \frac{1}{2}) \tag{4.41}$$

    The fine splitting of the hydrogen atom consists of three contributions which are of the order α^2, where α denotes Sommerfeld's fine structure constant

$$alpha = \frac{e^2}{4\pi\epsilon_0 \hbar c} \approx \frac{1}{137,..} \tag{4.42}$$

The first contribution is a relativistic correction to the kinetic energy of the electron

$$H = -\frac{p^4}{8m_0^3 c^2} \tag{4.43}$$

This contribution comes from the expansion

$$E = \sqrt{m_0^2 c^4 + c^2 p^2} = m_0 c^2 + \frac{p^2}{2m_0} - \frac{p^4}{8m_0^3 c^2} \tag{4.44}$$

The second contribution is the spin-orbit coupling. The third contirbution is due to the so-called Darwin term

$$H_{Darwin} = \frac{\hbar^2}{8m_0^2 c^4} 4\pi \frac{Ze^2}{4\pi\epsilon_0} \delta(r) \tag{4.45}$$

    The total effect has the form

$$E_{FS} = -\frac{E_n \alpha^2}{n}(\frac{1}{j+1/2} - \frac{3}{4n})Z^2 \tag{4.46}$$

    We take a fix value $S = 1/2$ and l. In this case J can talke the values

$$J = l + \frac{1}{2} \qquad J = l - \frac{1}{2} \tag{4.47}$$

The corresponding values of H are given by

$$H = a(r)\hbar^2[(l+\frac{1}{2})(l+\frac{3}{2}) - l(l+1) - \frac{3}{4}] = a(r)l\hbar^2 \tag{4.48}$$

there is a $2(l + 1/2) + 1 = 2l + 2$-fold degeneracy with respect to m.

$$H = a(r)\hbar^2[(l - \frac{1}{2})(l + \frac{1}{2}) - l(l+1) - \frac{3}{4}] = a(r)(-(l+1))\hbar^2 \qquad (4.49)$$

There is a $2l$-fold degeneracy.

4.4 Coupling of Angular Momenta: General Treatment

Angular moment

$$\mathbf{J_1}, \mathbf{J_2} \qquad (4.50)$$

Eigenvalue problems:

$$\begin{aligned}
\mathbf{J_1^2}|j_1, m_1 > &= \hbar^2 j_1(j_1 + 1)|j_1, m_1 > \\
J_{z,1}|j_1, m_1 > &= \hbar m_1|j_1, m_1 > \\
\mathbf{J_2^2}|j_2, m_2 > &= \hbar^2 j_2(j_2 + 1)|j_2, m_2 > \\
J_{z,2}|j_2, m_2 > &= \hbar m_2|j_2, m_2 >
\end{aligned} \qquad (4.51)$$

The product Hilbert space is the direct product of the spaces corresponding to the angular momentum operators $\mathbf{J}_1$, $\mathbf{J}_2$. This space is spanned by the vectors

$$|j_1 m_1; j_2 m_2 >= |j_1, m_1 > |j_2, m_2 > \qquad (4.52)$$

Expectation values are calculated by the scalar products.

The dimension of the product space is

$$dim[H(J_1) \times H(J_2)] = (2J_1 + 1)(2J_2 + 1) \qquad (4.53)$$

4.5 The Operator of Total Angular momentum, $\mathbf{J} = \mathbf{J_1} + \mathbf{J_2}$

Since the single operators form an algebra

$$[J_{i,1}, J_{j,1}] = i\hbar\epsilon_{ijk}J_{k,1} \qquad (4.54)$$

$$[J_{i,2}, J_{j,2}] = i\hbar\epsilon_{ijk}J_{k,2} \qquad (4.55)$$

the operators of the total angular momentum also defines an algebra momentum.

$$[J_i, J_j] = i\hbar\epsilon_{ijk}J_k \qquad (4.56)$$

We denote the eigenfunctions by

$$\begin{aligned}
\mathbf{J^2}|j, m > &= \hbar^2 j(j + 1)|j, m > \\
J_z|j, m > &= \hbar m|j, m >
\end{aligned} \qquad (4.57)$$

In the following we shall construct these eigenfunctions from the basis of the product space, (4.52). To this end we notice, however, that the following commutator relationships hold:

$$\left[\mathbf{J}^2, \mathbf{J}_1^2\right] = 0$$
$$\left[\mathbf{J}^2, \mathbf{J}_2^2\right] = 0$$
$$\left[\mathbf{J}^2, \mathbf{J}_z\right] = 0$$
$$\left[\mathbf{J}_1^2, \mathbf{J}_z\right] = 0$$
$$\left[\mathbf{J}_2^2, \mathbf{J}_z\right] = 0 \tag{4.58}$$

This indicates that there exist common eigenvectors, which we denote by

$$|j, j_1, j_2, m> \tag{4.59}$$

Since the operators $\mathbf{J}$ are operators of angular momentum we have the relationships

$$\mathbf{J}^2|j, j_1, j_2, m> = \hbar^2 j(j+1)|j, j_1, j_2, m>$$
$$J_z|jj_1j_2m> = \hbar m|j, j_1, j_2, m> \tag{4.60}$$

Furthermore, we know that j can take the values

$$j = 0, \frac{1}{2}, 1, \frac{3}{2}, \dots \tag{4.61}$$

and

$$-j \le m \le j \tag{4.62}$$

Since the eigenvectors are simultaneously eigenvectors of the operators $\mathbf{J}_1$, $\mathbf{J}_2$ the following relations hold:

$$\mathbf{J}_1^2|j, j_1, j_2, m> = \hbar^2 j_1(j_1+1)|j, j_1, j_2 m>$$
$$\mathbf{J}_2^2|j, j_1, j_2, m> = \hbar^2 j_2(j_2+1)|j, j_1, j_2 m> \tag{4.63}$$

Let us now determine the eigenfunctions as a superposition of the basis of the product space.

$$|j, j_1, j_2, m> = \sum_{m_1, m_2} C(jm, j_1m_1, j_2m_2)|j_1, m_1; j_2, m_2> \tag{4.64}$$

The coefficients are denoted as Clebsch-Gordan coefficients. Sometimes, they are also called Wigner coefficients.

We have to determine the possible eigenvalues j and m, as well as the corresponding eigenvectors $|j, j_1, j_2, m>$. This will be done in an operational way in several steps.

4.5.1 First step: Determination of m

We apply the operator J_z to the eigenstate $j, j_1, j_2, m >$. The definition yields

$$J_z|j, j_1, j_2, m > = m\hbar|j, j_1, j_2, m >$$
$$= \sum_{m_1, m_2} C(jm, j_1m_1, j_2m_2)\hbar(m_1 + m_2)|j_1m_1 > |j_2m_2 > \quad (4.65)$$

We have used the identity

$$[J_{z1} + J_{z2}]|j_1m_1; j_2m_2 >= \hbar(m_1 + m_2)|j_1m_1; j_2m_2 > \quad (4.66)$$

indicating that

$$C(jm, j_1m_1, j_2m_2) = \delta_{m, m_1 + m_2}\tilde{C}_{jm, j_1m_1, j_2m_2} \quad (4.67)$$

As a consequence, the eigenvalue m and the eigenvalues m_1, m_2 are related by

$$m = m_1 + m_2 \quad (4.68)$$

4.5.2 Multiplets

Due to the inequality

$$-j \leq m \leq j \quad (4.69)$$

there are (2j+1) eigenstates of the operator J_z, which are denoted as multiplets (singulets j=0, dublets j=1/2, triplets j=1, quadruplets j=3/2,etc.)

We look for the eigenfunction with maximal value of m. Due to (4.68) the maximal value of m is $m = j_1 + j_2$. the corresponding value of j is $j = j_1 + j_2$. The corresponding state is

$$|(j_1 + j_2), j_1, j_2, (j_1 + j_2) > \quad (4.70)$$

We have to represent this state as a superposition of the product states (4.52). Up to a phase factor, there is only a single product vector, which can be used for a representation

$$|(j_1 + j_2)j_1j_2(j_1 + j_2) >= |j_1j_1 > |j_2j_2 >= |j_1j_1; j_2j_2 > \quad (4.71)$$

The other states corresponding to the $j_1 + j_2$-multiplet can be obtained by the application of the ladder operator J_-

$$J_-|j, j_1, j_2, m >= \hbar\sqrt{j(j+1) - m(m-1)}|j, j_1, j_2, m - 1 > \quad (4.72)$$

The first application yields

$$J_-|j_1 + j_2, j_1, j_2, j_1 + j_2 > = \hbar\sqrt{2(j_1 + j_2)}|j_1 + j_2, j_1, j_2, j_1 + j_2 - 1 >$$
$$= \hbar[\sqrt{2j_1}|j_1j_1 - 1; j_2j_2 > + + \sqrt{2j_2}|j_1j_1; j_2j_2 \quad (4.73)$$

As a consequence, we obtain

$$|j_1+j_2, j_1, j_2, j_1+j_2-1> = \sqrt{\frac{j_1}{j_1+j_2}}|j_1, j_1-1; j_2 j_2> + \sqrt{\frac{j_2}{j_1+j_2}}|j_1, j_1; j_2, j_2-1>$$
$$(4.74)$$

from where we can read off the Clebsch Gordan coefficients.

It is important to notice that this eigenvector is normalized. The states $|j_1 + j_2, j_1, j_2, m>$ with descending values of m are obtained by a subsequent application of the operator J_-. We obtain $2(j_1 + j_2) + 1$ eigenvectors.

4.5.3 Further Multiplets

There is a further state, which is spanned by the two eigenvectors

$$|j_1, j_1; j_2, j_2 - 1>   , |j_1, j_1 - 1; j_2, j_2> \qquad (4.75)$$

This eigenvector has $m = j_1 + j_2 - 1$ and, in turn, belongs to the eigenvector $|j_1 + j_2 - 1, j_1, j_2, j_1 + j_2 - 1$. However, since this vector has to be orthogonal to the vector $|j_1 + j_2, j_1, j_2, j_1 + j_2 - 1$,

$$< j_1 + j_2 - 1, j_2, j_1, j_1 + j_2 - 1|j_1 + j_2, j_1, j_2, j_1 + j_2 - 1> = 0 \qquad (4.76)$$

it is uniquely given by

$$|j_1+j_2-1, j_1, j_2, j_1+j_2-1> = \sqrt{\frac{j_2}{j_1+j_2}}|j_1, j_1-1; j_2 j_2> - \sqrt{\frac{j_1}{j_1+j_2}}|j_1, j_1; j_2, j_2-1>$$
$$(4.77)$$

Application of the ladder operator L_- yields the multiplet corresponding to $j = j_1 + j_2 - 1$. We obtain $2(j_1 + j_2 - 1) + 1$ eigenvectors.

4.5.4 Iteration of the Procedure

The procedure starts anew. We obtain the vector $|j_1+j_2-1, j_1, j_2, j_1+j_2-2>$ as a linear combination of $j_1, j_1 - 2, j_2, j_2>$, $|j_1, j_1 - 1, j_2, j_2 - 1>$ and $j_1, j_1, j_2, j_2 - 2>$. These vectors, however, can be used to form a further vector, $|j_1 + j_2 - 2, j_1, j_2, j_1 + j_2 - 2>$. It has to be orthogonal with respect to $|j_1 + j_2 - 1, j_1, j_2, j_1 + j_2 - 2>$, as well as $j_1 + j_2, j_1, j_2, j_1 + j_2 - 2>$. This fact uniquely defines the vector $j_1 + j_2 - 2, j_1, j_2, j_1 + j_2 - 2>$.

If $j_2 > j_1$, this procedure terminates after $2j_1$ steps. This means

$$j \geq |j_2 - j_1| \qquad (4.78)$$

This condition has to be compared with the classical addition of angular momentum, which follows from the inequality

$$|\mathbf{J}_1 - \mathbf{J}_2 \leq |\mathbf{J}| \leq |\mathbf{J}_1 + \mathbf{J}_2| \qquad (4.79)$$

5

Schrödinger-, Heisenberg-, Interaction Picture

In this chapter we shall discuss various ways to deal with the dynamics of quantum systems. We shall introduce the so-called Schrödinger-, Heisenberg-, and interaction pictures. The starting point is a formal solution of the Schrödinger equation.

