

Week 10

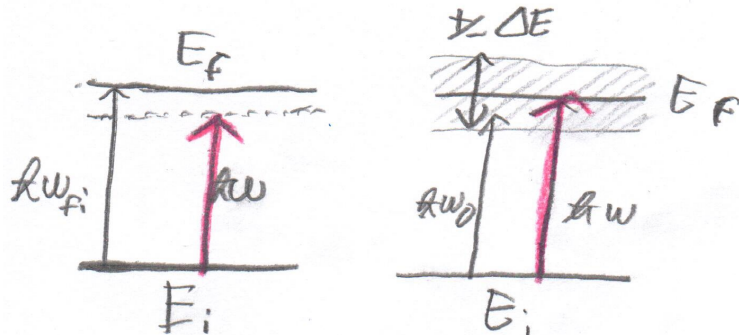
PHY 304 Quantum Mechanics-II

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These notes are provided for the students of the class above only. There is no guarantee for correctness, please contact me if you spot a mistake.

9.3.6 Fermi's golden rule

In section 9.3.2 and section 9.3.5 we had considered transitions between two discrete states of an atom.



left: What if the final state is embedded in a continuum, such as during photo-ionisation (photoelectric effect), as sketched on the left? The transition is thus into a scattering state with $E > 0$.

In that case it makes no sense to single out a single target state, but instead we have to add the probabilities to make a transition into a (possibly small but) finite energy interval, according to (9.24)

$$P = \int_{E_f - \Delta E/2}^{E_f + \Delta E/2} dE \frac{|V_{fi}|^2 \sin^2 [(\omega_0 - \omega) \frac{t}{2}]}{\hbar^2 |\omega_0 - \omega|^2} \rho(E), \quad (9.55)$$

where we assume that the perturbation is resonantly targeting a final energy E_f in the continuum, hence $\hbar\omega = E_f - E_i$. To use (9.24) we then set $\hbar\omega_0 = E - E_i$ and use the density of states $\rho(E)$ near energy E . This means that $\rho(E)dE$ is the number of final states in the energy interval $[E, E + dE]$.

Now recall from the figure in section 9.1.4 that the sinc function within the integrand becomes a very narrow function of ω , peaked near $\omega = \omega_0$ which implies $E = E_f$. In contrast, we assume that $\rho(E)$ is a much more slowly varying function, hence we can turn (9.55) into

$$P = \frac{|V_{fi}|^2}{\hbar^2} \rho(E_f) \int_{E_f - \Delta E/2}^{E_f + \Delta E/2} dE \frac{\sin^2 [(\omega_0 - \omega) \frac{t}{2}]}{|\omega_0 - \omega|^2} = \frac{2\pi}{\hbar} \frac{|V_{fi}|^2}{4} \rho(E_f) t. \quad (9.56)$$

For the last equality we used $\int_{-\infty}^{\infty} dE \sin^2[Et/(2\hbar)]/(E/\hbar)^2 = \pi\hbar t/2$. Writing $P = Rt$ for a transition rate R we reached:

Fermi's golden rule for the rate R of a transition from a bound state into a continuum

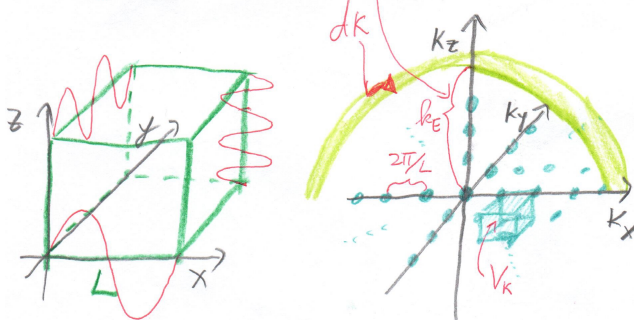
$$R = \frac{2\pi}{\hbar} \frac{|V_{fi}|^2}{4} \rho(E_f). \quad (9.57)$$

by a periodic perturbation of frequency ω .

- This is surprisingly simple, given the path we took to reach here, we only need to know the matrix element of the perturbation and the density of states at the target energy.

