Higher orders in perturbation theory

Three pictures of quantum dynamics

(1) The Schrödinger picture:

$$i\hbar \frac{d}{dt} |\psi_S(t)\rangle = \hat{H}_S(t) |\psi_S(t)\rangle = (\hat{H}_S^0 + \hat{H}_S^1(t)) |\psi_S(t)\rangle$$

States evolve with time; for time-independent systems, $\hat{H}_S^0$ is independent of time.

We can solve this Schrödinger equation formally as follows:

$$|\psi_S(t)\rangle = \hat{\mathcal{U}}_S(t,t_0) |\psi_S(t_0)\rangle$$

where the time evolution operator $\hat{\mathcal{U}}_S$ satisfies the EOM

$$\boxed{i\hbar \frac{d\hat{\mathcal{U}}_S(t,t_0)}{dt} = \hat{H}_S(t)\, \hat{\mathcal{U}}_S(t,t_0)}$$

$$\Rightarrow \hat{\mathcal{U}}_S(t,t_0) = \hat{T}\left(e^{-\frac{i}{\hbar}\int_{t_0}^{t} \hat{H}_S(t')dt'} \right) \equiv \lim_{N\to\infty} \prod_{n=0}^{N-1} e^{-\frac{i}{\hbar}\hat{H}_S(n\Delta)\cdot\Delta}$$

with $\Delta = \frac{t-t_0}{N}$

($\hat{T}$: time-ordering operator (latest time farthest to the left))

We remind ourselves of the following properties:

$$\hat{\mathcal{U}}^+ \hat{\mathcal{U}} = \hat{1} = \hat{\mathcal{U}}(t_1,t_1)$$

$$\hat{\mathcal{U}}(t_3,t_2)\,\hat{\mathcal{U}}(t_2,t_1) = \hat{\mathcal{U}}(t_3,t_1); \qquad \hat{\mathcal{U}}^+(t_2,t_1) = \hat{\mathcal{U}}(t_1,t_2)$$

(2) The Heisenberg picture

The Heisenberg picture is obtained from the Schrödinger picture by a (time-dependent) unitary transformation

$$\boxed{|\psi_H\rangle = \hat{U}_S(0,t)|\psi_S(t)\rangle} \iff \langle\psi_H| = \langle\psi_S(t)|\hat{U}_S^+(0,t) = \langle\psi_S(t)|\hat{U}_S(t,0)$$

Since $|\psi_S(t)\rangle = \hat{U}_S(t,0)|\psi_S(0)\rangle$, we see that

$$\boxed{|\psi_H\rangle = |\psi_S(0)\rangle} \quad \text{independent of time.}$$

This unitary transformation shifts all time evolution to the operators:

$$\langle\psi_S(t)|\hat{\Omega}_S(t)|\psi_S(t)\rangle \overset{!}{=} \langle\psi_H|\hat{\Omega}_H(t)|\psi_H\rangle$$

$$= \langle\psi_S(t)|\hat{U}_S(t,0)\hat{\Omega}_H(t)\hat{U}_S(0,t)|\psi_S(t)\rangle$$

$$\Rightarrow \boxed{\hat{\Omega}_H(t) = \hat{U}_S(0,t)\hat{\Omega}_S(t)\hat{U}_S(t,0)} \quad \text{for any observable } \hat{\Omega}$$

Even if the observable is time-independent in the Schrödinger picture, it is represented by a time-dependent operator in the Heisenberg picture.

In the Heisenberg picture we have

$$\frac{d}{dt}|\psi_H\rangle = 0$$

and

$$i\hbar \frac{d\hat{\Omega}_H}{dt} = i\hbar \frac{d\hat{U}_s(0,t)}{dt} \hat{\Omega}_s(t) \hat{U}_s(t,0) + \hat{U}_s(0,t)\, i\hbar \frac{\partial \hat{\Omega}_s}{\partial t} \hat{U}_s(t,0) + \hat{U}_s(0,t) \hat{\Omega}_s(t)\, i\hbar \frac{d\hat{U}_s(t,0)}{dt}$$

