Quantum mechanics

II

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1 Quantum dynamics

1.1 The time evolution operator

- The time-dependent Schrödinger equation is given by

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = H |\psi(t)\rangle .$$

- Assuming that the Hamiltonian H does not depend on time, its formal solution is

$$|\psi(t)\rangle = e^{-\frac{i}{\hbar}(t-t_0)H} |\psi(t_0)\rangle .$$

- In order to see that this is indeed the case, we make use of the series expansion of the exponential function:

$$i\hbar \frac{d}{dt} e^{-\frac{i}{\hbar}(t-t_0)H} |\psi(t_0)\rangle = i\hbar \frac{d}{dt} \sum_{k=0}^{\infty} \frac{1}{k!} \left(-\frac{i}{\hbar}(t-t_0)\right)^k H^k |\psi(t_0)\rangle$$

$$= i\hbar \sum_{k=1}^{\infty} \frac{1}{(k-1)!} \left(-\frac{i}{\hbar}\right)^k (t-t_0)^{k-1} H^k |\psi(t_0)\rangle$$

$$= H e^{-\frac{i}{\hbar}(t-t_0)H} |\psi(t_0)\rangle$$

- Defining the operator $U(t,t_0) = e^{-\frac{i}{\hbar}(t-t_0)H}$, we can write

$$i\hbar \frac{d}{dt} U(t,t_0) |\psi(t_0)\rangle = H\, U(t,t_0) |\psi(t_0)\rangle$$

and apparently the time-evolved state can be written as

$$|\psi(t)\rangle = U(t, t_0)\,|\psi(t_0)\rangle .$$

- The operator $U(t, t_0)$ evolves the state from time t_0 to time t and is thus called the time <u>evolution operator</u>.

- It has the following properties:

(i) $U(t_0, t_0) = \mathbb{1}$

(ii) $U^+(t, t_0)\,U(t, t_0) = \mathbb{1}$, i.e. $U^+(t, t_0)$ is a <u>unitary operator</u>. This follows from the normalisation condition of the state $|\psi(t)\rangle$:

$$1 = \langle\psi(t)|\psi(t)\rangle = \langle\psi(t_0)|U^+(t, t_0)\,U(t, t_0)|\psi(t_0)\rangle$$

$$\overset{!}{=} \langle\psi(t_0)|\psi(t_0)\rangle$$

$\hookrightarrow U^+(t, t_0)\,U(t, t_0) = \mathbb{1}$, since this has to be valid for any state

(iii) $U(t_1,t_0) = U(t_1,t)\,U(t,t_0)$, which follows from

$$|\psi(t_1)\rangle = U(t_1,t)\,|\psi(t)\rangle = U(t_1,t)\,U(t,t_0)\,|\psi(t_0)\rangle$$
$$\vdots$$
$$= U(t_1,t_0)\,|\psi(t_0)\rangle$$

- From property (iii) follows, by setting $t_1 = t_0$,

$$\mathbb{1} = U(t_0,t_0) = U(t_0,t)\,U(t,t_0),$$ and hence

$$U(t_0,t) = U^{-1}(t,t_0) = U^{+}(t,t_0)$$

↑ due to the unitarity of the time evolution operator

- So far we have considered only the case in which the Hamiltonian H is time-independent, and when $U(t,t_0)$ can be computed by exponentiation.
- However, as we will now show, $U(t,t_0)$ can also be constructed for time-dependent Hamiltonians $H(t)$
- Starting point is the time-dependent Schrödinger equation

$$i\hbar \frac{d}{dt} \underbrace{U(t,t_0)|\psi(t_0)\rangle}_{|\psi(t)\rangle} = H(t) \underbrace{U(t,t_0)|\psi(t_0)\rangle}_{|\psi(t)\rangle}$$

- Since this equation is valid for all $|\psi(t_0)\rangle$, it must hold that

$$i\hbar \frac{\partial}{\partial t} U(t, t_0) = H(t)\, U(t, t_0) .$$

- Integrating this differential equation for the time evolution operator with the initial condition $U(t_0, t_0) = \mathbb{1}$ yields

$$U(t, t_0) = \mathbb{1} - \frac{i}{\hbar} \int_{t_0}^{t} dt_1\, H(t_1)\, U(t_1, t_0)$$

- This equation can be solved by iteration, i.e. we insert the expression

$$U(t_1, t_0) = \mathbb{1} - \frac{i}{\hbar} \int_{t_0}^{t_1} dt_2\, H(t_2)\, U(t_2, t_0) ,$$

which yields

$$U(t, t_0) = \mathbb{1} - \frac{i}{\hbar} \int_{t_0}^{t} dt_1\, H(t_1) + \left(\frac{-i}{\hbar}\right)^2 \int_{t_0}^{t} dt_1\, H(t_1) \int_{t_0}^{t_1} dt_2\, H(t_2)\, U(t_2, t_0) ,$$

and repeat this procedure

- The final result can be written as

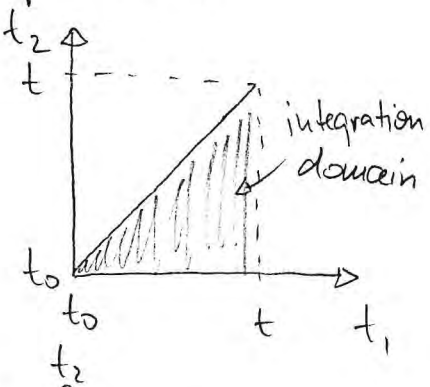
$$U(t, t_0) = \mathbb{1} + \sum_{n=1}^{\infty} U^{(n)}(t, t_0) = \sum_{n=0}^{\infty} U^{(n)}(t, t_0) ,$$

where

$$U^{(n)}(t,t_0) = \left(-\frac{i}{\hbar}\right)^n \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \cdots \int_{t_0}^{t_{n-1}} dt_n \, H(t_1) H(t_2) \cdots H(t_n) .$$

- Note that the order of the operators in the integrand matters, since generally $[H(t_n), H(t_m)] \neq 0$ for $n \neq m$.
- The order of their time arguments is such that $t \geq t_1 \geq t_2 \geq \cdots \geq t_n \geq t_0$.
- The operators are thus time ordered, which means that the operator containing the earliest time argument, t_n, is acting first on the state $|\psi(t_0)\rangle$.
- In the following we seek to derive a more compact expression for the time evolution operator.
- To illustrate the idea, we consider for the moment $U^{(n)}(t,t_0)$ with $n=2$

- This operator involves an integration over a triangle $\int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2$

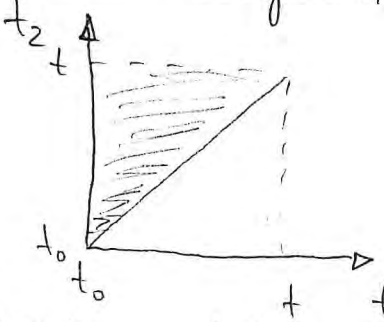


- More specifically, we have

$$U^{(2)}(t,t_0) \propto \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2\, H(t_1)\,H(t_2) = \int_{t_0}^{t} dt_2 \int_{t_0}^{t_2} dt_1\, H(t_2)H(t_1),$$

where the expression on the very right is obtained by the change of integration variables: $t_2 \leftrightarrow t_1$.

- However, after this change the integration proceeds over this domain:



- Since integrating over both domains yields the same result, we can write

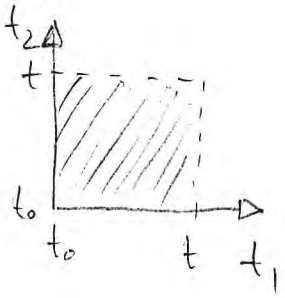
$$U^{(2)}(t,t_0) = \left(-\frac{i}{\hbar}\right)^2 \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2\, H(t_1)\,H(t_2)$$

$$= \left(-\frac{i}{\hbar}\right)^2 \frac{1}{2}\left[\int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2\, H(t_1)H(t_2) + \int_{t_0}^{t} dt_2 \int_{t_0}^{t_2} dt_1\, H(t_2)H(t_1)\right]$$

↑ factor $\frac{1}{2}$ to avoid double counting

$$= \frac{1}{2}\left(-\frac{i}{\hbar}\right)^2 \int_{t_0}^{t} dt_1 \int_{t_0}^{t} dt_2 \left[H(t_1) H(t_2) \Theta(t_1 - t_2) + H(t_2) H(t_1) \Theta(t_2 - t_1) \right]$$

- In the last step we have extended the integration domain to the square and introduced the Heaviside step function



$$\Theta(x) = \begin{cases} 1 & , \; x > 0 \\ 0 & , \; x < 0 \end{cases}$$

in order to restrict the integration domain for each of the two terms.

- We now introduce the so-called time ordering operator T, which is defined as

$$T\left[H(t_1) H(t_2)\right] = \begin{cases} H(t_1) H(t_2) & , \; t_1 > t_2 \\ H(t_2) H(t_1) & , \; t_2 > t_1 \end{cases}$$

- This operator orders the operators in its argument such that the operator with the largest time argument appears at the very left.

- Using the time ordering operator allows us to write

$$U^{(2)}(t,t_0) = \frac{1}{2}\left(-\frac{i}{\hbar}\right)^2 \int_{t_0}^{t} dt_1 \int_{t_0}^{t} dt_2 \, \mathcal{T}\left[H(t_1)\,H(t_2)\right].$$

- The advantage is that this expression no longer contains nested integrals.

- The construction can be extended to arbitrary $U^{(n)}(t,t_0)$, e.g. for $n=3$:

$$U^{(3)}(t,t_0) = \left(-\frac{i}{\hbar}\right)^3 \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \int_{t_0}^{t_2} dt_3 \, H(t_1)H(t_2)H(t_3)$$

$$= \frac{1}{6}\left(-\frac{i}{\hbar}\right)^3 \int_{t_0}^{t} dt_1 \int_{t_0}^{t} dt_2 \int_{t_0}^{t} dt_3 \, \underbrace{\mathcal{T}\left[H(t_1)\,H(t_2)\,H(t_3)\right]}$$

↑ 3! integration domains

example for $t_3 > t_1 > t_2$:
$\mathcal{T}\left[H(t_1)H(t_2)H(t_3)\right] = H(t_3)\,H(t_1)\,H(t_2)$

- The general result is

$$U^{(n)}(t,t_0) = \frac{1}{n!}\left(-\frac{i}{\hbar}\right)^n \int_{t_0}^{t} dt_1 \int_{t_0}^{t} dt_2 \ldots \int_{t_0}^{t} dt_n \, \mathcal{T}\left[H(t_1)\ldots H(t_n)\right],$$

- We can now construct the full time evolution operator:

$$U(t,t_0) = \sum_{n=0}^{\infty} U^{(n)}(t,t_0)$$

$$= \sum_{n=0}^{\infty} \frac{1}{n!} \left(-\frac{i}{\hbar}\right)^n \int_{t_0}^{t} dt_1 \dots \int_{t_0}^{t} dt_n \; \mathcal{T}\left[H(t_1) \dots H(t_n)\right]$$

$$= \mathcal{T}\left[\sum_{n=0}^{\infty} \frac{1}{n!} \left(-\frac{i}{\hbar}\right)^n \int_{t_0}^{t} dt_1 \dots \int_{t_0}^{t} dt_n \; H(t_1) \dots H(t_n) \right]$$

$$= \mathcal{T}\left[\sum_{n=0}^{\infty} \frac{1}{n!} \left(-\frac{i}{\hbar}\right)^n \left(\int_{t_0}^{t} dt' H(t') \right)^n \right]$$

$$= \underbrace{\mathcal{T} \exp\left(-\frac{i}{\hbar} \int_{t_0}^{t} dt' H(t')\right)}$$

time ordered exponential

- Note, that the time ordered exponential is a formal expression (defined by the series expansion)
- However, it is useful and obeys

$$i\hbar \frac{d}{dt} \mathcal{T} \exp\left(-\frac{i}{\hbar} \int_{t_0}^{t} dt' H(t')\right) = H(t)\, \mathcal{T} \exp\left(-\frac{i}{\hbar} \int_{t_0}^{t} dt' H(t')\right)$$

↑ has to appear at the left, because t is the largest time

1.2 Dynamical pictures of quantum theory

- Let us assume that we know the state $|\psi(t_0)\rangle$ of a quantum system at a given time t_0.

- A typical goal in quantum mechanics is to calculate the expectation value of an operator O at a later time t, i.e. for the state $|\psi(t)\rangle$: $\langle O \rangle = \langle \psi(t) | O | \psi(t) \rangle$

- This can be accomplished in different ways, which leads to the notion of „dynamical pictures" or „representations".

Schrödinger picture

- In this „standard" representation of quantum mechanics a state $|\psi(t)\rangle$ evolves according to

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = H |\psi(t)\rangle$$

or $|\psi(t)\rangle = U(t, t_0) |\psi(t_0)\rangle$.

- Operators are time independent unless the are constructed with an explicit time dependence, in which case $\frac{d}{dt} O = \frac{\partial}{\partial t} O$.

Heisenberg picture

- We consider the expectation value of an operator O in the time evolved state $|\psi(t)\rangle$:

$$\langle\psi(t)|O|\psi(t)\rangle = \langle\psi(t_0)|U^+(t,t_0)\,O\,U(t,t_0)|\psi(t_0)\rangle.$$

- Apparently, this can be interpreted as the expectation value of the time dependent operator $U^+(t,t_0)\,O\,U(t,t_0)$ evaluated in the time independent (initial) state $|\psi(t_0)\rangle$.

↳ idea behind the Heisenberg picture

- states are time independent

$$|\psi_H\rangle = |\psi(t_0)\rangle = U^+(t,t_0)\,|\psi(t)\rangle$$

↑ Heisenberg picture

- operators are time dependent

$$O_H = U^+(t,t_0)\,O\,U(t,t_0)$$

↑ operator in the Schrödinger picture

↳ operators acquire time dependence even when they are time independent in the Schrödinger picture

- For the expectation values in the two pictures, one finds $\langle \psi(t)|O|\psi(t)\rangle = \langle \psi_H|O_H(t)|\psi_H\rangle$.

- Furthermore, the following properties hold:

i) Scalar products remain unchanged

$$\langle \phi(t)|\psi(t)\rangle = \langle \phi(t)|UU^+|\psi(t)\rangle = \langle U^+\phi(t)|U^+\psi(t)\rangle$$
$$= \langle \phi_H|\psi_H\rangle$$

ii) Eigenvalues of operators remain unchanged

$$O|\psi(t)\rangle = \lambda|\psi(t)\rangle$$
$$OUU^+|\psi(t)\rangle = \lambda|\psi(t)\rangle$$
$$\underbrace{U^+OUU^+|\psi(t)\rangle}_{O_H(t)\ \ |\psi_H\rangle} = \lambda \underbrace{U^+|\psi(t)\rangle}_{|\psi_H\rangle}$$

iii) Products of operators keep their structure

$$C = AB \rightarrow C_H = U^+CU = U^+ABU = U^+AUU^+BU$$
$$= A_H B_H$$

Furthermore,

$$[x, p] = i\hbar \longrightarrow [x_H(t), p_H(t)] = i\hbar$$

and

$$H = H(x,p) \rightarrow H_H(t) = H(x_H(t), p_H(t))$$

iv) Provided the Hamiltonian H is time independent, and thus having $U(t,t_0) = e^{-\frac{i}{\hbar}(t-t_0)H}$, one can write

$$O_H(t) = e^{\frac{i}{\hbar}(t-t_0)H} \, O \, e^{-\frac{i}{\hbar}(t-t_0)H}$$

For $O = H$ one has $H_H = H$.

- Using the differential equation for the time evolution operator, and its adjoint equation

$$-i\hbar \frac{\partial}{\partial t} U^+(t,t_0) = U^+(t,t_0) \, H(t)$$

one finds the following evolution equation for operators:

$$\frac{d}{dt} O_H(t) = \frac{d}{dt} [U^+ O U]$$

$$= \left(\frac{\partial}{\partial t} U^+\right) O U + U^+ \left(\frac{\partial}{\partial t} O\right) U + U^+ O \left(\frac{\partial}{\partial t} U\right)$$

$$= \frac{i}{\hbar} U^+ H O U + U^+ \left(\frac{\partial}{\partial t} O\right) U - \frac{i}{\hbar} U^+ O H U$$

$$= \frac{i}{\hbar} [H_H, O_H] + \left(\frac{\partial}{\partial t} O\right)_H$$

- This is the <u>Heisenberg equation of motion</u>.

- It resembles the classical equation of motion of a function $F(x,p)$:

$$\frac{dF}{dt} = \underbrace{\{F, H\}}_{\text{Poisson bracket}} + \frac{\partial F}{\partial t}$$

$$\text{Poisson bracket} = \frac{\partial F}{\partial x}\frac{\partial H}{\partial p} - \frac{\partial F}{\partial p}\frac{\partial H}{\partial x}$$

Dirac picture / interaction picture

- The interaction picture is somewhat in between the Schrödinger and Heisenberg picture.
- It is usually used to deal with Hamiltonians with the structure

$$H = H_0 + \alpha V$$

- H_0: time independent Hamiltonian with known spectrum
- α: coupling constant which parameterises the strength of the perturbation
- V: perturbation (operator)

- In the interaction picture the operators evolve under the Hamiltonian H_0, while the wave functions evolve under the perturbing Hamiltonian $\propto V$.
- We use the time evolution operator,

$$U_0(t,t_0) = e^{-\frac{i}{\hbar}(t-t_0)H_0},$$

to define the interaction picture state

$$|\psi_D(t)\rangle = U_0^\dagger(t,t_0)\,|\psi(t)\rangle.$$

↑ often one uses the label 'I' or 'int'

- An operator in the interaction picture becomes

$$O_D(t) = U_0^\dagger(t,t_0)\, O\, U_0(t,t_0)$$
$$= e^{\frac{i}{\hbar}(t-t_0)H_0}\, O\, e^{-\frac{i}{\hbar}(t-t_0)H_0}$$

- With these definitions, the Schrödinger and interaction representation become identical at time $t = t_0$.
- What is left to show is what equation of motion governs the evolution of states and operators, respectively.

- states:

$$i\hbar \frac{d}{dt}|\psi_D(t)\rangle = i\hbar \left[\underbrace{\frac{\partial U_0^+}{\partial t}}_{= \frac{i}{\hbar} U_0^+ H_0} |\psi(t)\rangle + U_0^+ \underbrace{\frac{d}{dt}|\psi(t)\rangle}_{= -\frac{i}{\hbar}(H_0 + \alpha V)|\psi(t)\rangle} \right]$$

$$= -U_0^+ H_0 |\psi(t)\rangle + U_0^+ (H_0 + \alpha V)|\psi(t)\rangle$$

$$= U_0^+ \alpha V |\psi(t)\rangle = U_0^+ \alpha V U_0 U_0^+ |\psi(t)\rangle$$

$$= \alpha V_D |\psi_D(t)\rangle$$

↳ states evolve under the perturbation

- operators:

A calculation analogous to the one of the Heisenberg picture yields

$$\frac{d}{dt} O_D(t) = \frac{i}{\hbar} [H_0, O_D(t)] + \left(\frac{\partial O(t)}{\partial t} \right)_D$$

$H = H_0 + \alpha V$

	Schrödinger	Heisenberg	Dirac / interaction
$\|\psi\rangle$	time evolution governed by H	fixed	time evolution governed by αV
O	fixed	time evolution governed by H	time evolution governed by H_0

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perturbation theory example on p. 20

- electron confined in potential of harmonic oscillator in presence of electric field of form

$$\mathcal{E}(t) = \mathcal{E}_0 \, e^{-t^2/\tau^2}$$

- Hamiltonian

$$H = \frac{p^2}{2\mu} + \frac{1}{2}\mu\omega^2 x^2 + \underbrace{e x \mathcal{E}_0 \, e^{-t^2/\tau^2}}$$

(ω: oscillator frequency; μ: electron mass; $e x \mathcal{E}_0 \, e^{-t^2/\tau^2}$: electric potential)

- probability for transition between ground state $|0\rangle$ and first excited state $|1\rangle$
- $\omega_{01} = \omega_1 - \omega_0 = \frac{3}{2}\omega - \frac{1}{2}\omega = \omega$
- $P_{0\to 1} = \frac{e^2\mathcal{E}_0^2}{\hbar^2}\left|\int_{-\infty}^{\infty} dt_1 \, e^{i\omega t_1} e^{-t_1^2/\tau^2} \langle 1|x|0\rangle\right|^2$
- with $x = \sqrt{\frac{\hbar}{2\mu\omega}}(a^\dagger + a) \to \langle 1|x|0\rangle = \sqrt{\frac{\hbar}{2\mu\omega}}$

↳ $P_{0\to 1}(\infty) = \frac{\pi e^2 \mathcal{E}_0^2 \tau^2}{2\mu\hbar\omega} e^{-\frac{\omega^2\tau^2}{2}}$

1.3 Time dependent perturbation theory

- The interaction picture offers an elegant route for deriving time dependent perturbation theory.
- The solution of

$$i\hbar \frac{d}{dt} |\psi_D(t)\rangle = \alpha V_D(t) |\psi_D(t)\rangle$$

is given by

$$|\psi_D(t)\rangle = U_D(t, t_0) |\psi_D(t_0)\rangle$$

where

$$U_D(t, t_0) = \mathcal{T} \exp\left(-\frac{i}{\hbar} \int_{t_0}^{t} dt' \, \alpha V_D(t')\right)$$

$$= \mathbb{1} - \frac{i}{\hbar} \int_{t_0}^{t} dt' \, \alpha V_D(t') + \left(-\frac{i}{\hbar}\right)^2 \int_{t_0}^{t} dt_1 \, \alpha V_D(t_1) \int_{t_0}^{t_1} dt_2 \, \alpha V_D(t_2) + \ldots$$

is the so-called Dyson series.

- The advantage is that this expansion of the time evolution operator yields a series in powers of the small parameter α.

- Depending on the desired order of perturbation theory one chooses to truncate this series either at α (1st order), α^2 (2nd order) or even higher powers.

- We assume now that at time t_0 the system populates an eigenstate of the Hamiltonian H_0: (eigenstate, eigenvalue)

$$|\psi(t_0)\rangle = |\psi_0(t_0)\rangle = |n\rangle \quad ; \quad H_0|n\rangle = E_n^{(0)}|n\rangle$$

- The time evolution of this state within the interaction picture reads

$$|\psi_D(t)\rangle = |n\rangle - \frac{i}{\hbar}\int_{t_0}^{t} dt' \alpha V_D(t')|n\rangle + \left(-\frac{i}{\hbar}\right)^2 \int_{t_0}^{t} dt_1 \alpha V_D(t_1) \int_{t_0}^{t_1} dt_2 \alpha V_D(t_2)|n\rangle + \dots$$

- Moving back to the Schrödinger picture via $|\psi_D(t)\rangle = e^{\frac{i}{\hbar}(t-t_0)H_0}|\psi(t)\rangle$ and bringing the operator $e^{\frac{i}{\hbar}(t-t_0)H_0}$ to the right hand side yields:

$$|\psi(t)\rangle = e^{-\frac{i}{\hbar}(t-t_0)H_0}\Bigg[|n\rangle - \frac{i}{\hbar}\int_{t_0}^{t} dt' e^{\frac{i}{\hbar}(t_1-t_0)H_0} \alpha V(t_1) e^{-\frac{i}{\hbar}(t_1-t_0)H_0}|n\rangle$$

$$+\left(-\frac{i}{\hbar}\right)^2 \int_{t_1}^{t} dt_1 e^{\frac{i}{\hbar}(t_1-t_0)H_0} \alpha V_1(t_1) e^{-\frac{i}{\hbar}(t_1-t_0)H_0} \int_{t_0}^{t_1} dt_2 e^{\frac{i}{\hbar}(t_2-t_0)H_0} \alpha V(t_2) e^{-\frac{i}{\hbar}(t_2-t_0)H_0}|n\rangle + \dots \Bigg]$$

- We can now calculate the probability of the system to be found in the eigenstate $|m\rangle$ ($\neq |n\rangle$) of H_0 at time t.
- To this end we calculate the probability amplitude

$$\langle m|\psi(t)\rangle = -\frac{i}{\hbar} e^{-\frac{i}{\hbar}(t-t_0)E_m^{(0)}} \int_{t_0}^{t} dt_1\, e^{\frac{i}{\hbar}(t_1-t_0)E_m^{(0)}} \langle m|\alpha V(t_1)|n\rangle \underbrace{e^{-\frac{i}{\hbar}(t_1-t_0)H_0}|n\rangle}_{e^{-\frac{i}{\hbar}(t_1-t_0)E_n^{(0)}}}$$

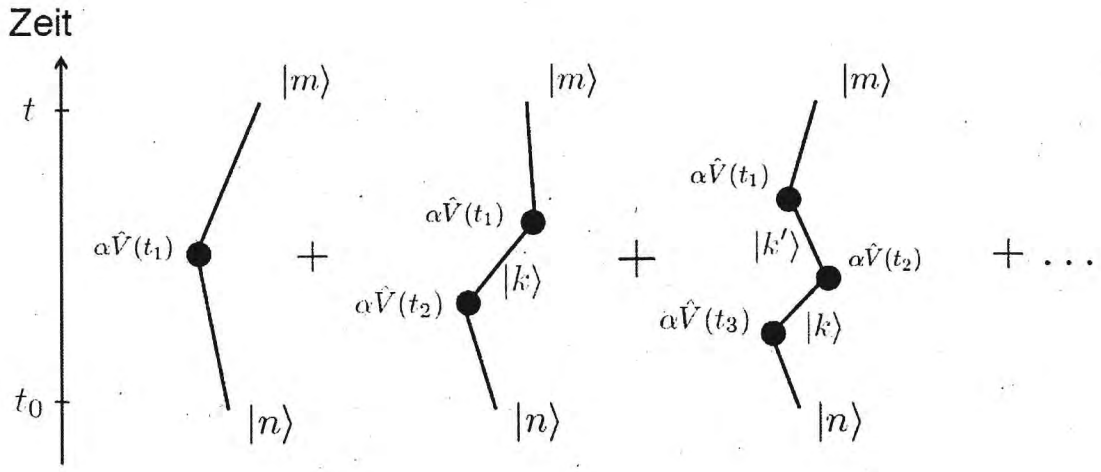
$$+ \left(-\frac{i}{\hbar}\right)^2 e^{-\frac{i}{\hbar}(t-t_0)E_m^{(0)}} \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2\, e^{\frac{i}{\hbar}(t_1-t_0)E_m^{(0)}} \langle m|\alpha V(t_1) e^{-\frac{i}{\hbar}(t_1-t_2)H_0} \alpha V(t_2)|n\rangle e^{-\frac{i}{\hbar}(t_2-t_0)E_n^{(0)}} + \ldots$$

- Using the abbreviation $\omega_{mn} = \frac{1}{\hbar}(E_m^{(0)} - E_n^{(0)})$ ("transition frequency") and inserting the resolution of the identity, $\mathbb{1} = \sum_k |k\rangle\langle k|$, in the second term yields

$$\langle m|\psi(t)\rangle = e^{-\frac{i}{\hbar}(E_m^{(0)}t - E_n^{(0)}t_0)} \left[-\frac{i}{\hbar} \int_{t_0}^{t} dt_1\, e^{i\omega_{mn}t_1} \langle m|\alpha V(t_1)|n\rangle \right.$$

$$\left. + \left(-\frac{i}{\hbar}\right)^2 \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \sum_k e^{i\omega_{mk}t_1} \langle m|\alpha V(t_1)|k\rangle\langle k|\alpha V(t_2)|n\rangle e^{i\omega_{kn}t_2} + \ldots \right]$$

Diagrammatic representation of the perturbative expansion



Skript zur Vorlesung
Fortgeschrittene Quantentheorie
(Quantenmechanik II)
Prof. Werner Vogelsang
Universität Tübingen
Wintersemester 2020/21

- The probability of a transition $|n\rangle \to |m\rangle$ can now be calculated by evaluating

$$P_{n\to m}(t) = |\langle m|\psi(t)\rangle|^2 .$$

- To first order in α we thus find

$$P_{n\to m}(t) = \frac{1}{\hbar^2}\left|\int_{t_0}^{t} dt'\, e^{i\omega_{mn}t'}\langle m|\alpha V(t')|n\rangle\right|^2 .$$

- As a first application of perturbation theory we consider the situation in which a perturbation is suddenly switched on at time $t_0 = 0$ and kept constant afterwards:

$$\alpha V(t) = \alpha V_0\,\Theta(t) .$$

↑ Heaviside step function

- Inserting this expression into the formula for the transition probability and considering only the first order in α yields

$$P_{n\to m}(t) = \frac{1}{\hbar^2}\left|\int_0^t dt'\, e^{i\omega_{mn}t'}\right|^2 \underbrace{|V_{mn}|^2}_{|\langle m|\alpha V_0|n\rangle|^2}$$

$$= \frac{|V_{mn}|^2}{\hbar^2}\left|\frac{e^{i\omega_{mn}t}-1}{i\omega_{mn}}\right|^2 = \frac{|V_{mn}|^2}{\hbar^2}\left(\frac{\sin\left(\frac{\omega_{mn}t}{2}\right)}{\left(\frac{\omega_{mn}}{2}\right)}\right)^2$$

- We evaluate this formula for different scenarios:

i) H_0 has a discrete, non-degenerate spectrum

- Since $E_n^{(0)} \neq E_m^{(0)}$ one has $\omega_{mn} \neq 0$ and thus $P_{n\to m}(t)$ oscillates with a period $\frac{2\pi}{|\omega_{mn}|}$. Such oscillations are characteristic for systems with discrete spectra.

The amplitude of the oscillations is $\frac{4|V_{mn}|^2}{\omega_{mn}^2}$, i.e. the transition probability becomes smaller between states that are far apart in energy.

ii) H_0 has a discrete spectrum and the energy $E_n^{(0)}$ is degenerate

- Given that $\lim_{x\to 0} \frac{\sin xt}{x} = t$ one finds in this case $P_{n\to m}(t) = \frac{|V_{mn}|^2}{\hbar^2} t^2$.

- This expression can only be sensible for sufficiently short times, $t \ll \frac{\hbar}{|V_{mn}|}$, since $P_{n\to m} \leq 1$.

- Long times require the consideration of higher orders.

iii) The spectrum of H_0 is continuous in the vicinity of $E_n^{(0)}$

- In order to investigate this case we need to take a closer look at the function $f(t) = \left(\frac{2 \sin(\omega_{mn} \frac{t}{2})}{\omega_{mn}} \right)^2$ to which $P_{n \to m}(t)$ is proportional.

- $f(t)$ has a peak at $\omega_{mn} = 0$, i.e. at $E_n^{(0)} = E_m^{(0)}$, and the hight of this peak it growing in time as t^2.

- Moreover, with growing time the peak becomes narrower so that transitions with $|\omega_{mn}| > 0$ become increasingly unlikely.

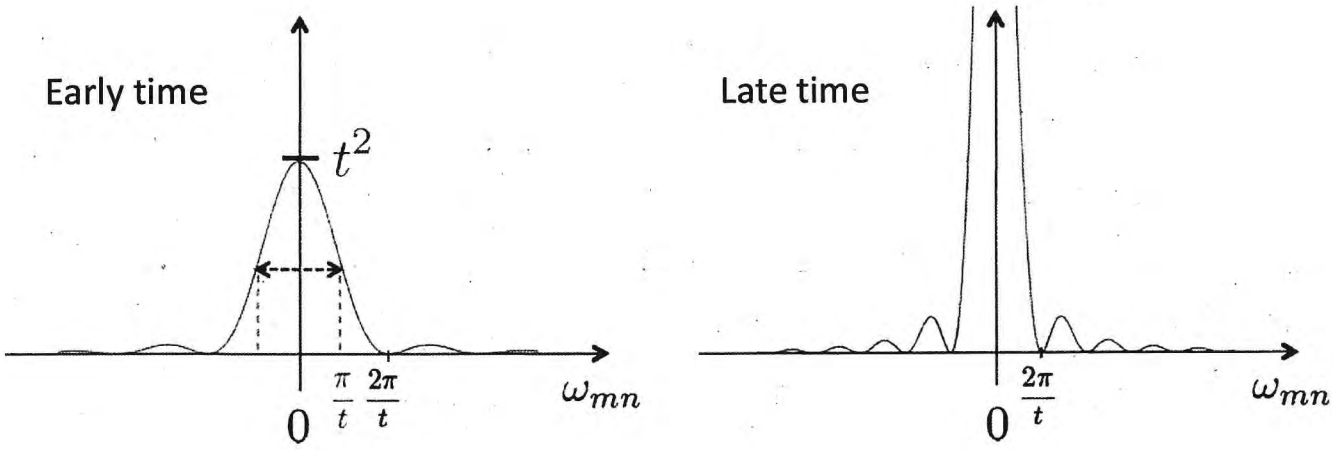
- In fact, $f(t)$ is closely related to a representation of the Dirac δ-function:

$$\delta(x) = \lim_{t \to \infty} \delta_t(x) = \lim_{t \to \infty} \frac{\sin^2(xt)}{\pi x^2 t}$$

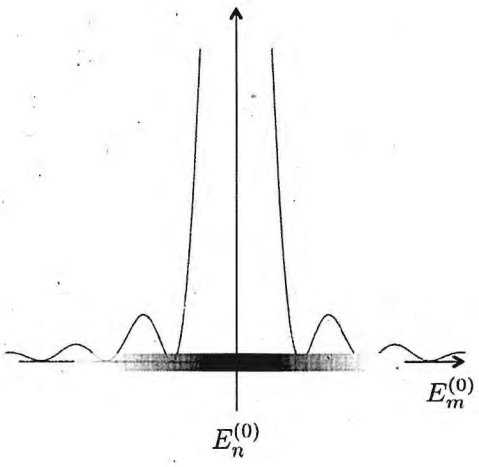
- Therefore, we can make for long times t the replacement

$$f(t) \longrightarrow \pi t \, \delta\left(\frac{\omega_{mn}}{2}\right)$$

The function f(t)



Continuous distribution of final state energies



Skript zur Vorlesung
Fortgeschrittene Quantentheorie
(Quantenmechanik II)
Prof. Werner Vogelsang
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- Using $\delta(ax) = \frac{1}{|a|}\delta(x)$ yields for the transition probability in this limit

$$P_{n\to m}(t) \approx \frac{|V_{mn}|^2}{\hbar^2}\pi t\,\delta\left(\frac{\omega_{mn}}{2}\right) = t\frac{2\pi}{\hbar}|V_{mn}|^2\delta\left(E_m^{(0)} - E_n^{(0)}\right)$$

- This expression allows us to calculate the transition rate

$$\Gamma_{n\to m} = \frac{dP_{n\to m}(t)}{dt} = \frac{2\pi}{\hbar}|V_{mn}|^2\delta\left(E_m^{(0)} - E_n^{(0)}\right)$$

- This derivation has a few issues:
  - i) We conveniently ignored the fact that the probability increases in time without being bounded, and at the same time we are considering the limit $t \to \infty$.
  - ii) A rate should be a measurable quantity and thus should not contain a δ-function.

- The δ-function can be given meaning by considering that we are actually dealing with a continuous spectrum of states into which transitions take place.
- The total transition probability must then be calculated according to

$$P = \sum_m P_{n\to m}(t) = \sum_{E_m^{(0)}} P_{n\to m}(t) = \int_{-\infty}^{\infty} dE_m^{(0)}\, \rho(E_m^{(0)})\, P_{n\to m}(t)$$

$\sum_m$: sum over all target states

$\sum_{E_m^{(0)}} \to \int dE_m^{(0)}\,\rho(E_m^{(0)})$: conversion of the sum over target state energies into integral involving the density of states

$\rho(E) = \frac{dN}{dE}$ (number of states N in energy interval $[E, E+dE]$)

$$= \int_{-\infty}^{\infty} dE_m^{(0)}\, \rho(E_m^{(0)})\, \frac{|V_{mn}|^2}{\hbar^2} \underbrace{\left(\frac{\sin(\omega_{mn}\frac{t}{2})}{\frac{\omega_{mn}}{2}} \right)^2}_{\text{function strongly peaked at } E_m^{(0)} = E_n^{(0)}}$$

$$\approx \left(\rho(E_m^{(0)})\, \frac{|V_{mn}|^2}{\hbar^2} \right)\Bigg|_{E_m^{(0)} = E_n^{(0)}} \underbrace{\int_{-\infty}^{\infty} dE_m^{(0)} \left(\frac{\sin(\omega_{mn}\frac{t}{2})}{\frac{\omega_{mn}}{2}} \right)^2}_{2\pi\hbar t}$$

$$= \frac{2\pi}{\hbar}\, \rho(E_n^{(0)})\, |V_{mn}|^2 t$$

- Calculating the corresponding transition rate leads to the so-called

Fermi's Golden Rule

$$\Gamma_{n\to m} = \frac{2\pi}{\hbar}\,\rho(E_n^{(0)})\,|V_{mn}|^2,$$

which despite the many approximations that were performed yields often rather accurate results.

- We now consider so-called harmonic perturbations which oscillate at a given frequency ω:

$$\propto V(t) = \left(\propto V_0\, e^{-i\omega t} + \propto V_0^{+} e^{i\omega t}\right)\Theta(t)$$

- Using $\int_0^t dt'\, e^{i(\omega_{mn}\pm\omega)t'} = \frac{e^{i(\omega_{mn}\pm\omega)t}-1}{i(\omega_{mn}\pm\omega)}$

and $V_{mn} = \langle m|\propto V_0|n\rangle$, $V_{nm}^{*} = \langle m|\propto V_0^{+}|n\rangle = \langle n|\propto V_0|m\rangle^{*}$,

we can write:

$$P_{n\to m}(t) = \frac{1}{\hbar^2}\left| V_{mn}\,\frac{e^{i(\omega_{mn}-\omega)t}-1}{i(\omega_{mn}-\omega)} + V_{nm}^{*}\,\frac{e^{i(\omega_{mn}+\omega)t}-1}{i(\omega_{mn}+\omega)}\right|^2$$

- Evaluating this expression yields

$$P_{n\to m}(t) = \frac{|V_{mn}|^2}{\hbar^2}\left(\frac{\sin\left(\frac{\omega_{mn}-\omega}{2}t\right)}{\frac{\omega_{mn}-\omega}{2}}\right)^2 + \frac{|V_{nm}|^2}{\hbar^2}\left(\frac{\sin\left(\frac{\omega_{mn}+\omega}{2}t\right)}{\frac{\omega_{mn}+\omega}{2}}\right)^2$$

$$+ 2\,\mathrm{Re}\left\{V_{mn}V_{nm}\,e^{-i\omega t}\,\frac{\sin\left(\frac{\omega_{mn}-\omega}{2}t\right)}{\frac{\omega_{mn}-\omega}{2}}\,\frac{\sin\left(\frac{\omega_{mn}+\omega}{2}t\right)}{\frac{\omega_{mn}+\omega}{2}}\right\}$$

at long times this „interference term" grows $\propto t$, while the other two terms grow $\propto t^2$

- For sufficiently long times the interference term can be neglected and the transition probability is approximately given by a sum of two δ-functions:

$$P_{n\to m}(t) \approx \frac{2\pi}{\hbar^2}\,t\,|V_{nm}|^2\,\delta(\omega_{mn}-\omega) + \frac{2\pi}{\hbar}\,t\,|V_{nm}|^2\,\delta(\omega_{mn}+\omega)$$

- The corresponding rate is

$$\Gamma_{n\to m} = \frac{2\pi}{\hbar}\left[|V_{mn}|^2\,\delta(E_m^{(0)}-E_n^{(0)}-\hbar\omega) + |V_{nm}|^2\,\delta(E_m^{(0)}-E_n^{(0)}+\hbar\omega)\right]$$

↳ the transitions that take place with high probability obey: $E_m^{(0)} = E_n^{(0)} \pm \hbar\omega$.

- Processes which increase / decrease the energy can be interpreted as absorption / emission.

- The next case we consider is that of an <u>adiabatic perturbation</u>.

- We parametrise the perturbation as

$$\alpha V(t) = \alpha V_0 e^{\epsilon t},$$

where ϵ determines the speed at which the perturbation is switched on.

- In the limit $\epsilon \to 0$ the perturbation becomes static.

- In the following we consider the case in which the evolution is starting at a time t_0 which is large and negative: $t_0 \to -\infty$.

- The evolution of the state is then given by (p. 18)

$$|\psi(t)\rangle = e^{-\frac{i}{\hbar}(t-t_0)H_0}\left[|n\rangle - \frac{i}{\hbar}\int_{t_0}^{t} dt_1\, e^{\frac{i}{\hbar}(t_1-t_0)H_0}\,\alpha V(t_1)\, e^{-\frac{i}{\hbar}(t_1-t_0)H_0}|n\rangle\right]$$

$$= e^{-\frac{i}{\hbar}(t-t_0)H_0}\left[|n\rangle - \frac{i}{\hbar}\sum_k |k\rangle \int_{t_0}^{t} dt_1\, e^{\frac{i}{\hbar}(t_1-t_0)(E_k^{(0)}-E_m^{(0)})}\langle k|\alpha V(t_1)|n\rangle\right]$$

- Separating the diagonal and off-diagonal terms in the sum of the second term, yields:

$$|\psi(t)\rangle = e^{-\frac{i}{\hbar}(t-t_0)E_n^{(0)}}\left[1-\frac{i}{\hbar}\int_{t_0}^{t} dt_1 \overbrace{\langle n|\alpha V_1(t)|n\rangle}^{V_{nn}}\right]|n\rangle$$

$$-\frac{i}{\hbar}\sum_{k\neq n} e^{-\frac{i}{\hbar}(t-t_0)E_k^{(0)}}|k\rangle \int_{t_0}^{t} dt_1\, e^{\overbrace{i\omega_{kn}(t_1-t_0)}^{(E_k^{(0)}-E_n^{(0)})/\hbar}} \underbrace{\langle k|\alpha V(t_1)|n\rangle}_{V_{kn}}.$$

- Integrating over t_1 and neglecting a term $\propto e^{\varepsilon t_0}$ in the off-diagonal part, which vanishes as $t_0 \to -\infty$, we find

$$|\psi(t)\rangle = e^{-\frac{i}{\hbar}(t-t_0)E_n^{(0)}}\left\{\left(1-\frac{i}{\hbar}\frac{e^{\varepsilon t}-e^{\varepsilon t_0}}{\varepsilon}V_{nn}\right)|n\rangle - \frac{1}{\hbar}\sum_{k\neq n}\frac{e^{\varepsilon t}V_{kn}}{\omega_{kn}-i\varepsilon}|k\rangle\right\}.$$

- In the limit $\varepsilon \to 0$ this result allows to recover static perturbation theory.
- To see this we evaluate the limit $\varepsilon \to 0$

↳ $$|\psi(t)\rangle = e^{-\frac{i}{\hbar}(t-t_0)E_n^{(0)}}\left\{\left(1-\frac{i}{\hbar}(t-t_0)V_{nn}\right)|n\rangle - \frac{1}{\hbar}\sum_{k\neq n}\frac{V_{kn}}{\omega_{kn}}|k\rangle\right\}.$$

- static perturbation theory predicts that eigenstates and eigenenergies of H_0 change under a perturbation $\propto V_0$ as

$$|n\rangle' = |n\rangle + \sum_{k\neq n}\frac{\langle k|\alpha V_0|n\rangle}{E_n^{(0)}-E_k^{(0)}}|k\rangle = |n\rangle - \sum_{k\neq n}\frac{V_{kn}}{\hbar\omega_{kn}}|k\rangle$$

and

$$E_n = E_n^{(0)} + \langle n|\alpha V|n\rangle = E_n^{(0)} + V_{nn} .$$

- To connect this to the previous result, one needs to consider the time evolution of $|n\rangle'$ which takes place under the action of $H = H_0 + \alpha V_0$.

- Using that $e^{-iHt}|n\rangle' = e^{-iE_n t}|n\rangle' = |n(t)\rangle'$ one has that

$$|n(t)\rangle' = e^{-\frac{i}{\hbar}E_n(t-t_0)}\left\{|n\rangle - \sum_{k\neq n}\frac{V_{kn}}{\hbar\omega_{kn}}|k\rangle\right\}$$

$$= e^{-\frac{i}{\hbar}(E_n^{(0)}+V_{nn})(t-t_0)}\left\{|n\rangle - \sum_{k\neq n}\frac{V_{kn}}{\hbar\omega_{kn}}|k\rangle\right\}$$

$$\approx e^{-\frac{i}{\hbar}E_n^{(0)}(t-t_0)}\left\{\left(1-\frac{i}{\hbar}(t-t_0)V_{nn}\right)|n\rangle - \sum_{k\neq n}\frac{V_{kn}}{\hbar\omega_{kn}}|k\rangle\right\}.$$

↳ expanding the exponential and neglecting terms of order $V_{nn}V_{kn}$

- This expression is identical with the previously derived one and shows that an adiabatic perturbation indeed allows to recover the result of static perturbation theory in the limit of $\varepsilon \to 0$.

- As the final application of perturbation theory – for the moment – we consider the <u>decay of a bound state</u> which is coupled to a continuum of states.