5.1 Formal Solution of the Schrödinger Equation

5.1.1 Time Independent Hamiltonian H

The solution of the Schrödinger equation with a time independent Hamiltonian H can be represented by the formal expression

$$|\psi(t)> = e^{-i/\hbar H t}|\psi(0)> \tag{5.1}$$

Thereby we define the function $F(A)$ of an operator A by the formal Taylor expansion of the function $F(x)$:

$$F(x) = \sum_{k=0} F_k x^k \tag{5.2}$$

and obtain

$$F(A) = \sum_{k=0} F_k x^k \tag{5.3}$$

The operator

$$U(t) = e^{-\frac{i}{\hbar}Ht} = \sum_{k=0} t^k \frac{1}{k!}\left(-\frac{i}{\hbar}\right)^k H^k \tag{5.4}$$

is given in terms of the Taylor series expansion of the exponential function e^x.

We now calculate the temporal derivative of the operator $U(t)$. To this end we use the Taylor expansion and calculate

$$\frac{d}{dt}U(t) = \frac{d}{dt}\sum_{k=0} t^k \frac{1}{k!}\left(-\frac{i}{\hbar}\right)^k H^k$$

$$= [\sum_{k=1} t^{k-1}\frac{1}{(k-1)!}\left(-\frac{i}{\hbar}\right)^{-1} k H^{k-1}]\frac{-i}{\hbar}H \tag{5.5}$$

The result can be summarized as

$$i\hbar\frac{d}{dt}U(t) = HU(t) = U(t)H \tag{5.6}$$

It is transparent from (5.5) that the operators H and $U(t)$ commute.

The time evolution operator $U(t)$ is an unitary operator, i.e.

$$U^\dagger(t)U(t) = E \tag{5.7}$$

5.1.2 Time Ordered Exponential

Liebe Frau Gurevich: Dies muss nicht gemacht werden

$$|\psi(t)> = |\psi(0)> + \frac{1}{i\hbar}\int_0^t dt' H|\psi(t')> \tag{5.8}$$

Iteration yields

$$|\psi(t)> = |\psi(0)> + \frac{1}{i\hbar}\int_0^t dt' H|\psi(0)> \frac{1}{(i\hbar)^2}\int_0^t dt' H\int_0^{t'} dt'' H|\psi(0)> \tag{5.9}$$

Formal Solution for time dependent Hamilton operator

$$|\psi(t)> = Te^{-i/\hbar\_0^t dt' H(t')}|\psi(0)> \tag{5.10}$$

5.2 Schrödinger Picture

The temporal evolution of the state vector of a quantum mechanical system is given by the Schrödinger equation. The knowledge of the evolution of the state vector allows one to calculate the expectation of a physical quantity $A(t)$, which may itself be explicitly time dependent, as the expectation value of the operator A(t):

$$< \psi(t)|A(t)|\psi(t) > \tag{5.11}$$

5.3 Heisenberg-Picture

We can use the formal solution (5.1) to calculate the expectation value of an operator A, which we assume to be time independent, according to

$$< \psi(t)|A|\psi(t) > = < e^{-i/\hbar Ht}\psi(0)|A|e^{-i/\hbar Ht}\psi(0) >$$
$$= < \psi(0)|e^{i/\hbar Ht}Ae^{-i/\hbar Ht}|\psi(0) > \qquad (5.12)$$

This relation suggests to introduce the operator $A_H(t)$ in the so-called *Heisenberg picture*

$$A_H(t) = e^{i/\hbar Ht}Ae^{-i/\hbar Ht} \qquad (5.13)$$

Thus, there are two possibilities to calculate the expectation of $A(t)$,

$$< \psi(t)|A|\psi(t) > = < \psi(0)|A_H(t)|\psi() > \qquad (5.14)$$

either using the time dependent state vector $|\psi(t) >$ and the operator $A(t)$ (the so-called *Schrödinger picture*) or the time independet initial state vector and the operator $A_H(t)$ in the *Heisenberg picture*.

In the Heisenberg picture, the state vector is constant, where as the operator $A_H(t)$ changes in time.

There are certain relationships for operators A, B in the Schrödinger and Heisenberg picture.

The first relation concernes commutators:

$$[A_H, B_H] = \{[A, B]\}_H \qquad (5.15)$$

This relation means that the commutator of two operators in the Heisenberg picture equals the commutator of the operators in the Schrödinger picture transformed to the Heisenberg picture.

The proof is strightforward:

$$[A_H, B_H] = e^{\frac{i}{\hbar}Ht}Ae^{-\frac{i}{\hbar}Ht}e^{\frac{i}{\hbar}Ht}Be^{-\frac{i}{\hbar}Ht} - e^{\frac{i}{\hbar}Ht}Be^{-\frac{i}{\hbar}Ht}e^{\frac{i}{\hbar}Ht}Ae^{-\frac{i}{\hbar}Ht}$$
$$= e^{\frac{i}{\hbar}Ht}[AB - BA]e^{-i\hbar Ht} = \{[A, B]\}_H \qquad (5.16)$$

The second relation concernes the Hamilton operator:

$$H_H = e^{\frac{i}{\hbar}Ht}He^{-\frac{i}{\hbar}Ht} = H \qquad (5.17)$$

This means explicitly for a quantum mechanical particle moving in the potential $U(x)$

$$H = \frac{\mathbf{p}^2}{2m} + U(\mathbf{x}) = \frac{\mathbf{p}_H^2}{2m} + U(\mathbf{x}_H) \qquad (5.18)$$

5.3.1 Heisenberg's Evolution Equation

It is convenient to determine the time dependence of the operator $A_H(t)$ by an evolution equation. To this end we calculate

$$\frac{d}{dt}A_H(t) = \frac{i}{\hbar}e^{\frac{i}{\hbar}Ht}[HA(t) - A(t)H]e^{-\frac{i}{\hbar}Ht} \qquad (5.19)$$

We can insert

$$E = e^{-\frac{i}{\hbar}Ht} e^{\frac{i}{\hbar}Ht} \tag{5.20}$$

and obtain the so-called *Heisenberg evolution equation* of the operator $A_H(t)$:

$$\frac{d}{dt} A_H(t) = \frac{i}{\hbar}[H, A_H(t)] \tag{5.21}$$

5.3.2 Relation to Poisson Brackets

We can compare this evolution equation with the evolution equation of a quantity $A(\mathbf{q}, \mathbf{p})$ in classical mechanics.

$$\frac{d}{dt} A(\mathbf{q}(t), \mathbf{p}(t)) = \dot{\mathbf{q}}(t) \cdot \nabla_q A + \dot{\mathbf{p}}(t) \cdot \nabla_p A \tag{5.22}$$

With the help of the Hamiltonian canonical equations we obtain

$$\frac{d}{dt} A(\mathbf{q}(t), \mathbf{p}(t), t = \nabla_p H \cdot \nabla_q A - \nabla_q H \cdot \nabla_p A$$
$$= \{H, A\} \tag{5.23}$$

The latter equation determines the Poisson bracket

$$\{H, A\} = \nabla_p H \cdot \nabla_q A - \nabla H_q \cdot \nabla_p A \tag{5.24}$$

We see that the formulation of classical mechanics based on the Poisson bracket has its counterpert in the Heisenberg evolution equation for the operator A_H in the Heisenberg picture.

The analogy between the formulation of classical Hamiltonian dynamics on the basis of the Poisson bracket and the Heisenberg operator allows one to perform the following quantization procedure, which may be considered to be an analogue of the quantization procedure based on Jordan's rule.

The quantization is summarized in the table

Classical Mechanics	Quantum Mechanics
Hamilton function $H(\mathbf{p}, \mathbf{q})$	Hamilton operator H
Physical Observable $A(\mathbf{q}, \mathbf{p})$	Operator A
$\frac{d}{dt}A = \{H, A\}$	$\frac{d}{dt}A_h = \frac{i}{\hbar}[H, A_H]$

5.3.3 Examples

Our first example is the harmonic oscillator with Hamiltonian

$$H = \frac{p^2}{2m} + \frac{m\omega^2}{2}x^2 \qquad (5.25)$$

The evolution equation for the operators $x_H(t)$ and $p_H(t)$ read

$$\dot{x}_H = \frac{i}{\hbar}[H, x]_H = \frac{i}{\hbar}\frac{1}{2m}[p_H^2, x_H]$$

$$\dot{p}_H = \frac{i}{\hbar}[H, p]_H = \frac{i}{\hbar}\frac{m\omega^2}{2}[x_H^2, p_H] \qquad (5.26)$$

For the commutators of two operators one can proof

$$[A_H, B_H] = \{[A, B]\}_H \qquad (5.27)$$

Since

$$[p^2, x] = p[p, x] + [p, x]p = 2\frac{\hbar}{i}p \qquad (5.28)$$

$$[x^2, p] = x[x, p] + [x, p]x = -2\frac{\hbar}{i}x \qquad (5.29)$$

we simply obtain the Heisenberg equation of motion for the operators x_H, p_H:

$$\dot{x}_H = \frac{p_H}{m}$$

$$\dot{p}_H = -m\omega_0^2 x_H \qquad (5.30)$$

It is straightforward to determine the equation of motion for the expectation values. In the Heisenberg picture we have

$$\frac{d}{dt} < \psi(0)|A_H|\psi > = < \psi(0)|\frac{d}{dt}A_H|\psi(0) > \qquad (5.31)$$

This yields

$$\frac{d}{dt} < x > = \frac{< p >}{m}$$

$$\frac{d}{dt} < p > = -m\omega^2 < x > \qquad (5.32)$$

which can be combined into

$$\frac{d^2}{dt^2} < x > = -\omega^2 < x > \qquad (5.33)$$

We now proceed to the harmonic oscillator in the occupation number representation

$$H = \hbar\omega[b^\dagger b + \frac{1}{2}] \tag{5.34}$$

We determine the Heisenberg evolution equation for the annihilation and creation operators $b^\dagger$, b. We obtain

$$\dot{b}_H = \frac{i}{\hbar}[H, b_H] = \frac{i}{\hbar}\hbar\omega[b^\dagger b, b]_H = -i\omega b_H$$

$$\dot{b}_H^\dagger = \frac{i}{\hbar}[H, b_H^\dagger] = \frac{i}{\hbar}\hbar\omega[b^\dagger b, b^\dagger]_H = i\omega b_H^\dagger \tag{5.35}$$

Thereby, we have used

$$[b^\dagger b, b] == -b \tag{5.36}$$

$$[b^\dagger b, b^\dagger] = b^\dagger \tag{5.37}$$

Therefore, the operators b, $b^\dagger$ in the interaction picture are

$$b_H(t) = e^{-i\omega t} b_S$$
$$b_H^\dagger(t) = e^{i\omega t} b_S^\dagger \tag{5.38}$$

5.4 Interaction Picture

Besides the Schrödinger and the Heisenberg picture there is the so-called Interaction picture, which is applied if the Hamilton operator can be spilt into H_0 and an interaction $W(t)$. The Schrödinger equation takes the form

$$i\hbar\frac{\partial}{\partial t}|\psi(t) > = [H_0 + W(t)]|\psi(t) > \tag{5.39}$$

The interaction picture is obtained through the ansatz

$$|\psi(t) > = e^{-i/\hbar H_0 t}|\psi_I(t) > \tag{5.40}$$

where the influence of the interaction term $W(t)$ is taken into account by the time dependence of $\psi_I(T) >$. For $W(t) \to 0$ the Interaction picture tends to the Heisenberg picture.