$$= \underbrace{\left(-i\hbar \frac{d}{dt} \hat{U}_s(t,0)\right)^{+}}_{-\hat{H}_s(t)\hat{U}_s(t,0)} \hat{\Omega}_s(t) \hat{U}_s(t,0) + \hat{U}_s(0,t)\, i\hbar \frac{\partial \hat{\Omega}_s}{\partial t} \hat{U}_s(t,0) + \hat{U}_s(0,t) \hat{\Omega}_s(t) \underbrace{\ }_{\hat{U}_s(t,0)\hat{U}_s(0,t)} H_s(t) \hat{U}_s(t,0)$$

$$= -\hat{U}_s(0,t) \hat{H}_s(t) \underbrace{\hat{U}_s(t,0) \hat{U}_s(0,t)}_{\hat{1}} \hat{\Omega}_s(t) \hat{U}_s(t,0)$$

$$+ i\hbar\, \hat{U}_s(0,t) \frac{\partial \hat{\Omega}_s}{\partial t} \hat{U}_s(t,0)$$

$$+ \underbrace{\hat{U}_s(0,t) \hat{\Omega}_s(t) \hat{U}_s(t,0)}_{\hat{\Omega}_H(t)} \underbrace{\hat{U}_s(0,t) \hat{H}_s(t) \hat{U}_s(t,0)}_{\hat{H}_H(t)}$$

$$= \left[\hat{\Omega}_H(t), \hat{H}_H(t)\right] + i\hbar \left(\frac{\partial \hat{\Omega}}{\partial t}\right)_H$$

$$\Rightarrow \boxed{i\hbar \frac{d\hat{\Omega}_H}{dt}(t) = \left[\hat{\Omega}_H(t), \hat{H}_H(t)\right] + i\hbar \left(\frac{\partial \hat{\Omega}}{\partial t}\right)_H}$$

Heisenberg equation of motion.

The overlap between Heisenberg picture state is time independent:

$\langle \varphi_H | \psi_H \rangle$ = independent of time

This overlap matrix element represents the following overlap of Schrödinger picture states:

$$\langle \varphi_H | \psi_H \rangle = \langle \varphi_s(t) | \hat{U}(t,0)\, \hat{U}_s(0,t) | \psi_s(t) \rangle$$

$$= \langle \varphi_s(t) | \psi_s(t) \rangle$$ (which is therefore also time independent)

$$= \langle \varphi_s(t) | \hat{U}_s(t,t_0) | \psi_s(t_0) \rangle$$

$$= \langle \varphi_s(\infty) | \hat{U}_s(\infty,-\infty) | \psi_s(-\infty) \rangle$$

(3) The interaction picture

If we split $\hat{H}(t)$ into an unperturbed ("non-interacting") part and an interaction term ("perturbation"),

$$\hat{H}(t) = \hat{H}_0(t) + \hat{H}'(t) \equiv \hat{H}_0(t) + \hat{V}(t)$$

we can split the time evolution between the states and the operators such that the operators evolve with $\hat{H}^0$ and the states evolve only with the perturbation. This is called the interaction picture.

In most applications one splits $\hat{H}(t)$ such that in the S-picture $\hat{H}_S^\circ$ is independent of time and all time-dependence goes into $\hat{V}(t)$. But let us develop the interaction picture first for the general case.

We define a "non-interacting" time evolution operator $\hat{\mathcal{U}}_S^\circ(t,t_0)$ by

$$i\hbar \frac{d}{dt}\hat{\mathcal{U}}_S^\circ(t,t_0) = H_S^\circ(t)\,\hat{\mathcal{U}}_S^\circ(t,t_0)$$

and the interaction picture state vectors through

$$|\psi_I(t)\rangle = \left(\hat{\mathcal{U}}_S^\circ(t,0)\right)^+ |\psi_S(t)\rangle$$
$$= \hat{\mathcal{U}}_S^\circ(0,t)\,|\psi_S(t)\rangle \quad ; \quad |\psi_I(0)\rangle = |\psi_S(0)\rangle$$

This is similar to the Heisenberg picture, except that we use only the non-interacting part of the Hamiltonian for our unitary transformation. If there are no interactions, $\hat{V} \equiv 0$, then the interaction picture states $|\psi_I(t)\rangle$ are time independent – interaction and Heisenberg picture agree in this case. Any time dependence of $|\psi_I(t)\rangle$ is thus entirely caused by $\hat{V}(t)$.

$\Rightarrow$ in the interaction picture, the states evolve with $\hat{V}(t)$ in time, while the time evolution of the observables is due to $\hat{H}^0(t)$.