Density of states for plane waves: Consider the states $|\phi_{\mathbf{k}}\rangle = e^{i\mathbf{k}\cdot\mathbf{r}}/\sqrt{\mathcal{V}}$ of a free particle with energy $E = \hbar^2\mathbf{k}^2/(2m)$. Instead of delta-function normalisation as in Eq. (2.4), we use box-normalisation for our plane waves: Integrating $|\phi(\mathbf{r})|^2$ over a huge cubic volume $\mathcal{V} = L^3$ with periodic boundary conditions clearly gives one.

We now want to find the density of these states $\rho(E)$. Since this is defined such that $\rho(E)dE$ is the number of states in the energy interval $[E, E + dE]$, we had to make our states countable, which was the purpose of the box above.



left: (left) Cubic quantisation volume with edge length L . (right) reciprocal space, with allowed \mathbf{k} as cyan dots and energy shell in bright green.

To meet the boundary conditions, the 3D wave vector must have the form,

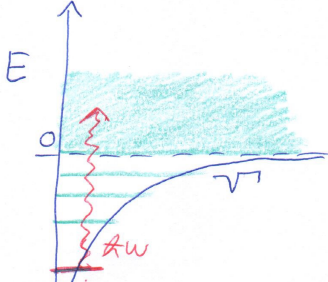
$$\mathbf{k} = [k_x, k_y, k_z]^T = k_x\mathbf{e}_x + k_y\mathbf{e}_y + k_z\mathbf{e}_z, \quad (9.58)$$

with $k_x = \frac{2\pi}{L}n_x$, $k_y = \frac{2\pi}{L}n_y$ and $k_z = \frac{2\pi}{L}n_z$ and integer n_k (including zero and negative values). We show the example $n_x = 1$, $n_y = 2$ and $n_z = 3$ in the figure above. In \mathbf{k} -space, also called reciprocal space, these allowed wavenumbers form a grid as shown above. In the limit $\mathcal{V} \rightarrow \infty$ ($L \rightarrow \infty$), this grid becomes infinitely dense. Without taking that limit, we can estimate the number of plane-waves with energy in the shell $[E, E + dE]$ by noting that each grid-point takes up a volume $V_k = (2\pi/L)^3$ of \mathbf{k} -space and the volume of the energy shell is $V_E = 4\pi k_E^2 dk = 2\pi(2m)^{3/2}E^{1/2}dE/\hbar^3$ (using $k_E = \sqrt{2mE}/\hbar$). Hence the number of states within the shell is $N_E \approx V_E/V_k = \rho(E)dE$, and we arrive at a density of states

$$\rho(E) = \mathcal{V} \frac{m^{3/2}(2E)^{1/2}}{2\pi^2\hbar^3}. \quad (9.59)$$

The quantisation volume \mathcal{V} must (and will) always cancel with normalisation factors $1/\sqrt{\mathcal{V}}$ of our box-normalised plane wave states, hence we can safely take the limit $\mathcal{V} \rightarrow \infty$ for physical observables such as the transition rate R in (9.57).

Example 75, Photoelectric effect:



left: A scenario where electrons make a transition from discrete states to continuum states due to a periodic perturbation (radiation) is photo-ionisation of a Hydrogen atom. We had already discussed in QM-I section ??, that for $E < 0$ (with $E = 0$ defined as a zero momentum electron at spatial infinity), the electron will be in discrete bound states $E_n < 0$, while for $E > 0$ we have continuum scattering states $E = \hbar^2 \mathbf{k}^2 / (2m)$.

For simplicity we assume the latter are not perturbed by the proton's potential, hence our initial state $|i\rangle = |nlm\rangle$ from Eq. (4.91) and the final states $|f_{\mathbf{k}}\rangle = e^{i\mathbf{k}\cdot\mathbf{r}}/\sqrt{\mathcal{V}}$, compare Eq. (2.4). Instead of delta-function normalisation as in Eq. (2.4), we use box-normalisation for our plane waves, see box above.