We can derive the evolution equation for the wave function $|\psi_I(t) >$ in the interaction picture. To this end we calculate

$$i\hbar\frac{\partial}{\partial t}e^{-i/\hbar H_0 t}|\psi_I(t) > = H_0 e^{-i/\hbar H_0 t}|\psi_I(t) > + e^{-i/\hbar H_0 t}i\hbar\frac{\partial}{\partial t}|\psi_I(t) > \tag{5.41}$$

Inserting this temporal derivative into the Schrödinger equation we obtain the evolution equation determining the time dependence of the wave function $|\psi_I(t) >$ in the interaction picture

$$i\hbar\frac{\partial}{\partial t}|\psi_I(t)> = e^{i/\hbar H_0 t}W(t)e^{-i/\hbar H t}|\psi_I(t)> \tag{5.42}$$

The expectation values of an arbitrary operator A can be evaluated according to

$$
\begin{aligned}
<\psi(t)|A(t)|\psi(t)> &= <e^{-i/\hbar H_0 t}\psi_I(t)|A(t)|e^{-i/\hbar H_0 t}\psi_I(t)> \\
&= <\psi_I(t)|e^{i/\hbar H_0 t}A(t)e^{-i/\hbar H_0 t}|\psi_I(t)> = <\psi_I(t)|A_I(t)|\psi_I(t)>
\end{aligned}
\tag{5.43}
$$

This defines the operators in the Interaction picture

$$A_I(t) = e^{i/\hbar H_0 t}A(t)e^{-i/\hbar H_0 t} \tag{5.44}$$

Application: Time dependent perturbation theory in the interaction picture

6

Perturbation Theory

6.1 Introductory Example

We consider the eigenvalue problem

$$H|\psi> = [H_0 + \epsilon W]|\psi> = E|\psi> \qquad (6.1)$$

with the symmetric 2×2 matrices

$$H_0 = \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix} \qquad , \qquad W = \begin{pmatrix} W_1 & w \\ w & W_2 \end{pmatrix} \qquad (6.2)$$

The eigenvalue problem is then related to the solution of the linear homogeneous system

$$\begin{pmatrix} E_1 + \epsilon W_1 - E & \epsilon w \\ \epsilon w & E_2 + \epsilon W_2 - E \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = 0 \qquad (6.3)$$

Nontrivial solutions are obtained provided

$$
\begin{aligned}
Det(H_0 + \epsilon W - EI) &= (E_1 + \epsilon W_1 - E)(E_2 + \epsilon W_2 - E) - \epsilon^2 w^2 \\
&= E^2 - (E_1 + E_2 + \epsilon(W_1 + W_2))E \\
&\quad + (E_1 + \epsilon W_1)(E_2 + \epsilon W_2) - \epsilon^2 w^2 = 0 \qquad (6.4)
\end{aligned}
$$

The characteristic equation can be solved

$$E_{1,2} = \frac{E_1^0 + E_2^0 + \epsilon(W_1 + W_2)}{2} \pm \sqrt{\frac{(E_1^0 - E_2^0 + \epsilon(W_1 - W_2))}{4} + \epsilon^2 w^2} \quad (6.5)$$

In order to obtain the eigenvalues for small values of ϵ, we can expand into a Taylor series with respect to the smallness parameter ϵ. To first order in ϵ we obtain

$$
\begin{aligned}
E_1 &= E_1^0 + \epsilon W_1 \\
E_2 &= E_2^0 + \epsilon W_2 \qquad (6.6)
\end{aligned}
$$

To second order in ϵ^2 the result reads

$$E_1 = E_1^0 + \epsilon W_1 + \epsilon^2 \frac{w^2}{2(E_1 - E_2)}$$

$$E_2 = E_2^0 + \epsilon W_2 + \epsilon^2 \frac{w^2}{2(E_2 - E_1)} \tag{6.7}$$

6.2 Perturbation Theory: Nondegenerate Case

In this section we shall generalize the above result to the time independent Hamilton operator:

$$[H_0 + \epsilon V]|\psi> = E|\psi> \tag{6.8}$$

We assume that the eigenfunctions $|n>$ and the eigenvalues E_n of the Hamiltonian H_0 are well-known:

$$H_0|n> = E_n^0|n> \tag{6.9}$$

In order to solve the linear eigenvalue problem we perform the following expansion

$$E = E^0 + \epsilon E^1 + \epsilon^2 E^2 + ...$$

$$|\psi> = |\psi^0> + \epsilon|\psi^1> + \epsilon^2|\psi^2> \tag{6.10}$$

Inserting this ansatz into the eigenvalue problem and collecting terms of the same order in ϵ we find

$$H_0|\psi^0> - E^0|\psi^0> = 0$$
$$H_0|\psi^1> - E^0|\psi^1> = -E^1|\psi^0> - V|\psi^0>$$
$$H_0|\psi^2> - E^0|\psi^2> = -E^2|\psi^0> - E^1|\psi^1> - V|\psi^1> \tag{6.11}$$

In general, one could write down the expansion in n-the order.

We shall now solve this set of equations order by order. In zeroth order we obtain the solution

$$E^0 = E_n^0 \quad , \quad |\psi^0> = |n> \tag{6.12}$$

where we consider in detail a perturbation of the n-th eigenfunction corresponding to the eigenvalue E_n^0.

Let us now preceed to the solution of the first order equation

$$(H_0 - E_n^0)|\psi^1> = E^1|n> - V|n> \tag{6.13}$$

We can immediately determine the first order correction E_n^1 to the energy value E_n^0 by forming the scalar product of this equation with the eigenvector $|n>$:

$$< n|(H_0 - E_n^0)|\psi^1 > = E^1 < n|n > - < n|V|n > \qquad (6.14)$$

The left hand side, however is zero, since

$$< n|(H_0 - E_n^0)|\psi^1 > = < (H_0 - E_n^0)n|\psi^1 > = (E_n^0 - E_n^0) < n|\psi > = 0 \quad (6.15)$$

As a result, we obtain the first order correction

$$E_n^1 = < n|V|n > \qquad (6.16)$$

We proceed to determine the first order correction to the eigenvector, which is determined by eq. (6.13). To this end we perform an expansion of the first order correction $|\psi^1 >$ in terms of the complete set of eigenvectors $|n >$

$$|\psi^1 > = \sum_k c_n^k |k > \qquad (6.17)$$

Equation (6.13) yields with the help of $H_0|k > = E_k^0|k >$

$$(H_0 - E_n^0) \sum_k c_n^k |k > = \sum_k (E_k^0 - E_n^0) c_n^k |k > = E_n^1 |n > -V|n > \qquad (6.18)$$

Projecting this equation onto the eigenvector $|m >$ yields

$$\sum_k (E_k^0 - E_n^0) C_n^k < m|k > = E^1 \delta_{mn} - < m|V|n > \qquad (6.19)$$

where we have exploited the fact that $< m|n > = \delta_{nm}$. We arrive at

$$(E_m^0 - E_n^0) c_n^m = E_n^1 \delta_{mn} - < m|V|n > \qquad (6.20)$$

Again, we see that taking $n = m$ we obtain as solvability condition the first order correction $E_n^1 = < n|V|n >$. For $n \neq m$ we can determine the coefficients c_n^m:

$$c_n^m = < \frac{< m|V|n >}{E_n^0 - E_m^0} \qquad (6.21)$$

Thereby, we have to assume that $E_n^0 \neq E_m^0$, i.e. that we have no degeneracy of the energy spectrum. This case will be treated below.

We can now summarize our results to first order in ϵ

$$E = E_n^0 + \epsilon E_n^1 = E_n^0 + \epsilon < n|V|n >$$

$$|\psi > = |n > + \sum_m \frac{< m|V|n >}{E_n^0 - E_m^0}|m > \qquad (6.22)$$

We shall proceed to the treatment of the second order corrections E_n^2 and $\psi_n^2 >$, which are determined by

$$H_0|\psi^2 > -E_n^0|\psi^2 > = E^2|n > +E^1|\psi^1 > -V|\psi^1 > \qquad (6.23)$$

Again, we can employ a solvability condition by forming the scalar product with $< n|$. The left hand side vanishes identically, whereas the right hand side yields the second order contribution

$$E^2 = < n|V|\psi_n^1 > = \sum_m < n|V|m > c_n^m = < \frac{|<m|V|n>|^2}{E_n^0 - E_m^0} \tag{6.24}$$

We can now summarize our results to second order in ϵ

$$E = E_n^0 + \epsilon < n|V|n > + \epsilon^2 \sum_{m \neq n} < \frac{|<m|V|n>|^2}{E_n^0 - E_m^0}$$

$$|\psi> = |n> + \sum_m \frac{<m|V|n>}{E_n^0 - E_m^0}|m> \tag{6.25}$$

The second order contribution to the eigenvector can bed determined in a straightforward manner.

6.3 Perturbation Theory for Degenerate States

Example:
$$\begin{pmatrix} E^0 & \epsilon w \\ \epsilon w & E^0 \end{pmatrix} \tag{6.26}$$

Characteristic equation:

$$(E - E_0)^2 - \epsilon^2 w^2 = 0 \tag{6.27}$$

$$E = E_0 \pm \epsilon w \tag{6.28}$$

General: Finite dimensional subspace

$$H_0|n, \alpha> = E_n^0|n, \alpha> \tag{6.29}$$

Ansatz:
$$|\psi> = \sum_\alpha c_{n\alpha}|n\alpha> + \epsilon \sum_{k \neq n} |k\beta> + .. \tag{6.30}$$

$$\epsilon W \sum_\alpha c_{n\alpha}|n\alpha> = \epsilon E_n^1 \sum_\alpha c_{n\alpha}|n\alpha> \tag{6.31}$$

Projection
$$\sum_\alpha [< n\alpha|W|n\beta> - E_n^1 \delta_{\alpha,\beta}]c_{n\alpha} = 0 \tag{6.32}$$

7

Atoms in Electric Field

7.1 Application of Perturbation Theory

We consider the Hamilton operator of a Hydrogen atom in an electric field

$$H = H_0 + e\mathbf{r} \cdot \mathbf{E} \tag{7.1}$$

In order to approximately determine the energy levels we take the direction of the electric field as the z-direction and introduce spherical coordinates. As a result we obtain

$$H = H_0 + er\cos\theta E \tag{7.2}$$

As we have seen in the section on time independent perturbation theory the various corrections are related to the matrix elements

$$< nlm|V|n'l'm' > = < nlm|r\cos\theta|n'l'm' > \tag{7.3}$$

where the eigenfunctions of the Hamilton operator H_0 are denoted by

$$|nlm> = R_{nl}(r)Y_l^m(\theta, \varphi) \tag{7.4}$$

The explicit expression for the matrix elements

$$
\begin{aligned}
< nlm|r\cos\theta|n'l'm' > = &\int_0^\infty r^2 dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\varphi R_{nl}(r) r R_{n'l'}(r) \\
&\times Y_l^m(\theta, \varphi)^* \cos\theta Y_{l'}^{m'}(\theta, \varphi)
\end{aligned} \tag{7.5}
$$

explicitly shows that the integrals factorizes according to

$$< nlm|V|n'l'm' > = M_{lm,l'm'} K_{nl,n'l'} \tag{7.6}$$

where the matrix elements $M_{lm,l'm'}$ involves integration with respect to the variables Θ, φ

$$M_{lm,l'm'} = \int_0^\pi sin\theta d\theta \int_0^{2\pi} d\varphi Y_l^m(\theta,\varphi)^* cos\theta Y_{l'}^{m'}(\theta,\varphi) \qquad (7.7)$$

and a matrix element in volving the integral

$$K_{nl,n'l'} = \int_0^\infty r^2 dr R_{n'l'}(r) r R_{nl}(r) \qquad (7.8)$$

It is convenient to represent $cos\theta$ as a spherical harmonics according to

$$cos\theta = \sqrt{\frac{4\pi}{3}} Y_1^0(\theta,\varphi) \qquad (7.9)$$

As a consequence, one has to evaluate the integrals

$$M_{lm,l'm'} = \int_0^\pi sin\theta d\theta \int_0^{2\pi} d\varphi Y_l^m(\theta,\varphi)^* Y_1^0(\theta,\varphi) Y_{l'}^{m'}(\theta,\varphi)$$
$$= < Y_l^m | Y_{l'}^{m'} Y_1^0 > \qquad (7.10)$$

We emphasize that this matrix element is an example of a *Clebsch-Gordon coefficient*.

Due to the fact that

$$Y_l^m = e^{im\varphi} L_{lm}(cos\theta) \qquad (7.11)$$

where L_{lm} are polynomial functions of $\cos\theta$ we immediately obtain the selection rule with respect to the quantum number m:

$$M_{lm;l'm'} = \delta_{m,m'} M_{lm;l'm'} \qquad (7.12)$$

Furthermore, there are selection rules with respect to l,l'. It can be shown that $M_{lm,l'm'}$ is different from zero only in the cases

$$l = l' + 1 \qquad l = l' - 1 \qquad (7.13)$$

7.2 Stark Effect of the Ground State n=1,l=0

We remind the reader that

$$Y_0^0(\theta,\varphi = \frac{1}{\sqrt{4\pi}} \qquad (7.14)$$

As a consequence, the matrix element

$$M_{l,m;00} = \delta_{m,0} \int_0^\pi sin\theta d\theta \int_0^{2\pi} d\varphi Y_l^m(\theta,\varphi)^* \sqrt{\frac{4\pi}{3}} Y_1^0(\theta,\varphi) \frac{1}{\sqrt{4\pi}}$$
$$= \delta_{l,1}\delta_{m,0} \frac{1}{\sqrt{3}} \qquad (7.15)$$

can be evaluated using the orthogonality condition of the spherical harmonics:

$$< Y_l^m(\theta, \varphi) Y_1^{m'}(\theta, \varphi) = \delta_{ll'} \delta_{mm'} \tag{7.16}$$

In order to apply perturbation theory we have to consider the following matrix elements which are given by the following integrals:

$$< nlm|rcos\theta|100 >= \delta_{l,1} \delta_{m,0} \frac{1}{\sqrt{3}} \int_0^\infty r^2 dr R_{n1} r R_{10} \tag{7.17}$$

We are now in the position to determine the corrections to the ground state $|1,0,0>$ of the hydrogen atom. The first order contribution vanishes

$$E_{100}^1 =< 100|rcos\theta|100 >= M_{00,00} K_{10,10} = 0 \tag{7.18}$$

since $M_{00,00} = 0$, according to (7.17). As a result, the ground state of the hydrogen atom does not exhibit the linear Stark effect.