- To this end we ask with which probability no transition takes place for a system that is initially prepared in an eigenstate $|n\rangle$ of the unperturbed Hamiltonian H_0. Using once more an adiabatic perturbation, $\propto V(t) = \propto V_0 e^{\varepsilon t}$, inserting this into the general expression (p. 18) for a time evolving state ($|\psi(t_0)\rangle = |n\rangle$), projecting onto $\langle n|$ and gathering all contributions up to order $\propto$ yields:

$$\langle n|\psi(t)\rangle = e^{-\frac{i}{\hbar}(t-t_0)E_n^{(0)}}\left[1 - \frac{i}{\hbar}\frac{e^{\varepsilon t}}{\varepsilon}V_{nn} + \left(-\frac{i}{\hbar}\right)^2 \frac{e^{2\varepsilon t}}{2\varepsilon^2}V_{nn}^2 + \frac{i}{\hbar^2}\sum_{k\neq n}\frac{e^{2\varepsilon t}}{2\varepsilon}\frac{1}{\omega_{kn} - i\varepsilon}|V_{kn}|^2\right]$$

(we also neglected some terms which vanish in the limit $\varepsilon \to 0$, which we consider soon)

$$\frac{\frac{d}{dt}\langle n|\psi(t)\rangle}{\langle n|\psi(t)\rangle} = -\frac{i}{\hbar}E_n^{(0)} + \frac{-\frac{i}{\hbar}e^{\varepsilon t}V_{nn} + \left(-\frac{i}{\hbar}\right)^2 \frac{e^{2\varepsilon t}}{\varepsilon}V_{nn}^2 + \frac{i}{\hbar^2}\sum_{k\neq n}\frac{e^{2\varepsilon t}}{\omega_{kn}-i\varepsilon}|V_{kn}|^2}{1 - \frac{i}{\hbar}\frac{e^{\varepsilon t}}{\varepsilon}V_{nn} + \mathcal{O}(V^3)}$$

$$\approx -\frac{i}{\hbar}E_n^{(0)} + \left(-\frac{i}{\hbar}\right)e^{\varepsilon t}V_{nn} + \left(-\frac{i}{\hbar}\right)^2\frac{e^{2\varepsilon t}}{\varepsilon}V_{nn}^2 + \frac{i}{\hbar^2}\sum_{k\neq n}\frac{e^{2\varepsilon t}}{\omega_{kn}-i\varepsilon}|V_{kn}|^2$$
$$+ \frac{i}{\hbar}\left(-\frac{i}{\hbar}\right)\frac{e^{2\varepsilon t}}{\varepsilon}V_{nn}^2 + \cdots$$

$$\approx -\frac{i}{\hbar}E_n^{(0)} - \frac{i}{\hbar}e^{\varepsilon t}V_{nn} + \frac{i}{\hbar^2}\sum_{k\neq n}\frac{e^{2\varepsilon t}}{\omega_{kn}-i\varepsilon}|V_{kn}|^2$$

- We now take the derivative with respect to time:

$$\frac{d}{dt}\langle n|\psi(t)\rangle = -\frac{i}{\hbar}E_n^{(0)}\langle n|\psi(t)\rangle$$

$$+ e^{-\frac{i}{\hbar}(t-t_0)E_n^{(0)}}\left[-\frac{i}{\hbar}e^{\varepsilon t}V_{nn} + \left(-\frac{i}{\hbar}\right)^2\frac{e^{2\varepsilon t}}{\varepsilon}V_{nn}^2\right.$$

$$\left. + \frac{i}{\hbar^2}\sum_{k\neq n} e^{2\varepsilon t}\frac{1}{\omega_{kn}-i\varepsilon}|V_{kn}|^2\right].$$

- In the next step we divide by $\langle n|\psi(t)\rangle$, and keeping track of the orders of α, when expanding $\frac{1}{\langle n|\psi(t)\rangle}$, one obtains:

$$\frac{1}{\langle n|\psi(t)\rangle}\frac{d}{dt}\langle n|\psi(t)\rangle = \frac{d\ln\langle n|\psi(t)\rangle}{dt}$$

$$= -\frac{i}{\hbar}E_n^{(0)} - \frac{i}{\hbar}e^{\varepsilon t}V_{nn} + \frac{i}{\hbar^2}\sum_{k\neq n} e^{2\varepsilon t}\frac{|V_{kn}|^2}{\omega_{kn}-i\varepsilon}.$$

- We now manipulate the last term by converting the sum into an integral:

$$\frac{1}{\hbar}\sum_{k\neq n}\frac{|V_{kn}|^2}{\omega_{kn}-i\varepsilon} = \sum_{k\neq n}\frac{|V_{kn}|^2}{E_k^{(0)}-E_n^{(0)}-i\varepsilon\hbar} \to \int_{-\infty}^{\infty} dE_k^{(0)}\,\rho(E_k^{(0)})\,\frac{|V_{kn}|^2}{E_k^{(0)}-E_n^{(0)}-i\varepsilon\hbar}$$

density of states

- To proceed, we take the limit $\epsilon \to 0$, using the identity

$$\lim_{\epsilon \to 0} \frac{1}{x \pm i\epsilon} = PV\left(\frac{1}{x}\right) \mp i\,\delta(x).$$

- Here PV stands for the so-called principal value, which is defined for a function $f(x)$, which is continuous at $x = 0$ as:

$$PV \int_{-\infty}^{\infty} dx\, \frac{f(x)}{x} = \lim_{\Delta \to 0} \left(\int_{-\infty}^{-\Delta} dx\, \frac{f(x)}{x} + \int_{+\Delta}^{\infty} dx\, \frac{f(x)}{x} \right).$$

- To understand the origin of this identity we start by writing

$$\frac{1}{x \pm i\epsilon} = \frac{x \mp i\epsilon}{(x \pm i\epsilon)(x \mp i\epsilon)} = \frac{x}{x^2+\epsilon^2} \mp \frac{i\epsilon}{x^2+\epsilon^2}.$$

- The imaginary part leads to a representation of the δ-function:

$$\lim_{\epsilon \to 0} \frac{\epsilon}{x^2+\epsilon^2} = \pi\,\delta(x).$$

- For the real part one obtains

$$\lim_{\epsilon \to 0} \int_{-\infty}^{\infty} dx\, \frac{x}{x^2+\epsilon^2} f(x) = \lim_{\epsilon \to 0} \lim_{\Delta \to 0} \left(\int_{-\infty}^{-\Delta} dx + \int_{+\Delta}^{\infty} dx \right) \frac{x}{x^2+\epsilon^2} f(x)$$

$$= \lim_{\Delta \to 0} \left(\int_{-\infty}^{-\Delta} dx + \int_{+\Delta}^{\infty} dx \right) \frac{1}{x} f(x)$$

$$= PV \int_{-\infty}^{\infty} dx\, \frac{f(x)}{x}.$$

- With this we find

$$\lim_{\varepsilon \to 0} \int_{-\infty}^{\infty} dE_k^{(0)} \rho(E_k^{(0)}) \frac{|V_{kn}|^2}{E_k^{(0)} - E_n^{(0)} - i\varepsilon\hbar}$$

$$= PV \int_{-\infty}^{\infty} dE_k^{(0)} \frac{|V_{kn}|^2 \rho(E_k^{(0)})}{E_k^{(0)} - E_n^{(0)}} + i\pi \int_{-\infty}^{\infty} dE_k^{(0)} \delta(E_k^{(0)} - E_n^{(0)}) |V_{kn}|^2 \rho(E_k^{(0)})$$

$$= PV \int_{-\infty}^{\infty} dE_k^{(0)} \rho(E_k^{(0)}) \frac{|V_{kn}|^2}{E_k^{(0)} - E_n^{(0)}} + i\pi |V_{kn}|^2 \rho(E_n^{(0)}) .$$

- Plugging this result into logarithmic derivative of the overlap, for $\varepsilon \to 0$, yields:

$$\frac{d \ln \langle n|\psi(t)\rangle}{dt} = \underbrace{-\frac{i}{\hbar} E_n^{(0)} - \frac{i}{\hbar} V_{nn} + \frac{i}{\hbar} PV \int_{-\infty}^{\infty} dE_k^{(0)} \rho(E_k^{(0)}) \frac{|V_{kn}|^2}{E_k^{(0)} - E_n^{(0)}}}_{\equiv -\frac{i}{\hbar} E_n} \underbrace{- \frac{\pi}{\hbar} |V_{kn}|^2 \rho(E_n^{(0)})}_{\equiv \gamma} ,$$

such that

$$\langle n|\psi(t)\rangle = e^{-\frac{i}{\hbar} E_n (t - t_0)} \cdot e^{-\gamma (t - t_0)}$$

phase due to coherent evolution under perturbed energy E_n

decay due to "loss" of probability amplitude into continuum states

- In order to obtain the transition rate, we take the squared modulus of the overlap:

$$|\langle n|\psi(t)\rangle|^2 \overset{t_0=0}{=} e^{-\Gamma t}$$

- Here $\Gamma = \frac{2\pi}{\hbar}|V_{kn}|^2 \rho(E_n^{(0)})$ is the transition rate, which is in fact again Fermi's Golden rule.

11 Light - matter interaction

11.1 Reminder on electromagnetic waves

- We start with the homogeneous Maxwell equations:

$$\nabla \cdot \vec{B} = 0 \quad \text{and} \quad \nabla \times \vec{E} + \frac{\partial \vec{B}}{\partial t} = 0$$

- From the first equation follows that the magnetic field $\vec{B}$ can be written as the curl of another vector field $\vec{A}$, which is referred to as the vector potential:

$$\vec{B} = \nabla \times \vec{A} \quad , \text{ since } \quad \nabla \cdot \nabla \times \vec{A} = 0.$$

- We can thus rewrite the second equation as

$$\nabla \times \left(\vec{E} + \frac{\partial \vec{A}}{\partial t} \right) = 0 .$$

- Given that the curl of a gradient vanishes, we can thus write the electric field $\vec{E}$ as

$$\vec{E} = -\nabla \phi - \frac{\partial \vec{A}}{\partial t} ,$$

where ϕ is the scalar potential.

- Let us now express the inhomogeneous Maxwell equations in terms of $\vec{A}$ and ϕ.

↳ $\frac{\rho}{\varepsilon_0} = \nabla \cdot \vec{E} = \nabla \cdot \left(-\nabla\phi - \frac{\partial \vec{A}}{\partial t}\right) = -\Delta\phi - \frac{\partial}{\partial t} \nabla \cdot \vec{A}$

(ρ: charge density; ε_0: vacuum permittivity; Δ: Laplacian)

$$\mu_0 \vec{j} = \nabla \times \vec{B} - \frac{1}{c^2} \frac{\partial \vec{E}}{\partial t} = \nabla \times (\nabla \times \vec{A}) + \frac{1}{c^2} \left(\frac{\partial}{\partial t} \nabla\phi + \frac{\partial^2}{\partial t^2} \vec{A}\right)$$

($\vec{j}$: current density; μ_0: vacuum permeability)

$$= \nabla (\nabla \cdot \vec{A}) - \Delta \vec{A} + \frac{1}{c^2} \left(\frac{\partial}{\partial t} \nabla\phi + \frac{\partial^2}{\partial t^2} \vec{A}\right)$$

$$= \frac{1}{c^2} \frac{\partial^2 \vec{A}}{\partial t^2} - \Delta \vec{A} + \vec{\nabla} \left(\vec{\nabla} \cdot \vec{A} + \underbrace{\frac{1}{c^2}}_{= \varepsilon_0 \mu_0} \frac{\partial \phi}{\partial t}\right)$$

- In the next step we employ the so-called gauge freedom to simplify the last equation.

- The gauge freedom means that the fields $\vec{E}$ and $\vec{B}$ are invariant under a change of the potentials which is of the form

$$\vec{A} \to \vec{A}' = \vec{A} + \nabla\chi$$

$$\phi \to \phi' = \phi - \frac{\partial}{\partial t} \chi,$$

where $\chi \equiv \chi(\vec{r}, t)$ is an arbitrary function.

- The utility of the gauge freedom can be seen as follows:
  - Suppose that $\nabla \cdot \vec{A} \neq 0$, but you want to enforce that $\nabla \cdot \vec{A}$ is zero in order to simplify the equations. (this is called Coulomb gauge)
  - Then choose χ such that

$$\nabla \cdot \vec{A}' = \nabla \cdot \vec{A} + \Delta \chi = 0 \rightarrow \Delta \chi = -\nabla \cdot \vec{A}$$

- Within the Coulomb gauge ($\nabla \cdot \vec{A} = 0$) the equations for the potentials become

$$\Delta \phi = -\frac{\rho}{\varepsilon_0}$$

$$\frac{1}{c^2}\frac{\partial^2 \vec{A}}{\partial t^2} - \Delta \vec{A} + \frac{1}{c^2}\frac{\partial}{\partial t}\nabla \phi = \mu_0 \vec{j},$$

where the first equation has the solution

$$\phi(\vec{r}, t) = \frac{1}{4\pi\varepsilon_0} \int d^3\vec{r}' \, \frac{\rho(\vec{r}', t)}{|\vec{r} - \vec{r}'|}.$$

- In the absence of charges and currents ($\rho = 0$, $\vec{j} = \vec{0}$), one has $\phi = 0$ and thus the equation for $\vec{A}$ simplifies to <u>the wave equation</u>

$$\frac{1}{c^2}\frac{\partial^2 \vec{A}}{\partial t^2} - \Delta \vec{A} = 0.$$

- The wave equation has plane wave solutions which are of the form

$$\vec{A}(\vec{r},t) = a\,\vec{\varepsilon}\,e^{i(\vec{k}\vec{r}-\omega t)} + a^*\vec{\varepsilon}^*\,e^{-i(\vec{k}\cdot\vec{r}-\omega t)}$$

$\vec{k}$ ... wave vector

$\vec{\varepsilon}$ ... polarisation vector

$\omega = c|\vec{k}| = ck$ ... frequency of the wave

- The Coulomb gauge, in which we are working, constrains the solutions:

$$\nabla\cdot\vec{A} = 0 \;\rightarrow\; a\,\vec{\varepsilon}\cdot\nabla e^{i(\vec{k}\cdot\vec{r}-\omega t)} = i a\,\vec{\varepsilon}\cdot\vec{k}\,e^{i(\vec{k}\cdot\vec{r}-\omega t)} \overset{!}{=} 0$$

$$\hookrightarrow \vec{k}\cdot\vec{\varepsilon} = \vec{k}\cdot\vec{\varepsilon}^* = 0$$

- This so-called transversality condition means that the polarisation vector has only two free components.

- For example, assuming that $\vec{k} = \begin{pmatrix}0\\0\\k\end{pmatrix}$, we can choose as polarisation bases

<u>linear polarisation</u>

$$\vec{\varepsilon}^{(1)} = \begin{pmatrix}1\\0\\0\end{pmatrix}$$

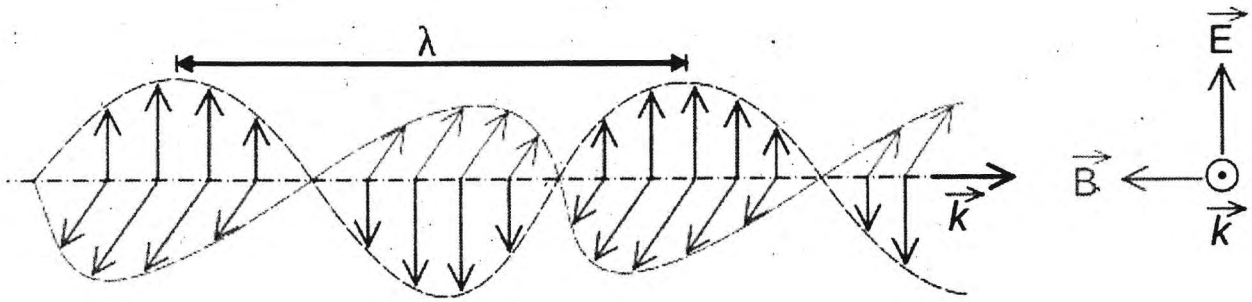
$$\vec{\varepsilon}^{(2)} = \begin{pmatrix}0\\1\\0\end{pmatrix}$$

<u>circular polarisation</u>

$$\vec{\varepsilon}^{(1)} = -\frac{1}{\sqrt{2}}\begin{pmatrix}1\\i\\0\end{pmatrix}$$

$$\vec{\varepsilon}^{(2)} = \frac{1}{\sqrt{2}}\begin{pmatrix}-1\\i\\0\end{pmatrix}$$

Plane wave



Wikipedia

$$|\vec{E}|^2 = \omega^2 \left(a\,\vec{\varepsilon}\,e^{i(\)} - a^*\vec{\varepsilon}^*e^{-i(\)}\right)\left(a^*\vec{\varepsilon}^*e^{-i(\)} - a\,\vec{\varepsilon}\,e^{i(\)}\right)$$

$$= \omega^2 \left(|a|^2\,\vec{\varepsilon}\cdot\vec{\varepsilon}^* + |a|^2\,\vec{\varepsilon}^*\cdot\vec{\varepsilon} - a^2\,\vec{\varepsilon}\cdot\vec{\varepsilon}\,e^{2i(\)} - a^{*2}\vec{\varepsilon}^*\cdot\vec{\varepsilon}^*e^{-2i(\)}\right)$$

$$|\vec{B}|^2 = |\vec{k}|^2\left(a\,\vec{n}\,e^{i(\)} - a^*\vec{n}^*e^{-i(\)}\right)\left(a^*\vec{n}^*e^{-2i(\)} - a\,\vec{n}\,e^{2i(\)}\right)$$

$$(\vec{n}\times\vec{\varepsilon})(\vec{n}\times\vec{\varepsilon}) = (\vec{n}\cdot\vec{n})(\vec{\varepsilon}\cdot\vec{\varepsilon}) - (\vec{\varepsilon}\cdot\vec{n})(\vec{n}\cdot\vec{\varepsilon})$$

$(\vec{n}\cdot\vec{n}) = 1$

$(\vec{\varepsilon}\cdot\vec{n}) = 0$ since $\vec{\varepsilon}\perp\vec{n}$

↑ Lagrange identity

- Using the plane wave solution one finds for the electric and magnetic fields:

$$\vec{E} = -\frac{\partial \vec{A}}{\partial t} = i\omega \left(a\vec{\varepsilon}\, e^{i(\vec{k}\cdot\vec{r}-\omega t)} - a^* \vec{\varepsilon}^*\, e^{-i(\vec{k}\cdot\vec{r}-\omega t)} \right)$$

$$\vec{B} = \nabla \times \vec{A} = a(i\vec{k}\times\vec{\varepsilon})\, e^{i(\vec{k}\cdot\vec{r}-\omega t)} - a^* (i\vec{k}\times\vec{\varepsilon}^*)\, e^{-i(\vec{k}\cdot\vec{r}-\omega t)}$$

- $\vec{E}$, $\vec{B}$ and $\vec{k}$ are perpendicular to each other.

- We can now generalise the solution of the wave equation to a superposition of many plane waves.
- The amplitude of a wave with wave vector $\vec{k}$ and polarisation vector $\vec{\varepsilon}^{(s)}$ is given by $A_s(\vec{k})$.
- With this we can write the general solution as

$$\vec{A}(\vec{r},t) = \sum_{s=1,2} \int \underbrace{\frac{d^3\vec{k}}{(2\pi)^3 2\omega}} \left[A_s(\vec{k})\, \vec{\varepsilon}^{(s)}\, e^{i(\vec{k}\cdot\vec{r}-\omega t)} + A_s^*(\vec{k})\, \vec{\varepsilon}^{(s)*}\, e^{-i(\vec{k}\cdot\vec{r}-\omega t)} \right]$$

($A_s(\vec{k})$: depends also on $\vec{k}$; $\vec{\varepsilon}^{(s)*}$: $\vec{k}$)

integration measure (different choices possible)

- Let us finally consider other important properties of plane wave, such as their energy and momentum
- The energy density is

$$u = \frac{1}{2}\left(\varepsilon_0 |\vec{E}|^2 + \frac{1}{\mu_0}|\vec{B}|^2\right) = \frac{\varepsilon_0}{2}\left(|\vec{E}|^2 + c^2|\vec{B}|^2\right) \overset{\text{for plane waves } |\vec{E}| = c|\vec{B}|}{=} \varepsilon_0 |\vec{E}|^2$$

$$= \varepsilon_0 \omega^2 \left(2|a|^2 \underbrace{- a^2 \vec{\varepsilon}\cdot\vec{\varepsilon}\, e^{2i(\vec{k}\cdot\vec{r}-\omega t)} - (a^*)^2 \vec{\varepsilon}^*\cdot\vec{\varepsilon}^*\, e^{-2i(\vec{k}\cdot\vec{r}-\omega t)}}_{\text{time dependent terms}}\right)$$

- Averaging over an oscillation period $T = \frac{2\pi}{\omega}$ yields the mean energy density:

$$\bar{u}(\vec{r}) = \frac{1}{T}\int_0^T dt\, u(\vec{r},t) = 2\varepsilon_0\omega^2|a|^2.$$

- Another important quantity is the pointing vector

$$\vec{S} = \frac{1}{\mu_0}(\vec{E}\times\vec{B}) \overset{\text{plane wave}}{=} \frac{1}{\mu_0}|\vec{E}||\vec{B}|\underbrace{\frac{\vec{k}}{|\vec{k}|}}_{\vec{n}} = \frac{1}{\mu_0 c}|\vec{E}|^2\vec{n}.$$

- Averaging over an oscillation period yields

$$\bar{S} = \frac{2\omega^2|a|^2}{\mu_0 c}\vec{n} = \frac{1}{\varepsilon_0\mu_0 c}u\vec{n} = \underbrace{c\,u\,\vec{n}}_{\text{energy flux}}$$

(c: velocity, u: energy density, $\vec{n}$: direction)

$$= I\cdot\vec{n}$$

(I: intensity)

- The pointing vector can be used to define a momentum density

$$\vec{p} = \frac{1}{c^2}\vec{S} = \varepsilon_0(\vec{E}\times\vec{B}),$$

whose time average obeys

$$c|\vec{p}| = \bar{u}.$$

II. 2 The hydrogen atom in the (classical) radiation field

- In the presence of electromagnetic field, characterised by the vector and scalar potential $\vec{A}, \phi$, the Hamiltonian of a hydrogen atom reads

$$H = \frac{1}{2\mu}\left(\vec{p} + e\vec{A}(\vec{r},t)\right)^2 - e\phi(\vec{r},t) + V(\vec{r})$$

($\vec{p}$: momentum operator of electron; μ: reduced mass; e: electronic charge, $q=-e$; $V(\vec{r})$: Coulomb potential)

$$\mu = \frac{m_{electron}\, m_{proton}}{m_{electron} + m_{proton}}$$

$$V(\vec{r}) = -\frac{e^2}{4\pi\varepsilon_0 |\vec{r}|}$$

- Note, that for the moment we do not consider the spin of the electron.

- We can now decompose the Hamiltonian into an unperturbed part H_0 and a perturbation H_1:

$$H_0 = \frac{\vec{p}^2}{2\mu} + V(\vec{r})$$

($V(\vec{r})$: electrostatic interaction)

$$H_1 = \underbrace{\frac{e}{2\mu}\left(\vec{p}\cdot\vec{A} + \vec{A}\cdot\vec{p}\right)}_{\text{diamagnetic term}} + \underbrace{\frac{e^2}{2\mu}\vec{A}^2}_{\text{paramagnetic term}} - e\phi$$

diamagnetic vs. paramagnetic term

$$E_{dia} = \left\langle \frac{e}{2\mu} \vec{p} \cdot \vec{A} \right\rangle \qquad \operatorname{div} \vec{A} = \vec{B}$$

$\hookrightarrow A \sim B \cdot r$

$p \propto \hbar \frac{\partial}{\partial x} \sim \hbar \frac{1}{r}$

$\hookrightarrow E_{dia} \sim B \frac{e}{2\mu} \hbar$

$$E_{para} = \left\langle \frac{e^2}{2\mu} \vec{A}^2 \right\rangle \sim \frac{e^2}{2\mu} B^2 \langle r^2 \rangle \sim \frac{e^2}{2\mu} B^2 a_0^2$$

$\hookrightarrow E_{dia} \sim E_{para} \rightarrow B \frac{e}{2\mu} \hbar \sim \frac{e^2}{2\mu} B^2 a_0^2$

$$\hookrightarrow B \sim \frac{\hbar}{e a_0^2} \sim \frac{10^{-34}\ \mathrm{Js}}{10^{-19}\ \mathrm{As} \cdot (5 \cdot 10^{-11})^2\ \mathrm{m}^2} \sim 10^6\ \frac{\mathrm{Vs}}{\mathrm{m}^2} = 10^6\ \mathrm{T}$$

- We now use that under the Coulomb gauge, we can write

$$(\vec{p}\cdot\vec{A})\psi = \frac{\hbar}{i}\nabla\cdot(\vec{A}\psi) = \frac{\hbar}{i}\left(\underbrace{(\nabla\cdot\vec{A})}_{=0}\psi + \vec{A}\cdot\nabla\psi\right) = \vec{A}\cdot(\vec{p}\psi)$$

and hence

$$\vec{p}\cdot\vec{A} + \vec{A}\cdot\vec{p} = \vec{A}\cdot\vec{p} + \vec{A}\cdot\vec{p} = 2\vec{A}\cdot\vec{p}.$$

- Moreover, we neglect the diamagnetic term, which for laboratory strength magnetic fields is dominated by the diamagnetic one.

↳ $H_1 \approx \frac{e}{\mu}\vec{p}\cdot\vec{A}$ ← in a homogeneous static magnetic field this term gives rise to the Zeeman splitting

- We can generalise this interaction Hamiltonian by introducing the probability current density operator

$$\vec{j}(\vec{r}') = \underbrace{\frac{\vec{p}}{2\mu}\delta^3(\vec{r}-\vec{r}') + \delta^3(\vec{r}-\vec{r}')\frac{\vec{p}}{2\mu}}_{\text{symmetrisation in principle needed, since } \vec{p} \text{ and } \vec{r} \text{ are non-commuting quantum mechanical operators}} \quad \text{"} = \text{"velocity} \times \left(\text{probability density}\right)$$

- With this definition we have

$$H_1 = e\int d^3\vec{r}'\ \vec{j}(\vec{r}')\cdot\vec{A}(\vec{r}',t).$$

$$H_1 = e \int d^3\vec{r}\, \vec{j}(\vec{r})\, \vec{A}(\vec{r},t)$$

$$= e \int d^3r\, \vec{j}(\vec{r})\, a\, \vec{\varepsilon}^{(s)} e^{i\vec{k}\cdot\vec{r}} e^{-i\omega t}$$

$$+ e \int d^3r\, j(r)\, a^*\, \vec{\varepsilon}^{*(s)} e^{-i\vec{k}\cdot\vec{r}} e^{i\omega t}$$

$$= ea \Big[\underbrace{\int d^3r\, \vec{j}(\vec{r}) e^{i\vec{k}\cdot\vec{r}}}_{\vec{j}(-\vec{k})} \Big] \cdot \vec{\varepsilon}^{(s)} e^{-i\omega t}$$

$$+ ea^* \Big[\underbrace{\int d^3r\, \vec{j}(\vec{r}) e^{-i\vec{k}\cdot\vec{r}}}_{\vec{j}(\vec{k})} \Big] \cdot \vec{\varepsilon}^{*(s)} e^{i\omega t}$$

$$= e \Big[a\, \vec{j}(-\vec{k}) \cdot \vec{\varepsilon}^{(s)} e^{-i\omega t} + a^* \vec{j}(\vec{k}) \cdot \vec{\varepsilon}^{*(s)} e^{i\omega t} \Big]$$

$$= e \Big[a\, j^+(\vec{k}) \cdot \vec{\varepsilon}^{(s)} e^{-i\omega t} + a^* \vec{j}(\vec{k}) \cdot \vec{\varepsilon}^{*(s)} e^{i\omega t} \Big]$$

- The vector potential thus couples to the electric current density: $q\,\vec{j}(\vec{r}) = \vec{v}\,\rho(\vec{r})$ (probability current; charge; velocity; charge density)
- H_1 is interaction energy of a current density in a magnetic field.
- To proceed, we define the Fourier transform of the probability current density:

$$\vec{j}(\vec{k}) = \int d^3r'\, e^{-i\vec{k}\cdot\vec{r}'}\,\vec{j}(\vec{r}') = \int d^3r'\, e^{-i\vec{k}\cdot\vec{r}'}\left(\frac{\vec{p}}{2\mu}\delta^3(\vec{r}-\vec{r}') + \delta^3(\vec{r}-\vec{r}')\frac{\vec{p}}{2\mu}\right)$$

$$= e^{-i\vec{k}\cdot\vec{r}}\frac{\vec{p}}{2\mu} + \frac{\vec{p}}{2\mu}e^{-i\vec{k}\cdot\vec{r}}.$$

- For the interaction of the atom with a monochromatic wave with wave vector $\vec{k}$ and polarisation s,

$$\vec{A}(\vec{r},t) = a\,\vec{\varepsilon}^{(s)}\,e^{i(\vec{k}\cdot\vec{r}-\omega t)} + a^*\,\vec{\varepsilon}^{(s)*}\,e^{-i(\vec{k}\cdot\vec{r}-\omega t)},$$

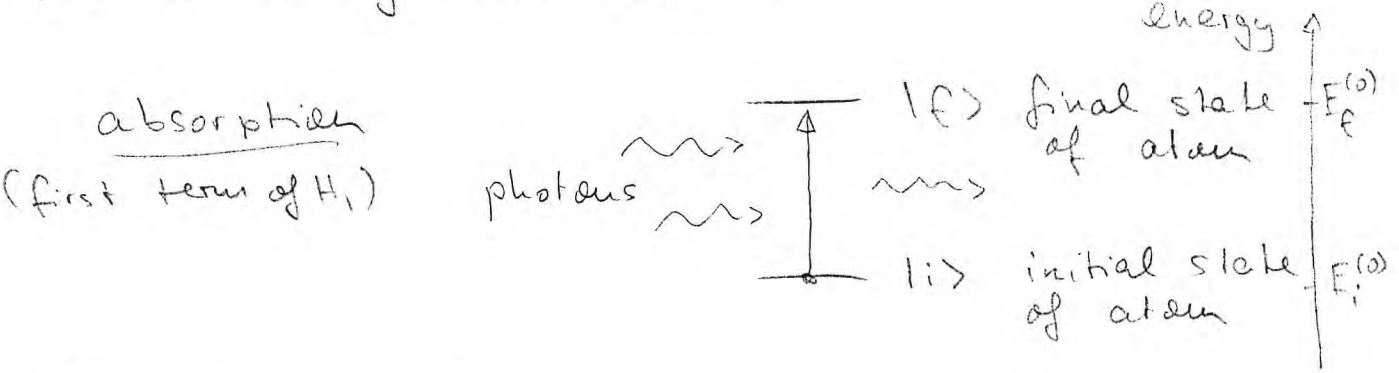
we can then write

$$H_1 = e\left[a\,\vec{\varepsilon}^{(s)}\cdot\vec{j}(-\vec{k})\,e^{-i\omega t} + a^*\,\vec{\varepsilon}^{(s)*}\cdot\vec{j}(\vec{k})\,e^{i\omega t}\right]$$

$$= e\left[a\,\vec{\varepsilon}^{(s)}\cdot\vec{j}^{\,+}(\vec{k})\,e^{-i\omega t} + a^*\,\vec{\varepsilon}^{(s)*}\cdot\vec{j}(\vec{k})\,e^{i\omega t}\right]$$

- For calculating this expression one exploits, e.g. that $(\vec{\varepsilon}^{(s)}\cdot\vec{p})\,e^{i\vec{k}\cdot\vec{r}} = \frac{\hbar}{i}(\vec{\varepsilon}^{(s)}\cdot\nabla)\,e^{i\vec{k}\cdot\vec{r}} = \hbar(\vec{k}\cdot\vec{\varepsilon}^{(s)})\,e^{i\vec{k}\cdot\vec{r}} = 0$ (Coulomb gauge)
- H_1 is a hermitean operator.

- The operator H_1 describes a harmonic perturbation, which was discussed in Sec 1.3.
- It leads to absorption and induced emission of photons from/into the electromagnetic field.
- These processes also lead to a change of the state of the atom:

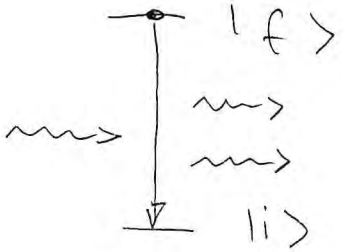


- The corresponding rate is given by Fermi's Golden Rule:

$$\Gamma_{i\to f}^{abs} = \frac{2\pi}{\hbar} |\langle f| a\, \vec{\varepsilon}^{(s)} \cdot \vec{j}(-\vec{k}) |i\rangle|^2 \, \delta(E_f^{(0)} - E_i^{(0)} - \hbar\omega)$$

$$= \frac{2\pi}{\hbar} e^2 |a|^2 |\langle f| \vec{\varepsilon}^{(s)} \cdot \vec{j}(-\vec{k}) |i\rangle|^2 \, \delta(E_f^{(0)} - E_i^{(0)} - \hbar\omega)$$

induced emission
(second term of H_1)



- Here the rate is

$$\Gamma_{f\to i}^{ind.em.} = \frac{2\pi e^2}{\hbar} |a|^2 |\langle f| \vec{\varepsilon}^{(s)} \cdot \vec{j}(-\vec{k}) |i\rangle|^2 \, \delta(E_i^{(0)} - E_f^{(0)} + \hbar\omega)$$

$$= |\langle i| \vec{\varepsilon}^{(s)*} \cdot \vec{j}(\vec{k}) |f\rangle|^2$$

$$= \Gamma_{i\to f}^{abs}$$

- Both rates are proportional to the factor $|a|^2$, which is the squared modulus of the amplitude of the vector potential $\vec{A}$.
  → the higher the intensity I of the electromagnetic field, the higher the rates

$$I = 2\varepsilon_0 c\omega^2 |a|^2 .$$

- In order to obtain a „normalised" quantity, which describes absorption and induced emission we define the absorption cross section:

$$\sigma_{i\to f}^{abs} = \frac{\text{absorbed energy per time unit}}{\text{incident energy flux}}$$

$$= \frac{\hbar\omega \times \Gamma_{i\to f}^{abs}}{I}$$

$$= \frac{\pi e^2}{\varepsilon_0 \omega c} |\langle f | \vec{\varepsilon}^{(s)} \cdot \vec{j}(-\vec{k}) | i \rangle|^2 \, \delta(E_f^{(0)} - E_i^{(0)} - \hbar\omega)$$

- The absorption cross section has the unit 'area', e.g. m^2.
- It can be interpreted as the size of an effective / fictitious area over which the entire incident current is absorbed.
- It is a quantity that characterises a given absorption process:

- In the following we will focus on the (approximate) calculation of the matrix element $\langle f | \vec{\varepsilon}^{(s)} \cdot \vec{j}(-\vec{k}) | i \rangle$, and we will also deal with the δ-function on which $\sigma^{abs}_{i \to f}$ (so far) depends.

- The first step consists of realising that the exponential factor $e^{i\vec{k}\cdot\vec{r}}$ in $\vec{j}(-\vec{k})$ varies only weakly over the typical size of an atom, i.e., the region in space where the states $|i\rangle$ (or $|f\rangle$) are non-zero:

- Typical values of $|\vec{k}|$ can be estimated by

$$|\vec{k}| = \frac{\omega}{c} = \frac{E_f^{(0)} - E_i^{(0)}}{\hbar c} < \frac{E_{Ry}}{\hbar c}$$

E_{Ry} ← Rydberg energy, $E_{Ry} = \frac{\mu e^4}{8\varepsilon_0 h^2}$

- Therefore $|\vec{k}||\vec{r}| \sim |\vec{k}| \cdot a_0 = \frac{E_{Ry} a_0}{\hbar c} = \frac{1}{2}\alpha \ll 1$.

↑ Bohr radius $a_0 = \frac{4\pi\varepsilon_0 \hbar}{\mu e^2}$

↑ fine structure constant $\alpha = \frac{1}{4\pi\varepsilon_0 c} \frac{e^2}{\hbar^2} \approx \frac{1}{137}$

- We can thus approximate

$$e^{\pm i\vec{k}\cdot\vec{r}} \approx 1 \quad \to \quad \vec{\varepsilon}^{(s)} \cdot \vec{j}(-\vec{k}) \approx \vec{\varepsilon}^{(s)} \cdot \frac{\vec{p}}{\mu}.$$

- To calculate the matrix element, we use that for the unperturbed Hamiltonian H_0 of the hydrogen atom the following relation holds:

$$[\vec{r}, H_0] = \left[\vec{r}, \frac{\vec{p}^{\,2}}{2\mu}\right] = \frac{i\hbar}{\mu}\vec{p}\,.$$

$$\hookrightarrow \langle f|\vec{\varepsilon}^{(s)}\cdot\vec{j}(\vec{k})|i\rangle \propto \langle f|\vec{\varepsilon}^{(s)}\cdot\frac{\vec{p}}{\mu}|i\rangle = \frac{1}{i\hbar}\langle f|\vec{\varepsilon}^{(s)}\cdot[\vec{r},H_0]|i\rangle$$

$$= \frac{E_i^{(0)} - E_f^{(0)}}{i\hbar}\langle f|\vec{\varepsilon}^{(s)}\cdot\vec{r}|i\rangle$$

$$= i\omega\langle f|\vec{\varepsilon}^{(s)}\cdot\vec{r}|i\rangle$$

$E_i^{(0)} - E_f^{(0)} = -\hbar\omega$ ⟶

- The last expression depends on the so-called <u>dipole matrix element</u> $\vec{d}_{fi} = \langle f|\vec{r}|i\rangle$

↑ sometimes this is defined with a factor e (electron charge).

- With this definition, we can write for the absorption cross section

$$\sigma_{i\to f}^{abs}(\omega, \vec{n}, s) = \frac{\pi e^2\omega}{\varepsilon_0 c}\left|\vec{d}_{fi}\cdot\vec{\varepsilon}^{(s)}(\vec{k})\right|^2 \delta(E_f^{(0)} - E_i^{(0)} - \hbar\omega).$$

frequency; direction of wave propagation $\vec{n} = \frac{\vec{k}}{|\vec{k}|}$; polarisation

- The dipole matrix element is only non zero if the angular momentum quantum numbers of the initial and final states $|i\rangle$ and $|f\rangle$ obey certain conditions.

- These conditions are called (dipole) <u>selection rules</u>.

- For the following derivation of these rules we consider the non-relativistic hydrogen atom with the initial and final states given by

$$|i\rangle = |n, \ell, m\rangle \qquad |f\rangle = |n', \ell', m'\rangle$$

(n: principal quantum number; ℓ: quantum number of $\vec{L}^2$ (angular momentum); m: quantum number of L_z (azimuthal))

- Since the following calculations do not involve the principal quantum numbers n, n', we omit them to keep the notation compact

- In order to calculate the selection rules for the azimuthal quantum numbers, we make use of the following commutators:

$$[L_z, z] = 0$$

$$[L_z, x \pm iy] = \pm \hbar (x \pm iy)$$

- The first commutator yields

$$0 = \langle f | [L_z, z] | i \rangle = \langle e', m' | (L_z z - z L_z) | l m \rangle$$

$$= \hbar (m' - m) \langle f | z | i \rangle = \hbar \Delta m \langle f | z | i \rangle ,$$

and apparently the z-component of the dipole matrix element can only be non-zero if $\Delta m = m' - m = 0$.

- From the second commutator one obtains

$$\pm \hbar \langle f | x \pm iy | i \rangle = \langle f | [L_z, x \pm iy] | i \rangle$$

$$= \hbar (m' - m) \langle f | x \pm iy | i \rangle$$

$$\hookrightarrow 0 = \hbar (m' - m \mp 1) \langle f | x \pm iy | i \rangle ,$$

which yields $\Delta m = \pm 1$.

- Therefore, the selection rules for the azimuthal quantum number for dipole transitions are

$$\Delta m = 0, \pm 1$$

- Note, that $\Delta m = 0$ corresponds to linearly and $\Delta m = \pm 1$ to circularly polarised light.

linear

$$\vec{d}_{fi} \cdot \vec{\varepsilon} = \vec{d}_{fi} \cdot \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} = \langle f | z | i \rangle ,$$

circular

$$\vec{d}_{fi} \cdot \vec{\varepsilon} \propto \vec{d}_{fi} \cdot \begin{pmatrix} 1 \\ \pm i \\ 0 \end{pmatrix} = \langle f | x \pm iy | i \rangle$$

- In order to calculate the selection rules for the angular momentum quantum number ℓ, we use

$$\left[\vec{L}^2,\left[\vec{L}^2,\vec{r}\right]\right] = 2\hbar^2\left(\vec{r}\,\vec{L}^2 + \vec{L}^2\,\vec{r}\right).$$

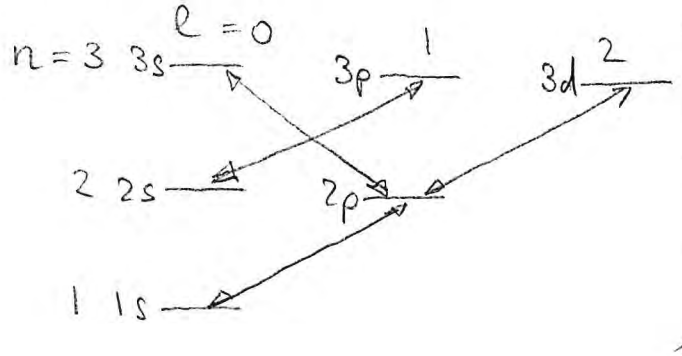
- This yields

$$\underbrace{\langle \ell' m'|}_{\langle f|}\left[\vec{L}^2,\left[\vec{L}^2,\vec{r}\right]\right]\underbrace{|\ell m\rangle}_{|i\rangle} = \hbar^4\left[\ell'(\ell'+1)-\ell(\ell+1)\right]^2\langle f|\vec{r}|i\rangle$$

$$= 2\hbar^2\langle \ell' m'|\vec{r}\,\vec{L}^2+\vec{L}^2\vec{r}\,|\ell m\rangle = 2\hbar^4\left[\ell'(\ell'+1)+\ell(\ell+1)\right]\langle f|\vec{r}|i\rangle$$

$$\hookrightarrow (\ell+\ell')(\ell+\ell'+2)\left[(\ell-\ell')^2-1\right]\langle f|\vec{r}|i\rangle = 0$$

- Given that $\ell,\ell' \geq 0$, the dipole matrix element can only be non-zero when $\ell=\ell'=0$ or when $\Delta\ell = \ell'-\ell = \pm 1$.
- The first case can be ruled out from symmetry considerations: $\langle 0,0|\vec{r}|100\rangle \propto \int d^3\vec{r}\,\vec{r} = 0$, and hence, the selection rule is $\Delta\ell = \pm 1$.



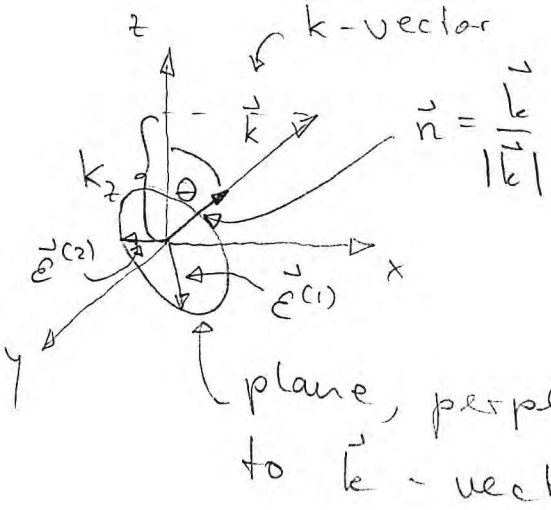
transition $2s \to 1s$ is not dipole allowed; the 2s state has a life time of 0.12 s; life time of 2p is 1.6 ns

- We are now calculating the total absorption cross section for electromag. radiation in the dipole approximation.
- This is obtained by averaging $\sigma^{abs}_{i\to f}(\omega, \vec{n}, s)$ over all polarisations and incidence angles.

$$\bar{\sigma}^{abs}_{i\to f} = \underbrace{\left(\frac{1}{4\pi}\int d\Omega\right)}_{\text{average over solid angle}} \underbrace{\left(\frac{1}{2}\sum_{s=1,2}\right)}_{\text{average over polarisations}} \sigma^{abs}_{i\to f}(\omega, \vec{n}, s)$$

$$= \frac{1}{8\pi}\,\frac{\pi e^2 \omega}{\varepsilon_0 c}\int d\Omega \sum_{s=1,2} (\vec{d}_{fi}\cdot\vec{\varepsilon}^{(s)})(\vec{d}_{fi}\cdot\varepsilon^{(s)})^{*}\,\delta(E_f^{(0)} - E_i^{(0)} - \hbar\omega).$$

- We now choose the coordinate system in a convenient fashion so as to simplify the evaluation of the integral over the $\vec{k}$-direction ($\vec{n}$) and the sum over the polarisations:



θ .. polar angle, i.e. angle between $\vec{k}$ and z-axis

- With this choice, we can now write

$$\int d\Omega \sum_{s=1,2} (\vec{d}_{fi}\cdot\vec{\varepsilon}^{(s)})(\vec{d}_{fi}\cdot\vec{\varepsilon}^{(s)})^* = 2\pi \int_0^\pi d\theta \sin\theta \sum_{s=1,2} |\vec{d}_{fi}\cdot\vec{\varepsilon}^{(s)}|^2$$

$$= 2\pi \int_0^\pi d\theta \sin\theta \left(\underbrace{|\vec{d}_{fi}|^2}_{= |\vec{d}_{fi}\cdot\vec{\varepsilon}^{(1)}|^2 + |\vec{d}_{fi}\cdot\vec{\varepsilon}^{(2)}|^2 + |\vec{d}_{fi}\cdot\vec{n}|^2} - |\vec{d}_{fi}\cdot\vec{n}|^2 \right)$$

$$= 2\pi \int_0^\pi d\theta \sin\theta \left(|\vec{d}_{fi}|^2 - |\vec{d}_{fi}|^2 \cos^2\theta \right)$$

$$= |\vec{d}_{fi}|^2 \cdot 2\pi \int_0^\pi d\theta \sin\theta (1-\cos^2\theta) = \frac{8\pi}{3} |\vec{d}_{fi}|^2 .$$

- This yields

$$\overline{\sigma}^{abs}_{i\to f} = \frac{\pi e^2 \omega}{3\varepsilon_0 c} |\vec{d}_{fi}|^2 \, \delta(E_f^{(0)} - E_i^{(0)} - \hbar\omega) .$$

- So far we have considered only processes in the hydrogen atom that are stimulated by the electromagnetic field, i.e. their rate was proportional to the squared amplitude of the vector potential $\vec{A}$.

- However, there is also the process of <u>spontaneous emission</u>, which takes place even when the vector potential is zero.
- The quantisation of the radiation field will ultimately allow us to understand the origin of this.
- Nevertheless, it is possible to derive the rate of spontaneous emission even without it, following an argument put forward by Einstein.
- To this end we consider an atom in the presence of the radiation field of a black body, whose spectral energy density is given by Planck's radiation law

$$u(\omega, T)\, d\omega = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1}\, d\omega$$

(u: energy per volume per frequency = energy density; T: temperature)

- Following the definition of the absorption cross section,

$$\sigma^{abs}_{i\to f} = \frac{\hbar\omega\, \Gamma^{abs}_{i\to f}}{\bar{u}\, c}$$

($\Gamma^{abs}_{i\to f}$: absorption rate; $\bar{u}$: average energy density)

we can define a average transition rate per frequency as

$$d\bar{\Gamma}^{abs}_{i\to f} = \bar{\sigma}^{abs}_{i\to f} \frac{c\, u(\omega,T)}{\hbar\omega} d\omega$$

($u(\omega,T)$: energy density of black body)

$\bar{\Gamma}$, $\bar{\sigma}$: quantities are averaged over polarisations and directions of $\vec{k}$-vector

The total absorption rate is then

$$\Gamma^{abs,tot}_{i\to f} = \int d\bar{\Gamma}^{abs}_{i\to f} = \int_0^\infty d\omega \frac{\pi e^2}{3\varepsilon_0 \hbar} |\vec{d}_{fi}|^2 u(\omega,T)\, \delta(E_f^{(0)} - E_i^{(0)} - \hbar\omega)$$

$$= \frac{\pi e^2}{3\varepsilon_0 \hbar^2} |\vec{d}_{fi}|^2 u(\omega_{fi},T),$$

where $\omega_{fi} = \frac{1}{\hbar}(E_f^{(0)} - E_i^{(0)})$.

- The total rate of induced emission is the same as the total absorption rate;

$$\Gamma^{ind.em,tot}_{f\to i} = \Gamma^{abs,tot}_{i\to f} = B\, u(\omega_{fi},T),$$

where $B = \frac{\pi e^2}{3\varepsilon_0 \hbar^2} |\vec{d}_{fi}|^2$ is the so-called Einstein B-coefficient.

- Einstein now postulated that there should be an additional process - spontaneous emission, whose rate is

$$\Gamma^{sp.em,tot}_{f\to i} = A \leftarrow \text{Einstein A-coefficient}$$

- Denoting by $P_{i/f}$ the probabilities of finding an atom in the initial / final state, it should hold in equilibrium that

$$\underbrace{\left[A + B u(\omega_{fi}, T)\right]}_{\text{rate for leaving the state } |f\rangle} P_f = \underbrace{B u(\omega_{fi}, T)}_{\text{rate for leaving the state } |i\rangle} P_i .$$

- On the other hand, in thermal equilibrium we find for the probabilities:

$$\frac{P_f}{P_i} = \frac{e^{-E_f^{(0)}/k_B T}}{e^{-E_i^{(0)}/k_B T}} = e^{-\frac{\hbar\omega_{fi}}{k_B T}}$$

- Inserting this into the above expressions allows to obtain the spontaneous emission rate:

$$\hookrightarrow A = B u(\omega_{fi}, T)\left(\frac{P_i}{P_f} - 1\right) = B u(\omega_{fi}, T)\left(e^{\frac{\hbar\omega_{fi}}{k_B T}} - 1\right)$$

$$= B\,\frac{\hbar\omega_{fi}^3}{\pi^2 c^3}$$

$$\hookrightarrow \Gamma^{\text{sp.em, tot}}_{f\to i} = \frac{e^2 \omega_{fi}^3}{3\varepsilon_0 \hbar c^3 \pi} |\vec{d}_{fi}|^2 .$$

- The fact that all (excited) states can decay spontaneously implies that the energy of these states cannot be determined to an arbitrary accuracy, as we will show now.
- In fact, all these states are characterised by a distribution of energies, i.e. the have a finite <u>natural line width</u>.
- To see this, we come back to a result of Sec. 1.3, which showed that the amplitude for remaining in an initially prepared eigenstate (here $|f\rangle$) is

$$\langle f|\psi(t)\rangle = e^{-\frac{i}{\hbar}E_f t - \frac{\Gamma}{2}t}$$

← here this is the spontaneous decay rate

- This expression can be written in terms of an integral of energies:

$$-\frac{1}{2\pi i}\int_{-\infty}^{\infty} dE\, \frac{e^{-\frac{i}{\hbar}Et}}{E-E_f+i\frac{\hbar\Gamma}{2}} = \frac{-1}{2\pi i}\,(-1)\,2\pi i\,\mathrm{Res}\left[\frac{e^{-\frac{i}{\hbar}Et}}{E-E_f+i\frac{\hbar\Gamma}{2}}\right]_{E=E_f-i\frac{\hbar\Gamma}{2}}$$

$$= e^{-\frac{i}{\hbar}E_f t - \frac{\Gamma}{2}t}$$

↓ due to integration along a contour with negative orientation

residue theorem

- The integrand $\frac{1}{E-E_f+i\frac{\hbar\Gamma}{2}}$ can be interpreted as the energy spectrum of the excited state (similar to a Fourier transform).