Let's check this:

$$i\hbar \frac{d}{dt}|\psi_I(t)\rangle = i\hbar \frac{d}{dt}\left(\hat{U}_S^{0\dagger}(t,0)\,|\psi_S(t)\rangle\right)$$

$$= \left(-i\hbar \frac{d}{dt}\hat{U}_S^0(t,0)\right)^\dagger |\psi_S(t)\rangle + \hat{U}_S^0(0,t)\, i\hbar\frac{d}{dt}|\psi_S(t)\rangle$$

$$= \left(-H_S^0(t)\hat{U}_S^0(t,0)\right)^\dagger |\psi_S(t)\rangle + \hat{U}_S^0(0,t)\,\hat{H}_S(t)|\psi_S(t)\rangle$$

$$= \hat{U}_S^0(0,t)\left[-\hat{H}_S^0(t) + \hat{H}_S(t)\right]|\psi_S(t)\rangle$$

$$= \underbrace{\hat{U}_S^0(0,t)\,\hat{V}_S(t)\,\hat{U}_S^0(t,0)}_{\hat{V}_I(t)\text{ = interaction in interaction picture}}\;\underbrace{\hat{U}_S^0(0,t)\,|\psi_S(t)\rangle}_{|\psi_I(t)\rangle}$$

(with $\hat{U}_S^0(t,0)\,\hat{U}_S^0(0,t) = \hat{\mathbb{1}}$)

$$\Rightarrow \boxed{i\hbar\frac{d}{dt}|\psi_I(t)\rangle = \hat{V}_I(t)|\psi_I(t)\rangle}$$ ✓ I-states evolve with $\hat{V}_I(t)$

For the operators: $\hat{\Omega}_I(t) = \hat{U}_S^0(0,t)\,\hat{\Omega}_S(t)\,\hat{U}_S^0(t,0)$

$$i\hbar\frac{d}{dt}\hat{\Omega}_I(t) = i\hbar\frac{d}{dt}\left(\hat{U}_S^0(0,t)\,\hat{\Omega}_S(t)\,\hat{U}_S^0(t,0)\right)$$

$$= -\hat{U}_S^0(0,t)\,\hat{H}_S^0(t)\,\hat{\Omega}_S(t)\,\hat{U}_S^0(t,0)$$

$$+\hat{U}_S^0(0,t)\, i\hbar\frac{\partial\hat{\Omega}_S}{\partial t}(t)\,\hat{U}_S^0(t,0)$$

$$+\hat{U}_S^0(0,t)\,\hat{\Omega}_S(t)\,\hat{H}_S^0(t)\,\hat{U}_S^0(t,0) =$$

$$= -\hat{\mathcal{U}}_S^0(0,t)\hat{H}_S^0(t)\hat{\mathcal{U}}_S^0(t,0)\,\hat{\mathcal{U}}_S^0(0,t)\hat{\Omega}_S(t)\hat{\mathcal{U}}_S^0(t,0)$$

$$+\hat{\mathcal{U}}_S^0(0,t)\left(i\hbar\frac{\partial\hat{\Omega}_S}{\partial t}\right)\hat{\mathcal{U}}_S^0(t,0)$$

$$+\underbrace{\hat{\mathcal{U}}_S^0(t)\hat{\Omega}_S(t)\hat{\mathcal{U}}_S^0(t,0)}_{\hat{\Omega}_I(t)}\,\underbrace{\hat{\mathcal{U}}_S^0(0,t)\hat{H}_S^0(t)\hat{\mathcal{U}}_S^0(t,0)}_{\hat{H}_I^0(t)}$$

$$\Rightarrow \boxed{i\hbar\frac{d\hat{\Omega}_I}{dt} = \left[\hat{\Omega}_I(t), H_I^0(t)\right] + i\hbar\left(\frac{\partial\hat{\Omega}}{\partial t}\right)_I} \checkmark$$

interaction-picture observables evolve with $\hat{H}_I^0(t)$

Let us now define the propagator $\hat{\mathcal{U}}_I$ in the interaction picture:

$$\boxed{|\psi_I(t)\rangle = \hat{\mathcal{U}}_I(t,t_0)\,|\psi_I(t_0)\rangle}$$

Because of $i\hbar\frac{d}{dt}|\psi_I(t)\rangle = \hat{V}_I(t)|\psi_I(t)\rangle$ this propagator satisfies the E.O.M.:

$$\boxed{i\hbar\frac{d}{dt}\hat{\mathcal{U}}_I(t,t_0) = \hat{V}_I(t)\,\hat{\mathcal{U}}_I(t,t_0)}$$