We proceed to calculate the second order correction to the energy eigenvalue E_1^0, which is given by

$$E_{100}^2 = e^2 E^2 \sum_{n,l} \frac{| < nl0|rcos\theta|100 > |^2}{E_{100} - E_{nl0}} \tag{7.19}$$

Due to the selection rule (7.17) only the matrix elements with l=1 contribute and we obtain explicitly

$$E_{100}^2 = e^2 E^2 \sum_n \frac{1}{3} \frac{|K_{n1,10}|^2}{E_{100} - E_{nl0}} \tag{7.20}$$

with the integrals

$$K_{n1,00} = \int_0^\infty r^2 dr r R_{n1}(r) R_{10}(r) \tag{7.21}$$

involving the (normalized) radial functions of the Hydrogen problem.

Taking the contribution with n=2 and neglecting the contirbutions from the higher order functions $R_{n1}(r)$ we obtain our final estimate for the second order contirbutions

$$E_{100}^{(2)} = -\frac{9}{4} a_B^3 E^2 e^2 \tag{7.22}$$

We can summarize: The ground state of the Hydrogen atom exhibits the quadratic Stark effect.

7.2.1 Induced Dipole Moment

Energy of a dipol in the electric field:

$$\Delta E = -\int d(E)dE = -\frac{\alpha}{2}E^2 = -\frac{d}{2}E \qquad (7.23)$$

As a consequence:

$$<d> = \frac{9}{2}Ea_B^3 \qquad (7.24)$$

Polarization

$$P = \rho <d> = \chi_e E \qquad (7.25)$$

7.3 Linear Stark Effect

The linear Stark effect arises for the case of a degenerate energy level. We consider the states with principal quantum number $n = 2$. The energy level $E_2^0 = -Ry/4$ is fourfold degenerate and we denote the corresponding eigenstates by $|n\alpha>$, according to our notation in the section on perturbation theory:

$$\begin{aligned}
|2,1> &= |2,0,0> \\
|2,2> &= |2,1,0> \\
|2,3> &= |2,1,1> \\
|2,4> &= |2,1,-1>
\end{aligned} \qquad (7.26)$$

In order to calculate the splitting of the degeneracy by the external electric field we have to calculate the matrix elements

$$<2\alpha|rcos\theta|2\beta> \qquad (7.27)$$

Due to selection rules only the matrix elements

$$<22|rcos\theta|20> = W = <20|rcos\theta|22> \qquad (7.28)$$

is different from zero. It is explicitly given by

$$W = M_{10,00}K_{21,20} \qquad (7.29)$$

with

$$M_{10,00} = \frac{1}{\sqrt{3}} \qquad (7.30)$$

and

$$K_{21,20} = \int r^2 dr r R_{20}(r)R_{21}(r) = \int_0^\infty r^2 dr \frac{2}{\sqrt{3}(2a)^3}e^{-r/a}(1-\frac{r}{a})\frac{r}{a}r \quad (7.31)$$

The radial wave functions are given by

$$R_{20} = \frac{2}{(2a)^{3/2}}(1-\rho)e^{-\rho/2}$$

$$R_{21} = \frac{1}{\sqrt{3}}\frac{1}{(2a)^{3/2}}\rho e^{-\rho} \tag{7.32}$$

a: Bohr's radius

As a consequence we obtain

$$W = 3eaE \tag{7.33}$$

Let us now consider the perturbation theory in first order. We make the following ansatz for the eigenvector

$$|\psi> = \sum_{\alpha=1}^{4} c_2^{\alpha}|2\alpha>$$
$$= c_1|200> +c_2|210> +c_3|211> +c_4|21-1> \tag{7.34}$$

We obtain the following eigenvalue problem

$$\sum_{\beta=1}^{4} <2\alpha|V|2\beta> c_2^{\beta} = E_2^1 c_2^{\alpha} \tag{7.35}$$

Explicitly,

$$\begin{pmatrix} 0 & W & 0 & 0 \\ W & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = E_2^1 \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} \tag{7.36}$$

This linear set of equations has only nontrivial solutions for eigenvalues E_2^1 determined by the characteristic equation

$$Det[< 2\alpha|V|2\beta> -E_2^1\delta_{\alpha\beta}] = 0 \tag{7.37}$$

The characteristic equation reads

$$(E_2^1)^2(E_2^1 - W^2) = 0 \tag{7.38}$$

with the four roots

$$E_2^1 = 0 \quad , \quad E_2^1 = 0 \quad , \quad E_2^1 = W \quad , \quad E_2^1 = -W \tag{7.39}$$

In first order the energy eigenvalues split into three groups. The states $|2,1,1>$ and $|21-1>$ remain degenerate and there is not change of the eigenvalue in lowest order. The states $|210>$ and $|200>$ are coupled by the external field and the energy eigenvalues split:

$$E^1 = 3eaE \qquad |\psi> = \frac{1}{\sqrt{2}}[|210> +|200>]$$

$$E^2 = -3eaE \qquad |\psi> = \frac{1}{\sqrt{2}}[|210> -|200>] \tag{7.40}$$

The corresponding eigenstates (to lowest) order are linear superpositions.

7.3.1 Convergence of Perturbation theory

8

Variational Approximation: Rayleigh-Ritz-Method

8.1 General Treatment

We consider a Hermitian Operator L, which has a minimal eigenvalues λ_{min}. The Rayleigh-Ritz-Method allows one to determine approximations to the eigenvalues λ_i and eigenfunctions φ_i of the linear eigenvalue problem

$$L|\varphi_i> = \lambda_i|\varphi_i> \tag{8.1}$$

It is based on the following optimization problem.

We consider an arbitrary vector $|\psi>$, which is normalized:

$$<\psi|\psi> = 1 \tag{8.2}$$

and calculate the expectation value of the operator L:

$$<\psi|L|\psi> = <L> \tag{8.3}$$

This expectation value depends on the choosen function $|\psi>$, i.e. it is a functional. This functional maps a vector $|\psi>$ onto a real value $<L>$. We can now pose the question, which vector $|\psi>$ of the Hilbert space, which is normalized according to (8.2), minimalizes the functional $<L>$.

In order to solve this problem we consider the following functional:

$$V = <\psi|L|\psi> + \lambda(1- <\psi|\psi>) \tag{8.4}$$

The so-called *Lagrange multiplier* λ has been included for the following reason. The vectors $|\psi>$ have to be normalized. This should be kept in mind when varying the vectors $|\psi>$. On the other hand, we can allow for arbitrary, i.e. not normalized vectors, by introducing a secondary term to the functional, which contains a free parameter λ.

For the following we assume that there is a single extremal vector, which we shall denote as $|\varphi>$. We consider deviations from this extremal vector:

$$|\psi> = |\varphi> + \epsilon|\delta\varphi> \qquad (8.5)$$

Inserting this ansatz we obtain the functional

$$
\begin{aligned}
V = & <\varphi|L|\varphi> + \lambda(1- <\varphi|\varphi>) \\
& + \epsilon <\delta\varphi|L|\varphi> - <\delta\varphi|\varphi>) \\
& + \epsilon <L\varphi|\delta\varphi> - <\varphi|\delta\varphi>) + O(\epsilon^2) \qquad (8.6)
\end{aligned}
$$

We have neglected terms of order ϵ and have already taken into account that L is a Hermitian operator: $L = L^\dagger$.

In order that $|\varphi>$ actually is an extremalizing vector, the terms of first order in ϵ have to vanish. Since the variation $|\delta\varphi>$ is completely arbitrary, we obtain the condition

$$L|\varphi> = \lambda|\varphi> \qquad (8.7)$$

which defines the extremal vector, $\varphi>$. This shows that the Lagrange mutliplier is an eigenvalue of the operator L and $|\varphi>$ is the corresponding eigenvector.

8.1.1 Approximate Solutions of the Variational Problem

The variational formulation (8.4) of the eigenvalue problem (8.7) suggests to make an ansatz for solution in terms of the *trial function* $|\psi>$. One chooses a class of vectors depending on parameters $\alpha_1, .., \alpha_N$

$$|\psi> = |\psi(\alpha_1, .., \alpha_N)> \qquad (8.8)$$

The functional (8.4) then becomes a function of the parameter set α_i:

$$
\begin{aligned}
V(\alpha_1, .., \alpha_N) = & <\psi(\alpha_1, .., \alpha_N)|L|\psi(\alpha_1, .., \alpha_N)> \\
& + \lambda(1- <\psi(\alpha_1, .., \alpha_N)|\psi(\alpha_1, .., \alpha_N)>) \qquad (8.9)
\end{aligned}
$$

The minimum of this function can be determined from the set of algebraic equations

$$\frac{\partial}{\partial\alpha_i} V(\alpha_1, .., \alpha_N) = 0 \qquad , \qquad i = 1, .., N \qquad (8.10)$$

8.1.2 Application: Hamilton-Operator

We consider now the case where L is the Hamilton operator. In this case, there is an eigenstate with minimal energy E.

Harmonic Oscillator

We exemplify the variational principle for the case of the harmonic oscillator.
   As trial function we use

$$\psi = N e^{-\frac{\beta}{2}x^2} = (\frac{\beta}{\pi})^{1/4} e^{-\frac{\beta}{2}x^2} \tag{8.11}$$

The ansatz is already normalized. The following formula's are helpful

$$\int_{-\infty}^{\infty} e^{-\beta x^2} = \sqrt{\frac{\pi}{\beta}}$$

$$\int_{-\infty}^{\infty} x^2 e^{-\beta x^2} = \frac{1}{2}\sqrt{\frac{\pi}{\beta^3}} \tag{8.12}$$

We have to calculate the expectation value for the energy

$$E = \int dx\, \psi(x)[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{m\omega^2}{2}x^2]\psi(x) \tag{8.13}$$

We use

$$\psi' = -\beta x \psi$$
$$\psi'' = -\beta\psi + \beta^2 x^2 \psi \tag{8.14}$$

and obtain

$$E(\beta) = \int_{-\infty}^{\infty} dx[-\frac{\hbar^2}{2m}(-\beta + \beta^2 x^2)\psi^2 + \frac{m\omega^2}{2}x^2\psi^2]$$

$$= \frac{\hbar^2\beta}{2m} + \sqrt{\frac{\pi}{\beta}}(\frac{m\omega^2}{2} - \frac{\hbar^2}{2m}\beta^2]$$

$$= \frac{\hbar^2}{4m}\beta + \frac{m\omega^2}{4}\frac{1}{\beta} \tag{8.15}$$

We now consider the variation of $E(\beta)$

$$\frac{\partial E}{\partial \beta} = \frac{\hbar^2}{4m} - \frac{m\omega^2}{4\beta^2} \tag{8.16}$$

The result is

$$\beta = \frac{m\omega}{\hbar} \quad , \quad E = \frac{\hbar\omega}{2} \tag{8.17}$$

and we obtain the exact energy and eigenfunction of the ground state of the
harmonic oscillator.

8.1.3 Higher Eigenvalues

Higher eigenvalues and eigenvectors can be calculated approximately by performing an ansatz, which is orthogonal to the approximate ground state $|\varphi_0>$.

9

Time Dependent Perturbation Theory

9.0.4 Motivation

In the following section we consider a time dependent perturbation:

$$i\hbar|\dot{\psi}> = [H_0 + \epsilon W(t)]|\psi> \tag{9.1}$$

Such types of problems arises when an atom is exposed to time dependent electric or magnetic fields. In this case, one is interested in the transition probabilities between two eigenstates of the Hamiltonian H_0.