- Moreover, the normalised squared modulus of the integrand can be interpreted as a probability distribution, which states how likely it is to find the atom at energy E:

$$\phi(E) = \frac{\hbar\Gamma}{2\pi}\left|\frac{1}{E-E_f+i\frac{\hbar\Gamma}{2}}\right|^2 = \frac{1}{\pi}\,\frac{\frac{\hbar\Gamma}{2}}{(E-E_f)^2+\frac{\hbar^2\Gamma^2}{4}},$$

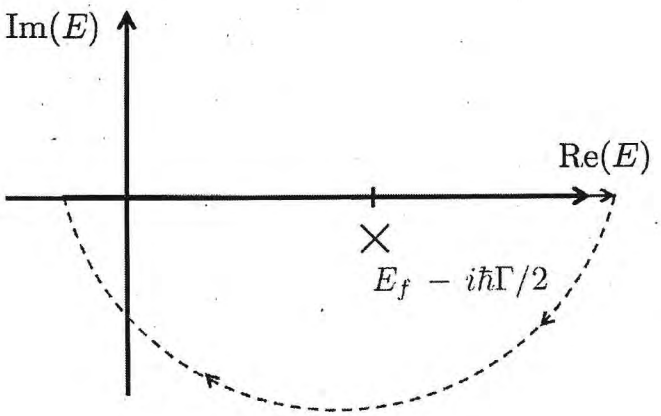
with $\int_{-\infty}^{\infty} dE\,\phi(E) = 1$.

- The function $\phi(E)$ is a so-called <u>Breit-Wigner profile</u> (or Lorentz curve).
- It is peaked at $E = E_f$ and has a width of $\hbar\Gamma$ (= natural linewidth).
- This width is directly related to the life time τ of the state, via $\tau = \frac{1}{\Gamma}$.
- In the limit $\tau \to \infty$, i.e. $\Gamma \to 0$, $\phi(E)$ approaches a Dirac δ-function.
- Since there are apparently no excited states with sharply defined energy, it makes sense to replace in all rates, that we so far calculated

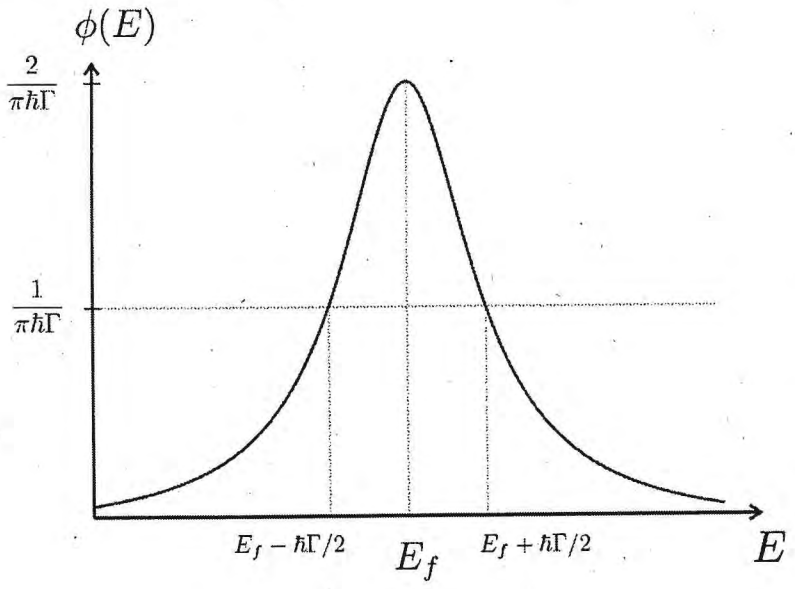
$$\delta(E_f^{(0)} - E_i^{(0)} - \hbar\omega) \to \underbrace{\int_{-\infty}^{\infty} dE\,\phi(E)\,\delta(E-E_i^{(0)}-\hbar\omega)}_{\text{integration over a "continuum" of final states}} = \phi(E_i^{(0)}+\hbar\omega)$$

- This yields well-defined expressions.

Integration contour for obtaining the Breit-Wigner profile



Breit-Wigner profile



Skript zur Vorlesung
Fortgeschrittene Quantentheorie
(Quantenmechanik II)
Prof. Werner Vogelsang
Universität Tübingen
Wintersemester 2020/21

11.3 Quantisation of the radiation field

- The treatment of radiation and its coupling to atom, as conducted so far, cannot be complete.
- For example, we were not able to derive the effect of spontaneous emission from first principles.
- Moreover, our „semi-classical" treatment of the radiation field revealed first indications hinting towards the existence of photons, i.e. absorption and emission involved an energy change of $\pm\hbar\omega$.
- The quantum theory of radiation will indeed show that this is related to the absorption and emission of discrete quanta, i.e. photons.

- We start from the decomposition of the vector potential into plane waves:

$$\vec{A}(\vec{r},t) = \sum_{s=1,2} \int \frac{d^3\vec{k}}{(2\pi)^3 2\omega} \left[A_s(\vec{k})\, \vec{\varepsilon}^{(s)}\, e^{i(\vec{k}\cdot\vec{r}-\omega t)} + A_s^*\, \vec{\varepsilon}^{(s)*}\, e^{-i(\vec{k}\cdot\vec{r}-\omega t)} \right]$$

- Note, that $\vec{\varepsilon}^{(s)} = \vec{\varepsilon}^{(s)}(\vec{k})$ and $\omega = c|\vec{k}|$
- For the following discussion it is convenient to introduce a quantisation volume V, which is finite.
- This makes the set of $\vec{k}$-modes countable, and thereby simplifies the analysis.
- We choose the volume to be a cube whose edges have length L, i.e. $V = L \times L \times L$.
- Moreover, we impose <u>periodic boundary conditions</u>, such that e.g.

$$\vec{A}(x = -\tfrac{L}{2}, y, z, t) \overset{!}{=} \vec{A}(x = \tfrac{L}{2}, y, z, t).$$

- This means that all plane waves have to satisfy

$$e^{i(-k_x \frac{L}{2} + k_y y + k_z z)} \overset{!}{=} e^{i(k_x \frac{L}{2} + k_y y + k_z z)} \rightarrow e^{-ik_x \frac{L}{2}} \overset{!}{=} e^{ik_x \frac{L}{2}}$$

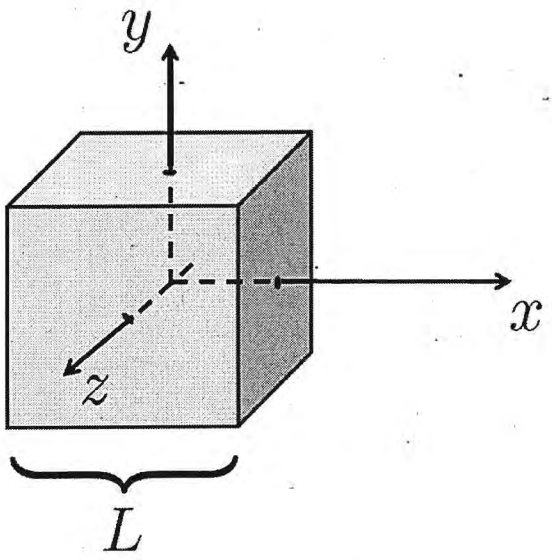
$$\hookrightarrow k_x L \overset{!}{=} k_x \cdot 2\pi \quad \text{with } k_x \in \mathbb{Z}$$

- Generalising this to the y and z directions, yields the possible $\vec{k}$-values:

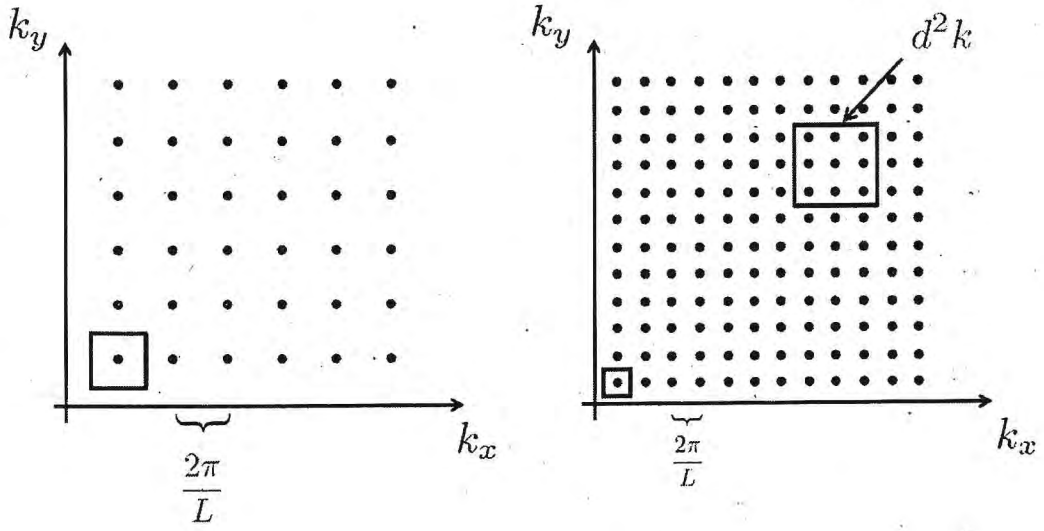
$$\vec{k} = \frac{2\pi}{L} \begin{pmatrix} k_x \\ k_y \\ k_z \end{pmatrix}, \quad k_x, k_y, k_z \in \mathbb{Z}$$

Quantisation of the radiation field

Finite quantisation volume



Discrete countable set of k-modes



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- When switching from the continuous to the discrete $\vec{k}$-values, we also have to take into account that the integral in the expression for $\vec{A}(\vec{r},t)$ becomes a sum

discrete		continuous
$\sum_{\vec{k}}$	$\longleftrightarrow$	$\frac{1}{\left(\frac{2\pi}{L}\right)^3}\int d^3\vec{k} = \frac{V}{(2\pi)^3}\int d^3\vec{k}$

$$\hookrightarrow \vec{A}(\vec{r},t) = \underbrace{\frac{V}{\sqrt{(2\pi)^3}}}_{\text{note, that normalisation constant may be different in different scripts/books}} \sum_{\vec{k},s} \frac{1}{\sqrt{2\omega}} \left[A_s(\vec{k})\,\vec{\varepsilon}^{(s)}\, e^{i(\vec{k}\vec{r}-\omega t)} + A_s^*(\vec{k})\,\vec{\varepsilon}^{(s)*}\, e^{-i(\vec{k}\vec{r}-\omega t)} \right]$$

- Note, that in case of discrete $\vec{k}$-values the plane waves are actually normalisable and obey

$$\int d^3\vec{r}\, e^{i(\vec{k}-\vec{k}')\cdot\vec{r}} = V \underbrace{\delta_{\vec{k}\vec{k}'}}_{\text{Kronecker delta}}$$

- After these preliminary considerations we are now in the position to calculate the energy, H_{rad}, of the radiation field using discrete $\vec{k}$-values.

$$H_{rad} = \int d^3\vec{r}\ \underbrace{u(\vec{r},t)}_{\text{energy density}}$$

$$\frac{\epsilon_0}{2}\left(|\vec{E}(\vec{r},t)|^2 + c^2\,|\vec{B}(\vec{r},t)|^2\right)$$

(see p. 39) $$= \frac{(2\pi)^3}{V}\frac{\epsilon_0}{2}\sum_{\vec{k},s}\omega\left[A_s(\vec{k})\,A_s^*(\vec{k}) + A_s^*(\vec{k})\,A_s(\vec{k})\right]$$

- Introducing the quantity

$$\tilde{a}_s(\vec{k}) = \sqrt{\frac{(2\pi)^3\epsilon_0}{\hbar V}}\,A_s(\vec{k}),$$

one can write this in a more compact way:

$$H_{rad} = \sum_{\vec{k},s}\frac{\hbar\omega}{2}\left[\tilde{a}_s(\vec{k})\,\tilde{a}_s^*(\vec{k}) + \tilde{a}_s^*(\vec{k})\,\tilde{a}_s(\vec{k})\right].$$

- This form of the energy looks similar to the Hamiltonian of a quantum harmonic oscillator, which in terms of creation and annihilation operator, a^+ and a, respectively, has the form

$$H_{osc} = \hbar\omega\left(a^+a + \frac{1}{2}\right) = \frac{\hbar\omega}{2}\left(aa^+ + a^+a\right)$$

- This suggests the following postulate, which leads to a <u>quantised radiation field</u>: Each mode (characterised by $\vec{k}$ and s) of the radiation field behaves like a harmonic oscillator. The free electromagnetic field is described by an infinite set of quantum harmonic oscillators.

- In the corresponding equations this entails the replacement

Fourier coefficient		operator	
$\tilde{a}_s(\vec{k})$	$\rightarrow$	$a_s(\vec{k})$	annihilation operator of mode $(\vec{k},s)$
$\tilde{a}_s^*(\vec{k})$	$\rightarrow$	$a_s^+(\vec{k})$	creation operator of mode $(\vec{k},s)$

- Oscillators corresponding to different modes are assumed to be independent, which leads to the following commutator relations:

$$\left[a_s(\vec{k}),\, a_{s'}^+(\vec{k}')\right] = \delta_{ss'}\,\delta_{\vec{k}\vec{k}'}$$

$$\left[a_s(\vec{k}),\, a_{s'}(\vec{k}')\right] = 0$$

$$\left[a_s^+(\vec{k}),\, a_{s'}^+(\vec{k}')\right] = 0$$

- The replacement of Fourier coefficients by operators also promotes the vector potential to an operator

$$\vec{A}(\vec{r},t) = \sum_{\vec{k},s} \sqrt{\frac{\hbar}{2\varepsilon_0 \omega V}} \left[a_s(\vec{k})\, \vec{\varepsilon}^{(s)} e^{i(\vec{k}\cdot\vec{r}-\omega t)} + a_s^+(\vec{k})\, \vec{\varepsilon}^{(s)*} e^{-i(\vec{k}\cdot\vec{r}-\omega t)} \right]$$

↑ we are not introducing a new symbol for this field operator; often one uses a "hat": $\vec{A} \to \hat{\vec{A}}$, but we omit the hat when the context is clear

- When expressed in terms of a_s and a_s^+ the energy of the radiation field is promoted to a quantum Hamiltonian:

$$H_{rad} = \sum_{\vec{k},s} \frac{\hbar\omega}{2} \left[a_s(\vec{k})\, a_s^+(\vec{k}) + a_s^+(\vec{k})\, a_s(\vec{k}) \right]$$

$$= \sum_{\vec{k},s} \hbar\omega \left(\underbrace{a_s^+(\vec{k})\, a_s(\vec{k})}_{= N_s(\vec{k})} + \frac{1}{2} \right) = \sum_{\vec{k},s} \hbar\omega \left(N_s(\vec{k}) + \frac{1}{2} \right)$$

$= N_s(\vec{k})$ ← number operator

- The number operator $\hat{n}_{\vec{k},s}$ obeys the eigenvalue relation (in analogy to the operator $N = a^+ a$ of the harmonic oscillator):

$$N_s(\vec{k}) \,|n_{\vec{k},s}\rangle = n_{\vec{k},s}\, |n_{\vec{k},s}\rangle .$$

- Here, the numbers $n_{\vec{k},s}$ can be interpreted as the number of photons that occupy the mode $(\vec{k}, s)$, i.e. <u>occupation numbers</u>.
- The state $|n_{\vec{k},s}\rangle$, which has a fixed number of photons is called <u>Fock state</u> (= eigenstate of the number operator).
- A state of the electromagnetic field, which contains a fixed number of photons in any of its modes $(\vec{k}_j, s_j)$ with $j = 1 \dots \infty$ reads

$$|\text{photons}\rangle = |n_{\vec{k}_1 s_1}\rangle \otimes |n_{\vec{k}_2 s_2}\rangle \otimes |n_{\vec{k}_3 s_3}\rangle \otimes \dots$$

(direct product (tensor product))

$$= |n_{\vec{k}_1 s_1}, n_{\vec{k}_2 s_2}, n_{\vec{k}_3 s_3}, \dots\rangle .$$

- These many-body Fock states form a complete orthonormal set, e.g.

$$\langle \text{photons} | \text{photons}' \rangle = \underbrace{\langle n_{\vec{k}_1 s_1} | n_{\vec{k}_1' s_1'} \rangle}_{\delta_{n_{\vec{k}_1 s_1}, n_{\vec{k}_1' s_1'}}} \underbrace{\langle n_{\vec{k}_2 s_2} | n_{\vec{k}_2' s_2'} \rangle}_{\delta_{n_{\vec{k}_2 s_2}, n_{\vec{k}_2' s_2'}}} \dots$$

↳ the scalar product is only non-zero when all occupation numbers coincide.

- An important role is taken by the vacuum state:

$$|\text{vac}\rangle = |0\rangle = |0, 0, \dots\rangle .$$

↑ all modes are empty

- States with a well-defined number of photons can then be constructed by the successive application of creation operators:

$$a_s^\dagger(\vec{k})\,|0\rangle = |0, 0, \dots, \underset{\downarrow}{1}_{\vec{k}s}, \dots\rangle \quad \left.\begin{array}{l}\\\\\end{array}\right\} \text{single photon state}$$

$$a_{s'}^\dagger(\vec{k}')\,a_s(\vec{k})\,|0\rangle = |0, \dots, \underset{\downarrow}{1}_{\vec{k}'s'}, \dots, \underset{\downarrow}{0}_{\vec{k}s}, \dots, \underset{\downarrow}{1}_{\vec{k}'s'}, \dots\rangle$$

$$a_s^\dagger(\vec{k})\,a_s^\dagger(\vec{k})\,|0\rangle = \sqrt{2}\,|0, \dots, \underset{\downarrow}{2}_{\vec{k}s}, \dots\rangle \quad \left.\begin{array}{l}\\\\\end{array}\right\} \text{two photon states}$$

- In general, one has for the creation and annihilation of photons the relations

$$a_s^\dagger(\vec{k})\,|\dots n_{\vec{k}s} \dots\rangle = \sqrt{n_{\vec{k}s}+1}\;|\dots n_{\vec{k}s}+1 \dots\rangle$$

$$a_s(\vec{k})\,|\dots n_{\vec{k}s} \dots\rangle = \sqrt{n_{\vec{k}s}}\;|\dots n_{\vec{k}s}-1 \dots\rangle$$

in close analogy with the quantum harmonic oscillator.

- Note, that the quantisation of the radiation field does not come without conceptual issues.

- For example, the energy of the vacuum state is actually infinite:

$$H_{rad}|0\rangle = \sum_{\vec{k}s} \hbar\omega \left(N_s(\vec{k}) + \tfrac{1}{2}\right)|0\rangle = \sum_{\vec{k}s} \hbar\omega \left(\underbrace{N_s(\vec{k})|0\rangle}_{0} + \tfrac{1}{2}|0\rangle\right)$$

$$= \left(\sum_{\vec{k}s} \frac{\hbar\omega}{2}\right)|0\rangle = \infty\,|0\rangle \quad \text{(infinite energy)}$$

- This problem is „cured" by assuming that not absolute energies but merely energy differences are measurable quantities.

- Therefore, we will in the following subtract this infinite energy and write

$$H_{rad} = \sum_{\vec{k}s} \hbar\omega\, a_s^+(\vec{k})\, a_s(\vec{k}) = \sum_{\vec{k}s} \hbar\omega\, N_s(\vec{k})$$

which acts on Fock states according to

$$H_{rad}|n_{\vec{k}_1 s_1}, n_{\vec{k}_2 s_2} \dots\rangle = \sum_{\vec{k}s} \hbar\omega\, n_{\vec{k}s}\, |n_{\vec{k}_1 s_1}, n_{\vec{k}_2 s_2}, \dots\rangle .$$

- To conclude, we define the momentum operator

(see p. 40) $\vec{P}_{rad} = \int d^3r\, \vec{p}(\vec{r},t) \xrightarrow{\text{quant.}} \sum_{\vec{k}s} \hbar\vec{k}\, N_s(\vec{k})$

$\hbar\vec{k}$: momentum of mode; $N_s(\vec{k})$: number of photons in mode

- We will now revisit the processes of absorption and emission of radiation by an atom, using the quantised radiation field.

- The interaction Hamiltonian is given by

$$H_1 = \frac{e}{\mu}\vec{p}\cdot\vec{A} = e\sum_{\vec{q}s'}\sqrt{\frac{\hbar}{2\varepsilon_0\omega_q V}}\left(a_{s'}(\vec{q})e^{i\omega_q t}\vec{\varepsilon}^{(s')}\cdot\vec{j}(-\vec{q}) + a^+_{s'}(\vec{q})e^{i\omega_q t}\vec{\varepsilon}^{(s')*}\cdot\vec{j}(\vec{q})\right),$$

with $\omega_q = c|\vec{q}|$ and $\vec{j}(\vec{q}) = \frac{\vec{p}}{\mu}e^{-i\vec{q}\cdot\vec{r}}$.

- The quantum states of the atom and the field, which are relevant for absorption and emission, have the structure

$$|\text{atom; photons}\rangle = |\text{atom}\rangle \otimes |\text{photons}\rangle.$$

- E.g. in case of <u>absorption</u> we have

$$|i; \ldots n_{\vec{k}s} \ldots\rangle \longrightarrow |f; \ldots n_{\vec{k}s}-1 \ldots\rangle$$

atom in state $|i\rangle$ and $n_{\vec{k}s}$ photons in mode $(\vec{k},s)$ → atom in state $|f\rangle$ and $n_{\vec{k}s}-1$ photons in mode $(\vec{k},s)$

- For evaluating the matrix elements of H_1, we use the relations

$$\langle \ldots n_{\vec{k}s}-1 \ldots | a_{s'}(\vec{q}) | \ldots n_{\vec{k}s} \ldots\rangle = \sqrt{n_{\vec{k}s}}\,\delta_{ss'}\,\delta_{\vec{q}\vec{k}}$$

$$\langle \ldots n_{\vec{k}s}-1 \ldots | a^+_{s'}(\vec{q}) | \ldots n_{\vec{k}s} \ldots\rangle = 0.$$

- Hence, we obtain for an absorption process the matrix element

$$\langle f; \dots n_{\vec{k}s}-1 \dots | H_1 | i; \dots n_{\vec{k}s} \dots \rangle =$$

$$= e \sum_{\vec{q}s'} \sqrt{\frac{\hbar}{2\varepsilon_0 \omega_q V}}\, \sqrt{n_{\vec{k}s}}\, \delta_{ss'} \delta_{\vec{q}\vec{k}} \langle f | \vec{\varepsilon}^{(s')} \cdot \vec{j}(-\vec{q}) | i \rangle e^{-i\omega_q t}$$

$$= e \sqrt{\frac{\hbar}{2\varepsilon_0 \omega V}}\, \sqrt{n_{\vec{k}s}} \langle f | \vec{\varepsilon}^{(s)} \cdot \vec{j}(-\vec{k}) | i \rangle e^{-i\omega t}$$

$\uparrow$ $\omega = c|\vec{k}|$

- This yields the absorption rate

$$\Gamma^{abs}_{i\to f} = \frac{2\pi}{\hbar} \frac{e^2 \hbar}{2\varepsilon_0 \omega V}\, n_{\vec{k}s}\, |\langle f | \vec{\varepsilon}^{(s)} \cdot \vec{j}(-\vec{k}) | i \rangle|^2 \delta(E_f^{(0)} - E_i^{(0)} - \hbar\omega)$$

$\uparrow$ rate depends on the number of photons.

- For calculating the <u>emission rate</u>, we need to consider the matrix elements of the states

$$|f; \dots n_{\vec{k}s} \dots\rangle \longrightarrow |i; \dots n_{\vec{k}s}+1 \dots\rangle ,$$

and using

$$\langle \dots n_{\vec{k}s}+1 \dots | a_{s'}(\vec{q}) | \dots n_{\vec{k}s} \dots \rangle = 0 ,$$

$$\langle \dots n_{\vec{k}s}+1 \dots | a^+_{s'}(\vec{q}) | \dots n_{\vec{k}s} \dots \rangle = \sqrt{n_{\vec{k}s}+1}\, \delta_{ss'} \delta_{\vec{q}\vec{k}}$$

yields

$$\langle i; \dots n_{\vec{k}s}+1 \dots | H_1 | f; \dots n_{\vec{k}s} \dots \rangle = e \sqrt{\frac{\hbar}{2\varepsilon_0 \omega V}} \sqrt{n_{\vec{k}s}+1}\, \langle i | \vec{\varepsilon}^{(s)*} \cdot \vec{j}(\vec{k}) | f \rangle e^{i\omega t}.$$

The emission rate then becomes

$$\Gamma^{\text{em}}_{f\to i} = \frac{\pi e^2}{\varepsilon_0 \omega V} (n_{\vec{k}s}+1) \underbrace{|\langle i | \vec{\varepsilon}^{(s)*} \cdot \vec{j}(\vec{k}) | f \rangle|^2}_{= |\langle i | \vec{\varepsilon}^{(s)} \cdot \vec{j}(-\vec{k}) | f \rangle|^2} \delta(E_f^{(0)} - E_i^{(0)} - \hbar\omega)$$

$n_{\vec{k}s}$: induced emission, $\Gamma^{\text{ind. em}}_{f\to i}$

$+1$: spontaneous emission, $\Gamma^{\text{sp. em}}_{f\to i}$

- Apparently, even in the absence of photons the quantised radiation field leads to an emission of a photon together with a deviation of the atom.
- The total rate of spontaneous emission is obtained by summing over all wave vectors and polarisations:

$$\Gamma^{\text{sp.em, tot}}_{f\to i} = \sum_{s=1,2} \sum_{\vec{k}} \frac{\pi e^2 \omega}{\varepsilon_0 V} |\vec{d}_{fi} \cdot \vec{\varepsilon}^{(s)}|^2 \delta(E_f^{(0)} - E_i^{(0)} - \hbar\omega)$$

$$= \sum_s \int \frac{d^3\vec{k}}{(2\pi)^3} \frac{\pi e^2 \omega}{\varepsilon_0} |\vec{d}_{fi} \cdot \vec{\varepsilon}^{(s)}|^2 \delta(E_f^{(0)} - E_i^{(0)} - \hbar\omega)$$

$$\overset{\omega = c|\vec{k}|}{=} \sum_s \int d\Omega \int_0^\infty d\omega\, \omega^2 \frac{\pi e \omega}{\varepsilon_0 c^3 (2\pi)^3} |\vec{d}_{fi} \cdot \vec{\varepsilon}^{(s)}|^2 \delta(E_f^{(0)} - E_i^{(0)} - \hbar\omega)$$

$$= \sum_s \int d\Omega \frac{\pi e^2 \omega_{fi}^3}{\varepsilon_0 c^3 (2\pi)^3 \hbar} |\vec{d}_{fi} \cdot \vec{\varepsilon}^{(s)}|^2 .$$

- Using the result from p. 52, i.e. that

$$\sum_{\varepsilon} \int d\Omega \, |\vec{d}_{fi} \cdot \vec{\varepsilon}^{(s)}|^2 = \frac{8\pi}{3} |\vec{d}_{fi}|^2,$$ we find

$$\Gamma_{f \to i}^{\text{sp. em., tot}} = \frac{e^2 \omega_{fi}^3}{3 \varepsilon_0 \hbar c^3 \pi} |\vec{d}_{fi}|^2$$

- This result coincides with the one that we obtained previously by following Einsteins argument.

- Let us finally study a bit more closely the vacuum state of the electromagnetic field.

- Using the vector potential of a given mode $(\vec{k}, s)$

$$\vec{A}_{\vec{k}s}(\vec{r}, t) = \sqrt{\frac{\hbar}{2\varepsilon_0 \omega V}} \left[a_s(\vec{k}) \, \vec{\varepsilon}^{(s)} e^{i(\vec{k}\vec{r} - \omega t)} + a_s^+(\vec{k}) \, \vec{\varepsilon}^{(s)*} e^{-i(\vec{k}\vec{r} - \omega t)} \right],$$

we can calculate the expectation value of the electric field using $\vec{E}_{\vec{k}s} = -\frac{\partial}{\partial t} \vec{A}_{\vec{k}s}$:

$$\langle \vec{E}_{\vec{k}s} \rangle_{\text{vac}} = \langle 0 | \vec{E}_{\vec{k}s} | 0 \rangle = \ldots \underbrace{\langle 0 | a_s(\vec{k}) | 0 \rangle}_{0} + \ldots \underbrace{\langle 0 | a_s^+(\vec{k}) | 0 \rangle}_{0}$$

$$= 0.$$

- On the other hand one finds

$$\langle \vec{E}_{\vec{k}s}^{\,2} \rangle_{\text{vac}} = \langle 0 | \vec{E}_{\vec{k}s}^{\,2} | 0 \rangle = \frac{\hbar \omega}{\varepsilon_0 V} \cdot \frac{1}{2}.$$

- Apparently, the electric field is only on average 0, and it fluctuates around this average value with a variance, that is $(\Delta \tilde{E}_{vs})^2 = \frac{\hbar\omega}{2\varepsilon_0 V}$.
- Both, this zero point fluctuation and the spontaneous emission are genuine quantum effects.

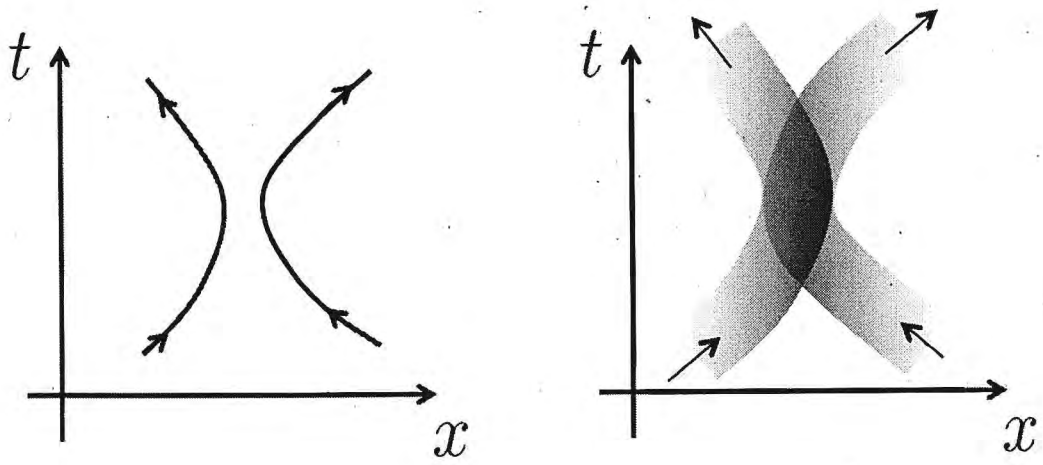
III Many particle systems

- In this chapter we will be considering systems that are composed of many particles, e.g. atoms with many electrons.
- We will show that the concept of exchange symmetry leads to the notion of bosonic and fermionic particles.
- We will also develop the so-called second quantisation formalism, which allows to describe many-body systems through creation and annihilation operators, in close analogy to our treatment of the quantised radiation field.

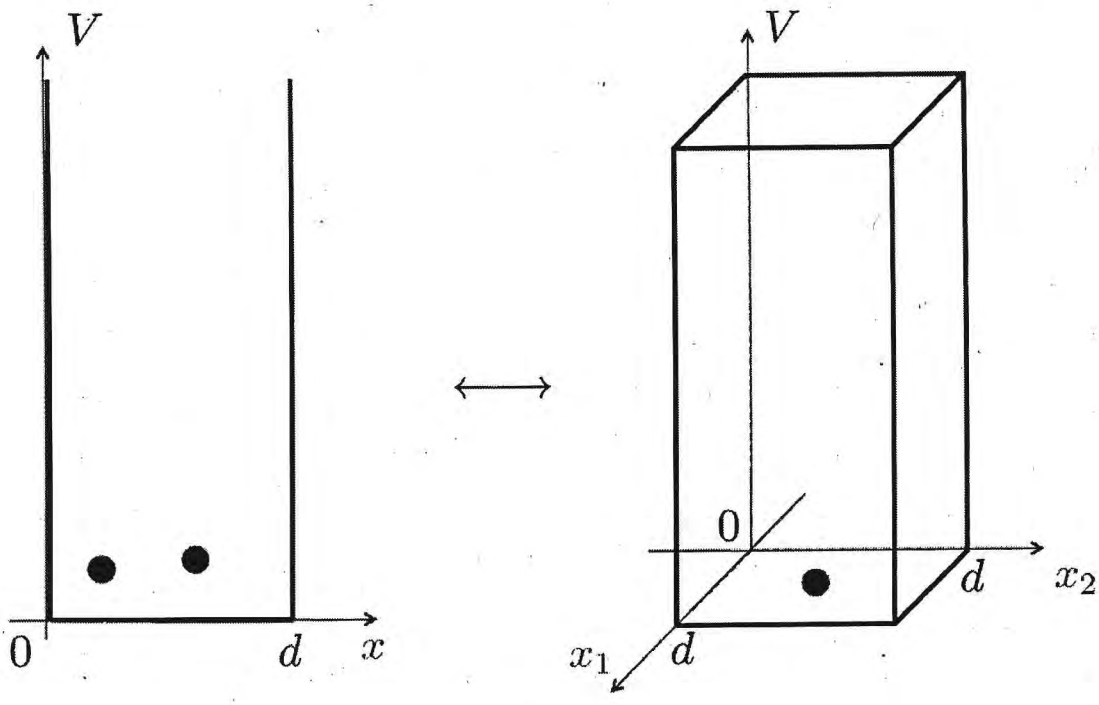
III.1 Identical particles

- In classical physics two identical particles can be distinguished, i.e. we can observe their trajectories and know at any time which one is which.
- For quantum mechanical particles this is not the case, e.g. two electrons or photons are truly identical and there is not even in principle a way to mark them in order to make them distinguishable.

Identical particles: classical vs. quantum



Two particles in a potential well



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- In systems composed of identical particles each particle "follows the exact same physics".
- This means that operators which describe these systems, such as H, L^2 or L_z, are symmetric under exchange of particles.
- In order to get an idea of what that means lets consider two identical particles contained in one-dimensional infinitely deep potential well.
- The corresponding potential is

$$V(x) = \begin{cases} 0 & 0 \le x \le d \\ \infty & \text{elsewhere} \end{cases}$$

- The stationary Schrödinger equation of this system is

$$\underbrace{\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x_1^2} - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial x_2^2} \right]}_{\text{Hamiltonian, } H(x_1,x_2)} u(x_1,x_2) = \underbrace{E}_{\text{energy}}\, u(x_1,x_2)$$

$u(x_1,x_2)$: wave function

$x_{1/2}$: coordinate of particle 1/2

m: particle mass

- The Hamiltonian is indeed symmetric under the exchange of particles:

$$H(x_1, x_2) = H(x_2, x_1)$$

- The problem is formally equivalent to a single particle confined in a two-dimensional potential well, which can be solved by separating variables.

- The normalised solutions are

$$u_{n_1 n_2}(x_1, x_2) = \frac{2}{d} \sin\left(\frac{n_1 \pi}{d} x_1\right) \sin\left(\frac{n_2 \pi}{d} x_2\right),$$

where $n_1, n_2 \in \mathbb{N}$ are the quantum numbers

- The eigenvalues of the energy are

$$E_{n_1 n_2} = \frac{\hbar^2}{2m} \frac{\pi^2}{d^2} (n_1^2 + n_2^2).$$

- Let us consider the case $n_1 = 2$, $n_2 = 3$.

- Given that $u_{n_1 n_2}(x_1, x_2)$ solves the Schrödinger equation, one would expect that $|u_{n_1 n_2}(x_1, x_2)|^2$ is the probability for encountering particle 1 at position x_1 and particle 2 at position x_2.

- However, this does not yield a consistent result, since

$$\underbrace{|u_{23}(x_1,x_2)|^2_{\substack{x_1=\frac{d}{2}\\ x_2=\frac{d}{3}}}}_{\text{probability to find particle 1(2) at position } \frac{d}{2}\,(\frac{d}{3})} \neq \underbrace{|u_{23}(x_1,x_2)|^2_{\substack{x_1=\frac{d}{3}\\ x_2=\frac{d}{2}}}}_{\text{probability to find particle 1(2) at position } \frac{d}{3}\,(\frac{d}{2})}$$

$$= 0 \qquad \neq 0$$

- This result is certainly not compatible with having indistinguishable particles, whose quantum state $\psi(x_1,x_2)$ should obey

$$|\psi(x_1,x_2)|^2 = |\psi(x_2,x_1)|^2,$$

i.e. it should not matter for the probability density whether particle 1(2) is at position x_1 (x_2) or vice versa.

- To fix the problem, we make use of the fact that $u_{23}(x_2,x_1) = u_{32}(x_1,x_2)$, and that both of these wave functions have the same energy eigenvalue

$$E_{23} = E_{32} = \frac{13\hbar^2\pi^2}{2md^2}.$$

- This means that any superposition of those two states is again a valid wave function.
- In particular one finds that

$$u_{23}^{(S)}(x_1,x_2) = \frac{1}{\sqrt{2}}\left(u_{23}(x_1,x_2) + u_{23}(x_2,x_1)\right)$$

$$u_{23}^{(A)}(x_1,x_2) = \frac{1}{\sqrt{2}}\left(u_{23}(x_1,x_2) - u_{23}(x_2,x_1)\right),$$

which obey

$$u_{23}^{(S)}(x_1,x_2) = u_{23}^{(S)}(x_2,x_1) \quad \text{symmetric state}$$

$$u_{23}^{(A)}(x_1,x_2) = -u_{23}^{(A)}(x_2,x_1) \quad \text{antisymmetric state}$$

satisfy the required symmetry condition

$$|u_{23}^{(S,A)}(x_1,x_2)|^2 = |u_{23}^{(S,A)}(x_2,x_1)|^2.$$

- In principle, one can also construct other superpositions which obey this property, but it turns out that only the symmetric and antisymmetric ones are realised in nature.
- In fact, the symmetry property is intimately connected with the spin of the particles, which is referred to as <u>spin-statistics theorem</u>.

- Particles with integer-valued spin $0, 1, 2, \ldots$ (photons, ^4He, ...) are so-called <u>bosons</u> and their many-body wave function is symmetric under particle exchange.

- Particles with half-integer-valued spin $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}$ (electron, quarks, proton) are refered to as <u>fermions</u> and their many-body wave function is antisymmetric under particle exchange.

- Note, that unlike the probability density of the symmetric state, we find that $|u_{23}^{(A)}(x,x)|^2 = 0$.

- This means that the probability to find two particles with an antisymmetric state at the same spatial position is zero.

- This is a manifestation of the Pauli principle, which states that two fermions cannot occupy the same state.

- In what follows, we will generalise these considerations to a system consisting of N identical particles.

- A general Hamiltonian of a system of indistinguishable particles must be fully symmetric under exchange of the labels, corresponding to the degrees of freedom of these particles, i.e

$$H(\underbrace{1,2,3,\dots N}_{\text{labels}}) = H(2,1,3,\dots,N) = \dots$$

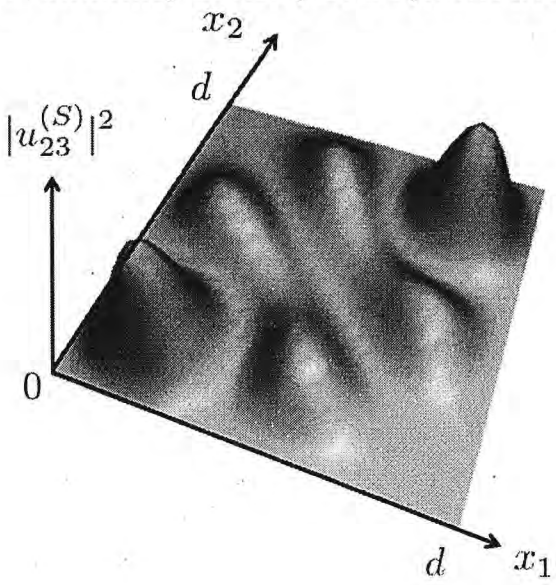
- A typical example is a Hamiltonian of an atom with nuclear charge Z:

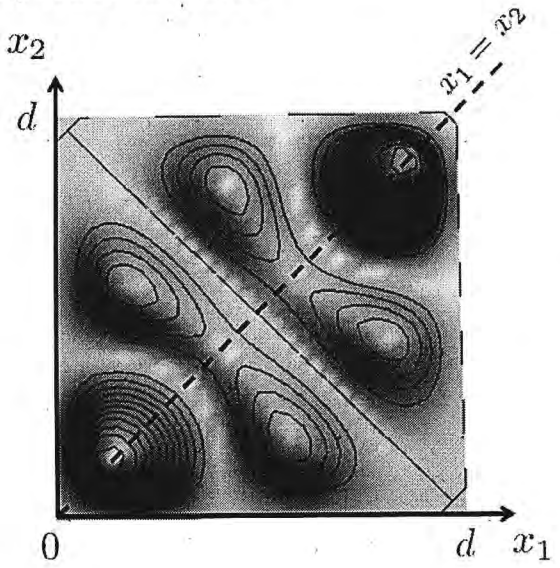
$$H = \underbrace{\sum_{i=1}^{N=Z} \left(\frac{\vec{p}_i^{\,2}}{2\mu} - \frac{Ze^2}{4\pi\varepsilon_0 |\vec{r}_i|} \right)}_{\text{kinetic energy of electrons and Coulomb interaction between electrons and nucleus}} + \underbrace{\sum_{\substack{i,j=1 \\ i<j}}^{N=Z} \frac{1}{4\pi\varepsilon_0} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}}_{\text{Coulomb interaction among electrons}}$$

- For the sake of simplicity we have omitted interactions related to the spin of the electrons.

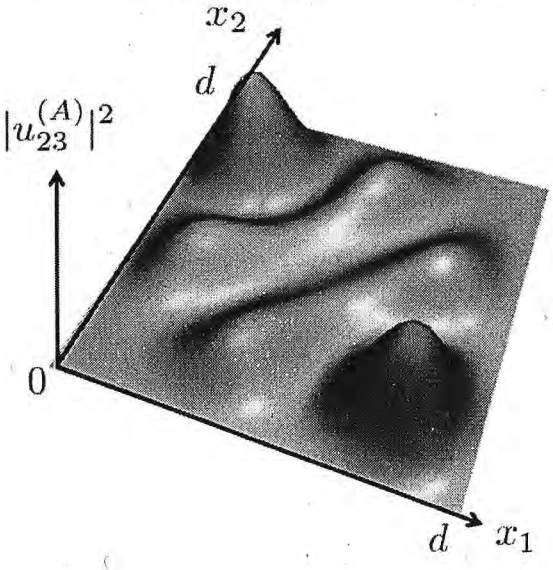
Identical particles

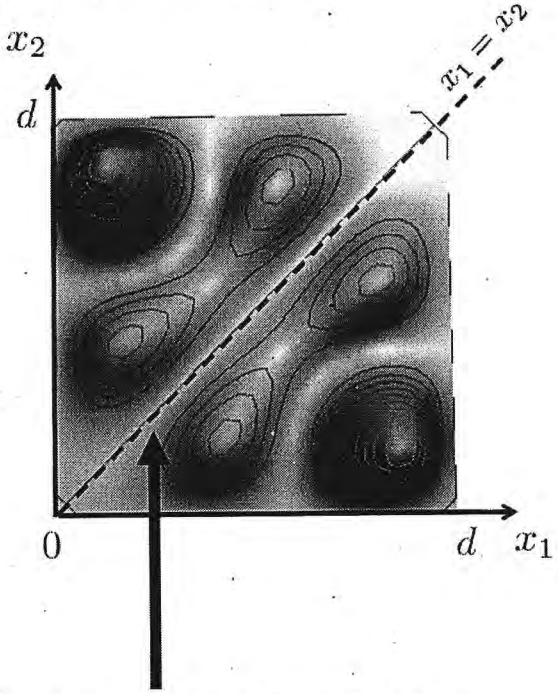
Probability density of a symmetric two-body wave function





Probability density of an antisymmetric two-body wave function





Particles are not found at the same spatial position
(Manifestation of Pauli principle)

Skript zur Vorlesung
Fortgeschrittene Quantentheorie
(Quantenmechanik II)
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- The wave function of such many-body system can be written in the form

$$\Psi(\xi_1, \dots, \xi_N),$$

where ξ_i contains the variables that characterise a particle, e.g. position, spin, ...

↳ $\xi_i = \{\vec{r}_i, s_{i,z}, \dots\}$

- Like for the Hamiltonian before, we use the short hand notation

$$\Psi(\xi_1, \dots, \xi_N) = \Psi(\underbrace{1, \dots, N}_{\text{particle labels}}).$$

- For the following discussion it is useful to define the <u>transposition operator</u> T_{ij},

$$T_{ij}\, \Psi(\dots, i, \dots, j, \dots) = \Psi(\dots, j, \dots, i, \dots)$$

which swaps the labels i and j in the argument of Ψ.

- For example:

$$T_{23}\, T_{12}\, \Psi(1,2,3) = T_{23}\, \Psi(2,1,3) = \Psi(2,3,1).$$

- In total there are $\frac{N(N-1)}{2}$ transpositions, with $i < j$.

- The transposition operators have the following properties:

i) $T_{ij}^2 = \mathbb{1}$

ii) Different transposition operators do not commute in general, e.g.

$$T_{12}\,T_{23}\,\psi(1,2,3) = T_{12}\,\psi(1,3,2) = \psi(\underset{3}{2},\underset{1}{3},\underset{2}{1}) \neq T_{23}\,T_{12}\,\psi(1,2,3)$$

iii) The transposition operator commutes with the Hamiltonian, i.e

$$[H, T_{ij}] = 0 .$$

This is shown as follows:

$$T_{ij}\,H(\ldots,i,\ldots,j,\ldots)\,\psi(\ldots i,\ldots,j\ldots) = H(\ldots j,\ldots,i\ldots)\,\psi(\ldots j,\ldots,i\ldots)$$

$$\overset{\text{Symmetry of the Hamiltonian}}{=} H(\ldots i,\ldots,j\ldots)\,\psi(\ldots j,\ldots,i\ldots)$$

$$= H(\ldots i,\ldots,j\ldots)\,T_{ij}\,\psi(\ldots i,\ldots,j\ldots)$$

Analogously, any operator O that is symmetric under particle exchange commutes with T_{ij}: $[O, T_{ij}] = 0$.

- The next operator, that we are going to need for the subsequent discussion is the <u>permutation operator</u> $P_{P(1)\ldots P(N)}$, which replaces the labels $1,\ldots,N$ in the wave function by $P(1),\ldots,P(N)$.

↳ $P_{P(1)\ldots P(N)}\,\psi(\ldots,1,\ldots,N,\ldots,1,\ldots) = \psi(\ldots,P(1),\ldots,P(N),\ldots,P(1),\ldots)$

$P(1)$ $P(N)$ $P(1)$

- For example: $P_{231}\,\psi(1,2,3) = \psi(2,3,1)$

  or $P_{231}\,\psi(2,3,1) = \psi(3,1,2)$.