Matrix elements between relevant states are

$$\begin{aligned}
 V_{fi} &\stackrel{\text{Eq. (9.46)}}{=} \langle \phi_{\mathbf{k}} | ezE_0 | nlm \rangle = \frac{eE_0}{\sqrt{\mathcal{V}}} \int d^3\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} z \phi_{nlm}(\mathbf{r}) \\
 &= \frac{eE_0}{\sqrt{\mathcal{V}}} \frac{\partial}{\partial k_z} \int d^3\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} \phi_{nlm}(\mathbf{r}) \stackrel{\text{Eq. (2.74)}}{\text{in 3D}} \frac{eE_0(2\pi)^{3/2}}{\sqrt{\mathcal{V}}} \frac{\partial}{\partial k_z} \tilde{\phi}_{nlm}(\mathbf{k}), \quad (9.60)
 \end{aligned}$$

which we recognise as related to the Fourier transform of the initial wavefunction. We cannot quite directly use Eq. (9.57) since in its derivation we assumed V_{fi} to be independent of the target state in the continuum, but we can already see that \mathcal{V} will cancel as promised above. A detailed discussion of photo-ionisation is deferred to PHY402.

9.4 Higher order time-dependent perturbation theory

We had seen first order time-dependent perturbation theory in section 9.1. To move this to higher orders, it is useful to first develop yet another picture of quantum time-evolution in addition to the Schrödinger and Heisenberg pictures that you had seen in section 3.9.1. (Please revise that section now if you have forgotten).

9.4.1 Interaction picture

Further reading: For this section (Interaction picture), please also refer to Shankar, section 18.3. (SH), or Sakurai (SA), chapter 5.

Assuming a Hamiltonian split as in (9.1), we want to handle the time-evolution due to $\hat{H}^{(0)}$ in something akin to the Heisenberg picture (move it into the operators), such that we only have to worry about the time evolution due to $\hat{H}'(t)$ in the Schrödinger picture. This is often applied to problems with interacting particles, such that the free particles are in $\hat{H}^{(0)}$ and the interactions in $\hat{H}'(t)$, hence it is called the interaction picture. In this section subscripts I denote states or

operators in the interaction picture, and S in the Schrödinger picture.

In Eq. (3.60) we had first encountered the time evolution operator. Let us redefine it with a variable initial time as:

$$\hat{U}(t, t_0) = e^{-i\frac{\hat{H}}{\hbar}(t-t_0)}. \quad (9.61)$$

Now we further define a specific variant of it, in which the time evolution is due to the unperturbed Hamiltonian only:

$$\hat{U}_S^{(0)}(t, t_0) = e^{-i\frac{\hat{H}^{(0)}}{\hbar}(t-t_0)}, \quad (9.62)$$

and the subscript indicates that it is in the Schrödinger picture. From that we define the

Quantum state in the interaction picture $|\Psi_I(t)\rangle$ as

$$|\Psi_I(t)\rangle = [\hat{U}_S^{(0)}(t, t_0)]^\dagger |\Psi_S(t)\rangle \quad (9.63)$$

- We are essentially cancelling the time-evolution due to the unperturbed Hamiltonian $\hat{H}^{(0)}$ such that $|\Psi_I(t)\rangle$ only evolves due to the other pieces of the Hamiltonian (the interactions). You will also see this called a “rotating frame” in the literature. The reason is that a unitary operator preserves the modulus of the Hilbertspace vector it acts upon, as a rotation would. However this rotation might take place in an abstract infinite dimensional complex vectorspace.
- We directly see that the interaction picture state $|\Psi_I(t)\rangle$ and the Schrödinger picture state $|\Psi_S(t)\rangle$ coincide at $t = t_0$ (this reference time for the pictures is up to our choice).
- Similarly to (6.7), we also define an operator in the interaction picture as

$$\bar{O}_I(t) = \hat{U}_S^{(0)\dagger}(t) \hat{O}_S^{(0)} \hat{U}_S(t). \quad (9.64)$$