In the following we assume that the energy eigenvalues E_n and the eigenstates $|n>$ of the unperturbed energy eigenvalue problem

$$H_0|n> = E_n|n> \tag{9.2}$$

are known explicitly. In order to determine the transition probability P_{nm} between the initial state —m¿ and the final state —n¿, we have to solve the time dependent Schrödinger equation (9.1) with the initial condition

$$|\psi(t=0)> = m \tag{9.3}$$

The probability to find the quantum system in the eigenstate $|n>$ at time t is then given by the projection of the state vector $|\psi(t)>$ onto the eigenstate $|n>$:

$$P_{nm}(t) = |<n|\psi(t)>|^2 \tag{9.4}$$

The transition probability can be used to determine the transition rate

$$p_{n\leftarrow m} = \frac{P_{nm}(t)}{t} \tag{9.5}$$

It is expected that this transition rate tends to a constant value in the long time limit $t \to \infty$.

9.0.5 Transition to the Interaction Picture

The central quantity is the wave function at time t with initial condition $\psi(0) >= |m>$. It is convenient to proceed to the interaction picture. The Schrödinger equation in the interaction picture reads

$$i\hbar \frac{\partial}{\partial t}|\psi_I(t)> = \epsilon W_I(t)|\psi_I(t)> \tag{9.6}$$

The interaction term has the form

$$W_I(t) = e^{\frac{i}{\hbar}H_0 t} W(t) e^{-\frac{i}{\hbar}H_0 t} \tag{9.7}$$

The state vector has the form

$$|\psi(t)> = e^{-\frac{i}{\hbar}H_0 t}|\psi_I(t)> \tag{9.8}$$

and we can read off the initial conditon

$$|\psi_I(0)> = |m> \tag{9.9}$$

The Schrdinger equation in the interaction picture can be solved iteratively by the transformation to the integral equation

$$|\psi_I(t)> = |m> +\epsilon\frac{1}{i\hbar}\int_0^t dt' W_I(t')|\psi_I(t')> \tag{9.10}$$

Iteration of this relation yields

$$|\psi_I(t)> = |m> +\epsilon\frac{1}{i\hbar}\int_0^t dt' W_I(t')|m>$$
$$+ \epsilon^2\frac{1}{(i\hbar)^2}\int_0^t dt' \int_0^{t'} dt'' W_I(t')W_I(t'')|\psi_I(t'')> \tag{9.11}$$

Further iteration yields the *Dyson series*

$$|\psi_I(t)> = |m> +\epsilon\frac{1}{i\hbar}\int_0^t dt_1 W_I(t_1)|m>$$
$$+ \epsilon^2\frac{1}{(i\hbar)^2}\int_0^t dt_1 \int_0^{t_1} dt_2 W_I(t_1)W_I(t_2)|m>$$
$$+ \epsilon^k\frac{1}{(i\hbar)^k}\int_0^t dt_1... \int_0^{t_{k-1}} dt_k W_I(t_1)....W_I(t_k)|m> +... \tag{9.12}$$

Formally, the Dyson series is usually written as the so-called *time ordered exponential*

$$U(t,t_0) = Te^{-\frac{i}{\hbar}\epsilon\int_{t_0}^t dt' W_I(t')} \tag{9.13}$$

The matrix element $< n|\psi(t) >$ can be written in the form

$$< n|\psi(t) > \; = \; < n|e^{-\frac{i}{\hbar}H_0 t}|\psi_I(t >$$

$$= \; < n||e^{-\frac{i}{\hbar}H_0 t}\, T e^{-\frac{i}{\hbar}\epsilon \int_{t_0}^{t} dt' W_I(t')}|m > \qquad (9.14)$$

with the first order approximation

$$< n|\psi(t) > \; = \; < n|e^{-\frac{i}{\hbar}H_0 t}[1 + \frac{1}{i\hbar}\epsilon \int_0^t dt' W_I(t')]|m > +O(\epsilon^2)$$

$$= \; e^{\frac{i}{\hbar}E_n^0 t}[< n|m > +\epsilon\frac{1}{i\hbar} \int_0^t dt' < n|W_I(t)|m > \qquad (9.15)$$

We consider $n \neq m$ and obtain for the transition probability

$$P_{nm} = \epsilon^2 \frac{1}{\hbar^2} \int_0^t dt' \int_0^t dt'' < n|W_I(t')|m >< m|W_I(t'')|n > \qquad (9.16)$$

9.0.6 Fermi's Golden Rule

Time independent Perturbation

For the time independent perturbation we obtain

$$\int_0^t dt' < m|e^{\frac{i}{\hbar}H_0 t}w e^{-\frac{i}{\hbar}H_0 t}|n > \; = \; \int_0^t dt' e^{i\omega_{mn}t} < m|w|n >$$

$$= \; \frac{[e^{i\omega_{mn}t} - 1]}{i\omega_{mn}} < m|w|n > \qquad (9.17)$$

Thereby, we have introduced

$$\omega_{mn} = \frac{E_m - E_n}{\hbar} \qquad (9.18)$$

As a consequence, the transition rate reads

$$p_{nm} = lim_{t\to\infty} \frac{P_{nm}(t)}{t} = |< m|w|n >|^2 2\frac{[1 - cos\omega_{mn}t]}{\omega_{mn}^2 t}$$

$$= |< m|w|n >|^2 \frac{sin^2 \frac{\omega_{mn}}{2}t}{(\frac{\omega_{mn}}{2})^2 t} \qquad (9.19)$$

The function $\frac{sin^2 \frac{\omega_{mn}}{2}t}{(\omega_{mn}/2)^2 t}$ gets sharply peaked at $\omega_{mn} = 0$ for large times. In fact,

$$2\pi\delta(\omega) = \frac{sin^2 \frac{\omega}{2}t}{(\frac{\omega}{2})^2 t} \qquad (9.20)$$

Therefore, there are only transitions with $E_n = E_m$

We now consider transitions for the case of a continuous energy spectrum. Then

$$p_{nm} = \int dE\delta(\omega - \omega_m)\frac{2\pi}{\hbar^2}| < m|w|n > |^2$$

$$= \rho(E_m)\frac{2\pi}{\hbar}| < m|w|n > |^2 \tag{9.21}$$

where we have defined the density of states

$$\rho(E_m) = \int dE\delta(E - E_m) \tag{9.22}$$

Harmonic Perturbation

For the following we assume that the perturbation is periodic in time

$$W(t) = w cos\omega t = \frac{1}{2}[we^{i\omega t} + w^\dagger e^{-i\omega t}] \tag{9.23}$$

Here, w is and operator, $w^\dagger$ denotes the adjoint operator. The perturbationa $W(t)$ is hermitian.

The matrix element $< m|W_I(t)|m >$ in the interaction picture then takes the form

$$< m|W_I(t)|n > = < e^{-\frac{i}{\hbar}H_0 t}m|W(t)|e^{-\frac{i}{\hbar}H_0 t} >$$

$$= \frac{1}{2}e^{i\omega_{mn} t}[< m|w|n > e^{i\omega t} + < m|w^\dagger|n > e^{-i\omega t}] \tag{9.24}$$

Therby, we have defined the frequency difference

$$\omega_{mn} = \frac{E_m - E_n}{\hbar} \tag{9.25}$$

We calculate the time integral

$$\int_0^t dt'\frac{1}{2}e^{i\omega_{mn} t} < m|w|n > [e^{i\omega t} + e^{-i\omega t}]$$

$$= \frac{1}{2} < m|w|n > (\frac{[e^{i(\omega_{mn} + \omega)t} - 1]}{i(\omega_{mn} + \omega)}$$

$$+ \frac{[e^{i(\omega_{mn} - \omega)t} - 1]}{i(\omega_{mn} - \omega)}) \tag{9.26}$$

As a consequence, we obtain

$$P_{nm} = \frac{\epsilon^2}{4\hbar^2}| < n|w|m > |^2$$

$$\times [|F(\omega)|^2 + |F(-\omega)|^2 + F(\omega)F(-\omega)^* + F(-\omega)F(\omega)^*] \tag{9.27}$$

where we have defined

$$F(\omega) = \frac{[e^{i(\omega_{mn} - \omega)t} - 1]}{i(\omega_{mn} - \omega)} \tag{9.28}$$

such that

$$|F(\omega)|^2 = \frac{2}{(\omega_{mn} - \omega)^2}[1 - cos(\omega_{mn} - \omega)t] = 4\frac{\sin^2 \frac{(\omega_{mn} - \omega)}{2}t}{(\omega_{mn} - \omega)^2} \tag{9.29}$$

The transition rate then reads

$$p_{nm} = lim_{t \to \infty} \frac{P_{nm}}{t}$$

$$= \frac{\epsilon^2}{\hbar^2}| < n|w|m > |^2[\frac{\sin^2 \frac{(\omega_{mn} - \omega)}{2}t}{(\frac{(\omega_{mn} - \omega)}{2})^2 t} + \frac{\sin^2 \frac{(\omega_{mn} + \omega)}{2}t}{(\frac{(\omega_{mn} + \omega)}{2})^2 t}] \tag{9.30}$$

Again , we use the representation of the δ-function

$$2\pi\delta(\omega - \omega_{mn}) = [\frac{\sin^2 \frac{(\omega_{mn} - \omega)}{2}t}{(\frac{(\omega_{mn} - \omega)}{2})^2 t} \tag{9.31}$$

In the long time limit the transition rate gets only significant contributions provided

$$|\omega_{nm} + \omega| < \frac{2\pi}{t} \qquad , \qquad |\omega_{nm} - \omega| < \frac{2\pi}{t} \qquad , \tag{9.32}$$

We consider again transitions to a continuous spectrum. Then,

$$p_{nm} = 2\pi\frac{\epsilon^2}{\hbar}| < n|w|m > |^2\delta(\omega - \omega_{nm}) \tag{9.33}$$

Using the relation

$$\delta(E - e_{nm}) = \frac{1}{\hbar}\delta(\omega - \omega_{nm}) \tag{9.34}$$

we obtain:

$$p_{nm} = \frac{2\pi\epsilon^2}{\hbar}| < n|w|m > |^2\delta(E - E_{nm}) \tag{9.35}$$

If we have introduce the energy density of states

$$\rho(E - E_0)dE_0 \tag{9.36}$$

i.e. $\rho(E - E_0)dE_0$ calculates the number of states in the interval dE_0, then an integration of () with respect to E yields

$$p_{nm} = \frac{2\pi\epsilon^2}{\hbar}| < n|w|m > |^2\rho(E_{nm}) \tag{9.37}$$

This is expression is usually denoted as Fermi's golden rule.

9.0.7 Radiation Transitions: Selection Rules

We now consider the Hydrogen atom in an external electromagnetic field. The Hamilton operator is just

$$H = H_0 - \mathbf{d} \cdot \mathbf{E} = H_0 + \int d\omega e\mathbf{r} \cdot [\mathbf{E}_0(\omega)e^{-i\omega t} + \mathbf{E}_0^*(\omega)e^{i\omega t}] \qquad (9.38)$$

The transition rate is then given by

$$p_{nm} = 2\pi \frac{\epsilon^2}{\hbar} |\langle n|\mathbf{r} \cdot \mathbf{E}_0|m\rangle^2 \delta(E - E_{nm}) \qquad (9.39)$$

We introduce the matrix elements of the dipol operator

$$\mathbf{d}_{nm} = - <n|e\mathbf{r}|m> \qquad (9.40)$$

and obtain the relation

$$p_{nm} = 2\pi \frac{1}{\hbar} |d_{nm} \cdot \mathbf{E}(\omega_{nm})|^2 \rho(E_{nm}) \qquad (9.41)$$

The matrix element d_{nm} is related to the selection rules. A transition between level E_n and E_m are forbidden, provided

$$d_{nm} = 0 \qquad (9.42)$$

It is allowed if $d_{nm} \neq 0$.

We consider transitions between the eigenstates of the hydrogen atom. We consider the z-component of the dipol moment, which is the only component, which is necessary, since we can assume that $\mathbf{E} = Ee_z$. Then

$$d_{nlm;n'l'm'} = -e \int dr r^2 \int d\Omega (Y_l^m)^* cos\theta Y_{l'}^{m'} R_{nl}(r)r R_{n'l'}(r)$$

$$= \int d\Omega (Y_l^m)^* cos\theta Y_{l'}^{m'} \int dr r^2 R_{nl}(r)r R_{n'l'}(r) \qquad (9.43)$$

The integral factorizes. Integration with respect to the angles yields

$$\int d\Omega (Y_l^m)^* cos\theta Y_{l'}^{m'} \approx \delta_{m,m'} \delta_{l,l'\pm1} \qquad (9.44)$$

Allowed transitions are obtained only between states with $l, l \pm 1$.