- In total, there are $N!$ permutations.
- Each permutation can be decomposed into a sequence of transpositions, e.g. $P_{231} = T_{23}T_{12}$.
- The sign (signum or signature) of a permutation is odd (even) when it can be decomposed into an odd (even) number of transpositions

number of transpositions

$(-1)^{\pi_P}$

Sign of permutation

$\begin{cases} 1, & \text{when } P \text{ is a product of an even number of transpositions} \\ -1, & \text{when } P \text{ is a product of an odd number of transpositions} \end{cases}$

- The permutation operator commutes with the Hamiltonian: $[H,P]=0$.
- When ψ is an eigenfunction of H, then also $P\psi$ is an eigenfunction with the same eigenvalue:

$H\psi = E\psi \rightarrow PH\psi = EP\psi \rightarrow H(P\psi) = E(P\psi)$

- We now come back to the notion of bosons and fermions, whose wave functions have to obey

$$\text{bosons:} \quad T_{ij}\,\psi^{(S)}(1,\dots,N) = +\psi^{(S)}(1,\dots,N) \quad \forall_{ij}$$

$$\text{fermions:} \quad T_{ij}\,\psi^{(A)}(1,\dots,N) = -\psi^{(A)}(1,\dots,N) \quad \forall_{ij}$$

- For $N=2$, there is only one non trivial transposition, and the corresponding symmetric and antisymmetric states are

$$\psi^{(S)} = \mathcal{N}\,(\psi(1,2) + \psi(2,1))$$

$\mathcal{N}$: normalisation factor

$$\psi^{(A)} = \mathcal{N}\,(\psi(1,2) - \psi(2,1))$$

- For $N=3$, there are three transpositions (T_{12}, T_{13}, T_{23}) and 3! permutations, and the anti(symmetric) states are:

$$\psi^{(S)} = \mathcal{N}\,(\psi(1,2,3) + \psi(2,1,3) + \psi(2,3,1) + \psi(1,3,2) + \psi(3,1,2) + \psi(3,2,1))$$

terms with odd number of transpositions

$$\psi^{(A)} = \mathcal{N}\,(\psi(1,2,3) \underset{\downarrow}{-} \psi(2,1,3) + \psi(2,3,1) \underset{\downarrow}{-} \psi(1,3,2) + \psi(3,1,2) \underset{\downarrow}{-} \psi(3,2,1))$$

- Generalising these results leads to the following wave functions:

Symmetric state (bosons)

$$\psi^{(S)} = \mathcal{N} \sum_P P\, \psi(1,\dots,N) \equiv \psi^B$$

anti-symmetric state (fermions)

$$\psi^{(A)} = \mathcal{N} \sum_P (-1)^{\pi P} P\, \psi(1,\dots,N) \equiv \psi^F$$

$(-1)^{\pi P}$ ← sign of the permutation

$\sum_P$ ← Sum over all permutations

- Let us now discuss the consequences of the fact that in nature we encounter only symmetric or antisymmetric many-body states.

(i) Pauli exclusion principle

- Since $\psi^F(1,2,\dots,N) = -\psi^F(2,1,\dots N)$ one has immediately $\psi^F(1,1,\dots,N) = 0$.

  ↳ Two identical fermions must not occupy the same quantum state. This has far-reaching consequences concerning the composition of atoms and matter in general.

(ii) Symmetry properties of wave functions for spatial and spin degrees of freedom

- Lets consider two fermions whose wave function has a spatial and a spin part:

$$\psi^F(1,2) = \psi^F(\vec{r}_1, s_{1,z}; \vec{r}_2, s_{2,z}) = \underbrace{\varphi(\vec{r}_1, \vec{r}_2)}_{\text{spatial wave function}} \underbrace{\chi(s_{1,z}, s_{2,z})}_{\text{spin state}}$$

- Two spin $\frac{1}{2}$ particles can couple to form triplet (total spin $S=1$) or singlet (total spin $S=0$) states:

(S: total spin quantum number; m: spin projection quantum number)

$$|1,1\rangle = |\uparrow\uparrow\rangle$$

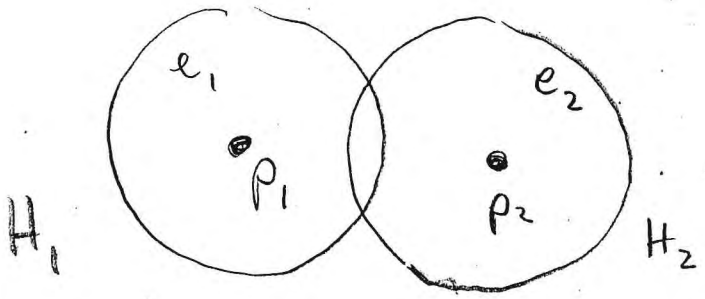
$$|1,0\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right)$$

$$|1,-1\rangle = |\downarrow\downarrow\rangle$$

} triplet

$$|0,0\rangle = \frac{1}{2}\left(|\uparrow\downarrow\rangle - |\uparrow\downarrow\rangle\right) \quad \text{singlet}$$

- The singlet (triplet) states are antisymmetric (symmetric) under the exchange of particles.


e_1
e_2
p_1
p_2
H_1
H_2

- In order for the total state (combination of spatial and spin part) to be antisymmetric, the spatial wavefunction $\psi(\vec{r}_1, r_2)$ has to be antisymmetric (symmetric), when the spins are in the triplet (singlet) state.
- This has measurable consequences for the structure of multi-electron atoms.

(iii) Composite particles

- When a particle is composed from other particles, the following rule applies:

  If the particle is composed of an odd number of fermions it is a fermion, otherwise it is a boson.

- To illustrate this, we consider two hydrogen atoms, whose state is given by

$$\psi(H_1; H_2) = \psi(e_1, p_1; e_2, p_2).$$

- Exchanging the two electrons yields

$$\psi(e_1, p_1; e_2, p_2) \overset{e_1 \leftrightarrow e_2}{=} -\psi(e_2, p_1; e_1, p_2)$$

and exchanging the two protons yields

$$\psi(e_1, p_1; e_2, p_2) \overset{p_1 \leftrightarrow p_2}{=} -\psi(e_1, p_2; e_2, p_1).$$

- Hence $\Psi(e_1, p_1; e_2, p_2) \overset{\substack{e_1 \leftrightarrow e_2 \\ p_1 \leftrightarrow p_2}}{=} \Psi(e_2, p_2; e_1, p_1)$

and thus $\Psi(H_1; H_2) \overset{H_1 \leftrightarrow H_2}{=} + \Psi(H_2; H_1)$.

↑ boson!

- In the following we construct the (anti-) symmetric wave functions of a non-interacting many-particle problem.
- These are usually a good starting point for perturbative expansions of interacting many-particle systems.
- The Hamiltonian we study, has the form

$$H = \sum_{i=1}^{N} \left(\frac{\vec{p}_i^{\,2}}{2m} + V_{ext}(\vec{r}_i) \right) = \sum_{i=1}^{N} H_i .$$

↑ external potential

- In order to solve the stationary Schrödinger equation $H \Psi(1, \ldots, N) = E \Psi(1, \ldots, N)$ we make the separation ansatz

$$\Psi(1, \ldots, N) = u^{(1)}(1)\, u^{(2)}(2) \ldots u^{(N)}(N),$$

where the $u^{(i)}$ are single-particle wave functions that obey the single particle Schrödinger equation

$$H_i u^{(i)} = E^{(i)} u^{(i)}$$

- Inserting the ansatz into the many-body Schrödinger equation, one sees that this is indeed solved:

$$H\,\Psi(1,\dots,N) = \sum_{i=1}^{N} H_i\, u^{(1)}(1)\dots u^{(N)}(N) = \underbrace{\left(\sum_{i=1}^{N} E^{(i)}\right)}_{\text{energy eigenvalue}} u^{(1)}(1)\dots u^{(N)}(N).$$

- Each of the functions $u^{(i)}$ can be one of the eigenstates $u_1, u_2, u_3, \dots$ with eigenenergies $E_1, E_2, E_3, \dots$ of the single-body Schrödinger equation.
- Therefore, the product wave function is generally of the form

$$\Psi(1,\dots,N) = u_{n_1}(1)\, u_{n_2}(2) \dots u_{n_N}(N).$$

& quantum number(s) labelling the energy eigenstate of the first particle

- The energy eigenvalue of the many-body system is then composed of the energy eigenvalues of the individual particles via

$$E = E_{n_1} + E_{n_2} + \dots + E_{n_N}.$$

- Let us now construct the symmetric eigenstates of bosons.

- $N=2$: $\psi^B(1,2) = \frac{1}{\sqrt{2}}\left(u_{n_1}(1)\,u_{n_2}(2) + u_{n_1}(2)\,u_{n_2}(1)\right)$

  ↑ normalisation factor

- $N=3$ with two bosons in state u_{n_1} and one boson in state u_{n_3}:

$$\begin{aligned}\psi^B(1,2,3) = \mathcal{N}\big(&u_{n_1}(1)\,u_{n_1}(2)\,u_{n_3}(3) + u_{n_1}(2)\,u_{n_1}(1)\,u_{n_3}(3)\\ &+ u_{n_1}(2)\,u_{n_1}(3)\,u_{n_3}(1) + u_{n_1}(1)\,u_{n_1}(3)\,u_{n_3}(2)\\ &+ u_{n_1}(3)\,u_{n_1}(1)\,u_{n_3}(2) + u_{n_1}(3)\,u_{n_1}(2)\,u_{n_3}(1)\big)\\ = 2\mathcal{N}\big(&u_{n_1}(1)u_{n_1}(2)u_{n_3}(3) + u_{n_1}(1)u_{n_1}(3)u_{n_3}(2) + u_{n_1}(3)u_{n_1}(2)u_{n_3}(1)\big)\end{aligned}$$

Since all u_n are normalised and mutually orthogonal, the normalisation factor is given by $1 = 4\mathcal{N}^2 \cdot 3 \rightarrow \mathcal{N} = \frac{1}{2\sqrt{3}} = \frac{1}{\sqrt{2!3!}}$.

- Generalising these considerations leads to

$$\psi^B(1,\dots,N) = \frac{1}{\sqrt{N!\,N_{n_1}!N_{n_2}!\dots N_{n_N}!}} \sum_P u_{n_1}(P(1))\dots u_{n_N}(P(N))$$

↑ number of bosons in state u_{n_1}.

- When all bosons occupy the same state, e.g. u_{n_1}, then $N_{n_1} = N$ and all the other $N_m = 1$ and the wave function simplifies to

$$\psi^{(B)}(1,\dots,N) = u_{n_1}(1)\dots u_{n_N}(N).$$

- If the state u_{n_1} is the ground state $\psi^{(B)}$ describes a so-called Bose-Einstein condensate (predicted 1924 by Bose and Einstein; experimentally realised in 1995 by Cornell, Ketterle, Wieman (Nobel prize 2001)).

- For the case of fermionic particles, we construct the many-body wave function according to

$$\psi^{(F)}(1,\dots,N) = \frac{1}{\sqrt{N!}} \sum_P (-1)^{\Pi_P} u_{n_1}(P(1)) \dots u_{n_N}(P(N)).$$

- For $N=2$ this yields the known result

$$\psi^F(1,2) = \frac{1}{\sqrt{2}} \left(u_{n_1}(1) u_{n_2}(2) - u_{n_1}(2) u_{n_2}(1) \right)$$

$$= \frac{1}{\sqrt{2}} \det \begin{pmatrix} u_{n_1}(1) & u_{n_1}(2) \\ u_{n_2}(1) & u_{n_2}(2) \end{pmatrix},$$

whose generalisation yields the so-called Slater determinant:

$$\psi^F(1,\dots,N) = \frac{1}{\sqrt{N!}} \det \begin{pmatrix} u_{n_1}(1) & \cdots & u_{n_1}(N) \\ \vdots & & \vdots \\ u_{n_N}(1) & \cdots & u_{n_N}(N) \end{pmatrix}$$

- Here, the Pauli principle is reflected by the fact that the determinant vanishes when two columns or rows are identical.

III.2 The helium atom

- The helium atom contains two electrons and its Hamiltonian reads

$$H = \underbrace{\frac{\vec{p}_1^{\,2}}{2\mu} + \frac{\vec{p}_2^{\,2}}{2\mu} - \frac{Ze^2}{4\pi\varepsilon_0|\vec{r}_1|} - \frac{Ze^2}{4\pi\varepsilon_0|\vec{r}_2|}}_{\text{nuclear charge } Z=2} + \frac{e^2}{4\pi\varepsilon_0|\vec{r}_1-\vec{r}_2|}$$

$$= \underbrace{H_0}_{\text{two non-interacting hydrogen atoms}} + \frac{e^2}{4\pi\varepsilon_0|\vec{r}_1-\vec{r}_2|}.$$

- We can thus compose the problem into a many-body Hamiltonian, H_0, of non-interacting particles and an interaction term.

- The ground state of the non-interacting problem is given by

$$\psi_{1s1s}(\vec{r}_1,\vec{r}_2) = \psi_{1s}(\vec{r}_1)\,\psi_{1s}(\vec{r}_2),$$

where $\psi_{1s}(\vec{r}) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-\frac{Zr}{a_0}}$ is the ground state (1s-state) of the single-body problem, i.e. the hydrogen atom.

- Since the spatial wave function of the ground state is apparently symmetric, the electrons need to be in an anti-symmetric spin state, i.e. the $S=0$ singlet state.

- The ground state of the non-interacting problem is thus

$$\psi(\vec{r}_1, s_{z,1}; \vec{r}_2, s_{z,2}) = \psi_{1s}(\vec{r}_1)\,\psi_{1s}(\vec{r}_2)\,\frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right).$$

- The ground state energy is given by.

$$H_0\,\psi_{1s1s}(\vec{r}_1, \vec{r}_2) = \underbrace{2E_{1s}^{(0)}}\,\psi_{1s1s}(\vec{r}_1, \vec{r}_2)$$

$$= -2Z^2 E_{Ryd}$$

$$= -108.8\ eV$$

- This is relatively far from the experimentally measured result, $E_{1s1s}^{(exp)} = -78.98\ eV$, for helium.

- The discrepancy stems from electron-electron interaction term.

- Its contribution can be estimated through first order perturbation theory, which yields the correction

$$\Delta E_{1s1s}^{(1)} = \frac{e^2}{4\pi\varepsilon_0}\int d^3\vec{r}_1 \int d^3\vec{r}_2\, \frac{|\psi_{1s}(\vec{r}_1)|^2\,|\psi_{1s}(\vec{r}_2)|^2}{|\vec{r}_1 - \vec{r}_2|}$$

$$\overset{Z=2}{=} \frac{5}{2} E_{Ryd} = 34\ eV$$

↳ $E_{1s1s}^{(0)} + \Delta E_{1s1s}^{(1)} = -\frac{11}{2} E_{Ryd} = -74.8\ eV$

- The agreement of this corrected value with the experiment is fairly good.

- To conclude, we briefly discuss the excited states of helium.

- Here one of the electrons is excited to the state $\psi_{n=2,\ell,m}(\vec{r})$, and the spatial wave function of the non-interacting two-electron system is

Sign depends on symmetry of spin state ↓

$$\psi_{1s|2\ell m}(\vec{r}_1,\vec{r}_2) = \frac{1}{\sqrt{2}}\left(\psi_{1s}(\vec{r}_1)\psi_{2\ell m}(\vec{r}_2) \pm \psi_{1s}(\vec{r}_2)\psi_{2\ell m}(\vec{r}_1)\right).$$

- The energy of this state (under the action of H_0) is

$$E^{(0)}_{1s|2\ell m} = -Z^2 E_{Rgd}\left(1+\frac{1}{4}\right) = -5\,E_{Rgd} = -68\,eV.$$

- We can now use again perturbation theory to calculate the energy correction due to the electron-electron interaction:

$$\Delta E^{(1)}_{1s|2\ell m} = \frac{1}{2}\frac{e^2}{4\pi\varepsilon_0}\int d^3\vec{r}_1 \int d^3\vec{r}_2 \frac{\left|\psi_{1s}(\vec{r}_1)\psi_{2\ell m}(\vec{r}_2) \pm \psi_{1s}(\vec{r}_2)\psi_{2\ell m}(\vec{r}_1)\right|^2}{|\vec{r}_1-\vec{r}_2|}$$

$$= \frac{e^2}{4\pi\varepsilon_0}\int d^3\vec{r}_1 d^3\vec{r}_2 \frac{|\psi_{1s}(\vec{r}_1)|^2\,|\psi_{2\ell m}(\vec{r}_2)|^2 \pm \psi^*_{1s}(\vec{r}_1)\psi^*_{2\ell m}(\vec{r}_2)\psi_{1s}(\vec{r}_2)\psi_{2\ell m}(\vec{r}_1)}{|\vec{r}_1-\vec{r}_2|}$$

$$= I_{\ell m} \pm K_{\ell m}$$

↑ electrostatic energy

↑ exchange energy

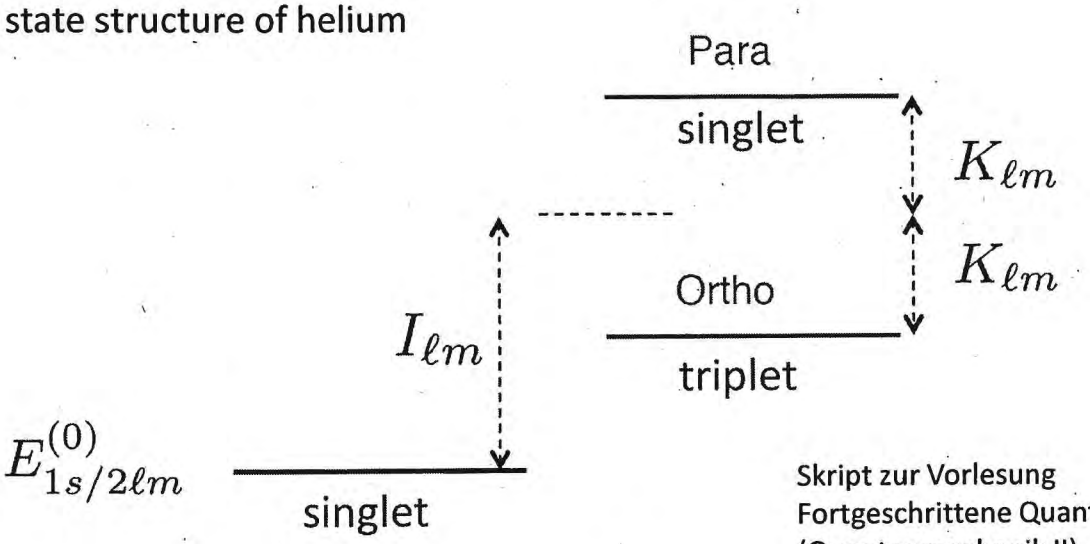
- For an anti-symmetric spatial wave function (the electrons are in the triplet state) the energy correction is

$$\Delta E^{(1)}_{1s\,12\,em} = I_{em} - K_{em}.$$

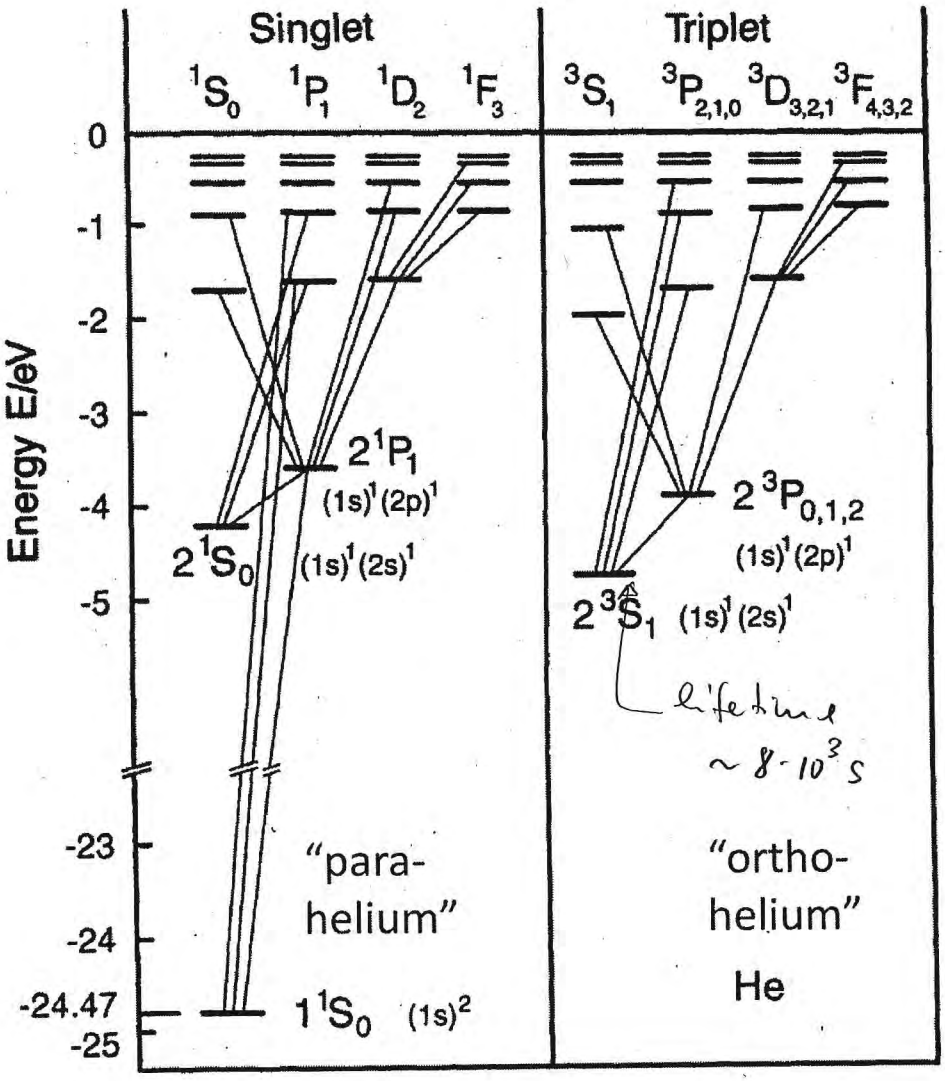
- Since $K_{em} > 0$ this state has a lower energy compared to the state in which the electron spins form a singlet.
- The Pauli principle thus introduces a spin-dependence of the energies, although the Hamiltonian that we studied, does not explicitly depend on the spin degrees of freedom.

- Helium where spins form a singlet (triplet) is also refered to as para (ortho) helium.
- The triplet state is extremely long-lived ($\sim 10^8$ s lifetime), which comes from the fact that external perturbations that couple singlet and triplet states are extremely weak.

Ground state structure of helium



Skript zur Vorlesung
Fortgeschrittene Quantentheorie
(Quantenmechanik II)
Prof. Werner Vogelsang
Universität Tübingen
Wintersemester 2020/21



Haken and Wolf,
The Physics of Atoms
and Quanta,
Springer

III.3 Heavier atoms

- The treatment of heavier atoms, i.e. atoms with a larger number of electrons, becomes increasingly complicated.
- This requires the utilisation of approximation methods, which we discuss in the following.
- Starting point is the Hamiltonian

$$H = \underbrace{\sum_{i=1}^{N=Z} \left(-\frac{\hbar^2}{2\mu}\Delta - \frac{Ze^2}{4\pi\varepsilon_0 |\vec{r}_i|} \right)}_{\text{sum of single electron operators}} + \underbrace{\frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^{N=Z} \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_i - \vec{r}_j|}}_{\frac{N(N-1)}{2} \text{ interaction terms}}$$

- Unlike in the case of the helium atom the electron - electron interaction can typically not be treated as a perturbation.
- However, a simplifying assumption that is made for heavier atoms is that each electron experiences an average potential, which is generated by all other electrons.
- This allows to formulate a single-body Schrödinger equation for each electron, which however contains a potential that depends on the wave functions of all the other electrons.

- This system of coupled equations can then be solved in an iterative fashion.

- A first ansatz of this kind is the so-called Hartree approximation (developed in 1927).

- Here, the many-body electron wave function is written in terms of single-electron states u_i:

$$\Psi(1, \dots, N) = u_1(1)\, u_2(2) \dots u_N(N) .$$

- In order to respect the Pauli principle one assumes that all u_i are different.

- However, no antisymmetrisation is performed.

- With the above ansatz one can formulate a charge density $\rho_j(\vec{r})$ which is associated with the j-th atom:

$$\rho_j(\vec{r}) = -e\, |u_j(\vec{r})|^2$$

($-e$: electron charge; $|u_j(\vec{r})|^2$: probability density of j-th electron)

From electrostatics we know that the associated electric potential is given by

$$\int d^3\vec{r}\,' \frac{\rho_j(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|} = -e \int d^3\vec{r}\,' \frac{|u_j(\vec{r}\,')|^2}{|\vec{r} - \vec{r}\,'|} .$$

- Therefore, the interaction of the i-th electron with all remaining electrons and the nucleus is described by the potential

$$V_i(\vec{r}) = \int d^3\vec{r}' \frac{e^2}{4\pi\varepsilon_0|\vec{r}-\vec{r}'|} \sum_{j\neq i} |u_j(\vec{r}')|^2 - \frac{Ze^2}{4\pi\varepsilon_0|\vec{r}|},$$

and the associated single electron Schrödinger equation - also referred to as <u>Hartree equation</u> - is

$$\left(-\frac{\hbar^2}{2m}\Delta + V_i(\vec{r})\right) u_i(\vec{r}) = \varepsilon_i u_i(\vec{r}).$$

- One now proceeds as follows:

  i) Select a set of orthonormal start functions $u_i^{(0)}$, e.g. eigenstates of hydrogen (with spin).

  ii) Calculate the potentials V_i using the $u_i^{(0)}$.

  iii) Solve the associated Hartree equations and determine from them the new u_i and the eigenenergies ε_i.

  iv) Calculate the potentials with the new u_i and restart until convergence (u_i and ε_i no longer change).

- We now calculate the energy of the many-electron system with the Hartree approximation.

- Calculating the expectation value $\langle H \rangle$ within the Hartree ansatz yields

$$\langle H \rangle = \int d^3\vec{r}_1 \dots d^3\vec{r}_N \; u_1^*(\vec{r}_1) \dots u_N^*(\vec{r}_N) \; H \; u_1(\vec{r}_1) \dots u_N(\vec{r}_N)$$

$$= \sum_{i=1}^{N=Z} \int d^3\vec{r}_i \; u_i^*(\vec{r}_i) \left(-\frac{\hbar^2}{2\mu} \Delta_i - \frac{Ze^2}{4\pi\varepsilon_0 |\vec{r}_i|} \right) u_i(\vec{r}_i)$$

$$+ \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^{N=Z} \int d^3\vec{r}_i \, d^3\vec{r}_j \; \frac{e^2 |u_j(\vec{r}_j)|^2 |u_i(\vec{r}_i)|^2}{4\pi\varepsilon_0 |\vec{r}_i - \vec{r}_j|}$$

- This expression can be simplified by multiplying the Hartree equation from the left by $u_i^*(\vec{r})$ and integrating over $\vec{r}$, which yields

$$\varepsilon_i = \int d^3\vec{r} \; u_i^*(\vec{r}) \left(-\frac{\hbar^2}{2\mu} \Delta - \frac{Ze^2}{4\pi\varepsilon_0 |\vec{r}|} \right) u_i(\vec{r}) + \sum_{j \neq i} \int d^3\vec{r} \, d^3\vec{r}' \; \frac{e^2 |u_j(\vec{r}')|^2 |u_i(\vec{r})|^2}{4\pi\varepsilon_0 |\vec{r} - \vec{r}'|} .$$

- Using this expression to replace the first term on the right hand side of $\langle H \rangle$ yields:

$$\langle H \rangle = \sum_{i=1}^{N} \varepsilon_i - \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^{N} \int d^3\vec{r}_i \, d^3\vec{r}_j \; \frac{e^2 |u_j(\vec{r}_j)|^2 |u_i(\vec{r}_i)|^2}{4\pi\varepsilon_0 |\vec{r}_i - \vec{r}_j|}$$

corrects the double counting when summing over Hartree energies (electron i interacts with j and vice versa)

- The energies ε_i can be interpreted as single electron ionisation energies, assuming that the wave functions of the other electrons do not change after the removal of this electron.

- An improvement over the Hartree method can be achieved via the so-called Hartree-Fock ansatz, which was developed in 1935.

- Here the electronic wave function is chosen to have the form of a Slater determinant

$$\Psi(1,\dots,N) = \frac{1}{\sqrt{N!}} \det \begin{pmatrix} u_1(1) & \dots & u_1(N) \\ \vdots & \ddots & \vdots \\ u_N(1) & \dots & u_N(N) \end{pmatrix},$$

the u_i contain spatial and spin parts

which is a far more accurate description of the electronic many-body state.

- Using this ansatz, the energy expectation value evaluates to:

$$\langle H \rangle = \sum_{i=1}^{N=Z} \int d^3\vec{r}_i \, u_i^*(\vec{r}_i) \left(-\frac{\hbar^2}{2\mu}\Delta_i - \frac{Ze^2}{4\pi\varepsilon_0 |\vec{r}_i|} \right) u_i(\vec{r}_i)$$

$$+ \frac{1}{2} \sum_{\substack{i,j=1 \\ i\neq j}}^{N=Z} \int d^3\vec{r}_i \, d^3\vec{r}_j \, \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_i - \vec{r}_j|} \left(|u_j(\vec{r}_j)|^2 |u_i(\vec{r}_i)|^2 - \underbrace{\delta_{s_i s_j} u_i^*(\vec{r}_i) u_j^*(\vec{r}_j) u_i(\vec{r}_j) u_j(\vec{r}_i)}_{\text{exchange term, which only contributes when electron } i \text{ and } j \text{ are in the same spin state}} \right)$$

- The appearance of the exchange term is new, compared to the Hartree approximation, and a consequence of the antisymmetrisation of the electronic wave function.
- The exchange term is „non-local", i.e. it necessitates the evaluation of an electronic wave function at two distinct spatial points.
- The wave functions u_i, which are still unknown, can be derived using the variational principle due to Ritz, i.e. one finds the set that minimises $\langle H \rangle$ under the constraint, that all u_i shall be normalised.
- This leads to the <u>Hartree-Fock equation</u>

$$\varepsilon_i u_i(\vec{r}) = \left(-\frac{\hbar^2}{2\mu}\Delta - \frac{Ze^2}{4\pi\varepsilon_0 |\vec{r}|} \right) u_i(\vec{r})$$

$$+ \int d^3\vec{r}' \, \frac{e^2}{4\pi\varepsilon_0 |\vec{r}-\vec{r}'|} \sum_{j=1}^{N=7} u_j^*(\vec{r}') \left[u_j(\vec{r}') u_i(\vec{r}) - \delta_{s_{i,z} s_{j,z}} u_j(\vec{r}) u_i(\vec{r}') \right] .$$

- Here, the ε_i are Lagrangian parameters (due to the constrained minimisation), which again can be interpreted as ionisation energies.
- From the Hartree-Fock equation one sees that the effective single electron potential depends on the anti-symmetrised spatial wave function, when the i-th and j-th atom are in the same spin state.
- This is yet another manifestation of the Pauli principle.

- Hartree-Fock ground state energies

	HF	experiment
He	−5.72	−5.8
Li	−14.86	−14.96
Ne	−257.10	−257.88
Ar	−1053.64	−1055.20

energies in units of E_{Ryd}

- variational principle

Hartree-Fock orbitals: $|u_k\rangle$

Slater determinant: $|\phi\rangle$

functional to be minimized under the constraint that orbitals remain normalised

$$\delta F = \delta \left[\langle \phi | H | \phi \rangle - \sum_i \varepsilon_i \langle u_i | u_i \rangle \right] = 0$$

variation: $|u_k\rangle \rightarrow |u_k\rangle + \delta |u_k\rangle$

- The Hartree - Fock approach allows to develop a systematic picture of the atomic structure and the periodic table of elements.

- The effective potential emerging in the Hartree - Fock equation is to a good degree of approximation spherically symmetric.

- The single electron wave functions u_i can therefore be chosen as eigenfunctions of the angular momentum operators $\vec{L}^2$ and L_z.

- We can thus write the single electron states in the form

$$|n, \ell, m, s_z\rangle$$

- n: principal quantum number
- ℓ: angular momentum q.n.
- m: angular momentum projection q.n.
- s_z: spin projection q.n.

- Since the Hartree - Fock potential is not a pure Coulomb potential, the energy eigenvalues of the Hartree - Fock equation will depend on the principal quantum number n and the angular momentum quantum number ℓ

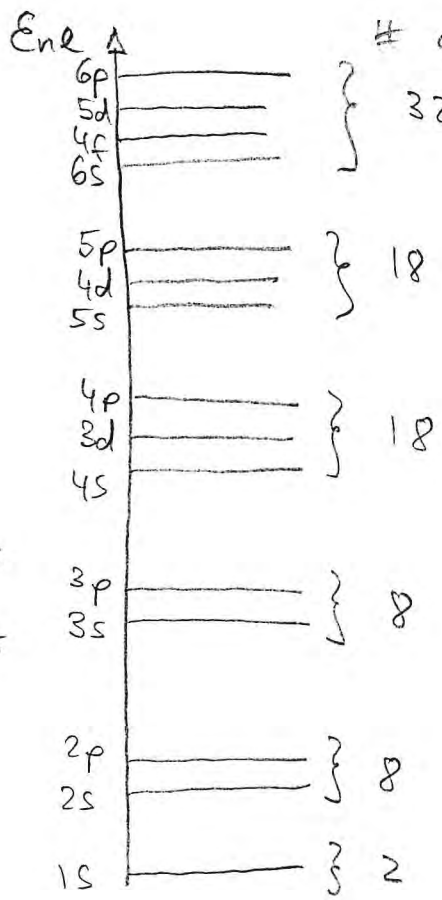
$\hookrightarrow E_{n\ell}$.

- Each of the energy levels has a degeneracy of $2\,\underbrace{(2\ell+1)}$, where 2 = number of possible s_z-values and $(2\ell+1)$ = number of possible m-values.
- These $2(2\ell+1)$ electronic states, which one also calls orbitals, form a shell.
- Each orbital can contain one electron.
  - s-shell ($\ell=0$) — 2 electrons
  - p-shell ($\ell=1$) — 6 electrons
  - d-shell ($\ell=2$) — 10 electrons
  - f-shell ($\ell=3$) — 14 electrons
- To construct the ground state configuration of a given element with Z electrons, one fills the orbitals one by one (no orbital can be populated by more than one electron).
- In which order the orbitals are filled depends on a number of factors.
- One important aspect is the energy $\varepsilon_{n\ell}$ of the orbitals, and one always populates the orbital with lowest available energy.
- In general, for given n, the energy increases with increasing ℓ.

$$\underbrace{\varepsilon_{1s}}_{2} < \underbrace{\varepsilon_{2s}}_{2} < \underbrace{\varepsilon_{2p}}_{6} < \underbrace{\varepsilon_{3s}}_{2} < \underbrace{\varepsilon_{3p}}_{6} < \underbrace{\varepsilon_{3d}}_{10}$$

orbitals

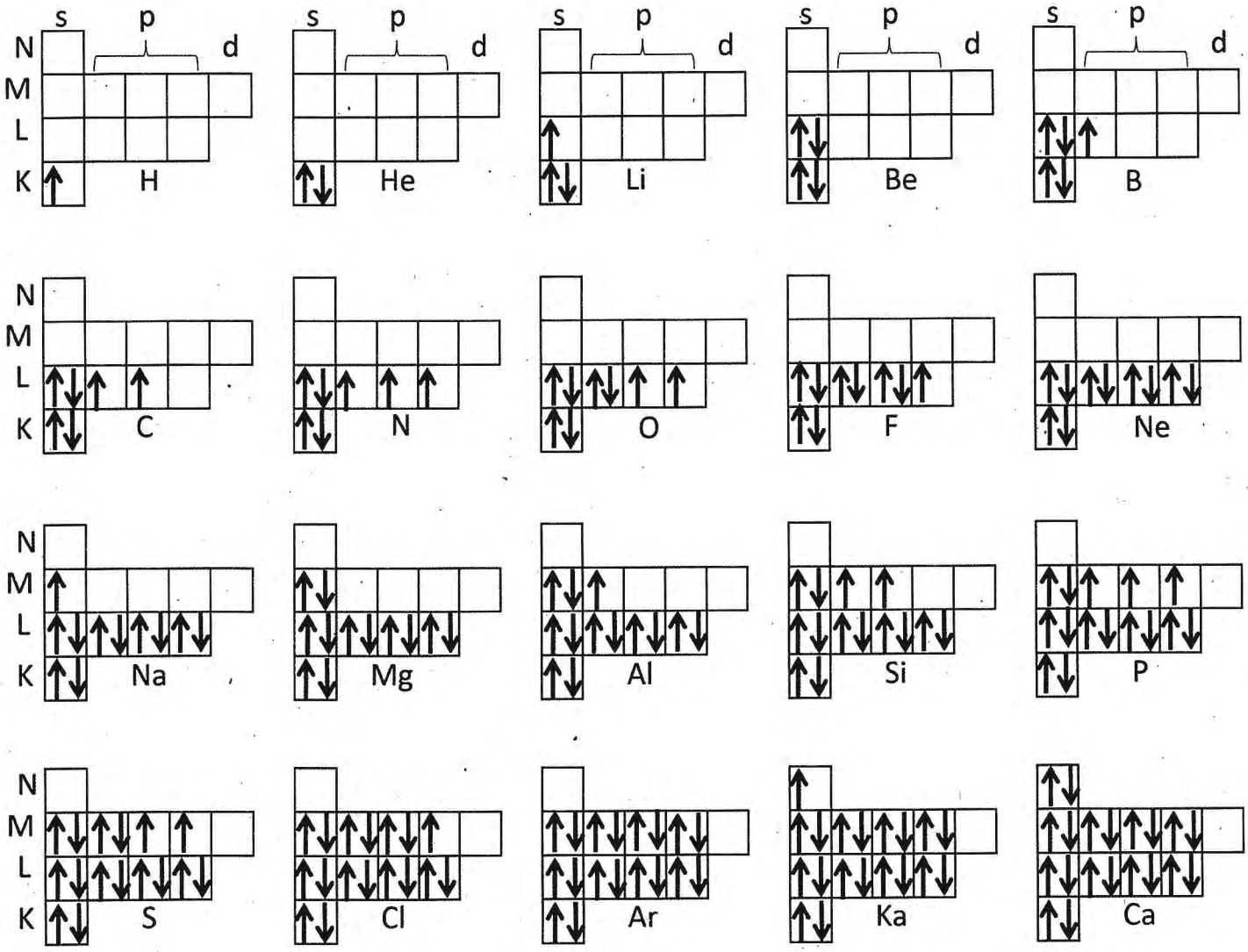
- However, due to screening effects (higher l electrons are further away from the nucleus), s-states with principle quantum numbers $n+1$ can be lower in energy than, e.g., d-states with principle quantum number n (see 3d vs. 4s).



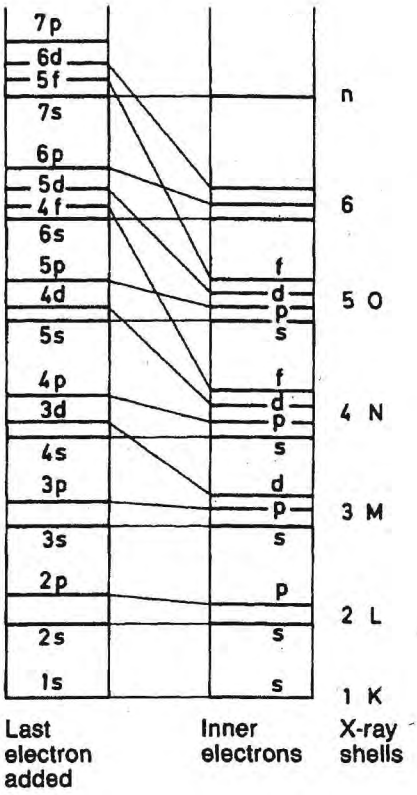
- Considering this, one can construct the entire periodic table:

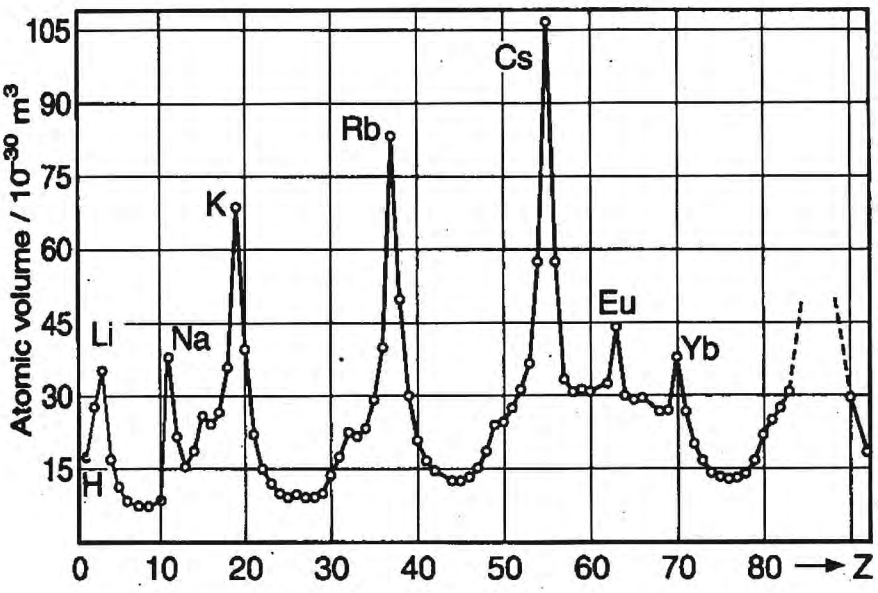
  - Hydrogen has one electron in 1s orbital and helium has the 1s orbital fully occupied
  - Filling the 2s-shell yields Li and Be, and the 2p-shell is filled from B to Ne.
  - Ne has fully filled 1s, 2s, 2p-shells.
  - The systematics of the $n=2$ shells is repeated for $n=3$: Na to Ar.
  - For $n=4$ first the s-shell is filled (K, Ca), but this is followed by 3d (Sc to Zn) and only then by 4p (Ga to Kr).
  - This systematics is repeated for (5s, 4d, 5p).
  - Next, one fills the shells in the order 6s, 4f, 5d, 6p).