Thus physics (expectation values) are the same in either picture:

$$\langle \Psi_S(t) | \hat{O}_S | \Psi_S(t) \rangle = \langle \Psi_S(t) | \underbrace{[\hat{U}_S^{(0)}(t, t_0)] [\hat{U}_S^{(0)\dagger}(t, t_0)]}_{=1} \hat{O}_S \underbrace{[\hat{U}_S^{(0)}(t, t_0)] [\hat{U}_S^{(0)\dagger}(t, t_0)]^\dagger}_{=1} | \Psi_S(t) \rangle = \langle \Psi_I(t) | \hat{O}_I | \Psi_I(t) \rangle \quad (9.65)$$

We can now insert (9.63) into the TDSE (3.8) to find out how the interaction picture state evolves in time:

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} |\Psi_I(t)\rangle &= \underbrace{\left(i\hbar \frac{\partial}{\partial t} [\hat{U}_S^{(0)}(t, t_0)]^\dagger \right)}_{\text{Eq. (3.63)} \quad -[\hat{H}^{(0)} \hat{U}_S^{(0)}(t, t_0)]^\dagger = -\hat{U}_S^{(0)}(t, t_0)^\dagger \hat{H}^{(0)\dagger}} |\Psi_S(t)\rangle + [\hat{U}_S^{(0)}(t, t_0)]^\dagger \underbrace{\left(i\hbar \frac{\partial}{\partial t} |\Psi_S(t)\rangle \right)}_{\text{Eq. (3.8)} \quad [\hat{H}^{(0)} + \hat{H}'(t)] |\Psi_S(t)\rangle} \\ &= [\hat{U}_S^{(0)}(t, t_0)]^\dagger \hat{H}'(t) |\Psi_S(t)\rangle = \hat{U}_S^{(0)}(t, t_0)^\dagger \hat{H}'(t) \underbrace{[\hat{U}_S^{(0)}(t, t_0)] [\hat{U}_S^{(0)\dagger}(t, t_0)]^\dagger}_{=1} |\Psi_S(t)\rangle \\ &\stackrel{\text{Eq. (9.63)}}{=} \underbrace{\hat{U}_S^{(0)}(t, t_0)^\dagger \hat{H}'(t) \hat{U}_S^{(0)}(t, t_0)}_{\text{Eq. (9.64)} \quad \hat{H}'_I(t)} |\Psi_I(t)\rangle. \end{aligned} \quad (9.66)$$

We also want to know how an interaction picture operator evolves in time:

$$\begin{aligned}
i\hbar \frac{\partial}{\partial t} \bar{O}_I(t) &\stackrel{\text{Eq. (9.64)}}{=} \left[i\hbar \frac{\partial}{\partial t} \hat{U}_S^{(0)\dagger}(t) \right] \hat{O}_S \hat{U}_S^{(0)}(t) + \hat{U}_S^{(0)\dagger} \hat{O}_S \left[i\hbar \frac{\partial}{\partial t} \hat{U}_S^{(0)}(t) \right] \\
&\stackrel{\text{Eq. (3.63)}}{=} \left[-\hat{U}_S^{(0)\dagger}(t) \hat{H}^{(0)\dagger} \right] \hat{O}_S \hat{U}_S^{(0)}(t) + \hat{U}_S^{(0)\dagger} \hat{O}_S \left[\hat{H}^{(0)} \hat{U}_S^{(0)}(t, t_0) \right] \\
&= \hat{U}_S^{(0)\dagger}(t) [\hat{O}_S, \hat{H}^{(0)}] \hat{U}_S^{(0)}(t) = [\hat{O}_I, \hat{H}_I^{(0)}]. \tag{9.67}
\end{aligned}$$

Alltogether we see the following

Evolution equations in the interaction picture for quantum states and operators

$$i\hbar \frac{\partial}{\partial t} |\Psi_I(t)\rangle = \hat{H}'_I |\Psi_I(t)\rangle, \tag{9.68}$$

$$i\hbar \frac{\partial}{\partial t} \hat{O}_I(t) = [\hat{O}_I, \hat{H}_I^{(0)}], \tag{9.69}$$

- States evolve according to the interaction/perturbation Hamiltonian only, and operators according to the free Hamiltonian only.
- The interaction picture is thus somewhat in between the Heisenberg and Schrödinger picture.
- We skip a practical example since the interaction picture is required here for the next section only, and will be used heavily in many more advanced courses.