We can relate $\hat{\mathcal{U}}_I$ to $\hat{\mathcal{U}}_S$ and $\hat{\mathcal{U}}_S^0$:

$$|\psi_I(t)\rangle = \hat{\mathcal{U}}_I(t,t_0)\,|\psi_I(t_0)\rangle$$
$$\hat{\mathcal{U}}_S^0(0,t)|\psi_S(t)\rangle = \hat{\mathcal{U}}_I(t,t_0)\,\hat{\mathcal{U}}_S^0(0,t_0)|\psi_S(t_0)\rangle$$

$$\hat{U}_S^\circ(0,t)\,\hat{U}_S(t,t_0)|\psi_S(t_0)\rangle = \hat{U}_I(t,t_0)\,\hat{U}_S^{\circ +}(t_0,0)|\psi_S(t_0)\rangle$$

$$\Rightarrow \boxed{\hat{U}_I(t,t_0) = \hat{U}_S^\circ(0,t)\,\hat{U}_S(t,t_0)\,\hat{U}_S^\circ(t_0,0)}$$

I-propagator; S-propagator

(transforms like any other operator)

For $t_0 = 0$ (i.e. at the time when the 3 pictures coincide) this simplifies to

$$\hat{U}_I(t,0) = \hat{U}_S^\circ(0,t)\,\hat{U}_S(t,0)$$

or

$$\hat{U}_S(t,0) = \hat{U}_S^\circ(t,0)\,\hat{U}_I(t,0) \qquad (*)$$

We chose to make the 3 pictures coincide at $t=0$; we could, however, have chosen any other reference time t_{ref}. <u>We can change this simply a posteriori by replacing all time arguments "0" by "t_{ref}".</u> <u>For example:</u>

$$\hat{U}_I(t_1,t_2) = \hat{U}_S^\circ(t_{ref},t_1)\,\hat{U}_S(t_1,t_2)\,\hat{U}_S^\circ(t_2,t_{ref})$$

<u>Note</u>: Shankar uses the notation t_0 for t_{ref}.

His t_0 should not be confused with our t_0 which is a free time parameter unrelated to the reference time where the pictures coincide.

Perturbation theory in the interaction picture:

In the interaction picture, the states evolve only in response to the interaction:

$$|\psi_I(t)\rangle = \hat{\mathcal{U}}_I(t,t_0)\,|\psi_I(t_0)\rangle$$

$$i\hbar\frac{d}{dt}|\psi_I(t)\rangle = \hat{V}_I(t)\,|\psi_I(t)\rangle$$

$$i\hbar\frac{d}{dt}\hat{\mathcal{U}}_I(t,t_0) = \hat{V}_I(t)\,\hat{\mathcal{U}}_I(t,t_0)$$

We can solve the last equation formally by integrating both sides from t_0 to t:

$$\boxed{\hat{\mathcal{U}}_I(t,t_0) = \hat{\mathbb{1}} - \frac{i}{\hbar}\int_{t_0}^{t} dt'\,\hat{V}_I(t')\,\hat{\mathcal{U}}_I(t',t_0)}$$

except that this is not really a solution but an <u>integral equation</u> for $\hat{\mathcal{U}}_I$. It is useful because it can be solved iteratively, with each iteration corresponding to the next higher order in the perturbative series:

<u>Zeroth order</u>: drop all terms containing $\hat{V}$

$$\Longrightarrow \hat{\mathcal{U}}_I^{(0)}(t,t_0) = \hat{\mathbb{1}} \quad , \quad |\psi_I^{(0)}(t)\rangle = |\psi_I^{(0)}(t_0)\rangle$$

The interaction-picture states do not evolve.

<u>First order</u> Keep only linear terms in $\hat{V}$

$\Rightarrow$ can set $\hat{\mathcal{U}}_I(t', t_0) = \hat{\mathcal{U}}_I^{(0)}(t', t_0) = \mathbb{1}$ on the r.h.s.

$$\Rightarrow \hat{\mathcal{U}}_I^{(1)}(t, t_0) = \hat{\mathbb{1}} - \frac{i}{\hbar} \int_{t_0}^{t} dt' \, \hat{V}_I(t')$$

Let us use this to compute

$$c_f(t) = \langle f_S^0 | e^{i E_f^0 (t - t_{ref})} \hat{\mathcal{U}}_S(t, t_{ref}) | i_S^0 \rangle$$

i.e. the transition amplitude to the state $|f_S^0\rangle$ at time t for a system that started (in the Schrödinger picture) in state $|i_S^0\rangle$ at the reference time t_{ref}.