Ground state configuration of atoms



Experimental evidence for shell model





Haken and Wolf,
The Physics of Atoms
and Quanta,
Springer

- The position of the elements in the periodic table also determines their chemical properties:
  - Nobel gases have fully occupied shells and are chemically inert.
  - Elements of the first group (except H) posses only one weakly bound valence electron (Li, Na, ...) and are therefore chemically very reactive.
  - The halogenides (7. group) are also very reactive since only one p-electron is missing for completing the noble gas configuration.
- Let us finally consider atoms whose shells are neither fully nor nearly closed.
- Their electronic configuration is given by <u>Hund's rules</u>.

  i) The electrons fill the orbitals such that their total spin S is maximised. This leads to a spin wave function, that is as symmetric as possible. In turn this means that the spatial wave function is antisymmetric which reduces the probability for two electrons to be at the same position and therefore lowers their electrostatic interaction

ii) Is there more than one possibility to have a state with maximum total electron spin, then the state with maximum possible orbital angular momentum is chosen.

iii) If a shell is less than half-filled, the total angular momentum of the electronic ground state is $J = |L-S|$. Conversely, for a filling greater than half, the electronic ground state has $J = L+S$.

example: Carbon atom

- $Z = 6$; 1s & 2s filled
- 2 p electrons

H1 → maximisation of spin $s_{1,z} + s_{2,z} = 1$

↳ $S = 1$, which is symmetric

the possible orbital angular momentum states are $|\alpha| = 0, 1, 2$

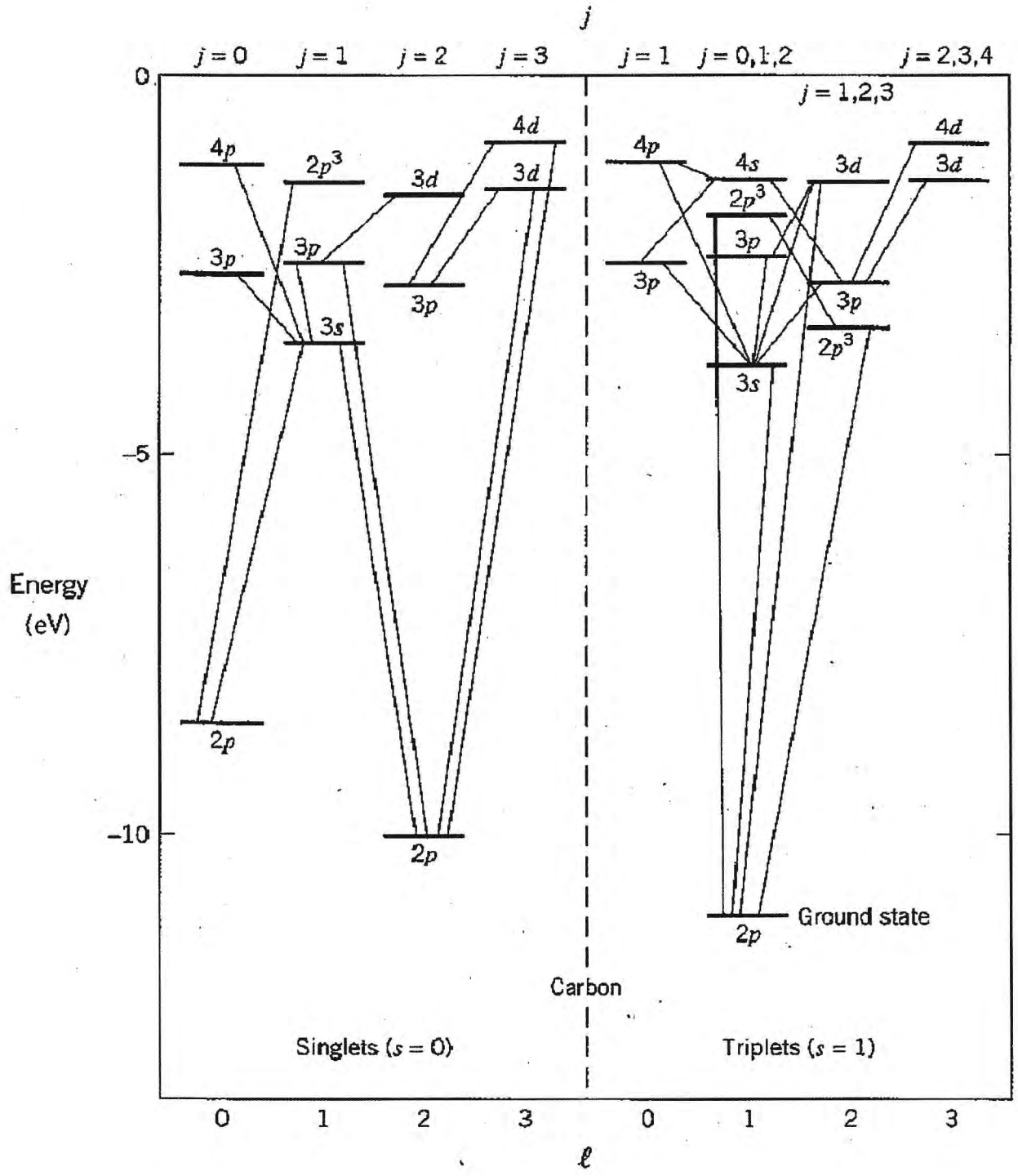
H2 → the highest L, that is antisymmetric is $L = 1 \hat{=}$ maximum possible orbital angular momentum

H3 → shell is less than half filled

→ $J = |L - S| = 0$

↳ ground state $n \; {}^{2S+1}L_J = 2\,{}^3P_0$

Carbon level spectrum



https://quantummechanics.ucsd.edu/ph130a/130_notes/node392.html

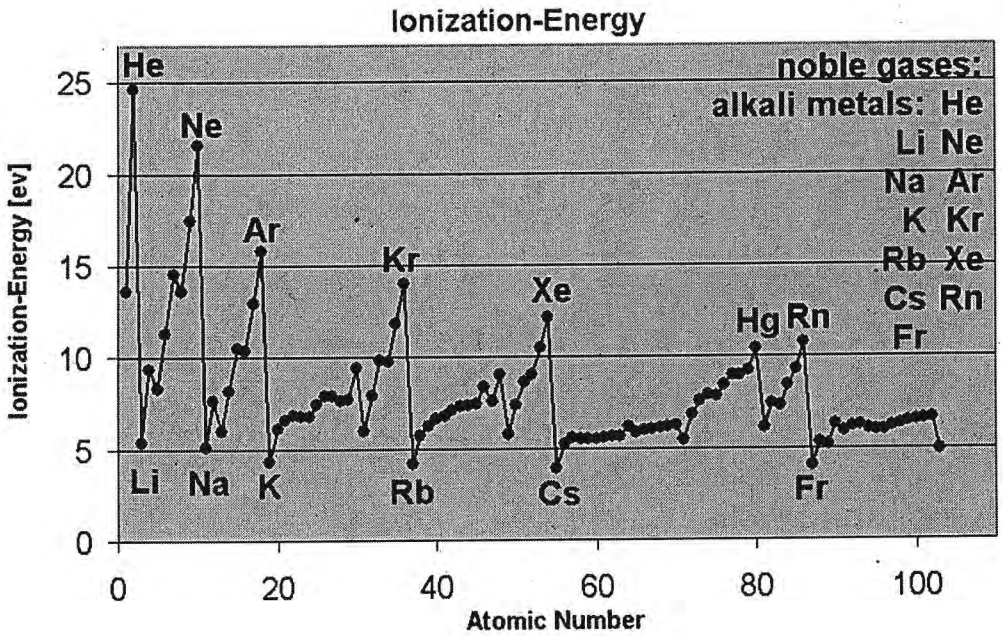
Periodic table of elements

V·T·E

Periodic table

Group	1 Hydrogen & alkali metals	2 Alkaline earth metals	3	4	5	6	7	8	9	10	11	12	13	14	15 Pnictogens	16 Chalcogens	17 Halogens	18 Noble gases
Period 1	Hydrogen 1 H 1.008																	Helium 2 He 4.0026
2	Lithium 3 Li 6.94	Beryllium 4 Be 9.0122											Boron 5 B 10.81	Carbon 6 C 12.011	Nitrogen 7 N 14.007	Oxygen 8 O 15.999	Fluorine 9 F 18.998	Neon 10 Ne 20.180
3	Sodium 11 Na 22.990	Magnesium 12 Mg 24.305											Aluminium 13 Al 26.982	Silicon 14 Si 28.085	Phosphorus 15 P 30.974	Sulfur 16 S 32.06	Chlorine 17 Cl 35.45	Argon 18 Ar 39.95
4	Potassium 19 K 39.098	Calcium 20 Ca 40.078	Scandium 21 Sc 44.956	Titanium 22 Ti 47.867	Vanadium 23 V 50.942	Chromium 24 Cr 51.996	Manganese 25 Mn 54.938	Iron 26 Fe 55.845	Cobalt 27 Co 58.933	Nickel 28 Ni 58.693	Copper 29 Cu 63.546	Zinc 30 Zn 65.38	Gallium 31 Ga 69.723	Germanium 32 Ge 72.630	Arsenic 33 As 74.922	Selenium 34 Se 78.971	Bromine 35 Br 79.904	Krypton 36 Kr 83.798
5	Rubidium 37 Rb 85.468	Strontium 38 Sr 87.62	Yttrium 39 Y 88.906	Zirconium 40 Zr 91.224	Niobium 41 Nb 92.906	Molyb-denum 42 Mo 95.95	Technetium 43 Tc [97]	Ruthenium 44 Ru 101.07	Rhodium 45 Rh 102.91	Palladium 46 Pd 106.42	Silver 47 Ag 107.87	Cadmium 48 Cd 112.41	Indium 49 In 114.82	Tin 50 Sn 118.71	Antimony 51 Sb 121.76	Tellurium 52 Te 127.60	Iodine 53 I 126.90	Xenon 54 Xe 131.29
6	Caesium 55 Cs 132.91	Barium 56 Ba 137.33	* Lutetium 71 Lu 174.97	Hafnium 72 Hf 178.49	Tantalum 73 Ta 180.95	Tungsten 74 W 183.84	Rhenium 75 Re 186.21	Osmium 76 Os 190.23	Iridium 77 Ir 192.22	Platinum 78 Pt 195.08	Gold 79 Au 196.97	Mercury 80 Hg 200.59	Thallium 81 Tl 204.38	Lead 82 Pb 207.2	Bismuth 83 Bi 208.98	Polonium 84 Po [209]	Astatine 85 At [210]	Radon 86 Rn [222]
7	Francium 87 Fr [223]	Radium 88 Ra [226]	** Lawrencium 103 Lr [266]	Ruther-fordium 104 Rf [267]	Dubnium 105 Db [268]	Seaborgium 106 Sg [269]	Bohrium 107 Bh [270]	Hassium 108 Hs [269]	Meitnerium 109 Mt [278]	Darm-stadtium 110 Ds [281]	Roent-genium 111 Rg [282]	Copernicium 112 Cn [285]	Nihonium 113 Nh [286]	Flerovium 114 Fl [289]	Moscovium 115 Mc [290]	Livermorium 116 Lv [293]	Tennessine 117 Ts [294]	Oganesson 118 Og [294]

*	Lanthanum 57 La 138.91	Cerium 58 Ce 140.12	Praseo-dymium 59 Pr 140.91	Neodymium 60 Nd 144.24	Promethium 61 Pm [145]	Samarium 62 Sm 150.36	Europium 63 Eu 151.96	Gadolinium 64 Gd 157.25	Terbium 65 Tb 158.93	Dysprosium 66 Dy 162.50	Holmium 67 Ho 164.93	Erbium 68 Er 167.26	Thulium 69 Tm 168.93	Ytterbium 70 Yb 173.05
**	Actinium 89 Ac [227]	Thorium 90 Th 232.04	Protactinium 91 Pa 231.04	Uranium 92 U 238.03	Neptunium 93 Np [237]	Plutonium 94 Pu [244]	Americium 95 Am [243]	Curium 96 Cm [247]	Berkelium 97 Bk [247]	Californium 98 Cf [251]	Einsteinium 99 Es [252]	Fermium 100 Fm [257]	Mende-levium 101 Md [258]	Nobelium 102 No [259]



Wikipedia

III. 4 Second quantisation

- Second quantisation is a formalism that allows to construct in a rather elegant way fully (anti)symmetric many-body states of (fermions) bosons.
- It moreover delivers a general representation of operators in terms of creation and annihilation operators.
- It is based on the description of bosonic and fermionic wave functions in terms of number states.

- To begin the discussion we consider a single mode (state, orbital) that can be populated by bosonic or fermionic particles.
- The state in which no particle is occupying this mode is the <u>vacuum state</u> $|0\rangle$, which is normalised: $\langle 0|0\rangle = 1$.
- We know that in the case of bosons, the mode can be populated by an arbitrary number of particles, and the state in which the mode is occupied by N particles is denoted by $|N\rangle$ (= number state).

- Following the discussion of the quantization of the radiation field, we now introduce bosonic creation ($a^\dagger$) and annihilation (a) operators, whose commutator is

$$[a, a^\dagger] = 1 .$$

- When acting on the number state, they obey

$$a|N\rangle = \sqrt{N}\,|N-1\rangle$$
$$a^\dagger|N\rangle = \sqrt{N+1}\,|N+1\rangle ,$$

which is consistent with the commutator:

$$[a, a^\dagger]|N\rangle = (aa^\dagger - a^\dagger a)|N\rangle = \left((\sqrt{N+1})^2 - (\sqrt{N})^2\right)|N\rangle = |N\rangle .$$

- The number state $|N\rangle$ can be constructed from the vacuum according to:

$$|N\rangle = \frac{(a^\dagger)^N}{\sqrt{N!}}|0\rangle$$

- Moreover, the application of the annihilation operator to the vacuum yields

$$a|0\rangle = 0 \quad \leftarrow \text{ zero-"vector"}$$

- Let us now discuss the case of fermions.
- The difference compared to bosons is that there are only two available states:

vacuum $|0\rangle$, single fermion $|1\rangle$

- Applying the creation and annihilation operators to both we find:

$$a|0\rangle = 0 \qquad a|1\rangle = |0\rangle$$

$$a^+|0\rangle = |1\rangle \qquad \underbrace{a^+|1\rangle = 0}$$

application of creation operator on already occupied mode does not create a physical state

- We can deduce from these expressions, that $a^2 = 0$, $a^{+2} = 0$.

- Moreover, we find that

$$(aa^+ + a^+a)|1\rangle = 0 + |1\rangle = |1\rangle$$

$$(aa^+ + a^+a)|0\rangle = |0\rangle + 0 = |0\rangle,$$

and therefore

$$\underbrace{\{a, a^+\}} = aa^+ + a^+a = 1.$$

anti-commutator

- Summarising these results yields.

bosons: $[a, a^+] = 1$, $[a, a] = [a^+, a^+] = 0$

fermions: $\{a, a^+\} = 1$, $\{a, a\} = \{a^+, a^+\} = 0$

- In both cases the number operator is a^+a:

$$a^+a|N\rangle = N|N\rangle.$$

- We will now generalise these considerations to many modes.

- We begin with bosons and write the fully symmetrised many-body state of N particles as (using Dirac notation),

$$|\psi^B\rangle = \frac{1}{\sqrt{N!\, N_{n_1}! \dots N_{n_N}!}} \sum_P |n_1\rangle_{P(1)} \dots |n_N\rangle_{P(N)} .$$

- Here we have used the single-body states

$|n_i\rangle_j$ — n_i: quantum number of the single particle state; j: label of the particle.

- The numbers N_{n_i} specify how many particles occupy the single-body state with quantum number n_i.

- As an example consider a state of $N = 18$ bosons, where 5 are in state $|1\rangle$, 4 in state $|4\rangle$ and 9 in state $|12\rangle$:

$$|\psi^B\rangle' = \frac{1}{\sqrt{18!\,5!\,4!\,9!}} \sum_P |1\rangle_{P(1)} \cdots |1\rangle_{P(5)} |4\rangle_{P(6)} \cdots |4\rangle_{P(9)} |12\rangle_{P(10)} \cdots |12\rangle_{P(18)} .$$

- This state is fully determined by the occupation numbers 5, 4 and 9, and the other occupation numbers being zero.

- We can therefore write it also as

$$|\psi_B\rangle' = |5, 0, 0, 4, 0, 0, 0, 0, 0, 0, 0, 9, 0, \dots\rangle .$$

- Generally, this leads to the occupation number representation:

$$|\psi^B\rangle = |N_1, \dots, N_n, \dots\rangle \quad , \quad N = \sum_k N_k$$

N_1: number of particles in $|1\rangle$; N_n: number of particles in $|n\rangle$

- These states obey the orthogonality relation

$$\langle N_1', N_2' \dots | N_1, N_2 \dots \rangle = \delta_{N_1 N_1'} \delta_{N_2 N_2'} \dots$$

and the vacuum state is

$$|0\rangle = |0, 0, \dots, 0, \dots\rangle .$$

- These states live in a Hilbert space, which is the tensor product of N single body Hilbert spaces, where all states are symmetrised: $\mathcal{H}_N^{sym} = \mathcal{H} \otimes \mathcal{H} \otimes \dots \otimes \mathcal{H}$.

- Example:

$$|\psi^B\rangle'' = \frac{1}{\sqrt{6}} \left(|0,0,1,1,0,\dots\rangle - |0,0,2,0,0,\dots\rangle + 2i\,|2,0,0,0,0,\dots\rangle \right)$$

$$= \frac{1}{\sqrt{6}} \left(\frac{1}{\sqrt{2}} \left(|3\rangle_1 |4\rangle_2 + |4\rangle_1 |3\rangle_2 \right) - |3\rangle_1 |3\rangle_2 + 2i\,|1\rangle_1 |1\rangle_2 \right)$$

- Also, note that

$$\underbrace{|1,1,0,\dots\rangle}_{\text{two particle state}} \neq \underbrace{|1,0,0,\dots\rangle + |0,1,0,\dots\rangle}_{\text{single particle state}}$$

- The particle number representation can be also extended to arbitrary N, which introduces the so-called Fock-space.
- This space can be written as a direct sum of all Hilbert spaces $\mathcal{H}_N^{sym}$.

$$\mathcal{F}^{sym} = \mathcal{H}_0^{sym} \oplus \mathcal{H}_1^{sym} \oplus \mathcal{H}_2^{sym} \oplus \dots$$

- These Hilbert spaces are spanned by the following bases:

$\mathcal{H}_0^{sym}$: $|0,0,\dots\rangle$

$\mathcal{H}_1^{sym}$: $|1,0,0,\dots\rangle, |0,1,0,\dots\rangle \dots$

$\mathcal{H}_2^{sym}$: $|2,0,0,\dots\rangle, |0,2,0,\dots\rangle \dots$

$|1,1,0,\dots\rangle, |1,0,1,\dots\rangle, |0,1,1,\dots\rangle \dots$

- For fermions the construction of the particle number states follows a similar procedure.
- We write

$$|\Psi^F\rangle = \frac{1}{\sqrt{N!}} \sum_P (-1)^{\pi_P} |n_1\rangle_{P(1)} \dots |n_N\rangle_{P(N)}$$

$$= \frac{1}{\sqrt{N!}} \det \begin{pmatrix} |n_1\rangle_1 & \dots & |n_N\rangle_1 \\ \vdots & & \\ |n_1\rangle_N & & |n_N\rangle_N \end{pmatrix} = |N_1, \dots, N_n \dots\rangle$$

N_n: number of fermions in single particle state $|n\rangle$

n: number of fermions in single particle state $|1\rangle$

- The occupation numbers can only take the values $N_i = 0, 1$.
- For fixed $N = \sum_i N_i$ these particle numbers states span the N-particle Hilbert space $\mathcal{H}_N^{\text{antisym}}$, which consists only of antisymmetric states constructed from tensor products of single-particle states.
- For example, the space $\mathcal{H}_2^{\text{antisym.}}$ is spanned by $|1,1,0,0,\dots\rangle$, $|1,0,1,0,\dots\rangle$, $|0,1,1,0,\dots\rangle$ etc.
- The direct sum $\mathcal{H}_0^{\text{antisym.}} \oplus \mathcal{H}_1^{\text{antisym}} \oplus \mathcal{H}_2^{\text{antisym}} \oplus \dots$ (identical to bosons) spans the Fock space $\mathcal{F}^{\text{antisym}}$.

- We proceed by studying the action of annihilation and creation operators on bosonic particle number state.
- Since all modes are independent, we have

$$a_n |N_1, N_2, \dots, N_n, \dots\rangle = \sqrt{N_n}\, |N_1, N_2, \dots, N_n - 1, \dots\rangle$$
$$a_n^\dagger |N_1, N_2, \dots, N_n, \dots\rangle = \sqrt{N_n + 1}\, |N_1, N_2, \dots, N_n + 1, \dots\rangle,$$

and the commutation relations are

$$[a_n, a_m^\dagger] = \delta_{nm}, \quad [a_n, a_m] = [a_n^\dagger, a_m^\dagger] = 0.$$

- Furthermore, the particle number operator of the n-th mode obeys

$$a_n^+ a_n |N_1, N_2, \dots, N_n, \dots\rangle = N_n |N_1, N_2, \dots, N_n, \dots\rangle,$$

and a number state can be written as

$$|N_1, N_2, \dots, N_n, \dots\rangle = \dots \frac{(a_n^+)^{N_n}}{\sqrt{N_n!}} \dots \frac{(a_2^+)^{N_2}}{\sqrt{N_2!}} \frac{(a_1^+)^{N_1}}{\sqrt{N_1!}} |0\rangle .$$

$|0\rangle$ ← vacuum

- The action of a creation operator on a symmetrised bosonic state $|\psi^B\rangle$ with N particles is defined as follows:

$$a_n^+ |\psi^B\rangle = \frac{1}{\sqrt{N+1}} \mathrm{Sym}\left[|n\rangle \otimes |\psi^B\rangle\right]$$

↑ creates boson in single-particle state $|n\rangle$

↑ this means that the particle is inserted symmetrically into all $N+1$ possible „positions"

For example:

$$|\psi^B\rangle = a_3^+ a_4^+ |0\rangle = \frac{1}{\sqrt{2}} \left(|3\rangle_1 |4\rangle_2 + |4\rangle_1 |3\rangle_2\right) = |0,0,1,1,\dots\rangle$$

$$\hookrightarrow a_3^+ |\psi^B\rangle = \mathcal{N} \frac{1}{\sqrt{2}} \left(|3\rangle_1 |4\rangle_2 |3\rangle_3 + |4\rangle_1 |3\rangle_2 |3\rangle_3 + |3\rangle_1 |3\rangle_2 |4\rangle_3 + |4\rangle_1 |3\rangle_2 |3\rangle_3 + |3\rangle_1 |3\rangle_2 |4\rangle_3 + |3\rangle_1 |4\rangle_2 |3\rangle_2\right)$$

$$= \mathcal{N} \sqrt{2} \left(|3\rangle_1 |4\rangle_2 |3\rangle_3 + |3\rangle_1 |3\rangle_2 |4\rangle_3 + |4\rangle_1 |3\rangle_2 |3\rangle_3\right).$$

↳ since $a_3^+ |\psi^B\rangle = a_3^+ |0,0,1,1,..\rangle = \sqrt{2}\,|0,0,2,1,..\rangle$
it follows that $\mathcal{N} = \frac{1}{\sqrt{3}}$.

- The requirement that the application of a creation operator leads to symmetric state is „built into" the commutator relations.
- In order to treat a bosonic many-body system we therefore do not have to bother with the explicit construction of the many-particle states, but instead solely need to work with the algebraic properties of the creation and annihilation operators.

- Next, we turn to number states of fermionic systems and the action of fermionic annihilation and creation operators.
- Generalising the algebra of the latter to many modes leads to the anti-commutation relations

$$\{a_n, a_m^+\} = \delta_{nm}\,, \quad \{a_n, a_m\} = \{a_n^+, a_m^+\} = 0$$

- A general number state is constructed via

$$|N_1, N_2, \ldots, N_n, \ldots\rangle = \ldots (a_n^+)^{N_n} \ldots (a_2^+)^{N_2} (a_1^+)^{N_1} \underbrace{|0_1, 0_1, \ldots, 0_1, \ldots\rangle}_{=|0\rangle, \text{ vacuum}}.$$

- Since the occupation numbers N_i are either 0 or 1 there is no additional normalisation factor appearing.
- What is important to note is that we occupied in the construction of the above state the fermionic operators in a given order.
- This order is arbitrary, but it matters, since creation operators corresponding to different modes do not commute.
- In the following we therefore stick to the convention that the mode with the lowest index is filled first, and after that all other modes in ascending order
- The action of a fermionic creation operator on an antisymmetrised state $|\psi^F\rangle$ with N particles is defined as

$$a_n^\dagger |\mathcal{A}^F\rangle = \frac{1}{\sqrt{N+1}} \text{Antisym}\left[|n\rangle \otimes |\mathcal{A}^F\rangle\right].$$

↑ creates fermion in mode $|n\rangle$

↑ single particle state is inserted such that the resulting wave function is antisymmetric

For example:

$$|\mathcal{A}^F\rangle = a_4^\dagger a_3^\dagger |0\rangle = \underbrace{|0,0,1,1,0,\dots\rangle}_{=} = \frac{1}{\sqrt{2}}\left(|3\rangle_1 |4\rangle_2 - |4\rangle_1 |3\rangle_2\right) = \frac{1}{\sqrt{2}} \det\begin{pmatrix} |3\rangle_1 & |3\rangle_2 \\ |4\rangle_1 & |4\rangle_2 \end{pmatrix}$$

$$= -\frac{1}{\sqrt{2}} \det\begin{pmatrix} |4\rangle_1 & |4\rangle_2 \\ |3\rangle_1 & |3\rangle_2 \end{pmatrix}$$

The order matters; we need to stick to our convention!

$$= -a_3^\dagger a_4^\dagger |0\rangle \quad (\neq -|0,0,1,1,0,\dots\rangle)$$

↳ the antisymmetrisation of the state is reflected in the anticommutator relations

- To add a particle in mode 5, one adds a row from below and a column from the right to the Slater determinant:

$$a_5^\dagger a_4^\dagger a_3^\dagger |0\rangle = \frac{1}{\sqrt{6}} \det\begin{pmatrix} |3\rangle_1 & |3\rangle_2 & |3\rangle_3 \\ |4\rangle_1 & |4\rangle_2 & |4\rangle_3 \\ |5\rangle_1 & |5\rangle_2 & |5\rangle_3 \end{pmatrix}.$$

↑ normalisation factor changes: $\frac{1}{\sqrt{2}} \frac{1}{\sqrt{2+1}}$

Using the properties of the Slater determinant one can then show that, e.g.

$$a_5^+ |0,0,1,1,0\ldots\rangle = a_5^+ a_4^+ a_3^+ |0\rangle = -a_4^+ a_5^+ a_3^+ |0\rangle .$$

- Acting with a creation operator onto a general state thus yields

$$a_n^+ |\ldots, \underset{\uparrow n}{0}, \ldots\rangle = (-1)^{\eta_n} |\ldots, \underset{\uparrow n}{1}, \ldots\rangle ,$$

with $\eta_n = \sum_{m>n} N_m$ (number of fermions to the "left" of mode n).

- Likewise, one finds for the annihilation operator

$$a_n |\ldots, \underset{\uparrow n}{1}, \ldots\rangle = (-1)^{\eta_n} |\ldots, 1, \ldots\rangle ,$$

such that the combination $a_n^+ a_n$, which obeys

$$a_n^+ a_n |\ldots, 1, \ldots\rangle = \left[(-1)^{\eta_n}\right]^2 |\ldots, 1, \ldots\rangle = |\ldots, 1, \ldots\rangle ,$$

can be interpreted, like in the case of bosons, as number operator.

- To be able to work efficiently with the second quantisation formalism, we will now derive the representation of many-body operators in terms of creation and annihilation operators.

- We begin with operators which can be written as a sum of single-body operators:

$$T = \sum_{\alpha=1}^{N} t_\alpha$$

(t_α: single-body operator acting on particle α)

- The single-particle states $|n\rangle_\alpha$ associated with the particle α form a complete basis:

$$\mathbb{1} = \sum_n |n\rangle_\alpha {}_\alpha\langle n|$$

- We can thus write

$$t_\alpha = \mathbb{1}\, t_\alpha\, \mathbb{1} = \sum_{mn} |m\rangle_\alpha {}_\alpha\langle m|\, t_\alpha\, |n\rangle_\alpha {}_\alpha\langle n| .$$

- Note, that the matrix element

$$_\alpha\langle m|\, t_\alpha\, |n\rangle_\alpha = \int d^3 r_\alpha\, u_m^*(\vec{r}_\alpha)\, \underbrace{t_\alpha}_{= t(\vec{r}_\alpha)}\, u_n(\vec{r}_\alpha)$$

does not depend on α, since it is the same for any particle.

$\hookrightarrow \alpha\langle m|t_\alpha|n\rangle_\alpha = \langle m|t|n\rangle = t_{mn}$.

- Therefore, $t_\alpha = \sum_{mn} t_{mn} |m\rangle_\alpha{}_\alpha\langle n|$

and $$T = \sum_{mn} t_{mn} \sum_\alpha |m\rangle_\alpha{}_\alpha\langle n| .$$

- In the following we show that

$$\sum_\alpha |m\rangle_\alpha{}_\alpha\langle n| = a_m^+ a_n ,$$

i.e., we can express the sum over the outer product of single particle states as a product of an annihilation and creation operator, when applied to number states.

- Lets start with an example for bosons:

$$|2,0,1,0..\rangle = \frac{1}{\sqrt{3}}\left(|1\rangle_1|1\rangle_2|3\rangle_3 + |1\rangle_1|3\rangle_2|1\rangle_3 + |3\rangle_1|1\rangle_2|1\rangle_3\right)$$

- Applying the operator $\sum_\alpha |3\rangle_\alpha{}_\alpha\langle 1|$ yields

$$\left(|3\rangle_1{}_1\langle 1| + |3\rangle_2{}_2\langle 1| + |3\rangle_3{}_3\langle 1|\right)|2,0,1,0..\rangle$$

$$= \left(|3\rangle_1{}_1\langle 1| + |3\rangle_2{}_2\langle 1| + |3\rangle_3{}_3\langle 1|\right)\frac{1}{\sqrt{3}}\left(|1\rangle_1|1\rangle_2|3\rangle_3 + |1\rangle_1|3\rangle_2|1\rangle_3 + |3\rangle_1|1\rangle_2|1\rangle_3\right)$$

$$= \frac{1}{\sqrt{3}}\left(|3\rangle_1|1\rangle_2|3\rangle_3 + |3\rangle_1|3\rangle_2|1\rangle_3 + |1\rangle_1|3\rangle_2|3\rangle_3 + |3\rangle_1|3\rangle_2|1\rangle_3 + |1\rangle_1|3\rangle_2|3\rangle_3 + |3\rangle_1|1\rangle_2|3\rangle_3\right)$$

$$= \frac{2}{\sqrt{3}}\left(|3\rangle_1|1\rangle_2|3\rangle_3 + |3\rangle_1|3\rangle_2|1\rangle_3 + |1\rangle_1|3\rangle_2|3\rangle_3\right) = 2\,|1,0,2,0..\rangle$$

$$= a_3^+ a_1 |2,0,1,..\rangle$$

- For a general state

$$|N_1,\dots,N_n,\dots,N_m,\dots\rangle = \frac{1}{\sqrt{N!\,N_1!\dots N_n!\dots N_m!\dots}} \times$$

$$\times \sum_P \underbrace{|1\rangle_{P(1)}\dots|1\rangle_{P(N_1)}}_{N_1 \text{ terms}} \cdots \underbrace{|n\rangle_{P(\dots)}\dots|n\rangle_{P(\dots+N_n)}}_{N_n \text{ terms}} \cdots \underbrace{|m\rangle_{P(\dots)}\dots|m\rangle_{P(\dots+N_m)}}_{N_m \text{ terms}} \cdots$$

one finds

factor must be introduced to ensure correct normalisation

$$\Big(\sum_\alpha |m\rangle_\alpha \langle n|\Big)\,|N_1,\dots,N_n,\dots,N_m\dots\rangle = N_n \sqrt{\frac{(N_m+1)!\,(N_n-1)!}{N_m!\,N_n!}}\;|N_1,\dots,N_n-1,\dots,N_m+1,\dots\rangle$$

$$= \sqrt{N_m+1}\,\sqrt{N_n}\,|N_1,\dots,N_n-1,\dots,N_m+1,\dots\rangle$$

$$= a_m^+ a_n\,|N_1,\dots,N_n,\dots,N_m,\dots\rangle$$

- This result also holds for fermions, so that we can write in general for a single-body operator:

$$T = \sum_{mn} t_{mn}\, a_m^+ a_n = \sum_{mn} \langle m|t|n\rangle\, a_m^+ a_n .$$

- For example: Assume that T is a sum of single-body Hamiltonians,

$$T = H_0 = \sum_\alpha h_\alpha \qquad \text{with } h|n\rangle = E_n|n\rangle .$$

Then $H_0 = \sum_{mn} \underbrace{\langle m|h|n\rangle}_{E_n|n\rangle} a_m^+ a_n = \sum_n E_n a_n^+ a_n$

$= \sum_n E_n \hat{N}_n$, ← number operator

and $H_0 |N_1, N_2, \ldots\rangle = \left(\sum_n E_n N_n\right) |N_1, N_2, \ldots\rangle$

↑ the total energy is the sum over all occupation numbers multiplied by the energy of the corresponding single-particle state

- Let us now consider the representation of sums of <u>two-body operators</u> in the second quantisation formalism
- Such operator can be generally written as $V = \frac{1}{2} \sum_{\substack{\alpha,\beta=1 \\ \alpha \neq \beta}}^{N} V_{\alpha\beta}$ ← operator acts on two particles simultaneously, e.g. electron-electron interaction

- We can now write, by inserting identities,

$$V = \frac{1}{2} \sum_{\substack{\alpha,\beta \\ \alpha \neq \beta}} \sum_{mjnk} |m\rangle_\alpha |j\rangle_\beta \left({}_\alpha\langle m| \, {}_\beta\langle j| \right) v_{\alpha\beta} \left(|n\rangle_\alpha |k\rangle_\beta \right) {}_\alpha\langle n| \, {}_\beta\langle k|$$

$$= \frac{1}{2} \sum_{\substack{\alpha,\beta \\ \alpha \neq \beta}} \sum_{mjnk} |m\rangle_\alpha |j\rangle_\beta \, \langle m,j|v|n,k\rangle \, {}_\alpha\langle n| \, {}_\beta\langle k|$$

$$= \frac{1}{2} \sum_{mjnk} V_{mjnk} \sum_{\substack{\alpha,\beta \\ \alpha \neq \beta}} |m\rangle_\alpha \, {}_\alpha\langle n| \, |j\rangle_\beta \, {}_\beta\langle k| \, .$$

- We have used that the matrix element

$$v_{mjnk} = \langle m,j|v|n,k\rangle = \int d^3\vec{r}_\alpha \int d^3\vec{r}_\beta \, u_m^*(\vec{r}_\alpha) u_j^*(\vec{r}_\beta) \, v(\vec{r}_\alpha, \vec{r}_\beta) \, u_n(\vec{r}_\alpha) \, u_k(\vec{r}_\beta)$$

does not depend on α and β.

- We now rewrite

$$\sum_{\substack{\alpha,\beta \\ \alpha \neq \beta}} |m\rangle_\alpha \, {}_\alpha\langle n| \, |j\rangle_\beta \, {}_\beta\langle k| = \sum_{\alpha,\beta} |m\rangle_\alpha \, {}_\alpha\langle n| \, |j\rangle_\beta \, {}_\beta\langle k| - \sum_\alpha |m\rangle_\alpha \underbrace{{}_\alpha\langle n|j\rangle_\alpha}_{\delta_{nj}} \, {}_\alpha\langle k|$$

(unconstrained summation)

$$= a_m^\dagger a_n a_j^\dagger a_k - a_m^\dagger \delta_{nj} a_k$$

$$= a_m^\dagger a_n a_j^\dagger a_k - \begin{cases} a_m^\dagger [a_n, a_j^\dagger] a_k & \text{bosons} \\ a_m^\dagger \{a_n, a_j^\dagger\} a_k & \text{fermions} \end{cases}$$

using (anti) commutators $\rightsquigarrow$

$$= \begin{cases} a_m^\dagger a_j^\dagger a_n a_k & \text{bosons} \\ -a_m^\dagger a_j^\dagger a_n a_k & \text{fermions} \end{cases}$$

- This yields the final result

$$V = \frac{1}{2} \sum_{mjnk} v_{mjnk}\, a_j^\dagger a_m^\dagger a_n a_k ,$$

and a typical Hamiltonian, which contains single and two-body terms reads in its second quantised form

$$H = \sum_{mn} \langle m|t|n\rangle a_m^\dagger a_n + \frac{1}{2} \sum_{mjnk} \langle m,j|v|n,k\rangle a_j^\dagger a_m^\dagger a_n a_k .$$

- We are now going to adress the question concerning how the second quantised form of operators behaves und a change of basis.

- The new (old) basis shall be denoted as $(|n\rangle)\ |\lambda\rangle$, and we can expand the new basis states in terms of the old ones according to

$$|\lambda\rangle = \sum_n \underbrace{\langle n|\lambda\rangle}_{\substack{\text{expansion} \\ \text{coefficients}}} |n\rangle$$

- Using the expansion coefficients, we can also relate the creation and annihilation operators of the old states $(a_n, a_n^\dagger)$ with the new ones $(b_\lambda, b_\lambda^\dagger)$.

$$b_\lambda^\dagger = \sum_n \langle n|\lambda\rangle a_n^\dagger$$

$$b_\lambda = \sum_n \langle\lambda|n\rangle a_n$$

adjoint equation

- The (anti) commutation relations remain unchanged when changing the basis, e.g. for bosons:

$$[b_\lambda, b_{\lambda'}^\dagger] = \sum_{nm} \langle\lambda|n\rangle\langle m|\lambda'\rangle \underbrace{[a_n, a_m^\dagger]}_{\delta_{nm}}$$

$$= \sum_n \langle\lambda|n\rangle\langle n|\lambda'\rangle = \langle\lambda|\lambda'\rangle = \delta_{\lambda\lambda'} .$$

- The operator $b_\lambda^\dagger$ creates a single particle in the state $|\lambda\rangle$, and a general particle number state reads

$$|N_{\lambda_1}, .., N_{\lambda_i}, ..\rangle = \frac{\cdots (b_{\lambda_i}^\dagger)^{N_{\lambda_i}} \cdots (b_{\lambda_1}^\dagger)^{N_{\lambda_1}}}{\cdots \sqrt{N_{\lambda_i}!} \cdots \sqrt{N_{\lambda_1}!}} |0 \ldots 0\rangle \quad \text{new basis}$$

$$|N_{n_1}, .., N_{n_i}, ..\rangle = \frac{\cdots (a_{n_i}^\dagger)^{N_{n_i}} \cdots (a_{n_1}^\dagger)^{N_{n_1}}}{\cdots \sqrt{N_{n_i}!} \cdots \sqrt{N_{n_1}!}} \underbrace{|0 \ldots 0\rangle}_{\text{vacuum state is the same in both bases}} \quad \text{old basis}$$

- The total number operator has the same appearance in both bases

$$\sum_\lambda b_\lambda^\dagger b_\lambda = \sum_{mn} \sum_\lambda \langle m|\lambda\rangle\langle\lambda|n\rangle a_m^\dagger a_n = \sum_{mn} \langle m|n\rangle a_m^\dagger a_n = \sum_n a_n^\dagger a_n = \hat{N}.$$

- Also, the form of a generic Hamiltonian remains unchanged:

$$H = \sum_{\lambda\lambda'} \langle\lambda|t|\lambda'\rangle\, b^+_\lambda b_{\lambda'} + \frac{1}{2}\sum_{\lambda\lambda'\mu\mu'} \langle\lambda,\lambda'|v|\mu,\mu'\rangle\, b^+_{\lambda'} b^+_\lambda b_\mu b_{\mu'}.$$

- A particular important basis is associated with the real-space representation.

$$b^+_{\vec{r}} = \sum_n \langle n|\vec{r}\rangle\, a^+_n = \sum_n u^*_n(\vec{r})\, a^+_n \equiv \psi^+(\vec{r})$$

$\langle n|\vec{r}\rangle$: spatial mode (wave function); a^+_n: adjoint field operator

- The field operator obeys the commutation relations

$$\left[\psi(\vec{r}), \psi^+(\vec{r}')\right] = \sum_{mn} u_n(\vec{r})\, u^*_m(\vec{r}')\, [a_n, a^+_m]$$

$$= \underbrace{\sum_n u_n(\vec{r})\, u^*_n(\vec{r}') = \delta^3(\vec{r}-\vec{r}')}_{\text{completeness relation}}$$

and

$$[\psi(\vec{r}), \psi(\vec{r}')] = [\psi^+(\vec{r}), \psi(\vec{r}')] = 0.$$

- Fermions follow the corresponding anti-commutation relations.

- A particle number state has now the form

$$|N_{\vec{r}_1}, \dots, N_{\vec{r}_i}, \dots\rangle = \frac{\dots \left(\Psi^+(\vec{r}_i)\right)^{N_{\vec{r}_i}} \dots \left(\Psi^+(\vec{r}_1)\right)^{N_{\vec{r}_1}} |0,0,\dots\rangle}{\dots \sqrt{N_{\vec{r}_i}!} \dots \sqrt{N_{\vec{r}_1}!}},$$

and the $N_{\vec{r}_i}$ give the number of particles found at position $\vec{r}_i$.

- The particle number operator we can write by introducing the <u>particle density operator</u>

$$\rho(\vec{r}) = \Psi^+(\vec{r})\,\Psi(\vec{r})$$

as $$\hat{N} = \int d^3\vec{r}\,\rho(\vec{r}) = \int d^3\vec{r} \left(\sum_m u_m^*(\vec{r})\, a_m^+\right)\left(\sum_n u_n(\vec{r})\, a_n\right)$$

$$= \sum_{mn} a_m^+ a_n \underbrace{\int d^3\vec{r}\, u_m^*(\vec{r})\, u_n(\vec{r})}_{\delta_{mn}} = \sum_n a_n^+ a_n .$$

- For a single-particle operator one obtains the representation:

$$\sum_{mn} \langle m|t|n\rangle\, a_m^+ a_n = \sum_{mn} a_m^+ a_n \int d^3\vec{r}\, u_m^*(\vec{r})\, t\, u_n(\vec{r})$$

$$= \int d^3\vec{r}\, \Psi^+(\vec{r})\, t\, \Psi(\vec{r})$$

t ↑ spatial representation of the operator t

- For example:

$$H_0 = \sum_{\alpha=1}^{N} \left(-\frac{\hbar^2}{2\mu} \Delta_\alpha + V_{ext}(\vec{r}_\alpha) \right)$$

$$= \int d^3\vec{r}\; \psi^+(\vec{r}) \left(-\frac{\hbar^2}{2\mu} \Delta + V_{ext}(\vec{r}) \right) \psi(\vec{r})$$

looks like the expectation value for a single particle energy, but the wave functions are replaced by field operators

- For a two-particle operator one obtains the representation:

$$V = \frac{1}{2} \sum_{mjnk} \langle m,j | v | n,k \rangle\, a_j^+ a_m^+ a_n a_k$$

$$= \frac{1}{2} \sum_{mjnk} a_j^+ a_m^+ \int d^3\vec{r} \int d^3\vec{r}'\; u_m^*(\vec{r})\, u_j^*(\vec{r}')\, v(\vec{r},\vec{r}')\, u_n(\vec{r})\, u_k(\vec{r}')\, a_n a_k$$

$$= \frac{1}{2} \int d^3\vec{r} \int d^3\vec{r}'\; \underbrace{\psi^+(\vec{r})\, \psi^+(\vec{r})}_{= \left(\psi(\vec{r})\, \psi(\vec{r}')\right)^+}\, v(\vec{r},\vec{r}')\, \psi(\vec{r})\, \psi(\vec{r}')$$

- Rather often it is useful to introduce creation and annihilation operators in momentum space.
- Considering a finite quantisation volume $V = L \times L \times L$, the eigenvalues of the momentum operator are

$$\vec{p} = \frac{2\pi\hbar}{L} \begin{pmatrix} k_x \\ k_y \\ k_z \end{pmatrix}.$$

- The corresponding eigenstates are plane waves $\langle \vec{r} | \vec{p} \rangle = \frac{1}{\sqrt{V}} e^{i \frac{\vec{p} \cdot \vec{r}}{\hbar}}$.

- The expansion of momentum eigenstates in terms of spatial eigenfunctions is

$$|\vec{p}\rangle = \int d^3\vec{r} \, \langle \vec{r} | \vec{p} \rangle \, |\vec{r}\rangle$$

and thus

$$a^+_{\vec{p}} = \frac{1}{\sqrt{V}} \int d^3\vec{r} \, e^{i \frac{\vec{p} \cdot \vec{r}}{\hbar}} \, \psi^+(\vec{r})$$

$$a_{\vec{p}} = \frac{1}{\sqrt{V}} \int d^3\vec{r} \, e^{-i \frac{\vec{p} \cdot \vec{r}}{\hbar}} \, \psi(\vec{r})$$

$a_{\vec{p}}$: creation and annihilation operators of a particle with momentum $\vec{p}$

$\psi(\vec{r})$: field operators

- The inverse transformation is

$$\psi^+(\vec{r}) = \frac{1}{\sqrt{V}} \sum_{\vec{p}} e^{-i \frac{\vec{p} \cdot \vec{r}}{\hbar}} a^+_{\vec{p}}, \quad \psi(\vec{r}) = \frac{1}{\sqrt{V}} \sum_{\vec{p}} e^{i \frac{\vec{p} \cdot \vec{r}}{\hbar}} a_{\vec{p}},$$

from which follows

$$\left[a_{\vec{p}}, a^+_{\vec{p}'}\right] = \frac{1}{V} \int d^3\vec{r} \int d^3\vec{r}' \, e^{-i \frac{\vec{p} \cdot \vec{r}}{\hbar}} e^{i \frac{\vec{p}' \cdot \vec{r}'}{\hbar}} \left[\psi(\vec{r}), \psi^+(\vec{r}')\right]$$

$$= \frac{1}{V} \int d^3\vec{r} \, e^{i \frac{\vec{r}}{\hbar} \cdot (\vec{p}' - \vec{p})} = \frac{1}{V} \, V \, \delta_{\vec{p}\vec{p}'} = \delta_{\vec{p}\vec{p}'}.$$

- For fermions, again, the appropriate anticommutator holds.

Examples

- kinetic energy:

$$\int d^3\vec{r}\, \psi^\dagger(\vec{r}) \left(-\frac{\hbar^2}{2\mu}\Delta\right)\psi(\vec{r}) = \frac{1}{V}\sum_{\vec{p}\vec{p}'} a^\dagger_{\vec{p}} a_{\vec{p}'} \int d^3\vec{r}\, e^{-i\frac{\vec{p}\cdot\vec{r}}{\hbar}}\left(-\frac{\hbar^2}{2\mu}\Delta\right) e^{i\frac{\vec{p}'\cdot\vec{r}}{\hbar}}$$

$$= \frac{1}{V}\sum_{\vec{p}\vec{p}'} \frac{\vec{p}'^2}{2\mu} a^\dagger_{\vec{p}} a_{\vec{p}'} \underbrace{\int d^3\vec{r}\, e^{-i\frac{(\vec{p}-\vec{p}')\cdot\vec{r}}{\hbar}}}_{V\delta_{\vec{p}\vec{p}'}}$$

$$= \sum_{\vec{p}} \frac{\vec{p}^2}{2\mu} a^\dagger_{\vec{p}} a_{\vec{p}}$$

- single particle potential:

$$\int d^3\vec{r}\, \psi^\dagger(\vec{r}) V_{ext}(\vec{r}) \psi(\vec{r}) = \frac{1}{V}\sum_{\vec{p}\vec{p}'} \tilde{V}_{ext}(\vec{p}-\vec{p}')\, a^\dagger_{\vec{p}} a_{\vec{p}'}$$

with $\tilde{V}_{ext}(\vec{q}) = \int d^3\vec{r}\, V_{ext}(\vec{r})\, e^{-i\frac{\vec{q}\cdot\vec{r}}{\hbar}}$

being the Fourier transformed potential

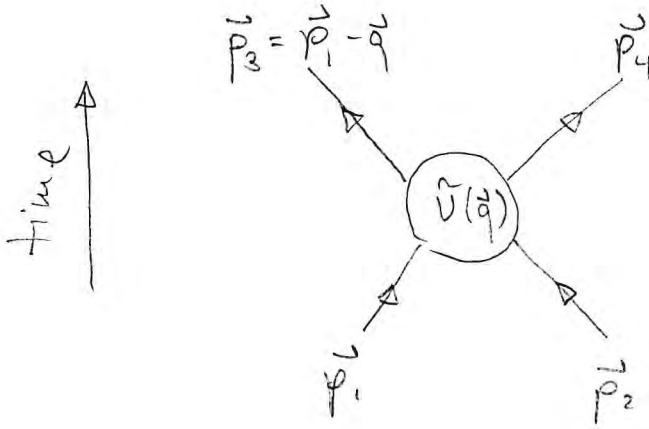
- two-particle interaction, $v(\vec{r},\vec{r}') = v(\vec{r}-\vec{r}')$

$$\frac{1}{2}\int d^3\vec{r}\int d^3\vec{r}'\, \psi^\dagger(\vec{r}')\psi^\dagger(\vec{r})\, v(\vec{r}-\vec{r}')\,\psi(\vec{r})\psi(\vec{r}') = \frac{1}{2V}\sum_{\vec{p}_1,\vec{p}_2,\vec{q}} \tilde{v}(\vec{q})\, a^\dagger_{\vec{p}_2+\vec{q}}\, a^\dagger_{\vec{p}_1-\vec{q}}\, a_{\vec{p}_1} a_{\vec{p}_2}$$

with $\tilde{v}(\vec{q}) = \int d^3\vec{r}\, v(\vec{r})\, e^{-i\frac{\vec{q}\cdot\vec{r}}{\hbar}}$.

- The second quantisation formalism in momentum space is of great importance in scattering theory.

- The Fourier transform of the interaction potential for a given momentum $\vec{q}$ determines for example the strength of a scattering event of the type



- The fact that there are as many creation as annihilation operators appearing in the interaction term means that the particle number is conserved (number of incoming = number of outgoing particles).

- We will now revisit the <u>Harbee-Fock approach</u> using the second quantisation formalism.

- The Hamiltonian of a many-electron atom is

$$H = \sum_{\alpha=1}^{N=7} \underbrace{\left(-\frac{\hbar^2}{2\mu}\Delta_\alpha - \frac{Ze^2}{4\pi\varepsilon_0 |\vec{r}_\alpha|} \right)}_{t_\alpha} + \frac{1}{2} \sum_{\substack{\alpha,\beta=1 \\ \alpha \neq \beta}}^{N=7} \underbrace{\frac{e^2}{4\pi\varepsilon_0 |\vec{r}_\alpha - \vec{r}_\beta|}}_{V_{\alpha\beta}}$$

- The trial state for the electrons is a (antisymmetrized) particle number state, i.e.

$$|\Psi\rangle = a_N^\dagger \dots a_1^\dagger |0, \dots 0\rangle .$$

- The expectation value of the energy for this state is

$$\langle H\rangle = \sum_{mn} \langle m|t|n\rangle \langle \Psi|a_m^\dagger a_n|\Psi\rangle + \frac{1}{2}\sum_{mjnk} \langle mj|V|nk\rangle \langle \Psi|a_j^\dagger a_m^\dagger a_n a_k|\Psi\rangle .$$

- For the matrix elements we obtain

$$\langle \Psi|a_m^\dagger a_n|\Psi\rangle = \delta_{mn} \quad (a_m^\dagger a_n|\Psi\rangle \text{ is orthogonal to } |\Psi\rangle \text{ unless } m=n)$$

$$\langle \Psi|a_j^\dagger a_m^\dagger a_n a_k|\Psi\rangle = \delta_{mn}\delta_{jk}\langle \Psi|a_k^\dagger a_n^\dagger a_n a_k|\Psi\rangle$$

(indices of one annihilation and creation operators must be the same)

$$+ \delta_{mk}\delta_{jn}\langle \Psi|a_n^\dagger a_k^\dagger a_n a_k|\Psi\rangle$$

$$= (-\delta_{mn}\delta_{jk} + \delta_{mk}\delta_{jn})\langle \Psi|a_n^\dagger a_k^\dagger a_n a_k|\Psi\rangle$$

$a_k^\dagger a_n = -a_n a_k^\dagger + \delta_{nk}$ (does not contribute, since all indices will be the same)

$$= (\delta_{mn}\delta_{jk} - \delta_{mk}\delta_{jn})\langle \Psi|\overbrace{a_n^\dagger a_n}^{N_n}\overbrace{a_k^\dagger a_k}^{N_k}|\Psi\rangle$$

$$= \delta_{mn}\delta_{jk} - \delta_{mk}\delta_{jn}$$

- We thus find

$$\sum_{mn} \langle m|t|n\rangle \langle 4|a_m^+ a_n|4\rangle = \sum_n \langle n|t|n\rangle = \sum_n t_{nn}$$

and

$$\frac{1}{2}\sum_{mjk} \langle m,j|v|n,k\rangle \langle 4|a_j^+ a_m^+ a_n a_k|4\rangle = \frac{1}{2}\sum_{\substack{m,k=1\\ m\neq k}} \left(\langle m,k|v|m,k\rangle - \langle m,k|v|k,m\rangle\right)$$

$$= \frac{1}{2}\sum_{\substack{m,k=1\\ m\neq k}} \left(v_{mkmk} - v_{mkkm}\right).$$

- Translating this to the real space representation yields the result that we previously obtained:

$$\langle 4|H|4\rangle = \sum_{n=1}^{N=2} \int d^3\vec{r}\, u_n^*(\vec{r}) \left[-\frac{\hbar^2}{2\mu}\Delta - \frac{2e^2}{4\pi\varepsilon_0|\vec{r}|}\right] u_n(\vec{r})$$

$$+\frac{1}{2}\sum_{\substack{m,k=1\\ m\neq k}} \int d^3\vec{r}\int d^3\vec{r}\,' \frac{e^2}{4\pi\varepsilon|\vec{r}-\vec{r}\,'|}\left(|u_m(\vec{r})|^2|u_k(\vec{r}\,')|^2 - \underbrace{\delta_{s_{m,2}s_{k,2}}}\, u_m^*(\vec{r})\, u_k^*(\vec{r}\,')\, u_k(\vec{r})\, u_m(\vec{r}\,')\right)$$

we made explicit here, that the interaction is diagonal in the spin

- As another application of the second quantization formalism, we consider the Fermi gas.