9.4.2 Time-dependent perturbation series

Let us define further the

Interaction picture propagator as the time evolution operator

$$\hat{U}_I(t, t_0) |\Psi_I(t_0)\rangle = |\Psi_I(t)\rangle, \tag{9.70}$$

that evolves an interaction picture state from t_0 to t

As stated earlier, we assume that solving Eq. (9.69) based on $\hat{H}^{(0)}$ is easy/solved, so once we know also $\hat{U}_I(t, t_0)$, which amounts to solving (9.68), we can calculate all expectation values (9.65) and thus solved the quantum dynamics problem. We can also revert back to the Schrödinger picture using

$$\hat{U}_S(t, t_0) = \hat{U}_S^{(0)}(t, t_0) \hat{U}_I(t, t_0), \tag{9.71}$$

which we can show from Eq. (9.63) and Eq. (9.70) (exercise).

Due to (9.68) and by comparison with Eq. (3.61) and Eq. (3.63) we know that $\hat{U}_I(t, t_0)$ obeys:

$$i\hbar \frac{\partial}{\partial t} \hat{U}_I(t, t_0) = \hat{H}'_I(t) \hat{U}_I(t, t_0) \quad (9.72)$$

We can formally integrate both sides over time to write:

$$\hat{U}_I(t, t_0) = \mathbb{1} - \frac{i}{\hbar} \int_{t_0}^t dt' \hat{H}'_I(t') \hat{U}_I(t', t_0), \quad (9.73)$$

where we have converted Eq. (9.72) into an integral equation. This is not yet too helpful, since the LHS and RHS both contain the operator $\hat{U}_I(t, t_0)$ that we seek to find, and the RHS does so in a messy way within an operator-integrand. But similarly to our integral form of the TISE (8.37), it is now a good starting point for an approximation series in powers of $\hat{H}'_I(t')$.

Zeroth order: If we ignore all powers of $\hat{H}'_I(t')$ we have $\hat{U}_I(t, t_0) = \mathbb{1}$ implying no evolution, which makes sense since we figured in Eq. (9.68) that states in the interaction picture evolve only due to the interaction Hamiltonian.

First order: To first order we insert this zeroth order result for $\hat{U}_I(t', t_0)$ within the integral on the RHS of (9.73), reaching

$$\hat{U}_I(t, t_0) = \mathbb{1} - \frac{i}{\hbar} \int_{t_0}^t dt' \hat{H}'_I(t'). \quad (9.74)$$

This equation is equivalent to the first-order time-dependent perturbation theory result we had seen in Eq. (9.10). To see this, you have to convert back to the Schrödinger picture and then sandwich the time-evolution operator between $\langle f |$ and $| i \rangle$ (exercise).

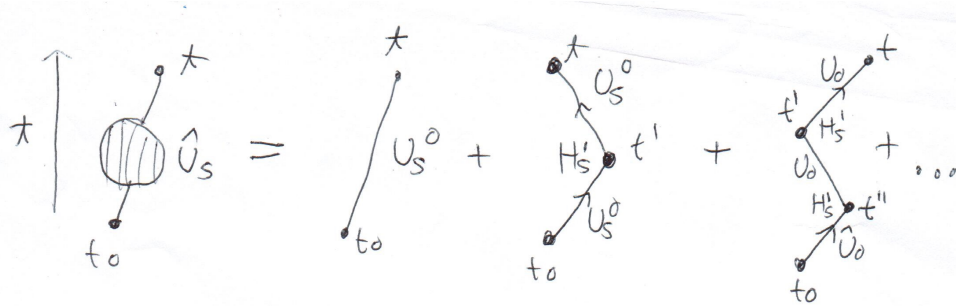
Higher orders: We can now keep repeating these insertions, to generate the interaction picture propagator systematically to any order in the interaction Hamiltonian that is desired

$$\begin{aligned} \hat{U}_I(t, t_0) = & \mathbb{1} - \frac{i}{\hbar} \int_{t_0}^t dt' \hat{H}'_I(t') + \left(-\frac{i}{\hbar}\right)^2 \int_{t_0}^t dt' \int_{t_0}^{t'} dt'' \hat{H}'_I(t') \hat{H}'_I(t'') \\ & + \left(-\frac{i}{\hbar}\right)^3 \int_{t_0}^t dt' \int_{t_0}^{t'} dt'' \int_{t_0}^{t''} dt''' \hat{H}'_I(t') \hat{H}'_I(t'') \hat{H}'_I(t''') + \dots \end{aligned} \quad (9.75)$$

This is called the Dyson series.