We assume here (as we had earlier) that $\hat{H}_S^0$ is time independent. Then $\hat{\mathcal{U}}_S^0(t, t_{ref})$ is simply

$$\hat{\mathcal{U}}_S^0(t, t_{ref}) = e^{-i/\hbar \, \hat{H}_S^0 (t - t_{ref})}$$

Using Eq. (*) on p. 79 for $0 \to t_{ref}$ we can rewrite $c_f(t)$ as

$$c_f(t) = \langle f_S^0 | \hat{\mathcal{U}}_S^{0\dagger}(t, t_{ref}) \hat{\mathcal{U}}_S(t, t_{ref}) | i_S^0 \rangle$$
$$= \langle f_S^0 | \hat{\mathcal{U}}_I(t, t_{ref}) | i_S^0 \rangle$$

This holds with the exact interaction picture propagator $\hat{\mathcal{U}}_I(t, t_{ref})$.

Using the first-order approximation for it we find

$$\underset{\sim\sim}{c_f^{(1)}(t)} = \langle f_S^0 | \hat{1} - \frac{i}{\hbar} \int_{t_{ref}}^{t} dt' \, \hat{V}_I(t') | i_S^0 \rangle$$

$$= \delta_{fi} - \frac{i}{\hbar} \int_{t_{ref}}^{t} dt' \, \langle f_S^0 | \hat{V}_I(t') | i_S^0 \rangle$$

$$= \delta_{fi} - \frac{i}{\hbar} \int_{t_{ref}}^{t} dt' \langle f_S^0 | \hat{U}_S^0(t_{ref}, t') \hat{V}_S(t') \hat{U}_S^0(t', t_{ref}) | i_S^0 \rangle$$

$$= \delta_{fi} - \frac{i}{\hbar} \int_{t_{ref}}^{t} dt' \langle f_S^0 | e^{-\frac{i}{\hbar} E_f^0 (t_{ref} - t')} \hat{V}_S(t') e^{-i/\hbar \, E_i^0 (t' - t_{ref})} | i_S^0 \rangle$$

$$= \delta_{fi} - \frac{i}{\hbar} \int_{t_{ref}}^{t} dt' \langle f_S^0 | \hat{V}_S(t') | i_S^0 \rangle e^{i \omega_{fi} (t' - t_{ref})}$$

This agrees with our earlier result if we set $t_{ref} = 0$.

<u>Higher orders:</u> If we keep feeding the result for $\hat{U}_I(t', t_{ref})$ at a given order into the right hand side of the integral equation to generate the next higher order approximation, we get

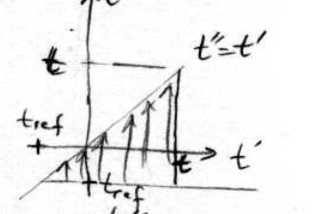
$$\hat{U}_I(t, t_{ref}) = \hat{1} - \frac{i}{\hbar} \int_{t_{ref}}^{t} dt' \, \hat{V}_I(t') + \left(\frac{-i}{\hbar}\right)^2 \int_{t_{ref}}^{t} dt' \int_{t_{ref}}^{t'} dt'' \, \hat{V}_I(t') \hat{V}_I(t'')$$

$$+ \left(\frac{-i}{\hbar}\right)^3 \int_{t_{ref}}^{t} dt' \int_{t_{ref}}^{t'} dt'' \int_{t_{ref}}^{t''} dt''' \, \hat{V}_I(t') \hat{V}_I(t'') \hat{V}_I(t''') + \ldots$$

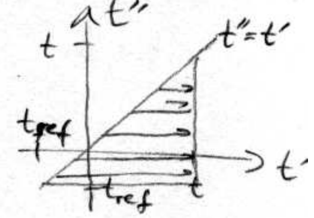
Note that the $\hat{V}_I$ factors under the integral are time-ordered, with largest time argument to the left and smallest to the right.

