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:

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

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

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

- 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 $|\psi(t)\rangle$:

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

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

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

$$|\psi(t_1)\rangle = \mathcal{U}(t_1, t)\,|\psi(t)\rangle = \mathcal{U}(t_1, t)\,\mathcal{U}(t, t_0)\,|\psi(t_0)\rangle$$
$$\overset{!}{=} \mathcal{U}(t_1, t_0)\,|\psi(t_0)\rangle$$

- From property (iii) follows, by setting $t_1 = t_0$,
$\mathbb{1} = \mathcal{U}(t_0, t_0) = \mathcal{U}(t_0, t)\,\mathcal{U}(t, t_0)$, and hence

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

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 $\mathcal{U}(t, t_0)$ can be computed by exponentiation.
- However, as we will now show, $\mathcal{U}(t, t_0)$ can also be constructed for time-dependent Hamiltonians $H(t)$
- Starting point is the time-dependent Schrödinger equation

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

- 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

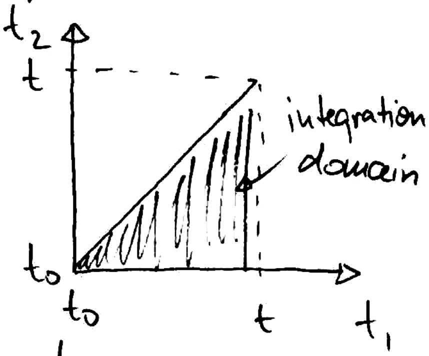
$$U(t,t_0) = \mathbb{1} + \sum_{n=1}^{\infty} U^{(n)}(t,t_0) = \sum_{n=0}^{\infty} U^{(n)}(t,t_0) ,$$

where

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

- 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 $t \geq t_1 \geq t_2 \geq \ldots \geq t_n \geq t_0$.
- The operators are thus <u>time ordered</u>, 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 $\int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2$

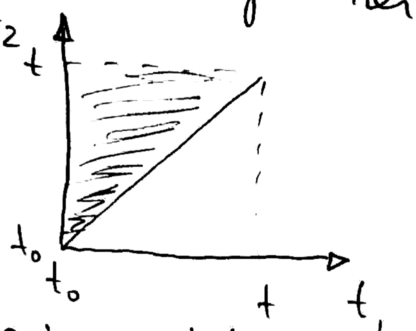


- More specifically, we have

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

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:



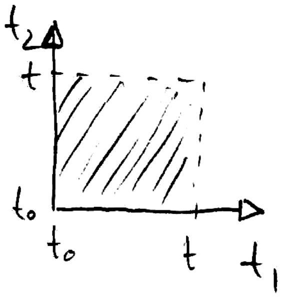
- Since integrating over both domains yields the same result, we can write

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

$$= \underset{\substack{\uparrow \\ \text{factor } \frac{1}{2} \text{ to avoid double counting}}}{\left(-\frac{i}{\hbar}\right)^2 \frac{1}{2}} \left[\int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2\, H(t_1)H(t_2) + \int_{t_0}^{t} dt_2 \int_{t_0}^{t_2} dt_1\, H(t_2)H(t_1)\right]$$

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

- 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:

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

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

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

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

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

- 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

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

iii) Products of operators keep their structure

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

Furthermore,

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

and

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

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:

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

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

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

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

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

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

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

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 of the structure

$$H = H_0 + \alpha V$$

time independent Hamiltonian with known spectrum

perturbation (operator)

coupling constant which parametrises the strength of the perturbation

- In the interaction picture the operators evolve under the Hamiltonian H_0, while the wave functions evolve under the perturbing Hamiltonian αV.
- 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

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

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

- An operator in the interaction picture becomes

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

- 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

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

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

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

$$= \mathbb{1} - \frac{i}{\hbar}\int_{t_0}^{t} dt' \, \alpha V_D(t')$$

$$+ \left(-\frac{i}{\hbar}\right)^2 \int_{t_0}^{t} dt_1 \, \alpha V_D(t_1) \int_{t_0}^{t_1} dt_2 \, \alpha V_D(t_2) + \ldots$$