10

Electromagnetic Field: Quantization

In this section we perform the quantization of the free electromagnetic field. To this end we consider a box of volume V assuming periodic boundary conditions for the fields.

10.1 The Classical Electromagnetic Field

In the classical theory the electromagnetic field is determined by Maxwell's Equations:

$$\nabla \cdot \mathbf{E} = 0$$
$$\nabla \times \mathbf{E} = -\frac{\partial}{\partial t}\mathbf{B}$$
$$\nabla \cdot \mathbf{B} = 0$$
$$\nabla \times \mathbf{B} = \frac{1}{c^2}\frac{\partial}{\partial t}\mathbf{E} \tag{10.1}$$

The energy density takes the form

$$u = \frac{1}{2}[\mathbf{E} \cdot \mathbf{D} + \mathbf{B} \cdot \mathbf{H}$$
$$= \frac{\epsilon_0}{2}[\mathbf{E}^2 + c^2\mathbf{B}^2] \tag{10.2}$$

The energy contained in a volume V is just given by

$$E = \int_V d\mathbf{x}\, u(\mathbf{x}, t) \tag{10.3}$$

The energy density $u(\mathbf{x}, t)$ obeys the continuity equation

$$\frac{\partial}{\partial t}h(\mathbf{x}, t) + \nabla_\mathbf{x} \cdot \mathbf{S}(\mathbf{x}, t) = 0 \tag{10.4}$$

$S(\mathbf{x}, t)$ denotes the Poynting vector

$$\mathbf{S} = \mathbf{E} \times \mathbf{H} = \frac{1}{\mu_0}[\mathbf{E} \times \mathbf{B}] \qquad (10.5)$$

It is convenient to introduce the electromagnetic potentials $\mathbf{A}$, Φ via the relations

$$\mathbf{B} = \nabla \times \mathbf{A}$$
$$\mathbf{E} = -\nabla\Phi - \dot{\mathbf{A}} \qquad (10.6)$$

In the following we shall use the gauge $\Phi = 0$, the so-called *radiation gauge*. In this case the electromagnetic energy density takes the form

$$u = \frac{\epsilon_0}{2}\{(\dot{\mathbf{A}})^2 + c^2[\nabla \times \mathbf{A}]^2\} \qquad (10.7)$$

10.1.1 Periodic Boundaries: Cavity

We investigate the free electromagnetic field in a cavity of volume V. (For the sake of simplicity we consider a cube of length L). We postulate periodic boundary conditions. In that case we can represent the vector potential as a Fourier series

$$\mathbf{A}(\mathbf{x}, t) = \frac{1}{\sqrt{V}}\sum_{\mathbf{k}}\sum_{j=1}^{2}\mathbf{e}_j(\mathbf{k})N(k)A_{\mathbf{k},j}(t)e^{i\mathbf{k}\cdot\mathbf{x}} \qquad (10.8)$$

Transversality condition, $\nabla \cdot \mathbf{A} = 0$, requires

$$\mathbf{k} \cdot \mathbf{e}_j(\mathbf{k}) = 0 \qquad (10.9)$$

Furthermore, we take

$$\mathbf{e}_1(\mathbf{k}) \cdot \mathbf{e}_2(\mathbf{k}) = 0 \qquad (10.10)$$

The normalization constant $N(k)$ will be fixed below.

Periodic boundary conditions require

$$\mathbf{k} = \frac{2\pi}{L}[l_x, l_y, l_z] \qquad , \qquad l_i = -\infty, ..., -1, 0, 1, .. + \infty \qquad (10.11)$$

As a consequence the electric field and the magnetic induction also are represented as Fourier series:

$$\mathbf{E}(\mathbf{x}, t) = -\dot{\mathbf{A}}(\mathbf{x}, t) = -\frac{1}{\sqrt{V}}\sum_{\mathbf{k}}\sum_{j=1}^{2}\mathbf{e}_j(\mathbf{k})N(k)\dot{A}_{\mathbf{k},j}(t)e^{i\mathbf{k}\cdot\mathbf{x}} \qquad (10.12)$$

$$\mathbf{B}(\mathbf{x}, t) = \nabla \times \mathbf{A}(\mathbf{x}, t) = \frac{1}{\sqrt{V}} \sum_{\mathbf{k}} \sum_{j=1}^{2} i[\mathbf{e}_j(\mathbf{k}) \times \mathbf{k}] N(k) A_{\mathbf{k},j}(t) e^{i\mathbf{k}\cdot\mathbf{x}} \quad (10.13)$$

The energy of the free electromagnetic field in a volume V with periodic boundary conditions reads

$$E = \frac{\epsilon_0}{2} \sum_{\mathbf{k}} \sum_{j=1}^{2} N(k)^2 \left(\dot{A}_{\mathbf{k},j} \dot{A}_{-\mathbf{k},j} + \mathbf{c^2} k^2 A_{\mathbf{k},j} A_{-\mathbf{k},j} \right) \quad (10.14)$$

This follows from the fact that

$$\sum_{\mathbf{k}} \sum_{\mathbf{k}'} N(k) N(k') \int d\mathbf{x} C_{\mathbf{k}} \mathbf{e}_j(\mathbf{k}) \cdot \mathbf{e}_l(\mathbf{k}') C_{\mathbf{k}'} \frac{e^{i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{x}}}{V}$$
$$= \sum_{\mathbf{k}} C_{-\mathbf{k}} N(k)^2 C_{\mathbf{k}} \mathbf{e}_j(\mathbf{k}) \cdot \mathbf{e}_l(-\mathbf{k}) \quad (10.15)$$

The amplitudes $\mathbf{A}_{\mathbf{k},j}$ obey the wave equation

$$\frac{1}{c^2} \frac{\partial^2}{\partial t^2} A_{\mathbf{k},j} + \mathbf{k}^2 A_{\mathbf{k},j} = 0 \quad (10.16)$$

whose solution is

$$A_{\mathbf{k},j} = N[b_{\mathbf{k},j} e^{-i\omega_k t} + b_{-\mathbf{k},j}^\dagger e^{i\omega_k t}] \quad (10.17)$$

This ansatz ensures that the vector potential, and, in turn, the electric and magnetic fields, are real quantities.

For a proof we consider

$$\mathbf{A}(\mathbf{x}, t) = \frac{1}{\sqrt{V}} \sum_{\mathbf{k}} \sum_{j=1}^{2} \mathbf{e}_j(\mathbf{k}) N(\mathbf{k})[b_{\mathbf{k},j} e^{-i\omega_k t} + b_{-\mathbf{k},j}^\dagger e^{i\omega_k t}] e^{i\mathbf{k}\cdot\mathbf{x}} \quad (10.18)$$

Taking the complex conjugate, we obtain

$$\mathbf{A}(\mathbf{x}, t) = \frac{1}{\sqrt{V}} \sum_{\mathbf{k}} \sum_{j=1}^{2} \mathbf{e}_j(\mathbf{k}) N(\mathbf{k})[b_{\mathbf{k},j}^* e^{i\omega_k t} + b_{-\mathbf{k},j} e^{-i\omega_k t}] e^{-i\mathbf{k}\cdot\mathbf{x}} \quad (10.19)$$

Replacing $\mathbf{k}$ with $-\mathbf{k}$ in the sum over $\mathbf{k}$ we can explicitly proof that ansatz leads to a real vector potential.

We are now in the position to explicitly determine the electromagnetic energy in terms of the amplitudes $a_{\mathbf{k},j}$ $a_{\mathbf{k},j}^\dagger$. A straightforward calculation yields

$$H = \frac{1}{2} \sum_{\mathbf{k}} \sum_{j=1}^{2} \hbar \omega_k [b_{\mathbf{k},j} b_{\mathbf{k},j}^\dagger + b_{\mathbf{k},j}^\dagger b_{\mathbf{k},j}] \quad (10.20)$$

Thereby, we have choosen the normalization constant $N(\mathbf{k})$ as

$$N(\mathbf{k}) = \sqrt{\frac{\hbar}{2\epsilon_0 \omega_k}} \tag{10.21}$$

The vector potential, the electri and magnetic fields read

$$\mathbf{A}(\mathbf{x}, t) = \sum_{\mathbf{k}} \sum_j \sqrt{\frac{\hbar}{2\epsilon_0 \omega_k}} \mathbf{e}_j(\mathbf{k}) \left[b_{\mathbf{k},j} e^{-i\omega_k t} e^{i\mathbf{k}\cdot\mathbf{x}} + b_{\mathbf{k},j}^\dagger e^{i\omega_k t} e^{-i\mathbf{k}\cdot\mathbf{x}} \right]$$

$$\mathbf{E}(\mathbf{x}, t) = -i \sum_{\mathbf{k}} \sum_j \sqrt{\frac{\hbar\omega_k}{2\epsilon_0}} \mathbf{e}_j(\mathbf{k}) \left[b_{\mathbf{k},j} e^{-i\omega_k t} e^{i\mathbf{k}\cdot\mathbf{x}} - b_{\mathbf{k},j}^\dagger e^{i\omega_k t} e^{-i\mathbf{k}\cdot\mathbf{x}} \right]$$

$$\mathbf{B}(\mathbf{x}, t) = \sum_{\mathbf{k}} \sum_j \sqrt{\frac{\hbar}{2\epsilon_0 \omega_k}}$$

$$\times\, i[\mathbf{e}_j(\mathbf{k}) \times \mathbf{k}] \left[b_{\mathbf{k},j} e^{-i\omega_k t} e^{i\mathbf{k}\cdot\mathbf{x}} - b_{\mathbf{k},j}^\dagger e^{i\omega_k t} e^{-i\mathbf{k}\cdot\mathbf{x}} \right] \tag{10.22}$$

10.1.2 Hamiltonian Formulation: Free Electromagnetic Field

It is possible to extend the Hamilton formalism of classical mechanics to the treatment of the classical free electromagnetic field. To this end we consider H to be the Hamilton function of the free electromagnetic field. The canonical equations should produce the evolution equations

$$\dot{b}_{\mathbf{k},j} = -i\omega_k b_{\mathbf{k},j}$$
$$\dot{b}_{\mathbf{k},j}^\dagger = i\omega_k b_{\mathbf{k},j}^\dagger \tag{10.23}$$

These evolution equations can be obtained via the canonical equations

$$\dot{b}_{\mathbf{k},j} = -i\frac{\partial}{\partial b_{\mathbf{k},j}^\dagger} H$$

$$\dot{b}_{\mathbf{k},j}^\dagger = i\frac{\partial}{\partial b_{\mathbf{k},j}} H \tag{10.24}$$

We can convince ourselves that the canonical equations lead to the correct evolution equations for the classical mode amplitudes $b_{\mathbf{k},j}$, $b_{\mathbf{k},j}^\dagger$

We can summarize: The free electromagnetic field can be described as a collection of harmonic oscillators described by the complex amplitudes $b_{\mathbf{k},j}$, $b_{\mathbf{k},j}^\dagger$. Each amplitude corresponds to a field mode with polarization $\mathbf{e}_j(\mathbf{k})$, $j = 1, 2$.

10.2 Quantization of the Electromagnetic Field

The quantization of the electromagnetic field as a collection of noninteracting harmonic oscillators is based on the quantization procedure of the single harmonic oscillator.

We consider the amplitudes $b_{\mathbf{k},j}$, $b^\dagger_{\mathbf{k},j}$ as creation and annihilation operators obeying the following commutation rules

$$[b_{\mathbf{k},i}, b^\dagger_{\mathbf{k}',j}] = \delta_{\mathbf{k},\mathbf{k}'}\delta_{ij}$$
$$[b_{\mathbf{k},i}, b_{\mathbf{k}',j}] = 0$$
$$\left[b^\dagger_{\mathbf{k},i}, b^\dagger_{\mathbf{k}',j}\right] = 0 \tag{10.25}$$

The Hamilton operator of the free electromagnetic field then can be written in terms of the creation and annihilation operators as

$$H = \sum_{\mathbf{k}} \sum_i \hbar\omega_{\mathbf{k}}[b^\dagger_{\mathbf{k},i}b_{\mathbf{k},i} + \frac{1}{2}] \tag{10.26}$$

As a basis of the corresponding Hilbert space we take

$$|...n_{\mathbf{k},j}....n_{\mathbf{k}',j'}... > = ...\frac{1}{\sqrt{n_{\mathbf{k},j}!}}(b^\dagger_{\mathbf{k},i})^{n_{\mathbf{k},j}}....\frac{1}{\sqrt{n_{\mathbf{k}',j'}!}}(b^\dagger_{\mathbf{k}',j})^{n_{\mathbf{k}',j'}}|0 > \tag{10.27}$$

The basis vectors describe states with $n_{\mathbf{k},j}$ photons with wave vector $\mathbf{k}$ and polarization j.