With a little trick we can resum this series:

We write



$$\int_{t_{ref}}^{t} dt' \int_{t_{ref}}^{t'} dt'' \, \hat{V}(t')\hat{V}(t'') = \frac{1}{2}\int_{t_{ref}}^{t} dt' \int_{t_{ref}}^{t'} dt'' \, \hat{V}(t')\hat{V}(t'')$$



$$+\frac{1}{2}\int_{t_{ref}}^{t} dt'' \int_{t''}^{t} dt' \, V(t')V(t'')$$

$$= \underbrace{\frac{1}{2}\int_{t_{ref}}^{t} dt' \int_{t_{ref}}^{t'} dt'' \, \hat{V}(t')\hat{V}(t'')}_{t'>t''} + \underbrace{\frac{1}{2}\int_{t_{ref}}^{t} dt' \int_{t'}^{t} dt'' \, \hat{V}(t'')\hat{V}(t')}_{t''>t'}$$

$$= \frac{1}{2}\int_{t_{ref}}^{t} dt' \int_{t_{ref}}^{t} dt'' \, \hat{T}\left[\hat{V}(t')\hat{V}(t'')\right]$$

wher $\hat{T}[\hat{V}(t')\hat{V}(t'')] = \theta(t'-t'')\hat{V}(t')\hat{V}(t'') + \theta(t''-t')\hat{V}(t'')\hat{V}(t')$

$$= \begin{cases} \hat{V}(t')\hat{V}(t'') & \text{if } t'>t'' \\ \hat{V}(t'')\hat{V}(t') & \text{if } t''>t' \end{cases}$$

is the time-ordered product of $\hat{V}(t')$ and $\hat{V}(t'')$

$$\Rightarrow \hat{U}_I(t,t_{ref}) = \hat{\mathbb{1}} - \frac{i}{\hbar}\int_{t_{ref}}^{t} dt' \hat{V}_I(t') + \frac{1}{2}\left(\frac{-i}{\hbar}\right)^2 \int_{t_{ref}}^{t} dt' \int_{t_{ref}}^{t} dt'' \, \hat{T}\left[\hat{V}_I(t')\hat{V}(t'')\right]$$

$$+ \frac{1}{3!}\left(-\frac{i}{\hbar}\right)^3 \int_{t_{ref}}^{t} dt' \int_{t_{ref}}^{t} dt'' \int_{t_{ref}}^{t} dt''' \, \hat{T}\left[\hat{V}(t')\hat{V}(t'')\hat{V}(t''')\right] + \ldots$$

and finally

$$\hat{U}_I(t,t_{ref}) = \hat{T}\, e^{-\frac{i}{\hbar}\int_{t_{ref}}^{t} dt'\, \hat{V}_I(t')}$$

The Taylor expansion of the exponential function generates the perturbation series.

We can also get the Schrödinger picture propagator:

$$\hat{U}_S(t,t_{ref}) \overset{(p.79)}{=} \hat{U}_S^0(t,t_{ref})\,\hat{U}_I(t,t_{ref})$$

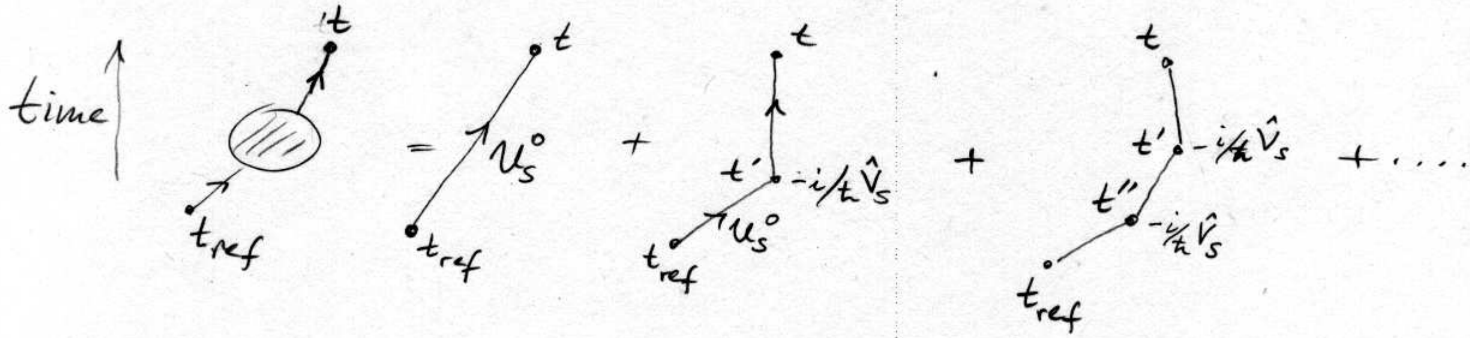
$$= e^{-\frac{i}{\hbar}\hat{H}_S^0(t-t_{ref})}\,\hat{T}\, e^{-\frac{i}{\hbar}\int_{t_{ref}}^{t} dt'\, \hat{V}_I(t')}$$