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:

$$|\psi(t_0)\rangle = |\psi_D(t_0)\rangle = |n\rangle \quad ; \quad H_0 \underset{\text{eigenstate}}{|n\rangle} = \underset{\text{eigenvalue}}{E_n^{(0)}} |n\rangle$$

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

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

- 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:

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

$$+\left(-\frac{i}{\hbar}\right)^2 \int_{t_1}^{t} dt_1\, e^{\frac{i}{\hbar}(t_1-t_0)H_0}\,\alpha V_1(t_1)\, e^{-\frac{i}{\hbar}(t_1-t_0)H_0}\int_{t_0}^{t_1} dt_2\, e^{\frac{i}{\hbar}(t_2-t_0)H_0}\,\alpha V(t_2)\, e^{-\frac{i}{\hbar}(t_2-t_0)H_0} + \ldots\Big]$$

- 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

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

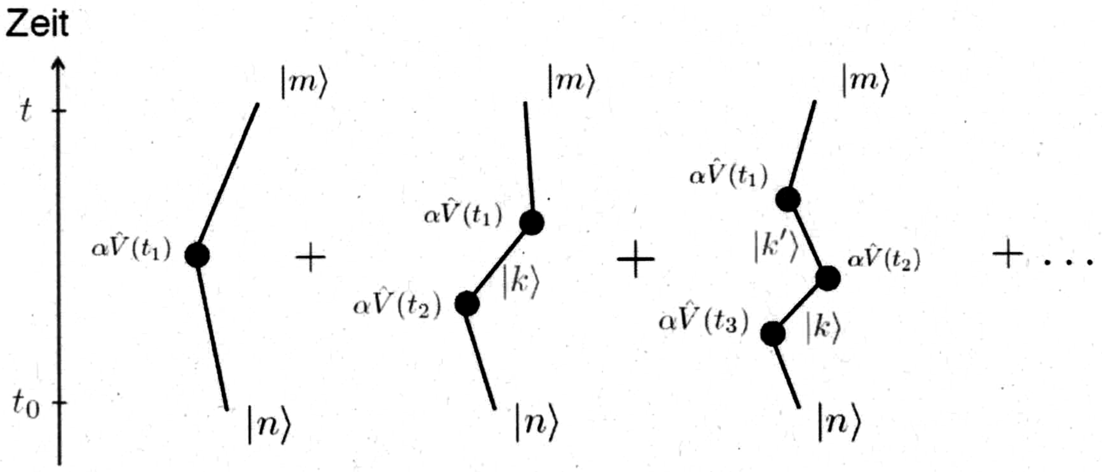
$$+\left(-\frac{i}{\hbar}\right)^2 e^{-\frac{i}{\hbar}(t-t_0)E_m^{(0)}} \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2\, e^{\frac{i}{\hbar}(t_1-t_0)E_m^{(0)}} \langle m|\alpha V(t_1)\, e^{-\frac{i}{\hbar}(t_1-t_2)H_0}\, \alpha V(t_2)|n\rangle\, e^{-\frac{i}{\hbar}(t_2-t_0)E_n^{(0)}} + \ldots$$

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

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

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

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

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

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

- We evaluate this formula for different scenarios:

i) <u>H_0 has a discrete, non-degenerate spectrum</u>

- 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 $\frac{2\pi\hbar}{|\omega_{mn}|}$. 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) <u>H_0 has a discrete spectrum and the energy $E_n^{(0)}$ is degenerate</u>

- Given that $\lim\limits_{x\to 0} \frac{\sin xt}{x} = t$ 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:

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

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

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

- Using $\delta(ax) = \frac{1}{|a|}\delta(x)$ yields for the transition probability in this limit

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

- This expression allows us to calculate the transition rate

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

- 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

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

sum over all target states

Conversion of the sum over target state energies into integral involving the density of states