- A system of N noninteracting fermions confined in a box of volume $V = L\times L\times L$ is described by the Hamiltonian

$$H_{kin} = \sum_{\vec{p},s} \frac{\vec{p}^{\,2}}{2\mu} a^+_{\vec{p},s} a_{\vec{p},s}, \qquad \vec{p} = \frac{2\pi\hbar}{L}\begin{pmatrix} k_x\\ k_y\\ k_z\end{pmatrix}$$

momentum quantum numbers

s ← spin projection

- The smaller the momentum, the smaller the energy.
- Therefore, the ground state is constructed by filling up all momentum states, starting from $\vec{p}=0$ and ending at $|\vec{p}|=p_F$, where p_F is the Fermi momentum, which depends on N and V.
- Ground state: $$|\phi_0\rangle = \prod_{\substack{\vec{p} \\ |\vec{p}|\le p_F}} \prod_{s} a^+_{\vec{p},s} |0\rangle$$
- The total particle number obeys

$$N = \sum_{\vec{p},s} N_{\vec{p},s} = \sum_{\vec{p},s} \langle \phi_0 | \hat{N}_{\vec{p},s} | \phi_0 \rangle = \sum_{\substack{\vec{p},s \\ |\vec{p}|\le p_F}} 1 = \sum_{\substack{\vec{p} \\ |\vec{p}|\le p_F}} 2$$

$$= \frac{2V}{(2\pi\hbar)^3} \underbrace{\int_{|\vec{p}|\le p_F} d^3p}_{\text{volume of a sphere with radius } p_F} = \frac{V}{3\pi^2\hbar^3} p_F^3$$

↳ Fermi momentum: $p_F^3 = 3\pi^2\hbar^3 \frac{N}{V} = 3\pi^2\hbar^3 \nu$ (ν: particle density)

- The total energy is given by

$$E = \sum_{\substack{\vec{p},s \\ |\vec{p}|\le p_F}} \frac{\vec{p}^2}{2\mu} = \frac{2V}{(2\pi\hbar)^3} \int_{|\vec{p}|\le p_F} d^3p \, \frac{\vec{p}^2}{2\mu} = \frac{2V}{(2\pi\hbar)^3} \frac{4\pi}{2\mu} \int_0^{p_F} dp \, p^4 = \frac{V}{10\pi^2\mu\hbar^3} p_F^5$$

$$= \frac{3}{5} N \frac{p_F^2}{2\mu} = \frac{3}{5} N E_F$$

(E_F: Fermi energy)

- We now turn to the more interesting case of an interacting Fermi gas, which is embedded in a uniform positive charge density $\rho = e\frac{N}{V}$, which mimics ions of a metal.
- This charge density is chosen such that it cancels the charge of the electrons, so that overall the system is neutral
- This is the so-called <u>Jellium model</u>.
- Its Hamiltonian is

$$H = H_{kin} + H_{e,ion} + H_{ee} + E_{ion,ion}$$

H_{kin}	$H_{e,ion}$	H_{ee}	$E_{ion,ion}$
kinetic energy of electrons	electron ion interaction	electron-electron interaction	ion-ion interaction (energy shift)

- We assume the the ground state $|\phi_0\rangle$ of a non interacting Fermi gas is a good approximation for this system and calculate the contribution of the perturbations $H_{e,ion}$ and H_{ee} in first order perturbation theory.

- Electron - ion interaction:

$$\langle \phi_0 | H_{e,ion} | \phi_0 \rangle = \langle \phi_0 | \frac{1}{V} \sum_{\vec{p}\vec{p}'} \sum_{ss'} \tilde{V}_{ext}(\vec{p}-\vec{p}')\, a^+_{\vec{p}s} a_{\vec{p}'s'} | \phi_0 \rangle ,$$

with $\tilde{V}_{ext}(\vec{q}) = \int d^3\vec{r}\, V_{ext}(\vec{r})\, e^{i\vec{q}\cdot\vec{r}}$ and

$$V_{ext}(\vec{r}) = -e \int d^3\vec{r}' \frac{\rho(\vec{r}')}{4\pi\varepsilon_0 |\vec{r}-\vec{r}'|} = -N \int d^3\vec{r}' \frac{e^2}{4\pi\varepsilon_0 |\vec{r}-\vec{r}'|} .$$

This yields:

$$\langle \phi_0 | H_{e,ion} | \phi_0 \rangle = \frac{1}{V} \sum_{\vec{p}\vec{p}'} \sum_{ss'} \tilde{V}_{ext}(\vec{p}-\vec{p}') \underbrace{\langle \phi_0 | a^+_{\vec{p}s} a_{\vec{p}'s'} | \phi_0 \rangle}_{\delta_{\vec{p}\vec{p}'}\delta_{ss'} N_{\vec{p},s} \; = 1 \text{ for } |\vec{p}| \le p_F}$$

$$= \frac{1}{V} \sum_{\substack{\vec{p}s \\ |\vec{p}| \le p_F}} \tilde{V}_{ext}(0) = \frac{N}{V} \int d^3\vec{r}\, V_{ext}(\vec{r})$$

$$= -N^2 \underbrace{\int d^3\vec{r} \int d^3\vec{r}' \frac{e^2}{4\pi\varepsilon_0 |\vec{r}-\vec{r}'|}}$$

$$= -N^2 \cdot U \quad \leftarrow \text{large constant}$$

- Electron - electron interaction:

$$\langle \phi_0 | H_{ee} | \phi_0 \rangle = \frac{1}{2} \int d^3\vec{r} \int d^3\vec{r}'\, v(\vec{r}-\vec{r}') \sum_{ss'} \underbrace{\langle \phi_0 | \psi^+_{s'}(\vec{r}')\, \psi^+_s(\vec{r})\, \psi_s(\vec{r})\, \psi_{s'}(\vec{r}') | \phi_0 \rangle}_{\text{pair correlation function}}$$

$$G_{ss'}(\vec{r}-\vec{r}') = \left(\frac{N}{2}\right)^2 \begin{cases} 1 & , s \neq s' \\ 1 - \left(\frac{3(\sin x - x\cos x)}{x^3}\right)^2 & , s = s' \end{cases}$$

with $x = \frac{p_F}{\hbar} |\vec{r}-\vec{r}'|$

- With the Coulomb potential $v(|\vec{r}-\vec{r}'|) = \frac{e^2}{4\pi\varepsilon_0|\vec{r}-\vec{r}'|}$ this yields

$$\langle\phi_0|H_{ee}|\phi_0\rangle = \frac{1}{2}\int d^3\vec{r}\int d^3\vec{r}'\, v(|\vec{r}-\vec{r}'|)\left[2\left(\frac{\nu}{2}\right)^2 + 2\left(\frac{\nu}{2}\right)^2\left(1-\left(\frac{3(\sin x - x\cos x)}{x^3}\right)^2\right)\right]$$

$$= \frac{\nu^2}{2}U - \frac{9\nu^2}{4}\frac{e^2 p_F}{4\pi\varepsilon_0 4}\int d^3\vec{r}\int d^3\vec{r}'\,\frac{(\sin x - x\cos x)^2}{x^7}$$

$$= \frac{\nu^2}{2}U - \frac{9}{4}\nu^2 V\frac{e^2 p_F}{4\pi\varepsilon_0 4}\frac{\pi 4^3}{p_F^3}$$

$$= \frac{\nu^2}{2}U - \frac{3}{4\pi}\frac{e^2}{4\pi\varepsilon_0 4}p_F N$$

- Ion-ion interaction energy shift:

$$E_{ion,ion} = \frac{1}{2}\int d^3\vec{r}\int d^3\vec{r}'\,\frac{\rho(\vec{r})\rho(\vec{r}')}{4\pi\varepsilon_0|\vec{r}-\vec{r}'|}$$

$$= \frac{\nu^2}{2}\int d^3\vec{r}\int d^3\vec{r}'\,\frac{e^2}{4\pi\varepsilon_0|\vec{r}-\vec{r}'|} = \frac{\nu^2}{2}U.$$

↳ cancels all other U-dependent terms

- Adding all contributions together, yields

$$E_{ground} = \langle\phi_0|H|\phi_0\rangle = \frac{3}{5}E_F N - \nu^2 U + \frac{\nu^2}{2}U - \frac{3}{4\pi}\frac{e^2}{4\pi\varepsilon_0 4}p_F N + \frac{\nu^2}{2}U.$$

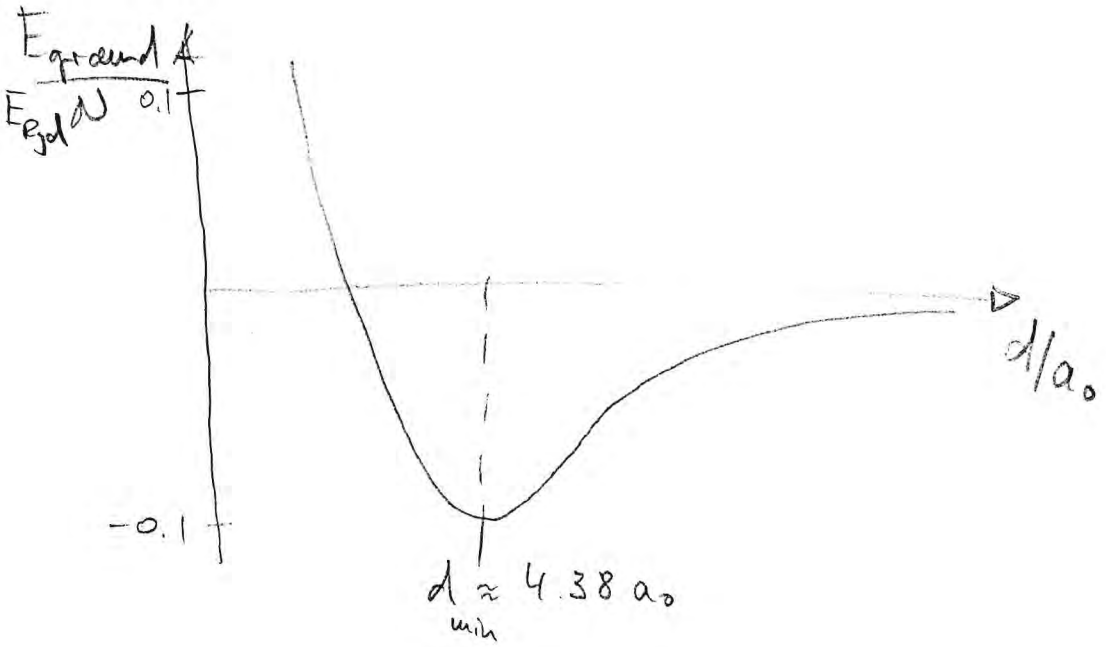
↳ $$\frac{E_{ground}}{N} = \frac{3}{5}E_F - \frac{3}{4\pi}\frac{e^2}{4\pi\varepsilon_0 4}p_F$$

$$= E_{Ryd}\left[\frac{3}{5}\left(\frac{9\pi}{4}\right)^{2/3}\left(\frac{a_0}{d}\right)^2 - \frac{3}{2\pi}\left(\frac{9\pi}{4}\right)^{1/3}\left(\frac{a_0}{d}\right)\right]$$

E_{Ryd}: Rydberg energy; a_0: Bohr's radius

with $d = \sqrt[3]{\frac{9\pi}{4}}\frac{4}{p_F}$.

- The quantity d is a length, which characterises the typical distance between electrons.
- It depends on p_F and therefore on N and V.
- Interestingly, the function $\frac{E_{ground}}{N}$ has a minimum and one would therefore expect that an electron gas adjusts p_F (N and V) such that the ground state energy is minimised.

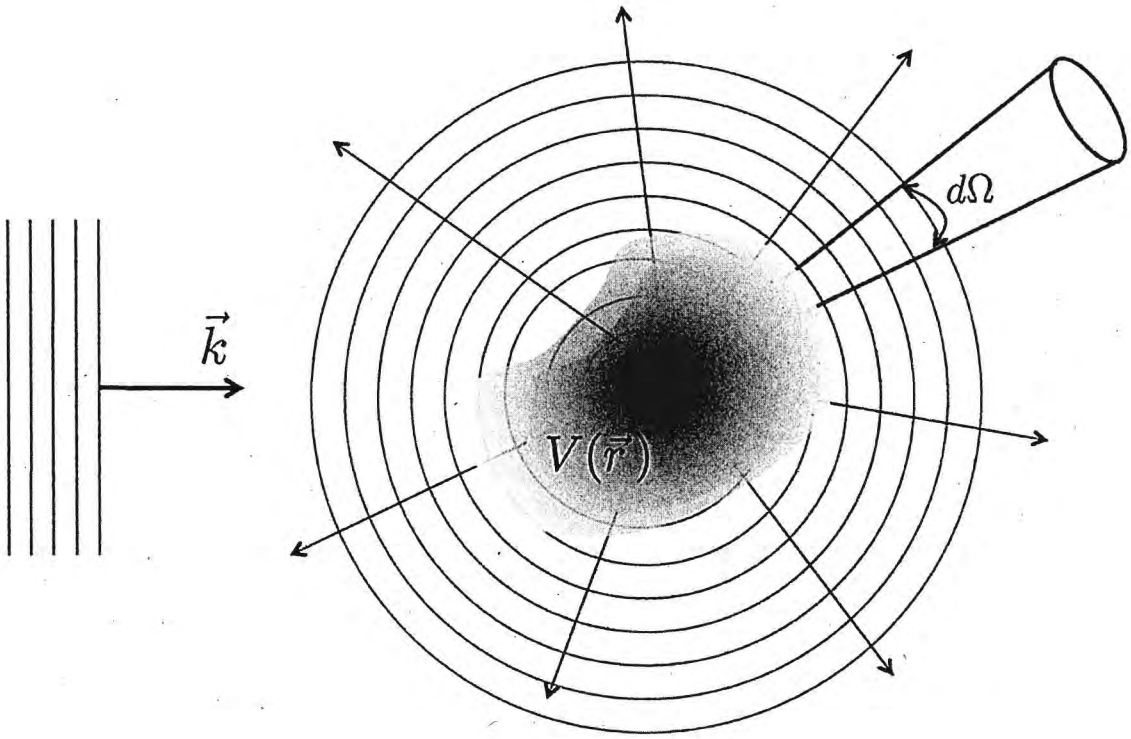


- The minimisation yields $d_{min} \approx 4.38\, a_0$ and $\left.\frac{E_{ground}}{N}\right|_{d=d_{min}} \approx -0.1\ E_{Ryd}$.
- This is comparable with actual metals, such as sodium ($d = 3.96\, a_0$) and potassium ($d = 4.86\, a_0$).

IV Scattering theory

- Scattering is of fundamental importance for making the structure of Nature "visible".
- The application of scattering has led to the discovery of the atomic nucleus (Rutherford) and scattering protons off one another is the standard tool at LHC (CERN) for searching for „new physics".
- In the following we consider the scattering of a particle of mass μ off a localised potential (i.e. the potential has a finite range, dropping off with distance $|\vec{r}|$ from the particle, sufficiently fast).
  The particle is approaching the potential from a far-away initial position.
  The particle is modelled by a wave packet, and the question we are going to ask is: What is the probability (cross section) for the particle to be scattered into the solid angle element $d\Omega$.

Scattering problem



Skript zur Vorlesung
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IV.1 Scattering states and scattering cross section

- The scattering potential $U(\vec{r})$ shall be localised in the vicinity of $\vec{r} = 0$.
- The wave packet of the particle at initial time t_0 is given by

$$\psi(\vec{r}, t_0) = \int \frac{d^3\vec{k}}{(2\pi)^3}\, a(\vec{k})\, e^{i\vec{k}\cdot\vec{r}}$$

↑ Fourier transform of the wave packet

- The maximum of the Fourier components $a(\vec{k})$ shall be at $\vec{k}_0$, such that the particle is moving with group velocity $\frac{\hbar\vec{k}_0}{\mu}$ towards the scattering centre (potential).
- Each plane wave

$$u_k^{(0)}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}$$

is a solution of the free, stationary Schrödinger equation

$$-\frac{\hbar^2}{2\mu}\Delta u_k^{(0)}(\vec{r}) = E_k\, u_k^{(0)}(\vec{r})$$

with the kinetic energy

$$E_k = \frac{\hbar^2\vec{k}^2}{2\mu} = \frac{\hbar^2 k^2}{2\mu} > 0 .$$

- Our goal is to solve the time dependent Schrödinger equation

$$i\hbar \frac{\partial \psi(\vec{r},t)}{\partial t} = \left[-\frac{\hbar^2}{2\mu}\Delta + V(\vec{r}) \right] \psi(\vec{r},t)$$

($V(\vec{r})$: scattering potential)

with the boundary condition $\psi(\vec{r},t_0)$.

- In order to do this we consider at first the associated stationary problem,

$$\left[-\frac{\hbar^2}{2\mu}\Delta + V(\vec{r}) \right] u_k(\vec{r}) = E_k u_k(\vec{r}).$$

- Here, the energy shell be fixed to $E_k = \frac{\hbar^2 k^2}{2\mu}$, which means that we are considering <u>elastic scattering</u> ($E_k > 0$, no bound states).

- The solutions $u_k(\vec{r})$ are referred to as <u>elastic scattering states.</u>

- We expect that the initial wave function can be expanded in these scattering states:

$$\psi(\vec{r},t_0) = \int \frac{d^3\vec{k}}{(2\pi)^3} A(\vec{k})\, u_k(\vec{r})$$

($A(\vec{k})$: expansion coefficients)

- The time evolved state, that we want to find is thus

$$\psi(\vec{r},t) = \int \frac{d^3\vec{k}}{(2\pi)^3} A(\vec{k})\, u_k(\vec{r})\, e^{-\frac{i}{\hbar}E_k(t-t_0)}.$$

- The „only" things left to find are the wave functions $u_k(\vec{r})$ and the expansion coefficients $A(\vec{k})$.

- In order to find the $u_k(\vec{r})$ we rewrite the stationary Schrödinger equation as

$$(\Delta + k^2)\, u_k(\vec{r}) = \underbrace{\frac{2\mu}{\hbar^2} V(\vec{r})\, u_k(\vec{r})}_{f(\vec{r})} .$$

- This looks like an inhomogeneous differential equation (it is not, because the inhomogeneity depends on $u_k(\vec{r})$).

- The next step towards solving the problem is to introduce the Green's function $G_k(\vec{r})$ which obeys

$$(\Delta + k^2)\, G_k(\vec{r}) = \delta^{(3)}(\vec{r}) .$$

- Once this is found, the stationary Schrödinger equation is „solved" by the function

$$\int d^3\vec{r}'\, G_k(\vec{r} - \vec{r}')\, f(\vec{r}')$$

↳ $(\Delta + k^2) \int d^3\vec{r}'\, G_k(\vec{r}' - \vec{r})\, f(\vec{r}') = \int d^3\vec{r}'\, \delta(\vec{r} - \vec{r}')\, f(\vec{r}') = f(\vec{r})$

- The Green's function is found most easily in Fourier space:

$$G_k(\vec{r}) = \int \frac{d^3\vec{q}}{(2\pi)^3}\, \tilde{G}_k(\vec{q})\, e^{i\vec{q}\cdot\vec{r}} .$$

- Then $(\Delta + k^2)\, G_k(\vec{r}) = \int \frac{d^3\vec{q}}{(2\pi)^3}\, \tilde{G}_k(\vec{q})\,(\Delta + k^2)\, e^{i\vec{q}\cdot\vec{r}}$

$$= \int \frac{d^3\vec{q}}{(2\pi)^3}\, \tilde{G}_k(\vec{q})\,(-\vec{q}^2 + k^2)\, e^{i\vec{q}\cdot\vec{r}}$$

$$\overset{!}{=} \delta^3(\vec{r}) = \int \frac{d^3\vec{q}}{(2\pi)^3}\, 1\, e^{i\vec{q}\cdot\vec{r}}$$

$$\hookrightarrow \tilde{G}_k(\vec{q}) = \frac{1}{k^2 - \vec{q}^2} = \frac{1}{k^2 - q^2}$$

- In order to obtain the Green's function in real space, we need to calculate the Fourier transform

$$G_k(\vec{r}) = \int \frac{d^3\vec{q}}{(2\pi)^3}\, \frac{e^{i\vec{q}\cdot\vec{r}}}{k^2 - q^2} = \frac{1}{(2\pi)^3} \int_0^\infty dq\, q^2 \int_{-1}^{1} d\cos\theta \int_0^{2\pi} d\varphi\, \frac{e^{iqr\cos\theta}}{k^2 - q^2}$$

$$= \frac{2\pi}{(2\pi)^3} \int_0^\infty dq\, \frac{q^2}{k^2 - q^2} \int_{-1}^{1} d\cos\theta\, e^{iqr\cos\theta}$$

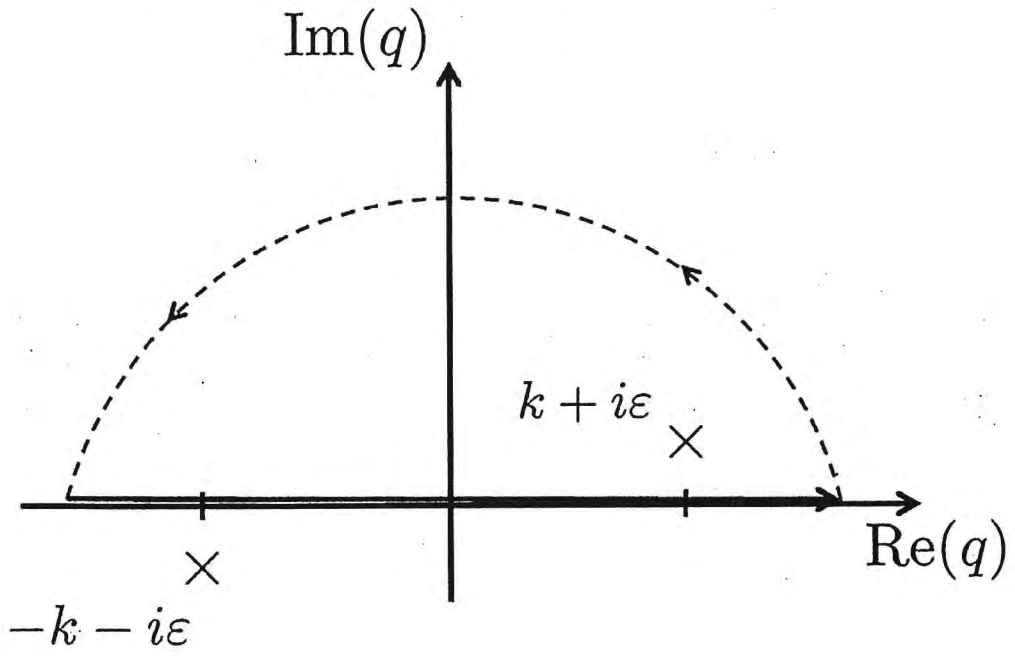
$$= \frac{1}{(2\pi)^2} \int_0^\infty dq\, \frac{q^2}{k^2 - q^2}\, \frac{1}{iqr}\, (e^{iqr} - e^{-iqr})$$

$$= -\frac{1}{(2\pi)^2}\, \frac{1}{2ir} \int_{-\infty}^{\infty} dq\, \left(\frac{1}{q-k} + \frac{1}{q+k}\right) e^{iqr}.$$

- The integrals diverge, which means that the inverse of $\Delta^2 + k^2$ is not uniquely defined.
- To nevertheless solve the integration, we introduce an imaginary part to the k

↳ $k \to k + i\varepsilon \quad (\varepsilon > 0)$.

Integration contour for Green's function



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- We can now use the residue theorem to calculate the integral.

- Closing the contour in the upper half-plane, since here the factor e^{iqr} is suppressing the contribution of the contour, yields

$$\int_{-\infty}^{\infty} dq \left(\frac{1}{q-(k+i\varepsilon)} + \frac{1}{q+(k+i\varepsilon)} \right) e^{iqr} = 2\pi i \, \mathrm{Res} \left(\frac{e^{iqr}}{q-(k+i\varepsilon)} \right)_{q=k+i\varepsilon}$$

$$= 2\pi i \, e^{i(k+i\varepsilon)r} \xrightarrow{\varepsilon \to 0} 2\pi i \, e^{ikr}$$

- Hence, the Green's function is

$$G_k(\vec{r}) = -\frac{1}{4\pi} \frac{e^{ikr}}{r},$$

which represents a spherical wave.

- With its help the solution of the stationary Schrödinger equation is given by

$$u_k(\vec{r}) = -\frac{1}{4\pi} \int d^3\vec{r}' \, \frac{e^{ik|\vec{r}-\vec{r}'|}}{|\vec{r}-\vec{r}'|} f(\vec{r}').$$

- This expression describes a wave that is outgoing with respect to the scattering centre.

- This is seen by the fact that the combination with the phase factor of the free time evolution yields $e^{i(k|\vec{r}-\vec{r}'| - \frac{E_k}{\hbar}(t-t_0))}$, and therefore shells of constant phase have a radius that grows with time.

- For that reason one refers also to the calculated Green's function as <u>retarded Green's function</u>.

- Note, that choosing $\varepsilon < 0$ would have led to the advanced Green's function, $G_k(\vec{r}) = -\frac{1}{4\pi} \frac{e^{-ikr}}{|\vec{r}-\vec{r}'|}$, which we do not consider for physical reasons.

- The solution for $u_k(\vec{r})$ that we constructed is still incomplete, which is seen by the fact that it vanishes for $V(\vec{r}) = f(\vec{r}) = 0$, and therefore it is not compatible with the imposed boundary condition

- This is cured by adding the incoming plane wave $u_k^{(0)}(\vec{r})$, which solves the equation $(\Delta + k^2) u_k^{(0)}(\vec{r}) = 0$ and thus does not change the fact that $u_k(\vec{r})$ must solve the inhomogeneous problem.

- With this modification we obtain the so-called <u>Lippmann - Schwinger equation:</u>

$$u_k(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} - \frac{1}{4\pi} \int d^3r' \, \frac{e^{ik|\vec{r}-\vec{r}'|}}{|\vec{r}-\vec{r}'|} \frac{2\mu}{\hbar} V(\vec{r}') \, u_k(\vec{r}').$$

- This equation can be solved by iteration.
- It shows that the solution of the scattering problem is composed of an incoming plane wave and a scattered wave, which is a superposition of spherical waves.

- In the next step we simplify the integrand, assuming that the detector, with which we probe the scattering solution is far away from the scattering centre.
- We use

$$|\vec{r}-\vec{r}'| = \sqrt{r^2 - 2\vec{r}\cdot\vec{r}' + r'^2} = r\sqrt{1 - \frac{2\vec{r}\cdot\vec{r}'}{r^2} + \left(\frac{r'}{r}\right)^2}$$

$$\approx r\left(1 - \frac{\vec{r}\cdot\vec{r}'}{r^2}\right) = r - \vec{e}_r\cdot\vec{r}'$$

$\vec{e}_r$: radial unit vector

and make the approximations

$$\frac{1}{|\vec{r}-\vec{r}'|} \approx \frac{1}{r} \quad \text{and} \quad e^{ik|\vec{r}-\vec{r}'|} \approx e^{ikr}\, e^{-ik\vec{e}_r\cdot\vec{r}'}$$

first order is sufficient

- This yields

$$u_k(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} - \frac{1}{4\pi}\frac{e^{ikr}}{r}\int d^3r'\, e^{-ik\vec{e}_r\cdot\vec{r}'}\frac{2\mu}{\hbar}V(\vec{r}')\,u_k(\vec{r}')$$

$$\equiv e^{i\vec{k}\cdot\vec{r}} + f_k(\theta,\varphi)\frac{e^{ikr}}{r}.$$

- In the last step we have introduced the so-called <u>scattering amplitude</u>

$$f_k(\theta,\varphi) = -\frac{1}{4\pi}\int d^3r'\, e^{-ik\,\vec{e}_r\cdot\vec{r}'}\,\frac{2\mu}{\hbar^2}\,V(\vec{r}')\,u_k(\vec{r}').$$

- Note, that $f_k(\theta,\varphi)$ only depends on $\vec{e}_r$ and has the unit 'length'.

- The position vector $\vec{r}$ is the vector at which one observes the scattering solution with the detector.

- Moreover, the vector $\vec{k}' = k\,\vec{e}_r$ points into the direction of $\vec{r}$.

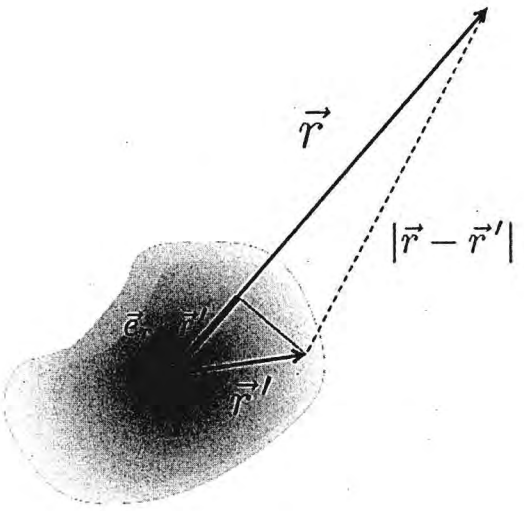
- This means that $f_k(\theta,\varphi)$ is the probability amplitude for the scattering of the incoming wave into the direction $\vec{k}'$.

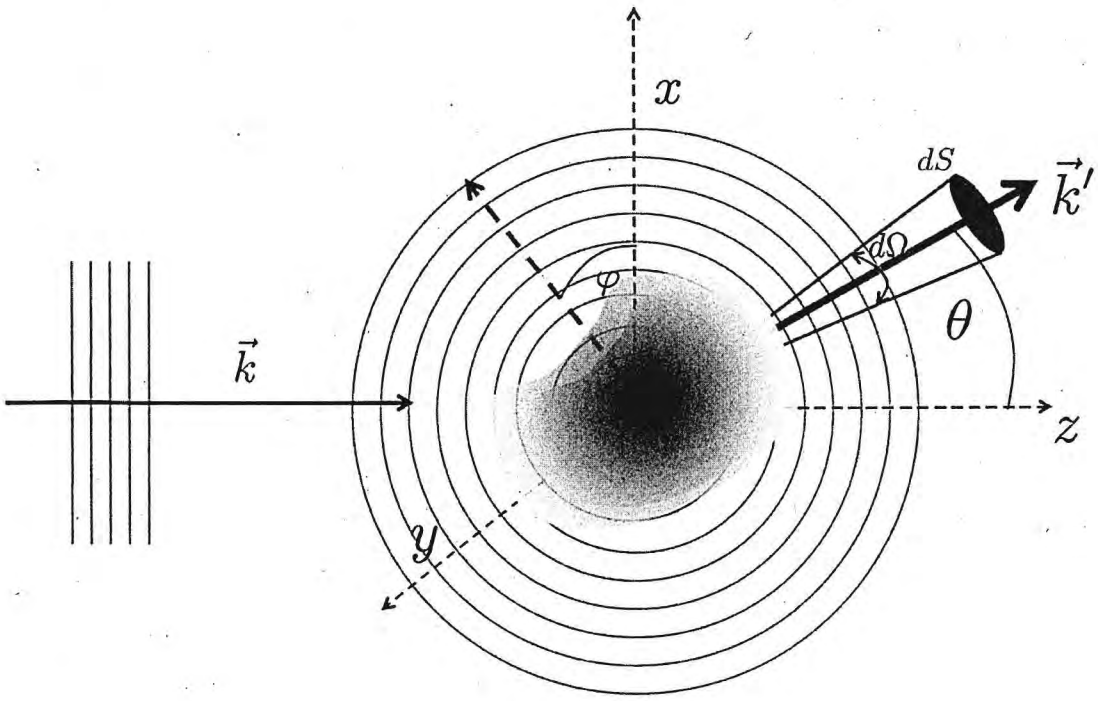
- It is also the probability amplitude for detecting the scattered particle at position $\vec{r}$.

- The fact that $|\vec{k}'| = |\vec{k}|$ is once again a manifestation of elastic scattering.

- It is common to align the z-axis of the coordinate system with the wave vector of the incoming wave: $\vec{k} = k\,\vec{e}_z$.

Geometry of the scattering problem





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- We now imagine a scenario in which a particle beam (the particles do not interact with one another) scatters off the scattering centre.

- We can then define the scattering cross section $d\sigma$ for the scattering of a particle into the solid angle element $d\Omega$:

$$d\sigma = \frac{\#\text{ particles per time scattered into } d\Omega}{\text{incoming particle flux}}$$

$$= \frac{|\vec{j}^{\,out}(\vec{k}')|\, dS}{|\vec{j}^{\,in}(\vec{k})|} = \frac{|\vec{j}^{\,out}(\vec{k}')|\, \overbrace{r^2 d\Omega}^{dS\ldots\text{surface element}}}{|\vec{j}^{\,in}(\vec{k})|}$$

- The incoming and outgoing currents we calculate using $u_k^{(0)} = e^{i\vec{k}\cdot\vec{r}}$ and

$$\vec{j}^{\,in} = \frac{\hbar}{2\mu i}\left[(u_k^{(0)})^* \nabla u_k^{(0)} - (\nabla u_k^{(0)})^* u_k^{(0)}\right] = \frac{\hbar\vec{k}}{\mu}$$

as well as $u_k^{out} = f(\theta,\varphi)\,\frac{e^{ikr}}{r}$ and

$$\vec{j}^{\,out} = \frac{\hbar}{2\mu i}\left[(u_k^{out})^* \nabla u_k^{out} - (\nabla u_k^{out})^* u_k^{out}\right]$$

$$= \frac{\hbar k\,\vec{e}_r}{\mu}\,\frac{|f_k(\theta,\varphi)|^2}{r^2} = \frac{\hbar\vec{k}'}{\mu}\,\frac{|f_k(\theta,\varphi)|^2}{r^2}$$

- Hence, we find

$$d\sigma = \underbrace{\frac{|\vec{k}'|}{|\vec{k}|}}_{=1} \frac{|f_k(\theta,\varphi)|^2}{r^2} r^2 d\Omega ,$$

and for the <u>differential scattering cross section</u> we obtain

$$\frac{d\sigma}{d\Omega} = |f_k(\theta,\varphi)|^2 ,$$

which has the unit $(\text{length})^2$.

- The total scattering cross section then follows from integration:

$$\sigma = \int d\Omega \frac{d\sigma}{d\Omega} = \int d\Omega |f_k(\theta,\varphi)|^2 .$$

- From these expressions it becomes apparent that all relevant information on the scattering problem is contained in the scattering amplitude $f_k(\theta,\varphi)$.

- We will now start to solve the Lippmann-Schwinger equation, in order to calculate an (approximate) expression for the scattering amplitude.

- To this end we insert the Lippmann-Schwinger equation into itself:

$$u_k(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} + \int d^3\vec{r}'\, G_k(\vec{r}-\vec{r}')\,\frac{2\mu}{\hbar^2}\,V(\vec{r}')\,u_k(\vec{r}')$$

$$= e^{i\vec{k}\cdot\vec{r}} + \int d^3\vec{r}'\, G_k(\vec{r}-\vec{r}')\,\frac{2\mu}{\hbar^2}\,V(\vec{r}')\,e^{i\vec{k}\cdot\vec{r}'}$$

$$+ \int d^3\vec{r}'\, G_k(\vec{r}-\vec{r}')\,\frac{2\mu}{\hbar}\,V(\vec{r}') \int d^3\vec{r}''\, G_k(\vec{r}'-\vec{r}'')\,\frac{2\mu}{\hbar}\,V(\vec{r}'')\,u_k(\vec{r}'')$$

- Such iteration step can of course be repeated indefinitely, yielding the <u>Born series</u>

$$u_k(\vec{r}) = \sum_{n=0}^{\infty} u_k^{(n)}(\vec{r})$$

with $u_k^{(0)}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}$

and $u_k^{(n)}(\vec{r}) = \int d^3\vec{r}'\, G(\vec{r}-\vec{r}')\,\frac{2\mu}{\hbar^2}\,V(\vec{r}')\,u_k^{(n-1)}(\vec{r}')$.

- Truncation of this series at the n-th term corresponds to the Born approximation of order n.
- In the following we consider the Born approximation of order 1 (first Born approximation) more closely:

$$u_k(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} - \frac{1}{4\pi}\int d^3\vec{r}'\,\frac{e^{ik|\vec{r}-\vec{r}'|}}{|\vec{r}-\vec{r}'|}\,\frac{2\mu}{\hbar^2}\,V(\vec{r}')\,e^{i\vec{k}\cdot\vec{r}'}$$

$|\vec{r}|$ is much larger than interaction range $\approx$

$$\approx e^{i\vec{k}\cdot\vec{r}} - \frac{1}{4\pi}\,\frac{e^{ikr}}{r}\int d^3\vec{r}'\, e^{-ik\vec{e}_r\cdot\vec{r}'+i\vec{k}\cdot\vec{r}'}\,V(\vec{r}')$$

(- This first Born approximation usually works well, when the interaction is weak or the energy of the incident particle is high.)

- Comparing this result with the general scattering solution (p 144) yields the scattering amplitude:

$$f_k^B(\theta,\varphi) = -\frac{1}{4\pi}\frac{2\mu}{\hbar^2}\int d^3\vec{r}\,' e^{-ik\vec{e}_r\cdot\vec{r}\,' + i\vec{k}\cdot\vec{r}\,'} V(\vec{r}\,')$$

- Writing $-ik\vec{e}_r\cdot\vec{r}\,' + i\vec{k}\cdot\vec{r}\,' = i(\vec{k}-\vec{k}')\cdot\vec{r}\,' = i\vec{q}\cdot\vec{r}\,'$ yields the more compact expression ($\vec{q}$: momentum transfer)

$$f_k^B(\theta,\varphi) = -\frac{\mu}{2\pi\hbar^2}\int d^3\vec{r}\,' e^{i\vec{q}\cdot\vec{r}\,'} V(\vec{r}\,').$$

- Hence the scattering amplitude within the first Born approximation is the Fourier transform of the interaction potential with respect to the momentum transfer, and the differential cross-section becomes

$$\frac{d\sigma^B}{d\Omega} = |f_k^B(\theta,\varphi)|^2 = \frac{\mu^2}{4\pi^2\hbar^4}\left|\int d^3\vec{r}\, e^{i\vec{q}\cdot\vec{r}} V(\vec{r})\right|^2.$$

- An important case is the scattering off a spherically symmetric potential, $V(\vec{r}) = V(r)$, for which one obtains

$$f_k^B(\theta) = -\frac{\mu}{2\pi\hbar^2}\int_0^\infty dr\, r^2 V(r)\int_0^{2\pi} d\varphi \int_{-1}^{1} d\cos\theta\, e^{iqr\cos\theta}$$

$$= -\frac{\mu}{\hbar^2}\int_0^\infty dr\, r^2 V(r)\,\frac{1}{iqr}\left(e^{iqr} - e^{-iqr}\right)$$

$$= -\frac{2\mu}{q\hbar^2}\int_0^\infty dr\, r\, V(r)\,\sin(qr)$$

- The relation between the scattering angle θ and the momentum transfer q is established via the relation

$$q = |\vec{k} - \vec{k}'| = \sqrt{k^2 + k'^2 - 2\vec{k}\cdot\vec{k}'} = k\sqrt{2(1-\cos\theta)} = 2k\sin\left(\frac{\theta}{2}\right).$$

- Example: Yukawa-potential, which serves as a model potential for describing nuclear forces.

$$V(r) = -g^2 \frac{e^{-ar}}{r}$$

(a: inverse interaction range; g^2: interaction strength)

↳ $$f_k^B(\theta) = \frac{2\mu g^2}{q\hbar^2} \int_0^\infty dr\, e^{-ar} \sin(qr)$$

$$= \frac{2\mu g^2}{\hbar^2} \frac{1}{a^2+q^2} = \frac{2\mu g^2}{\hbar^2} \frac{1}{a^2 + 4k^2 \sin^2\frac{\theta}{2}}$$

↳ $$\frac{d\sigma^B}{d\Omega} = \frac{4\mu^2 g^4}{\hbar^4} \frac{1}{\left[a^2 + 4k^2 \sin^2\frac{\theta}{2}\right]^2}.$$

- Let us now return to the description of the <u>scattering process in terms of wave packets</u>, with which we started the discussions of this chapter.

- We write the wave packet of the incoming particle as

$$\psi^{in}(\vec{r}, t_0) = \int \frac{d^3\vec{k}}{(2\pi)^3}\, a(\vec{k})\, e^{i\vec{k}\cdot\vec{r}}.$$

- The coefficients $a(\vec{k})$ shall be peaked around a certain $\vec{k}_0$, e.g.

$$a(\vec{k}) \sim e^{-g(\vec{k}-\vec{k}_0)^2}$$

(g: constant controls width of wave packet, $g > 0$)

for a Gaussian wave packet.

- We also assume that the wave packet is well localised in real space, i.e., the constant g cannot be too large.

- We now look for an expansion of the wave packet in terms of the scattering solutions $u_k(\vec{r})$:

$$\psi^{in}(\vec{r}, t_0) = \int \frac{d^3\vec{k}}{(2\pi)^3}\, A(\vec{k})\, u_k(\vec{r}).$$

- Rewriting the Lippmann-Schwinger equation yields

$$e^{i\vec{k}\cdot\vec{r}} = u_k(\vec{r}) + \frac{1}{4\pi}\int d^3r'\, \frac{e^{ik|\vec{r}-\vec{r}'|}}{|\vec{r}-\vec{r}'|}\, \frac{2\mu}{\hbar^2}\, V(\vec{r}')\, u_k(\vec{r}').$$

- Inserting this expression into the expansion of $\psi^{in}(\vec{r}, t_0)$ in terms of plane waves leads to

$$\psi^{in}(\vec{r}, t_0) = \int \frac{d^3\vec{k}}{(2\pi)^3} a(\vec{k}) \left[\underbrace{u_k(\vec{r})}_{\text{has the form we are looking for}} + \underbrace{\frac{1}{4\pi} \int d^3\vec{r}' \frac{e^{ik|\vec{r}-\vec{r}'|}}{|\vec{r}-\vec{r}'|} \frac{2\mu}{\hbar^2} V(\vec{r}') u_k(\vec{r}')}_{\text{term can be neglected, when integrating over } \vec{k}} \right]$$

- We consider only the $\vec{k}$-dependent parts of the second term:

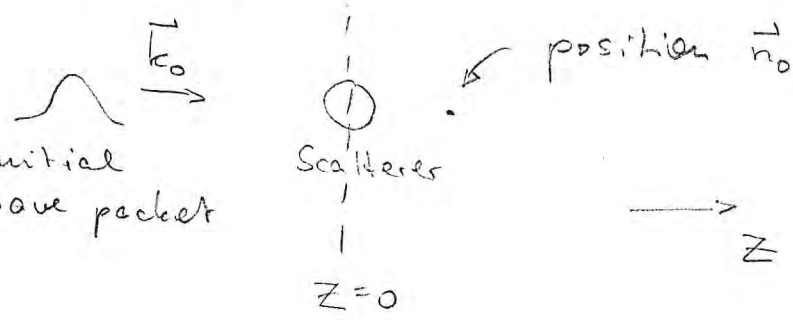
$$\int \frac{d^3\vec{k}}{(2\pi)^3} \underbrace{a(\vec{k})}_{\text{peaked at } \vec{k}=\vec{k}_0} e^{ik|\vec{r}-\vec{r}'|} \underbrace{u_k(\vec{r}')}_{\approx u_{k_0}(\vec{r}')} \approx u_{k_0}(\vec{r}) \underbrace{\int \frac{d^3\vec{k}}{(2\pi)^3} a(\vec{k}) e^{i\vec{k}\cdot\vec{n}_0|\vec{r}-\vec{r}'|}}_{\psi^{in}(\vec{n}_0|\vec{r}-\vec{r}'|, t_0)}$$

($\vec{n}_0 = \frac{\vec{k}_0}{|\vec{k}_0|}$)

$$\approx e^{i\left(\vec{k}\cdot\frac{\vec{k}_0}{|\vec{k}_0|}\right)|\vec{r}-\vec{r}'|}$$

projection of $\vec{k}$ onto direction of $\vec{k}_0$

- The second term thus depends on the value of the initial wave packet at position $\vec{n}_0|\vec{r}-\vec{r}'|$, which is a point to the right of the scattering centre:



- However, here the wave packet is zero and thus the second term vanishes

- Therefore,

$$\psi^{in}(\vec{r}, t_0) = \int \frac{d^3\vec{k}}{(2\pi)^3} a(\vec{k})\, u_k(\vec{r})$$

↳ $A(\vec{k}) = a(\vec{k})$, i.e. the expansion coefficients are the same as for plane waves.