$$= \hat{U}_S^0(t,t_{ref}) - \frac{i}{\hbar}\int_{t_{ref}}^{t} dt'\, \hat{U}_S^0(t,t_{ref})\,\hat{U}_S^0(t_{ref},t')\,\hat{V}_S(t')\,\hat{U}_S^0(t',t_{ref}) + \dots$$

$$= \hat{U}_S^0(t,t_{ref}) - \frac{i}{\hbar}\int_{t_{ref}}^{t} dt'\, \hat{U}_S^0(t,t')\,\hat{V}_S(t')\,\hat{U}_S^0(t',t_{ref})$$

$$+\left(-\frac{i}{\hbar}\right)^2 \int_{t_{ref}}^{t} dt' \int_{t_{ref}}^{t'} dt''\, \hat{U}_S^0(t,t')\,\hat{V}_S(t')\,\hat{U}_S^0(t',t'')\,\hat{V}_S(t'')\,\hat{U}_S^0(t'',t_{ref})$$

$$+ \dots$$



The complete Schrödinger picture propagator is a sum of terms with 0, 1, 2, ... actions of $\hat{V}_S$ at intermediate times, with free propagation U_S^0 between the interactions.

The intermediate times when $\hat{V}_S$ acts are integrated over from initial time t_{ref} to final time t.

For the transition amplitude this implies

$$c_f(t) = \langle f_S^\circ | \hat{\mathcal{U}}_I(t, t_{ref}) | i_S^\circ \rangle =$$

$$= \langle f_S^\circ | \hat{\mathcal{U}}_S^\circ(t_{ref}, t)\, \hat{\mathcal{U}}_S(t, t_{ref}) | i_S^\circ \rangle$$

$$= \langle f_S^\circ | e^{-\frac{i}{\hbar}E_f^\circ (t_{ref}-t)}\, \hat{\mathcal{U}}_S(t, t_{ref}) | i_S^\circ \rangle$$

$$= \delta_{fi} - \frac{i}{\hbar}\int_{t_{ref}}^{t} dt'\, e^{-\frac{i}{\hbar}E_f^\circ(t_{ref}-t')} \langle f_S^\circ | \hat{V}_S(t') | i_S^\circ \rangle\, e^{-\frac{i}{\hbar}E_i^\circ (t'-t_{ref})}$$

$$+ \left(-\frac{i}{\hbar}\right)^2 \int_{t_{ref}}^{t} dt' \int_{t_{ref}}^{t'} dt'' \sum_n e^{-iE_f^\circ(t_{ref}-t')} \langle f_S^\circ | \hat{V}_S(t') | n_S^\circ \rangle\, *$$

$$* \, e^{-\frac{i}{\hbar}E_n^\circ (t'-t'')} \langle n_S^\circ | \hat{V}_S(t'') | i_S^\circ \rangle\, e^{-i/\hbar\, E_i^\circ (t''-t_{ref})} + \ldots$$

Dropping the S subscripts everywhere and simplifying this gives

$$c_f(t) = e^{-i\omega_{fi} t_{ref}} * \Big[\delta_{fi} - \frac{i}{\hbar}\int_{t_{ref}}^{t} dt' \langle f^\circ | \hat{V}(t') | i^\circ \rangle\, e^{i\omega_{fi} t'}$$

$$+ \left(-\frac{i}{\hbar}\right)^2 \int_{t_{ref}}^{t} dt' \int_{t_{ref}}^{t'} dt'' \sum_n \langle f^\circ | \hat{V}(t') | n^\circ \rangle\, e^{i\omega_{fn} t'} \langle n^\circ | \hat{V}(t'') | i^\circ \rangle\, e^{i\omega_{ni} t''}$$

$$+ \ldots \Big]$$