The electric and magnetic fields become operators. We obtain

$$\mathbf{E}(\mathbf{x},t) = -\sum_{\mathbf{k},j} \sqrt{\frac{\hbar\omega_k}{2\epsilon_0}}\mathbf{e}_j(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{x}}i[b_{\mathbf{k},j}e^{-i\omega_k t} - b^\dagger_{-\mathbf{k},j}e^{i\omega_k t}]$$

$$\mathbf{B}(\mathbf{x},t) = \sum_{\mathbf{k},j} \sqrt{\frac{\hbar}{2\epsilon_0\omega_k}}i[\mathbf{e}_j(\mathbf{k}) \times \mathbf{k}]e^{i\mathbf{k}\cdot\mathbf{x}}[b_{\mathbf{k},j}e^{-i\omega_k t} - b^\dagger_{-\mathbf{k},j}e^{i\omega_k t}] \tag{10.28}$$

11

Absorption, Induced, and Spontaneous Emission

11.1 Einstein' s Derivation of Planck's Formula

This formula determines the total energy of the electromagnetic field per unit volume in terms of the energy densities $u(\nu, T)$

$$
\begin{aligned}
U &= \int d\nu u(\nu, T) = \int dk \frac{c}{2\pi} u(k, T) \\
&= \frac{1}{V} \frac{c}{2\pi} \sum_k n_{\mathbf{k}}(T) \hbar \omega_k
\end{aligned}
\tag{11.1}
$$

Thereby, the sum in the last expression is approximated by the integral

$$
\sum_{\mathbf{k}} \ldots = \frac{V}{(2\pi)^3} \sum_{\mathbf{k}} \Delta^3 \mathbf{k} \ldots = \frac{V}{(2\pi)^3} \int d^3 \mathbf{k} \ldots
\tag{11.2}
$$

and the integral is evaluated in spherical coordinates

$$
\int d^3 \mathbf{k} = \int dk k^2 \int d\Omega
\tag{11.3}
$$

Planck presented the following formula for the spectral energy density $u(\nu, T)$:

$$
u(\nu, T) = 2 \frac{8\pi h \nu^3}{c^3} \frac{1}{e^{\frac{h\nu}{kT}} - 1}
\tag{11.4}
$$

In the following we discuss Einstein's derivation of Planck's formula for black body radiation.

He considered two-level system with energy levels $E_n > E_m$. He postulated that the radiation field is in equilibrium with the set of two-level atoms, contained e.g. in the walls of a black body. He hypothezised the existence of the following processes:

- **Absorption**: A two level atom absorbs a photon with frequency $\omega = \frac{E_n - E_m}{\hbar}$. The transition rate is given by

$$\frac{dP_{nm}^A}{dt} = B_{nm} u(\nu, T) \tag{11.5}$$

  Here, $u(\nu, T)$ denotes the energy density of the electromagnetic field
- **Stimulated Emission**: A two level atom emittes a photon with frequency $\omega = \frac{E_n - E_m}{\hbar}$. The transition rate of this process is given by

$$\frac{dP_{mn}^{IE}}{dt} = B_{mn} u(\nu, T) \tag{11.6}$$

  Stimulated emission is the process inverse to absorption. Therefore, transition rate contains the coefficients B_{nm} in reverse order.
- **Spontaneous Emission**: A two level atom in the upper state emits spontaneously a photon. The transition rate is given by

$$\frac{dP_{nm}^{SE}}{dt} = A_{nm} \tag{11.7}$$

  The transition rate is assumed to be independent on the energy density of the electromagnetic field.

In thermal equilibrium we have a balance of the three processes. The number of atoms emitting a photon per unit time has to equal the number of atoms absorbing a photon per unit time. The number of atoms absorbing a photon is given by the transition rate times the number of atoms N_m in the ground state E_m.

$$N_m \frac{dP_{nm}^A}{dt} \tag{11.8}$$

The number of atoms emitting a photon is give by the sum of the transition rates of induced and spontaneous emission times the number of atoms N_n in the excited state E_n:

$$N_n \left[\frac{dP_{mn}^{SE}}{dt} + \frac{dP_{mn}^{IE}}{dt} \right] \tag{11.9}$$

In thermodynamic equilibrium the number of absorbed and emitted photons have to be equal:

$$N_m \frac{dP_{nm}^A}{dt} = N_n \left[\frac{dP_{mn}^{SE}}{dt} + \frac{dP_{mn}^{IE}}{dt} \right] \tag{11.10}$$

As a consequence,

$$N_m B_{nm} u = N_n [B_{mn} u + A_{mn}] \tag{11.11}$$

and we can solve for the energy density u

$$u(\nu, T) = \frac{Amn}{Bnm} \frac{1}{\frac{N_m}{N_n} - 1} \tag{11.12}$$

The temperature enters via the ratio $\frac{N_m}{N_n}$. In thermal equilibrium, however, we have

$$\frac{N_m}{N_n} = e^{\beta\hbar\omega} = e^{h\nu/kT} \tag{11.13}$$

and we obtain Planck's radiation formula

$$u(\nu, T) = \frac{Amn}{Bnm}\frac{1}{e^{\beta h\nu} - 1} \tag{11.14}$$

The fraction $\frac{A_{mn}}{B_{nm}}$ can be obtained from Wien's law.

11.2 Quantum Mechanical Treatment

We start by considering the Hamilton operator, which is the sum of the Hamilton operator of the free electromagnetic field and the two-level atom, described by H_0.

$$H = H_0 + \mathbf{d} \cdot \mathbf{E} \tag{11.15}$$

We consider a single field mode, for which the electric field operator is given by

$$\mathbf{E}(\mathbf{x}, t) = -i\mathbf{e}\sqrt{\frac{\hbar\omega_k}{2\epsilon_0}}[b_{\mathbf{k}}e^{-i\omega_k t}e^{i\mathbf{k}\cdot\mathbf{x}} - b_{\mathbf{k}}^{\dagger}e^{i\omega_k t}e^{-i\mathbf{k}\cdot\mathbf{x}}] \tag{11.16}$$

Provided the wavelength $\lambda = \frac{\pi}{k}$ is larger than the size of the atom, i.e. larger than Bohr's radius, we can approximate

$$e^{i\mathbf{k}\cdot\mathbf{x}} \approx 1 \tag{11.17}$$

and obtain the Hamilton operator

$$H = H_0 - \mathbf{d} \cdot \mathbf{e}(\mathbf{k})\sqrt{\frac{\hbar\omega_k}{2\epsilon_0}}i[b_{\mathbf{k}}e^{-i\omega_k t} - b_{\mathbf{k}}^{\dagger}e^{i\omega_k t}] \tag{11.18}$$

We denote the states of the unperturbed Hamilton opertor H_0 by

$$|m_{\mathbf{k}}, m\rangle \tag{11.19}$$

and consider transitions to states $|n_{\mathbf{k}}, n\rangle$. Perturbation theory yields

$$\begin{aligned}
P_{nm} = \frac{1}{\hbar^2}\frac{\hbar\omega_k}{2\epsilon_0 V}| &\int_0^t dt' \langle n_{\mathbf{k}}n|\mathbf{d}\cdot\mathbf{e}(\mathbf{k})b_{\mathbf{k}}|m_{\mathbf{k}}m\rangle e^{i(\omega_{nm}-\omega_k)t} \\
&- \langle n_{\mathbf{k}}n|\mathbf{d}\cdot\mathbf{e}(\mathbf{k})b_{\mathbf{k}}^{\dagger}|m_{\mathbf{k}}m\rangle e^{i(\omega_{nm}-\omega_k)t}|^2
\end{aligned} \tag{11.20}$$

This yields

$$\frac{dP_{nm}}{dt} = \frac{2\pi}{\hbar^2} \frac{\hbar\omega_k}{2\epsilon_0 V} [\delta(\omega_{nm} - \omega_k)|\langle n_{\mathbf{k}} n|\mathbf{d} \cdot \mathbf{e}(\mathbf{k})b_{\mathbf{k}}|m_{\mathbf{k}} m\rangle|^2$$
$$+ \delta(\omega_{nm} + \omega_k)|\langle n_{\mathbf{k}} n|\mathbf{d} \cdot \mathbf{e}(\mathbf{k})b_{\mathbf{k}}^{\dagger}|m_{\mathbf{k}} m\rangle|^2] \tag{11.21}$$

The matrix elements factor:

$$\langle n_{\mathbf{k}} n|\mathbf{d} \cdot \mathbf{e}(\mathbf{k})b_{\mathbf{k}}|m_{\mathbf{k}} m\rangle = \langle n|\mathbf{d} \cdot \mathbf{e}(\mathbf{k})m\rangle|^2 \langle n_{\mathbf{k}}|b_{\mathbf{k}}|m_{\mathbf{k}}\rangle$$
$$D_{nm}\langle n_{\mathbf{k}}|b_{\mathbf{k}}^{\dagger}|m_{\mathbf{k}}\rangle \tag{11.22}$$

$$\langle n_{\mathbf{k}} n|\mathbf{d} \cdot \mathbf{e}(\mathbf{k})b_{\mathbf{k}}|m_{\mathbf{k}} m\rangle = \langle n|\mathbf{d} \cdot \mathbf{e}(\mathbf{k})m\rangle|^2 \langle n_{\mathbf{k}}|b_{\mathbf{k}}^{\dagger}|m_{\mathbf{k}}\rangle$$
$$D_{nm}\langle n_{\mathbf{k}}|b_{\mathbf{k}}^{\dagger}|m_{\mathbf{k}}\rangle \tag{11.23}$$

The matrix elements

$$\langle n_{\mathbf{k}}|b_{\mathbf{k}}^{\dagger}|m_{\mathbf{k}}\rangle = \sqrt{m_{\mathbf{k}}}\delta_{n_{\mathbf{k}}, m_{\mathbf{k}}-1}$$
$$\langle n_{\mathbf{k}}|b_{\mathbf{k}}^{\dagger}|m_{\mathbf{k}}\rangle = \sqrt{m_{\mathbf{k}} + 1}\delta_{n_{\mathbf{k}}, m_{\mathbf{k}}+1} \tag{11.24}$$

Thereby, we have used the fact that

$$b_{\mathbf{k}}|m_{\mathbf{k}}\rangle = \sqrt{m_{\mathbf{k}}}|m_{\mathbf{k}} - 1\rangle$$
$$b_{\mathbf{k}}^{\dagger}|m_{\mathbf{k}}\rangle = \sqrt{m_{\mathbf{k}} + 1}|m_{\mathbf{k}} + 1\rangle \tag{11.25}$$

11.3 Transition Rate: Absorption and Emission

11.3.1 Absorption

According to Fermi's golden rule, the transition rate of absorption is

$$\frac{dP_{n_{\mathbf{k}}-1,n;n_{\mathbf{k}},m}}{dt} = \frac{2\pi}{\hbar}|D_{nm}|^2 \frac{1}{2\epsilon_0 V} n_k \hbar\omega_k \delta(E_k - E_{nm}) \tag{11.26}$$

11.3.2 Emission

Now we determine the transition rate for emission of a photon

$$\frac{dP_{n_{\mathbf{k}}+1,m;n_{\mathbf{k}},n}}{dt} \tag{11.27}$$

The transition rate reads

$$\frac{dP_{n_{\mathbf{k}}+1,m;n_{\mathbf{k}},n}}{dt} = \frac{1}{2\hbar\epsilon_0 V}\delta(E_k - E_{nm})|D_{nm}|^2(n_{\mathbf{k}} + 1)\hbar\omega_k \tag{11.28}$$

As we see, there are two contributions. The part due to stimulated emission is given by

$$\frac{dP^{IE}_{n_{\mathbf{k}}+1,m;n_{\mathbf{k}},n}}{dt} = \frac{1}{2\hbar\epsilon_0 V}\delta(E_k - E_{nm})|D_{nm}|^2 n_{\mathbf{k}}\hbar\omega_k \tag{11.29}$$

The contribution of spontaneous emission is

$$\frac{dP^{SE}_{n_{\mathbf{k}}+1,m;n_{\mathbf{k}},n}}{dt} = \frac{1}{2\hbar\epsilon_0 V}\delta(E_k - E_{nm})|D_{nm}|^2\hbar\omega_k \tag{11.30}$$

The transition rates are

$$w_{in} = \frac{1}{2\hbar\epsilon_0 V}|D_{nm}|^2 n_k\hbar\omega_k$$

$$w_{spo} = \frac{1}{2\hbar\epsilon_0 V}|D_{nm}|^2\hbar\omega_k \tag{11.31}$$

We see that the rate of stimulated emission is, indeed proportional to $n_k\hbar\omega_k$, i.e. proportional to the spectral energy density.