Since we are more used to thinking in the Schrödinger picture, it is instructive to convert Eq. (9.75) back into that picture. For this we multiply from the left with $\hat{U}_S^{(0)}(t, t_0)$, use Eq. (9.71) and Eq. (9.64) to re-express $\hat{H}'_I(t)$ in terms of $\hat{H}'_S(t)$. We reach:

$$\begin{aligned} \hat{U}_S(t, t_0) = & \hat{U}_S^{(0)}(t, t_0) - \frac{i}{\hbar} \int_{t_0}^t dt' \hat{U}_S^{(0)}(t, t_0) \hat{U}_S^{(0)\dagger}(t', t_0) \hat{H}'_S(t') \hat{U}_S^{(0)}(t', t_0) \\ & + \left(-\frac{i}{\hbar}\right)^2 \int_{t_0}^t dt' \int_{t_0}^{t'} dt'' \hat{U}_S^{(0)}(t, t_0) \hat{U}_S^{(0)\dagger}(t', t_0) \hat{H}'_S(t') \hat{U}_S^{(0)}(t', t_0) \hat{U}_S^{(0)\dagger}(t'', t_0) \hat{H}'_S(t'') \hat{U}_S^{(0)}(t'', t_0) + \dots \\ = & \hat{U}_S^{(0)}(t, t_0) - \frac{i}{\hbar} \int_{t_0}^t dt' \hat{U}_S^{(0)}(t, t') \hat{H}'_S(t') \hat{U}_S^{(0)}(t', t_0) \\ & + \left(-\frac{i}{\hbar}\right)^2 \int_{t_0}^t dt' \int_{t_0}^{t'} dt'' \hat{U}_S^{(0)}(t, t') \hat{H}'_S(t') \hat{U}_S^{(0)}(t', t'') \hat{H}'_S(t'') \hat{U}_S^{(0)}(t'', t_0) + \dots \end{aligned} \quad (9.76)$$



top: The equation offers the interpretation of the perturbation series visualised above: Consider the last term/rightmost diagram first: In words it says, evolve under the free/unperturbed Hamiltonian from time t_0 to t'' , at that time interact with the perturbation once, then again evolve freely until time t' interact a second time, then evolve freely until the end-time t_0 . The complete time-evolution operator (propagator) is the coherent sum of all such amplitudes.

Finally let us number the eigenstates of $\hat{H}^{(0)}$ by $|n\rangle$, insert a complete set $\mathbf{1} = \sum_n |n\rangle\langle n|$ before and after each occurrence of \hat{H}' in (9.76) and consider the transition amplitude from some defined initial to a final state $d_{i \rightarrow f} = \langle f | \hat{U}_S(t, t_0) | i \rangle$. With the help of (9.76) we can see the

Perturbation expansion of the transition amplitude from $|i\rangle$ to $|f\rangle$:

$$\begin{aligned}
 d_{i \rightarrow f} &= \langle f | \hat{U}_S(t, t_0) | i \rangle = \delta_{fi} e^{-iE_0(t-t_0)/\hbar} - \frac{i}{\hbar} \int_{t_0}^t dt' e^{-iE_f(t-t')/\hbar} \langle f | \hat{H}'_I(t') | i \rangle e^{-iE_i(t'-t_0)/\hbar} \\
 &+ \left(-\frac{i}{\hbar}\right)^2 \int_{t_0}^t dt' \int_{t_0}^{t'} dt'' \sum_n e^{-iE_f(t-t')/\hbar} \langle f | \hat{H}'_I(t') | n \rangle e^{-iE_n(t'-t'')/\hbar} \langle n | \hat{H}'_I(t'') | i \rangle e^{-iE_0(t''-t_0)/\hbar} + \dots
 \end{aligned}
 \tag{9.77}$$