- The time evolved state then becomes

$$\psi^{out}(\vec{r}, t) = \int \frac{d^3\vec{k}}{(2\pi)^3} a(\vec{k})\, u_k(\vec{r})\, e^{-i\frac{E_k}{\hbar}(t-t_0)} \qquad E_k = \frac{\hbar^2 k^2}{2\mu}$$

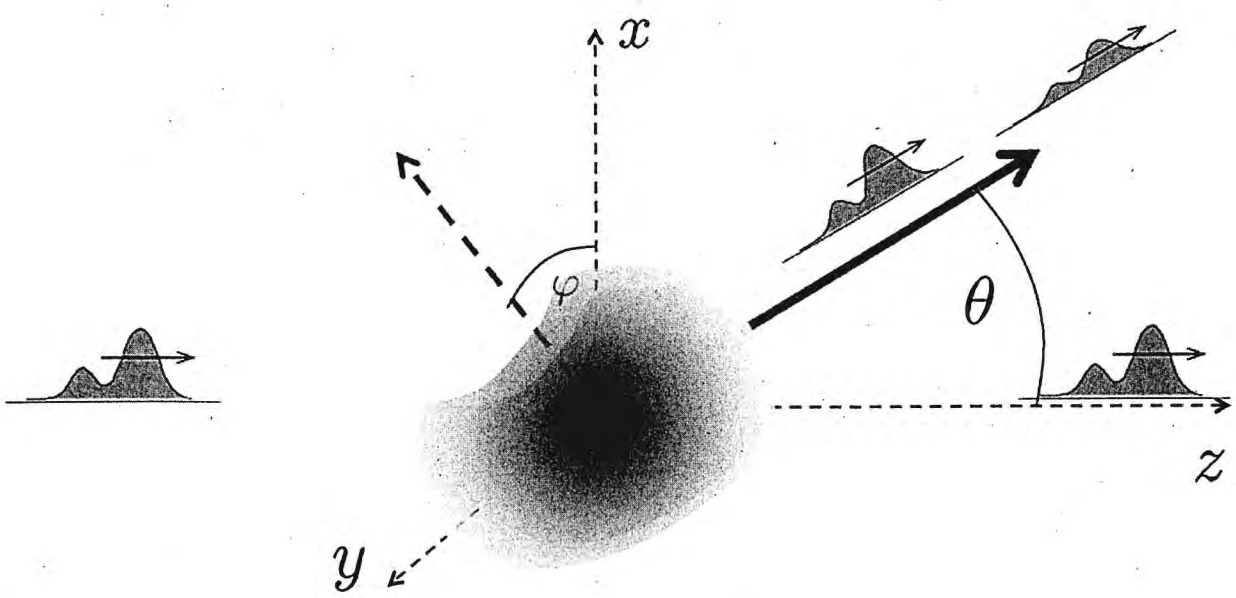
$$= \int \frac{d^3\vec{k}}{(2\pi)^3} a(\vec{k}) e^{i\vec{k}\cdot\vec{r}} e^{-i\frac{E_k}{\hbar}(t-t_0)} + \int \frac{d^3\vec{k}}{(2\pi)^3} a(\vec{k})\, f_k(\theta,\varphi) \frac{e^{ikr}}{r} e^{-i\frac{E_k}{\hbar}(t-t_0)}$$

$$\approx \int \frac{d^3\vec{k}}{(2\pi)^3} a(\vec{k}) e^{i\left(\vec{k}\cdot\vec{r} - \frac{E_k}{\hbar}(t-t_0)\right)} + \frac{f_{k_0}(\theta,\varphi)}{r} \int \frac{d^3\vec{k}}{(2\pi)^3} a(\vec{k})\, e^{i\left[(\vec{n}_0\cdot\vec{k})r - \frac{E_k}{\hbar}(t-t_0)\right]}$$

↑ exploiting that $a(\vec{k})$ is peaked around $\vec{k}_0$

$$= \psi^{in}(\vec{r}, t) + \frac{f_{k_0}(\theta,\varphi)}{r}\, \underbrace{\psi^{in}(\vec{n}_0 r, t)}_{\text{incoming wave packet evaluated at new position}}$$

Scattering process with wave packets



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- To interpret this expression it is instructive to study a Gaussian initial wave packet

incoming wave packet: $\psi^{in}(\vec{r},t) \sim e^{-g'(\vec{r}-\vec{v}_g t)^2}$

$\vec{v}_g$ ↑ group velocity

$\vec{v}_g = \frac{\hbar \vec{k}_0}{\mu} = \frac{\hbar k_0}{\mu}\vec{n}_0$

Wave packet moves into the direction of $\vec{v}_g$

$\vec{n}_0 \parallel \vec{v}_g$

scattered wave packet: $\psi^{in}(r\vec{n}_0,t) \sim e^{-g'(\vec{n}_0 r - \vec{v}_g t)^2} = e^{-g'(r-|\vec{v}_g|t)^2}$

Wave packet is moving radially outwards, i.e. the wave front has the shape of a sphere

- In the following we study the probability current more closely, which will lead us to the so-called <u>optical theorem</u>

- The probability density $\rho = |\psi|^2$ and the current $\vec{j} = \frac{\hbar}{2\mu i}(\psi^* \nabla\psi - \psi \nabla\psi^*)$ of a state ψ are connected by the continuity equation

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \vec{j} = 0 .$$

- In a stationary situation one has $\frac{\partial \rho}{\partial t} = 0$ and therefore $\nabla \cdot \vec{j} = 0$.

- Integration of this expression over the volume of a large sphere, which encloses the scattering centre yields

$$0 = \int_{\text{sphere}} d^3\vec{r}\, \nabla \cdot \vec{j} = \int_{\text{surface}} d\vec{A} \cdot \vec{j} = r^2 \int_{\text{surface}} d\Omega\, \underbrace{\vec{j} \cdot \vec{e}_r}_{\text{radial current component}} = r^2 \int_{\text{surface}} d\Omega\, \underbrace{j_r}_{\text{radial current component}}$$

- We calculate in the following the radial component, j_r, of the current for the scattering state

$$u_k(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} + f_k(\theta,\varphi)\frac{e^{i\vec{k}\cdot\vec{r}}}{r}$$

$$j_r = \frac{\hbar}{2\mu i}\left(u_k^* \frac{\partial}{\partial r} u_k - u_k \frac{\partial}{\partial r} u_k^*\right) = \frac{\hbar}{\mu}\,\mathrm{Im}\left[u_k^* \frac{\partial}{\partial r} u_k\right]$$

$\vec{k} = k\vec{e}_z$

$$= \frac{\hbar}{\mu}\,\mathrm{Im}\left[\left(e^{-ikr\cos\theta} + f_k^* \frac{e^{-ikr}}{r}\right)\frac{\partial}{\partial r}\left(e^{ikr\cos\theta} + f_k \frac{e^{ikr}}{r}\right)\right]$$

neglected

large r

$$\approx \frac{\hbar}{\mu}\,\mathrm{Im}\left[\left(e^{-ikr\cos\theta} + f_k^* \frac{e^{-ikr}}{r}\right)\left(ik\cos\theta\, e^{ikr\cos\theta} + ik f_k \frac{e^{ikr}}{r} + \mathcal{O}\left(\frac{1}{r^2}\right)\right)\right]$$

$$= \underbrace{\frac{\hbar}{\mu} k\cos\theta}_{j_r^{\text{in}}} + \underbrace{\frac{\hbar k}{\mu}\frac{|f_k|^2}{r^2}}_{j_r^{\text{out}}} + \underbrace{\frac{\hbar k}{\mu r}\,\mathrm{Im}\left[i\left(f_k^* e^{-ikr(1-\cos\theta)}\cos\theta + f_k e^{ikr(1-\cos\theta)}\right)\right]}_{j_r^{\text{int}}}$$

j_r^{in}: incoming; j_r^{out}: outgoing; j_r^{int}: interference current

- Integrating the current of the incoming wave yields $\int d\Omega\, j_r^{in} = 0$.

- For the current of the outgoing spherical wave one obtains the integral.

$$\int d\Omega\, j_r^{out} = \frac{\hbar k}{\mu} \int d\Omega\, \frac{|f_k(\theta,\varphi)|^2}{r^2} = \frac{\hbar k}{\mu r^2}\,\sigma$$

↑ total scattering cross section

- The current of the interfering incoming and outgoing wave yields the integral

$$\int d\Omega\, j_r^{int} = \int_0^{2\pi} d\varphi \int_{-1}^{1} d\cos\theta\, \frac{\hbar k}{\mu r}\, \mathrm{Im}\left[i \left(f_k^*(\theta,\varphi)\, e^{-ikr(1-\cos\theta)} \cos\theta + f_k(\theta,\varphi)\, e^{ikr(1-\cos\theta)} \right) \right]$$

- For large r-values the exponential functions are rapidly oscillating, except when $\theta = 0$ ($\cos\theta = 1$).
- Choosing r sufficiently large, the only contribution to the integral comes therefore from angles around $\theta = 0$.
- Moreover, at $\theta = 0$ there is no dependence of the scattering amplitude f_k on φ ($f_k(0,\varphi) \to f_k(0)$)
- We can therefore approximate:

$$\int d\Omega\, j_r^{int} \approx \frac{2\pi\hbar k}{\mu r} \int_{-1}^{1} d\cos\theta\, \mathrm{Im}\left[i \left(f_k^*(0)\, e^{-ikr(1-\cos\theta)} + f_k(0)\, e^{ikr(1-\cos\theta)} \right) \right]$$

$$\approx \frac{2\pi\hbar k}{\mu r}\, \mathrm{Im}\left[\frac{f_k^*(0)}{ikr} - \frac{f_k(0)}{ikr} \right] = -\frac{4\pi\hbar}{\mu r^2}\, \mathrm{Im}\left[f_k(0) \right].$$

- Note, that after the integration step we omitted terms of the form $e^{\pm 2ikr}$ which also rapidly oscillate for large r.
- Putting everything together yields

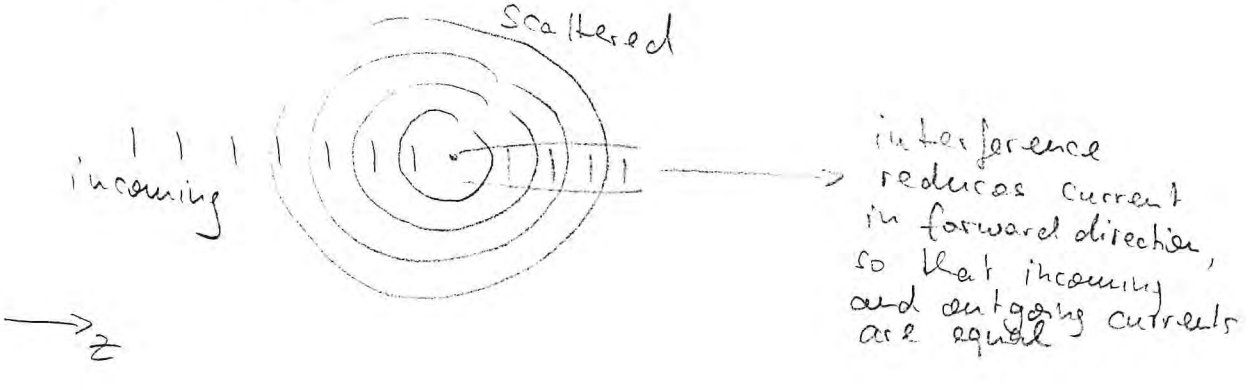
$$0 = \underbrace{0}_{j_r^{in}} + \underbrace{\frac{t_k k}{\mu r^2}\sigma}_{j_r^{out}} - \underbrace{\frac{4\pi t_k}{\mu r^2}\,\mathrm{Im}\left[f_k(0)\right]}_{j_r^{int}}$$

$$\hookrightarrow \quad \sigma = \frac{4\pi}{k}\,\mathrm{Im}\left[f_k(\theta=0)\right].$$

- This relationship between the total scattering cross section and the imaginary part of the scattering amplitude in forward direction is the so-called <u>optical theorem</u>.
- It has the following interpretation / consequences:

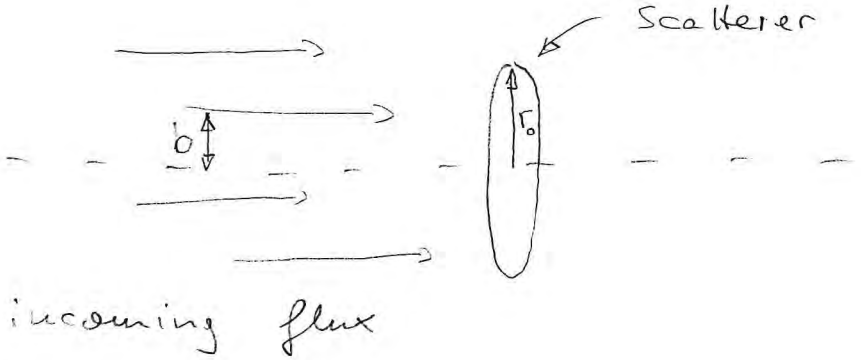
i) The current of the outgoing (scattered) wave and the current related to the interference of the scattered and incoming wave cancel.

ii) The scattering amplitude cannot be real everywhere.



IV.2 Partial wave decomposition

- We will now focus more closely on the case of a spherically symmetric scatterer
- In this case we have conservation of angular momentum.
- It is then convenient to decompose the incident wave packet into its angular momentum components, since each one of these scatters independently.
- This idea is called <u>partial wave decomposition</u>, and to see that this can be indeed advantageous, lets consider this „classical" setting



- The angular momentum of an incoming particle is $L = b \cdot p$ ← momentum
  ↑ distance from the axis (impact parameter)
- According to the sketch only particles with $b \leq r_0$ are hitting the disk of the scatterer.
- Quantum mechanically $L \approx \hbar l$.
  ↑ angular momentum quantum number

- Thus, for particles that undergo scattering off the scattering disk we find

$$L \approx \hbar l \leq r_0 p = r_0 \hbar k$$

$$\hookrightarrow \quad l \leq k r_0 .$$

- One would thus expect that the quantity kr_0 determines how many partial waves (angular momentum components) have to be considered in the scattering process.

- To study this problem rigorously, we consider the Hamiltonian for a particle in a spherically symmetric potential $V(r)$:

$$H = -\frac{\hbar^2}{2\mu}\Delta + U(r) = -\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2} r + \frac{\vec{L}^2}{2\mu r^2} + U(r),$$

with $\vec{L}^2$ being the squared angular momentum operator.

- The operators H, $\vec{L}^2$ and L_z commute and the eigenfunctions of H can be constructed such that they are eigenfunctions to all of these operators.

- They have the form

$$\psi(r, \theta, \varphi) = R(r)\, Y_{lm}(\theta, \varphi)$$

(Y_{lm}: spherical harmonics; $R(r)$: radial eigenfunctions)

- The radial eigenfunctions obey the differential equation (radial equation):

$$\left[-\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{d^2}{dr^2}r + \frac{\hbar\,\ell(\ell+1)}{2\mu r^2} + U(r)\right]R(r) = E_k\,R(r).$$

- Since we are dealing with elastic scattering, the energy $E_k = \frac{\hbar k^2}{2\mu} > 0$ is fixed.
- Since, k and ℓ appear in the above equation, we write $R(r) = R_{k,\ell}(r)$.
- Let us first consider the case $U(r)=0$, which describes the situation long before and after the scattering event:

$$\hookrightarrow \left[\frac{1}{r}\frac{d^2}{dr^2}r + k^2 - \frac{\ell(\ell+1)}{r^2}\right]R_{k,\ell}(r) = 0 \quad , \quad \text{or}$$

$$r^2 R''_{k,\ell} + 2r R'_{k,\ell} + (k^2r^2 - \ell(\ell+1))R_{k,\ell} = 0.$$

- This equation is known as <u>Bessel differential equation</u>.
- Its solutions are given by the <u>spherical Bessel functions</u>.

$$j_\ell(x) = (-x)^\ell\left(\frac{1}{x}\frac{d}{dx}\right)^\ell\frac{\sin x}{x}$$

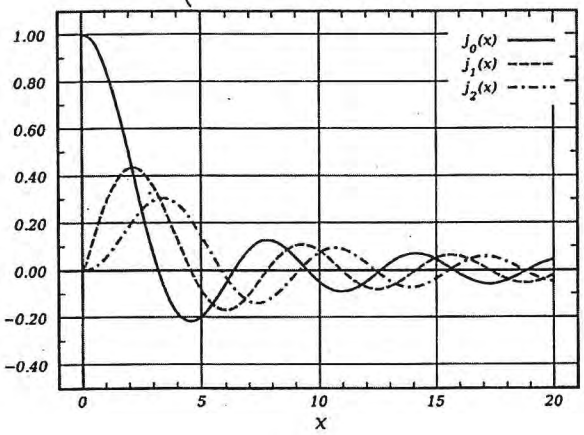
$$y_\ell(x) = -(-x)^\ell\left(\frac{1}{x}\frac{d}{dx}\right)^\ell\frac{\cos x}{x}$$

} often also referred to as spherical Neumann functions

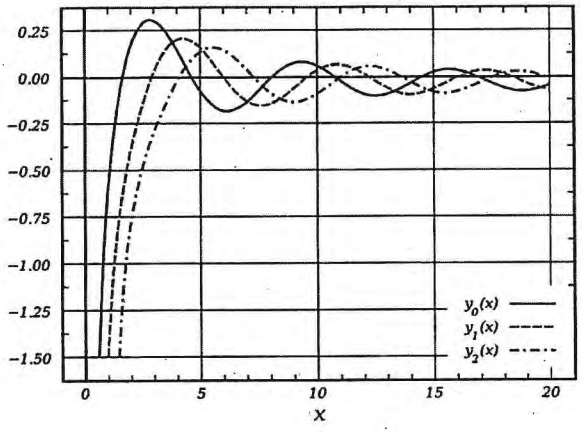
- The general solution of the free ($U(r)=0$) stationary Schrödinger equation is a superposition of terms proportional to $j_\ell(kr)\,Y_{\ell m}(\theta,\varphi)$ and $y_\ell(kr)\,Y_{\ell m}(\theta,\varphi)$, for all ℓ and m.

Spherical Bessel and Neumann functions

first kind



second kind



$$j_0(x) = \frac{\sin x}{x}, \qquad j_1(x) = \frac{\sin x}{x^2} - \frac{\cos x}{x}, \qquad j_2(x) = \left(\frac{3}{x^2} - 1\right)\frac{\sin x}{x} - \frac{3\cos x}{x^2}$$

$$y_0(x) = -\frac{\cos x}{x}, \qquad y_1(x) = -\frac{\cos x}{x^2} - \frac{\sin x}{x}, \qquad y_2(x) = \left(-\frac{3}{x^2} + 1\right)\frac{\cos x}{x} - \frac{3\sin x}{x^2}$$

Wikipedia

- The functions $y_\ell(x)$ diverge at $x=0$.
- For problems for which one is interested in the behaviour of the wave functions at the origin, the $y_\ell(x)$ must be discarded, since they cannot be normalised.
- The asymptotic behaviours of the Bessel functions for large $x = kr$ is given by

$$j_\ell(x) \overset{x\gg 1}{\approx} \frac{\sin\left(x - \ell\frac{\pi}{2}\right)}{x}$$

$$y_\ell(x) \overset{x\gg 1}{\approx} -\frac{\cos\left(x - \ell\frac{\pi}{2}\right)}{x}$$

- To see how this result is obtained, consider (Rayleigh's formula) $j_\ell(x) = (-x)^\ell \left(\frac{1}{x}\frac{d}{dx}\right)^\ell \frac{\sin x}{x} = (-x)^\ell \left(\frac{1}{x}\frac{d}{dx}\right)^{\ell-1}\left(\frac{\cos x}{x^2} - \frac{\sin x}{x^3}\right)$.
- The leading term (with the lowest power of $\frac{1}{x}$) is alternating between sin and cos, and with every differentiation its power increases by one.

↳ $$j_\ell(x) \overset{x\gg 1}{\approx} (-x)^\ell \frac{1}{x^{\ell+1}} \frac{d^\ell}{dx^\ell} \sin x = (-1)^\ell \frac{1}{x} (-1)^\ell \sin\left(x - \ell\frac{\pi}{2}\right)$$

$$= \frac{\sin\left(x - \ell\frac{\pi}{2}\right)}{x}$$

- A similar reasoning yields the asymptotic behaviour of the y_ℓ.

- For a spherically symmetric scattering potential the scattering amplitude does not depend on the azimuthal angle φ.
- (Note, that the $\vec{k}$ vector of the incoming particle is aligned with the z-axis.)
- This symmetry restricts the set of spherical harmonics which are required to describe the scattering process to

$$Y_{l0}(\theta, \varphi) = \sqrt{\frac{2l+1}{4\pi}}\, P_l(\cos\theta)$$

($P_l(\cos\theta)$: no φ-dependence; 0: azimuthal quantum number is set to zero)

- Here, the P_l are the Legendre polynomials

$$P_l(\cos\theta) = \frac{(-1)^l}{2^l l!} \frac{d^l}{d\cos\theta^l} \sin^{2l}\theta .$$

- One can show that a plane wave can actually be expanded in terms of Bessel functions and Legendre polynomials:

$$\underbrace{e^{ikz}}_{\text{incoming } \vec{k} \text{ is aligned with } z\text{-axis}} = e^{ikr\cos\theta} = \sum_{l=0}^{\infty} i^l (2l+1)\, j_l(kr)\, P_l(\cos\theta)$$

- We are now considering the asymptotic form of this expression, far away from the scattering centre:

$$e^{ikz} \approx \sum_{\ell=0}^{\infty} i^\ell (2\ell+1) \overbrace{\frac{\sin\left(kr - \ell\frac{\pi}{2}\right)}{kr}}^{\text{asymptotics of } j_\ell} P_\ell(\cos\theta)$$

$$= \sum_{\ell=0}^{\infty} \frac{2\ell+1}{2ikr} \left[i^\ell e^{ikr} e^{-i\ell\frac{\pi}{2}} - i^\ell e^{-ikr} e^{i\ell\frac{\pi}{2}} \right] P_\ell(\cos\theta)$$

$$= \sum_{\ell=0}^{\infty} \frac{2\ell+1}{2ikr} \left[e^{ikr} - (-1)^\ell e^{-ikr} \right] P_\ell(\cos\theta)$$

- In the next step we take a look at the general scattering solution

$$u_k(\vec{r}) = e^{ikz} + f_k(\theta) \frac{e^{ikr}}{r}$$

- Also the scattering amplitude $f_k(\theta)$ can be expanded in terms of Legendre polynomials

$$f_k(\theta) = \sum_{\ell=0}^{\infty} (2\ell+1) f_{k,\ell} P_\ell(\cos\theta)$$

it turns out to be convenient to have this factor

expansion coefficients, also called <u>partial wave amplitudes</u>.

- Plugging this expression and the expansion of the plane wave into the scattering solution yields

$$u_k(\vec{r}) = \sum_{\ell=0}^{\infty} \frac{2\ell+1}{2ikr}\left[e^{ikr} - (-1)^\ell e^{-ikr}\right] P_\ell(\cos\theta) + \frac{e^{ikr}}{r}\sum_{\ell=0}^{\infty}(2\ell+1) f_{k,\ell} P_\ell(\cos\theta)$$

$$= \sum_{\ell=0}^{\infty}(2\ell+1) P_\ell(\cos\theta)\, \frac{e^{ikr}\overbrace{(1+2ik f_{k,\ell})}^{S_\ell} - (-1)^\ell e^{-ikr}}{2ikr}$$

$$= \sum_{\ell=0}^{\infty}(2\ell+1) P_\ell(\cos\theta)\, \frac{e^{ikr} S_\ell - (-1)^\ell e^{-ikr}}{2ikr}$$

- The factor S_ℓ is called <u>scattering matrix element</u>.
- The reason for this name is that in a general (non-spherically symmetric) scattering potential the so-called scattering matrix (or S-matrix) $S_{\ell\ell'}$ appears, which depends on the incoming and outgoing angular momenta ℓ, ℓ'.
- As previously discussed, the radial component j_r of the probability current has to vanish when integrating over a spherical shell with radius r around the scatterer.
- This has to hold for all ℓ-components

$$u_{k\ell}(r) = (2\ell+1) P_\ell(\cos\theta)\, \frac{e^{ikr} S_\ell - (-1)^\ell e^{-ikr}}{2ikr}$$

separately.

- For the radial current one finds

$$\int d\Omega\, j_{r,\ell} = \int d\Omega \frac{\hbar}{2\mu i}\left(u^*_{k,\ell}\frac{du_{k,\ell}}{dr} - \frac{du^*_{k,\ell}}{dr}u_{k,\ell}\right)$$

$$= \frac{(2\ell+1)\hbar}{\mu k r^2}\left(|S_\ell|^2 - 1\right) \overset{!}{=} 0 .$$

- Hence, we find that $|S_\ell| = 1$ and thus the scattering matrix element can be parametrised as

$$S_\ell = e^{2i\delta_\ell} \quad , \qquad \left(-\tfrac{\pi}{2} \le \delta_\ell \le \tfrac{\pi}{2}\right)$$

where δ_ℓ is the <u>scattering phase</u>, which depends on ℓ as well as on the momentum k.

- Using δ_ℓ, we can write the scattering state as

$$u_k(\vec{r}) = \sum_{\ell=0}^{\infty} (2\ell+1)\, P_\ell(\cos\Theta)\, \frac{e^{i(kr+2\delta_\ell)} - (-1)^\ell e^{-ikr}}{2ikr} ,$$

which is the so-called <u>partial wave decomposition</u>.

- From this expression it becomes apparent, that the outgoing spherical wave, e^{ikr}, acquires a phase shift of $2\delta_\ell$, in which the information about the scatterer is contained.

- We can now write (p. 164)

$$f_{k,\ell} = \frac{S_\ell - 1}{2ik} = \frac{e^{2i\delta_\ell} - 1}{2ik} = \frac{e^{i\delta_\ell}}{k} \sin\delta_\ell ,$$

and inserting this into the expansion of the scattering amplitude yields

$$f_k(\theta) = \frac{1}{k} \sum_{\ell=0}^{\infty} (2\ell+1)\, \underbrace{e^{i\delta_\ell} \sin\delta_\ell}\, P_\ell(\cos\theta) .$$

scattering phases determine scattering amplitude

- The differential scattering cross section is defined as

$$\frac{d\sigma}{d\Omega} = |f_k(\theta)|^2 ,$$

and it will in general have a complicated shape due to the interference of many partial wave components.

- For the total cross section one obtains

$$\sigma = \int d\Omega |f_k(\theta)|^2 = \frac{1}{k^2} \int d\Omega \sum_{\ell,\ell'=0}^{\infty} (2\ell+1)(2\ell'+1)\, e^{i\delta_\ell - i\delta_{\ell'}} \sin\delta_\ell \sin\delta_{\ell'} P_\ell(\cos\theta) P_{\ell'}(\cos\theta) ,$$

which simplifies drastically after using the orthogonality relation of the Legendre polynomials

$$\int d\Omega\, P_\ell(\cos\theta) P_{\ell'}(\cos\theta) = 2\pi \delta_{\ell\ell'} \frac{2}{2\ell+1} .$$

$$\hookrightarrow \quad \sigma = \sum_{\ell=0}^{\infty} \frac{4\pi}{k^2}(2\ell+1)\sin^2\delta_\ell = \sum_{\ell=0}^{\infty} \sigma_\ell$$

knowledge of the scattering phases solves the scattering problem

each partial wave yields a separate contribution to the scattering cross section

- The partial wave decomposition also leads to the optical theorem:

$$\mathrm{Im}\left[f_k(\theta)\right] = \sum_{\ell=0}^{\infty}(2\ell+1)\frac{\sin^2\delta_\ell}{k} P_\ell(\cos\theta),$$

which for $\theta = 0$ becomes (using $P_\ell(1) = 1$)

$$\mathrm{Im}\left[f_k(0)\right] = \sum_{\ell=0}^{\infty}(2\ell+1)\frac{\sin^2\delta_\ell}{k} = \frac{k}{4\pi}\sigma$$

$$\hookrightarrow \quad \sigma = \frac{4\pi}{k}\mathrm{Im}\left[f_k(\theta=0)\right]$$

- The total cross section associated with a certain ℓ-value is proportional to $\sin^2\delta_\ell$ and thus becomes maximal for $\delta_\ell = \pm\frac{\pi}{2}$.

- Such maximum is associated with a <u>scattering resonance</u> as we will show in the following for $\delta_\ell = +\frac{\pi}{2} \equiv \delta_\ell^R$ resonance.

- To investigate the behaviour of the partial wave amplitude near such resonance, we write it as

$$f_{k,\ell} = \frac{\sin\delta_\ell}{k(\cos\delta_\ell - i\sin\delta_\ell)} = \frac{\tan\delta_\ell}{k(1-i\tan\delta_\ell)}$$

- For $\delta_\ell = \delta_\ell^R = \frac{\pi}{2}$ one finds

$$f_{k,\ell}^R \equiv f_{k,\ell}(\delta_\ell^R) = -\frac{1}{ik},$$

since $\lim_{\delta_\ell \to \delta_\ell^R} \tan\delta_\ell = \infty$.

- In the vicinity of δ_ℓ^R we can expand the tangent into a Laurent series:

$$\tan\delta_\ell = -\frac{1}{\delta_\ell - \delta_\ell^R} + \mathcal{O}(1)$$

- Next, we consider that the scattering phase δ_ℓ is a function of energy, i.e. $\delta_\ell(E)$, and we denote as E_ℓ^R the energy at which $\delta_\ell(E_\ell^R) = \delta_\ell^R = \frac{\pi}{2}$.

- Expanding around E_ℓ^R yields:

$$\delta_\ell(E) = \underbrace{\delta_\ell^R}_{\delta_\ell(E_\ell^R)} + \delta_\ell'(E_\ell^R)(E - E_\ell^R) + \mathcal{O}((E-E_\ell^R)^2).$$

- Defining $\Gamma_\ell = -\frac{2}{\delta_\ell'(E_\ell^R)}$ we can write

$$\tan\delta_\ell \approx \frac{\frac{\Gamma_\ell}{2}}{E - E_\ell^R}$$

and the partial wave amplitude becomes

$$f_{k,\ell} = \frac{1}{k} \frac{\frac{1}{2}\Gamma_\ell}{E - E_\ell^R - i\frac{1}{2}\Gamma_\ell}$$

- The contribution of this partial wave to the total scattering cross section thus becomes

$$\sigma_\ell = \frac{4\pi}{k^2}(2\ell+1)\sin^2\delta_\ell \overset{\text{p. 166}}{=} \frac{4\pi}{k^2}(2\ell+1)\,k^2\,|f_{k,\ell}|^2$$

($\sin^2\delta_\ell = |\sin\delta_\ell|^2$)

$$= \frac{4\pi}{k^2}(2\ell+1)\frac{\frac{1}{4}\Gamma_\ell^2}{(E-E_\ell^R)^2 + \frac{1}{4}\Gamma_\ell^2}.$$

- This is a Breit-Wigner profile with width Γ_ℓ.
- Such resonances are related to the emergence of bound states, such as the (temporary) creation of new particles, during a scattering process.

- We conclude this chapter by discussion some properties of the scattering phases for spherically symmetric potentials that vanish outside a given radius r_0:

$$V(r) = \begin{cases} W(r) & , r \le r_0 \\ 0 & , r > r_0 . \end{cases}$$

- For $r > r_0$ the solution of the radial Schrödinger equation is

$$R_{k,\ell}(r) = a\, j_\ell(kr) + b\, y_\ell(kr).$$

(a, b: complex coefficients)

- It is now convenient to introduce the so-called spherical Hankel functions

$$h_\ell(kr) = j_\ell(kr) + i\, y_\ell(kr)$$
$$h_\ell^*(kr) = j_\ell(kr) - i\, y_\ell(kr),$$

which allows us to write

$$R_{k,\ell}(kr) = A\, h_\ell(kr) + B\, h_\ell^*(kr)$$

- For large r we find the asymptotic behaviour

$$h_\ell(kr) \overset{kr\gg 1}{\approx} \frac{\sin(kr - \ell\frac{\pi}{2})}{kr} - i\,\frac{\cos(kr-\ell\frac{\pi}{2})}{kr} = \frac{e^{i(kr-\ell\frac{\pi}{2})}}{ikr}$$

and thus

$$R_{k\ell}(r) \overset{kr\gg 1}{\approx} \frac{A e^{i(kr-\frac{\pi}{2}\ell)} - B e^{-i(kr-\frac{\pi}{2}\ell)}}{ikr} = B e^{-i\ell\frac{\pi}{2}}\,\frac{\frac{A}{B} e^{ikr} - (-1)^\ell e^{-ikr}}{ikr}.$$

- In order for this to be a scattering solution we must require $\frac{A}{B} = e^{2i\delta_\ell}$ and thus we find for $r > r_0$ the radial solution

$$R_{k,\ell}(r) = B\left(h_\ell(kr)\, e^{2i\delta_\ell} + h_\ell^*(kr)\right).$$

- This solution has to be matched with the the solution $\bar{R}_{k\ell}$ inside the region $r \leq r_0$.
- At the matching point r_0 both logarithmic derivatives have to be equal:

$$\alpha_\ell \equiv \frac{\bar{R}'_{k,\ell}(r_0)}{\bar{R}_{k,\ell}(r_0)} = k\,\frac{h'_\ell(kr_0)\, e^{2i\delta_\ell} + h^{*\prime}_\ell(kr_0)}{h_\ell(kr_0)\, e^{2i\delta_\ell} + h^*_\ell(kr_0)}$$

↑ value of the logarithmic derivative of $\bar{R}_{k\ell}$ at $r = r_0$.

- Solving for the scattering phases δ_ℓ yields

$$\tan\delta_\ell = \frac{k\, j'_\ell(kr_0) - \alpha_\ell\, j_\ell(kr_0)}{k\, y'_\ell(kr_0) - \alpha_\ell\, y_\ell(kr_0)}.$$

- For a hard sphere potential, i.e. $W(r) \to \infty$, one has $\bar{R}_{k,\ell}(r_0) \to 0$ and thus $\alpha_\ell \to \infty$.
- This yields for the scattering phase shifts

$$\tan\delta_\ell = \frac{j_\ell(kr_0)}{y_\ell(kr_0)}$$

which for $\ell = 0$ leads to $\delta_0 = -kr_0$.

- This is a manifestation of a more general result, namely that the scattering phases become negative for a repulsive potential.

- Let us now return to the general expression for $\tan\delta_\ell$ and investigate it for small energies, i.e. $k \to 0$.

- Using the expansion

$$j_\ell(x) \overset{x\ll 1}{\approx} \frac{x^\ell}{(2\ell+1)!!}, \quad y_\ell(x) \overset{x\ll 1}{\approx} -\frac{x^{-\ell-1}}{(2\ell-1)!!}$$

yields

$$\tan\delta_\ell \sim k^{2\ell+1}$$

for $k \to 0$.

- The scattering phase thus decreases with k, and the larger ℓ the faster this decrease becomes.

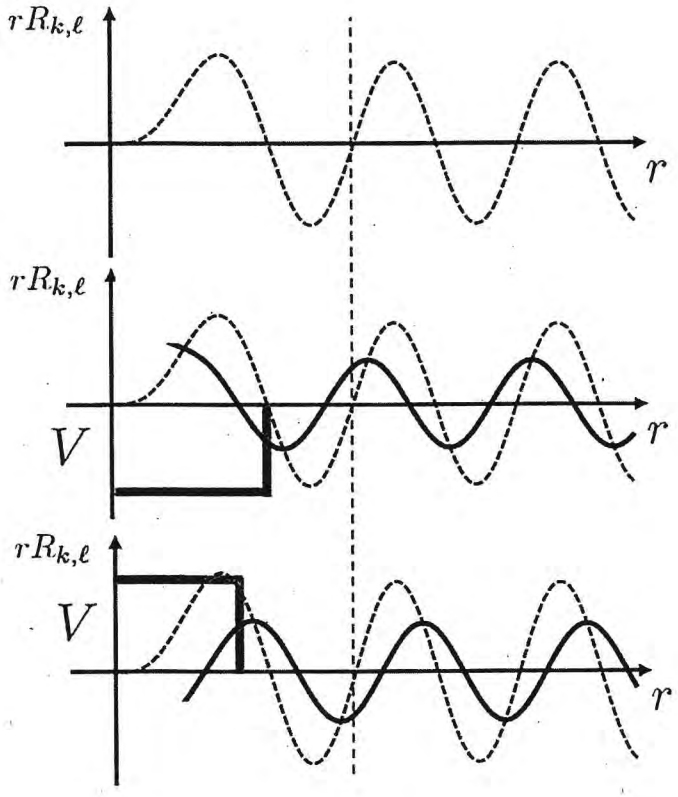
- For sufficiently small energy the dominant contribution to the scattering thus comes from the $\ell=0$ component, which is referred to <u>s-wave scattering</u>.

- In this case

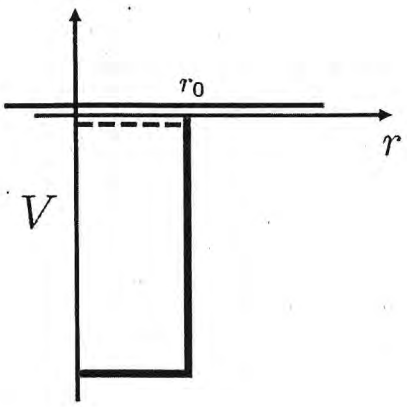
$$\frac{d\sigma}{d\Omega} = |f_k(\theta)|^2 = \frac{\sin^2\delta_0}{k^2} \sim \text{const.}$$

$\delta_0 \sim k$ ← does not depend on energy

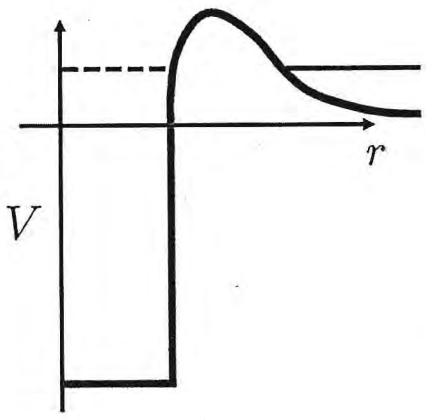
Qualitative behaviour of the scattering phase



Bound state



Metastable state



Skript zur Vorlesung
Fortgeschrittene Quantentheorie
(Quantenmechanik II)
Prof. Werner Vogelsang
Universität Tübingen
Wintersemester 2020/21

- One can now define the so-called s-wave <u>scattering length</u> a_s:

$$\lim_{k \to 0} k \cdot \cot(\delta_0) = -\frac{1}{a_s}.$$

- With this definition, the scattering cross section becomes at low energies

$$\sigma = 4\pi a_s^2,$$

and for a hard sphere of radius r_0 one finds $a_s = r_0$.

- The s-wave scattering length is positive for repulsive potentials.

- For attractive potentials it is negative, but can also become positive, when the potential permits bound states.

- To see this lets consider an attractive potential, $W(r) = -W$, which has a bound state close to $E = 0$. (bound state energy: $E_B < 0$)

- The associated radial wave function is

$$R_{k,\ell=0}(r) \sim \frac{e^{-kr}}{kr},$$

with $\frac{\hbar^2 k^2}{2\mu} = E_B$.

- This solution corresponds to a scattered wave function with $k = ik$.

- Evaluating the scattering phase shift by matching the logarithmic derivatives at r_0, yields

$$\tan \delta_0 = -i ,$$

and hence

$$e^{2i\delta_0} = - \frac{(\tan \delta_0 - i)^2}{1 + \tan^2 \delta_0} = \infty$$

↳ the scattering matrix element has a pole in the complex plane, which corresponds to the bound state.

- Generally, one finds for the behaviour of the total scattering cross section in the vicinity of a bound state

$$\sigma = \frac{2\pi t^2}{\mu} \frac{1}{E - E_B} .$$

V Relativistic quantum mechanics

- The free Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \psi(\vec{x},t) = -\frac{\hbar^2}{2m} \Delta \psi(\vec{x},t)$$

is based on the non-relativistic energy-momentum relation

$$E = \frac{\vec{p}^2}{2m}.$$

- This is a limiting case of the relativistic relation

$$E = \sqrt{\vec{p}^2 c^2 + m^2 c^4}$$

- In this chapter we will discuss how one can construct a „relativistic Schrödinger equation", based on this more general expression.
- This connection between quantum theory and special relativity leads to new phenomena and also requires new interpretations, e.g. it shows that a many-particle theory is ultimately necessary in order to arrive at a consistent picture.

VI The Klein-Gordon equation

- The free Schrödinger equation is obtained by making the substitutions

$$E \to i\hbar \frac{\partial}{\partial t}$$

$$\vec{p} \to \frac{\hbar}{i} \nabla$$

in the energy momentum relation $E = \frac{p^2}{2m}$.

- Attempting this for the relativistic expression leads to

$$i\hbar \frac{\partial}{\partial t} \psi(\vec{x},t) = \sqrt{-\hbar^2 c^2 \Delta + m^2 c^4}\, \psi(\vec{x},t)$$

$$= mc^2 \sqrt{1 - \lambda\!\!\!^{-2} \Delta}\, \psi(\vec{x},t).$$

$\lambda\!\!\!^{-}$ (reduced) Compton wavelength

$$\lambda\!\!\!^{-} = \frac{\hbar}{mc}$$

- This equation has problems, which stem from the square root, whose series expansion leads to arbitrarily high powers of Δ.
- This neither leads to a simple theory, nor does it lead to a local and causal description of the physics (wave packets propagate arbitrarily fast).

- On the other hand, this approach cannot be entirely incorrect, since the expansion

$$\sqrt{\vec{p}^2c^2 + m^2c^4} \approx mc^2 + \frac{\vec{p}^2}{2m} - \frac{\vec{p}^4}{8m^3c^2}$$

leads to relativistic corrections of the bound state energies of hydrogen (fine structure), which are measurable and rather accurately described.

- To get rid of the square root we revise our starting point and use the squared energy-momentum relationship:

$$E^2 = \vec{p}^2c^2 + m^2c^4$$

- This results in the Klein-Gordon equation, which has the form of a wave equation:

$$\left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \Delta + \left(\frac{mc}{\hbar}\right)^2\right)\psi(\vec{x},t) = 0$$

- Note, that this equation is of second order in the time variable, i.e. we would need two initial values, $\psi(\vec{x},0)$ and $\frac{\partial}{\partial t}\psi(\vec{x},t)\big|_{t=0}$, to propagate it.
- Just like the Schrödinger equation, the Klein-Gordon equation has plane wave solutions:

$$\psi(\vec{x},t) = e^{\frac{i}{\hbar}(\vec{p}\cdot\vec{x} - E(p)t)}$$

- In order to see which energies $E(p)$ are permissible, we insert the plane waves into the equation.

$$\hookrightarrow -\frac{E^2}{c^2\hbar^2} + \frac{\vec{p}^2}{\hbar^2} + \left(\frac{mc}{\hbar}\right)^2 = 0$$

$$\hookrightarrow E^2 = \vec{p}^2c^2 + m^2c^4 \rightarrow E = \pm\sqrt{\vec{p}^2c^2 + m^2c^4}$$

- For given $\vec{p}$ the plane waves thus have the form $\psi(\vec{x},t) = e^{\frac{i}{\hbar}(\vec{p}\cdot\vec{x} \pm \sqrt{\vec{p}^2c^2 + m^2c^4}\,t)}$.

- Apparently, there are solutions with negative energy and moreover the energy is not bounded from below.

- This is problematic, because it is unclear what the lowest energy state (ground state) of a free particle would be.

- Moreover, the appearance of negative energies affects the interpretation of the wave function as probability amplitude, as we show now:

- For the Schrödinger equation there exists the continuity equation

$$\frac{\partial \rho}{\partial t} + \nabla\cdot\vec{j} = 0, \text{ with } \rho = \psi^*\psi \text{ and } \vec{j} = \frac{\hbar}{2mi}\left(\psi^*\nabla\psi - (\nabla\psi^*)\psi\right).$$

- Here ρ is the positive definite probability density and $\vec{j}$ the probability current.
- To obtain the continuity equation that corresponds to the Klein-Gordon equation we calculate

$$\psi^* \underbrace{\left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \Delta + \left(\frac{mc}{\hbar}\right)^2\right)\psi}_{\text{Klein-Gordon equation}} - \psi \underbrace{\left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \Delta + \left(\frac{mc}{\hbar}\right)^2\right)\psi^*}_{\text{conjugate Klein-Gordon equation}} = 0$$

$$\hookrightarrow \frac{1}{c^2}\left(\psi^* \frac{\partial^2}{\partial t^2}\psi - \psi \frac{\partial^2}{\partial t^2}\psi^*\right) - \left(\psi^* \Delta \psi - \psi \Delta \psi^*\right) = 0$$

$$\hookrightarrow \frac{1}{c^2}\frac{\partial}{\partial t}\left(\psi^* \frac{\partial}{\partial t}\psi - \psi \frac{\partial}{\partial t}\psi^*\right) - \nabla \cdot \left(\psi^* \nabla \psi - \psi \nabla \psi^*\right) = 0$$

- Here we can identify the following quantities:

$$\vec{j} = \frac{\hbar}{2mi}\left(\psi^* \nabla \psi - \psi \nabla \psi^*\right) \quad \ldots \text{probability current}$$

$$\rho = \frac{i\hbar}{2mc^2}\left(\psi^* \frac{\partial \psi}{\partial t} - \psi \frac{\partial \psi^*}{\partial t}\right) \quad \ldots \text{"probability density"}$$

- Unlike for the Schrödinger equation, ρ contains a derivative of the wave function.
- Inserting plane waves, one finds that ρ is not positive definite:

$$\hookrightarrow \rho = \frac{i\hbar}{2mc^2}\left(-\frac{iE}{\hbar} - \frac{iE}{\hbar}\right) = \frac{E}{mc^2} \quad \text{E can be negative!}$$

- Interestingly, Schrödinger first attempted to formulate a relativistic wave equation, but then discarded his attempts due to such problem.
- The issue is „fixed" within the framework of quantum field theory.
- Here one can use the Klein-Gordon equation for describing spin-less particles and their anti particles.
- The negative „probability density" is cured by multiplying it with the particle charge and interpreting it as charge density.

V. 2 The Dirac equation

- Dirac was wondering whether there exists an equation which is relativistically covariant (like the wave equation), but which contains only a first derivative with respect to time.
- The latter would fix the issue with the negative probability density.
- He constructed indeed an equation of the form

$$i\hbar \frac{\partial}{\partial t} \psi = H_{\text{Dirac}} \psi ,$$

with a Hamiltonian H_{Dirac} that is linear in the momentum operator $\vec{p}$.

- This equation also obeys the relativistic energy-momentum relation, reduces to the Schrödinger equation in the nonrelativistic limit and also introduces the spin in a natural way.
- To arrive at his equation, Dirac made the ansatz

$$H_{Dirac} = c\vec{\alpha}\cdot\vec{p} + \beta mc^2 = \frac{\hbar c}{i}\vec{\alpha}\cdot\nabla + \beta mc^2,$$

with α^j and β being constant „coefficients".

- The Dirac equation then reads

$$i\hbar\frac{\partial\psi(\vec{x},t)}{\partial t} = \left(\frac{\hbar c}{i}\vec{\alpha}\cdot\nabla + \beta mc^2\right)\psi(\vec{x},t) = \left(\frac{\hbar c}{i}\alpha^j\partial_j + \beta mc^2\right)\psi(\vec{x},t),$$

where we used the short hand notation $\partial_j = \frac{\partial}{\partial x_j}$ and also the Einstein convention, i.e. the implied summation over indices that appear twice.

- To determine the coefficients, we „square" the equation:

$$-\hbar^2\frac{\partial^2\psi}{\partial t^2} = \left(\frac{\hbar c}{i}\alpha^j\partial_j + \beta mc^2\right)\left(\frac{\hbar c}{i}\alpha^k\partial_k + \beta mc^2\right)\psi$$

$$= -\hbar c^2\frac{1}{2}\left(\alpha^j\partial_j\alpha^k\partial_k + \alpha^k\partial_k\alpha^j\partial_j\right)\psi - i\hbar mc^3\left(\alpha^j\beta + \beta\alpha^j\right)\partial_j\psi$$

$$+ \beta^2 m^2c^4\psi$$

- Imposing the relativistic energy momentum relation we have to require that this equation becomes the Klein-Gordon equation

$$-\hbar^2 \frac{\partial^2 \psi}{\partial t^2} = -\hbar^2 c^2 \Delta \psi + m^2 c^4 \psi .$$

- Comparing the two equations, we find that the coefficients have to obey

$$\alpha^j \alpha^k + \alpha^k \alpha^j = 2\delta^{jk}$$
$$\alpha^j \beta + \beta \alpha^j = 0$$
$$\beta^2 = 1$$

- These conditions cannot we satisfied using complex numbers, but instead one has to choose α^k and β to be matrices.
- These matrices have to be hermitean (since H_{Dirac} has to be hermitean).
- The last equation shows that β has to be invertible, with $\beta^{-1} = \beta$.
- Making use of this fact, allows to rewrite the second equation as $\alpha^j = -\beta \alpha^j \beta$, and thus

$$Tr(\alpha^j) = Tr(-\beta \alpha^j \beta) = Tr(-\beta^2 \alpha^j) = -Tr(\alpha^j)$$

$$\hookrightarrow Tr(\alpha^j) = 0 .$$

- Using $(\alpha^j)^2 = 1$, which follows from the first equation, one finds $Tr(\beta) = 0$.