11.3.3 Determination of the Einstein Coefficients A_{nm}, B_{nm}

We now determine Planck's radiation formula. To this end we have to to relate the energy density of the modes with wave-vector $k = |\mathbf{k}|$

$$u_{\mathbf{k}} = \frac{1}{V}n_k\hbar\omega_k \tag{11.32}$$

to the spectral energy density $u(\nu)$.

We perform the continuum limit

$$\sum_{\mathbf{k}} = \frac{V}{(2\pi)^3}\int d^3\mathbf{k} = \int dk k^2 \int d\Omega \frac{V}{(2\pi)^3} \tag{11.33}$$

We introduce the density u_k by averaging over all wave vectors with modulus k:

$$u_k = \frac{V}{(2\pi)^3}\int d\Omega \frac{1}{V}k^2 n_k\hbar\omega_k$$

$$= \frac{1}{(2\pi)^3}k^2 n_k\hbar\omega_k 4\pi \tag{11.34}$$

The factor 4π stems from averaging over a sphere in k-space. Now, the spectral energy density is

$$u(\nu)d\nu = u_k dk \tag{11.35}$$

which yields, using $2\pi\nu = ck$,

$$u(\nu) = u_k\frac{dk}{d\nu} = u_k\frac{2\pi}{c} = \frac{4\pi}{c^3}\nu^2 n_k\hbar\omega_k \tag{11.36}$$

As a consequence we obtain

$$\frac{A_{mn}}{B_{nm}} = \frac{\hbar\omega}{n_k \hbar \omega_k} u(\nu)$$
$$= \frac{4\pi}{c^3} \nu^2 h\nu \tag{11.37}$$

Since there are two different polarizations we finally obtain the ratio

$$\frac{A_{mn}}{B_{nm}} = \frac{8\pi}{c^3} \nu^2 h\nu \tag{11.38}$$

and, in turn, Planck's formula:

$$u(\nu) = \frac{8\pi}{c^3} \nu^2 h\nu \frac{1}{e^{h\nu/kT} - 1} \tag{11.39}$$

11.4 Interaction of Two-Level Atoms with Light

11.4.1 Two-Level Systems

In this subsection we are interested in the dynamical behaviour of a two-level system under the influence of an external perturbation $W(t)$. The time dependent Schrödinger equation reads

$$i\hbar |\dot\psi(t)\rangle = [H_0 + W]|\psi(t)\rangle \tag{11.40}$$

The ansatz

$$|\psi(t)\rangle = c_1(t)|1\rangle + c_2(t)|2\rangle \tag{11.41}$$

leads us to the set of equations

$$\dot c_1 = -i\omega_1 c_1 + H_{12}(t)c_2$$
$$\dot c_2 = -i\omega_2 c_2 + H_{21}(t)c_1 \tag{11.42}$$

with the definitions

$$\omega_i = \frac{E_i}{\hbar} \quad , \quad H_{ij} = \frac{1}{i\hbar}\langle i|W|j\rangle \tag{11.43}$$

Now, we can switch to the interaction picture

$$\frac{d}{dt}\tilde c_1 = e^{i(\omega_1 - \omega_2)t} H_{12}(t)\tilde c_2$$
$$\dot{d}dtc_2 = e^{i(\omega_2 - \omega_1)t} H_{21}(t)\tilde c_1 \tag{11.44}$$

We assume that the time dependence of the perturbation is harmonic in time,

$$H_{ij} = h_{ij} e^{-i\omega t} + h_{ij}^* e^{i\omega t} \tag{11.45}$$

such that we obtain

$$\frac{d}{dt}\tilde{c}_1 = [e^{i(\omega_1 - \omega_2 - \omega)t}h_{12}(t) + e^{i(\omega_1 - \omega_2 + \omega)t}h_{12}^*(t)]\tilde{c}_2$$

$$\frac{d}{dt}\tilde{c}_2 = [e^{i(\omega_2 - \omega_1 - \omega)t}h_{21}(t) + e^{i(\omega_2 - \omega_1 + \omega)t}h_{21}^*(t)]\tilde{c}_1 \qquad (11.46)$$

We perform the *rotating wave approximation.*

This leads us to

$$\frac{d}{dt}\tilde{c}_1 = = h_{12}\tilde{c}_2$$

$$\frac{d}{dt}\tilde{c}_2 = h_{21}^*\tilde{c}_1 \qquad (11.47)$$

and the solution is

$$\tilde{c}_1 = N cos\Omega t$$

$$\tilde{c}_2 = N\frac{h_{21}^*}{\Omega}sin\Omega t \qquad (11.48)$$

with

$$\Omega^2 = h_{12}h_{21}^* \qquad (11.49)$$

and the normalization constant

$$N = 1 \qquad (11.50)$$

The transition probability is then given explicitly by

$$|c_2|^2 = sin^2\Omega t \qquad (11.51)$$

11.4.2 Semiclassical Treatment

We consider a single atom and assume that the interaction with the electromagnetic field only involves two energy states. Such an atom is described by the Hamilton-operator

$$H = H_0 - \mathbf{E} \cdot \mathbf{\Theta} \qquad . \qquad (11.52)$$

Here, we have introduced the dipole operator Θ, which in a simple picture of an atom consisting of a single electron at distance $\mathbf{r}$ from a positively charged core is given by

$$\Theta = -e\mathbf{r} \qquad . \qquad (11.53)$$

An electromagnetic field may introduce a dipol moment. The contribution of all dipol moments of the atoms in a volume element add up to form the macroscopic polarization $P(\mathbf{x}, t)$ of the medium.

The unperturbed Hamiltonian H_0 is assumed to possess two energy levels E_1, E_2 with eigenstates $|1>$, $|2>$:

$$H_0|i> = E_i|i> \qquad , \qquad i = 1, 2 \qquad . \qquad (11.54)$$

The quantum mechanical state of the atom is a linear superposition of the eigenstates $|1>$, $|2>$:

$$|\psi> = c_1(t)|1> + c_2(t)|2> \qquad (11.55)$$

The electromagnetic field $\mathbf{E}$ will introduce transitions between these states. The dynamical evolution of the state vector $|\psi>$ is given by the time dependent Schrödinger equation:

$$i\hbar\frac{\partial}{\partial t}|\psi> = [H_0 - \mathbf{E}\cdot\mathbf{\Theta}]|\psi> \qquad . \qquad (11.56)$$

Evolution equations for the amplitues $c_i(t)$ can be obtained by inserting the ansatz into the equation (11.56) and projecting onto the both eigenstates $|1>$, $|2>$:

$$i\hbar\dot{c}_1 = E_1 c_1 - \mathbf{E}\cdot\mathbf{\Theta}_{12}c_2 \qquad ,$$
$$i\hbar\dot{c}_2 = E_2 c_2 - \mathbf{E}\cdot\mathbf{\Theta}_{21}c_1 \qquad . \qquad (11.57)$$

Thereby, we have defined the dipole matrix elements

$$\mathbf{\Theta}_{12} = <1|\Theta|2> = \mathbf{\Theta}_{21}^* \qquad (11.58)$$

The diagonal dipole matrix elements are assumed to vanish, which means that the two states do not possess a permanent dipole moment:

$$\mathbf{\Theta}_{11} = <1|\Theta|1> = \mathbf{\Theta}_{22} = <2|\Theta|2> = 0 \qquad (11.59)$$

This is the case if the eigenstates are spherically symmetric, as can be seen using the representation (11.53).

The following two combinations of the amplitudes c_1, c_2 have an immediate physical interpretation. The atomic inversion d,

$$d = c_2^* c_2 - c_1^* c_1 \qquad , \qquad (11.60)$$

is the difference between the probabilities of finding the atom in the states 1 ($|c_1|^2$) and 2 ($c_2|^2$), respectively. If we consider an ensemble of atoms, it is proportinal to the difference of the number of atoms in the excited and the ground states.

The second quantity α is related to the expectation value of the dipole moment and is defined according to:

$$\alpha = c_1^* c_2 \qquad . \qquad (11.61)$$

The atomic dipole moment can be calculated as the expectation value of the dipole operator $\mathbf{\Theta}$

$$<\psi(t)|\mathbf{\Theta}|\psi(t)> = c_1^* c_2 \mathbf{\Theta}_{12} + c_1 c_2^* \mathbf{\Theta}_{21} = \alpha\mathbf{\Theta}_{12} + \alpha^*\mathbf{\Theta}_{21} \qquad . \qquad (11.62)$$

A set of equations for the quantities α and d directly follows from the evolution equations for c_1, c_2 ($\omega = \omega_2 - \omega_1$):

$$\dot{\alpha} = -i\omega\alpha - \frac{i}{\hbar}\mathbf{E} \cdot \Theta_{21}d$$

$$\dot{d} = -\frac{2i}{\hbar}[\mathbf{E} \cdot \Theta_{12}a - \mathbf{E} \cdot \Theta_{21}\alpha^*] \tag{11.63}$$

For the following we shall introduce the abbreviations

$$p^+ = \alpha\mathbf{\Theta}_{12} \qquad , \qquad p^- = \alpha^*\mathbf{\Theta}_{21} \qquad . \tag{11.64}$$

The set of equations for the dynamics of the single atom in an electric field takes the form:

$$\frac{d}{dt}d = -\frac{2i}{\hbar}\mathbf{E} \cdot [\mathbf{p}^+ - \mathbf{p}^-] \qquad ,$$

$$\frac{d}{dt}\mathbf{p}^+ = -i\omega\mathbf{p}^+ - \frac{i}{\hbar}\mathbf{\Theta_{12}}\mathbf{E} \cdot \mathbf{\Theta}_{21}d \qquad . \tag{11.65}$$

Thereby, we have defined the transition frequency ω:

$$\omega = \frac{E_2 - E_1}{\hbar} \qquad . \tag{11.66}$$

Eqs. (11.65) allow us to evaluate the dynamical behaviour of a single two level atom with dipole moment Θ_{12} in an external electric field by looking at the inversion d and the polarization p^+.

11.4.3 Macroscopic Polarization and Inversion

The set of equations (11.65) describe the dynamics of a single atom. Since we are interested in the macroscopic behaviour of laseractive materials, in which a large number of two-level atoms participate, we introduce macroscopic quantities:

$$D(\mathbf{x}, t) = \sum_\mu d_\mu\delta(\mathbf{x} - \mathbf{x}_\mu)$$

$$\tilde{P}^\pm(\mathbf{x}, t) = \sum_\mu \mathbf{p}_\mu^\pm\delta(\mathbf{x} - \mathbf{x}_\mu) \tag{11.67}$$

Thereby, the location of an atom characterized by the index μ is denoted by $\mathbf{x}_\mu$. It is characterized by polarization $\mathbf{p}_\mu$ and inversion d_μ .
It is convenient to introduce the new variable P according to

$$P = i\tilde{P} \qquad P^* = -i\tilde{P}^* \tag{11.68}$$

This leads us to the following set of equations describing the propagation of electromagnetic waves in a material consisting of two level atoms:

$$\frac{\partial}{\partial t}D(\mathbf{x},t) = \frac{2}{\hbar}\mathbf{E}(\mathbf{x},t)\cdot[P(\mathbf{x},t)+P^*(\mathbf{x},t)]$$

$$\frac{\partial}{\partial t}P(\mathbf{x},t) = -i\omega P(\mathbf{x},t) + \frac{1}{\hbar}\mathbf{E}(\mathbf{x},t)\cdot\mathbf{\Theta}_{21}\mathbf{\Theta}_{12}D(\mathbf{x},t)$$

$$\{\Delta - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\}\mathbf{E}(\mathbf{x},t) = \frac{4\pi\sigma}{c^2}\frac{\partial}{\partial t}\mathbf{E}(\mathbf{x},t) + \frac{4\pi i}{c^2}\frac{\partial^2}{\partial t^2}[\mathbf{P}(\mathbf{x},t)-\mathbf{P}^*(\mathbf{x},t)]$$ (11.69)