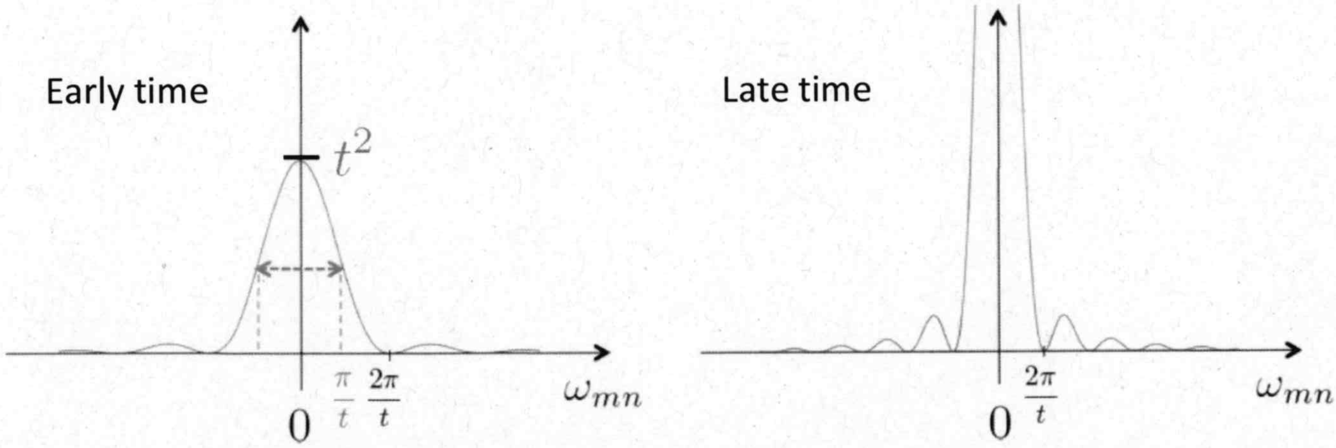
$\rho(E) = \frac{dN}{dE}$ (number of states N in energy interval $[E, E+dE]$)

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

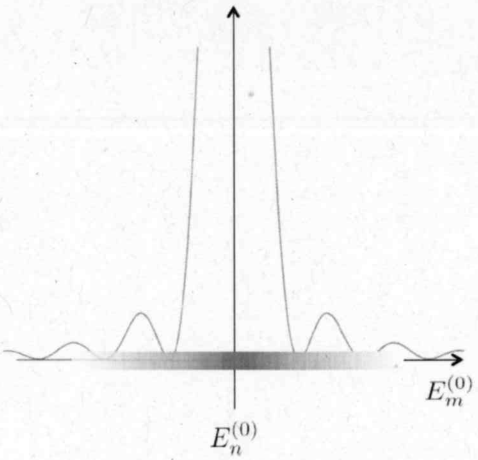
$$\approx \left(\rho(E_m^{(0)}) \frac{|V_{mn}|^2}{\hbar^2} \right)\Bigg|_{E_m^{(0)}=E_n^{(0)}} \underbrace{\int_{-\infty}^{\infty} dE_m^{(0)} \left(\frac{\sin(\omega_{mn}\frac{t}{2})}{\frac{\omega_{mn}}{2}} \right)^2}_{2\pi\hbar t}$$

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

The function f(t)



Continuous distribution of final state energies



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

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

<u>Fermi's Golden Rule</u>

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

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

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

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

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

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

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

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

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

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

↳ 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 adiabatic perturbation.
- 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)

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

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

- Separating the diagonal and off-diagonal terms in the sum of the second term, yields: (2p)

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

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

- 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 $\varepsilon\to 0$

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

- static perturbation theory predicts that eigenstates and eigenenergies of H_0 change under a perturbation αV_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

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

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

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

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

- We now take the derivative with respect to time: (31)

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

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

- 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:

$$\frac{1}{\hbar}\sum_{k\neq n}\frac{|V_{kn}|^2}{\omega_{kn}-i\varepsilon} = \sum_{k\neq n}\frac{|V_{kn}|^2}{E_k^{(0)}-E_n^{(0)}-i\varepsilon\hbar} \rightarrow \int_{-\infty}^{\infty} dE_k^{(0)}\,\underset{\substack{\uparrow\\ \text{density of states}}}{\rho(E_k^{(0)})}\,\frac{|V_{kn}|^2}{E_k^{(0)}-E_n^{(0)}-i\varepsilon\hbar}$$

- 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.