- The lowest dimension for which matrices with this property can be constructed is 4.
- There are different possibilities to choose them, with the standard choice being

$$\alpha^j = \begin{pmatrix} 0 & \sigma^j \\ \sigma^j & 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} \mathbb{1} & 0 \\ 0 & -\mathbb{1} \end{pmatrix}$$

σ^j: 2×2 Pauli matrices; $\mathbb{1}$: 2×2 identity matrix

$$\sigma^1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma^2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma^3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

- Given the fact that H_{Dirac} is a 4×4 matrix, the wave function acquires four components:

$$\psi(\vec{x},t) = \begin{pmatrix} \psi_1(\vec{x},t) \\ \psi_2(\vec{x},t) \\ \psi_3(\vec{x},t) \\ \psi_4(\vec{x},t) \end{pmatrix}$$

- This object is called a <u>spinor</u>. (Note, that this is not a vector, as it transforms differently.)
- In summary, the free Dirac equation reads

$$i\hbar \frac{\partial \psi(\vec{x},t)}{\partial t} = \left(\frac{c\hbar}{i} \vec{\alpha} \cdot \nabla + \beta mc^2 \right) \psi(\vec{x},t), \quad \text{or}$$

$$i\hbar \frac{\partial}{\partial t} \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix} = \begin{pmatrix} mc^2\psi_1 - ic\hbar\left(\frac{\partial \psi_4}{\partial x} - i\frac{\partial \psi_4}{\partial y}\right) - ic\hbar \frac{\partial \psi_3}{\partial z} \\ mc^2\psi_2 - ic\hbar\left(\frac{\partial \psi_3}{\partial x} + i\frac{\partial \psi_3}{\partial y}\right) + ic\hbar \frac{\partial \psi_4}{\partial z} \\ -mc^2\psi_3 - ic\hbar\left(\frac{\partial \psi_2}{\partial x} - i\frac{\partial \psi_2}{\partial y}\right) - ic\hbar \frac{\partial \psi_1}{\partial z} \\ mc^2\psi_4 - ic\hbar\left(\frac{\partial \psi_1}{\partial x} + i\frac{\partial \psi_1}{\partial y}\right) + ic\hbar \frac{\partial \psi_2}{\partial z} \end{pmatrix}.$$

- To construct the continuity equation, we define the adjoint spinor

$$\psi^+ = (\psi_1^*, \psi_2^*, \psi_3^*, \psi_4^*)$$

(we will later introduce a different object as adjoint Dirac spinor)

and the adjoint Dirac equation

$$-i\hbar\frac{\partial \psi^+}{\partial t} = -\frac{c\hbar}{i}(\nabla\psi^+)\cdot\vec{\alpha}^+ + \psi^+\beta^+ mc^2 = -\frac{c\hbar}{i}(\vec{\nabla}\psi^+)\cdot\vec{\alpha} + \psi^+\beta mc^2$$

- We now multiply the Dirac equation from the left with ψ^+ and the adjoint equation from the right with ψ.
- Subtracting the two expressions yields

$$\psi^+ i\hbar\frac{\partial \psi}{\partial t} - \left(-i\hbar\frac{\partial \psi^+}{\partial t}\right)\psi = \frac{c\hbar}{i}\psi^+\vec{\alpha}\cdot\nabla\psi + mc^2\psi^+\beta\psi - \left(-\frac{c\hbar}{i}(\nabla\psi^+)\cdot\vec{\alpha}\psi + mc^2\psi^+\beta\psi\right),$$

which can be written as

$$i\hbar\frac{\partial}{\partial t}(\psi^+\psi) = \frac{c\hbar}{i}\vec{\nabla}(\psi^+\vec{\alpha}\psi).$$

- This allows to identify the probability current

$$\vec{j} = c\,\psi^+\vec{\alpha}\psi$$

and the probability density

$$\rho = \psi^+\psi = \sum_{i=1}^{4}|\psi_i|^2,$$

which is clearly positive definite.

V.3 Theory of relativity basics

- We already mentioned that the Dirac equation is compatible with the principle of relativity, i.e. the Dirac equation is covariant

- To understand and analyse what this means precisely, we revisit in the following the basics of the theory of relativity.

- Einstein's postulates:

  i) The laws of physics acquire the same form in any inertial frame of reference, i.e. it is not possible to detect experimentally absolute motion.

  ii) The speed of light is the same in any inertial frame of reference, i.e. it is a universal constant, independently of the reference frame.

- From the second postulate follows, that time cannot be absolute, but that it is connected with space such that when changing between inertial frames of reference also the notion of time must change.

- Such change between reference frames is conducted through a Lorentz transformation, and the invariance of physical laws under this transformation is the central claim of the theory of relativity.

- A space-time point is determined by a four-vector

contravariant four-vector (index at top)

$$x \equiv (ct, \vec{x}) = (ct, x, y, z) \equiv (x^0, x^1, x^2, x^3) \equiv (x^\mu)$$

- We consider now two inertial frames of reference, IS and IS', which at $t = 0$ have the same origin $\vec{x} = 0$.

- The system IS' moves with constant velocity v into the positive x'-direction.

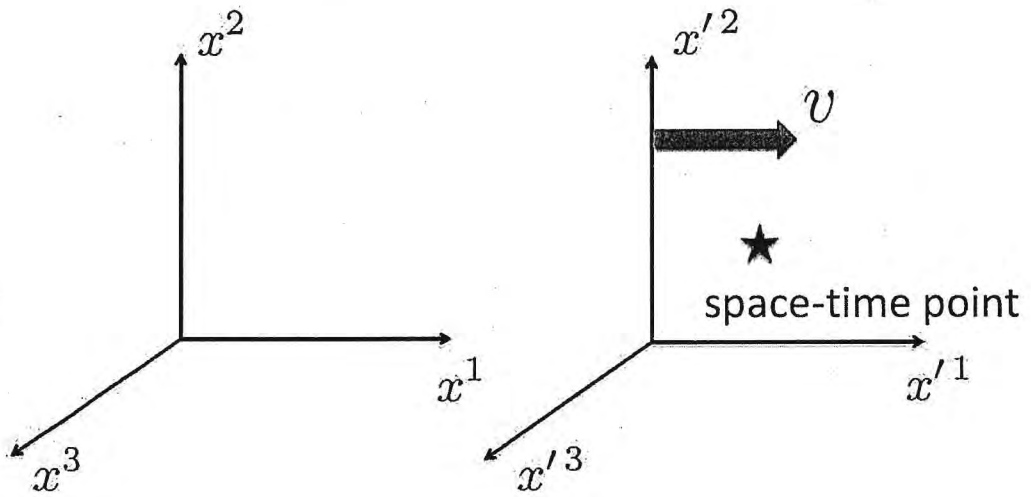
- These two inertial frames of reference are linked by the Lorentz-boost

$$\begin{aligned} x'^0 &= \gamma x^0 - \beta\gamma x^1 \\ x'^1 &= -\beta\gamma x^0 + \gamma x^1 \\ x'^2 &= x^2 \\ x'^3 &= x^3 \end{aligned}$$

coordinates in IS' | coordinates in IS

where $\beta = \frac{v}{c}$ and $\gamma = \frac{1}{\sqrt{1-\beta^2}}$.

Intertial frames of reference



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- One can show that

$$(x'^0)^2 - (\vec{x}')^2 = (x^0)^2 - \vec{x}^2,$$

which is a consequence of the invariance of the speed of light (the wave front of a light pulse starting from the centre of an inertial frame of reference moves at the speed of light in any frame).

- There are other transformations that leave $(ct)^2 - \vec{x}^2$ invariant, such as rotations of two inertial frames of reference with respect to one another ($\vec{x}$ is invariant under rotations). Other examples are parity, $\vec{x} \to -\vec{x}$, and time reversal, $t \to -t$.

- We continue by introducing the so-called covariant four-vector

$$(x_\mu) = (x_0, x_1, x_2, x_3) \equiv (ct, -\vec{x})$$

- With its help we can write

$$(ct)^2 - \vec{x}^2 = \sum_{\mu=0,1,2,3} x^\mu x_\mu \equiv \underbrace{x^\mu x_\mu}_{\text{Summation convention}} \equiv x \cdot x .$$

- For two different space-time points x and y one has

$$x^0 y^0 - \vec{x} \cdot \vec{y} = x^\mu y_\mu \equiv x \cdot y$$

- It turns out to be useful to introduce the <u>metric tensor</u> $g_{\mu\nu}$, which is defined via

$$x_\mu = \sum_\nu g_{\mu\nu} x^\nu \equiv g_{\mu\nu} x^\nu .$$

(x_μ: covariant four-vector; x^ν: contravariant four-vector)

- Likewise, one has

$$x^\mu = g^{\mu\nu} x_\nu .$$

- The matrix representation of the metric tensor is

$$(g_{\mu\nu}) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} = (g^{\mu\nu}),$$

with which one finds

$$x \cdot y = x^\mu y_\mu = x^\mu g_{\mu\nu} y^\nu = x_\nu y^\nu = x_\nu g^{\nu\mu} y_\mu .$$

- The quantity $x \cdot y$ is the scalar product (or inner product) of four-vectors.
- It does not change under a Lorentz-transformation, which can be written as

$$x'^\mu = \Lambda^\mu{}_\nu x^\nu \quad \text{or} \quad x' = \Lambda x .$$

- The transformation matrix Λ for the Lorentz-boost on p. 186 reads

$$(\Lambda^{\mu}{}_{\nu}) = \begin{pmatrix} \gamma & -\beta\gamma & 0 & 0 \\ -\beta\gamma & \gamma & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \quad \text{with } \beta = \frac{v}{c},\ \gamma = \frac{1}{\sqrt{1-\beta^2}}.$$

- For a rotation around the x^3-axis by an angle Θ, one finds

$$(\Lambda^{\mu}{}_{\nu}) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos\Theta & \sin\Theta & 0 \\ 0 & -\sin\Theta & \cos\Theta & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}.$$

- We now investigate how certain quantities behave under a Lorentz transformation.
- As mentioned before, the scalar product of two four-vectors, e.g. $x \cdot y$, is the same in any coordinate system.
- Such quantity is called <u>(Lorentz-) scalar</u>, e.g. mass, charge, speed of light and scalar products of four-vectors.
- Any quantity, that transforms like x^{μ}, is a <u>contravariant four-vector</u>, e.g.

$(V^{\mu}) = (V^0, V^1, V^2, V^3)$ with $V'^{\mu} = \Lambda^{\mu}{}_{\nu} V^{\nu}$.

- Covariant four-vectors transform according to

$$V'_\mu = \Lambda_\mu{}^\nu V_\nu .$$

- Examples:

i) Four-momentum:

$$(p^\mu) = \begin{pmatrix} p^0 \\ \vec{p} \end{pmatrix} = \begin{pmatrix} E/c \\ \vec{p} \end{pmatrix}$$

(relativistic energy)

- The quantity $p^\mu p_\mu$ is a scalar:

$$p^\mu p_\mu = \frac{E^2}{c^2} - \vec{p}^2 = m^2 c^2 , \text{ i.e.}$$

$$E = \sqrt{\vec{p}^2 c^2 + m^2 c^4}$$

ii) Four-gradient:

$$\left(\frac{\partial}{\partial x^\mu}\right) = \left(\frac{\partial}{\partial x^0}, \frac{\partial}{\partial x^1}, \frac{\partial}{\partial x^2}, \frac{\partial}{\partial x^3}\right) \equiv \left(\frac{1}{c}\frac{\partial}{\partial t}, \nabla\right)$$

- Using the chain rule one finds that this quantity transforms like a covariant vector and thus one writes $\frac{\partial}{\partial x^\mu} \equiv \partial_\mu$.

- The corresponding contravariant four-vector is

$$(\partial^\mu) = \left(\frac{\partial}{\partial x_\mu}\right) \equiv \left(\frac{1}{c}\frac{\partial}{\partial t}, -\nabla\right).$$

- With the four-gradient we can calculate the four-divergence, e.g. of the four-vector $(j^\mu) = (j^0, \vec{j})$:

$$\partial_\mu j^\mu = \frac{1}{c}\frac{\partial}{\partial t} j^0 + \vec{\nabla}\cdot\vec{j},$$

which is a Lorentz-invariant quantity.

- We also find that the d'Alembert-operator

$$\partial_\mu \partial^\mu = \frac{1}{c^2}\frac{\partial}{\partial t^2} - \Delta^2$$

is a Lorentz-scalar.

iii) Four-vectorpotential:

$$(A^\mu) = \begin{pmatrix} A^0 \\ \vec{A} \end{pmatrix} = \begin{pmatrix} \frac{1}{c}\phi \\ \vec{A} \end{pmatrix}$$

($\frac{1}{c}\phi$: scalar potential; $\vec{A}$: vector potential)

V.4 Covariant form of the Dirac equation

- In order to investigate the relativistic covariance of the Dirac-equation we change its representation, by introducing the matrices

$$\gamma^0 \equiv \beta \quad \text{and} \quad \gamma^j \equiv \beta\alpha^j.$$

- Multiplying the Dirac equation from the left with $\beta = \gamma^0$, dividing by c and rearranging it, leads to

$$\left(i\hbar\gamma^0\frac{1}{c}\frac{\partial}{\partial t} - \frac{\hbar}{i}\vec{\gamma}\cdot\nabla - mc\right)\Psi(x) = 0.$$

(x: four-vector argument)

- When introducing $(\gamma^\mu) = (\gamma^0, \vec{\gamma})$ and the notation

$$\not{a} \equiv \gamma^\mu a_\mu = \gamma_\mu a^\mu = \gamma^0 a^0 - \vec{\gamma}\cdot\vec{a},$$

(four-vector; $\not{a}$: "a-slash")

we can write the Dirac equation even more compactly,

$$(i\hbar\not{\partial} - mc)\,\psi(x) = 0,$$

or, with the four-momentum operator

$$(\hat{\not{p}} - mc)\,\psi(x) = 0 \quad , \quad (\hat{p}^\mu) = i\hbar(\partial^\mu).$$

- The matrices, that we introduced at the beginning of this section are the so-called <u>Dirac-matrices or Gamma-matrices</u>.
- Their standard representation is

$$\gamma^0 = \begin{pmatrix} \mathbb{1} & 0 \\ 0 & -\mathbb{1} \end{pmatrix} \quad , \quad \gamma^j = \begin{pmatrix} 0 & \sigma^j \\ -\sigma^j & 0 \end{pmatrix}.$$

- They obey the anti-commutator

$$\{\gamma^\mu, \gamma^\nu\} = 2g^{\mu\nu},$$

from which follows that

$$(\gamma^0)^2 = -(\gamma^j)^2 = 1.$$

- A useful relation is

$$(\gamma^\mu)^\dagger = \gamma^0\gamma^\mu\gamma^0 \iff \begin{cases} (\gamma^0)^\dagger = \gamma^0 \\ (\gamma^j)^\dagger = -\gamma^j \end{cases}$$

- Finally, we construct the four-current density for the Dirac-spinor

$$j^\mu = (c\varrho, \vec{j}).$$

($c\varrho$: probability density; $\vec{j}$: current density)

- Using $(\gamma^0)^2 = \mathbb{1}$, one finds

$$c\varrho = c\psi^+\psi = c\psi^+\gamma^0\gamma^0\psi = c\bar{\psi}\gamma^0\psi,$$

where $\bar{\psi} \equiv \psi^+\gamma^0$ is the adjoint Dirac-spinor.

- Furthermore,

$$j^k = c\psi^+\alpha^k\psi = c\psi^+\gamma^0\underbrace{\gamma^0\alpha^k}_{=\beta\alpha^k=\gamma^k}\psi = c\bar{\psi}\gamma^k\psi.$$

- The four-current density is thus

$$j^\mu = c\bar{\psi}\gamma^\mu\psi,$$

and it obeys the continuity equation

$$\partial_\mu j^\mu = 0.$$

V.5 Solution of the free Dirac equation

- We make the plane wave ansatz

$$\psi(x) = u(p)\, e^{-\frac{i}{\hbar}p\cdot x} = u(p)\, e^{-\frac{i}{\hbar}(Et - \vec{p}\cdot\vec{x})},$$

with the spinor $u(p)$ that has as its argument the four-momentum $p = (\frac{E}{c}, \vec{p})$.

- This has the four linearly independent solutions:

$$E = mc^2: \begin{pmatrix}1\\0\\0\\0\end{pmatrix}, \begin{pmatrix}0\\1\\0\\0\end{pmatrix} \quad ; \quad E = -mc^2: \begin{pmatrix}0\\0\\1\\0\end{pmatrix}, \begin{pmatrix}0\\0\\0\\1\end{pmatrix}.$$

- We consider now the expression

$$\begin{aligned}(\not{p} - mc)(\not{p} + mc) &= \not{p}\not{p} - m^2c^2 = p_\mu p_\nu \gamma^\mu \gamma^\nu - m^2c^2 \\ &= p_\mu p_\nu \tfrac{1}{2}\{\gamma^\mu, \gamma^\nu\} - m^2c^2 \\ &= p^2 - m^2c^2 \\ &= \frac{E^2}{c^2} - \vec{p}^2 - m^2c^2 = 0 .\end{aligned}$$

- This means that for any given spinor w, the spinor $(\not{p} + mc)w$ is a solution of the Dirac equation.

- Using the matrix representation of $\not{p} + mc$ with energy E^+ and applying it to the spinors $\begin{pmatrix}1\\0\\0\\0\end{pmatrix}$ and $\begin{pmatrix}0\\1\\0\\0\end{pmatrix}$ yields the positive energy solutions, which allow to construct the normalised wave functions

$$\psi^{(1)}(x) = e^{-\frac{i}{\hbar} p(E^+)\cdot x} u^{(1)}(p(E^+)) = \underbrace{\frac{e^{-\frac{i}{\hbar}(E^+ t - \vec{p}\cdot\vec{x})}}{\sqrt{2mc^2(E^+ + mc^2)}}}_{\text{normalisation constant}} \underbrace{\begin{pmatrix} E^+ + mc^2 \\ 0 \\ cp^z \\ c(p^x + ip^y)\end{pmatrix}}_{u^{(1)}(p(E^+))}$$

and

$$\psi^{(2)}(x) = \frac{e^{-\frac{i}{\hbar}(E^+ t - \vec{p}\cdot\vec{x})}}{\sqrt{2mc^2(E^+ + mc^2)}} \begin{pmatrix} 0 \\ E^+ + mc^2 \\ c(p^x - ip^y) \\ -cp^z \end{pmatrix}.$$

- For constructing the wave functions associated with the rest frame spinors $\begin{pmatrix}0\\0\\1\\0\end{pmatrix}$ and $\begin{pmatrix}0\\0\\0\\1\end{pmatrix}$ we use $E = E^-$ (we cannot use again E^+, because the operator $\not{p} + mc$ does not have full rank, and thus does not map four linearly independent solutions onto another four linearly independent solutions).

- The negative energy solutions are thus

$$\psi^{(3)}(x) = e^{-\frac{i}{\hbar} p(E^-)\cdot x}\, u^{(3)}(p(E^-)) = \frac{e^{-\frac{i}{\hbar}(E^- t - \vec{p}\cdot\vec{x})}}{\sqrt{2mc^2(-E^- + mc^2)}} \begin{pmatrix} -cp^z \\ -c(p^x + ip^y) \\ -E^- + mc^2 \\ 0 \end{pmatrix}$$

and

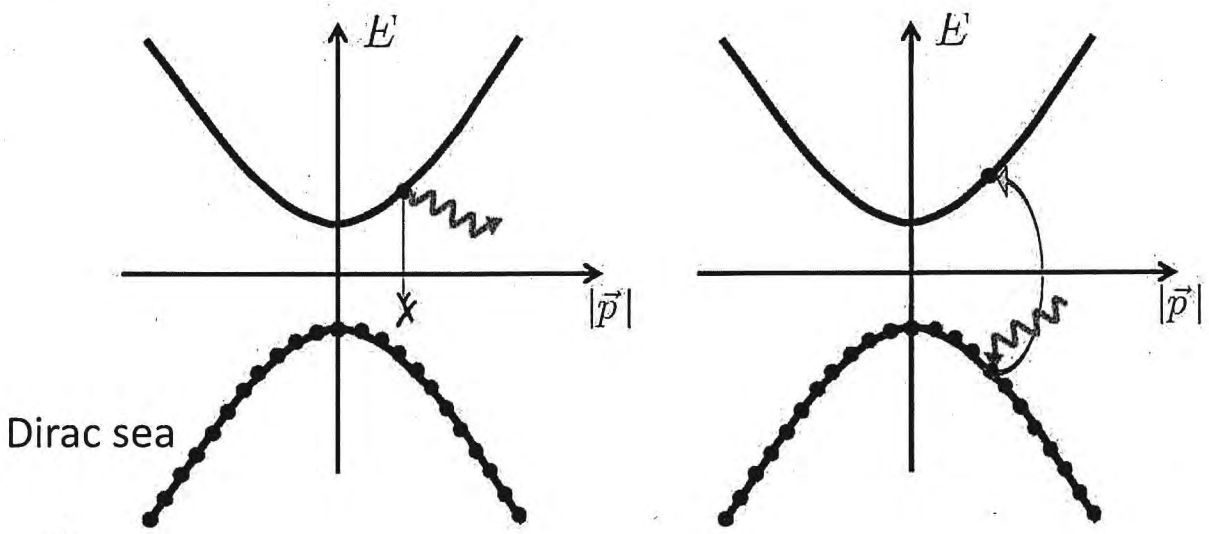
$$\psi^{(4)}(x) = \frac{e^{-\frac{i}{\hbar}(E^- t - \vec{p}\cdot\vec{x})}}{\sqrt{2mc^2(-E^- + mc^2)}} \begin{pmatrix} -c(p^x - ip^y) \\ cp^z \\ 0 \\ -E^- + mc^2 \end{pmatrix}.$$

- These solutions with negative energy are indeed necessary in order to span a complete basis for the spinor wave functions.

- However, like in the case of the Klein-Gordon equation this poses a problem; namely, it is unclear what the ground state of a free Dirac particle (e.g. an electron) is.

- To overcome this problem Dirac proposed in 1930 his hole-theory.
- This states that all states with negative energy are completely filled, which is (at least in principle) possible because Dirac particles are fermions (Dirac sea).
- This means that no particle with positive energy can decay under the emission of a photon into a negative energy state, because of the Pauli principle.
- Conversely, it should be possible to excite a particle with negative energy, e.g. by irradiating a photon with energy $+2\sqrt{\vec{p}^2c^2+m^2c^4}$, into one of the positive energy state.
- This creates a hole in the Dirac sea.
- Such absence of a particle in the Dirac sea is interpreted as an oppositely charged particle with positive energy.
- The excitation of a particle from the Dirac sea thus creates two particles with opposite charge and positive energy, which are interpreted as particle - anti-particle pair.

Hole-theory and Dirac sea



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- Note, that for the Klein-Gordon equation, which describes bosons, such „Dirac sea" construction is not possible.
- Let us now construct the solutions for the anti-particles.
- To this end we construct the four-current density of the solutions for the Dirac equation.
- $\psi^{(1)}$ and $\psi^{(2)}$ lead to

$$(j^\mu) = \frac{1}{mc}\begin{pmatrix} \frac{E^+}{c} \\ \vec{p} \end{pmatrix}.$$

- $\psi^{(3)}$ and $\psi^{(4)}$ result in

$$(j^\mu) = \frac{1}{mc}\begin{pmatrix} -\frac{E^-}{c} \\ -\vec{p} \end{pmatrix},$$

and for these solutions the current density $\vec{j}$ points into the direction that is opposite to the momentum.

- The same is true for the phase velocity of the negative energy solutions, since $e^{-\frac{i}{\hbar}(E^- t - \vec{p}\cdot\vec{x})}$, ($E^-$: negative)
- Inverting the direction of momentum in both solutions, therefore would lead to wave functions propagating along the direction of $\vec{p}$.

Using from now on $E \equiv + \sqrt{\vec{p}^2 c^2 + m^2 c^4}$, this yields the following set of solutions for the Dirac equation:

particle solutions:

$$\psi_p^{(1)}(x) = e^{-\frac{i}{\hbar} p\cdot x} u^{(1)}(p) \quad , \quad \psi_p^{(2)}(x) = e^{-\frac{i}{\hbar} p\cdot x} u^{(2)}(p)$$

with

$$u^{(1)}(p) = \sqrt{\frac{E+mc^2}{2mc^2}} \begin{pmatrix} 1 \\ 0 \\ \frac{cp^z}{E+mc^2} \\ \frac{c(p^x+ip^y)}{E+mc^2} \end{pmatrix}, \quad u^{(2)}(p) = \sqrt{\frac{E+mc^2}{2mc^2}} \begin{pmatrix} 0 \\ 1 \\ \frac{c(p^x+ip^y)}{E+mc^2} \\ -\frac{cp^z}{E+mc^2} \end{pmatrix}$$

These solutions obey the equation

$$(\not{p} - mc)\, u(p) = 0 .$$

anti-particle solutions

$$\psi_A^{(1)}(x) = e^{\frac{i}{\hbar} p\cdot x} v^{(1)}(p) \quad , \quad \psi_A^{(2)}(x) = e^{\frac{i}{\hbar} p\cdot x} v^{(2)}(p)$$

with

$$v^{(1)}(p) = \sqrt{\frac{E+mc^2}{2mc^2}} \begin{pmatrix} \frac{c(p^x-ip^y)}{E+mc^2} \\ -\frac{cp^z}{E+mc^2} \\ 0 \\ 1 \end{pmatrix}, \quad v^{(2)}(p) = \sqrt{\frac{E+mc^2}{2mc^2}} \begin{pmatrix} \frac{cp^z}{E+mc^2} \\ \frac{c(p^x+ip^y)}{E+mc^2} \\ 1 \\ 0 \end{pmatrix}$$

These solutions obey the equation

$$(\not{p} + mc)\, v(p) = 0 .$$

- To conclude, we provide some useful relations for the spinors.

i) inner products:

$$[u^{(r)}(p)]^+ u^{(s)}(p) = [v^{(r)}(p)]^+ v^{(s)}(p) = \frac{E}{mc^2}\delta^{rs},$$

$$\bar{u}^{(r)}(p)\, u^{(s)}(p) = -\bar{v}^{(r)}(p)\, v^{(s)}(p) = \delta^{rs},$$

$$\bar{u}^{(r)} v^{(s)} = \bar{v}^{(r)} u^{(s)} = 0.$$

ii) outer products (completeness relations):

$$\sum_{s=1}^{2} u^{(s)}(p)\, \bar{u}^{(s)}(p) = \frac{\not{p} + mc}{2mc},$$

$$\sum_{s=1}^{2} v^{(s)}(p)\, \bar{v}^{(s)}(p) = \frac{\not{p} - mc}{2mc}.$$

V.6 Covariance of the Dirac equation

- In order to get an understanding of what covariance actually means, we begin with the Klein-Gordon equation, which can be written as

$$\left(\partial_\mu \partial^\mu + \left(\frac{mc}{\hbar}\right)^2\right) \psi(x) = 0.$$

- The coordinates x and the derivatives refer to a specific inertial frame of reference, IS.

- An observer in a different inertial frame of reference, IS', would write the Klein-Gordon equation in exactly the same way:

$$\left(\partial'_\mu \partial'^\mu + \left(\frac{mc}{\hbar}\right)^2\right) \psi'(x') = 0 .$$

- The question is now how the wave functions $\psi(x)$ and $\psi'(x')$ are related to one another.

- Since it is possible to transform between different inertial frames of reference via the Lorentz transform, it should also be possible to find a transformation law that directly connects the wave functions $\psi(x)$ and $\psi'(x')$, such that $\psi'(x')$ solves the Klein-Gordon equation in IS' when $\psi(x)$ solves the Klein-Gordon equation in IS.

- This property is referred to as <u>relativistic covariance</u>.

- The Klein-Gordon equation depends on $\partial_\mu \partial^\mu$ which is a Lorentz-scalar, and hence when transforming from IS to IS' one finds $\partial'_\mu \partial'^\mu = \partial_\mu \partial^\mu$.

- The term $\left(\frac{mc}{\hbar}\right)^2$ is also a scalar and these fore the Klein-Gordon equation is indeed relativistically covariant.
- For the wave functions we find

$$\psi'(x') = \psi(x),$$

which is also reflected by the free solutions:

$$\psi(x) = e^{\frac{i}{\hbar}(\vec{p}\cdot\vec{x} - Et)} = e^{-\frac{i}{\hbar}p\cdot x} = e^{-\frac{i}{\hbar}p'\cdot x'} \equiv \psi'(x').$$

- For calculating the wave function in IS' it is just sufficient to transform the argument of the wave function via a Lorentz-transform, $x' = \Lambda x$.
- The wave function is thus a Lorentz-scalar, i.e. it has at the same space-time point the same value, no matter whether we are in IS or IS'.
- Let us now focus on the Dirac equation where the situation is a bit more involved.
- In the inertial frame of reference IS' is should read

$$(i\hbar\gamma^\mu\partial'_\mu - mc)\,\psi'(x') = 0.$$

- The problem is that $\gamma^\mu \partial_\mu$ is not a Lorentz-scalar, which is due to the fact that (γ^μ) is a vector of constant matrices and thus does not transform like a four-vector.
- This issue is fixed by the fact that the spinor ψ transforms in a non-trivial fashion, unlike the wave function of the Klein-Gordon equation.
- We make the ansatz

$$\psi'(x') = S(\Lambda)\psi(x).$$

- To determine the 4×4 transformation matrix $S(\Lambda)$ we multiply the Dirac equation from the left with $S(\Lambda)$ and write $\psi(x) = S^{-1}(\Lambda)\psi'(x')$.

$$(i\hbar\gamma^\mu\partial_\mu - mc)\psi(x) = 0$$

$$\hookrightarrow S(i\hbar\gamma^\mu\partial_\mu - mc)S^{-1}\psi'(x') = 0$$

$$\hookrightarrow (i\hbar S\gamma^\mu S^{-1}\partial_\mu - mc)\psi'(x') = 0$$

- If we find an S that satisfies

$$S\gamma^\mu S^{-1}\partial_\mu = \gamma^\nu\partial'_\nu$$

we have shown the covariance of the Dirac equation.

- Using $\partial'_\nu = \Lambda_\nu^{\ \mu}\,\partial_\mu$ we find that $S(\Lambda)$ is determined by the equation

$$S(\Lambda)\,\gamma^\mu\,S^{-1}(\Lambda) = \gamma^\nu \Lambda_\nu^{\ \mu}.$$

- Different Lorentz-transformations Λ thus give rise to a different transformation matrix S:

i) Lorentz-boost in x^1-direction

$$(\Lambda^\mu_{\ \nu}) = \begin{pmatrix} \gamma & -\beta\gamma & 0 & 0 \\ -\beta\gamma & \gamma & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \quad \beta = \tanh(\eta) \quad \begin{pmatrix} \cosh\eta & -\sinh\eta & 0 & 0 \\ -\sinh\eta & \cosh\eta & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

$$\hookrightarrow S(\Lambda) = \begin{pmatrix} \cosh\frac{\eta}{2} & 0 & 0 & -\sinh\frac{\eta}{2} \\ 0 & \cosh\frac{\eta}{2} & -\sinh\frac{\eta}{2} & 0 \\ 0 & -\sinh\frac{\eta}{2} & \cosh\frac{\eta}{2} & 0 \\ -\sinh\frac{\eta}{2} & 0 & 0 & \cosh\frac{\eta}{2} \end{pmatrix}$$

ii) Boost in arbitrary direction, i.e. IS' moves with velocity $\vec{v}$ with respect to IS

$$S(\Lambda) = \exp\left(-\frac{\eta}{2}\,\frac{\vec{\alpha}\cdot\vec{v}}{|\vec{v}|}\right) = \mathbb{1}\cosh\frac{\eta}{2} - \frac{\vec{\alpha}\cdot\vec{v}}{|\vec{v}|}\sinh\frac{\eta}{2}.$$

iii) Rotation about the x^3-axis by angle Θ

$$(\Lambda^\mu_{\ \nu}) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos\Theta & \sin\Theta & 0 \\ 0 & -\sin\Theta & \cos\Theta & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

↳ $S(\Lambda) = \mathbb{1} \cos\frac{\Theta}{2} + i \sum^3 \sin\frac{\Theta}{2}$

Pauli matrix

with $\sum^3 = \begin{pmatrix} \sigma^3 & 0 \\ 0 & \sigma^3 \end{pmatrix}$

iv) Rotation about a general axis $\vec{n}$

$$S(\Lambda) = \exp\left(i \frac{\Theta}{2} \vec{\sum} \cdot \vec{n}\right) = \mathbb{1} \cos\frac{\Theta}{2} + i \vec{n} \cdot \vec{\sum} \sin\frac{\Theta}{2}$$

with $\vec{\sum} = \begin{pmatrix} \vec{\sigma} & 0 \\ 0 & \vec{\sigma} \end{pmatrix}$

↑ Pauli matrices, $\vec{\sigma} = \begin{pmatrix} \sigma^1 \\ \sigma^2 \\ \sigma^3 \end{pmatrix}$

↑ closely related to spin operator

- From the last expression one reads off that the spinor apparently returns to its original state only if one rotates by an angle 4π.
- Such behaviour is typical for spin-$\frac{1}{2}$-particles.
- Despite the fact that a spinor has a special behaviour under Lorentz-transformation, one can construct quantities with typical transformation behaviour when combining the spinor ψ with its Dirac-adjoint spinor $\bar{\psi}$.
- Examples:

$\bar{\psi}(x)\psi(x)$ is a Lorentz-scalar

$\bar{\psi}(x)\gamma^\mu\psi(x)$ is a four-vector

V.7 Spin

- In the Schrödinger equation spin needed to be introduced by hand, while the concept of spin emerges rather naturally in the Dirac equation.
- We define the spin operator

$$\vec{S} = \frac{\hbar}{2}\vec{\Sigma} = \frac{\hbar}{2}\begin{pmatrix} \vec{\sigma} & 0 \\ 0 & \vec{\sigma} \end{pmatrix},$$

whose components obey the angular momentum algebra

$$[S^i, S^j] = i\hbar S^k \varepsilon_{ijk}.$$

- Furthermore, $\vec{S}^2 = \frac{3}{4}\hbar^2 \mathbb{1}$.
- One can show that the Dirac Hamiltonian

$$H_{\text{Dirac}} = c\,\vec{\alpha}\cdot\vec{p} + \beta mc^2$$

does not commute with $\vec{S}$, i.e. $[H_{\text{Dirac}}, \vec{S}] \neq 0$.

- It also does not commute with the orbital angular momentum operator $\vec{L} = \vec{r} \times \vec{p}$.
- However, one can show that

$$[H_{\text{Dirac}}, \vec{L} + \vec{S}] = 0,$$

and thus the total angular momentum, $\vec{L} + \vec{S}$, is conserved for a particle that evolves under the free Dirac Hamiltonian.

- One can construct another, spin-related operator, with which H_{Dirac} commutes and according to whose eigenvalues states can be classified.

- This is the so-called <u>helicity-operator</u>

$$h(\vec{p}) = \frac{1}{2} \frac{\vec{\Sigma} \cdot \vec{p}}{|\vec{p}|}$$

(note, that $\vec{p}$ is not an operator here)

- This operator corresponds to the projection of the spin onto the direction of the momentum.

- The eigenvalues of $h(\vec{p})$ are

$\lambda = \frac{1}{2}$: positive / right-handed helicity
(the spin points into the direction of the momentum)

$\lambda = -\frac{1}{2}$: negative / left-handed helicity
(the spin points opposite to the direction of the momentum)

- For the simple case $\vec{p} = |\vec{p}| \vec{e}_z$ we can write

$$h(\vec{p}) = \frac{1}{2} \Sigma^3 = \frac{1}{2} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}.$$

- The spinors in the solution of the free Dirac equation with defined helicity are

$$u^{(1)}(p) = \sqrt{\frac{E+mc^2}{2mc^2}} \begin{pmatrix} 1 \\ 0 \\ \frac{c|\vec{p}|}{E+mc^2} \\ 0 \end{pmatrix}, \quad u^{(2)}(p) = \sqrt{\frac{E+mc^2}{2mc^2}} \begin{pmatrix} 0 \\ 1 \\ 0 \\ -\frac{c|\vec{p}|}{E+mc^2} \end{pmatrix}$$

$$v^{(1)}(p) = \sqrt{\frac{E+mc^2}{2mc^2}} \begin{pmatrix} 0 \\ -\frac{c|\vec{p}|}{E+mc^2} \\ 0 \\ 1 \end{pmatrix}, \quad v^{(2)}(p) = \sqrt{\frac{E+mc^2}{2mc^2}} \begin{pmatrix} \frac{c|\vec{p}|}{E+mc^2} \\ 0 \\ 1 \\ 0 \end{pmatrix}.$$

- They are simultaneous eigenstates of H_{Dirac} and $h(p)$:

$$\left.\begin{aligned} \frac{1}{2}\frac{\vec{\Sigma}\cdot\vec{p}}{|\vec{p}|}u^{(1)}(p) &= +\frac{1}{2}u^{(1)}(p) \\ \frac{1}{2}\frac{\vec{\Sigma}\cdot\vec{p}}{|\vec{p}|}u^{(2)}(p) &= -\frac{1}{2}u^{(2)}(p) \end{aligned}\right\} \text{particle states}$$

$$\left.\begin{aligned} \left(-\frac{1}{2}\frac{\vec{\Sigma}\cdot\vec{p}}{|\vec{p}|}\right)v^{(1)}(p) &= +\frac{1}{2}v^{(1)}(p) \\ \left(-\frac{1}{2}\frac{\vec{\Sigma}\cdot\vec{p}}{|\vec{p}|}\right)v^{(2)}(p) &= -\frac{1}{2}v^{(2)}(p) \end{aligned}\right\} \begin{array}{l}\text{anti particle states,} \\ \text{where we use} \\ \vec{\Sigma} \to -\vec{\Sigma}, \text{ since } \vec{S} \to -\vec{S} \\ \text{(we already changed} \\ \vec{p} \to -\vec{p} \text{ before)}\end{array}$$

- For anti particles we have $\vec{p} \to -\vec{p}$ and $\vec{S} \to -\vec{S}$.

V.8 The Dirac equation with an electromagnetic field

- We want to investigate the Dirac equation in the presence of a vector potential $\vec{A}(\vec{x},t)$ and a scalar potential $\phi(\vec{x},t)$.
- A (classical) particle couples to these potentials via its charge, q, which is reflected by the minimal substitution

$$E \to E - q\phi \quad , \quad \vec{p} \to \vec{p} - q\vec{A}.$$

- Using the correspondence principle this amounts to

$$i\hbar\frac{\partial}{\partial t} \to i\hbar\frac{\partial}{\partial t} - q\phi \quad , \quad \frac{\hbar}{i}\nabla \to \frac{\hbar}{i}\vec{\nabla} - q\vec{A} \quad ,$$

which, by making use of the four-vectors $(p^\mu) = (\frac{E}{c}, \vec{p})$ and $(A^\mu) = (\phi/c, \vec{A})$, can be compactly written as

$$\hat{p}^\mu \to \hat{p}^\mu - qA^\mu \quad .$$

- Making this substitution, the Dirac equation becomes

$$(i\hbar\not{\partial} - q\not{A}(x) - mc)\psi(x) = 0 \quad .$$

- Before continuing, let us briefly come back to the construction of anti-particle states:
- One can show, that the so-called

<u>charge conjugated spinor</u>

$$\psi_c(x) = iy^2\psi^*(x) = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \\ 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}\psi(x)$$

satisfies the above equation, but with charge $-q$.

- Moreover, one finds that the charge conjugation operation actually yields the anti-particle spinors when applied to the particle spinors.
- From this follows that particles and anti-particles carry opposite charges

- Let us now focus on the <u>non-relativistic limit</u> of the Dirac equation.
- We start with the non-covariant form

$$i\hbar \frac{\partial}{\partial t}\psi(\vec{x},t) = \left[c\vec{\alpha}\cdot\underbrace{\left(\frac{\hbar}{i}\nabla - q\vec{A}\right)}_{\vec{\pi} = \vec{p} - q\vec{A} \;\ldots\; \text{kinetic momentum}} + q\phi + \beta mc^2 \right] \psi(\vec{x},t)$$

- We now make the following ansatz for the spinor:

$$\psi = \begin{pmatrix} \tilde{\varphi} \\ \tilde{\chi} \end{pmatrix} = \underbrace{e^{-\frac{i}{\hbar}mc^2 t}}_{\text{we separate this fast oscillation}} \overbrace{\begin{pmatrix} \varphi \\ \chi \end{pmatrix}}^{\text{"slowly evolving"}}$$

- The two-component spinors are "slowly" evolving, i.e. on timescales that are much longer than $\frac{\hbar}{mc^2}$.
- Inserting the ansatz into the Dirac equation yields

$$mc^2 \begin{pmatrix} \varphi \\ \chi \end{pmatrix} + i\hbar \frac{\partial}{\partial t} \begin{pmatrix} \varphi \\ \chi \end{pmatrix} = \left(c\vec{\alpha}\cdot\vec{\pi} + q\phi + \beta mc^2 \right) \begin{pmatrix} \varphi \\ \chi \end{pmatrix},$$

which becomes after using the explicit forms of the α^i and β-matrices

$$i\hbar \frac{\partial}{\partial t} \begin{pmatrix} \varphi \\ \chi \end{pmatrix} = c\,\vec{\sigma}\cdot\vec{\pi} \begin{pmatrix} \chi \\ \varphi \end{pmatrix} + q\phi \begin{pmatrix} \varphi \\ \chi \end{pmatrix} - 2mc^2 \begin{pmatrix} 0 \\ \chi \end{pmatrix}.$$

- The second row is dominated by the last term: $|mc^2\chi| \gg |q\phi\chi|, \left|i\hbar\frac{\partial}{\partial t}\chi\right|$.

- Neglecting the time derivative and the term proportional to $q\phi$, the second line becomes an algebraic equation, which is solved by

$$\chi = \frac{\vec{\sigma}\cdot\vec{\pi}}{2mc}\varphi$$

(χ: upper / large spinor component; φ: lower / small spinor component)

- This relation shows, that in the non-relativistic limit $|\chi| \ll |\varphi|$, since here the velocity $|\vec{v}| \approx \left|\frac{\vec{\pi}}{m}\right|$ should be much smaller than the speed of light.

- We can now eliminate χ from the upper line, which yields the equation of motion for the upper spinor component

$$i\hbar\frac{\partial}{\partial t}\varphi(\vec{x},t) = \left[\frac{1}{2m}(\vec{\sigma}\cdot\vec{\pi})^2 + q\phi\right]\varphi(\vec{x},t)$$

- One can show that

$$(\vec{\sigma}\cdot\vec{\pi})(\vec{\sigma}\cdot\vec{\pi}) = \vec{\pi}^2 + i\sigma\cdot(\vec{\pi}\times\vec{\pi}).$$

- For the x-component of the cross product of operators in the second term on finds

$$\begin{aligned}(\vec{\pi}\times\vec{\pi})^x\varphi &= (\pi^y\pi^z - \pi^z\pi^y)\varphi \\ &= \left((\hat{p}^y - qA^y)(\hat{p}^z - qA^z) - (\hat{p}^z - qA^z)(\hat{p}^y - qA^y)\right)\varphi \\ &= q\frac{\hbar}{i}\left(-\frac{\partial}{\partial y}A^z - A^y\frac{\partial}{\partial z} + \frac{\partial}{\partial z}A^y + A^z\frac{\partial}{\partial y}\right)\varphi \\ &= q\frac{\hbar}{i}\left(-\frac{\partial A^z}{\partial y} + \frac{\partial A^y}{\partial z}\right)\varphi = i\hbar q B^x\varphi\end{aligned}$$

- Following an analogous calculation for the other components leads to the equation

$$i\hbar \frac{\partial}{\partial t} \varphi(\vec{x},t) = \left[\frac{1}{2m}(\vec{p} - q\vec{A})^2 - \frac{q\hbar}{2m} \vec{\sigma} \cdot \vec{B} + q\phi \right] \varphi(\vec{x},t)$$

- For a homogeneous magnetic field, $q = -e$ and the Coulomb potential $q\phi = -\frac{e^2}{4\pi\varepsilon_0 |\vec{r}|}$ this leads to the Pauli-equation for the Hydrogen atom (using $(\vec{p} + e\vec{A})^2 \approx \vec{p}^2 + e\vec{B}\cdot\vec{L}$)

$$i\hbar \frac{\partial}{\partial t} \begin{pmatrix} \psi_\uparrow \\ \psi_\downarrow \end{pmatrix} = \left[\frac{\vec{p}^2}{2m} - \frac{e^2}{4\pi\varepsilon_0 |\vec{r}|} + \frac{\mu_B}{\hbar} \vec{L} \cdot \vec{B} + \frac{g_s}{2} \mu_B \vec{\sigma} \cdot \vec{B} \right] \begin{pmatrix} \psi_\uparrow \\ \psi_\downarrow \end{pmatrix}$$

with the Bohr magneton $\mu_B = \frac{e\hbar}{2m}$ and the Landé factor $g_s = 2$.

- The prediction of g_s is a huge success of Dirac's theory.

- One can systematically improve the approximation describing the non-relativistic limit, e.g. through the so-called Foldy-Wouthuysen transformation.

- This leads for time-independent fields to

$$i\hbar \frac{\partial}{\partial t} \varphi(\vec{x},t) = \left[\frac{1}{2m}(\vec{p} - q\vec{A})^2 - \frac{q\hbar}{2m} \vec{\sigma} \cdot \vec{B} + q\phi \right.$$
$$\left. - \frac{\vec{p}^4}{8m^3c^2} - \frac{q\hbar}{4m^2c^2} \vec{\sigma} \cdot (\vec{E} \times (\vec{p} - q\vec{A})) - \frac{q\hbar^2}{8m^2c^2} (\vec{\nabla} \cdot \vec{E}) \right] \varphi(\vec{x},t).$$

- The three terms in the second row also contribute when there is only a scalar potential present and $\vec{A} = 0$.

i) The term $\frac{\vec{p}^4}{8m^3c^2}$ is the first relativistic correction stemming from the expansion of the relativistic energy-momentum relation $E = \sqrt{\vec{p}^2c^2 + m^2c^4}$

ii) The second term in the second line becomes with $q = -e$ and the Coulomb potential $(-e)\phi = -\frac{e^2}{4\pi\varepsilon_0|\vec{r}|}$

$$\frac{e\hbar}{4m^2c^2}\vec{\sigma}\cdot(\vec{E}\times\vec{p}) = -\frac{e\hbar}{4m^2c^2}\frac{d\phi}{dr}\frac{1}{r}\vec{\sigma}\cdot(\vec{r}\times\vec{p})$$

$$= \frac{\hbar}{4m^2c^2}\frac{e^2}{4\pi\varepsilon_0 r^3}\vec{\sigma}\cdot\vec{L}$$

$$= \frac{e^2}{4\pi\varepsilon_0 m^2c^2}\frac{\vec{L}\cdot\vec{S}}{2r^3}.$$

This is the spin-orbit coupling term with the correct „Thomas"-factor $\frac{1}{2}$!

iii) For the last term we use Maxwell's equation

$$\nabla\cdot\vec{E} = \frac{\rho}{\varepsilon_0} = \frac{e}{\varepsilon_0}\delta^{(3)}(\vec{r}),$$

with $\rho = e\,\delta^{(3)}(\vec{r})$ being the charge density of the point-like nucleus.

With this the term becomes

$$\frac{e^2\hbar^2}{8m^2c^2\varepsilon_0}\delta^{(3)}(r),$$

which is the so-called Darwin term.

- Finally, we remark that the Dirac equation can actually be solved exactly in the presence of the Coulomb potential.
- This yields the energy eigenvalues

$$E_{nj} = mc^2\left[1+\frac{\alpha_{FS}^2}{\left(n-(j+\frac{1}{2})+\sqrt{(j+\frac{1}{2})^2-\alpha_{FS}^2}\right)^2}\right]^{-\frac{1}{2}}.$$

principal quantum number

total angular momentum quantum number

- Expanding in the fine-structure constant $\alpha_{FS} = \frac{e^2}{4\pi\varepsilon_0\hbar c} \approx \frac{1}{137}$ yields

$$E_{nj} = mc^2\left[1-\frac{\alpha_{FS}^2}{2n^2}+\frac{\alpha_{FS}^4}{2n^4}\left(\frac{3}{4}-\frac{n}{j+\frac{1}{2}}\right)+\mathcal{O}(\alpha_{FS}^6)\right]$$

$$= mc^2 - \underbrace{\frac{E_{Ry}}{n^2}}_{\text{Rydberg energies}} + \underbrace{\frac{\alpha_{FS}^2 E_{Ry}}{n^4}\left(\frac{3}{4}-\frac{n}{j+\frac{1}{2}}\right)}_{\text{hydrogen fine-structure}} + \mathcal{O}(\alpha_{FS}^6)$$

$$E_{Ry} = \frac{1}{2}\alpha_{FS}^2 mc^2 \approx 13.6\ \text{eV}.$$