- The purpose of this lengthy derivation was not so much to provide the formula Eq. (9.77) for practical calculations, but rather for the physical insight into the nature of quantum dynamics that it provides: Let us decypher it reading one of the higher order terms from right to left, transport the statement after (9.76) into the eigenstate basis: Starting in the initial state $|i\rangle$ at time t_0 , the system first evolves in that state until t'' , gathering the appropriate phase factor $e^{-iE_i(t'-t_0)/\hbar}$. At time t'' it may then make a transition into any intermediate state $|n\rangle$ towards which the interaction Hamiltonian has a nonvanishing matrix element $\langle n | \hat{H}'(t'') | i \rangle$, in which it then evolves up to time t' , gathering a phase. At time t' it then makes a similar transition into the final state $|f\rangle$ where it is found at the final time t . Note that the integrals ensure the logical time-ordering $t_0 < t'' < t' < t$, but within that constraint integrate over all possible choices of interaction times.

9.4.3 Time-ordered exponentials [BONUS]

Suppose we have a time-ordering operator \mathcal{T} which orders operators according to their time argument:

$$\mathcal{T}\hat{O}(t_1)\hat{O}(t_2) = \begin{cases} \hat{O}(t_1)\hat{O}(t_2), & \text{if } t_1 > t_2, \\ \hat{O}(t_2)\hat{O}(t_1), & \text{if } t_2 > t_1 \end{cases} \quad (9.78)$$

such that earlier times are on the right.

Looking e.g. at the second term in the Dyson series (9.75), we can then write

$$\left(-\frac{i}{\hbar}\right)^2 \int_{t_0}^t dt' \int_{t_0}^{t'} dt'' \hat{H}'_I(t')\hat{H}'_I(t'') = \frac{1}{2}\mathcal{T} \left[\left(-\frac{i}{\hbar}\right)^2 \int_{t_0}^t dt' \int_{t_0}^t dt'' \hat{H}'_I(t')\hat{H}'_I(t'') \right] = \mathcal{T} \left[-\frac{i}{\hbar} \int_{t_0}^t dt'' \hat{H}'_I(t'') \right]^2. \quad (9.79)$$

In the first equality we have only extended the upper limit of the dt'' integration from t' to t . All additional pairs of times that we get are brought into the correct time ordering by the application of \mathcal{T} , and we added a factor of $1/2$ in front to compensate that we now integrate over each pair of times (t', t'') twice.

Similar arguments in all the higher order terms allows one to write a neat form for the

Dyson series as time-ordered exponential

$$\hat{U}_I(t, t_0) = \mathcal{T} \exp \left[-\frac{i}{\hbar} \int_{t_0}^t dt' \hat{H}'_I(t') \right] \quad (9.80)$$

- This is very elegant since it looks quite similar to (??), and very dangerous since all complications within (9.75) are hidden in the innocent looking time-ordering operator.

9.4.4 Quantum dynamics through virtual states

We have now seen in multiple slightly different but related contexts, that quantum mechanics progresses by involving all possible intermediate states that a system can access from some initial to a final state. This was quite clearly worked out for the time-dependent perturbation series in the preceding section, but also had arisen in our higher orders of scattering theory, in section 8.51. Note, that there we were using a time-independent picture, so the meaning of “intermediate” states would be “waves involved in between a fixed incoming and fixed outgoing wave”. Also in higher orders of time-independent perturbation theory, in section 7.1.2, we had seen that higher order states and energies are obtained by some prescription of mixing in contributions of all accessible eigenstates of the Hamiltonian.

A common feature of these was also, that these intermediate states are involved regardless of whether they have the same energy as the initial/perturbed states, however with their contribution reduced more if the energy mismatch is larger.

A particularly beautiful formulation of quantum mechanics where this access over all possible path from the initial to the final state is most evident, is provided by the Feynman path integral. This will be shown properly in lectures on quantum field theory, for an incomplete preview see my lectures notes on classical mechanics PHY305, week 11.